PHYSICAL CHEMISTRY



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Physical Chemistry

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1: THE DAWN OF THE QUANTUM THEORY

"A profound change has taken place during the present century in the opinions physicists have held on the mathematical foundations of their subject. Previously they supposed that the principles of Newtonian mechanics would provide the basis for the description of the whole of physical phenomenon and that all the theoretical physicists had to do was suitably to develop and apply these principles. With the recognition that there is no logical reason why Newtonian and classical principles should be valid outside the domains in which they have been experimentally verified has come the realization that departures from these principles are indeed necessary. Such departures find their expression through the introduction of new mathematical formalisms, new schemes of axioms and rules of manipulation, into the methods of theoretical physics." **P. A. M. Dirac, "Quantum Mechanics" (1930).**

1.1: Blackbody Radiation Cannot Be Explained Classically

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1.E: The Dawn of the Quantum Theory (Exercises)

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1.1: Blackbody Radiation Cannot Be Explained Classically

Learning Objectives

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation. Objectives for this section include

- Be familiar with black-body radiators
- Apply Stefan-Boltzmann's Law to estimate total light output from a radiator
- Apply Wien's Displacement Law to estimate the peak wavelength (or frequency) of the output from a black body radiator
- Understand the Rayleigh-Jeans Law and how it fails to properly model black-body radiation

All normal matter at temperatures above absolute zero emits electromagnetic radiation, which represents a conversion of a body's internal thermal energy into electromagnetic energy, and is therefore called *thermal radiation*. Conversely, all normal matter *absorbs* electromagnetic radiation to some degree. An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody. When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called *blackbody radiation*.

A room temperature blackbody appears black, as most of the energy it radiates is infra-red and cannot be perceived by the human eye. Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey, even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it becomes yellow, white, and ultimately blue-white.



Figure 1.1.1 : Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

Blackbody radiation has a characteristic, continuous frequency spectrum that experimentally depends only on the body's temperature. In fact, we can be much more precise:

> A body emits radiation at a given temperature and frequency *exactly* as well as it absorbs the same radiation.

This statement was proved by Gustav Kirchhoff: the essential point is that if we *instead* suppose a particular body can absorb better than it emits, then in a room full of objects all at the same temperature, it will absorb radiation from the other bodies better than it radiates energy back to them. This means it will get hotter, and the rest of the room will grow colder, contradicting the second law of thermodynamics. *Thus, a body must emit radiation exactly as well as it absorbs the same radiation at a given temperature and frequency in order to not violate the second law of thermodynamics.*

Any body at any temperature above absolute zero **will** radiate to some extent, the intensity and frequency distribution of the

radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter*. So how do we construct a perfect absorber in the laboratory? In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find (Figure 1.1.2).

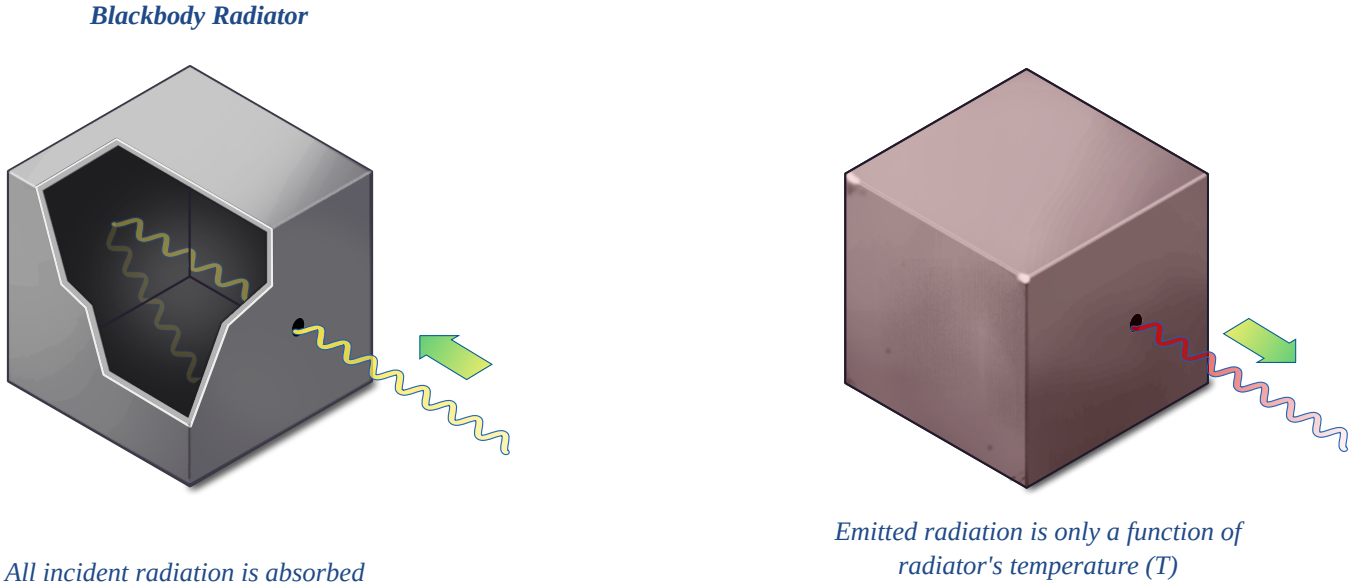


Figure 1.1.2 : Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya via LibreTexts)

By the 1890's, experimental techniques had improved sufficiently that it was possible to make fairly precise measurements of the energy distribution of blackbody radiation. In 1895, at the University of Berlin, Wien and Lummer punched a small hole in the side of an otherwise completely closed oven, and began to measure the radiation coming out. The beam coming out of the hole was passed through a diffraction grating, which sent the different wavelengths/frequencies in different directions, all towards a screen. A detector was moved up and down along the screen to find how much radiant energy was being emitted in each frequency range. They found a radiation intensity/frequency curve close to the distributions in Figure 1.1.3 .

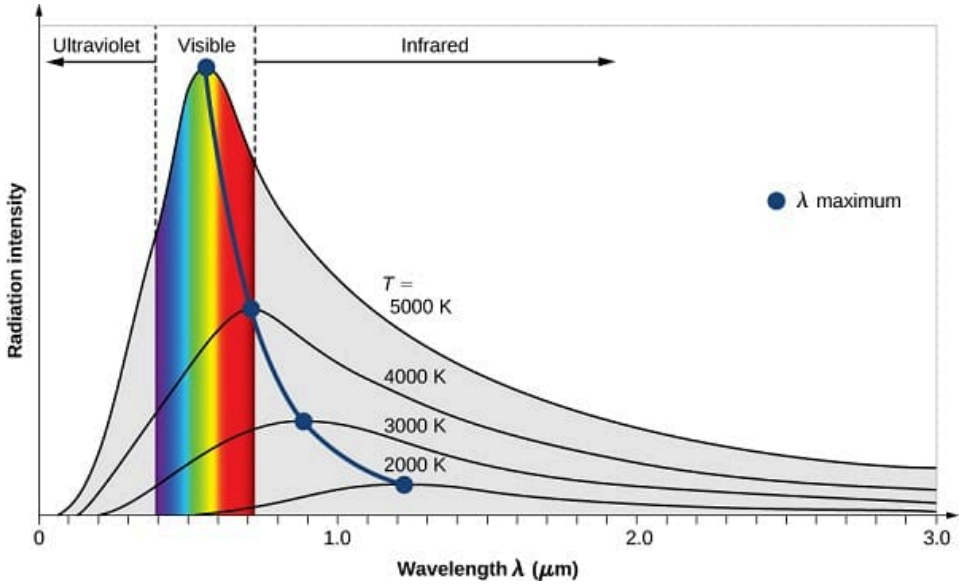
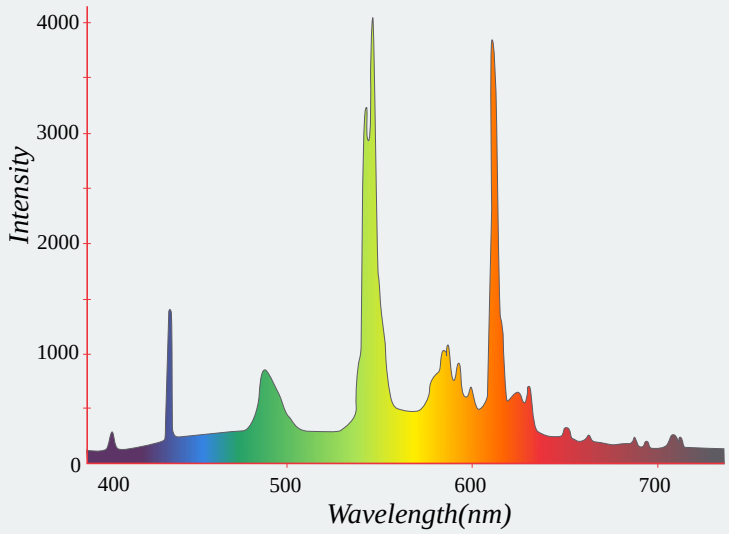


Figure 1.1.3 : Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength with increasing temperature. (CC-BY 4.0; OpenStax)

By measuring the blackbody emission curves at different temperatures (Figure 1.1.3), they were also able to construct two important phenomenological Laws (i.e., formulated from experimental observations, not from basic principles of nature): **Stefan-Boltzmann's Law** and **Wien's Displacement Law**.

Not all radiators are blackbody radiators

The radiation of a blackbody radiator is produced by the thermal activity of the material, not the nature of the material, nor how it got thermally excited. Some examples of blackbodies include incandescent light bulbs, stars, and hot stove tops. The emission appears as a continuous spectrum (Figure 1.1.3) with multiple coexisting colors. However, not every radiator is a blackbody radiator. For example, the emission of a fluorescence bulb is not one. The following spectrum show the distribution of light from a fluoresce light tube and is a mixture of discrete bands at different wavelengths of light in contrast to the continuous spectra in Figure 1.1.3 for blackbody radiators.



Fluorescent lighting spectrum with emission peaks. Graph of Intensity (counts) vs. Wavelength (nm) in the visible spectrum. (CC BY-NC; Ümit Kaya via LibreTexts).

Fluorescent light bulbs contain a mixture of inert gases (usually argon and neon) together with a drop of mercury at low pressure. A different mix of visible colors blend to produce a light that appears to us white with different shadings.

The Stefan-Boltzmann Law

The first quantitative conjecture based on experimental observations was the **Stefan-Boltzmann Law** (1879) which states the total power (i.e., integrated over all emitting frequencies in Figure 1.1.3) radiated from one square meter of black surface goes as the *fourth power* of the absolute temperature (Figure 1.1.4):

$$P = \sigma T^4 \tag{1.1.1}$$

where

- P is the total amount of radiation emitted by an object per square meter ($Watts/m^2$)
- σ is a constant called the Stefan-Boltzman constant ($5.67 \times 10^{-8}\ Watts\ m^{-2}K^{-4}$)
- T is the absolute temperature of the object (in K)

The Stefan-Boltzmann Law is easily observed by comparing the integrated value (i.e., under the curves) of the experimental black-body radiation distribution in Figure 1.1.3 at different temperatures. In 1884, Boltzmann derived this T^4 behavior from theory by applying classical thermodynamic reasoning to a box filled with electromagnetic radiation, using Maxwell's equations to relate pressure to energy density. That is, the tiny amount of energy coming out of the hole (Figure 1.1.2) would of course have the same

temperature dependence as the radiation intensity inside.

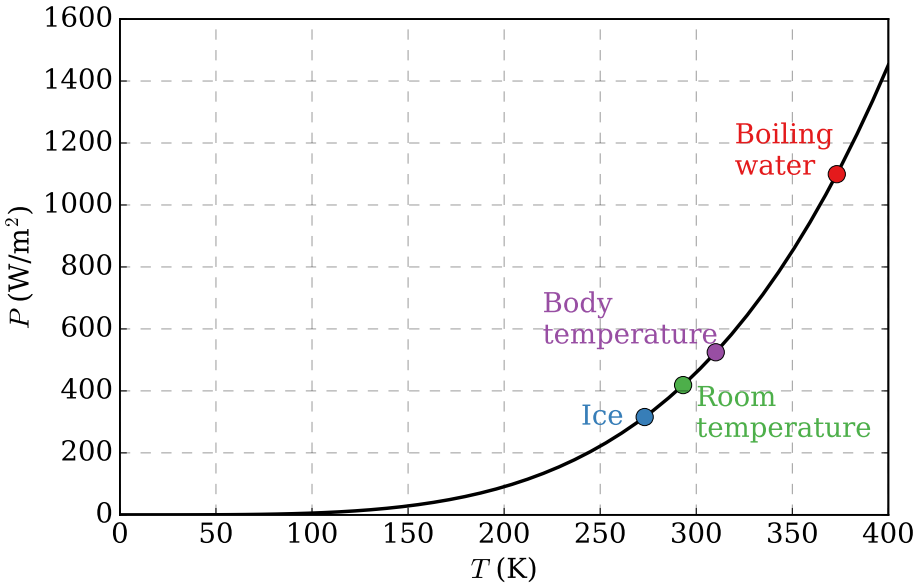


Figure 1.1.4 : Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature T according to the Stefan–Boltzmann law. (CC BY-SA 4.0; Nicoguaro)

Example 1.1.1

The sun's surface temperature is 5700 K.

a. How much power is radiated by the sun?
b. Given that the distance to earth is about 200 sun radii, what is the maximum power possible from a one square kilometer solar energy installation?

Solution A

First, we calculate the area of the sun followed by the flux (power). The sun has a radius of $6.96 \times 10^8 m$

The area of the sun is $A = 4\pi R^2$.

$$A = 4(3.1416)(6.96 \times 10^8 m)^2$$
$$= 6.08 \times 10^{18} m^2$$

The power radiated from the sun (via Stefan-Boltzmann Law) is $P = \sigma T^4$ (Equation 1.1.1).

$$P = (5.67 \times 10^{-8}\, Watts\, m^{-2} K^{-4})(5700K)^4$$
$$= 5.98 \times 10^7 Watts/m^2$$

This value is per square meter.

Solution B

To calculate the total power radiated by the sun is thus:

$$P_{total} = PA = (5.98 \times 10^7 Watts/m^2)(6.08 \times 10^{18} m^2)$$
$$= 3.6 \times 10^{26} Watts$$

Wien's Displacement Law

The second phenomenological observation from experiment was **Wien's Displacement Law**. Wien's law identifies the dominant (peak) wavelength, or color, of light coming from a body at a given temperature. As the oven temperature varies, so does the frequency at which the emitted radiation is most intense (Figure 1.1.3). In fact, that frequency is directly proportional to the absolute temperature:

$$\nu_{max} \propto T \tag{1.1.2}$$

where the proportionality constant is $5.879 \times 10^{10} Hz/K$.

Wien himself deduced this law theoretically in 1893, following Boltzmann's thermodynamic reasoning. It had previously been observed, at least semi-quantitatively, by an American astronomer, Langley. This upward shift in ν_{max} with T is familiar to everyone—when an iron is heated in a fire (Figure 1.1.1), the first visible radiation (at around 900 K) is deep red, the lowest frequency visible light. Further increase in T causes the color to change to orange then yellow, and finally blue at very high temperatures (10,000 K or more) for which the peak in radiation intensity has moved beyond the visible into the ultraviolet.

Another representation of Wien's Law (Equation 1.1.2) in terms of the peak wavelength of light is

$$\lambda_{max} = \frac{b}{T} \tag{1.1.3}$$

where T is the absolute temperature in kelvin and b is a constant of proportionality called **Wien's displacement constant**, equal to $2.89 \times 10^{-3} m\ K$, or more conveniently to obtain wavelength in micrometers, $b \approx 2900\ \mu m \cdot K$. This is an inverse relationship between wavelength and temperature. So the higher the temperature, the shorter or smaller the wavelength of the thermal radiation. The lower the temperature, the longer or larger the wavelength of the thermal radiation. For visible radiation, hot objects emit bluer light than cool objects.

Example 1.1.2

If surface body temperature is 90 °F.

a. How much radiant energy in $W\ m^{-2}$ would your body emit?
b. What is the peak wavelength of emitted radiation?
c. What is the total radiant energy emitted by your body in Watts? Note: The average adult human male has a body surface area of about 1.9 m^2 and the average body surface area for a woman is about 1.6 m^2.

Solution A

90 °F is 305 K. We use Stefan-Boltzmann Law (Equation 1.1.1). The total amount of radiation emitted will be $P = \sigma T^4$.

$$\begin{aligned} P &= (5.67 \times 10^{-8}\, Watts\, m^{-2} K^{-4})(305K)^4 \\ &= 491 W\, m^{-2} \end{aligned}$$

Solution B

The peak wavelength of emitted radiation is found using Wien's Law:

$$\begin{aligned} \lambda_{max} &= \frac{2.898 \times 10^{-3} m \cdot K}{T} \\ &= \frac{2.898 \times 10^{-3} m \cdot K}{305K} \\ &= 9.5 \times 10^{-6} m = 9.5 \mu m \end{aligned}$$

Solution C

The total radiant energy density in Watts is :

$$\text{Energy}_{\text{male}} = (491W\,m^{-2})(1.9m^2) = 933W$$
$$\text{Energy}_{\text{female}} = (491W\,m^{-2})(1.6m^2) = 786W$$

Example 1.1.3 : The Temperature of the Sun

For example, if the Sun has a surface temperature of 5700 K, what is the wavelength of maximum intensity of solar radiation?

Solution

If we substitute 5700 K for T in Equation 1.1.3, we have

$$\lambda_{max} = \frac{0.0029}{5700}$$
$$= 5.1 \times 10^{-7}\,m$$

Knowing that violet light has a wavelength of about 4.0×10^{-7} meters, yellow about 5.6×10^{-7} meters, and red about 6.6×10^{-7} meters, what can we say about the color of the Sun's peak radiation? The peak wavelength of the Sun's radiation is at a slightly shorter wavelength than the color yellow, so it is a slightly greenish yellow. To see this greenish tinge to the Sun, you would have to look at it from space. It turns out that the Earth's atmosphere scatters some of the shorter waves of sunlight, which shifts its peak wavelength to pure yellow.

Remember that thermal radiation always spans a wide range of wavelengths (Figure 1.1.2) and Equation 1.1.3 only specifies the single wavelength that is the **peak** of the spectrum. So although the Sun appears yellowish-white, when you disperse sunlight with a prism you see radiation with all the colors of the rainbow. Yellow just represents a characteristic wavelength of the emission.

Exercise 1.1.1

a. At what wavelength does the sun emit most of its radiation if it has a temperature of 5,778 K?
b. At what wavelength does the earth emit most of its radiation if it has a temperature of 288 K?

Answer a available at the end of this section.

The Rayleigh-Jeans Law

Lord Rayleigh and J. H. Jeans developed an equation which explained blackbody radiation at low frequencies. The equation which seemed to express blackbody radiation was built upon all the known assumptions of physics at the time. *The big assumption which Rayleigh and Jean implied was that infinitesimal amounts of energy were continuously added to the system when the frequency was increased.* Classical physics assumed that energy emitted by atomic oscillations could have any continuous value. This was true for anything that had been studied up until that point, including things like acceleration, position, or energy. Their resulting **Rayleigh-Jeans Law** was

$$d\rho\left(\nu, T\right) = \rho_{\nu}\left(T\right) d\nu \tag{1.1.4}$$
$$= \frac{8\pi k_B T}{c^3}\nu^2 d\nu \tag{1.1.5}$$

Experimental data performed on the black box showed slightly different results than what was expected by the Rayleigh-Jeans law (Figure 1.1.5). The law had been studied and widely accepted by many physicists of the day, but the experimental results did not lie, something was different between what was theorized and what actually happens. The experimental results showed a bell type of curve, but according to the Rayleigh-Jeans law the frequency diverged as it neared the ultraviolet region (Equation 1.1.5). Ehrenfest later dubbed this the "ultraviolet catastrophe". It is important to emphasizing that Equation 1.1.5 is a **classical** result: the only inputs are classical dynamics and Maxwell's electromagnetic theory.

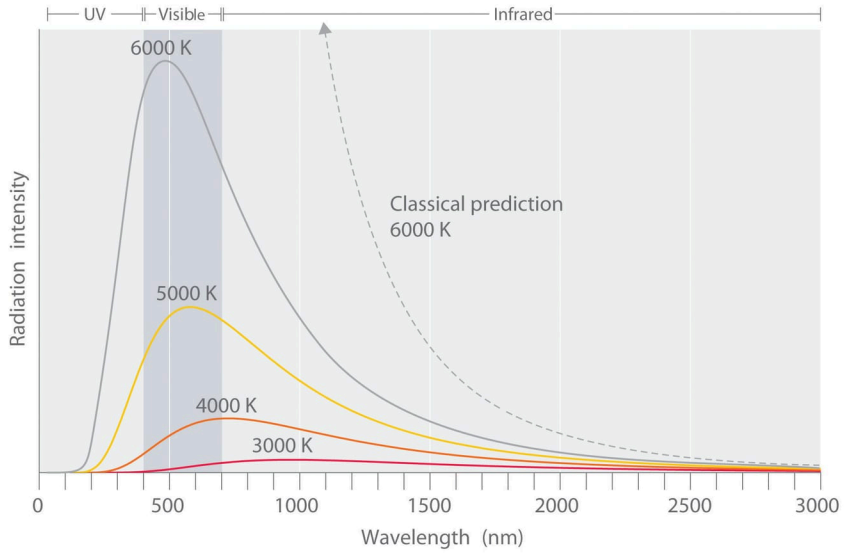


Figure 1.1.5 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 1.1.5 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. (CC BY-SA-NC 3.0; anonymous)

Differential vs. Integral Representation of the Distribution

Radiation is understood as a continuous distribution of amplitude vs. wavelength or, equivalently, amplitude vs. frequency (Figure 1.1.5). According to Rayleigh-Jeans law, the intensity at a specific frequency ν and temperature is

$$\rho(\nu, T) = \frac{8\pi k_b T \nu^2}{c^3}.$$

However, in practice, we are more interested in frequency intervals. An exact frequency is the limit of a sequence of smaller and smaller intervals. If we make the assumption that, for a sufficiently small interval, $\rho(\nu, T)$ does not vary, we get your definition for the differential $d\rho(\nu, T)$ in Equation 1.1.5:

The assumption is fair due to the continuity of $\rho(\nu, T)$. This is the approximation of an integral on a very small interval $d\nu$ by the height of a point inside this interval ($\frac{8\pi k_b T \nu^2}{c^3}$) times its length ($d\nu$). So, if we sum an infinite amount of small intervals like the one above we get an integral. The total radiation between ν_1 and ν_2 will be:

$$\begin{aligned}\int_{\nu_1}^{\nu_2} \mathrm{d}\rho(\nu, T) &= \int_{\nu_1}^{\nu_2} \rho(\nu, T)\, \mathrm{d}\nu \\ &= \int_{\nu_1}^{\nu_2} \frac{8\pi k_b T \nu^2}{c^3} \mathrm{d}\nu \\ &= 8\pi k_b T \frac{v_2^3 - v_1^3}{3c^3}.\end{aligned}$$

Observe that $\rho(\nu, T)$ is quadratic in ν.

Example 1.1.4 : The Ultraviolet Catastrophe

What is the total spectral radiance of a radiator that follows the Rayleigh-Jeans law for its emission spectrum?

Solution

The total spectral radiance $\rho_{tot}(T)$ is the combined emission over all possible wavelengths (or equivalently, frequencies), which is an integral over the relevant distribution (Equation 1.1.5 for the Rayleigh-Jeans Law).

$$\begin{aligned}\rho_{tot}(T) &= \int_0^\infty d\rho\,(\nu, T) \\ &= \int_0^\infty \frac{8\pi k_B T}{c^3}\nu^2 d\nu\end{aligned}$$

but the integral

$$\int_0^\infty x^2 \mathrm{d}x$$

does not converge. Worse, it is infinite,

$$\lim_{k\to\infty}\int_0^k x^2 \mathrm{d}x = \infty$$

Hence, the classically derived Rayleigh-Jeans law predicts that the radiance of a blackbody is **infinite**. Since radiance is power per angle and unit area, this also implies that the total power and hence the energy a blackbody emitter gives off is infinite, which is patently absurd. This is called the ultraviolet catastrophe because the absurd prediction is caused by the classical law not predicting the behavior at high frequencies/small wavelengths correctly (Figure 1.1.5).

Contributors and Attributions

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- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).
- ACuriousMind (StackExchange)

Answers

500 nm
10.0 microns

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1.2: Quantum Hypothesis Used for Blackbody Radiation Law

Learning Objectives

- To understand how energy is quantized in blackbody radiation

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could not be explained by the theories available at the time.

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation (Figure 1.2.1). Attempts to explain or calculate this spectral distribution from classical theory were complete failures. A theory developed by Rayleigh and Jeans predicted that the intensity should go to infinity at short wavelengths. Since the intensity actually drops to zero at short wavelengths, the Rayleigh-Jeans result was called the **ultraviolet catastrophe** (Figure 1.2.1 dashed line). There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

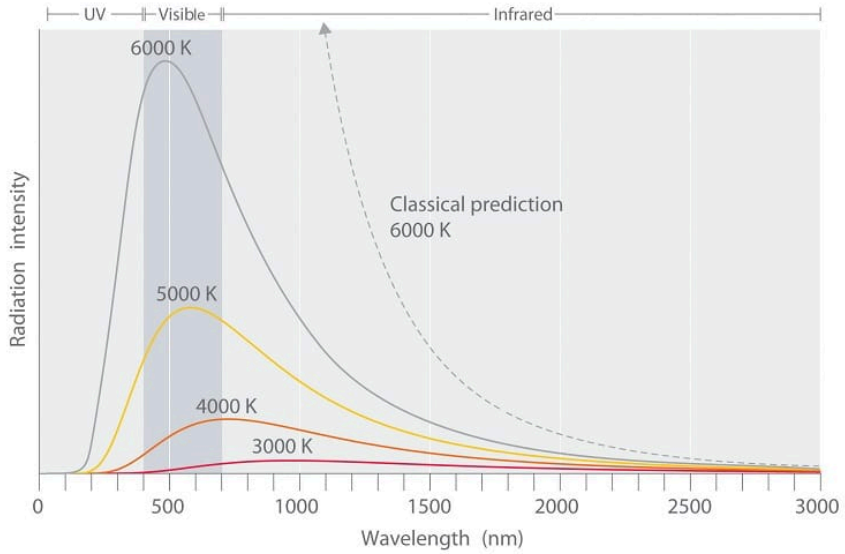


Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun. Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity. (CC BY-SA-NC; anonymous).

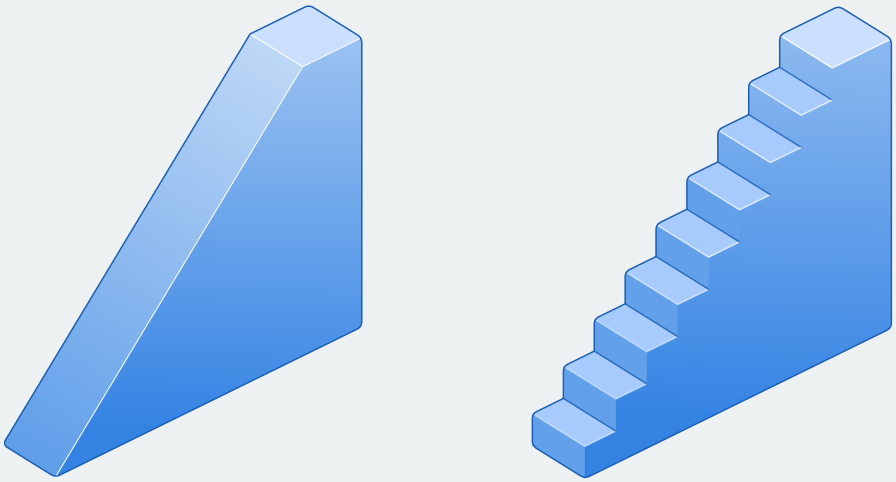
Quantizing Electrons in the Radiator

In 1900, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1.2.1 , so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral

multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum.

Quantization

Although quantization may seem to be an unfamiliar concept, we encounter it frequently in quantum mechanics (hence the name). For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. It is also similar to going up and down a hill using discrete stair steps rather than being able to move up and down a continuous slope. Your potential energy takes on discrete values as you move from step to step. Even electrical charge is quantized: an ion may have a charge of –1 or –2, but *not* –1.33 electron charges.



A continuous vs. a quantized (gravitationaly) potential energy system. In the continuous case (left) a system can have any potential energy, but in the quantized case (right), a system can only have certain values (other values are not allowed). (CC BY-NC; Ümit Kaya via LibreTexts)

Planck's quantization of energy is described by the his famous equation:

$$E = h\nu \tag{1.2.1}$$

where the proportionality constant h is called **Planck's constant**, one of the most accurately known fundamental constants in science

$$h = 6.626070040(81) \times 10^{-34}\, J \cdot s$$

However, for our purposes, its value to four significant figures is sufficient:

$$h = 6.626 \times 10^{-34}\, J \cdot s$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 1.2.1 . We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1.2.1 , and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

Max Planck explain the spectral distribution of blackbody radiation as result from oscillations of electrons. Similarly, oscillations of electrons in an antenna produce radio waves. Max Planck concentrated on modeling the oscillating charges that must exist in the oven walls, radiating heat inwards and—in thermodynamic equilibrium—themselves being driven by the radiation field. He found he could account for the observed curve if he required these oscillators not to radiate energy continuously, as the classical theory would demand, but they could **only** lose or gain energy in chunks, called **quanta**, of size $h\nu$, for an oscillator of frequency ν (Equation 1.2.1).

With that assumption, Planck calculated the following formula for the radiation energy density inside the oven:

$$d\rho(\nu,T) = \rho_\nu(T)d\nu \tag{1.2.2}$$

$$= \frac{8\pi h\nu^3}{c^3}\cdot\frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{1.2.3}$$

with

- $\pi = 3.14159$
- h = $6.626\times10^{-34}J\cdot s$
- c = $3.00\times10^{8}\ m/s$
- ν = $1/s$
- k_B = $1.38\times10^{-23}J/K$
- T is absolute temperature (in Kelvin)

Planck's radiation energy density (Equation 1.2.3) can also be expressed in terms of wavelength λ.

$$\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda k_BT}-1}\right) \tag{1.2.4}$$

With a wavelength of maximum energy density at:

$$\lambda_{max} = \frac{hc}{4.965kT}$$

This can be used to calculate the radiance emitted from surface per unit frequency

$$dB_\nu(\nu,T) = \rho_\nu(T)d\nu$$

$$= \frac{2h\nu^3}{c^2}\cdot\frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{1.2.5}$$

or

$$B_\lambda(\lambda,T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/(\lambda k_BT)}-1} \tag{1.2.6}$$

Planck's equation (Equation 1.2.4) gave an excellent agreement with the experimental observations for all temperatures (Figure 1.2.2).

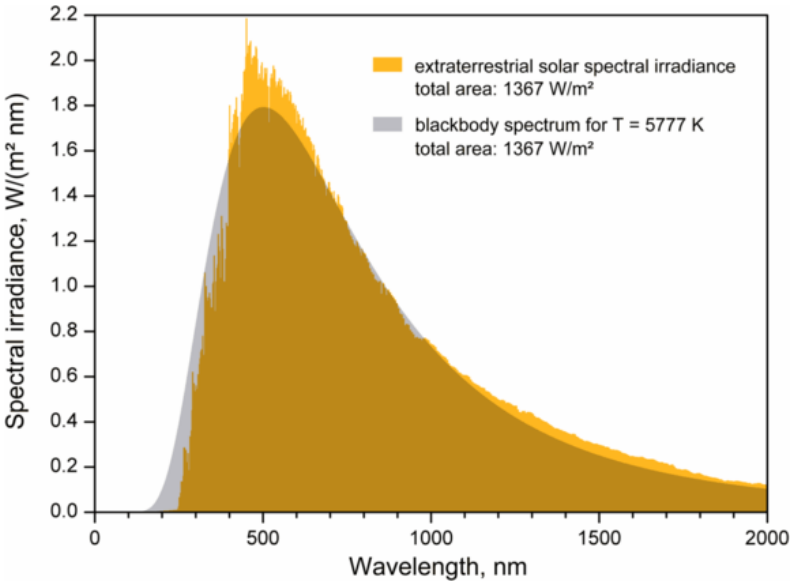
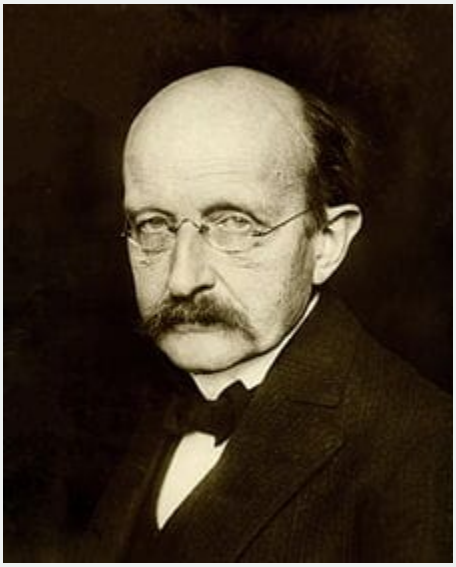


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

Max Planck (1858–1947)

Planck made many substantial contributions to theoretical physics, but his fame as a physicist rests primarily on his role as the originator of quantum theory. In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



MAX-PLANCK-GESELLSCHAFT

(left) The German physicist Max Planck had a major influence on the early development of quantum mechanics, being the first to recognize that energy is sometimes quantized. Planck also made important contributions to special relativity and classical physics. (Public Domain; Library of Congress via Wikimedia) (left) The society's logo features Minerva, the Roman goddess of wisdom. (Fair use)

One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Exercise 1.2.1

Use Equation 1.2.4 to show that the units of $\rho(\lambda, T)\ d\lambda$ are J/m^3 as expected for an energy density.

The near perfect agreement of this formula with precise experiments (e.g., Figure 1.2.3), and the consequent necessity of energy quantization, was the most important advance in physics in the century. His blackbody curve was completely accepted as the correct one: more and more accurate experiments confirmed it time and again, yet the radical nature of the quantum assumption did not sink in. Planck was not too upset—he didn't believe it either, he saw it as a technical fix that (he hoped) would eventually prove unnecessary.

> Part of the problem was that Planck's route to the formula was long, difficult and implausible—he even made contradictory assumptions at different stages, as Einstein pointed out later. However, the result was correct anyway!

The mathematics implied that the energy given off by a blackbody was not continuous, but given off at certain specific wavelengths, in regular increments. If Planck assumed that the energy of blackbody radiation was in the form

$$E = nh\nu$$

where n is an integer, then he could explain what the mathematics represented. This was indeed difficult for Planck to accept, because at the time, there was no reason to presume that the energy should only be radiated at specific frequencies. Nothing in Maxwell's laws suggested such a thing. It was as if the vibrations of a mass on the end of a spring could only occur at specific energies. Imagine the mass slowly coming to rest due to friction, but not in a continuous manner. Instead, the mass jumps from one fixed quantity of energy to another without passing through the intermediate energies.

> To use a different analogy, it is as if what we had always imagined as smooth inclined planes were, in fact, a series of closely spaced steps that only presented the illusion of continuity.

Summary

The agreement between Planck's theory and the experimental observation provided strong evidence that the energy of electron motion in matter is quantized. In the next two sections, we will see that the energy carried by light also is quantized in units of $h\bar{\nu}$. These packets of energy are called "photons."

Contributors and Attributions

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1.3: Photoelectric Effect Explained with Quantum Hypothesis

Learning Objectives

- To be familiar with the photoelectron effect for bulk materials
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light wavelength
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light intensity
- Describe what a workfunction is and relate it to ionization energy
- Describe the photoelectric effect with Einstein's quantized photon model of light

Nature, it seemed, was quantized (non-continuous, or discrete). If this was so, how could Maxwell's equations correctly predict the result of the blackbody radiator? Planck spent a good deal of time attempting to reconcile the behavior of electromagnetic waves with the discrete nature of the blackbody radiation, to no avail. It was not until 1905, with yet another paper published by Albert Einstein, that the wave nature of light was expanded to include the particle interpretation of light which adequately explained Planck's equation.

The photoelectric effect was first documented in 1887 by the German physicist Heinrich Hertz and is therefore sometimes referred to as the Hertz effect. While working with a spark-gap transmitter (a primitive radio-broadcasting device), Hertz discovered that upon absorption of certain frequencies of light, substances would give off a visible spark. In 1899, this spark was identified as light-excited electrons (called **photoelectrons**) leaving the metal's surface by J.J. Thomson (Figure 1.3.1).

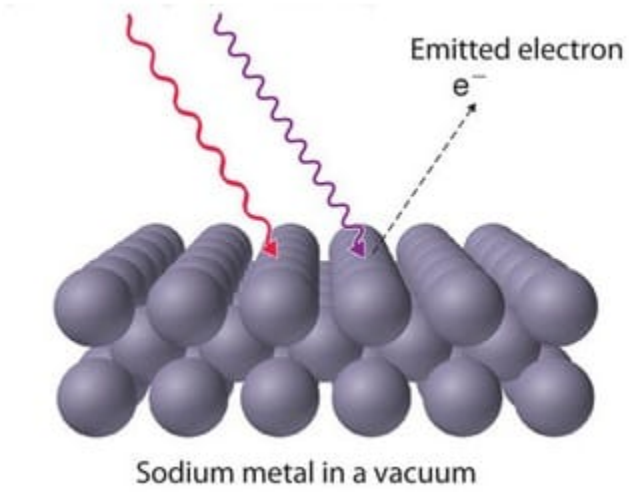


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

The classical picture underlying the photoelectron effect was that the atoms in the metal contained electrons, that were shaken and caused to vibrate by the oscillating electric field of the incident radiation. Eventually some of them would be shaken loose, and would be ejected from the cathode. It is worthwhile considering carefully how the *number* and *speed* of electrons emitted would be expected to vary with the *intensity* and *color* of the incident radiation along with the time needed to observe the photoelectrons.

- Increasing the intensity of radiation would shake the electrons more violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average.
- Increasing the frequency of the radiation would shake the electrons faster, so it might cause the electrons to come out faster. For very dim light, it would take some time for an electron to work up to a sufficient amplitude of vibration to shake loose.

Lenard's Experimental Results (Intensity Dependence)

In 1902, Hertz's student, Philipp Lenard, studied how the energy of the emitted photoelectrons varied with the intensity of the light. He used a carbon arc light and could increase the intensity a thousand-fold. The ejected electrons hit another metal plate, the collector, which was connected to the cathode by a wire with a sensitive ammeter, to measure the current produced by the illumination (Figure 1.3.2). To measure the energy of the ejected electrons, Lenard charged the collector plate negatively, to repel the electrons coming towards it. Thus, only electrons ejected with enough kinetic energy to get up this potential hill would contribute to the current.

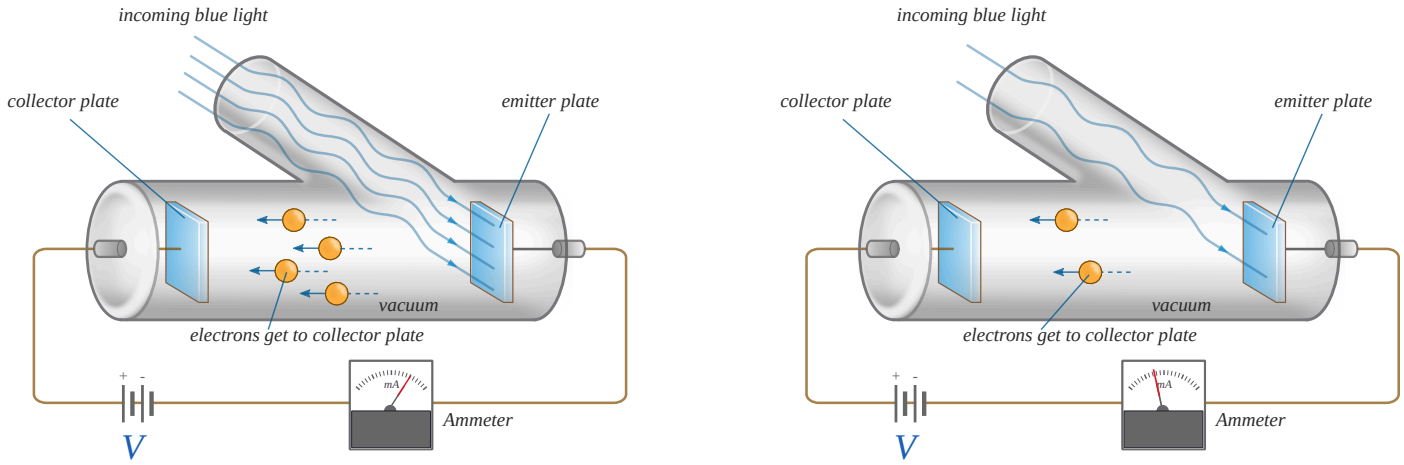


Figure 2: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Lenard discovered that there was a well defined minimum voltage that stopped any electrons getting through (V_{stop}). To Lenard's surprise, he found that V_{stop} did not depend at all on the intensity of the light! Doubling the light intensity doubled the *number* of electrons emitted, but did not affect the *kinetic energies* of the emitted electrons. The more powerful oscillating field ejected more electrons, but the maximum individual energy of the ejected electrons was the same as for the weaker field (Figure 1.3.2).

Millikan's Experimental Results (Wavelength Dependence)

The American experimental physicist Robert Millikan followed up on Lenard's experiments and using a powerful arc lamp, he was able to generate sufficient light intensity to separate out the colors and check the photoelectric effect using light of different colors. He found that the maximum energy of the ejected electrons *did* depend on the color - the shorter wavelength, higher frequency light eject photoelectrons with greater kinetic energy (Figures 1.3.3).

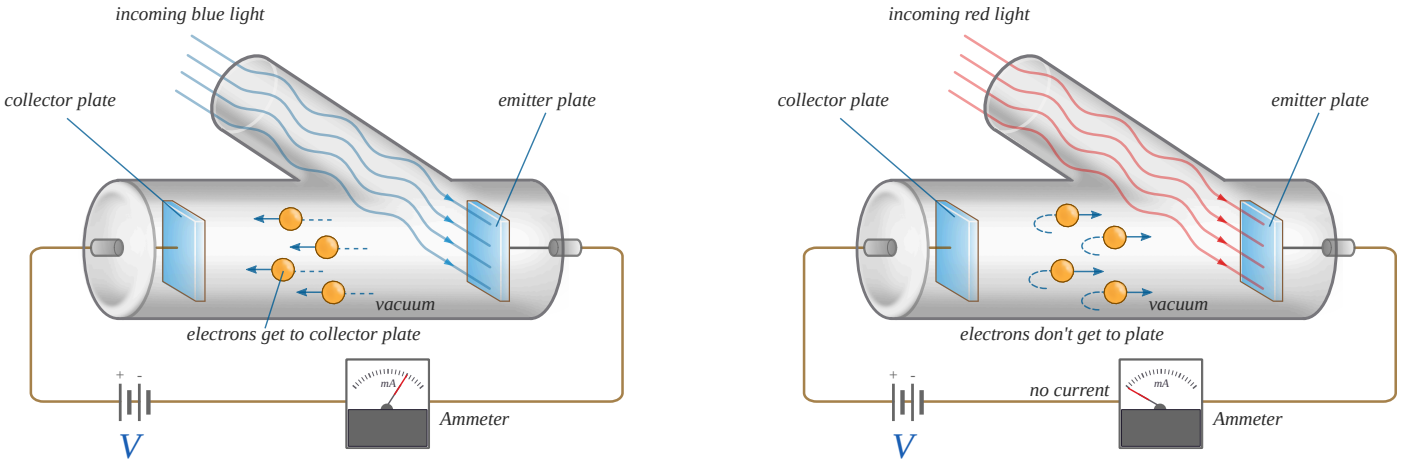


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than V_{stop}, for blue light. (right) Indicent low-energy red light. Since the electrons ejected by the red light are not getting to the collector plate, the potential supplied by the battery exceeds V_{stop} for red light. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 1.3.4 , just the opposite behavior from classical is observed from Lenard's and Millikan's experiments. The intensity affects the number of electrons, and the frequency affects the kinetic energy of the emitted electrons. From these sketches, we see that

- the kinetic energy of the electrons is linearly proportional to the frequency of the incident radiation above a threshold value of ν_0 (no current is observed below ν_0), and the kinetic energy is independent of the intensity of the radiation, and
- the number of electrons (i.e. the electric current) is proportional to the intensity and independent of the frequency of the incident radiation above the threshold value of ν_0 (i.e., no current is observed below ν_0).

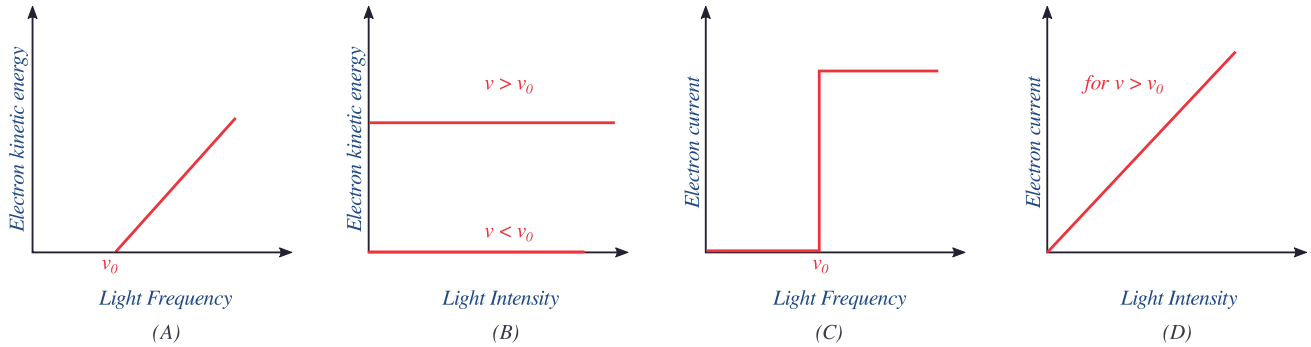


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the light intensity above the threshold frequency and zero below. (C) The number of electrons emitted per second (i.e. the electric current) is independent of light frequency above the threshhold frequency and zero below. (D) The number of electrons increases linearly with the light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Classical Theory does not Describe Experiment

Classical theory predicts that energy carried by light is proportional to its amplitude independent of its frequency, and this fails to correctly explain the observed wavelength dependence in Lenard's and Millikan's observations.

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex

physics and instrumentation, which will be ignored for now.

Einstein's Quantum Picture

In 1905 Einstein gave a very simple interpretation of Lenard's results and borrowed Planck's hypothesis about the quantized energy from his blackbody research and assumed that the incoming radiation should be thought of as quanta of energy $h\nu$, with ν the frequency. In photoemission, one such quantum is absorbed by one electron. If the electron is some distance into the material of the cathode, some energy will be lost as it moves towards the surface. There will always be some electrostatic cost as the electron leaves the surface, which is the workfunction, Φ. The most energetic electrons emitted will be those very close to the surface, and they will leave the cathode with kinetic energy

$$KE = h\nu - \Phi \tag{1.3.1}$$

On cranking up the negative voltage on the collector plate until the current just stops, that is, to V_{stop}, the highest kinetic energy electrons (KE_e) must have had energy eV_{stop} upon leaving the cathode. Thus,

$$eV_{stop} = h\nu - \Phi \tag{1.3.2}$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and V_{stop} plotted as a function of frequency, the slope of the line should be $\frac{h}{e}$ (Figure $1.3.4A$). It is also clear that there is a minimum light frequency for a given metal ν_o, that for which the quantum of energy is equal to Φ (Equation 1.3.1). Light below that frequency, no matter how bright, will not eject electrons.

> According to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum *frequency* ν_0 needed to eject an electron with no residual energy.

Since every photon of sufficient energy excites only one electron, increasing the light's intensity (i.e. the number of photons/sec) only increases the *number* of released electrons and not their kinetic energy. In addition, no time is necessary for the atom to be heated to a critical temperature and therefore the release of the electron is nearly instantaneous upon absorption of the light. Finally, because the photons must be above a certain energy to satisfy the workfunction, a threshold frequency exists below which no photoelectrons are observed. This frequency is measured in units of Hertz (1/second) in honor of the discoverer of the photoelectric effect.

Einstein's Equation 1.3.1 explains the properties of the photoelectric effect quantitatively. A strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy $E = h\nu$ can be transferred to an actual particle (an electron), imparting kinetic energy to it, just as in an elastic collision between to massive particles such as billiard balls.

> Robert Millikan initially did not accept Einstein's theory, which he saw as an attack on the wave theory of light, and worked for ten years until 1916, on the photoelectric effect. He even devised techniques for scraping clean the metal surfaces inside the vacuum tube. For all his efforts he found disappointing results: he confirmed Einstein's theory after ten years. In what he writes in his paper, Millikan is still desperately struggling to avoid this conclusion. However, by the time of his Nobel Prize acceptance speech, he has changed his mind rather drastically!

Einstein's simple explanation (Equation 1.3.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new field of photoelectron spectroscopy. Einstein's theory of the photoelectron presented a completely different way to measure Planck's constant than from black-body radiation.

The Workfunction (Φ)

The **workfunction** is an intrinsic property of the metal. While the workfunctions and ionization energies appear as similar concepts, they are independent. The workfunction of a metal is the minimum amount of energy (E) necessary to remove an electron from the surface of the bulk (*solid*) metal (sometimes referred to as **binding energy**).

$$\mathrm{M(s) + \Phi \rightarrow M^+(s) + e^-(free\ with\ no\ kinetic\ energy)}$$

The workfunction is qualitatively similar to ionization energy (IE), which is the amount of energy required to remove an electron from an atom or molecule in the *gaseous* state.

$$\mathrm{M(g) + IE\ \rightarrow M^+(g) + e^-(free\ with\ no\ kinetic\ energy)}$$

However, these two energies differ in magnitude (Table 1.3.1). For instance, copper has a workfunction of about 4.7 eV, but has a higher ionization energy of 7.7 eV. Generally, the ionization energies for metals are greater than the corresponding workfunctions (i.e., the electrons are less tightly bound in bulk metal).

Table 1.3.1 : Workfunctions and Ionization Energies of Select Elements

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Lithium (Li)	2.93	5.39
Beryllium (Be)	4.98	9.32
Boron (B)	4.45	8.298
Carbon (C)	5.0	11.26
Sodium (Na)	2.36	5.13
Aluminum (Al)	4.20	5.98
Silicon (Si)	4.85	8.15
Potassium (K)	2.3	4.34
Iron (Fe)	4.67	7.87
Cobalt (Co)	4.89	7.88
Copper (Cu)	4.7	7.7
Gallium (Ga)	4.32	5.99
Germanium (Ge)	5.0	7.89
Arsenic (As)	3.75	9.81
Selenium (Se)	5.9	9.75
Silver (Ag)	4.72	7.57
Tin (Sn)	4.42	7.34
Cesium (Cs)	1.95	3.89
Gold (Au)	5.17	9.22
Mercury $(Hg)_{liquid}$	4.47	10.43
Bismuth (Bi)	4.34	7.29

Example 1.3.1 : Calcium

a. What is the energy in joules and electron volts of a photon of 420-nm violet light?
b. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the workfunction for calcium metal is 2.71 eV?

Strategy

To solve part (a), note that the energy of a photon is given by $E = h\nu$. For part (b), once the energy of the photon is calculated, it is a straightforward application of Equation 1.3.1 to find the ejected electron's maximum kinetic energy, since Φ is given.

Solution for (a)

Photon energy is given by

$$E = h\nu$$

Since we are given the wavelength rather than the frequency, we solve the familiar relationship $c = \nu\lambda$ for the frequency, yielding

$$\nu = \frac{c}{\lambda}$$

Combining these two equations gives the useful relationship

$$E = \frac{hc}{\lambda}$$

Now substituting known values yields

$$\begin{aligned} E &= \frac{(6.63 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{420 \times 10^{-9}\ m} \\ &= 4.74 \times 10^{-19}\ J \end{aligned}$$

Converting to eV, the energy of the photon is

$$\begin{aligned} E &= (4.74 \times 10^{-19}\ J)\left(\frac{1\ eV}{1.6 \times 10^{-19}\ J}\right) \\ &= 2.96\ eV. \end{aligned}$$

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of Equation 1.3.1. Substituting the photon energy and binding energy yields

$$\begin{aligned} KE_e &= h\nu – \Phi \\ &= 2.96\ eV – 2.71\ eV \\ &= 0.246\ eV. \end{aligned}$$

Discussion

The energy of this 420-nm photon of violet light is a tiny fraction of a joule, and so it is no wonder that a single photon would be difficult for us to sense directly—humans are more attuned to energies on the order of joules. But looking at the energy in electron volts, we can see that this photon has enough energy to affect atoms and molecules. A DNA molecule can be broken with about 1 eV of energy, for example, and typical atomic and molecular energies are on the order of eV, so that the UV photon in this example could have biological effects.

The ejected electron (called a photoelectron) has a rather low energy, and it would not travel far, except in a vacuum. The electron would be stopped by a retarding potential of 0.26 eV. In fact, if the photon wavelength were longer and its energy less than 2.71 eV, then the formula would give a negative kinetic energy, an impossibility. This simply means that the 420-nm photons with their 2.96-eV energy are not much above the frequency threshold. You can show for yourself that the threshold wavelength is 459 nm (blue light). This means that if calcium metal is used in a light meter, the meter will be insensitive to wavelengths longer than those of blue light. Such a light meter would be insensitive to red light, for example.

Exercise 1.3.1 : Silver

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver? Is this in the visible range?

Answer available at the end of this section.

Exercise 1.3.2

Why is the workfunction of an element generally lower than the ionization energy of that element?

Answer available at the end of this section.

Summary

Although Hertz discovered the photoelectron in 1887, it was not until 1905 that a theory was proposed that explained the effect completely. The theory was proposed by Einstein and it made the claim that electromagnetic radiation had to be thought of as a series of particles, called photons, which collide with the electrons on the surface and emit them. This theory ran contrary to the belief that electromagnetic radiation was a wave and thus it was not recognized as correct until 1916 when Robert Millikan experimentally confirmed the theory

The photoelectric effect is the process in which electromagnetic radiation ejects electrons from a material. Einstein proposed photons to be quanta of electromagnetic radiation having energy $E = h\nu$ is the frequency of the radiation. All electromagnetic radiation is composed of photons. As Einstein explained, all characteristics of the photoelectric effect are due to the interaction of individual photons with individual electrons. The maximum kinetic energy KE_e of ejected electrons (photoelectrons) is given by $KE_e = h\nu$–Φ, where $h\nu$ is the photon energy and Φ is the workfunction (or binding energy) of the electron to the particular material.

Conceptual Questions

1. Is visible light the only type of electromagnetic radiation that can cause the photoelectric effect?
2. Which aspects of the photoelectric effect cannot be explained without photons? Which can be explained without photons? Are the latter inconsistent with the existence of photons?
3. Is the photoelectric effect a direct consequence of the wave character of electromagnetic radiation or of the particle character of electromagnetic radiation? Explain briefly.
4. Insulators (nonmetals) have a higher Φ than metals, and it is more difficult for photons to eject electrons from insulators. Discuss how this relates to the free charges in metals that make them good conductors.
5. If you pick up and shake a piece of metal that has electrons in it free to move as a current, no electrons fall out. Yet if you heat the metal, electrons can be boiled off. Explain both of these facts as they relate to the amount and distribution of energy involved with shaking the object as compared with heating it.

Contributors and Attributions

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Answers

Given that the workfunction is 4.72 eV from Table 1.3.1 , then only photons with wavelengths lower than 263 nm will induce photoelectrons (calculated via $E = h\nu$). This is ultraviolet and not in the visible range.

The workfunction of a metal refers to the minimum energy required to extract an electron from the surface of a (**bulk**) metal by the absorption a photon of light. The workfunction will vary from metal to metal. In contrast, ionization energy is the energy needed to detach electrons from **atoms** and also varies with each particular atom, with the valence electrons require less energy to extract than core electrons (i.e., from lower shells) that are more closely bound to the nuclei. The electrons in the metal lattice there less bound (i.e., free to move within the metal) and removing one of these electrons is much easier than removing an electron from an atom because the metallic bonds of the bulk metal reduces their binding energy. As we will show in subsequent chapters, the more delocalized a particle is, the lower its energy.

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1.4: The Hydrogen Atomic Spectrum

Overview

- To introduce the concept of absorption and emission line spectra and describe the Balmer equation to describe the visible lines of atomic hydrogen.

The first person to realize that white light was made up of the colors of the rainbow was Isaac Newton, who in 1666 passed sunlight through a narrow slit, then a prism, to project the colored spectrum on to a wall. This effect had been noticed previously, of course, not least in the sky, but previous attempts to explain it, by Descartes and others, had suggested that the white light became colored when it was refracted, the color depending on the angle of refraction. Newton clarified the situation by using a second prism to reconstitute the white light, making much more plausible the idea that the white light was composed of the separate colors. He then took a monochromatic component from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

Atomic Line Spectra

The spectrum of hydrogen *atoms*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Ångström in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Ångström, the son of a country minister, was a reserved person, not interested in the social life that centered around the court. Consequently, it was many years before his achievements were recognized, at home or abroad (most of his results were published in Swedish).

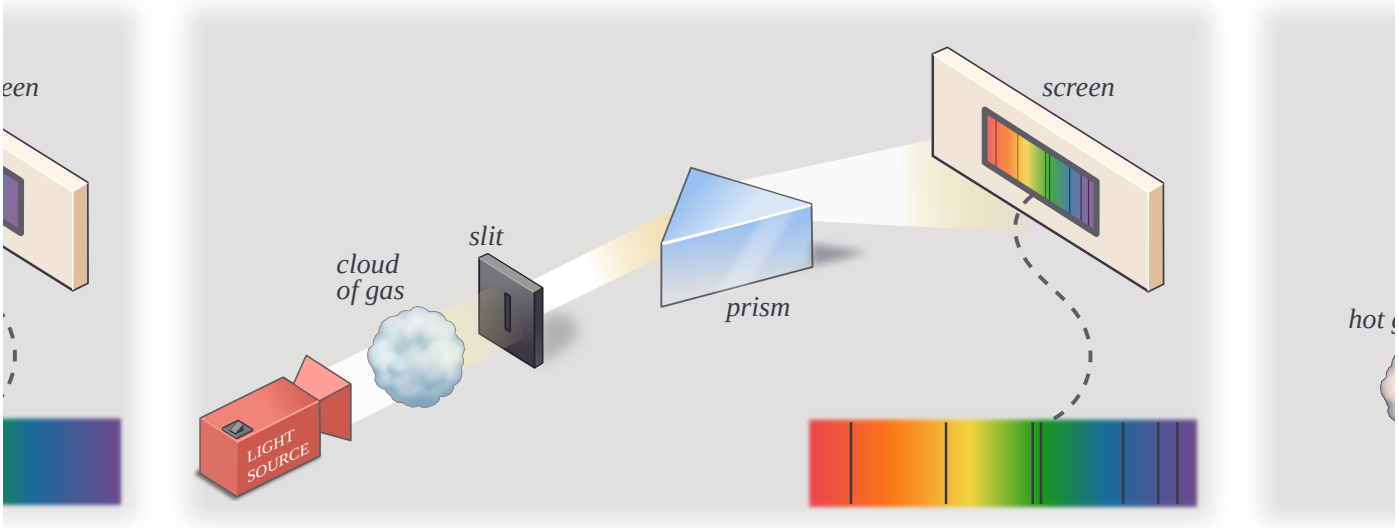


Figure 1.4.1 : Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen without the continuous source behind it, its atoms produce emission lines. We can learn which types of atoms are in the gas cloud from the pattern of absorption or emission lines. (CC BY-NC; Ümit Kaya via LibreTexts).

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.4.1 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure (e.g., blackbody radiation is a continuum). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas,

consisting of a series of dark lines characteristic of the composition of the gas.

Fraunhofer Lines

In 1802, William Wollaston in England had discovered that the solar spectrum had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table 1.4.1). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

Table 1.4.1 : Major Fraunhofer lines and the elements they are associated with.

Designation	Element	Wavelength (nm)
y	O_2	898.765
Z	O_2	822.696
A	O_2	759.370
B	O_2	686.719
C	H	656.281
a	O_2	627.661
D_1	Na	589.592
D_2	Na	588.995
D_3 or d	He	587.5618

The Fraunhofer lines are typical spectral absorption lines. These dark lines are produced whenever a cold gas is between a broad spectrum photon source and the detector. In this case, a decrease in the intensity of light in the frequency of the incident photon is seen as the photons are absorbed, then re-emitted in random directions, which are mostly in directions different from the original one. This results in an *absorption line*, since the narrow frequency band of light initially traveling toward the detector, has been turned into heat or re-emitted in other directions.

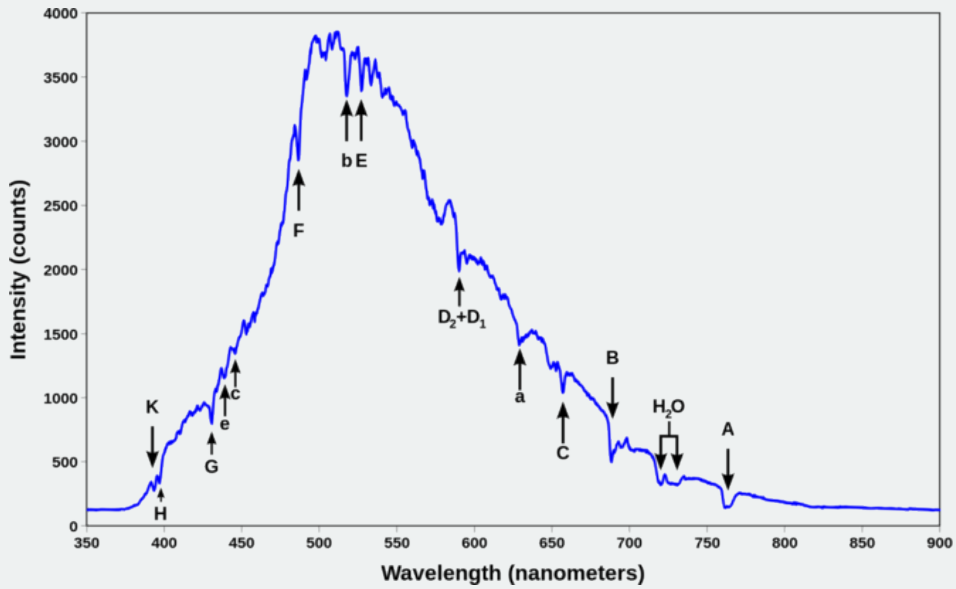


Figure 1.4.2 : Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun, Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure 1.4.3 .

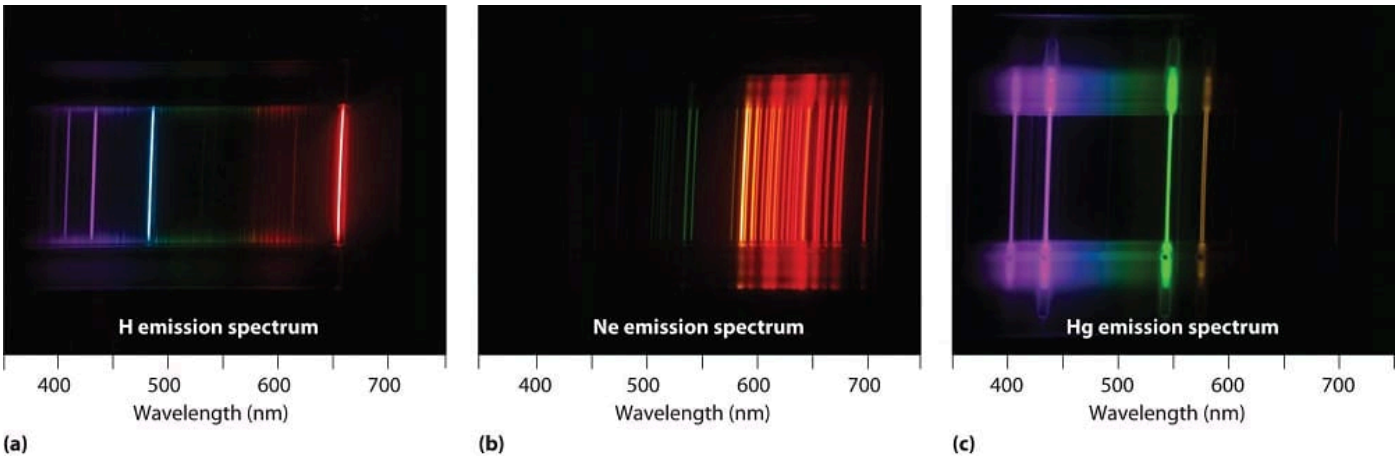


Figure 1.4.3 : The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV; these are not shown. (CC BY-SA-NC; Anonymous by request).

The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specific atom (in contract to the mixture that Fraunhofer lines represent), that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before and made his great discovery when he was almost sixty.

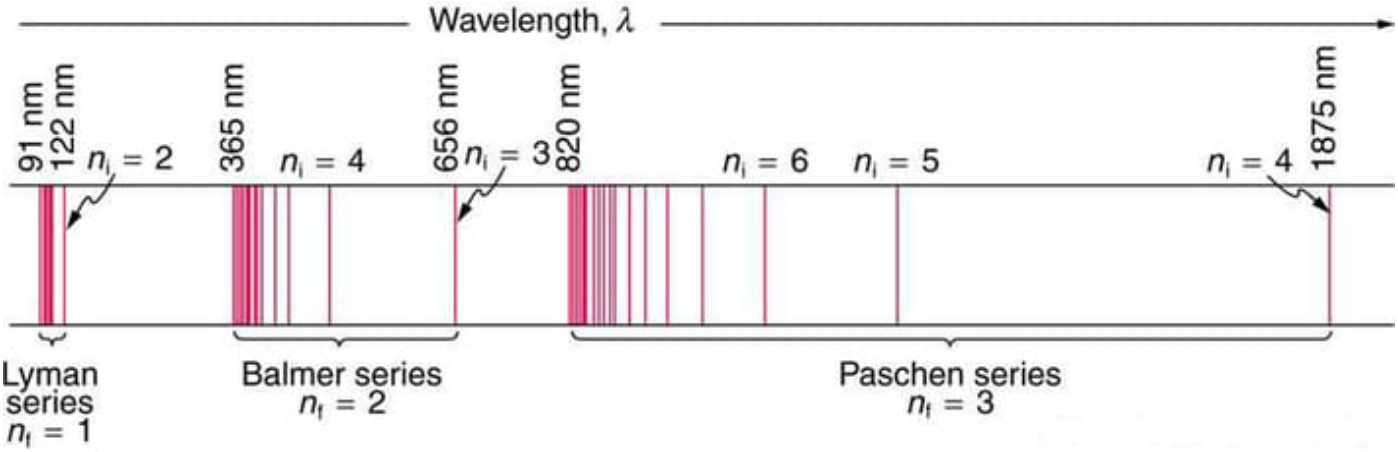


Figure 1.4.4 : A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and n_i are shown for some of the lines (CC BY-SA; OpenStax).

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Ångström had

measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure 1.4.4). Balmer concentrated on just these four numbers, and found they were represented by the phenomenological formula:

$$\lambda = b\left(\frac{n_2^2}{n_2^2 - 4}\right) \tag{1.4.1}$$

where b = 364.56 nm and $n_2 = 3, 4, 5, 6$.

The first four wavelengths of Equation 1.4.1 (with n_2 = 3, 4, 5, 6) were in excellent agreement with the experimental lines from Ångström (Table 1.4.2). Balmer predicted that other lines exist in the ultraviolet that correspond to $n_2 \geq 7$ and in fact some of them had already been observed, unbeknown to Balmer.

Table 1.4.2 : The Balmer Series of Hydrogen Emission Lines

n_2	3	4	5	6	7	8	9	10
λ	*656*	*486*	*434*	*410*	397	389	383	380
color	*red*	*teal*	*blue*	*indigo*	violet	not visible	not visible	not visible

The n_2 integer in the Balmer series extends theoretically to infinity and the series represents a monotonically increasing energy (and frequency) of the absorption lines with increasing n_2 values. Moreover, the energy difference between successive lines decreased as n_2 increases (1.4.4). This behavior converges to a highest possible energy as Example 1.4.1 demonstrates. If the lines are plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure 1.4.4 ; these lines are called the **Balmer series**.

Balmer's general formula (Equation 1.4.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.4.2}$$

$$= R_H\left(\frac{1}{4} - \frac{1}{n_2^2}\right) \tag{1.4.3}$$

where $n_2 = 3, 4, 5, 6$ and R_H is the Rydberg constant (discussed in the next section) equal to 109,737 cm^{-1}.

He further conjectured that the 4 could be replaced by 9, 16, 25, ... and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines.

The Wavenumber as a Unit of Frequency

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda\nu = c$$

In the SI system of units the wavelength, (λ) is measured in meters (m) and since wavelengths are usually very small one often uses the nanometer (nm) which is 10^{-9} m. The frequency (ν) in the SI system is measured in reciprocal seconds 1/s – which is called a Hertz (after the discover of the photoelectron effect) and is represented by Hz.

It is common to use the reciprocal of the wavelength in centimeters as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by ($\tilde{\nu}$) and is defined by

$$\tilde{\nu} = \frac{1}{\lambda}$$
$$= \frac{\nu}{c}$$

Wavenumbers is a convenient unit in spectroscopy because it is directly proportional to energy.

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= hc \times \frac{1}{\lambda} \\ &= hc\tilde{\nu} \\ &\propto \tilde{\nu} \end{aligned}$$

Example 1.4.1 : Balmer Series

Calculate the longest and shortest wavelengths (in nm) emitted in the Balmer series of the hydrogen atom emission spectrum.

Solution

From the behavior of the Balmer equation (Equation 1.4.1 and Table 1.4.2), the value of n_2 that gives the longest (i.e., greatest) wavelength (λ) is the smallest value possible of n_2, which is (n_2=3) for this series. This results in

$$\begin{aligned} \lambda_{longest} &= (364.56\ nm)\left(\frac{9}{9-4}\right) \\ &= (364.56\ nm)\,(1.8) \\ &= 656.2\ nm \end{aligned}$$

This is also known as the H_α line of atomic hydrogen and is bright red (Figure $1.4.3a$).

For the shortest wavelength, it should be recognized that the shortest wavelength (greatest energy) is obtained at the limit of greatest (n_2):

$$\lambda_{shortest} = \lim_{n_2 \to \infty} (364.56\ nm)\left(\frac{n_2^2}{n_2^2-4}\right)$$

This can be solved via L'Hôpital's Rule, or alternatively the limit can be expressed via the equally useful energy expression (Equation 1.4.3) and simply solved:

$$\begin{aligned} \tilde{\nu}_{greatest} &= \lim_{n_2 \to \infty} R_H\left(\frac{1}{4} - \frac{1}{n_2^2}\right) \\ &= \lim_{n_2 \to \infty} R_H\left(\frac{1}{4}\right) \\ &= 27,434\ cm^{-1} \end{aligned}$$

Since $\frac{1}{\tilde{\nu}} = \lambda$ in units of cm, this converts to 364 nm as the shortest wavelength possible for the Balmer series.

The Balmer series is particularly useful in astronomy because the Balmer lines appear in numerous stellar objects due to the abundance of hydrogen in the universe, and therefore are commonly seen and relatively strong compared to lines from other elements.

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1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum

Learning Objectives

- Describe Rydberg's theory for the hydrogen spectra.
- Interpret the hydrogen spectrum in terms of the energy states of electrons.

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in atomic hydrogen in what we now know as the Balmer series. Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg suggested that all atomic spectra formed families with this pattern (he was unaware of Balmer's work). It turns out that there are families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the Balmer formula, and low values of n_2 predicted wavelengths that deviate considerably.

Rydberg's phenomenological equation is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.5.1}$$

$$= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.5.2}$$

where R_H is the **Rydberg constant** and is equal to 109,737 cm^{-1} ($2.18 \times 10^{-18}\ J$) and n_1 and n_2 are integers (whole numbers) with $n_2 > n_1$.

For the Balmer lines, $n_1 = 2$ and n_2 can be any whole number between 3 and infinity. The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

Other Series

The results given by Balmer and Rydberg for the spectrum in the visible region of the electromagnetic radiation start with $n_2 = 3$, and $n_1 = 2$. Is there a different series with the following formula (e.g., $n_1 = 1$)?

$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{1.5.3}$$

The values for n_2 and wavenumber $\tilde{\nu}$ for this series would be:

Table 1.5.1 : The Lyman Series of Hydrogen Emission Lines ($n_1 = 1$)

n_2	2	3	4	5	...
λ (nm)	121	102	97	94	...
$\tilde{\nu}$ (cm^{-1})	82,2291	97,530	102,864	105,332	...

Do you know in what region of the electromagnetic radiation these lines are? Of course, these lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of more series. For example, the series with $n_1 = 3$ and $n_2 = 4, 5, 6, 7, \ldots$ is called **Paschen series**.

Other Series

The spectral lines are grouped into series according to n_1 values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. For example, the ($n_1 = 1/n_2 = 2$) line is called "Lyman-alpha" (Ly-α), while the ($n_1 = 3/n_2 = 7$) line is called "Paschen-delta" (Pa-δ). The first six series have specific names:

- Lyman series with $n_1 = 1$
- Balmer series with $n_1 = 2$
- Paschen series (or Bohr series) with $n_1 = 3$
- Brackett series with $n_1 = 4$
- Pfund series with $n_1 = 5$
- Humphreys series with $n_1 = 6$

Example 1.5.1 : The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the *n* = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy

A. Substitute the appropriate values into Equation 1.5.2 (the Rydberg equation) and solve for λ.
B. Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution

We can use the Rydberg equation (Equation 1.5.2) to calculate the wavelength:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Solution A

For the Lyman series, $n_1 = 1$.

$$\begin{aligned} \frac{1}{\lambda} &= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= 1.097 \times 10^7 \, m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) \\ &= 8.228 \times 10^6 \, m^{-1} \end{aligned}$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit (wavenumbers) is particularly convenient. We can convert the answer in part A to cm^{-1}.

$$\begin{aligned}\tilde{\nu} &= \frac{1}{\lambda} \\ &= 8.228 \times 10^6 \cancel{m^{-1}} \left(\frac{\cancel{m}}{100\ cm}\right) \\ &= 82,280\ cm^{-1}\end{aligned}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm$$

This emission line is called Lyman alpha and is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

Solution B

his wavelength is in the ultraviolet region of the spectrum.

Exercise 1.5.1 : The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n_1 = 5$. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer available at the end of this section.

The above discussion presents only a phenomenological description of hydrogen emission lines and fails to provide a probe of the nature of the atom itself. Clearly a continuum model based on classical mechanics is not applicable, and as the next Section demonstrates, a simple connection between spectra and atomic structure can be formulated.

Answers

$4.65 \times 10^3\ nm$; infrared

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1.6: Matter Has Wavelike Properties

Learning Objectives

- To introduce the wave-particle duality of light extends to matter
- To describe how matter (e.g., electrons and protons) can exhibit wavelike properties, e.g., interference and diffraction patterns
- To use algebra to find the de Broglie wavelength or momentum of a particle when either one of these quantities is given

The next real advance in understanding the atom came from an unlikely quarter - a student prince in Paris. Prince Louis de Broglie was a member of an illustrious family, prominent in politics and the military since the 1600's. Louis began his university studies with history, but his elder brother Maurice studied x-rays in his own laboratory, and Louis became interested in physics. After World War I, de Broglie focused his attention on Einstein's two major achievements, the theory of special relativity and the quantization of light waves. He wondered if there could be some connection between them. Perhaps the quantum of radiation really should be thought of as a particle. De Broglie suggested that if waves (photons) could behave as particles, as demonstrated by the photoelectric effect, then the converse, namely that particles could behave as waves, should be true. He associated a wavelength λ to a particle with momentum p using Planck's constant as the constant of proportionality:

$$\lambda = \frac{h}{p} \tag{1.6.1}$$

which is called the **de Broglie wavelength**. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the **wave-particle duality**.

Deriving the de Broglie Wavelength

From the discussion of the photoelectric effect, we have the first part of the particle-wave duality, namely, that electromagnetic waves can behave like particles. These particles are known as *photons*, and they move at the speed of light. Any particle that moves at or near the speed of light has kinetic energy given by Einstein's special theory of relatively. In general, a particle of mass m and momentum p has an energy

$$E = \sqrt{p^2c^2 + m^2c^4} \tag{1.6.2}$$

Note that if $p = 0$, this reduces to the famous rest-energy expression $E = mc^2$. However, photons are massless particles (technically rest-massless) that always have a finite momentum p. In this case, Equation 1.6.2 becomes

$$E = pc.$$

From Planck's hypothesis, one quantum of electromagnetic radiation has energy $E = h\nu$. Thus, equating these two expressions for the kinetic energy of a photon, we have

$$h\nu = \frac{hc}{\lambda} = pc \tag{1.6.3}$$

Solving for the wavelength λ gives Equation 1.6.1:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

where v is the velocity of the particle. Hence, de Broglie argued that if particles can behave as waves, then a relationship like this, which pertains particularly to waves, should also apply to particles.

Equation 1.6.1 allows us to associate a wavelength λ to a particle with momentum p. As the momentum increases, the wavelength decreases. In both cases, this means the energy becomes larger. i.e., short wavelengths *and* high momenta correspond to high

energies.

> It is a common feature of quantum mechanics that particles and waves with short wavelengths correspond to high energies and vice versa.

Having decided that the photon might well be a particle with a rest mass, even if very small, it dawned on de Broglie that in other respects it might not be too different from other particles, especially the very light electron. In particular, maybe the electron also had an associated wave. The obvious objection was that if the electron was wavelike, why had no diffraction or interference effects been observed? But there was an answer. If de Broglie's relation between momentum and wavelength also held for electrons, the wavelength was sufficiently short that these effects would be easy to miss. As de Broglie himself pointed out, the wave nature of light is not very evident in everyday life. As the next section will demonstrate, the validity of de Broglie's proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both electrons (i.e., matter) and electromagnetic radiation (i.e., light).

Example 1.6.1 : Electron Waves

Calculate the de Broglie wavelength for an electron with a kinetic energy of 1000 eV.

Solution

To calculate the de Broglie wavelength (Equation 1.6.1), the momentum of the particle must be established and requires knowledge of both the mass and velocity of the particle. The mass of an electron is $9.109383 \times 10^{-28}\ g$ and the velocity is obtained from the given kinetic energy of 1000 eV:

$$\begin{aligned} KE &= \frac{mv^2}{2} \\ &= \frac{p^2}{2m} = 1000\ eV \end{aligned}$$

Solve for momentum

$$p = \sqrt{2mKE}$$

convert to SI units

$$p = \sqrt{(1000\ \cancel{eV})\left(\frac{1.6 \times 10^{-19}\ J}{1\ \cancel{eV}}\right)(2)(9.109383 \times 10^{-31}\ kg)}$$

expanding definition of joule into base SI units and cancel

$$\begin{aligned} p &= \sqrt{(3.1 \times 10^{-16}\ kg \cdot m^2/s^2)(9.109383 \times 10^{-31}\ kg)} \\ &= \sqrt{2.9 \times 10^{-40}\, kg^2\ m^2/s^2} \\ &= 1.7 \times 10^{-23} kg \cdot m/s \end{aligned}$$

Now substitute the momentum into the equation for de Broglie's wavelength (Equation 1.6.1) with Planck's constant ($h = 6.626069 \times 10^{-34}\ J \cdot s$). After expanding units in Plank's constant

$$\begin{aligned}\lambda &= \frac{h}{p} \\ &= \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{1.7 \times 10^{-23} kg \cdot m/s} \\ &= 3.87 \times 10^{-11}\ m \\ &= 38.9\ pm\end{aligned}$$

Exercise 1.6.1 : Baseball Waves

Calculate the de Broglie wavelength for a fast ball thrown at 100 miles per hour and weighing 4 ounces. Comment on whether the wave properties of baseballs could be experimentally observed.

Answer available at the end of this section.

Exercise 1.6.2 : Electrons vs. Protons

If an electron and a proton have the same velocity, which would have the longer de Broglie wavelength?

a. The electron
b. The proton
c. They would have the same wavelength

Answer available at the end of this section.

This was the prince's Ph.D. thesis, presented in 1924. His thesis advisor was somewhat taken aback, and was not sure if this was sound work. He asked de Broglie for an extra copy of the thesis, which he sent to Einstein. Einstein wrote shortly afterwards: "*I believe it is a first feeble ray of light on this worst of our physics enigmas*" and the prince got his Ph.D.

Answers

Following the unit conversions below, a 4 oz baseball has a mass of 0.11 kg. The velocity of a fast ball thrown at 100 miles per hour in m/s is 44.7 m/s.

$$m = (4\ \cancel{oz})\left(\frac{0.0283\ kg}{1\ \cancel{oz}}\right) = 0.11kg$$

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{hr}}\right)\left(\frac{1609.34\ m}{\cancel{mi}}\right)\left(\frac{1\ \cancel{hr}}{3600\ s}\right) = 44.7\ m/s$$

The de Broglie wavelength of this fast ball is:

$$\lambda = \frac{h}{mv} = \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{(0.11\ kg)(44.7\ m/s)} = 1.3 \times 10^{-34} m$$

Equation 1.6.1 shows that the de Broglie wavelength of a particle's matter wave is inversely proportional to its momentum (mass times velocity). Therefore the smaller mass particle will have a smaller momentum and longer wavelength. The electron is the lightest and will have the longest wavelength.

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1.7: de Broglie Waves can be Experimentally Observed

Learning Objectives

- To present the experimental evidence behind the wave-particle duality of matter

The validity of de Broglie's proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. The interference pattern was just like that produced when water waves pass through two holes in a barrier to generate separate wave fronts that combine and interfere with each other. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both matter (e.g., electrons and neutrons) and electromagnetic radiation. Diffraction patterns are obtained if the wavelength is comparable to the spacing between scattering centers.

Diffraction occurs when waves encounter obstacles whose size is **comparable** with its wavelength.

Continuing with our analysis of experiments that lead to the new quantum theory, we now look at the phenomenon of electron diffraction.

Diffraction of Light (Light as a Wave)

It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of light diffraction is the Young double slit experiment (Figure 1.7.1). Here, light as waves (pictured as waves in a plane parallel to the double slit apparatus) impinge on the two slits. Each slit then becomes a point source for spherical waves that subsequently interfere with each other, giving rise to the light and dark fringes on the screen at the right.

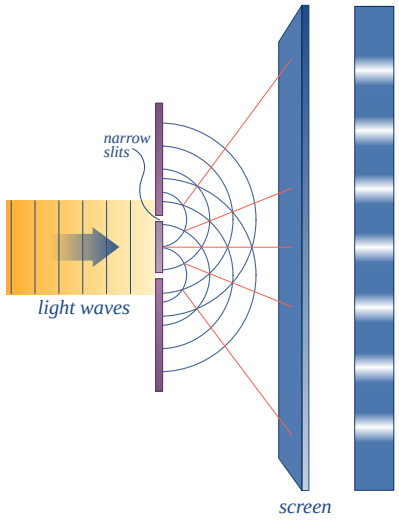


Figure 1.7.1 : Young double slit experiment. Two slits are illuminated by a plane light waves. (CC BY-NC; Ümit Kaya via LibreTexts)

The double-slit experiments are direct demonstration of wave phenomena via observed interference. These types of experiment were first performed by Thomas Young in 1801, as a demonstration of the wave behavior of light. In the basic version of this experiment, light is illuminated only a plate pierced by two parallel slits, and the light passing through the two slits is observed on a screen behind the plate (Figures 1.7.1 and 1.7.2).

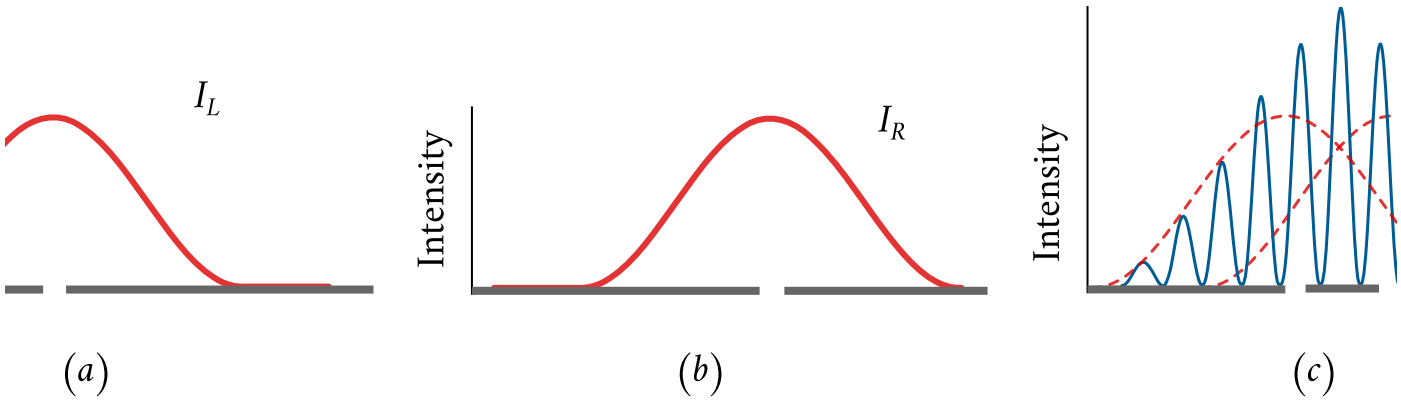


Figure 1.7.2 : Amplitude of particles through (a) left slit, (b) right slit, (c) through both slits. In absence of wavelength interference behavior, the intensity will be the sum of each single slit results (red) and when there is interference, pronounced oscillations in intensity is observed (blue curve). (CC BY; Ümit Kaya via LibreTexts)

The wave nature of light causes the light waves passing through the two slits to interfere, producing bright and dark bands on the screen – a result that would not be expected if light consisted of classical particles (Figure $1.7.0c$). However, the light is always found to be absorbed at the screen at discrete points, as individual particles (not waves); the interference pattern appears via the varying density of these particle hits on the screen. Furthermore, versions of the experiment that include detectors at the slits find that each detected photon passes through one slit (as would a classical particle), and not through both slits (as would a wave).

> Interference is a wave phenomenon in which two (or more) *waves* superimpose to form a resultant wave of greater or lower amplitude. It is the primary property used to identify wave behavior.

Diffraction of Electrons (Electrons as Waves)

According to classical physics, electrons should behave like particles - they travel in straight lines and do not curve in flight unless acted on by an external agent, like a magnetic field. In this model, if we fire a beam of electrons through a double slit onto a detector, we should get two bands of "hits", much as you would get if you fired a machine gun at the side of a house with two windows - you would get two areas of bullet-marked wall inside, and the rest would be intact (Figure 1.7.3 (left) and Figure 1.7.2).

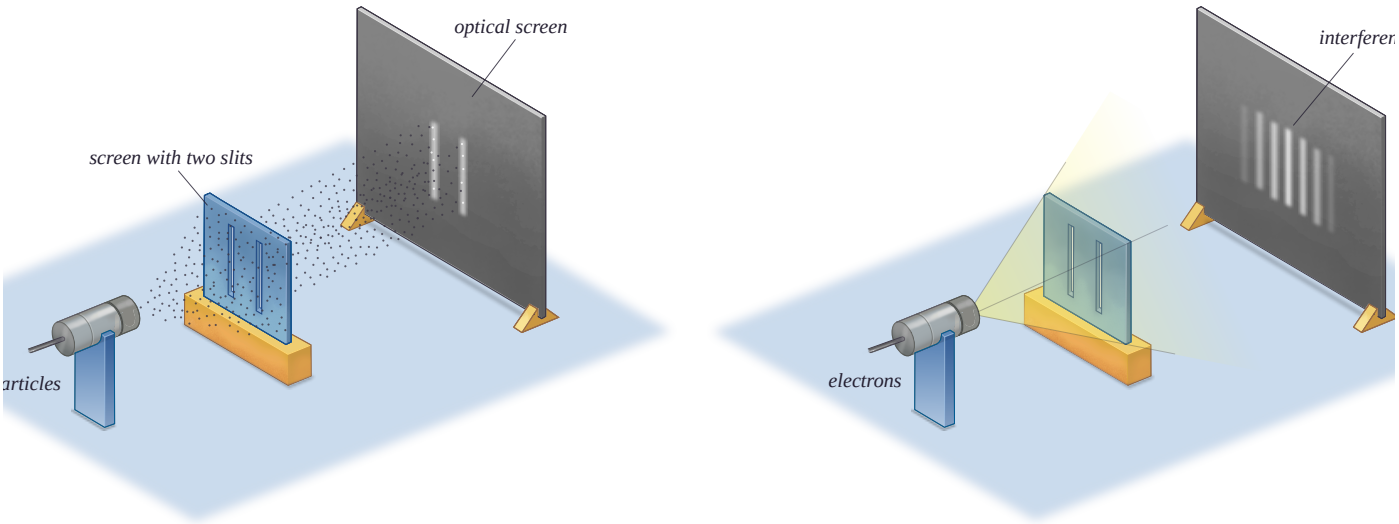


Figure 1.7.3 : (left) classical model of electrons. (right) wave property of electrons. (CC BY-NC; Ümit Kaya via LibreTexts)

However, if the slits are made small enough and close enough together, we actually observe the electrons are *diffracting* through the slits and *interfering* with each other just like waves (Figure 1.7.3 (right) and Figure 1.7.2 a,b). This means that the electrons

have **wave-particle duality**, just like photons, in agreement with de Broglie's hypothesis discussed previously. In this case, they must have properties like wavelength and frequency. We can deduce the properties from the behavior of the electrons as they pass through our diffraction grating.

This was a pivotal result in the development of quantum mechanics. Just as the photoelectric effect demonstrated the particle nature of light, the Davisson–Germer experiment showed the wave-nature of matter, and completed the theory of wave-particle duality. For physicists this idea was important because it meant that not only could any particle exhibit wave characteristics, but that one could use wave equations to describe phenomena in matter if one used the de Broglie wavelength.



Figure 1.7.4 : An image of an ant in a scanning electron microscope based on the wave properties of electrons. (Public Domain; United States Geological Survey, an agency of the United States Department of the Interior)

An electron microscope use a beam of accelerated electrons as a source of illumination. Since the wavelength of electrons can be up to 100,000 times shorter than that of visible light photons, electron microscopes have a higher resolving power than light microscopes and can reveal the structure of smaller objects. A transmission electron microscope can achieve better than 50 pm resolution and magnifications of up to about 10,000,000x whereas most light microscopes are limited by diffraction to about 200 nm resolution and useful magnifications below 2000x (Figure 1.7.4).

Is Matter a Particle or a Wave?

An electron, indeed any particle, is neither a *particle* nor a *wave*. Describing the electron as a particle is a mathematical model that works well in some circumstances while describing it as a wave is a different mathematical model that works well in other circumstances. When you choose to do some calculation of the electron's behavior that treats it either as a particle or as a wave, you're not saying the electron **is** a particle or **is** a wave: you're just choosing the mathematical model that makes it easiest to do the calculation.

Neutron Diffraction (Neutrons as Waves)

Like all quantum particles, neutrons can also exhibit wave phenomena and if that wavelength is short enough, atoms or their nuclei can serve as diffraction obstacles. When a beam of neutrons emanating from a reactor is slowed down and selected properly by their speed, their wavelength lies near one angstrom (0.1 nanometer), the typical separation between atoms in a solid material. Such a beam can then be used to perform a diffraction experiment. Neutrons interact directly with the nucleus of the atom, and the contribution to the diffracted intensity depends on each isotope; for example, regular hydrogen and deuterium contribute differently. It is also often the case that light (low Z) atoms contribute strongly to the diffracted intensity even in the presence of large Z atoms.

Example 1.7.1 : Neutron Diffraction

Neutrons have no electric charge, so they do not interact with the atomic electrons. Hence, they are very penetrating (e.g., typically 10 cm in lead). Neutron diffraction was proposed in 1934, to exploit de Broglie's hypothesis about the wave nature of matter. Calculate the momentum and kinetic energy of a neutron whose wavelength is comparable to atomic spacing ($1.8 \times 10^{-10}\ m$).

Solution

This is a simple use of de Broglie's equation

$$\lambda = \frac{h}{p}$$

where we recognize that the wavelength of the neutron must be comparable to atomic spacing (let's assumed equal for convenience, so $\lambda = 1.8 \times 10^{-10}\ m$). Rearranging the de Broglie wavelength relationship above to solve for momentum (p):

$$\begin{aligned} p &= \frac{h}{\lambda} \\ &= \frac{6.6 \times 10^{-34} Js}{1.8 \times 10^{-10} m} \\ &= 3.7 \times 10^{-24}\, kg\ m\ s^{-1} \end{aligned}$$

The relationship for kinetic energy is

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

where v is the velocity of the particle. From the reference table of physical constants, the mass of a neutron is $1.6749273 \times 10^{-27}\ kg$, so

$$\begin{aligned} KE &= \frac{(3.7 \times 10^{-24}\, kg\ m\ s^{-1})^2}{2(1.6749273 \times 10^{-27}\, kg)} \\ &= 4.0 \times 10^{-21} J \end{aligned}$$

The neutrons released in nuclear fission are 'fast' neutrons, i.e. much more energetic than this. Their wavelengths be much smaller than atomic dimensions and will not be useful for neutron diffraction. We slow down these fast neutrons by introducing a "moderator", which is a material (e.g., graphite) that neutrons can penetrate, but will slow down appreciably.

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1.8: The Bohr Theory of the Hydrogen Atom

Learning Objectives

- Introduce the fundamentals behind the Bohr Atom and demonstrate it can predict the Rydberg's equation for the atomic spectrum of hydrogen

Rutherford's Failed Planetary Atom

Ernest Rutherford had proposed a model of atoms based on the α-particle scattering experiments of Hans Geiger and Ernest Marsden. In these experiments helium nuclei (α-particles) were shot at thin gold metal foils. Most of the particles were not scattered; they passed unchanged through the thin metal foil. Some of the few that were scattered were scattered in the backward direction; i.e. they recoiled. This backward scattering requires that the foil contain heavy particles. When an α-particle hits one of these heavy particles it simply recoils backward, just like a ball thrown at a brick wall. Since most of the α-particles don't get scattered, the heavy particles (the nuclei of the atoms) must occupy only a very small region of the total space of the atom. Most of the space must be empty or occupied by very low-mass particles. These low-mass particles are the electrons that surround the nucleus.

There are some basic problems with the Rutherford model. The Coulomb force that exists between oppositely charge particles means that a positive nucleus and negative electrons should attract each other, and the atom should collapse. To prevent the collapse, the electron was postulated to be orbiting the positive nucleus. The Coulomb force (discussed below) is used to change the direction of the velocity, just as a string pulls a ball in a circular orbit around your head or the gravitational force holds the moon in orbit around the Earth. The origin for this hypothesis that suggests this perspective is plausible is the similarity of gravity and Coulombic interactions. The expression for the force of gravity between two masses (Newton's Law of gravity) is

$$F_{gravity} \propto \frac{m_1 m_2}{r^2} \tag{1.8.1}$$

with m_1 and m_2 representing the **mass** of object 1 and 2, respectively and r representing the distance between the objects centers

The expression for the Coulomb force between two charged species is

$$F_{Coulomb} \propto \frac{Q_1 Q_2}{r^2} \tag{1.8.2}$$

with Q_1 and Q_2 representing the **charge** of object 1 and 2, respectively and r representing the distance between the objects centers.

However, this analogy has a problem too. An electron going around in a circle is constantly being accelerated because its velocity vector is changing. A charged particle that is being accelerated emits radiation. This property is essentially how a radio transmitter works. A power supply drives electrons up and down a wire and thus transmits energy (electromagnetic radiation) that your radio receiver picks up. The radio then plays the music for you that is encoded in the waveform of the radiated energy.

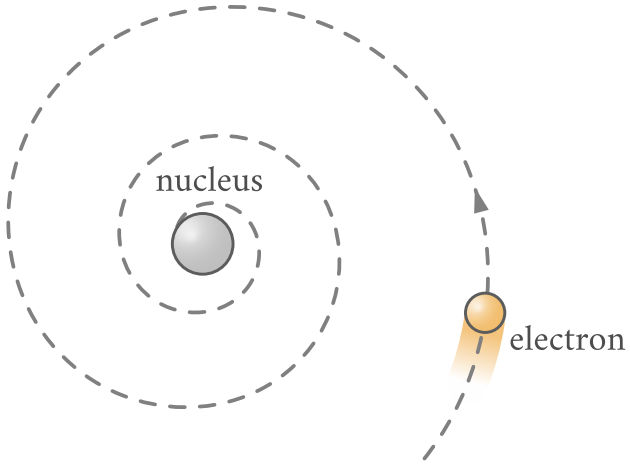


Figure 1.8.1 : The classical death spiral of an electron around a nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

If the orbiting electron is generating radiation, it is losing energy. If an orbiting particle loses energy, the radius of the orbit decreases. To conserve angular momentum, the frequency of the orbiting electron increases. The frequency increases continuously as the electron collapses toward the nucleus. Since the frequency of the rotating electron and the frequency of the radiation that is emitted are the same, both change continuously to produce a continuous spectrum and not the observed discrete lines. Furthermore, if one calculates how long it takes for this collapse to occur, one finds that it takes about 10^{-11} seconds. This means that nothing in the world based on the structure of atoms could exist for longer than about 10^{-11} seconds. Clearly something is terribly wrong with this classical picture, which means that something was missing at that time from the known laws of physics.

Conservative Forces can be explained with Potentials

A conservative force is dependent only on the position of the object. If a force is conservative, it is possible to assign a numerical value for the potential at any point. When an object moves from one location to another, the force changes the potential energy of the object by an amount that does not depend on the path taken. The potential can be constructed as simple derivatives for 1-D forces:

$$F = -\frac{dV}{dx}$$

or as gradients in 3-D forces

$$F = -\nabla V$$

where ∇ is the vector of partial derivatives

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

The most familiar conservative forces are gravity and Coulombic forces.

The Coulomb force law (Equation 1.8.2) comes from the corresponding Coulomb potential (sometimes call electrostatic potential)

$$V(r) = \frac{kQ_1Q_2}{r} \tag{1.8.3}$$

and it can be easily verified that the Coulombic force from this interaction ($F(r)$) is

$$F(r) = -\frac{dV}{dr} \tag{1.8.4}$$

As r is varied, the energy will change, so that we have an example of a potential energy curve $V(r)$ (Figure $1.8.2; left$). If Q_1 and Q_2 are the same sign, then the curve which is a purely **repulsive potential**, i.e., the energy increases monotonically as the charges are brought together and decreases monotonically as they are separated. From this, it is easy to see that like charges (charges of the same sign) repel each other.

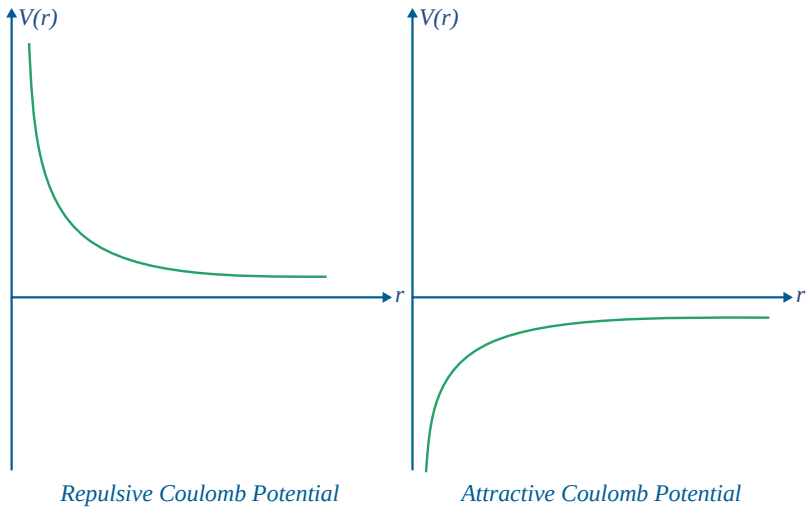


Figure 1.8.2 : Potential energy curve for the Coulomb interactions between two charges of same sign (left) and opposite signs (right). (CC BY-NC; Ümit Kaya via LibreTexts)

If the charges are of opposite sign, then the curve appears roughly Figure $1.8.2; right$ and this is a purely **attractive potential**. Thus, the energy decreases as the charges are brought together, implying that opposite charges attract

The Bohr Model

It is observed that line spectra discussed in the previous sections show that hydrogen atoms absorb and emit light at only discrete wavelengths. This observation is connected to the discrete nature of the allowed energies of a quantum mechanical system. Quantum mechanics postulates that, in contrast to classical mechanics, the energy of a system can only take on certain discrete values. This leaves us with the question: How do we determine what these allowed discrete energy values are? After all, it seems that Planck's formula for the allowed energies came out of nowhere.

The model we will describe here, due to Niels Bohr in 1913, is an early attempt to predict the allowed energies for single-electron atoms such as H, He^{+}, Li^{2+}, Be^{3+}, etc. Although Bohr's reasoning relies on classical concepts and hence, is not a correct explanation, the reasoning is interesting, and so we examine this model for its historical significance.

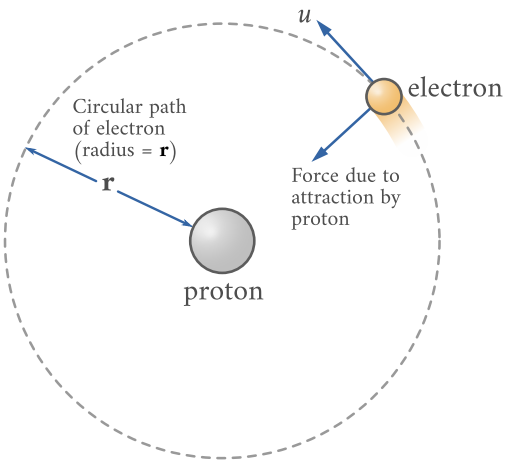


Figure 1.8.3 : Bohr atom with an electron revolving around a fixed nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

Consider a nucleus with charge $+Ze$ and one electron orbiting the nucleus. In this analysis, we will use another representation of the constant k in Coulomb's law (Equation 1.8.3), which is more commonly represented in the form:

$$k = \frac{1}{4\pi\epsilon_0} \tag{1.8.5}$$

where ϵ_0 is known as the **permittivity of free space** with the numerical value $\epsilon_0 = 8.8541878 \times 10^{-12}\ C^2 J^{-1} m^{-1}$.

The total energy of the electron (the nucleus is assumed to be fixed in space at the origin) is the sum of kinetic and potential energies:

$$E_{total} = \underbrace{\frac{p^2}{2m_e}}_{\text{kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{potential energy}}$$

The force on the electron is

$$\vec{F} = -\frac{Ze^2}{4\pi\epsilon_0 r^3} r$$

and its magnitude is

$$F = |\vec{F}| = \frac{Ze^2}{4\pi\epsilon_0 r^3}|r| = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

since $\vec{F} = m_e\vec{a}$, the magnitude, it follows that $|\vec{F}| = m_e|\vec{a}|$. If we assume that the orbit is circular, then the acceleration is *purely centripetal*, so

$$|a| = \frac{v^2}{r}$$

where v is the velocity of the electron. Equating force $|F|$ to $m_e|a|$, we obtain

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = m_e\frac{v^2}{r}$$

or

$$\frac{Ze^2}{4\pi\epsilon_0} = m_e v^2 r$$

or

$$\frac{Ze^2m_er}{4\pi\epsilon_0} = (m_evr)^2 \tag{1.8.6}$$

The reason for writing the equation this way is that the quantity m_evr is the classical orbital angular momentum of the electron. Bohr was familiar with Maxwell's theory of classical electromagnetism and knew that in a classical theory, the orbiting electron should radiate energy away and eventually collapse into the nucleus (Figure 1.8.1). He circumvented this problem by following Planck's idea underlying blackbody radiation and positing that the orbital angular momentum m_evr of the electron could only take on specific values

$$m_evr = n\hbar \tag{1.8.7}$$

with $n = 1, 2, 3, ...$

Note that the electron must be in motion, so $n = 0$ is not allowed.

Substituting Equation 1.8.7 into the Equation 1.8.6, we find

$$\frac{Ze^2m_er}{4\pi\epsilon_0} = n^2(\hbar)^2 \tag{1.8.8}$$

Equation 1.8.8 implies that orbits could only have certain allowed radii

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{Ze^2m_e}n^2 \tag{1.8.9}$$

$$= \frac{a_0}{Z}n^2 \tag{1.8.10}$$

with $n = 1, 2, 3, ...$ The collection of constants has been defined to be a_0

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2m_e}$$

a quantity that is known as the **Bohr radius**.

We can also calculate the allowed momenta since $m_evr = n\hbar$, and $p = m_ev$. Thus,

$$\begin{aligned} p_nr_n &= n\hbar \\ p_n &= \frac{n\hbar}{r_n} \\ &= \frac{\hbar Z}{a_0n} \\ &= \frac{Ze^2m_e}{4\pi\epsilon_0\hbar n} \end{aligned}$$

From p_n and r_n, we can calculate the allowed energies from

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0r_n}$$

Substituting in the expressions for p_n and r_n and simplifying gives

$$E_n = -\frac{Z^2e^4m_e}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{e^4m_e}{8\epsilon_0^2h^2}\frac{Z^2}{n^2} \tag{1.8.11}$$

We can redefine a new energy scale by defining **the Rydberg** as

$$1\ Ry = \frac{e^4m_e}{8\epsilon_0^2h^2} = 2.18 \times 10^{-18}\ J.$$

and this simplifies the allowed energies predicted by the Bohr model (Equation 1.8.11) as

$$E_n = -(2.18 \times 10^{-18})\frac{Z^2}{n^2}\ J = -\frac{Z^2}{n^2}\ R_y \tag{1.8.12}$$

Hence, the energy of the electron in an atom also is quantized. Equation 1.8.12 gives the energies of the electronic states of the hydrogen atom. It is very useful in analyzing spectra to represent these energies graphically in an energy-level diagram. An energy-level diagram has energy plotted on the vertical axis with a horizontal line drawn to locate each energy level (Figure 1.8.4).

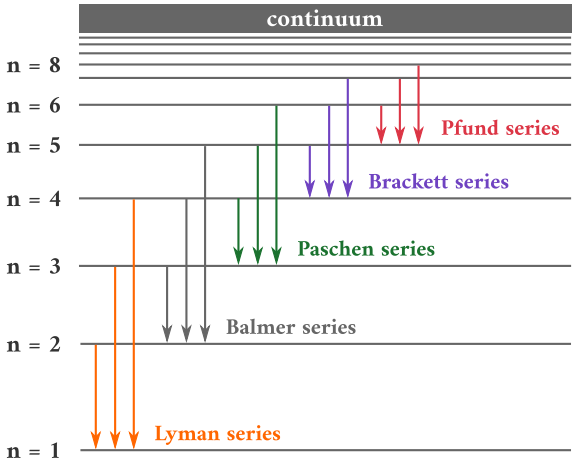


Figure 1.8.4 : Energy levels predicted by the Bohr model of hydrogen ($Z = 1$). (CC BY-NC; Ümit Kaya via LibreTexts)

These turn out to be the correct energy levels, apart from small corrections that cannot be accounted for in this pseudo-classical treatment. Despite the fact that the energies are essentially correct, the Bohr model masks the true quantum nature of the electron, which only emerges from a fully quantum mechanical analysis.

Exercise 1.8.1

Calculate a value for the Bohr radius using Equation 1.8.8 to check that this equation is consistent with the value 52.9 pm. What would the radius be for $n = 1$ in the Li^{2+} ion?

Answer available at the end of this section.

Exercise 1.8.2 : Rydberg states

How do the radii of the hydrogen orbits vary with n? Prepare a graph showing r as a function of n. States of hydrogen atoms with $n = 200$ have been prepared (called Rydberg states). What is the diameter of the atoms in these states?

Answer available at the end of this section.

The Wave Argument for Quantization

The above discussion is based off of a classical picture of an orbiting electron with the quantization from the angular momentum (Equation 1.8.7) requirement lifted from Planck's quantization arguments. Hence, only allows certain trajectories are stable (with differing radii). However, as discussed previously, the electron will have a wavelike property also with a de Broglie wavelength λ

$$\lambda = \frac{h}{p}$$

Hence, a larger momentum p implies a shorter wavelength. That means as n increases (Equation 1.8.12), the wavelength must also increase; this is a common feature in quantum mechanics and will be often observed. In the Bohr atom, the circular symmetry and the wave property of the electron requires that the electron waves have an integer number of wavelengths (Figure $1.8.1A$). If not, then the waves will overlap imperfectly and cancel out (i.e., the electron will cease to exist) as demonstrated in Figure $1.8.1B$.

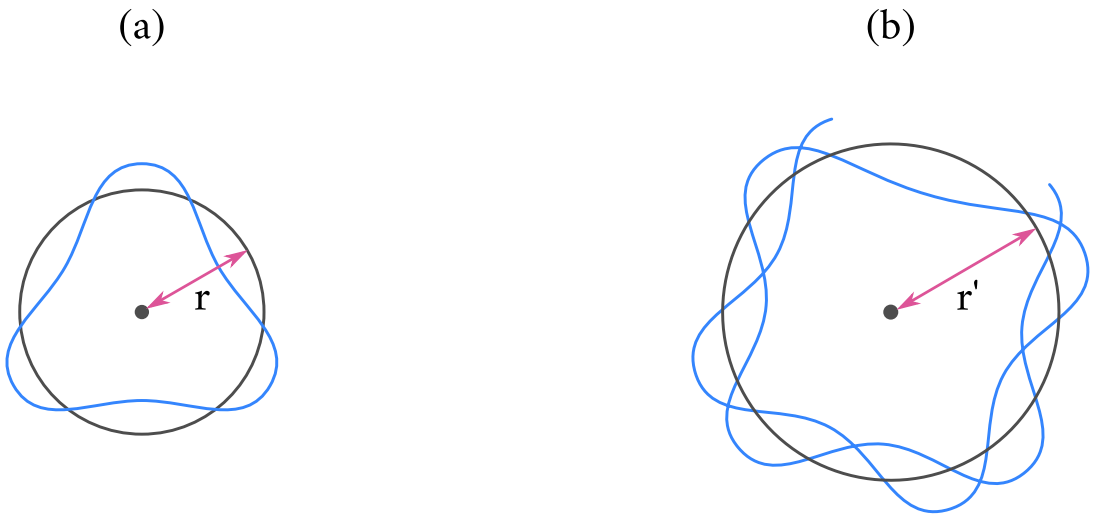


Figure 1.8.5 : Waves on a string have a wavelength related to the length of the string, allowing them to interfere constructively. (A) If we imagine the string bent into a closed circle, we get a rough idea of how electrons in circular orbits can interfere constructively. (B) If the wavelength does not fit into the circumference, the electron interferes destructively; it cannot exist in such an orbit. (CC BY-NC; Ümit Kaya via LibreTexts)

A more detailed discussion of the effect of electron waves in atoms will be discuss in the following chapters.

Derivation of the Rydberg Equation from Bohr Model

Given a prediction of the allowed energies of a system, how could we go about verifying them? The general experimental technique known as *spectroscopy* permits us to probe the various differences between the allowed energies. Thus, if the prediction of the actual energies, themselves, is correct, we should also be able to predict these differences. Let us assume that we are able to place the electron in Bohr's hydrogen atom into an energy state E_n for $n > 1$, i.e. one of its so-called *excited states*. The electron will rapidly return to its lowest energy state, known as the *ground state* and, in doing so, emit light. The energy carried away by the light is determined by the condition that the total energy is conserved (Figure 1.8.6).

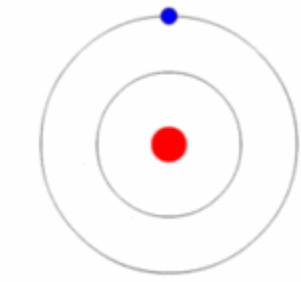


Figure 1.8.6 : A simple illustration of Bohr's model of the atom, with an electron making quantum leaps. (CC BY-SA 3.0 unported; Kurzon via Wikipedia)

Thus, if n_i is the integer that characterizes the initial (excited) state of the electron, and n_f is the final state (here we imagine that

$n_f = 1$, but is applicable in cases that $n_f < n_i$, i.e., emission)

$$E_{nf} = E_{ni} - h\nu$$

or

$$\nu = \frac{E_{ni} - E_{nf}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{1.8.13}$$

We can now identify the Rydberg constant R_H with the ratio of constants on the right hand side of Equation 1.8.13

$$R_H = \frac{m_e e^4}{8\epsilon_0^2 h^3}$$

Evaluating R_H from the fundamental constants in this formula gives a value within 0.5% of that obtained experimentally from the hydrogen atom spectrum.

Thus, by observing the emitted light, we can determine the energy difference between the initial and final energy levels, which results in the emission spectra discussed in Sections 1.4 and 1.5. Different values of n_f determine which emission spectrum is observed, and the examples shown in the figure are named after the individuals who first observed them. The figure below shows some of the transitions possible for different n_f and n_i values discussed previously.

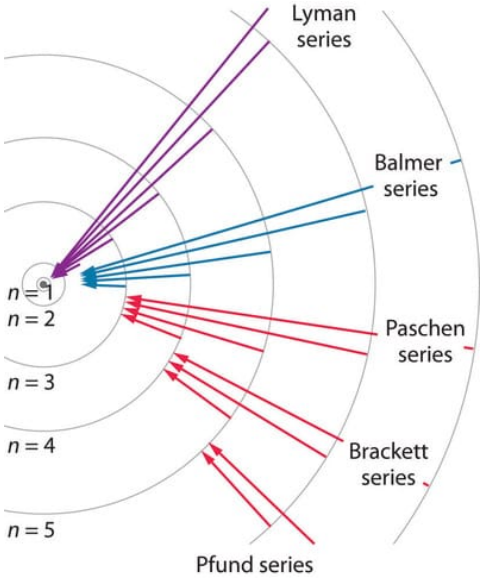


Figure 1.8.7 : Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. Orbits are not drawn to scale. (CC BY-NC-SA 3.0; anonymous)

If the atom absorbs light it ends up in an excited state as a result of the absorption. The absorption is only possible for light of certain frequencies, and again, conservation of energy determines what these frequencies are. If light is absorbed, then the final energy E_{nf} will be related to the initial energy E_{ni} with $n_f > n_i$ by

$$E_{nf} = E_{ni} + h\nu$$

or

$$\nu = \frac{E_{nf} - E_{ni}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Exercise 1.8.3

a. Calculate the energy of a photon that is produced when an electron in a hydrogen atom goes from an orbit with $n = 4$ to an orbit with $n = 1$.
b. What happens to the energy of the photon as the initial value of n approaches infinity?

Answer available at the end of this section.

Bohr's proposal explained the hydrogen atom spectrum, the origin of the Rydberg formula, and the value of the Rydberg constant. Specifically it demonstrated that the integers in the Rydberg formula are a manifestation of quantization. The energy, the angular momentum, and the radius of the orbiting electron all are quantized. This quantization also parallels the concept of stable orbits in the Bohr model. Only certain values of E, M, and r are possible, and therefore the electron cannot collapse onto the nucleus by continuously radiating energy because it can only have certain energies, and it cannot be in certain regions of space. The electron can only jump from one orbit (quantum state) to another. The quantization means that the orbits are stable, and the electron cannot spiral into the nucleus in spite of the attractive Coulomb force.

Although Bohr's ideas successfully explained the hydrogen spectrum, they failed when applied to the spectra of other atoms. In addition a profound question remained. Why is angular momentum quantized in units of $\hbar$? As we shall see, de Broglie had an answer to this question, and this answer led Schrödinger to a general postulate that produces the quantization of angular momentum as a consequence. This quantization is not quite as simple as proposed by Bohr, and we will see that it is not possible to determine the distance of the electron from the nucleus as precisely as Bohr thought. In fact, since the position of the electron in the hydrogen atom is not at all as well defined as a classical orbit (such as the moon orbiting the earth) it is called an orbital. An electron orbital represents or describes the position of the electron around the nucleus in terms of a mathematical function called a wavefunction that yields the **probability** of positions of the electron.

Contributors and Attributions

- Mark Tuckerman (New York University)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Template:Contriboundless

Answers

Starting from Equation 1.8.8 and solving for r:

$$\frac{Ze^2m_e r}{4\pi\epsilon_0} = n^2\hbar^2$$
$$r = \frac{4n^2\hbar^2\pi\epsilon_0}{Ze^2m_e}$$

with

- e is the fundamental charge: $e = 1.60217662 \times 10^{-19}C^2$
- m_e is the mass of an electron: $m_e = 9.10938356 \times 10^{-31}kg$
- ϵ_o is the permittivity of free space: $\epsilon_o = 8.854 \times 10^{-12}C^2N^{-1}m^{-2}$
- $\hbar$ is the reduced planks constant: $\hbar = 1.0546 \times 10^{-34}m^2kg/s$

For the ground-state of the hydrogen atom: $Z = 1$ and $n = 1$.

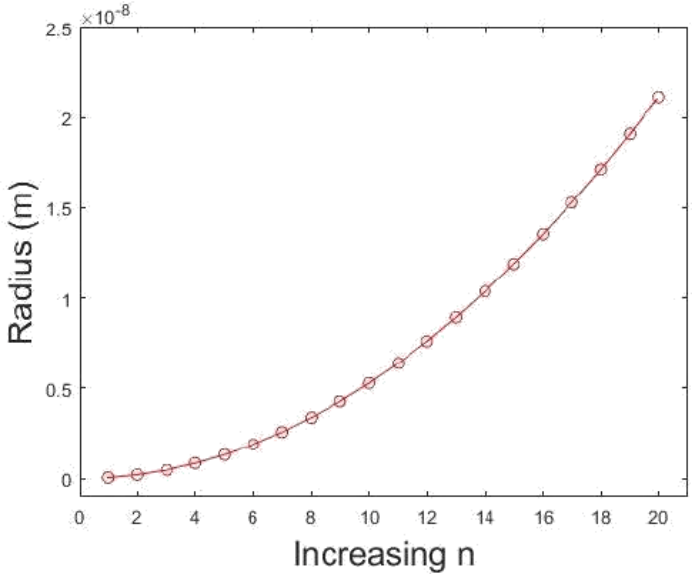
$$\begin{aligned} r &= \frac{4\hbar^2\pi\epsilon_0}{e^2m_e} \\ &= \frac{4(1.0546 \times 10^{-34}m^2kg/s)^2 \times \pi \times 8.854 \times 10^{-12}C^2N^{-1}m^{-2}}{(1.60217662 \times 10^{-19}C)^2(9.10938356 \times 10^{-31}kg)} \\ &= 5.29 \times 10^{-11}m = 52.9\,pm \end{aligned}$$

For the ground-state of the lithium +2 ion: $Z = 3$ and $n = 1$

$$\begin{aligned} r &= \frac{4\hbar^2\pi\epsilon_0}{3e^2m_e} \\ &= \frac{4(1.0546 \times 10^{-34}m^2kg/s)^2 \times \pi \times 8.854 \times 10^{-12}C^2N^{-1}m^{-2}}{3(1.60217662 \times 10^{-19}C)^2(9.10938356 \times 10^{-31}kg)} \\ &= 1.76 \times 10^{-11}m = 17.6\,pm \end{aligned}$$

As expected, the Li^{2+} has a smaller radius than the H atoms because of the increased nuclear charge.

This is a straightforward application of Equation of 1.8.10. The hydrogen atom has only certain allowable radii and these radii can be predicted from the equation that relates them with each n. Note that the electron must be in motion so $n = 0$ is not allowed.



This plot shows the relationship of radius as a function of n. Note that at $n = 1$ the radius is not zero. (CC BY-NC; Ümit Kaya via LibreTexts)

$4\pi\epsilon_0 = 1.113 \times 10^{-10}\mathrm{C}^2\mathrm{J}^{-1}\mathrm{m}^{-1}$ and $\hbar = 1.054 \times 10^{-34}\mathrm{Js}$, also knowing

$$e = 1.602 \times 10^{-19}\mathrm{C} \text{ with}$$
$$m_e = 9.109 \times 10^{-31}\mathrm{kg}$$

and Z is the nuclear charge, we use this equation directly. A simplification can be made by taking advantage of the fact that

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$$

resulting in

$$r_n = \frac{a_0}{Z}n^2$$

where $a_0 = 5.292 \times 10^{-11}\mathrm{m}$ which is the Bohr Radius.

Suppose we want to find the radius where $n = 200.n^2 = 40000$ so plugging in directly we have

$$r_n = \frac{(5.292 \times 10^{-11})}{(1)}(40000)$$
$$= 2.117 \times 10^{-6}m$$

for the radius of a hydrogen atom with an electron excited to the $\mathrm{n} = 200$ state. The diameter is then $4.234 \times 10^{-6}\mathrm{m}$.

a:

$$E_{\mathrm{nf}} = E_{ni} - h\nu$$
$$E_{photon} = h\nu = E_{nf} - E_{ni}$$
$$= \frac{Z^2 e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$
$$= \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{1^2} - \frac{1}{4^2}\right)$$
$$= 2.18 \times 10^{-18}\left(1 - \frac{1}{16}\right)$$
$$= 2.04 \times 10^{-18}J$$

b:

As $n_i \to \infty$

$$E_{photon} = \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$
$$\frac{1}{n_i^2} \to 0$$
$$E_{photon} \to \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2}\right)$$

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1.9: The Heisenberg Uncertainty Principle

Learning Objectives

- To understand that sometime you cannot know everything about a quantum system as demonstrated by the Heisenberg uncertainly principle.

In classical physics, studying the behavior of a physical system is often a simple task due to the fact that several physical qualities can be measured simultaneously. However, this possibility is absent in the quantum world. In 1927 the German physicist Werner Heisenberg described such limitations as the Heisenberg Uncertainty Principle, or simply the Uncertainty Principle, stating that it is not possible to measure both the momentum and position of a particle simultaneously.

The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously. Until the dawn of quantum mechanics, it was held as a fact that all variables of an object could be known to exact precision simultaneously for a given moment. Newtonian physics placed no limits on how better procedures and techniques could reduce measurement uncertainty so that it was conceivable that with proper care and accuracy all information could be defined. Heisenberg made the bold proposition that there is a lower limit to this precision making our knowledge of a particle inherently uncertain.

Probability

Matter and photons are waves, implying they are spread out over some distance. What is the position of a particle, such as an electron? Is it at the center of the wave? The answer lies in how you measure the position of an electron. Experiments show that you will find the electron at some definite location, unlike a wave. But if you set up exactly the same situation and measure it again, you will find the electron in a different location, often far outside any experimental uncertainty in your measurement. Repeated measurements will display a statistical distribution of locations that appears wavelike (Figure 1.9.1).

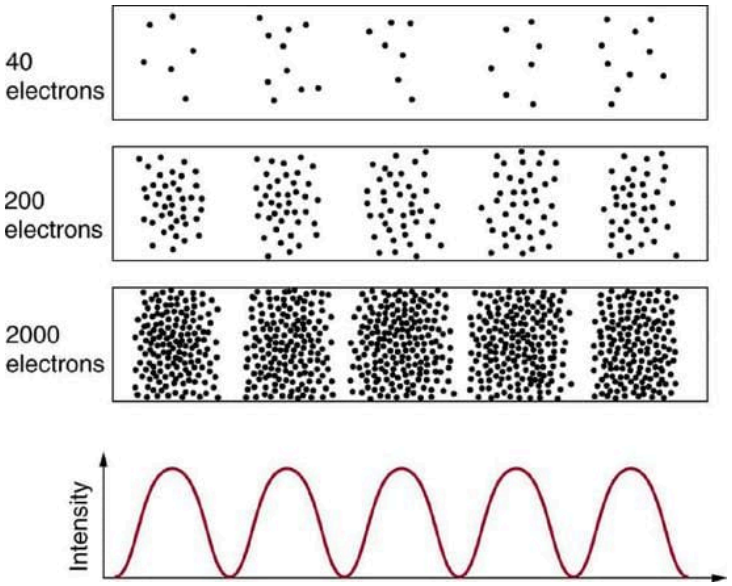


Figure 1.9.1 : The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength of the electrons (CC BY 4.0; OpenStax).

After de Broglie proposed the wave nature of matter, many physicists, including Schrödinger and Heisenberg, explored the consequences. The idea quickly emerged that, *because of its wave character, a particle's trajectory and destination cannot be precisely predicted for each particle individually*. However, each particle goes to a definite place (Figure 1.9.1). After compiling

enough data, you get a distribution related to the particle's wavelength and diffraction pattern. There is a certain *probability* of finding the particle at a given location, and the overall pattern is called a **probability distribution**. Those who developed quantum mechanics devised equations that predicted the probability distribution in various circumstances.

It is somewhat disquieting to think that you cannot predict exactly where an individual particle will go, or even follow it to its destination. Let us explore what happens if we try to follow a particle. Consider the double-slit patterns obtained for electrons and photons in Figure 1.9.2 . The interferrence patterns build up statistically as individual particles fall on the detector. This can be observed for photons or electrons—for now, let us concentrate on electrons. You might imagine that the electrons are interfering with one another as any waves do. To test this, you can lower the intensity until there is never more than one electron between the slits and the screen. The same interference pattern builds up!

This implies that a particle's probability distribution spans both slits, and the particles actually interfere with themselves. Does this also mean that the electron goes through both slits? An electron is a basic unit of matter that is not divisible. But it is a fair question, and so we should look to see if the electron traverses one slit or the other, or both. One possibility is to have coils around the slits that detect charges moving through them. What is observed is that an electron always goes through one slit or the other; it does not split to go through both.

But there is a catch. If you determine that the electron went through one of the slits, you no longer get a double slit pattern—instead, you get single slit interference. There is no escape by using another method of determining which slit the electron went through. Knowing the particle went through one slit forces a single-slit pattern. If you do not observe which slit the electron goes through, you obtain a double-slit pattern. How does knowing which slit the electron passed through change the pattern? The answer is fundamentally important—*measurement affects the system being observed*. Information can be lost, and in some cases it is impossible to measure two physical quantities simultaneously to exact precision. For example, you can measure the position of a moving electron by scattering light or other electrons from it. Those probes have momentum themselves, and by scattering from the electron, they change its momentum *in a manner that loses information*. There is a limit to absolute knowledge, even in principle.

Heisenberg's Uncertainty Principle

It is mathematically possible to express the uncertainty that, Heisenberg concluded, always exists if one attempts to measure the momentum and position of particles. First, we must define the variable "x" as the position of the particle, and define "p" as the momentum of the particle. The momentum of a photon of light is known to simply be its frequency, expressed by the ratio h/λ, where h represents Planck's constant and λ represents the wavelength of the photon. The position of a photon of light is simply its wavelength (λ). To represent finite change in quantities, the Greek uppercase letter delta, or Δ, is placed in front of the quantity. Therefore,

$$\Delta p = \frac{h}{\lambda} \tag{1.9.1}$$

$$\Delta x = \lambda \tag{1.9.2}$$

By substituting Δx for λ into Equation 1.9.1, we derive

$$\Delta p = \frac{h}{\Delta x} \tag{1.9.3}$$

or,

$$\Delta p \Delta x = h \tag{1.9.4}$$

early form of uncertainty principle

A Common Trend in Quantum Systems

Equation 1.9.4 can be derived by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let $\Delta p = mv$, and $\Delta x = h/(mv)$ (from De Broglie's expression for the wavelength of a particle). Substituting in Δp for mv in the second equation leads to Equation 1.9.4.

Equation 1.9.4 was further refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

$$\Delta p_x \Delta x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{1.9.5}$$

with $\hbar = \frac{h}{2\pi} = 1.0545718 \times 10^{-34}\ m^2 \cdot kg/s$.

Equation 1.9.5 reveals that the more accurately a particle's position is known (the smaller Δx is), the less accurately the momentum of the particle in the x direction (Δp_x) is known. Mathematically, this occurs because the smaller Δx becomes, the larger Δp_x must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known (Figure 1.9.2).

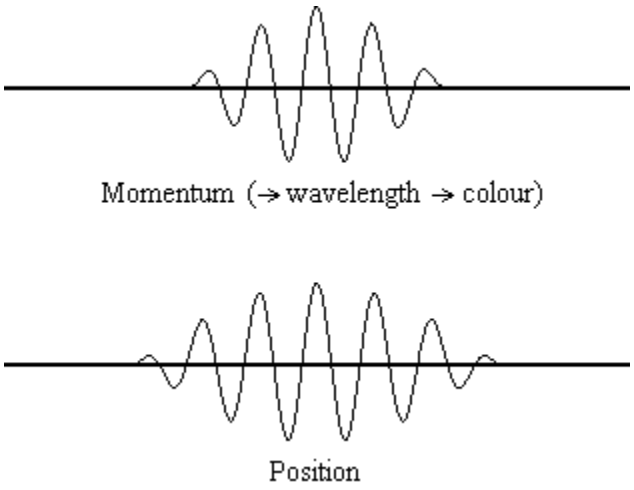


Figure 1.9.2 : The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength can be determined (and hence a specific color of the light).

What is the Proper Definition of Uncertainty?

Equation 1.9.5 relates the uncertainty of momentum and position. An immediate questions that arise is if Δx represents the full range of possible x values or if it is half (e.g., $\langle x \rangle \pm \Delta x$). Δx is the standard deviation and is a statistic measure of the spread of x values. The use of half the possible range is more accurate estimate of Δx. As we will demonstrated later, once we construct a wavefunction to describe the system, then both x and Δx can be explicitly derived. However for now, Equation 1.9.5 will work.

For example: If a problem argues a particle is trapped in a box of length, L, then the uncertainly of it position is $\pm L/2$. So the value of Δx used in Equation 1.9.5 should be $L/2$, not L.

Example 1.9.1

An electron is confined to the size of a magnesium atom with a 150 pm radius. What is the **minimum** uncertainty in its velocity?

Solution

The uncertainty principle (Equation 1.9.5):

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

can be written

$$\Delta p \geq \frac{\hbar}{2\Delta x}$$

and substituting $\Delta p = m\Delta v$ since the mass is not uncertain.

$$\Delta v \geq \frac{\hbar}{2\ m\ \Delta x}$$

the relevant parameters are

- mass of electron $m = m_e = 9.109383 \times 10^{-31}\ \ kg$
- uncertainty in position: $\Delta x = 150 \times 10^{-12} m$

$$\Delta v \geq \frac{1.0545718 \times 10^{-34}\ \cancel{kg}\ m^{\cancel{2}}/s}{(2)\ (9.109383 \times 10^{-31}\ \cancel{kg})\ (150 \times 10^{-12}\ \cancel{m})}$$
$$= 3.9 \times 10^{5}\ m/s$$

Exercise 1.9.1

What is the maximum uncertainty of velocity the electron described in Example 1.9.1 ?

Answer available at the end of this section.

Understanding the Uncertainty Principle through Wave Packets and the Slit Experiment

It is hard for most people to accept the uncertainty principle, because in classical physics the velocity and position of an object can be calculated with certainty and accuracy. However, in quantum mechanics, the wave-particle duality of electrons does not allow us to accurately calculate both the momentum and position because the wave is not in one exact location but is spread out over space. A "wave packet" can be used to demonstrate how either the momentum or position of a particle can be precisely calculated, but not both of them simultaneously. An accumulation of waves of varying wavelengths can be combined to create an average wavelength through an interference pattern: this average wavelength is called the "wave packet". The more waves that are combined in the "wave packet", the more precise the position of the particle becomes and the more uncertain the momentum becomes because more wavelengths of varying momenta are added. Conversely, if we want a more precise momentum, we would add less wavelengths to the "wave packet" and then the position would become more uncertain. Therefore, there is no way to find both the position and momentum of a particle simultaneously.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Several scientists have debated the Uncertainty Principle, including Einstein. Einstein created a slit experiment to try and disprove the Uncertainty Principle. He had light passing through a slit, which causes an uncertainty of momentum because the light behaves like a particle and a wave as it passes through the slit. Therefore, the momentum is unknown, but the initial position of the particle is known. Here is a video that demonstrates particles of light passing through a slit and as the slit becomes smaller, the final possible array of directions of the particles becomes wider. As the position of the particle becomes more precise when the slit is narrowed, the direction, or therefore the momentum, of the particle becomes less known as seen by a wider horizontal distribution of the light.

Example 1.9.2

The speed of a 1.0 g projectile is known to within $10^{-6}\ m/s$.

a. Calculate the *minimum* uncertainty in its position.
b. What is the *maximum* uncertainty of its position?

Solution a

From Equation 1.9.5, the $\Delta p_x = m\Delta v_x$ with $m = 1.0\ g$. Solving for Δx to get

$$\begin{aligned}\Delta x &= \frac{\hbar}{2m\Delta v} \\ &= \frac{1.0545718 \times 10^{-34}\ m^2 \cdot kg/s}{(2)(0.001\ kg)(10^{-6}\ m/s)} \\ &= 5.3 \times 10^{-26}\, m\end{aligned}$$

This negligible for all intents and purpose as expected for any macroscopic object.

Solution b

Unlimited (or the size of the universe). The Heisenberg uncertainty principles does not quantify the maximum uncertainty.

Exercise 1.9.2

Estimate the minimum uncertainty in the speed of an electron confined to a hydrogen atom within a diameter of $1 \times 10^{-10} m$?

Answer available at the end of this section.

Heisenberg's Uncertainty Principle not only helped shape the new school of thought known today as quantum mechanics, but it also helped discredit older theories. Most importantly, the Heisenberg Uncertainty Principle made it obvious that there was a fundamental error in the Bohr model of the atom. Since the position and momentum of a particle cannot be known simultaneously, Bohr's theory that the electron traveled in a circular path of a fixed radius orbiting the nucleus was obsolete. Furthermore, Heisenberg's uncertainty principle, when combined with other revolutionary theories in quantum mechanics, helped shape wave mechanics and the current scientific understanding of the atom.

Humor: Heisenberg and the Police

- Heisenberg get pulled over for speeding by the police. The officer asks him "Do you know how fast you were going?"
- Heisenberg replies, "No, but we know exactly where we are!"
- The officer looks at him confused and says "you were going 108 miles per hour!"
- Heisenberg throws his arms up and cries, "Great! Now we're lost!"

Answers

Infinity. There is no limit in the maximum uncertainty, just the minimum uncertainty.

We need to quantify the uncertainty of the electron in position. We can estimate that as $\pm 5 \times 10^{-10} m$. Hence, substituting the relavant numbers into Equation 1.9.5 and solving for Δv we get

$$\Delta v = 1.15 \times 10^{6}\, km/s$$

Notice that the uncertainty is significantly greater for the electron in a hydrogen atom than in the magnesium atom (Example 1.9.1) as expected since the magnesium atom is appreciably bigger.

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1.E: The Dawn of the Quantum Theory (Exercises)

Solutions to select questions can be found online.

1.1A

Sodium metal has a threshold frequency of 4.40×10^{14} Hz. What is the kinetic energy of a photoelectron ejected from the surface of a piece of sodium when the ejecting photon is 6.20×10^{14} Hz? What is the velocity of this photoelectron? From which region of the electromagnetic spectrum is this photon?

1.1B

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver, given that the work function is 4.73 eV? Is this in the visible range?

Solution

263 nm

1.1C

Find the longest-wavelength photon that can eject an electron from potassium, given that the work function is 2.24 eV. Is this visible electromagnetic radiation?

1.1C

What is the work function in eV of electrons in magnesium, if the longest-wavelength photon that can eject electrons is 337 nm?

Solution

3.69 eV

1.1D

Calculate the work function in eV of electrons in aluminum, if the longest-wavelength photon that can eject the electromagnetic is 304 nm.

1.1E

What is the maximum kinetic energy in eV of electrons ejected from sodium metal by 450-nm electromagnetic radiation, given that the work function is 2.28 eV?

Solution

0.483 eV

1.1F

UV radiation having a wavelength of 120 nm falls on gold metal, to which electrons are bound by 4.82 eV. What is the maximum kinetic energy of the ejected photoelectrons?

1.1G

Violet light of wavelength 400 nm ejects electrons with a maximum kinetic energy of 0.860 eV from sodium metal. What is the work function of electrons to sodium metal?

Solution

2.25 eV

1.1H

UV radiation having a 300-nm wavelength falls on uranium metal, ejecting 0.500-eV electrons. What is the work function of electrons to uranium metal?

1.1I

What is the wavelength of electromagnetic radiation that ejects 2.00-eV electrons from calcium metal, given that the work function is 2.71 eV? What type of electromagnetic radiation is this?

Solution

(a) 264 nm

(b) Ultraviolet

1.1J

Find the wavelength of photons that eject 0.100-eV electrons from potassium, given that the work function is 2.24 eV. Are these photons visible?

1.1K

What is the maximum velocity of electrons ejected from a material by 80-nm photons, if they are bound to the material by 4.73 eV?

Solution

1.95×10^{6} m/s

1.1L

Photoelectrons from a material with a work function of 2.71 eV are ejected by 420-nm photons. Once ejected, how long does it take these electrons to travel 2.50 cm to a detection device?

1.1M

A laser with a power output of 2.00 mW at a wavelength of 400 nm is projected onto calcium metal. (a) How many electrons per second are ejected? (b) What power is carried away by the electrons, given that the work function is 2.71 eV?

Solution

(a) $4.02 \times 10^{15}/s$

(b) 0.256 mW

1.1N

(a) Calculate the number of photoelectrons per second ejected from a 1.00-mm 2 area of sodium metal by 500-nm electromagnetic radiation having an intensity of $1.30\ kW/m^2$ (the intensity of sunlight above the Earth's atmosphere). (b) Given that the work function is 2.28 eV, what power is carried away by the electrons? (c) The electrons carry away less power than brought in by the photons. Where does the other power go? How can it be recovered?

1.1O

Red light having a wavelength of 700 nm is projected onto magnesium metal to which electrons are bound by 3.68 eV. (a) Use $KE_e = h\nu - \Phi$ to calculate the kinetic energy of the ejected electrons. (b) What is unreasonable about this result? (c) Which assumptions are unreasonable or inconsistent?

Solution

(a) –1.90 eV–1.90 eV

(b) Negative kinetic energy

(c) That the electrons would be knocked free.

Unreasonable Results

1.1P

(a) What is the work function of electrons to a material from which 4.00-eV electrons are ejected by 400-nm electromagnetic radiation? (b) What is unreasonable about this result? (c) Which assumptions are unreasonable or inconsistent?

1.2A

a. Suppose the electron in a hydrogen atom is in the circular Bohr orbit with n = 30. How many times per second does it go around?
b. Suppose now the electron drops to the n = 29 state, emitting a single photon. What is the frequency of this photon, in cycles per second?
c. Comment on the relation between your answers in (a), (b) above. What would you guess the relation to be for n = 300?

1.2B

The μ (muon) is a cousin of the electron, the only difference being its mass is 207 times greater. The μ has a lifetime of about 2 ms. If a beam of muons is directed at a solid, the muons will go into orbit around nuclei. The Bohr atom, with a muon replacing the electron, is a useful model for picturing this.

1. For a nucleus of charge Ze, how large is the n = 1 μ orbit compared with the electron orbit?
2. What is the frequency of the photon emitted by the μ in the n = 2 to n = 1 transition?
3. For the gold nucleus, the $n = 1$ μ orbit is inside the nucleus. Find the frequency of the emitted photon for $n = 2$ to $n = 1$ in this case. (Hint: you'll need the radius of the gold nucleus. Assume here that the positive charge is uniformly spread throughout the nucleus.)

1.3

Past Infrared region, in direction of the lower energies, the microwave region is located. In this region, radiation usually is characterized by frequency (ν) which is expressed in units of MHz, where Hz is a cycle per second. Given a microwave frequency of $2.0 \times 10^4\ \mathrm{MHz}$, calculate v, λ, and energy per photon for this radiation and then compare the results with figure below.

8d4e0e72466bee4ef6a8faaad3f9f7d3.jpg

Solution

The frequency(v) of the microwave radiation is given and once convert to Hz get the following

$$v=2.0e^{4}MHz(1e^{6}Hz/1MHz)= 2.0e^{10}s^{-1}\ Hz$$

now we find the wavelength using formula and get

$$\lambda = \frac{c}{v} = \frac{2.998 \times 10^8 m\, s^{-1}}{2.0 \times 10^{10}\, s^{-1}} = 1.5 \times 10^{-2}\, m$$

finally we use E=hv to calculate the energy

$$E=hv=(6.626e^{-34}J*s)(2.0e^{10}s^{-1})= 1.3e^{-23}J$$

1.4

Compare the Planck Distribution and the Rayleigh-Jean Distributions. For large values of ν, which one would be greater?

Solution

The Planck Distribution is

$$d\rho = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1} d\nu$$

And the Rayleigh Jean Distribution is

$$d\rho = \frac{8\pi \rho^2 k_B T}{c^3} d\nu$$

For larger ν, the Rayleigh Jean Distribution increases, while the Planck Distribution decreases because of the exponential term in the denominator outweighing the ν^3 term.

1.4

Plancks principal assumption was that energies of electronic oscillator can only have values $E = nh\nu$ and $\Delta E = h\nu$. In fact, as v → 0 then ΔE → 0 and E becomes continuous. It should be expected that the nonclassical Plank distribution to go over to the classical Rayleigh-Jeans distribution at low frequencies, where ΔE → 0. Prove that Equation 1.2 reduces to Equation 1.1 as v → 0.

Note: The Taylor expansion of an exponential

$$e^x \approx 1 + x + \left(\frac{x^2}{2!}\right) + ...$$

can truncated to $e^x \approx 1 + x$ when x is small.

Solution

Important to know Planks equation and put it into use:

$$dp(v,T)=P_v(T)dv=(8\pi h/c^3)(v^3 dv/e^{hv/k_bT}-1)$$

Note: $P_v(T)dv \Rightarrow$ is the radiant energy density between frequencies v and v+dv

Now for small x we have $e^x \approx 1+x$

and as v → 0, $hv/k_bT \rightarrow 0$ once we have this we get the following

$$dp(v,T)=(8\pi h/c^3)*((v^3 dv)/(1+(hv/k_bT)-1))= 8\pi hv^3 k_B T dv/c^3 hv = 8\pi v^2 k_B T dv/c^3$$

and this is the classical Rayleigh-Jeans distribution.

1.5

The visible spectrum is in the 400-700 nm range, and contains about 40% of the sun's radiation intensity. Using the Planck Distribution, write an integral expression that can be evaluated to give this result (do not evaluate the integral).

Solution

The Planck Blackbody distribution in terms of wavelength is

$$\rho_\lambda(\lambda,T)d\lambda = \frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

And so the intensity contained in the visible spectrum (from 400 nm and 700 nm) is

$$\int_{400}^{700}\rho_\lambda(\lambda,T)d\lambda = \int_{400\,nm}^{700\,nm}\frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

The intensity contained in the whole spectrum can be given by

$$\int_0^{\infty}\rho_\lambda(\lambda,T)d\lambda = \int_0^{\infty}\frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

And thus

$$40\% = 100\% \times \frac{\rho_{visible}}{\rho_{total}} = 100\% \times \frac{\int_{400}^{700}\frac{8phc}{\lambda^5\left(e^{\frac{hc}{\lambda k_b T}}-1\right)}d\lambda}{\int_0^{\infty}\frac{8phc}{\lambda^5\left(e^{\frac{hc}{\lambda k_b T}}-1\right)}d\lambda}$$

1.13

What is the frequency and energy of a single 310 nm photon?

Solution

Given: λ = 310 nm.

To find the frequency:

$$\nu = \frac{c}{\lambda}$$

]

$$\nu = \frac{2.99\times10^8\frac{m}{s}}{310\ nm}$$

$$\nu = 9.67\times10^{14}s^{-1}$$

To find the energy:

$$E = h\nu$$

$$E = (6.626\times10^{-34})\times\nu$$

$$E = 6.41\times10^{-19}J$$

1.14

A laser emits 3.3×10^{17}photons per second. If the energy per photon is $6.4 \times 10^{-20} J$ per photon, find the a) wattage and b) wavelength of the laser. in what electromagnetic spectra is the laser in?

Solution

a)

$$W = (6.4 \times 10^{-20} J)(3.3 \times 10^{17} \frac{1}{s})$$

$$W = 0.02112 \frac{J}{s}$$

b)

$$E = h\frac{c}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{(3 \times 10^{8} \frac{m}{s})(6.626 \times 10^{-34} Js)}{6.4 \times 10^{-20} J}$$

$$\lambda = 3.106 \times 10^{-6} m$$

c)

infrared spectrum

1.15

What is the max wavelength with a given temperature of 7500K?

Solution

For a given temperature, the maximum wavelength allowed is given by:

$$T = \frac{2.9 \times 10^{-3} \text{mK}}{\lambda_{\text{max}}}$$

Given: T = 7500K

$$7500 = \frac{2.9 \times 10^{-3} \text{mK}}{\lambda_{\text{max}}}$$

$$\lambda_{\text{max}} = \frac{2.9 \times 10^{-3} \text{mK}}{7500 \text{K}}$$

$$\lambda_{\text{max}} = 3.8 \times 10^{-7} \text{m}$$

Q1.15

A light bulb is a blackbody radiator. What temperature is required such that $\lambda_{max} = \ 400nm$?

Solution

$$T = \frac{(2.90 \times 10^{-3} \ m \cdot K)}{400 \times 10^{-9} \ m} = 7250 \ K.$$

1.16

An unknown elemental metal has work function of $\Phi = 8.01 \times 10^{-19} J$. Upon illumination with UV light of wavelength 162 nm, electrons are ejected with velocity of at $2.95 \times 10^3 \frac{m}{s}$. What is the threshold wavelength? What is the work function in units of eV? What metal does this correspond to (you will need to consult Table B1)?

Solution

This question involves a bit of a trick in that neither the wavelength of radiation nor the velocity of electrons are necessary to solve for the threshold wavelength or material as requested. To solve for the threshold wavelength, we employ the concept that kinetic energy is 0 at threshold frequency and then use a relation equation to solve for threshold wavelength.

$$\frac{1}{2}mv^2 = h\nu - \Phi$$

So,

$$\nu_{threshold} = \frac{\Phi}{h} = 1.21 \times 10^{15} s^{-1}$$

and

$$\lambda_{threshold} = \frac{c}{\nu_{threshold}} = 248nm$$

With a basic conversion of

$$1\ J = 6.242 \times 10^{18} eV$$

we see that the work function is 5 eV. Using Table B1, we see that this value corresponds to Cobalt (discovered by Georg Brandt).

1.16

Given the work function of sodium is 1.87 eV, find the kinetic energy of the ejected electrons when light of frequency 2.3 times greater than the threshold frequency is used to excite the electrons.

Solution

step 1: convert work function from electron volts to joules

$$\phi = 1.87\ eV$$

1 eV = $1.602 \times 10^{-19} J$

$$\phi = 1.87 eV \times \frac{1.602 \times 10^{-19} J}{1\ eV} = 2.995 \times 10^{-19} J$$

Step 2: Solve for the threshold frequency

$$\phi = hf$$

$$\frac{\phi}{h} = f$$

$$\frac{2.995 \times 10^{-19} J}{6.626 \times 10^{-34} Js} = f$$

$$4.5 \times 10^{14} Hz = f$$

Step 3: Use threshold frequency to solve for kinetic energy at desired conditions

$$KE = h(2.3f - f)$$

$$KE = h(1.3f)$$

$$KE = (6.626 \times 10^{-34} Js)(1.3(4.5 \times 10^{14} Hz))$$

$$KE = 3.87 \times 10^{-19} J$$

Q1.17

Find kinetic energy emitted off surface of tungsten that is radiated with radiation of 250 nm. Work function of tungsten 4.50 eV.

Solution

Kinetic energy is represented by

$$E = h\nu$$

we then use $c = \nu\lambda$ for the frequency to find

$$E = \frac{hc}{\lambda}$$

Then substitute values to get

$$E = \frac{(6.626 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{250 \times 10^{-9}\ m} = 7.95 \times 10^{-19}\ J$$

Convert to eV, to get

$$E = (7.95 \times 10^{-19}\ J)\frac{1\ eV}{1.6 \times 10^{-19}\ J} = 4.97\ eV.$$

Use $KE_e = h\nu – \Phi$ to finally get

$$KE_e = h\nu – \Phi = 4.97\ eV – 4.50\ eV = 0.47\ eV.$$

1.18

A smooth silver Thanksgiving platter and serving spoon (the pilgrims had knives and spoons but no forks) are irradiated with light of wavelength 317 nm. The work function is $\Phi = 6.825 \times 10^{-19} J$. What is the kinetic energy of the ejected electrons [eV]? The threshold frequency?

Solution

We first solve for the threshold frequency.

$$\frac{hc}{\lambda} = \Phi \ = h\nu$$

Rearrange to solve for ν

$$\nu = \frac{\Phi}{h}$$
$$= 1.03 \times 10^{15} s^{-1}$$

Now we solve for kinetic energy.

$$\frac{1}{2}mv^2 = h\nu - \Phi$$

where

$$\nu = \nu_{radiation}$$

and we recall that

$$\nu = \frac{c}{\lambda_{radiation}}$$

Using the right hand side of that kinetic energy equation, we find the result to be

$$KE = 2.55 \times 10^{-19}$$

Q1.18

When a clean surface of silver is irradiated with light of wavelength 255 nm, the work function of ejected electrons is 4.18 eV. Calculate the kinetic energy in eV of the silver and the threshold frequency.

Solution

Kinetic Energy of the electrons can be represented with the formula

$$KE = h\nu - \Phi$$

We have to solve for the Kinetic energy in eV

$$KE = h\nu - \Phi$$

substituting known values gives

$$KE = (6.626 \times 10^{-}34 Js)(\frac{3 \times 10^{8} m/s}{255 \times 10^{-}9 m}) - 6.69 * 10^{-}19 J$$

$$KE = 1.105 \times 10^{-}19 J \approx .690 eV$$

The second part of the question asks us to solve for the threshold frequency

$$\nu_o = \frac{\Phi}{h}$$

$$\nu_o = \frac{6.69 \times 10^{-}19J}{6.626 \times 10^{-}34J * s}$$

$$= 1.01 \times 10^{15} Hz$$

Q1.21

A line in the Paschen series of hydrogen has a wavelength of 1.01 x 10^{-6} m. Find the original energy of the electron.

Solution

For the Paschen series n_1= 3. To find n_2 we have to use the Rhydberg formula:

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

substituting our known values will give us

$$\frac{1}{1.01 \times 10^{-6} m} = 109677 cm^{-1} \left(\frac{1}{3^2} + \frac{1}{n_2^2} \right)$$

converting our units and using algebra gives us

$$0.0903 = \left(\frac{1}{9} - \frac{1}{n_2^2} \right)$$

where

$$n_2 = 6.93 \approx 7$$

We approximate to 7 since n is an integer.

1.22

How does the energy change when a particle absorbs and releases a photon? Show the effects on the state that the particle is in and the energy itself.

Solution

The energy would increase when a photon is absorbed and decrease when a photon is released. We have two equations

$$E = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = 109680 \left(\frac{1}{n_1} - \frac{1}{n_2} \right)$$

When a photon is absorbed, λ is positive and when a photon is released λ is negative. From the first equation, we can see that E only depends on the sign of λ. So when a photon is absorbed, energy is positive (increases) and when it is released, energy is negative (decreases).

The second equation shows that when λ is negative, n_1 must be greater than n_2 so the final state is at a lower quantum number than the initial and vice versa for when a photon is absorbed.

1.23

Show that the (a) wavelength of 100 nm occurs within the Lyman series, that (b) wavelength of 500 nm occurs within the Balmer series, and that (c) wavelength of 1000 nm occurs within the Paschen series. Identify the spectral regions to which these wavelengths correspond.

Solution

We can show the where the wavelengths occurs by calculate the maximum and minimum wavelengths of each series using the Rydberg formula.

a) Lyman Series:

$$Max: \frac{1}{\lambda} = 109680\left(1 - \frac{1}{2^2}\right) cm^{-1}$$

$$\lambda = 121.6nm$$

$$Min: \frac{1}{\lambda} = 109680\left(1 - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 91.2nm$$

The range for the Lyman series from 91.2 nm to 121.6 nm, therefore a wavelength of 100 nm occurs within the Lyman series. This corresponds to the ultraviolent region of the spectrum.

b) Balmer Series:

$$Max: \frac{1}{\lambda} = 109680\left(\frac{1}{2^2} - \frac{1}{3^2}\right) cm^{-1}$$

$$\lambda = 656.5nm$$

$$Min: \frac{1}{\lambda} = 109680\left(\frac{1}{2^2} - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 364.7nm$$

The range for the Balmer series from 364.7 nm to 656.5 nm, therefore a wavelength of 500 nm occurs within the Balmer series. This corresponds to the near ultraviolent region of the spectrum.

c) Paschen Series:

$$Max: \frac{1}{\lambda} = 109680\left(\frac{1}{3^2} - \frac{1}{4^2}\right) cm^{-1}$$

$$\lambda = 1875.6nm$$

$$Min: \frac{1}{\lambda} = 109680\left(\frac{1}{3^2} - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 820.6nm$$

The range for the Paschen series from 820.6 nm to 1875.6 nm, therefore a wavelength of 1000 nm occurs within the Paschen series. This corresponds to the near infrared region of the spectrum.

1.24

Calculate the wavelength and the energy of a photon associated with the series limit of the Balmer series.

Solution

First find the minimum wavelength for the Balmer series.

$$\frac{1}{\lambda} = 109,680 cm^{-1} \left(\frac{1}{2^2} - \frac{1}{\infty} \right)$$
$$\lambda = 364.7\, nm$$

Now we can use the wavelength to find the energy.

$$E = \frac{hc}{\lambda}$$
$$= \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{364.7 \times 10^{-9}}$$
$$= 5.45 \times 10^{-19}\, J$$

1.25

For the following particles (a) an electron with a kinetic energy of 50eV, (b) a proton with a kinetic energy of 50eV , and (c) an electron in the second Bohr orbit of a hydrogen atom, calculate the de Broglie wavelength of each.

Solution

We use $\lambda = \frac{h}{p}$ in all cases to find λ.

a.

$$KE = \frac{mv^2}{2}$$

$$50eV\left(\frac{1.602\times10^{-19}J}{1eV}\right) = \frac{(v^2)(9.109\times10^{-31}kg)}{2}$$

$$v = 4.19\times10^{6}\,m\cdot s^{-1}$$

So

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$
$$= \frac{6.626\times10^{-34}J\cdot s}{(9.109\times10^{-31}kg)(4.19\times10^{6}m\cdot s^{-1})}$$
$$= 1.23\times10^{-10}m = 0.123\,nm$$

b. Replace m_e with m_p in (a) to find $\lambda = 2.86\times10^{-3}nm$.

c. We must first determine the velocity of an electron in the second Bohr orbit of a hydrogen atom. The velocity of an electron is given by the following equation:

$$v = \frac{nh}{2(\pi)m_e r}$$

and we know

$$r = \frac{\epsilon_0 h^2 n^2}{(\pi)m_e e^2}$$

substituting the two equations we find that

$$v = \frac{e^2}{2nh\epsilon_0}$$

For $n = 2$, because we are talking about the second orbit

$$v = \frac{(1.602\times10^{-19}C)^2}{2(2)(6.626\times10^{-34}J\cdot s)(8.854\times10^{-12}C^2J^{-1}m^{-1})}$$
$$= 1.09\times10^{6}m\cdot s^{-1}$$

So

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$
$$= \frac{6.626\times10^{-34}J\cdot s}{(9.109\times10^{-31}kg)(1.09\times10^{6}m\cdot s^{-1}}$$
$$= 6.64\times10^{-10}m = 0.664\,nm$$

Q1.26

a. What is the velocity and wavelength of an electron with a voltage increase of 75 V?

b. What is the momentum of an electron with a de Broglie wavelength of 20 nm?(mass of an electron is $9.109 \times 10^{-31}\ kg$)

Solution

a.

$$\begin{aligned} KE &= (\text{electron charge}) \times (\text{potential}) \\ &= (1.602 \times 10^{-19}\, C)(75\, V) \\ &= 1.2 \times 10^{-17}\, J \\ &= (1/2)mv^2 \end{aligned}$$

$$v = \sqrt{\frac{2(KE)}{m}} = \sqrt{\frac{2(1.2 \times 10^{-17} J)}{(9.109 \times 10^{-31} kg)}} = 5.133 \times 10^{6} m * s^{-1}$$

$$\begin{aligned} \lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} J * S}{(9.109 \times 10^{-31} kg)(5.133 \times 10^{6} m * s^{-1})} \\ &= 1.2267\, m \end{aligned}$$

b.

$$\lambda = \frac{h}{p}$$

$$\begin{aligned} p &= \frac{h}{\lambda} \\ &= \frac{6.626 \times 10^{-34} J * S}{20 \times 10^{-6} m} \\ &= 3.313 \times 10^{-29} kg * m * s^{-1} \end{aligned}$$

1.27

Through what potential a proton must initially at rest fall so its de Broglie wavelength is $1.83 \times 10^{-10}\ m$?

Q1.28

Calculate the energy and wavelength associated with a β particle that has fallen through a potential difference of 3.2 V. Take the mass of a β particle to be 9.1×10^{-31}kg.

Solution

A beta particle is an electron, so it has a -1 charge.

$$KE = (\beta \text{particle charge}) \times \text{ Potential} = |-1.602 \times 10^{-19}\text{C}| \ \times \ 3.2\text{V}$$

$$KE = 5.126 \times 10^{-19}\text{J per } \beta \text{ particle}$$

$$\lambda = \frac{h}{p}$$

$$KE = \frac{mv^2}{2} = \frac{p^2}{2m}$$

$$p = \sqrt{2\ KE\ m} = \sqrt{2\ \times\ 5.126 \times 10^{-19}\text{J}\ \times\ 9.1 \times 10^{-31}\text{kg}}$$

$$p = 5.66 \times 10^{-25}\text{kg m } s^{-1}$$

$$\lambda = \frac{6.626 \times 10^{-34}\text{J s}}{5.66 \times 10^{-25}\text{kg m s}^{-1}} = 6.86 \times 10^{-10}\text{m}$$

Q1.28

If a proton is going through a potential difference of 3.0V, what is the momentum and wavelength associated with this proton? (mass of a proton is equal to $1.6726 \times 10^{-27}\ kg$)

Solution

$$(charge) * (potential) = KE$$

$$charge = 1.602 \times 10^{-19} C$$

$$(1.602 \times 10^{-19} C) * (3.0V) = KE$$

$$KE = 4.806 \times 10^{-19} J$$

$$KE = \frac{p^2}{2m}$$

$$p = \sqrt{2(KE)m} = \sqrt{2(4.806 \times 10^{-19} J)(1.6726 \times 10^{-27} kg)} = 4.01 \times 10^{-23} kg * m * s^{-1}$$

$$\lambda = h/p = \frac{6.626 \times 10^{-34} J * S}{4.01 \times 10^{-23} kg * m * s^{-1}} = 1.65 \times 10^{-11} m = 0.165\, pm$$

1.29

Neutron diffraction is a modern technique to study structure. In the neutron diffraction, a collimated beam of neutrons was generated at some temperature from high-energy neutron source. This is achieved at several accelerator facilities around the world. If the speed of neutron is $v_n = (3k_BT/m)^{1/2}$ with m as the mass of neutron. What is the required temperature so that neutrons have a de Broglie wavelength of 200 pm? The mass of a neutron to be $1.67 \times 10^{-27}\ kg$.

1.29

While studying quantum mechanics one day, you wondered what temperature would be required for the Jumbo Jawbreaker you were about to eat to have a de Broglie wavelength of 1.9×10^{-24} meters? Assuming that the speed of a Jumbo Jawbreaker can be calculated from the equation $\nu_n = (\frac{3k_BT}{m})\frac{1}{2}$. You quickly measure the mass of your Jumbo Jawbreaker and found it to be $0.1kg$.

Solution

Knowing that the de Broglie wavelength has the form,

$$\lambda = \frac{h}{m\nu_n}$$

we can substitute the given equation for speed into the de Broglie wavelength equation

$$\lambda = \frac{h}{\sqrt{3mk_BT}}$$

rearrange to solve for temperature

$$T = \frac{h^2}{3mk_B\lambda^2}$$

Substituting in constants we can solve for temperature in Kelvin. Using $h = 6.626 \times 10^{-34} J*s$, $m = 0.1kg$, $k_B = 1.381 \times 10^{-21} J*K^{-1}$, and $\lambda = 1.9 \times 10^{-24}$ meters.

We find that

$$T = \frac{(6.626 \times 10^{-34} J*s)^2}{3(0.1kg)(1.381 \times 10^{-21} J*K^{-1})(1.9 \times 10^{-24})^2}$$

Therefore

$$\begin{aligned} T &= 293.5K \\ &= 20.35^{\circ}C \end{aligned}$$

1.30

For linear motion, show that a small change in the momentum, $\Delta \mathrm{p}$, changes a change in kinetic energy, $\Delta \mathrm{KE}$, of

$$\Delta \mathrm{KE} = \frac{p_0}{m}\Delta \mathrm{p}$$

where p_0 is initial momentum.

Solution

Since $\Delta \mathrm{p} = dp$ and $\Delta \mathrm{KE} = dKE$,

$$KE = \frac{p^2}{2m}$$

$$dKE = \frac{p_0}{m}dp$$

$$\Delta \mathrm{KE} = \frac{p_0}{m}\Delta \mathrm{p}$$

1.31

Derive the Bohr formula for $\frac{1}{\lambda_{vac}}$ for a multi-proton and single electron atom such as He^{+} or Li^{2+}.

Solution

The number of protons (Z) in the nucleus interact with the single electron with the same coulomb force (f). The total force of a nucleus with charge Z can be written as the sum of each proton individually interacting with the electron.

$$f_{Total} = \sum_{i=0}^{Z} \frac{e^2}{4r^2\pi\epsilon_\circ}$$

Simplifying this expression we find that

$$f_{Total} = \frac{Ze^2}{4r^2\pi\epsilon_\circ}$$

To prevent the electron from spiraling into or away from the nucleus, the centrifugal force $f = \frac{m_e v^2}{r}$ is equal to the Coulombic force. Therefore

$$\frac{Ze^2}{4r^2\pi\epsilon_\circ} = \frac{m_e\nu^2}{r}$$

For stability purposes a condition requires electrons to have a set number of complete wavelengths around the circumference of the orbit or

$$2\pi r = n\lambda \ , \ where \ n = 1, 2, 3...$$

using the de Broglie wavelength formula $\lambda = \frac{h}{p} = \frac{h}{m\nu}$ we find that

$$m_e\nu r = \frac{nh}{2\pi}$$

Solving for ν and substituting into our force relationship $\frac{Ze^2}{4r^2\pi\epsilon_\circ} = \frac{m_e\nu^2}{r}$ We find that

$$r = \frac{n^2h^2\epsilon_\circ}{m_e e^2 Z\pi}$$

Now solving for the total energy of the system

$$E = KE + V(r)$$
$$= \frac{1}{2}m_e\nu^2 - \frac{Ze^2}{4r\pi\epsilon_\circ}$$

Substituting in $m_e\nu^2$ found above into the kinetic energy portion we find

$$E = \frac{Ze^2}{8r\pi\epsilon_\circ} - \frac{Ze^2}{4r\pi\epsilon_\circ} = -\frac{Ze^2}{8r\pi\epsilon_\circ}$$

Substituting r from above we quantize the energy such that

$$E_n = \frac{-Z^2 m_e e^4}{8n^2h^2\epsilon_\circ^2}$$

Since this energy is quantized, the change in energy states will occur where electrons are excited by light or $h\nu$ into higher quantum states. Therefore

$$\Delta E = \frac{-Z^2 m_e e^4}{8h^2\epsilon_\circ^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu$$

Finally solve for $\frac{1}{\lambda_{vac}}$ remembering that $h\nu = \frac{hc}{\lambda_{vac}}$ where c is the speed of light. We obtain our final solution

$$\boxed{\frac{1}{\lambda_{vac}} = \frac{-Z^2 m_e e^4}{8h^3 c\epsilon_\circ^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

1.32

The series in the He^+ spectrum that corresponds to the set of transitions where the electron falls from a higher level into the n = 4 state is called the Pickering series, an important series in solar astronomy. Derive the formula for the wavelengths of the observed lines in this series. In what region of the spectrum does it occur?

Solution

If we derive the Bohr formula for $\tilde{v} = Z^2 R_H \left(\frac{1}{(n^2)_1} - \frac{1}{(n^2)_2}\right)$

In the Pickering series, the helium spectrum is in $Z = 2$ and $n_2 = 4$

$$\tilde{v} = 4(109,680 cm^-1)\left(\frac{1}{4^2} - \frac{1}{n_1^2}\right) \tag{1.E.1}$$

where \(n_1 = 5, 6, 7, 8.... \]).

$$n_1 = 5, \tilde{v}\ = 9871\,\mathrm{cm}^-1$$

or

$$\lambda = 1.013 * 10^{-6} meters$$

1.33A

Using the Bohr model, find the third ionization energy for the Lithium atom in eV and in J.

Solution

Energy transitions for a hydrogen like atom are given by $\Delta E = Z^2 R_y(1/n_i^2 - 1/n_f^2)$

where Z is the atomic number and R_y is 13.6 eV

When a hydrogen like atom is ionized, the electron transitions to its highest bound state, at n = infinity,so its quantum number nf goes to infinity, making $1/n_f^2 = 0$.

So $E_{ionization} = (3)^2(13.6)(1/(1)^2 - 0) = 122.9$ eV.

$122.9 \text{ eV} * 1.6 * 10^{-19} = 1.96 * 10^{-17}$ J

1.33B

Find the ionization energy in eV and $kJ \cdot mol^{-1}$ of singly ionized helium in the $n = 3$ state using Bohr theory

Solution

To find the ionization energy of helium, consider the case where we move an electron from the $n = 3$ state to an infinite distance from the nucleus.

Using the Bohr formula for $\tilde{v}$.

$$\tilde{v} = Z^2 R_H (\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

$$\tilde{v} = 2^2 (109680\, cm^{-1}) \left(\frac{1}{3^2} - \frac{1}{\infty^2} \right)$$

$$\tilde{v} = 4.87467 \times 10^4 cm^{-1}$$

Then plugging into $E = hc\tilde{v}$

$$E = (6.626 \times 10^{-34} J \cdot s)(2.998 \times 10^8 m \cdot s^{-1})(4.87467 \times 10^6 m^{-1})$$

$$E = 9.68 \times 10^{-19} J = 583 kJ \cdot mol^{-1} = 6eV$$

1.34A

The speed of electron in an *n*th Bohr orbit is given by the equation:

$$v = \frac{e^2}{2\epsilon_0 nh}$$

The force acting between an electron and proton a distance r from one another is given by Coulomb's law:

$$f = \frac{e^2}{4\pi\epsilon_0 r^2}$$

The centrifugal force acts in opposition to the Coulombic force and is given by the equation:

$$f = \frac{mv^2}{r}$$

Find the values of v for the Bohr orbits of n = 4, n = 5, and n = 6, and find the total force in an atom between a proton and electron a distance of 5 x 10^{-11} m away from one another, with the electron moving at a speed of 2 x 10^{6} m/s.

Solution

To find v simply substitute the values for n into the equation:

$$v = \frac{e^2}{2\epsilon_0 nh}$$

For the values of v at n = 4, n = 5, n = 6, we get

n = 1

$$v_1 = 546,923\ m \cdot s^{-1}$$

n = 2

$$v_2 = 437,538\ m \cdot s^{-1}$$

n = 3

$$v_3 = 364,615\ m \cdot s^{-1}$$

To find the force between a proton and electron, simply subtract the Coulombic force from the Centrifugal force and substitute appropriate values for the constants:

$$f = \frac{mv^2}{r} - \frac{e^2}{4\pi\epsilon_0 r^2}$$

For which we attain:

$$f = 7.2875 \times 10^{-8} N$$

1.34B

Prove that the speed of electron in an *n*th Bohr orbit is $v = \frac{e^2}{2\epsilon_0 nh}$

Then find the first few values of v the Bohr orbit.

Solution

First we have to know that the angular moment of the electron revolving in the nth Bohr orbit is quantized then

$$mvr = \frac{nh}{2\pi}$$

where r is the radius of the nth Bohr orbit.

Kinetic energy of the electron is given as $\frac{mv^2}{2} = \frac{e^2}{2(4\pi\epsilon_0)r}$

So the radius, r must equal $r = \frac{e^2}{(4\pi\epsilon_0)mv^2}$

Now after substituting the value above into the first equation, we get

$mv(\frac{e^2}{(4\pi\epsilon_0)mv^2} = \frac{nh}{2\pi}$

Thus the speed of the electron in the n Bohr orbit is

$v = \frac{e^2}{2\epsilon_0 nh}$

For the first few values of v in the nth Bohr orbit, we get

n = 1

$v = 2.188 \times 10^6 m * s^-1$

n = 2

$v_2 = 1.094 \times 10^6 m * s^-1$

n = 3

$v_3 = 7.292 \times 10^5 m * s^-1$

1.35

What is the uncertainty in an electron's position if the uncertainty in measuring its velocity is 5 $m \cdot s^{-1}$.

Solution

According to the Heisenburg Uncertainty Principle

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

$$\Delta x \geq \frac{\hbar}{2\Delta p}$$

Then by definition $\Delta p = m\Delta v$

$$\Delta x \geq \frac{\hbar}{2m\Delta v}$$

$$\Delta x \geq \frac{6.626 \times 10^{-34} J \cdot s}{4\pi(9.109 \times 10^{-31} kg)(5m \cdot s^{-1})}$$

$$\Delta x \geq 1.16 \times 10^{-5} m$$

1.35

What is the *uncertainty* in the speed of an electron if we locate it to within 50 pm?

Solution

It is known that the uncertainty of momentum is given by the expression

$$\Delta p = m\Delta v$$

and Heisenberg's Uncertainty Principle states that

$$\Delta x \Delta p \geq h$$

Then

$$\begin{aligned} \Delta x(m\Delta v) &\geq h \\ \Delta v &\geq \frac{h}{m\Delta x} \\ &\geq \frac{6.626 \cdot 10^{-34} J \cdot s}{(9.109 \cdot 10^{-31} kg)(50 \cdot 10^{-12} m)} \\ &\geq 1.45 \cdot 10^{7} m \cdot s \end{aligned}$$

1.35

If we know the velocity of an electron to within $3.5 \times 10^{7} \frac{m}{s}$, then what is the uncertainty in its position?

Solution

Using the Heisenberg Uncertainty Principle,

$$\Delta x \Delta p \geq h = \Delta x \times m\Delta v \geq h$$

and rearranging to solve for uncertainty in velocity,

$$\Delta x \geq \frac{h}{m\Delta v}$$

we can use $h = 6.626 \times 10^{-34} J \cdot s$, $m = 9.109 \times 10^{-31} kg$, and $\Delta v = 3.5 \times 10^{7} \frac{m}{s}$ and find that

$$\Delta x \geq \frac{(6.626 \times 10^{-34} J \cdot s)}{(9.109 \times 10^{-31} kg)(3.5 \times 10^{7} \frac{m}{s})}$$

and thus

$$\Delta x \geq 2.078 \times 10^{-11} meters$$

1.35

If a proton is located to within 1 angstrom, what is its uncertainty in velocity?

Solution

The Heisenberg uncertainty principle states

$\Delta x \Delta p = h/4\pi$

$\Delta x m \Delta v = h/4\pi$

$\Delta v = h/(4m_p\pi\Delta x)$ where m_p is the mass of a proton

$x \sim \Delta x$ the uncertainty in position is on the same order as the location it is confined to, here 1 angstrom

$\Delta v = h/(4m_p\pi x) = (6.626*10^{-34})/(4*(1.67*10^{-27})*3.14*10^{-10})$

= 315.7 m/s

1.36

If the position of an electron is within the 10 pm interval, what is the uncertainty of the momentum? Is this value similar to that of an electron in the first Bohr orbit?

Solution

According to the uncertainty principle for position and momentum,

$$\Delta x \Delta p \geq h$$
$$\Delta p \geq \frac{h}{\Delta x}$$

by substituting the respective values we get,

$$\Delta p \geq \frac{6.626 \times 10^{-34} J.s}{10.0 \times 10^{-12} m}$$
$$\geq 2.9 \times 10^{-23} kg.m.s^{-}1$$

Therefore, uncertainty in the momentum of an electron will be $2.9 \times 10^{-23} kg.m.s^{-}1$.

We can calculate the momentum of an electron in the first Bohr radius by using v since we know that,

$$p = m_e v$$
$$= (9.109 \times 10^{-31} kg)(2.188 \times 10^{6} m \cdot s^{-1})$$
$$= (1.992 \times 10^{-24} kg \cdot m \cdot s^{-1})$$

The uncertainty of the momentum of an electron somewhere in a 10 pm interval is greater that the momentum of an electron in the first Bohr radius.

1.37

The Heisenberg Uncertainty Principle

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Show both sides have the same units

Solution

$$\Delta x = meters$$

$$\Delta p = m\Delta v$$

Planck's Constant has units of

$$J \cdot s$$

and

$$J = \frac{kg \cdot m^2}{s^2}$$

so apply these equations we get

$$m\frac{kg \cdot m}{s} \geq \frac{kg \cdot m^2 \cdot s}{s^2}$$

and simplify

$$\frac{kg \cdot m^2}{s} \geq \frac{kg \cdot m^2}{s}$$

Therefore Both sides have same units

1.38

The relationship between energy and time can be seen through the following uncertainty principle: $\Delta E \Delta t \geq h$. Through this relationship, it can be interpreted that a particle of mass m, the energy (E=mc^2) can come from nothing and return to nothing within a time Δt ≤ h/(mc^2). A real particle is one that lasts for time (Δt) or more; likewise, a particle that lasts for less than time (Δt) are called virtual particles. For a charged subatomic particle, a pion, the mass is $2.5 \times 10^{-28} kg$. For a pion to be considered a real particle, what is its minimum lifetime?

Solution

Based on the uncertainty principle for energy and time:

$$\Delta E \Delta t \geq h$$

$$\Delta t \geq \frac{h}{mc^2}$$

therefore $E = mc^2$. By plugging in the values, you get

$$\Delta t \geq \frac{6.626 \times 10^{-34} Js}{(2.5 \times 10^{-28} kg)(2.998 \times 10^8 ms^{-1})^2}$$
$$\geq 2.9 \times 10^{-23} s$$

Therefore, the minimum lifetime if the pion is to be considered a real particle will be $2.9 \times 10^{-23} s$.

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2: THE CLASSICAL WAVE EQUATION

The aim of this section is to give a fairly brief review of waves in various shaped elastic media—beginning with a taut string, then going on to an elastic sheet, a drumhead, first of rectangular shape then circular, and finally considering elastic waves on a spherical surface, like a balloon. The reason we look at this material here is that these are “real waves”, hopefully not too difficult to think about, and yet mathematically they are the solutions of the same wave equation the Schrödinger wavefunction obeys in various contexts, so should be helpful in visualizing solutions to that equation, in particular for the hydrogen atom.

2.1: The One-Dimensional Wave Equation

2.2: The Method of Separation of Variables

2.3: Oscillatory Solutions to Differential Equations

2.4: The General Solution is a Superposition of Normal Modes

2.5: A Vibrating Membrane

2.E: The Classical Wave Equation (Exercises)

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2.1: The One-Dimensional Wave Equation

Learning Objectives

- To introduce the wave equation including time and position dependence

In the most general sense, waves are particles or other media with wavelike properties and structure (presence of crests and troughs).

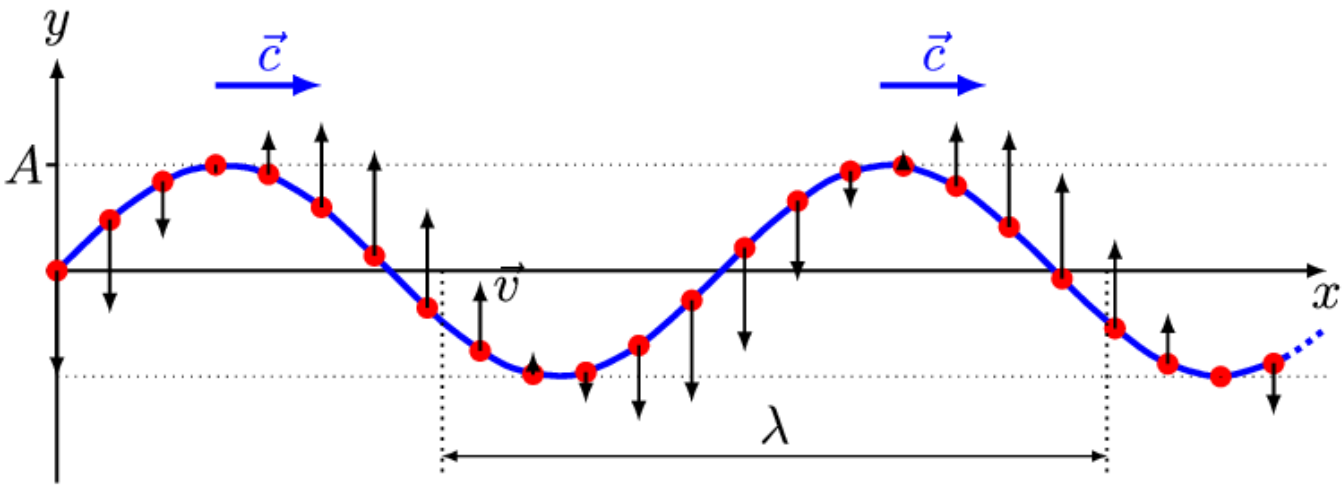


Figure 2.1.1 : A simple translational (transverse) wave. (CC BY-SA 4.0 International; And1mu via Wikimedia Commons)

The simplest wave is the (spatially) one-dimensional sine wave (Figure 2.1.1) with an varing amplitude A described by the equation:

$$A(x,t) = A_o \sin(kx - \omega t + \phi)$$

where

- A_o is the maximum amplitude of the wave, maximum distance from the highest point of the disturbance in the medium (the crest) to the equilibrium point during one wave cycle. In Figure 2.1.1 , this is the maximum vertical distance between the baseline and the wave.
- x is the space coordinate
- t is the time coordinate
- k is the wavenumber
- ω is the angular frequency
- ϕ is the phase constant.

One can categorize “waves” into two different groups: *traveling waves* and *stationary waves*.

Traveling Waves

Traveling waves, such as ocean waves or electromagnetic radiation, are waves that “move,” meaning that they have a frequency and are propagated through time and space. Another way of describing this property of “wave movement” is in terms of energy transmission – a wave travels, or transmits energy, over a set distance. The most important kinds of traveling waves in everyday life are electromagnetic waves, sound waves, and perhaps water waves, depending on where you live. It is difficult to analyze

waves spreading out in three dimensions, reflecting off objects, etc., so we begin with the simplest interesting examples of waves, those restricted to move along a line. Let's start with a rope, like a clothesline, stretched between two hooks. You take one end off the hook, holding the rope, and, keeping it stretched fairly tight, wave your hand up and back once. If you do it fast enough, you'll see a single bump travel along the rope:

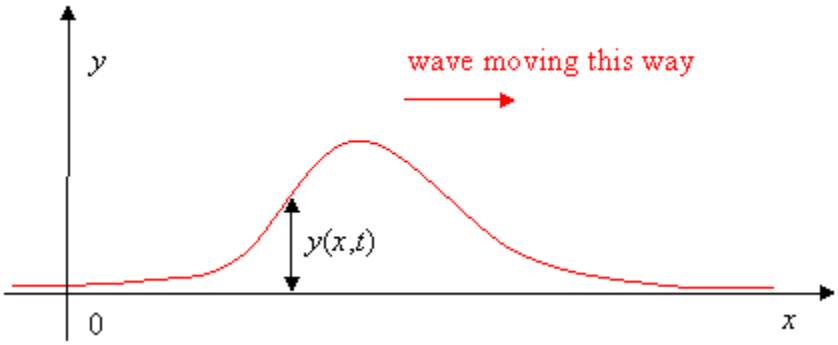


Figure 2.1.2 : A one-dimensional traveling wave at one instance of time t.

This is the simplest example of a *traveling wave*. You can make waves of different shapes by moving your hand up and down in different patterns, for example an upward bump followed by a dip, or two bumps. You'll find that the traveling wave *keeps the same shape* as it moves down the rope. Taking the rope to be stretched tightly enough that we can take it to be horizontal, we'll use its rest position as our *x*-axis (Figure 2.1.1). The y-axis is taken vertically upwards, and we only wave the rope in an up-and-down way, so actually $y(x,t)$ will be how far the rope is from its rest position at x at time t: that is, Figure 2.1.2 shows where the rope is at a single time t.

We can now express the observation that the wave "keeps the same shape" more precisely. Taking for convenience time $t = 0$ to be the moment when the peak of the wave passes $x = 0$, we graph here the rope's position at t = 0 and some later times t as a movie (Figure 2.1.3). Denoting the first function by $y(x,0) = f(x)$, then the second $y(x,t) = f(x - vt)$: it is the same function with the "same shape," but just moved over by vt, where v is the velocity of the wave.

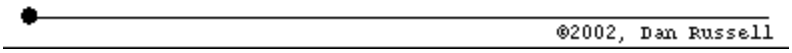


Figure 2.1.3 : A one-dimensional traveling wave at as a function of time. Traveling waves propagate energy from one spot to another with a fixed velocity v. (CC BY-NC-ND; Daniel A. Russell).

To summarize: on sending a traveling wave down a rope by jerking the end up and down, from observation the wave travels at constant speed and keeps its shape, so the displacement *y* of the rope at any horizontal position at x at time t has the form

$$y(x,t) = f(x - vt) \tag{2.1.1}$$

We are neglecting frictional effects—in a real rope, the bump gradually gets smaller as it moves along.

Standing Waves

In contrast to traveling waves, *standing waves,* or stationary waves, remain in a constant position with crests and troughs in fixed intervals. One way of producing a variety of standing waves is by plucking a melody on a set of guitar or violin strings. When placing one's finger on a part of the string and then plucking it with another, one has created a standing wave. The solutions to this problem involve the string oscillating in a sine-wave pattern (Figure 2.1.4) with no vibration at the ends. There is also no vibration at a series of equally-spaced points between the ends; these "quiet" places are *node*s. The places of maximum oscillation are *antinode*s.

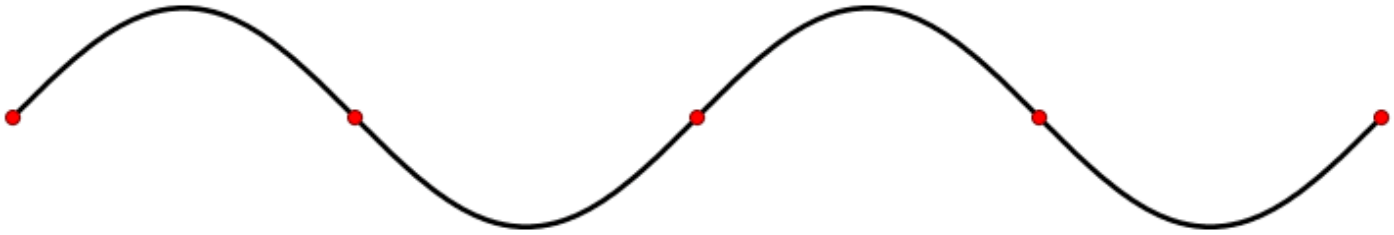


Figure 2.1.4 : Animation of standing wave in the stationary medium with marked wave nodes (red circles). (public domain; LucasVB).

Bound vs. Free particles and Traveling vs. Stationary Waves

Traveling waves exhibit movement and propagate through time and space and stationary wave have crests and troughs at fixed intervals separated by nodes. "Free" particles like the photoelectron discussed in the photoelectron effect, exhibit traveling wave like properties. In contrast, electrons that are "bound" waves will exhibit stationary wave like properties. The latter was invoked for the Bohr atom for quantizing angular moment of an electron bound within a hydrogen atom.

The Wave Equation

The mathematical description of the one-dimensional waves (both traveling and standing) can be expressed as

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{2.1.2}$$

with u is the amplitude of the wave at position x and time t, and v is the velocity of the wave (Figure 2.1.2).

Equation 2.1.2 is called the classical wave equation in one dimension and is a *linear partial differential equation*. It tells us how the displacement u can change as a function of position and time and the function. The solutions to the wave equation ($u(x,t)$) are obtained by appropriate integration techniques. It may not be surprising that not all possible waves will satisfy Equation 2.1.2 and the waves that do must satisfy both **the initial conditions** and the **boundary conditions**, i.e. on how the wave is produced and what is happening on the ends of the string.

For example, for a standing wave of string with length L held taut at two ends (Figure 2.1.3), the boundary conditions are

$$u(0,t) = 0 \tag{2.1.3}$$

and

$$u(L,t) = 0 \tag{2.1.4}$$

for all values of t. As expected, different system will have different boundary conditions and hence different solutions.

Mathematical Origin of Quantization

The initial conditions and the boundary conditions used to solve the wave equation will result in restrictions of "allowed" waves to exist in a similar fashion that only certain solutions exist for the electrons in the Bohr atom.

The first six wave solutions $u(x,t)$ to Equation 2.1.2 subject to the boundary conditions in Equations 2.1.3 and 2.1.4 (discussed in detail later) results in the wave in Figure 2.1.5 . These are standing waves that exist with frequencies based on the number of *nodes* (0, 1, 2, 3,...) they exhibit (more discussed in the following Section).



Figure 2.1.5 : Standing waves in a string (both spatially and temporally). The first six solutions ($u(x,t)$. from Wikipedia.

Curvature of Wave Solutions

Since the acceleration of the wave amplitude (right side of Equation 2.1.2) is proportional to $\frac{\partial^2}{\partial x^2}$, the greater curvature in the material produces a greater acceleration, i.e., greater changing velocity of the wave (Figure 2.1.4) and greater frequency of oscillation. As discussed later, the higher frequency waves (i..e, more nodes) are higher energy solutions; this as expected from the experiments discussed in Chapter 1 including Plank's equation $E = h\nu$.

Summary

Waves which exhibit movement and are propagated through time and space. The two basic types of waves are traveling and stationary. Both exhibit wavelike properties and structure (presence of crests and troughs) which can be mathematically described by a wavefunction or amplitude function. Both wave types display movement (up and down displacement), but in different ways.Traveling waves have crests and troughs which are constantly moving from one point to another as they travel over a length or distance. In this way, energy is transmitted along the length of a traveling wave. In contrast, standing waves have nodes at fixed positions; this means that the wave's crests and troughs are also located at fixed intervals. Therefore, standing waves only experience vibrational movement (up and down displacement) on these set intervals - no movement or energy travels along the length of a standing wave.

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2.2: The Method of Separation of Variables

Learning Objectives

- To be introduced to the *Separation of Variables* technique as method to solved wave equations

Solving the wave equation involves identifying the functions $u(x,t)$ that solve the partial differential equation that represent the amplitude of the wave at any position x at any time t

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{2.2.1}$$

This wave equation is a type of second-order partial differential equation (PDE) involving two variables - x and t. PDEs differ from ordinary differential equations (ODEs) that involve functions of only one variable. However, this difference makes PDEs appreciably more difficult to solve. In fact, the vast majority of PDE cannot be solved analytically and those classes of special PDEs that can be solved analytically invariably involve converting the PDE into one or more ODEs and then solving independently. One of these approaches is the the method of *separation of variables*.

Method of Separation of Variables

The general application of the *Method of Separation of Variables* for a wave equation involves three steps:

1. We find all solutions of the wave equation with the general form
$$u(x,t) = X(x)T(t)$$
for some function $X(x)$ that depends on x but not t and some function $T(t)$ that depends only on t, but not x. It is of course too much to expect that all solutions of Equation 2.2.1 are of this form, however, if we find a set of solutions $\{X_i(x)T_i(t)\}$ since the wave equation is a *linear equation*,
$$u(x,t) = \sum_i c_i X_i(x) T_i(t) \tag{2.2.2}$$
is also a solution for *any choice* of the constants c_i.
2. Impose constraints on the solutions based on the knowledge of the system. These are called the **boundary conditions**, which specify the values of $u(x,t)$ at the extremes ("boundaries"). This is a similar constraint to the solution as in initial value problems which the conditions $x(t_i)$ are specified at a specific time t_i. The goal is then to select the constants c_i in Equation 2.2.2 so that the boundary conditions are also satisfied.

Method of separation of variables is one of the most widely used techniques to solve partial differential equations and is based on the *assumption* that the solution of the equation is separable, that is, the final solution can be represented as a product of several functions, each of which is only dependent upon a single independent variable. If this assumption is incorrect, then clear violations of mathematical principles will be obvious from the analysis.

A Vibrating Spring Held Fixed Between Two Points

As discussed in Section 2.1, the solutions to the string example $u(x,t)$ for all x and t would be assumed to be a product of two functions: $X(x)$ and $T(t)$, where $X(x)$ is a function of only x, not t and $T(t)$ is a function of t, but not x.

$$u(x,t) = X(x)T(t) \tag{2.2.3}$$

Substitute Equation 2.2.3 into the one-dimensional wave equation (Equation 2.2.1) gives

$$\frac{\partial^2 X(x)T(t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 X(x)T(t)}{\partial t^2} \tag{2.2.4}$$

Since X is not a function of t and T is not a function of x, Equation 2.2.4 can be simplified

$$T(t)\frac{\partial^2 X(x)}{\partial x^2} = \frac{1}{v^2}X(x)\frac{\partial^2 T(t)}{\partial t^2} \tag{2.2.5}$$

Collecting the expressions that depend on x on the left side of Equation 2.2.5 and of t on the right side results in

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} = \frac{1}{v^2}\frac{1}{T(t)}\frac{\partial^2 T(t)}{\partial t^2} \tag{2.2.6}$$

Equation 2.2.6 is an interesting equation since each side can be set to a fixed constant K as that is the only solution that works for all values of t and x. Therefore, the equation can be separated into two *ordinary differential equations:*

$$\frac{d^2 T(t)}{dt^2} - Kv^2 T(t) = 0 \tag{2.2.7}$$

$$\frac{d^2 X(x)}{dx^2} - KX(x) = 0 \tag{2.2.8}$$

Hence, by substituting the new product solution form (Equation 2.2.3) into the original wave equation (Equation 2.2.1), we converted a partial differential equation of two variables (x and t) into two *ordinary differential equations* (differential equation containing a function or functions of one independent variable and its derivatives). Each differential equation involves only one of the independent variables (x or t).

- If $K = 0$, then the solution is the trivial $u(x, y,) = 0$ solution (i.e., no wave exists).
- If $K > 0$, then the general solution of Equation 2.2.8 is

$$X(x) = Ae^{\sqrt{K}x} + Be^{-\sqrt{K}x} \tag{2.2.9}$$

At this stage, Equation 2.2.9 implies that the solution to the two ordinary differential wave equations will be an infinite number of waves with no quantization to limit those that are allowed (i.e., any values of A and B are possible). Narrowing down the general solution to a specific solution occurs when taking the boundary conditions into account.

The boundary conditions for this problem is that the wave amplitude equal to zero at the ends of the string

$$u(0, t) = X(x)T(t) = 0 \tag{2.2.10}$$

$$u(L, t) = X(x)T(t) = 0 \tag{2.2.11}$$

for all times t.

Applying the two boundary conditions in Equations 2.2.10 and 2.2.11 into the general solution in Equation 2.2.9 results into relationships between A and B:

$$X(x = 0) = A + B = 0 \tag{2.2.12}$$

and

$$X(x = L) = Ae^{\sqrt{K}L} + Be^{-\sqrt{K}L} = 0 \tag{2.2.13}$$

Ignore the Trivial Solution

One solution to this is that $A = B = 0$, but this is the trivial solution from $K = 0$ and one we ignore since it provides no physical solution to the problem other than the knowledge that $0 = 0$, which is not that inspiring of a result.

Both Equations 2.2.7 and 2.2.8 can be generalized into the following equations

$$\frac{d^2 y(x)}{dx^2} - k^2 y(x) = 0 \tag{2.2.14}$$

where k is a real constant (i.e., not complex). Equation 2.2.14 is a *homogeneous* second order linear differential equation. The general solution to these types of differential equations has the form

$$y(x) = e^{\alpha x} \tag{2.2.15}$$

where α is a constant to be determined by the constraints of system. Substituting Equation 2.2.15 into Equation 2.2.14 results in

$$\left(\alpha^2 - k^2\right) y(x) = 0 \tag{2.2.16}$$

For this equation to be satisfied, either

- $\alpha^2 - k^2 = 0$ or
- $y(x) = 0$.

The later is the trivial solution and is ignored and therefore

$$\alpha^2 - k^2 = 0 \tag{2.2.17}$$

so

$$\alpha = \pm k \tag{2.2.18}$$

Hence, there are two solutions to the general Equation 2.2.14, as expected for a second order differential equation (first order differential equations have one solution), which are a result from substituting the α values from Equation 2.2.18 into Equation 2.2.15

$$y(x) = e^{k\,x}$$

$$y(x) = e^{-k\,x}$$

The general solution can then be any linear combination of these two equations

$$y(x) = c_1 e^{k\,x} + c_2 e^{-k\,x} \tag{2.2.19}$$

Example 2.2.1 : General Solution

Solve

$$y'' + 3y' - 4y = 0$$

Solution

The strategy is to search for a solution of the form

$$y = e^{\alpha t}$$

The reason for this is that long ago some geniuses figured this stuff out and it works. Now calculate derivatives

$$y' = \alpha e^{\alpha t}$$

$$y'' = \alpha^2 e^{\alpha t}$$

Substituting into the differential equation gives

$$\alpha^2 e^{\alpha t} + 3(\alpha e^{\alpha t}) - 4(e^{\alpha t}) = 0$$

$$(\alpha^2 + 3\alpha - 4)e^{\alpha t} = 0$$

Now divide by $e^{\alpha t}$ to get

$$\alpha^2 + 3\alpha - 4 = 0$$
$$(\alpha - 1)(\alpha + 4) = 0$$
$$\alpha = 1$$

and

$$\alpha = -4$$

We can conclude that two solutions are

$$y_1 = e^t$$

and

$$y_2 = e^{-4t}$$

Now let

$$L(y) = y'' + 3y' - 4y$$

It is easy to verify that if y_1 and y_2 are solutions to

$$L(y) = 0$$

then

$$y = c_1 y_1 + c_2 y_2$$

is also a solution. More specifically we can conclude that

$$y = c_1 e^t + c_2 e^{-4t}$$

Represents a two dimensional family (vector space) of solutions. Later we will prove that this is the most general description of the solution space.

Example 2.2.2 : Boundary Conditions

Solve

$$y'' - y' - 6y = 0$$

with $y(0) = 1$ and $y'(0) = 2$.

Solution

As before we seek solutions of the form

$$y = e^{rt}$$

Now calculate derivatives

$$y' = re^{rt}$$
$$y'' = r^2 e^{rt}$$

Substituting into the differential equation gives

$$r^2 e^{rt} + (re^{rt}) - 6(e^{rt}) = 0$$
$$(r^2 - r - 6)e^{rt} = 0$$

Now divide by e^{rt} to get

$$r^2 - r - 6 = 0$$
$$(r-3)(r+2) = 0$$

We can conclude that two solutions are

$$y_1 = e^{3t}$$

and

$$y_2 = e^{-2t}$$

We can conclude that

$$y = c_1 e^{3t} + C_2 e^{-2t}$$

Represents a two dimensional family (a "vector space") of solutions. Now use the initial conditions to find that

$$1 = c_1 + c_2$$

We have that

$$y' = 3C_1 e^{3t} - 2C_2 e^{-2t}$$

Plugging in the initial condition with y', gives

$$2 = 3c_1 - 2c_2$$

This is a system of two equations and two unknowns. We can use linear algebra to arrive at

$$c_1 = \frac{4}{5}$$

and

$$C_2 = \frac{1}{5}$$

The final solution is

$$y = \frac{4}{5} e^{3t} + \frac{1}{5} e^{-2t}$$

When $K > 0$, the general solutions of Equations 2.2.7 and 2.2.8 are oscillatory in time and space, respectively, as discussed in the following section.

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2.3: Oscillatory Solutions to Differential Equations

Learning Objectives

- Explore the basis of the oscillatory solutions to the wave equation
- Understand the consequences of boundary conditions on the possible solutions
- Rationalize how satisfying boundary conditions forces quantization (i.e., only solutions with specific wavelengths exist)

The boundary conditions for the string held to zero at both ends argue that $u(x,t)$ collapses to zero at the extremes of the string (Figure 2.3.1).

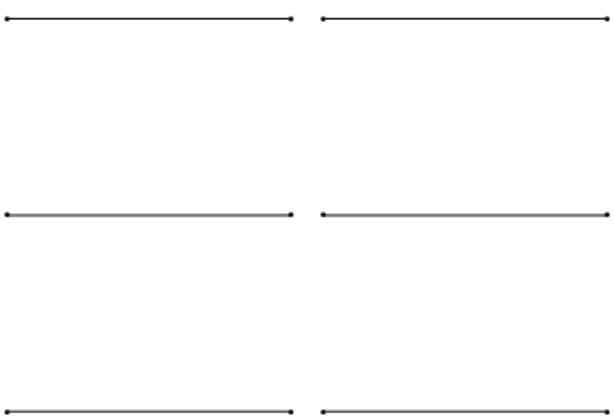


Figure 2.3.1 : Standing waves in a string (both spatially and temporally). from Wikipedia.

Unfortunately, when $K > 0$, the general solution (Equation 2.2.7) results in a sum of exponential decays and growths that cannot achieve the boundary conditions (except for the trivial solution); hence $K < 0$. This means we must introduce complex numbers due to the $\sqrt{K}$ terms in Equation 2.2.5. So we can rewrite K:

$$K = -p^2 \tag{2.3.1}$$

and Equation 2.2.4b can be

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0 \tag{2.3.2}$$

The general solution to differential equations of the form of Equation 2.3.2 is

$$X(x) = Ae^{ipx} + Be^{-ipx} \tag{2.3.3}$$

Example 2.3.1

Verify that Equation 2.3.3 is the general form for differential equations of the form of Equation 2.3.2, which when substituted with Equation 2.3.1 give

$$X(x) = Ae^{ipx} + Be^{-ipx}$$

Solution

Expand the complex exponentials into trigonometric functions via Euler formula ($e^{i\theta} = \cos\theta + i\sin\theta$)

$$X(x) = A\left[\cos(px) + i\sin(px)\right] + B\left[\cos(px) - i\sin(px)\right]$$

collecting like terms

$$X(x) = (A+B)\cos(px) + i(A-B)\sin(px) \tag{2.3.4}$$

Introduce new *complex* constants $c_1 = A + B$ and $c_2 = i(A - B)$ so that the general solution in Equation 2.3.4 can be expressed as oscillatory functions

$$X(x) = c_1\cos(px) + c_2\sin(px) \tag{2.3.5}$$

Now let's apply the boundary conditions from Equation 2.2.7 to determine the constants c_1 and c_2. Substituting the first boundary condition ($X(x=0) = 0$) into the general solutions of Equation 2.3.5 results in

$$\begin{aligned} X(x=0) = c_1\cos(0) + c_2\sin(0) &= 0 \\ c_1 + 0 &= 0 \\ c_1 &= 0 \end{aligned} \tag{2.3.6}$$

and substituting the second boundary condition ($X(x=L) = 0$) into the general solutions of Equation 2.3.5 results in

$$X(x=L) = c_1\cos(pL) + c_2\sin(pL) = 0 \tag{2.3.7}$$

we already know that $c_1 = 0$ from the first boundary condition so Equation 2.3.7 simplifies to

$$c_2\sin(pL) = 0 \tag{2.3.8}$$

Given the properties of sines, Equation 2.3.7 simplifies to

$$pL = n\pi \tag{2.3.9}$$

with $n = 0$ is the *trivial solution* that we ignore so $n = 1, 2, 3....$

$$p = \frac{n\pi}{L} \tag{2.3.10}$$

Substituting Equations 2.3.10 and 2.3.6 into Equation 2.3.5 results in

$$X(x) = c_2\sin\left(\frac{n\pi x}{L}\right)$$

which can simplify to

$$X(x) = c_2\sin(\omega x)$$

with

$$\omega = \frac{n\pi}{L}$$

A similar argument applies to the other half of the *ansatz* ($T(t)$).

Exercise 2.3.1

Given two traveling waves:

$$\psi_1 = \sin(c_1x + c_2t) \quad \text{and} \quad \psi_2 = \sin(c_1x - c_2t)$$

a. Find the wavelength and the wave velocity of ψ_1 and ψ_2
b. Find the following and identify nodes:

$$\psi_+ = \psi_1 + \psi_2 \quad \text{and} \quad \psi_- = \psi_1 - \psi_2$$

Solution a

ψ_1 is a sin function. At every integer $n\pi$ where $n = 0, \pm1, \pm2, ...$, a sin function will be zero. Thus, $\psi_1 = 0$ when $c_1x + c_2t = \pi n$. Solving for the x, while ignoring trivial solutions:

$$x = \frac{n\pi - c_2t}{c_1}$$

The velocity of this wave is:

$$\frac{dx}{dt} = -\frac{c_2}{c_1}$$

Similarly for ψ_2. At every integer $n\pi$ where $n = 0, \pm1, \pm2, ...$, a sin function will be zero. Thus, $\psi_2 = 0$ when $c_1x - c_2t = \pi n$. Solving for x, for ψ_2:

$$x = \frac{n\pi + c_2t}{c_1}$$

The velocity of this wave is:

$$\frac{dx}{dt} = \frac{c_2}{c_1}$$

The wavelength for each wave is twice the distance between two successive nodes. In other words,

$$\lambda = 2(x_n - x_{n-1}) = \frac{2\pi}{c_1}$$

Solution b

Find $\psi_+ = \psi_1 + \psi_2 \quad \text{and} \quad \psi_- = \psi_1 - \psi_2$.

$$\begin{aligned}\psi_+ &= \sin(c_1x + c_2t) + \sin(c_1x - c_2t)\\ &= \sin(c_1x)\cos(c_2t) + \cancel{\cos(c_1x)\sin(c_1t)} + \sin(c_1x)\cos(c_2t) - \cancel{\cos(c_1x)\sin(c_1t)}\\ &= 2\sin(c_1x)\cos(c_2t)\end{aligned}$$

This should have a node at every $x = n\pi/c_1$ and

$$\begin{aligned}\psi_- &= \sin(c_1x + c_2t) - \sin(c_1x - c_2t)\\ &= \cancel{\sin(c_1x)\cos(c_2t)} + \cos(c_1x)\sin(c_1t) - \cancel{\sin(c_1x)\cos(c_2t)} + \cos(c_1x)\sin(c_1t)\\ &= 2\cos(c_1x)\sin(c_2t)\end{aligned}$$

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2.4: The General Solution is a Superposition of Normal Modes

Learning Objectives

- Separate the wave equation into individual spatial and temporal problems and solve them.
- Demonstrate that the general solution can be a superposition of solutions (normal modes)

As discussed previously, the solutions to the string example $u(x,t)$ for all x and t would be assumed to be a product of two functions: $X(x)$ and $T(t)$, where $X(x)$ is a function of only x, not t and $T(t)$ is a function of t, but not x.

$$u(x,t) = X(x)T(t)$$

By substituting the new product solution form into the original wave equation, one can obtain two *ordinary differential equations* (differential equation containing a function or functions of one independent variable and its derivatives). Each differential equation would involve only one of the independent variables (x or t).

Spatial Dependence of the Solution: $X(x)$

The boundary conditions for the string held to zero at both ends argue that $u(x,t)$ collapses to zero at the extremes of the string. Unfortunately, when $K > 0$, the general solution to the wave equation results in a sum of exponential decays and growths that cannot achieve the boundary conditions (except for the trivial solution that $u(x,t) = 0$); hence $K < 0$. This means we must introduce complex numbers due to the $\sqrt{K}$ terms in Equation 2.4.5. So we can rewrite K:

$$K = -p^2 \tag{2.4.1}$$

and Equation 2.4.4b can be

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0 \tag{2.4.2}$$

The general solution to differential equations of the form of Equation 2.4.2 is

$$X(x) = Ae^{\sqrt{K}x} + Be^{-\sqrt{K}x} \tag{2.4.3}$$

that when substituted with Equation 2.4.1 give

$$X(x) = Ae^{ipx} + Be^{-ipx}$$

The complex exponentials in Equation 2.4.1 can be expressed as trigonometric functions via Euler formula ($e^{i\theta} = \cos\theta + i\sin\theta$)

$$X(x) = A\left[\cos(px) + i\sin(px)\right] + B\left[\cos(px) - i\sin(px)\right]$$

collecting like terms

$$X(x) = (A+B)\cos(px) + i(A-B)\sin(px) \tag{2.4.4}$$

The general solution in Equation 2.4.4 can be expressed as oscillatory functions by introducing new *complex* constants $C = A + B$ and $D = i(A - B)$:

$$X(x) = C\cos(px) + D\sin(px) \tag{2.4.5}$$

Exercise 2.4.1

Verify that Equation 2.4.3 is the general form for differential equations of the form of Equation 2.4.2.

Answer available at the end of this section.

Now let's apply the boundary conditions from Equation 2.4.5 to determine the constants C and D. Substituting the first boundary condition ($X(x=0)=0$) into the general solutions of Equation 2.4.5 results in

$$\begin{aligned} X(x=0) &= 0 \\ C\cos(0) + D\sin(0) &= 0 \\ C + 0 &= 0 \\ C &= 0 \end{aligned} \tag{2.4.6}$$

and substituting the second boundary condition ($X(x=L)=0$) into the general solutions of Equation 2.4.5 results in

$$X(x=L) = C\cos(pL) + D\sin(pL) = 0 \tag{2.4.7}$$

we already know that $C=0$ from the first boundary condition so Equation 2.4.7 simplifies to

$$D\sin(pL) = 0$$

Given the properties of sines, Equations 2.4.7 simplifies to

$$pL = n\pi$$

with $n=0$ is the *trivial solution* that we ignore so $n=1,2,3....$

$$p = \frac{n\pi}{L} \tag{2.4.8}$$

Substituting Equations 2.4.8 and 2.4.6 into Equation 2.4.5 results in

$$X(x) = D\sin\left(\frac{n\pi x}{L}\right) \tag{2.4.9}$$

Equation 2.4.9 presents a set of solutions to the spatial part of the solution to the wave equation subject to the boundary conditions (Figure 2.4.1). This set of solutions is infinitely large with individual solutions that are distinguished from each other by the n parameter introduced to account for the boundary conditions. This number is an example of a "quantum number" that are ubiquitously in quantum mechanics and are uniquely defined for each system.

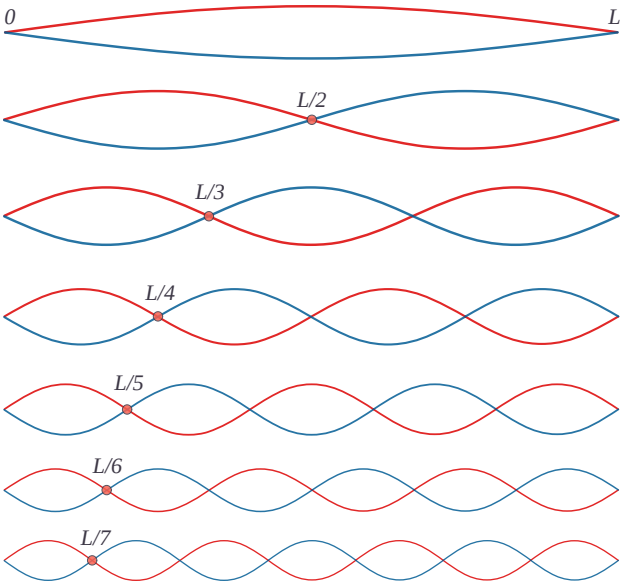


Figure 2.4.1: The first seven $X(x)$ solutions of a vibrating string of length L at the two times of maximum displacement (red and blue). (CC BY-NC; Ümit Kaya via LibreTexts).

Time Dependence of the Solution: $T(t)$

A similar argument applies to the other half of the *ansatz* ($T(t)$) originally proposed for the classical wave equation was obtain from solving Equation 2.4.4a, which qualitatively resembles the original spatial differential equation solved above (Equation 2.4.4b).

$$\frac{d^2T(t)}{dt^2} - Kv^2T(t) = 0$$

However, the constraints extracted from solving spatial dependence apply to the time dependence. When Equations 2.4.1 and 2.4.8 are substituted into Equation 2.4.4a, a more simplified expression is obtained

$$\frac{d^2T(t)}{dt^2} + p^2v^2T(t) = \frac{d^2T(t)}{dt^2} + \left(\frac{nv\pi}{L}\right)^2 T(t) = 0 \tag{2.4.10}$$

Define a new constant: ω_n

$$\omega_n = \left(\frac{nv\pi}{L}\right)$$

and substitute into Equation 2.4.10

$$\frac{d^2T(t)}{dt^2} + \omega_n^2T(t) = 0$$

This is the same functional form of Equation 2.4.2

$$T(t) = E\cos(\omega_n t) + F\sin(\omega_n t) \tag{2.4.11}$$

In contrast to the spatial dependence solution, we have no boundary conditions to use to identify the constants E and F.

The Principle of Superposition

Now let's revisit the original *ansatz* solution to the classical wave equation (Equation 2.4.1), which can be substituted with Equations 2.4.9 and 2.4.11

$$\begin{aligned} u(x,t) &= X(x)T(t) \\ &= \left[D\sin\left(\frac{n\pi x}{L}\right)\right](E\cos(\omega_n t) + F\sin(\omega_n t)) \end{aligned}$$

we can collect constants again with $G = DE$ and $H = DF$ and introduce a n dependence to each since E and F may be n dependence.

$$u_n(x,t) = \underbrace{[G_n\cos(\omega_n t) + H_n\sin(\omega_n t)]}_{\text{temporal solution}}\underbrace{\sin\left(\frac{n\pi x}{L}\right)}_{\text{spatial solution}} \tag{2.4.12}$$

The functions represented in Equation 2.4.12 are set of solutions including both spatial and temporal features that solve the wave equation of a string held tight on two ends.

Linearity of the Wave Equation

The wave equation has a very important property: if we have two solutions to the equation, then the sum of the two is *also* a solution to the equation. It's easy to check this:

$$\frac{\partial^2(f+g)}{\partial x^2} = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 g}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 f}{\partial t^2} + \frac{1}{v^2}\frac{\partial^2 g}{\partial t^2} = \frac{1}{v^2}\frac{\partial^2(f+g)}{\partial t^2}$$

Any differential equation for which this property holds is called *a linear differential equation*. Also note that $af(x,t) + bg(x,t)$ is also a solution to the equation if a, b are constants. So you can add together—superpose—multiples of any two solutions of the wave equation to find a new function satisfying the equation.

The linearity property is easy to interpret *visually*: if you can draw two wave solutions, then at each point on the string simply add the displacement $u_n(x,t)$ of one wave to the other $u_m(x,t)$—the sum of the two waves together is a solution. So, for example, as two traveling waves moving along the string in opposite directions meet each other, the displacement of the string at any point at any instant is just the sum of the displacements it would have had from the two waves singly.



Figure 2.4.2: Interference of Multiple Pulses. ("for non-profit educational purposes."; Tom Walsh via ophysics.com)

This simple addition of the displacements is interference, doubtless because if the waves meeting have displacements in opposite directions, the string will be displaced less than by a single wave. This is also called the ***Principle of Superposition***.

Principle of Superposition

The *Principle of Superposition* is the sum of two or more solutions is also a solution.

Since the wave equation is a linear homogeneous differential equation, the total solution can be expressed as a sum of all

possible solutions described by Equation 2.4.12.

$$u(x,t) = \sum_{n=1}^{\infty} u_n(x,t) \tag{2.4.13}$$

$$= \sum_{n=1}^{\infty} \left(G_n \cos(\omega_n t) + H_n \sin(\omega_n t)\right) \sin\left(\frac{n\pi x}{L}\right) \tag{2.4.14}$$

Each $u_n(x,t)$ solution is called a **normal mode** of the system and can be characterized via their corresponding frequencies $\frac{n\pi}{L}$ with $n = 1, 2, 3....$ The spatial dependence of the first seven normal modes are shown in Figure 2.4.1 and are standing waves. The first term with $n = 1$ is typically called the *fundamental* and each subsequent modes is called an *overtone* or *harmonic*. The temporal dependence of the normal modes is sinusoidal with angular frequencies ω_n that can be expanded to natural frequencies ν_n via

$$\nu_n = \frac{\omega_n}{2\pi} = \frac{nv}{2L} \tag{2.4.15}$$

Hence, as the spatial curvature of the normal mode increases, the temporal oscillation of that mode also increases. This is a common trait in quantum mechanical systems and is a direct consequence of the wave equation.

Answers

In order to show that

$$X(x) = Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x} \tag{2.4.16}$$

is a general solution to the differential equation

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0.$$

We then have to take the second derivative of Equation 2.4.16 and substitute it and the original function into the appropriate locations in Equation 2.4.3 and verify that it does in fact equal 0.

First we have to take the first and then second derivative of Equation 2.4.16

$$\frac{d}{dx}\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) = \sqrt{k}Ae^{\sqrt{k}x} - \sqrt{k}Be^{-\sqrt{k}x}$$

$$\frac{d^2}{dx^2}\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) = kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x}$$

Now that we have the second derivative of Equation 2.4.16 we plug the relevant values into Equation 2.4.2

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0$$

$$kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x} + p^2\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) \stackrel{?}{=} 0$$

We are given in Equation 2.4.2 that

$$k = -p^2$$

So

$$p^2 = -k$$

Now we can plug that into our differential equation to simplify

$$kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x} - k\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) \stackrel{?}{=} 0$$

$$\cancel{kAe^{\sqrt{k}x}} + \cancel{kBe^{-\sqrt{k}x}} - \cancel{kAe^{\sqrt{k}x}} - \cancel{kBe^{-\sqrt{k}x}} \stackrel{\checkmark}{=} 0$$

As all of these terms cancel to equal 0, we prove that the solution given is a general solution to the differential equation. It is important to remember though that it is not the only solution to the differential equation.

This page titled 2.4: The General Solution is a Superposition of Normal Modes is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Michael Fowler.

2.5: A Vibrating Membrane

Learning Objectives

- To apply the wave equations to a two-dimensional membrane (rectangles and circles)
- To recognize the possible geometries of a nodes in two-dimensional systems

So far, we've looked at waves in one dimension, traveling along a string or sound waves going down a narrow tube. However, waves in higher dimensions than one are very familiar—water waves on the surface of a pond, or sound waves moving out from a source in three dimensions. It is pleasant to find that these waves in higher dimensions satisfy wave equations which are a very natural extension of the one we found for a string, and—very important—they also satisfy the *Principle of Superposition*, in other words, if waves meet, you just add the contribution from each wave. In the next two paragraphs, we go into more detail, but this Principle of Superposition is the crucial lesson.

The Wave Equation and Superposition in More Dimensions

What happens in higher dimensions? Let's consider two dimensions, for example waves in an elastic sheet like a drumhead. If the rest position for the elastic sheet is the (x, y) plane, so when it's vibrating it's moving up and down in the z-direction, its configuration at any instant of time is a function. $u(x, y, t)$

In fact, we could do the same thing we did for the string, looking at the total forces on a little bit and applying Newton's Second Law. In this case that would mean taking one little bit of the drumhead, and instead of a small stretch of string with tension pulling the two ends, we would have a small *square* of the elastic sheet, with tension pulling all around the edge. Remember that the net force on the bit of string came about because the string was curving around, so the tensions at the opposite ends tugged in slightly different directions, and did not cancel. The $\frac{\partial^2}{\partial x^2}$ term measured that curvature, the rate of change of slope. In two dimensions, thinking of a small square of the elastic sheet, things are more complicated. Visualize the bit of sheet to be momentarily like a tiny patch on a balloon, you'll see it curves in two directions, and tension forces must be tugging all around the edges. The total force on the little square comes about because the tension forces on opposite sides are out of line if the surface is curving around, now we have to add *two* sets of almost-opposite forces from the two pairs of sides. The math is now shown here, but it is at least plausible that the equation is:

$$\frac{\partial^2 u(x,y,t)}{\partial x^2} + \frac{\partial^2 u(x,y,t)}{\partial y^2} = \frac{1}{v^2}\frac{\partial^2 u(x,y,t)}{\partial t^2} \tag{2.5.1}$$

The physics of this equation is that the acceleration of a tiny bit of the sheet comes from out-of-balance tensions caused by the sheet curving around in *both* the *x*- and *y*-directions, this is why there are the two terms on the left hand side.

And, going to three dimensions is easy: add one more term to give

$$\frac{\partial^2 u(x,y,,z,t)}{\partial x^2} + \frac{\partial^2 u(x,y,z,t)}{\partial y^2} + \frac{\partial^2 u(x,y,z,t)}{\partial z^2} = \frac{1}{v^2}\frac{\partial^2 u(x,y,z,t)}{\partial t^2} \tag{2.5.2}$$

This sum of partial differentiations in space is so common in physics that there's a shorthand:

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2}, \frac{\partial^2}{\partial y^2}, \frac{\partial^2}{\partial z^2}\right)$$

so Equation 2.5.2 can be more easily written as

$$\nabla^2 u(x,y,z,t) = \frac{1}{v^2}\frac{\partial^2 u(x,y,z,t)}{\partial t^2}$$

Just as we found in one dimension traveling harmonic waves (no boundary conditions)

$$u(x,t) = A\sin(kx - \omega t)$$

with $\omega = \nu k$, you can verify that the *three*-dimensional equation has harmonic solutions

$$u(x, y, z, t) = A \sin(k_x x + k_x + k_z z - \omega t)$$

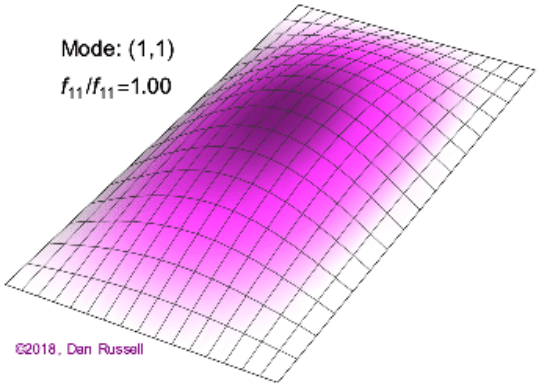
with $\omega = \nu|\vec{k}|$ where $|k| = \sqrt{k_x^2 + k_y^2 + k_z^2}$.

$\vec{k}$ is a vector in the direction the wave is moving. The electric and magnetic fields in a radio wave or light wave have just this form (or, closer to the source, a very similar equivalent expression for outgoing spheres of waves, rather than plane waves).

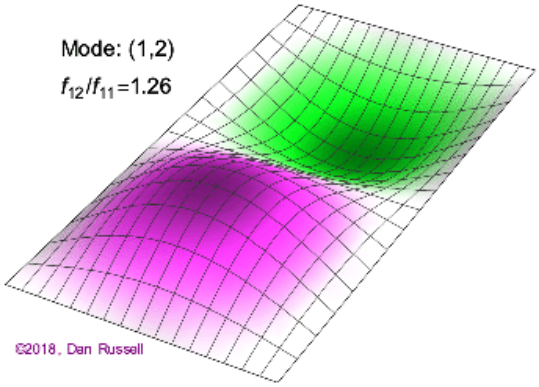
> It's important to realize that the 2D wave equation (Equation 2.5.1) is still a ***linear*** equation, so the Principle of Superposition still holds. If two waves on an elastic sheet, or the surface of a pond, meet each other, the result at any point is given by simply adding the displacements from the individual waves. We'll begin by thinking about waves propagating freely in two and three dimensions, than later consider waves in restricted areas, such as a drum head.

Vibrational Modes of a Rectangular Membrane

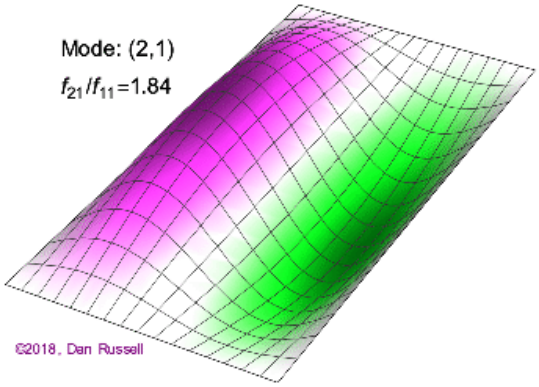
A one-dimensional wave does not have a choice in how it propagates: it just moves along the line (well, it could get partly reflected by some change in the line and part of it go backwards). However, when we go to higher dimensions, how a wave disturbance starting in some localized region spreads out is far from obvious. But we can begin by recalling some simple cases: dropping a pebble into still water causes an outward moving circle of ripples. If we grant that light is a wave, we notice a beam of light changes direction on going from air into glass. Of course, it is not immediately evident that light *is* a wave: we'll talk a lot more about that later. A few solutions (both temporal and spatials) are shown below together with their quantum numbers (n_x and n_y).



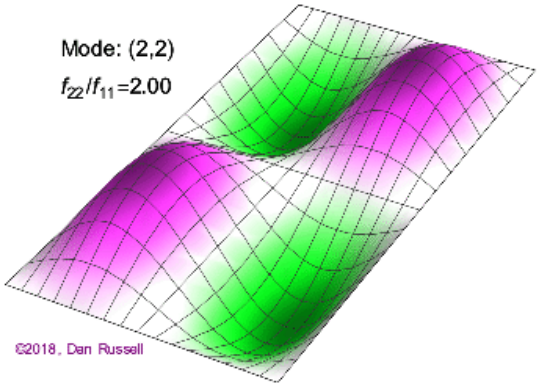
The ($n_x = 1$, $n_y = 1$) Solution



The ($n_x = 1$, $n_y = 2$) Solution



The ($n_x = 2$, $n_y = 1$) Solution



The ($n_x = 2$, $n_y = 2$) Solution

Figure 2.5.1: Select Vibrational Modes of a Rectangular Membrane. Animations courtesy of Dr. Dan Russell via Grad. Prog. Acoustics, Penn State).

Solving for the function $u(x, y, t)$ in a vibrating, rectangular membrane is done in a similar fashion by separation of variables, and setting boundary conditions. The solved function is very similar, where

$$u(x, y, t) = A_{nm} \cos(\omega_{nm} t + \phi_{nm}) \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \tag{2.5.3}$$

where

- a is the length of the rectangular membrane and b is the width, and
- n_x and n_y are two quantum numbers (one in each dimension).

As with the solutions to 1-D wave equations, a **node** is a point (or line) on a structure that does not move while the rest of the

structure is vibrating.

Example 2.5.1: Nodal Geometries in Rectangular Membranes

For the following 2-D solutions in Figure 2.5.1, how many nodes are there, what is the geometry and how would you characterize them?

a. ($n_x = 1$, $n_y = 1$
b. ($n_x = 2$, $n_y = 1$

Solution a

The ($n_x = 1$, $n_y = 1$ solution in Figure 2.5.1 has zero nodes. That is, no spot in the membrane (other than the boundaries) is not moving during the motion of the membrane.

Solution b

The ($n_x = 2$, $n_y = 1$ solution in Figure 2.5.1 has one node. It is a line at half the length of the x direction and extends over the entire length of the y direction.

Exercise 2.5.1

For the ($n_x = 2$, $n_y = 2$ solution to a rectangular membrane in Figure 2.5.1 : how many nodes are there, what is the geometry and how would you characterize them?

Answer available at the end of this section.

Vibrational Modes of a Circular Membrane

The basic principles of a vibrating rectangular membrane applies to other 2-D members including circular membranes. However, the mathematics and solutions are a bit more complicated. The solutions are best represented in polar notation (instead of rectangular like in Equation 2.5.3) and have the following functional form

$$u(r, \theta, t) = J_m\left(\lambda_{mn} r\right) \cos m\theta \cos c\lambda_{mn} t$$

where J_m are Bessel functions (these are oscillatory functions) and λ are constants. This system has two quantum numbers (m and n) that serve the same function as n_x and n_y do in the rectangular membranes. In the animations in Figure 2.5.2 , the nodal diameters and circles show up as white regions that do not oscillate, while the red and blue regions indicate positive and negative displacements.

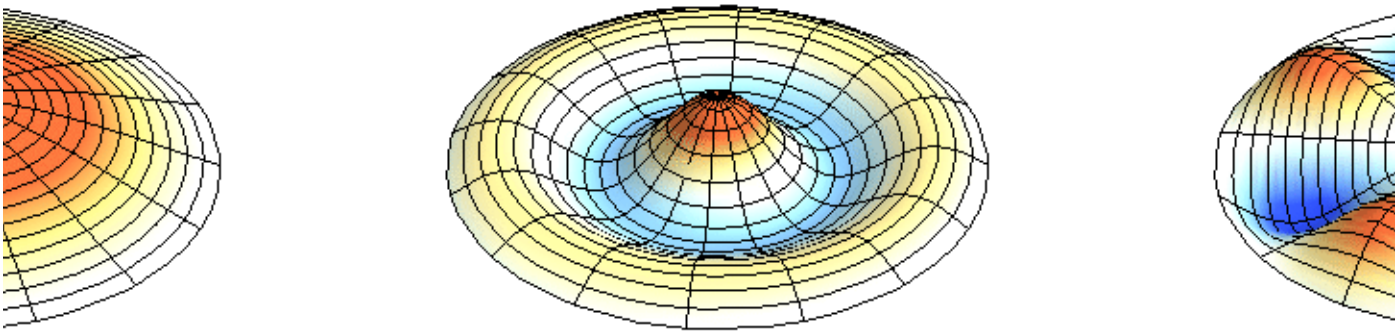


Figure 2.5.2: Select Vibrational Modes of a Circular Membrane. (CC BY-SA-ND 4.0; Dan Russell, via Grad. Prog. Acoustics, Penn State.

Figure 2.5.2 (left) shows the fundamental mode shape for a vibrating circular membrane, while the other two modes are excited modes with more complex nodal character.

Exercise 2.5.2

How many nodes are there in the three solutions for a circular membrane in Figure 2.5.2, what are their geometries, and how would you characterize them?

Answer available at the end of this section.

Answers

Exercise 2.5.1

There are two nodes. They are lines and one is at half the length of the x direction and extends over the entire length of the y direction and one if and one is at half the length of the y direction and extends over the entire length of the x direction

Exercise 2.5.2

(left) zero nodes

(middle) two nodes. They are circular at approximately 1/3 and 2/3 the radius (these are radial nodes = at fixed radii)

(right) four nodes. They are lines at 45° angle from the center (these are angular nodes = at fixed angles).

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2.E: The Classical Wave Equation (Exercises)

Solutions to select questions can be found online.

2.1A

Find the general solutions to the following differential equations:

a. $\frac{d^2y}{dx^2} - 4y = 0$
b. $\frac{d^2y}{dx^2} - 3\frac{dy}{dx} - 54y = 0$
c. $\frac{d^2y}{dx^2} + 9y = 0$

2.1B

Find the general solutions to the following differential equations:

a. $\frac{d^2y}{dx^2} - 16y = 0$
b. $\frac{d^2y}{dx^2} - 6\frac{dy}{dx} + 27y = 0$
c. $\frac{d^2y}{dx^2} + 100y = 0$

2.1C

Find the general solutions to the following differential equations:

a. $\frac{dy}{dx} - 4\sin(x)y = 0$
b. $\frac{d^2y}{dx^2} - 5\frac{dy}{dx} + 6y = 0$
c. $\frac{d^2y}{dx^2} = 0$

2.2A

Practice solving these first and second order homogeneous differential equations with given boundary conditions:

a. $\frac{dy}{dx} = ay$ with $y(0) = 11$
b. $\frac{d^2y}{dt^2} = ay$ with $y(0) = 6$ and $y'(0) = 4$
c. $\frac{d^2y}{dt^2} + \frac{dy}{dt} - 42y = 0$ with $y(0) = 2$ and $y'(0) = 0$

2.3A

Prove that $x(t) = \cos(\theta)$ oscillates with a frequency

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Prove that $x(t) = \cos(\theta)$ also has a period

$$T = 2\pi\sqrt{\frac{m}{k}}$$

where k is the force constant and m is mass of the body.

2.3B

Try to show that

$$x(t) = \sin(\omega t)$$

oscillates with a frequency

$$\nu = \omega/2\pi$$

Explain your reasoning. Can you give another function of x(t) that have the same frequency.

2.3C

Which two functions oscillate with the same frequency?

a. $x(t) = \cos(\omega t)$
b. $x(t) = \sin(2\omega t)$
c. $x(t) = A\cos(\omega t) + B\sin(\omega t)$

2.3D

Prove that $x(t) = \cos(\omega(t))$ oscillates with a frequency

$$\nu = \frac{\omega}{2\pi}.$$

Prove that $x(t) = A\cos(\omega(t) + B\sin(\omega(t))$ oscillates with the same frequency:

$$\nu = \frac{\omega}{2\pi}.$$

2.4

Show that the differential equation:

$$\frac{d^2y}{dx^2} + y(x) = 0$$

has a solution

$$y(x) = 2\sin x + \cos x$$

2.7

For a classical harmonic oscillator, the displacement is given by

$$\xi(t) = v_0\sqrt{\frac{m}{k}}\sin\sqrt{\frac{k}{m}}t$$

where $\xi = x - x_0$. Derive an expression for the velocity as a function of time, and determine the times at which the velocity of the oscillator is zero.

2.11

Verify that

$$Y(x,t) = A\sin\left(\frac{2\pi}{\lambda}(x - vt)\right)$$

has a frequency $\nu = v/\lambda$ and wavelength λ traveling right with a velocity v.

2.13A

Explain (in words) how to expand the Hamiltonian into two dimensions and use it solve for the energy

2.13B

Given that the Schrödinger equation for a two-dimensional box, with sides a and b, is

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{(8\pi^2 mE)}{h^2}\Psi(x,y) = 0$$

and it has the boundary conditions of

$$\Psi(0,y) = \Psi(a,y) = 0 \text{ and } \Psi(o,x) = \Psi(x,b) = 0$$

for all x and y values, show that

$$E_{2,2} = \left(\frac{h^2}{2ma^2}\right) + \left(\frac{h^2}{2mb^2}\right).$$

2.14

Explain, in words, how to expand the Schrödinger Equations into a three-dimensional box

2.18

Solving for the differential equation for a pendulum gives us the following equation,

$$\phi(x) = c_1 \cos\sqrt{\frac{g}{L}} + c_2 \sin\sqrt{\frac{g}{L}}$$

Assuming $c_1 = 2$, $c_3 = 5$, $g = 7$ and $L = 3$, what is the position of the pendulum initially? Does this make sense in the real world. Why or why not? (We can ignore units for this problem).

2.23

Consider a Particle of mass m in a one-dimensional box of length a. Its average energy is given by

$$\langle E\rangle = \frac{1}{2m}\langle p^2\rangle$$

Because

$$\langle p\rangle \ = 0$$

$$\langle p^2\rangle = \sigma_p^2$$

where σ_p can be called the uncertainty in p. Using the Uncertainty Principle, show that the energy must be at least as large as $\hbar/8ma^2$ because σ_x, the uncertainty in x, cannot be larger than a.

2.33

Prove $y(x,t) = A\cos[2\pi/\lambda(x - vt)]$ is a wave traveling to the right with velocity v, wavelength λ, and period λ/v.

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3: THE SCHRÖDINGER EQUATION AND A PARTICLE IN A BOX

The particle in a box model (also known as the infinite potential well or the infinite square well) describes a particle free to move in a small space surrounded by impenetrable barriers. The model is mainly used as a hypothetical example to illustrate the differences between classical and quantum systems. In classical systems, for example a ball trapped inside a large box, the particle can move at any speed within the box and it is no more likely to be found at one position than another. However, when the well becomes very narrow (on the scale of a few nanometers), quantum effects become important. The particle may only occupy certain positive energy levels. The particle in a box model provides one of the very few problems in quantum mechanics which can be solved analytically, without approximations. This means that the observable properties of the particle (such as its energy and position) are related to the mass of the particle and the width of the well by simple mathematical expressions. Due to its simplicity, the model allows insight into quantum effects without the need for complicated mathematics. It is one of the first quantum mechanics problems taught in undergraduate physics courses, and it is commonly used as an approximation for more complicated quantum systems.

3.1: The Schrödinger Equation

3.2: Linear Operators in Quantum Mechanics

3.3: The Schrödinger Equation is an Eigenvalue Problem

3.4: Wavefunctions Have a Probabilistic Interpretation

3.5: The Energy of a Particle in a Box is Quantized

3.6: Wavefunctions Must Be Normalized

3.7: The Average Momentum of a Particle in a Box is Zero

3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

3.9: A Particle in a Three-Dimensional Box

3.E: The Schrödinger Equation and a Particle in a Box (Exercises)

3.S: The Schrödinger Equation and a Particle in a Box (Summary)

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3.1: The Schrödinger Equation

Learning Objectives

- To be introduced to the general properties of the Schrödinger equation and its solutions.

De Broglie's doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in the fall of 1925 Pieter Debye, Professor of Theoretical Physics at Zurich and Einstein's successor, suggested to Erwin Schrödinger that he give a seminar on de Broglie's work. Schrödinger gave a polished presentation, but at the end Debye remarked that he considered the whole theory rather childish: why should a wave confine itself to a circle in space? It wasn't as if the circle was a waving circular string, real waves in space diffracted and diffused, in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem and constructing his equation. There is no rigorous derivation of Schrödinger's equation from previously established theory, but it can be made very plausible by thinking about the connection between light waves and photons, and construction an analogous structure for de Broglie's waves and electrons (and later, other particles).

The Schrödinger Equation: A Better Approach

While the Bohr model is able to predict the allowed energies of any single-electron atom or cation, it by no means, a general approach. Moreover, it relies heavily on classical ideas, clumsily grafting quantization onto an essentially classical picture, and therefore, provides no real insights into the true quantum nature of the atom. Any rule that might be capable of predicting the allowed energies of a quantum system must also account for the *wave-particle duality* and implicitly include a wave-like description for particles. Nonetheless, we will attempt a heuristic argument to make the result at least plausible. In classical electromagnetic theory, it follows from Maxwell's equations that each component of the electric and magnetic fields in vacuum is a solution of the 3-D wave equation for electromagnetic waves:

$$\nabla^2\Psi(x,y,z,t) - \frac{1}{c^2}\frac{\partial^2\Psi(x,y,z,t)}{\partial t^2} = 0 \tag{3.1.1}$$

The wave equation in Equation 3.1.1 is the three-dimensional analog to the wave equation presented earlier (Equation 2.1.1) with the velocity fixed to the known speed of light: c. Instead of a partial derivative $\dfrac{\partial^2}{\partial x^2}$ in one dimension, the Laplacian (or "del-squared") operator is introduced:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{3.1.2}$$

Corresponding, the solution to this 3D equation wave equation is a function of *four* independent variables: x, y, z, and t and is generally called the **wavefunction** ψ.

We will attempt now to create an analogous equation for de Broglie's matter waves. Accordingly, let us consider a only 1-dimensional wave motion propagating in the *x*-direction. At a given instant of time, the form of a wave might be represented by a function such as

$$\Psi(x) = f\left(\frac{2\pi x}{\lambda}\right) \tag{3.1.3}$$

where $f(\theta)$ represents a sinusoidal function such as $\sin\theta$, $\cos\theta$, $e^{i\theta}$, $e^{-i\theta}$ or some linear combination of these. The most suggestive form will turn out to be the complex exponential, which is related to the sine and cosine by Euler's formula

$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta \tag{3.1.4}$$

Each of the above is a periodic function, its value repeating every time its argument increases by 2π. This happens whenever x increases by one wavelength λ. At a fixed point in space, the time-dependence of the wave has an analogous structure:

$$T(t) = f(2\pi\nu t) \tag{3.1.5}$$

where ν gives the number of cycles of the wave per unit time. Taking into account both x and t dependence, we consider a wavefunction of the form

$$\Psi(x,t) = exp\left[2\pi i\left(\frac{x}{\lambda} - \nu t\right)\right] \tag{3.1.6}$$

representing waves traveling from left to right. Now we make use of the Planck formula ($E = h\nu$) and de Broglie formulas ($p = \frac{h}{\lambda}$) to replace ν and λ by their particle analogs. This gives

$$\Psi(x,t) = \exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{3.1.7}$$

where

$$\hbar \equiv \frac{h}{2\pi} \tag{3.1.8}$$

Since Planck's constant occurs in most formulas with the denominator 2π, the $\hbar$ symbol was introduced by Paul Dirac. Equation 3.1.5 represents in some way the wavelike nature of a particle with energy E and momentum p. The time derivative of Equation 3.1.7 gives

$$\frac{\partial\Psi}{\partial t} = -\left(\frac{iE}{\hbar}\right)\exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{3.1.9}$$

Thus from a simple comparison of Equations 3.1.7 and 3.1.9

$$i\hbar\frac{\partial\Psi}{\partial t} = E\Psi \tag{3.1.10}$$

or analogously differentiation of Equation 3.1.9 with respect to x

$$-i\hbar\frac{\partial\Psi}{\partial x} = p\Psi \tag{3.1.11}$$

and then the second derivative

$$-\hbar^2\frac{\partial^2\Psi}{\partial x^2} = p^2\Psi \tag{3.1.12}$$

The energy and momentum for a *nonrelativistic* free particle (i.e., all energy is kinetic with no potential energy involved) are related by

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{3.1.13}$$

Substituting Equations 3.1.12 and 3.1.10 into Equation 3.1.13 shows that $\Psi(x,t)$ satisfies the following partial differential equation

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} \tag{3.1.14}$$

Equation 3.1.14 is the applicable differential equation describing the wavefunction of a *free particle* that is not bound by any external forces or equivalently not in a region where its potential energy $V(x,t)$ varies.

For a particle with a non-zero potential energy $V(x)$, the total energy E is then a sum of kinetics and potential energies

$$E = \frac{p^2}{2m} + V(x) \tag{3.1.15}$$

we postulate that Equation 3.1.3 for matter waves can be generalized to

$$\underbrace{i\hbar\frac{\partial\Psi(x,t)}{\partial t}=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\Psi(x,t)}_{\text{time-dependent Schrödinger equation in 1D}} \tag{3.1.16}$$

For matter waves in three dimensions, Equation 3.1.6 is then expanded

$$\underbrace{i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\Psi(\vec{r},t)}_{\text{time-dependent Schrödinger equation in 3D}} \tag{3.1.17}$$

Here the potential energy and the wavefunctions Ψ depend on the three space coordinates x, y, z, which we write for brevity as $\vec{r}$. Notice that the potential energy is assumed to depend on position only and not time (i.e., particle motion). This is applicable for conservative forces that a potential energy function $V(\vec{r})$ can be formulated.

The Laplacian Operator

The three second derivatives in parentheses together are called the Laplacian operator, or del-squared,

$$\begin{aligned}\nabla^2 &= \nabla\cdot\nabla \\ &= \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\end{aligned} \tag{3.1.18}$$

with the del operator,

$$\nabla=\left(\vec{x}\frac{\partial}{\partial x}+\vec{y}\frac{\partial}{\partial y}+\vec{z}\frac{\partial}{\partial z}\right) \tag{3.1.19}$$

Remember from basic calculus that when the del operator is direclty operates on a field (e.g, $\nabla f(x,y,x)$, it denotes the gradient (i.e, the locally steepest slope) of the field. The symbols with arrows in Equation 3.1.19 are unit vectors.

Equation 3.1.17 is the *time-dependent Schrödinger* equation describing the wavefunction amplitude $\Psi(\vec{r},t)$ of matter waves associated with the particle within a specified potential $V(\vec{r})$. Its formulation in 1926 represents the start of modern quantum mechanics (Heisenberg in 1925 proposed another version known as matrix mechanics).

For *conservative* systems, the energy is a constant, and the time-dependent factor from Equation 3.1.7 can be separated from the space-only factor (via the *Separation of Variables* technique discussed in Section 2.2)

$$\Psi(\vec{r},t)=\psi(\vec{r})e^{-iEt/\hbar} \tag{3.1.20}$$

where $\psi(\vec{r})$ is a wavefunction dependent (or time-independent) wavefuction that only depends on space coordinates. Putting Equation 3.1.20 into Equation 3.1.17 and cancelling the exponential factors, we obtain the time-independent Schrödinger equation:

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r})=E\psi(\vec{r})}_{\text{time-independent Schrödinger equation}} \tag{3.1.21}$$

The overall form of the Equation 3.1.21 is not unusual or unexpected as it uses the principle of the **conservation of energy**. Most of our applications of quantum mechanics to chemistry will be based on this equation (with the exception of spectroscopy). The terms of the time-independent Schrödinger equation can then be interpreted as total energy of the system, equal to the system kinetic energy plus the system potential energy. In this respect, it is just the same as in classical physics.

Time Dependence to the Wavefunctions

Notice that the wavefunctions used with the time-independent Schrödinger equation (i.e., $\psi(\vec{r})$) do not have explicit t dependences like the wavefunctions of time-dependent analog in Equation 3.1.17 (i.e., $\Psi(\vec{r},t)$). That does **not imply** that there is no time dependence to the wavefunction. Equation 3.1.20 argues that the time-dependent (i.e., full spatial and temporal) wavefunction ($\Psi(\vec{r},t)$) differs from from the time-independent (i.e., spatial only) wavefunction $\psi(\vec{r})$ by a "phase factor" of constant magnitude. Using the Euler relationship in Equation 3.1.4, the total wavefunction above can be expanded

$$\Psi(\vec{r},t) = \psi(\vec{r})\left(\cos\frac{Et}{\hbar} - i\,\sin\frac{Et}{\hbar}\right) \tag{3.1.22}$$

This means the total wavefunction has a **complex behavior** with a real part and an imaginary part. Moreover, using the trigonometry identity $\sin(\theta) = \cos(\theta - \pi/2)$ Equation 3.1.22 can further simplified to

$$\Psi(\vec{r},t) = \psi(\vec{r})\cos\left(\frac{Et}{\hbar}\right) - i\psi(\vec{r})\cos\left(\frac{Et}{\hbar} - \frac{\pi}{2}\right)$$

This shows that both the real and the imaginary components of the total wavefunction oscillate, the imaginary part of the total wavefunction oscillates **out of phase** by $\frac{\pi}{2}$ with respect to the real part.

Note that while all wavefunctions have a time-dependence, that dependence may not impact in simple quantum problems as the next sections discuss and can often be ignored.

Before we embark on this, however, let us pause to comment on the validity of quantum mechanics. Despite its weirdness, its abstractness, and its strange view of the universe as a place of randomness and unpredictability, quantum theory has been subject to intense experimental scrutiny. It has been found to agree with experiments to better than $10^{-10}\%$ for all cases studied so far. When the Schrödinger Equation is combined with a quantum description of the electromagnetic field, a theory known as *quantum electrodynamics*, the result is one of the most accurate theories of matter that has ever been put forth. Keeping this in mind, let us forge ahead in our discussion of the quantum universe and how to apply quantum theory to both model and real situations.

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3.2: Linear Operators in Quantum Mechanics

Learning Objectives

- Classical-Mechanical quantities are represented by linear operators in Quantum Mechanics
- Understand that "algebra" of scalars and functions do not always to operators (specifically the commutative property)

The bracketed object in the time-independent Schrödinger Equation (in 1D)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.2.1}$$

is called an *operator*. An operator is a generalization of the concept of a function applied to a function. Whereas a function is a rule for turning one number into another, an operator is a rule for turning one function into another. For the time-independent Schrödinger Equation, the operator of relevance is the Hamiltonian operator (often just called the Hamiltonian) and is the most ubiquitous operator in quantum mechanics.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$$

We often (but not always) indicate that an object is an operator by placing a 'hat' over it, eg, $\hat{H}$. So time-independent Schrödinger Equation can then be simplified from Equation 3.2.1 to

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.2.2}$$

Equation 3.2.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a scalar (i.e., a number, a quantity and observable) times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an eigenfunction, and the resulting numerical value is called the eigenvalue. Eigen here is the German word meaning self or own. We will discuss this in detail in later Sections.

Fundamental Properties of Operators

Most properties of operators are straightforward, but they are summarized below for completeness.

1. The sum and difference of two operators $\hat{A}$ and $\hat{B}$ are given by
$$(\hat{A} \pm \hat{B})f = \hat{A}f \pm \hat{B}f$$
2. The product of two operators is defined by
$$\hat{A}\hat{B}f \equiv \hat{A}[\hat{B}f]$$
3. Two operators are equal if
$$\hat{A}f = \hat{B}f$$
for **all** functions f.
4. The identity operator $\hat{1}$ does nothing (or multiplies by 1)
$$\hat{1}f = f$$
5. The n-th power of an operator $\hat{A}^n$ is defined as n successive applications of the operator, e.g.
$$\hat{A}^2 f = \hat{A}\hat{A}f$$
6. The *associative law* holds for operators
$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$

7. The *commutative law* does **not** generally hold for operators. In general, but not always,

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}. \tag{3.2.3}$$

To help identify if the inequality in Equation 3.2.3 holds for any two specific operators, we define the commutator.

Definition: The Commutator

It is convenient to define the **commutator** of $\hat{A}$ and $\hat{B}$

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

If $\hat{A}$ and $\hat{B}$ commute, then

$$[\hat{A}, \hat{B}] = 0.$$

If the commutator is not zero, the order of operating matters and the operators are said to "not commute." Moreover, this property applies

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}].$$

Linear Operators

The action of an operator that turns the function $f(x)$ into the function $g(x)$ is represented by

$$\hat{A}f(x) = g(x) \tag{3.2.4}$$

The most common kind of operator encountered are *linear operators* which satisfies the following two conditions:

$$\underset{\text{Condition A}}{\hat{O}(f(x) + g(x)) = \hat{O}f(x) + \hat{O}g(x)} \tag{3.2.5}$$

and

$$\underset{\text{Condition B}}{\hat{O}cf(x) = c\hat{O}f(x)} \tag{3.2.6}$$

where

- $\hat{O}$ is a linear operator,
- c is a constant that can be a complex number ($c = a + ib$), and
- $f(x)$ and $g(x)$ are functions of x

If an operator fails to satisfy either Equations 3.2.5 or 3.2.6 then it is not a linear operator.

Example 3.2.1

Is this operator $\hat{O} = -i\hbar\dfrac{d}{dx}$ linear?

Solution

To confirm is an operator is linear, both conditions in Equation 3.2.6 must be demonstrated.

Condition A (Equation 3.2.5):

$$\hat{O}(f(x)+g(x)) = -i\hbar\frac{d}{dx}\left(f(x)+g(x)\right)$$

From basic calculus, we know that we can use the **sum rule for differentiation**

$$\begin{aligned}\hat{O}(f(x)+g(x)) &= -i\hbar\frac{d}{dx}f(x) - i\hbar\frac{d}{dx}g(x)\\ &= \hat{O}f(x)+\hat{O}g(x) \quad \checkmark\end{aligned}$$

Condition A is confirmed. Does Condition B (Equation 3.2.6) hold?

$$\hat{O}cf(x) = -i\hbar\frac{d}{dx}cf(x)$$

Also from basic calculus, this can be factored out of the derivative

$$\begin{aligned}\hat{O}cf(x) &= -ci\hbar\frac{d}{dx}f(x)\\ &= c\hat{O}f(x) \quad \checkmark\end{aligned}$$

Yes. This operator is a linear operator (this is the linear momentum operator).

Exercise 3.2.1

Confirm if the square root operator $\sqrt{f(x)}$ linear or not?

Answer available at the end of this section.

The most operators encountered in quantum mechanics are *linear operators*.

Hermitian Operators

An important property of operators is suggested by considering the Hamiltonian for the particle in a box:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Let $f(x)$ and $g(x)$ be arbitrary functions which obey the same boundary values as the eigenfunctions of $\hat{H}$ (e.g., they vanish at $x = 0$ and $x = a$). Consider the integral

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = -\frac{\hbar^2}{2m}\int_0^a f(x)\,g''(x)\,\mathrm{d}x$$

Now, using integration by parts,

$$\int_0^a f(x)\,g''(x)\,\mathrm{d}x = -\int_0^a f'(x)\,g'(x)\,\mathrm{d}x + \left.f(x)\,g'(x)\right|_0^a \tag{3.2.7}$$

The boundary terms vanish by the assumed conditions on f and g. A second integration by parts transforms Equation 3.2.7 to

$$\int_0^a f''(x)\,g(x)\,\mathrm{d}x - \left.f'(x)\,g(x)\right|_0^a$$

It follows therefore that

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \int_0^a g(x)\,\hat{H}\,f(x)\,\mathrm{d}x$$

An obvious generalization for complex functions will read

$$\int_0^a f^*(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \left(\int_0^a g^*(x)\,\hat{H}\,f(x)\,\mathrm{d}x\right)^*$$

In mathematical terminology, an operator $\hat{A}$ for which

$$\int f^*\,\hat{A}\,g\,\mathrm{d}\tau = \left(\int g^*\,\hat{A}\,f\,\mathrm{d}\tau\right)^*$$

for all functions f and g which obey specified boundary conditions is classified as *Hermitian* or *self-adjoint*. Evidently, the Hamiltonian is a **Hermitian operator**. It is postulated that *all* quantum-mechanical operators that represent dynamical variables are Hermitian. The term is also used for specific times of matrices in linear algebra courses.

All quantum-mechanical operators that represent dynamical variables are Hermitian.

Answers

To confirm is an operator is linear, both conditions in Equations 3.2.5 and 3.2.6 must be demonstrated. Let's look first at Condition B.
Does Condition B (Equation 3.2.6) hold?

$$\hat{O}cf(x) = c\hat{O}f(x)$$
$$\sqrt{cf(x)} \neq c\sqrt{f(x)}$$

Condition B does not hold, therefore the square root operator is not linear.

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3.3: The Schrödinger Equation is an Eigenvalue Problem

Learning Objectives

- To recognize that each quantum mechanical observable is determined by solve by an eigenvalue problem with different operators for different observable
- Confirm if a specific wavefunction is an eigenfunction of a specific operation and extract the corresponding obserable (the eigenvalue)
- To recognize that the Schrödinger equation, just like all measurable, is also an eigenvalue problem with the eigenvalue ascribed to total energy
- Identity and manipulate several common quantum mechanical operators

As per the definition, an operator acting on a function gives another function, however a special case occurs when the generated function is proportional to the original

$$\hat{A}\psi \propto \psi \tag{3.3.1}$$

This case can be expressed in terms of a equality by introducing a proportionality constant k

$$\hat{A}\psi = k\psi \tag{3.3.2}$$

Not all functions will solve an equation like in Equation 3.3.2. If a function does, then ψ is known as an **eigenfunction** and the constant k is called its **eigenvalue** (these terms are hybrids with German, the purely English equivalents being "characteristic function" and "characteristic value", respectively). Solving eigenvalue problems are discussed in most linear algebra courses.

In quantum mechanics, every experimental measurable a is the eigenvalue of a specific operator ($\hat{A}$):

$$\hat{A}\psi = a\psi \tag{3.3.3}$$

The a eigenvalues represents the possible measured values of the $\hat{A}$ operator. Classically, a would be allowed to vary continuously, but in quantum mechanics, a typically has only a sub-set of allowed values (hence the quantum aspect). Both time-dependent and time-independent Schrödinger equations are the best known instances of an eigenvalue equations in quantum mechanics, with its eigenvalues corresponding to the allowed energy levels of the quantum system.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.3.4}$$

The object on the left that acts on $\psi(x)$ is an example of an **operator**.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right] \tag{3.3.5}$$

In effect, what is says to do is "take the second derivative of $\psi(x)$, multiply the result by $-(\hbar^2/2m)$ and then add $V(x)\psi(x)$ to the result of that." Quantum mechanics involves many different types of operators. This one, however, plays a special role because it appears on the left side of the Schrödinger equation. It is called the **Hamiltonian** *operator* and is denoted as

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{3.3.6}$$

Therefore, the time-dependent Schrödinger equation can be (and it more commonly) written as

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \tag{3.3.7}$$

and the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \tag{3.3.8}$$

Note that the functional form of Equation 3.3.8 is the same as the general eigenvalue equation in Equation 3.3.2 where the eigenvalues are the (allowed) total energies (E).

The Hamiltonian, named after the Irish mathematician Hamilton, comes from the formulation of Classical Mechanics that is based on the total energy, $H = T + V$, rather than Newton's second law, $F = ma$. Equation 3.3.8 says that the Hamiltonian operator operates on the wavefunction to produce the energy E, which is a scalar (e.g., expressed in Joules) times the wavefunction.

Correspondence Principle

Note that $\hat{H}$ is derived from the classical energy $p^2/2m + V(x)$ simply by replacing $p \rightarrow -i\hbar(d/dx)$. This is an example of the **Correspondence Principle** initially proposed by Niels Bohr that states that the behavior of systems described by quantum theory reproduces classical physics in the limit of large quantum numbers.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is then the eigenvalue, and the system is said to be in an eigenstate. Equation 3.3.8 states this principle mathematically for the case of energy as the observable. If the wavefunction is not the eigenfunction of the operation, then the measurement will give an eigenvalue (by definition), but not necessarily the same one for each measurement (this will be discussed in more detail in later section).

Common Operators

Although we could theoretically come up with an infinite number of operators, in practice there are a few which are much more important than any others.

- **Linear Momentum:**

  The linear momentum operator of a particle moving in one dimension (the x-direction) is

  $$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.3.9}$$

  and can be generalized in three dimensions:

  $$\hat{\vec{p}} = -i\hbar\nabla \tag{3.3.10}$$

- **Position**

  The position operator of a particle moving in one dimension (the x-direction) is

  $$\hat{x} = x \tag{3.3.11}$$

  and can be generalized in three dimensions:

  $$\hat{\vec{r}} = \vec{r} \tag{3.3.12}$$

  where $\vec{r} = (x, y, z)$.

- **Kinetic Energy**

  Classically, the kinetic energy of a particle moving in one dimension (the x-direction), in terms of momentum, is

  $$KE_{classical} = \frac{p_x^2}{2m} \tag{3.3.13}$$

Quantum mechanically, the corresponding kinetic energy operator is

$$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{3.3.14}$$

and can be generalized in three dimensions:

$$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m}\nabla^2 \tag{3.3.15}$$

- **Angular Momentum:**

  Angular momentum requires a more complex discussion, but is the cross product of the position operator $\hat{\vec{r}}$ and the momentum operator $\hat{p}$

$$\hat{\vec{L}} = -i\hbar(\vec{r} \times \nabla) \tag{3.3.16}$$

- **Hamiltonian:**

  The Hamiltonian operator corresponds to the total energy of the system

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{3.3.17}$$

  and it represents the total energy of the particle of mass m in the potential $V(x)$. The Hamiltonian in three dimensions is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{3.3.18}$$

- **Total Energy:**

  The energy operator from the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t) \tag{3.3.19}$$

  The right hand side of Equation 3.3.6 is the Hamiltonian Operator. In addition determining system energies, the Hamiltonian operator dictates the time evolution of the wavefunction

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{3.3.20}$$

  This aspect will be discussed in more detail elsewhere.

Eigenstate, Eigenvalues, Wavefunctions, Measurables, and Observables

In general, the **wavefunction** gives the "state of the system" for the system under discussion. It stores all the information available to the observer about the system. Often in discussions of quantum mechanics, the terms *eigenstate* and *wavefunction* are used interchangeably. The term eigenvalue is used to designate the value of measurable quantity associated with the wavefunction.

- If you want to measure the energy of a particle, you have to operate on the wavefunction with the Hamiltonian operator (Equation 3.3.6).
- If you want to measure the momentum of a particle, you have to operate on wavefunction with the momentum operator (Equation 3.3.9).
- If you want to measure the position of a particle, you have to operate on wavefunction with the position operator (Equation 3.3.11).
- If you want to measure the kinetic energy of a particle, you have to operate on wavefunction with the kinetic energy operator (Equation 3.3.14).

When discussing the eigenstates of the Hamiltonian ($\hat{H}$), the associated eigenvalues represent energies and within the context

of the momentum operators, the associated eigenvalues refer to the momentum of the particle. However, not all wavefunctions (ψ) are eigenstates of an operator (ϕ) – and if they are not, they can be usually be written as superpositions of eigenstates.

$$\psi = \sum_i c_i \phi_i$$

This will be discussed in more detail in later sections.

While the wavefunction may not be the eigenstate of an observable, when that operator operates on that wavefunction, the wavefunction **becomes** an eigenstate of that observable and only eigenvalues can be observed. Another way to say this is that the wavefunction "collapses" into an eigenstate of the observable. Because quantum mechanical operators have different forms, their associated eigenstates are similarly often (i.e., most of the time) different. For example, when a wavefunction is an eigenstate of total energy, it will **not** be an eigenstate of momentum.

> If a wavefunction is an eigenstate of one operator, (e.g., momentum), that state is not necessarily an eigenstate of a different operator (e.g., energy), although not always.

The wavefunction immediately after a measurement is an eigenstate of the operator associated with this measurement. What happens to the wavefunction after the measurement is a different topic.

Example 3.3.1

Confirm that the following wavefunctions are eigenstates of linear momentum and kinetic energy (or neither or both):

a. $\psi = A\sin(ax)$
b. $\psi = Ne^{-ix/\hbar}$

Strategy

This question is asking if the eigenvalue equation holds for the operators and these wavefunctions. This is just asking if these wavefunctions are solutions to Equation 3.3.2 using the operators in Equations 3.3.9 and 3.3.14, i.e., are these equations true:

$$\hat{p}_x\psi = p_x\psi \tag{3.3.21}$$

$$\hat{KE}\psi = KE\psi \tag{3.3.22}$$

where p_x and KE are the measurables (eigenvalues) for these operators.

Solution a

Let's evaluate the left side of the linear momentum eigenvalue problem (Equation 3.3.21)

$$-i\hbar\frac{\partial}{\partial x}A\sin(ax) = -i\hbar Aa\cos(ax)$$

and compare to the the right side of Equation 3.3.21

$$p_x A\sin(ax)$$

These are **not** the same so this wavefunction is not an eigenstate of momentum.

Let's look at the left side of the kinetic energy eigenvalue problem (Equation 3.3.22)

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}A\sin(ax) &= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}Aa\cos(ax) \\ &= +\frac{\hbar^2}{2m}Aa^2\sin(ax) \end{aligned}$$

and compare to the right side

$$KEA\sin(ax)$$

These are same, so this specific wavefunction is an eigenstate of kinetic energy. Moreover, the measured kinetic energy will be

$$KE = +\frac{\hbar^2}{2m}a^2$$

Solution b

Let's look at the left side of Equation 3.3.21 for linear momentum

$$-i\hbar\frac{\partial}{\partial x}Ne^{-ix/\hbar} = -Ne^{-ix/\hbar}$$

and the right side of Equation 3.3.21

$$p_x Ne^{-ix/\hbar}$$

These are the same so this wavefunction is an eigenstate of momentum with momentum $p_x = -N$.

Let's look at the left side of Equation 3.3.22 for kinetic energy

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}Ne^{-ix/\hbar} &= +i\frac{\hbar}{2m}\frac{\partial}{\partial x}Ne^{-ix/\hbar} \\ &= +\frac{1}{2m}Ne^{-ix/\hbar} \end{aligned}$$

and the right side

$$KENe^{-ix/\hbar}$$

These are same so this wavefunction is an eigenstate of kinetic energy. And the measured kinetic energy will be

$$KE = \frac{1}{2m}$$

This wavefunction is an eigenstate of both momentum and kinetic energy.

Exercise 3.3.1

Are $\psi = Me^{-bx}$ functions eigenstates of linear momentum and kinetic energy (or neither or both)?

Answer available at the end of this section.

Answers

ψ is an eigenstate of linear momentum with a eigenvalue of $bi\hbar$ and also an eigenstate of kinetic energy with an eigenvalue of b^2.

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3.4: Wavefunctions Have a Probabilistic Interpretation

Learning Objectives

- To understand that wavefunctions can have probabilistic interpretations.
- To calculate the probabilities directly from a wavefunctions

For a single-particle system, the wavefunction $\Psi(\vec{r},t)$, or $\psi(\vec{r})$ for the time-independent case, represents the amplitude of the still vaguely defined matter waves. Since wavefunctions can in general be complex functions, the physical significance cannot be found from the function itself because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the **square of the modulus** (also called absolute value).

$$P(\vec{r},t) = \Psi^*(\vec{r},t)\Psi(\vec{r},t) \tag{3.4.1}$$

$$= |\Psi(\vec{r},t)|^2 \tag{3.4.2}$$

where $\vec{r}$ is a vector (x,y,z) specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field.

Born proposed in 1926, the most commonly accepted interpretation of the wavefunction **that the square of the modulus** (Equation 3.4.2) is **proportional** to the **probability density** (probability per unit volume) that the electron is in the volume $d\tau$ located at r_i. Since the wavefunction represents the wave properties of matter, the probability amplitude $P(x,t)$ will also exhibit wave-like behavior. Probability density is the three-dimensional analog of the diffraction pattern that appears on the two-dimensional screen in the double-slit diffraction experiment for electrons. The idea that we can understand the world of atoms and molecules only in terms of probabilities is disturbing to some, who are seeking more satisfying descriptions through ongoing research.

> The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the probability density, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability P

The probability that a single quantum particle moving in one spatial dimension will be found in a region $x^{\text{int}}[a,b]$ if a measurement of its location is performed is

$$P(x^{\text{int}}[a,b]) = \int_a^b |\psi(x)|^2 dx \tag{3.4.3}$$

In three dimensions, Equation 3.4.3 is represented differently

$$P(x^{\text{int}}[a,b]) = \int_V |\psi(\vec{\tau})|^2 d\tau \tag{3.4.4}$$

This integration extends over a specified volume (V) with the symbol $d\tau$ designating the appropriate volume element (including a Jacobian) of the coordinate system adopted:

- Cartesian:

$$d\tau = dx\, dy\, dz$$

- Spherical:

$$d\tau = r^2 \sin\phi\, dr\, d\theta\, d\phi$$

- Cylindrical:

$$d\tau = r\, dr\, d\phi\, dz.$$

For rectilinear Cartesian space, Equation 3.4.4 can be is expanded with dimension explicitly indicated

$$P(x^{\text{int}}[a,b]) = \int_{a_x}^{b_x}\int_{a_y}^{b_y}\int_{a_z}^{b_z} |\psi(x,y,z)|^2 dx\, dy\, dz \tag{3.4.5}$$

where the limits of integration are selected to encompass the volume V of consideration.

The Born interpretation (Equation 3.4.2) of relating the wavefunction to probability forces certain demands on its mathematical behavior of wavefunctions and not any mathematical function can be a valid wavefunction.

Required Properties of Wavefunction

- The wavefunction must be a *single-valued function* of all its coordinates, since the probability density ought to be *uniquely determined* at each point in space.
- The wavefunction should be both *finite* as an infinite probability has no meaning.
- The wavefunction should be *continuous everywhere*, as expected for a physically-meaningful probability density.

The conditions that the wavefunction be single-valued, finite and continuous--in short, "well behaved"-- lead to restrictions on solutions of the Schrödinger equation such that only certain values of the energy and other dynamical variables are allowed. This is called *quantization* and is in the feature that gives *quantum* mechanics its name.

It is important to note that this interpretation implies the wavefunction does **not** mean the particle is distributed over a large region as a sort of "charge cloud". The wavefunction is used to describe the electron motion that behaves like waves and satisfies a wave equation. This is akin to how a grade distribution in a large class does not represent a smearing of grades for a single student, but only makes sense when taking into account that the distribution is the result of many measurables (e.g., student performances).

Example 3.4.1

Show that the square of the modulus of $\Psi(\vec{r},t) = \psi(\vec{r})e^{-i\omega t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Example 3.4.2

According to the Born interpretation, what is the physical significance of $e\psi^*(r_0)(r_0)d\tau$?

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3.5: The Energy of a Particle in a Box is Quantized

Learning Objectives

- Solve the particle-in-a-box model used to describing a trapped particle in 1 D well
- Characterize the particle-in-a-box eigenstates (i.e., wavefunctions) and the eigenenergies as a function of the quantum number
- Demonstrate that the eigenstates are orthogonal

The *particle in the box* model system is the simplest non-trivial application of the Schrödinger equation, but one which illustrates many of the fundamental concepts of quantum mechanics. For a particle moving in one dimension (again along the x- axis), the Schrödinger equation can be written

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x)$$

Assume that the particle can move freely between two endpoints $x = 0$ and $x = L$, but cannot penetrate past either end. This is equivalent to a potential energy dependent on x with

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & x < 0 \; and \; x > L \end{cases}$$

This potential is represented in Figure 3.5.1 . The infinite potential energy constitutes an impenetrable barrier since the particle would have an infinite potential energy if found there, which is clearly impossible.

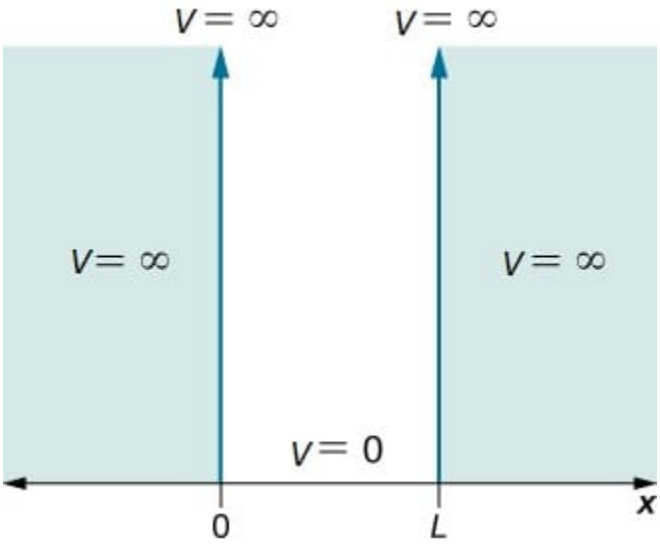


Figure 3.5.1 : The barriers outside a one-dimensional box have infinitely large potential, while the interior of the box has a constant, zero potential. (CC-BY 4.0; OpenStax).

The particle is thus bound to a "*potential well*" since the particle cannot penetrate beyond $x = 0$ or $x = L$

$$\psi(x) = 0 \quad for \;\; x < 0 \;\; and \;\; x > L \tag{3.5.1}$$

By the requirement that the wavefunction be continuous, it must be true as well that

$$\psi(0) = 0 \quad and \quad \psi(L) = 0 \tag{3.5.2}$$

which constitutes a pair of boundary conditions on the wavefunction within the box. Inside the box, $V(x) = 0$, so the Schrödinger

equation reduces to the free-particle form:

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x) \tag{3.5.3}$$

with $0 \le x \le L$.

We again have the differential equation

$$\psi''(x) + k^2\psi(x) = 0 \tag{3.5.4}$$

with

$$k^2 = \frac{2mE}{\hbar^2} \tag{3.5.5}$$

The general solution can be written

$$\psi(x) = A\ \sin\ kx\ +\ B\ \cos\ kx \tag{3.5.6}$$

where A and B are constants to be determined by the boundary conditions in Equation 3.5.2. By the first condition, we find

$$\psi(0) = A\ \sin\ 0\ +\ B\ \cos\ 0\ =\ B\ = 0 \tag{3.5.7}$$

The second boundary condition at $x = L$ then implies

$$\psi(a) = A\ \sin\ kL\ =\ 0 \tag{3.5.8}$$

It is assumed that $A \neq 0$, for otherwise $\psi(x)$ would be zero everywhere and the particle would disappear (i.e., the trivial solution). The condition that $\sin kx = 0$ implies that

$$kL\ =\ n\pi \tag{3.5.9}$$

where n is a integer, positive, negative or zero. The case $n = 0$ must be excluded, for then $k = 0$ and again $\psi(x)$ would vanish everywhere. Eliminating k between Equation 3.5.4 and 3.5.9, we obtain

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}\ n^2 = \frac{h^2}{8mL^2}n^2 \tag{3.5.10}$$

with $n = 1, 2, , 3....$

These are the only values of the energy which allows solutions of the Schrödinger Equation 3.5.3 consistent with the boundary conditions in Equation 3.5.2. The integer n, called a **quantum number**, is appended as a subscript on E to label the allowed energy levels. Negative values of n add nothing new because the energies in Equation 3.5.10 depends on n^2.

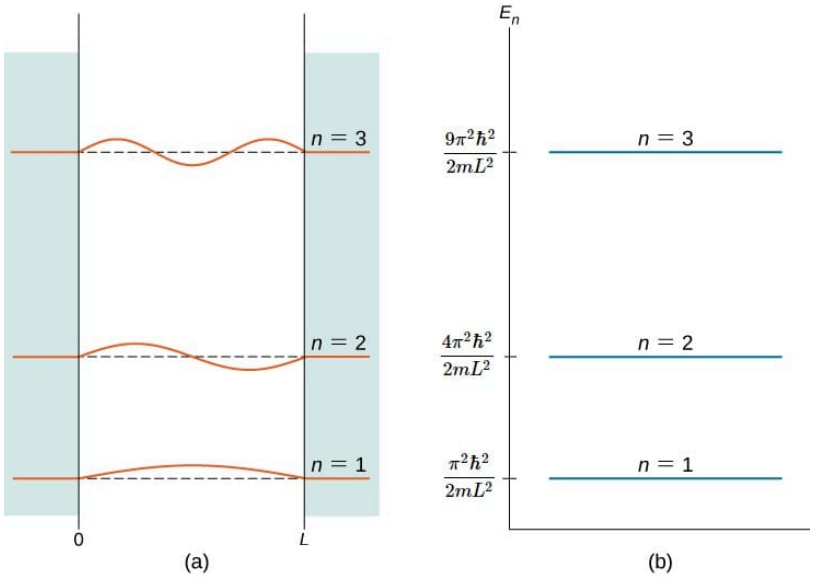


Figure 3.5.2 : A plot of $\psi_n(x)$ for the first four wavefunctions. (CC-BY 4.0; OpenStax).

Figure 3.5.2 shows part of the energy-level diagram for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space. For the free particle, the absence of confinement allowed an energy continuum. Note that, in both cases, the number of energy levels is infinite-denumerably infinite for the particle in a box, but nondenumerably infinite for the free particle.

The particle in a box assumes its lowest possible energy when $n = 1$, namely

$$E_1 = \frac{h^2}{8mL^2} \tag{3.5.11}$$

The state of lowest energy for a quantum system is termed its *ground state*.

Zero Point Energy

An interesting point is that $E_1 > 0$, whereas the corresponding classical system would have a minimum energy of zero. This is a recurrent phenomenon in quantum mechanics. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as **zero point energy**. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero. The minimum value of momentum is found by equating E_1 to $p^2/2m$, giving $p_{min} = \pm h/2L$. This can be expressed as an *uncertainty* in momentum given by $\Delta p \approx h/L$. Coupling this with the uncertainty in position, $\Delta x \approx L$, from the size of the box, we can write

$$\Delta x \Delta p \approx h \tag{3.5.12}$$

This is in accord with the *Heisenberg uncertainty principle*.

The particle-in-a-box eigenfunctions are given by Equation 3.5.13, with $B = 0$ and $k = n\pi/L = a$, in accordance with Equation 3.5.9

$$\psi_n(x) = A \sin \frac{n\pi x}{L} \tag{3.5.13}$$

with $n = 1, 2, 3....$

These, like the energies, can be labeled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi_n(x)$ is normalized. The normalization condition is, in this case,

$$\int_0^a [\psi_n(x)]^2 \, dx = 1 \tag{3.5.14}$$

the integration running over the domain of the particle $0 \leq x \leq L$. Substituting Equation 3.5.13 into Equation 3.5.14,

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = A^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2 \theta \, d\theta \tag{3.5.15}$$

$$= A^2 \frac{L}{2} = 1 \tag{3.5.16}$$

We have made the substitution $\theta = n\pi x/L$ and used the fact that the average value of $\sin^2 \theta$ over an integral number of half wavelengths equals 1/2 (alternatively, one could refer to standard integral tables). From Equation 3.5.16, we can identify the general normalization constant

$$A = \sqrt{\frac{2}{L}}$$

for all values of n. Finally we can write the normalized eigenfunctions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{3.5.17}$$

with $n = 1, 2, 3....$

The first few eigenfunctions and the corresponding probability distributions are plotted in Figure 3.5.3 . There is a close analogy between the states of this quantum system and the modes of vibration of a violin string. The patterns of standing waves on the string are, in fact, identical in form with the wavefunctions in Equation 3.5.17.

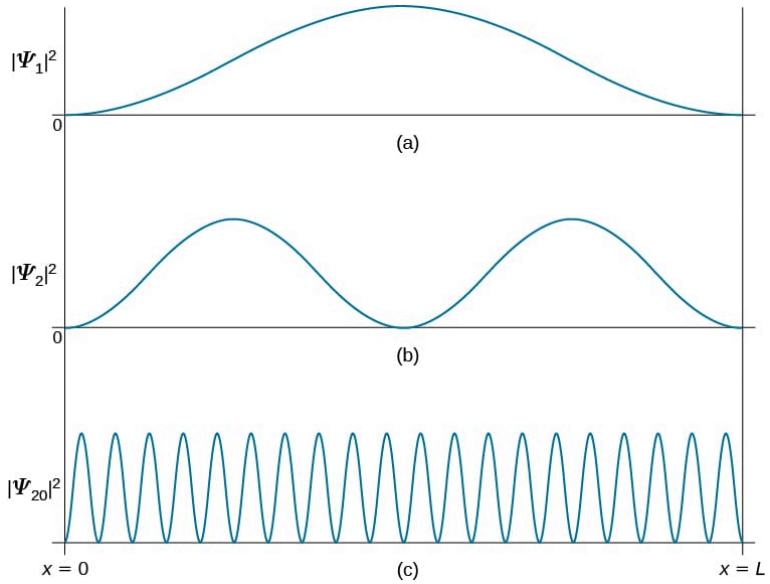


Figure 3.5.3 : The probability density distribution $|\psi_n(x)|^2$ for a quantum particle in a box for: (a) the ground state, $n = 1$; (b) the first excited state, $n = 2$; and, (c) the nineteenth excited state, $n = 20$. (CC-BY 4.0; OpenStax).

Nodes and Curvature

A significant feature of the particle-in-a-box quantum states is the occurrence of *node*s. These are points, other than the two end points (which are fixed by the boundary conditions), at which the wavefunction vanishes. At a node there is exactly zero probability of finding the particle. The *n*th quantum state has, in fact, $n - 1$ nodes. It is generally true that the number of nodes increases with the energy of the quantum state, which can be rationalized by the following qualitative argument. As the number of nodes increases, so does the number and the steepness of the 'wiggles' in the wavefunction. It's like skiing down a slalom course. Accordingly, the average curvature, given by the second derivative, must increase. But the second derivative is proportional to the kinetic energy operator. Therefore, the more nodes, the higher the energy. This will prove to be an invaluable guide in more complex quantum systems.

Example 3.5.1 : Excited State Probabilities

For a particle in a one-dimensional box of length L, the second excited state wavefunction ($n = 3$) is

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

a. What is the probability that the particle is in the left half of the box?
b. What is the probability that the particle is in the middle third of the box?

Strategy

Probability that the particle will be found between a and b is

$$P(a,b) = \int_a^b \psi^2 \, dx$$

For this problem,

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

therefore,

$$\begin{aligned} P(a,b) &= \frac{2}{L} \int_a^b \sin^2 \frac{3\pi x}{L} \, dx \\ &= \frac{2}{L} \left(\frac{x}{2} - \frac{L \sin\left(\frac{6\pi x}{L}\right)}{12\pi} \right) \Bigg|_a^b \\ &= \frac{b-a}{L} - \frac{1}{6\pi} \left[\sin\left(\frac{6\pi b}{L}\right) - \sin\left(\frac{6\pi a}{L}\right) \right] \end{aligned}$$

Solution a

The probability that the particle is in the left half of the box is

$$\begin{aligned} P\left(0, \frac{L}{2}\right) &= \frac{\frac{L}{2} - 0}{L} - \frac{1}{6\pi} \left[\sin\left(\frac{6\pi\left(\frac{L}{2}\right)}{L} \right) - \sin\left(\frac{6\pi(0)}{L}\right) \right] \\ &= \frac{1}{2} \end{aligned}$$

Solution b

The probability that the particle is in the middle third of the box

$$\begin{aligned} P\left(\frac{L}{3}, \frac{2L}{3}\right) &= \frac{\frac{2L}{3} - \frac{L}{3}}{L} - \frac{1}{6\pi} \left[\sin \frac{6\pi\left(\frac{2L}{3}\right)}{L} - \sin \frac{6\pi\left(\frac{L}{3}\right)}{L} \right] \\ &= \frac{1}{3} \end{aligned}$$

Exercise 3.5.1 : Ground State Probability

For a particle in a one-dimensional box, the ground state wavefunction is

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{x\pi}{L}$$

What is the probability that the particle is in the left half of the box in the ground state?

Answer available at the end of this section.

Time Dependence and Complex Nature of Wavefunctions

Recall that the time-dependence of the wavefunction with time-independent potential was discussed in Section 3.1 and is expressed as

$$\Psi(x,t) = \psi(x) e^{-iEt/\hbar}$$

so for the particle in a box, these are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} e^{-iE_n t/\hbar} \tag{3.5.18}$$

with E_n given by Equation 3.5.10.

The phase part of Equation 3.5.18 can be expanded into a real part and a complex components. So the total wavefunction for a particle in a box is

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right)\left(\cos \frac{E_n t}{\hbar}\right)}_{\text{real part}} - i \underbrace{\left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right)\left(\sin \frac{E_n t}{\hbar}\right)}_{\text{imaginary part}}$$

which can be simplified (slightly) to

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right)\left(\cos \frac{E_n t}{\hbar}\right)}_{\text{real part}} - i \underbrace{\left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right)\left(\cos \frac{E_n t}{\hbar} - \frac{\pi}{2}\right)}_{\text{imaginary part}}$$

As discussed previously, the imaginary part of the total wavefunction oscillates out of phase by $\pi/2$ with respect to the real part (we call this "out of phase"). This is demonstrated in the time-dependent behavior of the first three eigenfunctions in Figure 3.5.4 .

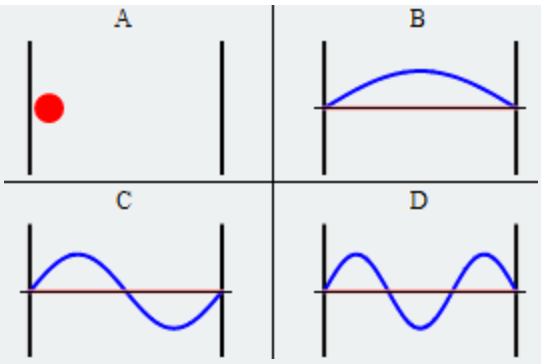


Figure 3.5.4 : Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-D). In (B-D), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B, C, D) are energy eigenstates. (Public Domain; Sbyrnes321 via Wikipedia).

Note that as n increased, the energy of the wavefunction increases (Equation 3.5.10) and both the number of nodes and antinodes increase and the frequency of oscillation of the wavefunction increases.

It is generally true in quantum systems (not just for particles in boxes) that the number of nodes in a wavefunction increases with the energy of the quantum state.

Orthonormality of the Eigenstates

Another important property of the eigenfunctions in Equation 3.5.17 applies to the integral over a product of two *different* eigenfunctions (Equation 3.5.17). It is easy to see from Figure 3.5.5 that the integral

$$\int_0^L \psi_2(x)\psi_1(x)dx = 0 \tag{3.5.19}$$

The integral in Equation 3.5.19 is zero when the two eignestates differ and when integrated over the entire range of the system (from $-\infty$ to ∞ for a 1-D particle in the box, but this can be a narrow region of 0 to L since the eigenstates are zero outside of the box).

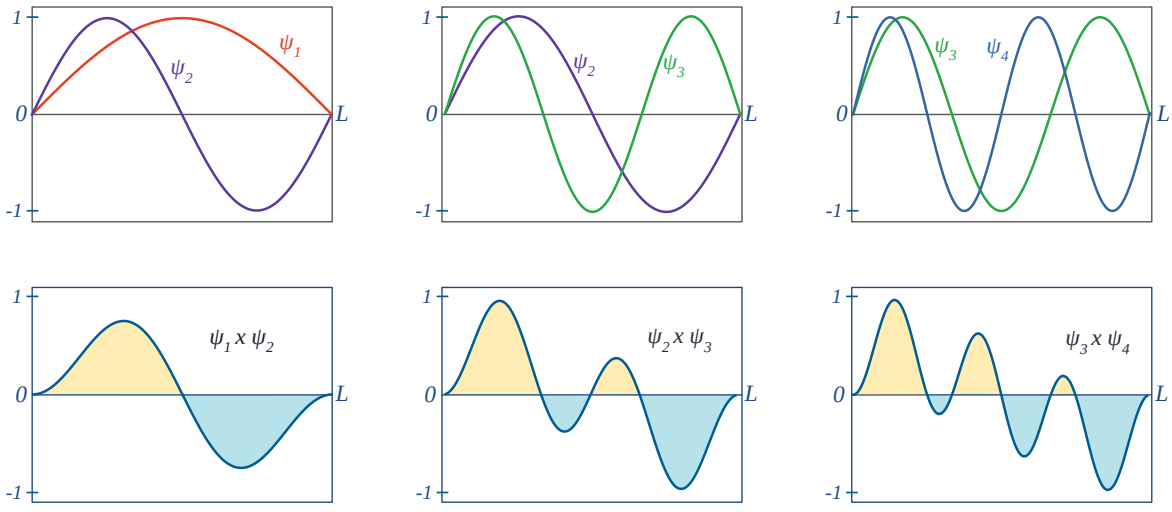


Figure 3.5.5 : (Top Row): Select plots of the $n = 1$ (red curves), $n = 2$ (purple curves), $n = 3$ (green curves), and $n = 4$ (blue curves) eigenfunctions. (Bottom Row): Product of different eigenstates with positive (tan) and negative (cyan) areas emphasized. Note that the negative and positive areas perfectly cancel when added together. Created via fooplot (CC BY-NC; Ümit Kaya via LibreTexts)

To prove Equation 3.5.19 for a particle in a box model, we can use the trigonometric identity

$$\sin\,\alpha\,\sin\,\beta = \frac{1}{2}\left[\cos(\alpha-\beta)-\cos(\alpha+\beta)\right] \tag{3.5.20}$$

to show that

$$\int_0^L \psi_m(x)\psi_n(x)dx = 0 \quad if \quad m \neq n \tag{3.5.21}$$

This property is called **orthogonality**. We will show in the next chapter, that this is a general result from quantum-mechanical eigenfunctions. The normalization (Equation 3.5.19) together with the orthogonality (Equation 3.5.21) can be combined into a single relationship

$$\int_0^L \psi_m(x)\psi_n(x)dx = \delta_{mn} \tag{3.5.22}$$

In terms of the *Kronecker delta*

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \tag{3.5.23}$$

A set of functions $\{\psi_n\}$ which obeys Equation 3.5.22 is called *orthonormal*.

Example 3.5.2

Evaluate

a. $\langle\psi_3|\psi_3\rangle$
b. $\langle\psi_4|\psi_4\rangle$
c. $\langle\psi_3|\psi_4\rangle$
d. $\langle\psi_4|\psi_3\rangle$

for the normalized wavefunctions:

$$|\psi_3\rangle = \sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}$$

and

$$|\psi_4\rangle = \sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}$$

Strategy

These are four different integrals and we can solve them directly or use orthonormality (Equation 3.5.23) to evaluate.

Solution a

$$\begin{aligned}\langle\psi_3|\psi_3\rangle &= \int_{-\infty}^{+\infty}\left(\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}\right)\left(\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_{-\infty}^{+\infty}\sin^2\frac{3\pi x}{L}\,dx\end{aligned}$$

This is an integration over an even function, so it cannot be tossed out via symmetry. We can use the Trigonometry relationship in Equation 3.5.20 to get

$$\frac{2}{L}\int_{-\infty}^{+\infty}\sin^2\frac{3\pi x}{L}\,dx = \frac{2}{L}\int_{-\infty}^{+\infty}\frac{1}{2}\left(1-\cos\frac{6\pi x}{L}\right)dx$$

and we can continue the fun. However, there is no need. Since the we can recognize that $\langle\psi_3|\psi_3\rangle$ is 1 by the normalization criteria which is folded into the orthonormal criteria (Equation 3.5.23).

Therefore $\langle\psi_3|\psi_3\rangle = 1$.

Solution b

$$\begin{aligned}\langle\psi_4|\psi_4\rangle &= \int_{-\infty}^{+\infty}\left(\sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}\right)\left(\sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_{-\infty}^{+\infty}\sin^2\frac{4\pi x}{L}\,dx\end{aligned}$$

We can expand and solve, but again there is no need. The wavefunctions are normalized therefore $\langle\psi_4|\psi_4\rangle = 1$.

Solution c

$$\begin{aligned}\langle\psi_3|\psi_4\rangle &= \int_{-\infty}^{+\infty}\left(\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}\right)\left(\sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_{-\infty}^{+\infty}\sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{4\pi x}{L}\right)dx\end{aligned}$$

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.5.23).

Solution d

$$\begin{aligned}\langle\psi_4|\psi_3\rangle &= \int_{-\infty}^{+\infty}\left(\sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}\right)\left(\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_{-\infty}^{+\infty}\sin\left(\frac{4\pi x}{L}\right)\sin\left(\frac{3\pi x}{L}\right)dx\end{aligned}$$

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd function), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.5.23).

However, since the wavefunctions are real, then

$$\langle\psi_4|\psi_3\rangle = \langle\psi_3|\psi_4\rangle$$

which also means

$$\langle\psi_4|\psi_3\rangle = 0$$

from the results of section c.

Answers

$$\begin{aligned}P\left(0,\frac{L}{2}\right) &= \frac{2}{L}\int_0^{\frac{L}{2}}\sin^2\frac{x\pi}{L}dx \\ &= \frac{2}{L}\frac{\frac{L\pi}{L}+\sin 0+\sin\frac{L\pi}{L}}{\frac{4\pi}{L}} \\ &= \frac{1}{2}\end{aligned}$$

This is the same answer as for the ψ_3 state in Example 3.5.1 . This is because the eigenstate squared (.e., probability density) for the particle in a 1D box will always be symmetric around the center of the box. So there will be equal probability to be on either side (i.e., no side is favored).

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3.6: Wavefunctions Must Be Normalized

Learning Objectives

- Calculate the probability of an event from the wavefunction
- Understand the utility and importance of normalizing wavefunctions
- Demonstrate how to normalize an arbitrary wavefunction

Extracting Probabilities

Since wavefunctions can in general be complex functions, the physical significance of wavefunctions cannot be found from the functions themselves because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the **square of the modulus**.

$$\Psi^*(r,t)\Psi(r,t) = |\Psi(r,t)|^2 \tag{3.6.1}$$

where r is a vector specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field. Remember that the Born interpretation is that $\psi^*(r_i)\psi(r_i)$ $d\tau$ is the **probability** that the electron is in the volume $d\tau$ located at r_i. The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the **probability density**, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability.

Since the squared magnitude $|\psi|^2$ of the wavefunction of a particle can be interpreted as the probability density, then the probability for a one-dimensional wavefunction between the points $x = a$ and $x = b$ can be calculated by

$$P_{1D} = \int_a^b |\psi(x)|^2 \mathrm{d}x \tag{3.6.2}$$

This is just the area under the under the $|\psi|^2$ curve (Figure 3.6.1).

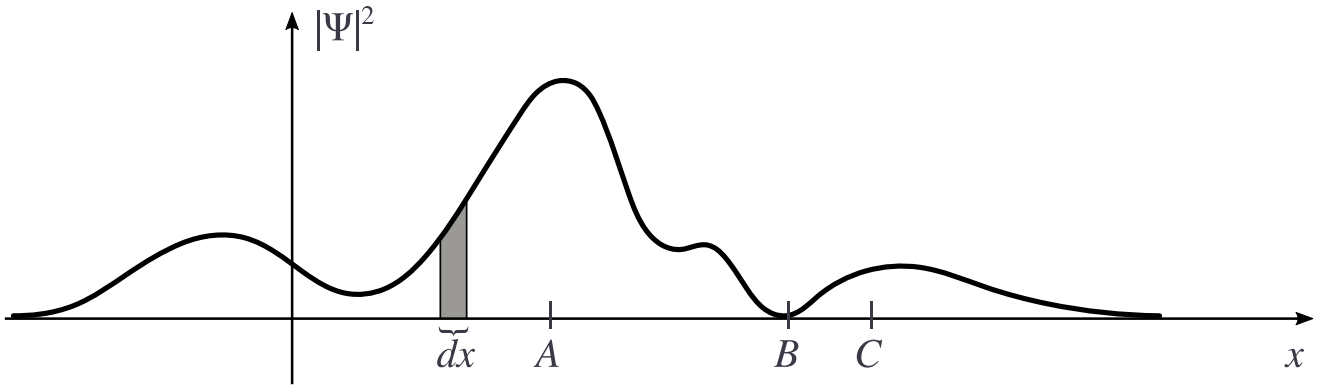


Figure 3.6.1 : The probability can be interpreted as an area under the probability density $|\psi|^2$. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

If the probability of a two-dimensional wavefunction is being evaluated, then Equation 3.6.2 will be amended to included a double integral:

$$P_{2D} = \iint_{a_1,a_2}^{b_1,b_2} |\psi(x,y)|^2 \mathrm{d}x\mathrm{d}y$$

and similarly a triple integral would be used for calculating probabilities of three-dimensional wavefunctions:

$$P_{3D} = \iiint_{a_1,a_2,a_3}^{b_1,b_2,b_3} |\psi(x,y,z)|^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z$$

Example 3.6.1 : Probability of a Particle in a Box

Calculate the probability of finding an electron at $L/2$ in a box of infinite height within an interval ranging from $\frac{L}{2} - \frac{L}{200}$ to $\frac{L}{2} + \frac{L}{200}$ for the $n = 1$ and $n = 2$ states. Since the length of the interval, $L/100$, is small compared to L, you can get an approximate answer without explicitly integrating.

Solution

The wavefunction for the particle in a box is

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

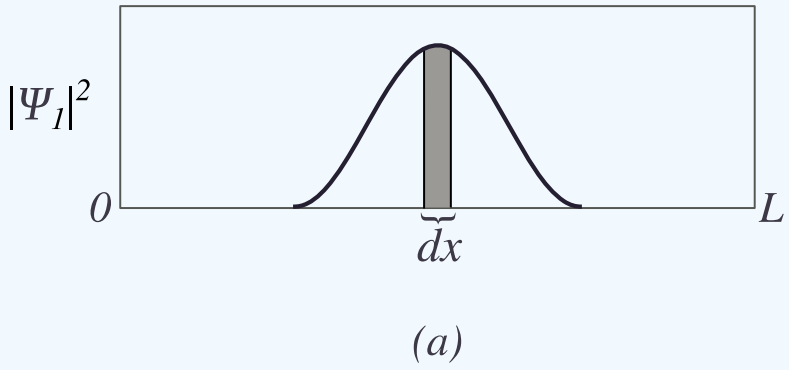
and the wavefunction for the $n = 1$ state is

$$\psi_{n=1} = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

From the interpretation that the wavefunction modulus squared is the probability density, we can establish the following integral to solve the problem (note the limits of integration)

$$|\psi_{n=1}|^2 = \frac{2}{L} \int_{\frac{99L}{200}}^{\frac{101L}{200}} \sin^2\left(\frac{\pi x}{L}\right) dx \tag{3.6.3}$$

We can solve this, but we can also recognize that Equation 3.6.3 is just calculating an area that can be approximated as the area of a rectangle with a height ($\frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$ at $x = L/2$) and width $\Delta x = L/100$ (Figure 3.6.2).



(a)

Figure 3.6.2 : The probability can be interpreted as an area under the probability density $|\psi_1|^2$. (CC BY-NC; Ümit Kaya via LibreTexts)

This area can be computed:

$$\begin{aligned} |\psi_{n=1}|^2 &\approx \frac{2}{L} \sin^2\left(\frac{\pi(L/2)}{L}\right)^{1} \Delta x \\ &\approx \left(\frac{2}{L}\right)(L/100) \\ &\approx 1/50 = 0.02 \end{aligned}$$

Given that the wavefunction is sinusoidal, the actual probability of finding an electron within the given interval at $\frac{L}{2}$ should be slightly less because of the behavior of the sinusoid at $\frac{L}{2}$ is at its peak of the wavefunction (Figure 3.6.2).

The wavefunction for the $n = 2$ state

$$\psi_{n=2} = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$$

so the integral that we need to construct and solve is

$$|\psi_{n=2}|^2 = \frac{2}{L} \int_{\frac{99L}{200}}^{\frac{101L}{200}} \sin^2\left(\frac{2\pi x}{L}\right) dx$$

We can use the same graphical interpretation as above, but using the probability density of the ψ_2 wavefunction (Figure 3.6.3).

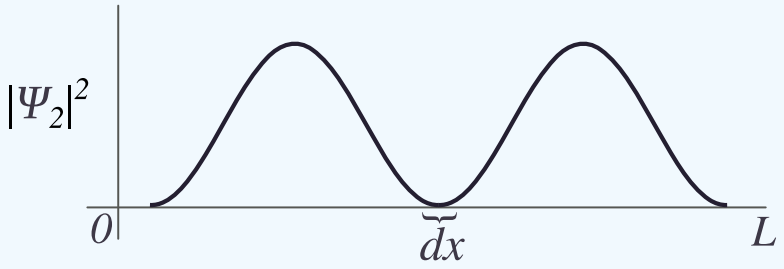


Figure 3.6.3 : The probability can be interpreted as an area under the probability density $|\psi_2|^2$. (CC BY-NC Copyright; Ümit Kaya via LibreTexts)

$$|\psi_{n=1}|^2 \approx \frac{2}{L} \sin^2\left(\frac{2\pi(L/2)}{L}\right)^{0} \Delta x$$
$$\approx 0$$

The probability of finding an electron in a box at $\frac{L}{2}$ for $n = 2$ is approximately zero.

Exercise 3.6.1

Show that the square of the modulus of $\Psi(r,t) = \psi(r)e^{-i\omega t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Solution

The square of the modulus of a wavefunction is $\Psi(r,t)^*\Psi(r,t)$ so for wavefunctions of this form, the square of the modulus is

$$\Psi(r,t)^*\Psi(r,t) = \psi(r)\cancel{e^{+i\omega t}}\,\psi(r)\cancel{e^{-i\omega t}}$$
$$= \psi(r)^2$$

Hence, there is no time dependence to the modulus of wavefunctions of this work, which from the probability interpretation of the wavefunction means that the probability density is time-independent.

Normalizing of the Wavefunction

A probability is a real number between 0 and 1, inclusive. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. According to Equation 3.6.1, the probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x^{\rm int}-\infty:\infty}(t) = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx. \tag{3.6.4}$$

However, a measurement of x *must* yield a value between $-\infty$ and $+\infty$, since the particle has to be located somewhere. It follows that $P_{x^{\rm int}-\infty:\infty}(t) = 1$, or

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1, \tag{3.6.5}$$

which is generally known as the **normalization condition** for the wavefunction.

Example 3.6.2 : Normalizing a Gaussian Wavepacket

Normalize the wavefunction of a Gaussian wave packet, centered on $x = x_o$ with characteristic width σ:

$$\psi(x) = \psi_0 {\rm e}^{-(x-x_0)^2/(4\sigma^2)}. \tag{3.6.6}$$

Solution

To determine the normalization constant ψ_0, we simply substitute Equation 3.6.6 into Equation 3.6.5, to obtain

$$|\psi_0|^2 \int_{-\infty}^{\infty} {\rm e}^{-(x-x_0)^2/(2\sigma^2)} dx = 1.$$

Changing the variable of integration to $y = (x - x_0)/(\sqrt{2}\sigma)$, we get

$$|\psi_0|^2 \sqrt{2}\sigma \int_{-\infty}^{\infty} {\rm e}^{-y^2} dy = 1.$$

However, from an integral table we know

$$\int_{-\infty}^{\infty} {\rm e}^{-y^2} dy = \sqrt{\pi},$$

which implies that

$$|\psi_0|^2 = \frac{1}{(2\pi\sigma^2)^{1/2}}.$$

Hence, a general normalized Gaussian wavefunction takes the form

$$\psi(x) = \frac{e^{{\rm i}\phi}}{(2\pi\sigma^2)^{1/4}} e^{-(x-x_0)^2/(4\sigma^2)}$$

where ϕ is an arbitrary real phase-angle.

Exercise 3.6.2

Normalize this wavefunction for a particle in a harmonic well:

$$\psi = xe^{-x^2}$$

Answer available at the end of this section.

Time Dependence to the Wavefunction

Now, it is important to demonstrate that if a wavefunction is initially normalized then it stays normalized as it evolves in time according to the time-dependent Schrödinger's equation. If this is not the case then the probability interpretation of the wavefunction is untenable, since it does not make sense for the probability that a measurement of x yields *any* possible outcome (which is, manifestly, unity) to change in time. Hence, we require that

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi(x,t)|^2 dx = 0$$

for wavefunctions satisfying the time-dependent Schrödinger's equation (this results from the time-dependent Schrödinger's equation and Equation 3.6.5). The above equation gives

$$\frac{d}{dt}\int_{-\infty}^{\infty}\psi^*\psi\, dx = \int_{-\infty}^{\infty}\left(\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t}\right)dx = 0. \tag{3.6.7}$$

Now, multiplying Schrödinger's equation by $\psi^*/(\mathrm{i}\hbar)$, we obtain

$$\psi^*\frac{\partial\psi}{\partial t} = \frac{\mathrm{i}}{2m}\psi^*\frac{\partial^2\psi}{\partial x^2} - \frac{\mathrm{i}}{\hbar}V|\psi|^2 \tag{3.6.8}$$

The complex conjugate of this expression yields

$$\psi\frac{\partial\psi^*}{\partial t} = -\frac{\mathrm{i}}{2m}\psi\frac{\partial^2\psi^*}{\partial x^2} + \frac{\mathrm{i}}{\hbar}V|\psi|^2 \tag{3.6.9}$$

since

- $(AB)^* = A^*B^*$,
- $A^{**} = A$, and
- $i^* = -i$.

Summing Equation 3.6.8 and 3.6.9 results in

$$\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t} = \frac{\mathrm{i}}{2m}\left(\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right) \tag{3.6.10}$$

$$= \frac{\mathrm{i}}{2m}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right). \tag{3.6.11}$$

Equations 3.6.7 and 3.6.11 can be combined to produce

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2 dx = \frac{\mathrm{i}}{2m}\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{3.6.12}$$

The above equation is satisfied provided the wavefunction converges

$$\lim_{|x|\to\infty}|\psi| = 0 \tag{3.6.13}$$

However, this is a necessary condition for the integral on the left-hand side of Equation 3.6.5 to converge. Hence, we conclude that all wavefunctions which are *square-integrable* [i.e., are such that the integral in Equation 3.6.5 converges] have the property that if the normalization condition Equation 3.6.5 is satisfied at one instant in time then it is satisfied at all subsequent times.

Not all Wavefunctions can be Normalized

Not all wavefunctions can be normalized according to the scheme set out in Equation 3.6.5. For instance, a planewave wavefunction for a quantum free particle

$$\Psi(x,t) = \psi_0 \mathrm{e}^{\mathrm{i}(kx-\omega t)}$$

is not square-integrable, and, thus, cannot be normalized. For such wavefunctions, the best we can say is that

$$P_{x^{\mathrm{int}}a:b}(t) \propto \int_a^b |\Psi(x,t)|^2 dx.$$

In the following, all wavefunctions are assumed to be square-integrable and normalized, unless otherwise stated.

Answers

$$\psi = 2\left(\frac{2}{\pi}\right)^{1/4} x e^{-x^2}$$

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3.7: The Average Momentum of a Particle in a Box is Zero

Learning Objectives

- Calculate the expectation value for a measurement
- Apply the expectation value concept to calculate average properties of a participle in a box model
- Understand the origin of a zero-point energy/zero-point motion.
- Extend the concept of orthogonality from vectors to mathematical functions (and wavefunctions).

Now that we have mathematical expressions for the wavefunctions and energies for the particle-in-a-box, we can answer a number of interesting questions. The answers to these questions use quantum mechanics to predict some important and general properties for electrons, atoms, molecules, gases, liquids, and solids. Key to addressing these questions is the formulation and use of expectation values. This is demonstrated below and used in the context of evaluating average properties (momentum of the particle in a box for the case below).

Classical Expectation Values

The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It is not the most probable value of a measurement; indeed the expectation value may even have zero probability of occurring. The expected value (or expectation, mathematical expectation, mean, or first moment) refers to the value of a variable one would "expect" to find if one could repeat the random variable process an infinite number of times and take the average of the values obtained. More formally, the expected value is a weighted average of all possible values.

Example 3.7.1 : Classical Expectation Value of Exam Scores (a discretized example)

A classical example is calculating the expectation value (i.e. average) of the exam grades in the class. For example if the class scores for an exam were

65	67	94	43	67	76	94	67

The discrete way is to sum up all scores and divide by the number of students:

$$\langle s \rangle = \frac{\sum_{i}^{N} s(i)}{N} \tag{3.7.1}$$

which of this example of scores is

$$\begin{aligned} \langle s \rangle &= \frac{65+67+94+43+67+76+94+76}{8} \\ &= 71.625 \end{aligned}$$

Notice that the average is not an allowable score on an individual exam. Equation 3.7.1 can be rewritten with "probability" or "probability weights"

$$\langle s \rangle = \sum_{i}^{N} s(i) P_s(i) \tag{3.7.2}$$

where $P_s(i)$ is the probability of observing a score of s. This is just the number of times it occurs in a dataset divided by the number of elements in that data set. Applying Equation 3.7.2 to the set of scores, we need to calculate these weights:

Score	65	67	94	43	76
P_s	1/8	3/8	2/8	1/8	1/8

As with all probabilities, the sum of all probabilities possible must be one. These confirm that for the weights here:

$$\frac{1}{8}+\frac{3}{8}+\frac{2}{8}+\frac{1}{8}+\frac{1}{8}=\frac{8}{8}=1$$

This is the discretized "normalization" criterion (the same as why we normalize wavefunctions).

So, now we can use Equation 3.7.2 properly

$$\begin{aligned}\langle s\rangle &= 65\times\frac{1}{8}+67\times\frac{3}{8}+94\times\frac{2}{8}+43\times\frac{1}{8}+76\times\frac{1}{8}\\ &= 71.625\end{aligned}$$

Hence, Equation 3.7.2 gives the same result, as expected, from Equation 3.7.1.

Quantum Expectation Values

The extension of the classical expectation (average) approach in Example 3.7.1 using Equation 3.7.2 to evaluating quantum mechanical expectation values requires three small changes:

1. Switch from descretized to continuous variables
2. Substitute the wavefunction squared for the probability weights (i.e., the probability distribution)
3. Use an operator instead of the scalar

Hence, the quantum mechanical expectation value $\langle o\rangle$ for an observable, o, associated with an operator, $\hat{O}$, is given by

$$\langle o\rangle=\int_{-\infty}^{+\infty}\psi^*\hat{O}\psi\,dx \tag{3.7.3}$$

where x is the range of space that is integrated over (i.e., an integration over all possible probabilities). The expectation value changes as the wavefunction changes and the operator used (i.e, which observable you are averaging over).

> In general, changing the wavefunction changes the expectation value for that operator for a state defined by that wavefunction.

Average Energy of a Particle in a Box

If we generalize this conclusion, such integrals give the average value for any physical quantity by using the operator corresponding to that physical observable in the integral in Equation 3.7.3. In the equation below, the symbol $\langle H\rangle$ is used to denote the average value for the total energy.

$$\langle H\rangle=\int_{-\infty}^{\infty}\psi^*(x)\hat{H}\psi(x)dx \tag{3.7.4}$$

$$=\int_{-\infty}^{\infty}\psi^*(x)\hat{KE}\psi(x)dx+\int_{-\infty}^{\infty}\psi^*(x)\hat{V}\psi(x)dx \tag{3.7.5}$$

$$=\underbrace{\int_{-\infty}^{\infty}\psi^*(x)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x)dx}_{\text{average kinetic energy}}+\underbrace{\int_{-\infty}^{\infty}\psi^*(x)\hat{V}(x)\psi(x)dx}_{\text{average potential energy}} \tag{3.7.6}$$

The Hamiltonian operator consists of a kinetic energy term and a potential energy term. The kinetic energy operator involves

differentiation of the wavefunction to the right of it. This step must be completed before multiplying by the complex conjugate of the wavefunction. The potential energy, however, usually depends only on position and not momentum (i.e., it involves conservative forces). The potential energy operator therefore only involves the coordinates of a particle and does not involve differentiation. For this reason we do not need to use a caret over V in Equation 3.7.6.

Equation 3.7.6 can be simplified

$$\langle H \rangle = \langle KE \rangle + \langle V \rangle \tag{3.7.7}$$

The potential energy integral then involves only products of functions, and the order of multiplication does not affect the result, e.g. 6×4 = 4×6 = 24. This property is called the **commutative property**. The average potential energy therefore can be written as

$$\langle V \rangle = \int_{-\infty}^{\infty} V(x)\psi^*(x)\psi(x)dx \tag{3.7.8}$$

This integral is telling us to take the probability that the particle is in the interval dx at x, which is $\psi^*(x)\psi(x)dx$, multiply this probability by the potential energy at x, and sum (i.e., integrate) over all possible values of x. This procedure is just the way to calculate the average potential energy $\langle V \rangle$ of the particle.

Exercise 3.7.2 : Particle in Box

Evaluate the two integrals in Equation 3.7.6 for the PIB wavefunction $\psi(x) = \sqrt{\frac{2}{L}}\sin(kx)$ with the potential function $V(x) = 0$ from 0 to the length of a box L with $k = \frac{\pi}{L}$.

Solution

The *average kinetic energy* is

$$\begin{aligned}
\langle KE \rangle &= \int_0^L \left(\sqrt{\frac{2}{L}}\right)\sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\left(\sqrt{\frac{2}{L}}\right)\sin(kx)dx \\
&= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial}{\partial x}\cos(kx)(k)dx \\
&= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\sin(kx)(k)(-k)dx \\
&= \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx
\end{aligned}$$

We can solve this intergral using the standard half-angle representation from an integral table. Or we can recognize that we already did this integral when we normalized the PIB wavefunction by rewriting this integral:

$$\langle KE \rangle = \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx$$

$$= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \left(\frac{2}{L}\right)\sin^2(kx)dx$$

$$= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \psi^*(x)\psi(x)dx \quad (= 1)$$

$$= \frac{k^2\hbar^2}{2m}$$

Thus, the average value for the total energy of this particular system is

$$\langle KE \rangle = \frac{k^2\hbar^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2}$$

Hence, the average kinetic energy of the wavefunction is dependent on the n quantum number

The *average potential energy* is

$$\langle V \rangle = \int_{-\infty}^{\infty} \sin(kx)0\sin(kx)dx = 0$$

Thus, the average potential energy of the PIB is 0 irrespective of the wavefunction.

Hence via Equation 3.7.7 for this system and set of wavefunctions

$$\langle H \rangle = \frac{\pi^2\hbar^2}{2mL^2}$$

This is the same result obtained from solving the eigenvalue equation for the PIB. However, if the wavefunctions used were NOT eigenstates of energy, then we cannot use the eigenvalue approach and need to rely on the expectation values to describe the energy of the system.

What is the lowest energy for a particle in a box? The lowest energy level is E_1, and it is important to recognize that this lowest energy of a particle in a box is not zero. This finite energy is called the **zero-point energy**, and the motion associated with this energy is called the zero-point motion. Any system that is restricted to some region of space is said to be bound. The zero-point energy and motion are manifestations of the wave properties and the Heisenberg Uncertainty Principle, and are general properties of bound quantum mechanical systems.

Exercise 3.7.2 : Progressing to the Classical Limit

What happens to the energy level spacing for a particle-in-a-box when mL^2 becomes much larger than h^2? What does this result imply about the relevance of quantization of energy to baseballs in a box between the pitching mound and home plate? What implications does quantum mechanics have for the game of baseball in a world where h is so large that baseballs exhibit quantum effects?

Answer available at the end of this section.

The first derivative of a function is the rate of change of the function, and the second derivative is the rate of change in the rate of change, also known as the curvature. A function with a large second derivative is changing very rapidly. Since the second derivative of the wavefunction occurs in the Hamiltonian operator that is used to calculate the energy by using the Schrödinger equation, a wavefunction that has sharper curvatures than another, i.e. larger second derivatives, should correspond

to a state having a higher energy. A wavefunction with more nodes than another over the same region of space must have sharper curvatures and larger second derivatives, and therefore should correspond to a higher energy state.

Exercise 3.7.3 : Nodes and Energies

Identify a relationship between the number of nodes in a wavefunction and its energy by examining the graphs you made above. A node is the point where the amplitude passes through zero. What does the presence of many nodes mean about the shape of the wavefunction?

Average Position of a Particle in a Box

We can calculate the most probable position of the particle from knowledge of probability distribution, $\psi^*\psi$. For the ground-state particle in a box wavefunction with $n = 1$ (Figure $3.7.1a$)

$$\psi_{n=1} = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \tag{3.7.9}$$

This state has the following probability distribution (Figure $3.7.1b$):

$$\psi^*_{n=1}\psi_{n=1} = \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$$

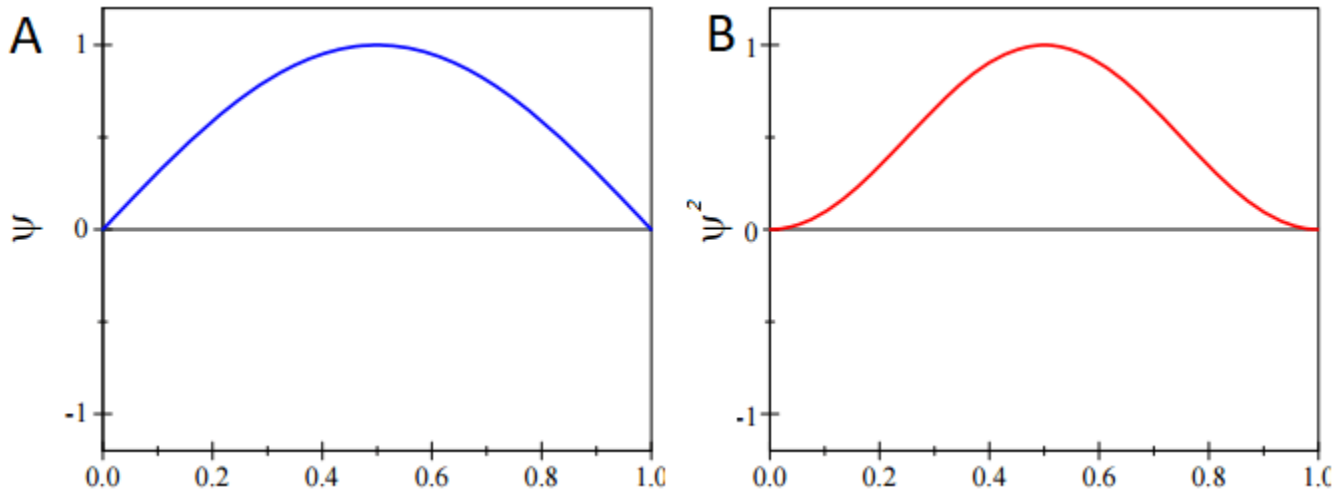


Figure 3.7.1 : (left) The ground-state ($n = 1$) wavefunction for a particle in a box. (right) The ground-state ($n = 1$) probability for a particle in a box.

The expectation value for position with the $\hat{x} = x$ operation for any wavefunction (Equation 3.7.3) is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* x \psi \, dx$$

which for the ground-state wavefunction (Equation 3.7.9) shown in Figure 3.7.1 is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) x \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \tag{3.7.10}$$

$$= \frac{2}{L} \int_{-\infty}^{+\infty} x \sin^2\left(\frac{\pi x}{L}\right) \tag{3.7.11}$$

Solution by Inspection

Without even having to evaluate Equation 3.7.11, we can get the expectation value from simply inspecting $\psi^*_{n=1}\psi_{n=1}$ in (Figure $3.7.1; right$). This is a symmetric distribution around the center of the box ($L/2$) so it is just as likely to be found in the left half than the right half. Moreover, specifically at any point a fixed distance away from the mean, i.e.

$$\psi^*_{n=1}\psi_{n=1}(L/2+\Delta x) = \psi^*_{n=1}\psi_{n=1}(L/2-\Delta x)$$

Therefore, the particle is most likely to be found at the center of the box. So

$$\langle x\rangle = \frac{L}{2}$$

Exercise 3.7.4

Use the general form of the particle-in-a-box wavefunction for any n to find the mathematical expression for the position expectation value $\langle x\rangle$ for a box of length L. How does $\langle x\rangle$ depend on n?

Average Momentum of a Particle in a Box

What is the average momentum of a particle in the box? We start with Equation 3.7.3 and use the momentum operator

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.7.12}$$

We note that the particle-in-a-box wavefunctions are **not** eigenfunctions of the momentum operator (Exercise 3.7.4). However, this does not mean that Equation 3.7.3 is inapplicable as Example 3.7.2 demonstrates.

Example 3.7.3 : The Average Momentum of a Particle in a Box is Zero

Even though the wavefunctions are not momentum eigenfunctions, we can calculate the expectation value for the momentum. Show that the expectation or average value for the momentum of an electron in the box is zero in every state (i.e., arbitrary values of n).

Strategy

First write the expectation value integral (Equation 3.7.3) with the momentum operator. Then insert the expression for the wavefunction and evaluate the integral as shown here.

Solution

$$\begin{aligned}\langle p\rangle &= \int_0^L \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)dx \\ &= \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)\left(-i\hbar\frac{d}{dx}\right)\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -i\hbar\left(\frac{2}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(\frac{d}{dx}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -i\hbar\left(\frac{2}{L}\right)\left(\frac{n\pi}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx \\ &= 0\end{aligned}$$

Note that this makes sense since the particles spends an equal amount of time traveling in the $+x$ and $-x$ direction.

Interpretation

It may seem that this means the particle in a box does not have any momentum, which is incorrect because we know the energy is never zero. In fact, the energy that we obtained for the particle-in-a-box is entirely kinetic energy because we set the potential energy at 0. Since the kinetic energy is the momentum squared divided by twice the mass, it is easy to understand how the average momentum can be zero and the kinetic energy finite

Exercise 3.7.5

Show that the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator (Equation 3.7.12).

Answer available at the end of this section.

Exercise 3.7.6

Write the particle-in-a-box wavefunction as a normalized linear combination of the momentum eigenfunctions e^{ikx} and e^{-ikx} by using Euler's formula. Show that the momentum eigenvalues for these two functions are $p = +\hbar k$ and $-\hbar k$.

The interpretation of the results of Exercise 3.7.6 is physically interesting. The exponential wavefunctions in the linear combination for the sine function represent the two opposite directions in which the electron can move. One exponential term represents movement to the left and the other term represents movement to the right (Figure 3.7.2).

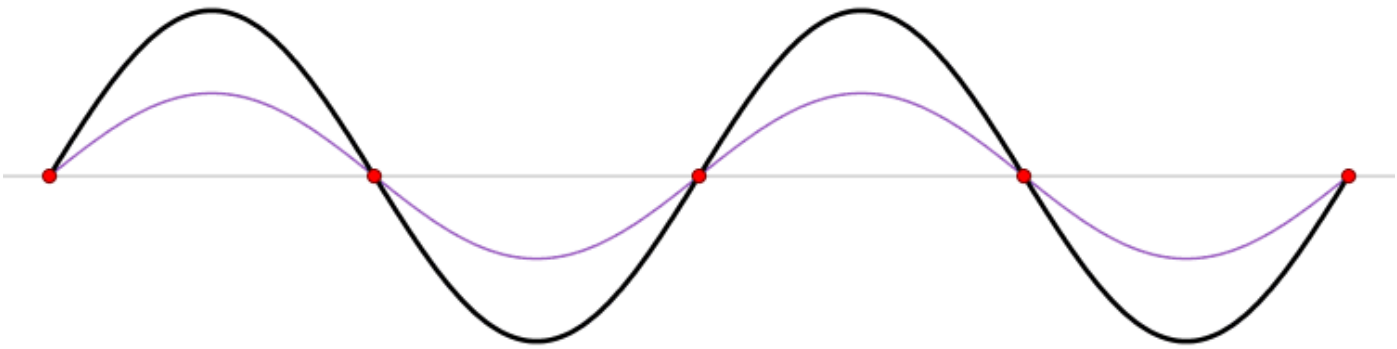


Figure 3.7.2 : Two waves traveling in opposite directions across the same medium combine linearly. In this animation, both waves have the same wavelength and the sum of amplitudes results in a standing wave. (Public Domain; LucasVB).

The electrons are moving, they have kinetic energy and momentum, yet the average momentum is zero.

Did we just Violate the Uncertainty Principle?

Does the fact that the average momentum of an electron is zero and the average position is $L/2$ violate the Heisenberg Uncertainty Principle? No, because the Heisenberg Uncertainty Principle pertains to the uncertainty in the momentum and in the position, not to the average values. Quantitative values for these uncertainties can be obtained to compare with the limit set by the Heisenberg Uncertainty Principle for the product of the uncertainties in the momentum and position. However, to do this we need a quantitative definition of uncertainty, which is discussed in the following Section.

Orthogonality

In vector calculus, *orthogonality* is the relation of two lines at right angles to one another (i.e., perpendicularity), but is generalized into n dimensions via zero amplitude "dot products" or "inner products." Hence, orthogonality is thought of as describing **non-overlapping**, **uncorrelated**, or **independent** objects of some kind. The concept of orthogonality extends to functions (wavefunctions or otherwise) too. Two functions ψ_A and ψ_B are said to be orthogonal if

$$\int_{allspace} \psi_A^* \psi_B d\tau = 0 \tag{3.7.13}$$

In general, eigenfunctions of a quantum mechanical operator with different eigenvalues are orthogonal. Are the eigenfunctions of the particle-in-a-box Hamiltonian orthogonal?

Exercise 3.7.7

Evaluate the integral $\int \psi_1^* \psi_3 dx$ for all possible pairs of particle-in-a-box eigenfunctions from $n = 1$ to $n = 3$ (use symmetry arguments whenever possible) and explain what the results say about orthogonality of the functions.

Answers

As mL^2 becomes much larger than h^2, as everyday objects are, the spacing between energy levels becomes much smaller. This shows how the quantizations of energy levels become irrelevant for an everyday object, as the quantizations of the energy of baseballs in a box between the pitching mound and home plate would appear particularly continuous for such a relatively large mass and box length. If h were so large that a baseball experiences quantum effects then a game of baseball would be far less predictable, in a classical world the position of a baseball can be easily predicted by the everyday understanding of projectile motion, however, in such a quantum world the baseball would not behave with expected projectile motion but instead behave wave-like with a probability of being in a certain position.

The easiest way to address this question is asking if the PIB wavefunction also satisfies the eigenvalue equation using the momentum operation instead of the Hamiltonian operator (3rd postulate of QM). That is

$$\hat{p}_x\psi(n) = p\psi(n)$$

with the following PIB wavefunctions

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

and

$$\hat{p} = -i\hbar\frac{d}{dx}$$

and p is a real scalar (since it is a measurable).

$$\begin{aligned}\hat{p}_x\psi_n &= -i\hbar\frac{d}{dx}\left[\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\right]\\ &= -i\hbar\sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right)\left(\frac{n\pi}{L}\right)\\ &\neq p\psi_n\end{aligned}$$

Hence, the PIB wavefunctions are NOT eigenfunctions of the momentum operator.

Alternative Solution

An alternative, albeit more complicated, approach is to recognize that the uncertainty of p must be zero if the wavefunction is an eigenstate of the momentum operator. Hence

$$\sqrt{\langle p^2\rangle - \langle p\rangle^2} = 0$$

This requires calculating the $\langle p^2\rangle$ and $\langle p\rangle$ expectation values:

$$\begin{aligned}\langle p\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]\psi dx\\ &= -i\hbar\int_0^L \frac{2}{L}\sin\left(\frac{n\pi x}{L}\right)\frac{d}{dx}x\sin\left(\frac{n\pi x}{L}\right)dx\\ &= -i\frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx\\ &= 0\end{aligned}$$

This integral is zero via orthonormality of the sine and cosine functions (although you can expand the integrand and confirm this).

$$\begin{aligned}\langle p^2\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]^2\psi dx\\ &= \frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{L}\right)dx\\ &= \frac{-\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx\\ &= -\frac{\mathrm{h}^2}{L}\end{aligned}$$

Now the integral above is 1 using orthonormality (although you can expand the integrand and confirm this). Now we calculate the uncertainty in momentum in the PIB wavefunctions:

$$\begin{aligned}\sqrt{\langle p^2\rangle - \langle p\rangle^2} &= \sqrt{\frac{-\mathrm{h}^2}{L} - 0^2}\\ &= \sqrt{\frac{-\mathrm{h}^2}{L}}\\ &\neq 0 \rightarrow\end{aligned}$$

Since the uncertainty is not 0, different measurements (experiments) will results in different values of momentum being quantified. Hence, the PIB wavefunctions are **not** eigenfunctions of the momentum operator.

It must be equally likely for the particle-in-a-box to have a momentum $-p$ as $+p$. The average of $+p$ and $-p$ is zero, yet p^2 and the average of p^2 are not zero. The information that the particle is equally likely to have a momentum of $+p$ or $-p$ is contained in the wavefunction. In fact, the sine function is a representation of the two momentum eigenfunctions e^{+ikx} and e^{-ikx} (Figure 3.7.2).

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3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

Learning Objectives

- Expand on the introduction of Heisenberg's Uncertainty Principle by calculating the Δx or Δp directly from the wavefunction

As will be discussed in Section 4.6, the operators $\hat{x}$ and $\hat{p}$ are not compatible and there is **no** measurement that can precisely determine the coresponding observables (x and p) simultaneously. Hence, there must be an uncertainty relation between them that specifies how uncertain we are about one quantity given a definite precision in the measurement of the other. Presumably, if one can be determined with infinite precision, then there will be an infinite uncertainty in the other. The uncertainty in a general quantity A is

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \tag{3.8.1}$$

where $\langle A^2 \rangle$ and $\langle A \rangle$ are the expectation values of $\hat{A}^2$ and $\hat{A}$ operators for a specific wavefunction. Extending Equation 3.8.1 to x and p results in the following uncertainties

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{3.8.2}$$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{3.8.3}$$

These quantities can be expressed explicitly in terms of the (time-dependent) wavefunction $\Psi(x,t)$ using the fact that

$$\langle x \rangle = \langle \Psi(t) | \hat{x} | \Psi(t) \rangle \tag{3.8.4}$$

$$= \int \Psi^*(x,t) x \Psi(x,t)\, dx \tag{3.8.5}$$

and

$$\langle x^2 \rangle = \langle \Psi(t) | \hat{x}^2 | \Psi(t) \rangle \tag{3.8.6}$$

$$= \int \Psi^*(x,t) x^2 \Psi(x,t)\, dx \tag{3.8.7}$$

The middle terms in both Equations 3.8.4 and 3.8.6 are the integrals expressed in Dirac's Bra-ket notation. Similarly using the definition of the linear momentum operator:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}.$$

So

$$\langle p \rangle = \langle \Psi(t) | \hat{p} | \Psi(t) \rangle \tag{3.8.8}$$

$$= \int \Psi^*(x,t) - i\hbar \frac{\partial}{\partial x} \Psi(x,t)\, dx \tag{3.8.9}$$

and

$$\langle p^2 \rangle = \langle \Psi(t) | \hat{p}^2 | \Psi(t) \rangle \tag{3.8.10}$$

$$= \int \Psi^*(x,t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \Psi(x,t)\, dx \tag{3.8.11}$$

Time-dependent vs. time-independent wavefunction

The expectation values above are formulated with the total time-dependence wavefunction $\psi(x,t)$ that are functions of x and t. However, it is easy to show that the same expectation value would be obtained if the time-independent wavefunction $\psi(x)$ that are functions of only x are used. If $V(x)$ in $\hat{H}$ is time independent, then the wavefunctions are stationary and the expectation value are time-independent. You can easily confirm that by comparing the expectation values using the general formula for a stationary wavefunction

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

and for $\psi(x)$.

The Heisenberg uncertainty principle can be quantitatively connected to the properties of a wavefunction, i.e., calculated via the expectation values outlined above:

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{3.8.12}$$

This essentially states that the greater certainty that a measurement of x or p can be made, the greater will be the *uncertainty* in the other. Hence, as Δp approaches 0, Δx must approach ∞, which is the case of the free particle (e.g, with $V(x) = 0$) where the momentum of a particles can be determined precisely.

Example 3.8.1 : Uncertainty with a Gaussian wavefunction

A particle is in a state described by the wavefunction

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \tag{3.8.13}$$

where a is a constant and $-\infty \leq x \leq \infty$. Verify that the value of the product $\Delta p \Delta x$ is consistent with the predictions from the uncertainty principle (Equation 3.8.12).

Solution

Let's calculate the average of x:

$$\begin{aligned}
\langle x \rangle &= \int_{-\infty}^{\infty} \psi^* x \psi \, dx \\
&= \int_{-\infty}^{\infty} (2a/\pi)^{\frac{1}{4}} e^{-ax^2} x (2a/\pi)^{\frac{1}{4}} e^{-ax^2} \, dx \\
&= \int_{-\infty}^{\infty} x (2a/\pi)^{\frac{1}{2}} e^{-2ax^2} \, dx \\
&= 0
\end{aligned}$$

since the integrand is an odd function (an even function times an odd function is an odd function). This makes sense given that the gaussian wavefunction is symmetric around $x = 0$.

Let's calculate the average of x^2:

$$\begin{aligned}\langle x^2\rangle &= \int_{-\infty}^{\infty} \psi^* x^2 \psi \, dx \\ &= \int_{-\infty}^{\infty} (2a/\pi)^{\frac{1}{4}} e^{-ax^2} (x^2) (2a/\pi)^{\frac{1}{4}} e^{-ax^2} \, dx \\ &= \int_{-\infty}^{\infty} x^2 (2a/\pi)^{\frac{1}{2}} e^{-2ax^2} \, dx \\ &= \frac{1}{4a}\end{aligned}$$

Let's calculate the average in p:

$$\begin{aligned}\langle p\rangle &= \int_{-\infty}^{\infty} \psi^* p \psi \, dx \\ &= \int_{-\infty}^{\infty} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} - i\hbar \frac{d}{dx} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \, dx \\ &= \int_{-\infty}^{\infty} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} (-i\hbar) \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} (-2ax) \, dx \\ &= 0\end{aligned}$$

since the integrand is an odd function.

Let's calculate the average of p^2:

$$\begin{aligned}\langle p^2\rangle &= \int_{-\infty}^{\infty} \psi^* p^2 \psi dx \\ &= -\hbar^2 \left(\frac{2a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} 2a(ax^2 - 1) e^{-2ax^2} dx \\ &= -4\hbar^2 a^2 \left(\frac{2a}{\pi}\right)^{1/2} \int_0^{\infty} x^2 e^{-2ax^2} dx + 4\hbar^2 a \left(\frac{2a}{\pi}\right)^{1/2} \int_0^{\infty} e^{-2ax^2} dx \\ &= a\hbar^2\end{aligned}$$

We use Equation 3.8.1 to check on the uncertainty

$$\begin{aligned}\Delta x^2 &= \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{4a} - 0 \\ \Delta x &= \sqrt{\Delta x^2} = \frac{1}{2\sqrt{a}} \\ \Delta p^2 &= \langle p^2\rangle - \langle p\rangle^2 = a\hbar^2 - 0 \\ \Delta p &= \sqrt{\Delta p^2} = \hbar\sqrt{a}\end{aligned}$$

Finally we have

$$\Delta p \Delta x = \left(\frac{1}{2\sqrt{a}}\right)(\hbar\sqrt{a}) = \frac{\hbar}{2}$$

Not only does the Heisenburg uncertainly principle hold (Equation 3.8.12), but the equality is established for this wavefunction. This is because the Gaussian wavefunction (Equation 3.8.13) is special as discussed later.

Exercise 3.8.1

A particle is in a state described by the ground state wavefunction of a particle in a box

$$\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

where L is the length of the box and $0 \leq x \leq L$. Verify that the value of the product $\Delta p \Delta x$ is consistent with the predictions from the uncertainty principle (Equation 3.8.12).

The uncertainty principle is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space.

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3.9: A Particle in a Three-Dimensional Box

Learning Objectives

- To demonstrate how the particle in 1-D box problem can extend to a particle in a 3D box
- Introduction to nodal surfaces (e.g., nodal planes)

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimensions as demonstrated elsewhere for a quantum particle in a 2D box. Here we continue the expansion into a particle trapped in a 3D box with three lengths L_x, L_y, and L_z. As with the other systems, there is NO FORCE (i.e., no potential) acting on the particles *inside* the box (Figure 3.9.1).

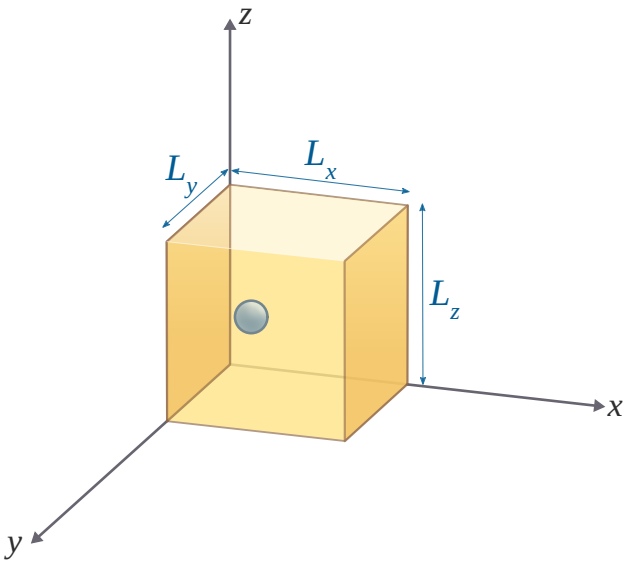


Figure 3.9.1 : A particle in 3D box with three lengths L_x, L_y, and L_z. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The potential for the particle inside the box

$$V(\vec{r}) = 0$$

- $0 \leq x \leq L_x$
- $0 \leq y \leq L_y$
- $0 \leq z \leq L_z$
- $L_x < x < 0$
- $L_y < y < 0$
- $L_z < z < 0$

$\vec{r}$ is the vector with all three components along the three axes of the 3-D box: $\vec{r} = L_x\hat{x} + L_y\hat{y} + L_z\hat{z}$. When the potential energy is infinite, then the wavefunction equals zero. When the potential energy is zero, then the wavefunction obeys the Time-Independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{3.9.1}$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrondinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \tag{3.9.2}$$

The easiest way in solving this partial differential equation is by having the wavefunction equal to a **product** of individual function for each independent variable (e.g., the Separation of Variables technique):

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{3.9.3}$$

Now each function has its own variable:

- $X(x)$ is a function of variable x only
- $Y(y)$ is a function of variable y only
- $Z(z)$ is a function of variable z only

Now substitute Equation 3.9.3 into Equation 3.9.2 and divide it by the xyz product:

$$\frac{d^2\psi}{dx^2} = YZ\frac{d^2X}{dx^2} \Rightarrow \frac{1}{X}\frac{d^2X}{dx^2}$$

$$\frac{d^2\psi}{dy^2} = XZ\frac{d^2Y}{dy^2} \Rightarrow \frac{1}{Y}\frac{d^2Y}{dy^2}$$

$$\frac{d^2\psi}{dz^2} = XY\frac{d^2Z}{dz^2} \Rightarrow \frac{1}{Z}\frac{d^2Z}{dz^2}$$

$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right) = E \tag{3.9.4}$$

E is an energy constant, and is the sum of x, y, and z. For this to work, each term must equal its own constant. For example,

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

Now separate each term in Equation 3.9.4 to equal zero:

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

$$\frac{d^2Y}{dy^2} + \frac{2m}{\hbar^2}\varepsilon_y Y = 0$$

$$\frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2}\varepsilon_z Z = 0$$

Now we can add all the energies together to get the total energy:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \tag{3.9.5}$$

Do these equations look familiar? They should because we have now reduced the 3D box into three particle in a 1D box problems!

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{3.9.6}$$

Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,

$$n = 1, 2, ..\infty$$

Use the normalization wavefunction equation for each variable:

$$\psi(x) = \begin{cases} \sqrt{\dfrac{2}{L_x}}\sin\dfrac{n\pi x}{L_x} & \text{if } 0 \le x \le L \\ 0 & \text{if } L < x < 0 \end{cases}$$

Normalization wavefunction equation for each variable (that substitute into Equation 3.9.3):

$$X(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi x}{L_x}\right) \tag{3.9.7}$$

$$Y(y) = \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi y}{L_y}\right) \tag{3.9.8}$$

$$Z(z) = \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.9.9}$$

The limits of the three quantum numbers

- $n_x = 1, 2, 3, ...\infty$
- $n_y = 1, 2, 3, ...\infty$
- $n_z = 1, 2, 3, ...\infty$

For each constant use the de Broglie Energy equation:

$$\varepsilon_x = \frac{n_x^2 h^2}{8mL_x^2} \tag{3.9.10}$$

with $n_x = 1...\infty$

Do the same for variables n_y and n_z. Combine Equation 3.9.3 with Equations 3.9.7-3.9.9 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.9.11}$$

with

$$V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}}$$

To find the Total Energy, add Equation 3.9.10 and Equation 3.9.5.

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{3.9.12}$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.9.12) and a 1D box.

Degeneracy in a 3D Cube

The energy of the particle in a 3-D cube (i.e., $L_x = L_y = L$) in the *ground state* is given by Equation 3.9.12 with $n_x = 1$, $n_y = 1$, and $n_z = 1$. This energy ($E_{1,1,1}$) is hence

$$E_{1,1,1} = \frac{3h^2}{8mL^2}$$

The ground state has only one wavefunction and no other state has this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 3-D cubical box potential the energy of a state depends upon the sum of the squares of the quantum numbers (Equation 3.9.11). The particle having a particular value of energy in the excited state *MAY* has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be **degenerate**.

For the first excited state, three combinations of the quantum numbers $(n_x,\ n_y,\ n_z)$ are $(2,\ 1,\ 1)$, $(1, 2, 1)$, $(1, 1, 2)$. The sum of squares of the quantum numbers in each combination is same (equal to 6). Each wavefunction has same energy:

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2}$$

Corresponding to these combinations three different wavefunctions and **three** different states are possible. Hence, the first

excited state is said to be three-fold or triply degenerate. The number of independent wavefunctions for the stationary states of an energy level is called as the **degree of degeneracy** of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

as well as the degree of degeneracy are depicted in Table 3.9.1 .

Table 3.9.1 : Degeneracy properties of the particle in a 3-D cube with $L_x = L_y = L$.

$n_x^2 + n_y^2 + n_z^2$	Combinations of Degeneracy (n_x, n_y, n_z)						Total Energy (E_{n_x,n_y,n_z})	Degree of Degeneracy
3	(1,1,1)						$\frac{3h^2}{8mL^2}$	1
6	(2,1,1)	(1,2,1)	(1,1,2)				$\frac{6h^2}{8mL^2}$	3
9	(2,2,1)	(1,2,2)	(2,1,2)				$\frac{9h^2}{8mL^2}$	3
11	(3,1,1)	(1,3,1)	(1,1,3)				$\frac{11h^2}{8mL^2}$	3
12	(2,2,2)						$\frac{12h^2}{8mL^2}$	1
14	(3,2,1)	(3,1,2)	(2,3,1)	(2,1,3)	(1,3,2)	(1,2,3)	$\frac{14h^2}{8mL^2}$	6
17	(2,2,3)	(3,2,2)	(2,3,2)				$\frac{17h^2}{8mL^2}$	3
18	(1,1,4)	(1,4,1)	(4,1,1)				$\frac{18h^2}{8mL^2}$	3
19	(1,3,3)	(3,1,3)	(3,3,1)				$\frac{19h^2}{8mL^2}$	3
21	(1,2,4)	(1,4,2)	(2,1,4)	(2,4,1)	(4,1,2)	(4,2,1)	$\frac{21h^2}{8mL^2}$	6

Example 3.9.1 : Accidental Degeneracies

When is there degeneracy in a 3-D box when none of the sides are of equal length (i.e., $L_x \neq L_y \neq L_z$)?

Solution

From simple inspection of Equation 3.9.12 or Table 3.9.1 , it is clear that degeneracy originates from different combinations of n_x^2/L_x^2, n_y^2/L_y^2 and n_z^2/L_z^2 that give the same value. These will occur at common multiples of at least two of these quantities (the Least Common Multiple is one example). For example

if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}$$

there will be a degeneracy. Also degeneracies will exist if

$$\frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}$$

or if

$$\frac{n_x^2}{L_x^2} = \frac{n_z^2}{L_z^2}$$

and especially if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}.$$

There are two general kinds of degeneracies in quantum mechanics: degeneracies due to a symmetry (i.e., $L_x = L_y$) and accidental degeneracies like those above.

Exercise 3.9.1

The 6th energy level of a particle in a 3D Cube box is 6-fold degenerate.

a. What is the energy of the 7th energy level?
b. What is the degeneracy of the 7th energy level?

Answer a available at the end of this section.

References

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Answers

$\frac{17h^2}{8mL^2}$
three-fold (i.e., there are three wavefunctions that share the same energy.

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3.E: The Schrödinger Equation and a Particle in a Box (Exercises)

Solutions to select questions can be found online.

3.2

Determine from the following operators which are linear and nonlinear:

a. $\hat{A}f(x) = f(x)^2$ [square f(x)]
b. $\hat{A}f(x) = f^*(x)$ [form the complex conjugate of f(x)]
c. $\hat{A}f(x) = 0$ [multiply f(x) by zero]
d. $\hat{A}f(x) = [f(x)]^{-1}$ [take the reciprocal of f(x)]
e. $\hat{A}f(x) = f(0)$ [evaluate f(x) at x=0]
f. $\hat{A}f(x) = \ln f(x)$ [take the log of f(x)]

Solution

It is important to note that an operator $\hat{A}$ is *linear* if

$$\underbrace{\hat{A}[c_1 f(x) + c_2 f_2(x)]}_{\text{left side}} = \underbrace{c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x)}_{\text{right side}}$$

and the operator is *nonlinear* if

$$\underbrace{\hat{A}[c_1 f_1(x) + c_2 f_2(x)]}_{\text{left side}} \neq \underbrace{c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x)}_{\text{right side}}$$

a)

Evaluate the left side

$$\begin{aligned}\hat{A}[c_1 f(x) + c_2 f_2(x)] &= [c_1 f_1(x) + c_2 f_2(x)]^2 \\ &= c_1^2 f_1(x)^2 + 2c_1 f_1(x) c_2 f_2(x) + c_2^2 f_2(x)^2\end{aligned}$$

Evaluate the right side

$$c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x) = c_1[f_1(x)]^2 + c_2[f_2(x)]^2 \neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

b)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1^* f_1^*(x) + c_2^* f_2^*(x)$$

Evaluate the right side

$$\begin{aligned}c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x) &= c_1 f_1^*(x) + c_2 f_2^*(x) \\ &= \hat{A}[c_1 f_1(x) + c_2 f_2(x)]\end{aligned}$$

This operator is linear

c)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = 0$$

Evaluate the right side

$$c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x) = c_1 f_1(x) + c_2 f_2(x) = 0$$

$$= \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is linear

d)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = \frac{1}{c_1 f_1(x) + c_2 f_2(x)}$$

Evaluate the right side

$$c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = \frac{c_1}{f_1(x)} + \frac{c_2}{f_2(x)}$$

$$\neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

e)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 f_1(0) + c_2 f_2(0)$$

Evaluate the right side

$$= c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

This operator is linear

f)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = \ln[c_1 f_1(x) + c_2 f_2(x)]$$

Evaluate the right side

$$c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = c1 \ln f_1(x) + c_2 \ln f_2(x)$$

$$\neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

3.8

Show that for a particle in a box with length a with state $n = 3$ that there are 3 locations along the x axis where the probability density is at a maximum.

Solution

The probability density for a particle in a box for state $n = 3$ is

$$\psi^*\psi = \frac{2}{a}\sin^2\frac{3px}{a}$$

To maximize the probability density, take its derivative and set it equal to zero and solve for x .

$$\frac{d}{dx}\left[\frac{2}{a}\sin^2\frac{3\pi x}{a}\right] = \frac{2}{a}\cdot 2\cdot \sin\frac{3\pi x}{a}\cdot\cos\frac{3\pi x}{a}\cdot\frac{3\pi}{a} = 0$$

$$\sin\frac{3\pi x}{a}\cos\frac{3\pi x}{a} = 0$$

We want to not choose values of x that make $\sin\frac{3\pi x}{a} = 0$, as that means that the probability density will be zero. We will only choose the zeros of $\cos\frac{3\pi x}{a}$. So the possible values for x which make

$$\cos\frac{3\pi x}{a} = 0$$

are

$$\frac{3px}{a} = \frac{2m+1}{2}p \qquad m = 0, 1, 2, ...$$

$$x = \frac{(2m+1)\,a}{6}$$

We only choose $m = 0, 1, 2$ and not 3 because $m = 3$ would give $x = \frac{7a}{6}$ which is outside the box. So the locations are

$$x = \frac{a}{6}$$

$$x = \frac{a}{2}$$

$$x = \frac{5a}{6}$$

3.13

What range for L is possible for σ_x given:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

where L is the length of the 1-D box? Hint: Remember that σ_x is the uncertainty in the position of a particle in a box.

Solution

For a particle in a box:

$$\langle x \rangle = \frac{\mathrm{L}}{2}$$

and

$$\langle x^2 \rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

$$\sigma_x = \sqrt{\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - (\frac{\mathrm{L}}{2})^2}$$

By inspection, only values of σ_x less than L will make this statement true.

3.14

Using the trigonometric identity

$$\cos(2x) = 2\cos^2 x - 1$$

show that

$$\int_0^a 2\cos^2 \frac{n\pi x}{a} - 1 dx = 0$$

$$\int_0^a \cos \frac{2n\pi x}{a} dx = 0$$

$$\frac{a}{2n\pi} \sin(2n\pi) = 0$$

3.18

Is the wavefunction $\phi_n = \sqrt{\frac{2}{L}} \sin(\frac{n\pi x}{L})$ orthonormal over $0 \leq x \leq L$. Explain your reasoning.

Solution

For a wavefunction to be orthonormal, it has to satisfy these conditions 1.) it has to be orthogonal and 2.) it has to be normalized.

To show that it is orthogonal:

$$\int_0^L \phi_m \phi *_n \, dx = 0$$

when $m \neq$ n

To show that that the wavefunction is normalized it must follow that

$$\int_0^L \phi_n \phi *_n \, dx = 1$$

when m=n

Because our wavefunction satisfies both conditions, it is an orthonormal function.

We find that

$$\langle \psi_3 | \psi_3 \rangle = \int_{-\infty}^{\infty} \frac{2}{L} (\sin \frac{3\pi x}{L})^2 dx = 1$$

and

$$\langle \psi_4 | \psi_4 \rangle = \int_{-\infty}^{\infty} \frac{2}{L} (\sin \frac{3\pi x}{L})(\sin \frac{4\pi x}{L}) dx = 0$$

From orthogonality, we can learn that if n is not equal to m, our dot product will always be zero. But if n = m our dot product will equal 1.

3.22

What is the Heisenberg Uncertainty Principle? Do position and momentum follow the uncertainty principle; why or why not? If they do, what is the minimum uncertainty in the velocity of an electron if it is known to be within 1.5nm of a nucleus?

Solution

The Heisenberg Uncertainty Principle states that two properties that follow cannot be **simultaneously** measured to **arbitrary** precision. Position and momentum follow the principle. If one were to try and commute these two operators, one would not get zero and therefore the properties do not commute. If they do not commute then they cannot be measured to arbitrary precision.

We know that

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

And that p = mv. This gives

$$m\Delta x \Delta v \geq \frac{\hbar}{2}$$

The mass of an electron is known is $m_e \approx 9.1 \times 10^{-31}\ kg$. The problem also gives Δx to be 1.5 nm. From here, it becomes a plug and chug to solve for Δv.

$$\Delta v = 3.86 \times 10^{4}$$

3.23

Describe the degeneracies of a two-dimensional box whose two sides have different lengths.

Solution

The energies of a two-dimensional box is given by,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

We can see that even if $a \neq b$, the energy levels will not necessarily be degenerate.

3.26

How many degenerate states do the first three energy levels for a three-dimensional particle in a box have if $a = b = c$?

3.27

Metal porphyrin molecules are commonly in many proteins and it has the general structure.

220px-Porphyrin.svg.png

This molecule is planar, so we can approximate π electrons as being confined inside a square. What are energy levels and corresponding degeneracies of a particle in a square of side m? Porphyrin molecules have 18 π electrons. If the length of the molecule is 850 pm, what is the lowest energy absorption of the porphyrin molecules? (the experimental value ≈ 17,000 cm^{-1})

Solution

The first energy level is $E_{(1,1,1)}$ which has no degeneracy.

The second energy state is $E_{(2,1,1)}=E_{(1,2,1)}=E_{(1,1,2)}$, therefore it has three degenerate states.

The third energy state is $E_{(2,2,1)}=E_{(2,1,2)}=E_{(1,2,2)}$, therfeore it has three degenerate states.

3.26

For a two dimensional box of width w and height $h = \sqrt{a}w$, calculate all possible energy combinations between E_{11} and E_{33} note any degeneracy.

Solution

The energy of a two dimensional particle in the box has the form,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{w^2} + \frac{n_y^2}{h^2}\right)$$

In this specific case $h = \sqrt{a}w$ so we can simplify the problem to,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{w^2} + \frac{2n_y^2}{w^2}\right)$$

Now we can tabulate the energy level indicating degeneracy.

E_{xy}	Degeneracy	$\frac{E8mw^2}{h^2}$
E_{11}	1	3
E_{12}. E_{31}	2	5
E_{21}	1	4
E_{22}	1	6
E_{13}. E_{32}	2	7
E_{23}	1	8
E_{33}	1	9

3.32

In this problem, we will explore the quantum-mechanical problem of a free particle that is not restricted to a finite region. Remember quantized energies of a particle in a box is a direct result from the boundary conditions set by the confines of the box.

When the potential energy $V(x)$ is equal to zero and the Schrodinger equation become

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

The two solutions to this Schrodinger equation are

$$\psi_1(x) = A_1 e^{ikx}$$

$$\psi_2(x) = A_2 e^{-ikx}$$

where

$$k = \frac{(2mE)^(1/2)}{\hbar}$$

Show that $\psi_1(x)$ and $\psi_2(x)$ are solution to the Schrodinger equation where the potential energy $V(x)$ is equal to zero

Solution

In order to prove that $\psi_1(x)$ and $\psi_2(x)$ are solutions we need to mention a few values

$$p = \hbar k \rightarrow k = p/\hbar \rightarrow k = \frac{(2mE)^{1/2}}{\hbar}$$

Now we have

$$\frac{d^2 Ae^{\pm ikx}}{dx^2} + \frac{2mE}{\hbar^2}Ae^{\pm ikx} = 0$$

$$A(\pm ik)^2 e^{\pm ikx} + \frac{2mE}{\hbar^2}Ae^{\pm ikx} = 0 \rightarrow -k^2 + \frac{2mE}{\hbar^2} = 0$$

Cancel the like terms

Thus, $k = \frac{(2mE)^{1/2}}{\hbar}$, which equals the original k value

3.32

Show that E had to be a positive value, since when E is negative the wave function become unbounded for large x values

Solution

If E < 0 then k becomes imaginary, $k = ik$

$\psi = Ae^{\pm ikx} = Ae^{\pm i(ik)x}Ae^{\pm kx}$

For $\psi_1(x) = A_1 e^{-kx}$ this will blow up for x → - ∞

For $\psi_2(x) = A_2 e^{kx}$ this will blow up for x → ∞

3.32

With $\hat{P}\ \psi_1(x)$ and $\hat{P}\ \psi_2(x)$ as eigenvalue equations, show that

$$\hat{P}\psi_1(x) = -i\hbar\frac{d\psi_1}{dx} = \hbar k\psi_1$$

and

$$\hat{P}\psi_2(x) = -i\hbar\frac{d\psi_2}{dx} = -\hbar k\psi_2$$

Solution

$$\hat{P}\psi_1(x) = -i\hbar\frac{d\psi_1}{dx} = -i\hbar\frac{d}{dx}A_1e^{+ikx} = -i\hbar A_1(ik)e^{ikx} = +\hbar kA_1e^{ikx} = +\hbar k\psi_1$$

$$\hat{P}\psi_2(x) = -i\hbar\frac{d\psi_2}{dx} = -i\hbar\frac{d}{dx}A_2e^{-ikx} = -i\hbar A_2(-ik)e^{ikx} = -\hbar kA_1e^{-ikx} = -\hbar k\psi_2$$

Now we can show that

$$E = \frac{p^2}{2m} = \frac{\pm(\hbar)^2}{2m} = \frac{\hbar^2k^2}{2m}$$

3.32

Show that $\psi_1^*\psi_1(x) = A_1^*A_1 = |A_1|^2$ and that $\psi_2^*\psi_2(x) = A_2^*A_2 = |A_2|^2$

Solution

$$\begin{aligned}\psi_1^*\psi_1(x) &= (A_1e^{ikx})^*A_1e^{ikx} \\ &= A_1^*A_1e^{-ikx}e^{ikx} \\ &= A_1^*A_1e^{-ikx+ikx} = A_1^*A_1e^0 \\ &= A_1^*A_1\end{aligned}$$

$$\begin{aligned}\psi_2^*\psi_2(x) &= (A_2e^{-ikx})^*A_2e^{-ikx} \\ &= A_2^*A_2e^{ikx-ikx} \\ &= A_2^*A_2e^0 = A_2^*A_2\end{aligned}$$

ψ has equal probability to be everywhere when $\Delta x = \infty$ and $\Delta p = 0$

3.33A

Assuming that a particle is characterized by a standing de Broglie wave, come up with an equation for the allowed energies of a particle in a one-dimensional box.

Solution

The de Broglie relationship is

$$\lambda = \frac{h}{p}$$

Because the waves are standing waves, an integral number of half wave-lengths will fit in the box or:

$$a = \frac{n\lambda}{2}$$

and

$$a = \frac{nh}{2p}$$

Solving for p yields

$$p = \frac{nh}{2a}$$

and the corresponding energy is

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{1}{2m}\frac{n^2h^2}{4a^2} = \frac{n^2h^2}{8ma^2}$$

3.33B

Derive the lowest allowed velocity for a proton in a box of length 10^{-14} m (approximate size of nucleus), assuming the particle is described by a standing deBroglie wave.

Solution

The de Broglie wavelength is

$$\lambda = \frac{h}{p} = \frac{h}{m_p v}$$

For a one dimensional wave that has nodes on both ends of a box, an integer number of half wavelengths can fit, so

$$n\left(\frac{\lambda}{2}\right) = L$$

Substituting this wavelength in the de Broglie relationship, one gets

$$\nu = \frac{hn}{2m_L}$$

lowest allowed velocity will have $n = 1$

$$\begin{aligned}\nu &= \frac{(6.626 \times 10^{-34})(1)}{2 \times (1.67 \times 10^{-27})(10^{-14})} \\ &= 19.8 \times 10^{6} m/s\end{aligned}$$

3.33C

If a particle in a one-dimensional box is described by standing de Broglie waves within the box, derive an equation for the allowed energies. Then use that equation to find the transition energy from n=1 to n=2 given the length of the box is 350 pm and the mass of an electron is $9.109 \times 10^{-31} kg$.

Solution

The de Broglie formula is

$$\lambda = \frac{h}{p}$$

An integral number of half-wavelengths will fit in the box because the waves are standing waves so

$$\frac{n\lambda}{2} = a$$

$$\frac{nh}{2p} = a$$

Then solving for p

$$p = \frac{nh}{2a}$$

Therefore the energy equation is

$$E = \frac{mv^2}{2} = \frac{p^2}{2,m} = \frac{1}{2m}\frac{n^2h^2}{4a^2} = \frac{n^2h^2}{8ma^2}$$

Just plug into the equation to find the transition energy

$$\Delta E = \frac{h^2}{8m_e a^2}(2^2 - 1^2)$$

$$\Delta E = \frac{(6.626 \times 10^{-34} J \cdot s)^2(3)}{8(9.109 \times 10^{-31} kg)(350 \times 10^{-12} m)^2}$$

$$\Delta E = 1.47 \times 10^{-18} J$$

3.35A

Consider the two wavefunctions

$$\psi_n(x) = \sin \frac{n\pi x}{a}$$

with even n numbers and

$$\psi_n(x) = \cos \frac{n\pi x}{a}$$

with odd n numbers.

Prove that the wavefunctions can be symmetric and antisymmetric by using the operation x to -x, a is a constant.

Given that the Schrödinger equation has the expression:

$$\hat{H}(x)\psi_n(x) = E_n\psi_n(x)$$

Through the operation x to -x, the equation now becomes:

$$\hat{H}(-x)\psi_n(-x) = E_n\psi_n(-x)$$

Show that

$$\hat{H}(x) = \hat{H}(-x)$$

is true to prove the Schrödinger equation.

Solution

Substituting x by $-x$, for odd n numbers,

$$\hat{\psi}_n(-x) = \cos \frac{-n\pi x}{a} = \cos \frac{n\pi x}{a} = \hat{\psi}_n(x) \tag{3.E.1}$$

For even n numbers,

$$\hat{\psi}_n(-x) = sin\frac{-n\pi x}{a} = -sin\frac{n\pi x}{a} = -\hat{\psi}_n(x) \tag{3.E.2}$$

Thus, the wavefunction for odd n number is symmetric and even n numbers is antisymmetric.

And,

$$\hat{H}(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} = \hat{H}(x) \tag{3.E.3}$$

$$\hat{H}(-x) = -\frac{\hbar^2}{2m}\frac{d^2}{d(-x)^2} = \hat{H}(x) \tag{3.E.4}$$

Thus,

$$\hat{H}(x) = \hat{H}(-x)$$

and

$$\hat{H}(x)$$

is an even function of x.

3.35B

Show that the Hamiltonian for a Rigid Rotor Model is odd.

Solution

$$\hat{H}(x) = \hat{H}(-x)$$

so

$$\hat{H} = -\frac{h^2}{4\pi\mu}\nabla^2$$

$$\nabla^2 = \frac{d^2y}{dx^2}\frac{d^2y}{dy^2}\frac{d^2y}{dz^2}$$

so

$$\frac{d^2y}{dx^2}(x) = 0$$

and

$$\frac{d^2y}{dx^2}(-x) = 0$$

so

$$\hat{H}(x) = 0$$

and

$$\hat{H}(-x) = 0$$

so

$$\hat{H}(x) = \hat{H}(-x)$$

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3.S: The Schrödinger Equation and a Particle in a Box (Summary)

Particle in a box

The Hamiltonian inside the box ($0 < x < L$) is simply:

$$\op H = -\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}.$$

Substituting this Hamiltonian into the Schrödinger equation and rearranging tells us that valid wavefunctions must satisfy:

$$\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}|\psi\rangle - E|\psi\rangle = 0,$$

subject to the boundary conditions that $\psi(0) = 0$ and $\psi(L) = 0$.

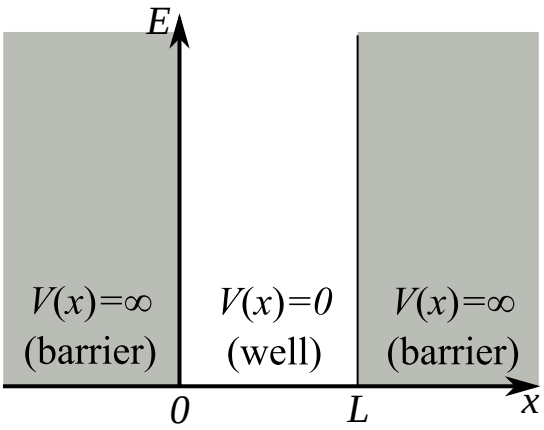


Figure 1.1: Particle in a box model system

The general solution for this wave equation is

$$\psi(x) = A\cos\frac{\sqrt{2mE}}{\hbar}x + B\sin\frac{\sqrt{2mE}}{\hbar}x.$$

The first boundary condition tells us that $A = 0$, because $\cos 0 = 1$. To satisfy the second boundary condition, we know that $\sin n\pi = 0$, and therefore $\psi(L) = 0$ when

$$\frac{\sqrt{2mE}}{\hbar}L = n\pi \quad n = 1, 2, ...$$

Note that $n = 0$ gives a physically uninteresting solution: the wavefunction everywhere is zero. Under the Born interpretation of the wavefunction, that means there is no particle in the box at all, and that's not what we're interested in. Now we can solve for energy

$$E_n = \frac{\pi^2\hbar^2 n^2}{2mL^2} = \frac{h^2 n^2}{8mL^2} \quad n = 1, 2, ...$$

and substitute this into our wave equation to get (after normalizing: $\langle\psi\rangle\psi = 1$)

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \quad n = 1, 2, ..., \quad 0 \le x \le L$$

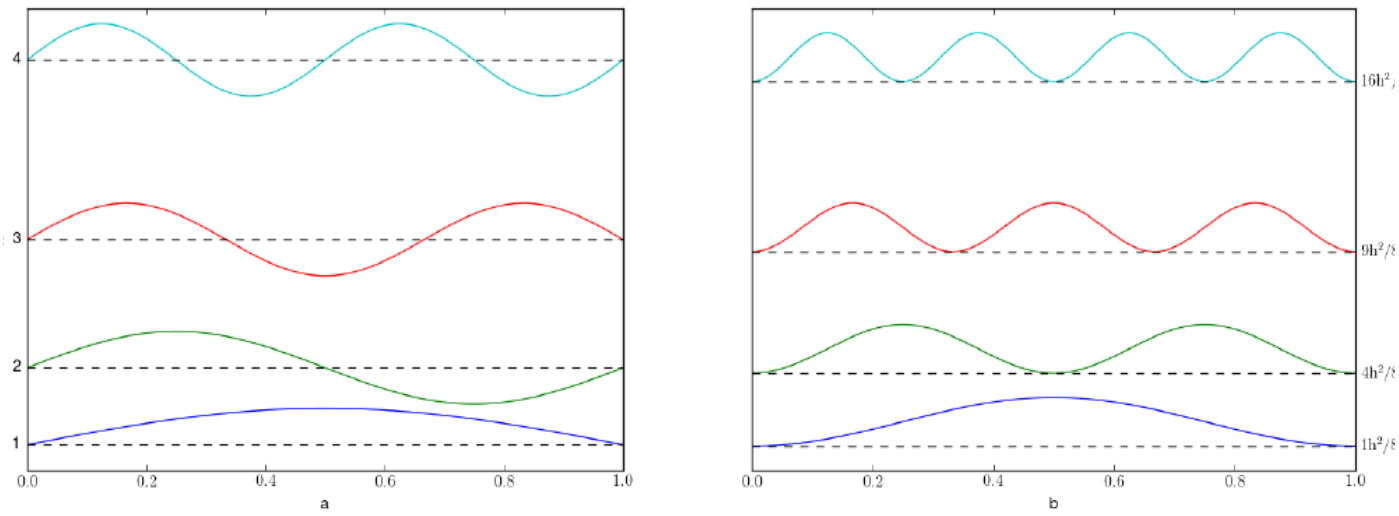


Figure 1.2: Wavefunctions (a) and probability densities (b) for a particle in a one-dimensional box. Note that the number of nodes is n - 1.

The one-dimensional particle in a box is sometimes used to estimate the energy of a π electron in a conjugated polyene.

Particle in a 3D box

It is straightforward to show that a particle in a 3D box is simply an extension of the 1D problem. The wavefunction $\psi(x,y,z)$ can be written as a product of independent one-dimensional functions $\phi(x)\phi(y)\phi(z)$, and the energy can consequently be shown to be $E = E_x + E_y + E_z$. This is actually an extremely important point– anytime a wavefunction can be expressed as a product of 1D functions, the individual components can be treated separately, and the total energy computed from a sum of the individual energies.

The particle in a 3D box, therefore, has (normalized) wavefunctions:

$$\psi(x,y,z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\frac{n_x \pi x}{L_x} \sin\frac{n_y \pi y}{L_y} \sin\frac{n_z \pi z}{L_z} \quad n_x, n_y, n_z = 1, 2, \ldots$$

and energies

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \quad n_x, n_y, n_z = 1, 2, \ldots$$

In the special case of a particle in a cube, $L_x = L_y = L_z$, and we find that many of the states have the same energy (i.e., they are degenerate). The energies are

$$E_{n_x,n_y,n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

so they only depend on the sum of the squares of the x, y, and z quantum numbers. If we denote the wavefunctions in Dirac notation as $|n_x, n_y, n_z\rangle$, the $|1,1,2\rangle$, $|1,2,1\rangle$, and $|2,1,1\rangle$ states all have energy $(6h^2)/(8mL^2)$. These degeneracies arise naturally as a result of the symmetry of the system, and we will explore this concept in more detail when we talk about group theory.

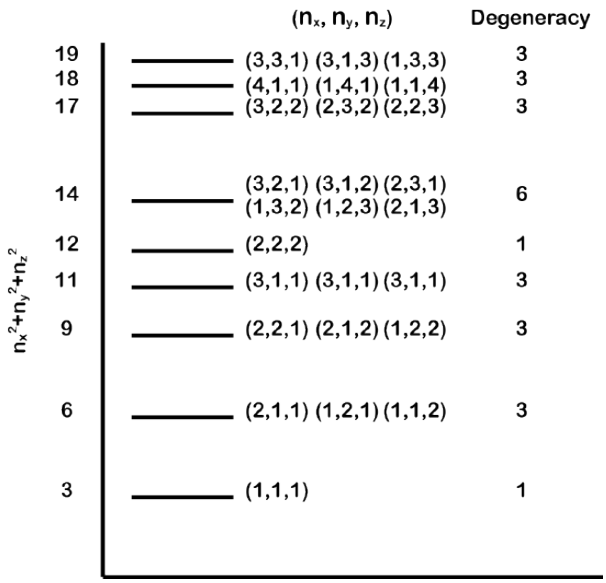


Figure 1.3: Energy levels and degeneracies of a particle in a cube.

The particle in a 3D box can be used to model the confinement energy of electrons as a function of nanoparticle size.

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4: POSTULATES AND PRINCIPLES OF QUANTUM MECHANICS

4.1: The Wavefunction Specifies the State of a System

4.2: Quantum Operators Represent Classical Variables

4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

4.4: The Time-Dependent Schrödinger Equation

4.5: Eigenfunctions of Operators are Orthogonal

4.6: Commuting Operators Allow Infinite Precision

4.E: Postulates and Principles of Quantum Mechanics (Exercises)

4.S: Postulates and Principles of Quantum Mechanics (Summary)

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4.1: The Wavefunction Specifies the State of a System

Learning Objectives

- Introduce the first postulate of quantum mechanics
- Recognize invalid wavefunction categories

In classical mechanics, the configuration or state of a system is given by a point (x, p) in the space of coordinates and momenta. This specifies everything else in the system in a fully deterministic way, in that any observable Q that can be expressed as $Q(x, p)$ can be found, and any that cannot is irrelevant. Yet, as we have seen with the diffraction of electrons, it is **impossible** to know both the position and momentum of the electron exactly at every point along the trajectory. This is mathematically expressed as the famous position-momentum uncertainty principle. Hence, specifying a state by (x, p) in classical mechanics clearly will not work in quantum mechanics. So what specifies the state of a quantum system? This is where the **first Postulate of quantum mechanics** comes in.

Postulate I

The state of the system is **completely** specified by ψ. All possible information about the system can be found in the wavefunction ψ.

The properties of a quantum mechanical system are determined by a wavefunction $\psi(r, t)$ that depends upon the spatial coordinates of the system and time, r and t. For a single particle system, r is the set of coordinates of that particle $r = (x_1, y_1, z_1)$. For more than one particle, r is used to represent the complete set of coordinates $r = (x_1, y_1, z_1, x_2, y_2, z_2, ... x_n, y_n, z_n)$. Since the state of a system is defined by its properties, ψ specifies or identifies the state and sometimes is called the state function rather than the wavefunction.

What does ψ mean? This is best answered in terms of the probability density $P(x)$ that determines the probability (density) that an object in the state $\psi(x)$ will be found at position x (the Born interpretation).

$$P(x) = \psi^*(x)\psi(x) \tag{4.1.1}$$

$$= |\psi(x)|^2 \tag{4.1.2}$$

Hence, for valid (e.g., well-behaved) wavefunctions, the normalized probability in Equation 4.1.2 holds true, such that the integral over all space is equal to 1.

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\, dx = 1 \tag{4.1.3}$$

Equation 4.1.3 means that the chance to find a particle is 100% somewhere within all space (e.g. somewhere between $-\infty$ and $+\infty$). A wavefunction is said to be **square-integrable** if Equation 4.1.3 can be satisfied (so that the Born Interpretation to be applicable).

Definition: Square-Integrable Functions

A complex-valued function, $f(x)$, is a *square-integrable* function if the integral of the square of the absolute value is finite.

$$\int_{-\infty}^{\infty} f^*(x)f(x)\, dx < \infty$$

For this to be true, the integrals of the positive and negative portions of the real and imaginary parts of $f(x)$ must both be finite.

Let us examine this set of examples in further detail in Figure 4.1.1 . The first wavefunction ψ_1 is sharply peaked at a particular value of x, and the probability density, being its square, is likewise peaked there as well. This is the wavefunction for a particle well localized at a position given by the center of the peak, as the probability density is high there, and the width of the peak is small, so the uncertainty in the position is very small.

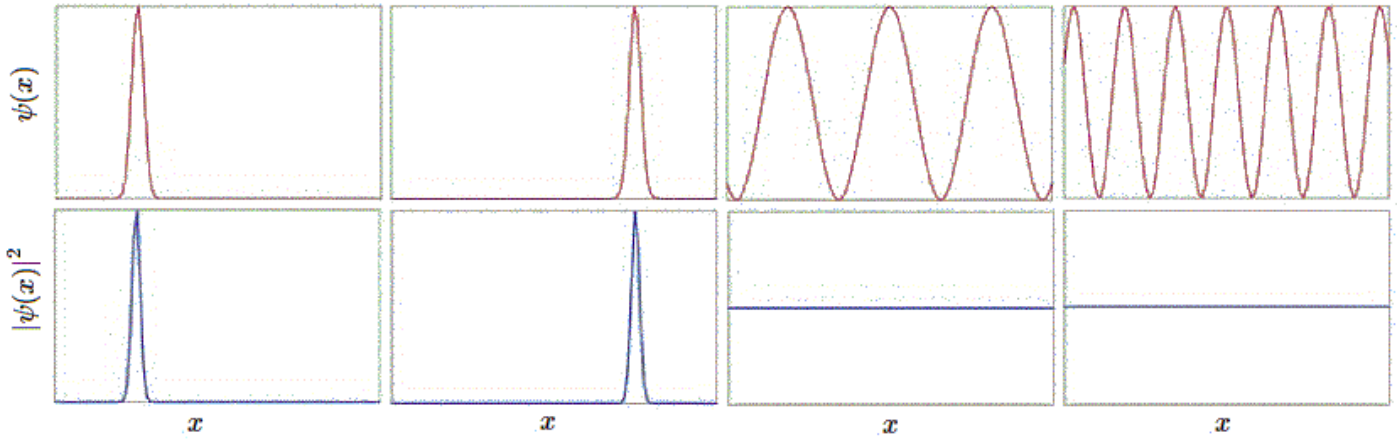


Figure 4.1.1 : Examples of good wavefunctions, $\psi(x)$, (red, top) and corresponding probability densities, $P(x)$, (blue, bottom).

The second wavefunction ψ_2 has the same peak profile, but shifted to a different position center. All of the properties of the first wavefunction hold here too, so this simply describes a particle that is well-localized at that different position. The third and fourth wavefunctions ψ_3 and ψ_4 respectively look like sinusoids of different spatial periods. The wavefunctions are actually complex of the form

$$\psi(x) = Ne^{ikx}$$

so only the real part is being plotted in Figure 4.1.1 . Note that even though the periods, k, of the oscillating wavefunctions are different,

$$\begin{aligned} P(x) &= \psi^*(x)\psi(x) \\ &= |e^{ikx}|^2 \\ &= N^2 \left(e^{-ikx}\right)\left(e^{ikx}\right) \\ &= N^2 \end{aligned}$$

for all k, so the corresponding probability densities, $P(x)$, are the same except for the normalization constant (Equation 4.1.2). We saw before that it does not make a whole lot of sense to think of a sinusoidal wave as being localized in some place. Indeed, the positions for these two wavefunctions are ill-defined, so they are not well-localized, and the uncertainty in the position is large in each case. This is Heisenberg Uncertainty Principle in action.

Ill-behaved (invalid) Wavefunctions

The Born interpretation in Equation 4.1.2 means that many wavefunctions which would be acceptable mathematical solutions of the Schrödinger equation are **not acceptable** because of their implications for the physical properties of the system. To satisfy this interpretation, wavefunctions must be:

- single valued,
- continuous, and
- finite.

These aspects mean that the valid wavefunction must be one-to-one, it cannot have an undefined slope, and cannot go to $-\infty$ or

$+\infty$. For example, the wavefunction must not be infinite over any finite region. If it is, then the integral in Equation 4.1.3 is equal to infinity. This implies that the particle described by such a wavefunction has a zero probability of being anywhere where the wavefunction is not infinite, but is certain to be found at all points where the wavefunction is infinite.

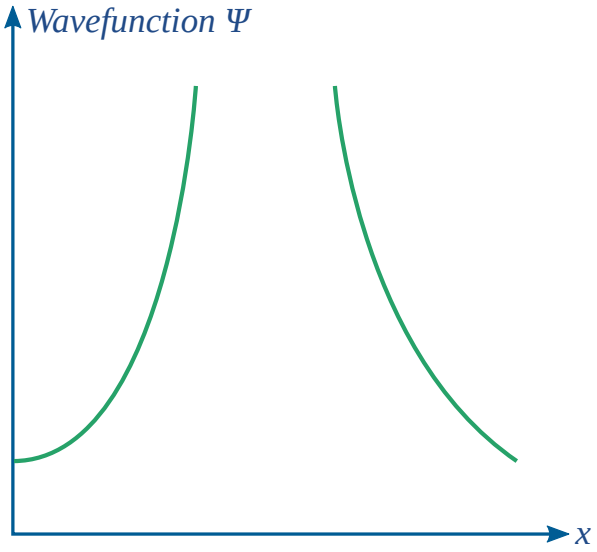


Figure 4.1.2 : This function is an invalid wavefunction since the amplitude is going to infinity over a region (the middle in this case). (CC BY-NC; Ümit Kaya via LibreTexts)

The Born interpretation also renders unacceptable solutions of the Schrödinger equation for which $|\psi(x)|^2$ has more than one value at any point. This would suggest that there were multiple different probabilities of finding the particle at that point, which is clearly absurd. The requirement that the square modulus of the wavefunction must be single-valued usually implies that the wavefunction itself must be single valued. The function in Figure 4.1.3 violates this requirement. The grey lines indicate the region where the wavefunction is multivalued.

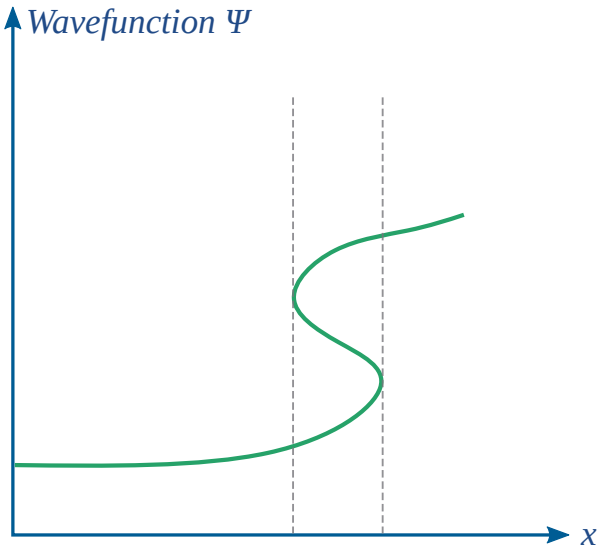


Figure 4.1.3 : This function is an invalid wavefunction since it is not a proper function (i. e., not one-to-one). (CC BY-NC; Ümit Kaya via LibreTexts)

Further restrictions arise because the wavefunction must satisfy the Schrödinger equation, which is a second-order differential equation. This implies that the second derivative of the function must exist, which implies that the first derivative of the wavefunction to exist (otherwise the second derivative is also undefined and the wavefunction cannot be a solution of the Schrödinger equation). The functions in Figure 4.1.4 are also not acceptable for these reasons.

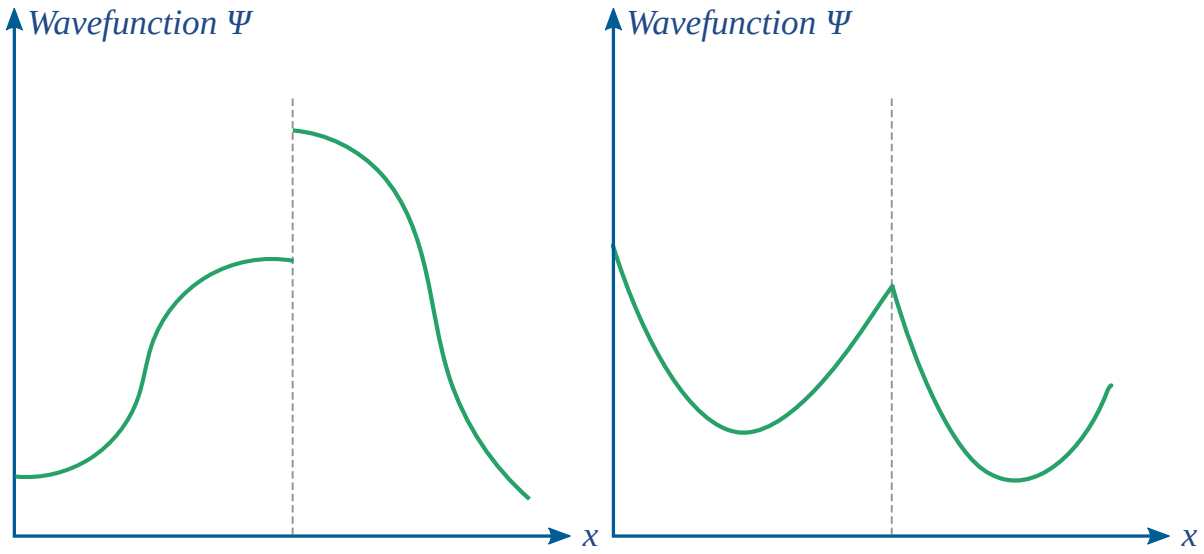


Figure 4.1.4 : These functions are invalid wavefunctions. (left) The first derivative of a function gives its gradient at a given point, and it thus exists as long as the function is continuous - only if there is a break in the function is there a point at which its first derivative does not exist. (right) The second derivative of this wavefunction is discontinuous at the point indicated, where the gradient of the line changes by more than 180°. In practice, this requirement may be somewhat flexible, particularly if the potential energy of the system shows rapid changes with distance. (CC BY-NC; Ümit Kaya via LibreTexts)

Exercise 4.1.1

Determine if each of the following functions is acceptable as a wavefunction over the indicated regions:

a. $\cos x$ over $(0, \infty)$
b. e^{x} over $(-\infty, \infty)$
c. e^{-x} over $[0, \infty)$
d. $\tan \theta$ over $[0, 2\theta]$

Solution a available at the end of this section.

Solution b available at the end of this section.

Solution c available at the end of this section.

Solution d available at the end of this section.

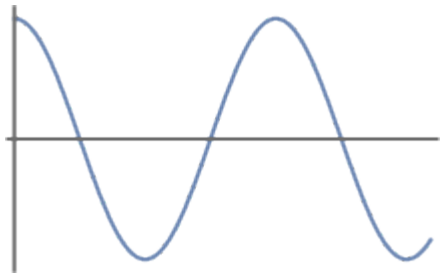
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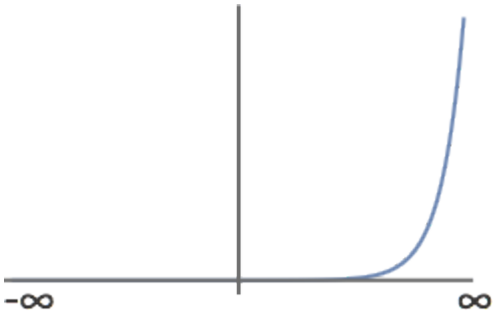
Answers

This is not an acceptable wavefunction. It is **single-valued** across the entire range. There is a single value for each value of x. It is **continuous** over the defined limits of integration, as we can see from a plot given below. However, it is not square-integrable.

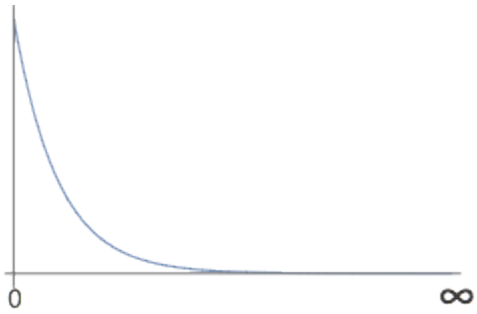
$$\int_{0}^{\infty} |\cos(x)|^{2} dx \not< \infty$$



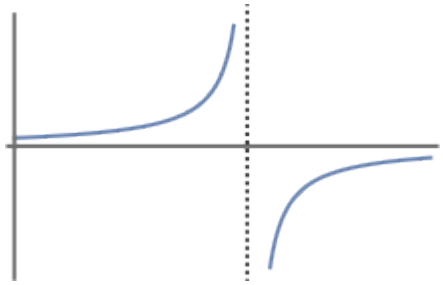
This is not an acceptable wavefunction. Over the limits of integration from $-\infty$ to ∞, this function is not square-integrable. Note in the plot below, how the function is indefinite approaching the limits of ∞.



This is an acceptable wavefunction over the given limits. It is **finite** over the given limits. It is **continuous** within given limits. It is **single-valued.** It is square-integrable with $\int_0^\infty |\Psi(x)|^2 dx = \frac{1}{2}$.



This is not an acceptable wavefunction. It is discontinuous over the limits of integration.



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4.2: Quantum Operators Represent Classical Variables

Learning Objectives

- Understand how the correspondence principle argues that a unique quantum operator exist for every classical observable.
- Recognize several of the commonly used quantum operators

An observable is a dynamic variable of a system that can be experimentally measured (e.g., position, momentum and kinetic energy). In systems governed by classical mechanics, it is a real-valued function (never complex), however, in quantum physics, every observable in quantum mechanics is represented by an independent operator that is used to obtain physical information about the observable from the wavefunction. It is a general principle of quantum mechanics that there is an operator for every physical observable. For an observable that is represented in classical physics by a function $Q(x,p)$, the corresponding operator is $Q(\hat{x},\hat{p})$.

Postulate II: The Correspondence Principle

For every observable property of a system there is a corresponding quantum mechanical operator. This is often referred to as the **Correspondence Principle**.

Classical dynamical variables, such as x and p, are represented in quantum mechanics by *linear operators* which act on the wavefunction. The operator for position of a particle in three dimensions is just the set of coordinates x, y, and z, which is written as a vector, r:

$$\vec{r} = (x,y,z) \tag{4.2.1}$$

$$= x\vec{i} + y\vec{j} + z\vec{k} \tag{4.2.2}$$

The operator for a component of linear momentum is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{4.2.3}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = \left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \tag{4.2.4}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \tag{4.2.5}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2 \tag{4.2.6}$$

The total energy operator is called the Hamiltonian operator, $\hat{H}$ and consists of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{4.2.7}$$

The Hamiltonian Operator

The Hamiltonian operator is named after the Irish mathematician William Hamilton and comes from the his formulation of Classical Mechanics that is based on the total energy:

$$\hat{H} = \hat{T} + \hat{V}$$

rather than Newton's second law,

$$\vec{F} = m\vec{a}$$

In many cases only the kinetic energy of the particles and the electrostatic or Coulomb potential energy due to their charges are considered, but in general all terms that contribute to the energy appear in the Hamiltonian. These additional terms account for such things as external electric and magnetic fields and magnetic interactions due to magnetic moments of the particles and their motion.

Table 4.2.1 : Some common Operators in Quantum Mechanics

Name	Observable Symbol	Operator Symbol	Operation
Position (in 1D)	x	$\hat{X}$	Multiply by x
Position (in 3D)	$\vec{r}$	$\hat{R}$	Multiply by $\vec{r}$
Momentum (in 1D)	p_x	$\hat{P}_x$	$-\imath\hbar\frac{d}{dx}$
Momentum (in 3D)	$\vec{p}$	$\hat{P}$	$-\imath\hbar\left[\hat{i}\ \frac{d}{dx} + \hat{j}\frac{d}{dy} + \hat{k}\frac{d}{dz}\right]$
Kinetic Energy (in 1D)	T_x	$\hat{T}_x$	$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$
Kinetic Energy (in 3D)	T	$\hat{T}$	$\frac{-\hbar^2}{2m}\left[\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right]$ Which can be simplified to $\frac{-\hbar^2}{2m}\bigtriangledown^2$
Potential Energy (in 1D)	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
Potential Energy (in 3D)	$V(x,y,z)$	$\hat{V}(x,y,z)$	Multiply by $V(x,y,z)$
Total Energy	E	$\hat{E}$	$\frac{-\hbar^2}{2m}\nabla^2 + V(x,y,z)$
Angular Momentum (x axis component)	L_x	$\hat{L_x}$	$-\imath\hbar\left[y\frac{d}{dz} - z\frac{d}{dy}\right]$
Angular Momentum (y axis component)	L_y	$\hat{L_y}$	$-\imath\hbar\left[z\frac{d}{dx} - x\frac{d}{dz}\right]$
Angular Momentum (z axis component)	L_z	$\hat{L_z}$	$-\imath\hbar\left[x\frac{d}{dy} - y\frac{d}{dx}\right]$

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4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

Learning Objectives

- To be introduced to the role of eigenvalue equations in obtaining observables from a system
- Understand how expectation values are calculated if the wavefunctions is not an eigenstate of the operator for the observable.

Recall, that we can identify the total energy operator, which is called the Hamiltonian operator, $\hat{H}$, as consisting of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{4.3.1}$$

Using this notation, we write the Schrödinger Equation as

$$\hat{H}|\psi(x,y,z)\rangle = E|\psi(x,y,z)\rangle \tag{4.3.2}$$

Equation 4.3.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a number, (a quantity of Joules), times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an **eigenfunction**, and the resulting numerical value is called the **eigenvalue**. Eigen here is the German word meaning self or own.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is the eigenvalue, and the system is said to be in an eigenstate. Equation 4.3.2 states this principle mathematically for the case of energy as the observable.

Postulate III: Obtaining Observables Requires Solving Eigenvalue Problems

If a system is described by the eigenfunction Ψ of an operator $\hat{A}$ then the value measured for the observable property corresponding to $\hat{A}$ will always be the eigenvalue a, which can be calculated from the eigenvalue equation.

$$\hat{A}|\Psi\rangle = a|\Psi\rangle \tag{4.3.3}$$

Consider a general real-space operator $A(x)$. When this operator acts on a general wavefunction $\psi(x)$ the result is usually a wavefunction with a completely different shape. However, there are certain special wavefunctions which are such that when A acts on them the result is just a multiple of the original wavefunction. These special wavefunctions are called *eigenstates*, and the multiples are called *eigenvalues*. Thus, if

$$A|\psi_a(x)\rangle = a|\psi_a(x)\rangle \tag{4.3.4}$$

where a is a complex number, then ψ_a is called an **eigenstate** of A corresponding to the eigenvalue a.

Suppose that A is an operator corresponding to some physical dynamical variable. Consider a particle whose wavefunction is ψ_a. The expectation of value A in this state is simply

$$\begin{aligned}\langle A\rangle &= \int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \\ &= a\int_{-\infty}^{\infty} \psi_a^* \psi_a dx \\ &= a.\end{aligned}$$

where use has been made of Equation 4.3.4 and the normalization condition. Moreover,

$$\begin{aligned}\langle A^2\rangle &= \int_{-\infty}^{\infty} \psi_a^* A^2 \psi_a dx \\ &= a\int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \\ &= a^2\int_{-\infty}^{\infty} \psi_a^* \psi_a dx \\ &= a^2.\end{aligned}$$

So the variance of A is

$$\begin{aligned}\sigma_A^2 &= \langle A^2\rangle - \langle A\rangle^2 = a^2 - a^2 \\ &= 0.\end{aligned}$$

The fact that the variance is *zero* implies that every measurement of A is bound to yield the same result: namely, a. Thus, the eigenstate ψ_a is a state which is associated with a *unique* value of the dynamical variable corresponding to A. This unique value is simply the associated eigenvalue determined by Equation 4.3.4.

Expectation Values

We have seen that $|\psi(x,t)|^2$ is the probability density of a measurement of a particle's displacement yielding the value x at time t. Suppose that we made a large number of independent measurements of the displacement on an equally large number of identical quantum systems. In general, measurements made on different systems will yield different results. However, from the definition of probability, the mean of all these results is simply

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx \tag{4.3.5}$$

Here, $\langle x\rangle$ is called the *expectation value* of x. Similarly the expectation value of any function of x is

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi|^2 dx. \tag{4.3.6}$$

Postulate IV

The average value of an observable measurement of a state in (*normalized*) wavefunction ψ with operator $\hat{A}$ is given by the expectation value $\langle a\rangle$:

$$\langle a\rangle = \langle\psi|a|\psi\rangle \tag{4.3.7}$$

$$= \int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx \tag{4.3.8}$$

If an unnormalized wavefunction where used, then Equation 4.3.8 changes to

$$\langle a \rangle = \frac{\langle \psi | a | \psi \rangle}{\langle \psi | \psi \rangle} \tag{4.3.9}$$

$$= \frac{\int_{-\infty}^{\infty} \psi^* \hat{A} \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx} \tag{4.3.10}$$

The denominator is just the normalization requirement discussed earlier. In general, the results of the various different measurements of x will be scattered around the expectation value $\langle x \rangle$. The degree of scatter is parameterized by the quantity

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 |\psi|^2 dx \tag{4.3.11}$$

$$\equiv \langle x^2 \rangle - \langle x \rangle^2, \tag{4.3.12}$$

which is known as the *variance* of x. The square-root of this quantity, σ_x, is called the *standard deviation* of x. We generally expect the results of measurements of x to lie within a few standard deviations of the expectation value (Figure 4.3.1).

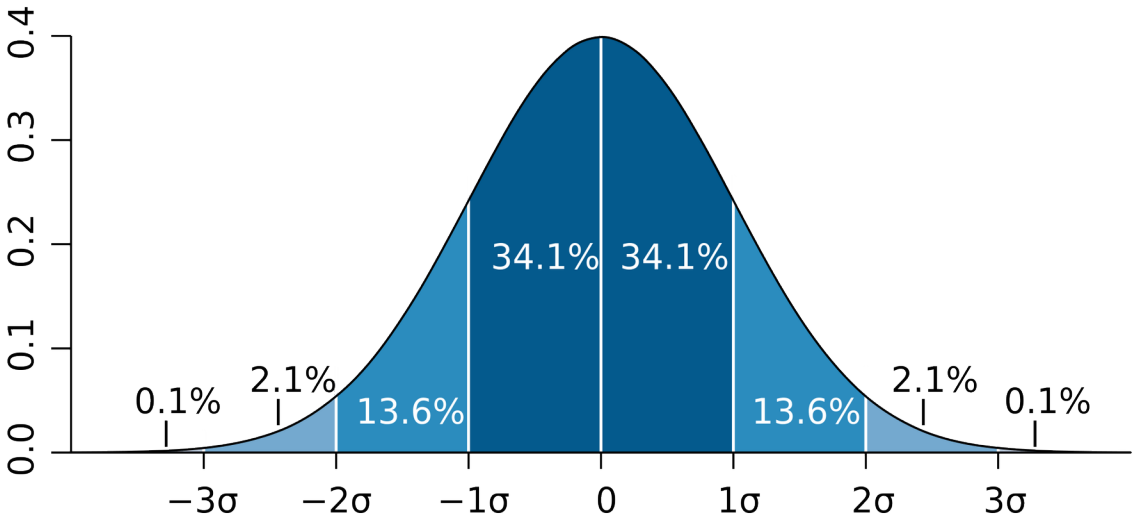


Figure 4.3.1 : A plot of a normal distribution (or bell-shaped curve) where each band has a width of 1 standard deviation. image usd with permission from Wikipedia.

Example 4.3.1

For a particle in a box in its ground state, calculate the expectation value of the

a. *position*,
b. the *linear momentum*,
c. the *kinetic energy*, and
d. the total energy

Solution

First the wavefunction needs to be defined. From the particle in the box solutions, the ground state wavefunction ($n = 1$) is

$$\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

We can confirm that the wavefunction is normalized.

$$\int \psi^* \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \, dx = 1$$

Hence, the Equation 4.3.8 is the relevant equation to use.

Solution a

The expectation value of the **position** is:

$$\begin{aligned} \langle x \rangle &= \int \psi^* x \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} x \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \, dx \\ &= \frac{2}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) \, dx \\ &= \frac{L}{2} \end{aligned}$$

Solution b

The expectation value of the **momentum** is:

$$\begin{aligned} \langle p \rangle &= \int \psi^* \hat{p} \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \, dx \\ &= \frac{2i\hbar\pi}{L^2} \int_0^L \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) \, dx \\ &= 0 \end{aligned}$$

Solution c

The expectation value of the **kinetic energy** is:

$$\begin{aligned} \langle T \rangle &= \int \psi^* \hat{K} \psi \, d\tau = \frac{2}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\right) \sin\left(\frac{\pi x}{L}\right) \, dx \\ &= \frac{\hbar^2 \pi^2}{2mL^2} \frac{2}{L} \int_0^L \sin^2\left(\frac{\pi x}{L}\right) \, dx \\ &= \frac{\hbar^2 \pi^2}{2mL^2} \end{aligned}$$

A position "on average" is in the middle of the box ($L/2$). It has equal probability of traveling towards the left or right, so the average momentum and velocity must be zero.

Solution d

The average kinetic energy must be equal to the total energy of the ground state of the particle in the box, as there is no other energy component (i.e, $V = 0$).

Expanding the Wavefunction

It is also possible to demonstrate that the eigenstates of an operator attributed to a observable form a **complete set** (*i.e.*, that any general wavefunction can be written as a linear combination of these eigenstates). However, the proof is quite difficult, and we shall not attempt it here.

In summary, given an operator $\hat{A}$, any general wavefunction, $\psi(x)$, can be written

$$\psi = \sum_i c_i \phi_i$$

where the c_i are complex weights, and the $\phi(x)$ are the properly normalized (and mutually orthogonal) eigenstates of $\hat{A}$: i.e.,

$$A\phi_i = a_i\phi_i$$

where a_i is the eigenvalue corresponding to the eigenstate ϕ_i, and

$$\int_{-\infty}^{\infty} \phi_i^* \phi_j dx = \delta_{ij}. \tag{4.3.13}$$

Here, δ_{ij} is called the **Kronecker delta-function**, and takes the value unity when its two indices are equal, and zero otherwise. It follows from Equations 4.3.10 and 4.3.13 that

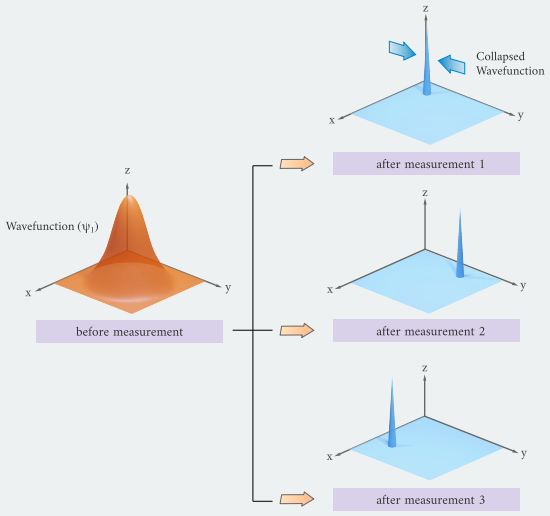
$$c_i = \int_{-\infty}^{\infty} \phi_i^* \psi dx. \tag{4.3.14}$$

Thus, the expansion coefficients in Equation 4.3.14 are easily determined, given the wavefunction ψ and the eigenstates ϕ_i. Moreover, if ψ is a properly normalized wavefunction then Equations 4.3.10 and 4.3.13 yield

$$\sum_i |c_i|^2 = 1.$$

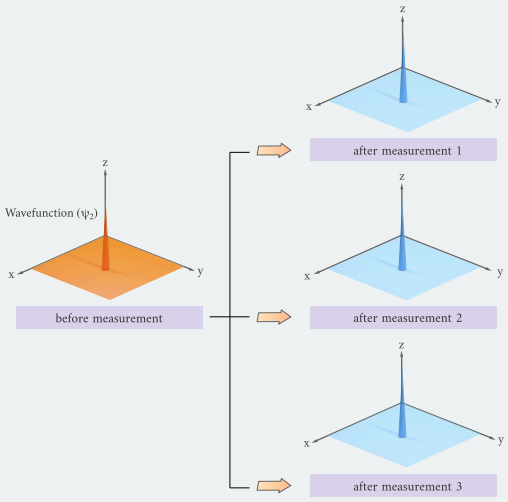
Collapsing the Wavefunction

Wavefunction collapse is said to occur when a wavefunction—initially in a superposition of several eigenstates—appears to reduce to a single eigenstate (by "observation"). A particle (or a system in general) can be found in a given state $\psi(x,t)$. Suppose now a measurement is performed on the wavefuction to characterize a specific property of the system.



The measurement of position (with the position operator) effectively collapses this wavefunction that is a superposition of position eigenstates, which are delta-functions and are continuous - i.e. not quantized. Using a different measurement operation may in quantized values (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Mathematically, an operator $\hat{A}$ is associated with this measurement process, which you suppose has a *complete orthonormal set* of eigenvalues: $\{\phi_i\}$ that is typically an infinite set of functionals that depend on quantum number n. The wavefunction Ψ can be expand and a set of basis functions can be selected to specifies the wavefunction is the coefficients $\{c_n\}$ of the expansion. Therefore, if the system is perturbed, then your wavefunction will have another set of coefficients $\{c_n'\}$.



The measurement of position (with the position operator) does not collapse this wavefunction since it is in a position eigenstate in contrast to the wavefunction above. Using a different measurement operation (e.g., kinetic energy) may "collapse" the wavefunction into a different eigenstate (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

If you wavefunction is in the eigenstate of the operator, then each measurement via that operator will give the same result.

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4.4: The Time-Dependent Schrödinger Equation

Learning Objectives

- Recognize the differences between the time-dependent and the time-independent Schrödinger equations
- To distinguish between stationary and non-stationary wavefunctions

There are two "flavors" of Schrödinger equations: the time-dependent and the time-independent versions. While the time-dependent Schrödinger equation predicts that wavefunctions can form standing waves (called stationary states), that if classified and understood, then it becomes easier to solve the time-dependent Schrödinger equation for any state. Stationary states can also be described by the time-independent Schrödinger equation (used only when the Hamiltonian is not explicitly time dependent). However, it should be noted that the solutions to the time-independent Schrödinger equation still have time dependencies.

Time-Dependent Wavefunctions

Recall that the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \tag{4.4.1}$$

yields the allowed energies and corresponding wavefunctions. However, it does not tell us how the system evolves in time. It would seem that something is missing, since, after all, classical mechanics tells us how the positions and velocities of a classical system evolve in time. The time dependence is given by solving Newton's second law

$$m\frac{d^2x}{dt^2} = F(x) \tag{4.4.2}$$

But where is t in quantum mechanics? First of all, what is it that must evolve in time? The answer is that the wavefunction (and associated probability density) must evolve. Suppose, therefore, that we prepare a system at $t = 0$ according to a particular probability density $p(x, 0)$ related to an amplitude $\Psi(x, 0)$ by

$$p(x, 0) = |\Psi(x, 0)|^2 \tag{4.4.3}$$

How will this initial amplitude $\Psi(x, 0)$ look at time t later? Note, by the way, that $\Psi(x, 0)$ does *not* necessarily need to be one of the eigenstates $\psi_n(x)$. To address this, we refer to the time-dependent Schrödinger equation that tells us how $\Psi(x, t)$ will evolve starting from the initial condition $\Psi(x, 0)$:

$$\hat{H}\Psi(x, t) = i\hbar\frac{\partial}{\partial t}\Psi(x, t) \tag{4.4.4}$$

It is important to know how it works physically and when it is sufficient to work with the time-independent version of the Schrödinger equation (Equation 4.4.1).

Postulate V

The time dependence of wavefunctions is governed by the Time-Dependent Schrödinger Equation (Equation 4.4.4).

Stationary States

Suppose that we are lucky enough to choose

$$\Psi(x, 0) = \psi_n(x)$$

with corresponding probability density

$$p(x,0) = |\psi_n(x)|^2 \tag{4.4.5}$$

We will show that

$$\Psi(x,t) = \psi_n(x)e^{-iE_nt/\hbar} \tag{4.4.6}$$

From the time-dependent Schrödinger equation

$$\frac{d\Psi}{dt} = \psi_n(x)\left(\frac{-iE_n}{\hbar}\right)e^{-iE_nt/\hbar}$$
$$i\hbar\frac{d\Psi}{dt} = E_n\psi_n(x)e^{-iE_nt/\hbar}$$

Similarly

$$\begin{aligned}\hat{H}\Psi(x,t) &= e^{-iE_nt/\hbar}\hat{H}\psi_n(x)\\ &= e^{-iE_nt/\hbar}E_n\psi_n(x)\end{aligned}$$

Hence $\psi_n(x)exp(-iE_nt/\hbar)$ satisfies the Time-Dependent Schrödinger Equation (Equation 4.4.4).

Consider the probability density for this wavefunction: $p(x,t) = |\Psi(x,t)|^2$

$$\begin{aligned}p(x,t) &= \left[\psi_n(x)e^{iE_nt/\hbar}\right]\left[\psi_n(x)e^{-iE_nt/\hbar}\right]\\ &= \psi_n^2(x)e^{iE_nt/\hbar}e^{-iE_nt/\hbar}\\ &= |\psi_n(x)|^2 = p(x,0)\end{aligned}$$

the probability does not change in time and for this reason, $\psi_n(x)$ is called a *stationary state*. In such a state, the energy remains **fixed** at the well-defined value E_n.

Nonstationary States

Suppose, however, that we had chosen $\Psi(x,0)$ to be some arbitrary linear combination of the two lowest energy states:

$$\Psi(x,0) = a\psi_1(x) + b\psi_2(x) \tag{4.4.7}$$

for example

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)] \tag{4.4.8}$$

as in the previous example. Then, the probability density at time t

$$p(x,t) = |\Psi(x,t)|^2 \neq p(x,0) \tag{4.4.9}$$

For such a mixture to be possible, there must be sufficient energy in the system that there is some probability of measuring the particle to be in its excited state.

Finally, suppose we start with a state

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)]$$

and we let this state evolve in time. At any point in time, the state $\Psi(x,t)$ will be some mixture of $\psi_1(x)$ and $\psi_2(x)$, and this mixture changes with time. Now, at some specific instance in time t, we measure the energy and obtain a value E_1. What is the state of the system *just after* the measurement is made? Once we make the measurement, then we know with 100% certainty that the energy is E_1. From the above discussion, there is only one possibility for the state of the system, and that has to be the wavefunction $\psi_1(x)$, since in this state we know with 100% certainty that the energy is E_1. Hence, just after the measurement, the state *must*

be $\psi_1(x)$, which means that because of the measurement, any further dependence on $\psi_2(x)$ drops out, and for all time thereafter, there is *no* dependence on $\psi_2(x)$. Consequently, any subsequent measurement of the energy would yield the value E_1 with 100% certainty. This discontinuous change in the quantum state of the system as a result of the measurement is known as the **collapse of the wavefunction**. The idea that the evolution of a system can change as a result of a measurement is one of the topics that is currently debated among quantum theorists.

The Quantum Observer Effect

The fact that measuring a quantum system changes its time evolution means that the experimenter is now coupled to the quantum system. This **observer effect** means that the act of observing will influence the phenomenon being observed. In classical mechanics, this coupling does not exist. A classical system will evolve according to Newton's laws of motion independent of whether or not we observe it. This is not true for quantum systems. The very act of observing the system changes how it evolves in time.

Put another way, by simply observing a system, we change it!

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4.5: Eigenfunctions of Operators are Orthogonal

Learning Objectives

- Understand the properties of a Hermitian operator and their associated eigenstates
- Recognize that all experimental obervables are obtained by Hermitian operators

Consideration of the quantum mechanical description of the particle-in-a-box exposed two important properties of quantum mechanical systems. We saw that the eigenfunctions of the Hamiltonian operator are orthogonal, and we also saw that the position and momentum of the particle could not be determined exactly. We now examine the generality of these insights by stating and proving some fundamental theorems. These theorems use the Hermitian property of quantum mechanical operators that correspond to observables, which is discuss first.

Hermitian Operators

Since the eigenvalues of a quantum mechanical operator correspond to measurable quantities, the eigenvalues must be real, and consequently a quantum mechanical operator must be Hermitian. To prove this, we start with the premises that ψ and φ are functions, $\int d\tau$ represents integration over all coordinates, and the operator $\hat{A}$ is **Hermitian** by definition if

$$\int \psi^* \hat{A} \psi \, d\tau = \int (\hat{A}^* \psi^*) \psi \, d\tau \tag{4.5.1}$$

This equation means that the complex conjugate of $\hat{A}$ can operate on ψ^* to produce the same result after integration as $\hat{A}$ operating on φ, followed by integration. To prove that a quantum mechanical operator $\hat{A}$ is Hermitian, consider the eigenvalue equation and its complex conjugate.

$$\hat{A}\psi = a\psi \tag{4.5.2}$$

$$\hat{A}^* \psi^* = a^* \psi^* = a\psi^* \tag{4.5.3}$$

Note that $a^* = a$ because the eigenvalue is real. Multiply Equation 4.5.2 and 4.5.3 from the left by ψ^* and ψ, respectively, and integrate over the full range of all the coordinates. Note that ψ is normalized. The results are

$$\int \psi^* \hat{A} \psi \, d\tau = a \int \psi^* \psi \, d\tau = a \tag{4.5.4}$$

$$\int \psi \hat{A}^* \psi^* \, d\tau = a \int \psi \psi^* \, d\tau = a \tag{4.5.5}$$

Since both integrals equal a, they must be equivalent.

$$\int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau \tag{4.5.6}$$

The operator acting on the function,

$$\hat{A}^* \int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau_*$$

produces a new function. Since functions commute, Equation 4.5.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{4.5.7}$$

This equality means that $\hat{A}$ is Hermitian.

Orthogonality Theorem

Eigenfunctions of a Hermitian operator are orthogonal if they have different eigenvalues.

Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.

Proof

ψ and φ are two eigenfunctions of the operator Â with real eigenvalues a_1 and a_2, respectively. Since the eigenvalues are real, $a_1^* = a_1$ and $a_2^* = a_2$.

$$\hat{A}\psi = a_1\psi$$

$$\hat{A}^*\psi^* = a_2\psi^*$$

Multiply the first equation by φ^* and the second by ψ and integrate.

$$\int \psi^* \hat{A}\psi \, d\tau = a_1 \int \psi^*\psi \, d\tau$$

$$\int \psi \hat{A}^*\psi^* \, d\tau = a_2 \int \psi\psi^* \, d\tau \tag{4.5.8}$$

Subtract the two equations in Equation 4.5.8 to obtain

$$\int \psi^* \hat{A}\psi \, d\tau - \int \psi \hat{A}^*\psi^* \, d\tau = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{4.5.9}$$

The left-hand side of Equation 4.5.9 is zero because $\hat{A}$ is Hermitian yielding

$$0 = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{4.5.10}$$

If a_1 and a_2 in Equation 4.5.10 are not equal, then the integral **must** be zero. This result proves that **nondegenerate eigenfunctions** of the same operator are orthogonal.

□

Two wavefunctions, $\psi_1(x)$ and $\psi_2(x)$, are said to be *orthogonal* if

$$\int_{-\infty}^{\infty} \psi_1^* \psi_2 \, dx = 0. \tag{4.5.11}$$

Consider two eigenstates of $\hat{A}$, $\psi_a(x)$ and $\psi_{a'}(x)$, which correspond to the two *different* eigenvalues a and a', respectively. Thus,

$$A\psi_a = a\psi_a \tag{4.5.12}$$

$$A\psi_a' = a'\psi_a' \tag{4.5.13}$$

Multiplying the complex conjugate of the first equation by $\psi_{a'}(x)$, and the second equation by $\psi_{a'}^*(x)$, and then integrating over all x, we obtain

$$\int_{-\infty}^{\infty} (A\psi_a)^* \psi_{a'} dx = a \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx, \tag{4.5.14}$$

$$\int_{-\infty}^{\infty} \psi_a^* (A\psi_{a'}) dx = a' \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx. \tag{4.5.15}$$

However, from Equation 4.5.9, the left-hand sides of the above two equations are equal. Hence, we can write

$$(a - a') \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0.$$

By assumption, $a \neq a'$, yielding

$$\int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0.$$

In other words, eigenstates of an Hermitian operator corresponding to *different* eigenvalues are automatically *orthogonal*.

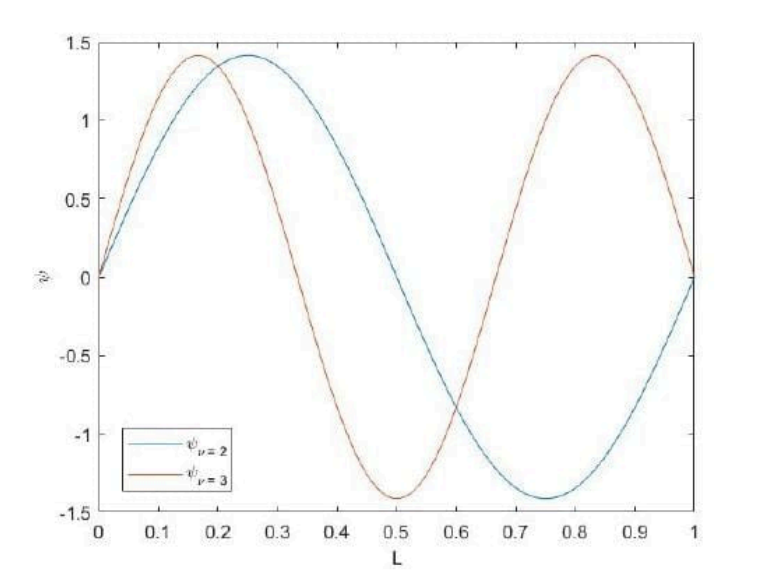
> The eigenvalues of operators associated with experimental measurements are all *real*.

Example4.5.1

Draw graphs and use them to show that the particle-in-a-box wavefunctions for $\psi(n = 2)$ and $\psi(n = 3)$ are orthogonal to each other.

Solution

The two PIB wavefunctions are qualitatively similar when plotted



These wavefunctions are orthogonal when

$$\int_{-\infty}^{\infty} \psi(n = 2)\psi(n = 3)dx = 0$$

and when the PIB wavefunctions are substituted this integral becomes

$$\int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{2n}{L}x\right) \sqrt{\frac{2}{L}} \sin\left(\frac{2n}{L}x\right) dx = ?$$

$$\frac{2}{L} \int_0^L \sin\left(\frac{2}{L}x\right) \sin\left(\frac{3}{L}x\right) = ?$$

We can expand the integrand using trigonometric identities to help solve the integral, but it is easier to take advantage of the symmetry of the integrand, specifically, the $\psi(n=2)$ wavefunction is even (blue curves in above figure) and the $\psi(n=3)$ is odd (purple curve). Their product (even times odd) is an odd function and the integral over an odd function is zero. Therefore $\psi(n=2)$ and $\psi(n=3)$ wavefunctions are orthogonal.

This can be repeated an infinite number of times to confirm the entire set of PIB wavefunctions are mutually orthogonal as the Orthogonality Theorem guarantees.

Orthogonality of Degenerate Eigenstates

Consider two eigenstates of $\hat{A}$, ψ_a and ψ'_a, which correspond to the *same* eigenvalue, a. Such eigenstates are termed **degenerate**. The above proof of the orthogonality of different eigenstates fails for degenerate eigenstates. Note, however, that *any* linear combination of ψ_a and ψ'_a is also an eigenstate of $\hat{A}$ corresponding to the eigenvalue a. Thus, even if ψ_a and ψ'_a are not orthogonal, we can always choose two linear combinations of these eigenstates which are orthogonal. For instance, if ψ_a and ψ'_a are properly normalized, we can define the **overlap integral**

$$S = \int_{-\infty}^{\infty} \psi_a^* \psi'_a dx, \tag{4.5.16}$$

It is easily demonstrated (but not here) that

$$\psi''_a = \frac{|S|}{\sqrt{1-|S|^2}} \left(\psi_a - S^{-1}\psi'_a\right) \tag{4.5.17}$$

is a properly normalized eigenstate of $\hat{A}$, corresponding to the eigenvalue a, which is orthogonal to ψ_a. It is straightforward to generalize the above argument to three or more degenerate eigenstates. Hence, we conclude that the eigenstates of a Hermitian operator are, or can be chosen to be, **mutually orthogonal.**

Theorem: Gram-Schmidt Orthogonalization

Degenerate eigenfunctions are **not** automatically orthogonal, but can be made so mathematically via the Gram-Schmidt Orthogonalization.

The above theorem argues that if the eigenvalues of two eigenfunctions are the same then the functions are said to be degenerate and linear combinations of the degenerate functions can be formed that will be orthogonal to each other. Since the two eigenfunctions have the same eigenvalues, the linear combination also will be an eigenfunction with the same eigenvalue. The proof of this theorem shows us one way to produce orthogonal degenerate functions.

Proof

If ψ_a and ψ'_a are degenerate, but not orthogonal, we can define a new composite wavefunction $\psi''_a = \psi'_a - S\psi_a$ where S is the overlap integral:

$$S = \langle \psi_a | \psi'_a \rangle$$

then ψ_a and ψ''_a will be orthogonal.

$$\begin{aligned}
\langle \psi_a | \psi''_a \rangle &= \langle \psi_a | \psi'_a - S\psi_a \rangle \\
&= \cancelto{S}{\langle \psi_a | \psi'_a \rangle} - S \cancelto{1}{\langle \psi_a | \psi_a \rangle} \\
&= S - S = 0
\end{aligned}$$

$$\int \psi_a^* \psi_a d\tau$$

then ψ_a and Φ will be orthogonal.

$$\begin{aligned}\int \psi_A^* \Phi d\tau &= \int \psi_a^* (\psi_a' - S\psi_a) d\tau \\ &= \int \psi_a^* \psi_a' d\tau - S \int \psi_a^* \psi_a d\tau \\ &= S - S = 0\end{aligned}$$

□

Exercise 4.5.2

Find N that normalizes ψ if $\psi = N(\varphi_1 - S\varphi_2)$ where φ_1 and φ_2 are normalized wavefunctions and S is their overlap integral.

$$S = \langle \varphi_1 | \varphi_2 \rangle$$

Answer available at the end of this section.

We conclude that the eigenstates of operators are, or can be chosen to be, **mutually orthogonal**.

Contributors and Attributions

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Answers

Remember that to normalize an arbitrary wavefunction, we find a constant N such that $\langle \psi | \psi \rangle = 1$. This equates to the following procedure:

$$\begin{aligned}\langle \psi | \psi \rangle &= \langle N(\varphi_1 - S\varphi_2) | N(\varphi_1 - S\varphi_2) \rangle = 1 \\ N^2 \langle (\varphi_1 - S\varphi_2) | (\varphi_1 - S\varphi_2) \rangle &= 1 \\ N^2 \left[\cancelto{1}{\langle \varphi_1 | \varphi_1 \rangle} - S \cancelto{S}{\langle \varphi_2 | \varphi_1 \rangle} - S \cancelto{S}{\langle \varphi_1 | \varphi_2 \rangle} + S^2 \cancelto{1}{\langle \varphi_2 | \varphi_2 \rangle} \right] &= 1 \\ N^2 (1 - S^2 \cancel{- S^2 + S^2}) &= 1 \\ N^2 (1 - S^2) &= 1\end{aligned}$$

therefore

$$N = \frac{1}{\sqrt{1 - S^2}}$$

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4.6: Commuting Operators Allow Infinite Precision

Learning Objectives

- To connect the Heisenberg Uncertainty principle to the commutation relations.
- Develop proficiency in calculating the commutator of two operators.

If two operators commute then both quantities can be measured at the same time with infinite precision, if not then there is a tradeoff in the accuracy in the measurement for one quantity vs. the other. This is the mathematical representation of the Heisenberg Uncertainty principle.

Commuting Operators

One important property of operators is that the order of operation matters. Thus in general

$$\hat{A}\hat{E}f(x) \neq \hat{E}\hat{A}f(x)$$

unless the two operators **commute**. Two operators commute if the following equation is true:

$$\left[\hat{A},\hat{E}\right] = \hat{A}\hat{E} - \hat{E}\hat{A} = 0$$

To determine whether two operators commute first operate $\hat{A}\hat{E}$ on a function $f(x)$. Then operate$\hat{E}\hat{A}$ the same function $f(x)$. If the same answer is obtained subtracting the two functions will equal zero and the two operators will commute.on

If two operators commute, then they can have the same set of eigenfunctions. By definition, two operators $\hat{A}$ and $\hat{B}$ commute if the effect of applying $\hat{A}$ then $\hat{B}$ is the same as applying $\hat{B}$ then $\hat{A}$, i.e.

$$\hat{A}\hat{B} = \hat{B}\hat{A}.$$

For example, the operations brushing-your-teeth and combing-your-hair commute, while the operations getting-dressed and taking-a-shower do not. This theorem is very important. If two operators commute and consequently have the same set of eigenfunctions, then the corresponding physical quantities can be evaluated or measured exactly simultaneously with no limit on the uncertainty. As mentioned previously, the eigenvalues of the operators correspond to the measured values.

If $\hat{A}$ and $\hat{B}$ commute and ψ is an eigenfunction of $\hat{A}$ with eigenvalue b, then

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \tag{4.6.1}$$

Equation 4.6.1 says that $\hat{A}\psi$ is an eigenfunction of $\hat{B}$ with eigenvalue b, which means that when $\hat{A}$ operates on ψ, it cannot change ψ. At most, $\hat{A}$ operating on ψ can produce a constant times ψ.

$$\hat{A}\psi = a\psi \tag{4.6.2}$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \tag{4.6.3}$$

Equation 4.6.3 shows that Equation 4.6.2 is consistent with Equation 4.6.1. Consequently ψ also is an eigenfunction of $\hat{A}$ with eigenvalue a.

Example 4.6.1

Do the following pairs of operators commute?

a. $\hat{A} = \dfrac{d}{dx}$ and $\hat{E} = x^2$
b. $\hat{B} = \dfrac{\hbar}{x}$ and $\hat{C}\{f(x)\} = f(x) + 3$
c. $\hat{J} = 3x$ and $\hat{O} = x^{-1}$

Solution a available at the end of this section.

Solution b available at the end of this section.

Solution c available at the end of this section.

General Heisenberg Uncertainty Principle

Although it will not be proven here, there is a general statement of the uncertainty principle in terms of the commutation property of operators. If two operators $\hat{A}$ and $\hat{B}$ do not commute, then the uncertainties (standard deviations σ) in the physical quantities associated with these operators must satisfy

$$\sigma_A \sigma_B \geq \left| \int \psi^* [\hat{A}\hat{B} - \hat{B}\hat{A}] \psi \, d\tau \right| \tag{4.6.4}$$

where the integral inside the square brackets is called the **commutator**, and $\left|\ \right|$ signifies the modulus or absolute value. If $\hat{A}$ and $\hat{B}$ commute, then the right-hand-side of Equation 4.6.4 is zero, so either or both σ_A and σ_B could be zero, and there is no restriction on the uncertainties in the measurements of the eigenvalues a and b. If $\hat{A}$ and $\hat{B}$ do not commute, then the right-hand-side of Equation 4.6.4 will not be zero, and neither σ_A nor σ_B can be zero unless the other is infinite. Consequently, both a and b cannot be eigenvalues of the same wavefunctions and cannot be measured simultaneously to arbitrary precision.

Exercise4.6.1

Show that the commutator for position and momentum in one dimension equals $-i\hbar$ and that the right-hand-side of Equation 4.6.4 therefore equals $\hbar/2$ giving $\sigma_x \sigma_{px} \geq \frac{\hbar}{2}$.

Applications

Operators are very common with a variety of purposes. They are used to figure out the energy of a wavefunction using the Schrödinger Equation.

$$\hat{H}\psi = E\psi$$

They also help to explain observations made in the experimentally. An example of this is the relationship between the magnitude of the angular momentum and the components.

$$\left[\hat{L}^2, \hat{L}_x^2\right] = \left[\hat{L}^2, \hat{L}_y^2\right] = \left[\hat{L}^2, \hat{L}_z^2\right] = 0$$

However the components do not commute themselves. An additional property of commuters that commute is that both quantities can be measured simultaneously. Thus, the magnitude of the angular momentum and ONE of the components (usually z) can be known at the same time however, NOTHING is known about the other components.

The physical quantities corresponding to operators that commute can be measured simultaneously to any precision.

4.6.2AExa

Determine whether the following two operators commute:

$$\hat{K} = \alpha \int [1]^{[\infty]} d[x]$$

and

$$\hat{H} = d/dx$$

Solution available at the end of this section.

4.6.2B Exa

Determine whether the following two operators commute:

$$\hat{I} = 5$$

and

$$\hat{L} = \int_{[1]}^{[\infty]} d[x]$$

Solution available at the end of this section.

4.6.2C Exe

Show that the components of the angular momentum do not commute.

$$\hat{L}_x = -i\hbar \left[-\sin\left(\phi \frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi \frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_y = -i\hbar \left[\cos\left(\phi \frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi \frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_z = -i\hbar \frac{\delta}{\delta\theta}$$

Solution available at the end of this section.

References

1. Gohberg, I. Basic Operator Theory; Birkhäuser: Boston, 2001
2. McQuarrie, D.A. Quantum Chemistry, 2nd Edition; University Science Books:Sausalito, 2008
3. Schechter, M. Operator Methods in Quantum Mechanics; Dover Publications, 2003

Answers

This requires evaluating $\left[\hat{A}, \hat{E}\right]$, which requires solving for $\hat{A}\{\hat{E}f(x)\}$ and $\hat{E}\{\hat{A}f(x)\}$ for arbitrary wavefunction $f(x)$ and asking if they are equal.

$$\hat{A}\{\hat{E}f(x)\} = \hat{A}\{x^2 f(x)\} = \frac{d}{dx}\{x^2 f(x)\} = 2xf(x) + x^2 f'(x)$$

From the product rule of differentiation.

$$\hat{E}\{\hat{A}f(x)\} = \hat{E}\{f'(x)\} = x^2 f'(x)$$

Now ask if they are equal

$$\left[\hat{A}, \hat{E}\right] = 2xf(x) + x^2 f'(x) - x^2 f'(x) = 2xf(x) \neq 0$$

Therefore the two operators do not commute.

This requires evaluating $\left[\hat{B}, \hat{C}\right]$ like in Example 4.6.1 .

$$\hat{B}\{\hat{C}f(x)\} = \hat{B}\{f(x)+3\} = \frac{h}{x}(f(x)+3) = \frac{hf(x)}{x} + \frac{3h}{x}$$

$$\hat{C}\{\hat{B}f(x)\} = \hat{C}\{\frac{h}{x}f(x)\} = \frac{hf(x)}{x} + 3$$

Now ask if they are equal

$$\left[\hat{B},\hat{C}\right] = \frac{hf(x)}{x} + \frac{3h}{x} - \frac{hf(x)}{x} - 3 \neq 0$$

The two operators do **not** commute.

This requires evaluating $\left[\hat{J},\hat{O}\right]$

$$\hat{J}\{\hat{O}f(x)\} = \hat{J}\{f(x)3x\} = f(x)3x/x = 3f(x)$$

$$\hat{O}\{\hat{J}f(x)\} = \hat{O}\{\frac{f(x)}{x}\} = \frac{f(x)3x}{x} = 3f(x)$$

$$\left[\hat{J},\hat{O}\right] = 3f(x) - 3f(x) = 0$$

Because the difference is zero, the two operators commute.

Evaluate

$$\left[\hat{K},\hat{H}\right]$$

The identity operator, $\hat{I}$ is a real number and commutes with everything. Thus, these two operators commute. We can also directly evaluate the commutator:

$$\left[\hat{I},\hat{L}\right]$$

$$\left[\hat{I},\hat{L}\right]f(x) = 5\int_1^\infty f(x)d(x) - \int_1^\infty 5f(x)d(x) = 0$$

This requires evaluating the following commucators:

$$\left[\hat{L}_z,\hat{L}_x\right] = i\hbar\hat{L}_y$$

$$\left[\hat{L}_x,\hat{L}_y\right] = i\hbar\hat{L}_z$$

$$\left[\hat{L}_y,\hat{L}_z\right] = i\hbar\hat{L}_x$$

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4.E: Postulates and Principles of Quantum Mechanics (Exercises)

Solutions to select questions can be found online.

4.3

The function $\psi^*\psi$ has to be real, nonnegative, finite, and of definite value everywhere. Why?

Solution

If we follow the Born interpretation of wavefuntions, then $\psi^*\psi$ is a probability density and hence must follow standard probability properties including being non-negative, finite and of a definite value at any relevant point in the space of the wavefunction. Moreover, the integral of $\psi^*\psi$ over all this space must be equal to 1.

4.5

Why are the following functions not acceptable wave functions for a 1D particle in a box with length a ? N is a normalization constant.

a. $\psi = N\cos\dfrac{n\pi x}{L}$
b. $\psi = \dfrac{N}{\sin\dfrac{n\pi x}{a}}$
c. $\psi = N\tan\dfrac{n\pi x}{a}$

Solution

The boundary conditions that need to be met are $\psi(0) = \psi(a) = 0$. This does not meet them. The proposed wavefunction blows up to infinity at $x = 0$ and $x = a$ Tan is not defined for $x = \dfrac{a}{2}$

4.12

Show that the sets of functions: $\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ where n = 1,2,3... is orthonormal.

Solution

Let

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

Because $\psi^* = \psi$ and is real, then

$$\int_0^L \psi^*\psi dx = \int_0^L \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{m\pi x}{L}\right)dx$$

Letting $n = m$

$$\begin{aligned}\int_0^L \psi^*\psi dx &= \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx \\ \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx &= 1\end{aligned}$$

Letting $n \neq m$

$$\begin{aligned}\int_0^L \psi^*\psi dx &= \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right)dx \\ &= \frac{2}{L}\frac{1}{2}\int_0^L \left[\cos\left(\frac{(n-m)\pi x}{L}\right) - \cos\left(\frac{(n+m)\pi x}{L}\right)\right]dx \\ &= \frac{1}{L}\left[\frac{L}{(n-m)\pi}\left[\sin\left(\frac{(n-m)\pi L}{L}\right) - \sin\left(\frac{(n-m)\pi 0}{L}\right)\right] - \frac{L}{(n+m)\pi}\left[\sin\left(\frac{(n+m)\pi L}{L}\right) - \sin\left(\frac{(n+m)\pi 0}{L}\right)\right]\right] = 0\end{aligned}$$

and thus $\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ (n=1, 2, 3, ...) are orthonormal.

4.13

Show that $a \cdot b \cdot c = \sum_{ik} a_i b_i c_k e_k$

$$\sum_i a_i e_i \cdot \sum_j b_j e_j \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$\sum_i \sum_j a_i b_j (e_i \cdot e_j) \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$e_i \cdot e_j = \delta_{ij} = 1$$

when $i = j$

$$\sum_i a_i b_i \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$\sum_{ik} a_i b_i c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

4.14

Determine if the following operators commute

$$\hat{B} = \frac{d}{dx}$$

and

$$\hat{C} = x^5$$

Solution

We must solve $\left[\hat{B}, \hat{C}\right]$, by solving for $\hat{B}\{\hat{C}f(x)\}$ and $\hat{C}\{\hat{B}f(x)\}$ for a wavefunction $f(x)$ and see if they are equal.

$$\hat{B}\{\hat{C}f(x)\} = \hat{B}\{x^5 f(x)\} = \frac{d}{dx}\{x^5 f(x)\} = 5xf(x) + x^5 f'(x)$$

$$\hat{C}\{\hat{B}f(x)\} = \hat{C}\{f'(x)\} = x^5 f'(x)$$

since

$$\left[\hat{B}, \hat{C}\right] = 5xf(x) + x^5 f'(x) - x^2 f'(x) = 5xf(x) \neq 0$$

The two operators do not commute.

4.15

Do the following combinations of angular momentum operators commute? Show work to the justify the answer (do not just write "yes" or no").

a. $\mathbf{L}_x$ and $\mathbf{L}_y$
b. $\mathbf{L}_y$ and $\mathbf{L}_z$
c. $\mathbf{L}_z$ and $\mathbf{L}_x$

with

$$\mathbf{L}_x = -\mathrm{i}\,\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\mathbf{L}_y = -\mathrm{i}\,\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\mathbf{L}_z = -\mathrm{i}\,\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Estimate the answer to Part C based on the pattern gathered from parts A and B; no work necessary for Part C.

Solution

a.

$$[\mathbf{L}_x, \mathbf{L}_y] = (yp_z - zp_y)(zp_x - xp_z)\Psi - (zp_x - xp_z)(yp_z - zp_y)\Psi,$$

$$= (zp_xyp_z - z^2p_xp_y - xyp_zp_z - xzp_yp_z)\Psi - (yp_zzp_x - yxp_zp_z + z^2p_yp_x + zxp_zp_y)\Psi$$

$$[\mathbf{L}_x, \mathbf{L}_y] = i\hbar\mathbf{L}_z,$$

Does **not** commute, i.e., is not zero.

b.

$$[\mathbf{L}_y, \mathbf{L}_z] = (zp_x - xp_z)(xp_y - yp_x)\Psi - (xp_y - yp_x)(zp_x - xp_z)\Psi$$

$$= (xp_yzp_x - x^2p_yp_z - yzp_xp_x - yxp_zp_x)\Psi - (zp_xxp_y - zyp_xp_x + x^2p_zp_y + xyp_xp_z)\Psi$$

$$[\mathbf{L}_y, \mathbf{L}_z] = i\hbar\mathbf{L}_x,$$

Does **not** commute, i.e., is not zero.

c. This part only requires that we notice the rotation of variables and consistency of format/equations. In doing so, we better understand the relation between the parts of the angular momentum operator. The work below does not need to be shown for credit, but it may clarify things or make the solution clearer if you are still having trouble assessing and using the pattern.

$$[\mathbf{L}_z, \mathbf{L}_x] = (xp_y - yp_x)(yp_z - zp_y)\Psi - (yp_z - zp_y)(xp_y - yp_x)\Psi$$

$$= (yp_zxp_y - y^2p_zp_x - zxp_yp_y - zyp_xp_y)\Psi - (xp_yyp_z - xzp_yp_y + y^2p_xp_z + yzp_yp_x)\Psi$$

$$[\mathbf{L}_z, \mathbf{L}_x] = i\hbar\mathbf{L}_y,$$

Does not commute, i.e., is not zero.

These calculations show that you can have only one well-defined component of the angular momentum because of the uncertainty principle says the others will not be known (since they do not commute).

4.17

For two operators to commute, what property must hold? Use the operators $\hat{L^2}$ and $\hat{L}_z$ as an example to show that this property holds.

Solution

The commuters when applied to a wavefunction must equal the 0 eigenfunction.

$$\hat{L^2}\hat{L}_z\psi(x) - \hat{L}_z\hat{L^2}\psi(x) = 0$$

$$\hat{L^2}\hat{L}_z - \hat{L}_z\hat{L^2}\psi(x) = \hat{0}\psi(x)$$

$$\hat{L^2}\hat{L}_z - \hat{L}_z\hat{L^2} = 0$$

4.21

Show that the angular momentum and kinetic energy operators commute and therefore can be measured simultaneously to arbitrary precision.

Solution

Show that

$$[\hat{K}, \hat{L}] \; = \; 0$$

where the operators can be broken up into 3 components

$$L_x = -\mathrm{i}\,\hbar\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right)$$

$$L_y = -\mathrm{i}\,\hbar\left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z}\right)$$

$$L_z = -\mathrm{i}\,\hbar\left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right)$$

and $\hat{K_x} \; = \; \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. The same can be written for $\hat{K}$ in the y and z directions.

$$[\hat{K}, \hat{L}] = [\hat{K_x}, \hat{L_x}] + [\hat{K_y}, \hat{L_y}] + [\hat{K_z}, \hat{L_z}]$$

For the x-direction

$$[\hat{K_x}, \hat{L_x}] = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, -i\hbar\Big(y\frac{d}{dz} - z\frac{d}{dy}\Big)\Big)\right]$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Big(-i\hbar\Big(y\frac{d}{dz} - z\frac{d}{dy}\Big)\Big) - -i\hbar\Big(y\frac{d}{dz} - z\frac{d}{dy}\Big)\Big)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\frac{i\hbar^3}{2m}\Big(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\Big) - \frac{i\hbar^3}{2m}\Big(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\Big) \; = \; 0$$

The process can be repeated for the y and z directions and following the same steps the commutations turn out to be 0. Therefore, kinetic energy and angular momentum commute.

4.22

Show that the position and angular momentum operator commutes. Can the position and angular momentum be measured simultaneously to a arbitrary precision?

Solution

First, we must prove that the position operator, $\hat{\mathbf{R}} = \mathbf{i}\hat{x} + \mathbf{j}\hat{y} + \mathbf{k}\hat{z}$, and the angular momentum operator $\hat{\mathbf{L}} = \mathbf{i}\hat{L_x} + \mathbf{j}\hat{L_y} + \mathbf{k}\hat{L_z}$, commute.

In order to prove the commutation,

$$[\hat{\mathbf{R}}, \hat{\mathbf{L}}] = [\mathbf{i}\hat{x} + \mathbf{j}\hat{y} + \mathbf{k}\hat{z}, \mathbf{i}\hat{L_x} + \mathbf{j}\hat{L_y} + \mathbf{k}\hat{L_z}]$$

$$= [\hat{x}, \hat{L_x}] + [\hat{y}, \hat{L_y}] + [\hat{z}, \hat{L_z}]$$

$$= 0$$

where we have used the fact that

$$\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = \mathbf{k} \cdot \mathbf{k} = 1$$

and

$$\mathbf{i} \cdot \mathbf{j} = \mathbf{j} \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{i} = 0$$

Now that we have proved that the two operators commute, the relationship of commutation means that the position and total angular momentum of any electrons can be measured simultaneously to arbitrary precision.

4.25

If both $|\Psi_n\rangle$ and $|\Psi_m\rangle$ satisfy the **time-independent** Schrödinger Equation (these are called *stationary states*)

$$|\Psi_n(x,t)\rangle = \Psi_n(x)e^{-iE_nt/\hbar}$$

and

$$|\Psi_m(x,t)\rangle = \Psi_m(x)e^{-iE_mt/\hbar}$$

show that any linear superposition of the two wavefunctions

$$|\Psi(x,t)\rangle = c_n|\Psi_n(x,t)\rangle + c_m|\Psi_m(x,t)\rangle$$

also satisfies the **time-dependent** Schrödinger Equation.

Solution

The time-dependent Schrödinger Equation is

\[\hat{H}Ψ(x,t) =iħ ∂Ψ(x,y)/∂t\nonumber \]

Plug Ψ(x,t) into the time-dependent equation.

\[\hat{H}c_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + c_mΨ$_m$(x)e$^{-iE_mt/ ħ}$ = iħ ∂/∂tc_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + c_mΨ$_m$(x)e$^{-iE_mt/ ħ}$ \nonumber \]

\[\hat{H}c_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + c_mΨ$_m$(x)e$^{-iE_mt/ ħ}$ = E_nc_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + E_mc_mΨ$_m$(x)e$^{-iE_mt/ ħ}$\nonumber \]

\[∂/∂tc_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + c_mΨ$_m$(x)e$^{-iE_mt/ ħ}$ = -[(iE$_m$c$_m$e$^{-iE_mt/ ħ}$Ψ$_m$(x))/ħ]-[(iE$_n$c$_n$e$^{-iE_nt/ ħ}$Ψ$_n$(x))/ħ]\nonumber \]

combine all the constants (except for E) into c_n and c_m

\[iħ [-[(ic$_m$e$^{-iE_mt/ ħ}$Ψ$_m$(x))/ħ]-[(ic$_n$e$^{-iE_nt/ħ}$ Ψ$_n$(x))/ħ]]=E$_n$c$_n$Ψ$_n$(x)e$^{-iE_nt/ ħ}$ + E$_m$c$_m$Ψ$_m$(x)e$^{-iE_mt/ ħ}$\nonumber \]

\[Since \hat{H}Ψ(x,t) and iħ ∂Ψ(x,y)/∂t are equal, they satisfy the time-dependent equation. \nonumber \]

4.26

Starting with

$$\langle x\rangle = \int \psi^*(x,t)x\psi(x,t)dx$$

and the time-independent Schrödinger equation, demonstrate that

$$\frac{d\langle x\rangle}{dt} = \int \psi^* \frac{i}{\hbar}(\hat{H}x - x\hat{H})\psi dx$$

Given that

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

show that

$$\hat{H}x - x\hat{H} = -2\frac{\hbar^2}{2m}\frac{d}{dx} = -\frac{\hbar^2}{m}\frac{i}{\hbar}\hat{P}_x = -\frac{ih}{m}\hat{P}_x$$

4.28

Derive the condition on operators that arises from forcing eigenvalues to be real with complex conjugates.

Solution

Starting with an eigenvalue problem with a $\hat{G}$ as our operator we recognize

$$\hat{G}\psi = \lambda\psi$$

Solving for our eigenvalue we must multiply by our complex conjugate wavefunction and integrate both sides to see

$$\int \psi^* \hat{G}\psi d\tau = \int \psi^* \lambda\psi d\tau = \lambda \int \psi^*\psi d\tau = \lambda$$

We can repeat this calculation but with a complex conjugate of our initial eigenvalue problem

$$\hat{G}^*\psi^* = \lambda^*\psi^*$$

Solving for our eigenvalue we multiply ψ and integrate both sides to find that

$$\int \psi\hat{G}^*\psi^* d\tau = \int \psi\lambda^*\psi^* d\tau = \lambda^* \int \psi\psi^* d\tau = \lambda$$

Since we restricted λ to be real both eigenvalue problems return the same eigenvalue. We can then relate the operator side of both equations to know that

$$\boxed{\int \psi^* \hat{G}\psi d\tau = \int \psi\hat{G}^*\psi^* d\tau}$$

4.31

Prove that the position operator is Hermitian.

Solution

We must see if the operator satisfies the following requirement to be in Hermitian:

$$\int_{-\infty}^{\infty} (\hat{A}\psi^*)\psi\, dx = \int_{-\infty}^{\infty} \psi^* \hat{A}\psi\, dx$$

Substitute $\hat{X}$ for $\hat{A}$ into the above equation:

$$\int_{-\infty}^{\infty} (\hat{A}\psi^*)\psi\, dx = \int_{-\infty}^{\infty} \psi^* \hat{A}\psi\, dx$$

$$\int_{-\infty}^{\infty} (\hat{X}\psi^*)\psi\, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi\, dx$$

$$\int_{-\infty}^{\infty} (\hat{X}\psi)^*\psi\, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi\, dx$$

$$\int_{-\infty}^{\infty} \psi^* \hat{X}^*\psi\, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi\, dx$$

Since $\hat{X}^* \equiv \hat{X}$:

$$\int_{-\infty}^{\infty} \psi^* \hat{X}\psi\, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi\, dx$$

Therefore the Position Operator is Hermitian.

4.31

Prove that the momentum operator is a Hermitian

Solution

Hermitian: $\int \psi_j^* \hat{H} \psi_i dx$

Momentum Operator: $\hat{P} = -i\hbar \frac{d}{dx}$

We will first start by showing you

$$\int_{-\infty}^{\infty} \psi_j (-i\hbar \frac{d}{dx}) psi_i dx$$

$\frac{d\psi_i}{dx} dx = d\psi_i$

$\int_{-\infty}^{\infty} \psi_j (-i\hbar \frac{d}{dx}) psi_i dx$ = iħ $\int_{-\infty}^{\infty} psi_j d\psi_i$

Using integration by parts with u = \psi_{j}*\ and dv = d\psi_{i}

We can notice now that for a confined particle the product \psi_{j}^{*}\psi_{i} will go to zero at each of the endpoints

We get in the end $-i\hbar \frac{d}{dx}$ = $-i\hbar \frac{d}{dx}$ → momentum operator

4.32

Which of the following operators are Hermitian:

a. x,
b. d/dx
c. hd^2/dx^2
d. id^2/dx^2

Solution

A Hermitian Operator $\hat{A}$ satisfies

$$< \Psi^*|A|\Psi >=< \Psi|A^*|\Psi* >$$

x

$$\int \Psi * x\Psi dx = \int \Psi x\Psi* dx$$

where $x^* = x$.

Operator x is Hermitian

d/dx

$$\int \Psi * d/dx\Psi dx$$

$$= \int \Psi* d\Psi$$

Here we can use Integration by Parts \int *vdu* = *uv* + \int *udv* with v=Ψ* and dv = dΨ

$$= [\Psi * \Psi] - \int \Psi d\Psi*$$

[Ψ*Ψ] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions

$$= - \int \Psi d/dx\Psi * dx$$

Here we inserted dx/dx into the integral

$$= \int \Psi(-d/dx)\Psi* dx$$

d/dx* = d/dx, not -d/dx,so this operator is **not Hermitian.**

hd^2/dx^2

$$\int \Psi * h(d^2/dx^2)\Psi dx$$

$$= h \int \Psi * (d^2/dx)\Psi$$

Here we can use Integration by Parts \int *vdu* = *uv* + \int *udv* with u=Ψ* and dv=d(dΨ/dx)

$$= h[\Psi * d\Psi/dx] - \int (d\Psi/dx)d\Psi*$$

$$= h[\Psi * d\Psi/dx] - \int (d\Psi * /dx)d\Psi$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ/dx, for example, also approach 0.

$$= -h \int (d\Psi * /dx) d\Psi$$

Here we can use Integration by Parts *int vdu = uv + \int udv* with u=dΨ*/dx and dv=dΨ

$$= -h([\Psi d\Psi * /dx] - \int \Psi d^2\Psi * /dx$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ*/dx, for example, also approaches 0.

$$= h \int \Psi (d^2\Psi * /dx)$$

$$= h \int \Psi (d^2\Psi * /dx^2) dx$$

$$= \int \Psi h (d^2/dx^2) \Psi * dx$$

$h(d^2/dx^2)^* = h(d^2/dx^2)$, so this operator is Hermitian

id^2/dx^2

$$\int \Psi * i (d^2/dx^2) \Psi dx$$

$$= i \int \Psi * (d^2/dx) \Psi$$

Here we can use Integration by Parts

$$\int v du = uv + \int u dv$$

with u=Ψ* and dv=d(dΨ/dx)

$$= i[\Psi * d\Psi/dx] - \int (d\Psi/dx) d\Psi *$$

$$= i[\Psi * d\Psi/dx] - \int (d\Psi * /dx) d\Psi$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ/dx, for example, also approach 0.

$$= -i \int (d\Psi * /dx) d\Psi$$

Here we can use Integration by Parts *int vdu = uv + \int udv* with u=dΨ*/dx and dv=dΨ

$$= -i([\Psi d\Psi * /dx] - \int \Psi d^2\Psi * /dx$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ*/dx, for example, also approach 0.

$$= i \int \Psi (d^2 \Psi * / dx)$$

$$= i \int \Psi (d^2 \Psi * / dx^2) dx$$

$$= \int \Psi i (d^2 / dx^2) \Psi * dx$$

$$i (d^2 / dx^2) * = -i (d^2 / dx^2)$$

so this operator is NOT Hermitian

4.32

Determine whether the following operators are Hermitian and whether they commute:

$$\hat{A} = i\frac{d}{dx}$$

and

$$\hat{B} = i\frac{d^2}{dx^2}$$

Given that -∞<x<∞ and the operators functions are well behaved.

Solution

If the operator satisfies this condition it is *Hermitian*

$$\int_{-\infty}^{\infty} f^*(x)\,\hat{A}f(x)\,dx = \int_{-\infty}^{\infty} f(x)\,\hat{A}f^*(x)\,dx$$

A)

$$\int_{-\infty}^{\infty} f^*\left(i\frac{df}{dx}\right)dx = i\int_{-\infty}^{\infty} f^*\frac{df}{dx}dx = i\left([_{-\infty}^{\infty} f^*f] - \int_{-\infty}^{\infty} f\frac{df^*}{dx}dx\right)$$

$$= -i\int_{-\infty}^{\infty} f\frac{df^*}{dx}dx = \int_{-\infty}^{\infty} f\left(-i\frac{d}{dx}\right)f^*dx$$

$$\int_{-\infty}^{\infty} f\left(i\frac{d}{dx}\right)^* f^*dx$$

This operator is Hermitian

B)

$$\int_{-\infty}^{\infty} f^*\left(i\frac{d^2f}{dx^2}\right)dx = [_{-\infty}^{\infty} f^*i\frac{df}{dx}] - \int_{-\infty}^{\infty}\frac{df^*}{dx}\frac{df}{dx}dx$$

$$= -i[_{-\infty}^{\infty} f\frac{df^*}{dx}] + i\int_{-\infty}^{\infty} f\frac{d^2f^*}{dx^2}dx$$

$$= -\int_{-\infty}^{\infty} f\frac{id^2}{dx^2}^* f^*dx$$

This operator is **not** Hermitian

If the operators commute they have to satisfy this condition

$$\hat{A}\hat{B}f = \hat{B}\hat{A}f$$

$$\hat{A}\hat{B}f = \frac{id}{dx}\left(\frac{d^2f}{dx^2}\right) = \frac{id^3f}{dx^3}$$

$$\hat{B}\hat{A}f = \frac{id^2}{dx^2}\left(\frac{df}{dx}\right) = \frac{id^3f}{dx^3}$$

This pair of operators commutes.

4.34

Consider two wavefunctions

$$\psi_1(x) = A\sin(k_1x) + B\cos(k_1x) \tag{4.E.1}$$

and

$$\psi_2(x) = C\sin(k_2x) + D\cos(k_2x)$$

Given the boundary conditions are:

$$\psi(0) = 0$$

and

$$\frac{d\psi_1}{dx} = \frac{d\psi_2}{dx} \quad atx = 0$$

$$A + B = C, k_1(A - B) = k_2C$$

and given a expression of

$$R = \frac{B^2}{A^2} \tag{4.E.2}$$

Derive the simplest expression of R based on the terms from the boundary conditions provided above.

Solution

Since

$$A + B = C, k_1(A - B) = k_2C \tag{4.E.3}$$

,

$$k_1(A - B) = k_2(A + B) \tag{4.E.4}$$

$$k_1A - k_1B = k_2A + k_2B \tag{4.E.5}$$

$$(k_1 - k_2)A = (k_1 + k_2)B \tag{4.E.6}$$

Thus,

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2} \tag{4.E.7}$$

$$R = \frac{B^2}{A^2} = \left(\frac{B}{A}\right)^2 = \left(\frac{k_1 - k2}{k_1 + k_2}\right)^2 \tag{4.E.8}$$

4.34

A particle is moving in a field. Half-way through the field, there is a line that represents potential energy. To the left of the line, the potential energy is

$$x < 0$$

and to the right of the line the potential energy is

$$x > 0$$

. If the particle's energy is less than the potential energy line will the particle reflect when the its energy is greater than the Potential energy barrier height?

Solution

When

$$x < 0$$

the Schrödinger equation is as followed:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} = E\psi_1$$

and the solution to this equation is:

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x}$$

where

$$k_1 = (\frac{2mE}{\hbar^2})^{1/2}$$

Region Two where $x > 0$:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V_0\psi_2 = E\psi_2$$

and the solution to the equation is:

$$\psi_2(x) = Ce^{ik_2x} + De^{-ik_2x}$$

and

$$k_2 = [\frac{2m(E - V_0)}{\hbar^2}]^{1/2}$$

Notice the difference between the two Schrödinger equations. Equation one does not have a potential energy component because it is before the potential energy field hence have zero potential energy. After the potential energy field, the Schrödinger equation has a potential energy component because the particle has potential energy at this moment.

When you solve the differential solutions to the Schrödinger equations you find that the amount that is reflected back of a particle by the line is equal to the amount that is transmitted after the line. This is all we can find out for the information given. However, if we solve this solution for when the Energy of the particle is greater than the potential energy line and compare the differential solutions to all four wave functions then we find that all particles will be reflected by the barrier.

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4.S: Postulates and Principles of Quantum Mechanics (Summary)

1. The state of a quantum system is completely specified by its wavefunction $|\psi\rangle$.
2. To every observable quantity in classical mechanics, there exists a **Hermitian quantum mechanical operator. For example:** kinetic energy in Classical Mechanics is

$$\text{kinetic energy} = \frac{p^2}{2m} \qquad \text{(classical mechanics)}$$

and in Quantum Mechanics is

$$\text{kinetic energy} = \frac{\hat{p}^2}{2m} = -\frac{\hbar}{2m}\nabla^2. \qquad \text{(quantum mechanics)}$$

3. Observable quantities in quantum mechanics are eigenvalues of their corresponding operators: $\op A|\phi_n\rangle = A_n|\phi_n\rangle$.
4. The set of eigenfunctions of an operator are orthogonal: $\langle\phi_n\rangle\phi_m = \delta_{nm}$. The Kronecker delta δ_{nm} is 1 if $n = m$, and zero otherwise. As a secondary point, the set of all eigenfunctions of an operator form a complete set. So if $|\phi_n\rangle$ ($n = 0$, 1, 2 ...) are the set of eigenfunctions of an operator $\op A$, then any other state in the same space can be expressed as a linear combination of these functions:

$$|\psi\rangle = \sum_n c_n|\phi_n\rangle,$$

where c_n are complex numbers (the exact values are $c_n = \langle\phi_n\rangle\psi$, as you can see by applying a projection operator on $|\psi\rangle$).
5. If two operators do not commute, then their corresponding observables cannot be measured simultaneously to arbitrary precision. The most famous example is position and momentum:

$$[\op x, \op p_x] = \op x\op p_x - \op p_x\op x = i\hbar,$$

and as a result

$$\Delta p_x \Delta x \geq \hbar/2.$$

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5: THE HARMONIC OSCILLATOR AND THE RIGID ROTOR

- **The harmonic oscillator is common:** It appears in many everyday examples: Pendulums, springs, electronics (such as the RLC circuit), standing waves on a string, etc. It's trivial to set up demonstrations of these phenomena, and we see them constantly.
- **The harmonic oscillator is intuitive:** We can picture the forces on systems such as pendulum or a plucked string. This makes it simple to study in the classroom. In contrast, there are many "everyday" examples that are not intuitive.
- **The harmonic oscillator is mathematically simple:** Math is part of physics. In studying simple harmonic motion, students can immediately use the formulas that describe its motion. These formulas are understandable: for example, the equation for frequency shows the intuitive result that increasing spring stiffness increases frequency.

5.1: A Harmonic Oscillator Obeys Hooke's Law

5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

5.3: The Harmonic Oscillator Approximates Molecular Vibrations

5.4: The Harmonic Oscillator Energy Levels

5.5: The Harmonic Oscillator and Infrared Spectra

5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials

5.7: Hermite Polynomials are either Even or Odd Functions

5.8: The Energy Levels of a Rigid Rotor

5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

5.S: The Harmonic Oscillator and the Rigid Rotor (Summary)

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5.1: A Harmonic Oscillator Obeys Hooke's Law

The motion of two atoms in a diatomic molecule can be separated into translational, vibrational, and rotational motions. Both rotation and vibrational motions are internal motions that do not change the center of mass for the molecule (Figure 5.1.1), which is described by translational motion. Quantum translational motions can be modeled with the particle in a box model discussed previously and rotation and vibration can be modeled via the **rigid rotor** and **harmonic oscillator** models, respectively.



Figure 5.1.1 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY, 3.0; www.cleonis.nl).

Before delving into the quantum mechanical harmonic oscillator, we will introduce the classical harmonic oscillator (i.e., involving classical mechanics) to build an intuition that we will extend to the quantum world. A classical description of the vibration of a diatomic molecule is needed because the quantum mechanical description begins with replacing the classical energy with the Hamiltonian operator in the Schrödinger equation. It also is interesting to compare and contrast the classical description with the quantum mechanical picture.

The Classical Harmonic Oscillator

Simple harmonic oscillators about a potential energy minimum can be thought of as a ball rolling frictionlessly in a curved dish or a pendulum swinging frictionlessly back and forth (Figure 5.1.2). The restoring forces are precisely the same in either horizontal direction.

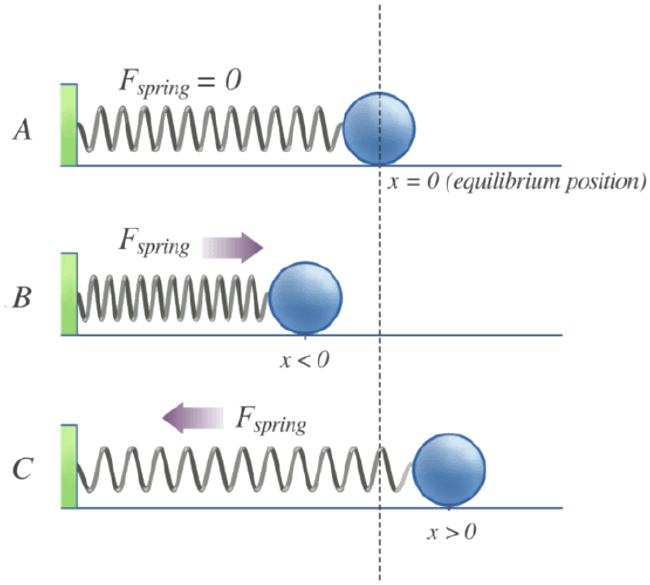


Figure 5.1.2 : A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (CC BY-NC; Ümit Kaya via LibreTexts)

If we consider the bond to behave like a mass on a spring (Figure 5.1.2), then this restoring force (F) is proportional to the displacement (x) from the equilibrium length (x_o) - this is *Hooke's Law*:

$$F = -kx \tag{5.1.1}$$

where k is the force constant. Hooke's Law says that the force is proportional to, but in opposite direction to, the displacement (x). The force constant reflects the **stiffness** of the spring. The idea incorporated into the application of Hooke's Law to a diatomic molecule is that when the atoms move away from their equilibrium positions, a restoring force is produced that increases proportionally with the displacement from equilibrium. The potential energy for such a system increases *quadratically* with the displacement.

$$V(x) = \frac{1}{2}kx^2 \tag{5.1.2}$$

Hooke's Law or the harmonic (i.e. quadratic) potential given by Equation 5.1.2 is an excellent *approximation* for the vibrational oscillations of molecules. The magnitude of the force constant k depends upon the nature of the chemical bond in molecular systems just as it depends on the nature of the spring in mechanical systems. The larger the force constant, the stiffer the spring or the stiffer the bond. Since it is the electron distribution between the two positively charged nuclei that holds them together, a double bond with more electrons has a larger force constant than a single bond, and the nuclei are held together more tightly.

Caution

A stiff bond with a large force constant is not necessarily a strong bond with a large dissociation energy. A harmonic oscillator has no dissociation energy since it CANNOT be broken - there is always a restoring force to keep the molecule together. This is one of many deficiencies in using the harmonic oscillator model to describe molecular vibrations.

Two atoms or one?

You may have questioned the applicability of the harmonic oscillator model involving one moving mass bound to a fix wall via a spring like in Figure 5.1.2 for the vibration of a diatomic molecule with two moving masses like in Figure 5.1.1 . It turned out the two are mathematically the same with internal vibration motion described by a single reduced particle with a reduced mass μ.

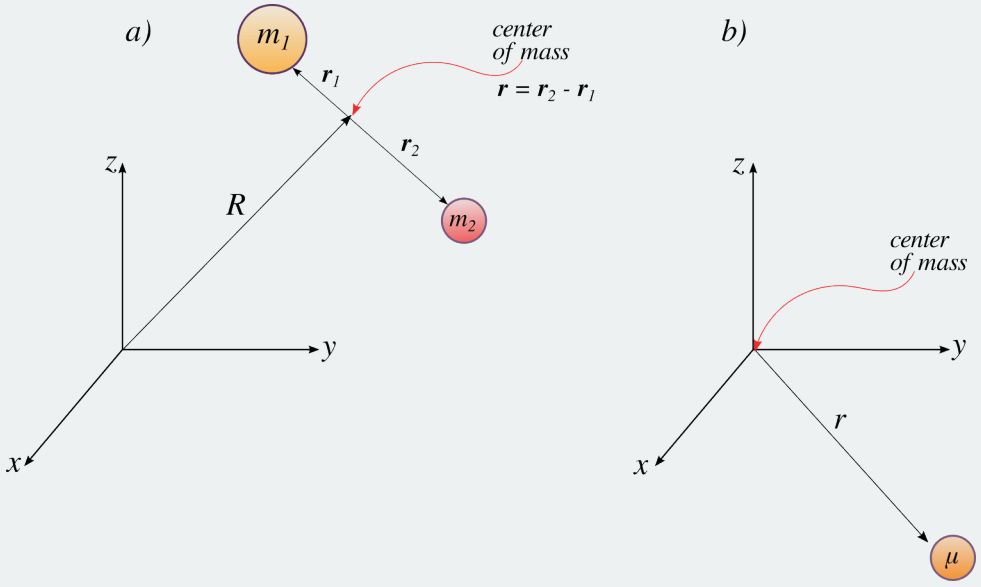


Figure 5.1.3 : Diagrams of the coordinate systems and relevant vectors for the motion of (a) a two-particle diatomic molecule with atoms of mass m_1 and m_2 and (b) the equivalent one-particle pseudo-particle of reduced mass μ. (CC BY-NC; Ümit Kaya via LibreTexts)

For a diatomic molecule, Figure 5.1.3 , the vector $\vec{r}$ corresponds to the internuclear axis. The magnitude or length of r is the bond length, and the orientation of r in space gives the orientation of the internuclear axis in space. Changes in the orientation correspond to rotation of the molecule, and changes in the length correspond to vibration. The change in the bond length from the equilibrium bond length is the **vibrational coordinate** for a diatomic molecule.

Example 5.1.1

a. Show that minus the first derivative of the harmonic potential energy function in Equation 5.1.2 with respect to x is the Hooke's Law force in Equation 5.1.1.
b. Show that the second derivative is the force constant, k.
c. At what value of x is the potential energy a minimum; at what value of x is the force zero?
d. Sketch graphs to compare the potential energy and the force for a system with a large force constant to one with a small force constant.

Solution a

Hooke's Law for a spring entails that the force applied on a spring F is equal to the force constant, $-k$ times the distance compressed or stretched, x (Equation 5.1.1). The derivative of $V(x) = 0.5kx^2$ is

$$V'(x) = (2)\left(\frac{1}{2}\right)kx = kx.$$

The negative of this is $-V'(x) = -kx$ which is exactly equal to Hooke's Law.

Solution b

The second derivative

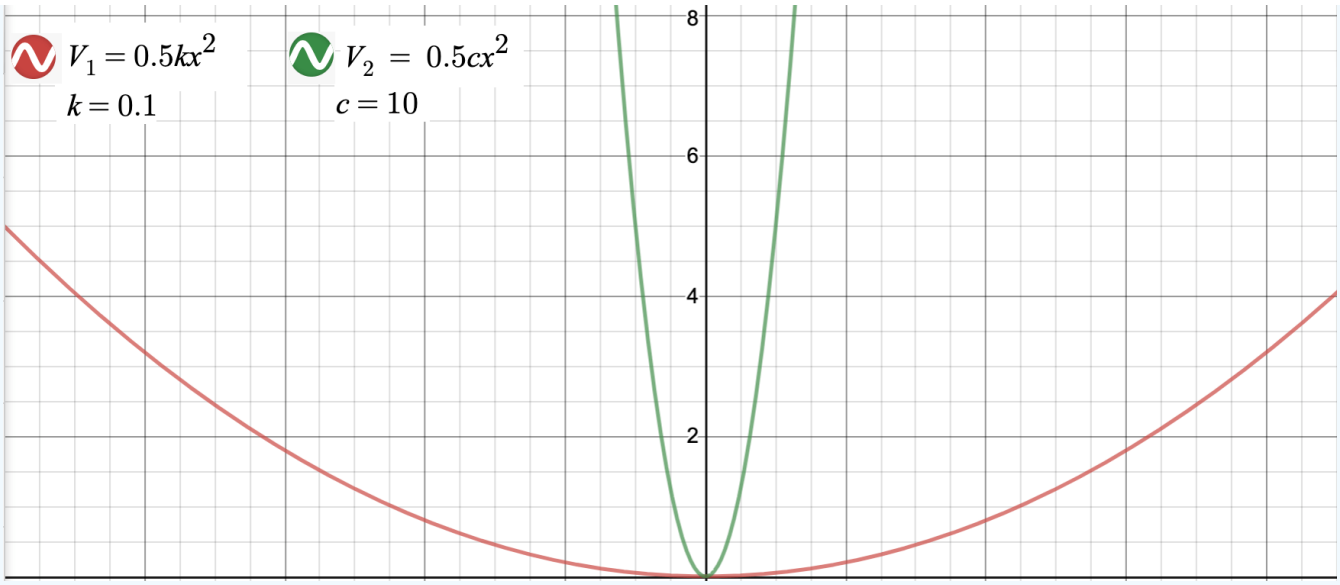
$$V''(x) = \frac{d}{dx}kx = k$$

Thus, the second derivative of this equation for potential energy is equal to the force constant, k.

Solution c

To find the minimum potential energy, it is easiest to set the first derivative equal to zero and solve for x. When $V'(x) = kx = 0$ then x must be equal to zero. Thus, the minimum potential energy is when x=0. Plugging this into Hooke's Law, $F(0) = -k(0) = 0$ so this is also the value for x when the force is zero.

Solution d



The force constant has a drastic effect on both the potential energy and the force. A system with a large force constant requires minimal change in x to have a drastic change in potential energy or force, whereas a system with a small force constant is the exact opposite phenomenon.

Solving the Harmonic Oscillator Model

The classical equation of motion for a one-dimensional simple harmonic oscillator with a particle of mass m attached to a spring having spring constant k is

$$m\frac{d^2x(t)}{dt^2} = -kx(t) \tag{5.1.3}$$

which can be rewritten in the standardform:

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0 \tag{5.1.4}$$

Equation 5.1.3 is a linear second-order differential equation that can be solved by the standard method of factoring and integrating. The resulting solution to Equation 5.1.3 is

$$x(t) = x_o \sin(\omega t + \phi) \tag{5.1.5}$$

with

$$\omega = \sqrt{\frac{k}{m}} \tag{5.1.6}$$

and the momentum has time dependence

$$\begin{aligned} p &= mv \\ &= mx_o\omega\cos(\omega t + \phi) \end{aligned}$$

Figure 5.1.4 show the displacement of the bond from its equilibrium length as a function of time. Such motion is called **harmonic**.

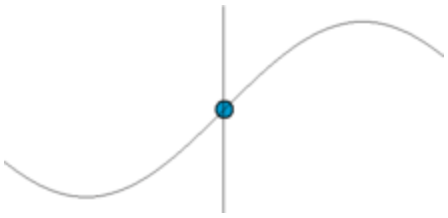


Figure 5.1.4 : Solution to the Harmonic Oscillator. Displacement (y-axis) is plotted as a function of time.

Example 5.1.2

Substitute the following functions into Equation 5.1.4 to demonstrate that they are both possible solutions to the classical equation of motion.

a. $x(t) = x_0 e^{i\omega t}$
b. $x(t) = x_0 e^{-i\omega t}$

where

$$\omega = \sqrt{\frac{k}{m}}$$

Note that the Greek symbol ω for frequency represents the angular frequency $2\pi\nu$.

Solution a

This requires simply placing the given function $x(t) = x_0 e^{i\omega t}$ into Equation 5.1.4.

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

$$\frac{d^2}{dt^2}\left(x_o e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} = 0$$

$$x_o \frac{d^2}{dt^2}\left(e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} = 0$$

$$x_o i^2\omega^2\left(e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} = 0$$

$$x_o i^2\omega^2 e^{i\omega t} + \frac{k}{m}x_o e^{i\omega t} = 0$$

$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$

$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \quad \text{with} \quad \omega = \sqrt{\frac{k}{m}}$$

Solution b

This requires simply placing the given function $x(t) = x_0 e^{-i\omega t}$ into Equation 5.1.4.

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

$$\frac{d^2}{dt^2}\left(x_o e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o\frac{d^2}{dt^2}\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 e^{-i\omega t} + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$

$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \quad \text{with} \quad \omega = \sqrt{\frac{k}{m}}$$

Exercise 5.1.1

Show that sine and cosine functions also are solutions to Equation 5.1.4.

Answer available at the end of this section.

Exercise 5.1.2

Identify what happens to the frequency of the motion as the force constant increases in one case and as the mass increases in another case. If the force constant is increased 9-fold and the mass is increased by 4-fold, by what factor does the frequency change?

Answer available at the end of this section.

Harmonic Oscillator Energies

The energy of the vibration is the sum of the kinetic energy and the potential energy. The momentum associated with the harmonic oscillator is

$$p = m\frac{dx}{dt} \tag{5.1.7}$$

so combining Equations 5.1.7 and 5.1.2, the total energy can be written as

$$E = T + V \tag{5.1.8}$$

$$= \frac{p^2}{2m} + \frac{k}{2}x^2 \tag{5.1.9}$$

The total energy of the harmonic oscillator is equal to the maximum potential energy stored in the spring when $x = \pm A$, called the *turning points* (Figure 5.1.5). The total energy (Equation 5.1.9) is continuously being shifted between potential energy stored in the spring and kinetic energy of the mass.

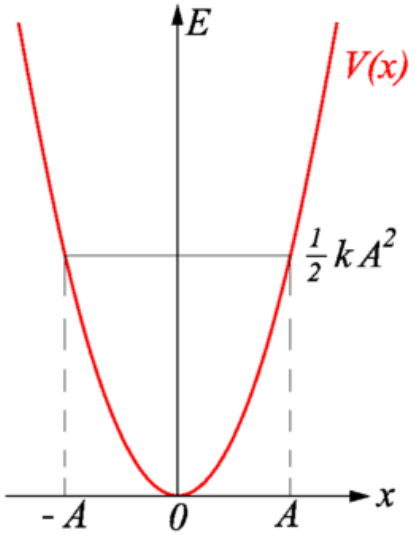


Figure 5.1.5 : The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x. The potential energy $V(x) = ½kx^2$ is shown in red. (Paul Wormer Wikipedia).

The motion of a classical oscillator is confined to the region where its kinetic energy is nonnegative, which is what the energy relation Equation 5.1.9 says. Physically, it means that a classical oscillator can never be found beyond its turning points, and its energy depends only on how far the turning points are from its equilibrium position. The energy of a classical oscillator changes in a continuous way. The lowest energy that a classical oscillator may have is zero, which corresponds to a situation where an object is at rest at its equilibrium position. The zero-energy state of a classical oscillator simply means no oscillations and no motion at all (a classical particle sitting at the bottom of the potential well in Figure 5.1.5). When an object oscillates, no matter how big or small its energy may be, it spends the longest time near the turning points, because this is where it slows down and reverses its direction of motion. Therefore, the probability of finding a classical oscillator between the turning points is highest near the turning points and lowest at the equilibrium position. (Note that this is not a statement of preference of the object to go to lower energy. It is a statement about how quickly the object moves through various regions.)

Example5.1.3

a. What happens to the frequency of the oscillation as the vibration is excited with more and more energy?
b. What happens to the maximum amplitude of the vibration as it is excited with more and more energy?

Solution

a. Frequency

The energy of the harmonic oscillator can be written as

$$E_v = hv\left(v + \frac{1}{2}\right)$$

and the frequency of oscillation is $\omega = \sqrt{\frac{k}{m}}$. Notice that the frequency depends only on the stiffness (k) and reduced mass (μ) of the oscillator and not on the energy. Hence, increasing the energy of the vibrations does not affects its frequency.

b. Amplitude

The kinetic and potential terms for energy of the harmonic oscillator can be written as

$$\begin{aligned} E &= K + V \\ &= \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t + \frac{1}{2}kA^2 \cos^2 \omega t \end{aligned}$$

with $\omega = \sqrt{\frac{k}{m}}$ so

$$E = \frac{1}{2}kA^2\left(\sin^2\omega t + \cos^2\omega t\right)$$
$$= \frac{1}{2}kA^2$$

The maximum amplitude of the vibration will **increase** as the energy **increases.**

Exercise 5.1.3

If a molecular vibration is excited by collision with another molecule and is given a total energy E_{hit} as a result, what is the maximum amplitude of the oscillation? Is there any constraint on the magnitude of energy that can be introduced?

Answer available at the end of this section.

Answers

Using Equation 5.1.4

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

with $\omega = \sqrt{\frac{k}{m}}$.

For

$$x(t) = x_o\sin(\omega t + \phi)$$

Take the second derivative of $x(t)$

$$\frac{d^2x(t)}{dt} = -\omega^2 x_o\sin(\omega t + \phi)$$
$$= \omega^2 x_o\sin(\omega t + \phi)$$
$$= -\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right)$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 5.1.4

$$-\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) + \frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) = 0$$

Hence, the sine equation is a solution to Equation 5.1.4

We do the same for the cosine function

$$x(t) = x_o\cos(\omega t + \phi)$$

Take the second derivative of $x(t)$

$$\frac{d^2x(t)}{dt} = -\omega^2 x_o\cos(\omega t + \phi)$$
$$= -\omega^2 x_o\cos(\omega t + \phi)$$
$$= -\frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t + \phi\right)$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 5.1.4

$$-\frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t + \phi\right) + \frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t + \phi\right) = 0$$

The cosine equation is also a solution to Equation 5.1.4.

This is a simple application of Equation 5.1.6. As the force constant increases, the frequency of the motion increases, while as the mass increases, the frequency of the motion decreases. If the force constant increased 9-fold and the mass increased 4-fold,

$$\omega = \sqrt{\frac{9k}{4m}} = \frac{3}{2}\left(\frac{k}{m}\right)$$

The entire frequency of motion would increase by a factor of 3/2.

The equation that defines the energy of a molecular vibration can be approximated is:

$$E_{hit} = T + V = \frac{p^2}{2m} + \frac{k}{2}x$$

The maximum amplitude of a harmonic oscillator is equal to x when the kinetic energy term of total energy equals zero

$$E_{hit} = \frac{k}{2}x$$

Solving for x gives the maximum amplitude:

$$x = \sqrt{\frac{2}{k}E_{hit}}$$

The constraint for the energy that can be introduced cannot be greater than the energy required to break the bond between atoms.

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5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For studying the energetics of molecular vibration we take the simplest example, a diatomic heteronuclear molecule AB. Let the respective masses of atoms A and B be m_A and m_B. For diatomic molecules, we define the reduced mass μ_{AB} by:

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \tag{5.2.1}$$

Reduced mass is the representation of a two-body system as a single-body one. When the motion (displacement, vibrational, rotational) of two bodies are only under mutual interactions, the inertial mass of the moving body with respect to the body at rest can be simplified to a reduced mass.

Reduced Mass

Viewing the multi-body system as a single particle allows the separation of the motion: vibration and rotation, of the particle from the displacement of the center of mass. This approach greatly simplifies many calculations and problems.

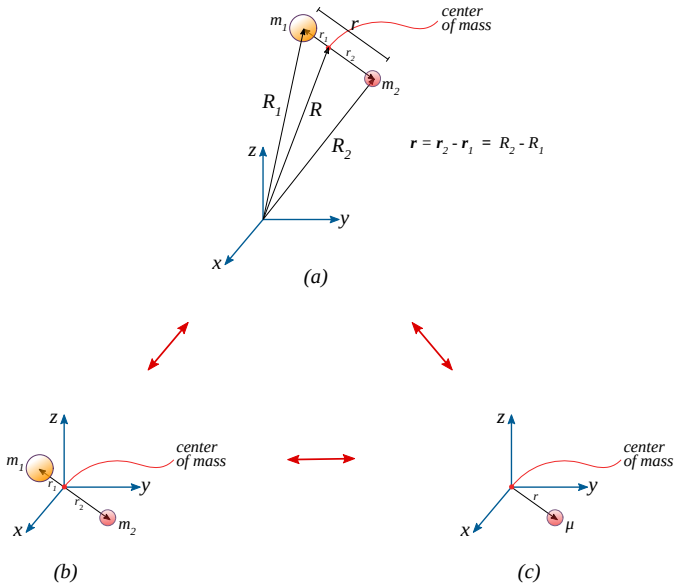


Figure 5.2.1 : a) the individual vectors to the particles m_1 and m_2 in the coordinate space and the resultant vector. b) center of mass. c) reduced mass. (CC BY-NC; Ümit Kaya via LibreTexts)

This concept is readily used in the general motion of diatomics, i.e. simple harmonic oscillator (vibrational displacement between two bodies, following Hooke's Law), the rigid rotor approximation (the moment of inertia about the center of mass of a two-body system), spectroscopy, and many other applications.

Example 5.2.1 : Reduced Mass

Determine the reduced mass of the two body system of a proton and electron with $m_{proton} = 1.6727 \times 10^{-27}\ kg$ and $m_{electron} = 9.110 \times 10^{-31}\ kg$).

Answer available at the end of this section.

The Quantum Harmonic Oscillator

The classical Harmonic Oscillator approximation is a simple yet powerful representation of the energetics of an oscillating spring system. Central to this model is the formulation of the quadratic potential energy

$$V(x) \approx \frac{1}{2}kx^2 \tag{5.2.2}$$

One problem with this classical formulation is that it is not general. We cannot use it, for example, to describe vibrations of diatomic molecules, where quantum effects are important. This require the formulation for Schrödinger Equation using Equation 5.2.2.

$$\hat{H}|\psi\rangle = \left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]|\psi\rangle = E|\psi\rangle$$

Solving this quantum harmonic oscillator is appreciably harder than solving the Schrödinger Equation for the simpler particle-in-the-box model and is outside the scope of this text. However, as with most quantum modules (and in contrast to the classical harmonic oscillator), the energies are quantized in terms of a quantum number (v in this case):

$$E_v = \hbar\left(\sqrt{\frac{k}{\mu}}\right)\left(v + \frac{1}{2}\right) \tag{5.2.3}$$

$$= h\nu\left(v + \frac{1}{2}\right) \tag{5.2.4}$$

with the natural vibrational frequency of the system given as

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.2.5}$$

and the mass, μ, is the reduced mass of the system (Equation 5.2.1).

Warning

Be careful to distinguish ν, the symbol for the natural frequency (as a Greek nu) from v the quantum harmonic oscillator quantum number (Latin v).

Caution: Do Not Use Atomic Weights to Calculate Reduced Masses

The vibrational frequencies given by Equation 5.2.5 depend on the force constants (k) and the atomic masses of the vibrating nuclei via the reduced mass (μ). It should be clear that the substitution of one isotope of an atom in a molecule for another isotope will affect the atomic masses and therefore the reduced mass (via Equation 5.2.1) and therefore the vibrational frequencies (via Equation 5.2.5).

It is important to remember that the Periodic Table gives only atomic weights of elements, which are scaled averages of atoms normally encountered in the laboratory (Table 5.2.1). To properly discuss vibrational frequencies of molecules, we need to know (or denote) the specific isotopes in the molecule. Check Table A4 for that information.

Table 5.2.1: Atomic Mass and Isotope Composition. Consult Table A4 for more extensive table.

isotope	atomic mass (in amu)	isotopic abundance (%)
^{1}H	1.007825	99.985
^{2}H	2.0140	0.015
^{35}Cl	35.968852	75.77

isotope	atomic mass (in amu)	isotopic abundance (%)
^{37}Cl	36.965903	24.23
^{79}Br	78.918336	50.69
^{81}Br	80.916289	49.31

Example 5.2.1 : Isotope Effect

What are the reduced mass for $^{1}H\,^{35}Cl$ and $^{1}H\,^{37}Cl$? If the spring constants for vibrations of both molecules are equal and estimated at $478\ N/m$, what are the natural vibrational frequencies of these two molecules?

Solution

The periodic table gives an atomic weight of 35.45 amu for chlorine, but remember this is the the average of the natural abundances of different chlorine isotopes which is dictated primary by two isotopes: ^{35}Cl and ^{37}Cl. For this problem, we need the exact mass of the ^{1}H, ^{35}Cl, and ^{37}Cl isotopes. Check Table A4 for that information.

For $^{1}H\,^{35}Cl$:

$$\begin{aligned}\text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{m_H m_{^{35}Cl}}{m_H + m_{^{35}Cl}} \\ &= \frac{(1.0078)(34.9688)}{1.0078 + 34.9688)}\, amu \\ &= 0.9796\, amu\end{aligned}$$

or when converted into kg is $1.629 \times 10^{-27}\ kg$.

For $^{1}H\,^{37}Cl$:

$$\begin{aligned}\text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{m_H m_{^{37}Cl}}{m_H + m_{^{37}Cl}} \\ &= \frac{(1.0078)(36.965)}{1.0078 + 36.965)}\, amu \\ &= 0.9810\, amu\end{aligned}$$

or when converted into kg is $1.6291 \times 10^{-27}\ kg$. This is only 0.29% bigger.

Equation 5.2.5 is used to predict the respective vibrational frequencies of these two molecules.

For $^{1}H\,^{35}Cl$:

$$\begin{aligned}\nu &= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2\pi}\sqrt{\frac{478\, N/m}{1.629 \times 10^{-27}\, kg}} \\ &= 8.6394 \times 10^{13} s^{-1}\end{aligned}$$

For $^{1}H\,^{37}Cl$:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$
$$= \frac{1}{2\pi}\sqrt{\frac{478\,N/m}{1.629\times10^{-27}\,kg}}$$
$$= 8.621\times10^{13}s^{-1}$$

As with the differences in the reduced masses, the differences in the vibrational frequencies of these two molecules is quite small. However, high resolution IR spectroscopy can easily distinguish the vibrations between these two molecules. Exercise 5.2.1 will demonstrate that this "**isotope effect**" is not always a small effect.

Exercise 5.2.1 : Hydrogen Chloride

The force constant is weakly sensitive to the specific isotopes in a molecule (and we typically assume it is isotope independent). If the $k = 478\ \ N/m$ for both $\mathrm{H}^{35}\mathrm{Cl}$ and $\mathrm{H}^{37}\mathrm{Cl}$. What are the vibration frequencies in these two diatomic molecules.

Answer available at the end of this section.

Answers

$$\mu_{pe} = \frac{(1.6727\times10^{-27})(9.110\times10^{-31})}{1.6727\times10^{-27}+9.110\times10^{-31}}$$
$$= 9.105\times10^{-31}kg$$

$\mathrm{H}^{35}\mathrm{Cl}$: 2886 cm^{-1}

$\mathrm{D}^{35}\mathrm{Cl}$: 2081 cm^{-1}

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5.3: The Harmonic Oscillator Approximates Molecular Vibrations

Learning Objectives

- Understand the utility and limits of using the quantum harmonic oscillator as a model for molecular vibrations

The quantum harmonic oscillator is one of the most important model systems in quantum mechanics. This is due in partially to the fact that an arbitrary potential curve $V(x)$ can usually be *approximated* as a harmonic potential at the vicinity of a stable equilibrium point. Furthermore, it is one of the few quantum-mechanical systems for which an exact, analytical solution exists. Solving other potentials typically require either approximations or numerical approaches to identify the corresponding eigenstates and eigenvalues (i.e., wavefunctions and energies).

A general potential energy ($V(x)$) curve for a molecular vibration can be expanded as a Taylor series

$$V(x) = V(x_0) + \frac{dV(x)}{dx}\bigg|_{x_0}^{x}(x-x_0) + \frac{1}{2!}\frac{d^2V(x)}{dx^2}\bigg|_{x_0}^{x}(x-x_0)^2 + \ldots + \frac{1}{n!}\frac{d^nV(x)}{dx^n}\bigg|_{x_0}^{x}(x-x_0)^n \tag{5.3.1}$$

It is important to note that this approximation is only good for x near x_0, and that x_0 stands for the equilibrium bond distance. $V(x)$ is often (but not always) shortened to the cubic term and can be rewritten as

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 \tag{5.3.2}$$

where $V(x_0) = 0$, k is the harmonic force constant (harmonic term), and γ is the first anharmonic term (i.e., cubic). As Figure 5.3.2 demonstrates, the harmonic oscillator (red curve) is a good approximation for the exact potential energy of a vibration (blue curve).

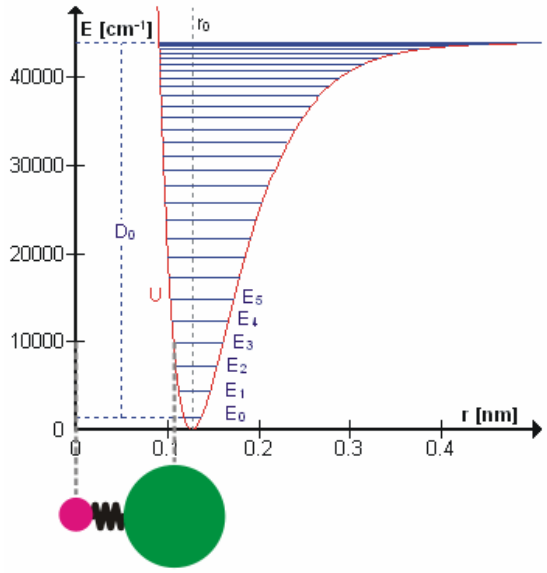


Figure 5.3.1: The vibration of the HCl molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, HCl is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed in wavenumbers. The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve. (CC BY-SA 3.0; Darekk2 via Wikipedia).

Adding anharmonic perturbations to the harmonic oscillator (Equation 5.3.2) better describes molecular vibrations. Anharmonic oscillation is defined as the deviation of a system from harmonic oscillation, or an oscillator not oscillating in simple harmonic

motion. Anharmonic oscillation is described as the restoring force is no longer proportional to the displacement. Adding the cubic term (Figure 5.3.2 ; green curve) improves the harmonic oscillation approximation especially under greater displacement from equilibrium.

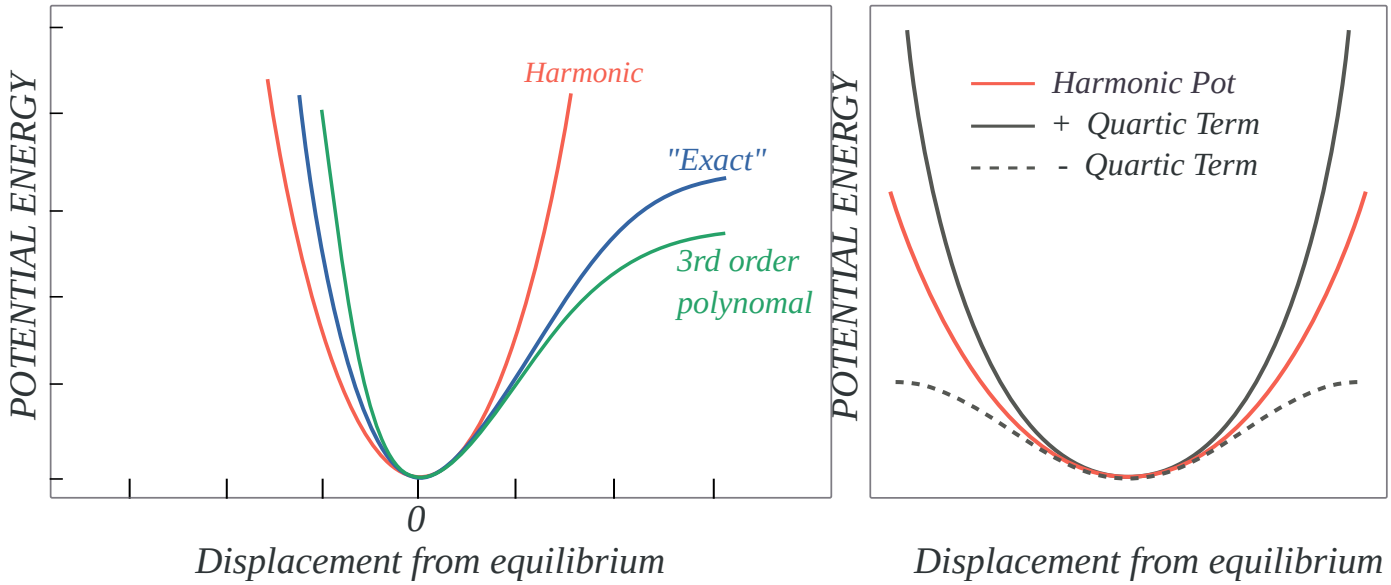


Figure 5.3.2: (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY 4.0; Ümit Kaya via LibreTexts)

Naturally, adding higher order anharmonic terms, like quartic terms (Figure $5.3.2; right$) improve the approximation. Almost all diatomics have experimentally determined potentials for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 with terms up to $n < 10$ determined of Equation $5.3.1$.

Figure 5.3.1 shows the the general potential with (numerically) calculated energy levels (E_0, E_1 etc.). D_o is the dissociation energy, which is different from the well depth D_e. These vibrational energy levels of this plot can be calculated using the harmonic oscillator model (i.e., Equation 5.3.1 with the Schrödinger equation) and have the general form

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + \text{higher terms}$$

where v is the vibrational quantum number and x_e and y_e are the first and second anharmonicity constants, respectively.

The $v = 0$ level is the vibrational ground state. Because this potential is less confining than a parabola used in the harmonic oscillator, the energy levels become **less widely** spaced at high excitation (Figure 5.3.1 ; top of potential).

Limitations of the Harmonic Oscillator Model for Molecular Vibrations

The harmonic oscillation is a great approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of energy, all transitions occur at the **same** frequency (i.e. single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

Morse Potentials are better Approximations of Vibrational Motion

A more powerful approach than just "patching up" the harmonic oscillator solution with anharmonic corrections is to adopt a different potential ($V(x)$). One such approach is the Morse potential, named after physicist Philip M. Morse, and a better approximation for the vibrational structure of the molecule than the harmonic oscillator because it explicitly includes the effects of *bond breaking* and accounts for the anharmonicity of real bonds (Figure 5.3.4).

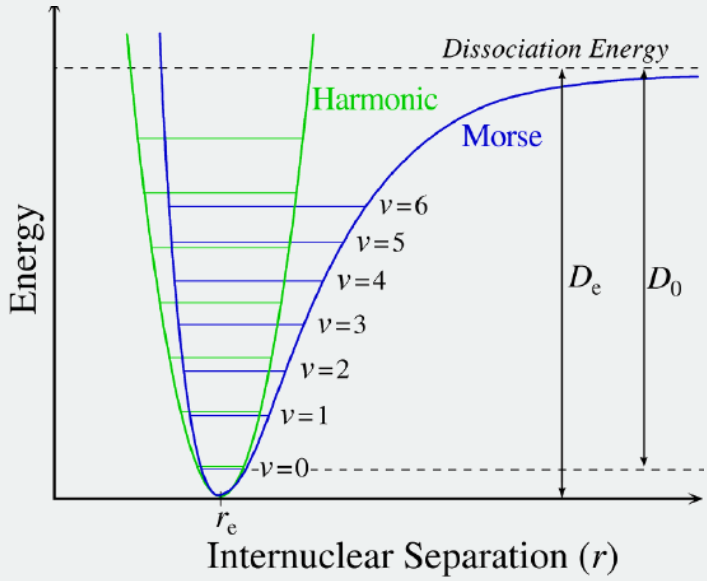


Figure 5.3.4: The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation D_0 due to the zero point energy of the lowest ($v = 0$) vibrational level. from Wikipedia.

The Morse Potential is a good approximation to $V(x)$ and is best when looking for a general formula for all x from 0 to ∞, not just applicable for the local region around the x_o:

$$V(x) = D(1 - e^{-\beta(x-x_0)})^2 \tag{5.3.3}$$

with $V(x = x_0) = 0$ and $V(x = \infty) = D$.

The Morse Potential (Figure 5.3.4) approaches zero at infinite r_e and equals $-D_e$ at its minimum (i.e. $r = r_e$). It clearly shows that the Morse potential is the combination of a short-range repulsion term (small r values) and a long-range attractive term (large r values).

Solving the Schrödinger Equation with the Morse Potential (Equation 5.3.3) is not trivial, but can be done analytically.

$$\hat{H}|\psi\rangle = E_n|\psi\rangle$$

with

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \frac{-\hbar^2 d^2}{2m\ dx^2} + D(1 - e^{-\beta(x-x_0)})^2\end{aligned}$$

The solutions and energies for the Morse potential will not be used in this course and will not be discussed in more detail.

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5.4: The Harmonic Oscillator Energy Levels

For a classical oscillator, we know exactly the position, velocity, and momentum as a function of time. The frequency of the oscillator (or normal mode) is determined by the reduced mass μ and the effective force constant k of the oscillating system and does not change unless one of these quantities is changed. There are no restrictions on the energy of the oscillator, and changes in the energy of the oscillator produce changes in the amplitude of the vibrations experienced by the oscillator.

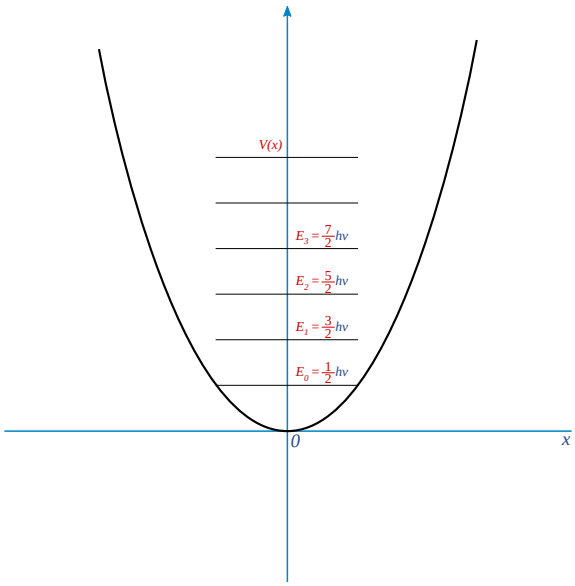


Figure 5.4.1 : Potential energy function and first few energy levels for harmonic oscillator. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For the quantum mechanical oscillator, the oscillation frequency of a given normal mode is still controlled by the mass and the force constant (or, equivalently, by the associated potential energy function). However, the energy of the oscillator is limited to certain values. The allowed quantized energy levels are equally spaced and are related to the oscillator frequencies as given by Equation 5.4.1 and Figure 5.4.1 .

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \left(v + \frac{1}{2}\right)h\nu \tag{5.4.1}$$

with

$$v = 0, 1, 2, 3, \cdots \infty$$

In a quantum mechanical oscillator, we cannot specify the position of the oscillator (the exact displacement from the equilibrium position) or its velocity as a function of time; we can only talk about the probability of the oscillator being displaced from equilibrium by a certain amount. This probability is given by

$$P_{Q \to Q+dQ} = \int_{Q}^{Q+dQ} \psi_v^*(Q)\psi_v(Q)dQ \tag{5.4.2}$$

We can, however, calculate the average displacement and the mean square displacement of the atoms relative to their equilibrium positions. This average is just $\langle Q \rangle$, the expectation value for Q, and the mean square displacement is $\langle Q^2 \rangle$, the expectation value for Q^2. Similarly we can calculate the average momentum $\langle P_Q \rangle$, and the mean square momentum $\left\langle P_Q^2 \right\rangle$, but we cannot specify the momentum as a function of time.

Physically what do we expect to find for the average displacement and the average momentum? Since the potential energy function is *symmetric* around $Q = 0$, we expect values of $Q > 0$ to be equally as likely as $Q < 0$. The average value of Q therefore should be zero.

These results for the average displacement and average momentum do not mean that the harmonic oscillator is sitting still. As for

the particle-in-a-box case, we can imagine the quantum mechanical harmonic oscillator as moving back and forth and therefore having an average momentum of zero. Since the lowest allowed harmonic oscillator energy, E_0, is $\frac{\hbar\omega}{2}$ and not 0, the atoms in a molecule must be moving even in the lowest vibrational energy state. This phenomenon is called the zero-point energy or the zero-point motion, and it stands in direct contrast to the classical picture of a vibrating molecule. Classically, the lowest energy available to an oscillator is zero, which means the momentum also is zero, and the oscillator is not moving.

Exercise 5.4.1

Compare the quantum mechanical harmonic oscillator to the classical harmonic oscillator at $v = 1$ and $v = 50$.

Answer available at the end of this section.

Since the average values of the displacement and momentum are all zero and do not facilitate comparisons among the various normal modes and energy levels, we need to find other quantities that can be used for this purpose. We can use the root mean square deviation (see also root-mean-square displacement) (also known as the standard deviation of the displacement) and the root-mean-square momentum as measures of the uncertainty in the oscillator's position and momentum.

For a molecular vibration, these quantities represent the standard deviation in the bond length and the standard deviation in the momentum of the atoms from the average values of zero, so they provide us with a measure of the relative displacement and the momentum associated with each normal mode in all its allowed energy levels. These are important quantities to determine because vibrational excitation changes the size and symmetry (or shape) of molecules. Such changes affect chemical reactivity, the absorption and emission of radiation, and the dissipation of energy in radiationless transitions.

The harmonic oscillator wavefunctions form an orthonormal set; this means that all functions in the set are normalized individually

$$\int_{-\infty}^{\infty} \psi_v^*(x)\psi_v(x)dx = 1 \tag{5.4.3}$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x)\psi_v(x)dx = 0 \;\text{ for }\; v' \neq v \tag{5.4.4}$$

The fact that a family of wavefunctions forms an orthonormal set is often helpful in simplifying complicated integrals. We will use these properties when we determine the harmonic oscillator selection rules for vibrational transitions in a molecule and calculate the absorption coefficients for the absorption of infrared radiation.

Finally, we can calculate the probability that a harmonic oscillator is in the classically forbidden region. What does this tantalizing statement mean? Classically, the maximum extension of an oscillator is obtained by equating the total energy of the oscillator to the potential energy, because at the maximum extension all the energy is in the form of potential energy. If all the energy weren't in the form of potential energy at this point, the oscillator would have kinetic energy and momentum and could continue to extend further away from its rest position. Interestingly, as we show below, the wavefunctions of the quantum mechanical oscillator extend beyond the classical limit, i.e. beyond where the particle can be according to classical mechanics.

The lowest allowed energy for the quantum mechanical oscillator is called the **zero-point energy,** $E_0 = \frac{\hbar\omega}{2}$. Using the classical picture described in the preceding paragraph, this total energy must equal the potential energy of the oscillator at its maximum extension. We define this classical limit of the amplitude of the oscillator displacement as Q_0. When we equate the zero-point energy for a particular normal mode to the potential energy of the oscillator in that normal mode, we obtain

$$\frac{\hbar\omega}{2} = \frac{kQ_0^2}{2} \tag{5.4.5}$$

The zero-point energy is the **lowest** possible energy that a quantum mechanical physical system may have. Hence, it is the energy of its ground state.

Recall that k is the effective force constant of the oscillator in a particular normal mode and that the frequency of the normal mode is given by Equation 5.4.1 which is

$$\omega = \sqrt{\frac{k}{\mu}} \tag{5.4.6}$$

Answers

At v=1 the classical harmonic oscillator poorly predicts the results of quantum mechanical harmonic oscillator, and therefore reality. At v=1 the particle will be near the ground state and the classical model will predict the particle to spend most it's time on the outer edges when the KE goes to zero and PE is at a maximum, while the quantum model says the opposite and that the particle will be more likely to be found in the center. At v=50 the quantum model will begin to match the classical much more closely, with the particle most likely to be found at the edges. The quantum model looking more like the classical at higher quantum numbers can be referred to as the correspondence principle.

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5.5: The Harmonic Oscillator and Infrared Spectra

Learning Objectives

- Understand how the quantum harmonic oscillator model can be used to interpret the infrared spectra of diatomic molecules
- Understand the origin of the transition moment integral and selection rules and how they are related

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups. IR spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

IR Spectroscopy

Transitions between vibrational energy levels can be induced about by absorption or emission of radiation. To understand this, knowledge of both the initial and final eigenstates is needed. The energy of the v^{th} eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.5.1}$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞. Equation 5.5.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \tag{5.5.2}$$

where ν_m is the vibrational frequency of the vibration. Equation 5.5.2 is often written as

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega$$

where ω is the angular frequency (i.e., $2\pi\nu$).

Transitions in vibrational energy levels can be brought about by absorption of radiation, provided the energy of the radiation ($h\nu_{photon}$) **exactly** matches the difference in energy ($\Delta E_{vv'}$) between the vibrational quantum state v to quantum state v'. This can be expressed as

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v)\, h\nu_m \end{aligned} \tag{5.5.3}$$

Let's consider only transitions between adjacent eigenstates (discussed in more details below) so

$$v' - v = \pm 1$$

which is positive if an IR photon is absorbed and negative if it is emitted. For the absorption of a IR photon, Equation 5.5.3 simplifies to

$$\begin{aligned} h\nu_{photon} &= h\nu_m \\ &= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \end{aligned} \tag{5.5.4}$$

The frequency of radiation ν_{photon} that will bring about this change is **identical** to the classical vibrational frequency of the bond ν.

The Wavenumber as a Unit of Energy

The cm^{-1} is the wavenumber scale and it can also be defined as 1/wavelength in cm. A wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{5.5.5}$$

$$= \frac{\nu\,(Hz)}{c\,(cm/s)} \tag{5.5.6}$$

Equation 5.5.3 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{5.5.7}$$

where c is the velocity of light (cm/s) and $\tilde{\nu}$ is the wavenumber of an absorption maximum (cm^{-1}).

Example 5.5.1: Hydrogen Halides

The force constants for typical diatomic molecules are in the range between 400 to 2000 $N \cdot m^{-1}$.

Molecule	HF	HCl	HBr	HI	CO	NO
Force constant, k ($N.m^{-1}$)	970	480	410	320	1860	1530

For the diatomic molecules listed above, calculate the following:

a. angular frequency ($\mathrm{rad} \cdot s^{-1}$)
b. natural frequency (Hz)
c. period (s)
d. separation between energy levels
e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$.

Solution

For HCl:

a. angular frequency

$$\omega = 5.45 \times 10^{14} \mathrm{rad} \cdot s^{-1}$$

b. natural frequency:

$$\nu = \frac{\omega}{2\pi} = 8.68 \times 10^{13}$$

c. period (s):

$$T = \frac{1}{\nu} = 1.15 \times 10^{-14}$$

d. separation between energy levels:

$$\Delta E = E_{v=1} - E_{v=0} = \hbar\omega = 5.75 \times 10^{-20}\ J$$

e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$:

$$3.46 \times 10^{-6}\, m$$

The electromagnetic radiation released (and absorbed) for vibrations is primarily in the infrared (IR) part of the spectrum. Calculating the above properties for the other molecules remains as an exercise.

Note: We did not designate the specific isotopes in the hydrogen halides above because that information was not required to solve these questions.

IR deals with the interaction between a molecule and radiation from the electromagnetic region ranging (4000- 40 cm^{-1}). The IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 μm. Conventionally the IR region is subdivided into three regions (Table 5.5.1): near IR, mid IR and far IR. Most of the IR used originates from the mid IR region.

Table 5.5.1: Regions of the IR Spectrum

Region	Wavelength	Wavenumbers ($\tilde{\nu}$), cm^{-1}	Frequencies (v), HZ
Near	0.78 -2.5	12800 - 4000	3.8 x 10^{14} - 1.2 x 10^{14}
Middle	2.5 - 50	4000 - 200	3.8 x 10^{14} - 1.2 x 10^{14}
Far	50 -100	200 -10	3.8 x 10^{14} - 1.2 x 10^{14}
Most Used	2.5 -15	4000 -670	3.8 x 10^{14} - 1.2 x 10^{14}

Example 5.5.2: Hydrogen Chloride

The $H^{35}Cl$ equilibrium bond length is 0.127 nm and the $v = 0$ to $v = 1$ transition is observed in the infrared at 2,886 cm^{-1}. Compute the vibrational energy of $H^{35}Cl$ in its lowest state.

a. Compute the classical limit for the stretching of the HCl bond from its equilibrium length in this state.
b. What percent of the equilibrium bond length is this extension?

Solution

The $H{-}Cl$ bond length is $0.127\ nm = 1.27 \times 10^{-10} m$ and the IR transition is observed at $2886\ cm^{-1}$. We first convert this to Hertz

$$2886\, cm^{-1}(3 \times 10^{10} cm/s) = 8.646 \times 10^{13} s^{-1} = 8.646 \times 10^{13}\, Hz$$

The equations for the energy of the v^{th} eigenstate of a harmonic oscillator is

$$E_v = (v + 1/2)\hbar\omega$$

So the ground state ($v = 0$) energy is

$$E_0 = \frac{1}{2}\hbar\omega$$

with

$$\begin{aligned}\omega &= 2\pi\nu \\ &= 5.54 \times 10^{14}\, rad/s\end{aligned}$$

We can then extra the ground state vibrational energy (aka zero-point energy) from

$$\begin{aligned}E_o &= \frac{1}{2}\hbar\omega \\ &= \frac{1}{2}\hbar(5.54 \times 10^{14} rad/s) \\ &= 2.916 \times 10^{-20}\, J\end{aligned}$$

The classical limit of the stretch is denoted as Q_0, this can be equated as potential energy in relation to the total E_0 found above as, at E_0, all of the energy would be potential energy in the form of the stretch. In comparison to the classic spring potential

$$V = \frac{1}{2}kQ_0^2$$

As described above, we can relate the two as

$$\frac{1}{2}\hbar\omega = \frac{1}{2}kQ_0^2$$

or,

$$2.916 \times 10^{-20} J = \frac{1}{2}481 Q_0^2$$

where $Q_0 = 1.10 \times 10^{-11} m = 0.0110\ nm$.

Lastly, this classical limit to length can be compared to the equilibrium bond length by a simple relation of

$$\begin{aligned}\text{Percent bond length} &= \frac{Q_0}{x_{eq}} \times 100\% \\ &= \frac{0.0110\, nm}{0.127\, nm} \times 100\% \\ &= 8.66\%\end{aligned}$$

Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can transition from one vibrational energy state to another. Which transitions between vibrational states are allowed? When discussing the Bohr hydrogen atom in Chapter 1, we identified multiple transitions between different states as being responsible for the line spectra emission of the hydrogen atom. No limitations were identified so that any transition between any starting state and ending state was possible and this resulted in a complex pattern in the spectra. As we will identify later on, when considering mulit-electron atoms, there are **selection rules** that limits which transitions will be observed (i.e., are allowed).

A similar situation exist for the harmonic oscillator and IR transitions and a set of selection rules must be satisfied to ensure a particular transition is allowed. Selection rules result from evaluating a **transition moment integral** that expresses the probability of a transition from the v to the v' eigenstates:

$$\mu_T = \langle \psi_{v'} | \hat{\mu}(x) | \psi_v \rangle \tag{5.5.8}$$

$$= \int_{-\infty}^{\infty} \psi^*_{v'}(x) \hat{\mu}(x) \psi_v(x) dx \tag{5.5.9}$$

When the transition moment integral is zero for two specific eigenstates (i.e., $\psi_v(x)$ and $\psi'_v(x)$), then the probability of observing that transition is zero. In this case, this transition is called a **forbidden transition** (i.e., it will not be obversed). Transitions with low probabilities are call "weakly allowed transitions" since they will have small amplitudes in spectra and transitions with high probabilities are "strongly allowed transitions" and will exhibit high amplitudes in spectra.

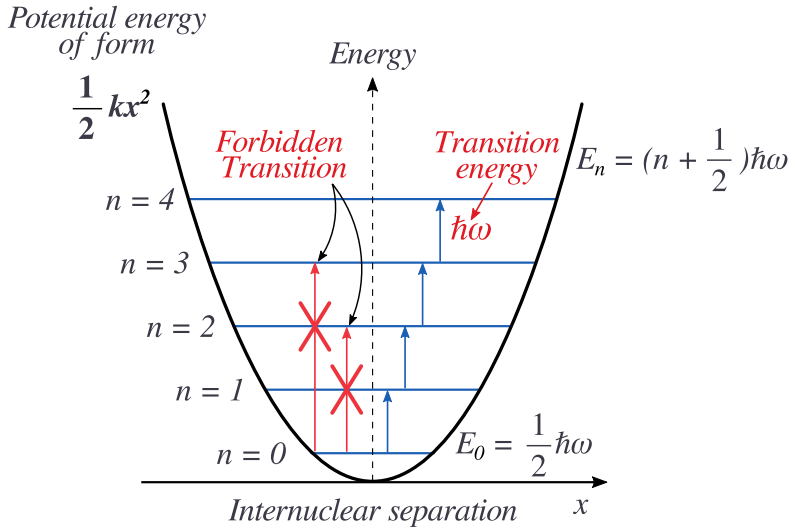


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 5.5.9, we need to express the dipole moment operator, $\hat{\mu}$, in terms of the magnitude of the vibration x. The dipole moment operator is defined as

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{5.5.10}$$

where the two sums are over all the electrons and nuclei and involve the particle charge ($-e$ or q) multiplying the position vector ($\vec{r}$ or $\vec{R}$, respectively). We can obtain this dipole moment operator in terms of the magnitude of the displacement coordinate, x, in a simple way by using a **Taylor series expansion** for the dipole moment around the equlibrium position ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left.\frac{d\mu(x)}{dx}\right|_{x=0} x + \left.\frac{d^2\mu(x)}{dx^2}\right|_{x=0} x^2 + \cdots \tag{5.5.11}$$

Retaining only the first two terms and substituting into Equation 5.5.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left.\frac{d\mu(x)}{dx}\right|_{x=0} \int_{-\infty}^{\infty} x\psi^*_{v'}(x)\psi_v(x)dx \tag{5.5.12}$$

where $\mu_{x=0}$ is the **dipole moment** of the molecule when the nuclei are at their equilibrium positions, and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

is the *linear* change in the dipole moment due to the displacement of the nuclei in the normal mode. The derivative is the linear change because it multiplies x and not a higher power of x in Equation 5.5.11. Both μ and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

are moved outside of the integral because they are constants that no longer depend on x because they are evaluated at $x = 0$.

The integral in the first term in Equation 5.5.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 5.5.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1 . Also note that the second term is zero if

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0} = 0 \tag{5.5.13}$$

Hence we can identify two "rules" that need to be satisfied for an IR photon to be absorb (or emitted) by a vibrating molecule.

Rules for IR Absorption

For IR absorption to occur two conditions must be met:

1. There must be a **change** in the dipole moment of the molecule as a result of a molecular vibration (or rotation). The change (or oscillation) in the dipole moment allows interaction with the alternating electrical component of the IR radiation. Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.
2. If the frequency of the radiation ν_{photon} matches the natural frequency of the vibration (ν_m), the IR photon can be absorbed and the amplitude of the vibration increases.

Exercise 5.5.1

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation 5.5.12 is 0 unless $v' = v \pm 1$.

If we are to observe absorption of infrared radiation due to a vibrational transition in a molecule, the transition moment cannot be zero. This condition requires that the dipole moment derivative Equation 5.5.13 **cannot** be zero and that the vibrational quantum number change by one unit. The normal coordinate motion must cause the dipole moment of the molecule to change in order for a molecule to absorb infrared radiation. If the normal coordinate oscillation does not cause the dipole moment to change then $\mu_T = 0$ and no infrared absorption is observed. So we can

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{5.5.14}$$

Consider oxygen and nitrogen molecules. Because they are symmetrical, their dipole moments are zero, $\mu = 0$. Since the vibrational motion (only bond stretching for a diatomic molecule) preserves this symmetry, the change in the dipole moment due to the vibrational motion also is zero, $\frac{d\mu(x)}{dx} = 0$. Consequently, oxygen and nitrogen do not absorb infrared radiation as a result of vibrational motion.

Exercise 5.5.2

Explain why the molar absorptivity or molar extinction coefficients (ϵ) in Beer's Law for the IR absorption of some vibrations are greater than others.

Answer available at the end of this section.

The case $v' = v + 1$ corresponds to going from one vibrational state to a higher energy one by absorbing a photon with energy $h\nu$. The case $v' = v - 1$ corresponds to a transition that emits a photon with energy $h\nu$. In the harmonic oscillator model infrared spectra are very simple; only the fundamental transitions, $\Delta = \pm 1$, are allowed. The associated transition energy is $\hbar\omega$, according

to Equation 5.5.4. The transition energy is the change in energy of the oscillator as it moves from one vibrational state to another, and it equals the photon energy.

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= h\upsilon_{photon} \\ &= \hbar\omega_{oscillator}\end{aligned}$$

For perfect harmonic oscillators, the only possible allowed transitions are $\Delta = \pm 1$ with all other transitions forbidden (Figure 5.5.1). This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of a single line since the energy levels are equally spaced in the harmonic oscillator model (Figure 5.5.1). If the vibration were anharmonic, then the levels would not be equally spaced and then transitions from $\upsilon = 0$ to $\upsilon = 1$ and from $\upsilon = 1$ to $\upsilon = 2$, etc. would occur at different frequencies.

Only the fundamental transitions, $\Delta = \pm 1$, are observed in infrared spectra within harmonic oscillator model.

The actual IR spectrum is more complex, especially at high resolution. There is a fine structure due to the rotational states of the molecule. These states will be discussed in the next chapter. The spectrum is enriched further by the appearance of lines due to transitions corresponding to $\Delta = \pm n$ where $n > 1$. These transitions are called **overtone** transitions and their appearance in spectra despite being forbidden in the harmonic oscillator model is due to the anharmonicity of molecular vibrations. Anharmonicity means the potential energy function is not strictly the harmonic potential. The first overtone, $\Delta\upsilon = 2$, generally appears at a frequency slightly less than twice that of the fundamental, i.e. the frequency due to the $\Delta\upsilon = 1$ transition.

Exercise 5.5.3: Hydrogen Chloride

Compute the approximate transition frequencies in wavenumber units for the first and second overtone transitions in HCl given that the fundamental is at 2,886 cm^{-1}.

Answers

Qualitatively, if the probability of transition is large, then the molar absorptivity is large. And similar if the transition were not allowed, then there will be no intensity and no observed peak in the spectrum. Transitions can be "partially allowed" as well, and these bands appear with a lower intensity than the full allowed transitions.

When looking at the Beer's Law

$$A = \epsilon\ c\ l$$

where A is absorbance. ϵ is the molar absorptivity, c is the molar concentration and l is the optical path length

We are only looking at the change in the molar absorptivity as the IR absorptions of vibrations vary. To do this we have to look at the transition moment integral

$$\mu_T = \langle \psi_{\upsilon'} | \not{\mu}(x) | \psi_{\upsilon} \rangle$$

When the transition moment integral is zero, there is no transition as it is not allowed under the selection rules. This means that the IR is not absorbing any vibrations and therefore the molar absorptivity is zero, which means that absorbance according to Beer's Law is zero. As the transition moment integral increases, the molar absorptivity also increases and the overall absorbance increases.

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5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials

Learning Objectives

- The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For a diatomic molecule, there is only one vibrational mode, so there will be only a single set of vibrational wavefunctions with associated energies for this system. For polytatomic molecules, there will be a set of wavefunctions with associated energy associated with each vibrational mode.

The Hamiltonian operator, the general quantum mechanical operator for energy, includes both a kinetic energy term, $\hat{T}$, and a potential energy term, $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \tag{5.6.1}$$

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero. As shown in Equation 5.6.1, the classical expression for the energy of a harmonic oscillator includes both a kinetic energy term and the harmonic potential energy term. Transforming this equation into the corresponding Hamiltonian operator gives,

$$\hat{H}(q) = \frac{1}{2\mu}\hat{P}_q^2 + \frac{k}{2}\hat{q}^2 \tag{5.6.2}$$

where $\hat{q}$ is the operator for the length of the normal coordinate, and $\hat{P}_q$ is the momentum operator associated with the normal coordinate. μ is an effective (reduced) mass, and k is an effective force constant, and these quantities will be different for each of the normal modes (vibrations).

Substituting the definitions for the operators yields

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{k}{2}q^2 \tag{5.6.3}$$

since the operator for position or displacement is just the position or displacement. The time-independent Schrödinger Equation then becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(q)}{dq^2} + \frac{k}{2}q^2\psi_v(q) = E_v\psi_v(q) \tag{5.6.4}$$

or upon rearranging

$$\frac{d^2\psi_v(q)}{dq^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{k}{2}q^2\right)\psi_v(q) = 0 \tag{5.6.5}$$

This differential equation is not straightforward to solve. Rather than fully develop the details of the solution, we will outline the method used because it represents a common strategy for solving differential equations. The steps taken to solve Equation 5.6.5 are to simplify the equation by collecting constants in the parameter β

$$\beta^2 = \frac{\hbar}{\sqrt{\mu k}} \tag{5.6.6}$$

and then changing the variable from q to x where

$$x = \frac{q}{\beta} \tag{5.6.7}$$

so that

$$\frac{d^2}{dq^2} = \frac{1}{\beta^2}\frac{d^2}{dx^2} \tag{5.6.8}$$

After substituting Equations 5.6.6 and 5.6.8 into Equation 5.6.5, the differential equation for the harmonic oscillator becomes

$$\frac{d^2\psi_v(x)}{dx^2} + \left(\frac{2\mu\beta^2 E_v}{\hbar^2} - x^2\right)\psi_v(x) = 0 \tag{5.6.9}$$

Exercise 5.6.1

Make the substitutions given in Equations 5.6.6 and 5.6.8 into Equation 5.6.5 to get Equation 5.6.9.

Solving for the Quantum Wavefunctions

A common strategy for solving differential equations, which is employed here, is to find a solution that is valid for large values of the variable and then develop the complete solution as a product of this asymptotic solution and a power series. Since the potential energy approaches infinity as x and the coordinate q approach infinity, the wavefunctions must approach zero (this is, the wavefunctions must **converge to zero**):

$$\lim_{x\to\infty} \psi_v(x) = 0 \tag{5.6.10}$$

The function that has this property and satisfies the differential equation for large values of x is the exponential function, i.e.,

$$\lim_{x\to\infty} \phi_v(x)\exp\left(\frac{-x^2}{2}\right) = 0 \tag{5.6.11}$$

where the wavefunctions are

$$\psi_v(x) \propto \phi_v(x)\exp\left(\frac{-x^2}{2}\right)$$

The general expression for a power series of $\phi_v(x)$ is

$$\begin{aligned}\phi_v(x) &= \sum_{n=0}^{\infty} c_n(v)x^n \\ &= c_n(v)x + c_n(v)x^2 + c_n(v)x^3 + \cdots\end{aligned}$$

which can be truncated after the first term, after the second term, after the third term, etc. to produce a set of polynomials. There is one polynomial for each value of v where v can be equal to any integer value including zero.

$$\sum_{n=0}^{v} c_n x^n \tag{5.6.12}$$

Each of the truncations of the power series in Equation 5.6.12 can be multiplied by the exponential function in Equation 5.6.11 to create a family of valid solutions to the differential equation in Equation 5.6.9.

$$\psi_v(x) = \sum_{n=0}^{v} c_n x^n \exp\left(\frac{-x^2}{2}\right) \tag{5.6.13}$$

Exercise 5.6.2

Write the first four polynomials, $v = 0$ to $v = 1$, $v = 12$, $v = 13$, $v = 14$ for Equation 5.6.12 and use suitable software to prepare plots of these polynomials. Identify the curves in the plots.

Exercise 5.6.3

Confirm that the wavefunction given by Equation 5.6.13 is a solution to the harmonic oscillator Schrödinger Equation in Equation 5.6.9 for $v = 0$ and $v = 1$.

Hermite Polynomials

While polynomials in general approach ∞ (or $-\infty$) as x approaches ∞, the decreasing exponential term overpowers the polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of x or $-x$. The exact forms of polynomials that solve Equation 5.6.9 are the **Hermite polynomials**, which are standard mathematical functions known from the work of Charles Hermite. The first eight Hermite polynomials, $H_v(x)$, are given below.

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$
- $H_6 = -120 + 720x^2 - 480x^4 + 64x^6$
- $H_7 = -1680x + 3360x^3 - 1344x^5 + 128x^7$

The first six Hermite polynomials are plotted in Figure 5.6.1 . Hermite polynomials will be discussed in more detail in the following Section.

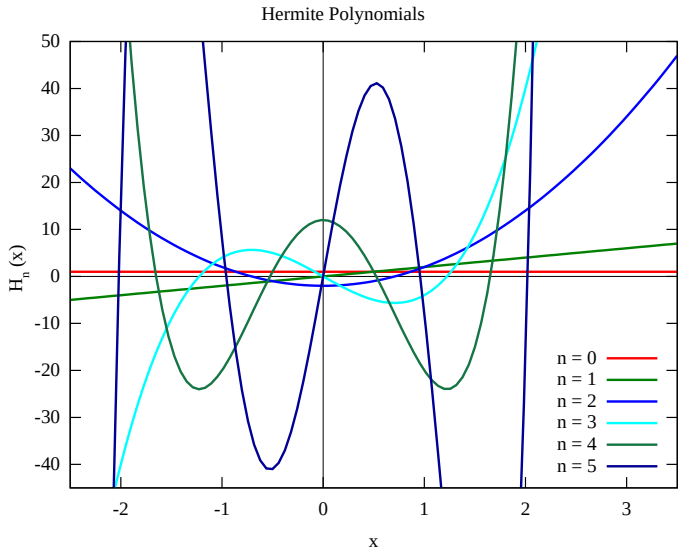


Figure 5.6.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

Exercise 5.6.4

Determine the units of β and the units of x in the Hermite polynomials.

Because of the association of the wavefunction with a probability density, it is necessary for the wavefunction to include a normalization constant, N_v.

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \tag{5.6.14}$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \tag{5.6.15}$$

Alternative and More Common Formulation of Harmonic Oscillator Wavefunctions

The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate (Equation 5.6.7) and a different constant α:

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

so Equation 5.6.15 becomes

$$\psi_v(x) = N_v'' H_v(\sqrt{\alpha} Q) e^{-\alpha Q^2/2}$$

with a slightly different normalization constant

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Exercise 5.6.5

Compute the normalization factor for $\psi_v(x)$ where $v = 0$ and $v = 4$. What is the purpose of N_v?

The energy eigenvalues for a quantum mechanical oscillator also are obtained by solving the Schrödinger equation. The energies are restricted to discrete values

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \tag{5.6.16}$$

with $v = 0, 1, 2, 3, \cdots$.

The energies depend both on the quantum number, v, and the oscillator frequency

$$\omega = \sqrt{\frac{k}{\mu}}$$

which in turn depends on the spring constant k and the reduced mass of the vibration μ.

Exercise 5.6.6

Determine the energy for the first ten harmonic oscillator energy levels in terms of $\hbar\omega$. Sketch an energy level diagram of these energies.

1. What insights do you gain from Equation 5.6.16, your calculations, and your diagram?
2. Is it possible to have a molecule that is not vibrating?
3. In terms of $\hbar\omega$, what is the energy of the photon required to cause a transition from one vibrational state to the next higher one?
4. If a transition from energy level $v = 9$ to $v = 10$ were observed in a spectrum, where would that spectral line appear relative to the one for the transition from level $v = 0$ to $v = 1$?
5. If a vibrational transition is observed at 3000 cm-1 in an infrared spectrum, what is the value of $\hbar\omega$ for the normal mode?
6. Identify all the possible meanings of $\Delta E = h\nu$ and the definition of the frequency, ν, in each case.

The normalized wavefunctions for the first four states of the harmonic oscillator are shown in Figure 5.6.2 , and the corresponding probability densities are shown in Figure 5.6.3 . You should remember the mathematical and graphical forms of the first few harmonic oscillator wavefunctions, and the correlation of v with E_v. The number of nodes in the wavefunction will help you to remember these characteristics. Also note that the functions fall off exponentially and that the symmetry alternates. For v equal to an even number, ψ_v is gerade; for v equal to an odd number, ψ_v is ungerade.

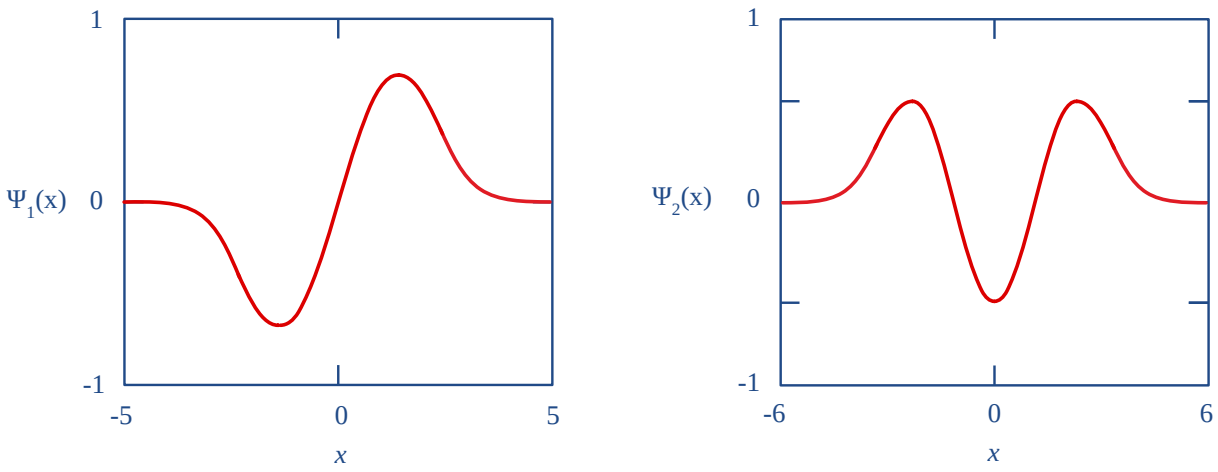


Figure 5.6.2 : The harmonic oscillator wavefunctions describing the four lowest energy states.

Exercise 5.6.7

Write a few sentences describing and comparing the plots in Figure 5.6.2 . How many nodes are there as a function of v? Do the wavefunctions converge at extreme displacement? Where is the most likely displacements for the oscillator to be found?

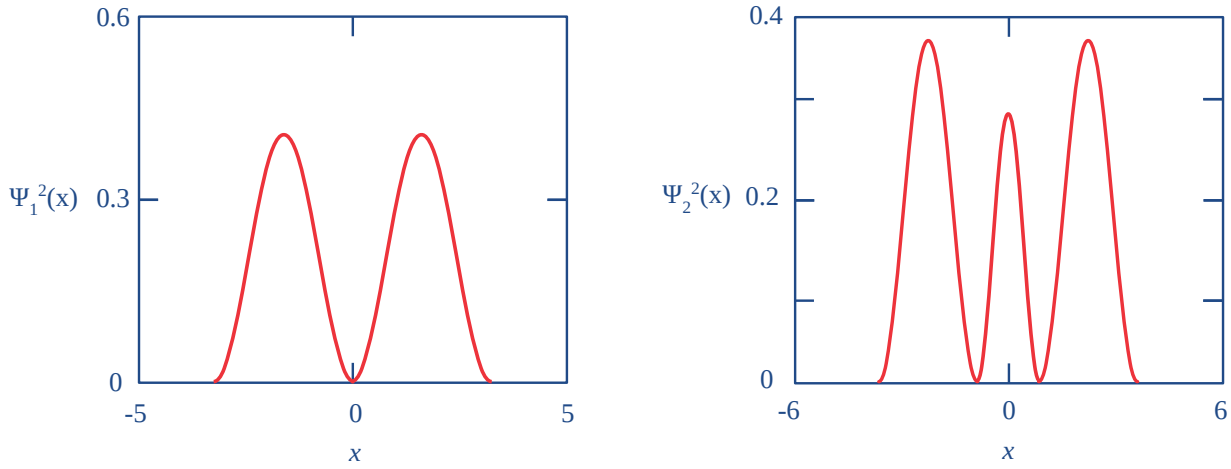


Figure 5.6.3 : The probability densities for the four lowest energy states of the harmonic oscillator.

Exercise 5.6.8

Explain how Figure 5.6.3 is related to Figure 5.6.2 . Explain the physical significance of the plots in Figure 5.6.3 in terms of the magnitude of the normal coordinate Q. Couch your discussion in terms of the HCl molecule. How would you describe the location of the atoms in each of the states? How does the oscillator position correspond to the energy of a particular level?

Answer available at the end of this section.

Exercise 5.6.9

Plot the probability density for energy level 10 of the harmonic oscillator. How many nodes are present? Plot the probability density for energy level 20. Compare the plot for level 20 with that of level 10 and level 1. Compare these quantum mechanical probability distributions to those expected for a classical oscillator. What conclusion can you draw about the probability of the location of the oscillator and the length of a chemical bond in a vibrating molecule? Extend your analysis to include a very high level, like level 50.

In completing Exercise 5.6.9 , you should have noticed that as the quantum number increases and becomes very large, the probability distribution approaches that of a classical oscillator. This observation is very general. It was first noticed by Bohr, and is called the Bohr Correspondence Principle. This principle states that classical behavior is approached in the limit of large values for a quantum number. A classical oscillator is most likely to be found in the region of space where its velocity is the smallest. This situation is similar to walking through one room and running through another. In which room do you spend more time? Where is it more likely that you will be found?

Examination of the quantum mechanical wavefunction for the lowest-energy state reveals that the wavefunction $\psi_0(x)$ extends beyond the classical limit (i.e., outside of the harmonic oscillator well, albeit slightly). Higher energy states have higher total energies, so the classical limits to the amplitude of the displacement will be larger for these states.

Tunneling in the Quantum Harmonic Oscillator

The observation that the wavefunctions are not zero at the classical limit means that the quantum mechanical oscillator has a finite probability of having a displacement that is larger than what is classically possible. The oscillator can be in a region of space where the potential energy is greater than the total energy. Classically, when the potential energy equals the total energy, the kinetic energy and the velocity are zero, and the oscillator cannot pass this point. A quantum mechanical oscillator, however,

has a finite probability of passing this point. For a molecular vibration, this property means that the amplitude of the vibration is larger than what it would be in a classical picture. In some situations, a larger amplitude vibration could enhance the chemical reactivity of a molecule.

Exercise 5.6.10

Plot the probability density for $v = 0$ and $v = 1$ states. Mark the classical limits on each of the plots, since the limits are different because the total energy is different for $v = 0$ and $v = 1$. Shade in the regions of the probability densities that extend beyond the classical limit.

We should be able to calculate the probability that the quantum mechanical harmonic oscillator is in the classically forbidden region for the lowest energy state of the harmonic oscillator, the state with $v = 0$. The classically forbidden region is shown by the shading of the regions beyond Q_0 in the graph you constructed for Exercise 5.6.3 . The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region (Figure 5.6.3). To calculate this probability, we use

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \tag{5.6.17}$$

because the integral from 0 to Q_0 for the allowed region can be found in integral tables and the integral from Q_0 to ∞ cannot. The form of the integral, $P[\text{allowed}]$, to evaluate is

$$P[\text{allowed}] = 2\int_0^{Q_0} \psi_0^*(Q)\psi_0(Q)dQ \tag{5.6.18}$$

The factor 2 appears in Equation 5.6.18 from the chancing the limits of integration from $-Q_0$ to $+Q_0$ into 0 to $+Q_0$; we can do this since the integrand is an even function, i. e., $f(-x) = f(x)$. To evaluate the integral in Equation 5.6.18, use the wavefunction and do the integration in terms of x. Recall that for $v = 0$, $Q = Q_0$ corresponds to $x = 1$. Including the normalization constant, Equation 5.6.18 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}}\int_0^1 \exp(-x^2)dx \tag{5.6.19}$$

The integral in Equation 5.6.19 is called an error function (ERF) and can only be evaluated numerically. Values can be found in books of mathematical tables. When the limit of integration is 1, ERF(l) = 0.843 and P[forbidden] = 0.157. This result means that the quantum mechanical oscillator can be found in the forbidden region 16% of the time. This effect is substantial and leads to the phenomenon called *quantum mechanical tunneling*.

Exercise 5.6.11

Numerically verify that $P[\text{allowed}]$ in Equation 5.6.19 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

Answers

Figure 5.6.2 is simply the wavefunction in Figure 5.6.1 squared. The normal coordinate is the linear combination of the atomic cartesian coordinates. As Q is often in relation to the energy (kinetic and potential), they would be displaced by a certain amount dependent on Q (energy) along with an increase in nodes. This displacement is apparent when comparing the ascending energy levels of each of the wavefunctions. In the n=0 (first) energy state, it is most probable to be found between -2, 2. (in a range of -4, 4) In the second energy state, it is likely to be between -2.5, 2.5 (range -5, 5), third level: (-3,3) (range -6,6), fourth level (-4,4) (range -6,6).

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5.7: Hermite Polynomials are either Even or Odd Functions

Learning Objectives

- Understand key properties of the Hermite polynomials including orthogonality and symmetry.
- Be proficient at using symmetries of integrands to quickly solve integrals.

Hermite polynomials were defined by Laplace (1810) though in scarcely recognizable form, and studied in detail by Chebyshev (1859). Chebyshev's work was overlooked and they were named later after Charles Hermite who wrote on the polynomials in 1864 describing them as new. They were consequently not new although in later 1865 papers Hermite was the first to define the multidimensional polynomials. The first six Hermite polynomial are plotted in Figure 5.7.1 .

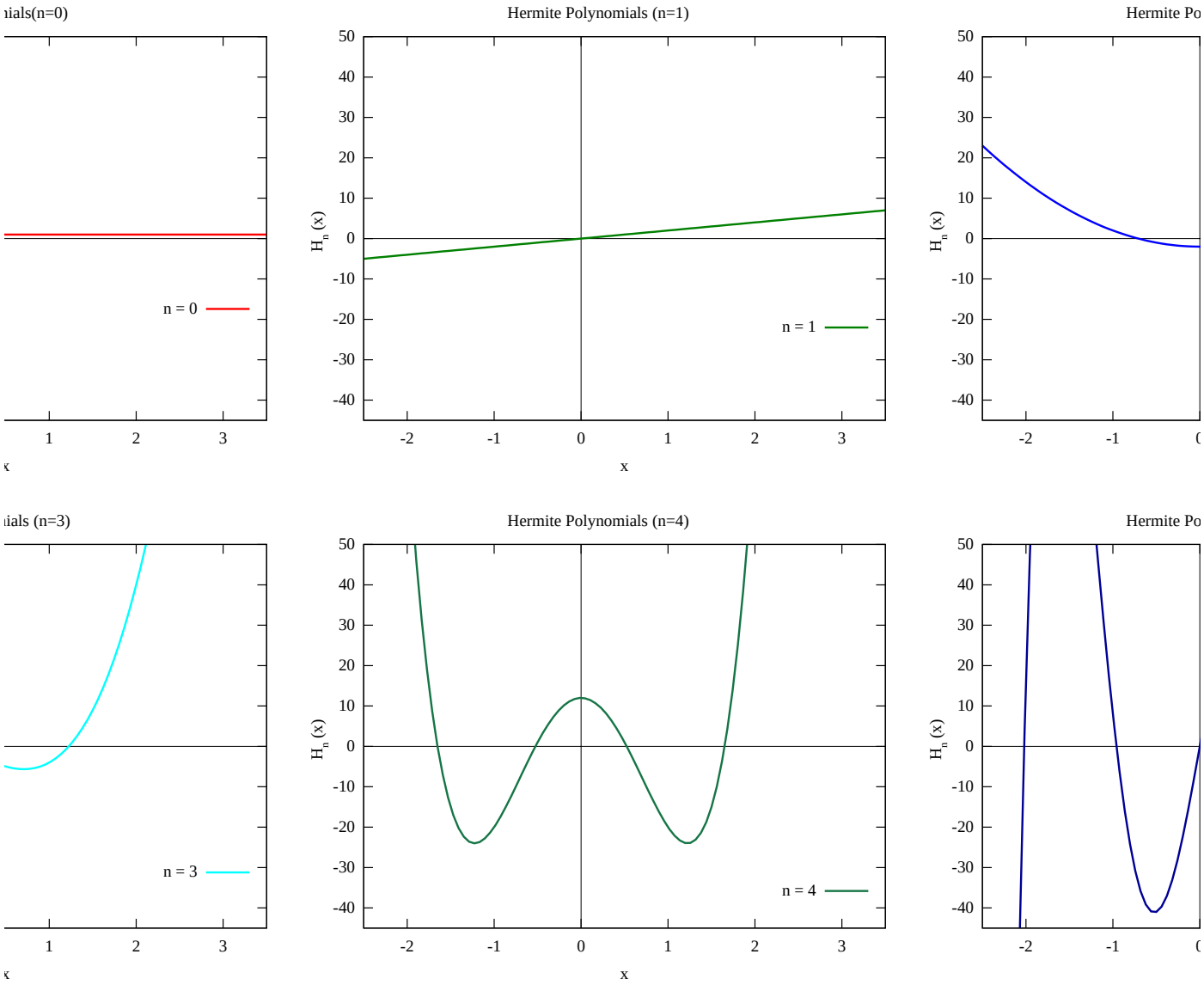


Figure 5.7.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

Generating Formula

Any Hermite polynomial $H_n(x)$ can be generated from a previous one $H_{n-1}(x)$ via the following using the recurrence relation

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x). \tag{5.7.1}$$

Hermite Polynomials are Symmetric

Let $f(x)$ be a real-valued function of a real variable.

- Then f is **even** if the following equation holds for all x and -x in the domain of f
$$f(x) = f(-x)$$
- Then f is **odd** if the following equation holds for all x and -x in the domain of f
$$-f(x) = f(-x)$$

Even and odd are terms used to describe particularly well-behaved functions. An *even* function is symmetric about the y-axis (Figure 5.7.2 ; left). That is, if we reflect the graph of the function in the y-axis, then it does not change. Formally, we say that f is even if, for all x and $-x$ in the domain of f, we have

$$f(-x) = f(x)$$

Two examples of even functions are $f(x) = x^2$ and $f(x) = \cos x$.

An *odd* function has rotational symmetry of order two about the origin (Figure 5.7.2 ; middle). That is, if we rotate the graph of the function 180° about the origin, then it does not change. Formally, we say that ff is odd if, for all x and $-x$ in the domain of f, we have

$$f(-x) = -f(x)$$

Examples of odd functions are $f(x) = x^3$ and $f(x) = \sin x$.

Naturally, not all functions can be classified as even or odd. For example $f = x^3 + 1$ shown in the right side of Figure 5.7.2 , is neither.

You can also think of these properties as symmetry conditions at the origin. More symmetries in 3D space are discussed in Group Theory.

Without proof, we can identify several key features involving multiplication properties of even and odd functions:

- The product of two **even** functions is an **even** function.
- The product of two **odd** functions is an **even** function.
- The product of an **even** function and an **odd** function is an odd function.

This can be shown graphically as a product table like that in Table 5.7.1 .

Table 5.7.1 : Product table of 1D Functions

Product table	Odd Function (anti-symmetric)	Even Function (symmetric)	No symmetry (neither)
Odd Function (anti-symmetric)	Even Function (symmetric)	Odd Function (anti-symmetric)	who knows
Even Function (symmetric)	Odd Function (anti-symmetric)	Even Function (symmetric)	who knows
No symmetry (neither)	who knows	who knows	who knows

Notice that the Hermite polynomials in Figure 5.7.1 oscillate from even to odd. We can take advantage of that aspect in our calculation of Harmonic Oscillator wavefunctions. Hermite Polynomial is an even or odd function depends on its degree n. Based on

$$H_n(-x) = (-1)^n H_n(x) \tag{5.7.2}$$

- $H_n(x)$ is an even function, when n is even.
- $H_n(x)$ is an odd function, when n is odd.

Integration over Symmetric Functions

You often consider integrals of the form

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x$$

If f is odd or even, then sometimes you can make solving this integral easier. For example, we can rewrite that integral in the following way:

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x = \int_{-a}^{0} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{5.7.3}$$

$$= \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{5.7.4}$$

For an even function, we have $f(-x) = f(x)$ and Equation 5.7.4 can be simplified

$$I = \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x$$
$$= 2\int_{0}^{a} f(x)\,\mathrm{d}x$$

For an odd function, we have $f(-x) = -f(x)$ and Equation 5.7.4 can be simplified

$$I = -\int_{0}^{a} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x$$
$$= 0$$

That's what it means to simplify the integration: the integral of an odd or even function over the interval $[-L, L]$ can be put into a nicer form (and sometimes we can see that it vanishes without ever computing an integral).

Example 5.7.1

Technically, evaluating the orthogonality of Hermite polynomials requires integrating over the $\exp(-x^2)$ weight function (Equations 5.7.5 and 5.7.6).

Solution

For the Hermite polynomials $H_n(x)$, the relevant inner product (using Dirac Notation)

$$\langle f, g\rangle = \int_{-\infty}^{\infty} f(x)g(x)\exp(-x^2)\,\mathrm{d}x$$

While the $H_2(x)H_3(x)$ product is indeed an odd function (Table 5.7.1), while $exp(-x^2)$ is even. Their product is odd, and thus $\langle f, g\rangle$ certainly ought to be zero.

Symmetry is an important aspect of quantum mechanics and mathematics, especially in calculating integrals. Using this symmetry, integrals can be identified to be equal to zero without explicitly solving them. For example, the integral of an odd

integrand over all possible values will **always** be zero irrespective of the exact nature of the function:

$$\int_{-\infty}^{\infty} f(x)\,dx = 0$$

This simplifies calculations greatly as demonstrated in the following chapters.

Hermite Polynomials are Orthogonal

Hermite polynomials $H_n(x)$ are *n*th-degree polynomials for *n* = 0, 1, 2, 3 and form an orthogonal set of functions for the weight function $e^{-x^2/2}$. The exact relation is:

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 0 \tag{5.7.5}$$

if $m \neq n$ and

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 2^n n!\sqrt{\pi} \tag{5.7.6}$$

if $m = n$.

This will not be proved, but can the demonstrated using any of the Hermite polynomials listed in the previous section. The orthogonality property becomes important when solving the Harmonic oscillator problems. Note that the integral of Equation 5.7.6 is important for normalizing the quantum harmonic oscillator wavefunctions discussed in last Section.

Example 5.7.2 : Hermite Polynomials are Orthogonal

Demonstrate that $H_2(x)$ and $H_3(x)$ are orthogonal.

Solution

We need to confirm

$$\int_{-\infty}^{\infty} H_2(x)H_3(x)dx = 0$$

or when substituted

$$\int_{-\infty}^{\infty} (4x^2-2)(8x^3-12x)dx = 0$$

because it says I need to show it's orthogonal on $[-\infty,\infty]$ or we can just evaluate it on a finite interval $[-L,L]$, where L is a constant.

$$\begin{aligned}\int_{-L}^{L} (4x^2-2)(8x^3-12x)dx &= 8\left(\frac{2x^6}{3}-2x^4+\frac{3x^2}{2}\right)\Bigg|_{-L}^{L} \\ &= 8\left(\frac{2L^6}{3}-2L^4+\frac{3L^2}{2}\right)-8\left(\frac{2(-L)^6}{3}-2(-L)^4+\frac{3(-L)^2}{2}\right) \\ &= 0.\end{aligned}$$

Concluding

Hermite polynomials are a component in the harmonic oscillator wavefunction that dictates the symmetry of the wavefunctions. If your integration interval is symmetric around 0, then the integral over *any* integrable odd function is zero, no exception. Therefore as soon as you've found that your integrand is odd and your integration interval is symmetric, you're done. Also, for general

functions, if you can easily split them into even and odd parts, you only have to consider the integral over the even part for symmetric integration intervals.

Another important property is that the product of two even or of two odd functions is even, and the product of an even and an odd function is odd. For example, if ff is even, $x \mapsto f(x)\sin(x)$ is odd, and therefore the integral over it is zero (provided it is well defined).

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5.8: The Energy Levels of a Rigid Rotor

Learning Objectives

- Compare the classical and quantum rigid rotor in three dimensions
- Demonstrate how to use the Separation of Variable technique to solve the 3D rigid rotor Schrödinger Equation
- Identify and interpret the two quantum numbers for a 3D quantum rigid rotor including the range of allowed values
- Describe the wavefunctions of the 3D quantum rigid rotor in terms of nodes, average displacements and most probable displacements
- Describe the energies of the 3D quantum rigid rotor in terms of values and degeneracies

Rigid rotor means when the distance between particles do not change as they rotate. A rigid rotor only approximates a rotating diatomic molecular if vibration is ignored.

The Classical Rigid Rotor in 3D

The **rigid rotor** is a mechanical model that is used to explain rotating systems. The linear rigid rotor model consists of two point masses located at fixed distances from their center of mass. The fixed distance between the two masses and the values of the masses are the only characteristics of the rigid model. However, for many actual diatomics this model is too restrictive since distances are usually not completely fixed and corrections on the rigid model can be made to compensate for small variations in the distance. Even in such a case the rigid rotor model is a useful model system to master.

For a rigid rotor, the total energy is the sum of kinetic (T) and potential (V) energies

$$E_{tot} = T + V \tag{5.8.1}$$

The potential energy, V, is set to 0 because the distance between particles does not change within the rigid rotor approximation. However, In reality, $V \neq 0$ because even though the average distance between particles does not change, the particles still vibrate. The rigid rotor approximation greatly simplifys our discussion.

Since $V = 0$ then $E_{tot} = T$ and we can also say that:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{5.8.2}$$

However, we have to determine v_i in terms of rotation since we are dealing with rotation motion. Since,

$$\omega = \frac{v}{r} \tag{5.8.3}$$

where ω is the **angular velocity**, we can say that:

$$v_i = \omega X r_i \tag{5.8.4}$$

Thus we can rewrite Equation 5.8.2 as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{5.8.5}$$

Since ω is a scalar constant, we can rewrite Equation 5.8.5 as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{5.8.6}$$

where l_i is the **angular momentum** of the i^{th} particle, and L is the angular momentum of the *entire system*. Also, we know from physics that,

$$L = I\omega \tag{5.8.7}$$

where I is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite Equation 5.8.2 as

$$T = \omega\frac{I\omega}{2} = \frac{1}{2}I\omega^2 \tag{5.8.8}$$

Equation 5.8.8 shows that the energy of the rigid rotor scales with increasing angular frequency (i.e., the faster is rotates) and with increasing moment of inertia (i.e, the inertial resistance to rotation). Also, as expected, the classical rotational energy is not quantized (i.e., all possible rotational frequencies are possible).

The Quantum Rigid Rotor in 3D

It is convenient to discuss rotation with in the spherical coordinate system rather than the Cartesian system (Figure 5.8.1).

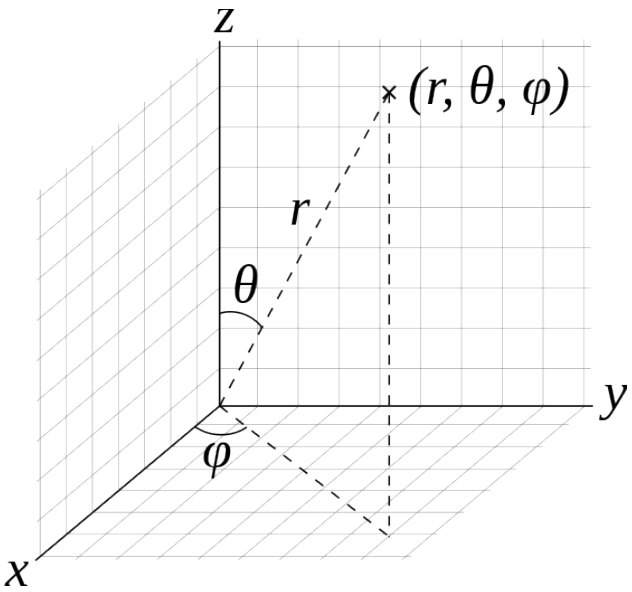


Figure 5.8.1 : The spherical coordinate system in terms of the Cartesian system. (Public Domain; Andeggs via Wikipedia).

To solve the Schrödinger equation for the rigid rotor, we will separate the variables and form single-variable equations that can be solved independently. Only two variables θ and φ are required in the rigid rotor model because the bond length, r, is taken to be the constant r_0. We first write the rigid rotor wavefunctions as the product of a theta-function depending only on θ and a phi-function depending only on φ

$$|\psi(\theta,\varphi)\rangle = |\Theta(\theta)\Phi(\varphi)\rangle \tag{5.8.9}$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 5.8.10

$$\hat{H}|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{5.8.10}$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{\partial}{\partial r_0}r_0^2\frac{\partial}{\partial r_0} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{5.8.11}$$

Since $r = r_0$ is constant for the **rigid rotor** and does not appear as a variable in the functions, the partial derivatives with respect to r are zero; i.e. the functions do not change with respect to r. We also can substitute the symbol I for the moment of inertia, μr_0^2 in the denominator of the left hand side of Equation 5.8.11, to give

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{5.8.12}$$

To begin the process of the Separating of Variables technique, multiply each side of Equation 5.8.12 by $\frac{2I}{\hbar^2}$ and $\frac{-\sin^2\theta}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi)=\frac{-2IE\sin^2\theta}{\hbar^2} \tag{5.8.13}$$

Simplify the appearance of the right-hand side of Equation 5.8.13 by defining a parameter λ:

$$\lambda=\frac{2IE}{\hbar^2}. \tag{5.8.14}$$

Note that this λ has no connection to a wavelength; it is merely being used as an algebraic symbol for the combination of constants shown in Equation 5.8.14.

Inserting λ, evaluating partial derivatives, and rearranging Equation 5.8.13 produces

$$\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta\right)\Theta(\theta)\right]=-\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) \tag{5.8.15}$$

Exercise 5.8.1

Carry out the steps leading from Equation 5.8.13 to Equation 5.8.15. Keep in mind that, if y is not a function of x,

$$\frac{dy}{dx}=y\frac{d}{dx}$$

Equation 5.8.15 says that the function on the left, depending only on the variable θ, always equals the function on the right, depending only on the variable φ, for all values of θ and φ. The only way two different functions of independent variables can be equal for all values of the variables is if both functions are equal to a constant (review separation of variables). We call this constant m_J^2 because soon we will need the square root of it. The two differential equations to solve are the θ-equation

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta-m_J^2\right)\Theta(\theta)=0 \tag{5.8.16}$$

and the φ-equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_J^2\Phi(\varphi)=0 \tag{5.8.17}$$

The partial derivatives have been replaced by total derivatives because only a single variable is involved in each equation.

Often m_J is referred to as just m for convenience.

Exercise 5.8.2

Show how Equations 5.8.16 and 5.8.17 are obtained from Equation 5.8.15.

Solving the φ Equation

The φ-equation is similar to the Schrödinger Equation for the free particle. Since we already solved this previously, we immediately write the solutions:

$$\Phi_m(\varphi)=Ne^{\pm im_J\varphi} \tag{5.8.18}$$

where we introduce the number m to track how many wavelengths of the wavefunction occur around one rotation (similar to the wavelength description of the Bohr atom).

Exercise 5.8.3

Substitute Equation 5.8.18 into Equation 5.8.17 to show that it is a solution to that differential equation.

Answer available at the end of this section.

The normalization condition, Equation 5.8.19 is used to find a value for N that satisfies Equation 5.8.18.

$$\int_0^{2\pi} \Phi^*(\varphi)\Phi(\varphi)d\varphi = 1 \tag{5.8.19}$$

The range of the integral is only from 0 to 2π because the angle φ specifies the position of the internuclear axis relative to the x-axis of the coordinate system and angles greater than 2π do not specify additional new positions.

Exercise 5.8.4

Use the normalization condition in Equation 5.8.19 to demonstrate that $N = 1/\sqrt{2\pi}$.

Answer available at the end of this section.

Values for m are found by using a **cyclic boundary condition**. The cyclic boundary condition means that since φ and $\varphi + 2\varphi$ refer to the same point in three-dimensional space, $\Phi(\varphi)$ must equal $\Phi(\varphi + 2\pi)$, i.e.

$$e^{im_J\varphi} = e^{im_J(\varphi+2\pi)} \tag{5.8.20}$$

$$= e^{im_J\varphi}e^{im_J2\pi} \tag{5.8.21}$$

For the equality in Equation 5.8.21 to hold, $e^{im_J2\pi}$ must equal 1, which is true only when

$$m_J = \cdots, -3, -2, -1, 0, 1, 2, 3, \cdots \tag{5.8.22}$$

In other words m_J can equal **any positive or negative integer or zero.**

Exercise 5.8.5 : Cyclic Boundary Conditions

Use Euler's Formula to show that $e^{im_J2\pi}$ equals 1 for m_J equal to zero or any positive or negative integer.

Thus, the Φ function is

$$\Phi_{m_J}(\varphi) = \sqrt{\frac{1}{2\pi}}e^{\pm im_J\varphi}$$

with

$$m_J = 0, \pm1, \pm2, \cdots$$

Solving the $\Theta(\theta)$ Equation

Finding the $\Theta(\theta)$ functions that are solutions to the θ-equation (Equation 5.8.16) is a more complicated process. Solutions are found to be a set of power series called *Associated Legendre Functions* (Table M2), which are power series of trigonometric functions, i.e., products and powers of sine and cosine functions. The $\Theta(\theta)$ functions, along with their normalization constants, are shown in the third column of Table 5.8.1 .

Table 5.8.1 : Spherical Harmonic Wavefunctions

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta,\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

The solution to the θ-equation requires that λ in Equation 5.8.15 be given by

$$\lambda = J(J+1) \tag{5.8.23}$$

where

$$J \geq |m_J| \tag{5.8.24}$$

J can be 0 or any positive integer greater than or equal to m_J. Each pair of values for the quantum numbers, J and m_J, identifies a rotational state with a wavefunction (Equation 5.8.9) and energy (below). Equation 5.8.24 means that J controls the allowed values of m_J.

> Each pair of values for the quantum numbers, J and m_J, identifies a rotational state and hence a specific wavefunction with associated energy.

The combination of Equations 5.8.14 and 5.8.23 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2\lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{5.8.25}$$

Using Equation 5.8.25, you can construct a rotational energy level diagram (Figure 5.8.2). For simplicity, use energy units of $\frac{\hbar^2}{2I}$.

- $J = 0$: The lowest energy state has $J = 0$ and $m_J = 0$. This state has an energy $E_0 = 0$. There is only **one state** with this energy, i.e. one set of quantum numbers, one wavefunction, and one set of properties for the molecule.
- $J = 1$: The next energy level is $J = 1$ with energy $\frac{2\hbar^2}{2I}$. There are **three states** with this energy because m_J can equal +1, 0, or -1. These different states correspond to different orientations of the rotating molecule in space. States with the same energy are said to be degenerate. The degeneracy of an energy level is the number of states with that energy. The degeneracy of the $J = 1$ energy level is 3 because there are three states with the energy $\frac{2\hbar^2}{2I}$.
- $J = 2$: The next energy level is for $J = 2$. The energy is $\frac{6\hbar^2}{2I}$, and there are **five states** with this energy corresponding to $m_J = +2,\ +1,\ 0,$ -1, -2. The energy level degeneracy is five. Note that the spacing between energy levels increases as J increases. Also note that the degeneracy increases. The degeneracy is always $2J + 1$ because m_J ranges from $+J$ to -J in

integer steps, including 0.

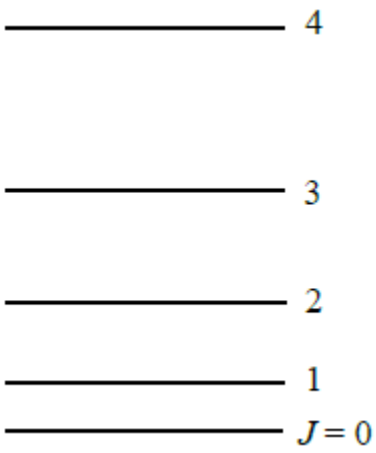


Figure 5.8.2 : Energy spacing for a rigid rotor (in 3D). Notice the energy depends only on J and not depend on m_J. That is, the energy of the rotor is not affected by its orientation.

Each allowed energy of rigid rotor is $(2J+1)$-fold degenerate. Hence, there exist $(2J+1)$ different wavefunctions with that energy.

Exercise 5.8.6

Compute the energy levels for a rotating molecule for $J=0$ to $J=5$ using units of $\frac{\hbar^2}{2I}$.

Answer available at the end of this section.

Exercise 5.8.7

For $J=0$ to $J=5$, identify the degeneracy of each energy level and the values of the m_J quantum number that go with each value of the J quantum number. Construct a rotational energy level diagram including $J=0$ through $J=5$. Label each level with the appropriate values for the quantum numbers J and m_J. Describe how the spacing between levels varies with increasing J.

Answer available at the end of this section.

Interpretation of Quantum Numbers for a Rigid Rotor

The m_J quantum number reflects the component of the angular momentum along the z direction (and hence is sometimes called the azimuthal quantum number). For a fixed value of J, the different values of m_J reflect the different **directions** the angular momentum vector could be pointing – for large, positive m_J the angular momentum is mostly along +z; if m_J is zero the angular momentum is orthogonal to z. Physically, the energy of the rotation does not depend on the direction, which is reflected in the fact that the energy depends only on J (Equation 5.8.25), which measures the length of the vector, not its direction given by m_J.

Example 5.8.7 : Molecular Oxygen

Calculate $J=0$ to $J=1$ rotational transition of the O_2 molecule with a bond length of 121 pm.

Solution

$$E = \frac{\hbar^2}{I} = \frac{\hbar^2}{\mu r^2}$$

$$\mu_{O2} = \frac{m_O m_O}{m_O + m_O} = \frac{(15.9994)(15.9994)}{15.9994 + 15.9994} = 7.9997$$

convert from atomic units to kilogram using the conversion: 1 au = 1.66 x 10^{-27} kg. Plug and chug.

$$E = 5.71 \times 10^{-27}\ Joules$$

Spherical Harmonics

A wavefunction that is a solution to the rigid rotor Schrödinger Equation (Equation 5.8.9) can be written as a single function $Y(\theta, \varphi)$, which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{5.8.26}$$

The spherical harmonic wavefunction is labeled with m_J and J because its functional form depends on both of these quantum numbers. These functions are tabulated above for $J = 0$ through $J = 2$ and for $J = 3$ in the Spherical Harmonics Table (M4) Polar plots of some of the θ-functions are shown in Figure 5.8.3 .

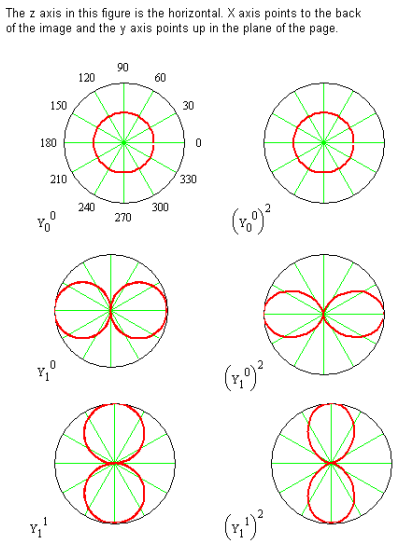


Figure 5.8.3 : Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

The two-dimensional space for a rigid rotor is defined as the surface of a sphere of radius r_0, as shown in Figure 5.8.2 .

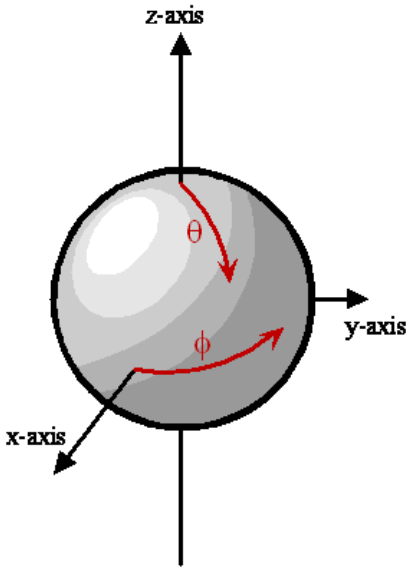


Figure 5.8.4 : Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

The probability of finding the internuclear axis at specific coordinates θ_0 and φ_0 within an infinitesimal area ds on this curved surface is given by

$$Pr\left[\theta_0, \varphi_0\right] = Y_J^{m_{J*}}(\theta_0, \varphi_0) Y_J^{m_J}(\theta_0, \varphi_0) ds \tag{5.8.27}$$

where the area element ds is centered at θ_0 and φ_0.

Within the Copenhagen interpretation of wavefunctions, the absolute square (or modulus squared) of the rigid rotor wavefunction $Y_J^{m_{J*}}(\theta, \varphi) Y_J^{m_J}(\theta, \varphi)$ gives the probability density for finding the internuclear axis oriented at θ to the z-axis and φ to the x-axis. In spherical coordinates the area element used for integrating θ and φ is

$$ds = \sin\theta \, d\theta \, d\varphi \tag{5.8.28}$$

Exercise 5.8.8

Use calculus to evaluate the probability of finding the internuclear axis of a molecule described by the $J = 1$, $m_J = 0$ wavefunction somewhere in the region defined by a range in θ of 0° to 45°, and a range in of 0° to 90°. Note that a double integral will be needed. Sketch this region as a shaded area on Figure 5.8.3 .

Consider the significance of the probability density function by examining the $J = 1$, $m_J = 0$ wavefunction. The Spherical Harmonic for this case is

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \tag{5.8.29}$$

The polar plot of $(Y_1^0)^2$ is shown in Figure 5.8.3 . For $J = 1$ and $m_J = 0$, the probability of finding the internuclear axis is independent of the angle φ from the x-axis, and greatest for finding the internuclear axis along the z-axis, but there also is a probability for finding it at other values of θ as well. So, although the internuclear axis is not always aligned with the z-axis, the probability is highest for this alignment. Also, since the probability is independent of the angle φ, the internuclear axis can be found in any plane containing the z-axis with equal probability.

The $J = 1$, $m_J = 0$ function is 0 when θ = 90°. Therefore, the entire xy-plane is a **node**. This fact means the probability of finding the internuclear axis in this particular horizontal plane is 0 in contradiction to our classical picture of a rotating molecule. In the classical picture, a molecule rotating in a plane perpendicular to the xy-plane must have the internuclear axis lie in the xy-plane

twice every revolution, but the quantum mechanical description says that the probability of being in the xy-plane is zero. This conclusion means that molecules are not rotating in the classical sense, but they still have some, but not all, of the properties associated with classical rotation. The properties they retain are associated with angular momentum.

Exercise 5.8.9

For each state with $J = 0$ and $J = 1$, use the function form of the Y spherical harmonics and Figure 5.8.1 to determine the most probable orientation of the internuclear axis in a diatomic molecule, i.e., the most probable values for θ and θ.

Exercise 5.8.10

Write a paragraph describing the information about a rotating molecule that is provided in the polar plot of $Pr[\theta, \theta]$ for the $J = 1$, $m_J = \pm 1$ state in Figure 5.8.1 . Compare this information to the classical picture of a rotating object.

Summary

There are two quantum numbers that describe the quantum behavior of a rigid rotor in three-deminesions: J is the total angular momentum quantum number and m_J is the z-component of the angular momentum. The spherical harmonics called $Y_J^{m_J}$ are functions whose probability $|Y_J^{m_J}|^2$ has the well known shapes of the s, p and d orbitals etc learned in general chemistry.

References

1. Anderson, J.M. Introduction to Quantum Chemistry, 1969, W.A. Benjamin, Inc, pg.91-100.
2. Atkins, Peter and de Paula, Julio. Physical Chemistry for the Life Sciences. New York: W.H. Freeman and Company. p. 515.

Contributors and Attributions

- Ian Huh
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Mark Tuckerman (New York University)
- MIT OpenCourseWare (Robert Guy Griffin and Troy Van Voorhis)

Answers

Substitute

$$\Phi_m(\varphi) = \mathrm{N}e^{\pm \mathrm{i}m_J\varphi}$$

into

$$\frac{d^2}{d\varphi^2}\Phi(\varphi) + m_J^2\Phi(\varphi) = 0$$

$$\begin{aligned}\frac{d^2}{d\varphi^2}\Phi_{\mathrm{m}}(\varphi) + m_J^2\Phi_{\mathrm{m}}(\varphi) =& \frac{d}{d\varphi}\left(\mathrm{N}\left(\pm \mathrm{i}m_J\right)e^{\pm \mathrm{i}m_J\varphi}\right) + m_J^2\Phi_{\mathrm{m}}(\varphi) \\ &= \mathrm{N}\left(\pm \mathrm{i}m_J\right)^2 e^{\pm \mathrm{i}m_J\varphi}\Big) + m_J^2\left(\mathrm{N}e^{\pm \mathrm{i}m_J\varphi}\right) \\ &= -\mathrm{N}m_J^2 e^{\pm \mathrm{i}m_J\varphi} + \mathrm{N}m_J^2 e^{\pm \mathrm{i}m_J\varphi} = 0\end{aligned}$$

Thus

$$\Phi_m(\varphi) = Ne^{\pm im_J\varphi}$$

is a solution to the differential equations.

We need to evaluate Equation 5.8.19 with $\psi(\varphi) = Ne^{\pm imJ\varphi}$

$$\psi^*(\varphi)\psi(\varphi) = Ne^{+imJ\varphi}Ne^{-imJ\varphi}$$
$$= N^2$$
$$1 = \int_0^{2\pi} N^*Nd\varphi = 1$$
$$N^2(2\pi) = 1$$
$$N = \sqrt{1/2\pi}$$

This rotating molecule can be assumed to be a rigid rotor molecule. From solving the Schrödinger equation for a rigid rotor we have the relationship for energies of each rotational eigenstate (Equation 5.8.25):

$$E = J(J+1)(\hbar^2/2I)$$

Using this equation, we can plug in the different values of the J quantum number so that

For J=0, $E = (0)(1)(\hbar^2/2I) = 0$ For J=1, $E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$

This shows that as J increases, the energy levels get farther apart (Figure 5.8.2).

- For J=2, $E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For J=3, $E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For J=4, $E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For J=5, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

This rotating molecule can be assumed to be a rigid rotor molecule. From solving the Schrödinger equation for a rigid rotor, we have:

$$\lambda = 2IE/\hbar^2$$

Where λ is an arbitrary parameter not related to wavelength. Additionally, λ is assigned a quantum relation so that

$$\lambda = J(J+1)$$

Thus, combining the two equations and solving for E yields

$$E = J(J+1)(\hbar^2/2I)$$

Using this equation, we can plug in the different values of J so that

- For J=0, $E = (0)(1)(\hbar^2/2I) = 0$
- For J=1, $E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$
- For J=2, $E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For J=3, $E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For J=4, $E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For J=5, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

This shows that as J increases, the energy levels get closer and closer together.

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5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

Learning Objectives

- Demonstrate how to use the 3D regid rotor to describe a rotating diatomic molecules
- Demonstate how microwave spectroscopy can get used to characterize rotating diatomic molecules
- Interprete a simple microwave spectrum for a diatomic molecule

To develop a description of the rotational states, we will consider the molecule to be a rigid object, i.e. the bond lengths are fixed and the molecule cannot vibrate. This model for rotation is called the rigid-rotor model. It is a good approximation (even though a molecule vibrates as it rotates, and the bonds are elastic rather than rigid) because the amplitude of the vibration is small compared to the bond length.

The rotation of a rigid object in space is very simple to visualize. Pick up any object and rotate it. There are orthogonal rotations about each of the three Cartesian coordinate axes just as there are orthogonal translations in each of the directions in three-dimensional space (Figures 5.9.1 and 5.9.2). These rotations are said to be *orthogonal* because one can not describe a rotation about one axis in terms of rotations about the other axes just as one can not describe a translation along the x-axis in terms of translations along the y- and z-axes. For a linear molecule, the motion around the interatomic axis (x-axis) is not considered a rotation.

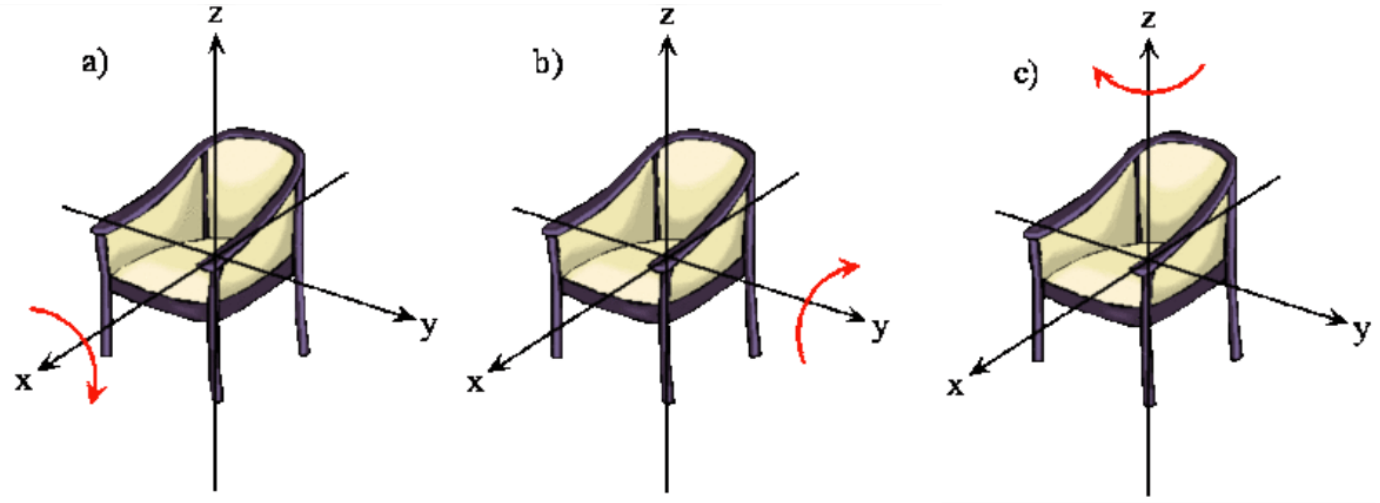


Figure 5.9.1 : Cartesian rotations of a chair. Rotations about the (a) x axis, (b) y axis, and (c) z axis.

In this section we examine the rotational states for a diatomic molecule by comparing the classical interpretation of the angular momentum vector with the probabilistic interpretation of the angular momentum wavefunctions. We want to answer the following types of questions. How do we describe the orientation of a rotating diatomic molecule in space? Is the molecule actually rotating? What properties of the molecule can be physically observed? In what ways does the quantum mechanical description of a rotating molecule differ from the classical image of a rotating molecule?

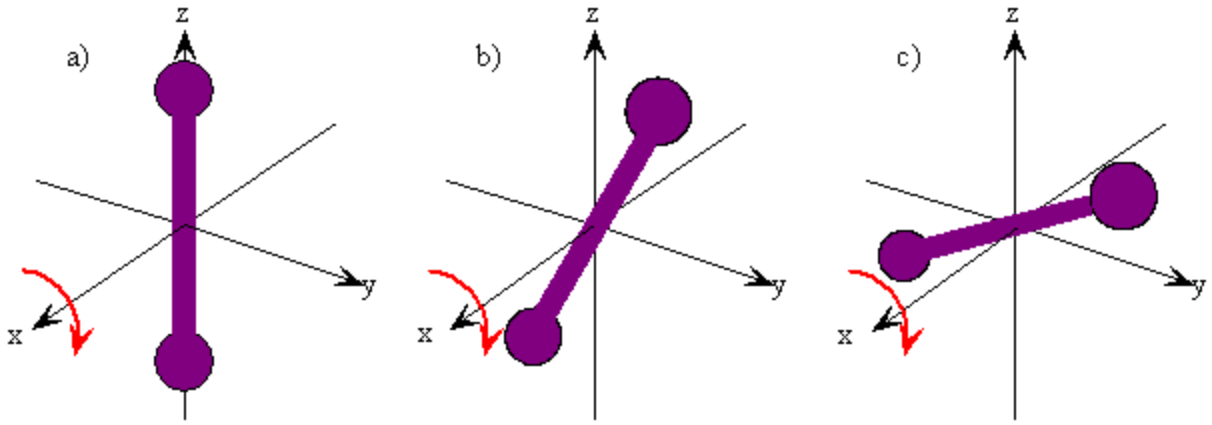


Figure 5.9.2 : Rotation of a diatomic molecule about the x axis.

Introduction to Microwave Spectroscopy

The permanent electric dipole moments of polar molecules can couple to the electric field of electromagnetic radiation. This coupling induces transitions between the rotational states of the molecules. The energies that are associated with these transitions are detected in the far infrared and microwave regions of the spectrum. For example, the microwave spectrum for carbon monoxide spans a frequency range of 100 to 1200 GHz, which corresponds to 3 - 40 cm^{-1}.

The selection rules for the rotational transitions are derived from the transition moment integral by using the spherical harmonic functions and the appropriate dipole moment operator, $\hat{\mu}$.

$$\mu_T = \int Y_{J_f}^{m_f *} \hat{\mu} Y_{J_i}^{m_i} \sin\theta \, d\theta \, d\varphi \tag{5.9.1}$$

or in braket notation

$$\mu_T = \langle Y_{J_f}^{m_f} | \hat{\mu} | Y_{J_i}^{m_i} \rangle \tag{5.9.2}$$

Evaluating the transition moment integral involves a bit of mathematical effort. This evaluation reveals that the transition moment depends on the square of the dipole moment of the molecule, μ^2 and the rotational quantum number, J, of the initial state in the transition,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \tag{5.9.3}$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \tag{5.9.4}$$

and

$$\Delta m_J = 0, \pm 1 \tag{5.9.5}$$

A photon is absorbed for $\Delta J = +1$ and emitted for $\Delta J = -1$.

Exercise 5.9.1

Explain why your microwave oven heats water, but not air. Hint: draw and compare Lewis structures for components of air and for water.

The energies of the J^{th} rotational levels are given by

$$E_J = J(J+1)\frac{\hbar^2}{2I} \tag{5.9.6}$$

with each J^{th} energy level having a degeneracy of $2J+1$ due to the different possible m_J values.

Microwave Transition Energies

The transition energies for absorption of radiation are given by

$$E_{photon} = \Delta E \tag{5.9.7}$$
$$= E_f - E_i \tag{5.9.8}$$
$$= h\nu \tag{5.9.9}$$
$$= hc\bar{\nu} \tag{5.9.10}$$

Substituting the relationship for energy (Equation 5.9.6) into Equation 5.9.8 results in

$$E_{photon} = E_f - E_i \tag{5.9.11}$$
$$= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \tag{5.9.12}$$

with J_i and J_f representing the rotational quantum numbers of the initial (lower) and final (upper) levels involved in the absorption transition.

Since microwave spectroscopists use frequency units and infrared spectroscopists use wavenumber units when describing rotational spectra and energy levels, both ν and $\bar{\nu}$ are important to calculate. When we add in the constraints imposed by the selection rules to identify possible transitions, J_f in Equation 5.9.12 can be replaced by J_i+1, since the selection rule requires J_f–$J_i = 1$ for the absorption of a photon (Equation 5.9.4). The equation for absorption transitions (Equation 5.9.12) then can be written in terms of the only the quantum number J_i of the initial state.

$$E_{photon} = h\nu \tag{5.9.13}$$
$$= hc\bar{\nu} \tag{5.9.14}$$
$$= 2(J_i+1)\frac{\hbar^2}{2I} \tag{5.9.15}$$

Equation 5.9.15 can be rewritten as

$$E_{photon} = 2B(J_i+1)$$

where B is the **rotational constant** for the molecule and is defined in terms of the *energy* of the absorbed photon

$$B = \frac{\hbar^2}{2I} \tag{5.9.16}$$

Often spectroscopists want to express the rotational constant in terms of *frequency* of the absorbed photon and do so by dividing Equation 5.9.16 by h

$$B(\text{in freq}) = \frac{B}{h} \tag{5.9.17}$$
$$= \frac{h}{8\pi^2\mu r_0^2} \tag{5.9.18}$$

More often, spectroscopists want to express the rotational constant in terms of *wavenumbers* ($\bar{\nu}$) of the absorbed photon by dividing Equation 5.9.16 by hc,

$$\tilde{B} = \frac{B}{hc} = \frac{h}{8\pi^2 c\mu r_0^2} \tag{5.9.19}$$

The rotational constant depends on the distance (R) and the masses of the atoms (via the reduced mass) of the nuclei in the

diatomic molecule.

Exercise 5.9.2

Construct a rotational energy level diagram for $J = 0$, 1, and 2 and add arrows to show all the allowed transitions between states that cause electromagnetic radiation to be absorbed or emitted.

Exercise 5.9.3

Complete the steps going from Equation 5.9.12 to Equation 5.9.16 and identify the units of B at the end.

Answer available at the end of this section.

Exercise 5.9.4

Infrared spectroscopists use units of wavenumbers. Rewrite the steps going from Equation 5.9.12 to Equation 5.9.16 to obtain expressions for $h\nu$ and B in units of wavenumbers. Note that to convert B in Hz to B in cm^{-1}, you simply divide the former by c.

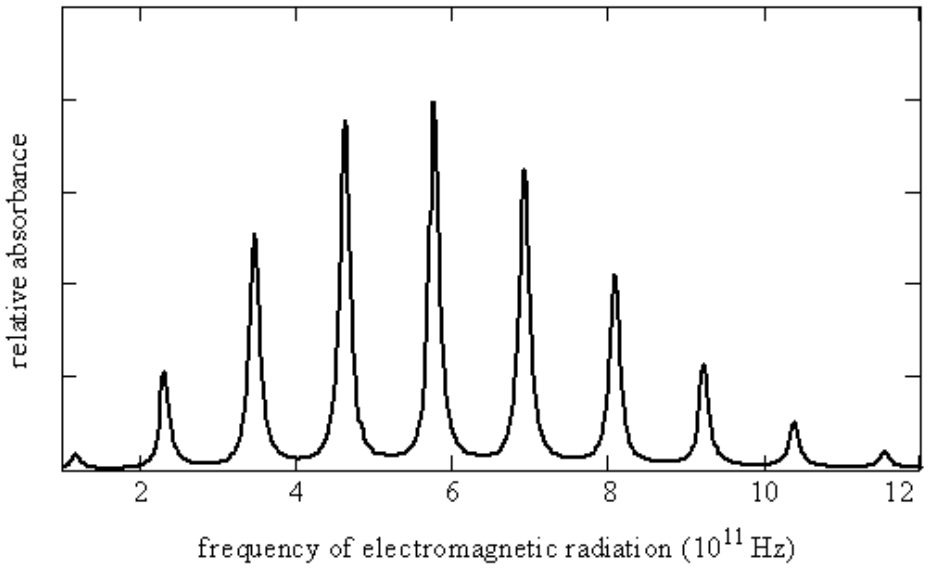


Figure 5.9.3: The rotation spectrum of $^{12}C^{16}O$ at 40 K. The peaks are tabulated in Table 5.9.1.

Figure 5.9.3 shows the rotational spectrum as a series of nearly equally spaced lines. The line positions ν_J, line spacings, and the maximum absorption coefficients (γ_{max}, the absorption coefficients associated with the specified line position) for each line in this spectrum are given here in Table 5.9.1.

Table 5.9.1 : Rotational Transitions in $^{12}C^{16}O$ at 40 K

J	ν_J (MHz)	Spacing from previous line (MHz)	γ_{max}
$0 \rightarrow 1$	115,271.21	0	0.0082
$1 \rightarrow 2$	230,538.01	115,266.80	0.0533
$2 \rightarrow 3$	345,795.99	115,257.99	0.1278
$3 \rightarrow 4$	461,040.76	115,244.77	0.1878

J	ν_J (MHz)	Spacing from previous line (MHz)	γ_{max}
$4 \rightarrow 5$	576,267.91	115,227.15	0.1983
$6 \rightarrow 6$	691,473.03	115,205.12	0.1618
$6 \rightarrow 7$	806,651.78	115,178.68	0.1064
$7 \rightarrow 8$	921,799.55	115,147.84	0.0576
$8 \rightarrow 9$	1,036,912.14	115,112.59	0.0262
$9 \rightarrow 10$	1,151,985.08	115,072.94	0.0103

Let's try to reproduce Figure 5.9.3 from the data in Table 5.9.1 by using the quantum theory that we have developed so far. Equation 5.9.19 predicts a pattern of exactly equally spaced lines. The lowest energy transition is between $J_i = 0$ and $J_f = 1$ so the first line in the spectrum appears at a frequency of $2B$. The next transition is from $J_i = 1$ to $J_f = 2$ so the second line appears at $4B$. The spacing of these two lines is $2B$. In fact the spacing of all the lines is $2B$, which is consistent with the experimental data in Table 5.9.1 showing that the lines are very nearly equally spaced. The difference between the first spacing and the last spacing is less than 0.2%.

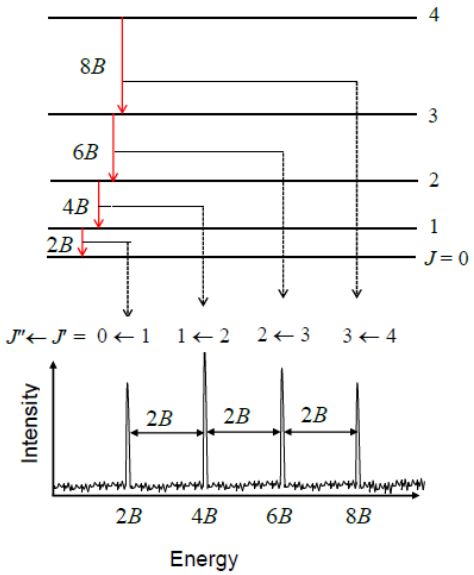


Figure 5.9.4 : Energy levels and line positions calculated in the rigid rotor approximation. (CC BY-SA 3.0; Nrrw via Wikipedia)

Exercise 5.9.5

Use Equation 5.9.19 to prove that the spacing of any two lines in a rotational spectrum is $2B$, i.e. derive:

$$\nu_{J_i+1} - \nu_{J_i} = 2B$$

Answer available at the end of this section.

Example 5.9.1 : Rotation of Sodium Hydride

The molecule NaH undergoes a rotational transition from $J = 0$ to $J = 1$ when it absorbs a photon of frequency $2.94 \times 10^{11}\ Hz$. What is the equilibrium bond length of the molecule?

Solution

We use $J = 0$ in the formula for the transition frequency

$$\nu = 2B = \frac{\hbar}{2\pi I} = \frac{\hbar}{2\pi\mu R_e^2}$$

Solving for R_e gives

$$R_e = \sqrt{\frac{\hbar}{2\pi\mu\nu}}$$

The reduced mass is given by

$$\begin{aligned}\mu &= \frac{m_{Na}m_H}{m_{Na}+m_H} \\ &= \frac{(22.989)(1.0078)}{22.989+1.0078} \\ &= 0.9655\end{aligned}$$

which is in atomic mass units or relative units. To convert to kilograms, we need the conversion factor $1\ au = 1.66 \times 10^{-27}\ kg$. Multiplying this by 0.9655 gives a reduced mass of $1.603 \times 10^{-27}\ kg$. Substituting in for R_e gives

$$\begin{aligned}R_e &= \sqrt{\frac{(1.055 \times 10^{-34}\ J \cdot s)}{2\pi(1.603 \times 10^{-27}\ kg)(2.94 \times 10^{11}\ Hz)}} \\ &= 1.899 \times 10^{-10}\ m \\ &= 1.89\ \mathring{A}\end{aligned}$$

Example 5.9.6

Use the frequency of the $J = 0$ to $J = 1$ transition observed for carbon monoxide to determine a bond length for $^{12}C^{16}O$.

Solution

- J=0: $v_0 = 115271.21\ \text{MHz}$
- J=1: $v_1 = 230538.01\ \text{MHz}$

$$\begin{aligned}\Delta v &= 230538.01\ \text{MHz} - 115271.21\,\text{MHz} \\ &= 115266.8\,\text{MHz} \\ &= 1.153 \times 10^{11}\ \text{Hz} \\ &= \frac{\hbar}{2\pi\mu R_e^2}\end{aligned}$$

The reduced mass is

$$\begin{aligned}\mu &= \frac{m_C m_O}{m_C+m_O} \\ &= \frac{12.01 \times 16.00}{12.01+16.00} \\ &= 6.86\,\text{amu}\end{aligned}$$

Convert to kg

$$6.86amu\left(\frac{1.661 \times 10^{-27}\ \text{kg}}{12\ \text{amu}}\right) = 1.139 \times 10^{-26}\ \text{kg}$$

$$
\begin{aligned}
R_e &= \sqrt{\frac{\hbar}{2\pi\mu\Delta v}} \\
&= \sqrt{\frac{1.055 \times 10^{-34}\ J \cdot s}{2\pi \cdot 1.139 \times 10^{-26}\ \text{kg} \cdot 1.153 \times 10^{11}\ \text{Hz}}} \\
&= 1.131 \times 10^{-10}\text{m} \\
&= 1.131\ \mathring{A}
\end{aligned}
$$

Advanced: Non-Rigid Rotors

Centrifugal stretching of the bond as J increases causes the decrease in the spacing between the lines in an observed spectrum (Table 5.9.1). This decrease shows that the molecule is not really a rigid rotor. As the rotational angular momentum increases with increasing J, the bond stretches. This stretching increases the moment of inertia and decreases the rotational constant (Figure 5.9.5).



Figure 5.9.5 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY 3.0; www.cleonis.nl).

The effect of centrifugal stretching is smallest at low J values, so a good estimate for B can be obtained from the $J = 0$ to $J = 1$ transition. From B, a value for the bond length of the molecule can be obtained since the moment of inertia that appears in the definition of B (Equation 5.9.16) is the reduced mass times the bond length squared. When the centrifugal stretching is taken into account quantitatively, the development of which is beyond the scope of the discussion here, a very accurate and precise value for B can be obtained from the observed transition frequencies because of their high precision. Rotational transition frequencies are routinely reported to 8 and 9 significant figures.

As we have just seen, quantum theory successfully predicts the line spacing in a rotational spectrum. An additional feature of the spectrum is the line intensities. The lines in a rotational spectrum do not all have the same intensity, as can be seen in Figure 5.9.3 and Table 5.9.1. This is related to the populations of the initial and final states. This aspect of spectroscopy will be discussed in more detail in the following chapters

Answers

$$\Delta E_{photon} = E_f - Ei$$

$$E_{r.rotor} = J(J+1)\frac{\hbar^2}{2I}$$

$$E_{photon} = h_\nu = hc\tilde{\nu} = J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I}$$

$$J_f - J_i = 1$$

$$J_f = 1 + J_i$$

$$E_{photon} = h_\nu = hc\tilde{\nu} = (1+J_i)(2+J_i)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I}$$

$$= \frac{\hbar^2}{2I}[2 + 3J_i + J_i^2 - J_i^2 - J_i]$$

$$= \frac{\hbar^2}{2I}2(J_i+1)$$

$$= 2B(J_i+1)$$

Now we do a standard dimensional analysis

$$B = \frac{\hbar^2}{2I} \equiv \left[\frac{kgm^2}{s^2}\right] = [J]$$

$$\frac{B}{h} = B(infreq.) = \frac{h}{8\pi^2\mu r_o^2} \equiv \left[\frac{1}{s}\right]$$

$$\frac{B}{hc} = \widetilde{B} = \frac{h}{8\pi^2\mu c r_o^2} \equiv \left[\frac{s}{m}\right]$$

To prove the relationship, evaluate the LHS. First, define the terms:

$$\nu_{J_i} = 2B(J_i+1), \nu_{J_i+1} = 2B((J_i+1)+1)$$

Substitute into the equation and evaluate:

$$2B((J_i+1)+1) - 2B(J_i+1) = 2B$$

$$2B(J_i+1) + 2B - 2B(J_i+1) = 2B$$

$$2B = 2B$$

LHS equals RHS.Therefore, the spacing between any two lines is equal to $2B$.

This page titled 5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski.

5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

Solutions to select questions can be found online.

5.7

Calculate the reduced mass of HCl molecule given that the mass of H atom is 1.0078 amu and the mass of Cl atom is 34.9688 amu. Note that 1 amu = 1.660565*10^{-27} kg.

Solution

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{1.0078\ amu \times 34.9688\ amu}{1.0078\ amu + 34.9688\ amu} = 0.9796\ amu$$

$$\mu = 0.9796\ amu \times \frac{1.660565 \cdot 10^{-27}\ kg}{1\ amu} = 1.627 \times 10^{-27} kg$$

5.8

Calculate the reduced mass for the Br_2, Cl_2, and I_2 diatomics.

Solution

From the periodic table, the atomic masses for Br, Cl, and I are 79.904, 35.453, and 126.904 respectively.

Covert the atomic mass to kg.

$Br = (79.904\ amu)(1.6606 \times 10^{-27}\ amu/kg) = 1.327 \times 10^{-25}\ kg\ Cl = (35.453\ amu)(1.6606 \times 10^{-27}\ amu/kg) = 5.887 \times 10^{-26}\ kg\ I = (126.904\ amu)(1.6606 \times 10^{-27}\ amu/kg) = 2.107 \times 10^{-25}\ kg$

$$\mu = \frac{m}{2}$$

therefore

μ_{Br2}=1.327x10^{-25} kg/2=6.635x10^{-26} kg μ_{Cl2}= 5.887x10^{-26}kg/2 = 2.9435x10^{-26}kg μ_{I2}=2.107x10^{-25}kg=1.0535x10-25kg

The equation for a reduced mass (μ) of a diatomic is

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

for a diatomic molecule with identical atoms ($m_1 = m_2 = m$) so

5.14

$^{79}Br^{79}Br$ has a force constant of $240\ N \cdot m^{-1}$. Given this information:

a. Calculate the fundamental vibrational frequency and
b. Calculate the $^{79}Br^{79}Br$ zero point energy.

Solution

We must first know which formula to use which is

$$\nu_{obs} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

calculate the reduced mass

$$\mu = \frac{(79\ amu)^2}{79\ amu + 79\ amu} = 39.5amu$$

and convert to Kg:

$1.66e^{-27}$ kg•amu^{-1}

substitute the given values

$$\nu = \frac{1}{2\pi}\sqrt{\frac{240kg\ m\ s^{-2}\ s}{39.5amu \times 1.66 \times 10^{-27}kg\ amu^{-1}}} = 9.63 \times 10^{12}s^{-1}$$

It can also be convert to wavenumber (inverse centimeter cm^{-1}):

$$\nu_{cm^{-1}} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{9.63 \times 10^{12}s^{-1}}{3.0 \times 10^{10}cm\ s^{-1}} = 321cm^{-1}$$

Zero Point Energy:

$$E_0 = \frac{1}{2}h\nu = \frac{1}{2}hc\nu_{cm^{-1}}$$

(formula to use)

E_0=1/2(6.626e^{-34}J•s)(2.998e^{10}cm•s^{-1})(321cm^{-1})

E_0= 3.19e^{-21}J

5.19

Prove that the second derivative of an even function is even and odd function is odd.

Solution

This is an example..not a proof

The following is an even function:

$$y(x) = a + bx^2 + cx^4 + dx^6$$

so

$$\frac{dy}{dx} = 2bx + 4cx^3 + 6dx^5$$

and

$$\frac{d^2y}{dx^2} = 2b + 12cx^2 + 30dx^4$$

which is an even function.

The following is an odd function:

$$f(x) = ax + bx^3 + cx^5$$

so

$$\frac{df}{dx} = a + 3bx^2 + 5cx^4$$

and

$$\frac{d^2f}{dx^2} = 6bx + 10cx^3$$

which is an odd function.

5.27

The Harmonic oscillator Hamiltonian obeys the reflective property:

$$\hat{H}(x) = \hat{H}(-x)$$

What does this say about the nature of the harmonic oscillator wave function?

Solution

The harmonic oscillator switches from odd to even due to the fact that the reflective property will alternate.

5.28

If $\langle x \rangle$ is an odd function, what does that say about p_x?

Hint: use

$$\frac{d\langle p_x \rangle}{dt} = \left\langle \frac{-dV}{dx} \right\rangle$$

also known as **Ehrenfest's Theorem**, where V is the potential of a one dimensional harmonic oscillator.

Hence, $\langle p_x \rangle$ does not depend on time.

5.32

Convert ∇^2 from Cartesian coordinates to cylindrical coordinates.

Solution

We have to start with the conversion of *Cartesian coordinates* $\{x, y, z\}$ to *cylindrical coordinates* $\{r, \theta, z\}$

$x = r\cos\theta \; y = r\sin\theta \; z = z$

Now putting it all together

$$\nabla^2 = \frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} + \frac{1}{r^2}\frac{d^2}{d\theta^2} + \frac{d^2}{dz^2}$$

$$r = \sqrt{x^2 + y^2}$$

$$\cos\theta = \frac{x}{\sqrt{x^2 + y^2}}$$

$$\sin\theta = \frac{x}{\sqrt{x^2 + y^2}}$$

Now by chain rule we get

$$\frac{d}{dx} = \frac{dr}{dx}\frac{d}{dr} + \frac{d\theta}{dx}\frac{d}{d\theta}$$

$$\frac{d}{dy} = \frac{dr}{dy}\frac{d}{dr} + \frac{d\theta}{dy}\frac{d}{d\theta}$$

$$\frac{dr}{dx} = \frac{x}{r} = \cos\theta$$

$$\frac{dr}{dx} = \sin\theta$$

using **implicit differentiation** and taking the second derivatives will yield

$$\frac{d^2}{dx^2} = \left(\cos\theta\frac{d}{dr} - \frac{\sin\theta}{r}\frac{d}{d\theta}\right)\left(\cos\theta\frac{d}{dr} - \frac{\sin\theta}{r}\frac{d}{d\theta}\right)$$

$$\frac{d^2}{dy^2} = \left(\sin\theta\frac{d}{dr} + \frac{\cos\theta}{r}\frac{d}{d\theta}\right)\left(\sin\theta\frac{d}{dr} + \frac{\cos\theta}{r}\frac{d}{d\theta}\right)$$

$$\frac{d^2}{dz^2} = \frac{d^2}{dz^2}$$

5.37

Find the magnitude of angular momentum and the z component of angular momentum for electrons in a hydrogen-like species with

a. quantum numbers $n = 1, l = 0, m = 0$; and
b. $n = 2, l = 0, m = 0$.

Compare your answers and explain your results.

Solution

The wave function for this problem is given by:

$$\psi_{100} = R(r)_{10}Y(\theta,\phi)_{00} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}}$$

Using that:

$$\hat{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1)Y_{lm}(\theta,\phi),$$

and

$$\hat{L_z} = m\hbar$$

Then $\hat{L}^2 = 0$ and $\hat{L_z} = 0$. Given that the values for l and m are the same as above, the answers would also be the same.

The reason why both answers are the same is that the operators for angular momentum only act on the angular part of the wave function. Since only the quantum number n varied between these two states, the angular momentum eigenvalues did not change.

5.38

Apply the angular momentum operator in the x direction to the following functions ($Y(\theta, \phi)$).

a. $\frac{5\pi}{4} + 7\exp(\pi^2)$
b. $3\pi\sin(\theta)$
c. $\frac{3}{2}\cos(\theta)\exp(i\phi)$

Solution

Let us begin by stating the angular momentum operator in terms of θ and ϕ.

$$\hat{L_x} = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta} + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\Big)$$

a) $Y(\theta, \phi) = \frac{5\pi}{4} + 7exp(\pi^2)$

$$\hat{L_x}(\frac{5\pi}{4} + 7exp(\pi^2)) = i\hbar\Big(\sin(\phi)\frac{\partial\frac{5\pi}{4} + 7exp(\pi^2)}{\partial\theta} + \cot(\theta)\cos(\phi)\frac{\partial\frac{5\pi}{4} + 7exp(\pi^2)}{\partial\phi}\Big)$$

$$= 0$$

The function does not depend on θ or ϕ so when the angular momentum operator is applied to the function, it equals 0.

b) $Y(\theta, \phi) = 3\pi\sin(\theta)$

$$\hat{L_x}(3\pi\sin(\theta)) = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta}3\pi\sin(\theta) + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}3\pi\sin(\theta)\Big)$$

$$= 3i\pi\hbar\sin(\phi)\cos(\theta)$$

c) $Y(\theta, \phi) = \frac{3}{2}\cos(\theta)exp(i\phi)$

$$\hat{L_x}(3\pi\sin(\theta)) = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta}\frac{3}{2}\cos(\theta)exp(i\phi) + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\frac{3}{2}\cos(\theta)exp(i\phi)\Big)$$

$$= i\hbar\Big(\frac{-3}{2}\sin(\phi)\sin(\theta)exp(i\phi) + \frac{3i}{2}\cot(\theta)\cos(\phi)\cos(\theta)exp(i\phi)\Big)$$

$$= \frac{3i\hbar exp(i\phi)}{2}(i\cot(\theta)\cos(\phi)\cos(\theta) - \sin(\phi)\sin(\theta))$$

5.41

Use the fact that $\hat{x}$ and $\hat{p}$ are Hermitian in the number operator

$$\hat{a}_- = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{p})$$

$$\hat{a}_+ = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{p})$$

and

$$\hat{H} = \frac{\hbar w}{2}(\hat{a}_-\hat{a}_+ + \hat{a}_+\hat{a}_-)$$

Show that

$$\int \psi_v^*\hat{v}\psi dx \geq 0$$

5.43

Determine the unnormalized wave function $\psi_{\circ}\left(x\right)$ given that $\hat{a}_{-} = 2^{-1/2}\left(\hat{x} + i\hat{p}\right)$ and that $\hat{a_{-}}\psi_{\circ} = 0$ Then find the unnormalized wave function for $\psi_{1}\left(x\right)$ using $\hat{a}_{+}$.

Solution

It was given that $\hat{a}_{-}\psi_{\circ} = 0$, so substituting in $\hat{a}_{-}$ so we know

$$\hat{a_{-}} = 2^{-1/2}\left(\hat{x} + i\hat{p}\right)\psi_{\circ} = 0$$

We can expand and simplify this expression to a first order partial differential equation

$$x\psi_{\circ} + \frac{d\psi_{\circ}}{dx} = 0$$

Solve by separating like terms

$$\frac{d\psi_{\circ}}{\psi_{\circ}} = -xdx$$

Solving this equation for $\psi_{\circ}\left(x\right)$ we find that

$$\psi_{\circ} = e^{\frac{-x^{2}}{2}}$$

To solve for ψ_{1} we understand that $\psi_{1} \backsim \hat{a_{+}}\psi_{\circ} \backsim \hat{x} - i\hat{p}\psi_{\circ}$, as well as that

$$\hat{x} - i\hat{p}\psi_{\circ} = x\psi_{\circ} - \frac{d\psi_{\circ}}{dx} = 2xe^{\frac{-x^{2}}{2}} = 2x\psi_{\circ}$$

So then we can say

$$\boxed{\psi_{1} \backsim xe^{\frac{-x^{2}}{2}}}$$

5.46

Find the reduced mass of an electron in a Tritium atom. Set the mass of the Tritium to be $5.008267 \times 10^{-27}\ kg$. Then find the value of the Rydberg constant for the Tritium atom.

Solution

To solve, use the reduced mass equation, and for mass 1 enter the mass of the electron, and for mass 2 enter the mass of the Tritium atom:

$$\mu = \frac{m_{1}m_{2}}{m_{1} + m_{2}}$$

For which one attains a value of $\mu = 9.1077x10^{-31}kg$

5.46

The mass of a deuterium atom is $3.343586 \times 10^{-27}\ kg$. First calculate the reduce mass of the deuterium atom. Then using the reduced mass calculated find the Rydberg constant for a deuterium atom.

Solution

μ = reduced mass

$$\mu_{deuterium} = \frac{(9.109390 \times 10^{-31} kg)(3.343586 \times 10^{-27} kg)}{(9.109390 \times 10^{-31} kg + 3.343586 \times 10^{-27} kg)}$$

$$\mu_{deuterium} = 9.106909 \times 10^{-31} kg = 0.9997277 m_e$$

R_H = Rydberg constant

$$R_H = (109,737.2 cm^{-1})(0.9997277 m_e) = 109,707.3 cm^{-1}$$

5.47

What is the ratio of the frequency of spectral lines of C-14 that has been ionized 5 times and C-12 that has been ionized 5 times?

Solution

Carbon that has been ionized 5 times is a hydrogen like ion, so we can use the Bohr model to find the desired ratio.

$$E = \frac{uZ^2e^4n^2}{8\varepsilon_0^2h^3c}$$

gives the placement of spectral lines. The coefficient of n^2 is proportional to the frequency of these lines, so the ratio of $E_{C\text{-}14}/E_{C\text{-}12}$ will give the ratio of frequency of the lines. The only difference between these two isotopes is the reduced mass u. So the problem reduces to $\mathbf{u_{C\text{-}14}/\ u_{C\text{-}12}}$. Mass in amu is used below. m_e = mass of electron = $5.4858*10^{-4}$ amu.

$$\mu_{C-14} = \frac{m_e m_{c-14}}{m_e + m_{c-14}} = \frac{(14.003)(5.4858 \times 10^{-4})}{14.003 + 5.4858 \times 10^{-4}} = 5.485585 \times 10^{-4}$$

$$\mu_{C-12} = \frac{m_e m_{c-12}}{m_e + m_{c-12}} = \frac{(12)(5.4858 \times 10^{-4})}{12 + 5.4858 \times 10^{-4}} = 5.485549 \times 10^{-4}$$

$$\frac{\mu_{C-14}}{\mu_{C-12}} = 1.0000065$$

5.47

Calculate the Rydberg constant for a deuterium atom and atomic hydrogen given the reduced mass of a deuterium atom is $9.106909 \times 10^{-31} kg$ and the reduced mass of hydrogen is $9.104431 \times 10^{-31} kg$. Compare both of these answers with the experimental result ($109677.6 cm^{-1}$). Then determine the ratio of the frequencies of the lines in the spectra of atomic hydrogen and atomic deuterium.

Solution

The Rydberg constant is found using

$$R_H = \frac{me^4}{8\epsilon_o^2 ch^3}$$

For a deuterium atom

$$R_H = \frac{(9.104431 \times 10^{-31} kg)(1.602 \times 10^{-19} C)^4}{8(8.854 \times 10^{-12} \frac{F}{m})^2(2.998 \times 10^8 \frac{m}{s})(6.626 \times 10^{-34} J \cdot s)^3}$$

$$R_H = 109707.3 cm^{-1}$$

This is different by $2.7 \times 10^{-2}\%$.

The ratio of the frequencies of the lines in the spectra of atomic hydrogen and atomic deuterium is equivalent to the ratio of the Rydberg constants we just found.

$$\frac{109707.3\ cm^{-1}}{109677.5\ cm^{-1}} = 1.000272$$

$$R_H = \frac{(9.106909 \times 10^{-31} kg)(1.602 \times 10^{-19} C)^4}{8(8.854 \times 10^{-12} \frac{F}{m})^2(2.998 \times 10^8 \frac{m}{s})(6.626 \times 10^{-34} J \cdot s)^3}$$

$$R_H = 109677.5 cm^{-1}$$

This is different by $9.1 \times 10^{-5}\%$.

For a hydrogen atom

5.46

Find the reduced mass of HCl where the mass of hydrogen in 1 amu and the mass of chloride is 35 amu.

Solution

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

$$\mu = \frac{(1.00)(35.00)}{36.00} 1.603 \times 10^{-27} kg = 1.558 \times 10^{-27} kg$$

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5.S: The Harmonic Oscillator and the Rigid Rotor (Summary)

Harmonic Oscillator

The harmonic oscillator is the model of a particle in a quadratic potential or, equivalently, two particles whose relative displacement sits in a quadratic potential. From the standpoint of chemistry, the harmonic oscillator is the simplest model for the vibration of a diatomic molecule (and even vibrations of the normal modes of a polyatomic molecule). If the potential between the two bodies is truly quadratic, then the Schrödinger equation can be solved exactly. However, any potential that has a smooth minimum can be approximated as a harmonic potential near that minimum. For any potential $V(x)$ where $x = l - l_0$ (i.e., the displacement relative to the separation at minimum potential l_0), a Taylor expansion gives

$$V(x) = V(0) + \left(\frac{dV}{dx}\right)_0 x + \frac{1}{2!}\left(\frac{d^2V}{dx^2}\right)_0 x^2 + \frac{1}{3!}\left(\frac{d^3V}{dx^3}\right)_0 x^3 + ... \tag{5.S.1}$$

The first term can be arbitrarily set to 0, and the second term is 0 because at $x = 0$, the derivative of the potential is zero (it's a minimum). Therefore, as long as x is small, we an truncate the series at the quadratic term and define the force constant $k = \left(\frac{d^2V}{dx^2}\right)_0$:

$$V(x) \approx \frac{1}{2}kx^2.$$

For the quantum harmonic oscillator involving two bodies with reduced mass $\mu = m_1^{-1} + m_2^{-1}$ and force constant k with displacement x, the Hamiltonian is

$$\op H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2,$$

and the Schrödinger equation tells us that the wavefunctions $\psi(x)$ must be the solutions of

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0.$$

It turns out that the solutions have the general form

$$\psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}, \quad v = 0, 1, 2, ...$$

where

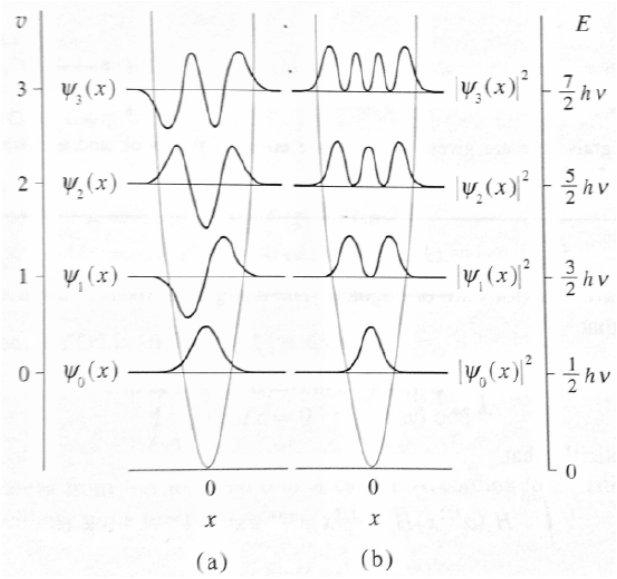
$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}, \quad N_v = (2^v v!)^{-1/2}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

and $H_v(\alpha^{1/2}x)$ are the Hermite polynomials, which are a series of polynomials of order v. It is conventional to use v as the quantum number for a harmonic oscillator.

If we define the angular frequency of the oscillator $\omega = \sqrt{k/\mu}$ or, alternatively, its frequency $\nu = \sqrt{k/\mu}/(2\pi)$, the energies are given by

$$E_v = \hbar\omega\left(v + \frac{1}{2}\right) = h\nu\left(v + \frac{1}{2}\right), \quad v = 0, 1, 2 ...$$

A unique feature of the harmonic oscillator is that its energy levels are evenly spaced, and that the lowest energy level is greater than the minimum of the potential. This means that even at absolute zero, the harmonic oscillator still has nonzero kinetic and potential energy, which is called zero-point energy.



Wavefunctions (a) and probability densities (b) of the harmonic oscillator, along with energies.

Rigid Rotor

The rigid rotor is the model system for both a rotating diatomic molecule and for the angular distribution of the electron in a hydrogen atom. This model starts with two bodies with reduced mass μ and a fixed separation r.

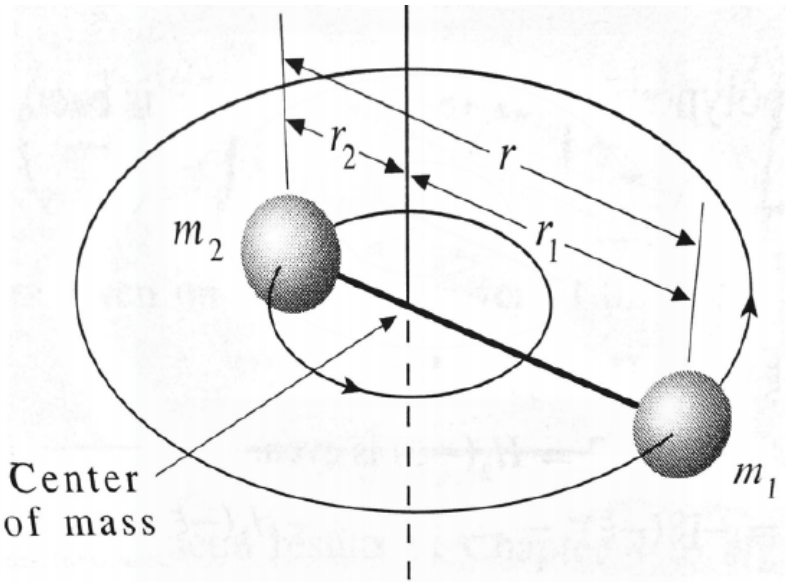


Figure 1.5: Model of a rigid rotor.

Since there is no preferred orientation of the body in free space, the Hamiltonian only has a kinetic energy term:

$$\op H = \op T = -\frac{\hbar^2}{2\mu}\nabla^2.$$

Because we're dealing with rotation, it's more natural to work in spherical coordinates, and after some tedious calculus it can be shown that:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta}$$

In the rigid rotor, r is constant, so we can eliminate the first term to get

$$\nabla^2 = \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta} \tag{5.S.2}$$

Recall from physics that angular momentum $L = I\omega$, where I is the moment of inertia and ω is the angular frequency. Relative to the center of mass, $I = m_1 r_1^2 + m_2 r_2^2$, and consequently in the center-of-mass frame $I = \mu r^2$. The kinetic energy of a rotating body is $T = L^2/(2I)$ (just like the linear quantity $T = p^2/(2m)$). If we now substitute Equation 5.S.2 into the Hamiltonian, we see

$$\op H = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta}\right],$$

and thus we find the quantum mechanical form of the square of the angular momentum operator:

$$\op L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta}\right].$$

The eigenfunctions of the Hamiltonian (and $\op L^2$) are the spherical harmonics $Y_l^m(\theta,\phi)$, where $l = 0, 1, 2, \ldots$ and $m = 0, \pm1, \pm2, \ldots, \pm l$. These spherical harmonics have the form:

$$Y_l^m(\theta,\phi) = \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\phi},$$

where $P_l^{|m|}(\cos\theta)$ are the associated Legendre functions.

The energies of the rigid rotor depend only on the l quantum number

$$E_l = \frac{\hbar^2}{2I}l(l+1), \quad l = 0, 1, 2, \ldots,$$

and each energy level has a degeneracy of $2l+1$ arising from the possible values of the m quantum number. While the quantum numbers l and m (often m_l) are used when describing the angular portion of the hydrogen atom wavefunction, typically the quantum numbers become J and m_J when discussing molecular rotation. They are equivalent in the case of linear molecules; for nonlinear molecules, additional quantum numbers are needed to specify the projection of the angular momentum onto some molecular axis, and the energy depends on these quantum number as well.

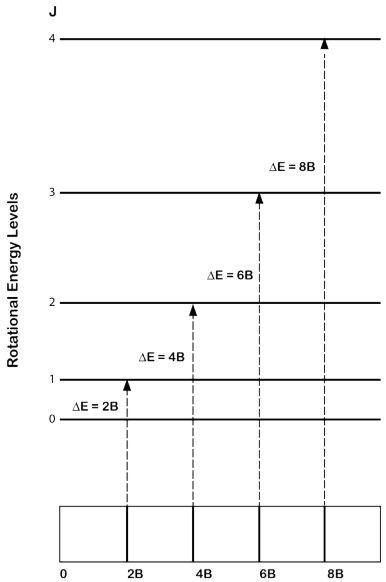


Figure 1.6: Energy level diagram of a rigid rotor. The gaps between successive levels are evenly spaced in energy.

As mentioned before, $\op L^2$ commutes with $\op H$, so the square of the total angular momentum has a definite value (l is a good quantum number). Looking at its components $\op L_x$, $\op L_y$, and $\op L_z$, we find that only $[\op L^2, \op L_z] = 0$, while $[\op L_i, \op L_j]$

$\neq 0$ if $i \neq j$. This means that we can know the total angular momentum l and its projection m onto one of three axes (under the coordinate system we've chosen, that axis is z, but different coordinate choices are possible).

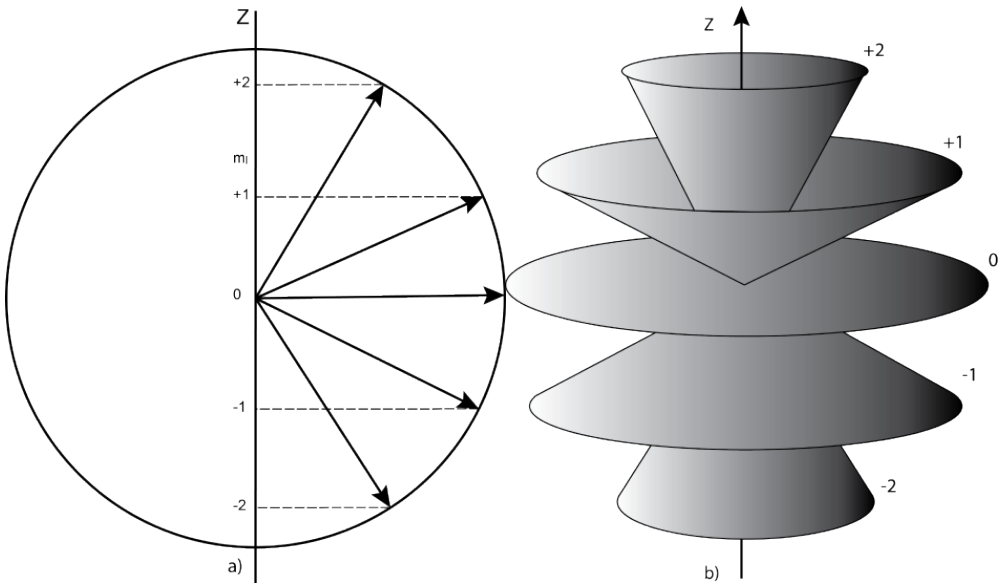


Figure 1.7: Vector representation of total angular momentum l and its projection ml onto the z axis. (a) is a two dimensional illustration, while (b) illustrates the uncertainty in the projection of the angular momentum onto the x and y axes.

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6: THE HYDROGEN ATOM

The solution of the Schrödinger equation (wave equation) for the hydrogen atom uses the fact that the Coulomb potential produced by the nucleus is isotropic (it is radially symmetric in space and only depends on the distance to the nucleus). Although the resulting energy eigenfunctions (the orbitals) are not necessarily isotropic themselves, their dependence on the angular coordinates follows completely generally from this isotropy of the underlying potential: the eigenstates of the Hamiltonian (that is, the energy eigenstates) can be chosen as simultaneous eigenstates of the angular momentum operator. This corresponds to the fact that angular momentum is conserved in the orbital motion of the electron around the nucleus. Therefore, the energy eigenstates may be classified by two angular momentum quantum numbers, ℓ and m (both are integers). The angular momentum quantum number $\ell = 0, 1, 2, \ldots$ determines the magnitude of the angular momentum. The magnetic quantum number $m = -\ell, \ldots, +\ell$ determines the projection of the angular momentum on the (arbitrarily chosen) z-axis.

6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly

6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

6.5: s-orbitals are Spherically Symmetric

6.6: Orbital Angular Momentum and the p-Orbitals

6.7: The Helium Atom Cannot Be Solved Exactly

6.E: The Hydrogen Atom (Exercises)

6.S: The Hydrogen Atom (Summary)

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6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass. This reduced particle is located at r, where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume throughout this chapter that the reduced mass equals the electron mass and the proton is located at the center of mass.

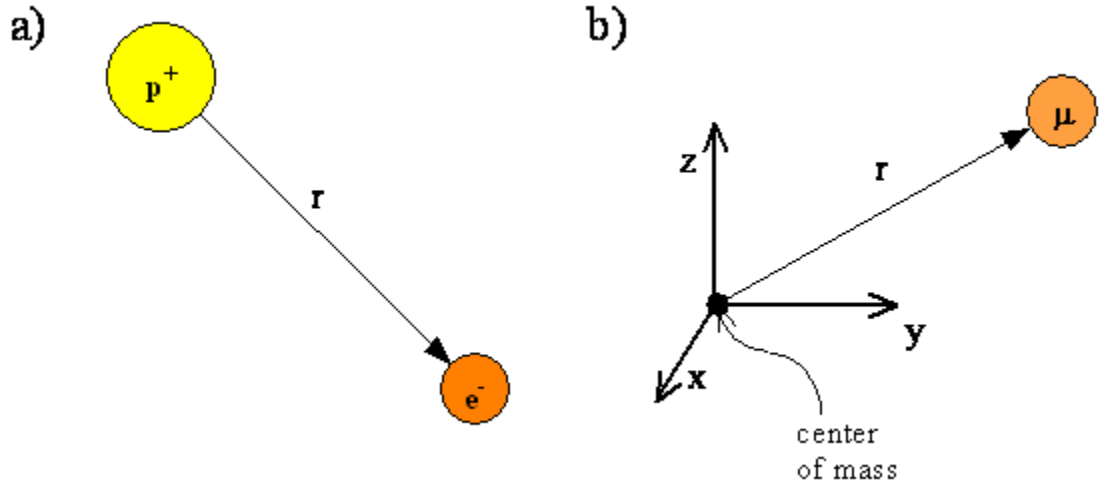


Figure 6.1.1 : (a) The proton (p^+) and electron (e^-) of the hydrogen atom. (b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Exercise 6.1.1

a. Assuming the Bohr radius gives the distance between the proton and electron, calculate the distance of the proton from the center of mass, and calculate the distance of the electron from the center of mass.
b. Calculate the reduced mass of the electron-proton system.
c. In view of your calculations in (a) and (b), comment on the validity of a model in which the proton is located at the center of mass and the reduced mass equals the electron mass.

Since the internal motion of any two-particle system can be represented by the motion of a single particle with a reduced mass, the description of the hydrogen atom has much in common with the description of a diatomic molecule discussed previously. The time-independent Schrödinger Equation for the hydrogen atom

$$\hat{H}(r,\theta,\varphi)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{6.1.1}$$

employs the same kinetic energy operator, $\hat{T}$, written in spherical coordinates. For the hydrogen atom, however, the distance, r , between the two particles can vary, unlike the diatomic molecule where the bond length was fixed and the rigid rotor model was applicable. The hydrogen atom Hamiltonian also contains a potential energy term, $\hat{V}$, to describe the attraction between the proton and the electron. This term is the Coulomb potential energy,

$$\hat{V}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{6.1.2}$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a **central potential**.

The full expression for $\hat{H}$ in spherical coordinates is

$$\hat{H}(r,\theta,\varphi) = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r} \tag{6.1.3}$$

The contributions from rotational and radial components of the motion become clearer if we write out the complete Schrödinger equation,

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{6.1.4}$$

multiply both sides of Equation 6.1.4 by $2\mu r^2$, and rearrange to obtain

$$\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2\left[E + \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(r,\theta,\varphi) =$$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi) \tag{6.1.5}$$

Manipulating the Schrödinger equation in this way helps us recognize the square of the angular momentum operator in Equation 6.1.5. The square of the angular momentum operator in Equation 6.1.6.

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{6.1.6}$$

Substituting Equation 6.1.6 into Equation 6.1.5 produces

$$\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2[E-\hat{V}]\psi(r,\theta,\varphi) = \hat{M}^2\psi(r,\theta,\varphi) \tag{6.1.7}$$

Exercise 6.1.2

Show the algebraic steps going from Equation 6.1.4 to 6.1.5 and finally to 6.1.7. Justify the statement that the rotational and radial motion are separated in Equation 6.1.7.

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 6.1.7 by using a product wavefunction, as we did previously for rigid rotors. We know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions (Table M4), $Y(\theta,\varphi)$, so a good choice for a product function is

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) \tag{6.1.8}$$

> The Spherical Harmonic functions provide information about where the electron is around the proton, and the radial function $R(r)$ describes how far the electron is away from the proton.

To separate variables, substitute the product function, Equation 6.1.8 into Equation 6.1.7, evaluate partial derivatives, divide each side by R(r) $Y(\theta,\varphi)$, and set each side of that resulting equation equal to a constant λ.

$$\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu r^2}{R(r)}[E-V]R(r) = \lambda \tag{6.1.9}$$

$$\frac{1}{Y(\theta,\varphi)}\hat{M}^2Y(\theta,\varphi) = \lambda \tag{6.1.10}$$

Equations 6.1.9 and 6.1.10 represent the radial differential equation and the angular differential equation, respectively. As we describe below, they are solved separately to give the $Y(\theta,\varphi)$ angular functions and the R(r) radial functions.

Exercise 6.1.3

Complete the steps leading from Equations 6.1.7 to 6.1.9 and 6.1.10.

Rearranging Equation 6.1.10 yields

$$\hat{M}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{6.1.11}$$

where we have added the indices l and m_l to identify a particular spherical harmonic function. Note that the notation has changed from that used with the Rigid Rotor; it is customary to use J and m_J to represent the angular momentum quantum numbers for rotational states, but for electronic states, it is customary to use l and m_l to represent the same thing. Furthermore, the electronic angular momentum is designated by L and the corresponding operator is called $\hat{L}$. In complete electronic notation, Equation 6.1.11 is

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{6.1.12}$$

Equation 6.1.12 says that $Y_l^{m_l}(\theta,\varphi)$ must be an eigenfunction of the angular momentum operator $\hat{L}^2$ with eigenvalue λ. We know from the discussion of the Rigid Rotor that the eigenvalue λ is $J(J+1)\hbar^2$, or in electronic notation, $l(l+1)\hbar^2$. Consequently, Equation 6.1.12 becomes

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta,\varphi) \tag{6.1.13}$$

Using this value for λ and rearranging Equation 6.1.9, we obtain

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) - E\right]R(r) = 0 \tag{6.1.14}$$

Exercise 6.1.4

Write the steps leading from Equation 6.1.9 to Equation 6.1.14.

The details for solving Equation 6.1.14 are provided elsewhere, but the procedure and consequences are similar to previously examined cases. As for the harmonic oscillator, an asymptotic solution (valid at large r) is found, and then the complete solutions are written as products of the asymptotic solution and polynomials arising from sequential truncations of a power series expansion.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

The solutions to the hydrogen atom Schrödinger equation are functions that are products of a spherical harmonic function and a radial function:

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_l^{m_l}(\theta,\phi) \tag{6.2.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and ϕ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the nucleus in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\phi)|^2$, evaluated at r, θ, and ϕ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and ϕ.

Exercise 6.2.1

What is the value of the integral (in braket notation)

$$\langle\psi(r,\theta,\phi)|\psi(r,\theta,\phi)\rangle \ ?$$

or expanded in integral notation (in Cartesian coordinates)

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} |\psi(x,y,z)|^2\,dx\,dy\,dz$$

or expanded in integral notation (in spherical coordinates)

$$\int_{0}^{+\infty}\int_{0}^{\pi}\int_{0}^{+2\pi} |\psi(r,\theta,\phi)|^2 r^2\sin\theta\,d\theta\,d\phi\,dr$$

Answer available at the end of this section.

The quantum numbers have names:

- n is called the principal quantum number,
- l is called the angular momentum quantum number, and
- m_l is called the magnetic quantum number because (as we will see, the energy in a magnetic field depends upon m_l).

Often l is called the azimuthal quantum number because it is a consequence of the θ-equation, which involves the azimuthal angle Θ, referring to the angle to the zenith. These quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, l can have the values 0 to n-1, and m_l can have $2l+1$ values ranging from $-l$ to $+l$ in unit or integer steps. The total number of orbitals with a particular value of n is n^2 - i.e., this is the **degeneracy** of the system.

Wavefunction Nomenclature

The values of the quantum number l usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l = 4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n, the magnitude of the angular momentum is given by l, and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_l.

The Φ function is found to have the quantum number m, where

$$\Phi_m(\phi) = A_m e^{im\phi}$$

and A_m is the normalization constant and $m = 0, \pm1, \pm2... \pm\infty$. The Θ function was solved and is known as *Legendre polynomials*, which have quantum numbers m and ℓ. When Θ and Φ are multiplied together, the product is known as **spherical harmonics** with labeling $Y_J^m(\theta, \phi)$.

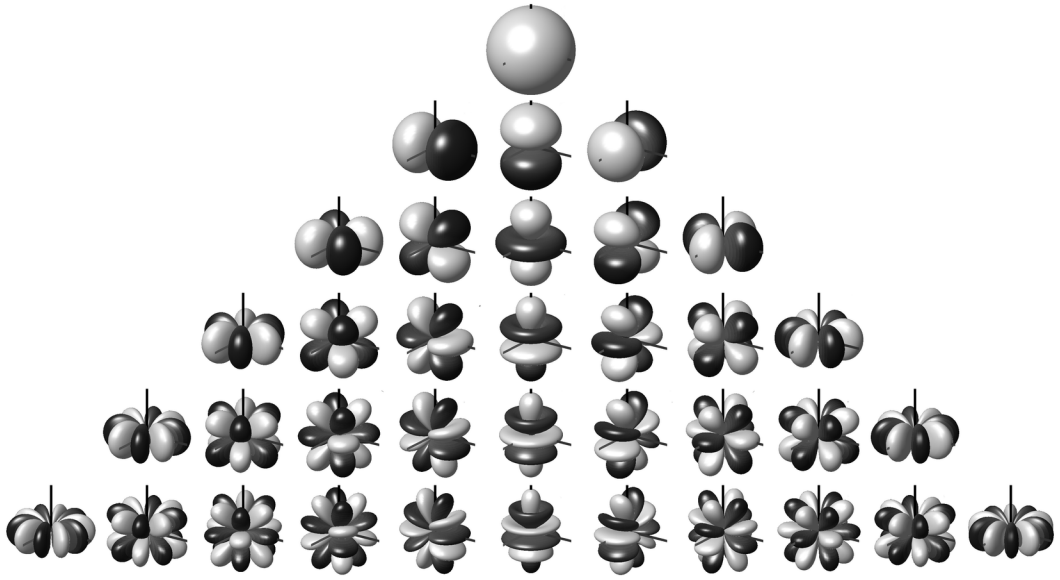


Figure 6.2.1: Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.

Figure 6.2.1 shows the spherical harmonics Y_J^M, which are solutions of the angular Schrödinger equation. These are explicitly written in Table 6.2.1 . Notice that these functions are complex in nature.

Table 6.2.1 : spherical harmonics Y_J^M

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta, \varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{-2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

Exercise 6.2.2

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 6.2.3

Construct a table summarizing the allowed values for the quantum numbers n, l, and m_l. for energy levels 1 through 7 of hydrogen.

Exercise 6.2.4

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom.

a. What are the values for n and l?
b. What are the values for the energy and angular momentum?
c. What are the possible values for the magnetic quantum number?
d. What are the possible orientations for the angular momentum vector?

Answer available at the end of this section.

Atomic Orbitals

The hydrogen atom wavefunctions, $\psi(r,\theta,\phi)$, are called **atomic orbitals**. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n=1$, $l=0$, and $m_l=0$ is called the 1s orbital, and an electron that is described by this function is said to be "in" the 1s orbital, i.e. have a 1s orbital state. The constraints on n, ℓ, and m_ℓ that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

The first few solutions of the Schrödinger equation for the H atom are:

Table 6.2.1 : The solutions to the Schrödinger equation for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho=\frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	m_l	ψ_{n,l,m_l}
ψ_{100}	1	0	$m_l=0$	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
ψ_{200}	2	0	$m_l=0$	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
ψ_{210}	2	1	$m_l=0$	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\cos\theta$
$\psi_{21\pm1}$	2	1	$m_l=\pm1$	$\frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\sin\theta e^{\pm i\phi}$
ψ_{300}	3	0	$m_l=0$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right) e^{-\frac{Zr}{3a_0}}$
ψ_{310}	3	1	$m_l=0$	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\cos\theta$
$\psi_{31\pm1}$	3	1	$m_l=\pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\sin\theta e^{\pm i\phi}$

	n	l	m_l	ψ_{n,l,m_l}
ψ_{320}	3	2	$m_l = 0$	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \left(3\cos^2\theta - 1\right)$
$\psi_{32\pm1}$	3	2	$m_l = \pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin\theta\cos\theta e^{\pm i\phi}$
$\psi_{32\pm2}$	3	2	$m_l = \pm2$	$\frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta e^{\pm 2i\phi}$

We can take superposition states of the solutions to obtain real wavefunctions that do not have any imaginary components:

Table 6.2.2 : The real solutions to the Schrödinger equation for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	m_l	$\psi_{n,l}$
ψ_{1s}	1	0	0	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
ψ_{2s}	2	0	0	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
ψ_{2p_z}	2	1	0	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \cos\theta$
ψ_{2p_x}	2	1	±1	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta\cos\phi$
ψ_{2p_y}	2	1	±1	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta\sin\phi$
ψ_{3s}	3	0	0	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-\frac{Zr}{3a_0}}$
ψ_{3p_z}	3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}} \cos\theta$
ψ_{3p_x}	3	1	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}} \sin\theta\cos\phi$
ψ_{3p_y}	3	1	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}} \sin\theta\sin\phi$
$\psi_{3d_{z^2}}$	3	2	0	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \left(3\cos^2\theta - 1\right)$
$\psi_{3d_{xz}}$	3	2	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin\theta\cos\theta\cos\phi$
$\psi_{3d_{yz}}$	3	2	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin\theta\cos\theta\sin\phi$
$\psi_{3d_{x^2-y^2}}$	3	2	±2	$\frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta\cos 2\phi$
$\psi_{3d_{xy}}$	3	2	±2	$\frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta\sin 2\phi$

These are the wavefunctions that are most often depicted. Visualizing the variation of an electronic wavefunction with r, θ, and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron-deficient part of one molecule is attracted to an electron-rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately do not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$. Do not confuse such plots with polar plots, which look similar. Probability densities also can be represented by contour maps, as shown in Figure 6.2.2 .

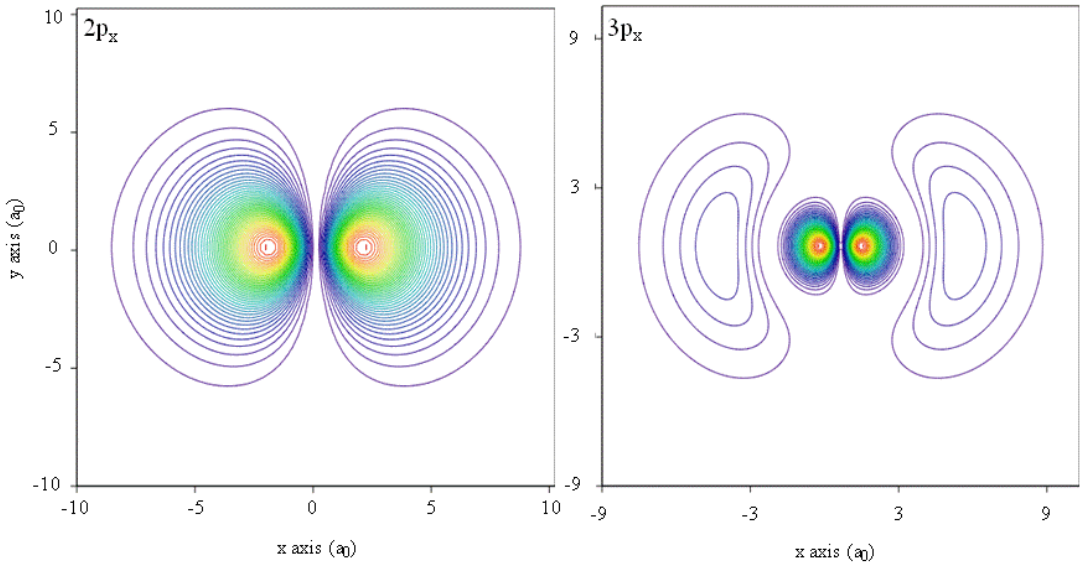


Figure 6.2.2: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical Harmonic functions.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s, 2s, and 2p orbitals plotted in Figure 6.2.3 .

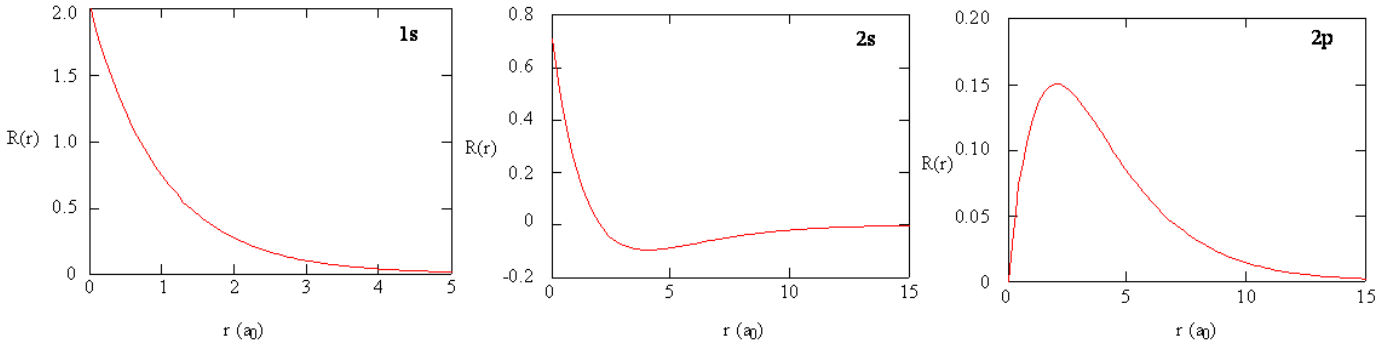


Figure 6.2.3: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

The 1s function in Figure 6.2.3 starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

Next notice how the radial function for the 2s orbital, Figure 6.2.3 , goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$, but p, d, f and all other functions go to zero at the origin. It is useful to remember that there are $n - 1 - l$ radial nodes in a wavefunction, which means that a 1s orbital has no radial nodes, a 2s has one radial node, and so on.

Exercise 6.2.5

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

Exercise 6.2.6

What mathematical feature of each of the radial functions controls the number of radial nodes?

Answer available at the end of this section.

Exercise 6.2.7 : Radial Node

At what value of r does the 2s radial node occur?

Answer available at the end of this section.

Exercise 6.2.8

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Answer available at the end of this section.

The quantity $R(r)^* R(r)$ gives the radial probability density; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three atomic orbitals are plotted in Figure 6.2.4 .

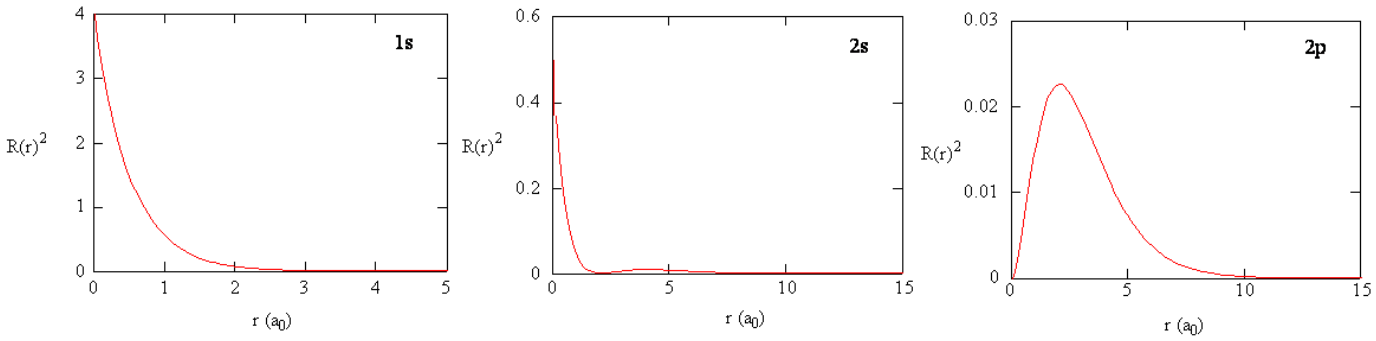


Figure 6.2.4: Radial probability densities for the 1s, 2s, and 2p orbitals.

Probabilities and Distribution Functions

When the **radial probability density** for every value of r is multiplied by the area of the spherical surface represented by that particular value of r, we get the radial distribution function. The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the **radial distribution function** is given by

$$\underbrace{4\pi r^2 R(r)^* R(r)}_{\text{radial probability density}}$$

Radial distribution functions are shown in Figure 6.2.5 . At small values of r, the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we increase r, the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to increase even though the radial probability density is beginning to decrease. At large values of r, the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

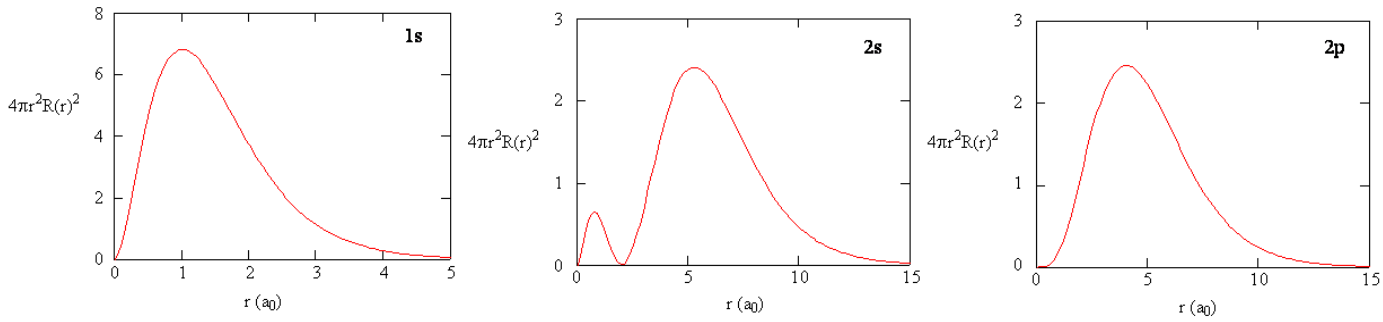


Figure 6.2.5: The radial distribution function for the 1s, 2s, and 2p orbitals.

Exercise 6.2.9

Write a quality comparison of the radial function and radial distribution function for the 2s orbital. See Figure 6.2.6 .

Answer available at the end of this section.

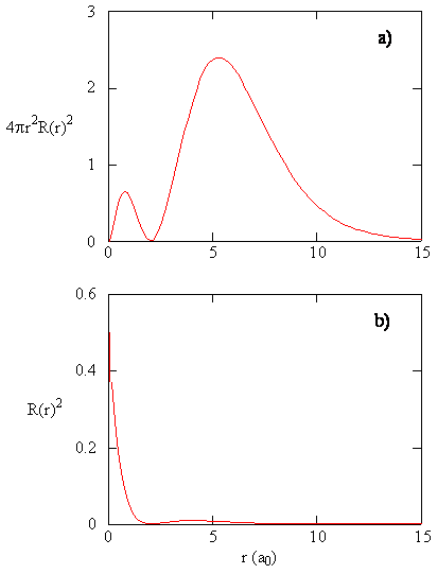


Figure 6.2.6: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

Answers

No need to know the functional form of the hydrogen atom eigenstates in any coordinate system. If the eigenstates (i.e., solutions to the hydrogen atom Schrödinger equation) are normalized - as we normally like them- then this integral will be 1.

a. $n = 3$ and $l = 2$
b. Energy:

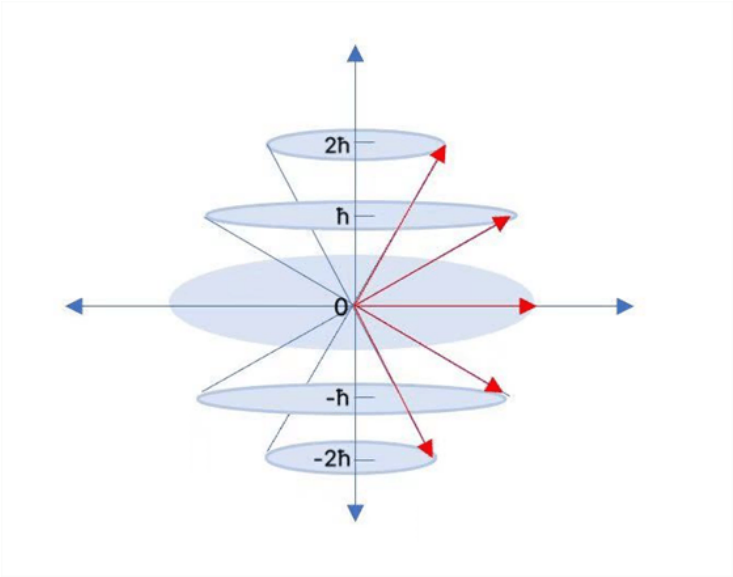
$$E_n = \frac{E_1}{n^2} = \frac{-13.6\text{eV}}{9} = -1.51\text{eV}$$

and angular momentum

$$\sqrt{l(l+1)}\hbar = \sqrt{2\times 3}\hbar = 2.584\times 10^{-34} J\cdot S$$

c. Magnetic quantum number:

$$m_l = -2, -1, 0, 1, 2$$



d.

The Laguerre polynomial controls the radial nodes with the number of roots for the Laguerre polynomial is the number of radial nodes.

A node exists when the radial portion of the wavefunction equals 0. The radial portion of the 2s wavefunction is:

$$R(r) = \left(\frac{1}{2\sqrt{2}}\right)\left(\frac{Z}{\alpha_0}\right)^{\frac{3}{2}}(2-\rho)e^{\frac{-\rho}{2}}$$

where $\rho = \frac{Zr}{\alpha_0}$, $Z = 1$ for the hydrogen atom and α_0 is the Bohr radius.

Therefore:

$$R(r) = \left(\frac{1}{2\sqrt{2}}\right)\left(\frac{1}{\alpha_0}\right)^{\frac{3}{2}}\left(2-\frac{r}{\alpha_0}\right)e^{\frac{-2r}{\alpha_0}}$$

For this wavefunction:

- $\left(\frac{1}{\alpha_0}\right)^{\frac{3}{2}}$ is a constant and will never equal 0.
- $e^{\frac{-2r}{\alpha_0}}$ is an exponential, and will also never equal 0.

Therefore, our node is when $\left(2-\frac{r}{\alpha_0}\right) = 0$ and

$$r = 2\alpha_0$$

Wavefunction	Energy	Total Nodes	Radial Nodes	Angular Nodes
1s	13.6 eV	0	0	0
2s	3.4 eV	1	1	0
2p	3.4 eV	1	0	1
3s	1.5 eV	2	2	0
3p	1.5 eV	2	1	1
3d	1.5 eV	2	0	2

The energy of the electron in each wavefunction is

$$E = \frac{Z^2 E_h}{2n^2}$$

The number of total nodes is (N-1\), the number of radial nodes is $N - L - 1$ and the number of angular nodes is L.

$R(r)$ is the radial function of the eigenstate and $4\pi r^2 R(r)^* R(r)$ gives the radial distribution function of the distance of electron at distance r from the nucleus (i.e., the probability integrated over all angles).

The radial probability function is low at small values of r because of a small surface area near nucleus, for example at 2s at a small value of r the radial probability function is low. At higher values of r the surface area increases while radial probability density decreases, this causes the radial distribution function to increase. In contrast the radial probability density is high at small surface area and when r is near the nucleus, i.e low values of r.

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- 6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

Learning Objectives

- Understand how to measure the orbital angular momentum of an electron around a nucleus.
- Understand how the Heisenburgh Uncertainty Principle extends to orbital angular momenta.
- Manipulate the angular momenta cyclic permutations that allow two of the three projects to be simultaneous measured

Consider a particle described by the Cartesian coordinates $(x, y, z) \equiv \vec{r}$ and their conjugate momenta $(p_x, p_y, p_z) \equiv \vec{p}$. The classical definition of the *orbital angular momentum* of such a particle about the origin is (i.e., via the vector cross product):

$$\vec{L} = \vec{r} \times \vec{p}$$

which can be separated into projections into each of the primary axes :

Multiple \label

Extending this discussion to the quantum mechanics, we can assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \vec{L}$ - that represent the components of orbital angular momentum in quantum mechanics - can be defined in an analogous manner to the corresponding components of classical angular momentum. In other words, we are going to assume that the above equations specify the angular momentum operators in terms of the position and linear momentum operators.

In Cartesian coordinates, the three operators for the orbital angular momentum components can be written as

$$\hat{L}_x = -\mathrm{i}\,\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{6.3.1}$$

$$\hat{L}_y = -\mathrm{i}\,\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \tag{6.3.2}$$

$$\hat{L}_z = -\mathrm{i}\,\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \tag{6.3.3}$$

These can be transforming to operators in standard spherical polar coordinates,

Multiple \label

we obtain

Multiple \label

We can introduce a new operator $\hat{L^2}$:

$$\hat{L^2} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{6.3.4}$$

$$= -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right) \tag{6.3.5}$$

The eigenvalue problem for $\hat{L^2}$ takes the form

$$\hat{L^2}|\psi\rangle = \lambda\,\hbar^2|\psi\rangle \tag{6.3.6}$$

where $\psi(r, \theta, \varphi)$ is the wavefunction, and λ is a number. Let us write

$$\psi(r, \theta, \varphi) = R(r)\,Y(\theta, \varphi) \tag{6.3.7}$$

By definition,

$$\boxed{L^2\,Y_l^{m_l} = l\,(l+1)\,\hbar^2\,Y_l^{m_l}} \tag{6.3.8}$$

where l is an integer. This is an important conclusion that argues the angular momentum is quantized with the square of the magnitude of the angular momentum only capable of assume one of the discrete set of values (Equation 6.3.8). From this, the **amplitude** of angular momentum can be expressed

$$\boxed{|\vec{L}| = \sqrt{L^2} = \sqrt{l(l+1)}\hbar} \tag{6.3.9}$$

Warning

We often refer to a particle in a state with angular momentum quantum number l as having angular momentum l, rather than saying that it has angular momentum of $\sqrt{l(l+1)}\hbar$ magnitude, primarily since it is awkward to say quickly.

The properties of spherical harmonics that the z-component of the angular momentum (L_z) is also quantized and can only assume a one of a discrete set of values

$$L_z\,Y_l^{m_l} = m\,\hbar\,Y_l^{m_l} \tag{6.3.10}$$

where m_l is an integer lying in the range $-l \leq m_l \leq l$.

- l is sometimes called "azimuthal quantum number" or "orbital quantum number"
- m_l is sometimes called "magnetic quantum number"

Simultaneous Measurements

Note that observables associated with $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ can, in principle, be measured. However, to determine if they can be measured *simultaneously* with infinite precision, the corresponding operators must **commute**. Remember that the fundamental commutation relations satisfied by the position and linear momentum operators are:

Multiple \label

where i and j stand for either x, y, or z. Consider the commutator of the operators $\hat{L}_x$ and $\hat{L}_z$:

Multiple \label

The **cyclic permutations** of the above result yield the fundamental commutation relations satisfied by the components of an orbital angular momentum:

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\,\hbar\,\hat{L}_z \tag{6.3.11}$$

$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\,\hbar\,\hat{L}_x \tag{6.3.12}$$

$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\,\hbar\,\hat{L}_y \tag{6.3.13}$$

The three commutation relations (Equations 6.3.11 - 6.3.13) are the foundation for the whole theory of angular momentum in quantum mechanics. Whenever we encounter three operators having these commutation relations, we know that the dynamical variables that they represent have identical properties to those of the components of an angular momentum (which we are about to derive). In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 6.3.11 - 6.3.13) represent the components of some sort of angular momentum.

> Any three operators that satisfy the cyclic commutation relations represent the components of some sort of angular momentum.

Example 6.3.1 : Commutators

Show that the $\hat{L^2}$ and $\hat{L}_x$ operators commute.

Solution

We want to confirm that $[\hat{L^2}, \hat{L}_x] = 0$ that from Equation 6.3.4 this can be expanded

$$[\hat{L^2}, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x]$$

from the properties of commutators, this can be expanded

$$[\hat{L^2}, \hat{L}_x] = [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]$$

However,

$$[\hat{L}_x^2, \hat{L}_x] = \hat{L}_x^2\hat{L}_x - \hat{L}_x\hat{L}_x^2 = \hat{L}_x\hat{L}_x\hat{L}_x - \hat{L}_x\hat{L}_x\hat{L}_x = 0$$

So

$$\begin{aligned}[\hat{L^2}, \hat{L}_x] &= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\ &= \hat{L}_y^2\hat{L}_x - \hat{L}_x\hat{L}_y^2 + \hat{L}_z^2\hat{L}_x - \hat{L}_x\hat{L}_z^2 \\ &= \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z\end{aligned}$$

Lets look at some related forms which can be used to simplify the above expression. The first two terms can and final two terms can be rewritten as different commutators

$$\begin{aligned}[\hat{L}_y, \hat{L}_x] &= \hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] \\ &= (\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y)\hat{L}_y + \hat{L}_y(\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y) \\ &= \cancel{\hat{L}_y\hat{L}_x\hat{L}_y} - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_y\hat{L}_y\hat{L}_x - \cancel{\hat{L}_y\hat{L}_x\hat{L}_y}\end{aligned}$$

The first & fourth terms cancel, giving

$$[\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] = \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y$$

Similarly,

$$[Lz, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] = \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z$$

So,

$$\begin{aligned}[\hat{L^2}, \hat{L}_x] &= [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\ &= -i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_z\hat{L}_y \\ &= 0\end{aligned}$$

One can also show similarly that

$$[\hat{L^2}, \hat{L}_y] = [\hat{L^2}, \hat{L}_z] = 0$$

Example 6.3.1 shows that while L_z can be known with certainty, L_x and L_y would **unknown**. This means that every vector with the appropriate length and *z*-component can drawn to represent $\vec{L}$, which forms a cone (Figure 6.3.1). The expected value of the angular momentum for a given ensemble of systems in the quantum state characterized by l and m_l could be somewhere on this cone while it cannot be defined for a single system (since the components of L do not commute with each other).

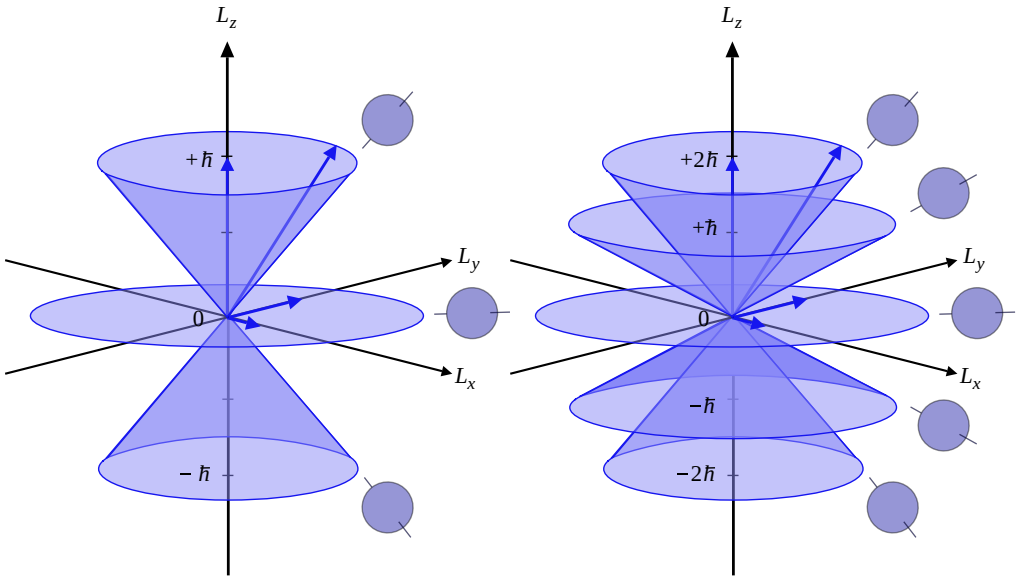


Figure 6.3.1 : Illustration of the vector model of orbital angular momentum. (left) A set of states with quantum numbers $l = 1$, and $m_l = -1, 0, +1$,. (right) A set of states with quantum numbers $l = 2$, and $m_l = -2, -1, 0, +1, +2$. (Public Domain; Maschen via Wikipedia)

The Meaning of Commutation of Two Operators

The mathematics of commutation relations is relatively straightforward, but what does it physically mean for an observable (Hermitian operator) to commute with another observable (Hermitian operator) in quantum mechanics?

If two operators $\hat{A}$ and $\hat{B}$ commute with each other then

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0,$$

which can be rearranged to

$$\hat{A}\hat{B} = \hat{B}\hat{A}.$$

This is not a trivial statement and many operations do not commute and hence the end-result depends on how you have ordered the operations.

If you recall that operators act on quantum mechanical states and give you a new state in return, then this means that with $\hat{A}$ and $\hat{B}$ commuting, the state you obtain from letting first $\hat{A}$ act and then $\hat{B}$ act on some initial state is the same as if you let first $\hat{B}$ and then $\hat{A}$ act on that state, i.e.,

$$\hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle.$$

Recall that when you perform a quantum mechanical measurement, you will always measure an eigenvalue of your operator, and after the measurement your state is left in the corresponding eigenstate. The eigenstates to the operator are precisely those states for which there is **no uncertainty** in the measurement: You will **always** measure the eigenvalue.

Therefore, $\hat{B}|a\rangle$ must be an eigenfunction of $\hat{A}$ with eigenvalue a just like $|a\rangle$ itself is. That is essentially saying that $|a\rangle$ is an eigenfunction of $\hat{B}$.

A key example of this is since $\hat{L}^2$ and $\hat{L}_x$ commute (Example 6.3.1) then both operators share the same eigenstates. Hence, we do no need to solve two eignevalue problems:

$$\hat{L}^2|\psi\rangle = \lambda|\psi\rangle$$

and

$$\hat{L}_x|\psi\rangle = \beta|\psi\rangle$$

If we solve one, we then know the eigenvalues ($|\psi\rangle$) for the other!

What does it mean when some observable $\hat{A}$ commutes with the Hamiltonian $\hat{H}$? First, we get all the result from above: There is a simultaneous eigenbasis of the energy-eigenstates and the eigenstates of $\hat{A}$. This can yield a tremendous simplification of the task of solving Schrödinger equations. For example, the Hamiltonian of the hydrogen atom commutes with $\hat{L}$, the angular momentum operator, and with $\hat{L}_z$, its z-component. This tells you that you can classify the eigenstates by an angular- and magnetic quantum number l and m.

Summary

In the quantum world, angular momentum is quantized. The square of the magnitude of the angular momentum (determined by the eigenvalues of the $\hat{L}^2$ operator) can only assume one of the discrete set of values

$$L^2 = l(l+1)\hbar^2$$

or the magnitude of the angular momentum

$$L = \sqrt{l(l+1)}\hbar$$

with $l = 0, 1, 2, ...$

The z-component of the angular momentum (i.e., projection of L onto the z-axis) is also quantized with

$$L_z = m_l\hbar$$

with $m_l = -l, 0-1, ..., 0, ... + l + 1, l$ for a given value of l. Hence, l and m_l are the *angular momentum quantum number* and the *magnetic quantum number,* respectively.

Contributors and Attributions

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6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

Learning Objectives

- Recognize how the hydrogen atomic orbitals vary as a function of the three primary quantum numbers

The solutions to the hydrogen atom Schrödinger equation discussed previously are functions that are products of a **spherical harmonic function** and a **radial function**.

$$\psi_{n,l,m_l}(r,\theta,\varphi) = \underbrace{R_{n,l}(r)}_{radial}\underbrace{Y_l^{m_l}(\theta,\varphi)}_{angular} \tag{6.4.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and φ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the proton in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\varphi)|^2$, evaluated at r, θ, and φ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and φ.

Exercise 6.4.1

Evaluate the following integrals

a. $\langle\psi(r,\theta,\varphi)|\psi(r,\theta,\varphi)\rangle$
b. $\langle\psi(r,\theta,\varphi)|\psi(r',\theta',\varphi')\rangle$

Answer available at the end of this section.

Answer available at the end of this section.

The quantum numbers n, l, and m_l have names:

- n is called the **principal quantum number**,
- l is called the **angular momentum quantum number**, and
- m_l is called the **magnetic quantum number** because the energy in a magnetic field depends upon m_l.

Often l is called the azimuthal quantum number because it is a consequence of the θ-equation, which involves the azimuthal angle Θ, referring to the angle to the zenith.

The three quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, l can have the values 0 to n-1, and m_l can have $2l+1$ values ranging from $-l$ to $+l$ in unit or integer steps. The values of the quantum number l usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l=4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n, the magnitude of the angular momentum is given by l, and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_l. The total number of orbitals with a particular value of n is n^2.

Exercise 6.4.4

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 6.4.5

Construct a table summarizing the allowed values for the quantum numbers n, l, and m_l for energy levels 1 through 7 of hydrogen.

Exercise 6.4.6

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom. What are the values for n and l ? What are the values for the energy and angular momentum? What are the possible values for the magnetic quantum number? What are the possible orientations for the angular momentum vector?

Radial Part of the Wavefunction

The asymptotic behavior (i.e., far away from the nucleus) to the radial part of the wavefunction is

$$R_{\text{asymptotic}}(r) \sim \exp\left(-\frac{r}{n}a_0\right) \tag{6.4.2}$$

where n will turn out to be a quantum number and a_0 is the Bohr radius (~52.9 pm). Note that this function decreases exponentially with distance, in a manner similar to the decaying exponential portion of the harmonic oscillator wavefunctions, but with a different distance dependence, r vs. r^2.

Exercise 6.4.2

What happens to the magnitude of $R_{\text{asymptotic}}(r)$ as the distance r from the proton approaches infinity? Sketch a graph of the function, $R_{\text{asymptotic}}(r)$. Why might this behavior be expected for an electron in a hydrogen atom?

Answer available at the end of this section.

The polynomials produced by the truncation of the power series are related to the associated Laguerre polynomials, $L_{n,l}(r)$, where the set of c_i are constant coefficients.

$$L_{n,l}(r) = \sum_{r=0}^{n-l-1} c_i r^i \tag{6.4.3}$$

These polynomials are identified by two indices or quantum numbers, n and l. Physically acceptable solutions require that n must be greater than or equal to $l+1$. The smallest value for l is zero, so the smallest value for n is 1. The angular momentum quantum number affects the solution to the radial equation because it appears in the radial differential equation, (Equation 6.4.1).

The $R(r)$ functions that solve the radial differential Equation 6.4.1, are products of the associated Laguerre polynomials and the exponential factor, multiplied by a normalization factor $(N_{n,l})$ and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,l}\left(\frac{r}{a_0}\right)^l L_{n,l}(r)e^{-\frac{r}{na_0}} \tag{6.4.4}$$

The decreasing exponential term overpowers the increasing polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of r. The first six radial functions are provided in Table 6.4.1 . Note that the functions in the table exhibit a dependence on Z, the atomic number of the nucleus. As discussed later in this chapter, other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$.

Table 6.4.3 : Radial functions for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	$R_{n,l}(\rho)$
R_{10}	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$
R_{20}	2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\rho)e^{-\rho/2}$
R_{21}	2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2}$
R_{30}	3	0	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3}$
R_{31}	3	1	$\frac{1}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (6\rho+\rho^2)e^{-\rho/3}$
R_{32}	3	2	$\frac{1}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}$

The constraint that n be greater than or equal to $l+1$ also turns out to quantize the energy, producing the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2}$$

Bohr Theory vs. Schrödinger Theory

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger and Bohr models differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $\sqrt{(l(l+1)}\hbar$.
3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

Exercise 6.4.3

Explain how the Schrödinger equation leads to the conclusion that the angular momentum of the hydrogen atom can be zero, and explain how the existence of such states with zero angular momentum contradicts Bohr's idea that the electron is orbiting around the proton in the hydrogen atom.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

Answers

a. This integral is equal to one since $\psi(r,\theta,\varphi)$ are normalized eigenstates.

b. However, we can explicitly evaluate this integral for any arbitrary pair of eigenstates

$$\langle\psi(r,\theta,\varphi)|\psi(r',\theta',\varphi')\rangle = \int_{allspace} \psi^*(r,\theta,\varphi)\psi(r',\theta',\varphi')d\tau$$

$$= \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi(r^2\sin(\theta)) \overbrace{\psi*(r,\theta,\varphi)}^{R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)} \overbrace{\psi(r,\theta,\varphi)}^{R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)}$$

$$= \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi(r^2\sin(\theta))[R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)][R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)]$$

$$= \left[\int_0^\infty r^2[R_{n,l}(r)R_{n',l'}(r)]dr\right]\left[\int_0^{2\pi}\int_0^\pi \sin(\theta)[Y_l^{m_l}(\theta,\varphi)Y_{l'}^{m_l'}(\theta,\varphi)]d\theta d\varphi\right]$$

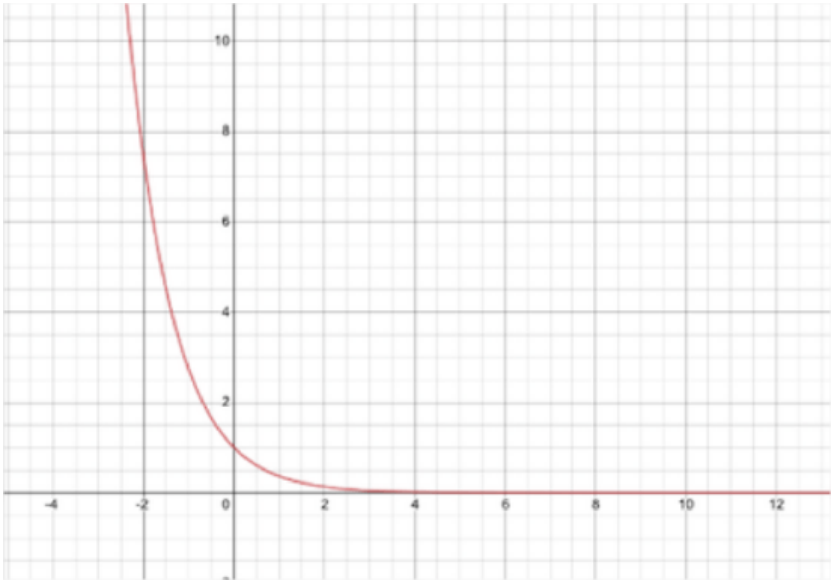
$$= \langle R_{n,l}(r)|R_{n',l'}(r)\rangle\langle Y_l^{m_l}(\theta,\varphi)|Y_{l'}^{m_l'}(\theta,\varphi)\rangle$$

$$= (\delta_{nn'}\delta_{ll'})(\delta_{ll'}\delta_{mm'}) = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$

While part a demonstrates normality of the eigenstates, part b demonstrates the orthogonality of the eigenstate (and normality too).

$$R(r) = e^{-\frac{c}{n}a_0}$$

As r approaches infinity, the exponential decay goes to zero, this is to be expected as the likelihood of an electron being found at an infinite distance away is almost zero too.



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6.5: s-orbitals are Spherically Symmetric

The hydrogen atom wavefunctions, $\psi(r, \theta, \varphi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1$, l = 0 is called the 1s orbital, and an electron that is described by this function is said to be “in” the ls orbital, i.e. have a 1s orbital state. The constraints on n, l, and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

Visualizing the variation of an electronic wavefunction with r, θ, and φ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

We can obtain an energy and one or more wavefunctions for every value of n, the principal quantum number, by solving Schrödinger's equation for the hydrogen atom. A knowledge of the wavefunctions, or probability amplitudes ψ_n, allows us to calculate the probability distributions for the electron in any given quantum level. When *n* = 1, the wavefunction and the derived probability function are independent of direction and depend only on the distance *r* between the electron and the nucleus. In Figure 6.5.1 , we plot both ψ_1 and P_1 versus r, showing the variation in these functions as the electron is moved further and further from the nucleus in any one direction. (These and all succeeding graphs are plotted in terms of the atomic unit of length, $a_0 = 0.529 \times 10^{-8}\ cm$.)

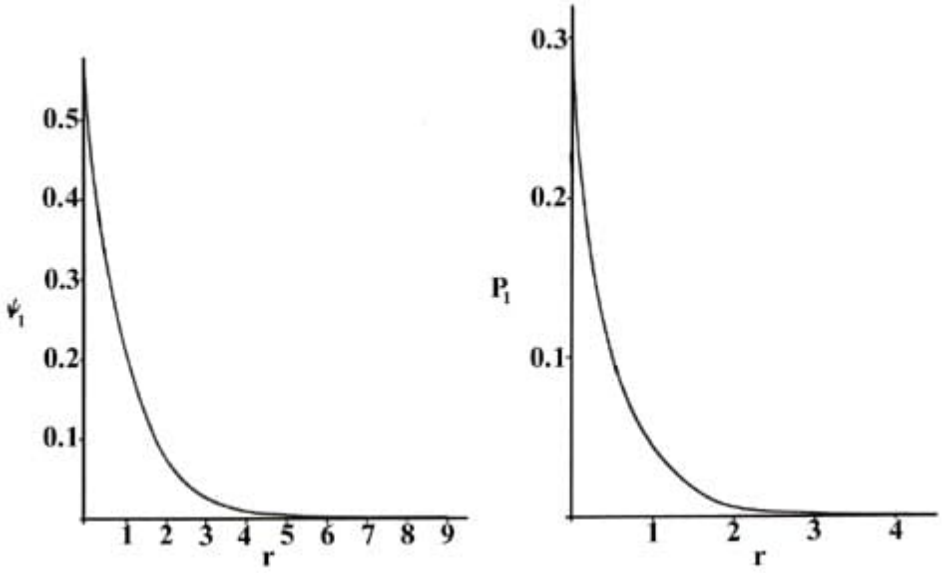


Figure 6.5.1 : The wavefunction and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

Two interpretations can again be given to the P_1 curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Figure 6.5.1 for P_1. That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing r. The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than 10^{-8} cm will be greater than K, the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret P_1 as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of P_n for every small volume element over all space adds up to unity, i.e., one electron and one

electronic charge.)

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately does not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane (Figure 6.5.2), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line (Figure 6.5.2). Since the electron density depends only on *r*, the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.

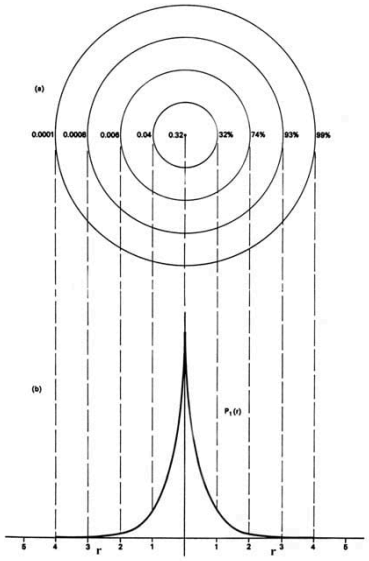


Figure 6.5.2 : (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter = $4.2 \times 10^{-8}\ cm$). (b) This is a profile of the contour map along a line through the nucleus. It is, of course, the same as that given previously in Figure 6.5.1 for P_1, but now plotted from the nucleus in both directions.

When the electron is in a definite energy level we shall refer to the P_n distributions as ***electron density distributions***, since they describe the manner in which the total electronic charge is distributed in space. The electron density is expressed in terms of the number of electronic charges per unit volume of space, e^-/V. The volume *V* is usually expressed in atomic units of length cubed, and one atomic unit of electron density is then e^-/a_0^3. To give an idea of the order of magnitude of an atomic density unit, 1 au of charge density e^-/a_0^3 = 6.7 electronic charges per cubic Ångstrom. That is, a cube with a length of $0.52917 \times 10^{-8}\ cm$, if uniformly filled with an electronic charge density of 1 au, would contain 6.7 electronic charges.

For every value of the energy E_n, for the hydrogen atom, there is a degeneracy equal to n^2. Therefore, for *n* = 1, there is but one atomic orbital and one electron density distribution. However, for *n* = 2, there are four different atomic orbitals and four different electron density distributions, all of which possess the same value for the energy, E_2. Thus for all values of the principal quantum number *n* there are n^2 different ways in which the electronic charge may be distributed in three-dimensional space and still possess the same value for the energy. For every value of the principal quantum number, ***one*** of the possible atomic orbitals is independent of direction and gives a spherical electron density distribution which can be represented by circular contours as has been exemplified above for the case of *n* = 1. The other atomic orbitals for a given value of *n* exhibit a directional dependence and predict density distributions which are not spherical but are concentrated in planes or along certain axes. The angular dependence of the atomic orbitals for the hydrogen atom and the shapes of the contours of the corresponding electron

density distributions are intimately connected with the angular momentum possessed by the electron.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s and 2s orbitals plotted in Figure 6.5.3 . The 1s function in Figure $6.5.3; left$ starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

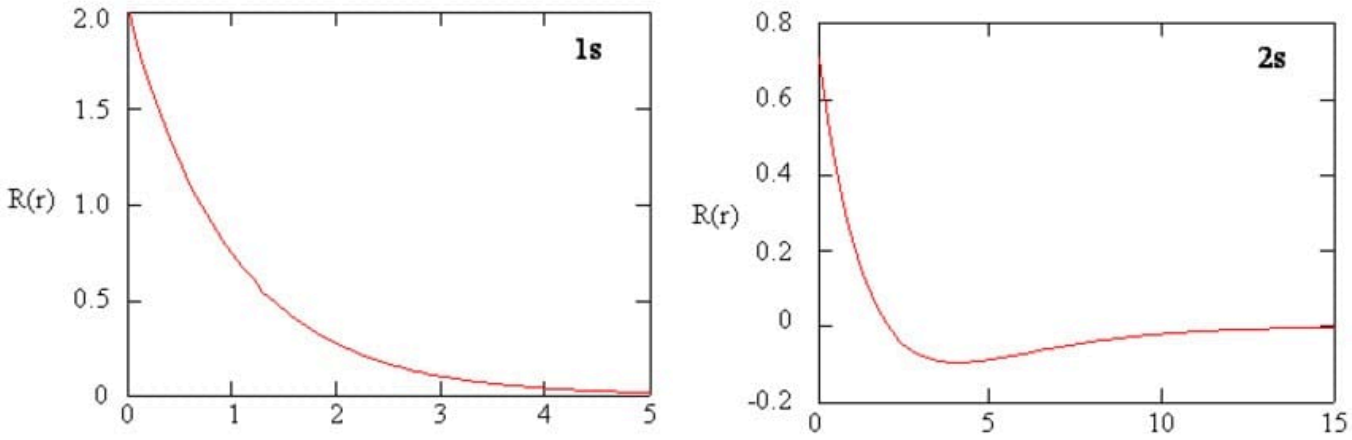


Figure 6.5.3 : Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click here.

Next notice how the radial function for the 2s orbital, Figure $6.5.3; right$, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$.

Exercise 6.5.1

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

Exercise 6.5.2

What mathematical feature of each of the radial functions controls the number of radial nodes?

Exercise 6.5.3 : Radial Nodes

At what value of r does the 2s radial node occur?

Exercise 6.5.4

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Answer available at the end of this section.

Radial probability densities for the 1s and 2s atomic orbitals are plotted in Figure 6.5.4 .

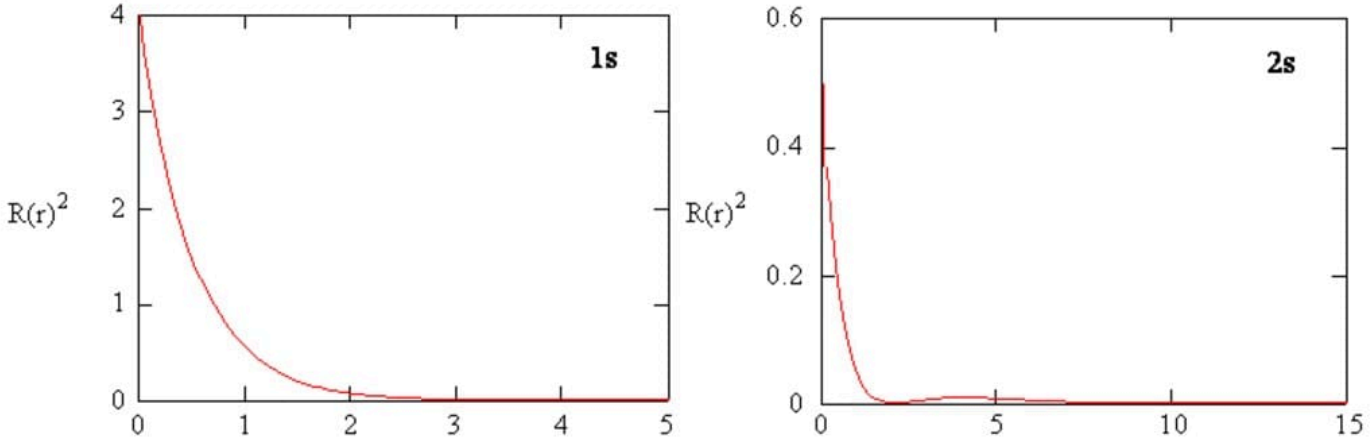


Figure 6.5.4 : Radial densities ($R(r)^*R(r)$) for the 1s and 2s orbitals.

Radial Distribution Functions

Rather than considering the amount of electronic charge in one particular small element of space, we may determine the total amount of charge lying within a thin spherical shell of space. Since the distribution is independent of direction, consider adding up all the charge density which lies within a volume of space bounded by an inner sphere of radius r and an outer concentric sphere with a radius only infinitesimally greater, say $r + \Delta r$. The area of the inner sphere is $4\pi r^2$ and the thickness of the shell is Δr. Thus the volume of the shell is $4\pi r^2 \Delta r$ and the product of this volume and the charge density $P_1(r)$, which is the charge or number of electrons per unit volume, is therefore the total amount of electronic charge lying between the spheres of radius r and $r + \Delta r$. The product $4\pi r^2 P_n$ is given a special name, the **radial distribution function**.

Volume Element for a Shell in Spherical Coordinates

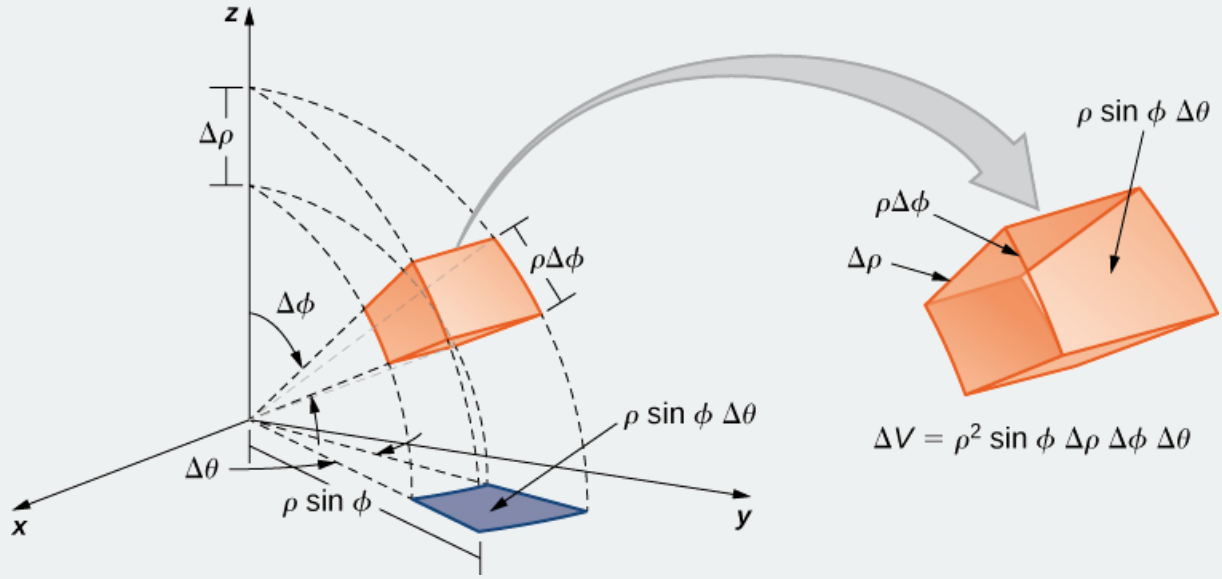
The reader may wonder why the volume of the shell is not taken as:

$$\frac{4}{3}\pi\left[(r+\Delta r)^3 - r^3\right]$$

the difference in volume between two concentric spheres. When this expression for the volume is expanded, we obtain

$$\frac{4}{3}\pi\left(3r^2\Delta r + 3r\Delta r^2 + \Delta r^3\right)$$

and for very small values of Δr the $3r\Delta r^2$ and Δr^3 terms are negligible in comparison with $3r^2\Delta r$. Thus for small values of Δr, the two expressions for the volume of the shell approach one another in value and when Δr represents an infinitesimal small increment in r they are identical.



The volume element of a box in spherical coordinates. (CC BY; OpenStax).

The radial distribution function is plotted in Figure 6.5.5 for the ground state of the hydrogen atom.

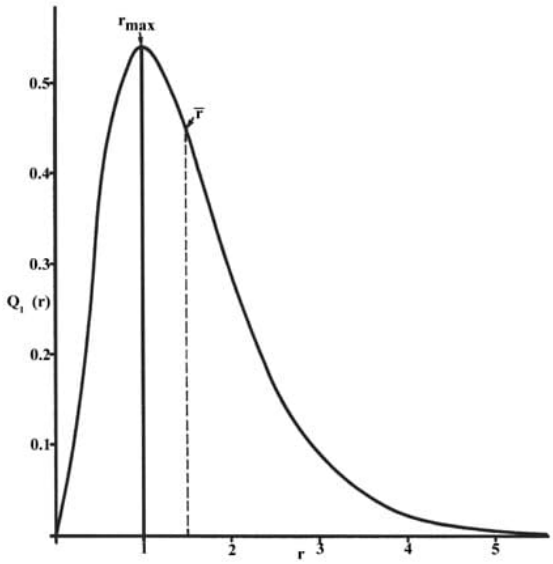


Figure 6.5.5 : The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r + \delta r$.

The curve passes through zero at $r = 0$ since the surface area of a sphere of zero radius is zero. As the radius of the sphere is increased, the volume of space defined by $4\pi r^2 Dr$ increases. However, as shown in Figure 6.5.4 , the absolute value of the electron density at a given point decreases with r and the resulting curve must pass through a maximum. This maximum occurs at $r_{max} = a_0$. Thus more of the electronic charge is present at a distance a_o, out from the nucleus than at any other value of r. Since the curve is unsymmetrical, the average value of r, denoted by $\bar{r}$, is not equal to r_{max}. The average value of r is indicated on the figure by a dashed line. A "picture" of the electron density distribution for the electron in the $n = 1$ level of the hydrogen atom would be a spherical ball of charge, dense around the nucleus and becoming increasingly diffuse as the value of r is increased.

> The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the radial distribution function is given by $4\pi r^2 R(r)^* R(r)$.

Radial distribution functions are shown in Figure 6.5.6 . At small values of r, the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we

increase r, the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to increase even though the radial probability density is beginning to decrease. At large values of r, the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

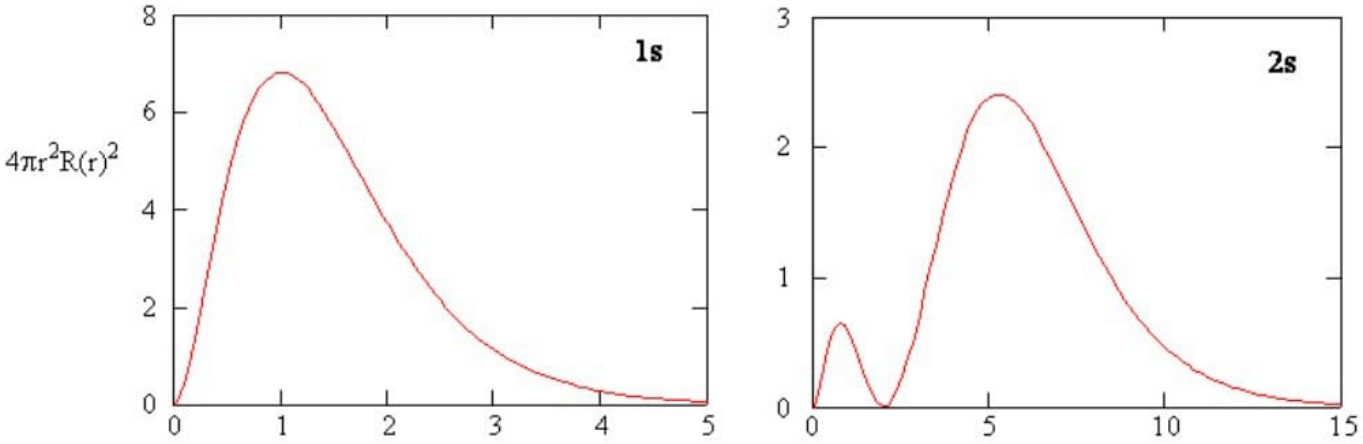


Figure 6.5.6 : The radial distribution function ($4\pi r^2 R(r)^* R(r)$) for the 1s and 2s orbitals. Compare to the radial functions in Figure 6.5.3 or the radial densities in Figure 6.5.4 . For an interactive graph click here.

Example 6.5.1 :

Calculate the probability of finding a 1s hydrogen electron being found within distance $2a_o$ from the nucleus.

Solution available at the end of this section.

Summary

This completes the description of the most stable state of the hydrogen atom, the state for which $n = 1$. Before proceeding with a discussion of the excited states of the hydrogen atom we must introduce a new term. When the energy of the electron is increased to another of the allowed values, corresponding to a new value for n, y_n and P_n change as well. The wavefunctions y_n for the hydrogen atom are given a special name, ***atomic orbitals***, because they play such an important role in all of our future discussions of the electronic structure of atoms. In general the word orbital is the name given to a wavefunction which determines the motion of a single electron. If the one-electron wavefunction is for an atomic system, it is called an atomic orbital.

Do not confuse the word orbital with the classical word and notion of an orbit. First, an orbit implies the knowledge of a definite trajectory or path for a particle through space which in itself is not possible for an electron. Secondly, an orbital, like the wavefunction, has no physical reality but is a mathematical function which when squared gives the physically measurable electron density distribution.

Contributors and Attributions

- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

Answers

	Energy 1.Particle in a Box ($h^2n^2/8m_eL^2$) 2.Harmonic Oscillator($(n+0.5)\hbar\omega$) 3.Hydrogen ($-13.6eV/n^2$)	Number of Radial Nodes (n-l-1)	Number of Angular Nodes l = (n-1) l : s =0 p = 1 d = 2	Total Number of Nodes
n = 1	1. 6.02 *10^{-38} J/L^2 2. 1.5$\hbar\omega$ 3. -13.6 eV	-	0	0
n = 2	1. 6.02 *10^{-38} J/L^2 2. 2.5$\hbar\omega$ 3. -3.4 eV	for s: 1 for p: 0	for s: 0 for p: 1	1
n = 3	1. 6.02 *10^{-38} J/L^2 2. 3.5$\hbar\omega$ 3. 1.51 eV	for s: 2 for p: 1 for d: 0	for s: 0 for p:1 for d: 2	2

For a particle in a box the energy is equivalent to $E_n = 6.02 \times 10^{-38} n^2 L^2$ where n is any value greater than and not equal to 0 and L is the length of the box.

Note the wavefunction of hydrogen 1s orbital which is

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\rho}$$

with $\rho = \frac{r}{a_0}$.

The probability of finding the electron within $2a_0$ distance from the nucleus will be:

$$prob = \underbrace{\int_0^{\pi} \sin\theta \, d\theta}_{over\ \theta} \overbrace{\frac{1}{\pi a_0^3} \int_0^{2a_0} r^2 e^{-2r/a_0} dr}^{over\ r} \underbrace{\int_0^{2\pi} d\phi}_{over\ \phi}$$

Since $\int_0^{\pi} \sin\theta d\theta = 2$ and $\int_0^{2\pi} d\phi = 2\pi$, we have

$$\begin{aligned}
prob &= 2 \times 2\pi \times \frac{1}{\pi a_0^3} \int_0^2 a_0(-a_0/2) r^2 de^{-2r/a_0} \\
&= \frac{4}{a_0^3} \left(-\frac{a_0}{2}\right) (r^2 e^{-2r/a_0}|_0^{2a_0} - \int_0^{2a_0} 2re^{-2r/a_0} dr) \\
&= -\frac{2}{a_0^2} [(2a_0)^2 e^{-4} - 0 - 2 \int_0^{2a_0} r \left(-\frac{a_0}{2}\right) de^{-2r/a_0}] \\
&= -\frac{2}{a_0^2} 4a_0^2 e^{-4} + \frac{4}{a_0^2} (-\frac{a_0}{2}) (re^{-2r/a_0}|_0^{2a_0} - \int_0^{2a_0} e^{-2r/a_0} dr) \\
&= -8e^{-4} - \frac{2}{a_0} \left[2a_0 e^{-4} - 0 - (-\frac{a_0}{2}) e^{-2r/a_0}|_0^{2a_0}\right] \\
&= -8e^{-4} - 4e^{-4} - e^{2r/a_0}|_0^{2a_0} \\
&= -12e^{-4} - (e^{-4} - 1) = 1 - 13e^{-4} = 0.762
\end{aligned}$$

There is a 76.2% probability that the electrons will be within $2a_o$ of the nucleus in the 1s eigenstate.

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6.6: Orbital Angular Momentum and the p-Orbitals

Learning Objectives

- To relate the classical orbital angular momentum for an particle to the quantum equivalent
- Characterize the mangnitude and orientation of orbital angular momentum for an electron in terms of quantum numbers

Classical Orbital Angular Momentum

The physical quantity known as angular momentum plays a dominant role in the understanding of the electronic structure of atoms. To gain a physical picture and feeling for the angular momentum it is necessary to consider a model system from the classical point of view. The simplest classical model of the hydrogen atom is one in which the electron moves in a circular orbit with a constant speed or angular velocity (Figure 6.6.1). Just as the linear momentum $m\vec{v}$ plays a dominant role in the analysis of linear motion, so angular momentum (L) plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.

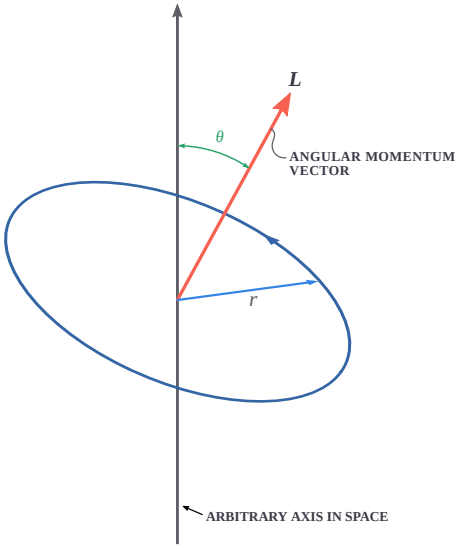


Figure 6.6.1 : The angular momentum vector for a classical model of the atom. (CC BY-NC; Ümit Kaya via LibreTexts)

In Figure 6.6.1 , m is the mass of the electron, $\vec{v}$ is the linear velocity (the velocity the electron would possess if it continued moving at a tangent to the orbit) and r is the radius of the orbit. The linear velocity $\vec{v}$ is a vector since it possesses at any instant both a magnitude and a direction in space. Obviously, as the electron rotates in the orbit the direction of $\vec{v}$ is constantly changing, and thus the linear momentum $m\vec{v}$ is ***not*** constant for the circular motion. This is so even though the speed of the electron (i.e, the magnitude of $\vec{v}$ which is denoted by $|\vec{v}|$) remains unchanged. According to Newton's second law, a force must be acting on the electron if its momentum changes with time. This is the force which prevents the electron from flying on tangent to its orbit. In an atom the attractive force which contains the electron is the electrostatic force of attraction between the nucleus and the electron, directed along the radius *r* at right angles to the direction of the electron's motion.

The angular momentum, like the linear momentum, is a vector and is defined as follows:

$$|\vec{L}| = m\nu r$$

The angular momentum vector $\vec{L}$ is directed along the axis of rotation. From the definition it is evident that the angular momentum vector will remain constant as long as the speed of the electron in the orbit is constant ($|\vec{v}|$ remains unchanged) and the plane and radius of the orbit remain unchanged. Thus for a given orbit, the angular momentum is constant as long as the angular velocity of

the particle in the orbit is constant. In an atom the only force on the electron in the orbit is directed along r; it has no component in the direction of the motion. The force acts in such a way as to change only the linear momentum. Therefore, while the linear momentum is not constant during the circular motion, the angular momentum is. A force exerted on the particle in the direction of the vector $\vec{v}$ would change the angular velocity and the angular momentum. When a force is applied which does change $\vec{L}$, a ***torque*** is said to be acting on the system. Thus angular momentum and torque are related in the same way as are linear momentum and force.

Quantum Angular Momentum

The important point of the above discussion is that both the angular momentum and the energy of an atom remain constant if the atom is left undisturbed. Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system. Thus both the energy and the angular momentum are quantized for an atom.

> Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system.

There is a quantum number, denoted by l, which governs the magnitude of the angular momentum, just as the quantum number n determines the energy. The ***magnitude*** of the angular momentum may assume only those values given by:

$$|L| = \sqrt{l(l+1)}\hbar \tag{6.6.1}$$

with $l = 0, 1, 2, 3, ...n - 1$.

Furthermore, the value of *n* limits the maximum value of the angular momentum as the value of *l* cannot be greater than *n* - 1. For the state *n* = 1 discussed above, l may have the value of zero only. When *n* = 2, *l* may equal 0 or 1, and for *n* = 3, *l* = 0 or 1 or 2, etc. When *l* = 0, it is evident from Equation 6.6.1 that the angular momentum of the electron is zero. The atomic orbitals which describe these states of zero angular momentum are called s orbitals. The *s* orbitals are distinguished from one another by stating the value of *n*, the principal quantum number. They are referred to as the 1s, 2s, 3s, etc., atomic orbitals.

The preceding discussion referred to the 1s orbital since for the ground state of the hydrogen atom $n = 1$ and $l = 0$. This orbital, and all s orbitals in general, predict spherical density distributions for the electron as discussed previously.

It is common usage to refer to an electron as being "in" an orbital even though an orbital is, but a mathematical function with no physical reality. To say an electron is in a particular orbital is meant to imply that the electron is in the quantum state which is described by that orbital. For example, when the electron is in the 2s orbital the hydrogen atom is in a state for which $n = 2$ and $l = 0$.

Comparing these results with those for the 1s orbital in Figure 6.6.2 we see that as n increases the average value of r increases. This agrees with the fact that the energy of the electron also increases as n increases. The increased energy results in the electron being on the average pulled further away from the attractive force of the nucleus. As in the simple example of an electron moving on a line, nodes (values of r for which the electron density is zero) appear in the probability distributions. The number of nodes increases with increasing energy and equals $n - 1$.

When the electron possesses angular momentum the density distributions are no longer spherical. In fact for each value of l, the electron density distribution assumes a characteristic shapes in Figure 6.6.2 .

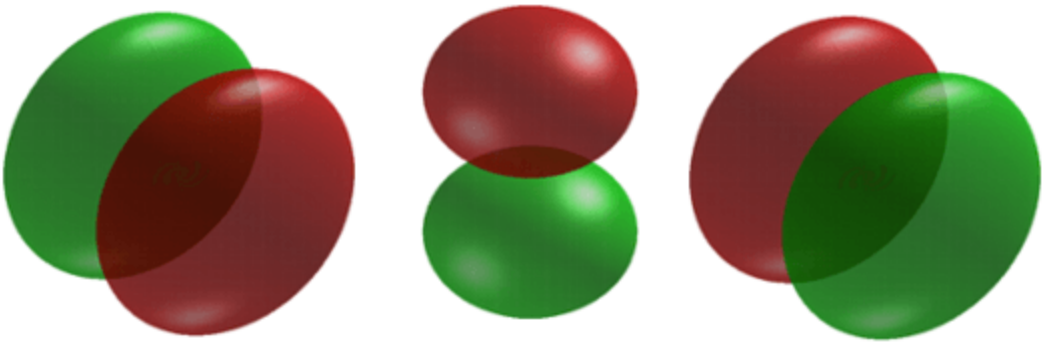


Figure 6.6.2 : The appearance of the three 2p orbitals in three-dimensional space. (CC BY-SA 3.0; I, Sarxos).

When $l = 1$, the orbitals are called *p* orbitals. In this case the orbital and its electron density are concentrated along a line (axis) in space. The 2*p* orbital or wavefunction is positive in value on one side and negative in value on the other side of a plane which is perpendicular to the axis of the orbital and passes through the nucleus. The orbital has a node in this plane, and consequently an electron in a 2*p* orbital does not place any electronic charge density at the nucleus. The electron density of a 1s orbital, on the other hand, is a maximum at the nucleus. The same diagram for the 2*p* density distribution is obtained for any plane which contains this axis. Thus in three dimensions the electron density would appear to be concentrated in two lobes, one on each side of the nucleus, each lobe being circular in cross section Figure 6.6.3 .

An electron possesses orbital angular momentum has a density distributions is no longer spherical.

The m_l Quantum Number and Magnetic Fields

The magnetic quantum number, designated by the letter m_l, is the third quantum numbers which describe the unique quantum state of an electron. The magnetic quantum number distinguishes the orbitals available within a subshell, and is used to calculate the azimuthal component of the orientation of the orbital in space. As with our discussion of rigid rotors, the quantum number m_l refers to the projection of the angular momentum in this arbitrarily chosen direction, conventionally called the z direction or quantization axis. L_z, the magnitude of the angular momentum in the z direction, is given by the formula

$$L_z = m_l \hbar$$

The quantum number m_l refers, loosely, to the direction of the angular momentum vector. The magnetic quantum number m_l only affects the electron's energy if it is in a magnetic field because in the absence of one, all spherical harmonics corresponding to the different arbitrary values of m_l are equivalent. The magnetic quantum number determines the energy shift of an atomic orbital due to an external magnetic field (this is called the Zeeman effect) - hence the name magnetic quantum number. However, the actual magnetic dipole moment of an electron in an atomic orbital arrives not only from the electron angular momentum, but also from the electron spin, expressed in the spin quantum number, which is the fourth quantum number. m_s and discussed in the next chapter.

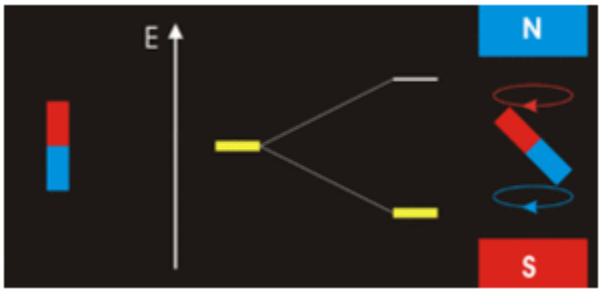


Figure 6.6.3 : The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left). However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative orientations of the magnet to the external field. (CC SA-BY 3.0; Darekk2).

m_l Which Number Corresponds to which p-Orbital?

The answer is complicated; while $m_l = 0$ corresponds to the p_z, the orbitals for $m_l = +1$ and $m_l = -1$ lie in the xy-plane (see Spherical Harmonics), but not on the axes. The reason for this outcome is that the wavefunctions are usually formulated in spherical coordinates to make the math easier, but graphs in the Cartesian coordinates make more intuitive sense for humans. The p_x and p_y orbitals are constructed via a linear combination approach from radial and angular wavefunctions and converted into xy (this was discussed previously). Thus, it is not possible to directly correlate the values of $m_l = \pm 1$ with specific orbitals. The notion that we can do so is sometimes presented in introductory courses to make a complex mathematical model just a little bit simpler and more intuitive, but it is incorrect.

The three wavefunctions for $n = 2$ and $l = 1$ are as follows.

$$|\psi_{2,1,0}\rangle = r\cos\theta R(r) \tag{6.6.2}$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2}\sin\theta e^{i\phi}R(r) \tag{6.6.3}$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2}\sin\theta e^{-i\phi}R(r) \tag{6.6.4}$$

The notation is $|\psi_{n,l,m_l}\rangle$ with $R(r)$ is the radial component of this wavefuction, θ is the angle with respect to the z-axis and ϕ is the angle with respect to the xz-plane.

$$R(r) = \sqrt{\frac{Z^5}{32\pi a_0^5}}\mathrm{e}^{-Zr/2a_0}$$

in which Z is the atomic number (or probably better nuclear charge) and a_0 is the Bohr radius.

In switching from spherical to Cartesian coordinates, we make the substitution $z = r\cos\theta$, so:

$$|\psi_{2,1,0}\rangle = zR(r)$$

This is ψ_{2p_z} since the value of ψ is dependent on z: when $z = 0$; $\psi = 0$, which is expected since $z = 0$ describes the xy-plane.

The other two wavefunctions are degenerate in the xy-plane. An equivalent statement is that these two orbitals do not lie on the x- and y-axes, but rather bisect them. Thus it is typical to take linear combinations of them to make the equation look prettier. If any set of wavefunctions is a solution to the Schrödinger equation, then any set of linear combinations of these wavefunctions must also be a solution (Section 2.4). We can do this because of the linearity of the Schrödinger equation.

In the equations below, we're going to make use of some trigonometry, notably Euler's formula:

$$\mathrm{e}^{\mathrm{i}\phi} = \cos\phi + \mathrm{i}\sin\phi \tag{6.6.5}$$

$$\sin\phi = \frac{\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi}}{2\mathrm{i}} \tag{6.6.6}$$

$$\cos\phi = \frac{\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}}{2} \tag{6.6.7}$$

We're also going to use $x = \sin\theta\cos\phi$ and $y = \sin\theta\sin\phi$.

$$\begin{aligned}\psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} - \psi_{2,1,-1}\right)\\ &= \frac{1}{2}\left(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}\right) r\sin\theta f(r)\\ &= r\sin\theta\cos\phi f(r) = x f(r)\\ \psi_{2p_y} &= \frac{\mathrm{i}}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right)\\ &= \frac{1}{2\mathrm{i}}\left(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi}\right) r\sin\theta f(r)\\ &= r\sin\theta\sin\phi f(r) = y f(r)\end{aligned}$$

So, while $m_l = 0$ corresponds to $|p_z\rangle$, $m_l = +1$ and $m_l = -1$ **cannot** be directly assigned to either $|p_x\rangle$ or $|p_y\rangle$, but rather a combination of $|p_x\rangle$ and $|p_y\rangle$. An alternative description is that $m_l = +1$ might correspond to $(|p_x\rangle + |p_y\rangle)$ and $m_l = -1$ might correspond to $(|p_x\rangle - |p_y\rangle)$.

d-Orbitals (even higher angular momenta wavefunctions)

When $l = 2$, the orbitals are called *d* orbitals and Figure 6.6.4 shows the contours in a plane for a 3*d* orbital and its density distribution. Notice that the density is again zero at the nucleus and that there are now two nodes in the orbital and in its density distribution. As the angular momentum of the electron increases, the density distribution becomes increasingly concentrated along an axis or in a plane in space. Only electrons in s orbitals with **zero angular momentum** give spherical density distributions and in addition place charge density at the position of the nucleus.

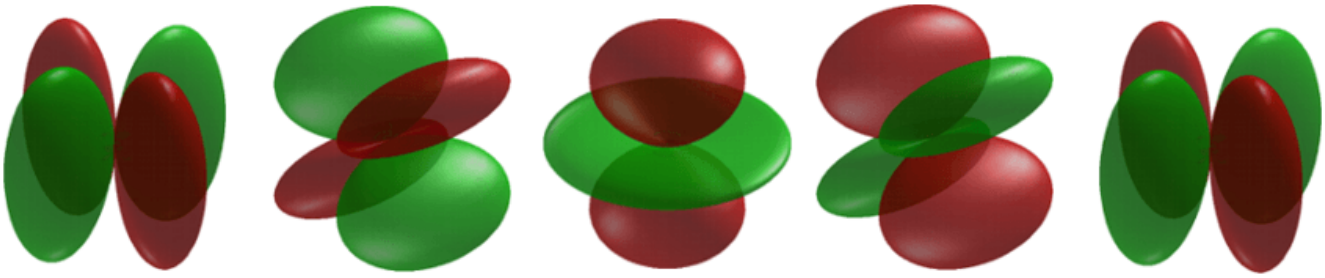


Figure 6.6.4 : The appearance of the 3d electron density distribution in three-dimensional space. (CC BY-SA 3.0; I, Sarxos)

As with the p-orbitals, the only d-orbital that a specific m_l can be ascribed is the d_{z^2} orbitals with $m_l = 0$. The rest are linear combinations of the hydrogen atom wavefunctions with complex spherical harmonic angular components.

There seems to be neither rhyme nor reason for the naming of the states corresponding to the different values of ℓ (s, *p, d, f* for *l* = 0, 1, 2, 3). This set of labels had its origin in the early work of experimental atomic spectroscopy. The letter s stood for sharp, *p* for principal, *d* for diffuse and *f* for fundamental in characterizing spectral lines. From the letter *f* onwards the naming of the orbitals is alphabetical $l = 4, 5, 6 \rightarrow g, h, i, ...$

We have not as yet accounted for the full degeneracy of the hydrogen atom orbitals which we stated earlier to be n^2 for every value of n. For example, when $n = 2$, there are four distinct atomic orbitals. The remaining degeneracy is again determined by the angular momentum of the system. Since angular momentum like linear momentum is a vector quantity, we may refer to the component of the angular momentum vector which lies along some chosen axis. For reasons we shall investigate, the number of values a particular component can assume for a given value of l is $(2l + 1)$. Thus when $l = 0$, there is no angular momentum and there is but a single orbital, an s orbital. When $l = 1$, there are three possible values for the component $(2 \times 1 + 1)$ of the total angular momentum which are physically distinguishable from one another. There are, therefore, three p orbitals. Similarly there are five d orbitals, $(2 \times 2 + 1)$, seven f orbitals, $(2 \times 3 + 1)$, etc. All of the orbitals with the same value of n and l, the three 2p orbitals for example, are similar but differ in their spatial orientations.

To gain a better understanding of this final element of degeneracy, we must consider in more detail what quantum mechanics

predicts concerning the angular momentum of an electron in an atom.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)
- Stack Exchange (Ben Norris and Loong)

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6.7: The Helium Atom Cannot Be Solved Exactly

Learning Objectives

- Adding electrons to the quantum hydrogen atom results in analytically unsolvable Schrödinger Equations (they exist, we just do not have analytical forms for them)
- A basic aspect of the corresponding multi-electron Hamiltonians is that they are NOT separable with respect to the spatial coordinate of each electron
- The solutions to multi-electron Schrödinger Equations are called multi-electron wavefunctions and they are often approximated as a product of single-electron wavefunctions (called the orbital approximation).

Multi-electron Hamiltonians

The second element in the periodic table provides our first example of a quantum-mechanical problem which *cannot* be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

Figure 6.7.1 shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors r_1 and r_2. The electrons are separated by a distance $r_{12} = |r_1 - r_2|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

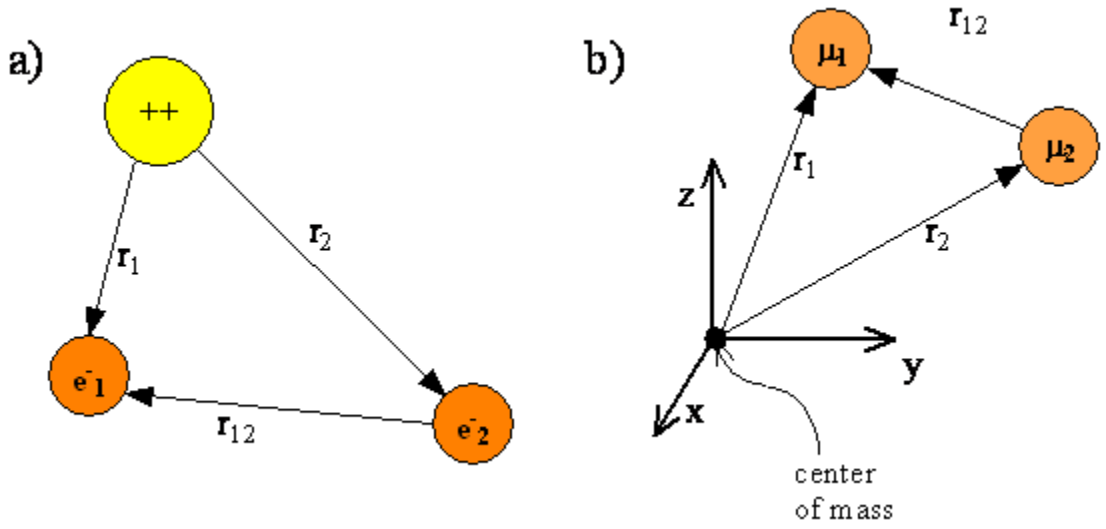


Figure 6.7.1 : (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Hamiltonian operator for the hydrogen atom serves as a reference point for writing the Hamiltonian operator for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} \tag{6.7.1}$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \tag{6.7.2}$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{6.7.3}$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{6.7.4}$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{6.7.5}$$

The two-electron Hamiltonian in Equation 6.7.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{6.7.6}$$

and including terms for the additional electrons. The subsequent multi-electron atom with n electron is

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i\neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \tag{6.7.7}$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 6.7.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 6.7.3 and 6.7.4). The other big difference between single electron systems and multi-electron systems is the presence of the $V_{ij}(r_{ij})$ terms which contain $1/r_{ij}$, where r_{ij} is the distance between electrons i and j. These terms account for the electron-electron repulsion that we expect between like-charged particles.

Exercise 6.7.1 : Multi-electron atom Hamiltonians

For the generalized multi-electron atom Hamiltonian (Equation 6.7.7):

a. Explain the origin of each of the three summations.
b. What do these summations over (i.e., what is the origin of the summing index)?
c. Write expressions for $V_i(r_i)$ and $V_{ij}(r_{ij})$.

Exercise 6.7.2 : Boron Atom

Boron is the fifth element of the periodic table (Z=5) and is located in Group 13.

a. Write the multi-electron Hamiltonian for a $^{11}\mathrm{B}$ atom.
b. Would it be any different for a $^{11}\mathrm{B}^+$ ion?
c. Would it be any different for a $^{10}\mathrm{B}$ atom?

Answer available at the end of this section.

Multi-electron Wavefunctions and the Orbital Approximation

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation in Equation 6.7.7 would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the

hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their Coulomb repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends *simultaneously* upon the coordinates of all the electrons; i.e., **a multi-electron wavefunction**,

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \cdots \vec{r}_n)$$

The modulus squared of such a wavefunction would describe the probability of finding the electrons (though not specific ones) at a designated volume (V) in the atom.

$$p(V) = \int_V |\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \cdots \vec{r}_n)|^2 d\tau$$

All of the electrons are described simultaneously by a multi-electron wavefunction, so the total amount of electron density represented by the wavefunction equals the number of electrons in the atom.

$$\int_{\text{all space}} |\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \cdots \vec{r}_i)|^2 d\tau = n$$

Unfortunately, the Coulomb repulsion terms (Equation 6.7.5) make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms and molecules even for two electrons atoms. We have to rely on approximations and the *orbital approximation* is central to basic chemistry concepts.

The Orbital Approximation

The most basic approximations to the exact solutions to a multi-electron atom Hamiltonian, $\hat{H}$, (Equation 6.7.7) involve writing a multi-electron wavefunction ($\psi(r_1, r_2, \cdots, r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1, r_2, \cdots, r_n) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_n(r_n) \tag{6.7.8}$$

or in Dirac notation

$$|\psi(r_1, r_2, \cdots, r_n)\rangle \approx |\varphi_1(r_1)\rangle|\varphi_2(r_2)\rangle\cdots|\varphi_n(r_n)\rangle \tag{6.7.9}$$

The energy of the atom in the state associated with a specific multi-electron wavefunction (E) is obtained from the multi-electron Schrödinger Equation

$$\hat{H}\psi(r_1, r_2, \cdots, r_n) = E\psi(r_1, r_2, \cdots, r_n)$$

Within the approximation in Equation 6.7.8, E can be expressed sum of the energies of the one-electron components (ϵ_i).

$$E \approx \sum_i \epsilon_i$$

This is called the **orbital approximation**.

By writing the multi-electron wavefunction as a product of single-electron functions (Equations 6.7.8 or 6.7.9), we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be separately identified. For atoms, these single-electron wavefunctions are called *atomic orbitals* and resemble the wavefunctions for hydrogen-like atoms. For molecules, as we will see in the following chapters, these are called *molecular orbitals*. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

Answers

a.

$$\hat{H}_{\mathrm{B}}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\vec{r}_5) = -\frac{\hbar^2}{2m_e}\sum_i^5 \nabla_i^2 + \sum_i^5 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{5,5} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

which expands to 20 terms

$$\begin{aligned}\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\vec{r}_5) = &-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{\hbar^2}{2m_e}\nabla_4^2 - \frac{\hbar^2}{2m_e}\nabla_5^2 \\ &- \frac{-5e^2}{4\pi\epsilon_0 r_1} - \frac{-5e^2}{4\pi\epsilon_0 r_2} - \frac{-5e^2}{4\pi\epsilon_0 r_3} - \frac{-5e^2}{4\pi\epsilon_0 r_4} - \frac{-5e^2}{4\pi\epsilon_0 r_5} \\ &+ \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{15}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{25}} + \frac{e^2}{4\pi\epsilon_0 r_{34}} + \frac{e^2}{4\pi\epsilon_0 r_{35}} + \frac{e^2}{4\pi\epsilon_0 r_{45}}\end{aligned}$$

b. Yes, $^{11}\mathrm{B}^+$ has one less electron than $^{11}\mathrm{B}$. Its Hamiltonian is

$$\hat{H}_{\mathrm{B}^+}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = -\frac{\hbar^2}{2m_e}\sum_i^4 \nabla_i^2 + \sum_i^4 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{4,4} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

or expanded to 14 terms

$$\begin{aligned}\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = &-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{\hbar^2}{2m_e}\nabla_4^2 \\ &- \frac{-5e^2}{4\pi\epsilon_0 r_1} - \frac{-5e^2}{4\pi\epsilon_0 r_2} - \frac{-5e^2}{4\pi\epsilon_0 r_3} - \frac{-5e^2}{4\pi\epsilon_0 r_4} \\ &+ \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{34}}\end{aligned}$$

c. No effect. Changing the number of neutrons in the nucleus does not affect kinetic nor potential energies of the electrons. The Hamilitonian for $^{10}\mathrm{B}$ is identical to $^{11}\mathrm{B}$. This is technically correct for this level of discussion, but as we we will see in later, if we expand the Hamiltonian with hyperfine structure the number of neutrons can play a role.

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6.E: The Hydrogen Atom (Exercises)

Solutions to select questions can be found online.

6.5

$$\int_{-1}^{1} T_n(x)T_m(x)\frac{1}{\sqrt{1-x^2}}dx = \begin{cases} 0, & n \neq m \\ \pi, & n = m = 0 \\ \pi/2, & n = m \neq 0 \end{cases}$$

First 6 Chebyshev Polynomials

$$T_0(x) = 1$$
$$T_1(x) = x$$
$$T_2(x) = 2x^2 - 1$$
$$T_3(x) = 4x^3 - 3x$$
$$T_4(x) = 8x^4 - 8x^2 + 1$$
$$T_5(x) = 16x^5 - 20x^3 + 5x$$

Use the orthogonality of Chebyshev polynomials to determine what the following polynomials are equal to

a. $\int_{-1}^{1} x^2 \frac{dx}{\sqrt{1-x^2}}$
b. $\int_{-1}^{1} 4x^3 - 2x \frac{dx}{\sqrt{1-x^2}}$
c. $\int_{-1}^{1} 1 \frac{dx}{\sqrt{1-x^2}}$
d. $\int_{-1}^{1} 4x^4 - 4x^2 + 1 \frac{dx}{\sqrt{1-x^2}}$

Solution

a. x^2= T_1*T_1; therefore the answer is π /2
b. here the following polynomial is not a product of either Chebyshev polynomials; therefore, answer is doesn't follow orthogonality conditions
c. 1=T_0*T_0; therefore, answer is π
d. x^4-4x^2+1= T_2*T_2; therefore the answer is π/2

6.6

Use Eq. 6.47 to generate the radial functions $R_{nl}(r)$ for $n = 1, 2$.

Solution

$$R_{10}(r) = \left\{ \frac{(1-0-1)!}{2(1)[(1+0)!]^3} \right\}^{\frac{1}{2}} \left(\frac{2}{1a_0} \right)^{\frac{0+3}{2}} r^0 e^{-\frac{r}{1a_0}} L_1^1 \left(\frac{2r}{1a_0} \right)$$

$$R_{10}(r) = -\left\{ \frac{1}{2} \right\}^{\frac{1}{2}} \left(\frac{2}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$$

$$R_{20}(r) = \left\{ \frac{(2-0-1)!}{2(2)[(2+0)!]^3} \right\}^{\frac{1}{2}} \left(\frac{2}{2a_0} \right)^{\frac{0+3}{2}} r^0 e^{-\frac{r}{2a_0}} L_2^1 \left(\frac{2r}{2a_0} \right)$$

$$R_{20}(r) = \left\{ \frac{1}{32} \right\}^{\frac{1}{2}} \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{2a_0}} \left(-2! \left(2 - \frac{r}{a_0} \right) \right)$$

$$R_{20}(r) = -2\left\{ \frac{1}{32} \right\}^{\frac{1}{2}} \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{2a_0}} \left(\left(2 - \frac{r}{a_0} \right) \right)$$

$$R_{21}(r) = \left\{ \frac{(2-1-1)!}{2(2)[(2+1)!]^3} \right\}^{\frac{1}{2}} \left(\frac{2}{2a_0} \right)^{\frac{1+3}{2}} r^1 e^{-\frac{r}{2a_0}} L_3^3 \left(\frac{2r}{2a_0} \right)$$

$$R_{21}(r) = -6\left\{ \frac{1}{864} \right\}^{\frac{1}{2}} \left(\frac{1}{a_0} \right)^2 r^1 e^{-\frac{r}{2a_0}}$$

6.29

Compare ψ_{310} and ψ_{311}.

Hint: What do the subscripts tell you about the wave function? What do they denote?

Solution

The first subscript tells you the quantum number n. The second denotes the angular momentum l. The last denotes the magnetic spin number m_l. These two functions have the same n values, and thus they are degenerate.

6.30

What is the probability density of the 3p orbital by evaluating

$$\left(\sum_{m=-1}^{1}\psi_{31m}^{2}\right)$$

Solution

$$\sum_{m=-1}^{1}\psi_{31m}^{2}=\left(\frac{2}{6561\pi}\right)\left(\frac{z^{3}}{a_{o}^{3}}\right)\sigma^{3}\left(6-\sigma\right)^{2}\exp\frac{-2\sigma}{3}\left(\cos^{2}\theta+\sin^{2}\theta\cos^{2}\phi+\sin^{2}\theta\sin^{2}\phi\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^{2}=\left(\frac{2z^{3}\sigma^{2}\left(6-\sigma\right)^{2}\exp\frac{-2\sigma}{3}}{6561\pi a_{o}^{3}}\right)\left(\cos^{2}\theta+\sin^{2}\theta\left(\cos^{2}\phi+\sin^{2}\phi\right)\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^{2}=\left(\frac{2z^{3}\sigma^{2}\left(6-\sigma\right)^{2}\exp\frac{-2\sigma}{3}}{6561\pi a_{o}^{3}}\right)$$

6.34

Find the energy, and wavefunction for a single electron located in the 2p orbital of the hydrogen atom. Include all possible wavefunctions.

Solution

Identify the quantum numbers for the electron of interest (in our case, $n=2$; $l=1$). Energy of the electron can be defined as

$$E_{n}=\frac{-m_{e}e^{4}}{8n^{2}\epsilon_{o}^{2}h^{2}}$$

this leads us to

$$E_{2}=\frac{-m_{e}e^{4}}{32\epsilon_{o}^{2}h^{2}}$$

we have two possible wave functions

$$\Psi_{210}=\frac{1}{\sqrt{32}}(\frac{z}{a_{o}})^{3/2}\sigma/e^{-\sigma/2}\cos\theta$$

and

$$\Psi_{21\pm1}=\frac{1}{\sqrt{32}}(\frac{z}{a_{o}})^{3/2}\sigma/e^{-\sigma/2}\sin\theta e^{\pm i\theta}$$

6.37

The Hamiltonian is given by $\hat{H} = \frac{-\hbar}{2m}\nabla^2 + V$ is an Hermitian Operator. Using this fact, show that

$$\int \psi^*[\hat{H}, \hat{A}]\psi d\tau = 0$$

where $\hat{A}$ is any operator.

Solution

Through the commutation relation

$$\int \psi^* \hat{H}\hat{A}\psi d\tau - \int \psi^* \hat{A}\hat{H}\psi d\tau = 0$$

because $\hat{H}$ is a *Hermitian* operator, the above goes to

$$\int (\psi\hat{H})^* \hat{A}\psi d\tau - \int \psi^* \hat{A}(\hat{H}\psi) d\tau = 0$$

$$E\int \psi^* \hat{A}\psi d\tau - E\int \psi^* \hat{A}\psi d\tau = 0$$

6.38

Prove that $\langle \hat{K} \rangle = \langle V \rangle = E/2$ for a harmonic oscillator using the virial theorem

Solution

The virial theorem gives us,

$$\left\langle x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z} \right\rangle = 2\langle \hat{K} \rangle$$

For a three-dimensional harmonic oscillator,

$$V(x, y, z) = \frac{k_x x^2}{2} + \frac{k_y y^2}{2} + \frac{k_z z^2}{2}$$

Therefore,

$$x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z} = k_x x^2 + k_y y^2 + k_z z^2 = 2V$$

and substituting into the equation given by the virial theorem gives us $2\langle V \rangle = 2\langle \hat{K} \rangle$. Because $\langle \hat{K} \rangle + \langle V \rangle = E$, we can also write

$$\langle \hat{K} \rangle = \langle V \rangle = \frac{1}{2}E$$

6.41

Find the expected values of $1/r$ and $1/r^2$ for a hydrogenlike atom in the $2p_z$ orbital.

Solution

The $2p_z$ orbital:

$$\Psi_{210} = \frac{1}{4\sqrt{2\pi}}(Z/a_0)^{3/2}\rho e^{-\rho}\sin\theta\cos\phi\, d\theta$$

where $\rho = Zr/a_o$

$$\langle 1/r\rangle_{\Psi 210} = \int_0^2 \pi\, d\theta \int_0^{\pi} \sin\theta\cos 2\phi d\theta \int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi}^{2*} r^2 p^* e^{-p*}(1/r)dr$$

$$\int_0^{2\pi} d\theta = 2\pi$$

$$\int_0^{\pi} \sin\theta\cos^2\,\phi\, d\theta = \frac{2}{3}$$

$$\int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi})^2 r^2\phi e - \rho(1/r)dr = (Z^3/a_o^3 32\pi)^*[3!/(Z/ao)^4]$$

$$\langle 1/r\rangle_{\Psi 210} = (Z^3/a_o^3 32\pi)(2\pi)(2/3)[3!/(Z/ao)^4]$$

Simplify to get:

$$\left\langle \frac{1}{r} \right\rangle_{\Psi_{210}} = \frac{Z}{4a_o}$$

For the hydrogen atom $Z = 1$, therefore

$$\langle \frac{1}{r} \rangle_{\Psi_{210}} = \frac{1}{4a_o}$$

For $\langle \frac{1}{r^2} \rangle$

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \int_0^2 \pi\, d\theta \int_0^{\pi} \sin\theta\cos^2\,\phi\, d\theta \int_0^{\infty} (Z^3/2/a_o^3/24\sqrt{2\pi})^2 r^2 p e^{-p}(1/r^2)dr$$

$$\int_0^{2\pi} d\theta = 2\pi$$

$$\int_0^{\pi} \sin\theta\cos^2\phi d\theta = 2/3$$

$$\int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi})^2 r 2pe^{-p}(1/r^2)dr = (Z^3/a_o^3 32\pi)[2!/(Z/ao)^3]$$

$$\langle 1/r^2\rangle \Psi_{210} = (Z^3/a_o^3 32\pi)(2\pi)(2/3)[2!/(Z/a_o)^3]$$

Simplify to get:

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \frac{Z^2}{12a_o^2}$$

where $Z = 1$

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \frac{1}{12a_o^2}$$

6.43

Derive the classical magnetic moment of an electron orbiting a nucleus in terms of charge, mass and angular momentum.

Solution

We can begin by recalling the classical expression for a magnetic moment,

$$\mu = IArea$$

Where I is the current the electron makes by revolving around the nucleus. The definition of current is

$$I = \frac{Q}{time}$$

In this case Q is simply the charge (q_e) of the electron and $time$ is the time it takes the electron to orbit the nucleus once. The area is the of loop that the electron takes when revolving around the nucleus. We also know from classical mechanics that $x = vt$. solving for t and evaluating x to be $2\pi r$ for a circle. We can figure out the time of revolution to be,

$$t = \frac{x}{v} = \frac{2\pi r}{v}$$

Our current equations becomes,

$$I = \frac{q_e v}{2\pi r}$$

To introduce angular momentum $L = m_e v r$ we can multiply the right side of our current equation by $\frac{m_e r}{m_e r}$ to arrive at

$$I = \frac{q_e m_e v r}{2\pi m_e r^2}$$
$$I = \frac{q_e L}{2\pi m_e r^2}$$

Substituting in the area of a circle (πr^2) we can show that,

$$\boxed{\mu = IArea = \frac{q_e L}{2m_e}}$$

6.46

Find the magnitude of the splitting shown in figure below. The magnetic field in the figure is at 20 T.

alt

Solution

We know from a previous problem that

$$\Delta E = E_2 - E_1 = \beta_e B_z (m_2 - m_1)$$

In the 1\s\ state where m = 0 and in the 2\p\ state where m = 0, \pm\ 1. The condition will cause (m_{2} - m_{1}) become equal to 0, or \pm\ 1 which will affect the magnitude of splitting, calculated below

$$\Delta E = (9.274 * 10^{-24} J * T^{-1})(20T)(1)$$

$$\Delta E = 1.8548 * 10^{-22} J * T^{-1} \text{ or } 0$$

6.47

Consider the transition between the $l = 1$ and the $l = 2$ states for atomic hydrogen. Determine the total number of possible allowed transitions between these two states in an external magnetic field given the following selection rules

a. Light whose electric field vector is parallel to the external magnetic field's direction has a selection rule of $\Delta m = 0$ for allowed transitions.
b. Light whose electric field vector is perpendicular to the external magnetic field's direction has a selection rule of $\Delta m = \pm 1$ for allowed transitions.

Solution

An external magnetic field splits a state with given values n and l into $2l + 1$ levels. So the $l = 1$ state will be split into three states ($m = 0, \pm 1$) and the $l = 2$ state will be split into five states ($m = 0, \pm 1, \pm 2$). This means that the $l = 1 \rightarrow l = 2$ transition will have a possible of 15 transitions (ignoring any selection rules that reduce this number).

Using the selection rule $\Delta m = 0$, then three transitions are possible: $m = 0$, $m = 1$, $m = -1$ Using the selection rule $\Delta m = \pm 1$, then six transitions are possible:

$l = 1$	$\rightarrow$	$l = 2$	Relative Orientation of light Polarization to Magnetic field
m=0		m=1	parallel
m=0		m=-1	parallel
m=1		m=2	perpendicular
m=1		m=0	perpendicular
m=-1		m=-2	perpendicular
m=-1		m=0	perpendicular

6.49

Prove that

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

given that

$$\hat{L_+} = \hat{L_x} + i\hat{L_y}$$

and

$$\hat{L_-} = \hat{L_x} - i\hat{L_y}.$$

Solution

$$\hat{L_+}\hat{L_-} = (\hat{L_x} + i\hat{L_y})(\hat{L_x} - i\hat{L_y}) = \hat{L_x^2} + \hat{L_y^2} - i\hat{L_x^2}\hat{L_y^2} + i\hat{L_y^2}\hat{L_x^2} = \hat{L_x^2} + \hat{L_y^2} + i[\hat{L_y}, \hat{L_x}]$$

$$\hat{L_+}\hat{L_-} = \hat{L^2} - \hat{L_z^2} + \hbar\hat{L_z}$$

and

$$\hat{L_-}\hat{L_+} = (\hat{L_x} - i\hat{L_y})(\hat{L_x} + i\hat{L_y}) = \hat{L_x^2} + \hat{L_y^2} + i\hat{L_x^2}\hat{L_y^2} - i\hat{L_y^2}\hat{L_x^2} = \hat{L_x^2} + \hat{L_y^2} + i[\hat{L_x}, \hat{L_y}]$$

$$\hat{L_-}\hat{L_+} = \hat{L^2} - \hat{L_z^2} - \hbar\hat{L_z}$$

thus

$$\hat{L_+}\hat{L_-} - hatL_-\hat{L_+} = \hat{L^2} - \hat{L_z^2} + \hbar\hat{L_z} - \hat{L^2} + \hat{L_z^2} - \hbar\hat{L_z}$$

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

6.49

Show that the commutative property applies to

$$\hat{L}_-\hat{L}_+$$

Solution

$$\hat{L}_-\hat{L}_+ = \hat{L}_+\hat{L}_-$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y$$

and

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$$

so

$$\hat{L}_-\hat{L}_+ = [\hat{L}_x - i\hat{L}_y][\hat{L}_x + i\hat{L}_y]$$

$$= \hat{L}_x^2 + i\hat{L}_x\hat{L}_y - i\hat{L}_x\hat{L}_y + \hat{L}_y^2$$

and

$$\hat{L}_+\hat{L}_- = [\hat{L}_x + i\hat{L}_y][\hat{L}_x - i\hat{L}_y]$$

$$= \hat{L}_x^2 - i\hat{L}_y\hat{L}_x + i\hat{L}_x\hat{L}_y + \hat{L}_y^2$$

which shows that

$$\hat{L}_-\hat{L}_+ = \hat{L}_+\hat{L}_-$$

Q7.29

Calculate the ground-state energy for particle in the box model using variational method.

Solution

Variational method equations is:

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$$

where the wavefunctions are unnormalized

The unnormalized Schrödinger equation for PIB:

$$\phi(x) = A\sin(\frac{xn\pi}{L})$$

$$\langle\phi|\phi\rangle$$

$$= A = \sqrt{\frac{2}{L}}$$

and

$$\langle\phi|\hat{H}|\phi\rangle$$

$$= \frac{n^2h^2}{8mL^2}\cdot\sqrt{\frac{2}{L}}$$

so

$$E_\phi = \frac{\frac{n^2h^2}{8mL^2}\cdot\sqrt{\frac{2}{L}}}{\sqrt{\frac{2}{L}}}$$

so

$$E_\phi = \frac{n^2h^2}{8mL^2}$$

where n=1 we get

$$E_\phi = \frac{h^2}{8mL^2}$$

6.50

If two functions commute, they have mutual eigenfunctions, such as $\hat{L}^2$ and $\hat{L}_z$. These mutual eigenfunctions are also known as spherical harmonics, $Y_l^m(\theta, \phi)$, however this information is not pertinent in this case. Let

$\psi_{\alpha\beta}$ be a mutual eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ so that

$$\hat{L}_z\,\psi_{\alpha\beta} = \beta^2\backslash_{\alpha\beta}$$

and

$$\hat{L}_z\,\psi_{\alpha\beta} = \alpha\psi_{\alpha\beta}$$

Now let

$$\psi_{\alpha\beta}{}^{+1} = \hat{L}_{+}\psi_{\alpha\beta}$$

Show that

$$\hat{L}_z\psi_{\alpha\beta}{}^{+1} = (\alpha + \hbar)\psi_{\alpha\beta}{}^{+1}$$

and

$$\hat{L}^2\psi_{\alpha\beta}{}^{+1} = \beta^2\psi_{\alpha\beta}{}^{+1}$$

This proves that if α is an eigenvalue of $\hat{L}_z$, then $\alpha + \hbar$ also is an eigenvalue.

Solution

Solve this problem as given below:

$\psi_{\alpha\beta}{}^{+1} = \hat{L}_{+}\psi_{\alpha\beta}$

$\hat{L}_z\ \psi_{\alpha\beta}{}^{+1} = \hat{L}_z\ \hat{L}_{+}\psi_{\alpha\beta}$

$= (\hat{L}_z\ \hat{L}_x + i\hat{L}_z\ \hat{L}_y\ )\psi_{\alpha\beta}$

$z,\ \hat{L}_x] + \hat{L}_x\ \hat{L}_z + i[\hat{L}_z,\ \hat{L}_y] + i\hat{L}_y\ \hat{L}_z)\psi_{\alpha\beta}$

$y + \hat{L}_z\hat{L}_x + i\hbar\hat{L}_x + \hat{L}_y\hat{L}_z)\ \psi_{\alpha\beta}$

$\hat{L}_{+}\hat{L}_z + \hbar\hat{L}_{+})\psi_{\alpha\beta}$

$+(\alpha + \hbar)\psi_{\alpha\beta}$

$\alpha\beta^{+1}$

Therefore proven.

Finally, you can write:

$\hat{L}^2\psi_{\alpha\beta}{}^{+1} = \hat{L}^2\hat{L}_{+}\psi_{\alpha\beta}$

$= (\hat{L}^2\hat{L}_x + i\hat{L}^2\hat{L}_y)\psi_{\alpha\beta}$

$=([\hat{L}^2,\hat{L}_x] + \hat{L}_x\hat{L}^2 + i[\hat{L}^2,\hat{L}_y] + i\hat{L}_y\hat{L}^2)\psi_{\alpha\beta}$

$x\hat{L}^2 + i\hat{L}_y\hat{L}^2)\psi_{\alpha\beta}$

$+\beta^2\psi_{\alpha\beta}$

$2\psi_{\alpha\beta}{}^{+1}$

Therefore proven.

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6.S: The Hydrogen Atom (Summary)

For the hydrogen atom, we let the nucleus be defined as the center of our coordinate system, and the Hamiltonian becomes:

$$\op H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r},$$

where r is the electron distance, ∇^2 is in spherical coordinates as before, e is the charge of the electron, and the Coulombic term is negative to indicate that the proton-electron potential is attractive (i.e., the proton and electron have charges that are opposite in sign). The factor $4\pi\epsilon_0$ comes from using SI units; the factor disappears if using atomic units. The solution to this equation is tedious, but it turns out that the method of separation of variables can be used to solve this system in terms of radial and angular components:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi).$$

The angular solutions are the same as those for the rigid rotor: the spherical harmonics $Y_l^m(\theta,\phi)$, so the hydrogen atom wavefunctions have quantum numbers l and m_l. You are already familiar with these from general chemistry, $l = 0$ corresponds to an s orbital, $l = 1$ is a p orbital, and so on.

It is found that the energy of the hydrogen atom depends only on a single quantum number n, even though full specification of the wavefunction also requires the quantum numbers l and m_l:

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}, \quad n = 1, 2, \dots,$$

where a_0 is the Bohr radius. The allowed quantum numbers are $n = 1, 2, 3, ...$, $0 \le l \le n$, and $0 \le |m_l| \le l$.

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7: APPROXIMATION METHODS

The Schrödinger equation for realistic systems quickly becomes unwieldy, and analytical solutions are only available for very simple systems - the ones we have described as *fundamental systems* in this module. Numerical approaches can cope with more complex problems, but are still (and will remain for a good while) limited by the available computer power. Approximations are necessary to cope with real systems. Within limits, we can use a pick and mix approach, *i.e.* use *linear combinations* of solutions of the fundamental systems to build up something akin to the real system. There are two mathematical techniques, *perturbation* and *variation* theory, which can provide a good approximation along with an estimate of its accuracy. These two approximation techniques are described in this chapter.

7.1: The Variational Method Approximation

7.2: Linear Variational Method and the Secular Determinant

7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

7.E: Approximation Methods (Exercises)

7.S: Approximation Methods (Summary)

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7.1: The Variational Method Approximation

Learning Objectives

- Appreciate the complexity of solving muliti-electron atoms
- Characterize multi-electron interactions within shielding and penetration concepts
- Use the variational method as an approximation to study insolvable problems
- User variational method to evaluate the effective nuclear charge for a specific atom

In this section we introduce the powerful and versatile variational method and use it to improve the approximate solutions we found for the helium atom using the independent electron approximation.

The True (Experimentally Determined) Energy of the Helium Atom

The helium atom has two electrons bound to a nucleus with charge $Z = 2$. The *successive* removal of the two electrons can be considered stepwise:

$$\mathrm{He} \xrightarrow{I_1} \mathrm{He}^+ + e^- \xrightarrow{I_2} \mathrm{He}^{++} + 2e^- \tag{7.1.1}$$

The *first ionization energy* I_1 is the minimum energy required to remove the first electron from helium gas and is experimentally determined:

$$I_1 = -E_{1s}(\mathrm{He}) = 24.59\ eV$$

While the second ionization energy, I_2 can be experimentally determined, it can also be calculated exactly from the hydrogen atom solutions since He^+ is a hydrogen-like ion with $Z = 2$. Hence, we have

$$\begin{aligned} I_2 &= -E_{1s}(\mathrm{He}^+) \\ &= \frac{Z^2}{2n^2} \\ &= 54.42\ \mathrm{eV} \end{aligned}$$

The energy of the three separated particles on the right side of Equation 7.1.1 is zero (by definition). Therefore the ground-state energy of helium atom is given by

$$\begin{aligned} E_{true} &= -(I_1 + I_2) \\ &= -79.02\ \mathrm{eV}. \end{aligned}$$

which can be expressed in terms of the ***Rydberg*** constant ($R_H = 13.6\ \ eV$) that also describes the lowest energy of the hydrogen atom

$$E_{true} = -5.8066\, R_H$$

We will attempt to reproduce this **true value**, as close as possible, by different theoretical approaches (all approximations).

The "Ignorance is Bliss" Approximation

The Hamiltonian for the Helium atom is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \cancel{\frac{e^2}{4\pi\epsilon_0 r_{12}}} \tag{7.1.2}$$

If we simply *ignore* the electron-electron repulsion term, then Equation 7.1.2 can be simplified to

$$\hat{H} \approx -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{7.1.3}$$

$$\approx h_1(r_1) + h_2(r_2) \tag{7.1.4}$$

where h_1 and h_2 are one electron Hamiltonians for electron 1 and 2, respectively, and are just the hydrogen-like Hamiltonians. The approximation in Equation 7.1.4 is convenient since electron 1 is *separable* from electron 2, so that the two-electron wavefunction is approximated as a product to two one-electron wavefunctions:

$$\Psi_{total} = \psi_{el_1}\psi_{el_2} \tag{7.1.5}$$

or in braket notation

$$|\Psi_{total}\rangle = \hat{H}|\psi_{el_1}\psi_{el_2}\rangle \tag{7.1.6}$$

With some operator algebra, something important arises - the one electron energies are **additive**:

$$\hat{H}\Psi_{total} = (\hat{H}_{el_1} + \hat{H}_{el_2})\psi_{n\ el_1}\psi_{n\ el_2} = (E_{n_1} + E_{n_2})\psi_{n\ el_1}\psi_{n\ el_2}$$

or in bra-ket notation

$$\begin{aligned}\hat{H}|\Psi_{total}\rangle &= \hat{H}|\psi_{el_1}\psi_{el_2}\rangle \\ &= (E_{n_1} + E_{n_2})|\psi_1\psi_2\rangle\end{aligned}$$

The energy for a ground state Helium atom (both electrons in lowest state) is then

$$\begin{aligned}E_{He_{1s}} &= \underbrace{E_{n_1}}_{\text{energy of single electron in helium}} + \underbrace{E_{n_2}}_{\text{energy of single electron in helium}} \\ &= -R_H\left(\frac{Z^2}{1}\right) - R_H\left(\frac{Z^2}{1}\right) \\ &= -8R_H\end{aligned}$$

This approximation significantly overestimates the true energy of the helium atom $E_{He_{1s}} = -5.8066\ \ R$. This is a poor approximation and we need to address electron-electron repulsion properly (or better at least).

Shielding and Penetration

One way to take electron-electron repulsion into account is to modify the form of the wavefunction. A logical modification is to change the nuclear charge, Z, in the wavefunctions to an effective nuclear charge (Z_{eff}), from +2 to a smaller value. The rationale for making this modification is that one electron partially shields the nuclear charge from the other electron, as shown in Figure 7.1.1 .

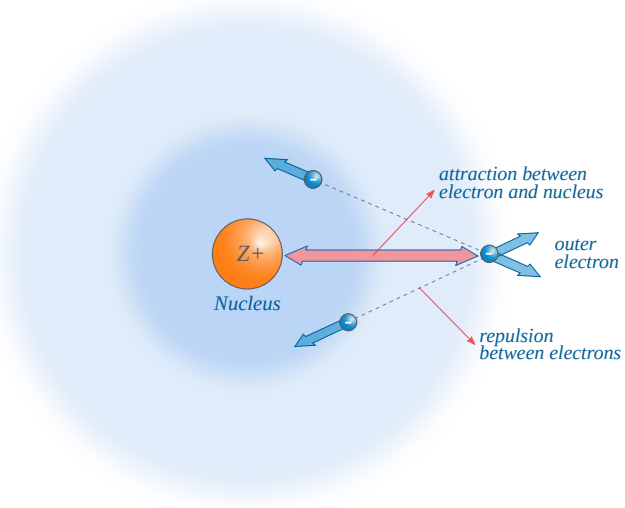


Figure 7.1.1 : Electron-electron shielding leading to a reduced effective nuclear charge. The attractive force of the nucleus on the outer electron is partially countered by the repulsive force between inner electrons and the outer electron. (CC BY-SA; Ümit Kaya via LibreTexts)

A region of negative charge density between one of the electrons and the +2 nucleus makes the potential energy between them more positive (decreases the attraction between them). We can effect this change mathematically by using $\zeta < 2$ in the wavefunction expression. If the shielding were complete, then Z_{eff} would equal 1. If there is no shielding, then $Z_{eff} = 2$. So a way to take into account the electron-electron interaction is by saying it produces a shielding effect. The shielding is not zero, and it is not complete, so the effective nuclear charge varies between one and two.

In general, a theory should be able to make predictions in advance of knowledge of the experimental result. Consequently, a principle and method for choosing the best value for Z_{eff} or any other adjustable parameter that is to be optimized in a calculation is needed. The Variational Principle provides the required criterion and method and says that the best value for any variable parameter in an approximate wavefunction is the value that gives the **lowest energy for the ground state**; i.e., the value that minimizes the energy. The variational method is the procedure that is used to find the lowest energy and the best values for the variable parameters.

A Better Approximation: The Variational Method

The variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions and is the variational principle. The method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an **upper bound** to the ground state energy.

The variational principle means that the expectation value for the binding energy obtained using an approximate wavefunction and the exact Hamiltonian operator will be higher than or equal to the true energy for the system. This idea is really powerful. When implemented, it permits us to find the best approximate wavefunction from a given wavefunction that contains one or more adjustable parameters, called a **trial wavefunction**. A mathematical statement of the variational principle is

$$E_{trial} \geq E_{true} \tag{7.1.7}$$

where

$$E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{7.1.8}$$

$$= \frac{\int \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int \psi^*_{trial} \psi_{trial} d\tau} \tag{7.1.9}$$

Equation 7.1.7 is called the variational theorem and states that for a time-independent Hamiltonian operator, any trial wavefunction will have an variational energy (i.e., expectation value) that is **greater than or equal** to the true ground state wavefunction corresponding to the given Hamiltonian (Equation 7.1.7). Because of this, the variational energy is an upper bound to the true ground state energy of a given molecule. The general approach of this method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible (Figure 7.1.2).

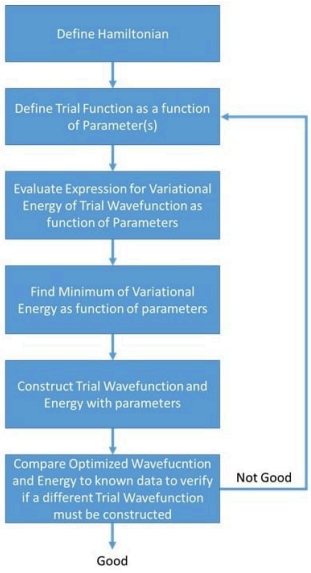


Figure 7.1.2 : Simplified algorithmic flowchart of the Variational Method approximation

The variational energy E_{trial} is only equal to the true energy E_{true} when the the corresponding trial wavefunction ψ_{trial} is equal to the true wavefunction ψ_{true}.

Application to the Helium atom Ground State

Often the expectation values (numerator) and normalization integrals (denominator) in Equation 7.1.9 can be evaluated analytically. For the case of the He atom, let's consider the trial wavefunction as the product wavefunction given by Equation 7.1.10 (this is called the **orbital approximation**),

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{7.1.10}$$

The adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ, and the Hamiltonian is the complete form given below (Note: quantum calculations typically refer to effective nuclear charge as ζ rather than Z_{eff} as we used previously).

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{7.1.11}$$

the adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ (would be equal to $\zeta = 2$ if fully unshielded), and the Hamiltonian is the complete form. When the expectation value for the trial energy (Equation 7.1.9) is evaluated for helium, the result is a variational energy that depends on the adjustable parameter, ζ.

$$E_{trial}(\zeta) = \frac{\mu e^4}{4\epsilon_0^2 h}\left(\zeta^2 - \frac{27}{8}\zeta\right) \tag{7.1.12}$$

This function is plotted in Figure 7.1.3 as a function of ζ. According to the variational principle (Equation 7.1.7), the minimum value of the energy on this graph is the best approximation of the true energy of the system, and the associated value of ζ is the best value for the adjustable parameter.

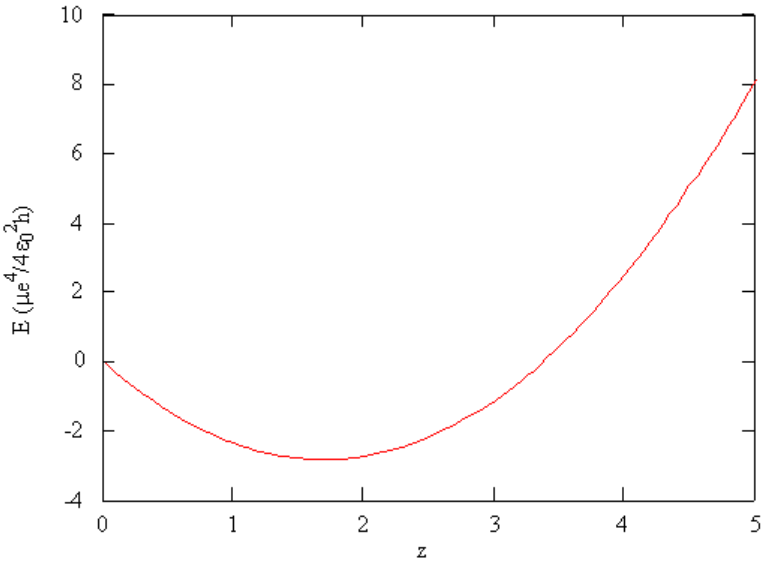


Figure 7.1.3 : Graph of trial energies for helium atom as a function of the adjustable parameter ζ in Equation 7.1.12 that represents the effective nuclear charge felt by the electrons.

Using the mathematical function for the energy of a system, the minimum energy with respect to the adjustable parameter can be found by taking the derivative of the energy with respect to that parameter, setting the resulting expression equal to zero, and solving for the parameter, in this case ζ. This is a standard method in calculus for finding maxima and minima.

Exercise 7.1.1

Find the value for ζ that minimizes the helium binding energy for the product trial wavefunction in Equation 7.1.10 with the Hamiltonian in Equation 7.1.11. and compare the binding energy to the experimental value. What is the percent error in the calculated value?

Solution

The variational method requires following the workflow in Figure 7.1.2 .

- Step 1: Define the Hamiltonian - This is given by Equation 7.1.11.
- Step 2: Define the trial wavefunction as a function of at least one parameter - This is given by Equation 7.1.10.
- Step 3: Evaluate variational energy (E_{trial} integral (Equation 7.1.9) - This procedure was already above in Equation 7.1.12.
- Step 4: Minimize the variational energy as a function of the parameter(s) - Following the standard approach to find extrema in calculus, evaluate the derivative of E_{trial} with respect to ζ and set to zero:

$$\frac{dE_{trial}}{d\zeta} = \frac{\mu e^4}{4\epsilon_0^2 h}\left(2\zeta - \frac{27}{8}\right) = 0$$

then find solve for the roots of this polynomial

$$2\zeta - \frac{27}{8} = 0$$

or

$$\zeta = \frac{27}{16} \approx 1.6875$$

- Step 5-6: The question does not ask for the optimized wavefunction (Step 5) or to compare the result with the true value to evaluate the quality of the approximation (Step 6). We can skip these steps.

From Exercise 7.1.1 , the $\zeta = 1.6875$ and the approximate energy we calculate using this approximation method, E_{approx} = -77.483 eV. Table 7.1.1 show that a substantial improvement in the accuracy of the computed binding energy is obtained by using shielding to account for the electron-electron interaction. Including the effect of electron shielding in the wavefunction reduces the error in the binding energy to about 2%. This idea is very simple, elegant, and significant.

Table 7.1.1 : Comparison of the results of three approximation methods to experiment.

Method	He binding energy (eV)
"Ignorance is Bliss" Approximation (neglect repulsion between electrons)	-108.8
Variational method with variable effective charge	-77.483
Experimental	-79.0

The improvement we have seen in the total energy calculations using a variable parameter ζ indicates that an important contribution of electron-electron interaction or repulsion to the total binding energy arises from the fact that each electron shields the nuclear charge from the other electron. It is reasonable to assume the electrons are independent; i.e., that they move independently, but the shielding must be taken into account in order to fine-tune the wavefunctions. The inclusion of optimizable parameters in the wavefunction allows us to develop a clear physical image of the consequences of our variation calculation. Calculating energies correctly is important, and it is also important to be able to visualize electron densities for multi-electron systems. In the next two sections, we take a temporary break from our consideration of approximation methods in order to examine multi-electron wavefunctions more closely.

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7.2: Linear Variational Method and the Secular Determinant

Learning Objectives

- Understand how the variational method can be expanded to include trial wavefunctions that are a linear combination of functions with coefficients that are the parameters to be varied.
- To be able to construct secular equations to solve the minimization procedure intrinsic to the variational method approach.
- To map the secular equations into the secular determinant
- To understand how the Linear Combination of Atomic Orbital (LCAO) approximation is a specific application of the linear variational method.

A special type of variation widely used in the study of molecules is the so-called **linear variation function**, where the trial wavefunction is a linear combination of N linearly independent functions (often atomic orbitals) that not the eigenvalues of the Hamiltonian (since they are not known). For example

$$|\psi_{trial}\rangle = \sum_{j=1}^{N} a_j |\phi_j\rangle \tag{7.2.1}$$

and

$$\langle\psi_{trial}| = \sum_{j=1}^{N} a_j^* \langle\phi_j| \tag{7.2.2}$$

In these cases, one says that a 'linear variational' calculation is being performed.

Linear Variational Basis Functions

The set of functions $\{\phi_j\}$ are called the 'linear variational' basis functions and are nothing more than members of a set of functions that are convenient to deal with. However, they are typically not arbitrary and are usually selected to address specific properties of the system:

- to obey all of the boundary conditions that the exact state $|\psi_{trial}\rangle$ obeys,
- to be functions of the the same coordinates as $|\psi_{trial}\rangle$,
- to be of the same symmetry as $|\psi_{trial}\rangle$, and
- to be convenient to evaluate Hamiltonian terms elements $\langle\phi_i|H|\phi_j\rangle$.

Beyond these conditions, nothing other than effort can limit the selection and number of such basis functions in the expansions in Equations 7.2.1 and 7.2.2.

As discussed in Section 7.1, the variational energy for a generalized trial wavefunction is

$$E_{trial} = \frac{\langle\psi_{trial}|\hat{H}|\psi_{trial}\rangle}{\langle\psi_{trial}|\psi_{trial}\rangle} \tag{7.2.3}$$

Substituting Equations 7.2.1 and 7.2.2 into Equation 7.2.3 involves addressing the numerator and denominator individually. For the numerator, the integral can be expanded thusly:

$$\langle \psi_{trial}|H|\psi_{trial}\rangle = \sum_{i}^{N}\sum_{j}^{N} a_i^* a_j \langle \phi_i|H|\phi_j\rangle. \tag{7.2.4}$$

$$= \sum_{i,\,j}^{N,\,N} a_i^* a_j \langle \phi_i|H|\phi_j\rangle. \tag{7.2.5}$$

We can rewrite the following integral in Equation 7.2.5 as a function of the basis elements (not the trial wavefunction) as

$$H_{ij} = \langle \phi_i|H|\phi_j\rangle$$

So the numerator of the right side of Equation 7.2.3 becomes

$$\langle \psi_{trial}|H|\psi_{trial}\rangle = \sum_{i,\,j}^{N,\,N} a_i^* a_j H_{ij} \tag{7.2.6}$$

Similarly, the denominator of the right side of Equation 7.2.3 can be expanded

$$\langle \psi_{trial}|\psi_{trial}\rangle = \sum_{i,\,j}^{N,\,N} a_i^* a_j \langle \phi_i|\phi_j\rangle \tag{7.2.7}$$

We often simplify the integrals on the right side of Equation 7.2.7 as

$$S_{ij} = \langle \phi_i|\phi_j\rangle$$

where S_{ij} are **overlap integrals** between the different $\{\phi_j\}$ basis functions. Equation 7.2.7 is thus expressed as

$$\langle \psi_{trial}|\psi_{trial}\rangle = \sum_{i,\,j}^{N,\,N} a_i^* a_j S_{ij} \tag{7.2.8}$$

Orthonormality of Basis Functions

There is no explicit rule that the $\{\phi_j\}$ functions have to be **orthogonal** or **normalized** functions, although they often are selected that way for convenience. Therefore, *a priori*, S_{ij} does not have to be δ_{ij}.

Substituting Equations 7.2.6 and 7.2.8 into the variational energy formula (Equation 7.2.3) results in

$$E_{trial} = \frac{\sum_{i,\,j}^{N,\,N} a_i^* a_j H_{ij}}{\sum_{i,\,j}^{N,\,N} a_i^* a_j S_{ij}} \tag{7.2.9}$$

For such a trial wavefunction as Equation 7.2.1, the variational energy depends quadratically on the 'linear variational' a_j coefficients. These coefficients can be varied just like the parameters in the trial functions of Section 7.1 to find the optimized trial wavefunction ($|\psi_{trial}\rangle$) that approximates the true wavefunction ($|\psi\rangle$) that we cannot analytically solve for.

Minimizing the Variational Energy

The expression for variational energy (Equation 7.2.9) can be rearranged

$$E_{trial}\sum_{i,\,j}^{N,\,N} a_i^* a_j S_{ij} = \sum_{i,\,j}^{N,\,N} a_i^* a_j H_{ij} \tag{7.2.10}$$

The optimum coefficients are found by searching for minima in the variational energy landscape spanned by varying the $\{a_i\}$ coefficients (Figure 7.2.1).

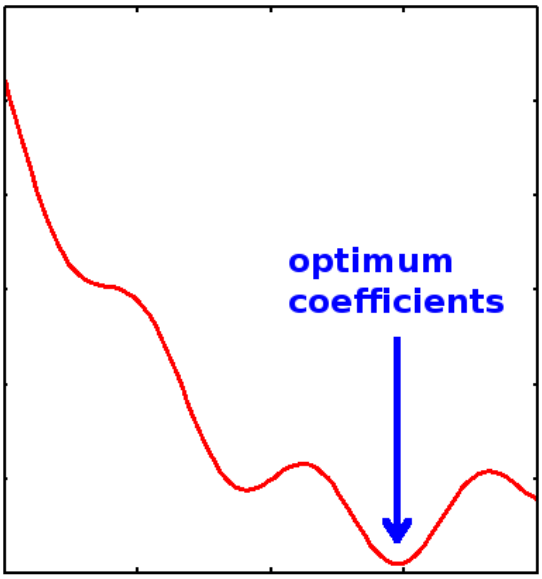


Figure 7.2.1 : Linear Variational Principle in action. Two (or more) wavefunctions are mixed by linear combination. The coefficients a_1, a_2 determine the weight each of them is given. The optimum coefficients are found by searching for minima in the potential landscape spanned by a_1 and a_2. (CC BY-SA-NC; Rudolf Winter; Aberystwyth University).

We want to minimize the energy with respect to the linear coefficients $\{a_i\}$, which requires that

$$\frac{\partial E_{trial}}{\partial a_i} = 0$$

for all i.

Differentiating both sides of Equation 7.2.10 for the k^{th} coefficient gives,

$$\frac{\partial E_{trial}}{\partial a_k} \sum_{i,\,j}^{N,\,N} a_i^* a_j S_{ij} + E_{trial} \sum_i \sum_j \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] S_{ij} = \sum_{i,\,j}^{N,\,N} \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] H_{ij} \tag{7.2.11}$$

Since the coefficients are independent

$$\frac{\partial a_i^*}{\partial a_k} = \delta_{ik}$$

and

$$S_{ij} = S_{ji}$$

and also since the Hamiltonian is a Hermitian Operator (see below)

$$H_{ij} = H_{ji}$$

then Equation 7.2.11 simplifies to

$$\frac{\partial E_{trial}}{\partial a_k} \sum_i \sum_j a_i^* a_j S_{ij} + 2 E_{trial} \sum_i a_i S_{ik} = 2 \sum_i a_i H_{ik} \tag{7.2.12}$$

At the minimum variational energy, when

$$\frac{\partial E_{trial}}{\partial a_k} = 0$$

then Equation 7.2.12 gives

$$\sum_{i}^{N} a_i(H_{ik}-E_{trial}S_{ik}) = 0 \tag{7.2.13}$$

for all k. The equations in 7.2.13 are called the **Secular Equations**.

Hermitian Operators

Hermitian operators are operators that satisfy the general formula

$$\langle\phi_i|\hat{A}|\phi_j\rangle = \langle\phi_j|\hat{A}|\phi_i\rangle \tag{7.2.14}$$

If that condition is met, then $\hat{A}$ is a Hermitian operator. For any operator that generates a real eigenvalue (e.g., observables), then that operator is Hermitian. The Hamiltonian $\hat{H}$ meets the condition of a Hermitian operator. Equation 7.2.14 can be rewriten as

$$A_{ij} = A^*_{ji}$$

where

$$A_{ij} = \langle\phi_i|\hat{A}|\phi_j\rangle$$

and

$$A_{ji} = \langle\phi_j|\hat{A}|\phi_i\rangle$$

Therefore, when applied to the Hamiltonian operator

$$H^*_{ij} = H_{ji}.$$

If the functions $\{|\phi_j\rangle\}$ are orthonormal, then the overlap matrix S reduces to the unit matrix (one on the diagonal and zero every where else) and the Secular Equations in Equation 7.2.13 reduces to the more familiar Eigenvalue form:

$$\sum_{i}^{N} H_{ij}a_j = E_{trial}a_i. \tag{7.2.15}$$

Hence, the secular equation, in either form, have as many eigenvalues E_i and eigenvectors $\{C_{ij}\}$ as the dimension of the H_{ij} matrix as the functions in $|\psi_{trail}\rangle$ (Example 7.2.1). It can also be shown that between successive pairs of the eigenvalues obtained by solving the secular problem at least one exact eigenvalue must occur (i.e.,$E_{i+1} > E_{exact} > E_i$, for all i). This observation is referred to as '*the bracketing theorem*'.

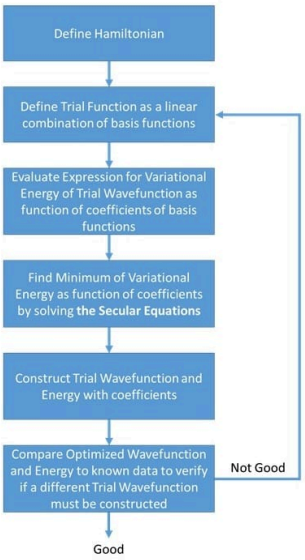


Figure 7.2.2 : Simplified algorithmic flowchart of the linear Variational Method approximation. Compared to the similar algorithmic flowchart for the "normal" Variational Method approximation.

Variational methods, in particular the linear variational method, are the most widely used approximation techniques in quantum chemistry. To implement such a method one needs to know the Hamiltonian H whose energy levels are sought and one needs to construct a trial wavefunction in which some 'flexibility' exists (e.g., as in the linear variational method where the a_j coefficients can be varied). This tool will be used to develop several of the most commonly used and powerful molecular orbital methods in chemistry.

The Secular Determinant

From the secular equations with an orthonormal functions (Equation 7.2.15), we have k simultaneous secular equations in k unknowns. These equations can also be written in matrix notation, and for a non-trivial solution (i.e. $c_i \neq 0$ for all i), the determinant of the secular matrix must be equal to zero.

$$|H_{ik}–ES_{ik}| = 0 \tag{7.2.16}$$

Properties of Determinants

- The determinant is a **real** number, it is **not** a matrix.
- The determinant can be a negative number.
- It is **not** associated with absolute value at all except that they both use vertical lines.
- The determinant **only** exists for square matrices (2×2, 3×3, ..., $n \times n$). The determinant of a 1×1 matrix is that single value in the determinant.
- The inverse of a matrix will exist only if the determinant is not zero.

Expanding Determinants

The determinant can be evaluated using an expansion method involving minors and cofactors. Before we can use them, we need to define them. It is the product of the elements on the main diagonal minus the product of the elements off the main diagonal. In the case of a 2×2 matrix, the specific formula for the determinant is

$$|A| = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc.$$

Similarly, suppose we have a 3×3 matrix A, and we want the specific formula for its determinant $|A|$:

$$|A| = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix}$$
$$= aei + bfg + cdh - ceg - bdi - afh.$$

To solve Equation 7.2.16, the determinate should be expanded and then set to zero. That generates a polynomial (called a **characteristic equation**) that can be directly solved with linear algebra methods or numerically.

Example 7.2.1 : A Simple Two Component Basis Set

If $|\psi_{trial}\rangle$ is a linear combination of two functions. In math terms,

$$|\psi_{trial}\rangle = \sum_{n=1}^{N=2} a_n |f_n\rangle = a_1|\phi_1\rangle + a_2|\phi_2\rangle$$

then the secular determinant (Equation 7.2.16), in matrix formulation would look like this

$$\begin{vmatrix} H_{11} - E_{trial}S_{11} & H_{12} - E_{trial}S_{12} \\ H_{12} - E_{trial}S_{12} & H_{22} - E_{trial}S_{22} \end{vmatrix} = 0$$

Solution

Solving the secular equations is done by finding E_{trial} and putting the value into the expansion of the secular determinant

$$a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22} = 0$$

and

$$a_1(H_{12} - E_{trial}S_{12}) + a_2(H_{22} - E_{trial}S_{22}) = 0$$

Equation 7.2.16 can be solved to obtain the energies E. When arranged in order of increasing energy, these provide approximations to the energies of the first k states (each having an energy higher than the true energy of the state by virtue of the variation theorem). To find the energies of a larger number of states we simply use a **greater number** of basis functions $\{\phi_i\}$ in the trial wavefunction (Example 7.2.1). To obtain the approximate wavefunction for a particular state, we substitute the appropriate energy into the secular equations and solve for the coefficients a_i.

Using this method it is possible to find all the coefficients $a_1 \ldots a_k$ in terms of one coefficient; normalizing the wavefunction provides the absolute values for the coefficients.

Example 7.2.2 : Linear Combination of Atomic Orbitals (LCAO) Approximation

Trial wavefunctions that consist of linear combinations of simple functions

$$|\psi(r)\rangle = \sum_i a_i |\phi_i(r)\rangle$$

form the basis of the Linear Combination of Atomic Orbitals (LCAO) method introduced by Lennard and Jones and others to compute the energies and wavefunctions of atoms and molecules. The functions $\{|\phi_i\rangle\}$ are selected so that matrix elements can be evaluated analytically. Two basis sets of atomic orbitals functions can be used: Slater type and Gaussian type:

Slater orbitals using Hydrogen-like wavefunctions

$$|\phi_i\rangle = Y_l^m(\theta, \phi)e^{-\alpha r}$$

and Gaussian orbitals of the form

$$|\phi_i\rangle = Y_l^m(\theta,\phi)e^{-\alpha r^2}$$

are the most widely used forms, where $Y_l^m(\theta,\phi)$ are the spherical harmonics that represent the angular part of the atomic orbitals. Gaussian orbitals form the basis of many quantum chemistry computer codes.

Because Slater orbitals give exact results for Hydrogen, we will use Gaussian orbitals to test the LCAO method on Hydrogen, following S.F. Boys, Proc. Roy. Soc. A 200, 542 (1950) and W.R. Ditchfield, W.J. Hehre and J.A. Pople, J. Chem. Phys. Rev. 52, 5001 (1970) with the basis set. Because products of Gaussians are also Gaussian, the required matrix elements are easily computed. The linear variational method is used extensively in molecular orbitals of molecules and further examples will be postponed until that discussion in Chapters 9.

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7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

Learning Objectives

- Demonstrate that variational problems can include changing parameters within the elements (normal variational method) and changing coefficients of a basis set (linear variational method)

An alternative approach to the general problem of introducing variational parameters into wavefunctions is the construction of a wavefunction as a linear combination of other functions each with one or multiple parameters that can be varied

For hydrogen, the radial function decays, or decreases in amplitude, exponentially as the distance from the nucleus increases. For helium and other multi-electron atoms, the radial dependence of the total probability density does not fall off as a simple exponential with increasing distance from the nucleus as it does for hydrogen. More complex single-electron functions therefore are needed in order to model the effects of electron-electron interactions on the total radial distribution function. One way to obtain more appropriate single-electron functions is to use a sum of exponential functions in place of the hydrogenic spin-orbitals.

An example of such a wavefunction created from a sum or linear combination of exponential functions is written as

$$\varphi_{1s}(r_1) = \sum_j c_j e^{-\zeta_j r_j / a_o} \tag{7.3.1}$$

The linear combination permits weighing of the different exponentials through the adjustable coefficients (c_j) for each term in the sum. Each exponential term has a different rate of decay through the zeta-parameter ζ_j. The exponential functions in Equation 7.3.1 are called **basis functions**. Basis functions are the functions used in linear combinations to produce the single-electron orbitals that in turn combine to create the product multi-electron wavefunctions. Originally the most popular basis functions used were the STO's, but today STO's are not used in most quantum chemistry calculations. However, they are often the functions to which more computationally efficient basis functions are fitted.

Physically, the ζ_j parameters account for the effective nuclear charge (often denoted with Z_{eff}). The use of several zeta values in the linear combination essentially allows the effective nuclear charge to vary with the distance of an electron from the nucleus. This variation makes sense physically. When an electron is close to the nucleus, the effective nuclear charge should be close to the actual nuclear charge. When the electron is far from the nucleus, the effective nuclear charge should be much smaller. See Slater's rules for a rule-of-thumb approach to evaluate Z_{eff} values.

A term in Equation 7.3.1 with a small ζ will decay slowly with distance from the nucleus. A term with a large ζ will decay rapidly with distance and not contribute at large distances. The need for such a linear combination of exponentials is a consequence of the electron-electron repulsion and its effect of screening the nucleus for each electron due to the presence of the other electrons.

Exercise 7.3.1

Make plots of φ in Equation 7.3.1 using three equally weighted terms with ζ = 1.0, 2.0, and 5.0. Also plot each term separately.

Computational procedures in which an exponential parameter like ζ is varied are more precisely called the Nonlinear Variational Method because the variational parameter is part of the wavefunction and the change in the function and energy caused by a change in the parameter is not linear. The optimum values for the zeta parameters in any particular calculation are determined by doing a variational calculation for each orbital to minimize the ground-state energy. When this calculation involves a nonlinear variational calculation for the zetas, it requires a large amount of computer time. The use of the variational method to find values for the coefficients, $\{c_j\}$, in the linear combination given by Equation 7.3.1 above is called the Linear Variational Method because the single-electron function whose energy is to be minimized (in this case φ_{1s}) depends linearly on the coefficients. Although the

idea is the same, it usually is much easier to implement the linear variational method in practice.

Nonlinear variational calculations are extremely costly in terms of computer time because each time a zeta parameter is changed, all of the integrals need to be recalculated. In the linear variation, where only the coefficients in a linear combination are varied, the basis functions and the integrals do not change. Consequently, an optimum set of zeta parameters were chosen from variational calculations on many small multi-electron systems, and these values, which are given in Table 7.3.1 , generally can be used in the STOs for other and larger systems.

Table 7.3.1 : Orbital Exponents for Slater Orbitals

Atom	ζ_{1s}	$\zeta_{2s,2p}$
H	1.24	-
He	1.69	-
Li	2.69	0.80
Be	3.68	1.15
B	4.68	1.50
C	5.67	1.72
N	6.67	1.95
O	7.66	2.25
F	8.56	2.55
Ne	9.64	2.88

Exercise 7.3.2

Compare the value ζ_{1s} = 1.24 in Table 7.3.1 for hydrogen with the value you obtained in Exercise 7.3.1 . and comment on possible reasons for any difference. Why are the zeta values larger for 1s than for 2s and 2p orbitals? Why do the ζ_{1s} values increase by essentially one unit for each element from He to Ne while the increase for the $\zeta_{2s,2p}$ values is much smaller?

Answer available at the end of this section.

The discussion above gives us some new ideas about how to write flexible, useful single-electron wavefunctions that can be used to construct multi-electron wavefunctions for variational calculations. Single-electron functions built from the basis function approach are flexible because they have several adjustable parameters, and useful because the adjustable parameters still have clear physical interpretations. Such functions will be needed in the Hartree-Fock method discussed elsewhere.

Answers

ζ values represent the rate of decay in the radial function of an orbital. ζ values are larger for 1s than 2s and 2p orbitals because 1s orbitals have a smaller radial function. As a result, 1s orbitals decrease faster in radial function as you move further from the nucleus, and have a larger ζ value to represent this faster decay. The ζ values for 1s increase essentially by one unit for each element from He to Ne because the 1s orbital is closest to the nucleus, and experiences the greatest effects from change in electronegativity as nuclear density increases from He to Ne. This increase in electronegativity causes the radial function to decay more and more rapidly as atomic number/nucleus density increase. The 2s and 2p orbitals don't experience as great a change in radial function decay rate because they are shielded by the 1s orbital.

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7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

Learning Objectives

- Use perturbation theory to approximate the energies of systems as a series of perturbation of a solved system.
- Use perturbation theory to approximate the wavefunctions of systems as a series of perturbation of a solved system.

It is easier to compute the changes in the energy levels and wavefunctions with a scheme of successive corrections to the zero-field values. This method, termed **perturbation theory**, is the single most important method of solving problems in quantum mechanics and is widely used in atomic physics, condensed matter and particle physics. Perturbation theory is another approach to finding approximate solutions to a problem, by starting from the exact solution of a related, simpler problem. A critical feature of the technique is a middle step that breaks the problem into "solvable" and "perturbation" parts. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a "small" term to the mathematical description of the exactly solvable problem.

Figure 7.4.1 : Perturbed Energy Spectrum. (CC BY-SA 2.0, Frontier via Wikipedia)

We begin with a Hamiltonian $\hat{H}^0$ having known eigenstates and eigenenergies:

$$\hat{H}^o|n^o\rangle = E_n^o|n^o\rangle \tag{7.4.1}$$

The task is to find how these eigenstates and eigenenergies change if a small term H^1 (an external field, for example) is added to the Hamiltonian, so:

$$(\hat{H}^0 + \hat{H}^1)|n\rangle = E_n|n\rangle \tag{7.4.2}$$

That is to say, on switching on $\hat{H}^1$ changes the wavefunctions:

$$\underbrace{|n^o\rangle}_{\text{unperturbed}} \Rightarrow \underbrace{|n\rangle}_{\text{Perturbed}} \tag{7.4.3}$$

and energies (Figure 7.4.1):

$$\underbrace{E_n^o}_{\text{unperturbed}} \Rightarrow \underbrace{E_n}_{\text{Perturbed}} \tag{7.4.4}$$

> The basic assumption in perturbation theory is that H^1 is sufficiently small that the leading corrections are the same order of magnitude as H^1 itself, and the true energies can be better and better approximated by a successive series of corrections, each of order H^1/H^o compared with the previous one.

The strategy is to **expand** the true wavefunction and corresponding eigenenergy as series in $\hat{H}^1/\hat{H}^o$. These series are then fed into Equation 7.4.2, and terms of the same order of magnitude in $\hat{H}^1/\hat{H}^o$ on the two sides are set equal. The equations thus generated are solved one by one to give progressively more accurate results.

To make it easier to identify terms of the same order in $\hat{H}^1/\hat{H}^o$ on the two sides of the equation, it is convenient to introduce a dimensionless parameter λ which always goes with $\hat{H}^1$, and then expand both eigenstates and eigenenergies as power series in λ,

$$|n\rangle = \sum_i^m \lambda^i |n^i\rangle \tag{7.4.5}$$

$$E_n = \sum_{i=0}^m \lambda^i E_n^i \tag{7.4.6}$$

where m is how many terms in the expansion we are considering. The ket $|n^i\rangle$ is multiplied by λ^i and is therefore of order $(H^1/H^o)^i$.

> λ is purely a bookkeeping device: we will set it equal to 1 when we are through! It's just there to keep track of the orders of magnitudes of the various terms.

For example, in first order perturbation theory, Equations 7.4.5 are truncated at $m = 1$ (and setting $\lambda = 1$):

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.7}$$

$$E_n \approx E_n^o + E_n^1 \tag{7.4.8}$$

However, let's consider the general case for now. Adding the full expansions for the eigenstate (Equation 7.4.5) and energies (Equation 7.4.6) into the Schrödinger equation for the perturbation Equation 7.4.2 in

$$(\hat{H}^o + \lambda \hat{H}^1)|n\rangle = E_n|n\rangle \tag{7.4.9}$$

we have

$$(\hat{H}^o + \lambda \hat{H}^1)\left(\sum_{i=0}^m \lambda^i |n^i\rangle\right) = \left(\sum_{i=0}^m \lambda^i E_n^i\right)\left(\sum_{i=0}^m \lambda^i |n^i\rangle\right) \tag{7.4.10}$$

We're now ready to match the two sides term by term in powers of λ. Note that the zeroth-order term, of course, just gives back the unperturbed Schrödinger Equation (Equation 7.4.1).

Let's look at Equation 7.4.10 with the first few terms of the expansion:

$$(\hat{H}^o + \lambda \hat{H}^1)\left(|n^o\rangle + \lambda|n^1\rangle\right) = \left(E_n^0 + \lambda E_n^1\right)\left(|n^o\rangle + \lambda|n^1\rangle\right) \tag{7.4.11}$$

$$\hat{H}^o|n^o\rangle + \lambda \hat{H}^1|n^o\rangle + \lambda H^o|n^1\rangle + \lambda^2 \hat{H}^1|n^1\rangle = E_n^0|n^o\rangle + \lambda E_n^1|n^o\rangle + \lambda E_n^0|n^1\rangle + \lambda^2 E_n^1|n^1\rangle \tag{7.4.12}$$

Collecting terms in order of λ and coloring to indicate different orders

$$\underset{\text{zero order}}{\hat{H}^o|n^o\rangle} + \underset{\text{1st order}}{\lambda(\hat{H}^1|n^o\rangle + \hat{H}^o|n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 \hat{H}^1|n^1\rangle} = \underset{\text{zero order}}{E_n^0|n^o\rangle} + \underset{\text{1st order}}{\lambda(E_n^1|n^o\rangle + E_n^0|n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 E_n^1|n^1\rangle} \tag{7.4.13}$$

If we expanded Equation 7.4.10 further we could express the energies and wavefunctions in higher order components.

Zero-Order Terms ($\lambda = 0$)

Collecting the zero order terms in the expansion (black terms in Equation 7.4.13) results in just the Schrödinger Equation for the unperturbed system

$$\hat{H}^o|n^o\rangle = E_n^o|n^o\rangle \tag{7.4.14}$$

First-Order Expression of Energy ($\lambda = 1$)

The summations in Equations 7.4.5, 7.4.6, and 7.4.10 can be truncated at any order of λ. For example, the first order perturbation theory has the truncation at $\lambda = 1$. Matching the terms that linear in λ (red terms in Equation 7.4.13) and setting $\lambda = 1$ on both

sides of Equation 7.4.13:

$$\hat{H}^o|n^1\rangle + \hat{H}^1|n^o\rangle = E_n^o|n^1\rangle + E_n^1|n^o\rangle \tag{7.4.15}$$

Equation 7.4.15 is the key to finding the first-order change in energy E_n^1. Taking the **inner product** of both sides with $\langle n^o|$:

$$\langle n^o|\hat{H}^o|n^1\rangle + \langle n^o|\hat{H}^1|n^o\rangle = \langle n^o|E_n^o|n^1\rangle + \langle n^o|E_n^1|n^o\rangle \tag{7.4.16}$$

since operating the zero-order Hamiltonian on the bra wavefunction (this is just the Schrödinger equation; Equation 7.4.14) is

$$\langle n^o|\hat{H}^o = \langle n^o|E_n^o \tag{7.4.17}$$

and via the orthonormality of the unperturbed $|n^o\rangle$ wavefunctions both

$$\langle n^o|n^o\rangle = 1 \tag{7.4.18}$$

and Equation 7.4.8 can be simplified

$$\cancel{E_n^o\langle n^o|n^1\rangle} + \langle n^o|H^1|n^o\rangle = \cancel{E_n^o\langle n^o|n^1\rangle} + E_n^1\cancel{\langle n^o|n^o\rangle^1} \tag{7.4.19}$$

since the unperturbed set of eigenstates are orthogonal (Equation 7.4.18) and we can cancel the other term on each side of the equation, we find that

$$E_n^1 = \langle n^o|\hat{H}^1|n^o\rangle \tag{7.4.20}$$

> The first-order change in the energy of a state resulting from adding a perturbing term $\hat{H}^1$ to the Hamiltonian is just the **expectation value** of $\hat{H}^1$ in the **unperturbed** wavefunctions.

That is, the first order energies (Equation 7.4.15) are given by

$$E_n \approx E_n^o + E_n^1 \tag{7.4.21}$$

$$\approx \underbrace{E_n^o + \langle n^o|H^1|n^o\rangle}_{\text{First Order Perturbation}} \tag{7.4.22}$$

7.4.1AExample : A Perturbed Particle in a Box

Estimate the energy of the ground-state and first excited-state wavefunction within first-order perturbation theory of a system with the following potential energy

$$V(x) = \begin{cases} V_o & 0 \le x \le L \\ \infty & x < 0 \text{ and } x > L \end{cases}$$

Solution

The first step in any perturbation problem is to write the Hamiltonian in terms of a unperturbed component that the solutions (both eigenstates and energy) are known and a perturbation component (Equation 7.4.2). For this system, the unperturbed Hamilonian and solutions is the particle in an infiinitely high box and the perturbation is a shift of the potential within the box by V_o.

$$\hat{H}^1 = V_o$$

Using Equation 7.4.20 for the first-order term in the energy of the ground-state

$$E_n^1 = \langle n^o|H^1|n^o\rangle$$

with the wavefunctions known from the particle in the box problem

$$|n^o\rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

At this stage we can do two problems independently (i.e., the ground-state with $|1\rangle$ and the first excited-state $|2\rangle$). However, in this case, the first-order perturbation to any particle-in-the-box state can be easily derived.

$$E_n^1 = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) V_o \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx$$

or better yet, instead of evaluating this integrals we can simplify the expression

$$E_n^1 = \langle n^o|H^1|n^o\rangle = \langle n^o|V_o|n^o\rangle = V_o\langle n^o|n^o\rangle = V_o$$

so via Equation 7.4.22, the energy of each perturbed eigenstate is

$$\begin{aligned} E_n &\approx E_n^o + E_n^1 \\ &\approx \frac{h^2}{8mL^2}n^2 + V_o \end{aligned}$$

While this is the first order perturbation to the energy, it is also the exact value.

7.4.1B Example : An Even More Perturbed Particle in a Box

Estimate the energy of the ground-state wavefunction within first-order perturbation theory of a system with the following potential energy

$$V(x) = \begin{cases} V_o & 0 \le x \le L/2 \\ \infty & x < 0 \; and \; x > L \end{cases}$$

Solution

As with Example 7.4.1 , we recognize that unperturbed component of the problem (Equation 7.4.2) is the particle in an infinitely high well. For this system, the unperturbed Hamiltonian and solution is the particle in an infinitely high box and the perturbation is a shift of the potential within half a box by V_o. This is essentially a step function.

Using Equation 7.4.20 for the first-order term in the energy of the any state

$$\begin{aligned} E_n^1 &= \langle n^o|H^1|n^o\rangle \\ &= \int_0^{L/2} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) V_o \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx + \int_{L/2}^{L} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) 0 \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx \end{aligned}$$

The second integral is zero and the first integral is simplified to

$$E_n^1 = \frac{2}{L}\int_0^{L/2} V_o \sin^2\left(\frac{n\pi}{L}x\right) dx$$

this is evaluated to

$$\begin{aligned} E_n^1 &= \frac{2V_o}{L}\left[\frac{-1}{2\frac{\pi n}{a}}\cos\left(\frac{n\pi}{L}x\right)\sin\left(\frac{n\pi}{L}x\right) + \frac{x}{2}\right]_0^{L/2} \\ &= \frac{2V_o}{\cancel{L}}\frac{\cancel{L}}{4} = \frac{V_o}{2} \end{aligned}$$

The energy of each perturbed eigenstate, via Equation 7.4.22, is

$$E_n \approx E_n^o + \frac{V_o}{2}$$
$$\approx \frac{h^2}{8mL^2}n^2 + \frac{V_o}{2}$$

First-Order Expression of Wavefunction ($\lambda = 1$)

The general expression for the first-order change in the *wavefunction* is found by taking the inner product of the first-order expansion (Equation 7.4.15) with the bra $\langle m^o|$ with $m \neq n$,

$$\langle m^o|H^o|n^1\rangle + \langle m^o|H^1|n^o\rangle = \langle m^o|E_n^o|n^1\rangle + \langle m^o|E_n^1|n^o\rangle \tag{7.4.23}$$

Last term on right side of Equation 7.4.23

The last integral on the right hand side of Equation 7.4.23 is zero, since $m \neq n$ so

$$\langle m^o|E_n^1|n^o\rangle = E_n^1\langle m^o|n^o\rangle \tag{7.4.24}$$

and

$$\langle m^o|n^0\rangle = 0 \tag{7.4.25}$$

First term on right side of Equation 7.4.23

The first integral is more complicated and can be expanded back into the H^o

$$E_m^o\langle m^o|n^1\rangle = \langle m^o|E_m^o|n^1\rangle = \langle m^o|H^o|n^1\rangle \tag{7.4.26}$$

since

$$\langle m^o|H^o = \langle m^o|E_m^o \tag{7.4.27}$$

so

$$\langle m^o|n^1\rangle = \frac{\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o} \tag{7.4.28}$$

and therefore the wavefunction corrected to first order is:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.29}$$
$$\approx \underbrace{|n^o\rangle + \sum_{m\neq n}\frac{|m^o\rangle\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o}}_{\text{First Order Perturbation Theory}} \tag{7.4.30}$$

Equation 7.4.30 is essentially is an expansion of the unknown wavefunction correction as a **linear combination** of known unperturbed wavefunctions 7.4.32:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.31}$$
$$\approx |n^o\rangle + \sum_{m\neq n} c_{m,n}|m^o\rangle \tag{7.4.32}$$

with the expansion coefficients determined by

$$c_{m,n} = \frac{\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o} \tag{7.4.33}$$

This is justified since the set of original zero-order wavefunctions forms a **complete basis set** that can describe any function.

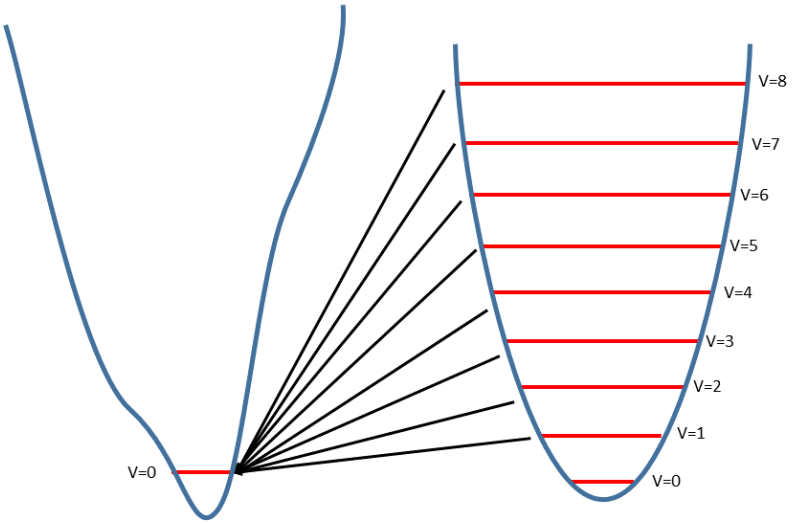


Figure 7.4.2 : The first order perturbation of the ground-state wavefunction for a perturbed (left potential) can be expressed as a linear combination of all excited-state wavefunctions of the unperturbed potential (Equation 7.4.32), shown as a harmonic oscillator in this example (right potential). Note that the ground-state harmonic oscillator wavefunction is not part of this expression and all wavefunctions need to be included in the expression, not just the first eight wavefunctions shown here. (CC BY 4.0; Delmar Larsen)

Calculating the first order perturbation to the wavefunctions is in general an infinite sum of off diagonal matrix elements of H^1 (Figure 7.4.2).

- However, the denominator argues that terms in this sum will be weighted by states that are of **comparable energy**. That means in principle, these sum can be truncated easily based off of some criterion.
- Another point to consider is that many of these matrix elements will equal zero depending on the symmetry of the $\{|n^o\rangle\}$ basis and H^1 (e.g., some $\langle m^o|H^1|n^o\rangle$ integrals in Equation 7.4.30 could be zero due to the integrand having an odd symmetry; see Example 7.4.3).

The denominators in Equation 7.4.30 argues that terms in this sum will be preferentially dictated by states that are of **comparable energy**. That is, eigenstates that have energies significantly greater or lower than the unperturbed eigenstate will weakly contribute to the perturbed wavefunction.

Example 7.4.2 : A Harmonic Oscillator with a Cubic Perturbation

Estimate the energy of the ground-state wavefunction associated with the Hamiltonian using perturbation theory

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \epsilon x^3$$

Solution

The first step in a perturbation theory problem is to identify the reference system with the known eigenstates and energies. For this example, this is clearly the harmonic oscillator model.

Energy

The first steps in flowchart for applying perturbation theory (Figure 7.4.1) is to separate the Hamiltonian of the difficult (or unsolvable) problem into a solvable one with a perturbation. For this case, we can rewrite the Hamiltonian as

$$\hat{H}^o + \hat{H}^1$$

where

- $\hat{H}^o$ is the Hamitonian for the standard Harmonic Oscillator with **known** eigenstates and eigenenergies

$$\hat{H}^{(0)} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

- $\hat{H}^1$ is the pertubtiation

$$\hat{H}^1 = \epsilon x^3$$

The first order perturbation is given by Equation 7.4.20, which for this problem is

$$E_n^1 = \langle n^o | \epsilon x^3 | n^o \rangle$$

Notice that the integrand has an odd symmetry (i.e., $f(x) = -f(-x)$) with the perturbation Hamiltonian being odd and the ground state harmonic oscillator wavefunctions being even. So

$$E_n^1 = 0$$

This means to first order pertubation theory, this cubic terms does not alter the ground state energy (via Equation 7.4.22). However, this is not the case if second-order perturbation theory were used, which is more accurate (not shown).

Wavefunction

Calculating the first order perturbation to the wavefunctions (Equation 7.4.30) is more difficult than energy since multiple integrals must be evaluated (an infinite number if symmetry arguments are not applicable). The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate:

$$|\Psi_v(x)\rangle = N_v'' H_v(\sqrt{\alpha}Q) e^{-\alpha Q^2/2}$$

with α

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

and

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Let's consider only the first six wavefunctions that use these Hermite polynomials $H_v(x)$:

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$

The first order perturbation to the ground-state wavefunction (Equation 7.4.30)

$$|0^1\rangle = \sum_{m \neq 0}^{5} \frac{|m^o\rangle\langle m^o|H^1|0^o\rangle}{E_0^o - E_m^o} \tag{7.4.34}$$

given these truncated wavefunctions (we should technically use the infinite sum) and that we are considering only the ground state with $n = 0$:

$$|0^1\rangle = \frac{\langle 1^o|H^1|0^o\rangle}{E_0^o - E_1^o}|1^o\rangle + \frac{\langle 2^o|H^1|0^o\rangle}{E_0^o - E_2^o}|2^o\rangle + \frac{\langle 3^o|H^1|0^o\rangle}{E_0^o - E_3^o}|3^o\rangle + \frac{\langle 4^o|H^1|0^o\rangle}{E_0^o - E_4^o}|4^o\rangle + \frac{\langle 5^o|H^1|0^o\rangle}{E_0^o - E_5^o}|5^o\rangle$$

We can use symmetry of the perturbation and unperturbed wavefunctions to solve the integrals above. We know that the unperturbed harmonic oscillator wavefunctions $\{|n^0\}\rangle$ alternate between even (when v is even) and odd (when v is odd) as shown previously. Since the perturbation is an odd function, only when $m = 2k + 1$ with $k = 1, 2, 3$ would these integrals be non-zero (i.e., for $m = 1, 3, 5, ...$).

So of the original five unperturbed wavefunctions, only $|m = 1\rangle$, $|m = 3\rangle$, and $|m = 5\rangle$ mix to make the first-order perturbed ground-state wavefunction so

$$|0^1\rangle = \frac{\langle 1^o|H^1|0^o\rangle}{E_0^o - E_1^o}|1^o\rangle + \frac{\langle 3^o|H^1|0^o\rangle}{E_0^o - E_3^o}|3^o\rangle + \frac{\langle 5^o|H^1|0^o\rangle}{E_0^o - E_5^o}|5^o\rangle$$

At this stage, the integrals have to be manually calculated using the defined wavefuctions above, which is left as an exercise. Notice that each unperturbed wavefunction that can "mix" to generate the perturbed wavefunction will have a reciprocally decreasing contribution (w.r.t. energy) due to the growing denominator in Equation 7.4.34.

Exercise 7.4.3 : Harmonic Oscillator with a Quartic Perturbation

Use perturbation theory to estimate the energy of the ground-state wavefunction associated with this Hamiltonian

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \gamma x^4.$$

Answer available at the end of this section.

Second-Order Terms ($\lambda = 2$)

There are higher energy terms in the expansion of Equation 7.4.5 (e.g., the blue terms in Equation 7.4.13), but are not discussed further here other than noting the whole perturbation process is an infinite series of corrections that ideally converge to the correct answer. It is truncating this series as a finite number of steps that is the approximation. The general approach to perturbation theory applications is giving in the flowchart in Figure 7.4.1 .

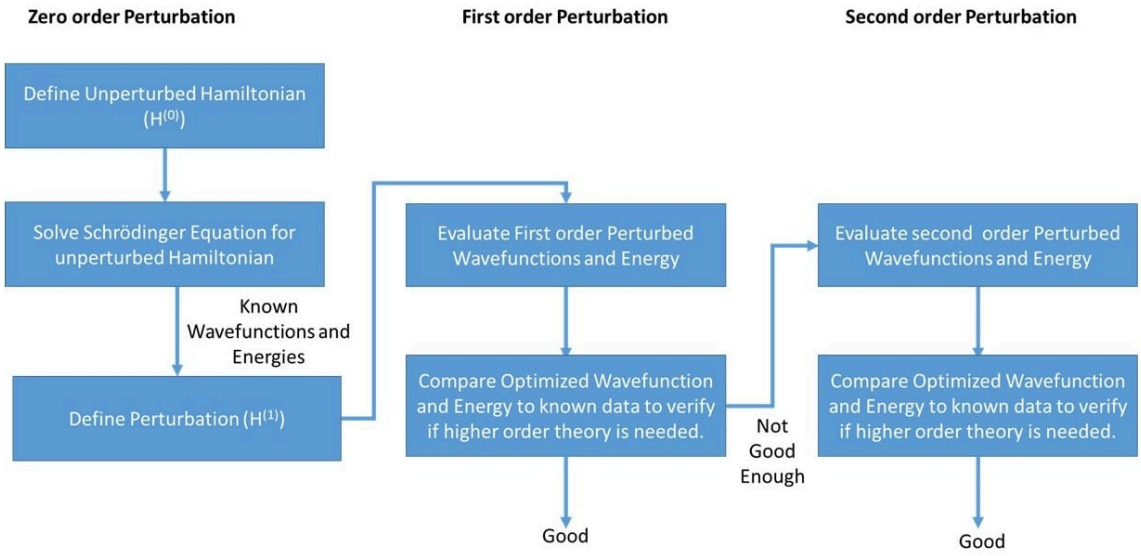


Figure 7.4.1 : Simplified algorithmic flowchart of the Perturbation Theory approximation showing the first two perturbation orders. The process can be continued to third and higher orders. (CC BY 4.0; Delmar Larsen)

Perturbation Theory Does not always Work

It should be noted that there *are* problems that cannot be solved using perturbation theory, even when the perturbation is very weak, although such problems are the exception rather than the rule. One such case is the one-dimensional problem of free particles perturbed by a localized potential of strength λ. Switching on an arbitrarily weak attractive potential causes the $k = 0$ free particle wavefunction to drop below the continuum of plane wave energies and become a localized bound state with binding energy of order λ^2. However, changing the sign of λ to give a repulsive potential there is no bound state, the lowest energy plane wave state stays at energy zero. Therefore the energy shift on switching on the perturbation **cannot** be represented as a power series in λ, the strength of the perturbation.

Answers

The model that we are using is the harmonic oscillator model which has a Hamiltonian

$$H^0 = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

Making the perturbed Hamiltonian

$$H^1 = \gamma x^4$$

To find the perturbed energy we approximate it using Equation 7.4.22

$$E^1 = \langle n^0 \left| H^1 \right| n^0 \rangle$$

where is the wavefunction of the ground state harmonic oscillator

$$n^0 = \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}}$$

When we substitute in the Hamiltonian and the wavefunction we get

$$E^1 = \left\langle \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}} \middle| \gamma x^4 \middle| \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}} \right\rangle$$

Changing this into integral form, and combining the wavefunctions,

$$E^1 = \int_{-\infty}^{\infty} \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} e^{\frac{-ax^2}{2}} \gamma x^4 dx$$
$$= \gamma \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx$$

Now we use the integral table value

$$\int_0^{\infty} x^{2\pi} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{m+1} a^n} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

Where we plug in $\mathrm{n} = 2$ and $\mathrm{a} = \alpha$ for our integral

$$E^1 = 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \int_0^{\infty} x^4 e^{-ax^2} dx$$
$$= 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \frac{1 \cdot 3}{2^3 a^2} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

This is our perturbed energy.
Now we have to find our ground state energy using the formula for the energy of a harmonic oscillator that we already know,

$$E_r^0 = \left(v + \frac{1}{2}\right) h\nu$$

Where in the ground state $v = 0$ so the energy for the ground state of the quantum harmonic oscillator is

$$E_{\mathrm{r}}^0 = \frac{1}{2} h\nu$$

Putting both of our energy terms together gives us the ground state energy of the wavefunction of the given Hamiltonian,

$$E = E^0 + E^1$$
$$= \frac{1}{2} h\nu + \gamma \frac{3}{4a^2}$$

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7.E: Approximation Methods (Exercises)

Solutions to select questions can be found online.

7.3

Calculate the ground state energy of Harmonic Oscillator using variation method with the following trial wavefunction

$$\phi(x) = |\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

You may require these definite integrals:

$$\int_{-\infty}^{\infty} \frac{dx}{(1+\beta x^2)^n} = \frac{(2n-3)(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)(2n-6)\ldots(2)\cdot\pi/\beta^{1/2}}$$

$$\int_{-\infty}^{\infty} \frac{dx}{(1-\beta x^2)^n} = \frac{(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)\ldots(2)\cdot\pi/\beta^{3/2}}$$

Solution

First, we must know the Hamiltonian operator for the harmonic oscillator, which is

$$\hat{H} = \frac{-\hbar}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

From this point on, the determination of E_{ϕ} can be found using the trail function

$$|\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

which once substitute get the following equation for the numerator portion:

$$\int_{-\infty}^{-\infty} \frac{1}{(1+\backslash\text{betax}^2)^2[\hbar^2/\mu * 2\beta/(1+\backslash\text{betax}^2)^3 - \hbar^2/\mu * 12\beta^2x^2/(1+\backslash\text{betax}^2)^4 + \frac{kx^2}{2}(1+\backslash\text{betax}^2)^2]}$$

$$= 2\beta\hbar^2/\mu * (7*5*3*1*\pi/8*6*4*2*\beta 1/2) - 12\beta^2\hbar^2/\mu * (7*5*3*1*\pi/10*8*6*4*2*\beta 1/2) + k/2 * (3*1*\pi$$

$$= \frac{7\pi\beta^{1/2}\hbar}{32\mu + k\pi/32\beta^{3/2}}$$

Now solving the denominator:

$$\int_{\infty}^{\infty} \phi^*\phi\, dx = \int_{\infty}^{\infty} \frac{1}{(1+\beta x^2)^4} = \frac{5*3*1*\pi}{6*4*2*\beta^{1/2}} = \frac{5\pi}{/16\beta^{1/2}}$$

After this we will find

$$E_{\phi} = \frac{7\pi\beta^{1/2}\hbar^2}{32\mu * (16\beta^{1/2}/5\pi)} + \frac{k\pi}{32\beta^{3/2} * (16\beta^{1/2}/5\pi)} = \frac{7/10 * \beta\hbar 2}{\mu} + \frac{1}{10}\frac{k}{\beta}$$

Then find minimum value

\[\dfrac{dE_\phi}{d \beta}= \dfrac{7 \hbar^2}{10μ} -\dfrac{ k}{10 \beta^2_{min} = 0\nonumber \]

therefore

$$\beta_{min} = \sqrt{\frac{\mu k}{7\hbar^2}}$$

\[E_{min}= \dfrac{7^{1/2} \hbar }{5 * (k/μ)^{1/2}} + \dfrac{7^{1/2} \hbar }{5 (k/μ)^{1/2} }= 71/2 \hbar /5 (k/μ)^{1/2} = 0.53 \hbar *(k/μ)^{1/2}\nonumber \]

Therefore overall get

$$E_{exact} = 0.500\hbar\sqrt{(k/\mu)}$$

⇒ this value differs by 6%.

7.8

What is the variational (trial) energy of the trial function

$$|\phi\rangle = e^{-ax^2}$$

for the ground-state of a harmonic oscillator? Just set up the integral, but do not evaluate. Use

$$\hat{H} = \frac{\hbar^2}{2m}\nabla n^2 + \frac{kx^2}{2}$$

Solution

The variational energy:

$$E_{trial}(a) = \frac{\langle\phi(a)|\hat{H}|\phi(a)\rangle}{\langle\phi(a)|\phi(a)\rangle} \geq E_{true}$$

numerator:

$$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty} e^{-2ax^2}dx$$

All combined together to extract the trial energy as a function of a:

$$E_{trial}(a) = \frac{\int_{-\infty}^{\infty} e^{-ax^2}\left[\frac{\hbar^2}{2m}\frac{d^2(e^{-ax^2})}{dx^2} + \frac{kx^2}{2}\right]e^{-ax^2}dx}{\int_{-\infty}^{\infty} e^{-2ax^2}dx}$$

Use the components of $\hat{H}$ to operate on ϕ

$$\langle\phi|\hat{H}|\phi\rangle = \int_{-\infty}^{\infty} e^{-ax^2}\left[\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{kx^2}{2}\right]e^{-ax^2}dx$$

denominator:

$$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty} e^{-ax^2}e^{-ax^2}dx$$

7.9

Use the trial function

$$|\exp^{\frac{-\alpha x^2}{2}}\rangle$$

to set up the integrals to find the ground state energy of a anharmonic oscillator whose potential is $V(x) = cx^5$, but do not evaluate.

Solution

$$E = \frac{\int_{-\infty}^{\infty} \phi^* \hat{H} \phi d\tau}{\int_{-\infty}^{\infty} \phi^* \phi d\tau}$$

$$\int_{-\infty}^{\infty} \phi^* \phi d\tau = \int_{-\infty}^{\infty} \exp^{-\alpha x^2} dx$$

$$\int_{-\infty}^{\infty} \phi^* \hat{H} \phi d\tau = \int_{-\infty}^{\infty} (\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} + cx^5) \exp^{-\alpha x^2} dx$$

$$E = \frac{\int_{-\infty}^{\infty} (\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} + cx^5) \exp^{-\alpha x^2} dx}{\int_{-\infty}^{\infty} \exp^{-\alpha x^2} dx}$$

7.12

Consider a particle of mass m in a box from $x = -a$ to $x = a$ with $V(x) = -V_0$ for $|x| \geq a$. Assume a trial function of the form

$$|\phi(x)\rangle = l^2 - x^2$$

for $-l < x < l$ and $\psi(x) = 0$ otherwise. l is the parameter. Does the trial function satisfy the requirements of a particle in a box wavefunction?

The result of the variational method was

$$E_\phi(s) = \frac{5}{16}\frac{\hbar^2}{ma^2}\left[\frac{4}{s^2} + \frac{4}{5}\left(8 - \frac{15}{s} + \frac{10}{s^3} - \frac{3}{s^5}\right)\right]$$

Where $s = \frac{l}{a}$ is a new variational parameter for convenience of expression. Derive a polynomial expression for s that can be solved to obtain the value of s that yields the ground state energy, but do not attempt to solve for this value of s .

Solution

Yes, it is finite over all x values, it's first and second derivatives are continuous, and it meets the boundary conditions $\psi(-a) = \psi(a) = 0$, and it is normalizable for a choice of l.

Taking the derivative of E with respect to s,

$$\frac{\partial E}{\partial s} = 0 = -\frac{8}{s^3} + \frac{4}{5}\left(\frac{15}{s^2} - \frac{30}{s^4} + \frac{15}{s^6}\right)$$

With some algebra, this becomes,

$$3s^4 - 2s^3 - 6s^2 + 3 = 0$$

With a calculator or other root finding procedure, s can be solved for.

7.13

Given a trial wavefunction equal to $\sin\lambda(x)$, explain in words a stepwise procedure on how you would go about solving for the energy of this trial wavefunction as well as how to minimize the error.

Solution

1. Denote $\sin(\lambda(x)) = \phi_n$

2. Solve the integral $\langle\phi_n^*|\phi_n\rangle$

3. Solve the integral $\langle\phi_n^*|\hat{H}|\phi_n\rangle$

4. Now that you solved for steps 2 and 3, plug into the equation

$$E_n = \frac{\langle\phi_n^*|\hat{H}|\phi_n\rangle}{\langle\phi_n^*|\phi_n\rangle}$$

5. Take the derivative of E_n with respect to λ and set equal to 0.

$$\frac{dE_n}{d\lambda}$$

6. Solve for λ and plug back into equation in step 4.

7.16

Using the variational method approximation, find the ground state energy of a particle in a box using this trial function:

$$|\phi\rangle = N\cos\left(\frac{\pi x}{L}\right)$$

How does is it compare to the true ground state energy?

Solution

The problem asks that we apply variational methods approximation to our trial wavefunction.

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_o$$

$$\langle\phi|\phi\rangle = 1 = \int_0^L N^2\cos^2\left(\frac{\pi x}{L}\right)$$

Performing this integral and solving for N yields

$$N = \sqrt{\frac{2}{L}}$$

The Hamiltonian for a particle in a one dimensional box is $\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\begin{aligned}\langle\phi|\hat{H}|\phi\rangle &= \langle N\cos\left(\frac{\pi x}{L}\right)\Big|\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Big|N\cos\left(\frac{\pi x}{L}\right)\rangle \\ &= \int_0^L N\cos\left(\frac{\pi x}{L}\right)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}N\cos\left(\frac{\pi x}{L}\right)dx \\ &= \frac{N^2\pi^2\hbar^2}{2mL^2}\int_0^L\cos^2\left(\frac{\pi x}{L}\right)dx\end{aligned}$$

where $N = \sqrt{\frac{2}{L}}$. The above equation after the integral becomes

$$\frac{\pi^2\hbar^2}{mL^3}\left(\frac{L}{2}\right)$$

$$E_\phi = \frac{\pi^2\hbar^2}{2mL^2}$$

This is equal to the ground state energy of the particle in a box that we calculated from the Schrodinger equation using

$$\psi = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$$

7.17

For the three-electron detrimental wavefunction

$$\psi = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \end{vmatrix}.$$

confirm that:

a. the interchange of two columns changes the sign of the wavefunction,
b. the interchange of two rows changes the sign of the wavefunction, and
c. the three electrons cannot have the same spin orbital.

Solution

First find the determinant

$$\psi = \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(2) \\ \phi_C(1) & \phi_C(2) \end{vmatrix}$$

$$= \phi_A(1)\ (\phi_B(2)\phi_C(3) - \phi_C(2)\phi_B(3)) - \phi_A(2)\ (\phi_B(1)\phi_C(3) - \phi_C(1)\phi_B(3)) + \phi_A(3)\ (\phi_B(1)\phi_C(2) - \phi_C(1)\phi_B(2))$$

$$\psi = \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(3)\phi_B(1)\phi_C(2) - \phi_A(3)\phi_C(1)\phi_B$$

a) Switch column 1 with column 2

$$\psi_{(a)} = \begin{vmatrix} \phi_A(2) & \phi_A(1) & \phi_A(3) \\ \phi_B(2) & \phi_B(1) & \phi_B(3) \\ \phi_C(2) & \phi_C(1) & \phi_C(3) \end{vmatrix}$$

Now find the determinant

$$\phi_{(a)} = \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(2) & \phi_B(1) \\ \phi_C(2) & \phi_C(1) \end{vmatrix}$$

$$\phi_{(a)} = \phi_A(2)\phi_B(1)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) + \phi_A(1)\phi_C(2)\phi_B(3) + \phi_A(3)\phi_B(2)\phi_C(1) - \phi_A(3)\phi_C(2)\phi$$

Comparing equation (5) with equation (6) we see that $\phi = -\phi_{(a)}$

b) Switch row 2 with row 3

$$\phi_{(b)} = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \end{vmatrix}.$$

Now find the determinant

$$\phi_{(b)} = \phi_A(1) \begin{vmatrix} \phi_C(2) & \phi_C(3) \\ \phi_B(2) & \phi_B(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_C(1) & \phi_C(3) \\ \phi_B(1) & \phi_B(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_C(1) & \phi_C(2) \\ \phi_B(1) & \phi_B(2) \end{vmatrix}$$

$$\phi_{(b)} = \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(3)\phi_C(1)\phi_B(2) - \phi_A(3)\phi_B(1)\phi$$

Comparing equation (5) with equation (7) we see that $\phi = -\phi_{(b)}$

c) Replace column 2 with column 1

$$\phi_{(c)} = \begin{vmatrix} \phi_A(1) & \phi_A(1) & \phi_A(3) \\ \phi_B(1) & \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(1) & \phi_C(3) \end{vmatrix}$$

Now find the determinant

$$\phi_{(c)} = \phi_A(1) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(1) \\ \phi_C(1) & \phi_C(1) \end{vmatrix}$$

The first two terms are identical but opposite so they cancel one another. The third has a determinant of zero.

$$\phi_{(c)} = 0 + \phi_A(3) \cdot (0) = 0$$

7.20

a. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for an oscillator that has a potential of

$$V(x) = (1/2)kx^2 + x^3 + x^4 + x^5?$$

b. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a particle in a box that has a potential of $V(x) = 0$ between 0<x<L?

c. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a hydrogenlike atom that has a potential of

$$V(x) = \frac{-e^2}{4\pi\epsilon_o r} + \frac{1}{2}\epsilon r\cos\theta?$$

Solution

For an oscillator:

$$\hat{H} = \frac{-\hbar 2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}kx^2 + x^3 + x^4 + x^6$$

$\hat{H}^{(0)}$ is the Hamiltonian for a simple harmonic oscillator, therefore

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}kx^2$$

$\hat{H}^{(1)}$ is what is added to the Hamiltonian for a simple harmonic oscillator. therefore

$$\hat{H}^{(1)} = x^3 + x^4 + x^5$$

$\Psi^{(0)}$ is the wave function for a simple harmonic oscillator, therefore

$$\Psi^{(0)} = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

$E^{(0)}$ is the energy for a simple harmonic oscillator, therefore

$$E^{(0)} = h\nu\left(v + \frac{1}{2}\right)$$

where v= 0,1, 2... ∞

Particle in a box

Using this as an example, we find that for a particle in a box with potential V(x) = 0 between 0<x<L

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$\hat{H}^{(0)} = -\frac{\hbar 2}{2m}\frac{\partial^2}{\partial x^2}$$

\[\hat{H}^{(1)} = 0\nonumber \]

$\Psi^{(0)}$ =B*sin(nπx/L)

$E^{(0)} = n^2h^2 / 8mL^2$ where n= 1, 2, 3 ... ∞

Hydrogen like Atom

For a hydrogen like atom that has a potential of

$$V(x) = -\frac{e^2}{4\pi\epsilon_o r} + (1/2)\epsilon r\cos\theta$$

\[\hat{H} = - ħ ^{2}/2μ ∂2 /∂x2 ∇^2 -e^2/(4πε$_o$r) + (1/2)εrcosθ\nonumber \]

\[\hat{H}^{(0)} = - ħ ^2/2μ ∂2 /∂x2 ∇^2 -e^2/(4πϵ_0r)\nonumber \]

\[\hat{H}^{(1)} =(1/2)ϵrcosθ\nonumber \]

$Ψ^{(0)} = Ψ_{n,l,m} (r,θ,ϕ)$

$E^{(0)} = μe^4 / 8ϵ_o^2h^2n^2$

7.21

Using a harmonic oscillator as the unperturbed problem, calculate the first-order correction to the energy of the $v = 0$ level for the system described as

$$V(x) = \frac{k}{2}x^2 + \frac{m}{6}x^3 + \frac{b}{24}x^4$$

7.22

Using the first order perturbation theory for particle in a box, calculate the ground-state energy for the system

$$V(x) = ax^3 \qquad 0 < x < b$$

Solution

$$\psi_1 = \sqrt{\frac{2}{b}}\sin(\frac{\pi x}{b})$$

$$\widehat{H} = \widehat{H}^0 + \widehat{H}^1$$

$$\widehat{H}^1 = ax^3$$

$$E_1 = E_1^0 + E_1^1$$

$$E_1^0 = \frac{h^2}{8mb^2}$$

$$E_1^1 = \langle\psi^1|\widehat{H}^1|\psi^1\rangle$$

$$= \int_0^b \frac{2a}{b}x^3\sin^2(\frac{\pi x}{b})dx$$

$$= \frac{2a}{b}\frac{(\pi^2-3)b^4}{8\pi^2}$$

$$= \frac{(\pi^2-3)ab^3}{4\pi^2}$$

$$E_1 = \frac{h^2}{8mb^2} + \frac{(\pi^2-3)ab^3}{4\pi^2}$$

7.23

In your chemistry lab you were able to manipulate an external electric field to have the strength κ. You're supervisor wants you to figure out what the first-order correction to the ground state energy of a hydrogen like atom of charge N in this electric field.

Solution

You should remember, or look up the ground state wavefunction for a hydrogen atom and find that

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{Z_\circ} \right)^{\frac{3}{2}} e^{-r/a_\circ}$$

Our change in energy equation has a familiar form

$$\Delta E = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau$$

For this problem you construct a Hamiltonian for a Hydrogen atom in an electron field with strength κ.

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ne^2}{4r\pi\kappa_\circ} + er\kappa \cos\theta$$

Luckily you have previously calculated $\hat{H}^{(1)}$ for this system in a previous experiment, simply allowing you to substitute your variables into your expressions to find that

$$\Delta E = \frac{Ne\kappa}{\pi} \left(\frac{1}{Z_\circ} \right)^3 \int_0^\infty r^3 e^{\frac{-r}{a_\circ}} dr \int_0^{2\pi} d\phi \int_0^\pi \sin\theta \cos\theta d\theta$$

Notice that the problem gets simplified by the fact that

$$\int_0^\pi \sin\theta \cos\theta d\theta = 0$$

So your answer is a trivial solution.

$$\boxed{\Delta E = 0}$$

7.25A

Use first-order perturbation theory to calculate ground-state energy of a harmonic oscillator with a cx^7 added to the end of the potential.

Solution

The Hamiltonian to the system can be formulated as

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^7$$

we then solve

$$E^1 = \langle\psi_0|cx^7|\psi_0\rangle$$

We know that the integral is of an odd function over a symmetric boundary is 0, so by symmetry we can conclude that the energy is 0.

7.25B

In order to calculate the first-order correction to the ground-state energy of the quartic oscillator, use first-order perturbation theory. The potential energy is $V(x) = cx^4$. For this potential use the harmonic oscillator as the unperturbed system. Solve for the perturbing potential as well.

Solution

The Hamiltonian operator is given below:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$$

To use a harmonic oscillator as the reference system, add and subtract $\frac{1}{2}kx^2$ from $\hat{H}$.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d}{dx^2} + \frac{1}{2}kx^2 \ + cx^4 - \frac{1}{2}kx^2$$

Hence we get :

$$\hat{H}^{(0)} = cx^4 - \frac{1}{2}kx^2$$

Now we have:

$$\Delta E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)} \ d\tau \ldots.$$

By putting the values in the equation above, we get:

$$\Delta E = \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} dx e^{-x^2\alpha}\left(cx^4 - \frac{1}{2}kx^2\right)$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} 2\left[\frac{3c}{8\alpha^2}\left(\frac{\pi}{\alpha}\right)^{1/2} - \frac{k}{8\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2}\right]$$

$$= \frac{3c}{4\alpha^2} - \frac{k}{4\alpha}$$

7.26

Solve the following integrals using this trial wavefunction

$$|\phi\rangle = c_1 x(a-x) + c_2 x^2 (a-x)^2$$

For simplicity purposes, we can assume that a = 1.

$$H_{11} = \frac{\hbar^2}{6m} \; S = \frac{1}{30}$$

$$H_{12} = H_{22} = \frac{\hbar^2}{30m} \; S_{12} = S_{21} = \frac{1}{140}$$

$$H_{22} = \frac{\hbar^2}{105m} \; S_{22} = \frac{1}{630}$$

Solution

We know that for a particle in a box

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

We also know the two components of the trial function that was given are

$$\phi_1 = x(a-x)$$

and

$$\phi_2 = x^2 (a-x)^2$$

Using this we will have

$$\hat{H}\phi_1 = \frac{\hbar^2}{2m}$$

and

$$\hat{H}\phi_2 = \frac{\hbar^2}{m}(a^2 - 6ax + 6x^2)$$

Using this we can solve for H_{ii} and S_{ij} using this integral

$$\int_0^1 x^m (1-x)^n dx = \frac{m!n!}{(m+n+1)!}$$

Letting $a = 1$, we can now solve for

$$H_{11} = \frac{\hbar^2}{m}$$

$$\int_0^1 x(1-x)dx = \frac{\hbar^2}{6m}$$

$$H_{12} = \frac{\hbar^2}{m}$$

$$\int_0^1 x(1-x)(1-6x+6x^2)dx = \frac{\hbar^2}{30m}$$

$$H_{21} = \frac{\hbar^2}{m}$$

$$\int_0^1 x^2(1-x)^2 dx = \frac{\hbar^2}{30m}$$

$$H_{22} = \frac{\hbar^2}{105m}$$

$$S_{11} = \int_0^1 x^2(1-x)^2 dx = \frac{4}{5!} = \frac{1}{30}$$

$$S_{12} = S_{21} = \int_0^1 x^3(1-x)^3 dx = \frac{36}{7!} = \frac{1}{140}$$

$$S_{22} = \int_0^1 x^4(1-x)^4 dx = \frac{576}{9!} = \frac{1}{630}$$

7.27

Use Perturbation Theory to add cubic and quartic perturbations to the SHO and find the first three SHO energy levels. Do this by expanding the Morse potential:

$$V(x) = D(1 - e^{-Bx})^2$$

into polynomials (i.e., a Taylor expansion). Show that the Hamiltonian can be written as

$$\frac{-h^2\nabla^2}{8\pi^2 m} + ax^2 + bx^3 + cx^4$$

Note which terms can be associated with H^0 and which are the H^1 perturbation. What are the relationships between a, b, c, and D, B? How do the new energy levels compare to the old ones?

Solution

The e^{-Bx} function can be expanded noting that

$$e^x \approx 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + ... + Ox^n$$

So e^{-Bx} will expand similarly, replacing x in the above expansion with -Bx, so

\[e^{-Bx] = 1 - Bx + B^2x^2/2 - B^3x^3/6 + ... + Ox^n\nonumber \]

The Morse Potential therefore is

$$D(1 - (1 - Bx + B^2\frac{x^2}{2} - B^3\frac{x^3}{6})^2$$

The expansion is shortened to 4 terms only.

$$= D(Bx - B^2x^2/2 + B^3x^3/6)^2$$

$$=D (B^6x^6/36 - B^5x^5/6 + 7B^4x^4/12 - B^3x^3 + B^2x^2)$$

$$= DB^6x^6/36 - DB^5x^5/6 + 7DB^4x^4/12 - DB^3x^3 + DB^2x^2$$

$$= 7DB^4x^4/12 - DB^3x^3 + DB^2x^2$$

(We have truncated above the quartic term)

Here, it is seen that DB^2x^2 corresponds to the H^0 potential, and $7DB^4x^4/12 - DB^3x^3$ is H^1

We can also see that $a = DB^2$, $b = - DB^3$, $c = 7DB^4/12$ in in the Hamiltonian potential: $ax^2 + bx^3 + cx^4$

Perturbation theory states that

$$E_n = E_n^0 + E_n^1 = E_n^0 + \int \Psi_n^0 H^1 \Psi_n^0 \, d\tau$$

Therefore, with $E^0_0 = h\nu/2$ and $\Psi^0_0 = (\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}$

$E^0_1 = 3h\nu/2$ and $\Psi^0_1 = (4\alpha^3/\pi)^{1/4}xe^{-\alpha(x^2)/2}$

$E^0_2 = 5\ h\nu/2$ and $\Psi^0_2 = (\alpha/4\pi)^{1/4}(2\alpha x^2 - 1)e^{-\alpha(x^2)/2}$

$H^1 = bx^2 + cx^2$

the first three energy levels are:

$E_0 = hv/2 + \int (\alpha/\pi)^{1/4} e^{-\alpha(x^2)/2} (bx^3 + cx^4)(\alpha/\pi)^{1/4} e^{-\alpha(x^2)/2} dx$

$= hv/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)} (bx^3 + cx^4) dx$

$= hv/2 + (\alpha/\pi)^{1/2} [\int e^{-\alpha(x^2)} bx^3 dx + \int e^{-\alpha(x^2)} cx^4 dx]$ (The cubic integral is odd so evaluates to 0)

$= hv/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)} cx^4 dx$

We can use $\int x^{2n} e^{-\alpha x^2} dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= hv/2 + 2 * c(\alpha/\pi)^{1/2} * 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}$

$= hv/2 + 3c/(4\alpha^2)$

$E_1 = 3hv/2 + \int (4\alpha^3/\pi)^{1/4} x e^{-\alpha(x^2)/2} (bx^3 + cx^4)(4\alpha^3/\pi)^{1/4} x e^{-\alpha(x^2)/2} dx$

$= 3hv/2 + (4\alpha^3/\pi)^{1/2} \int x^2 e^{-\alpha(x^2)} (bx^3 + cx^4) dx$

$= 3hv/2 + (4\alpha^3/\pi)^{1/2} [\int x^2 e^{-\alpha(x^2)} bx^3 dx + \int x^2 e^{-\alpha(x^2)} cx^4 dx]$ (First integral evaulates to 0)

$= 3hv/2 + c(4\alpha^3/\pi)^{1/2} \int x^6 e^{-\alpha(x^2)} dx$

We can use $\int x^{2n} e^{-\alpha x^2} dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= 3hv/2 + 2* c(4\alpha^3/\pi)^{1/2} * 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2}$

$= 3hv/2 + 15c/(4\alpha^2)$

$E_{2o} = 5hv/2 + \int (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha(x^2)/2} (bx^3 + cx^4) (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha(x^2)/2} dx$

$= 5hv/2 + (\alpha/4\pi)^{1/2} \int (bx^3 + cx^4)(2\alpha x^2 - 1)^2 e^{-\alpha(x^2)} dx$

$= 5hv/2 + (\alpha/4\pi)^{1/2} [\int bx^3 (2\alpha x^2 - 1)^2 e^{-\alpha(x^2)} dx + \int cx^4 e^{-\alpha(x^2)} (2\alpha x^2 - 1)^2 dx$

$= 5hv/2 + (\alpha/4\pi)^{1/2} \int cx^4 e^{-\alpha(x^2)} (2\alpha x^2 - 1)^2 dx$ (First integral evaluates to 0)

$= 5hv/2 + (\alpha/4\pi)^{1/2} \int 4c\alpha^2 x^8 e^{-\alpha(x^2)} - 4\alpha c x^6 e^{-\alpha(x^2)} + cx^4 e^{-\alpha(x^2)} dx$

We can use $\int x^{2n} e^{-\alpha x^2} dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= 5hv/2 + (\alpha/4\pi)^{1/2} [4c\alpha^2 * 2 * (105/(32\alpha^4)) * (\pi/\alpha)^{1/2} - \alpha c * 2 * 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2} + c * 2 * 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}]$

$= 5hv/2 + 39c/4\alpha^2$

It is evident that as the energy levels increase, the perturbation to the energy increases as well, making the Hooke potential increasingly bad as an approximation of intramolecular potential.

7.27

Use the perturbation theory to calculate the first - order corrections to the ground state energy of

a. A harmonic oscillator that arises from a cubic and quartic term.
b. A quartic oscillator that arises from only using a quartic term cx^4

and compare the results.

Solution

A) The Hamiltonian for this problem is

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2 + bx^3 + cx^4$$

We use the harmonic oscillator Hamiltonian for $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2$$

$$\hat{H}^{(1)} = bx^3 + cx^4$$

$$\psi^{(0)} = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

$$E^{(0)} = h\mu(v + \frac{1}{2})$$

$$E_0 = E_0^{(0)} + \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau$$

$$E_0 = \frac{\hbar\mu}{2} + b(\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx x^3 e^{-x^2\alpha} + c(\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx x^4 e^{-x^2\alpha}$$

$$E_0 = \frac{\hbar\mu}{2} + 0 + 2c\frac{\alpha}{\pi}^{1/2}\int_0^{\infty} dx x^4 e^{-x^2\alpha}$$

$$E_0 = \frac{\hbar\mu}{2} + \frac{3c}{4\alpha^2}$$

B) The Hamiltonian for this problem is

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$$

We use the harmonic oscillator Hamiltonian for $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2$$

$$\hat{H}^{(1)} = cx^4 - \frac{kx^2}{2}$$

$$E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau$$

$$E = (\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx e^{-x^2\alpha}(cx^4 - \frac{kx^2}{2})$$

$$E = (\frac{\alpha}{\pi})^{1/2}2(\frac{3c}{8\alpha^2}(\frac{\alpha}{\pi})^{1/2} - \frac{k}{8\alpha}(\frac{\alpha}{\pi})^{1/2})$$

$$E = \frac{3c}{4\alpha^2} + \frac{k}{4\alpha}$$

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7.S: Approximation Methods (Summary)

There are very few chemical systems for which the Schrödinger equation can be solved exactly, so most of the time approximations must be made. The most common approximation is the Born-Oppenheimer approximation, which says that the motion of the electrons is fast compared to the motion of the nuclei. Under the Born-Oppenheimer approximation, nuclear coordinates are held fixed and the electron system is solved exactly (one-electron systems) or approximately (multi-electron systems), and then the nuclear coordinates are systematically varied and the electronic system recalculated. In this manner, a **potential energy surface** (PES) is created, giving the potential energy of the system as a function of the nuclear coordinates, and the PES can be used to solve the vibrational and rotational parts of the molecular wavefunction. The Born-Oppenheimer approximation is specific for molecules; the approximation methods that follow are general for quantum mechanics.

Variational principle

The variational principle states that for a given operator, the expectation value of that operator with any normalized function will be greater than or equal to the lowest eigenvalue of that operator. For a molecular Hamiltonian, that means that the energy calculated with an arbitrary wavefunction will provide an upper bound for the ground state energy of the molecule. In equation form, the variational principle states that if $|\psi\rangle$ is a trial function, then

$$E = \frac{\langle\psi|\operatorname{op}H|\psi\rangle}{\langle\psi\rangle\psi}, \quad E \geq E_0, \tag{7.S.1}$$

where E is the energy associated with the trial function $|\psi\rangle$, and E_0 is the actual lowest eigenvalue of $\operatorname{op}H$. The trial function may have adjustable parameters which can be varied to minimize the calculated energy and therefore improve the estimate; this is usually done using specialized software packages.

A special type of linear variational calculation is called the Rayleigh–Ritz method. In this method, the trial function is simply a linear combination of orthogonal basis functions

$$|\psi\rangle = \sum_n c_n|\phi_n\rangle.$$

The solution to this problem involves calculating the c_n coefficients that minimize the variational energy. After some calculus, it can be shown that this is essentially an eigenvalue problem, and that the values of the coefficients can be obtained by solving the secular determinant

$$\begin{vmatrix} \langle\phi_0|\operatorname{op}H|\phi_0\rangle - E\langle\phi_0\rangle\phi_0 & \langle\phi_0|\operatorname{op}H|\phi_1\rangle - E\langle\phi_0\rangle\phi_1 & \cdots & \langle\phi_0|\operatorname{op}H|\phi_n\rangle - E\langle\phi_0\rangle\phi_n \\ \langle\phi_1|\operatorname{op}H|\phi_0\rangle - E\langle\phi_1\rangle\phi_0 & \langle\phi_1|\operatorname{op}H|\phi_1\rangle - E\langle\phi_1\rangle\phi_1 & \cdots & \langle\phi_1|\operatorname{op}H|\phi_n\rangle - E\langle\phi_1\rangle\phi_n \\ \vdots & \vdots & \ddots & \vdots \\ \langle\phi_n|\operatorname{op}H|\phi_0\rangle - E\langle\phi_n\rangle\phi_0 & \langle\phi_1|\operatorname{op}H|\phi_1\rangle - E\langle\phi_n\rangle\phi_1 & \cdots & \langle\phi_n|\operatorname{op}H|\phi_n\rangle - E\langle\phi_n\rangle\phi_n \end{vmatrix} = 0$$

Note that if the basis functions $|\phi_n\rangle$ are normalized, then $\langle\phi_n\rangle\phi_m = \delta_{nm}$, and the equation simplifies to

$$\begin{vmatrix} \langle\phi_0|\operatorname{op}H|\phi_0\rangle - E & \langle\phi_0|\operatorname{op}H|\phi_1\rangle & \cdots & \langle\phi_0|\operatorname{op}H|\phi_n\rangle \\ \langle\phi_1|\operatorname{op}H|\phi_0\rangle & \langle\phi_1|\operatorname{op}H|\phi_1\rangle - E & \cdots & \langle\phi_1|\operatorname{op}H|\phi_n\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle\phi_n|\operatorname{op}H|\phi_0\rangle & \langle\phi_1|\operatorname{op}H|\phi_1\rangle & \cdots & \langle\phi_n|\operatorname{op}H|\phi_n\rangle - E \end{vmatrix} = 0$$

This equation will result in n values for E, and for each value E_k, there will be a set of n coefficients c_k that give rise to that energy. If you take this argument further, you'll see that this is the general matrix formalism of quantum mechanics: wavefunctions $|\psi\rangle$ can be represented by vectors of coefficients c_n in the space of orthogonal unit vectors $|\phi_n\rangle$, and operators become matrices whose elements are the integrals $\langle\phi_n|\operatorname{op}A|\phi_m\rangle$.

$$|\psi\rangle = \begin{pmatrix} c_0 \\ c_1 \\ \vdots \\ c_n \end{pmatrix}, \quad \langle\psi| = \begin{pmatrix} c_0^* & c_1^* & \cdots & c_n^* \end{pmatrix}, \text{ and } \opH = \begin{pmatrix} \langle\phi_0|\opH|\phi_0\rangle & \langle\phi_0|\opH|\phi_1\rangle & \cdots & \langle\phi_0|\opH|\phi_n\rangle \\ \langle\phi_1|\opH|\phi_0\rangle & \langle\phi_1|\opH|\phi_1\rangle & \cdots & \langle\phi_1|\opH|\phi_n\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle\phi_n|\opH|\phi_0\rangle & \langle\phi_1|\opH|\phi_1\rangle & \cdots & \langle\phi_n|\opH|\phi_n\rangle \end{pmatrix}$$

Solving for the c_n coefficients that minimize the energy is equivalent to diagonalizing $\opH$ in this vector space; the eigenvalues are the energies and the eigenvectors are the coefficients on each basis function that make up the corresponding wavefunction. One can, for instance, estimate the ground state energy and wavefunction of a harmonic oscillator by using a trial function which is a linear combination of particle in a box wavefunctions.

Perturbation Theory

To use perturbation theory effectively, the problem must be expressed in terms of a separate problem that can be solved exactly together with a small correction term. That is, if $\opH$ is the problem, then we must be able to express it as

$$\opH = \opH_0 + \opV$$

where the eigenvalues and eigenfunctions of $\opH_0$ are known, and $\opV$ is relatively small. If we do this, then the eigenvalues ϵ_n and eigenfunctions $|\Psi_n\rangle$ can be expressed as

$$\epsilon_n = \epsilon_n^{(0)} + \epsilon_n^{(1)} + \epsilon_n^{(2)} + \ldots, \quad |\Psi_n\rangle = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \ldots$$

where the superscripts indicate the "order" of the approximation. You can think of this as similar to a type of expansion like a Taylor series.

The zeroth order terms in each of these equations are the eigenvalues E_n and eigenfunctions $|\phi_n\rangle$ of $\opH_0$, which are known exactly. It can be shown that the first order terms are

$$\epsilon_n^{(1)} = \langle\phi_n|\opV|\phi_n\rangle$$

and

$$|\psi_n^{(1)}\rangle = \sum_{k\neq n} -\frac{\langle\phi_k|\opV|\phi_n\rangle}{E_k - E_n}|\phi_k\rangle.$$

In this way, we can use the solutions to exactly-solvable problems and correct them for small perturbations. This is a second reason we spent so much time deriving the solutions to the model systems above; not only do the systems give us a mental picture of what's going on, they also provide a starting point for performing more accurate calculations while still maintaining the same qualitative physical picture. Perhaps the most common example of the use of perturbation theory is to calculate energies of anharmonic oscillators. Recall our earlier Taylor expansion of an arbitrary potential near the minimum, Equation ???. If we truncate the series at the fourth term instead of the third, we see that the Hamiltonian becomes

$$\opH = -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3,$$

where γ is the third derivative of the potential at the minimum. This problem can be treated with perturbation theory if we let

$$\opH_0 = -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{1}{2}kx^2, \text{ and } \opV = \frac{1}{6}\gamma x^3.$$

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8: MULTIELECTRON ATOMS

Electrons with more than one atom, such as Helium (He), and Nitrogen (N), are referred to as multi-electron atoms. Hydrogen is the only atom in the periodic table that has one electron in the orbitals under ground state. We will learn how additional electrons behave and affect a certain atom.

8.1: Atomic and Molecular Calculations are Expressed in Atomic Units

8.2: Perturbation Theory and the Variational Method for Helium

8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

8.4: An Electron has an Intrinsic Spin Angular Momentum

8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants

8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

8.8: Term Symbols Gives a Detailed Description of an Electron Configuration

8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

8.E: Multielectron Atoms (Exercises)

8.S: Multielectron Atoms (Summary)

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8.1: Atomic and Molecular Calculations are Expressed in Atomic Units

Learning Objectives

- Demonstrate how solving electron structure problems are less cluttered by switching to atomic units instead of SI units.

Atomic units (au or a.u.) form a system of natural units which is especially convenient for atomic physics calculations. Atomic units, like SI units, have a unit of mass, a unit of length, and so on. However, the use and notation is somewhat different from SI. Suppose a particle with a mass of *m* has 3.4 times the mass of electron. The value of mass m can be written in three ways:

- $m = 3.4\ \ m_e$: This is the clearest notation (but least common), where the atomic unit is included explicitly as a symbol.
- $m = 3.4\ \ a.u.$: This notation is ambiguous, but is common. Here, it means that the mass m is 3.4 times the atomic unit of mass. If considering a length L of 3.4 times the atomic unit of length, the equation would look the same, $L = 3.4\ \ a.u.$ The dimension needs to be inferred from context, which is sloppy.
- $m = 3.4$: This notation is similar to the previous one, and has the same dimensional ambiguity. It comes from formally setting the atomic units to 1 (Table 8.1.1).

This article deals with "Hartree type" of atomic units, where the numerical values of the following four fundamental physical constants are all unity by definition:

Table 8.1.1 : Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units	Value in Atomic Units
mass	electron rest mass	m_e	9.109×10^{-31} kg	1
charge	elementary charge	e	1.602×10^{-19} C	1
action	reduced Planck's constant	$\hbar = \frac{h}{2\pi}$	1.054×10^{-34} J·s	1
electric constant^{-1}	Coulomb force constant	$k_e = \frac{1}{4\pi\epsilon_o}$	8.987×10^{9} kg·m^3·s^{-2}·C^{-2}	1

Example 8.1.1 : Simplifying the Hamiltonian

Use the atomic units definitions in Table 8.1.1 to contrast the Hamiltonian for a Helium atom in Si units and in atomic units.

Solution

In SI units, the Hamiltonian for a Helium atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

In atomic units, the same Hamiltonian

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

All the units that make the SI version of the Hamiltonian disappear to emphasize the key aspects of the operator.

Atomic units are derived from certain fundamental properties of the physical world, and are free of anthropocentric

considerations. It should be kept in mind that atomic units were designed for atomic-scale calculations in the present-day universe, with units normalize the reduced Planck constant and also mass and charge of the electron are set to 1, and, as a result, the speed of light in atomic units is a large value, $1/\alpha \approx 137$. For example, the orbital velocity of an electron around a small atom is of the order of 1 in atomic units. Table 8.1.2 give a few derived units. Some of them have proper names and symbols assigned, as indicated in the table.

Table 8.1.2 : Derived atomic units

Dimension	Name	Symbol	Expression	Value in SI units	Value in more common units
length	bohr	a_o	$4\pi\epsilon_0\hbar^2/(m_e e^2) = \hbar/(m_e c\alpha)$	5.291×10^{-11} m	0.052 nm = 0.529 Å
energy	hartree	E_h	$m_e e^4/(4\pi\epsilon_0\hbar)^2 = \alpha^2 m_e c^2$	4.359×10^{-18} J	27.2 eV = 627.5 kcal·mol^{-1}
time			$\hbar/E_\mathrm{h}$	2.418×10^{-17} s	
velocity			$a_0 E_\mathrm{h}/\hbar = \alpha c$	2.187×10^{6} m·s^{-1}	

Bohr model in atomic units

Atomic units are chosen to reflect the properties of electrons in atoms. This is particularly clear from the classical Bohr model of the hydrogen atom in its ground state. The ground state electron orbiting the hydrogen nucleus has (in the classical Bohr model):

- Orbital velocity = 1
- Orbital radius = 1
- Angular momentum = 1
- Orbital period = 2π
- Ionization energy = $^1/_2$
- Electric field (due to nucleus) = 1
- Electrical attractive force (due to nucleus) = 1

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8.2: Perturbation Theory and the Variational Method for Helium

Learning Objectives

- Demonstrate that both perturbation theory and variational methods can be used to solve the electron structure of the helium atom.

Both perturbation theory and variation method (especially the linear variational method) provide good results in approximating the energy and wavefunctions of multi-electron atoms. Below we address both approximations with respect to the helium atom.

Perturbation Theory of the Helium Atom

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a **zero-order Hamiltonian**. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. For example, we call the simplified or starting Hamiltonian, $\hat{H}^0$, the zero order term, and the correction term $\hat{H}^1$.

$$\hat{H} = \hat{H}^0 + \hat{H}^1 \tag{8.2.1}$$

The Hamilonian for the helium atom (in atomic units) is:

$$\hat{H}^0 = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}}_{\text{H atom Hamiltonian}} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}}_{\text{H atom Hamiltonian}} \tag{8.2.2}$$

$$\hat{H}^1 = \frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \tag{8.2.3}$$

The expression for the first-order correction to the energy is

$$\begin{aligned} E^1 &= \langle \psi^0 | \hat{H}^1 | \psi^0 \rangle \\ &= \int \psi^{0*} \hat{H}^1 \psi^0 \, d\tau \end{aligned}$$

Equation ??? is a general expression for the first-order perturbation energy, which provides an improvement or correction to the zero-order energy we already obtained. Hence, E^1 is the average interaction energy of the two electrons calculated using wavefunctions that assume there is no interaction.

The solution to $\hat{H}^0$ (Equation 8.2.2) is the product of two single-electron hydrogen wavefunctions (scaled by the increased nuclear charge) since $\hat{H}^0$ can be separated into independent functions of each electron (i.e., Separation of Variables).

$$|\psi^0\rangle = |\varphi_{1s}(r_1)\varphi_{1s}(r_2)\rangle$$

So the integral in Equation ??? is

$$E^1 = \iint \varphi_{1s}(r_1)\varphi_{1s}(r_2)\frac{1}{r_{12}}\varphi_{1s}(r_1)\varphi_{1s}(r_2)\, d\tau_1 d\tau_2 \tag{8.2.4}$$

where the double integration symbol represents integration over all the spherical polar coordinates of both electrons $r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2$. The evaluation of these six integrals is lengthy. When the integrals are done, the result is E^1 = +34.0 eV so that the total energy calculated using our second approximation method, first-order perturbation theory, is

$$E_{approx2} = E^0 + E^1 = -74.8eV \tag{8.2.5}$$

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy:

$$E^0 = \frac{2}{n^2} + \frac{2}{n^2} = 4 \underbrace{E_h}_{hartrees} = 108.8\, eV$$

so the interaction of the two electrons is an important part of the total energy of the helium atom. We can continue with perturbation theory and find the additional corrections, E^2, E^3, etc. For example,

$$E^0 + E^1 + E^2 = -79.2\, eV.$$

So with two corrections to the energy, the calculated result is within 0.3% of the experimental value of -79.01 eV. It takes thirteenth-order perturbation theory (adding E^1 through E^{13} to E^0) to compute an energy for helium that agrees with experiment to within the experimental uncertainty. Interestingly, while we have improved the calculated energy so that it is much closer to the experimental value, we learn nothing new about the helium atom wavefunction by applying the first-order perturbation theory to the energy above. He need to expand the wavefunctions to first order perturbation theory, which requires more effort. Below, we will employ the variational method approximation to modify zero-order wavefunctions to address one of the ways that electrons are expected to interact with each other.

The Hartree Unit of Energy

The hartree is the atomic unit of energy (named after the British physicist Douglas Hartree) and is defined as

$$E_h = 2R_H hc$$

where R_H is the Rydberg constant, h is the Planck constant and c is the speed of light.

$$\begin{aligned} E_h &= 4.359 \times 10^{-18}\, J \\ &= 27.21\, eV. \end{aligned}$$

The hartree is usually used as a unit of energy in atomic physics and computational chemistry. As discussed before for hydrogen emission, IR, and microwave spectroscopies, experimental measurements prefer the electronvolt (eV) or the wavenumber (cm^{-1}).

Variational Method Applied to the Helium Method

As discussed in Section 6.7, because of the electron-electron interactions, the Schrödinger's Equation cannot be solved exactly for the helium atom or more complicated atomic or ionic species. However, the ground-state energy of the helium atom can be estimated using approximate methods. One of these is the variational method which requires the minimizing of the following variational integral.

$$E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{8.2.6}$$

$$= \frac{\int_0^\infty \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int_0^\infty \psi^2_{trial}\, d\tau} \tag{8.2.7}$$

The five trial wavefunctions discussions below are equally "valid" trial wavefunctions that describe the probability of finding each electron (technically the wavefunction squared). What separates the "poor" approximations from the "good" approximation is whether the trial wavefunction predicts experimental results. Consequently, for all the approximations used for the rest of this TextMap, it is important to compare the theoretical results to the "true" (i.e., experimental) results. No matter how complicated an approximation is, it is only as good as the accuracy of its predicted values to experimental values.

Trial Wavefunction #1: Simple Orbital Approximation with One Parameter

As is clear from Equation 8.2.6, the variational method approximation requires that a trial wavefunction with one or more adjustable parameters be chosen. A logical first choice for such a multi-electron wavefunction would be to assume that the electrons in the helium atom occupy two identical, but scaled, hydrogen 1s orbitals.

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{8.2.8}$$

$$= \exp\left[-\alpha(r_1 + r_2)\right] \tag{8.2.9}$$

The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.9) by varying α is

$$E_{trial} = -2.84766\ E_h$$

and the experimentally determined ground-state energy for the helium atom is the sum of first and second ionization energies

$$E_{\text{exp}} = I_1 + I_2 = -2.90372\ E_h \tag{8.2.10}$$

The deviation of energy for the optimized trial wavefunction from the experimental value is

$$\left|\frac{E_{trial}(\alpha) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.84766\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.11}$$

$$= 1.93\% \tag{8.2.12}$$

The value of -2.8477 hartrees is within 2% of the known ground-state energy of the helium atom. The error in the calculation is attributed to the fact that the wavefunction is based on the orbital approximation and, therefore, does not adequately take electron-electron interactions into account. In other words, this wavefunction gives the electrons too much independence, given that they have like charges and tend to avoid one another.

Trial Wavefunction #2: Orbital Approximation with Two Parameters

Some electron-electron interactions can be built into the multi-electron wavefunction by assuming that each electron is in an orbital which is a linear combination of two different and scaled hydrogen 1s orbitals.

$$\phi(r_1) = \exp(-\alpha r_1) + \exp(-\beta r_1) \tag{8.2.13}$$

Under the orbital approximation this assumption gives a trial wavefunction of the form

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{8.2.14}$$

$$= \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2) \tag{8.2.15}$$

Inspection of this trial wavefunction indicates that 50% of the time the electrons are in different orbitals, while for the first trial wavefunction the electrons were in the same orbital 100% of the time. Notice the enormous increase in the complexity of the variational expression for the energy for this trial wavefunction (Equation 8.2.7). However, the calculation is very similar to that using the previous trial wavefunction. The differences are that in this case the expression for the energy is more complex and that it is being minimized simultaneously with respect to two parameters (α and β) rather than just one (α).

The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.15) by varying α and β is

$$E_{trial} = -2.86035\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.86035\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.16}$$

$$= 1.49\% \tag{8.2.17}$$

Clearly introducing some electron-electron interactions into the trial wavefunction has improved the agreement between theory

and experiment (Equation 8.2.12 vs. 8.2.17).

Trial Wavefunction #3: Orbital Approximation with Two Parameters

The extent of electron-electron interactions can be increased further by eliminating the first and last term in the second trial wavefunction (Equation 8.2.15). This yields a multi-electron wavefunction of the form,

$$|\psi(1,2)\rangle_{trial} = \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) \tag{8.2.18}$$

This trial wavefunction places the electrons in different scaled hydrogen 1s orbitals 100% of the time this adds further improvement in the agreement with the literature value of the ground-state energy is obtained. The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.18) by varying α and β is

$$E_{trial} = -2.87566\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.87566\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.19}$$

$$= 0.97\% \tag{8.2.20}$$

This result is within 1% of the actual ground-state energy of the helium atom.

Trial Wavefunction #4: Approximation with Two Parameters

The third trial wavefunction, however, still rests on the orbital approximation and, therefore, does not treat electron-electron interactions adequately. Hylleraas took the calculation a step further by introducing electron-electron interactions directly into the first trial wavefunction by adding a term, r_{12}, involving the inter-electron separation.

$$|\psi_{trial}(1,2)\rangle = (\exp[-\alpha(r_1 + r_2)])\,(1 + \beta r_{12}) \tag{8.2.21}$$

In the trial multi-electron wavefunction of Equation 8.2.21, if the electrons are far apart, then r_{12} is large and the magnitude of the wavefunction increases to favor that configuration. The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.21) by varying α and β is

$$E_{trial} = -2.89112\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.89112\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.22}$$

$$= 0.43\% \tag{8.2.23}$$

This modification of the trial wavefunction has further improved the agreement between theory and experiment to within 0.5%.

Fifth Trial Wavefunction #5: Approximation with Three Parameters

Chandrasakar brought about further improvement by adding Hylleraas's r_{12} term to the third trial wavefunction (Equation 8.2.18) as shown here.

$$|\psi(1,2)\rangle_{trial} = [\exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)]\,[1 + \gamma r_{12}] \tag{8.2.24}$$

Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground-state energy. The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.24) by varying α, β and γ is

$$E_{trial} = -2.90143\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta,\gamma)-E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.90143+2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.25}$$

$$= 0.0789\% \tag{8.2.26}$$

Chandrasakar's wavefunction gives a result for helium that is within 0.07% of the experimental value for the ground-state energy.

Summary

The purpose of this section is to examine five trial wavefunctions for the helium atom used within the Perturbation Theory and Variational method approximation. For the Variational method approximation, the calculations begin with an uncorrelated wavefunction in which both electrons are placed in a hydrogenic orbital with scale factor α. The next four trial functions use several methods to increase the amount of electron-electron interactions in the wavefunction. As the summary of results that is appended shows this gives increasingly more favorable agreement with the experimentally determined value for the ground-state energy of the species under study. The detailed calculations show that the reason for this improved agreement with experiment is due to a reduction in electron-electron repulsion.

Five variational method calculations that have been outlined above for the helium atom ($Z = 2$) can be repeated for two-electron atoms (e.g., H^-, Li^+, Be^{2+}, etc). The hydride anion is a particularly interesting case because the first two trial wavefunctions do not predict a stable ion (i.e., they are poor approximations). This indicates that electron-electron interactions is an especially important issue for atoms and ions with small nuclear charge.

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8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

Learning Objectives

- Show how the Hartree approximation can be used to solve for the wavefunctions and energies of multi-electron atoms.
- Understand the orbital approach of independent orbitals is an approximation to a mutlti-electron system with the motions of all electrons coupled together.
- Demonstate how the Self-Consistant Field (SCF) calculation is needed to support the Hartree approximation

The Hartree method is used to approximate the wavefunction and the energy of a quantum multi-electron system in a stationary state. This approximation assumes that the exact N-body wavefunction of the system can be approximated by a product of single-electron wavefunctions. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree wavefunction and energy of the system. It is one step better than the "Ignorance is Bliss" approach, discussed previously, but still far from modern state-off-the-art methods.

Unsolvable Systems

The Hamiltonian for a generic multielectron atom includes nucleus-electron attraction terms for the additional electrons with a general charge Z; e.g.

$$V_{\text{nuclear-electron}}(r_1) = -\frac{Z}{|\mathbf{r}-\mathbf{R}|} \tag{8.3.1}$$

in atomic units with $|\mathbf{r}-\mathbf{R}|$ is the distance between the electron and the nucleus, The Hamiltonian must also have terms for electron-electron repulsion (also in atomic units)

$$V_{\text{electron-electron}}(r_{12}) = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

with $|\mathbf{r}-\mathbf{r}'|$ is the distance between electron 1 and electron 2. So the proper multi-electron Hamiltonian can be constructed

$$\hat{H}(r_1, r_2, ...r_n) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V_{\text{nuclear-electron}}(r_i) + \sum_{i\neq j} V_{\text{electron-electron}}(r_{ij}) \tag{8.3.2}$$

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their electron-electron repulsion (final term in Equation 8.3.2) means that an exact wavefunction for a multi-electron system would be a single function that depends **simultaneously** upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:

$$|\psi(r_1, r_2, \cdots r_i)\rangle \tag{8.3.3}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms.

The Hartree Approximation

The method for finding best possible one-electron wavefunctions that was published by Douglas Hartree in 1948 and improved two years later by Vladimir Fock. For the Schrödinger equation to be analytically solvable, the variables must be separable - the variables are the coordinates of the electrons. To separate the variables in a way that retains information about electron-electron interactions, the electron-electron term (Equation 8.3.1) must be approximated so it depends only on the coordinates of one electron. Such an approximate Hamiltonian can account for the interaction of the electrons in **an average way**. The exact one-electron eigenfunctions of this approximate Hamiltonian then can be found by solving the Schrödinger equation. These functions are the best possible **one-electron functions**.

The Hartree approximation starts by invoking an initial *ansatz* that the multi-electron wavefunction in Equation 8.3.3 can be expanded as a product of single-electron wavefunctions (i.e., orbitals)

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\rangle \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N)$$

from which it follows that the electrons are *independent*, and interact only via the mean-field Coulomb potential. This yields one-electron Schrödinger equations of the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

or

$$H_e(r)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

where $V(r)$ is the potential in which the electron moves; this includes both the nuclear-electron interaction

$$V_{nucleus}(\mathbf{r}) = -Ze^2\sum_R \frac{1}{|\mathbf{r}-\mathbf{R}|}$$

and the mean field arising from the $N-1$ other electrons. We smear the other electrons out into a smooth negative charge density $\rho(\mathbf{r}')$ leading to a potential of the form

$$V_{electron}(\mathbf{r}) = -e\int d\mathbf{r}'\rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

where

$$\rho(\mathbf{r}) = \sum_i^{\text{occupied}} |\psi(\mathbf{r})|^2.$$

The sum over runs over all occupied states; i.e., only the states of electrons that exist in the atom. The wavefunctions that from this approach with the Hamiltonian $H_e(r)$ involve possess three kinds of energies discussed below.

Three Energies within the Hartree Approximation

The total energy ϵ_j of the orbital ϕ_j, is the sum of the above three contributions:

1. **Kinetic Energy:** The Kinetic energy of the electron has an average value is computed by taking the expectation value of the kinetic energy operator

   $$\frac{-\hbar^2}{2m}\nabla^2$$

   with respect to any particular solution $\phi_j(r)$ to the Schrödinger equation:

   $$KE = \langle\phi_j|\frac{-\hbar^2}{2m}\nabla^2|\phi_j\rangle$$

2. **Nuclear-Electron Coulombic Attraction Energy:** Coulombic attraction energy with the nucleus of charge Z:

$$\langle \phi_j | \frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|} | \phi_j \rangle$$

3. **Electron-Electron Coulombic Repulsion Energy:** Coulomb repulsion energies with all of the $N-1$ other electrons, which are assumed to occupy other atomic orbitals denoted ϕ_K, with this energy computed as

$$\sum_{j \neq k} \langle \phi_j(r)\phi_k(r') | \frac{e^2}{|r-r'|} | \phi_j(r)\phi_k(r') \rangle. \tag{8.3.4}$$

The Dirac notation $\langle \phi_j(r)\phi_k(r') | \frac{e^2}{|r-r'|} | \phi_j(r)\phi_k(r') \rangle$ is used to represent the two-electron (six-dimensional) Coulomb integral

$$J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr'$$

that describes the Coulomb repulsion between the charge density $|\phi_j(r)|^2$ for the electron in ϕ_j and the charge density $|\phi_k(r')|^2$ for the electron in ϕ_k. Of course, the sum over k must be limited to exclude $k=j$ to avoid counting a "self-interaction" of the electron in orbital ϕ_j with itself.

Adding these all together to get the total energy ϵ_j of the orbital ϕ_j:

$$\epsilon_J = \langle \phi_j | \frac{-\hbar^2}{2m} \nabla^2 | \phi_j \rangle + \langle \phi_j | \frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|} | \phi_j \rangle + \sum_{j \neq k} \langle \phi_j(r)\phi_k(r') | \frac{e^2}{|r-r'|} | \phi_j(r)\phi_k(r') \rangle.$$

This treatment of the electrons and their orbitals is referred to as the **Hartree-level of theory**.

When screened hydrogenic atomic orbitals are used to approximate the ϕ_j and ϕ_K orbitals, the resultant ϵ_J values do **not** produce accurate predictions. For example, the negative of ϵ_J should approximate the ionization energy for removal of an electron from the orbitals ϕ_j. Such ionization potentials (IP s) can be measured, and the measured values do not agree well with the theoretical values when a crude screening approximation is made for the atomic orbitals.

The Self-Consistant Field (SCF) Approach to the Variational Method

The Hartree Equations are nonlinear and must be solved iteratively. This is because if particles interact, that interaction must be in the Hamiltonian. So until we know where the particles are, we cannot write down the Hamiltonian, but until we know the Hamiltonian, we cannot tell where the particles are.

The idea is to solve the Schrödinger equation for an electron moving in the potential of the nucleus and all the other electrons. We start with a guess for the trial electron charge density, solve N/2 one-particle Schrödinger equations (initially identical) to obtain N electron wavefunctions. Then we construct the potential for each wavefunction from that of the nucleus and that of all the other electrons, symmetrize it, and solve the N/2 Schrödinger equations again. This method is ideal for a computer, because it is easily written as an algorithm (Figure 8.3.1).

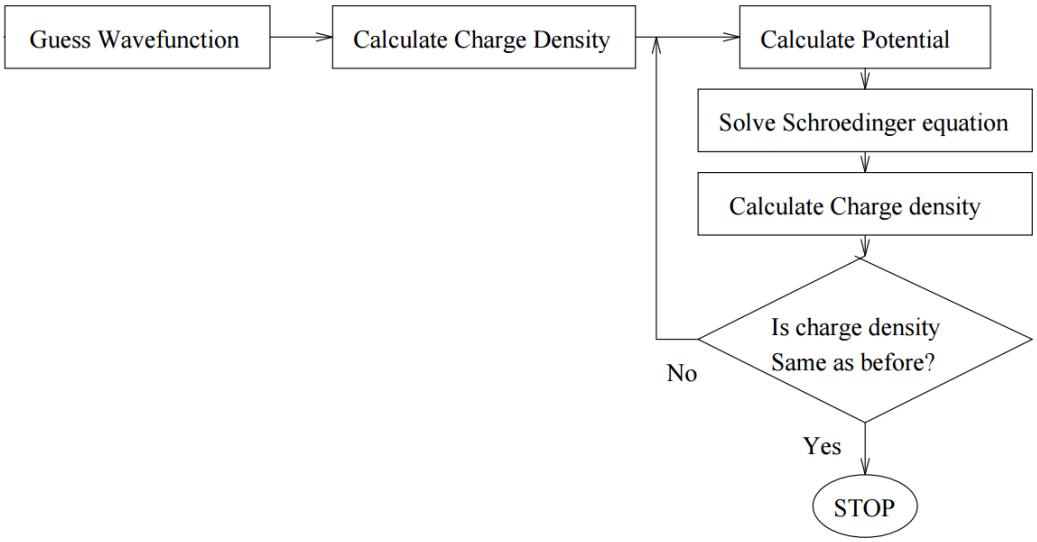


Figure 8.3.1 : Algorithm for Self-consistent field theory.

Although we are concerned here with atoms, the same methodology is used for molecules or even solids (with appropriate potential symmetries and boundary conditions). This is a variational method, so wherever we refer to wavefunctions, we assume that they are expanded in some appropriate basis set.

> Fock improved on Hartree's method by using proper "antisymmetrized wavefunctions" (called the Hartree-Fock method) instead of simple one-electron wavefunctions.

Shielding and Effective Charges Concepts are Useful

The hydrogen-like orbitals provide qualitative descriptions of orbitals of atoms with more than a single electron. By introducing the concept of screening as a way to represent the repulsive interactions among the electrons of an atom, an effective nuclear charge Z_{eff} can be used in place of Z in the hydrogenic $\psi_{n,l,m}$ and $E_{n,l}$ formulas to generate approximate atomic orbitals to be filled by electrons in a many-electron atom. For example, in the crudest approximation of a carbon atom, the two $1s$ electrons experience the full nuclear attraction so $Z_{\text{eff}} = 6$ for them, whereas the $2s$ and $2p$ electrons are screened by the two $1s$ electrons, so $Z_{\text{eff}} = 4$ for them. Within this approximation, one then occupies two $1s$ orbitals with $Z = 6$, two $2s$ orbitals with $Z = 4$ and two $2p$ orbitals with $Z = 4$ in forming the full six-electron product wavefunction of the lowest-energy state of carbon

$$|\psi(1,2,\ldots,6)\rangle = |\psi_{1s}(1)\psi_{1s}(2)\psi_{2s}(3)\ldots\psi_{1p}(6)\rangle. \tag{8.3.5}$$

However, such approximate orbitals are not sufficiently accurate to be of use in quantitative simulations of atomic and molecular structure. In particular, their energies do not properly follow the trends in atomic orbital (AO) energies that are taught in introductory chemistry classes (Figure 8.3.2).

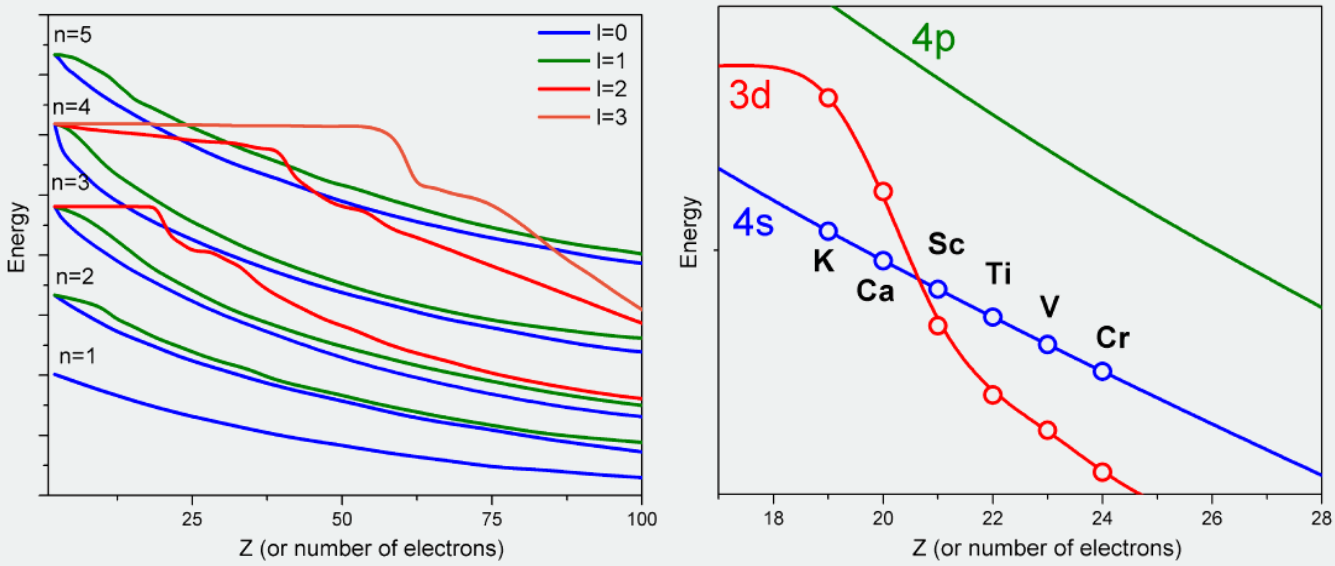


Figure 8.3.2 : Energies of Atomic Orbitals as Functions of the number of electrons in Neutral Atoms. (CC BY 4.0; Delmar Larsen).

For example, the relative energies of the $3d$ and $4s$ orbitals are not adequately described in a model that treats electron repulsion effects in terms of a simple screening factor. So, now it is time to examine how we can move beyond the screening model and take the electron repulsion effects, which cause the inter-electronic couplings that render the Schrödinger equation insolvable, into account in a more reliable manner.

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8.4: An Electron has an Intrinsic Spin Angular Momentum

Learning Objectives

- Understand the forth quantum number for electrons - spin.
- Understand how spin is connected to magnetic properties of the electrons and atoms.
- Understand how to break degeneracy via externally applied magnetic fields in electrons and atoms.

Imagine doing a hypothetical experiment that would lead to the discovery of electron spin. Your laboratory has just purchased a microwave spectrometer with variable magnetic field capacity. We try the new instrument with hydrogen atoms using a magnetic field of 10^4 Gauss and look for the absorption of microwave radiation as we scan the frequency of our microwave generator (Figure 8.4.1).

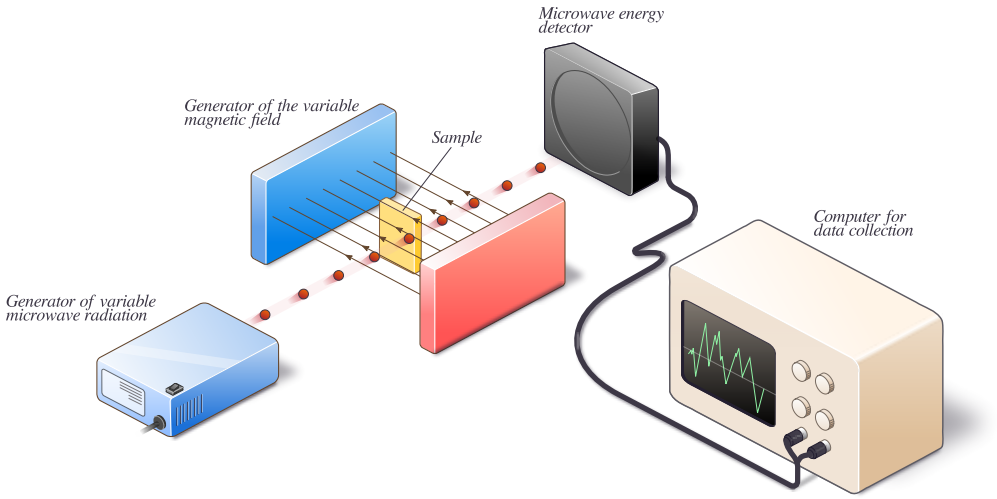


Figure 8.4.1 : Schematic diagram of a microwave spectrometer with the sample in a variable magnetic field. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Finally we see absorption at a microwave photon frequency of $28 \times 10^9\ Hz$ (28 gigahertz). This result is really surprising from several perspectives. Each hydrogen atom is in its ground state, with the electron in a 1s orbital. The lowest energy electronic transition that we predict based on existing theory (the electronic transition from the ground state (ψ_{100} to ψ_{21m}) requires an energy that lies in the vacuum ultraviolet (the lower Lyman line at 121 nm), not the microwave, region of the spectrum. Furthermore, when we vary the magnetic field we note that the frequency at which the absorption occurs varies in proportion to the magnetic field.

The Zeeman Effect: Breaking Degeneracies with Magnetic Fields

Magnetism results from the circular motion of charged particles. This property is demonstrated on a macroscopic scale by making an electromagnet from a coil of wire and a battery. Electrons moving through the coil produce a magnetic field, which can be thought of as originating from a magnetic dipole or a bar magnet. Electrons in atoms also are moving charges with angular momentum so they too produce a magnetic dipole, which is why some materials are magnetic. A **magnetic dipole** interacts with a magnetic field, and the energy of this interaction is given by the scalar product of the magnetic dipole moment, and the magnetic field, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{8.4.1}$$

Pieter Zeeman was one of the first to observe the splittings of spectral lines in a magnetic field caused by this interaction. Consequently such splittings are known as the Zeeman effect. (Figure 8.4.2). The expectation value calculated for the total energy in this case is the sum of the energy in the absence of the field, E_n, plus the Zeeman energy:

$$\langle E \rangle = E_n + \frac{e\hbar B_z m_l}{2m_e} \tag{8.4.2}$$

$$= E_n + \mu_B B_z m_l \tag{8.4.3}$$

The factor

$$\frac{e\hbar}{2m_e} = -\gamma_e \hbar = \mu_B \tag{8.4.4}$$

defines the constant μ_B, called the **Bohr magneton**, which is taken to be the fundamental magnetic moment. It has units of 9.2732×10^{-21} erg/Gauss or 9.2732×10^{-24} Joule/Tesla. This factor will help you to relate magnetic fields, measured in Gauss or Tesla, to energies, measured in ergs or Joules, for any particle with a charge and mass the same as an electron.

Equation 8.4.3 demonstrates that that m_l quantum number degeneracy of the hydrogen atom is removed by the externally applied magnetic field. For example, the three hydrogen atom eigenstates $|\psi_{211}\rangle$, $|\psi_{21-1}\rangle$, and $|\psi_{210}\rangle$ are degenerate in zero magnetic field, but have different energies in an externally applied magnetic field (Figure 8.4.2).

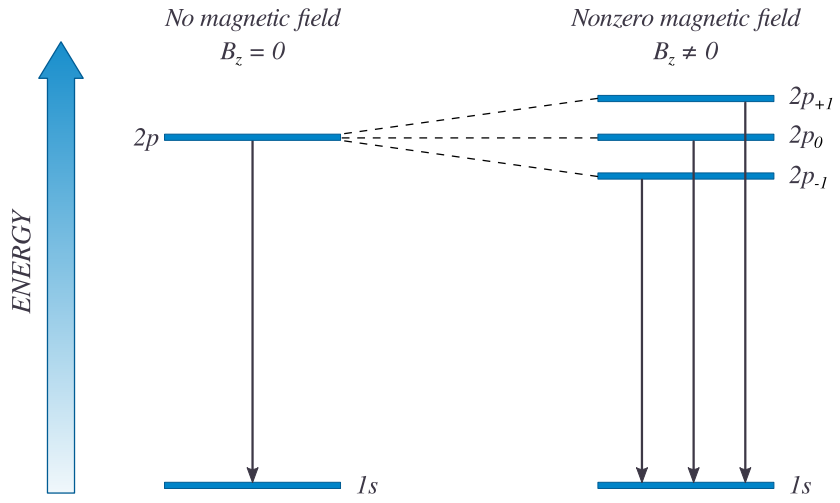


Figure 8.4.2 : The Zeeman effect for the $2s \rightarrow 1s$ transition. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field. (CC BY-NC; Ümit Kaya via LibreTexts)

The $m_l = 0$ state, for which the component of angular momentum and hence also the magnetic moment in the external field direction is zero, experiences no interaction with the magnetic field. The $m_l = +1$ state, for which the angular momentum in the z-direction is +ħ and the magnetic moment is in the opposite direction, against the field, experiences a raising of energy in the presence of a field. Maintaining the magnetic dipole against the external field direction is like holding a small bar magnet with its poles aligned exactly opposite to the poles of a large magnet. It is a higher energy situation than when the magnetic moments are aligned with each other.

Electron Spin and the Stern-Gerlach Experiment

To discover new things, experimentalists sometimes must explore new areas in spite of contrary theoretical predictions. Our theory of the hydrogen atom at this point gives no reason to look for absorption in the microwave region of the spectrum. By doing the crazy experiment outlines above, we discovered that when an electron is in the $|1s\rangle$ orbital of the hydrogen atom, there are two different states that have the same energy. When a magnetic field is applied, this degeneracy is removed, and microwave radiation can cause transitions between the two states. In the rest of this section, we see what can be deduced from this experimental observation. This experiment actually could be done with electron spin resonance spectrometers available today (Figure 8.4.1). To

explain our observations, a new model for the hydrogen atom. Our original model for the hydrogen atom accounted for the motion of the electron and proton in our three-dimensional world; the new model needs something else that can give rise to an additional Zeeman-like effect. We need a charged particle with angular momentum to produce a magnetic moment, just like that obtained by the orbital motion of the electron. We can postulate that our observation results from a motion of the electron that was not considered in the last section - electron spin. We have a charged particle spinning on its axis. We then have charge moving in a circle, angular momentum, and a magnetic moment, which interacts with the magnetic field and gives us the Zeeman-like effect that we observed (Figure 8.4.2).

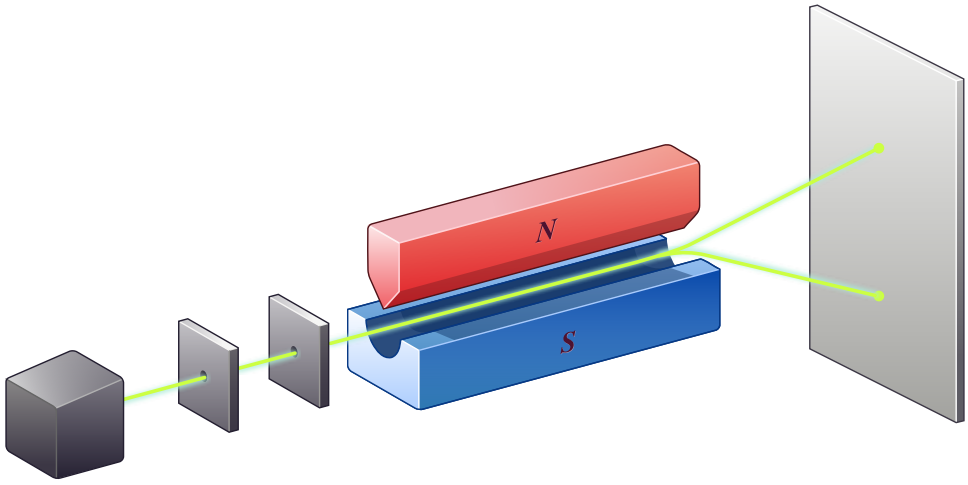


Figure 8.4.2 : Stern–Gerlach experiment: silver atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the **Electron Spin Quantum Number** and denoted by m_s. In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might by explained by assuming electrons act as if it has a spin, which can be denoted by an arrow pointing up, which is +1/2, or an arrow pointing down, which is -1/2. The Stern and Gerlach experiment which demonstrated this was done with a beam of vaporized silver atoms that split into two beams after passing through a magnetic field (Figure 8.4.2). An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the *one unpaired electron* in the atom will determine the spin.

Spin Eigenstates and Eigenvalues

To describe electron spin from a quantum mechanical perspective, we must have spin wavefunctions and spin operators. The properties of the spin states are deduced from experimental observations and by analogy with our treatment of the states arising from the orbital angular momentum of the electron. The important feature of the spinning electron is the spin angular momentum vector, which we label S by analogy with the orbital angular momentum L. We define spin angular momentum operators with the same properties that we found for the rotational and orbital angular momentum operators. After all, angular momentum is angular momentum, no matter if it is *orbital* or *spin* in nature.

We found that

$$\hat{L}^2|Y_l^{m_l}\rangle = l(l+1)\hbar^2|Y_l^{m_l}\rangle$$

so by analogy for the spin states, we must have

$$\hat{S}^2|\sigma_s^{m_s}\rangle = s(s+1)\hbar^2|\sigma_s^{m_s}\rangle$$

where σ is a spin wavefunction with quantum numbers s and m_s that obey the same rules as the quantum numbers l and m_l associated with the spherical harmonic wavefunction Y. We also found the project of the orbital angular momentum on the z-axis is

$$\hat{L}_z|Y_l^{m_l}\rangle = m_l\hbar|Y_l^{m_l}\rangle$$

so by analogy, we must have a similar projection for the spin angular momentum:

$$\hat{S}_z|\sigma_s^{m_s}\rangle = m_s\hbar|\sigma_s^{m_s}\rangle \tag{8.4.5}$$

Since m_l ranges in integer steps from $-l$ to $+l$, also by analogy m_s ranges in integer steps from $-s$ to $+s$. In our hypothetical experiment, we observed one absorption transition, which means there are two spin states. Consequently, the two values of m_s must be $+s$ and $-s$, and the difference in m_s for the two states, labeled f and i below, must be the smallest integer step, i.e., 1. The result of this logic is that

$$\begin{aligned} m_{s,f} - m_{s,i} &= 1 \\ (+s) - (-s) &= 1 \\ 2s &= 1 \\ s &= \frac{1}{2} \end{aligned} \tag{8.4.6}$$

Therefore our conclusion is that the magnitude of the spin quantum number is 1/2 and the values for m_s are +1/2 and -1/2. The two spin states correspond to spinning clockwise and counter-clockwise with positive and negative projections of the spin angular momentum onto the z-axis (Figure 8.4.3). The state with a positive projection, m_s = +1/2, is called α; the other is called β. These spin states are arbitrarily labeled α and β, and the associated spin wavefunctions also are designated by $|\alpha\rangle$ and $|\beta\rangle$.

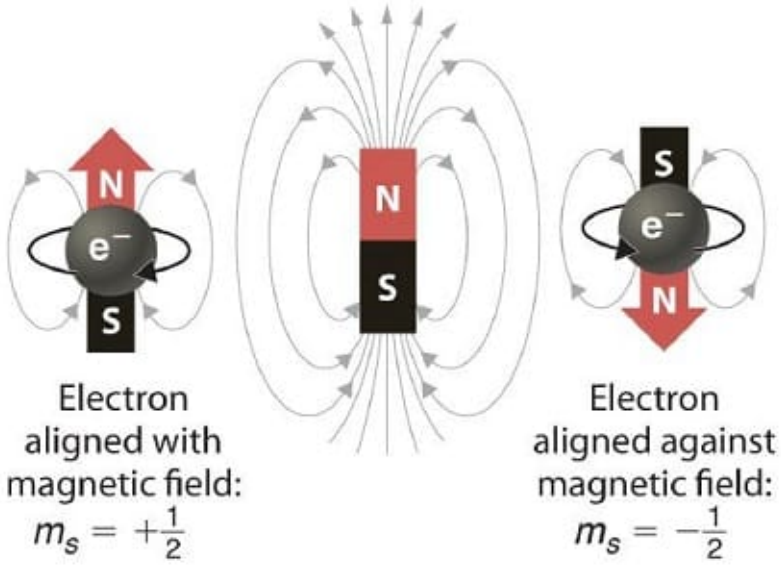


Figure 8.4.3 : Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden. (CC BY-SA-NC 3.0; Anonymous).

From Equation 8.4.5, the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s\hbar \tag{8.4.7}$$

so the value of S_z is $+\hbar/2$ for spin state α and $-\hbar/2$ for spin state β. Hence, we conclude that the α spin state, where the magnetic moment is aligned against the external field direction, has a **greater energy** than the β spin state.

Electrons are not Actually Spinning

Electron's hypothetical surface would have to be moving *faster* than the speed of light for it to rotate quickly enough to produce the observed angular momentum. Hence, an electron is not simply a spinning ball or ring and electron spin appears to be an *intrinsic angular moment* of the particle rather than a consequence of the rotation of a charge particle like Figure 8.4.3 suggests. Despite this, the term "electron spin" persists in quantum vernacular.

Properties of Spin Eigenstates

Even though we do not know their functional forms, the spin wavefunctions are taken to be normalized and orthogonal to each other.

$$\int \alpha^* \alpha \, d\tau_s = \int \beta^* \beta \, d\tau_s = 1 \tag{8.4.8}$$

or in braket notation

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \tag{8.4.9}$$

and

$$\int \alpha^* \beta \, d\tau_s = \int \beta^* \alpha \, d\tau_s = 0 \tag{8.4.10}$$

or in braket notation

$$\langle \alpha | \beta \rangle = \langle \alpha | \beta \rangle = 0 \tag{8.4.11}$$

where the integral is over the spin variable τ_s.

Now let's apply these deductions to the experimental observations in our hypothetical microwave experiment in Figure 8.4.1 . We can account for the frequency of the transition (ν= 28 gigahertz) that was observed in this hypothetical experiment in terms of the magnetic moment of the spinning electron and the strength of the magnetic field. The photon energy, $h\nu$, is given by the difference between the energies of the two states, E_α and E_β

$$\Delta E = h\nu \tag{8.4.12}$$

$$= E_\alpha - E_\beta \tag{8.4.13}$$

The energies of these two states consist of the sum of the energy of an electron in a 1s orbital, E_{1s}, and the energy due to the interaction of the spin magnetic dipole moment of the electron, μ_s, with the magnetic field, B.

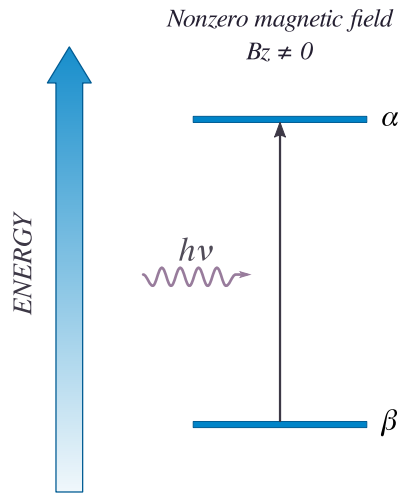


Figure 8.4.4 : Absorption of a photon to cause a transition from the β to the α state. (CC BY-NC; Ümit Kaya via LibreTexts)

The two states with distinct values for spin magnetic moment μ_s are denoted by the subscripts α and β (the spin version of Equation 8.4.1.

$$E_\alpha = E_{1s} - \mu_{s,\alpha} \cdot B$$
$$E_\beta = E_{1s} - \mu_{s,\beta} \cdot B$$

Substituting the two equations above into the expression for the photon (Equation 8.4.13) energy gives

$$h\nu = E_\alpha - E_\beta \tag{8.4.14}$$
$$= (E_{1s} - \mu_{s,\alpha} \cdot B) - (E_{1s} - \mu_{s,\beta} \cdot B) \tag{8.4.15}$$
$$= (\mu_{s,\beta} - \mu_{s,\alpha}) \cdot B \tag{8.4.16}$$

Again by analogy with the orbital angular momentum and magnetic moment discussed above, we take the spin magnetic dipole of each spin state, $\mu_{s,\alpha}$ and $\mu_{s,\beta}$, to be related to the total spin angular momentum of each state, S_α and S_β, by a constant **spin gyromagnetic ratio**, γ_s, as shown below.

$$\mu_s = \gamma_s S$$

or each of the two states

$$\mu_{s,\alpha} = \gamma_s S_\alpha$$
$$\mu_{s,\beta} = \gamma_s S_\beta$$

With the magnetic field direction defined as z, the scalar product in Equation 8.4.16 becomes a product of the z-components of the spin angular momenta, $S_{z,\alpha}$ and $S_{z,\beta}$, with the external magnetic field.

Inserting the values for $S_{z,\alpha} = +\frac{1}{2}\hbar$ and $S_{z,\alpha} = -\frac{1}{2}\hbar$ from Equation 8.4.7 and rearranging Equation 8.4.16 yields

$$\frac{h\nu}{B} = -\gamma_s \hbar$$

Calculating the ratio $\frac{h\nu}{B}$ from our experimental results, $\nu = 28 \times 10^9\ Hz$ when $B = 10^4\ gauss$, gives us a value for

$$-\gamma_s \hbar = 18.5464 \times 10^{-21}\, erg/gauss.$$

This value is about twice the Bohr magneton,$-\gamma_e \hbar$, found in Equation 8.4.4 i.e. $\gamma_s \hbar = 2.0023, \gamma_e \hbar$, or

$$\gamma_s = 2.0023\gamma_e \tag{8.4.17}$$

The factor of 2.0023 is called the **g-factor** and accounts for the deviation of the spin gyromagnetic ratio from the value expected for orbital motion of the electron. In other words, it accounts for the spin transition being observed where it is instead of where it would be if the same ratio between magnetic moment and angular momentum held for both orbital and spin motions. The value 2.0023 applies to a freely spinning electron; the coupling of the spin and orbital motion of electrons can produce other values for g.

Exercise 8.4.1

Carry out the calculations that show that the g-factor for electron spin is 2.0023.

Interestingly, the concept of electron spin and the value g = 2.0023 follow logically from *Dirac*'s *relativistic quantum theory*, which is beyond the scope of this discussion. Electron spin was introduced here as a postulate to explain experimental observations. Scientists often introduce such postulates parallel to developing the theory from which the property is naturally deduced.

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8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

Learning Objectives

- Interprete the consequence of exchanging two electrons in a multi-electron atom on the wavelengths
- Connect the Pauli's Exclusion Principle to the permutation symmetry of multi-electron atoms

Quantum mechanics allows us to predict the results of experiments. If we conduct an experiment with indistinguishable particles a correct quantum description cannot allow anything which distinguishes between them. For example, if the wavefunctions of two particles overlap, and we detect a particle, which one is it? The answer to this is not only that we do not know, but that we cannot know. Quantum mechanics can only tell us the probability of finding a particle in a given region. The wavefunction must therefore describe both particles.

The Schrödinger equation for the helium atom is then:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_1^2)-V(\mathbf{r}_1)-V(\mathbf{r}_2)+V_{12}(\mathbf{r}_1,\mathbf{r}_2)\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2)$$

where the subscripts label each particle, and there are six coordinates, three for each particle. While $|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ is a six dimensional wavefunction (three for each electron) and contains all the information we can measure (a Postulate of Quantum Mechanics), it only provide the probability of finding the electron at a specific volume element, and does **not** tell us which particle is which (e.g., is it electon 1 or electron 2?).

What basis states would be appropriate for $|\psi\rangle$? If we consider the orbital approximation that uses a product wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle=|\varphi_a(\mathbf{r}_1)\rangle|\varphi_b(\mathbf{r}_2)\rangle$$

where $|\varphi_a(\mathbf{r}_1)\rangle$ and $|\varphi_b(\mathbf{r}_2)\rangle$ are one-particle spin-orbitals (with both spin and spatial components) of atoms 1 and 2. This approximation allows us to separate the two particle equation into two one-electron equations:

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2+V(\mathbf{r}_1)\right]|\varphi_a(\mathbf{r}_1)\rangle=E|\varphi_a(\mathbf{r}_1)\rangle$$

$$\left[-\frac{\hbar^2}{2m}\nabla_2^2+V(\mathbf{r}_2)\right]|\varphi_b(\mathbf{r}_2)\rangle=E|\varphi_a(\mathbf{r}_2)\rangle$$

provided that the particles do not interact (e.g., ∇_1^2 does not act on $|\varphi_b(\mathbf{r}_2)\rangle$ and $V_{12}=0$).

Unfortunately, by doing this we have introduced unphysical *labels* to the indistinguishable particles. And this is wrong: the effect of it is that the particles do not interfere with each other because they are in different dimensions (six dimensional space - remember?). When we construct a two particle wavefunction out of two one-particle wavefunctions we must be ensure that the probability density (the measurable quantity $|\psi|^2$) is independent of the **artificial** labels.

The Exchange Operator

We can deepen our understanding of the quantum mechanical description of multi-electron atoms by examining the concepts of electron indistinguishability and the Pauli Exclusion Principle in detail. We will use the following statement as a guide to keep our explorations focused on the development of a clear picture of the multi-electron atom: "When a multi-electron wavefunction is built as a product of single-electron wavefunctions, the corresponding concept is that exactly one electron's worth of charge density is described by each atomic spin-orbital."

A subtle, but important part of the conceptual picture, is that the electrons in a multi-electron system are not distinguishable

from one another by any experimental means. Since the electrons are indistinguishable, the probability density we calculate by squaring the modulus of our multi-electron wavefunction also cannot change when the electrons are interchanged (permuted) between different orbitals. In general, if we interchange two identical particles, the world does not change. As we will see below, this requirement leads to the idea that the world can be divided into two types of particles based on their behavior with respect to permutation or interchange.

In order for the probability density to remain unchanged when two particles are permuted, the wavefunction itself can change only by a factor of $e^{i\varphi}$, which represents a complex number, when the particles described by that wavefunction are permuted. As we will show below, the $e^{i\varphi}$ factor is possible because the probability density depends on the absolute square of the function and all expectation values involve $\psi\psi^*$. Consequently $e^{i\varphi}$ disappears in any calculation that relates to the real world because $e^{i\varphi}e^{-i\varphi} = 1$.

We could symbolically write an approximate two-particle wavefunction as $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 ($\mathbf{r}_1$) for the coordinates of particle 2 ($\mathbf{r}_2$) and vice versa, to get the new wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This new wavefunction must have the property that

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = \psi(\mathbf{r}_2, \mathbf{r}_1)^*\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.1}$$

since the probability density of the electrons in the atom does **not** change upon permutation of the electrons.

Exercise 8.5.1

Permute the electrons the product function for He wavefunction:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = |\varphi_{1s}(\mathbf{r}_1)\rangle|\varphi_{1s}(\mathbf{r}_2)\rangle$$

Equation 8.5.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.2}$$

so that

$$\left(e^{-i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right)\left(e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.3}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi}e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \tag{8.5.4}$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature.

Exercise 8.5.2

Use Euler's Equality

$$e^{i\pi} + 1 = 0$$

to show that $e^{i2\varphi} = 1$ when $\varphi = 0$ or $n\pi$ and consequently $e^{i\varphi} = \pm 1$.

We can introduce the *exchange operator* $\hat{P}_{12}$: an operator which permutes the labels of the particles in a multi-particle wavefucntion. This is a rather strange operator, because it only changes the *unphysical* labels which we have attached to the one-particle wavefunctions in order to make the maths more easy. For a meaningful solution we must have a wavefunction which has a probability amplitude unchanged by $\hat{P}_{12}$: it must be either symmetric or antisymmetric with respect to exchange:

$$\hat{P}_{12}|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \pm|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle \tag{8.5.5}$$

Bosons and femions

Physical solutions must be eigenfunctions of $\hat{P}_{12}$ (i.e., $\hat{H}$ and $\hat{P}_{12}$ commute). Moveover, Equation 8.5.5 argues that the eigenvalues of the Exchange Operator are either +1 (bosons) or –1 (fermions).

Bosons

Wavefunctions for which $e^{i\varphi} = +1$ are defined as symmetric with respect to permutation, because the wavefunction is identical before and after a single permutation. Wavefunctions that are symmetric with respect to interchange of the particles obey the following mathematical relationship,

$$\hat{P}_{12}|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = +|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

The behavior of some particles requires that the wavefunction be symmetric with respect to permutation. These particles are called bosons and have integer spin such as deuterium nuclei, photons, and gluons.

Fermions

The behavior of other particles requires that the wavefunction be antisymmetric with respect to permutation $(e^{i\varphi} = -1)$. A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\hat{P}_{12}|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = -|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

These particles are called fermions and have half-integer spin and include electrons, protons, and neutrinos. Since electrons are fermion, any wavefunction used to describe multiple electrons **must** be antisymmetric with respect to permutation of the electrons. The requirement that the wavefunction be antisymmetric applies to all multi-electron functions $\psi(\mathbf{r}_1,\mathbf{r}_2,\cdots r_i)$, including those approximated as products of single electron functions

$$|\psi(\mathbf{r}_1,\mathbf{r}_2,\cdots r_i)\rangle \approx \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\cdots\varphi_i(r_i) \tag{8.5.6}$$

Exercise 8.5.4

What is meant by the term permutation symmetry?

Exercise 8.5.5

Explain why the product function $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ could describe two bosons (deuterium nuclei), but can not describe two fermions (e.g. electrons).

Answer available at the end of this section.

The Pauli's Exclusion Principle

Any physically meaningful Hamiltonian must commute with $\hat{P}_{12}$, otherwise $\hat{H}$ and $\hat{P}_{12}$ could not have common eigenfunctions and the system could not remain in an eigenstate of exchange. A simple product wavefunction like that in Equation 8.5.6 does **not** satisfy this (unless $\varphi_a = \varphi_b$). A **linear combination of all permutations** is required to satisfy indistinguishability constraints.

For a two particle system (e.g., Helium) there is the asymmetric combination

$$|\psi^{-}\rangle = \frac{1}{\sqrt{2}}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.7}$$

and symmetric combination

$$|\psi^{+}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle + C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle + C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.8}$$

where the C_{ab} terms are expansion and normalization parameters.

> Note that the antisymmetric combination (Equation 8.5.7) **cannot** include terms where both particles are in the same state (spin-orbital), but there are three possibilities for the symmetric state (Equation 8.5.8).

Although any linear combinations of C_{ab}, C_{bb}, and C_{aa} in Equation 8.5.8 is possible, there are three limiting expressions for possible symmetric combinations:

$$|\psi_1^{+i}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.9}$$

$$|\psi_2^{+i}\rangle = C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle \tag{8.5.10}$$

$$|\psi_3^{+i}\rangle = C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.11}$$

If $\varphi_a(\mathbf{r}_1) = \varphi_a(\mathbf{r}_2)$, then $|\varphi^{-i}\rangle = 0$. Thus there is no possible antisymmetric combination involving electrons in the same state (spin-orbit). This is the **Pauli exclusion principle**.

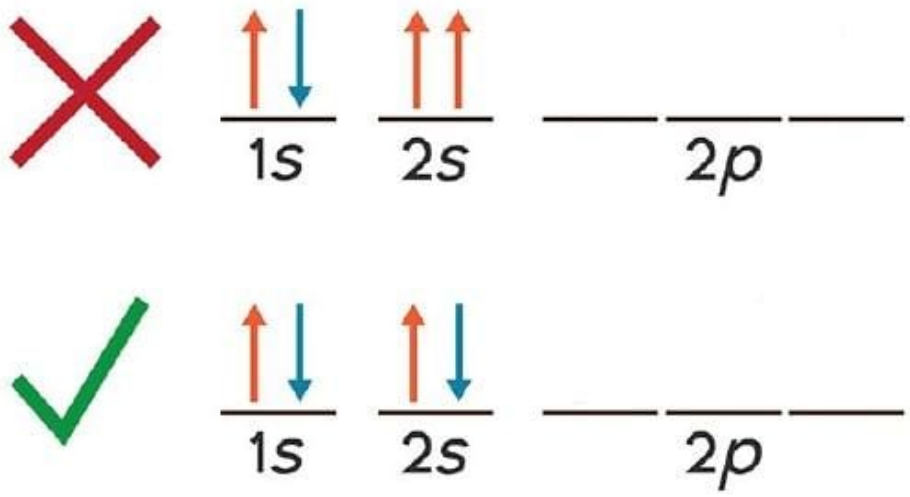


Figure 8.5.1 : The 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, since each electrons is described by a specific spin-orbital and each orbital (spatial) can hold either an α or a β electron (i.e., they must have opposite spins). Otherwise they will have the same four quantum numbers, in violation of the Pauli Exclusion Principle.

The Pauli Exclusion Principle argues that two electrons **could not** be described by the same spin-orbital. To see the relationship between this statement and the requirement that the wavefunction be antisymmetric for electrons, try to construct an anti-symmetric wavefunction for two electrons that are described by the same spin-orbital

$$|\varphi_b(\mathbf{r}_1)\rangle = \varphi_a(\mathbf{r}_2)\rangle$$

For example, if this were the case for the anti-symmetric combination for helium (Equation 8.5.7), then the wavefunction collapses to zero. We can only constructs wavefunctions that are antisymmetric with respect to permutation symmetry only if each electron is described by a different function.

> The Pauli Exclusion Principle is simply the requirement that the wavefunction be antisymmetric for electrons, since they are fermions.

Answers

Because if we switch $\mathbf{r}_1$ and $\mathbf{r}_2$, the product function becomes $\varphi(r_2)\varphi(r_1)$, which is equal to $\varphi(r_1)\varphi(r_2)$, which is consistent with the wavefunctions of bosons, because boson wavefunctions are symmetric. However, fermion wavefunctions are antisymmetric, which means that if switch r_1 and r_2, the result should be -1×the original wavefunction. Therefore, the product function $\varphi(r_1)\varphi(r_2)$ **cannot** describe fermions.

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8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants

Learning Objectives

- Understand how the Pauli Exclusion principle affects the electronic configuration of mulit-electron atoms
- Understand how determinantal wavefunctions (Slater determinents) ensure the proper symmetry to electron permutation required by Pauli Exclusion Principle.
- Connect the electron permutation symmetry requirement to multi-electron wavefunctions to the Aufbau principle taught in general chemistry courses

Let's try to construct an antisymmetric function that describes the two electrons in the ground state of helium. Blindly following the first statement of the Pauli Exclusion Principle, then each electron in a multi-electron atom **must** be described by a different spin-orbital. For the ground-state helium atom, this gives a $1s^2 2s^0 2p^0$ configuration (Figure 8.6.1).

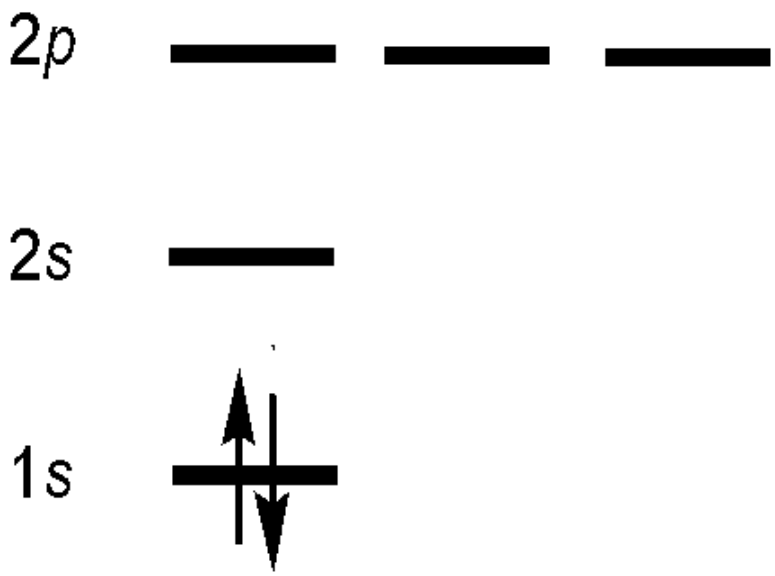


Figure 8.6.1 : Electron configuration for ground state of the helium atom.

We try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \varphi_{1s}\alpha(\mathbf{r}_1)\varphi_{1s}\beta(\mathbf{r}_2) \tag{8.6.1}$$

After permutation of the electrons, this becomes

$$|\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle = \varphi_{1s}\alpha(\mathbf{r}_2)\varphi_{1s}\beta(\mathbf{r}_1) \tag{8.6.2}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. Hence, the simple product wavefunction in Equation 8.6.1 does not satisfy the indistinguishability requirement since an antisymmetric function must produce the same function multiplied by (–1) after permutation of two electrons, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make **a linear combination of functions**. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 8.6.2 from the right-hand side of Equation 8.6.1 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be

normalized.

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s}\alpha(\mathbf{r}_1)\varphi_{1s}\beta(\mathbf{r}_2) - \varphi_{1s}\alpha(\mathbf{r}_2)\varphi_{1s}\beta(\mathbf{r}_1)] \tag{8.6.3}$$

In this orbital approximation, a single electron is held in a single s*pin-orbital* with an orbital component (e.g., the $1s$ orbital) determined by the n, l, m_l quantum numbers and a spin component determined by the m_s quantum number.

The wavefunction in Equation 8.6.3 can be decomposed into spatial and spin components:

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.4}$$

Example 8.6.1 : Symmetry to Electron Permutation

Show that the linear combination of spin-orbitals in Equation 8.6.3 is antisymmetric with respect to permutation of the two electrons.

Hint

Replace the minus sign with a plus sign (i.e. take the positive linear combination of the same two functions) and show that the resultant linear combination is symmetric.

Solution

First a reminder of permutation symmetries:

- If the wavefunction is symmetric with respect to permutation of the two electrons then
$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = |\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$
- If the wavefunction is antisymmetric with respect to permutation of the two electrons then
$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = -|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

We start with the original wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

and flip the position of electron 1 with electron 2 and vice versa

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1) - \varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)] \tag{8.6.5}$$

We then we ask if we can rearrange the left side of Equation 8.6.5 to either become $+|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (symmetric to permutation) or $-|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (antisymmetric to permutation).

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \frac{1}{\sqrt{2}}[-\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) + \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

or

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = -\frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

This is just the negative of the original wavefunction, therefore

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = -|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$$

The wavefunction is antisymemtric.

Exercise 8.6.1 : Symmetry

Is this linear combination of spin-orbitals

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) + \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

symmetric or antisymmetric with respect to permutation of the two electrons?

Answer available at the end of this section.

The electronic configuration of the first excited state of He is $1s^1 2s^1 2p^0$ and we can envision four microstates for this configuration (Figure 8.6.2). As spected, the wavefunctions associated for of these microstate must satisfy indistinguishability requirement just like the ground state.

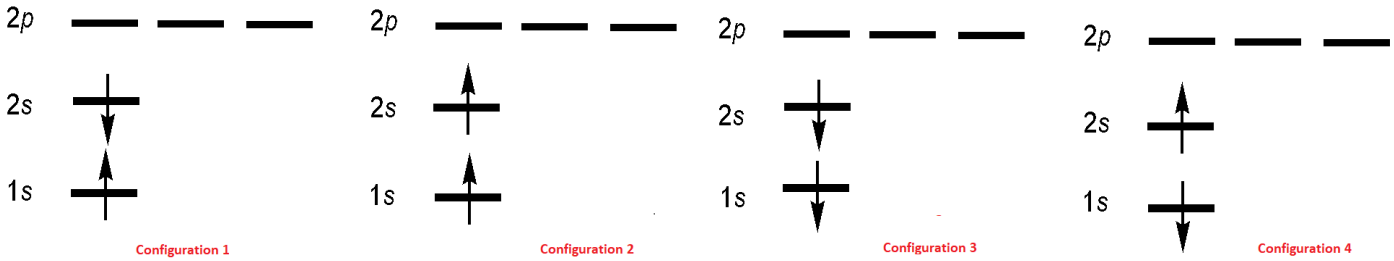


Figure 8.6.2 : Electron configurations for first-excited state of the helium atom.

These electron configurations are used to construct four possible excited-state two-electron wavefunctions (but not necessarily in a one-to-one correspondence):

$$|\psi_1(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2) + \varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.6}$$

$$|\psi_2(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2) - \varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\alpha(2)]}_{\text{spin component}} \tag{8.6.7}$$

$$|\psi_3(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2) - \varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2) + \alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.8}$$

$$|\psi_4(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2) - \varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\beta(1)\beta(2)]}_{\text{spin component}} \tag{8.6.9}$$

All four wavefunctions are antisymmetric as required for fermionic wavefunctions (which is left to an exercise). Wavefunctions $|\psi_2\rangle$ and $|\psi_4\rangle$ correspond to the two electrons both having spin up or both having spin down (Configurations 2 and 3 in Figure 8.6.2 , respectively). Wavefunctions $|\psi_1\rangle$ and $|\psi_3\rangle$ are more complicated and are antisymmetric (Configuration 1 - Configuration 4) and symmetric combinations (Configuration 1 + 4). That is, a single electron configuration does not describe the wavefunction. For many electrons, this ad hoc construction procedure would obviously become unwieldy. However, there is an elegant way to construct an antisymmetric wavefunction for a system of N identical particles.

Determinantal Wavefunctions

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a **Slater determinant**.

John C. Slater introduced the determinants in 1929 as a means of ensuring the antisymmetry of a wavefunction, however the determinantal wavefunction first appeared three years earlier independently in Heisenberg's and Dirac's papers.

The Slater determinant for the two-electron ground-state wavefunction of helium is

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix} \tag{8.6.10}$$

A shorthand notation for the determinant in Equation 8.6.10 is then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = 2^{-\frac{1}{2}} Det|\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)| \tag{8.6.11}$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is $(N!)^{-\frac{1}{2}}$ for N electrons.

The generalized Slater determinant for a multi-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1)\\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N)\end{vmatrix} \tag{8.6.12}$$

Example 8.6.2 : Helium Atom

Expand the Slater determinant in Equation 8.6.10 for the He atom.

Solution

To expand the Slater determinant of the Helium atom, the wavefunction in the form of a two-electron system:

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix}$$

This is a simple expansion exercise of a 2×2 determinant

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(1)\alpha(1)\varphi_{1s}(2)\beta(2) - \varphi_{1s}(2)\alpha(2)\varphi_{1s}(1)\beta(1)\right]$$

It is not unexpected that the determinant wavefunction in Equation 8.6.10 is the same as the form for the helium wavefunction that is given in Equation 8.6.3.

Exercise 8.6.2 : Lithium Atom

Write and expand the Slater determinant for the ground-state Li atom.

Answer available at the end of this section.

Now that we have seen how acceptable multi-electron wavefunctions can be constructed, it is time to revisit the “guide” statement of conceptual understanding with which we began our deeper consideration of electron indistinguishability and the Pauli Exclusion Principle. What does a multi-electron wavefunction constructed by taking specific linear combinations of product wavefunctions mean for our physical picture of the electrons in multi-electron atoms? Overall, the antisymmetrized product function describes the configuration (the orbitals, regions of electron density) for the multi-electron atom. Because of the

requirement that electrons be indistinguishable, we cannot visualize specific electrons assigned to specific spin-orbitals. Instead, we construct functions that allow each electron's probability distribution to be dispersed across each spin-orbital. The total charge density described by any one spin-orbital cannot exceed one electron's worth of charge, and each electron in the system is contributing a portion of that charge density.

The four configurations in Figure 8.6.2 for first-excited state of the helium atom can be expressed as the following Slater Determinants

$$|\phi_a(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} \tag{8.6.13}$$

$$|\phi_b(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix} \tag{8.6.14}$$

$$|\phi_c(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix} \tag{8.6.15}$$

$$|\phi_d(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} \tag{8.6.16}$$

Slater determinants are constructed by arranging spinorbitals in columns and electron labels in rows and are normalized by dividing by $\sqrt{N!}$, where N is the number of occupied spinorbitals. As you can imagine, the algebra required to compute integrals involving Slater determinants is extremely difficult. It is therefore most important that you realize several things about these states so that you can avoid unnecessary algebra:

- A Slater determinant corresponds to a single electron configuration diagram (Figure 8.6.2). Furthermore, recall that for the excited states of helium we had a problem writing certain stick diagrams as a (space)x(spin) product and had to make linear combinations of certain states to force things to separate (Equation 8.6.7 and 8.6.9). Because of the direct correspondence of configuration diagrams and Slater determinants, the same pitfall arises here: Slater determinants sometimes may not be representable as a (space)x(spin) product, in which case a linear combination of Slater determinants must be used instead. This generally only happens for systems with unpaired electrons (like several of the Helium excited-states).
- A Slater determinant is anti-symmetric upon exchange of any two electrons. We recall that if we take a matrix and interchange two its rows, the determinant changes sign.

The wavefunctions in 8.6.6-8.6.9 can be expressed in term of the four determinants in Equations 8.6.13-8.6.16.

$$\begin{aligned}|\psi_2\rangle &= |\phi_b\rangle\\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\\ |\psi_4\rangle &= |\phi_d\rangle\\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix}\end{aligned}$$

but the wavefunctions that represent combinations of spinorbitals and hence combinations of electron configurations (e.g., igure 8.6.2) are combinations of Slater determinants (Equation 8.6.13-8.6.15)

$$\begin{aligned}|\psi_1\rangle &= |\phi_a\rangle - |\phi_c\rangle\\ &= \frac{1}{2}\left(\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} - \begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\right)\\ |\psi_3\rangle &= |\phi_a\rangle + |\phi_c\rangle\\ &= \frac{1}{2}\left(\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} + \begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\right)\end{aligned}$$

Note the expected change in the normalization constants.

Example 8.6.3 : Carbon Atom

Write the Slater determinant for the ground-state carbon atom. If you expanded this determinant, how many terms would be in the linear combination of functions?

Solution

Carbon has 6 electrons which occupy the 1s 2s and 2p orbitals. Each row in the determinant represents a different electron and each column a unique spin-obital where the electron could be found. There are 6 rows, 1 for each electron, and 6 columns, with the two possible p orbitals both alpha (spin up), in the determinate. There are two columns for each s orbital to account for the alpha and beta spin possibilities. There are two different p orbitals because the electrons in their ground state will be in the different p orbitals and both spin up. N=6 so the normalization constant out front is 1 divided by the square-root of 6!

$$\psi(1,2,3,4,5,6) = \frac{1}{6!^{1/2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) & \varphi_{2px}(1)\alpha(1) & \varphi_{2py}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) & \varphi_{2px}(2)\alpha(2) & \varphi_{2py}(2)\alpha(2) \\ \varphi_{1s}(3)\alpha(3) & \varphi_{1s}(3)\beta(3) & \varphi_{2s}(3)\alpha(3) & \varphi_{2s}(3)\beta(3) & \varphi_{2px}(3)\alpha(3) & \varphi_{2py}(3)\alpha(3) \\ \varphi_{1s}(4)\alpha(4) & \varphi_{1s}(4)\beta(4) & \varphi_{2s}(4)\alpha(4) & \varphi_{2s}(4)\beta(4) & \varphi_{2px}(4)\alpha(4) & \varphi_{2py}(4)\alpha(4) \\ \varphi_{1s}(5)\alpha(5) & \varphi_{1s}(5)\beta(5) & \varphi_{2s}(5)\alpha(5) & \varphi_{2s}(5)\beta(5) & \varphi_{2px}(5)\alpha(5) & \varphi_{2py}(5)\alpha(5) \\ \varphi_{1s}(6)\alpha(6) & \varphi_{1s}(6)\beta(6) & \varphi_{2s}(6)\alpha(6) & \varphi_{2s}(6)\beta(6) & \varphi_{2px}(6)\alpha(6) & \varphi_{2py}(6)\alpha(6) \end{vmatrix}$$

Expanding this determinant would result in a linear combination of functions containing 720 terms. An expanded determinant will contain N! factorial terms, where N is the dimension of the matrix.

8.6.3AExercise : Excited-State of Helium Atom

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

Answer available at the end of this section.

8.6.3BExe

Critique the energy level diagram and shorthand electron configuration notation from the perspective of the indistinguishability criterion. Can you imagine a way to represent the wavefunction expressed as a Slater determinant in a schematic or shorthand notation that more accurately represents the electrons? (This is not a solved problem!)

Answers

Symmetric

Slater determinant for Li atom:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \det \begin{pmatrix} \varphi_{1s}\alpha(1) & \varphi_{1s}\beta(1) & \varphi_{2s}\alpha(1) \\ \varphi_{1s}\alpha(2) & \varphi_{1s}\beta(2) & \varphi_{2s}\alpha(2) \\ \varphi_{1s}\alpha(3) & \varphi_{1s}\beta(3) & \varphi_{2s}\alpha(3) \end{pmatrix}$$

Expansion of Slater determinant:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}[\varphi_{1s}\alpha(1)\varphi_{1s}\beta(2)\varphi_{2s}\alpha(3) - \varphi_{1s}\alpha(1)\varphi_{1s}\beta(3)\varphi_{2s}\alpha(2) + \varphi_{1s}\alpha(3)\varphi_{1s}\beta(1)\varphi_{2s}\alpha(2) - \varphi_{1s}\alpha(3)\varphi_{1s}\beta(2)\varphi_{1s}\alpha(1) + \varphi_{1s}\alpha(2)\varphi_{1s}\beta(3)\varphi_{2s}\alpha(3)]$$

Note that this is also a valid ground state wavefunction

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \det \begin{pmatrix} \varphi_{1s}\alpha(1) & \varphi_{1s}\beta(1) & \varphi_{2s}\beta(1) \\ \varphi_{1s}\alpha(2) & \varphi_{1s}\beta(2) & \varphi_{2s}\beta(2) \\ \varphi_{1s}\alpha(3) & \varphi_{1s}\beta(3) & \varphi_{2s}\beta(3) \end{pmatrix}$$

What is the difference between these two wavefunctions?

Since there are 2 electrons in question, the Slater determinant should have 2 rows and 2 columns exactly. Additionally, this means the normalization constant is $1/\sqrt{2}$.

Each element of the determinant is a different combination of the spatial component and the spin component of the $1s^1 2s^1$ atomic orbitals

$$\frac{1}{\sqrt{2}} \begin{bmatrix} \varphi_{1_s}(1)\alpha(1) & \varphi 2_s(1)\beta(1) \\ \varphi 1_s(2)\alpha(2) & \varphi 2_s(2)\beta(2) \end{bmatrix}$$

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8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

Learning Objectives

- Understand how the Hartree method is expanded to include symmetrized mulit-electron determential wavefunctions via the Hartree-Fock equations.
- Understand how to calculate the orbital energies from HF theory.
- Apply HF theory with Koopman's theory to estimate ionization energies and electron affinities.

The Hartree method discussed previously is useful as an introduction to the solution of many-particle system and to the concepts of self-consistency and of the self-consistent-field calculations, but its importance is confined to the history of physics. In fact the Hartree method is not just approximate, it is fundamentally wrong since its wavefunction is not antisymmetric to electron permutation! The Hartree-Fock approach discussed below is a better approach, which correctly takes into account the antisymmetric character of the trial wavefunctions.

Although the *Hartree equations* are numerically tractable via the self-consistent field method, it is not surprising that such a crude approximation fails to capture elements of the essential physics. The Pauli exclusion principle demands that the many-body wavefunction be antisymmetric with respect to interchange of any two electron coordinates, e.g.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) \tag{8.7.1}$$

which clearly cannot be satisfied by the multi-electron wavefunctions of the form used in the Hartree Approximation, i.e., the orbital approximation (Equation 8.7.2).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N) \tag{8.7.2}$$

This indistinguishability condition can be satisfied by forming a Slater determinant of single-particle orbitals

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N}} |\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \dots \psi(\mathbf{r}_N)| \tag{8.7.3}$$

This decouples the electrons resulting in N single-particle **Hartree-Fock** equations:

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})}_{\text{kinetic energy}} + \underbrace{V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{electron-nucleus potential}} + \underbrace{V_{electron}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{Hartree Term}} - \sum_j \int d\mathbf{r}' \frac{\psi_j^\star(\mathbf{r}')\psi_i^\star(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}). \tag{8.7.4}$$

As with the *Hartree equations*, the first term is the kinetic energy of the i^{th} electron

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})$$

and the second term is the electron-nucleus potential between the i^{th} electron and nucleus

$$V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})$$

The third term (sometimes called the “Hartree” term) is the electrostatic potential between the i^{th} electron and the **average** charge distribution of the other $N-1$ electrons.

$$V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) = J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr' \tag{8.7.5}$$

These three terms are identical to Hartree Equations with the product wavefunction ansatz (i.e., orbital approximation). The fourth term of Equation 8.7.4 is not in the Hartree Equations:

$$\sum_j \int d\mathbf{r}' \frac{\psi_j^\star(\mathbf{r}')\psi_i^\star(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

and is the *exchange* term. This term resembles the direct Coulomb term, but for the exchanged indices. It is a manifestation of the Pauli exclusion principle, and acts so as to separate electrons of the same spin. This "exchange" term acts only on electrons with the same spin and comes from the Slater determinant form of the wavefunction (Equation 8.7.3). Physically, the effect of exchange is for like-spin electrons to avoid each other. The exchange term adds considerably to the complexity of these equations.

The Hartree-Fock Equations in Equation 8.7.4 can be recast as series of Schrödinger-like equations:

$$\hat{F}|\varphi_i\rangle = \epsilon_i|\varphi_i\rangle \tag{8.7.6}$$

where $\hat{F}$ is called the **Fock operator** and $\{|\varphi_i\rangle\}$ are the Hatree-Fock orbitals with corresponding energies ϵ_i.

The Fock operator is a one-electron operator and solving a Hartree-Fock equation gives the energy and Hartree-Fock orbital for one electron. For a system with 2N electrons, the variable i will range from 1 to N; i.e there will be one equation for each orbital. The reason for this is that only the spatial wavefunctions are used in Equation 8.7.6. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving Equation 8.7.6 will be used to describe two electrons.

The nature of the Fock operator reveals how the Hartree-Fock (HF) or Self-Consistent Field (SCF) Method accounts for the electron-electron interaction in atoms and molecules while preserving the idea of **independent atomic orbitals**. The wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\begin{aligned}\hat{F} &= \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \\ &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)\end{aligned} \tag{8.7.7}$$

As shown by the expanded version on the far right, the first term in this equation, $\hat{H}^0$, is the familiar hydrogen-like operator that accounts for the kinetic energy of an electron and the potential energy of this electron interacting with the nucleus. The next term accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The $\hat{J}$ and $\hat{K}$ operators result from the electron-electron repulsion terms in the full Hamiltonian for a multi-electron system. These operators involve the one-electron orbitals as well as the electron-electron interaction energy.

The Fock operator (Equation 8.7.7) depends on **all occupied** orbitals (because of the exchange and Coulomb operators). Therefore, a specific orbital can only be determined if all the others are known. One must use iterative methods to solve the HF equations like the Self-consistent field method discussed previously for the Hartree Approximation.

Exchange Energy

The exchange interaction is a quantum mechanical effect that only occurs between identical particles. Despite sometimes being called an exchange force in analogy to classical force, **it is not a true force**, as it lacks a force carrier. The effect is due to the wavefunction of indistinguishable particles being subject to exchange symmetry, that is, either remaining unchanged (symmetric) or changing its sign (antisymmetric) when two particles are exchanged. Both bosons and fermions can experience the exchange interaction. For fermions, it is sometimes called Pauli repulsion and related to the Pauli exclusion principle. For bosons, the exchange interaction takes the form of an effective attraction that causes identical particles to be found closer together, as in Bose–Einstein condensation.

Example 8.7.1 : Hartree-Fock Energy of Helium

For example, the electron 1 in helium (with $Z = 2$), then

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}$$

The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we will call electron 1 throughout the following discussion), and the **average field created by all the other electrons** in the system is built in terms of the coordinates of a generic "other electron" (which we'll call electron 2) that is considered to occupy each orbital in turn during the summation over the N spatial orbitals. The best possible one-electron wavefunctions, by definition, will give the **lowest possible total energy** for a multi-electron system used with the complete multielectron Hamiltonian to calculate the expectation value for the total energy of the system. These wavefunctions are called the **Hartree-Fock wavefunctions** and the calculated total energy is the Hartree-Fock energy of the system.

As with the Hartree Equations, solving the Hartree-Fock Equations is mathematically equivalent to assuming each electron interacts only with the average charge cloud of the other electrons. This is how the electron-electron repulsion is handled. This also why this approach is also called the **Self-Consistant Field (SCF)** approach.

Hartree-Fock Energy

The Hartree-Fock equations $h_e\phi_i = \epsilon_i\phi_i$ imply that the orbital energies ϵ_i can be written as:

Multiple \label

where $T + V$ represents the kinetic (T) and nuclear attraction (V) energies, respectively. Thus, ϵ_i is the average value of the kinetic energy plus Coulombic attraction to the nuclei for an electron in ϕ_i plus the sum over all of the spin-orbitals occupied in ψ of Coulomb minus Exchange interactions of these electrons with the electron in ϕ_i.

If ϕ_i is an occupied spin-orbital, the $j = i$ term $[J_{i,i} - K_{i,i}]$ disappears in the above sum and the remaining terms in the sum represent the Coulomb minus exchange interaction of ϕ_i with all of the $N - 1$ other occupied spin-orbitals. If ϕ_i is a virtual spin-orbital, this cancelation does not occur because the sum over j does not include $j = i$. So, one obtains the Coulomb minus exchange interaction of ϕ_i with all N of the occupied spin-orbitals in ψ. Hence the energies of occupied orbitals pertain to interactions appropriate to a total of N electrons, while the energies of virtual orbitals pertain to a system with $N + 1$ electrons. This difference is very important to understand and to keep in mind.

To give an idea of how well HF theory can predict the ground state energies of several atoms, consider Table 8.7.1 below:

Table 8.7.1 : Hartree-Fock Calculations of Ground Energies of Select Atoms (all energies are in R_H)

Atom	Hartree-Fock Energy	Experiment
He	-5.72	-5.80
Li	-14.86	-14.96
Ne	-257.10	-257.88
Ar	-1053.64	-1055.20

Koopmans' Theorem

Koopmans' theorem states that the first ionization energy is equal to the negative of the orbital energy of the highest occupied molecular orbital. Hence, the ionization energy required to generated a cation and detached electron is represented by the removal of an electron from an orbital without changing the wavefunctions of the other electrons. This is called the "frozen orbital approximation." Let us consider the following model of the detachment or attachment of an electron in an N-electron system.

1. In this model, both the parent molecule and the species generated by adding or removing an electron are treated at the single-determinant level.
2. The Hartree-Fock orbitals of the parent molecule are used to describe both species. It is said that such a model neglects orbital relaxation (i.e., the re-optimization of the spin-orbitals to allow them to become appropriate to the daughter species).

Within this model, the energy difference between the daughter and the parent can be written as follows (ϕ_k represents the

particular spin-orbital that is added or removed:

- for electron detachment (vertical ionization energies)

$$E_{N-1} - E_N = -\epsilon_k \tag{8.7.8}$$

- and for electron attachment (electron affinities)

$$E_N - E_{N+1} = -\epsilon_k. \tag{8.7.9}$$

The Hartree-Fock equations deal with exchange exactly; however, the equations neglect more detailed correlations due to many-body interactions. The effects of electronic correlations are not negligible; indeed the failure of Hartree-Fock theory to successfully incorporate correlation leads to one of its most celebrated failures.

Example 8.7.2 : Electron Affinity

Let's derive this result for the case in which an electron is added to the $N+1^{st}$ spin-orbital. The energy of the N-electron determinant with spin-orbitals ϕ_1 through f_N occupied is

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \sum_{i=1}^{N} [J_{i,j} - K_{i,j}]$$

which can also be written as

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N} [J_{i,j} - K_{i,j}].$$

Likewise, the energy of the $N+1$-electron determinant wavefunction is

$$E_{N+1} = \sum_{i=1}^{N+1} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N+1} [J_{i,j} - K_{i,j}].$$

The difference between these two energies is given by

$$\begin{aligned} E_N - E_{N+1} = & - \langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \frac{1}{2} \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ & - \frac{1}{2} \sum_{j=1}^{N+1} [J_{N+1,j} - K_{N+1,j}] \\ & = - \langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ & = -\epsilon_{N+1}. \end{aligned}$$

That is, the energy difference is equal to minus the expression for the energy of the $N+1^{st}$ spin-orbital, which was given earlier.

Advanced: Electron Correlation and the "Exchange Hole"

In the Copenhagen Interpretation, the squared modulus of the wavefunction gives the probability of finding a particle in a given place. The many-body wavefunction gives the N-particle distribution function, i.e. $|\Phi(r_1, ..., r_N)|^2$ is the probability density that particle 1 is at r_1, ..., and particle N is at r_N. However, when trying to work out the interaction between electrons, what we want to know is the probability of finding an electron at r, given the positions of all the other electrons $\{r_i\}$. This implies that the electron behaves quantum mechanically when we evaluate its wavefunction, but as a classical point particle when it contributes to the potential seen by the other electrons.

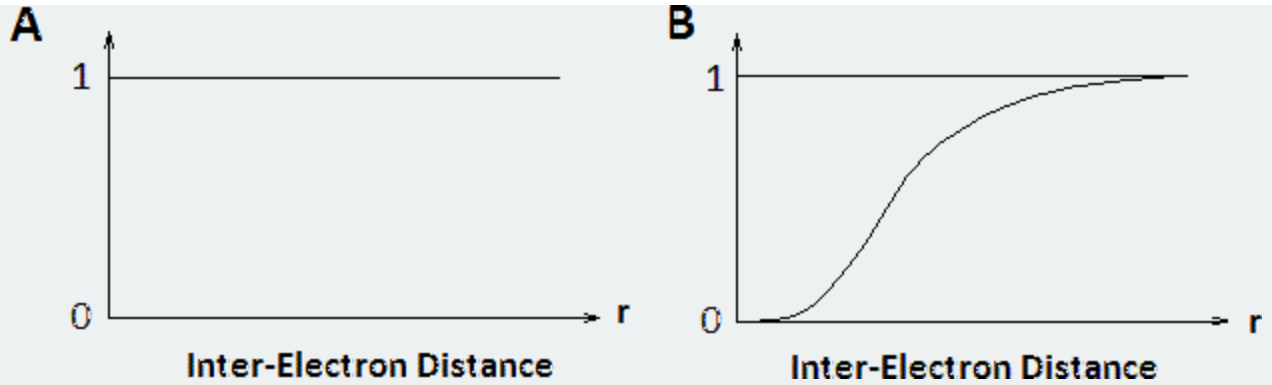


Figure 8.7.2 : Normalized Conditional Probability for from electron-electron interactions (excluding coulomb effects) in (A) the Hartree approximation and (B) the Hartree-Fock approximation.

The contributions of electron-electron interactions in N-electron systems within the Hartree and Hartree-Fock methods are shown in Figure 8.7.2 . The conditional electron probability distributions $n(r)$ of $N-1$ electrons around an electron with given spin situated at $r=0$. Within the Hartree approximation, all electrons are treated as independent, therefore $n(r)$ is structureless. However, within the Hartree-Fock approximation, the N-electron wavefunction reflects the Pauli exclusion principle and near the electron at $r=0$ the exchange hole can be seen where the the density of spins equal to that of the central electron is reduced. Electrons with opposite spins are **unaffected** (not shown).

Summary

So, within the limitations of the HF, frozen-orbital model, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to as Koopmans' theorem; it is used extensively in quantum chemical calculations as a means of estimating ionization potentials (Equation 8.7.8) and Electron Affinities (Equation 8.7.9) and often yields results that are qualitatively correct (i.e., ± 0.5 eV). In general Hartree-Fock theory gives a great first order solution (99%) to describing multi-electron systems, but that last 1% is still too great for quantitatively describing many aspects of chemistry and more sophisticated approaches are necessary. These are discussed elsewhere.

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8.8: Term Symbols Gives a Detailed Description of an Electron Configuration

Learning Objectives

- Understand how electron configurations results in different manifestations of angular momenta (both oribital and spin)
- Describe the manifestations in atoms via atomic term symbols

Atoms have quantum numbers that are directly analogous to the electronic quantum numbers.

The Total Orbital Angular Momentum Quantum Number: L

One might naively think that you could get the total angular momentum of an atom (L) by simply adding up the l values of the individual electrons. The problem with this idea is that the angular momenta of the various electrons are not necessarily pointing in the same direction. Let's consider the case of adding two 2p-orbitals together (i.e., with $l = 1$ quantum numbers).

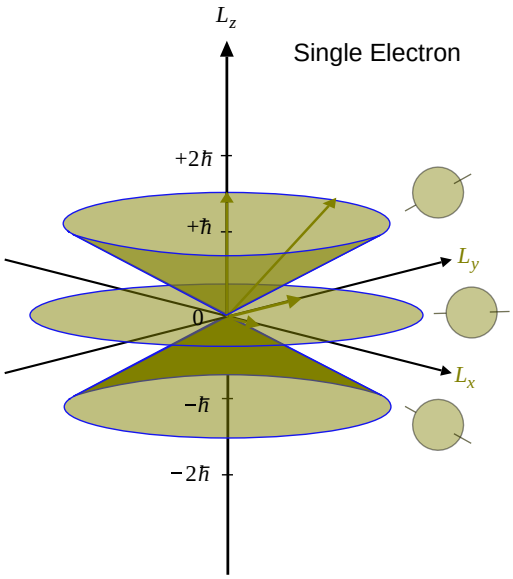


Figure 8.8.1 : The three possible angular momenta vectors for a p-orbital.

As discussed in Section 6.3, each of these electrons has $\sqrt{2}\hbar$ of angular momentum, but oriented in three different directions given by three different m_l values of 1, 0, and -1 (Figure 8.8.1).

$$L = \sum_{i}^{n} l_i \tag{8.8.1}$$

However, we must recognize that while the magnitude of angular momentum is a scalar (represented by l), angular momenta are really vector quantities and to add them together will require vector addition (vs. scalar addition) to do properly and must address all possible orientations of l for each electron.

For example, if two electrons are revolving in the same direction as each other (i.e., same m_l values), one would add just their l values together

$$L(\text{same direction}) = \sqrt{2}\hbar + \sqrt{2}\hbar = 2\hbar$$

If the two elections were revolving in opposites direction (e.., opposite m_l values, you subtract their values.

$$L(\text{same direction}) = \sqrt{2}\hbar - \sqrt{2}\hbar = 0$$

If they are revolving at some off-angle relative to each other (one revolving in a plane and one off plane), you would partially subtract them.

$$L(\text{same direction}) = \sqrt{2}\hbar + 0 = \sqrt{2}\hbar$$

To figure out all of the possible combinations of l for a pair of electrons, simply add them together to get the co-aligned case, subtract them to get the opposing case, and then fill in all the numbers in between to get the off-angle cases. For the two p-orbital case, there are no other possibilities (remember that l and hence L must be non-negative since they represent the magnitude of angular momenta (addressing the m_l values is a different story as we discuss below).

If you prefer to have a formula for the possibilities of L, you can use this:

$$L = |l_1 + l_2|, |l_1 + l_2\text{-}1|, \ldots, |l_1\text{-}l_2| \tag{8.8.2}$$

Technically, Equation 8.8.2 should include all electrons in a system, not just two, to account for all possible combinations of orbital angular momenta, however, there are some tricks that aid in applying this equations to address larger multi-electron atoms. First, electrons in s-orbitals have no orbital angular momentum, so they can be ignored. Second, if block of orbitals are completely filled (e.g., all six p-block spin-orbitals or all 10 d-block spin-orbitals), then the orbital angular momentum vector of each electron will be countered by another electron in the system; these are called **closed-shell** systems. Systems with partially unfilled blocks are called **open-shell** systems.

Hence, conveniently for chemists, an atom's electronic state depends entirely on its unfilled sub shells. Because electrons distribute themselves in a symmetric manner, the inner shell electrons end up canceling out each other's momenta. For an atom in the configuration $1s^2 2s^2 p^2$, only the two p-electrons matter. For an atom in the configuration $1s^2 2s^1 2p^1$, we have to examine only the 2s and 2p electrons (and can ignore the s electrons too).

Example 8.8.1 : Total Orbital Angular Momentum of Carbon

What are the possible L values for the electrons in the $1s^2 2s^2 2p^2$ configuration of carbon?

Solution

Both open-shell electrons (i.e., the 2p electrons) are $l = 1$. The possible combinations are 2, 1, 0.

Example 8.8.2 : Total Orbital Angular Momentum of Unknown Species

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We can ignore the electrons in the $[Xe]$ core and the electrons in the $6s$ block. So all we have to consider is the f electron $l = 3$ and d electron $l = 2$.

The two extremes possible (Equation 8.8.2) are

$$3 + 2 = 5$$

and

$$3\text{-}2 = 1$$

The possible combinations are thus 5, 4, 3, 2, and 1.

The Total Magnetic Quantum Number: M_l

The Total Magnetic Quantum Number M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much total angular momentum there is in the system, M_l tells you which direction it is pointing. Like L, a given configuration can have several possible values of M_l, depending on the electrons' relative orientation. Unlike L, M_l is allowed to have negative values. To list the possible M_l values for a two electron system, take the case where both m_l are positive, then take the case where they are both negative, and then fill in the numbers in between (Figure 8.8.1).

$$M_l = m_{l1} + m_{l2}, m_{l1} + m_{l2}\text{-}1, ..., \text{-}m_{l1}\text{-}m_{l2} \tag{8.8.3}$$

Note that there is no absolute value function in Equation 8.8.3 like in Equation 8.8.2.

Example 8.8.3 : Total Magnetic Quantum Number of the Zirconium Ground State

What are the possible values M_l of a zirconium atom with the $[Kr]5s^24d^2$ electron configuration?

Solution

Both open-shell electrons (i.e., the 4d electrons) are $l = 2$, so the values are 4, 3, 2, 1, 0, -1, -2, -3, -4.

The Total Spin Magnetic Quantum Number: M_s

M_s is the sum total of the z-components of the electrons' inherent spin. Do not confuse it with M_l, which is the sum total of the z-component of the **orbital angular momentum**. It is easily computed by finding all of the possible combinations of m_s. Since m_s for each individual electron can only be +1/2 or - 1/2, this isn't too complicated.

$$M_s = m_{s1} + m_{s2}, m_{s1} + m_{s2}\text{-}1, ..., m_{s1}\text{-}m_{s2} \tag{8.8.4}$$

Example 8.8.4 : Total Spin Magnetic Quantum Number of the Carbon Ground State

What are the M s values for $1s^22s^22p^2$?

Solution

$M_s = 1, 0, \text{-}1$

The Total Intrinsic Spin Quantum Number: S

The sum total of the spin vectors of all of the electrons is called S. The difference between S and M_s is subtle, but vital for understanding multiplicity. M_s measures the total z-component of the electrons' spins, while S measures the entire resultant vector. The values of S are computing in a manner very similar to M_s. Because S measures the magnitude of a vector, it cannot ever be negative.

$$S = |s_1 + s_2|, |s_1 + s_2\text{-}1|, ..., |s_1\text{-}s_2| \tag{8.8.5}$$

Example 8.8.5 : The Hydrogen Ground State

Find S for $1s^1$.

Solution

S clearly has to be ½ since that's the spin of a single electron and there's only one electron to worry about.

Example 8.8.6 : The Beryllium Excited State

Find S for $1s^2 2s^1 2p^1$.

Solution

$S = 1, 0$

Example 8.8.7 : The Carbon Ground State

Find S for carbon atoms with the $1s^2 2s^2 2p^2$ electron configuration.

Solution

$S = 1, 0$ This is the same as the previous problem. Notice that S is not affected by which orbitals the electrons are in. S only cares about how many **open-shell electrons** (i.e., unpaired electrons) there are, not about where they are. This is because S measures an inherent property of the electrons themselves

Example 8.8.8

Find S for nitrogen atoms with the $1s^2 2s^2 2p^3$ electron configuration.

Solution

We have not done a three electron case yet, but they are not hard. Find all the combinations for a single pair first, and then factor in the third electron. For two electrons, we already know that the two possible S values are S=1,0. A third electron can either add or subtract ½ from these values, so the final S can be $S = 3/2, 1, 1/2$.

The Total Angular Momentum Quantum Number J

The total orbital angular momentum of an atom (measured in terms of l), and the total spin angular momentum of an atom (measure in S) combine to form total angular momentum, a number that is quantized by the number J. L and S do not necessarily have to be pointing in the same direction (Figure 8.8.1), so J can range from $L + S$ to $|L–S|$.

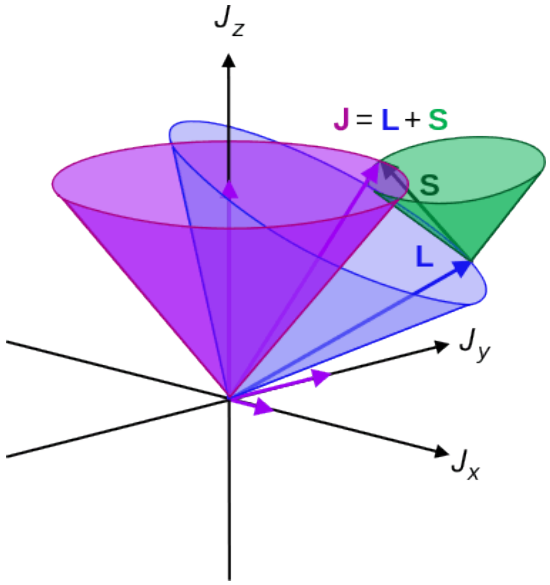


Figure 8.8.1 : Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

Table 8.8.1 : Quantum Numbers and associated ranges

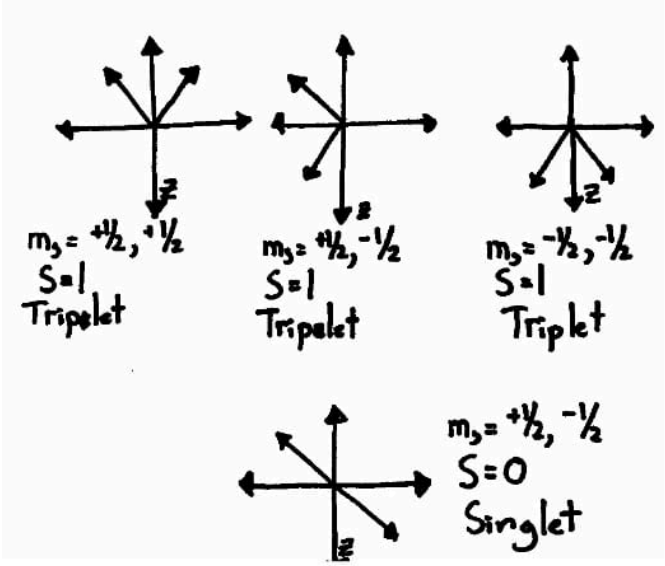
Symbol	Name	Allowed Range
l	Total orbital angular momentum	$\|l_1 + l_2\|, ..., \|l_1\text{-}l_2\|$
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, ..., \text{-}m_{l1}\text{-}m_{l2}]$
M_s	Spin Magnetic Quantum Number	$\|m_{s1} + m_{s2}\|, ..., \|m_{s1}\text{-}m_{s2}\|$
S	Inherent Spin Number	$\|s_1 + s_2\|, ..., \|s_1\text{-}s_2\|$
M	Multiplicity	2S+1
J	Total Angular Momentum	$L + S, ..., \|L - S\|$

Multiplicity

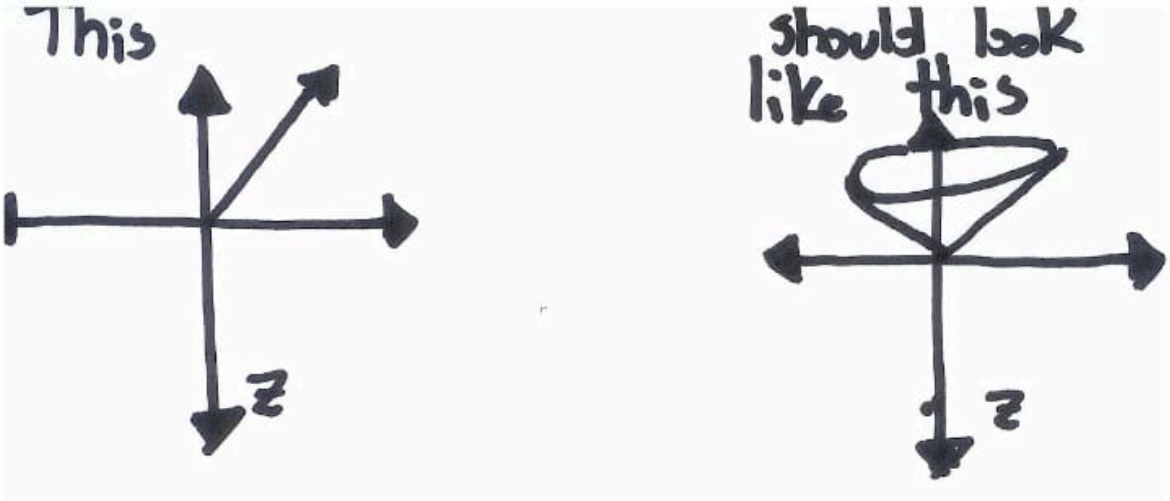
Multiplicity is a simple - sounding concept that defies simple explanations. You know from your first - year education that a singlet is when the net spin (S) is equal to zero (e.g. all the electrons are spin paired), and a triplet happens when the net spin is equal to 1 (e.g. two electrons are pointing in the same direction). They are called “singlet” and “triplet” because there are 3 ways to combine a pair of electron spins to get S=1, but only one way to get $S = 0$. If you draw a picture of the possible ways that two electrons can arrange their spins, you get something like this:



Figure 8.8.1 : When we call an electron spin “up,” what we really mean is that it has a positive z-component (e.g. $m_s = +½$).



While this picture is an improvement over the simple up-down model, it is still misleading. The three spin axes of an electron share a Heisenberg Uncertainty Principle. The more you know about S_x, the less you can know about either S_y or S_z. The same is true for all other combinations of x, y and z. Since we have defined S_z as a known and fixed value, the values of S_x and S_y must be **completely unknown**. This causes the x and y orientations of the electrons to become smeared out across all possible values:



Constructing Term Symbols

Atomic term symbols contain two pieces of information. They tell you the total orbital angular momentum of the atom (l), and they tell you the multiplicity (M). l is denoted by a simple code, similar to the code used to delineate the types of atomic orbitals:

- $L = 0 \rightarrow S$
- $L = 1 \rightarrow P$
- $L = 2 \rightarrow D$
- $L = 3 \rightarrow F$

Note that while the notation is similar, L does NOT say anything about what types of orbitals the electrons are in. A state that has the term symbol P does NOT necessarily have an open p-shell. The multiplicity is indicated by appending a number to the upper left of the symbol. A $L = 2$, $M = 3$ state would be represented by ${}^3D$. The secret to writing the term symbols for an atom is to

discover what combinations of l and M are possible for that atom with that specific electronic configuration. An atom that only has closed shells will always be $1S$.

Each term symbol represents a discrete energy level. We can place these levels in the correct order by using these simple rules:

- 1: High multiplicity values mean low energy
- 2: If there is a tie, high l values mean low energy
- 3a: If there is still a tie and the shell is less than half full, then low J means low energy
- 3b: If the shell is more than half full, then high J means low energy

These rules reliably predict the ground state. They have only erratic agreement with experiment when ordering the other levels.

Example 8.8.9 : Hydrogen Ground State

What are the term symbols for the microstates possible for $1s^1$ electronic configuration of hydrogen?

Solution

Since there is only one electron, this is a simple problem. $L = 0$ and $M = 1$, so the only possible term symbol is ^2S. With only one electron, $S = ½$, so $J = 0 + ½ = ½$. Only one microstate exists for this configuration and it has a term symbol of $^2S_{½}$.

Example 8.8.10 : Boron

What are the term symbols for the microstates possible for $1s^2 2s^2 2p^1$ electronic configuration of boron?

Solution

There still only one open shell electron, so $L = 1$, $M = 1$ and $S = ½$. We get a term symbol of the type ^2P, which gets split into separate symbols because $J = 3/2$ and $1/2$. Two possible microstates exist for this system with term symbols of $^2P_{3/2}$ and $^2P_{1/2}$.

Example 8.8.11 : Beryllium Excited State

What are the term symbols for the microstates possible for the $1s^2 2s^1 2p^1$ excited-state electronic configuration of Beryllium?

Solution

Now we have two electrons to worry about. Since $l_1 = 0$ and $l_2 = 1$, the only possible combination is $L = 1$. The possible combinations of S are: $S = 1, 0$. This means that $M = 3$ or $M = 1$. The term symbols will be of the form ^1P and ^3P. For the ^1P state, $L = 1$ and $S = 0$, so $J = 1$. For the second state, $L = 1$ and $S = 1$, so $J = 2, 1, 0$. There are four microstates for this configuration with term symbols of $^1P_1$ and $^3P_2$, $^3P_1$, and $^3P_0$.

Example 8.8.12 : Zirconium

What are the term symbols for the microstates possible for the $[Kr]5s^2 4d^2$ ground-state electronic configuration of zirconium?

Solution

This is a much harder problem. We will need to use a special technique to disentangle all of the possible combinations of l and M. Let's start be listing the relevant quantum numbers for the two open-shell electrons:

$l_1 = 2$	$l_2 = 2$
$m_{l1} = 2, 1, 0, -1, -2$	$m_{l2} = 2, 1, 0, -1, -2$
$m_{s1} = ½, -½$	$m_{s1} = ½, -½$

Let's combine these numbers to generate the atomic quantum numbers:

$$L = 4, 3, 2, 1, 0$$

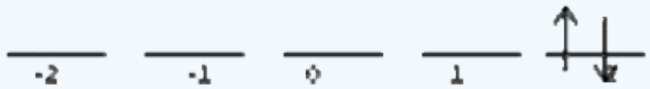
$$M_l = 4, 3, 2, 1, 0, -1, -2, -3, -4$$

$$M_s = 1, 0$$

We know that there will at least one each of S, P, D, F and G. It isn't immediately clear which of these will be singlets and which will be triplets. To figure this out, we need to systematically examine the possible microstates. It turns out that there are **45** possible ways to put distribute two electrons between 5 d orbitals. That's a lot! The easiest way to list the states is to organize them into a chart:

$M_s = -1$	$M_s = 0$	$M_s = +1$

Attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_l = 4$? It turns out there is only one possible combination that does this:

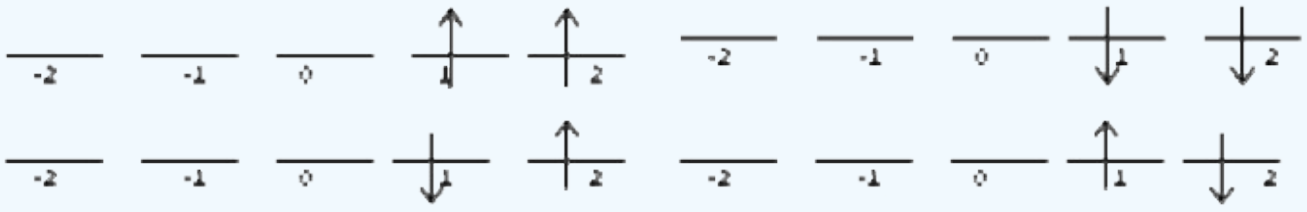


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This state is has $M_s = 0$. This means that there is only 1 microstate that corresponds to $M_l = 4$ and $M_s = 0$, and none that correspond to $M_l = 4$ and $M_s = \pm$-1. We add this microstate to the chart like this:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0

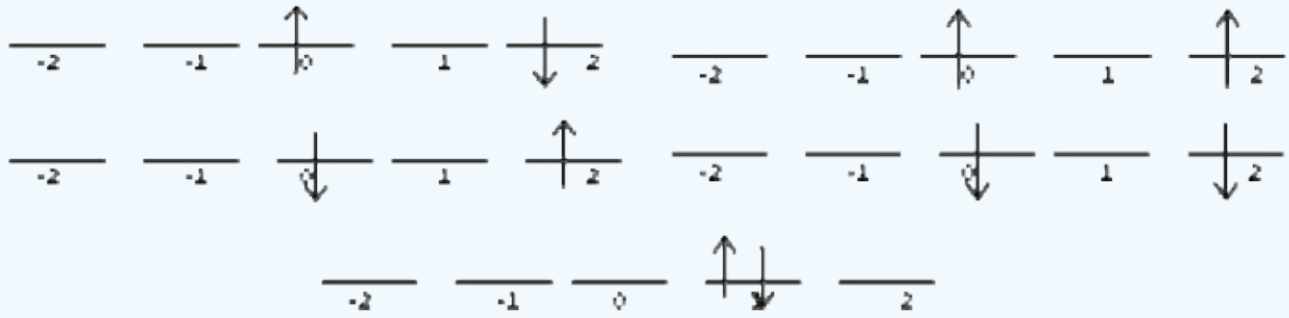
Now, how many ways are there to get $M_l = 3$?



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1

M_l	$M_s=-1$	$M_s=0$	$M_s=+1$

For $M_l=2$, we find the following states:



M_l	$M_s=-1$	$M_s=0$	$M_s=+1$
4	0	**1**	0
3	1	2	1
2	1	3	1

You should be able to draw the microstates on your own by now. You should find 8 states, four of which are singlet and four of which are triplets.

M_l	$M_s=-1$	$M_s=0$	$M_s=+1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2

There are only nine possible ways to arrange the electrons to get $M_l=0$

M_l	$M_s=-1$	$M_s=0$	$M_s=+1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$

The rest of the chart will be symmetric to the first half, so we do not need to do any more work:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	~~0~~	1	~~0~~
3	1	2	1
2	1	3	1
1	2	4	2
~~0~~	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	~~0~~	1	~~0~~

Now that we have a listing of all of the microstates, we need to figure out how to divide them up between the term symbols. It turns out that each term symbol can have, at most, one microstate from each box on the chart. The term symbols always end up claiming a “box” of microstates, centered on the middle of the chart. This is easier shown than said.

Attacking the chart from the top, we can see that the $M_l = 4$ $M_s = 0$ state clearly belongs to a ^1G symbol. The M_l = -4 $M_s = 0$ box also clearly belongs to this symbol. If I connect these states with a “box,” I get this:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
~~4~~	~~0~~	~~1~~	~~0~~
3	1	2	1
2	1	3	1
1	2	4	2
~~0~~	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
~~-4~~	~~0~~	~~1~~	~~0~~

The strickthough configurations all belong to the ^1G state. Let's subtract them from the chart to indicate that they are not available for other term symbols.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
3	1	2	1
2	1	3	1
1	2	4	2

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1

The next row indicates a $L = 3$ state. Because there are three M_s values available, this is a **triplet**. The term symbol will be ^3F, which reduces the chart down to

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	2	4	2
0	2	5	2
-1	2	4	2

The next state will be ^1D. Leaving us with

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	1	1	1
0	1	2	1
-1	1	1	1

Next is a ^3P state. The chart is getting pretty small now wtih

M_l	$M_s = 0$
	0

The last remaining microstate comprises the ^1S term symbol.

The total listing is

$$^1G,\ ^3F,\ ^1D,\ ^3P,\ ^1S.$$

Assigning J values, we get

$$^1G_4,\ ^3F_4,\ ^3F_3,\ ^3F_2,\ ^1D_2,\ ^3P_2,\ ^3P_1,\ ^3P_0,\ ^1S_0$$

If you can do this problem, you can do almost any atomic term symbol.

Note

The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration.

Shortcuts

There is a deep symmetry that connects different electronic configurations. It turns out that a p^1 configuration has the same term symbols as a p^5. Similarly, $p^2 = p^4$. A similar relationship can be used to figure out high electron number term symbols for the d

and f orbitals.

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8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

Learning Objectives

- Compate two spin-orbit coupling schemes that couple the total spin angular momenta and total orbital angular momenta of a multi-electron spectra

We need to be able to identify the electronic states that result from a given electron configuration and determine their relative energies. An electronic state of an atom is characterized by a specific energy, wavefunction (including spin), electron configuration, total angular momentum, and the way the orbital and spin angular momenta of the different electrons are coupled together. There are two descriptions for the coupling of angular momentum. One is called **j-j coupling**, and the other is called **L-S coupling**. The j-j coupling scheme is used for heavy elements (z > 40) and the L-S coupling scheme is used for the lighter elements. Only L-S coupling is discussed below.

L-S Coupling of Angular Momenta

L-S coupling also is called R-S or Russell-Saunders coupling. In L-S coupling, the orbital and spin angular momenta of all the electrons are combined separately

$$L = \sum_i l_i \tag{8.9.1}$$

$$S = \sum_i s_i \tag{8.9.2}$$

The total angular momentum vector then is the sum of the total orbital angular momentum vector and the total spin angular momentum vector.

$$J = L + S \tag{8.9.3}$$

The total angular momentum quantum number parameterizes the total angular momentum of a given particle, by combining its orbital angular momentum and its intrinsic angular momentum (i.e., its spin). Due to the spin-orbit interaction in the atom, the orbital angular momentum no longer commutes with the Hamiltonian, nor does the spin.

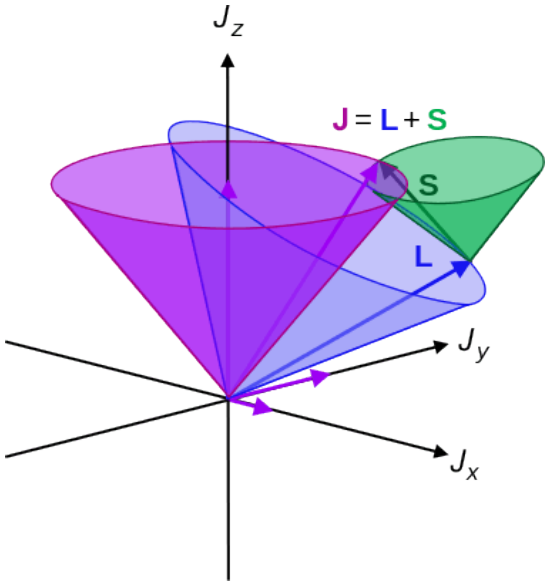


Figure 8.9.1 : "Vector cones" of total angular momentum J (purple), orbital L (blue), and spin S (green). The cones arise due to quantum uncertainty between measuring angular momentum components (see vector model of the atom). (Public Domain; Maschen).

However the total angular momentum J does commute with the Hamiltonian and so is a constant of motion (does not change in time). The relevant definitions of the angular momenta are:

Orbital Angular Momentum

$$|\vec{L}| = \hbar\sqrt{\ell(\ell+1)}$$

with its projection on the z-axis

$$L_z = m_\ell \hbar$$

Spin Angular Momentum

$$|\vec{S}| = \hbar\sqrt{s(s+1)}$$

with its projection on the z-axis

$$S_z = m_s \hbar$$

Total Angular Momentum

$$|\vec{J}| = \hbar\sqrt{j(j+1)}$$

with its projection on the z-axis

$$J_z = m_j \hbar$$

where

- l is the azimuthal quantum number of a single electron,
- s is the spin quantum number intrinsic to the electron,
- j is the total angular momentum quantum number of the electron,

The quantum numbers take the values:

$$m_\ell^{\text{int}}\{-\ell,-(\ell-1)\cdots\ell-1,\ell\},\quad \ell^{\text{int}}\{0,1\cdots n-1\} \tag{8.9.4}$$
$$m_s^{\text{int}}\{-s,-(s-1)\cdots s-1,s\}, \tag{8.9.5}$$
$$m_j^{\text{int}}\{-j,-(j-1)\cdots j-1,j\}, \tag{8.9.6}$$
$$m_j = m_\ell + m_s,\quad j=|\ell+s| \tag{8.9.7}$$

and the magnitudes are:

$$|\mathbf{J}| = \hbar\sqrt{j(j+1)} \tag{8.9.8}$$
$$|\mathbf{J}_1| = \hbar\sqrt{j_1(j_1+1)} \tag{8.9.9}$$
$$|\mathbf{J}_2| = \hbar\sqrt{j_2(j_2+1)} \tag{8.9.10}$$

in which

$$j^{\text{int}}\{|j_1-j_2|,|j_1-j_2|-1\cdots j_1+j_2-1,j_1+j_2\}$$

This process may be repeated for a third electron, then the fourth etc. until the total angular momentum has been found.

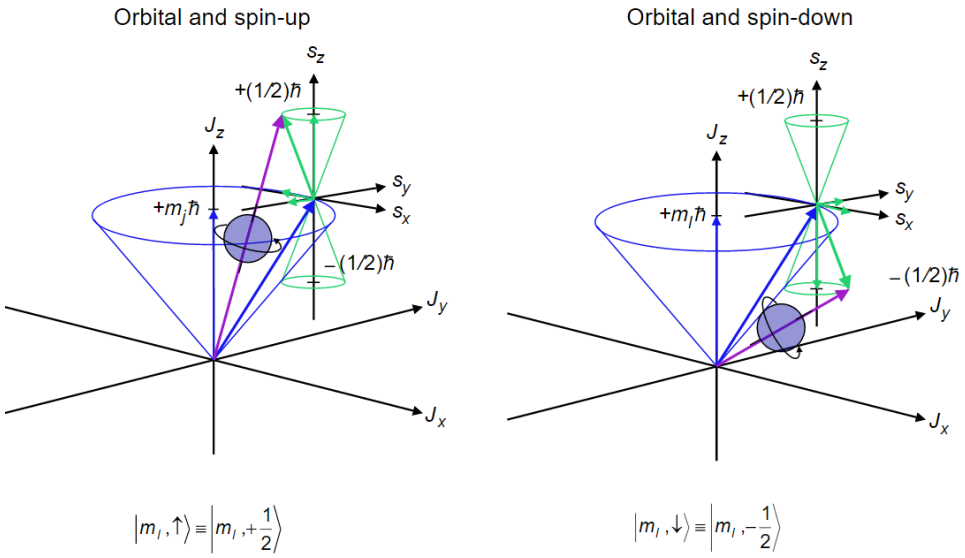


Figure 8.9.2 : Vector model of total angular momentum: spin and orbital coupling (spin-1/2 particles). (Public Domain; Maschen).

The result of these vector sums is specified in a code that is called a Russell-Saunders term symbol, and each term symbol identifies an energy level of the atom. Consequently, the energy levels also are called terms. A term symbol has the form ${}^{2s+1}L_J$ where the code letter that is used for the total orbital angular momentum quantum number L = 0, 1, 2, 3, 4, 5 is S, P, D, F, G, H, respectively. Note how this code matches that used for the atomic orbitals. The superscript $2S+1$ gives the spin multiplicity of the state, where S is the total spin angular momentum quantum number. The spin multiplicity is the number of spin states associated with a given electronic state. In order not to confuse the code letter S for the orbital angular momentum with the spin quantum number S, you must examine the context in which it is used carefully. In the term symbol, the subscript J gives the total angular momentum quantum number. Because of spin-orbit coupling, only J and M_j are valid quantum numbers, but because the spin-orbit coupling is weak L, M_l, S, and m_s still serve to identify and characterize the states for the lighter elements.

For example, the ground state, i.e. the lowest energy state, of the hydrogen atom corresponds to the electron configuration in which the electron occupies the 1s spatial orbital and can have either spin α or spin β. The term symbol for the ground state is ${}^2S_{1/2}$, which is read as “doublet S 1/2”. The spin quantum number is 1/2 so the superscript 2S+1 = 2, which gives the spin multiplicity of the state, i.e. the number of spin states equals 2 corresponding to α and β. The S in the term symbol indicates that the total orbital angular momentum quantum number is 0 (For the ground state of hydrogen, there is only one electron and it is in an s-orbital with $l=0$). The subscript ½ refers to the total angular momentum quantum number. The total angular momentum is the sum of the spin and orbital angular momenta for the electrons in an atom. In this case, the total angular momentum quantum number is just the spin angular momentum quantum number, ½, since the orbital angular momentum is zero. The ground state has a degeneracy of two because the total angular momentum can have a z-axis projection of $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, corresponding to m_J

= +1/2 or -1/2 resulting from the two electron spin states α and β. We also can say, equivalently, that the ground state term or energy level is two-fold degenerate.

Exercise 8.9.1

Write the term symbol for a state that has 0 for both the spin and orbital angular momentum quantum numbers.

Exercise 8.9.2

Write the term symbol for a state that has 0 for the spin and 1 for the orbital angular momentum quantum numbers

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8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

Learning Objectives

- Define Hund three rules
- Use Hunds three rules to predict the lowest energy configuration and term symbols for multi-electron systems

The Aufbau section discussed how that electrons fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there a problem with this rule. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. What about the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule, which make a lot more sense in the context of generated term symbols that are used to combine the various L and S values represent vector additions of possible microstates.

Hund's Rules

1. State with the largest value of S is most stable and stability decreases with decreasing S.
2. For states with same values of S, the state with the largest value of L is the most stable.
3. If states have same values of L and S then, for a subshell that is less than half filled, state with smallest J is most stable; for subshells that are more than half filled, state with largest value of J is most stable.

Example 8.10.1

Rank these terms associated with an electronic configuration of an atom based on energy (via Hund's rules):

$$^3D, ^3P, ^3S, ^1D, ^1P, ^1S$$

Hund's First Rule (Maximize Spin Multiplicity)

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus.

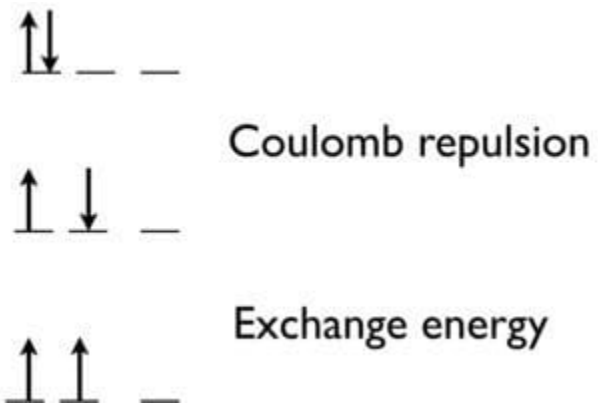


Figure 8.10.1 : Origin of Hund's First Rule. Hund's first rule is that for a given electron configuration, a state in which the spins are unpaired has lower total energy than one in which the spins are paired.

There's a Coulomb repulsion between two electrons to put them in the same orbital (a spin pairing energy often discussed in Crystal Field Theory). However, there's also a quantum mechanical effect. The *exchange energy* (which is favorable) increases with the number of possible exchanges between electrons with the same spin and energy. In transitioning from the top state to the middle state of Figure 8.10.1 , we remove the Coulomb repulsion between electrons in the same orbital. Moreover, In transitioning from the middle state to the bottom state (most stable state predicted by Hund's first rule), we *gain* the *exchange energy*, because these two electrons are indistinguishable.

Hund's Second Rule (Maximize Orbital Angular Multiplicity)

What matters is the total (scalar) angular momentum, not the direction. The negative and positive signs refer only to the direction of the angular momentum, not the magnitude. The direction is furthermore arbitrary (except in, say, a magnetic or electric field). So is the spin direction, incidentally. By convention we usually draw the first electron in each orbital as "up" (positive spin). However we could just as easily draw it "down". It makes no difference - in the absence of an external EM field, the energy is the same, if only because molecules/atoms are rotating with respect to the lab frame anyway. "Up" and "down", in other words, is artificial. What matters is the *relative* momentum vectors of the various electrons in the system, and hence their sum total.

Hund's Third Rule (Minimize less than half filled or maximize greater than half filled shells)

A long time ago someone offering a reasonably simple explanation related to the fact that when the shell is more than half full, it's easier to visualize the system as an interaction between the spin and orbital momenta of holes rather than electrons, in which case the energetic stabilization term is reversed in sign. This would be because the spin angular momentum of a single hole would be opposite in sign compared to the spin angular momentum of a single electron. Taking as an example - the three p-orbitals. A situation with 1 electron and 5 electrons are functionally similar, except that one has a single electron and one has a single hole. All things being equal, the total spin angular momentum of the 1 electron system would be opposite in sign to whatever the total spin angular momentum of the 5 electron system is. So the expectations for Hund's rules would be switched. You can kind of see this if you draw out all the microstates of the 1-electron and 5-electron configurations: the everything is pretty much changed in sign in the latter case.

Example 8.10.2

What terms and levels can arise from an atom with the ground-state configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^1 3d^1$? Which is the most stable (lowest in energy) state?

Solution

Possible states include:

$$^1F_3,\ ^1D_2,\ ^1P_1,\ ^3F_4,\ ^3F_3,\ ^3F_2,\ ^3D_3,\ ^3D_2,\ ^3D_1,\ ^3P_2,\ ^3P_1,\ ^3P_0.$$

There are two unpaired electrons in this system from the electron configuration.

- Rule 1 predicts that the ground state will be a triplet with $S = 1$ so $2S + 1 = 3$. So the ground state is from this more narrowed list: $^3F_4,\ ^3F_3,\ ^3F_2,\ ^3D_3,\ ^3D_2,\ ^3D_1,\ ^3P_2,\ ^3P_1,\ ^3P_0$.
- Rule 2 predicts a F state since that is the highest multiplicity with $L = 3$: So the ground state is from this more narrowed list: $^3F_4,\ ^3F_3,\ ^3F_2$
- Rule 3 predicts the lowest J term since the d shell is less than half full. That is the $J = 2$ state.

Therefore for this system, the atom will have a ground-state structure of

$$^3F_2$$

Example 8.10.3 : Titanium cation

The ground configuration of a Ti^{2+} ion is $[Ar]3d^2$. What is the term of lowest energy state?

Solution

- Rule 1: two unpaired electrons ⇒ highest S = 1 ⇒ 2S + 1 = 3
- Rule 2: two in d in parallel spin ⇒ highest L = 1 + 2 = 3 ⇒ 3F
- Rule 3:.L = 3, S = 1 ⇒ J = 4, 3, 2; less than half-filled ⇒ $^3F_2$

Exercise 8.10.3

What is the term of lowest energy state for the following atoms and ions.

- C: $[He]2s^22p^2$
- N: $[He]2s^22p^3$
- O: $[He]2s^22p^4$
- Cr^{3+}: $[Ar]3d^3$
- Mn^{3+}: $[Ar]3d^4$
- Fe^{3+}: $[Ar]3d^5$

Answer available at the end of this section.

Answers

$^3P_0$, $^4S_{3/2}$, $^3P_2$, $^4F_{3/2}$, $^5D_0$, and $^6S_{5/2}$, respectively.

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8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

Learning Objectives

- Demonstrate how spin-orbit coupling is experimentally observed in atomic spectra
- Use atomic terms symbols to ascribe transitions to specific angular momenta states described by atomic term symbols

Around 1930, several spectroscopists using high resolution instruments found that lines in the hydrogen atom spectrum actually are not single lines but they are multiplets as shown for an isotopic mixture of hydrogen,(H_α^1) and deuterium, (H_α^2), in Figure 8.11.1 . A multiplet consists of two or more closely spaced lines. Two lines together form a doublet, three a triplet, etc. Multiplets also are called fine structure. The term fine structure means the lines are spaced close together, i.e. finely spaced. Such fine structure also was found in spectra of one-electron ions such as He^+.

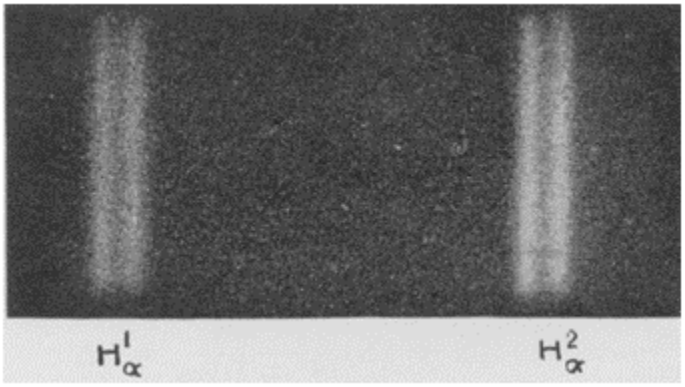


Figure 8.11.1 : Photograph of the first line in the Balmer series for atomic hydrogen and deuterium. These lines are identified as H_α^1 (hydrogen) and H_α^2 (deuterium), respectively. From H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) p. 132 and G.N. Lewis and F.H. Spedding, Phys. Rev. 43, 964 (1933). The doublet splitting for H_α^1 at 656.279 nm was measured to be 0.326 cm^{-1}.

You should recall that the H_α^1 line in the Balmer series at 656.279 nm was understood as resulting from a single transition of an electron from the n = 3 energy level to the n = 2 level. The observation of fine structure revealed that an orbital energy level diagram does not completely describe the energy levels of atoms. This fine structure also provided key evidence at the time for the existence of electron spin, which was used not only to give a qualitative explanation for the multiplets but also to furnish highly accurate calculations of the multiplet splittings.

Spin-Orbit Coupling

Specifying the orbital configuration of an atom does not uniquely identify the electronic state of the atom because the orbital angular momentum, the spin angular momentum, and the total angular momentum are not precisely specified. For example in the hydrogen $2p^1$ configuration, the electron can be in any of the three p-orbitals, m_l = +1, 0, and –1, and have spins with m_s = +1/2 or –1/2. Thus, there are 3 times 2 different possibilities or states. Also, the orbital and spin angular momentum of the electrons combine in multiple ways to produce angular momentum vectors that are characteristic of the entire atom not just individual electrons, and these different combinations can have different energies. This coupling of orbital and spin angular momentum occurs because both the electron spin and orbital motion produce magnetic dipole moments. As we have seen previously, the relationship between the angular momentum and the magnetic moment is given by the gyromagnetic ratio. These magnetic dipoles interact just like two tiny bar magnets attracting and repelling each other. This interaction is called **spin-orbit interaction**. The interaction energy is proportional to the scalar product of the magnetic dipole moments, which are proportional to the angular momentum vectors.

$$E_{s-o} \propto S \cdot L$$

with the following terms added to the Hamiltonian

$$\hat{H}_{s-o} \propto \hat{S} \cdot \hat{L}$$

where the constant of proportionality is called the spin-orbit coupling constant. The spin-orbit interaction couples the spin motion and orbital motion of all the electrons together. This coupling means that exact wavefunctions are not eigenfunctions of the spin and orbital angular momentum operators separately. Rather the total angular momentum $J = L + S$, the vector sum of the spin and orbital angular momentum, is required to be coupled for a completely accurate description of the system. Trying to describe the coupled system in terms of spin and orbital angular momentum separately is analogous to trying to describe the positions of two coupled bar magnets independently. It cannot be done; their interaction must be taken into account (Figure 8.11.1).

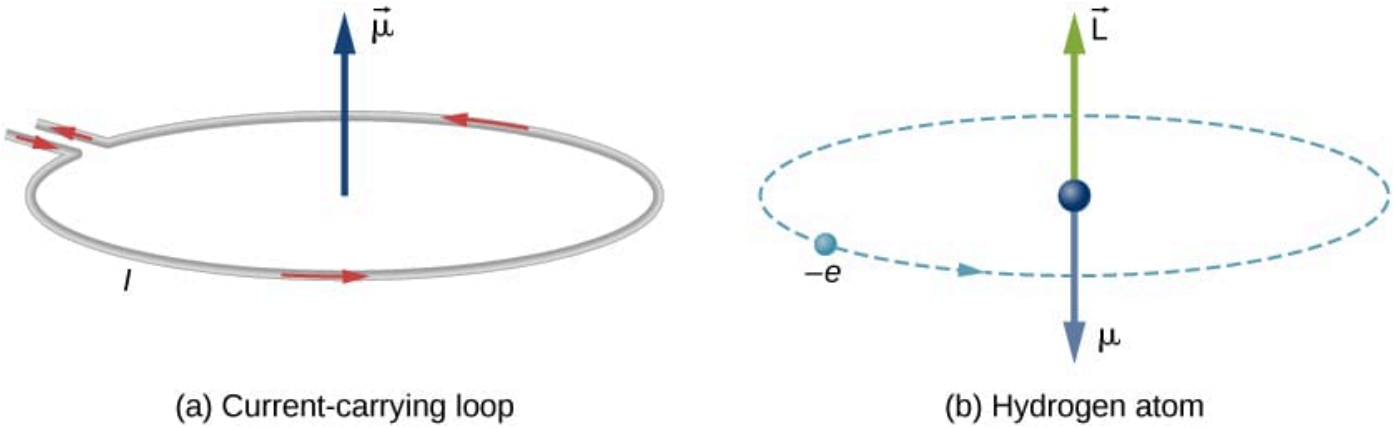


Figure 8.11.1 : An electron that orbits the nucleus induces a "current" and a magnetic field. Similarly, the rotating electron (really intrinsic spin) of the electron induces a different magnet. Both a magnetic (dipole) moments will interact with each other via spin-orbit coupling to generate fine structure atomic spectra.(CC-SA OpenStax).

Atomic Spectroscopy

Higher energy or excited orbital configurations also exist. The hydrogen atom can absorb energy, and the electron can be promoted to a higher energy orbital. The electronic states that result from these excited orbital configurations also are characterized or labeled by term symbols. The details of how to determine the term symbols for multi-electron atoms and for cases where both the orbital and spin angular momentum differ from zero are given elsewhere, along with rules for determining the relative energies of the terms.

We have found that the selection rules for promoting a single electron moving from one atomic orbital to another via the absorption or emission of light are

$$\Delta l = \pm 1$$
$$\Delta m_l = 0, \pm 1$$

These selection rules arise from the conservation fo angular momentum during a spectroscopic transition and the fact that a photon has a spin 1. Within the limits of L-S coupling, these rules can be expressed in terms of atomic term symbols resulting in the resulting Russell-Saunders selection rules:

$$\Delta S = 0 \tag{8.11.1}$$
$$\Delta L = 0, \pm 1 \tag{8.11.2}$$
$$\Delta J = 0, \pm 1, \tag{8.11.3}$$

but the $J = 0$ to $J = 0$ transition is forbidden

$$\Delta m_J = 0, \pm 1 \tag{8.11.4}$$

but the $m_J = 0$ to $m_J = 0$ transition is forbidden if $\Delta J = 0$.

These selection rules result from the general properties of angular momentum such as the conservation of angular momentum

and commutation relations. The $\Delta L = 0$ option in Equation 8.11.2 does not violate the conservation of angular momentum discussed previously, since $\Delta l = \pm 1$ is still required. The orbital angular momentum of an electron must change upon absorption, but this does not necessarily affect the overall momentum of the state given by Equation 8.11.2.

The selection rules apply only to atoms that can be described with Russell-Saunders (LS) coupling. These rules fail as the atomic number increases because the S and L quantum numbers become "bad" quantum numbers; this occurs when the jj-coupling coupling approach is more applicable. For example, the transition between single ($S = 1/2$ and triplet $S = 1$ states (violation of selection rule in Equation 8.11.1) are allowed and experimentally observed, in heavy atoms.

Example 8.11.1 : Sodium Atoms

An example of this fine structure is the emission of sodium atoms.



Figure above does not show this splitting).

616.07 nm	615.42 nm	589.00 nm	589.59 nm	568.82 nm	568.26 nm

How can these transitions be described in terms of transitions between microstates

Solution

We need to discussed states in terms of not only electron configurations, but in terms of microstates (i.e., term symbols) and the principal quantum number of the valence electron, n:

- The ground state has a $(Ne]ns^1$ configuration, which has only one microstate $^2S_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]np^1$, which has two microstates: $^2P_{3/2}$ and $^2P_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]nd^1$, which has two microstates of $^2D_{5/2}$ and $^2D_{3/2}$

Observed lines can be explained:

- $5S \rightarrow 3P$ gives two lines since the initial configuration has two microstates: 616.07, 615.42 nm
- $3P \rightarrow 3S$ gives two lines since the terminal configuration has two microstates: 589.00, 589.59 nm
- $4D \rightarrow 3P$ gives two lines since the terminal configuration has two microstates: 568.82, 568.26 nm

Splitting of the Sodium D Line

One notable atomic spectral line of sodium vapor is the so-called D-line, which may be observed directly as the sodium flame-test line and also the major light output of low -pressure sodium lamps (these produce pressure sodium lamps (these produce an unnatural yellow). The D-line is one of the classified Fraunhofer lines in Sodium vapor in the upper layers of lines. Sodium vapor in the upper layers of the sun creates a dark line in the emitted spectrum of electromagnetic radiation by absorbing visible light in a band of wavelengths around 589.5 nm. This wavelength corresponds to transitions in atomic sodium in which the valence-electron transitions from a 3s to 3p electronic state.

Closer examination of the visible spectrum of atomic sodium reveals that the D-line actually consists of two lines called the D_1 and D_2 lines at 589 6 nm and 589.0 nm, respectively. The splitting between these lines arises because of spin-orbit coupling. Na has one unpaired electron ($S = ½$). If we consider the $S \rightarrow P$ transition, then for the excited state, P, we have $L = 1$. Thus, $J = 3/2$ or $J = 1/2$.

Now we want to apply these ideas to understand why multiplet structure is found in the luminescence spectrum of hydrogen and single electron ions. As we have said, the H_α line in the Balmer series at 656.279 nm can be understood via a transition of an electron in a n = 3 atomic orbital to a n = 2 atomic orbital. When this spectral line was examined using high-resolution instruments, it was found actually to be a doublet, i.e. two lines separated by 0.326 cm^{-1}.

There are 9 degenerate orbitals associated with the n = 3 level, and 4 associated with the n = 2 level. Since an electron can be in any orbital with any one of two spins, we expect the total number of states to be twice the number of orbitals. The number of orbitals is given by n^2 so there should be 8 states associated with n = 2 and 18 states associated with n = 3. Using the ideas of vector addition of angular momentum, the terms that result from having an electron in any one of these orbitals are given in Table 8.11.1 .

Table 8.11.1 : H Atom Terms Originating from n = 1, 2, and 3

Orbital Configuration	Term Symbols	Degeneracy
$1s^1$	$^2S_{1/2}$	2
$2s^1$	$^2S_{1/2}$	2
$2p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3s^1$	$^2S_{1/2}$	2
$3p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3d^1$	$^2D_{3/2}$, $^2D_{5/2}$	4, 6

Table 8.11.1 shows that there are three terms associated with n = 2, and 5 terms associated with n = 3. In principle, each term can have a different energy. The degeneracy of each term is determined by the number of projections that the total angular momentum vector has on the z-axis. These projections depend on the m_J quantum number, which ranges from $+J$ to $-J$ in integer steps. J is the total angular momentum quantum number, which is given by the subscript in the term symbol. This relationship between m_J and J (m_J varies from $+J$ to $-J$ in integer steps) is true for any angular momentum vector.

Exercise 8.11.3

Confirm that the nine term symbols in Table 8.11.1 are correct.

Exercise 8.11.4

Confirm that the values for the degeneracy in Table 8.11.1 are correct and that the total number of states add up to 8 for n = 2 and 18 for n = 3.

The energies of the terms depend upon spin-orbit coupling and relativistic corrections that need to be included in the Hamiltonian operator in order to provide a more complete description of the hydrogen atom. As a consequence of these effects, all terms with the same n and (J\) quantum numbers have the **same energy,** while terms with different values for n or J have different energies. The theoretical term splittings as given by H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) pp. 132-137 and are shown in Figure 8.11.2 .

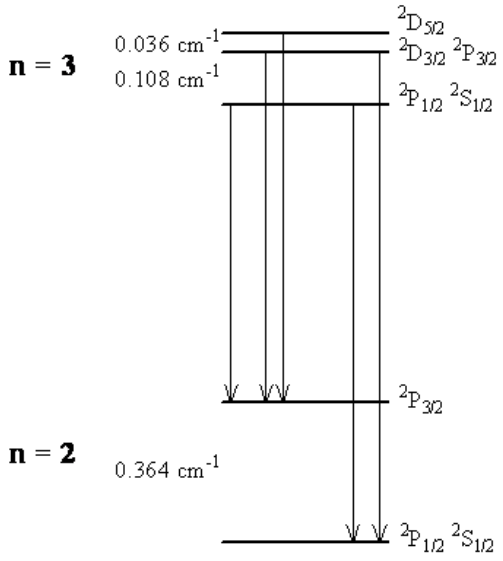


Figure 8.11.2 : Energy level diagram for the electronic states of hydrogen corresponding to an electron with the principal quantum number n = 3 and n = 2. While the relative energies of the terms are drawn to scale, the energy of n = 3 relative to n = 2 is not. Transitions to the $2P_{3/2}$ and ($2P_{1/2}$ and $2S_{1/2}$) levels correspond to the two lines in the H_α^1 band, which have a measured separation of 0.326 cm^{-1}.

Figure 8.11.2 shows 5 allowed transitions for the electron in the states associated with n = 3 to the states associated with n = 2. Of these five, two are most intense and are responsible for the doublet structure. These two transitions are indicated by the wide black lines at the bottom of the figure to correspond to the lines observed in the photographic spectrum shown in Figure 8.11.2 . The other transitions contribute to the width of these lines or are not observed. The theoretical value for the doublet splitting is 0.328 cm^{-1}, which is in excellent agreement with the measured value of 0.326 cm^{-1}. The value of 0.328 cm^{-1} is obtained by taking the difference, 0.364 – 0.036 cm^{-1},in the term splittings.

As we have just seen, the electronic states, as identified by the term symbols, are essential in understanding the spectra and energy level structure of atoms, but it also is important to associate the term symbols and states with the orbital electron configurations. The orbital configurations help us understand many of the general or coarse features of spectra and are necessary to produce a physical picture of how the electron density changes because of a spectroscopic transition.

Exercise 8.11.5

Use the Russell-Saunders selection rules to determine which transitions contribute to the H_α line in the hydrogen spectrum.

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8.E: Multielectron Atoms (Exercises)

Solutions to select questions can be found online.

8.4

Prove the speed of electron in first Bohr orbit is $e^2/4\pi\epsilon_0\hbar = 2.188 \times 10^6 m \bullet s^{-1}$. The speed is in atomic units.

Solution

Use following formula in order to make the calculations

$$v = \frac{\hbar}{m_e a_0}$$

$$v = \frac{\hbar}{m_e}\left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\right)$$

$$v = \frac{e^2}{4\pi\epsilon_0\hbar}$$

Substituting values get the following:

$$v = \frac{(1.6022 \times 10^{-19}\ C)^2}{(1.1127 \times 10^{-10} C^2 \cdot J^{-1} \cdot m^{-1})(1.0546 \times 10^{-34}\ J \cdot s)}$$

$$v = 2.1877 \times 10^6\ m \cdot s^{-1}$$

This is the speed in atomic units. Are either of the two separate terms in the two term helium Hartree-Fock Orbital acceptable wavefunctions by themselves?

$$\psi(r) = 0.81839e^{-1.44608r} + 0.52072e^{-2.86222r}$$

8.15

Explain why:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1 dr_2 d\sigma_1 d\sigma_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1 dr_2 d\sigma_1 d\sigma_2}$$

can be rewritten as:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1 dr_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1 dr_2}$$

Solution

The Hamiltonian does not depend on spin, so the spin integral can be factored out.

8.16

Why must you distinguish the two electrons in separated hydrogen atoms?

Solution

They must be distinguished from one another because they each belong to a separate nucleus, not to an individual one.

8.17

In both the Hartree-Fock approximation and hydrogen atomic wavefunction, why is the angular dependence the same?

Solution

Since the Hamiltonian used in the approximation only depends on r, the angular dependence is not affected in the Hartree-Fock approximation. So both the Hartree-Fock approximation and hydrogen atom will have the same angular dependence.

8.20

Given the two electron determinate wavefunction below, determine if the spin component of the system is symmetric, anti-symmetric, or neither.

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\alpha(2) \end{vmatrix}$$

Solution

We have to solve the determinate.

$$1s1\alpha(2)1s2\beta(2) - 1s1\beta(2)1s1\alpha(2)$$

Now we have to factor out the spatial part from the spin part.

$$1s11s2[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

We are focused on the spin part and by observation, we can tell that the spin component is anti-symmetric.

8.23

Given $\hat{S}_z\alpha = \frac{\hbar}{2}\alpha$ and $\hat{S}_z\alpha = \frac{-\hbar}{2}\beta$, show that Ψ_{200} is an eigenfunction of $S_{z,total} = \hat{S}_{za} + \hat{S}_{zB}$.

Solution

Start with $\Psi_{200} = C(\psi_{2sa} + \psi_{2sB})$.

$$\hat{S}_{z.total}\Psi = C(\hat{S}_{za} + \hat{S}_{zB})[\psi_{2sa} + \psi_{2sB}]$$

$$= C\left(\frac{\hbar}{2} - \frac{\hbar}{2}\right)[\psi_{2sa} + \psi_{2sB}]$$

$$= 0$$

8.24

For the wavefunction:

$$\psi = \begin{vmatrix} \psi_A(1) & \psi_A(2) \\ \psi_B(1) & \psi_B(2) \end{vmatrix}$$

discuss the effect on the wavefunction of (a) swapping rows of the matrix and (b) swapping columns of the matrix.

Solution

Let's expand the determinant to inspect the complete multi-electron wavefunction:

$$\psi = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1)$$

If we swap rows:

$$\psi_{RowSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

If we swap columns:

$$\psi_{ColumSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

Conclusion: swapping the either two rows or two columns of a Slater determinant changes the sign of the wavefunction.

8.27

What are the term symbols for carbon and oxygen atoms in the ground state?

Solution

Carbon: The electron configuration for carbon at ground state (lowest energy) is $1s^2 2s^2 2p^2$

Since the 1s and 2s orbitals are completely filled, they can be neglected when calculating for S. For the lowest energy, you need to use the highest values of S and L, therefore we find that S= 1/2 +1/2=1 and L=1 which corresponds to the letter P. Since the 2p orbital is less than half-way filled, we use J=|L-S|=|1-1|=0.

The term symbol is ${}^{2S+1}L_J$ which is ${}^3\mathrm{P}_0$ for the ground-state of carbon atoms.

Oxygen: The electron configuration for oxygen at ground state (lowest energy) is $1s^2 2s^2 2p^4$

Again, the 1s and 2s orbitals may be neglected when calculating for S.

$$S = 1/2 + 1/2 + 1/2 - 1/2 = 1$$

The last electron has a spin down due to the Pauli Exclusion Principle.

L=1 which corresponds to the letter P.

Since the 2p orbital for oxygen is more than half-filled,

$$J = L + S = 2$$

The term symbol for the ground-state oxygen atom is ${}^3\mathrm{P}_2$

8.28

Show that the number of sets of magnetic quantum number (m_l) and spin quantum number (m_s) associated with any term symbol is equal to $(2L+1)(2S+1)$. Apply this result to the np^2 case and show that symbol ${}^1S$, ${}^3P$ and ${}^1D$ account for all the possible sets of magnetic quantum numbers and spin quantum numbers

8.29

Calculate all possible numbers of term symbol for an np^1 electron configuration.

Solution

$$N = \frac{G!}{e!(G-e)!}$$

where G is the highest number of electrons that an orbital can hold and e is the highest number of electrons that a subshell can hold

$$N = \frac{6!}{2!(6-2)!} = 15$$

8.30

Determine the ground state term symbol for the electron configuration of the Halogens.

Solution

Halogens have the electron configurationnp^5 we can determine the term symbols for this configuration by mapping out all possible configurations the electrons can fit into the six spin orbitals. To quickly determine how many possible combinations there are we can use a statistical method of $N_{Comb.} = \binom{spinorbitals}{electrons}$

$$N_{comb} = \binom{6}{5} = \frac{6!}{5!(6!-5!)} = 6$$

Now we know that there are 6 different configurations that we can map out to determine the term symbols. Since we are working with the p orbital we know $l = 1$ and $m_s = -1,\ 0,\ 1$. I will denote spin using α as spin up $+\frac{1}{2}$ and β as spin down $-\frac{1}{2}$. M_L is the sum of the m_s values corresponding to the number of electrons in that energy level. For example if you have $\alpha\beta$ in $m_s = +1$ only, you then have 2 electrons in $m_s = +1$ resulting in $M_L = +1 + 1 = 2$. M_s is the sum of the spin up and spin down values.

+1	0	-1	M_L	M_s
$\alpha\beta$	$\alpha\beta$	α	+1	$+\frac{1}{2}$
$\alpha\beta$	α	$\alpha\beta$	0	$+\frac{1}{2}$
α	$\alpha\beta$	$\alpha\beta$	-1	$+\frac{1}{2}$
$\alpha\beta$	$\alpha\beta$	β	+1	$-\frac{1}{2}$
$\alpha\beta$	β	$\alpha\beta$	0	$-\frac{1}{2}$
β	$\alpha\beta$	$\alpha\beta$	-1	$-\frac{1}{2}$

Now we need to determine the maximum value of M_L andM_s. Looking at the table we see that

$$max\ M_L = 1$$
$$max\ M_s = \frac{1}{2}$$

From this we know our maximum value of L and S

$$L_{max} = 1$$
$$S_{max} = \frac{1}{2}$$

Our possible values for L and S are

$$L = 1,\ 0$$
$$S = \frac{1}{2}$$

Since S is only $\frac{1}{2}$ we know we can only have doublet term symbols since $2\left(\frac{1}{2}\right) + 1 = 2$. L ranges from 1 to 0 so our possible corresponding symbols will be P and S. This leaves us with the possibility of having

$$^2P,\ ^2S$$

To figure out what is there we start with the term symbol that has the largest L value, with is the P. We see that for P, $L = 1$ and $S = \frac{1}{2}$. For a value of $L = 1$ our m_l can be $+1,\ 0,\ -1$ and for an $S = \frac{1}{2}$ our $m_s = +\frac{1}{2},\ -\frac{1}{2}$. In the table above all rows that contain these possible combination include every row. Therefore all of the configurations are contained in this doublet P term symbol. Including values of J we know that $L + S \geq J \geq |L - S|$. Since $L = 1$ and $S = \frac{1}{2}$ our final term symbols are

$$^2P_{\frac{3}{2}},\ ^2P_{\frac{1}{2}}$$

Hund's rules say that when L and S are the same with a subshell more than half filled, you look to the largest J value to be the most stable. Therefore our final answer and the ground state term symbol for halogens is

$$\boxed{^2P_{\frac{3}{2}}}$$

8.33

^2P, ^2D, and ^4S are the term symbols for an atom with the np^3 electron configuration. Using the term symbols for the np^3 electron configuration, calculate the J values associated with each of the term symbol. Then find out which term symbol represent the ground state.

Solution

To calculate J we use this equation

$$J = L + S$$

This equation can be further expanded to be

$$J = L + S, L + S - 1, L + S - 2, \ldots |L - S|$$

Term Symbol	L	S	J	Full Term Symbol
^2P	1	$\frac{1}{2}$	$\frac{3}{2}, \frac{1}{2}$	$^2P_{3/2}$ and $^2P_{1/2}$
^2D	2	$\frac{1}{2}$	$\frac{5}{2}\ \frac{3}{2}$	$^4D_{5/2}$ and $^4D_{3/2}$
^4S	0	$\frac{3}{2}$	$\frac{3}{2}$	$^4S_{3/2}$

8.34

What are the ground state electron configuration and term symbol for Calcium?

Solution

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

or

$$[Ar]4s^2$$

For the term symbol:

Spin Multiplicity: S = 0 (all electrons paired)

$$J = S + L = 0$$

There is only one valid value of J, so the term symbol for this configuration is

$$^{2S+1}L_J = {}^1S0$$

$$2S + 1 = 1$$

Orbital Angular Multiplicity: L = 0 because we consider an s orbital. This corresponds to S.

8.34

Find the ground state term symbol for Ca.

Solution

ns^2 electron configurations have the term symbol $^1S_0$, so the term symbol for Ca in the ground state is $^1S_0$.

8.36

Write the electron configuration for vanadium and use this information to find the ground-state term symbol for V.

Solution

The electron configuration for vanadium is $[Ar]3d^3 4s^3$

Spin Multiplicity: The electron configuration predicts three unpaired electrons, so

$$S = 1/2 + 1/2 + 1/2 = 3/2$$

and the multiplicity of $2S + 1$ predicts that this will be a quartet. Orbital Angular Momentum: The electron configuration predicts three electrons with $l = 2$ and the rest so not contribute, so $L = 1 + 1 + 1 = 3$, which is an F state

The ground-state term symbol for vanadium is $^4F_{3/2}$ since vanadium has a half-filled 3d subshell.

- Total Angular Momentum: The shell is half full

8.36

What is the ground-state term symbol for Ne.

Solution

The term symbol is ${}^{2S+1}L_J$

where

S is the total electron spin L is the total orbital angular momentum

so $2S+1 = 2 \cdot 0 + 1 = 1$ and $J = 0 + 0 = 0$. So the term symbol for Ne is ${}^1S_0$.

and

$$J = L + S$$

The electron configuration for:Ne is $1s^2 2s^2 2p^6$ since Ne has spherical symmetry, we get:

$$L = 0 + 0 = S$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = 0$$

8.37

Looking at the $1s2p$ electron configuration for He. Solve for the term symbols (states) of the Helium configuration and the degeneracies. If electron spin orbit coupling is included, what effect will this have?

Solution

There are two possible sets of m_l and m_s for the ns electron and six possible sets of m_l and m_s for the np electron, so there are 2 × 6 = 12 possible sets of m_l and m_s for the system. We can denote values for the electron in the ns orbital as m_{1j} and those for the electron in the np orbital as m_{2j}. The allowed values are given below:

Microstate	$m_l(1)$	$m_s(1)$	$m_l(2)$	$m_s(2)$	M_L	M_S	M_J
	Electron 1 in $1s$ orbital		*Electron 2 in $2p$ orbital*		*Combined Angular Momenta of both Electrons*		
1	0	+ 1/2	1	+ 1/2	1	1	2
2	0	- 1/2	1	+ 1/2	1	0	0
3	0	+ 1/2	1	- 1/2	1	0	0
4	0	- 1/2	1	- 1/2	1	-1	1
5	0	+ 1/2	0	+ 1/2	0	1	0
6	0	- 1/2	0	+ 1/2	0	0	1
7	0	+ 1/2	0	- 1/2	0	0	0
8	0	- 1/2	0	- 1/2	0	-1	0
9	0	+ 1/2	-1	+ 1/2	-1	1	0
10	0	- 1/2	-1	+ 1/2	-1	0	-1
11	0	+ 1/2	-1	- 1/2	-1	0	-2
12	0	- 1/2	-1	- 1/2	-1	-1	-2

Entries 1, 2, 4, 5, 6, 8, 9, 10, and 12 correspond to L = 1 and S = 1, or ^{3}P term symbol, and entries 3, 7, and 11

correspond to L = 1 and S = 0, which is a ^{1}P term symbol. The values of J can be derived from the table or by using

$$J = (L + S), (L + S - 1), (L + S - 2), \ldots\ldots, (|L + S|),$$

The final results given the term symbols below:

$^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

$(L + S)$ $(L + S - 1)$ $(|L - S|)$ $(|L + S|)$

The states corresponding to this electron configuration and their degeneracies are:

Term symbol: $^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

Degeneracy: 5 3 1 3

According to Hund's rule, the ground state $^3P_0$. Including the effect of spin-orbit coupling removes the degeneracy of the electronic states, and no spin orbit coupling splits the lines in an atomic spectra.

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8.S: Multielectron Atoms (Summary)

- Hydrogen atom wavefunctions are used as a basis for multielectron atoms.
- Electrons in s orbitals "shield" the nuclear charge from p and higher orbitals, causing the s orbitals to lie lower in energy.
- Electrons have intrinsic spin angular momentum $\pm\hbar/2$. There is no classical analog for this.
- Pauli exclusion principle– wavefunctions must be antisymmetric with respect to permutations of fermions (particles with half-integer spin, such as electrons). Implication is that only two electrons may share the same wavefunction, and then only if they have opposite spin.
- Slater determinants of hydrogen atom wavefunctions can be used to construct antisymmetric total wavefunctions: these are called linear combinations of atomic orbitals.
- Term symbols ($^{2S+1}\mathbf{L}_{2J+1}$) describe the coupling of electron angular momenta– distinguish between otherwise identical electron configurations.
- Hund's rules predict the ground-state term symbol (i.e., ground-state electron configuration).

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9: CHEMICAL BONDING IN DIATOMIC MOLECULES

Our basis for understanding chemical bonding and the structures of molecules is the electron orbital description of the structure and valence of atoms, as provided by quantum mechanics. We assume an understanding of the periodicity of the elements based on the nuclear structure of the atom and our deductions concerning valence based on electron orbitals.

9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

9.2: The H_2^+ Prototypical Species

9.3: The Overlap Integral

9.4: Chemical Bond Stability

9.5: Bonding and Antibonding Orbitals

9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital

9.7: Molecular Orbitals Can Be Ordered According to Their Energies

9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle

9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals

9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

9.13: SCF-LCAO-MO Wavefunctions are Molecular Orbitals formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently

9.14: Molecular Term Symbols Describe Electronic States of Molecules

9.15: Molecular Term Symbols Designate Symmetry

9.16: Most Molecules Have Excited Electronic States

9.E: Chemical Bond in Diatomic Molecules (Exercises)

9.S: Chemical Bonding in Diatomic Molecules (Summary)

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9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

Learning Objectives

- Understand the need to introduce an approximation like the Born-Oppenheimer approximation to solve multi-electron systems
- Understand the basis of parameterization involved in using the Born-Oppenheimer approximation

Using quantum mechanics to predict the chemical bonding patterns, optimal geometries, and physical and chemical properties of molecules is a large and active field of research known as *molecular quantum mechanics* or more commonly as *quantum chemistry*. The density functional theory referred to in the previous lecture, for which the chemistry Nobel prize was given in 1998, has had a tremendous impact in quantum chemistry, with some of the papers in this subject having acquired some 10,000 citations each since their publication. In fact, the 1998 chemistry Nobel prize was shared between Walter Kohn, one of the inventors of density functional theory and John Pople, the developer of a commonly used quantum chemistry software package.

Quantum chemistry calculations allow the geometries of molecules to be computed as well as a wide range of properties. Quantum chemistry can also be used in a novel way, in which the electrons are treated using quantum mechanics but the nuclei are treated as classical particles. We use quantum mechanics to calculate the internuclear forces but then use these forces in Newton's Second Law to study the motion of the nuclei during chemical reactions. This gives us a microscopic window into the specific motions, the complex dance, executed by the nuclei during a simple or complex chemical process.

The methods of quantum chemistry have become very sophisticated, and there are various software packages that can be downloaded for carrying out the calculations of quantum chemistry. It should be noted that these packages use a series of approximations to solve the Schrödinger equation because for all but the simplest of molecules, exact solutions are not available. We will discuss some of these methods, but first we need to introduce some of the underlying theory.

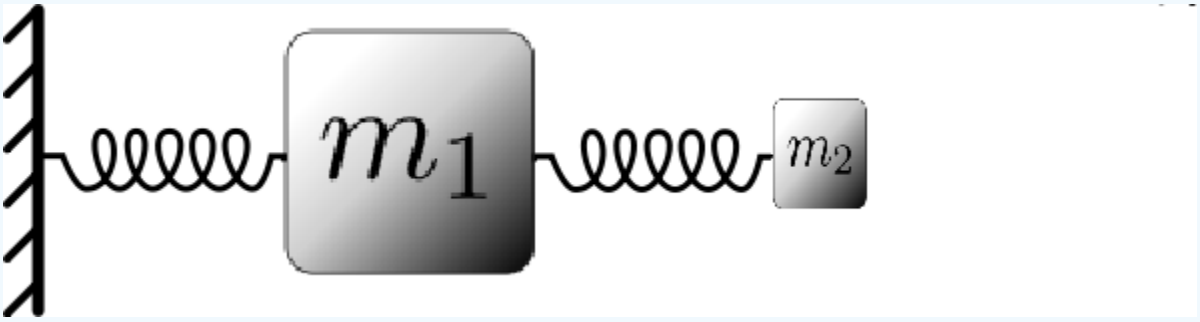
The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. We already made use of this approximation in the particle-in-a-box model when we explained the electronic absorption spectra of cyanine dyes without considering the motion of the nuclei. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. In this chapter we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times). Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of Ze^2/r^2 acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, a = F/m, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 2000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are not. You can imagine running a 100-yard dash against someone whose acceleration is a 2000 times greater than yours. That person could literally run circles around you.

Example 9.1.1 : Coupled Oscillators with Dissimilar Masses

If two particles interact in some way, and one is much heavier than the other, the light particle will move essentially as a "slave" of the heavy particle. That is, it will simply follow the heavy particle wherever it goes, *and*, it will move rapidly in response to the heavy particle motion. As an illustration of this phenomenon, consider the simple mechanical system pictured below:



(CC BY-SA 3.0 Unported; Jim.belk via Wikipedia).

Considering this as a classical system, we expect that the motion will be dominated by the large heavy particle (m_1), which is attached to a fixed wall by a spring. The small, light particle (m_2, which is attached to the heavy particle by a spring will simply follow the heavy particle and execute rapid oscillations around it.

So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei are not moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wavefunction can depend on the positions of the nuclei even though their motion is neglected.

Now we look at the mathematics to see what is done in solving the Schrödinger equation after making the Born-Oppenheimer approximation. For a diatomic molecule as an example, the Hamiltonian operator is grouped into three terms

$$\hat{H}(r,R) = \hat{T}_{nuc}(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} + \hat{H}_{elec}(r,R) \tag{9.1.1}$$

where

$$\hat{T}_{nuc}(R) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 \tag{9.1.2}$$

and

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \frac{-\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}\right) \tag{9.1.3}$$

In Equation 9.1.1, the first term represents the kinetic energy of the nuclei, the second term represents the Coulomb repulsion of the two nuclei, and the third term represents the contribution to the energy from the electrons, which consists of their kinetic energy, mutual repulsion for each other, and attraction for the nuclei. $\vec{r}$ and $\vec{R}$ are vectors specifying the positions of all the electrons and all the nuclei, respectively.

Exercise 9.1.1

Define all the symbols in Equations 9.1.1 through 9.1.3.

Answer available at the end of this section.

Exercise 9.1.2

Explain why the factor of 1/2 appears in the last term in Equation 9.1.3.

Answer available at the end of this section.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation 9.1.1, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction $\varphi_e(r, R)$ is found as a solution to the electronic Schrödinger equation

$$\hat{H}_{elec}(r, R)\varphi_e(r, R) = E_e(R)\varphi_e(r, R) \tag{9.1.4}$$

Even though the nuclear kinetic energy terms are neglected, the Born-Oppenheimer approximation still takes into account the variation in the positions of the nuclei in determining the electronic energy and the resulting electronic wavefunction depends upon the nuclear positions, R. As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product

$$\psi_{ne}(r, R) = X_{ne}(R)\varphi_e(r, R) \tag{9.1.5}$$

This product wavefunction is called the Born-Oppenheimer wavefunction. The function $X_{ne}(R)$ is the vibrational wavefunction, which is a function of the nuclear coordinates R and depends upon both the vibrational and electronic quantum numbers or states, n and e, respectively. The electronic function, $\varphi_e(r, R)$, is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, e. Translational and rotational motion is not included here. The translational and rotational wavefunctions simply multiply the vibrational and electronic functions in Equation 9.1.5 to give the complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

In the *Crude Born-Oppenheimer Approximation*, R is set equal to R_o, the equilibrium separation of the nuclei, and the electronic wavefunctions are taken to be the same for all positions of the nuclei (i.e., the nuclei never move). The electronic energy, $E_e(R)$, in Equation 9.1.4 combines with the repulsive Coulomb energy of the two nuclei, to form the potential energy function that controls the nuclear motion as shown in Figure 9.1.1 .

$$V_e(R) = E_e(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} \tag{9.1.6}$$

Consequently the Schrödinger equation for the vibrational motion is

$$(\hat{T}_{nuc}(R) + V(R))X_{ne}(R) = E_{ne}X_{ne}(R) \tag{9.1.7}$$

Potential Energy Curves and Surfaces

Previously, the potential energy was approximated as a harmonic potential or Morse potential depending on the displacement, R , of the nuclei from their equilibrium positions.

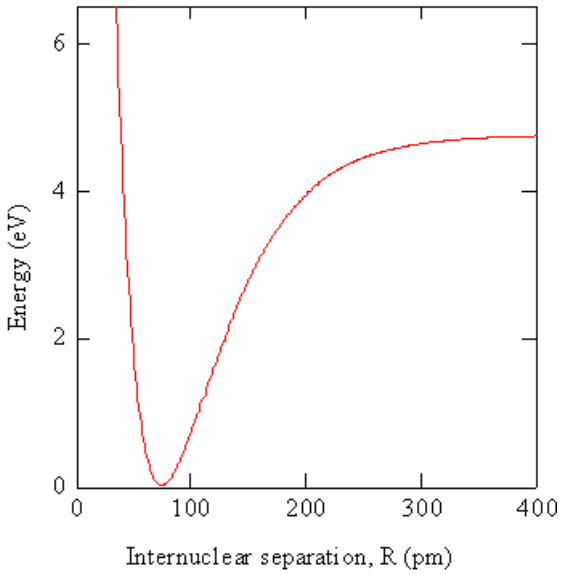


Figure 9.1.1 : The potential energy function for a diatomic molecule.

In practice the electronic Schrödinger equation is solved using approximations at particular values of R to obtain the wavefunctions $\varphi_e(r, R)$ and potential energies $V_e(R)$. The potential energies can be graphed as illustrated in Figure 9.1.1 .

The graph in Figure 9.1.1 is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When R is very large there are two atoms that are weakly interacting. As R becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of R, the internuclear repulsion is very large so the energy is large and positive. This energy function controls the motion of the nuclei. Previously, we approximated this function by a harmonic potential to obtain the description of vibrational motion in terms of the harmonic oscillator model. Other approximate functional forms could be used as well, e.g. the Morse potential. The equilibrium position of the nuclei is where this function is a minimum, i.e. at $R = R_0$. If we obtain the wavefunction at $R = R_0$ and use this function for all values of R, we have employed the *Crude Born-Oppenheimer* approximation.

Exercise 9.1.3

Relate Equation 9.1.7 to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

While the potential energy function, $V_e(R)$, for a diatomic molecule is a 1-D curve (Figure 9.1.1), molecules with more than two atoms will have multi-dimensional **potential energy surfaces** with 3N-6 (or 3N-5 for linear molecule) dimensions for the number of internal degrees of freedom.

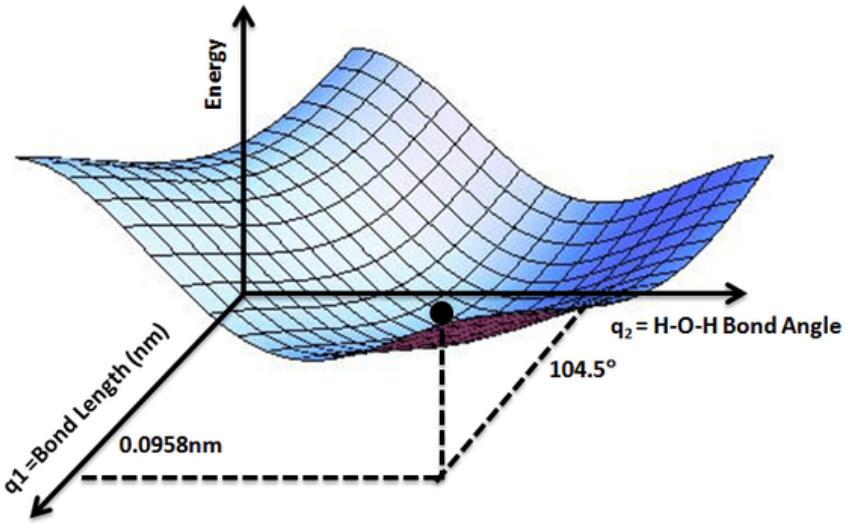


Figure 9.1.2 : The potential energy surface for a water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°. from Wikipeda (AimNature)

The potential energy surface concept can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction. Qualitatively the reaction coordinate diagrams (one-dimensional slices through the potential energy surfaces) have numerous applications. Chemists use reaction coordinate diagrams as both an analytical and pedagogical aid for rationalizing and illustrating kinetic and thermodynamic events. The purpose of energy profiles and surfaces is to provide a qualitative representation of how potential energy varies with molecular motion for a given reaction or process.

Exercise 9.1.4

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

Summary

In this section we started with the Schrödinger equation for a diatomic molecule and separated it into two equations, an electronic Schrödinger equation and a nuclear Schrödinger equation. In order to make the separation, we had to make an approximation. We had to neglect the effect of the nuclear kinetic energy on the electrons. The fact that this assumption works can be traced to the fact that the nuclear masses are much larger than the electron mass. We then used the solution of the electronic Schrödinger equation to provide the potential energy function for the nuclear motion. The solution to the nuclear Schrödinger equation provides the vibrational wavefunctions and energies.

Contributors and Attributions

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

Answers

$$\hat{H}(r,R) = \underbrace{\hat{T}_{nuc}(R)}_{\text{Kinetic Energy Term for nuclei}} + \underbrace{\frac{e^2}{4\pi\epsilon_o}\frac{Z_A Z_B}{R}}_{\text{Repulsion Term for nuclei}} + \underbrace{\hat{H}_{elec}(r,R)}_{\text{Hamiltonian for electrons}}$$

$$\hat{T}_{nuc}(R) = \underbrace{\frac{\hbar^2}{2m_A}\nabla_A^2}_{\text{Kinetic Energy Term for nuclei A}} - \underbrace{\frac{\hbar^2}{2m_b}\nabla_B^2}_{\text{Kinetic Energy Term for nuclei B}}$$

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \underbrace{\frac{-\hbar^2}{2m}\sum_i \nabla_i^2}_{\text{Kinetic Energy Term for electrons}} + \frac{e^2}{4\pi\epsilon_o}\left(- \underbrace{\sum_i \frac{Z_A}{r_{Ai}}}_{\text{Attraction Term between nuclei A and electron i}} - \underbrace{\sum_i \frac{Z_B}{R_{Bi}}}_{\text{Attraction Term between nuclei B and electron i}} + \underbrace{\frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}}_{\text{Repulsion Term between electrons}} \right)$$

where, $Z_x$is the charge of particle x, m_x is the mass of particle x and r_{xz} is the distance between particle x and z.

The 1/2 term is there to make sure we do not double count the potential energies via the two summations. Otherwise, we would independently add the potential energy of electron 1 with electron 2 and the potential energy of electron 2 with electron 1. These are the same and hence one has to be removed.

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9.2: The H_2^+ Prototypical Species

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion $\mathrm{H_2}^+$.

The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely $\mathrm{H_2}^+$. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry and it also has been detected in outer space. The Schrödinger equation for $\mathrm{H_2}^+$ can be solved exactly within the Born-Oppenheimer approximation (i.e., fixed nuclei). This ion consists of two protons held together by the electrostatic force of a single electron. Clearly the two protons, two positive charges, repeal each other. The protons must be held together by an attractive Coulomb force that opposes the repulsive Coulomb force. A negative charge density between the two protons would produce the required counter-acting Coulomb force needed to pull the protons together. So intuitively, to create a chemical bond between two protons or two positively charged nuclei, a high density of negative charge between them is needed. We expect the molecular orbitals that we find to reflect this intuitive notion.

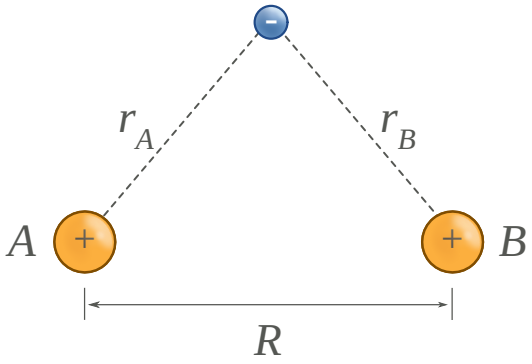


Figure 9.2.1 : Hydrogen molecular ion $\mathrm{H_2}^+$ with fixed nuclei A and B, internuclear distance R. (CC BY-NC; Ümit Kaya via LibreTexts)

The electronic Hamiltonian for $\mathrm{H_2}^+$ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{9.2.1}$$

where r_A and r_B are the distances electron from the A and B hydrogen nuclei, respectively and R is the distance between the two protons.

Although the Schrödinger equation for $\mathrm{H_2}^+$ can be solved exactly (albeit within the Born-Oppenheimer approximation where the nuclei are fixed) because there is only one electron, we will develop approximate solutions in a manner applicable to other diatomic molecules that have more than one electron.

Linear Combination of Atomic Orbitals

For the case where the protons in H_2^+ are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other. The electronic wavefunction would just be $1s_A(r)$ or $1s_B(r)$ depending upon which proton, labeled A or B, the electron is near. Here $1s_A$ denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position r of the electron is specified. Similarly $1s_B$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

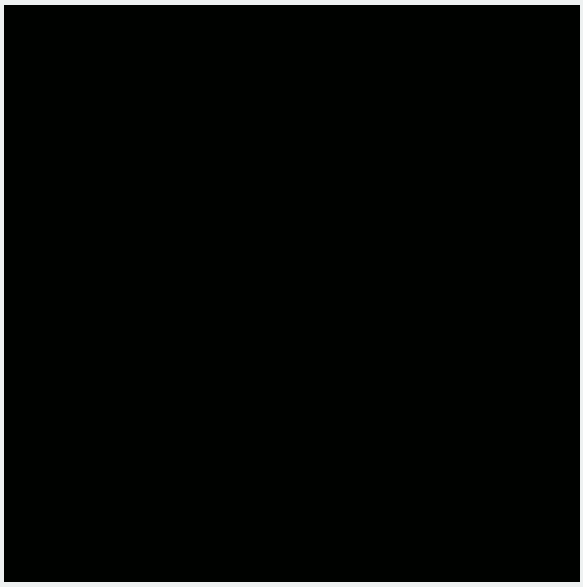
$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{9.2.2}$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals $1s_A$ and $1s_B$.

The Linear Combination of Atomic Orbitals (LCAO) Approximation and Interference

The LCAO approximation is an example of the linear variational method discussed previously with the true molecular orbital wavefunction approximated as an expansion of a basis set of atomic orbitals on each atom of the molecule with variable coefficients that can be optimized (e.g., via the secular equations). As discussed previously, the number of wavefunctions (solutions) extracted from solving the secular determinant is equal the number of elements in the expansion. So for the expansion in Equation 9.2.2 with two atomic orbitals contributing result in two molecule orbitals.

This method yields a approximate picture of the molecular orbitals in a molecules. The figure below shows two atoms approaching along the axis of one of their $2p$ states. In the top row, the two lobes facing one another have the same sign; in the bottom row they have opposite sign. These are two different linear combinations of the same two atomic states, on different atoms and with difference phases (i.e., signs of C_A vs. C_B in the expansion). In the first example, the electron density increases between the nuclei and in the second example, a very steep-sided node between the two nuclei causes all the probability density to face away from the atom opposite.



For H_2^+, the simplest molecule, the starting function is given by Equation 9.2.2. We must determine the values for the coefficients, C_A and C_B. We could use the variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition $|C_A|^2 = |C_B|^2$; namely, $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{9.2.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{9.2.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced (Figure 9.2.2 (bottom) between the two protons, whereas it is diminished for ψ_- as shown in Figures 9.2.2 (top). ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons.

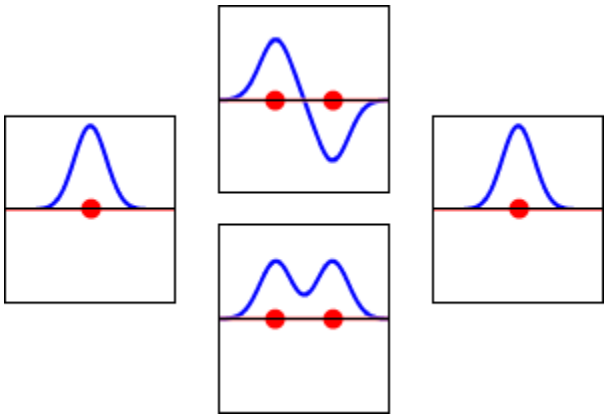


Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional .)

So ψ_+ is called a **bonding molecular orbital**. If the electron were described by ψ_-, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an **antibonding molecular orbital**.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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9.3: The Overlap Integral

For $H_2{}^+$, the simplest molecule, we must determine the values for the coefficients, C_A and C_B for the LCAO approximation for the molecular orbital as a linear combination of the two atomic orbitals

$$|\psi(r)\rangle = C_A 1s_A(r) + C_B 1s_B(r)$$

We could use the linear variational method to find a value for these coefficients, but for the case of $H_2{}^+$ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition

$$|C_A|^2 = |C_B|^2$$

so $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\underbrace{|\psi_+\rangle = C_+(1s_A + 1s_B)}_{\text{bonding molecular orbital}} \tag{9.3.1}$$

and

$$\underbrace{|\psi_-\rangle = C_-(1s_A - 1s_B)}_{\text{antibonding molecular orbital}} \tag{9.3.2}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for $|\psi_+\rangle$ is enhanced between the two protons, whereas it is diminished for $|\psi_-\rangle$ as shown in Figures 9.3.1 . ψ_- has a node in the middle while $|\psi_+\rangle$ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So $|\psi_+\rangle$ is called a *bonding molecular orbital*. If the electron were described by $|\psi_-\rangle$, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so $|\psi_-\rangle$ is called an *antibonding molecular orbital*.

Now we want to evaluate C_+ and C_- and then calculate the energy. The bonding and antibonding character of ψ_+ and ψ_- also should be reflected in the energy. If $|\psi_+\rangle$ indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts $H_2{}^+$ to be stable or not and also how much energy is required to dissociate this molecule.

The constants C_+ and C_- are evaluated from the standard normalization condition:

$$\int \psi_\pm^* \psi_\pm d\tau = \langle \psi_\pm | \psi_\pm \rangle = 1 \tag{9.3.3}$$

$$\langle C_\pm(1s_A \pm 1s_B) | C_\pm(1s_A \pm 1s_B) \rangle = 1 \tag{9.3.4}$$

$$|C_\pm|^2[\underbrace{\langle 1s_A|1s_A\rangle}_{1} + \underbrace{\langle 1s_B|1s_B\rangle}_{1} \pm \underbrace{\langle 1s_B|1s_A\rangle}_{S} \pm \underbrace{\langle 1s_A|1s_B\rangle}_{S^*}] = 1 \tag{9.3.5}$$

Since the atomic orbitals are normalized, the first two integrals are just 1. The last two integrals are called *overlap integrals* and are symbolized by S and S^*, respectively, since one is the complex conjugate of the other.

The overlap integrals are telling us to take the value of $1s_B$ at a point multiply by the value of $1s_A$ at that point and sum (integrate) such a product over all of space (Figure 9.3.1). If the functions do not overlap, i.e. if one is zero when the other one is not and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancelation of positive and negative contributions.

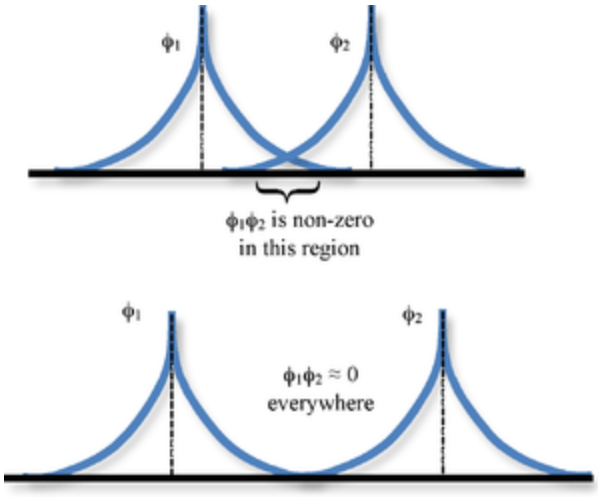


Figure 9.3.1 : The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close to zero.

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from $R = \infty$ to $R = 0$. Clearly when the protons are infinite distance apart, there is no overlap, and when $R = 0$ both functions are centered on one nucleus and $\langle 1s_A|1s_B\rangle$ becomes identical to $\langle 1s_B|1s_A\rangle$, which is normalized to 1, because $1s_A = 1s_B$.

With these considerations and using the fact that $1s$ wavefunctions are real so

$$\langle 1s_A|1s_B\rangle = \langle 1s_B|1s_A\rangle = S \tag{9.3.6}$$

Equation 9.3.5 becomes

$$|C_{\pm}|^2(2 \pm 2S) = 1 \tag{9.3.7}$$

The solution to Equation 9.3.7 is given by

$$C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} \tag{9.3.8}$$

Hence, the normalized molecular orbitals in Equations 9.3.1 and 9.3.1 are

$$|\psi_+\rangle = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B) \tag{9.3.9}$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B) \tag{9.3.10}$$

The energies associated with these wavefunctions requires a bit more effort to calculate though as demonstrated in the following section.

For the overlap integral of two 1s orbitals from the hydrogen dimer discussed above is difficult to evaluate analytically and is explained here. The final answer is:

$$S(R) = \langle 1s_A|1s_B\rangle \tag{9.3.11}$$

$$= e^{-R/a_o}\left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2}\right) \tag{9.3.12}$$

The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

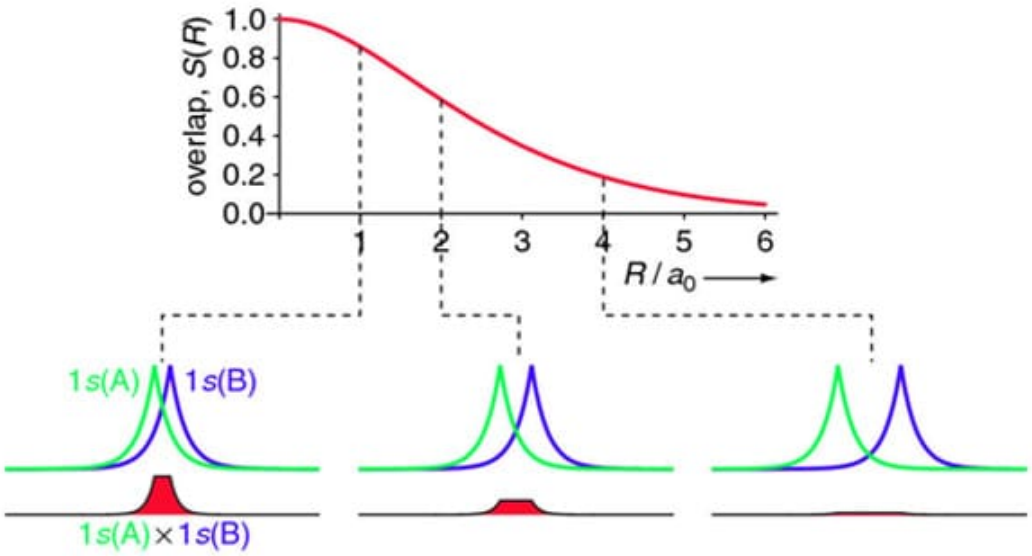


Figure 9.3.2 : The overlap integral at different proton separations.

Example 9.3.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for H_2^+ for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

Solution

The electronic charge density is calculated with the formula $|e\psi^2|$ where $e = 1.602 \times 10^{-19} C$

a: Bonding Molecular Orbital

First, squaring the bonding molecular orbital (Equation 9.3.9) gives us:

$$\begin{aligned}\psi_+^2 &= \frac{1}{2(1+S)}(1s_A + 1s_B)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3}\left(e^{-r_A/a_0} + e^{-r_B/a_0}\right)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3} \\ &= (0.561)^2 \times \left(\frac{1}{\pi \times (52.9\text{ pm})^3}\right) = 6.7672 \times 10^{-7}\text{ pm}^{-3}\end{aligned}$$

(Note: The value of C^2 is obtained from equation 9.3.12 and the value of S is from Equation 9.3.12)

To find the density at halfway between A and B for the bonding orbital evalulate at 1/2 R,

$$r_A = \frac{1}{2}R \text{ and } r_B = \frac{1}{2}R$$

$$\psi_+^2 = 3.7 \times 10^{-7}\text{ pm}^{-3}$$

Now multiply this answer by e to generate the electronic charge density,

$$P = \left(3.7 \times 10^{-7}\text{ pm}^{-3}\right) \times \left(1.602 \times 10^{-19}\right)\text{ C} = 5.93 \times 10^{-26} C/pm^3$$

b: Antibonding Molecular Orbital

To find the halfway between A and B for the anti-bonding orbital at $r_A = \frac{1}{2}R$ and $r_B = \frac{1}{2}R$. However, simple inspection of Equation 9.3.10 or Figure 9.3.1 shows this will be zero.

$$e\psi_-^2 = 0$$

Obviously, when multiplied by e, the answer is still zero. This makes logical sense as there would be no charge density between the two atoms as there lies a node with no probability of finding an electron.

Exercise 9.3.1

Show that for two arbitrary functions $\langle\varphi_B|\varphi_A\rangle$ is the complex conjugate of $\langle\varphi_A|\varphi_B\rangle$ and that these two integrals are equal if the functions are real.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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9.4: Chemical Bond Stability

Learning Objectives

- Identify the nature of the energy of molecular orbitals of a diatomic as a function of intermolecular distance
- Identify the three integrals involved in calculation the total Molecular Orbital Energy: coulomb Integral, exchange integral, and overlap integral

As shown previously, we can construct two molecular orbitals for the H_2^+ system using the LCAO approximation with a basis set of two 1s atomic orbitals (i.e., the $1s$ orbitals on hydrogen A ($1s_A$) and hydrogen B ($1s_B$):

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}}(1s_A \pm 1s_B) \tag{9.4.1}$$

The energy of these two molecular orbitals can be calculated from the expectation value integral of the Hamiltonian,

$$E_{\pm} = \left\langle \psi_{\pm} | \hat{H}_{elec} | \psi_{\pm} \right\rangle \tag{9.4.2}$$

which can be expanded using the expanded molecular orbital wavefunctions in Equations 9.4.1 to give

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[\underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{BA}} \right] \tag{9.4.3}$$

where S is the overlap integral between the two atomic orbitals of the basis. The four integrals in Equation 9.4.3 can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively.

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[H_{AA} + H_{BB} \pm H_{AB} \pm H_{BA} \right] \tag{9.4.4}$$

Exercise 9.4.1

Show that Equation 9.4.2 expands to give Equation 9.4.3 within the LCAO approximation that uses a basis set of only two 1s atomic orbitals.

Answer available at the end of this section.

Notice that A and B appear equivalently in the Hamiltonian operator for H_2^+. This equivalence means that integrals involving $1s_A$ must be the same as corresponding integrals involving $1s_B$, i.e.

$$H_{AA} = H_{BB} \tag{9.4.5}$$

and since the wavefunctions are real

$$|A\rangle = \langle A|$$

so

$$H_{AB} = H_{BA} \tag{9.4.6}$$

These two equalities simplify Equation 9.4.4:

$$E_{\pm} = \frac{1}{1 \pm S}(H_{AA} \pm H_{AB}) \tag{9.4.7}$$

Now examine the details of H_{AA} after inserting the Hamiltonian operator for $H_2{}^+$ (Equation 9.2.1):

$$H_{AA} = \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_A \right\rangle}_{E_H} + \frac{e^2}{4\pi\epsilon_0 R}\cancelto{1}{\langle 1s_A | 1s_A \rangle} - \underbrace{\left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle}_{J_{AB}} \tag{9.4.8}$$

- The first term is just the integral for the energy of the hydrogen atom of the 1s orbital, E_H.
- The second integral is equal to 1 by normalization; the prefactor is just the Coulomb repulsion of the two protons.
- The last integral, *including the minus sign*, is represented by J and is called the **Coulomb integral**.

Physically J_{AB} is the potential energy of interaction of the electron located around proton A with proton B. It is negative because it is an attractive interaction. It is the average interaction energy of an electron described by the $1s_A$ function with proton B.

The Coulomb Integral () J

The **Coulomb Integral** is the potential energy of electrostatic repulsion between the electron with the electron density in $1S_A$ and the the electron with the electron density function $1S_B$

Now consider H_{AB}.

$$H_{AB} = \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_B \right\rangle}_{E_H S} + \frac{e^2}{4\pi\epsilon_0 R}\cancelto{S}{\langle 1s_A | 1s_B \rangle} - \underbrace{\left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle}_{K_{AB}} \tag{9.4.9}$$

- In the first integral we have the hydrogen atom Hamiltonian and the H atom function $1s_B$. The function $1s_B$ is an eigenfunction of the operator with eigenvalue E_H. Since E_H is a constant it factors out of the integral, which then becomes the overlap integral, S. The first integral therefore reduces to $E_H S$.
- The second term is just the Coulombic energy of the two protons times the overlap integral.
- The third term, *including the minus sign*, is given the symbol K and is called the *exchange integral* because the electron is described by the $1s_A$ orbital on one side and by the $1s_B$ orbital on the other side of the operator. The electron changes or exchanges position in the molecule.

The Exchange Integral () K

In a **coulomb integral**, the electron always is in the same orbital; whereas, in an *Exchange Integral*, the electron is in one orbital on one side of the operator and in a different orbital on the other side.

Using the expressions for H_{AA} (Equation 9.4.8) and H_{AB} (Equation 9.4.9) and substituting into Equation 9.4.7 produces:

$$E_{\pm} = \frac{1}{1 \pm S}\left[\left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right)(1 \pm S) + J \pm K\right] \tag{9.4.10}$$

$$= E_H + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.4.11}$$

Equation 9.4.11 tells us that the energy of the $H_2{}^+$ molecule is the energy of a hydrogen atom plus the repulsive energy of two protons plus some additional electrostatic interactions of the electron with the protons. These additional interactions are given by the last term

$$\frac{J \pm K}{1 \pm S}.$$

If the protons are infinitely far apart then only E_H is nonzero, which we can set to zero by subtracting off:

$$\Delta E_{\pm} = E_{\pm} - E_H \tag{9.4.12}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.4.13}$$

To get a chemical bond and a stable $H_2{}^+$ molecule $\Delta E_{\pm}$ must be less than zero and have a minimum, i.e. $\frac{J \pm K}{1 \pm S}$ must be sufficiently negative to overcome the positive repulsive energy of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ for some value of R. For large R, these terms are zero, and for small R, the **Coulomb repulsion of the protons rises to infinity.**

Exercise 9.4.2

Show that Equation 9.2.1 follows from Equation 9.4.7

The Coulomb and Exchange Integrals

We will examine more closely how the Coulomb repulsion term and the integrals J, K, and S depend on the separation of the protons, but first we want to discuss the physical significance of J, the Coulomb integral, and K, the exchange integral. J and K have been defined as

$$J_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_A}(r)\frac{e^2}{4\pi\epsilon_0 r_B}d\tau \tag{9.4.14}$$

$$K_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_B}(r)\frac{e^2}{4\pi\epsilon_0 r_A}d\tau \tag{9.4.15}$$

Figure 9.4.2 shows graphs of the four terms contributing to the energy of $H_2{}^+$ (Equation 9.4.13). In Figure 9.4.2 , you can see that as the internuclear distance R approaches zero,

- the Coulomb repulsion of the two protons goes from near zero to a large positive number,
- the overlap integral goes for zero to one, and
- J and K become increasingly negative.

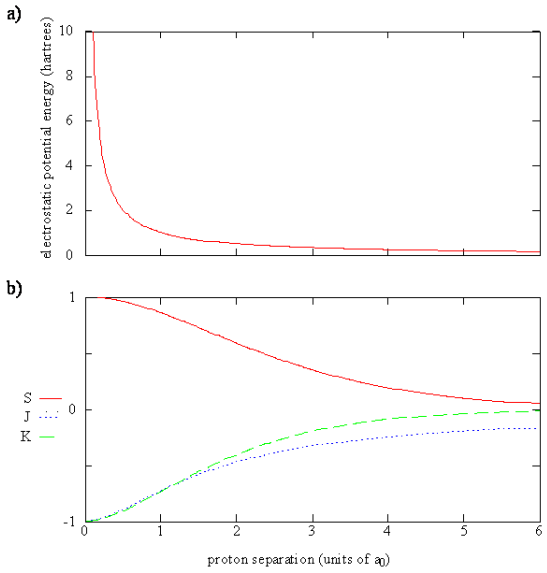


Figure 9.4.2 : (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). (b) The overlap (S), Coulomb (J), and exchange (K) integrals at different proton separations. The units for J and K are hartrees; S has no units.
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Note that both J and K integrals are **negative** since all quantities in the integrands of Equation 9.4.14 and 9.4.15 are positive. In the Coulomb integral, $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the charge density of the electron around proton A, since **r** represents the coordinates of the electron relative to proton A. Since r_B is the distance of this electron to proton B, the Coulomb integral gives the potential energy of the charge density around proton A interacting with proton B. J can be interpreted as an average potential energy of this interaction because $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the probability density for the electron at point r, and $\frac{e^2}{4\pi\epsilon_0 r_B}$ is the potential energy of the electron at that point due to the interaction with proton B. Essentially, J accounts for the attraction of proton B to the electron density of hydrogen atom A. As the two protons get further apart, this integral goes to zero because all values for r_B become very large and all values for $1/r_B$ become very small.

In the **exchange integral**, K, the product of the two functions is nonzero **only** in the regions of space where the two functions overlap. If one function is zero or very small at some point then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the $1/r$ values become zero. The product $e\varphi^*_{1s_A}(r)\varphi_{1a_B}(r)$ is called the *overlap charge density*. Since the overlap charge density is significant in the region of space between the two nuclei, it makes an important contribution to the chemical bond. The exchange integral, K, is the potential energy due to the interaction of the overlap charge density with one of the protons. While J accounts for the attraction of proton B to the electron density of hydrogen atom A, K accounts for the added attraction of the proton due the build-up of electron charge density between the two protons.

Exercise 9.4.3

Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for H_2^+.

Figure 9.4.3 shows the energy of H_2^+ relative to the energy of a separated hydrogen atom and a proton as given by Equation 9.4.11. For the electron in the ψ_- orbital, the energy of the molecule, $E_{el}(R)$, **always** is greater than the energy of the separated atom and proton.

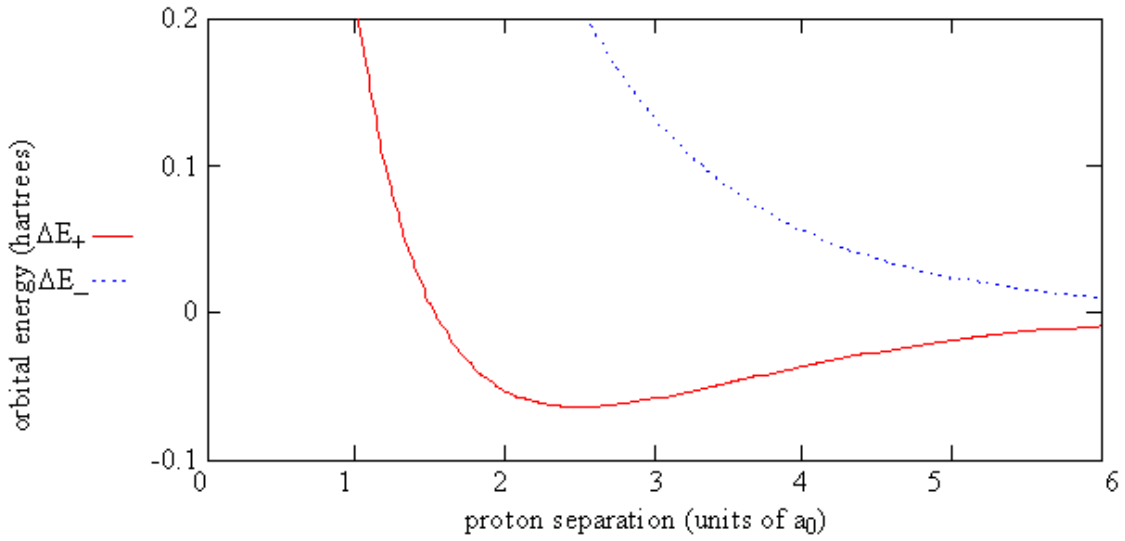


Figure 9.4.3 : Energy of the H_2^+ bonding molecular orbital ΔE_+ and the molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

For the electron in the ψ_+ orbital, you can see that the big effect for the energy of the bonding orbital, $E_+(R)$, is the balance between the repulsion of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ and J and K, which are both negative. J and K manage to compensate for the repulsion of the two protons until their separation is less than 100 pm (i.e the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. This minimum represents the formation of a chemical bond. The effect of S is small. It only causes the denominator in Equation 9.4.11 to increase from 1 to 2 as R approaches 0.

For the antibonding orbital, $-K$ is a positive quantity and essentially cancels J so there is not sufficient compensation for the Coulomb repulsion of the protons. The effect of the -K in the expression, Equation 9.4.11, for E_- is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for ψ_- is even lower than that given by the atomic orbitals.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

Answers

Here we have the wavefunction within the LCAO approximation that uses a basis set of only two 1s atomic orbitals (Equation 9.4.1).

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2(1 \pm S)}} \left(1_{Sa} \pm 1_{Sb}\right)$$

And our LCAO approximation is equivalent to this if we plug in the wavefunction directly.

$$E_\pm = \langle \psi_\pm | \hat{H} | \psi_\pm \rangle = N^2 \langle \left(1_{Sa} \pm 1_{Sb}\right) | \hat{H} | \left(1_{Sa} - 1_{Sb}\right) \rangle$$

We can see form above that the normalization constant squared results in:

$$N^2 = \frac{1}{2(1 \pm S)}$$

We now FOIL the mulitple (i.e., expaned term by term):

$$\langle 1_{Sa} | \hat{H} | 1_{Sa} \rangle + \langle 1_{Sb} | \hat{H} | 1_{Sb} \rangle \pm \langle 1_{Sa} | \hat{H} | 1_{Sb} \rangle \pm \langle 1_{Sb} | \hat{H} | 1_{Sa} \rangle$$

Now we can see this is now equivalent to Equation 9.4.3 if the equation above is inserted (and adding a subscript to emphasize this only applies to the electronic wavefunction):

$$E_\pm = \frac{1}{2(1 \pm S)} \left[\underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{BA}} \right]$$

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9.5: Bonding and Antibonding Orbitals

Learning Objectives

- Characterize the bonding and anti-bonding molecular orbitals in H^+

The two molecular orbitals of the H^+ ion were created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the j[th] molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$|\psi_J\rangle = \sum_i^N c_{J,i}|\phi_i\rangle \tag{9.5.1}$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 9.5.1). Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1s orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 9.5.1).

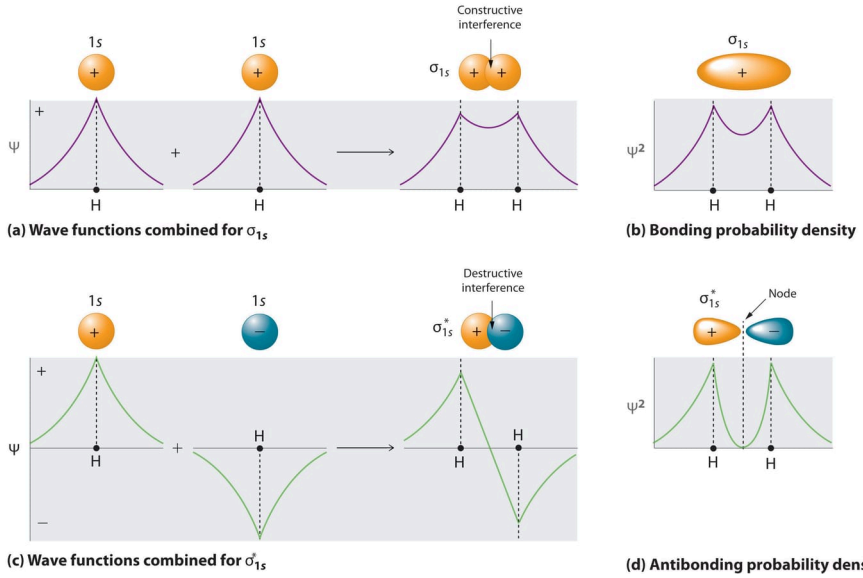


Figure 9.5.1 : Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wavefunctions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wavefunction (Ψ^2) for the bonding σ1s molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wavefunction.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the atomic orbital wavefunctions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wavefunction (Ψ2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei. (CC BY-SA-NC; anonymous).

In the sigma (σ) orbital, the electron density along the internuclear axis and between the nuclei has *cylindrical symmetry*; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1s denotes the atomic orbitals from which the molecular orbital was derived.

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}}\left(|1s_A\rangle + |1s_B\rangle\right) \tag{9.5.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 9.5.1

). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} and has a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$|\sigma^*_{1s}\rangle = \frac{1}{\sqrt{2(1-S)}}\left(|1s_A\rangle - |1s_B\rangle\right) \tag{9.5.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wavefunctions. In contrast, electrons in the $\sigma^\star_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^\star_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wavefunctions).

> Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1s atomic orbitals. Conversely, electrons in the $\sigma^\star_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1s atomic orbitals. Consequently, the $\sigma^\star_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1s atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1s atomic orbitals, and the $\sigma^\star_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 9.5.2

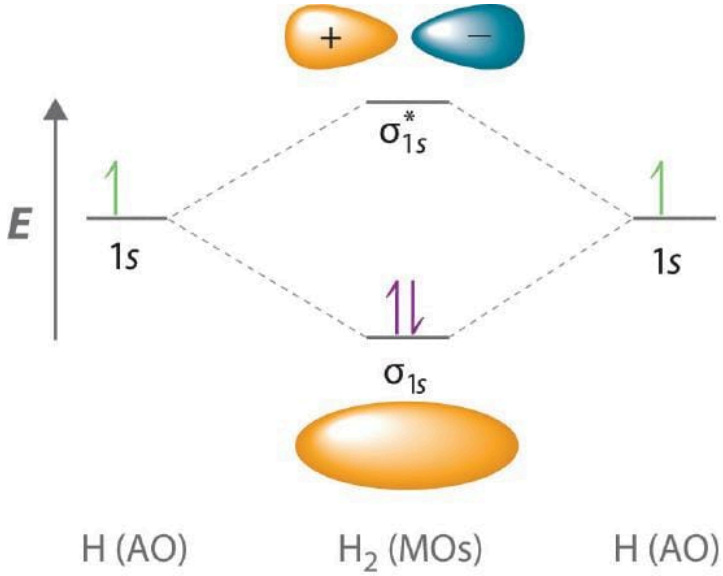


Figure 9.5.2 : Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).

Expanding Beyond the 1s Orbital Basis Set

This picture of bonding in H_2^+ in the previous section is very simple, but gives reasonable results when compared to an exact calculation. The equilibrium bond distance is 134 pm compared to 106 pm (exact), and a dissociation energy is 1.8 eV compared to 2.8 eV (exact). To better describe chemical bonding we need to account for the increase in electron density between the two nuclei. The 1s orbitals alone are not particularly good for this purpose because they are spherically symmetric and show no

preference for the space between the atomic nuclei. The use of additional atomic orbitals can correct this situation and provide additional parameters, which can be optimized by the linear variational method, to give a better function with a lower energy and more accurate description of the charge density.

The energy of the non-normalized molecular orbital can be calculated from the expectation value integral of the Hamiltonian,

$$E_J = \frac{\left\langle \psi_J | \hat{H}_{elec} | \psi_J \right\rangle}{\langle \psi_J | \psi_J \rangle} \tag{9.5.4}$$

This is the variational energy using $|\psi_J\rangle$ as the trail wavefunction. After substituting the LCAO expansion for $|\psi_J\rangle$ (Equation 9.5.1) into the energy expression of Equation 9.5.4 results in:

$$E_J = \frac{\left\langle \sum_i c_{J,i}^* \phi_i \middle| \hat{H}_{elec} \middle| \sum_j c_{J,i} \phi_j \right\rangle}{\left\langle \sum_i c_{J,i}^* \phi_j \middle| \sum_j c_{J,j} \phi_j \right\rangle} \tag{9.5.5}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle}{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \phi_j \rangle} \tag{9.5.6}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} H_{ij}}{\sum_{i,j} c_{J,i}^* c_{J,j} S_{ij}} \tag{9.5.7}$$

where H_{ij} is the Hamiltonian matrix element.

$$H_{ij} = \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle$$

Following the variational theorem, to determine the coefficients of the LCAO expansion c_i, we need to minimize E_J

$$\frac{\partial E_J}{\partial c_k} = 0 \tag{9.5.8}$$

for all k. This requires solving N linear equations to hold true (where N is the number of atomic orbitals in the basis)

$$\sum_{i=1}^{N} c_i (H_{ki} - E S_{ki}) = 0 \tag{9.5.9}$$

These equations are the **secular equations** and were discussed previously in the context of the linear variational method approximation. For the two basis set expansion (N) in Figure 9.5.1 , these are

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{9.5.10}$$

where c_1 and c_2 are the coefficients in the linear combination of the atomic orbitals used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{9.5.11}$$

Solving these secular equations with N different atomic orbitals in the expansion (Equation 9.5.1) requires finding the N roots of an N order polynomial.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \ldots \\ \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{9.5.12}$$

Each molecular orbital ($|\psi_J\rangle$) from this treatment has an energy E_J that is given by a different set of coefficients, $\{c_{ij}\}$ where i runs over all N functions in the basis (i.e., number of the atomic orbitals in the LCAO approximation of Equation 9.5.1), and J runs over molecular orbitals. Solve the set of linear equations using that specific E_J to determine c_{ij} values.

Steps in a Solving the Secular Equations

1. Select a set of N basis functions
2. Determine all N(N –1)/2 values of both H_{ij} and S_{ij}
3. Form the secular determinant; determine N roots E_j of secular equation
4. For each E_J solve the set of linear equations to determine the basis set coefficients \(c_{ij\}) for the j-th molecular orbital

For more information on solving the Secular equations check here.

The greater the number of atomic orbitals N that combine to genera the molecular orbitals (Equation 9.5.1), the more accurate the LCAO approximation is. This is expected based on our discussions of the variational method examples. Hence, the ψ_+ and ψ_- molecular orbitals for H_2^+ are better expressed with higher energy hydrogenic wavefunctions

$$|\psi_J\rangle = c_{J,1}1s_A + c_{J,2}1s_B + c_{J,3}2s_A + c_{J,4}2s_B + c_{J,5}2p_{z,A} + c_{J,6}2p_{z,B} \tag{9.5.13}$$

The reasons that only the p_z atomic orbitals are included in this expansion are discussed later.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$|\psi_i\rangle = \sum_j c_{ij}\varphi_j \tag{9.6.1}$$

where

- j is the index for the j^{th} basis function (e.g., atomic orbital)
- i is the i^{th} molecular orbitals and
- c_{ij} is the expansion coefficient of the j^{th} basis function for the i^{th} molecular orbital.

The variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. Just as for atoms, each electron in a molecule can be described by a product of spin-orbitals. Since electrons are fermions, the electronic wavefunction must be **antisymmetric** with respect to the permutation of any two electrons. A Slater determinant containing the molecular spin orbitals produces the antisymmetric wavefunction. For example for two electrons,

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1) \\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2) \end{vmatrix} \tag{9.6.2}$$

Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, ϵ. Following the Aufbau Principle, two electrons with different spins (α and β, consistent with the Pauli Exclusion Principle discussed for muliti-electron atoms) are assigned to each spatial molecular orbital in order of increasing energy. For the ground state of the 2n electron molecule, the n lowest energy spatial orbitals will be occupied, and the electron configuration will be given as $\psi_1^2\psi_2^2\psi_3^2 \ldots \psi_n^2$. The electron configuration also can be specified by an orbital energy level diagram as shown in Figure 9.6.1 . Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure 9.6.1 .

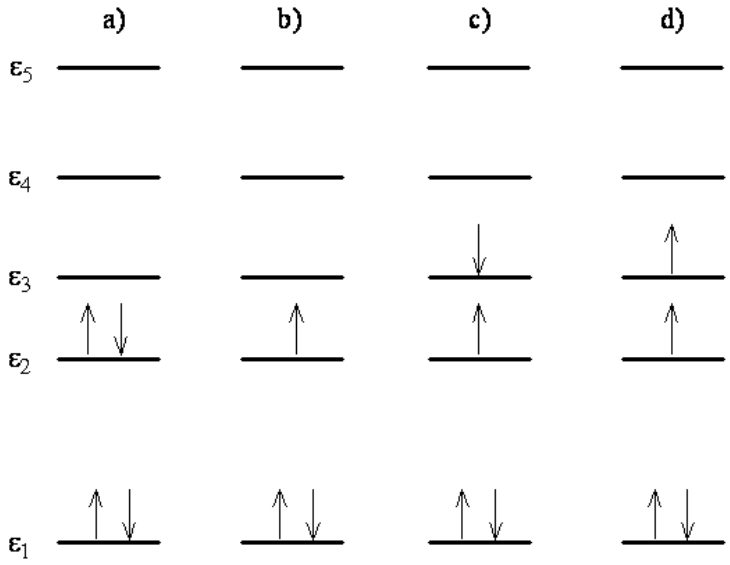


Figure 9.6.1 : a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

Symmetry

Molecular orbitals usually are identified by their symmetry or angular momentum properties. For example, a typical symbol used to represent an orbital in an electronic configuration of a diatomic molecule is $2\sigma_g^2$. The superscript in symbol means that this orbital is occupied by two electrons; the prefix means that it is the second sigma orbital with *gerade* symmetry.

Diatomic molecules retain a component of angular momentum along the internuclear axis. The molecular orbitals of diatomic molecule therefore can be identified in terms of this angular momentum. A Greek letter, e.g. σ or π, encodes this information, as well as information about the symmetry of the orbital. A σ means the component of angular momentum is 0, and there is no node in any plane containing the internuclear axis, so the orbital must be symmetric with respect to reflection in such a plane. A π means there is a node and the wavefunction is antisymmetric with respect to reflection in a plane containing the internuclear axis. For homonuclear diatomic molecules, a *g* or a *u* is added as a subscript to designate whether the orbital is symmetric or antisymmetric with respect to the center of inversion of the molecule.

A homonuclear diatomic molecule has a center of inversion in the middle of the bond. This center of inversion means that $\psi(x,y,z) = \pm\psi(-x,-y,-z)$ with the origin at the inversion center. Inversion takes you from (x,y,z) to $(-x,-y,-z)$. For a heteronuclear diatomic molecule, there is no center of inversion so the symbols g and u are not used. A prefix 1, 2, 3, etc. simply means the first, second, third, etc. orbital of that type. We can specify an electronic configuration of a diatomic molecule by these symbols by using a superscript to denote the number of electrons in that orbital, e.g. the lowest energy configuration of N_2 is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \tag{9.6.3}$$

Contrasting LCAO with other Quantum Chemistry Methods

As we have already seen, the LCAO approach is very approximate, yielding only qualitative results. It should be noted that the Hartree-Fock method discussed earlier for atoms can also be used for molecules. For example, the molecule He_2^+ has three electrons, and the Li atom also has three electrons. As usual with Hartree-Fock, the idea is to optimize the shapes of the single-electron orbitals $\psi_1(r)$, $\psi_2(r)$ and $\psi_3(r)$ by minimizing the guess to the ground state energy E_g. Of course, we will not get the same answer as for Li because there is a different V_{en} energy for He_2^+ due to the presence of two positively charge nuclei $(charge = +2e)$ separated by a distance R in contrast to the single $+3e$ charged nucleus for Li. When the shapes of the orbitals are optimized, we also obtain three energy ε_1, ε_2 and ε_3. Not unexpectedly, we find that two of the HF orbitals resemble $1\sigma_g$ while the third resembles $1\sigma_u^*$ and the first two energies ε_1 and ε_2 will be nearly equal, while the third ε_3 will

be noticeably higher. To contrast with the LCAO approach, in LCAO, we do not optimize the shapes of the orbitals (these are assumed *a priori* to be $1s$ shaped). All we do is choose the mixing coefficients so as to minimize the guess to the ground-state energy E_g.

We note, finally, that the density functional theory alluded to earlier can also be used for molecules. It is often the case that density functional theory yields a more accurate description than Hartree-Fock, but this depends on the molecule. In any case, both are more accurate than LCAO. There is also a hierarchy of methods called *post Hartree-Fock* methods, all of which are based on the wavefunction rather than the electron density, that can be used to improve upon the HF approximation systematically. The greater the accuracy that is desired for the calculation, the more costly computationally the post HF methods become, so quantum chemistry is often a trade-off between accuracy and efficiency, an issue that becomes more critical to take into account when calculations on large molecules must be carried out!

Contributors and Attributions

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9.7: Molecular Orbitals Can Be Ordered According to Their Energies

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they are often ignored in constructing molecular orbitals. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

Molecular Orbitals Formed from *ns* Orbitals

The molecular orbitals diagrams formatted for the dihydrogen species are similar to the diagrams to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 9.7.1 , where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

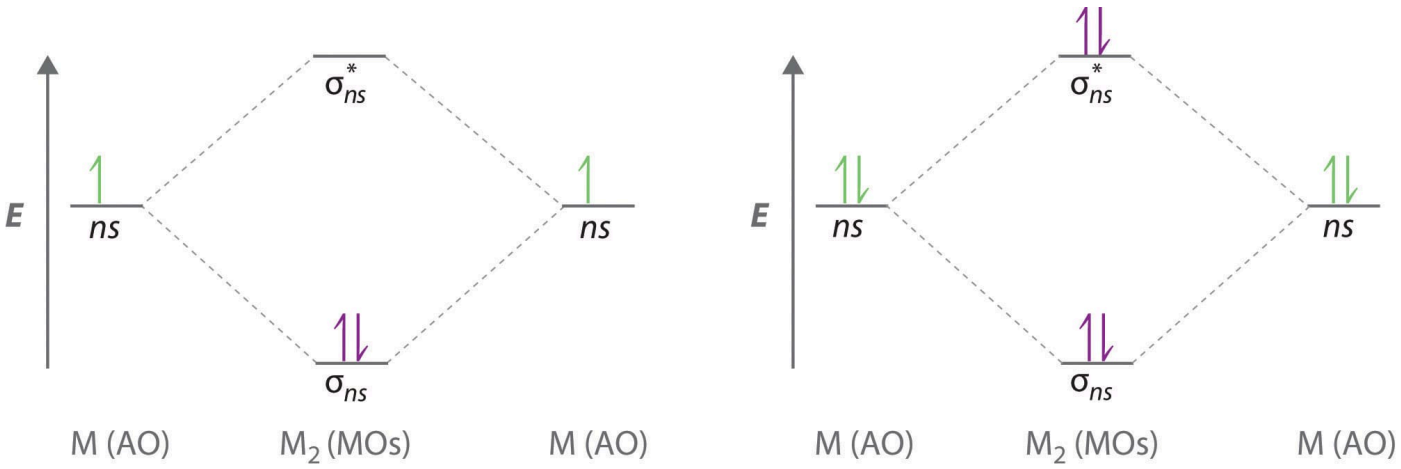


Figure 9.7.1 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ^*_{ns} (nonbonding) levels, leading to a predicted bond order of 0. (CC BY-SA-NC; anonymous).

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule. As shown in Figure $9.7.1b$, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 9.7.1 : Sodium Dimer Ion

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

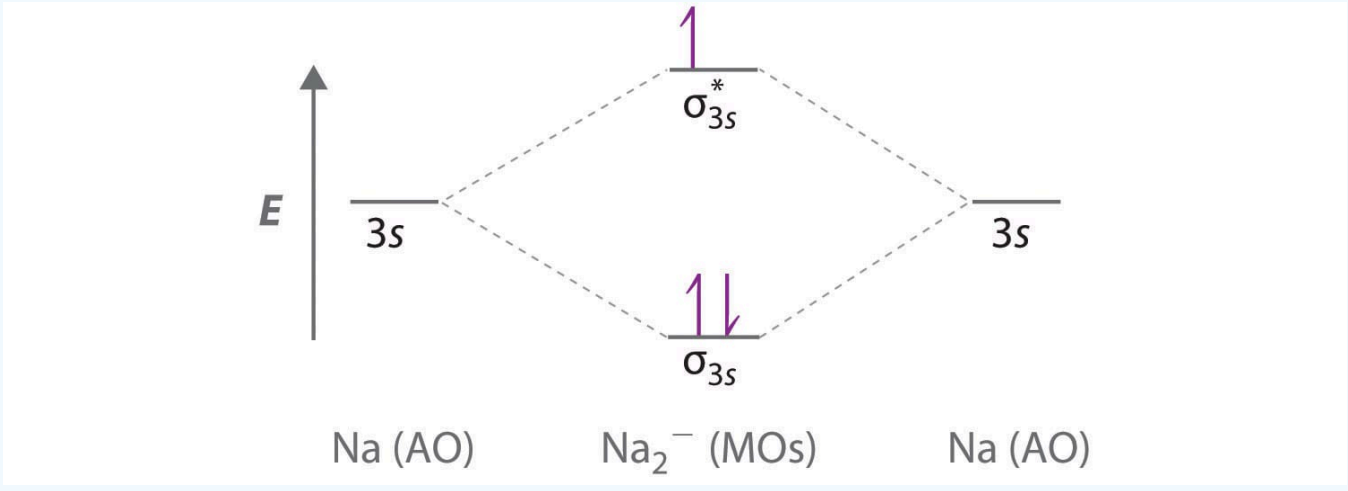
Strategy

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1s atomic orbitals.

B The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s^*} and a $(\sigma_{3s})^2(\sigma_{3s}^\star)^1$ electron configuration.



(CC BY-SA-NC; anonymous).

C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise 9.7.1 : Calcium Dimer Cation

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer available at the end of this section.

Molecular Orbitals Formed from n*p* Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{9.7.1}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 9.7.2 , it is the mathematical *difference* of their wavefunctions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{9.7.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{9.7.3}$$

In this combination, shown in part (b) in Figure 9.7.2 , the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

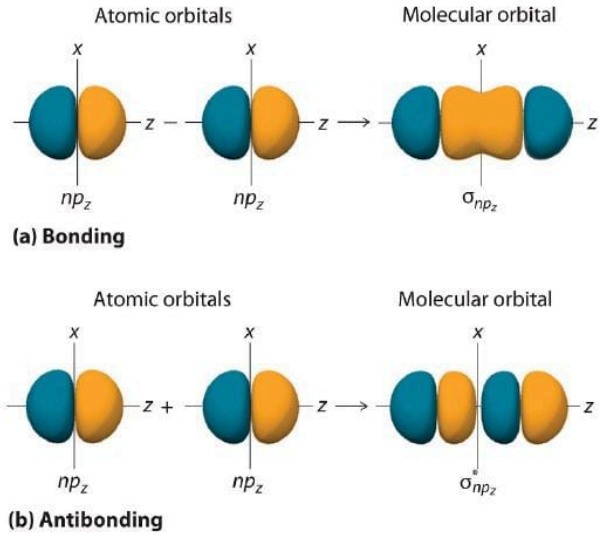


Figure 9.7.2 : Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate – + – +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 9.7.3 , we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on

one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{9.7.4}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{9.7.5}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

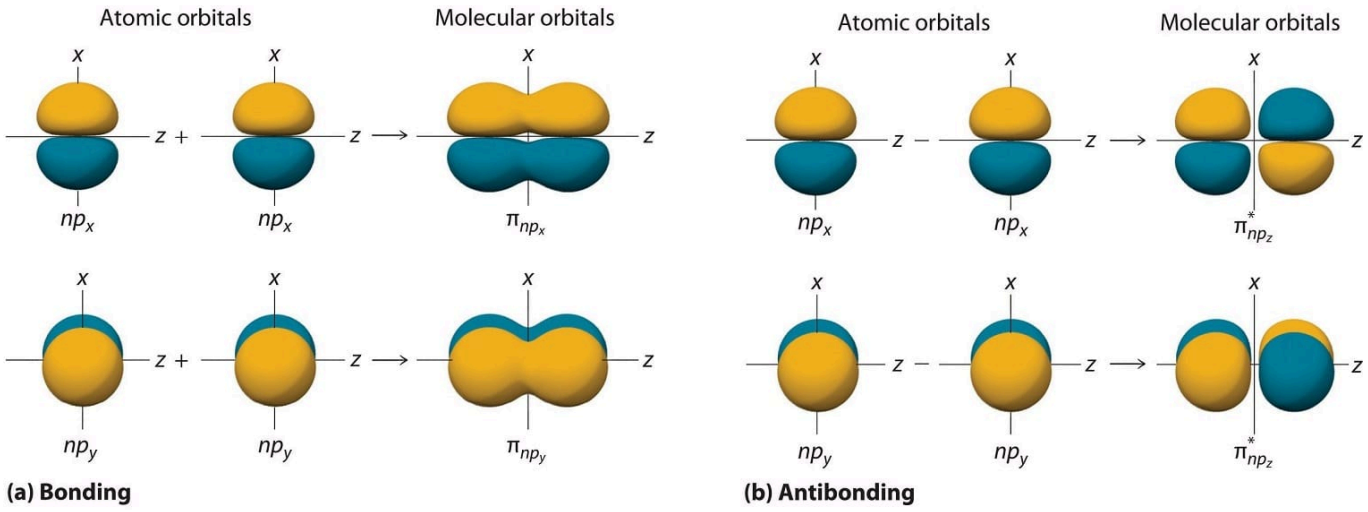


Figure 9.7.3 : Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

Energies for Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Figure 9.7.4 is an energy-level diagram that can be applied to two *identical* interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a

σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

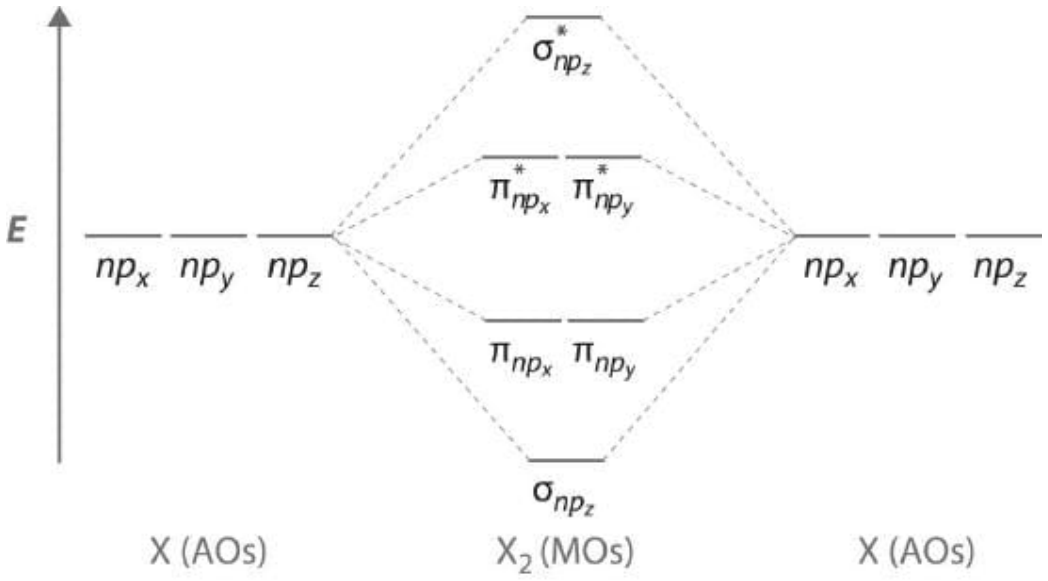


Figure 9.7.4 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals. (CC BY-SA-NC; anonymous).

The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in Figure $9.7.5a$; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^\star_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^\star_{2p_x}$ and $\pi^\star_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rules. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons.

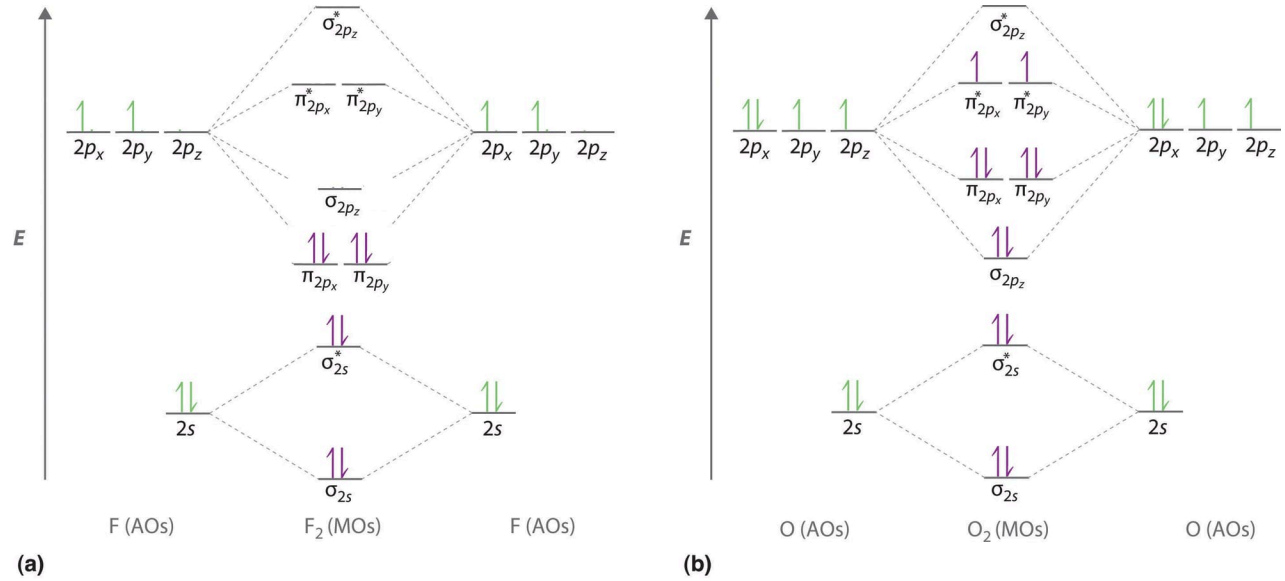


Figure 9.7.5 : Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; anonymous).

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2p_z orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 9.7.6 . Experimentally, the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 9.7.6). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

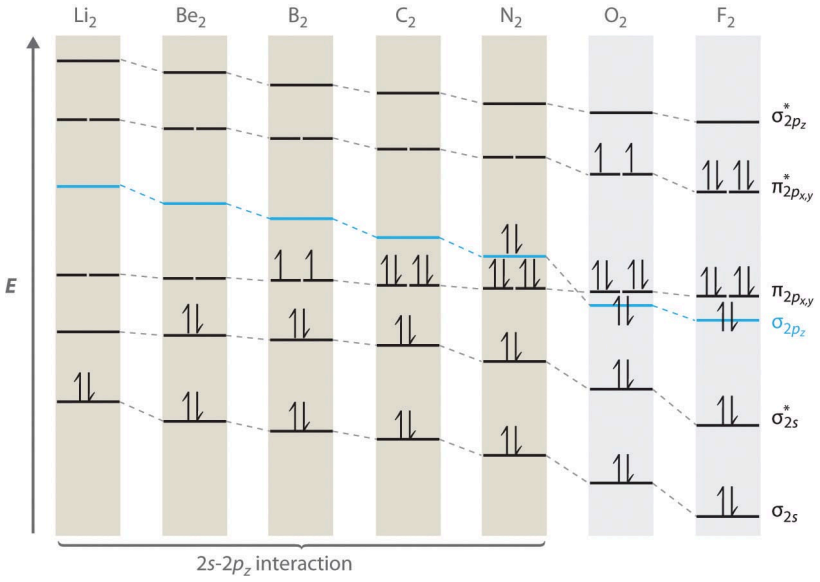


Figure 9.7.6 : Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2s and 2*p* atomic orbitals as the nuclear charge increases across the row. (CC BY-SA-NC; anonymous).

Example 9.7.2 : Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

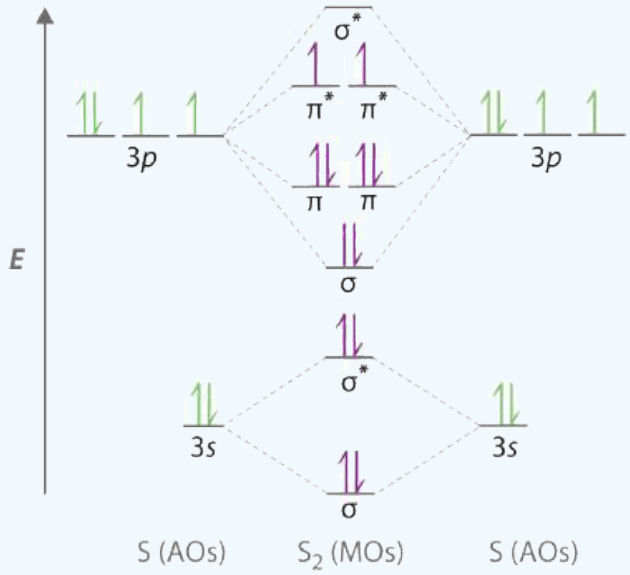
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figures 9.7.6 and 9.7.7 , we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases, the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



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Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ and $\pi^{\star}_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2 (\sigma^{\star}_{3s})^2 (\sigma_{3p_z})^2 (\pi_{3p_{x,y}})^4 (\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 – 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 9.7.2

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer available at the end of this section.

Molecular Orbitals Formed from *ns* with n*p* Orbitals

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 9.7.7 , the sum of the two atomic wavefunctions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

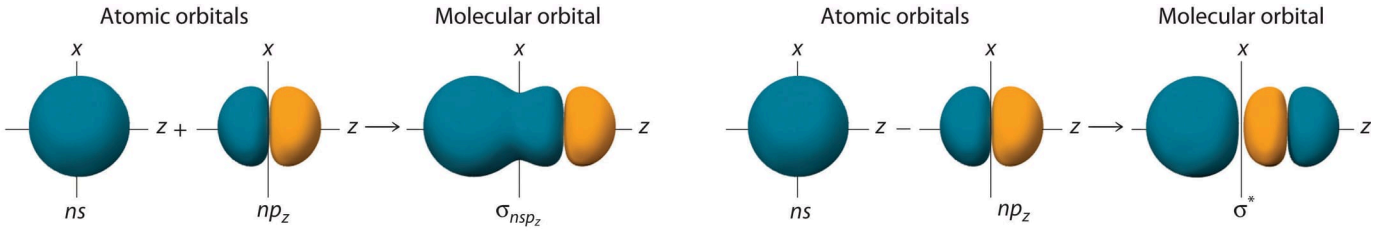


Figure 9.7.7 : Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

Answers

Ca_2^+ has a $(\sigma_{4s})^2 (\sigma_{4s}^\star)^1$ electron configurations and a bond order of 1/2 and should exist.

$(\sigma_{2s})^2 (\sigma_{2s}^\star)^2 (\sigma_{2p_z})^2 (\pi_{2p_{x,y}})^4 (\pi_{2p_{x,y}^\star})^4$ bond order of 1; no unpaired electrons

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9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

Learning Objectives

- Using bond order as a metric for the existance of molecules

Bond Order

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. Within the molecular orbital approach, *bond order* is defined as one-half the *net* number of bonding electrons:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{9.8.1}$$

To calculate the bond order of H_2, we know that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\text{bond order} = \frac{2-0}{2} = 1 \tag{9.8.2}$$

This result corresponds to the single covalent bond; double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams to describe the bonding in other pairs of atoms and ions where *n* = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's Rules.

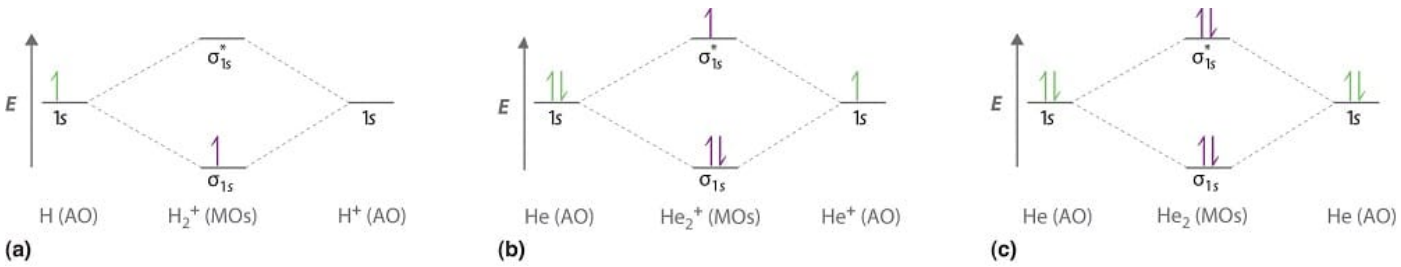


Figure 9.8.1 : Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. (CC BY-SA-NC; anonymous)

Figure $9.8.1a$ shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (via Equation 9.8.1)

$$\text{bond order} = \frac{1-0}{2} = 1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 9.8.1 , these predictions agree with the experimental data.

Table 9.8.1 : Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Species	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2 (\sigma^\star_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2 (\sigma^\star_{1s})^2$	0	5,500	4.6×10^{-5}

Figure $9.8.1b$ is the molecular orbital energy-level diagram for $\mathrm{He_2}^{2+}$. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma^\star_{1s}$ antibonding orbital, giving a $(\sigma_{1s})^2 (\sigma^\star_{1s})^1$ electron configuration. This electron configuration gives a bond order (via Equation 9.8.1) of

$$\text{bond order} = \frac{2-1}{2} = 1/2$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 9.8.1).

Example 9.8.1 : The ion $\mathrm{He_2}^{2+}$

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the $\mathrm{He_2}^{2+}$ ion.

Given: chemical species

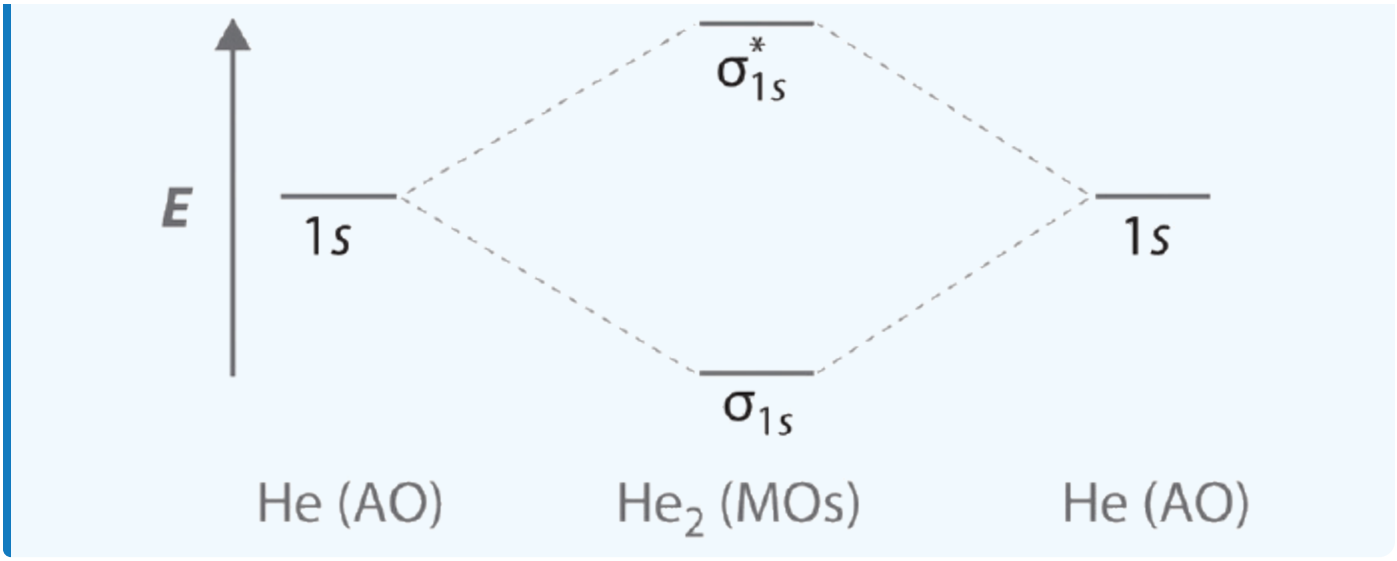
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

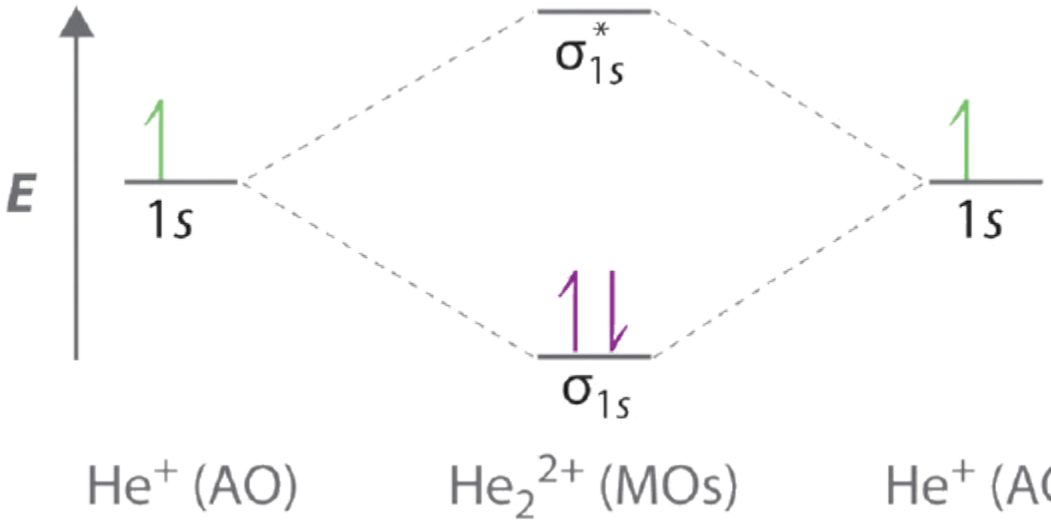
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1s atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma^\star_{1s}$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1s atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired.

C So the bond order is (via Equation 9.8.1)

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 9.8.1 : The Ion $H_2{}^{2-}$

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the $H_2{}^{2-}$ ion. Is this a stable species?

Answer available at the end of this section.

The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure $9.8.1c$ is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma^\star_{1s}$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2\,(\sigma^\star_{1s})^1$ electron configuration, with a predicted bond order (via Equation $9.8.1$) of

$$\text{bond order} = \frac{2-2}{2} = 0 \tag{9.8.3}$$

which indicates that the He_2 molecule has no net covalent bond and is not a stable species.

The ability to track bond order to bond strength is due to the fact that the energy difference between the anti-bonding $\sigma^\star_{1s}$ molecular orbital and the original $1s$ atomic orbital is *larger* than the energy difference between the bonding σ_{1s} molecular orbital and the $1s$ atomic orbitals. This was derived previously where the stabilization energy (ΔE_+) of the σ_{1s} molecular orbital is less than the destabilization energy (ΔE_-) of the anti-bonding $\sigma^\star_{1s}$ molecular orbital:

$$\Delta E_\pm = E_\pm - E_H \tag{9.8.4}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.8.5}$$

Hence, the anti-bonding $\sigma^\star_{1s}$ molecular orbital is more destabilized relative to the atomic orbitals than the bonding σ_{1s} molecular orbital is stabilized relative to the $1s$ atomic orbitals (E_H.

The fact that the anti-bonding MO energy difference is larger than the bonding σ_{1s} molecular orbital energy difference is the true reason that helium dimer is not predicted to exist with a covalent bond. Of the four valence electrons in helium dimer, two will fill the bonding σ_{1s} molecular orbital, and the other two will fill the anti-bonding $\sigma^\star_{1s}$ molecular orbital. The two electrons in the bonding σ_{1s} molecular orbital will achieve some stabilization relative to the $1s$ atomic orbitals, but the two electrons in the anti-bonding $\sigma^\star_{1s}$ molecular orbital will achieve *greater* de-stabilization relative to their position in the atomic orbitals. The net result is a less stable molecule than if the electrons remained in their respective $1s$ atomic orbitals.

> The *electrons in antibonding orbitals cancel (and exceed) the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature (at least as a covalently bonding complex).

However, Van der Waals Helium Dimers do exist

Based on molecular orbital theory discussed above, the He_2 molecule should not exist since no covalent bond formed between the helium atoms (Equation $9.8.3$). However, the molecular orbital description above neglects the van der Waals force that exists between the atoms as demonstrated by the existence of liquid helium (at 4 K). So a "molecule" composed of two helium atoms bound by the van der Waals force may exist by this attractive force instead - and it does.

A helium dimer molecule bound by Van der Waals forces was first proposed by John Clarke Slater in 1928 and observed in 1993 by Gentry and coworkers. Interestingly, He_2 is the largest known molecule of two atoms when in its ground state with an extremely long bond length with a separation of about 5,200 pm. The binding energy is only $4.6 \times 10^{-5}\ kJ/mol$, so the $He{-}He$ bond is 5,000 times weaker than the covalent bond in the hydrogen molecule (Table 9.8.1).

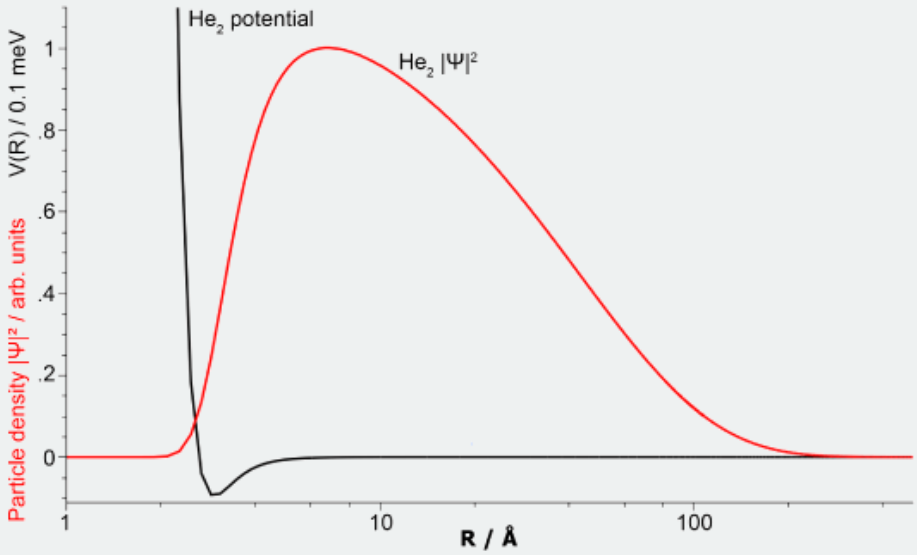


Figure 9.8.2 : The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i..e, tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses ($\mathrm{He_2}$ potential and wavefunction taken from Przybytek 2010), while the classical turning point is located at 13.6 Å, the overall wavefunction extends to more than 200 Å. (Inspire; http://inspirehep.net/record/1415151/plots)

Conclusion

The decrease in energy caused by the bonding orbital (constructive interference of the atomic orbitals) is canceled by the increase in energy caused by the antibonding orbital (destructive interference of the atomic orbitals), so it is not energetically favorable for the helium atoms to be in such proximity, so if that situation arises, they'll separate quickly since there's no force keeping them there.

Answers

$\mathrm{H_2}^{2-}$ has a valence electron configuration of $(\sigma_{1s})^2 (\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

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9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle

Just like with multielectron atoms, there are restrictions on how electrons occupy molecular orbitals. The most important of these rules is the Pauli exclusion principle, which we will not try to prove but will take as a fact. In general chemistry, you were told that the Pauli exclusion principle means that electrons in the same orbital must have opposite spin, and that only two electrons can be in each orbital. That is close, but not entirely accurate. The true statement of the Pauli exclusion principle is this: wavefunctions must be antisymmetric with respect to exchange of identical fermions, and symmetric with respect to exchange of identical bosons. A is a particle with half-integer spin, and a is a particle with integer spin. Recall that electrons are fermions (spin 1/2): we represent the two possible spin states as $|\alpha\rangle$ ($m_z = 1/2$) and $|\beta\rangle$ ($m_z = -1/2$), according to their spin projections.

Because all electrons are identical, the Pauli exclusion principle requires that the electronic wavefunction be antisymmetric with respect to exchanging any of them.[2] The word “antisymmetric” in this context means that if we swap two electrons (i.e., exchange their labels), the wavefunction must change sign. To denote both the orbital of an electron and its spin, we use a product of , each of the form $|\psi\sigma\rangle$, where ψ depends only on the spatial coordinates of the electrons, and σ depends only on their spins.

In the ground electronic state of , the electrons both occupy the $|1\sigma\rangle$ spatial orbital. Naively, we could write the following product of spin orbitals:

$$|\psi\rangle = |1\sigma^1\alpha^1\rangle|1\sigma^2\beta^2\rangle \tag{9.9.1}$$

where the superscript refers to the electron number. Note that since the spatial and spin coordinates are independent of one another, we can group them into kets in whichever way is most convenient for us at the time. Let us define the permutation operator $\hat{p}_{12}$, which swaps the labels of electrons 1 and 2, in order to test the wavefunction for asymmetry in accordance with the **Pauli Exclusion Principle**. It is clear that the electronic wavefunction we wrote above does not change sign under this permutation operation!

$$\hat{p}_{12}|\psi\rangle = |1\sigma^2\alpha^2\rangle|1\sigma^1\beta^1\rangle \neq -|\psi\rangle. \tag{9.9.2}$$

Instead, we can take a linear combination of spin functions to make a new wavefunction:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle - |1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle\right) \tag{9.9.3}$$

Since the Hamiltonian did not contain any terms that depend on spin, the energy of this new wavefunction is equal to the energy of our original wavefunction.[3] We can use the permutation operator $\hat{p}_{12}$ to see that this wavefunction is in fact antisymmetric:

$$\begin{aligned}\hat{p}_{12}|\psi\rangle &= \frac{1}{\sqrt{2}}\left(|1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle - |1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle\right)\\ &= -\frac{1}{\sqrt{2}}\left(|1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle - |1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle\right)\\ &= -|\psi\rangle.\end{aligned} \tag{9.9.4}$$

We see here that the orbital is not occupied by one electron of each spin, but in fact it is occupied electrons in a superposition of spin states. In larger systems, antisymmetrized wavefunctions show that each orbital is occupied by a superposition of all electrons in the system in both spin states. Although that is difficult to conceptualize, in most practical cases the electrons can still be thought of as localized in one particular orbital with one particular spin.

There is a standard procedure to generate an appropriately antisymmetrized electronic wavefunction from any set of single-electron functions. Like in multi-electron atoms, the general method for doing this is by use of a Slater determinant: a determinant in which each column contains the product of one molecular orbital and spin function for each possible labeling of the electrons. For our system above (two electrons in $|1\sigma\rangle$, one with spin α, and the other with spin β), we would write

$$|\psi\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} |1\sigma^1\alpha^1\rangle & |1\sigma^1\beta^1\rangle \\ |1\sigma^2\alpha^2\rangle & |1\sigma^2\beta^2\rangle \end{vmatrix}, \tag{9.9.5}$$

where once again the superscript indicated the label on the electron. The Slater determinant therefore contains all of the possible ways that we could assign numbers to the electrons in the system.

Note

A few things to know about Slater determinants:

- If two columns are swapped, the determinant changes sign (this is why it satisfies the exclusion principle!).
- If any two columns in a determinant are the same, the determinant is 0. This is why the Pauli exclusion principle only allows one electron of each spin to occupy a single orbital, which you learned way back in Gen Chem. It also directly leads to the "Aufbau" principle: when populating molecular orbitals, we fill up orbitals in order of increasing energy with two electrons each.
- The energy of a Slater determinant (in the independent particle approximation) is simply the sum of the orbitals that make it up (i.e., add up the energy of each electron in the MO diagram).
- The wavefunction described by a Slater determinant is normalized if the individual orbitals that make it up are normalized.
- Two Slater determinants are orthogonal if they differ in any single orbital.

Given an MO diagram, it is easy to generate a Slater determinant for the ground electronic state of a closed-shell molecule using general chemistry rules: the Aufbau principle and the Pauli exclusion principle. Each orbital can accommodate one electrons of each spin, and electrons are placed into orbitals from lowest to highest energy. A system with N electrons in the orbitals $|\phi_1\rangle$, $|\phi_2\rangle$, etc., will generate an $N \times N$ dimensional Slater determinant, and the general form is (if N is even):

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\phi_1^1\alpha^1\rangle & |\phi_1^1\beta^1\rangle & |\phi_2^1\alpha^1\rangle & |\phi_2^1\beta^1\rangle & \cdots & |\phi_{N/2}^1\alpha^1\rangle & |\phi_{N/2}^1\beta^1\rangle \\ |\phi_1^2\alpha^2\rangle & |\phi_1^2\beta^2\rangle & |\phi_2^2\alpha^2\rangle & |\phi_2^2\beta^2\rangle & \cdots & |\phi_{N/2}^2\alpha^2\rangle & |\phi_{N/2}^2\beta^2\rangle \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ |\phi_1^N\alpha^N\rangle & |\phi_1^N\beta^N\rangle & |\phi_2^N\alpha^N\rangle & |\phi_2^N\beta^N\rangle & \cdots & |\phi_{N/2}^N\alpha^N\rangle & |\phi_{N/2}^N\beta^N\rangle \end{vmatrix} \tag{9.9.6}$$

Once again, each column contains the orbital and spin state of one of the electrons in the diagram, and each row in the column corresponds to a different choice of label (1, 2, 3, etc...). Evaluating the determinant yields a normalized, antisymmetrized wavefunction. Therefore, an MO diagram can stand as an effective substitute for an electronic wavefunction; it is implied that the true wavefunction used in calculations comes from the Slater determinant described by the diagram.

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9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

Learning Objectives

- To describe the connection between bond order, bond length and bond energy in diatomic molecules
- To explain the observed paramagnetic properties of molecular oxygen with Molecular Orbital theory

In general chemistry courses, students learn that covalent bonds can come as either single, double or triple bonds, which are identifies by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases (Table 9.10.1).

Table 9.10.1 : General Correlation between Bond Strength, length and order in Covalent bonds

Bond	Bond Order	Bond Enthalpy (kJ/mol)	Bond Length (Å)
C−C	1	348	1.54
C=C	2	614	1.34
C≡C	3	839	1.20
N−N	1	163	1.47
N=N	2	418	1.24
N≡N	3	941	1.10

The above trend can be observed in the first row diatomics in Figure 9.10.1 . The bond order can be determined directly form the molecular orbital electron configurations. For diatomics, the occupations can correlate to bond length, bond energies (Figure 9.10.1).

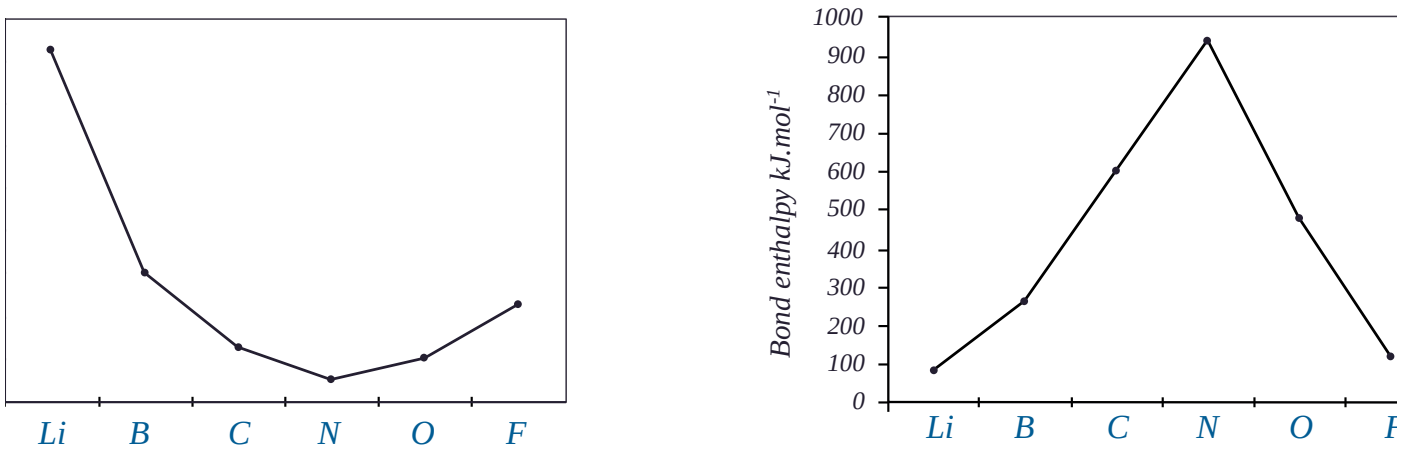


Figure 9.10.1 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

The trends in Figure 9.10.1 and Table 9.10.1 extend to molecular ions.

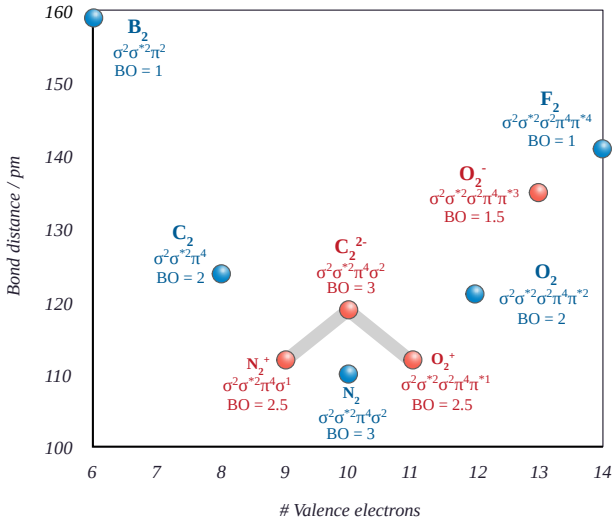


Figure 9.10.2 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

Example 9.10.1 : Molecular Oxygen

Arrange the following four molecular oxygen species in order of increasing bond length: O_2^+, O_2, O_2^-, and O_2^{2-}.

Solution

The bond length in the oxygen species can be explained by the positions of the electrons in molecular orbital theory. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in Figure 9.10.1 . We again fill the orbitals according to Hund's rules and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}^* orbitals, two more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's first rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving a multiplicity of 3 (a triplet state) with two unpaired electrons. This leads to a predicted bond order of

$$\frac{8-4}{2}=2$$

which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

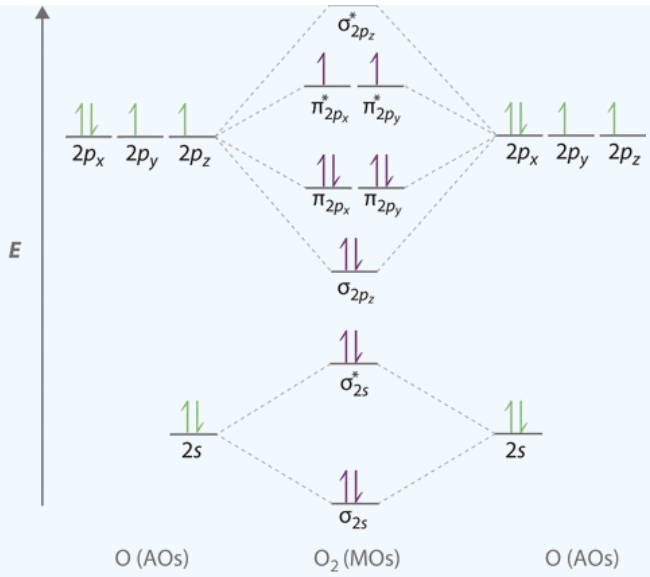


Figure 9.10.3 : Molecular Orbital Energy-Level Diagrams for O_2. With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^\star_{np_x},\ \pi^\star_{np_y}\right)$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; Anonymous by request).

The bond order is determined from the the electron configurations. The electron configurations for the four species are contrasted below.

- O_2:

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^1\pi_{2p_y}^{*\,1}$$

  From Equation ???, the bond order for O_2 is 2 (i.e., a double bond).
- O_2^+:

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^1\pi_{2p_y}^{*\,0}$$

  From Equation ???, the bond order for O_2^+ is 2.5. An alternative and equally valid configuration is

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^0\pi_{2p_y}^{*\,1}$$
- O_2^-:

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^2\pi_{2p_y}^{*\,1}$$

  From Equation ???, the bond order for O_2^- is 1.5. An alternative and equally valid configuration is

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^1\pi_{2p_y}^{*\,2}$$
- O_2^{2-}:

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^2\pi_{2p_y}^{*\,2}$$

  From Equation ???, the bond order for O_2^{2-} is 1.

The bond order decreases and the bond length increases in the order. The predicted order of increasing bondlength then is $O_2^+ < O_2 < O_2^- < O_2^{2-}$. This trend is confirmed experimentally with O_2^+ (112.2 pm), O_2 (121 pm), O_2^- (128 pm) and O_2^{2-} (149 pm).

Molecular Oxygen is Paramagnetic

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory or Lewis bonding) can predict the presence of two unpaired electrons in O_2

. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Video 9.10.1 , it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 9.10.1 : Liquid O_2 Suspended between the Poles of a Magnet. Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

Advanced: Spin Barriers

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*.

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9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{9.11.1}$$

You can see from Equation 9.11.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

Exercise 9.11.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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- 5.2: The Uncertainty Principle by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 9.12.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

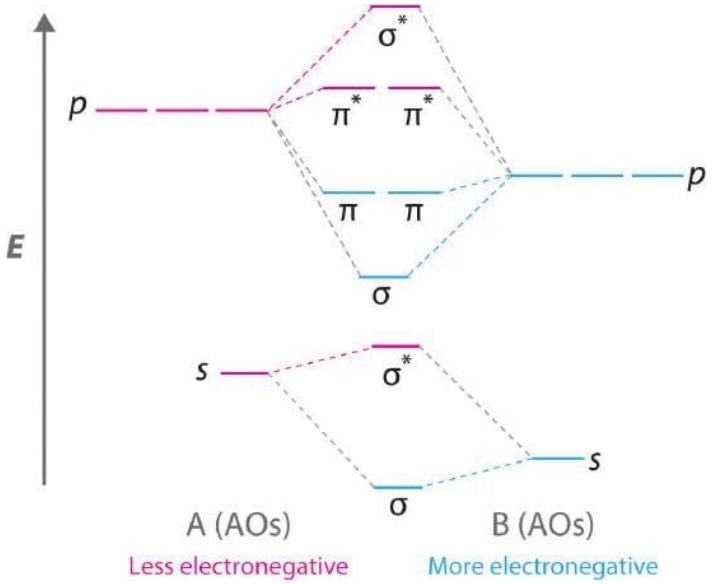


Figure 9.12.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 9.12.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 9.12.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

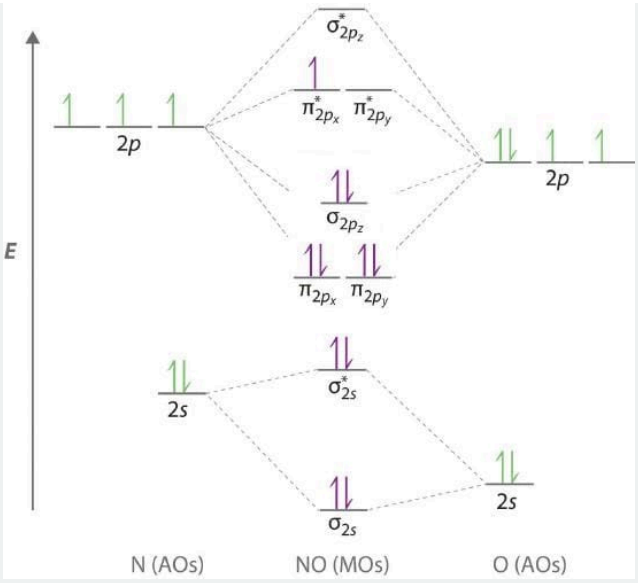


Figure 9.12.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_z},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\,(\sigma^{\star}_{2s})^2\,\left(\pi_{2p_{x,y}}\right)^4\,(\sigma_{2p_z})^2\,\left(\pi_{2p^{\star}_{x,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 9.12.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 9.12.13, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 9.12.6 that the 1s orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1s orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1s orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3s, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 – 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1s atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+} - -Cl^{\delta-}$.

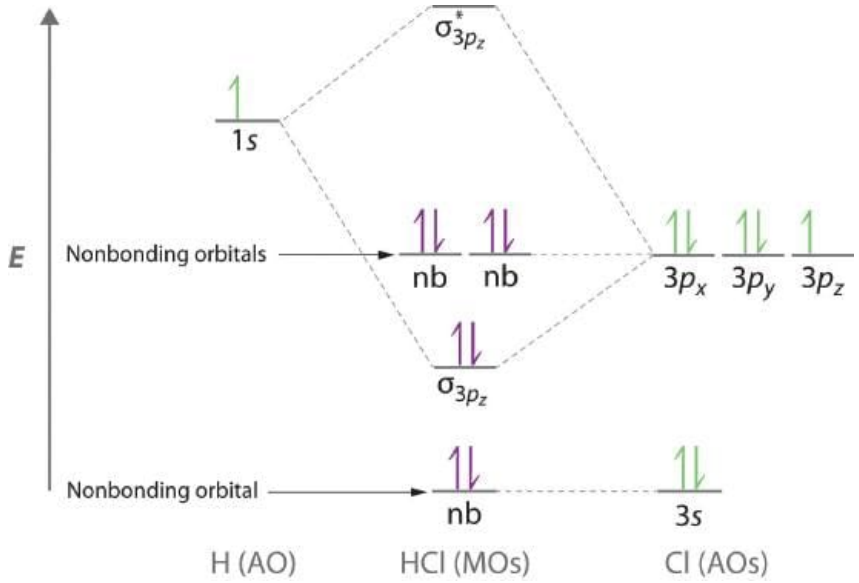


Figure 9.12.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Electrons in nonbonding molecular orbitals have no effect on bond order.

Example 9.12.4: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 9.12.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

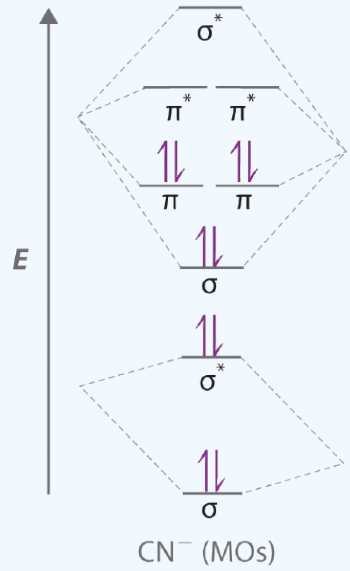
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 9.12.4 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the –1 charge. Placing these electrons in an energy-level diagram like Figure 9.12.4 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 – 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise 9.12.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer available at the end of this section.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

YouTube Video

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View this YouTube Video online

Summary

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With

such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

Answers

Exercise $9.12.4$**: The Hypochlorite Ion**

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

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9.13: SCF-LCAO-MO Wavefunctions are Molecular Orbitals formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently

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9.14: Molecular Term Symbols Describe Electronic States of Molecules

Molecular term symbols specify molecular electronic energy levels. Term symbols for diatomic molecules are based on irreducible representations in linear symmetry groups, derived from spectroscopic notations. They usually consist of four parts: spin multiplicity, azimuthal angular momentum, total angular momentum and symmetry. All molecular term symbols discussed here are based on Russel-Saunders coupling.

Introduction

Molecular term symbols mark different electronic energy levels of a diatomic molecule. These symbols are similar to atomic term symbols, since both follow the Russell-Saunders coupling scheme. Molecular term symbols employ symmetry labels from group theory. The possibility of an electronic transition can be deducted from molecular term symbols following selection rules. For multi-atomic molecules, symmetry labels play most of term symbols' roles.

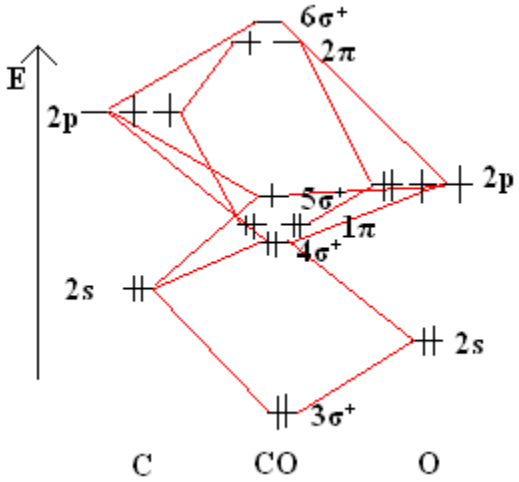
For homonuclear diatomics, the term symbol has the following form:

$$^{2S+1}\Lambda^{(+/-)}_{\Omega,(g/u)} \tag{9.14.1}$$

whereas Λ is the projection of the orbital angular momentum along the internuclear axis: Ω is the projection of the total angular momentum along the internuclear axis; *g*/*u* is the parity; and +/− is the reflection symmetry along an arbitrary plane containing the internuclear axis. Λ may be one of the greek letters in the sequence: Σ Π Δ Φ... when Λ = 0, 1, 2, 3..., respectively. For heteronuclear diatomics, the term symbol does not include the *g*/*u* part, for there is not inversion center in the molecule.

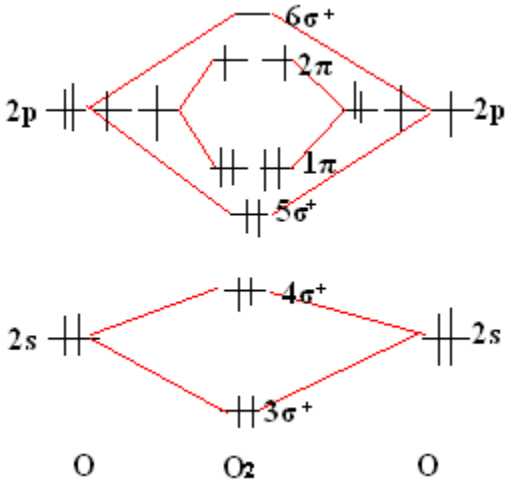
Determining term symbols of diatomics

Let's start with CO again. As we have seen before, the molecule has a close-shell configuration. Its ground state is a totally symmetric singlet, $^1\Sigma^+$, since the only possible values of (S, Λ) are (0, 0). If one of the HOMO electrons on the $5\sigma^+$ orbital has jumped to the LUMO, this molecule will be in an excited state as follows.



Suppose a CO molecule is in the excited state shown above. In order to know the term symbol of this state, a direct product of the labels is required for the two MO's with unpaired electrons. The multiplication is such as $\Pi \times \Sigma^+ = \Pi$. According to Pauli's exclusion rule, these two unpaired electrons can never share the same set of quantum numbers, therefore the spin degeneracy S can reach its maximum 3. The resulting term symbols are $^1\Pi$ and $^3\Pi$.

Now if we look at O_2, it does not have a close-shell configuration at its ground state. There are two unpaired electrons each occupying one of the two degenerate 2π orbitals, which can be seen in the diagram below.



The term symbol for oxygen molecule at its ground state is therefore derived such as $\Pi \times \Pi = \Sigma^+ + \Sigma^- + [\Delta]$, as the symbol in brackets does not allow the oxygen atoms to commute.

Transition between electronic states of diatomics

We'll focus on selection rules. Like atomic electronic states, different selection rules apply when differently incurred transitions occur. Usually for electric dipole field induced transitions, the selection rules are the same as for atoms.

1. $\Delta\Lambda = 0, \pm 1$ except $\Lambda = 0 \ddagger \Lambda' = 0$
2. $\Delta S = 0$
3. $\Delta\Omega = 0; \pm 1$ except $\Omega = 0 \ddagger \Omega' = 0$

References

1. Harris, Daniel C. (republished in 1989). *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*. Dover Publications. pp. 421-478. ISBN 0-486-66144-X
2. D. J. Willock (2009). *Molecular Symmetry*. John Wiley & Sons Ltd. ISBN 0-470-85348-4

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9.15: Molecular Term Symbols Designate Symmetry

The quantum numbers for diatomic molecules are similar from the atomic quantum numbers. Be cautious, because the rules for finding the possible combinations are different. The total orbital angular momentum quantum number For the molecular case, this number is called Λ instead of L. It follows the same naming convention as L, except that instead of using capital English letters, it uses capital Greek letters:

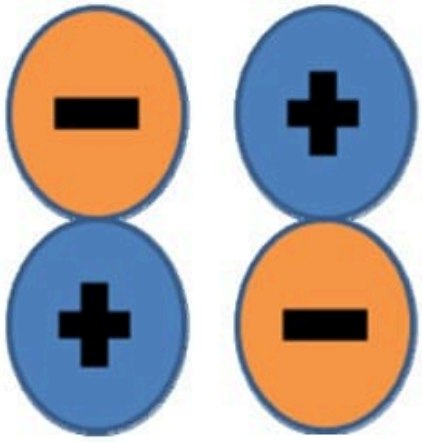
- $\Lambda = 0 \rightarrow \Sigma$
- $\Lambda = 1 \rightarrow \Pi$
- $\Lambda = 2 \rightarrow \Delta$
- $\Lambda = 3 \rightarrow \Phi$

Unlike L, there is not a general formula for finding the possible combinations of Λ. You have to examine the individual microstates. This is easier than it sounds.

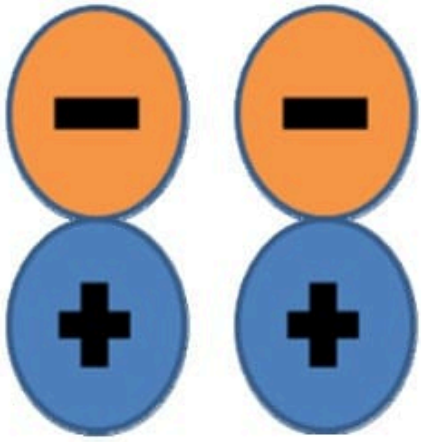
- **The total magnetic quantum number** M_L: M_L works like M_l with atoms, except that there is no formula for finding the combinations.
- **The total spin magnetic quantum number** M_S: M_S works exactly like M_s. Electrons can either point with or against the z -axis, and being in a molecular orbital versus an atomic orbital doesn't change this. M_S can range from $m_{s1} + m_{s2}$ to m_{s1}-m_{s2}.

Two New Symmetries: Parity and Reflection

Molecular orbitals are more complex than atomic ones and require more modifiers to completely define. **Parity** (sometimes called "inversion") tells you if the orbital is *symmetric* or *anti-symmetric* when an inversion operation is performed. The symmetry notation **u** and **g** are sometimes used when describing molecular orbitals. This refers to the operation of inversion, which requires starting at an arbitrary point in the orbital, traveling straight through the center, and then continuing outwards an equal distance from the center. The orbital is designated **g** (for gerade, even) if the phase is the same, and **u** (for ungerade, uneven) if the phase changes sign.



This pi orbital is gerade



This pi orbital is ungerade

To determine whether or not a given state is g or u, find the parity of each individual open-shell electron and uses these simple (Laporte rules):

- $g + g \rightarrow g$
- $g + u \rightarrow u$
- $u + u \rightarrow g$

Example 9.15.1: Closed Shell Configuration

What is the parity of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

Since both open shell electrons are ungerade, the overall parity is g. Helpful hint: bonding sigma orbitals and anti - bonding pi orbitals are always gerade. Anti - bonding sigmas and bonding pis are always ungerade. Draw them and see for yourself.

Reflection determines if a given orbital is symmetric or anti-symmetric upon reflection through a plane that contains both nuclei. The choice of symmetry planes is arbitrary. As long as you pick a plane and stick with it, you will always get the right answer. When an orbital is symmetric, it is labeled +. When an orbital is anti - symmetric, it is labeled - . To find the overall reflection of a state, use these rules:

- (+)(+) \rightarrow +
- (+)(-) \rightarrow -
- (-)(-) \rightarrow +

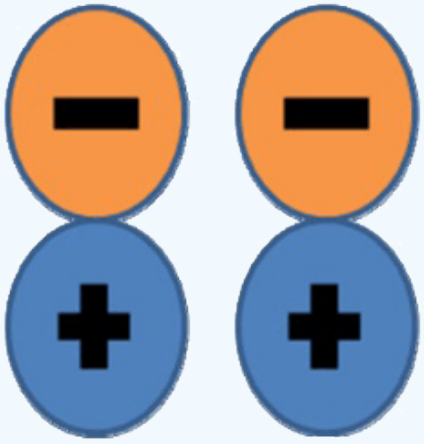
Reflection only applies to Σ states! For Λ > 0, there are no reflection labels! If you experiment with the rules, you will quickly realize why this is the case.

Example 9.15.2

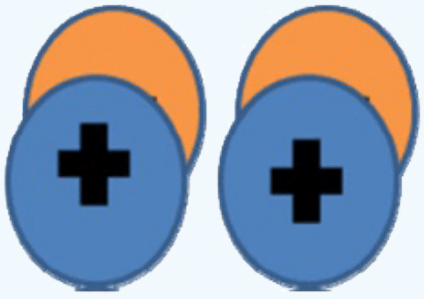
What is the reflection of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

You need to know what the orbitals look like. Draw a picture and then pick a plane. For this example, the plane of the page is selcted, but the orthogonal plane would have worked just as well.



The “vertical” orbital is +



The “horizontal” orbital is -

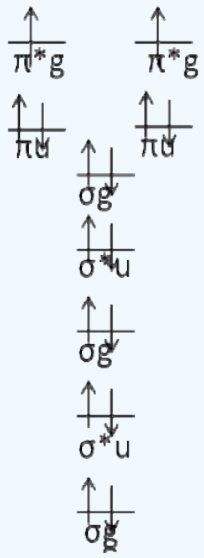
The “vertical” orbital is + The “horizontal” orbital is - Since one is + and one is - , the overall reflection is - . Try using the orthogonal plane and convince yourself that you still get the same answer.

Example 9.15.3: Oxygen

What are the term symbols for O_2 ?

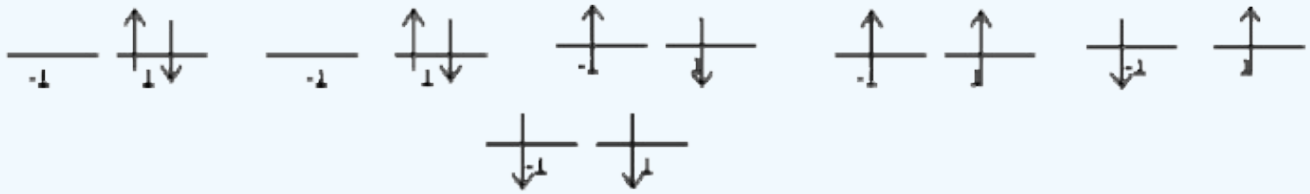
Solution

The molecular orbital diagram for O_2 is



Where I chose arbitrary configurations for the last two electrons.

There are two open - shell electrons occupying the anti-bonding π_g orbitals. These are the only electrons that matter. It is easiest to simply draw all of the permutations and figure out the bounds on Λ and M_L by inspection. If we do this, it is easy to see that $\Lambda = 2, 0$ and that $M_L = 2, 0, -2$



$M_s = -1$	$M_s = 0$	$M_s = 2$
0	**1**	0
1	2	1
0	1	0

The top row is a $\Lambda = 2$ $M_S = 0$ state, so it is $^1\Delta$. Both electrons are in the rightmost orbital. This orbital is gerade, and (g)(g) = g, so the parity label is g. We do not assign reflection labels to non Σ states, so the term symbol is $^1\Delta_g$. After removing the used up microstates, the chart becomes

$M_s = -1$	$M_s = 0$	$M_s = 2$

1	1	0

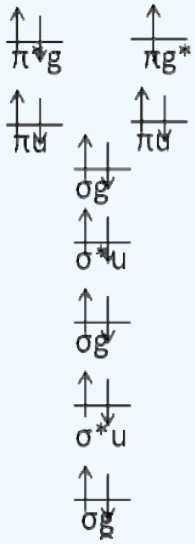
This is a Λ =0 state with three possible spin configurations, so it is $^3\Sigma$. We know that the electrons are in different sub-orbitals (if you cannot see this, try drawing all of the possible combinations that give $\Lambda = 0$). Both of the orbitals are gerade, so the overall parity is gerade. One of the orbitals will be +, the other will be - . The final answer is $^1\Delta_g \backslash (^3\Sigma_g^+$

Exercise 9.15.1

Write the term symbols for O_2^-

Solution

First draw the electron configuration diagram.



There are only two possible configurations. It should be easy to see that the term symbol is $^2\Pi_g$.

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9.16: Most Molecules Have Excited Electronic States

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9.E: Chemical Bond in Diatomic Molecules (Exercises)

Solutions to select questions can be found online.

9.3

The overlap integral and other integrals that arise in two-center systems like that of H_2 which is called a **two-center integral**. The two center integrals are much easier being evaluated by simply using the coordinate system, elliptic coordinates. In the coordinate system, where there are simply two fixed points which are separated by distance R.

Untitled 11111.png

A point P is given by three coordinates which are

- $\lambda = r_A + r_B/R$
- $\mu = r_A + r_B/R$

the angle ø is the angle that (r_A, r_B, R) triangle makes the interfocal axis. The differential volume element (elliptic coordinates) $\Leftrightarrow$ $dr = R^3/8(\lambda^2 - \mu^2)d\lambda \ d\mu \ d\phi$

Given definitions λ, μ, ϕ $\rightarrow$ prove that

- $1 \leq \lambda < \infty$
- $-1 \leq \mu \leq 1$
- $0 \leq \phi \leq 2\pi$

Use elliptic coordinates to evaluate the overlap integral.

Use Equation:

$$S = \int dr\, 1s_A 1s_B = \frac{Z^3}{\pi} \int dr\, e^{-Zr_A} e^{-Zr_B}$$

Solution

From simple inspection of the figure:

- Have $r_A + r_B$ is never less than that of R. Therefore, $1 \leq \lambda < \infty$.
- $r_A - r_B$ can never have a of magnitude greater that that of R, therefore have $-1 \leq \mu \leq 1$.
- The variable ϕ can undergo 1 complete revolution therefore have/get $0 \leq \phi \leq 2\pi$.

Knowing all of this information, we can now solve for this equation:

$$\begin{aligned}
S &= \frac{Z^3}{\pi} \int dr e^{-ZrA} e^{-Zr)B} \\
&= \frac{Z^3}{\pi} \int_0^{2\pi} d\phi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu R^3/8(\lambda^2 - \mu^2) e^{-Z(r_A + r_B)} \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) e^{-ZR\lambda} \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda e^{-ZR\lambda} \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda e^{-ZR\lambda} (2\lambda^2 - 2/3) \\
&= \frac{R^3 Z^3}{2} \left[(1/ZR + 2/Z^2R^2 + 2/Z^3R^3) e^{-ZR} - 1/3ZRe^{-ZR} \right] \\
&= e^{-ZR}(1 + ZR + Z^2R^2/3)
\end{aligned}$$

9.4

Repeat the calculation in 9.3 for $\psi_- = 1s_A - 1s_B$

Solution

$$E_- = \frac{\int dr \psi_-^* H \psi_-}{\int dr \psi_-^* \psi_-}$$

The denominator is

$$\int dr \psi_-^* \psi_- = 2(1 - S)$$

The numerator can be evaluated using equations 9.18, 9.19, 9.20, 9.21 with a simple exchange of a minus sign in equations 9.18 and 9.21,

$$\int dr \psi_-^* H \psi_- = 2E_{1s}(1 + S) + 2J - 2K$$

So

$$E_- = \frac{2E_{1s}(1 + S) + 2J - 2K}{2(1 - S)}$$

9.9

Show that the $2p_x$ and the $2p_y$ orbitals do not overlap. Use $2p_x \equiv C \cos\theta$ and $2p_y \equiv C \sin\theta \cos\theta$ and $f(r)$ as the radial component.

Solution

If $\int \Psi_1 \Psi_2 dr \neq 0$ then the orbitals overlap.

Substituting in:

$$\int C \cos^2\theta \sin\theta f(r)$$

$$C \int_0^{\pi} cos^2\theta \sin\theta \int_0^{\infty} f(r) \neq 0$$

This orbitals do not overlap.

9.10

what does the overlap integral represent?

Solution

The overlap integral represents the amount of overlap there is between the orbitals of 2 or more different nuclei. It is only significant for orbitals that have a large overlap. It is a component of the energy integral of the nuclei.

9.14

Which of the three species is the is the least stable due to bond order: O_2, O_2^+, O_2^{2-}. Hint it may be helpful to draw molecular orbitals for each species although it is not required.

Solution

We have to use the bond order formula for each of the situations.

$$\text{Bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of anti-bonding electrons})}{2}$$

For O_2: We have 12 valence electrons. Therefore

$$\text{Bond order} = \frac{10-8}{2} = 1$$

From the bond orders, we can see that O_2^{2-} is the least stable.

$$\text{Bond order} = \frac{10-5}{2} = \frac{5}{2}$$

For O_2^{2-}: We have 14 valence electrons. Therefore

$$\text{Bond order} = \frac{10-6}{2} = 2$$

For O_2^+: We have 11 valence electrons. Therefore

9.17

Write the electron configuration and bond order of carbon monoxide.

Solution

The electron configuration for carbon monoxide

$$CO : KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma 2_{p_z})^2$$

The bond order of CO is three.

9.17

Determine the bond order diphosphorus P_2.

Solution

Each phosphorus atom will contribute 5 valence electrons, so there will be a total of 10 valence electrons. We use these ten valence electrons to fill up atomic orbitals and we learn that the ground state electron configuration has 8 electron in bonding orbitals and 2 electrons in antibonding orbitals. To find bond order we take bonding electrons(8 electrons) minus antibonding (2 electrons) and divide by 2 to find the bond order of 3.

9.18

Determine the bond order for the bond in nitrogen oxide cation, NO^{+}.

Solution

The equation for bond order is

Misplaced '#'

There are 10 electrons total in the $2p$ level that have to fill the $\sigma_1, \sigma_1^*, \pi, \sigma_2, \pi^*\sigma_2^*$ in order of increasing energy, respectively. If one fills out the MO diagram, they will find that the number of bonding electrons is 8 and the number of antibonding electrons is 2.

Thus, the bond order is

$$\frac{1}{2}[8-2]=3$$

This indicates that there is triple bond for NO^{+}

9.18

What is the electron configuration and bond order of nitric oxide ion?

Solution

The electron configuration of NO^{+} is

$$NO^{+}: KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^1$$

The bond order of NO^{+} is $2\frac{1}{2}$

9.21

Determine the bond order for the NO molecule.

Solution

Bond Order = [(# of binding electrons) - (# of anitbonding electrons)] /2

From drawing the Molecular Orbital Diagram, we find that there are 6 binding electrons and 1 antibonding electron, therefore,

Bond Order = (6-1)/2 =5/2

9.22

How is the energy-level diagram for diatomic OH radical differ from that of NH? What is the highest occupied molecular orbital of OH?

9.23

If a light source generates a light at 73.4 nm while a photoelectron spectrometer is measuring the kinetic energy of the electrons ionized when the molecule absorbs this light, what is the largest electron binding energy that can be measured? Also, is it possible to determine the energy of the occupied molecular orbitals of a molecule using the kinetic energy of the ionized electrons measured? If yes, explain. *Hint* : Recall the photoelectron effect discussed in lecture 2.

Solution

The energy of the source light is

$$E = \frac{hc}{\lambda} = 2.71 \times 10^{-18}\ J$$

So 2.71 x 10^{-18} J is the largest electron binding energy that can be measured using this radiation source.

Using Einstein's explanation of the photoelectric effect, we know that

$$\varphi + KE = h\nu$$

Hence, if we know the kinetic energy of the ionized electrons, as well as the energy absorbed by the electron *v*, we can find φ, which is the energy of the molecular orbital occupied by the electron being ionized.

9.24

Why would the ionization energy of a $3p$ electron from HCl molecule be lower than a $3p$ electron from a chlorine atom?

Solution

The electrons that are shared between the two atoms in HCl are pulled closer to the Chlorine atom because it has a greater electronegativity than hydrogen. This creates a dipole moment and the bonding electrons become localized in such a way that they shield the nonbonding $3p$ electrons on the chlorine atom more than the inner shells of just a chlorine atom. Since shielding is greater for HCl the electrons require less energy to be pulled away from the molecule. Less shielded valence electrons will experience a greater attractive force decreasing the radius and increasing ionization energy.

9.27

Photoelectron spectroscopy involves the measurement of kinetic energy of photoelectrons to determine the binding energy, intensity and angular distributions of these electrons and use the information obtained to examine the electronic structure of molecules. It differs from the conventional methods of spectroscopy in that it detects electrons rather than photons to study electronic structures of a material. The O_2 photoelectron spectrum emits two bands of 52.3898 MJ* mol^{-1} and 52.311 MJ*mol^{-1}. This emission corresponds to the 1\(\s) ionization of the oxygen electron. In your own words explain the observation.

Solution

The two bands that oxygen is emitted corresponds to the spin $(+\frac{1}{2}, -\frac{1}{2})$ ionization in the 1s electron. The marginal difference in energy is due to the spin-orbit coupling, which is also known as spin-pairing. Spin-orbit coupling describes the weak magnetic interaction between the orbital motion and the particle spin in a particle

9.28

Would the ionization energies of non-bonding 1s electrons be different for HCl and Cl_2?

Solution

The shielding effects for the 1s electrons are different for these two systems. In HCl, the bonding electron is localized on the more electronegative Cl, while in Cl_2 the bonding electrons are right in between the two atoms. This means that the 1s electrons are more shielded in HCl than in Cl_2 , and so the electron is easier to rip off in HCl. So the ionization energy for 1s electrons in HCl is smaller than in Cl_2.

9.28

First write out the ground-state electron configuration for the homonuclear diatomic molecule F_2. Then given the experimental ionization energies for a 1s fluorine electron for HF and F_2 as 66.981 and 67.217 $MJ \cdot mol^{-1}$, explain why even though the 1s electrons of fluorine are not involved in the chemical bonds their ionization energies are different.

Solution

The ground state configuration is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^2(1\pi_g)^2$$

The ionization energies are different because the 1s electrons affect the attraction of those electrons to the nucleus, even though they are not involved in the actual bond. The F_2 bonding electrons are equally distributed between two atoms, whereas the HF bonding electrons are localized on the fluorine atom. Therefore there is increased shielding of the 1s orbital on HF which causes a smaller ionization energy.

9.30

Try to solve for the ground-state term symbols for the diatomic molecules H_2^+ and H_2, given that the ground-state electron configuration for H_2^+ is $(\sigma_g 1s)^1$ and for H_2 is $(\sigma_g 1s)^2$.

Solution

$(1\sigma_g)^1$ corresponds to M_L=0 and M_s=1/2, meaning that there is an unpaired electron in the symmetric molecular orbitals of g and there is change in the $1\sigma_g$ wavefunction. The ground-state term symbol for H_2^+ will then be

$$^2\Sigma_g^+ \tag{9.E.1}$$

$(1\sigma_g)^2$ corresponds to M_L=0 and M_s=0, meaning that there is an unpaired electron in the molecular orbitals of g and there is change in the $1\sigma_g$ wavefunction. The ground-state term symbol for H_2 will then be

$$^1\Sigma_g^+ \tag{9.E.2}$$

9.30

Find the ground-state term symbols for B_2.

Solution

The ground state electron configuration is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^1(1\pi_u)^1$$

We do not care about the filled orbitals because their

$$M_L = M_S = 0$$

The two unfilled orbitals are

$$(1\pi_u)^1(1\pi_u)^1$$

all possible combinations of

$$m_{l1}, m_{s1}, m_{l2}, m_{s2}$$

for B_2 are:

$$M_S, M_L :$$

$$(0, 2) : 1^+, 1^-$$

$$(0, 0) : 1^-, -1^+$$

$$(0, -2) : -1^+, -1^-$$

With these possible combinations we find the following to be possible ground state term symbols:

$$^1\Delta, ^3\Sigma, ^1\Sigma$$

Following Hund's Rule we detect $^3\Sigma$ to be our ground-state term symbol because the largest spin multiplicity will be the ground state of B_2. Now we take the two unoccupied orbitals and take the product to get the symmetry of the molecular orbital.

$$u \cdot u = g$$

So the ground-state term symbol for

$$B_2$$

is: $^3\Sigma_g^-$

9.31

Solve for the ground-state molecular term symbols for O_2, N_2, N_2^+, and O_2^+.

Solution

The ground state molecular term symbols are given below:

O_2

The molecular term symbol of O_2 without the ± designation is $^3\Sigma_g$. The electron configuration is (filled orbital) (1$\pi_g 2p_x$)^1(1$\pi_g 2p_y$)^1, so the symmetry with respect to a reflection through the x-z plane is (+) (-) = (-); therefore, the complete molecular term symbol of O_2 is $^3\Sigma_g^-$.

N_2

$(1\sigma_g)^2\ (1\sigma u)^2\ (2\sigma_g)^2(2\sigma u)^2(1\pi u)^2(1\pi u)^2(3\sigma_g)^2$ Corresponds to $|M_L| = 0$ and $|M_S| = 0$ of a $^1\Sigma$ term symbol. The symmetry of the molecule is g. The complete ground state term symbol of N_2 is $^1\Sigma_g{}^+$ because the molecular wave function does not change when reflected through a plane containing the two nuclei.

$N_2{}^+$

$(1\sigma_g)^2\ (1\sigma u)^2\ (2\sigma_g)^2(2\sigma u)^2(1\pi u)^2(1\pi u)^2(3\sigma_g)^1$ Corresponds to $|M_L| = 0$ and $|M_S| = 0.5$ of a $^2\Sigma$ term symbol. The symmetry of the molecule is g. The complete ground state term symbol of $N_2{}^+$ is $^2\Sigma_g{}^+$ because the molecular wave function does not change when reflected through a plane containing the two nuclei.

$O_2{}^+$

$(1\sigma_g)^2\ (1\sigma u)^2\ (2\sigma_g)^2(2\sigma u)^2(3\sigma_g)^2(1\pi u)^2(1\pi u)^2(1\pi g)^1$ Corresponds to $|M_L| = 1$ and $|M_S| = 0.5$ of a $^2\Pi$ term symbol. The symmetry of the molecule is g, since the only unfilled molecular orbital has symmetry g, so the complete ground state term symbol of $O_2{}^+$ is $^2\Pi_g$.

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9.S: Chemical Bonding in Diatomic Molecules (Summary)

- While not 100% accurate, molecular orbital theory provides intuitive and qualitative picture of bonding.
- When atomic orbitals overlap, they can do so in-phase (bonding orbitals) or out-of-phase (antibonding orbitals).
- Net stabilization occurs when atomic orbitals overlap in-phase from an “exchange integral” term– purely quantum-mechanical effect.
- Many atomic orbitals can be combined to produce bonding, antibonding, and non-bonding orbitals (LCAO–MO); these can be sorted by energy and filled in like atomic orbitals.
- Antibonding orbitals have nodal planes perpendicular to the internuclear axis.
- Bond order is estimated as the number of electrons in bonding orbitals minus number of electrons in antibonding orbitals, all divided by two. A bond order of 0 means that the bond is not predicted to be stable.
- σ orbitals are cylindrically symmetric about the internuclear axis, π orbitals have one nodal plane along the internuclear axis, δ orbitals have two nodal planes along the internuclear axis, etc...
- Molecular term symbols, like atomic term symbols, describe electron configurations. L is replaced by a Greek letter Λ in a molecular term symbol, and the $2J+1$ is gone because the total angular momentum now depends on the rotational state of the molecule in addition to the electron angular momentum.
- For homonuclear diatomics, the parity subscripts g and u tell whether the wavefunction is centrosymmetric (g is, u is not).
- For Σ states, a superscript $+/-$ indicates the symmetry with respect to a plane containing the internuclear axis. This only applies when π or higher MOs are involved. For each set of degenerate π MOs, one is symmetric and the other is not, so the net symmetry can be calculated by looking at the number of singly-occupied π orbitals. Similar logic applies for the δ and higher orbitals.

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10: BONDING IN POLYATOMIC MOLECULES

The concept of a molecular orbital is readily extended to provide a description of the electronic structure of a polyatomic molecule. Indeed molecular orbital theory forms the basis for most of the quantitative theoretical investigations of the properties of large molecules. In general a molecular orbital in a polyatomic system extends over all the nuclei in a molecule and it is essential, if we are to understand and predict the spatial properties of the orbitals, that we make use of the symmetry properties possessed by the nuclear framework.

10.1: Hybrid Orbitals Account for Molecular Shape

10.2: Hybrid Orbitals in Water

10.3: BeH_2 is Linear and H_2O is Bent

10.4: Photoelectron Spectroscopy

10.5: The pi-Electron Approximation of Conjugation (Hückel Theory)

10.6: Butadiene is Stabilized by a Delocalization Energy

10.7: Benzene and Aromaticity

10.E: Bonding in Polyatomic Molecules (Exercises)

10.S: Bonding in Polyatomic Molecules (Summary)

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10.1: Hybrid Orbitals Account for Molecular Shape

Learning Objectives

- Introduce hybrid orbital to explain non-linear molecular structure

Valence bond (VB) theory is one of two basic theories, along with **molecular orbital** (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

Review of Diatomics

Let us consider H_2. Recall that the Lewis structure for a single H atom is $H\cdot$ and for H_2, it is $H:H$. Thus, each hydrogen brings one unpaired electron to the bond. Let the two protons be denoted A and B and the two electrons 1 and 2. Now, consider the potential energy

$$V = V_{ee} + V_{en} + V_{nn} \tag{10.1.1}$$

$$= \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}}\right] \tag{10.1.2}$$

But as $R_{AB} \to \infty$, the $1/r_{12}$, $1/r_{1B}$, $1/r_{2A}$, and $1/R_{AB}$ terms vanish and the potential energy becomes simply that of two noninteracting hydrogen atoms

$$V \to -\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{1A}} + \frac{1}{r_{2B}}\right]$$

Since the potential energy becomes a simple sum of separate energies for electrons 1 and 2, the wavefunction should simply be a product $\psi_{1s}(r_1 - r_A)\psi_{1s}(r_2 - r_B)$. But as we let $R_{AB} \to R_e$, where R_e is the equilibrium bond length, the electrons mix, and we can no longer tell if electron 1 belongs to atom A or atom B and the same for electron 2. Thus, we need to construct a combination of products that is consistent with the Pauli exclusion principle. If we just consider the coordinates r_1 and r_2 of the electrons, then the only wavefunction we can construct from a product of 1s orbitals is

$$\psi_u(r_1, r_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

where the u designator indicates that this is an odd function. The constant C_u is the overall noramlization constant. Unfortunately, like in the LCAO method, such a wavefunction is antibonding and is not a good representation of the ground state. If, however, we construct the wavefunction

$$\psi_g(r_1, r_2) = C_g[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

where g designates that this is an even function (even in German is *gerade*), we violate the Pauli exclusion principle, even though such a wavefunction leads to a stable chemical bond.

What is missing here is the fact that we have not considered the spins of the electrons. Since the electrons are identical, if we exchange coordinates *and* spins, then the wavefunction should change sign. Thus, we can make both wavefunctions above consistent with the Pauli exclusion principle by multiplying by an appropriate spin wavefunction. We obtain

$$\psi_u(r_1, r_2, s_1, s_2) = \psi_u(x_1, x_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.3}$$

$$\psi_g(r_1, r_2, s_1, s_2) = \psi_g(x_1, x_2) = C_g[\psi^A_{1s}(r_1)\psi_{1s}B(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.4}$$

where s_1 and s_2 are the z-components of spin for electrons 1 and 2, respectively. We can now use ψ_g as an approximate 2-electron wavefunction that leads to a stable chemical bond in H_2.

The fact that ψ_u is antibonding can be easily determined by looking for a nodal plane between the two atoms, in this case, in the plane that exactly bisects the line joining the two atoms, midway between them. That this is, indeed, a nodal plane can be seen by considering two points r_1 and r_2 for the two electrons that are taken to lie in this plane. By symmetry, the functions $\psi_{1s}^A(r_1)$ and $\psi_{1s}^B(r_1)$ have the same value for r_1 in this plane, and the same for $\psi_{1s}^B(r_2)$ and $\psi_{1s}^A(r_2)$. Let us assign the following values:

$$\psi_{1s}^A(r_1) = \psi_{1s}^B(r_1) = A \tag{10.1.5}$$

$$\psi_{1s}^B(r_2) = \psi_{1s}^A(r_2) = A' \tag{10.1.6}$$

Substituting these into $\psi_u(x_1, x_2)$, we obtain

$$\psi_u(x_1, x_2) = C_u[AA' - A'A][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] = 0$$

Since the wavefunction has a node midway between the two atoms, it is clearly antibonding and should have a *higher energy* than the corresponding bonding wavefunction ψ_g.

A similar argument can be used for the molecule F_2. Each F has an electronic configuration

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

and the Lewis structure of $\mathrm{F_2}$ is



Figure 10.1.1 : Lewis structure of F_2.

Most of the electrons are in lone pairs, but the $2p_z$ electrons, which are unpaired in each F atom come together to form the bond. Thus, the bonding wavefunction should be a **2-electron wavefunction** constructed from $2p_z$ orbitals. The bonding wavefunction takes the "gerade" form as in $\mathrm{H_2}$:

$$\psi_g(r_1, r_2, s_1, s_2) = C_g[\psi_{2p_z}^A(r_1)\psi_{2p_z}^B(r_2) + \psi_{2p_z}^A(r_2)\psi_{2p_z}^B(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]$$

For HF, the $2p_z$ orbital on F and $1s$ orbital on H come together to form the bonding wavefunction. To be consistent with the Pauli principle, we need a wavefunction of the form

$$\psi(r_1, r_2, s_1, s_2) = [\psi_{1s}^H(1)\psi_{2p_z}^F(2) + \psi_{1s}^H(2)\psi_{2p_z}^F(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]) \tag{10.1.7}$$

Looking at the HF example, it becomes clear how much valence bond theory attempts to appear as a "quantum version" of the Lewis dot structure model. Valence bond theory attempts to construct very approximate wavefunctions for the bonding electrons in a Lewis structure, leaving the orbitals unused in the construction of the valence bond wavefunctions for the lone pair electrons. In the case of HF, we use the $2p_z$ orbitals of F, which leaves the $2s$, $2p_x$ and $2p_y$ orbitals unused. Since there are three lone pairs, these three orbitals are sufficient to hold each of the lone pairs as spin-up/spin-down couples.

Hybridization

For polyatomic molecules, the valence bond theory becomes a very poor approximation because the directionalities of the $2s$ and $2p$ orbitals is too restrictive to describe molecules with steric numbers ranging between 2 and 4. The example considered above of $\mathrm{H_2O}$ illustrates this rather dramatically! Let us consider an even simpler molecule, $\mathrm{BeH_2}$, which has a steric number of 2 and is linear. Let the atoms lie entirely along the z-axis in the arrangement $\mathrm{H{-}Be{-}H}$.

Although the Be atom has a ground-state electronic configuration of $1s^2 2s^2$, but if we "promote" one of the $2s$ electrons to a state with higher energy and allow its electronic structure to be $1s^2 2s 2p_z$, then the unpaired electrons in the $2s$ and $2p_z$ orbitals can combine with the unpaired electrons in each of the hydrogen atoms to form bonds. The energy needed to excite the electron in Be would be "repaid" by the energy gained in the formation of stable bonds. The two valence-bond wavefunctions we would construct would be

$$\psi_1(1,2) = C_1\left[\psi_{1s}^{H_1}(1)\psi_{2s}^{Be}(2) + \psi_{1s}^{H_1}(2)\psi_{2s}^{Be}(1)\right]\left[\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)\right] \tag{10.1.8}$$

$$\psi_2(1,2) = C_2\left[\psi_{1s}^{H_2}(1)\psi_{2p_z}^{Be}(2) + \psi_{1s}^{H_2}(2)\psi_{2p_z}^{Be}(1)\right]\left[\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)\right] \tag{10.1.9}$$

Unfortunately, even this simple scheme does not work entirely because the two $\mathrm{Be{-}H}$ bonds would be different due to their construction from different combinations of orbitals. By symmetry, however, we can see that the two $\mathrm{Be{-}H}$ bonds should be equivalent. A solution to this problem was proposed by Linus Pauling in the 1930s in the form of **orbital hybridization**, a scheme that we still use today.

Pauling used the fact that in the first and second periods, the $2s$ and $2p$ orbitals have similar energies. Indeed, for the H atom, the energies are exactly the same. Given that these energies are not that different, we can combine s and p orbitals and still have a valid solution of the Schrödinger equation. That is, a general orbital

$$\chi(r) = C_1\psi_{2s}(r) + C_2\psi_{2p_x}(r) + C_3\psi_{2p_y}(r) + C_4\psi_{2p_z}(r)$$

is also a solution of the Schrödinger equation with the same energy as a $2s$ or $2p$ orbitals individually (this is exactly true for H). In the case of $\mathrm{BeH_2}$, the external potential on the electrons in Be by the two hydrogens changes the energy levels and creates a near degeneracy between the $2s$ and $2p_z$ orbitals, hence, we are now free to combine the into linear combinations that are more suitable to the construction both of valence bond wavefunctions *and* MOs via the LCAO procedure.

sp Hybrid Orbitals

For Be, we now allow the s and p orbitals to mix and create two *hybrid* orbitals known as sp orbitals. The two new hybrid wavefunctions as linear combination of the functions for 2s and $2p_z$ (using Dirac Notation):

$$|\chi_i\rangle = a_1|2s\rangle + b_1|2p_z\rangle \tag{10.1.10}$$

$$|\chi_j\rangle = a_2|2s\rangle + b_2|2p_z\rangle \tag{10.1.11}$$

These two wavefunctions must be orthogonal.

$$\langle\chi_i|\chi_j\rangle = \delta_{ij}$$

Which can be separated into the following relationships:

$$\langle\chi_i|\chi_i\rangle = 1 \tag{10.1.12}$$

and

$$\langle\chi_j|\chi_j\rangle = 1 \tag{10.1.13}$$

and

$$\langle\chi_i|\chi_j\rangle = \langle\chi_j|\chi_i\rangle = 0 \tag{10.1.14}$$

Equations 10.1.12 and 10.1.13 are the **normality requirement** and Equation 10.1.14 is the **orthogonality requirement** for the new hybrid wavefunctions. Substituting 10.1.10 into 10.1.12 results in

$$\langle\chi_i|\chi_i\rangle = a_1^2\cancelto{1}{\langle 2s|2s\rangle} + a_1b_1\cancelto{0}{\langle 2s|2p_z\rangle} + a_1b_1\cancelto{0}{\langle 2p_z|2s\rangle} + b_1^2\cancelto{1}{\langle 2p_z|2p_z\rangle} = 1$$

and similarly for $\langle\chi_j|\chi_j\rangle$

$$\langle\chi_j|\chi_j\rangle = a_2^2\cancelto{1}{\langle 2s|2s\rangle} + a_2b_2\cancelto{0}{\langle 2s|2p_z\rangle} + a_2b_2\cancelto{0}{\langle 2p_z|2s\rangle} + b_2^2\cancelto{1}{\langle 2p_z|2p_z\rangle} = 1$$

results in the following relationships

$$\langle\chi_i|\chi_i\rangle = a_1^2 + b_1^2 = 1 \tag{10.1.15}$$

$$\langle\chi_j|\chi_j\rangle = a_2^2 + b_2^2 = 1 \tag{10.1.16}$$

and

$$\langle \chi_i | \chi_j \rangle = a_1 a_2 + b_1 b_2 = 0 \tag{10.1.17}$$

These are four unknowns and three equations. The fourth "constraint" is that we assume contribution of $|s\rangle$ is the same for both hybrid orbitals.

$$a_1 = a_2$$

Equations 10.1.15 to 10.1.17 revert to

$$a_1^2 + b_1^2 = 1 \tag{10.1.18}$$

$$a_1^2 + b_2^2 = 1 \tag{10.1.19}$$

$$b_1^2 = b_2^2 \tag{10.1.20}$$

Therefore

$$b_1 = -b_2$$

and

$$a_1 = b_1 \tag{10.1.21}$$

Insert Equation 10.1.21 into 10.1.20 to get

$$a_1 = \frac{1}{\sqrt{2}}$$

and the two hybrid orbitals are

$$\chi_1(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \tag{10.1.22}$$

$$\chi_2(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)] \tag{10.1.23}$$

Note that these orbitals are both normalized and orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \; ; \; \int |\chi_2(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_2(r) dV = 0$$

These orbitals appear as shown in Figure 10.1.3

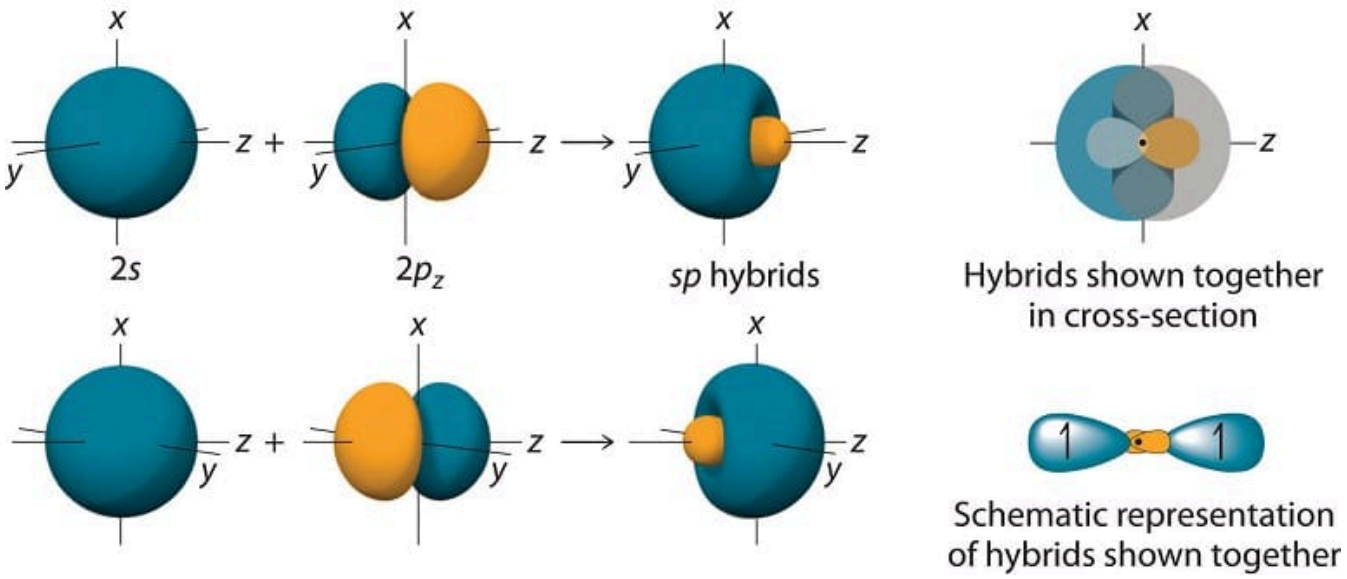


Figure 10.1.3 : The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

Given that the two sp hybrid orbitals are mirror images of each other, they can overlap with the $1s$ orbital of H (shown in the figure) and create two equal bonds, as needed for BeH_2. Using the valence bond formulation, now, one of the BeH bonds will be described by a wavefunction of the form:

$$\psi_1(1,2) = C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.24}$$

$$\psi_2(1,2) = C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.25}$$

In the above wavefunctions, it is clear that H_1 is on the right and H_2 is on the left, based on the directionalities of χ_1 and χ_2.

sp^2 Hybrid Orbitals

For trigonal planar molecules such as BH_3, we start with the electronic configuration of B, which is $1s^2 2s^2 2p_x$, and we promote one of the $2s$ electrons to a $2p_y$ orbital, so that we have $1s^2 2s 2p_x 2p_y$. Suppose the geometry of BH_3 is such that one of the hydrogen atoms lies along the positive x axis. The remaining hydrogen atoms would be in the 3rd and 4th quadrants, respectively (Figure 10.1.4).

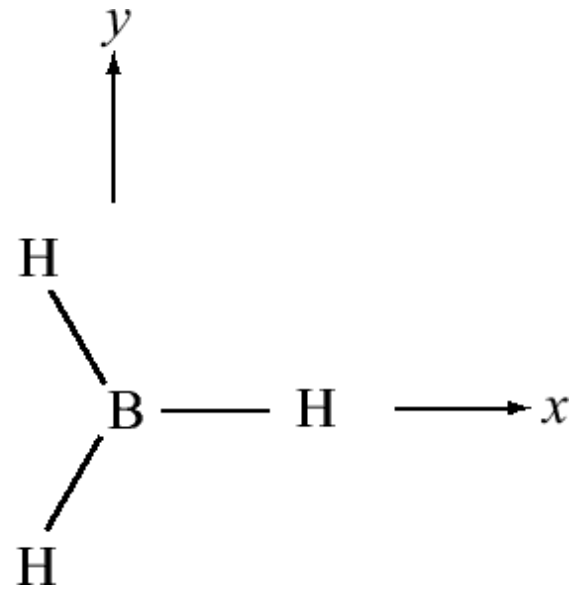


Figure 10.1.4: Geometry of BH_3.

If we simply combine the $2s$ with the $2p_x$ and $2p_y$ orbitals of boron, the resulting hybrid orbitals will not point in the correct direction. For this reason, we will create rotated versions of the p_x and p_y orbitals, which, as we will see are tantamount to taking new combinations of $2p_x$ and $2p_y$ orbitals to combine with the $2s$. Since the rotation occurs in the xy plane, the coordinate that controls this is the azimuthal angle ϕ. For the p_x and p_y orbitals, the ϕ dependence is

$$\psi_{2p_x} \sim \cos\phi \ ; \ \psi_{2p_y} \sim \sin\phi$$

If we rotate $2p_y$ by -30 degrees (Figure 10.1.5 ; blue is positive and red is negative), the ϕ dependence becomes

$$\psi_{2p_y}^{(rot)} \sim \sin(\phi + 30)$$

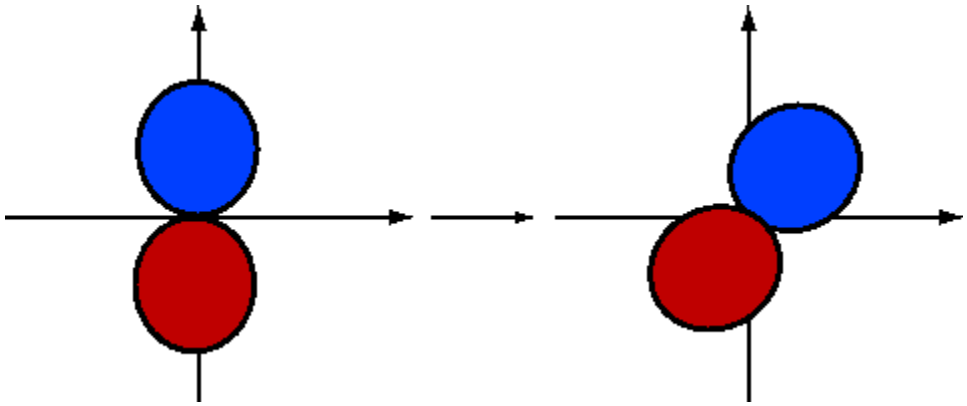


Figure 10.1.5: Rotation of a $2p_y$ orbital by -30 degrees.

Using the fact that

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm cos\alpha sin\beta$$

this rotation gives

$$\psi_{2p_y}^{(rot,1)} \sim \sin\phi\cos 30 + \cos\phi\sin 30 \tag{10.1.26}$$

$$\sim \left[\frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi\right] \tag{10.1.27}$$

$$\sim \left[\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x}\right] \tag{10.1.28}$$

Similarly, consider rotating $-\psi_{2p_y}$ by $+30$ degrees (Figure 10.1.6). This gives

$$-\psi_{2p_y}^{(rot,2)} \sim -\sin(\phi - 30) \tag{10.1.29}$$

$$\sim -\left[\frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi\right] \tag{10.1.30}$$

$$\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x} \tag{10.1.31}$$

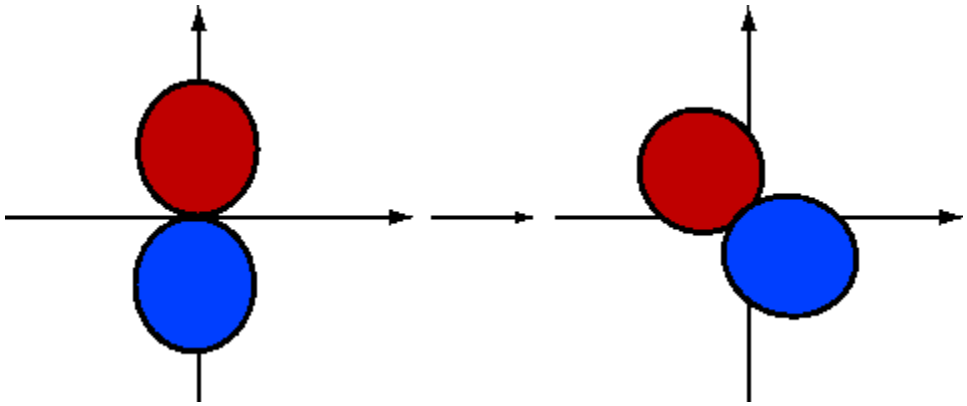


Figure 10.1.6: Rotation of a $-2p_y$ orbital by 30 degrees.

So, we now take the hybrid orbitals to be of the form

$$\chi_1(r) = a\psi_{2s}(r) - b\psi_{2p_x} \tag{10.1.32}$$

$$\chi_2(r) = c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \tag{10.1.33}$$

$$\chi_3(r) = c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r) \tag{10.1.34}$$

The coefficients a, b, and c are determined by requiring that the orbitals are normalized and mutually orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_2(r)dV = 0 \tag{10.1.35}$$

$$\int |\chi_2(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_3(r)dV = 0 \tag{10.1.36}$$

$$\int |\chi_3(r)|^2 dV = 1 \; ; \; \int \chi_2^*(r)\chi_3(r)dV = 0 \tag{10.1.37}$$

Carrying out the algebra, we obtain the following sp^2 hybrid orbitals:

$$\chi_1(r) = \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \tag{10.1.38}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.39}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.40}$$

The sp^2 hybrids allow bonding at 120° degrees, and these orbitals appear as shown in Figure 10.1.7:

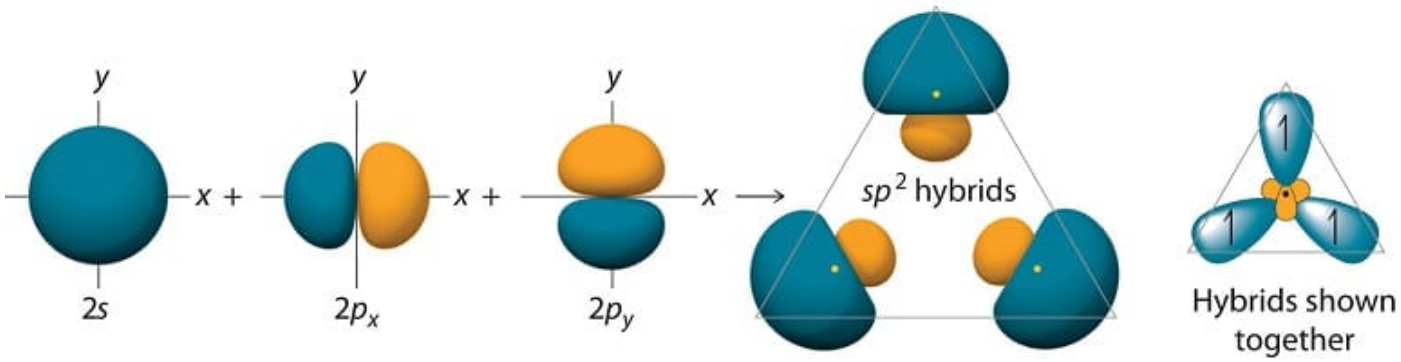


Figure 10.1.7: Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

The figure also shows the overlaps of these orbitals with the $1s$ orbitals of H.

sp^3 Hybrid Orbitals

Finally, we consider the case of methane CH_4. The electronic configuration of C is $1s^2 2s^2 2p_x 2p_y$. We now promote one of the $2s$ orbitals to the $2p_z$ orbital and write C as $1s^2 2s 2p_x 2p_y 2p_z$. We can now hybridize the $2s$ orbital with each of the $2p$ orbitals to create four hybrids:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.41}$$

$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.42}$$

$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.43}$$

$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.44}$$

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 10.1.8). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

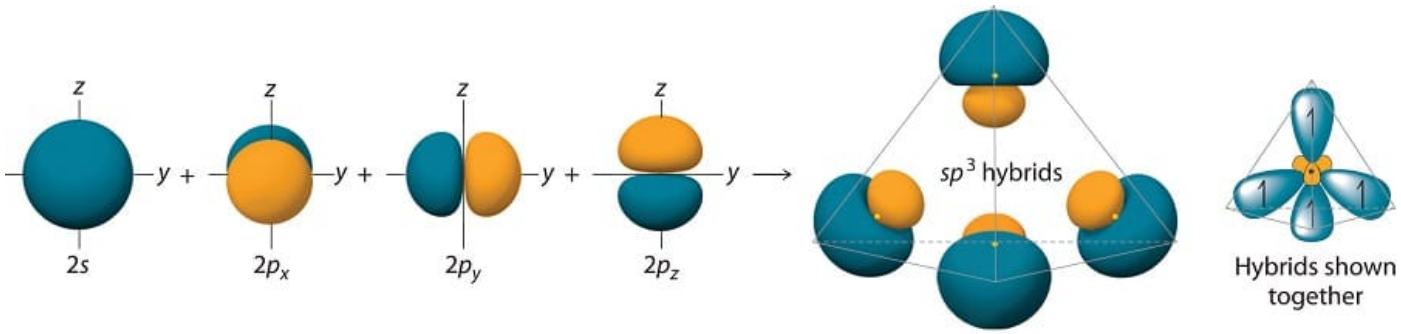


Figure 10.1.8 : Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Are hybrid orbitals Real?

Hybridization is an often misconceived concept. It only is a mathematical interpretation, which explains a certain bonding situation (in an intuitive fashion). In a molecule the equilibrium geometry will result from various factors, such as steric and electronic interactions, and further more interactions with the surroundings like a solvent or external field. The geometric arrangement will not be formed because a molecule is hybridized in a certain way, it is the other way around, i.e. a result of the geometry or more precise and interpretation of the wavefunction for the given molecular arrangement.

The justification we gave for invoking hybridization in molecules such as BeH_2, BF_3 and CH_4 was that the bonds in each are geometrically and chemically equivalent, whereas the atomic *s*- and *p*-orbitals on the central atoms are not. By combining these into new orbitals of *sp*, sp^2 and sp^3 types we obtain the required number of completely equivalent orbitals. This seemed easy enough to do on paper; we just drew little boxes and wrote "sp^2" or whatever below them. But what is really going on here?

The full answer is beyond the scope of this course, so we can only offer the following very general explanation. First, recall what we mean by "orbital": a mathematical function ψ having the character of a standing wave whose square ψ^2 is proportional to the probability of finding the electron at any particular location in space. The latter, the *electron density distribution*, can be observed (by X-ray scattering, for example), and in this sense is the only thing that is "real".

A given standing wave (ψ-function) can be synthesized by combining all kinds of fundamental wave patterns (that is, atomic orbitals) in much the same way that a color we observe can be reproduced by combining different sets of primary colors in various proportions. In neither case does it follow that these original orbitals (or colors) are actually present in the final product. So one could well argue that hybrid orbitals are not "real"; they simply turn out to be convenient for understanding the bonding of simple molecules at the elementary level, and this is why we use them.

Summary

The shape and bonding valecies of polyatomic molecules can be accounted for by hybrid orbitals. Molecular orbitals are formed from linear combinations of atomic orbitals which are similar in energy. These atomic orbitals could come from different atoms, or from the same atom. For example, the 2 sand 2patomic orbitals are very close energetically. When a linear combo of more than one atomic orbital from the **same atom** is formed, we have a hybrid orbital.

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10.2: Hybrid Orbitals in Water

The goal of applying Valence Bond Theory to water is to describe the bonding in $\mathrm{H_2O}$ and account for its structure (i.e., appropriate bond angle and two lone pairs predicted from VSEPR theory).

The ground state electronic configuration of atomic oxygen atom is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ and of course the ground state electronic configuration of atomic hydrogen atom is $1s^1$, i.e., a spherical atomic orbital with no preferential orientation. If only the unfilled $2p_y$ and $2p_z$ atomic orbitals of the oxygen were used as bonding orbitals, then two bonds would be predicted. These bonding wavefunctions would be mixture of only $|2p_y\rangle$ and $|2p_z\rangle$ orbitals on oxygen and the $|1s\rangle$ orbitals on the hydrogens (H_1 and H_2):

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + b_1|2p_y\rangle_O \tag{10.2.1}$$

$$|\chi_2\rangle = a_2|1s\rangle_{H_2} + b_2|2p_z\rangle_O \tag{10.2.2}$$

However, with a $\mathrm{H{-}O{-}H}$ bond angle for these bonds would be expected to be 90° since $2p_y$ and $2p_z$ are oriented 90° with respect to each other. Note that $|\chi_1\rangle$ and $|\chi_2\rangle$ are two-center bonding orbitals common to Valence Bond theory.

alt

Figure 10.2.1 : The three p-orbitals are aligned along perpendicular axis (CC-SA-BY-NC; Nick Greeves via ChemTube3D);

Using the oxygen atomic orbitals directly is obviously not a good model for describing bonding in water, since we know from experiment that the bond angle for water is 104.45° (Figure 10.2.2), which is also in agreement with VSEPR theory. Since the $2s$ orbital is spherical, mixing some $2s$ character into the $2p_z$ orbitals can adjust the bond angle as discussed previously by creating new hybrid orbitals.

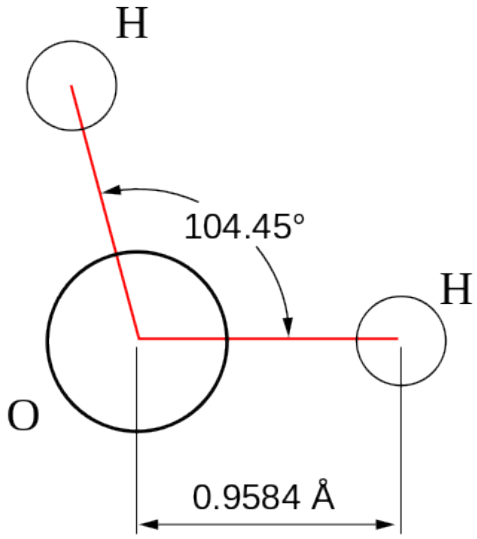


Figure 10.2.2 : Experimentally determined geometry of the water molecule (CC BY-SA 3.0; Booyabazooka).

Historically, Valence Bond theory was used to explain bend angles in small molecules. Of course, it was only qualitatively correct in doing this, as the following example shows. Let us construct the Valence Bond wavefunctions for the two bonding pairs in H_2O by mixing the $|2s\rangle$, $|2p_x\rangle$, $|2p_y\rangle$, and $|2p_z\rangle$ into four new sp^3 hybrid orbitals:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right]$$
$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right]$$
$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right]$$
$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right]$$

Hence, the three $2p$ orbitals of the oxygen atom combined with the $2s$ orbitals of the oxygen to form four sp^3 hybrid orbitals (Figure 10.2.3).

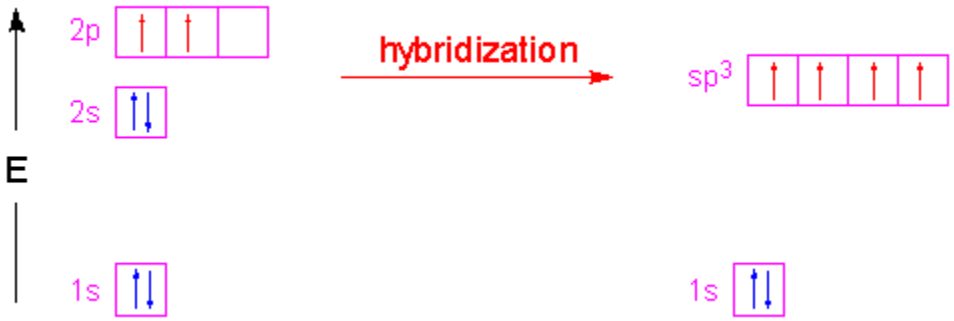


Figure 10.2.4: This would leave the $2s$ and $2p_z$ orbitals of oxygen left over for the two lone pairs on the oxygen.

The bond angle for four groups of electrons around a central atom is 109.5 degrees. However, for water the experimental bond angle is 104.45°. The VSPER picture (general chemistry) for this is that the smaller angle can be explained by the presence of the two lone-pairs of electrons on the oxygen atom. Since they take up more volume of space compared to a bonding pair of electrons the repulsions between lone pairs and bonding pairs is expected to be greater causing the H-O-H bond angle to be smaller than the ideal 109.5°.

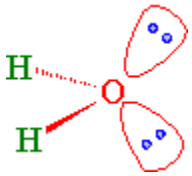


Figure 10.2.4 : Among the four hybrid orbitals, two are half filled and the remaining two are completely filled.

We can rationalize this by thinking about the s and p characters of the hybrids. In a perfectly sp^3 hybridized set of hybrid orbitals, each sp^3 orbital should have: 25% s character and and 75% p character. Since the bond angle is not 109.5° in water, the hybrid orbitals cannot have exactly this ratio of s and p character. So there there is uneven distribution of s and p character between the 4 hybrid orbitals. First we will write down the wavefunction and see what this means and then we will rationalize it.

Estimating Character of Hybrid Orbitals

The terminology we use for hybridization actually is just an abbreviation:

$$\mathrm{sp}^x = \mathrm{s}^{\frac{1}{x+1}}\mathrm{p}^{\frac{x}{x+1}}$$

In theory x can have any value, hence any of the following combinations constitute valid hybridization schemes for 1 s orbital and 3 p orbitals:

$$\begin{aligned} 1\times\mathrm{s}, 3\times\mathrm{p} &\rightsquigarrow 4\times\mathrm{sp}^3 \\ &\rightsquigarrow 3\times\mathrm{sp}^2, 1\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}, 2\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}^3, 1\times\mathrm{sp}, 1\times\mathrm{p} \\ &\rightsquigarrow \text{etc. pp.} \\ &\rightsquigarrow 2\times\mathrm{sp}^4, 1\times\mathrm{p}, 1\times\mathrm{sp}^{(2/3)} \end{aligned}$$

There are virtually infinite possibilities of combinations. Which one is "valid" is only determined by experiment (e.g., structure or spectroscopy). The generic sp^x hybrid orbitals wavefunction can be roughly written in terms of atomic orbital character:

$$|\chi_i\rangle = N(p + \gamma s) \tag{10.2.3}$$

where N is a normalization constant and γ is the relative contribution of s character to the hybrid orbital. For a pure sp^3 hybrid, γ would be 0.25 and for a pure sp hybrid, γ would be 1. The question is how to determine γ to get a better picture of the hybridization of water. Starting with the normalization criteria for wavefunctions:

$$\langle \chi_i | \chi_i \rangle = 1$$

and substituting Equation 10.2.3 into to get

$$\langle N(p + \gamma s) | N(p + \gamma s) \rangle = 1$$

which in integral notation is

$$\int N^2 (p + \gamma s)^2 d\tau = 1$$

where $d\tau$ represents all space. This is then expanded to

$$N^2 \cancelto{1}{\int p^2 \, d\tau} + N^2 2\gamma \cancelto{0}{\int sp \, d\tau} + N^2 \gamma^2 \cancelto{1}{\int s^2 \, d\tau} = 1 \tag{10.2.4}$$

These terms simplify either due to orthogonality or normality of the constitute atomic orbitals. Equation 10.2.4 simplifies to

$$N^2 + N^2 \gamma^2 = 1$$

and thus the normalization factor can be expressed in terms of γ

$$N = \frac{1}{\sqrt{1 + \gamma^2}}$$

and the generic normalized sp^x hybrid orbital (Equation 10.2.3) is

$$|\chi_i\rangle = \frac{1}{\sqrt{1 + \gamma^2}} (p + \gamma s) \tag{10.2.5}$$

The s and p characters to a hybrid orbital are now easy to obtain by squaring $|\chi_i\rangle$

- The magnitude of p-character is

$$\left(\frac{1}{\sqrt{1 + \gamma^2}} \right)^2 = \frac{1}{1 + \gamma^2} \tag{10.2.6}$$

  as $\gamma \to 0$, then the p character of the hybrid goes to 100%
- The magnitude of s-character is

$$\left(\frac{1}{\sqrt{1 + \gamma^2}} \gamma^2 \right)^2 = \frac{\gamma^2}{1 + \gamma^2} \tag{10.2.7}$$

  as $\gamma \to 1$, then the s character of the hybrid goes to 50%

As mentioned above, the geometric arrangement will **not** be formed because a molecule is hybridized in a certain way, it is the other way around. How do we choose the correct value of γ for the hybrid orbitals? The mixing coefficient γ is clearly related to the bond angle θ. Using some simple trigonometric relationships, it can be proven that:

$$\cos \theta = -\gamma^2 \tag{10.2.8}$$

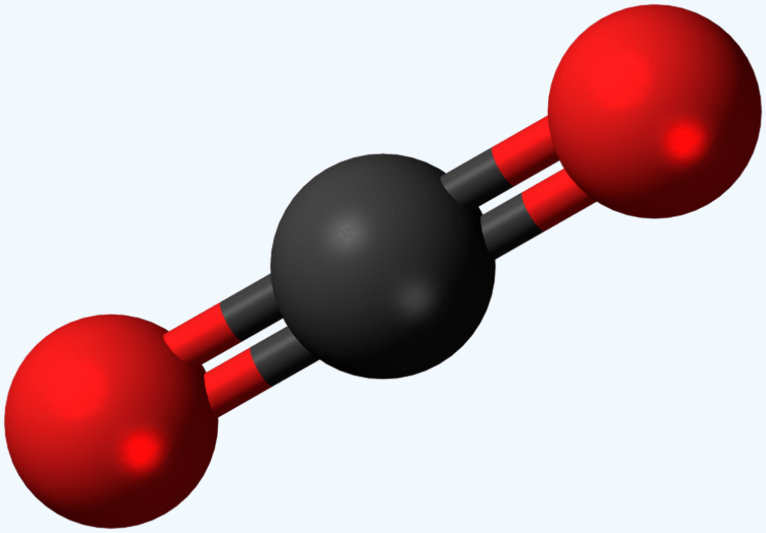
Equation 10.2.8 is an important equation as it related experimentally determined structure to the nature of the bonding and specifically, the composition of the atomic orbitals that create the hybrid orbitals used in the bonding.

Example 10.2.1 : Carbon Dioxide

What is the s-character in the hybrid orbitals for CO_2.

Solution

We know from simple VSEPR theory that the geometry of CO_2 is a linear triatomic molecule.



Thus $\theta = 180\ ^\circ$ and via Equation 10.2.8, $\gamma = 1$ since $\cos 180\ ^\circ = -1$. Hence, Equation 10.2.7 argues that the hybrid orbitals used in the bonding of CO_2 have 50% character; i.e., they are sp hybrid orbitals

$$|\chi_1\rangle = \frac{1}{\sqrt{2}}(s+p)$$

and

$$|\chi_2\rangle = \frac{1}{\sqrt{2}}(s-p)$$

Now, let's apply Equation 10.2.7 to water to find the character of the hybrid orbitals in water. The bond angle in water is 104.45° (Figure 10.2.2) hence

$$\cos 104.5° = -0.25$$

and

$$\gamma = \sqrt{0.25} = 0.5$$

From Equation 10.2.6, then the amount of p character in the hybrid orbitals are

$$\frac{1}{1+\gamma^2} = \frac{1}{1+0.5^2} = 0.80\%$$

which leave 20% for s character (Equation 10.2.7).

$$\frac{\gamma^2}{1+\gamma^2} = \frac{0.5^2}{1+0.5^2} = 0.20$$

The two hybridized atomic orbitals of oxygen involved in bonding are each 80% p and 20% s character. This are not perfect sp^3 hybrid orbitals, as expected. Actually, the orbitals involved in the bonds would be better described as sp^4 hybridized. It does not mean that there are 4 p-orbitals in the hybrid orbital, but that each hybrid consists of 20% of s and 80% of p atomic orbitals.

Lone Pairs

Water has two sets of non-bonding electron pairs (Figure 10.2.4). Without a bond angle to start from, we cannot derive γ that describes the nonbonding hybrid orbitals that they occupy. However, we do know that the O atom has three p orbitals. So the TOTAL absolute p-character in all hybrid orbitals must be 3.

Let x be the p-character in the lone pairs hybrid orbitals:

$$0.8 + 0.8 + x + x = 3$$

This is assuming the lone pairs are **identical**. Solving for this, x = 0.7 (i.e. 70% p and 30% s). From this we can estimate the angle between the lone pair using Equations 10.2.6 and 10.2.8

- p-character:

$$\frac{1}{1+\gamma^2} = 0.7$$

so

$$-\gamma^2 = \frac{1}{0.7-1} = -0.42$$

and $\theta = 115\ °$.

The angle between the lone pairs is greater (115°) than the bond angle (104.5°). The sp^3 hybrid atomic orbitals of the lone pairs have > 25% s-character. These hybrid orbitals are less directional and held more tightly to the O atom. The sp^3 hybrid atomic orbitals of the bonding pairs have < 25% s-character. They are more directional (i.e., more p-character) and electron density found in the bonding region between O and H.

Warning

It should be noted that the valence bond theory application described above predicts that the two lone electron pairs are in the same hybrid orbitals and hence have the same energies. As discussed in the next sections, that is not experimentally observed in photoelectron spectroscopy, which is a shortcoming of valence bond theory's application to water.

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10.3: BeH_2 is Linear and H_2O is Bent

In this section, we will construct approximate molecular orbitals for a water molecule by considering a simple linear triatomic of the general form HXH, where X is a second row element. We will take a multi-centered molecular orbital approach instead of the two-centered valence bond/hybrid approach discussed previously. As with previous discussions of Molecular Orbitals, we approximate them as a linear combinations of atomic orbitals (LCAO). In molecular orbital theory linear combinations of **all** available (atomic) orbitals will form molecular orbitals. These are spread over the whole molecule, or delocalized, and in a quantum chemical interpretation they are called canonical orbitals. Since it is absolutely wrong to assume that there are only three types of sp^x hybrid orbitals, it is possible, that there are multiple different types of orbitals involved in bonding for a certain atom.

AH_2 Molecules

We want to construct a reasonable argument for the energetic ordering and structure of the molecular orbitals. We first note that each H will donate a $1s$ orbital in the LCAO scheme, and A will likely donate at least $2s$ and possible $2p$ orbitals, depending on its chemical identity. In general, if we consider only the first row A elements, the molecule orbitals (via the LCAO) can be expressed as combination of $1s$ orbitals on the two Hydrogens (H_1 and H_2) and the four n=2 orbitals ($2s$ $2p_x$ $2p_y; 2p_z$) on the A atom:

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_2|1s\rangle_{H_2} + a_3|2s\rangle_A + a_4|2p_x\rangle_A + a_5|2p_y\rangle_A + a_6|2p_z\rangle_A \tag{10.3.1}$$

These molecular orbitals were created with six atomic orbitals and hence six different $|\chi\rangle$ molecular orbitals can be created. As with previous molecular orbitals problems, the coefficients of this expansion ($\{a_i\}$) are determined by solving the secular determinant.

If we consider only linear AH_2 molecules, then Equation 10.3.1 can be simplified by ignoring $2p_x$ and $2p_y$ atomic orbitals since they are perpendicular to the bonds and are hence non-bonding (only for linear AH_2 molecules). Moreover, the molecule is symmetric about the center (the position of A), hence the orbitals have to have the same symmetry.

Only the $2p$ orbital of A that will overlap with $1s$ of H is the $2p_z$. Hence, Equation 10.3.1 can be simplified to consider the combination

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A + a_6|2p_z\rangle_A \tag{10.3.2}$$

Note that the two coefficients in front of the $1s$ orbitals of hydrogen are the same by symmetry. This since no hydrogen is "special" and they must have the same contribution to the molecular orbital.

Mixing Amplitudes

How big should the $2s$ orbital contributors of A be compared to the $1s$ orbital of H?

This depends on several things. First, is the nuclear charge on A and the second is the **electronegativity** difference between H and A. The first determines how quickly the $2s$ orbitals, remembering that the exponential part is $exp(-Zr/a_0)$, and the electronegativity difference determines the relative magnitude of H_1 compared to H_2.

The six $|\chi\rangle$ molecular orbitals from Equation 10.3.1 are shown in Figure 10.3.1 .

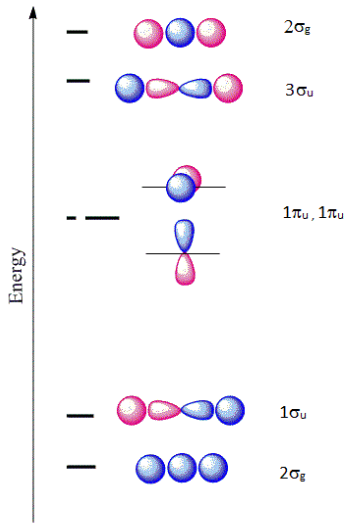


Figure 10.3.1 : The six molecular orbitals for the $\mathrm{AH_2}$ molecule constrained to a linear geometry. The symmetry labels for each molecular orbital are indicated.

The first molecular orbital $|\chi_1\rangle$ constructed from Equation 10.3.1 is purely bonding because the $2s$ orbital is positive near the A nucleus, but becomes negative as we go away from the nucleus. This orbital is also even (*garade symmetry*), so we can denote it as a $2\sigma_g$ orbital signifying that it is constructed from a $2s$ orbital of A combined with the two $1s$ orbitals of H. The only other MO that can be constructed that has the right symmetry is $|\chi_6\rangle$ which is denoted as $2\sigma_u$. This is an antibonding molecular orbital and is also even (*garade symmetry*). The corresponding wavefunctions are:

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A$$

$$|\chi_6\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} - a_3|2s\rangle_A$$

Next, if we combine a $2p_z$ orbital of A with the $1s$ of H, there are two possibilities that have the right symmetry. The first is

$$|\chi_2\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

which is a bonding orbital and denoted as $1\sigma_u$. This is purely antibonding and has an odd symmetry (*ungarede*). The other combination is

$$|\chi_5\rangle = a_1|1s\rangle_{H_1} - a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

Hence, we denote this as $2\sigma_g$. The orbitals $2p_x$ and $2p_y$ from X are nonbonding and become π_{2p_x} and π_{2p_y} nonbonding orbitals and designated as $1\pi_u$ orbitals:

$$|\chi_3\rangle = |2p_x\rangle_A$$

$$|\chi_4\rangle = |2p_y\rangle_A$$

Beryllium Hydride (BeH_2) is Linear

Consider the $\mathrm{BeF_2}$ molecule: Be has a $1s^2\ 2s^2$ electron configuration with is no unpaired electrons available for bonding. From a perspective of using only atomic orbitals to generate the bonding orbitals, we would conclude that the molecule could not exist since no free orientals exist on Be atom to bond. Clearly, atomic orbitals are not adequate to describe orbitals in molecules, but this can be solved by allowing the 2s and one 2p orbital on Be to mix to form sp hybrid orbitals. The experimental $\mathrm{H{-}Be{-}H}$ bond angle is 180°. Presumably, one electron from Be is shared with each unpaired electrons from H. We could promote and electron from the 2s orbital on Be to the 2p orbital to get two unpaired electrons for bonding (predicting 90° bond angles, not 180°). Thus the geometry is still not explained with atomic orbitals alone.

Be has 2s and 2p orbitals, and it is in the middle. H has 1s orbitals; there are two H atoms on the outside. We initially make

combinations of the H atomic orbitals that we previously used to make diatomic hydrogen, except there is no overlap (i.e., $S = 0$). These combinations will mix with the 2s and $2p_z$ on Be, as shown in Figure 10.3.2.

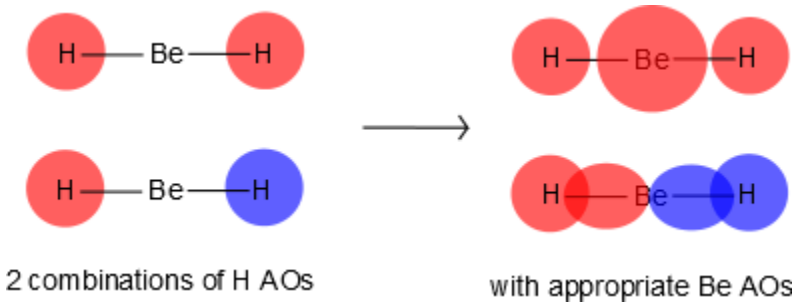


Figure 10.3.2: Forming molecular orbitals for $\mathrm{BeH_2}$.

Then we can put the Molecular Orbital diagram together, starting with the outside, drawing in bonding, non-bonding and anti-bonding MOs, and filling the electrons (Figure 10.3.3). The bond order is 2.

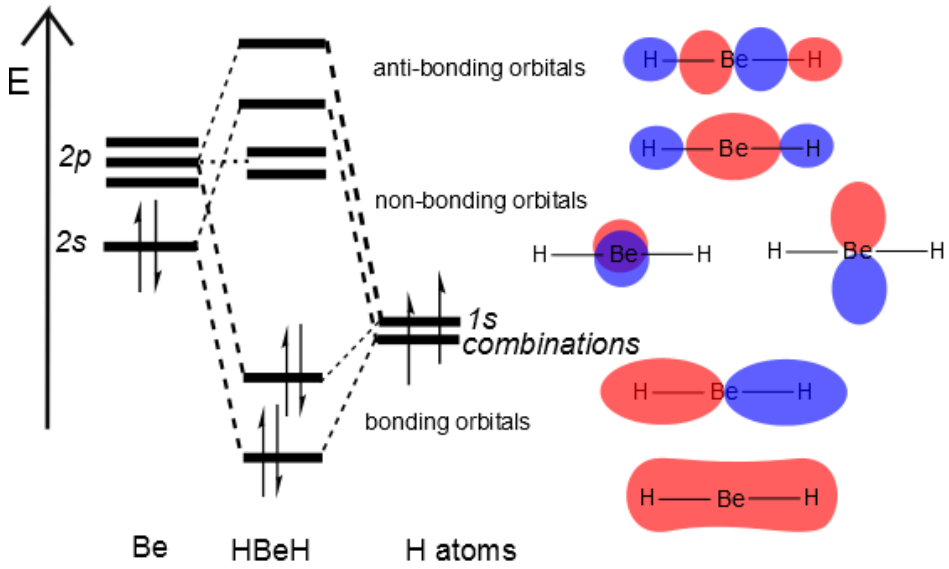


Figure 10.3.3: Molecular orbitals diagram for $\mathrm{BeH_2}$.

Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital energies of a molecule versus a distortion coordinate, used for making quick predictions about the geometries of small molecules. By plotting the change in molecular orbital levels of a molecule as a function of geometrical change, Walsh diagrams explain why molecules are more stable in certain spatial configurations (i.e. why water adopts a bent conformation).

Walsh Correlation Diagrams

A major application of Walsh diagrams is to explain the regularity in structure observed for related molecules having identical numbers of valence electrons (i.e. why $\mathrm{H_2O}$ and $\mathrm{H_2S}$ look similar), and to account for how molecules alter their geometries as their number of electrons or spin state changes. Additionally, Walsh diagrams can be used to predict distortions of molecular geometry from knowledge of how the LUMO (Lowest Unoccupied Molecular Orbital) affects the HOMO (Highest Occupied Molecular Orbital) when the molecule experiences geometrical perturbation. Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.

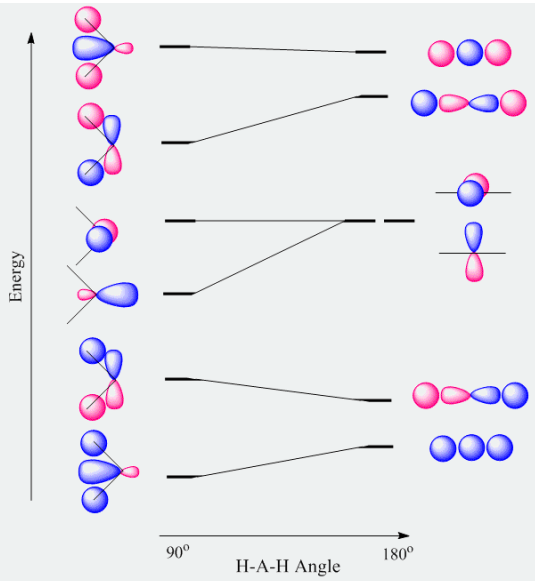


Figure 10.3.4: A Walsh diagram for an AH_2 molecule. (public domain).

For the AH_2 molecular system, Walsh produced the first angular correlation diagram by plotting the orbital energy curves for the canonical molecular orbitals while changing the bond angle from 90° to 180° (Figure 10.3.4). As the bond angle is distorted, the energy for each of the orbitals can be followed along the lines, allowing a quick approximation of molecular energy as a function of conformation.

A typical prediction result for water is an bond angle of 90°, which is not even close to the experimental value of 104°. At best, the method is able to differentiate between a bent and linear molecule.

> Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.

Figure 10.3.4 illustrates the difference between the actual linear case we just analyzed and the truly bent molecule, e.g. H_2O. The geometry changes the ordering somewhat, but the qualitative picture we obtain from the linear case makes it a useful construction. The oxygen atomic orbitals are labeled according to their symmetry (Figure 10.3.5) as a_1 for the 2s orbital and b_1 ($2p_x$), b_2 ($2p_y$) and a_1 ($2p_z$) for the three 2p orbitals. The two hydrogen 1s orbitals are premixed to form a_1 and b_2 molecular orbitals.

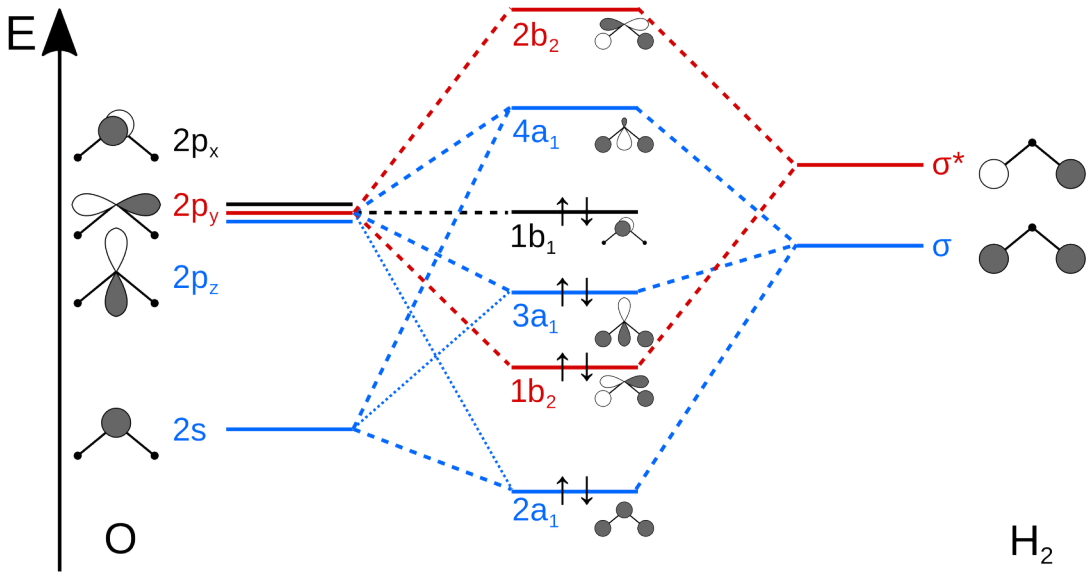


Figure 10.3.5: MO diagram for water. (CC-SA-BY-3.0; Officer781 via Wikipedia).

Mixing takes place between same-symmetry orbitals of comparable energy resulting a new set of MO's for water:

- $2a_1$ MO from mixing of the oxygen 2s atomic orbital and the hydrogen σ MO. Small oxygen $2p_z$ atomic orbital admixture strengthens bonding and lowers the orbital energy.
- $1b_2$ MO from mixing of the oxygen $2p_y$ atomic orbital and the hydrogen σ* MO.
- $3a_1$ MO from mixing of the oxygen $2p_z$ atomic orbital and the hydrogen σ MO. Small oxygen 2s atomic orbital admixture weakens bonding and raises the orbital energy.
- $1b_1$ nonbonding MO from the oxygen $2p_x$ atomic orbital (the p-orbital perpendicular to the molecular plane).

In the water molecule the highest occupied orbital, $(1b_1)$ is non-bonding and highly localized on the oxygen atom, similar to the non-bonding orbitals of hydrogen fluoride. The next lowest orbital $(2a_1)$ can be thought of as a non-bonding orbital, as it has a lobe pointing away from the two hydrogens. From the lower energy bonding orbitals, it is possible to see that oxygen also takes more than its "fair share" of the total electron density. The electronic configuration of water in the ground state (Figure 10.3.5) is therefore

$$(a_1)^2(b_2)^2(a_1)^2(b_1)^2$$

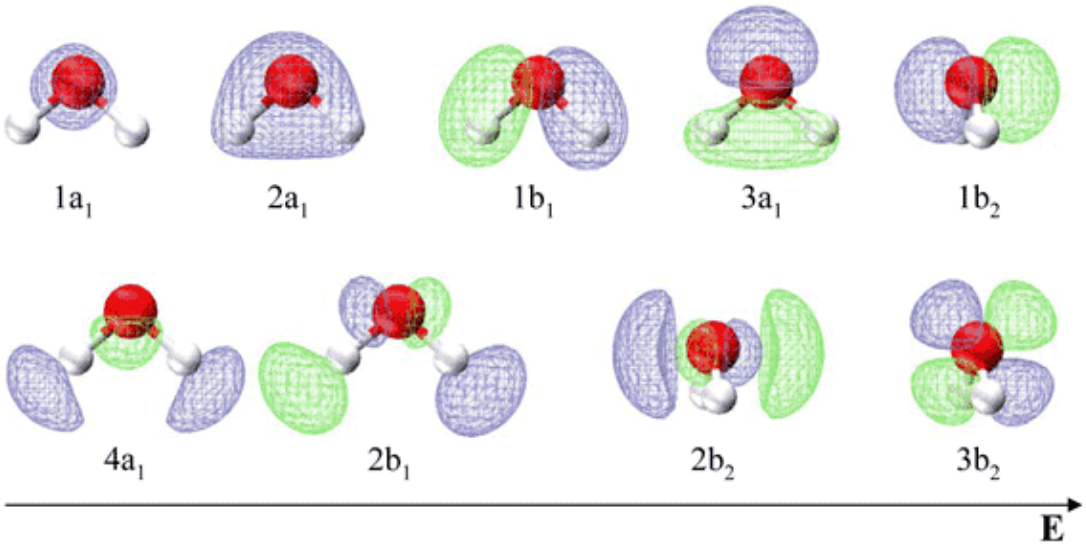


Figure 10.3.5. Image from Anna Krylov (USC)

Table 10.3.1 list the respective LCAO coefficients for the six atomic orbitals. Table 10.3.1 combines the energy values with the description derived from the character table for molecules of point group C_{2v}

Table 10.3.1: LCAO Coefficients of first six molecular orbitals of water

Energy	Symbol	s(H)	s(O)	p_x(O)	p_y(O)	p_z(O)	s(H)
6.728	$2b_2$	0.525	0	0	-0.669	0	-0.525
5.440	$3a_1$	-0.553	0.306	0	0	-0.544	0.553
-12.191	$1b_1$	0	0	-1.000	0	0	0
-14.467	$2a_1$	-0.309	0.354	0	0	0.827	-0.309
-19.113	$1b_2$	-0.473	0	0	-0.743	0	0.473
-40.032	$1a_1$	0.315	0.884	0	0	-0.143	0.315

Note in contrast to the valence bond theory discussed previous for water, the two lone electron pairs are **not in identical orbitals**. The $1b_1$ MO is a lone pair, while the $3a_1$, $1b_2$ and $2a_1$ MO's can be localized to give two O–H bonds and an in-plane lone pair. This is in agreement with the experimentally measured photoelectron spectrum discussed in the next section.

Summary

Walsh correlation diagram is a plot of molecular orbital energy as a function of some systematic change in molecular geometry. For example, the correlation between orbital energies and bond angle for an $\mathrm{AH_2}$ molecule. The geometry of a molecule is determined by which possible structure is lowest in energy. We can use the Walsh diagram to determine the energy trends based on which orbitals are occupied.

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10.4: Photoelectron Spectroscopy

Learning Objectives

- Demonstrate how photoelectron spectroscopy can be used to resolve the absolute energies of molecular orbitals.

Photoelectron spectroscopy (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

- **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels.
- **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.

Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:

$$E = h\nu \tag{10.4.1}$$

where h is Planck constant and ν is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the topic of this page.

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy). In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

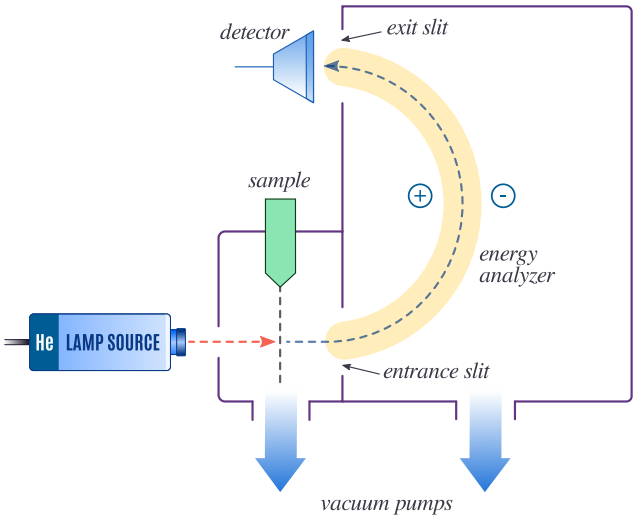


Figure 10.4.1: Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit. (CC BY 4.0; Ümit Kaya via LibreTexts)

The process of photoionization can be considered in several ways. One way is to look at the overall process for a species A:

$$A + \text{photon} \rightarrow A^{+} + e^{-} \tag{10.4.2}$$

Conservation of energy then requires that (after using Equation 10.4.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{10.4.3}$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^-) = KE$$

Equation 10.4.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - \left[E(A^+) - E(A)\right] \tag{10.4.4}$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the **vertical ionization energy** (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE \tag{10.4.5}$$

or

$$IE = h\nu - KE \tag{10.4.6}$$

The vertical ionization energy is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (i.e., a free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

Note

Equation 10.4.5 may look familiar to you as it the same equation Einstein used to describe the photoelectric effect except the vertical ionization energy (IE) is substituted for workfunction Φ. Both vertical ionization energy and workfunctions are metrics for the binding energy of an electron in the sample.

At a fundamental level, ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the molecular orbitals detailed and specific quantitative information regarding the electronic structure and bonding in molecules.

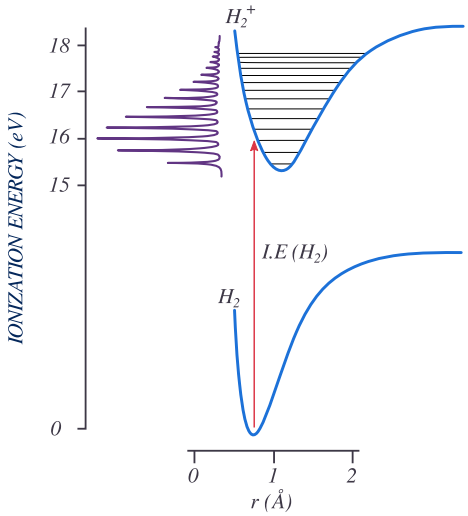


Figure 10.4.2: Vertical ionization process for molecular hydrogen. (CC BY 4.0; Ümit Kaya via LibreTexts)

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 10.4.6 and as illustrated in the Figure 10.4.2. Nonetheless, the information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals by Koopmans' theorem, which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the *vertical ionization energy* to the ion state formed by removal of an electron from that orbital (Figure 10.4.3), provided the distributions of the remaining electrons do not change (i.e., frozen).

$$I_j = -\epsilon_j \tag{10.4.7}$$

There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.

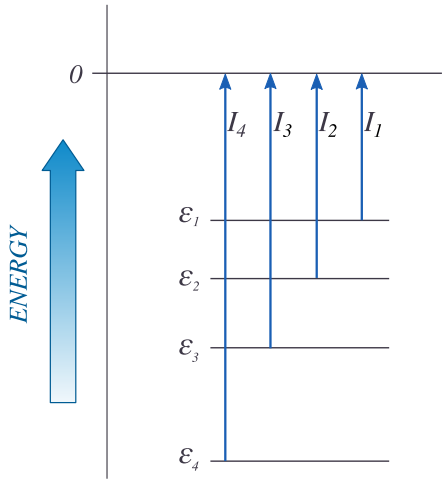


Figure 10.4.3: Within Koopmans' Theorem, the energies of the orbitals ϵ have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization potential (I). (CC BY 4.0; Ümit Kaya via LibreTexts)

Koopmans' Theorem

Koopmans' theorem argues that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital.

Several different ionization energies can be defined, depending on the degree of vibrational excitation of the cations. In general, the following two types of ionization energies are considered (Figure 10.4.4):

- Adiabatic ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''= 0) + h\nu \rightarrow M^+(x, v' = 0) + e^-$$

  Adiabatic ionization energy that is, the minimum energy required to eject an electron from a molecule in its ground vibrational state and transform it into a cation in the lowest vibrational level of an electronic state x of the cation.
- Vertical ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''= 0) + h\nu \rightarrow M^+(x, v' = n) + e^-$$

where, the value n of the vibrational quantum number v' corresponds to the vibrational level whose wavefunction gives the largest overlap with the v" = 0 wavefunction. This is the most probable transition and usually corresponds to the vertical transition where the internuclear separations of the ionic state are similar to those of the ground state.

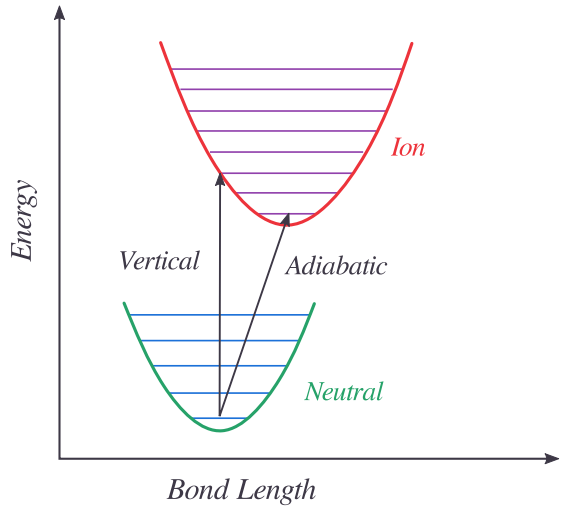


Figure 10.4.4: Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system. (CC BY 4.0; Ümit Kaya via LibreTexts)

The geometry of an ion may be different from the neutral molecule. The measured ionzation energy in a PES experiment can refer to the vertical ionization energy, in which case the ion is in the same geometry as the neutral, or to the adiabatic ionzaiton energy, in which case the ion is in its lowest energy, relaxed geometry (mostly the former though). This is illustrated in the Figure 10.4.4. For a diatomic the only geometry change possible is the bond length. The figure shows an ion with a slightly longer bond length than the neutral. The harmonic potential energy surfaces are shown in green (neutral) and red (ion) with vibrational energy levels. The vertical ionzation energy is **always greater** than the adiabatic ionzation energy.

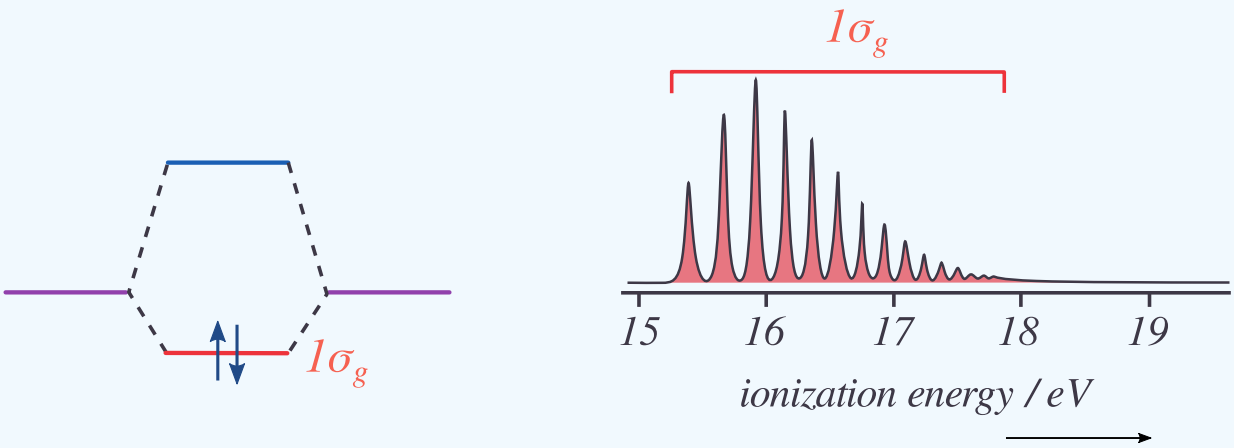
Differing Ionization Energies

You have been exposed to three metrics of ionization energies already, which are similar, but with distinct differences:

- The *ionization energy* (also called *adiabatic ionization energy*) is the lowest energy required to effect the removal of an electron from a molecule or atom, and corresponds to the transition from the lowest electronic, vibrational and rotational level of the isolated molecule to the lowest electronic, vibrational and rotational level of the isolated ion.
- The *binding energy* (also called *vertical ionization energy*) is the energy change corresponding to an ionization reaction leading to formation of the ion in a configuration which is the same as that of the equilibrium geometry of the ground state neutral molecule.
- The *workfunction* is the minimum energy needed to remove an electron from a (bulk) solid to a point in the vacuum.

Example 10.4.1: Molecular Hydrogen

As you remember, the molecular orbital description of molecular hydrogen involves two $|1s\rangle$ atomic orbitals generating a bonding $1\sigma_g$ and antibonding $2\sigma_u^*$ molecular orbitals. The two electrons that are responsible for the H_2 bond are occupied in the $1\sigma_g$.

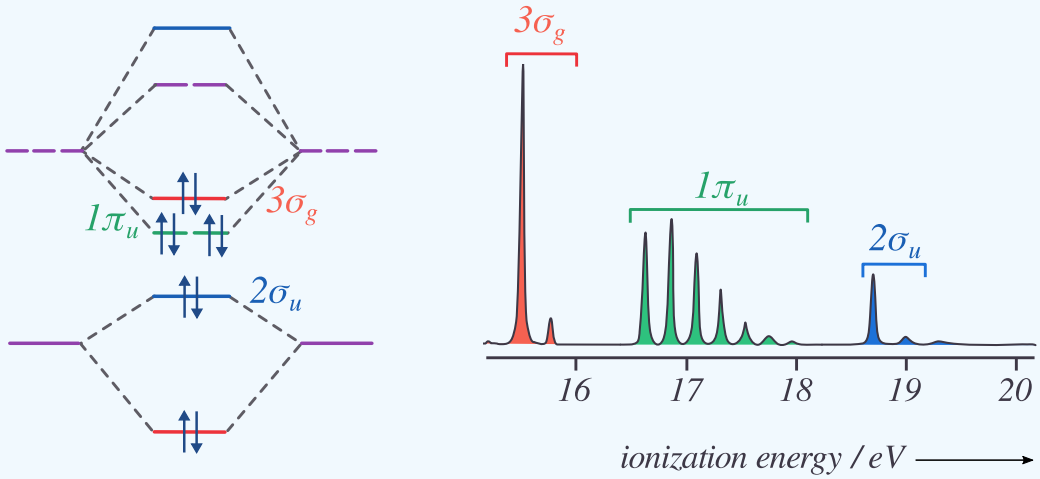


MO diagram and PES spectrum of H_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

The PES spectrum has a single band that corresponds to the ionization of a $1\sigma_g$ electron. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length since the bond order has been reduced).

Example 10.4.2: Molecular Nitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Four molecular orbitals are occupied (the two $1\pi_u$ orbitals are both occupied). The UV photoelectron spectrum of N_2, has three bands corresponding to $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ occupied molecular orbitals. Both $3\sigma_g$ and $2\sigma_u$ are weakly bonding and antibonding. The $1\sigma_g$ orbital is not resolved in this spectrum since the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital.



MO diagram and PES spectrum of N_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

Note that extensive vibrational structure for the $1\pi_u$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

Hydrogen Chloride

The molecular energy level diagram for HCl is reproduced in Figure 10.4.5

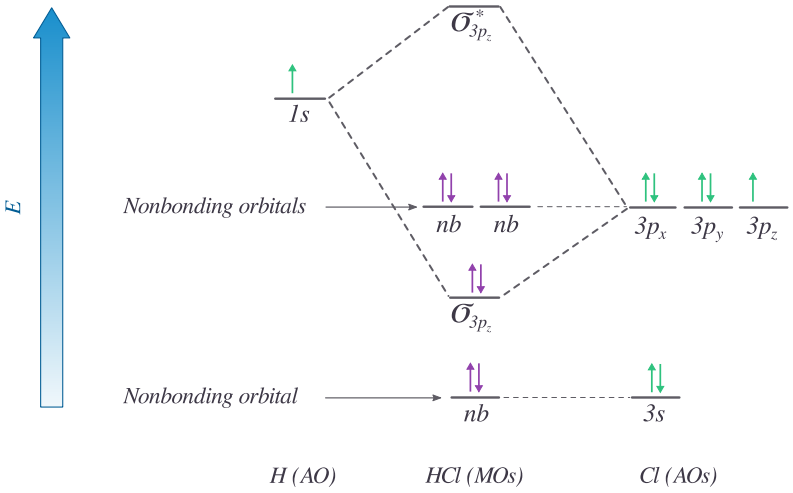


Figure 10.4.5: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1. (CC BY 4.0; Ümit Kaya via LibreTexts)

Important aspects of molecular orbital diagram in Figure 10.4.5:

- The H 1s energy lies well above the Cl 2s and 2*p* atomic orbitals;
- The valence electron configuration can be written $3\sigma^2 1\pi^4$;
- The H 1s orbital contributes only to the σ molecular orbitals, as does one of the Cl 2*p* orbitals (hence the lines in Figure 10.4.5 connecting these atomic orbitals and the 3σ and 4σ molecular orbitals);
- The remaining Cl 2*p* orbitals (ie those perpendicular to the bond axis) are unaffected by bonding, and these form the 1π molecular orbitals;
- The 1π orbitals are nonbonding - they are not affected energetically by the interaction between the atoms, and are hence neither bonding nor antibonding;
- The 3σ orbital is weakly bonding, and largely Cl 2*p*;
- The 3σ* orbital is antibonding, and primarily of H 1s character;

Figure 10.4.6 shows the analogous MO diagram and photoelectron spectrum for HCl. The spectrum has two bands corresponding to non-bonding 1*p* (or 1π) molecular orbitals (with negligible vibrational structure) and the 3s bonding molecular orbital (vibrational structure).

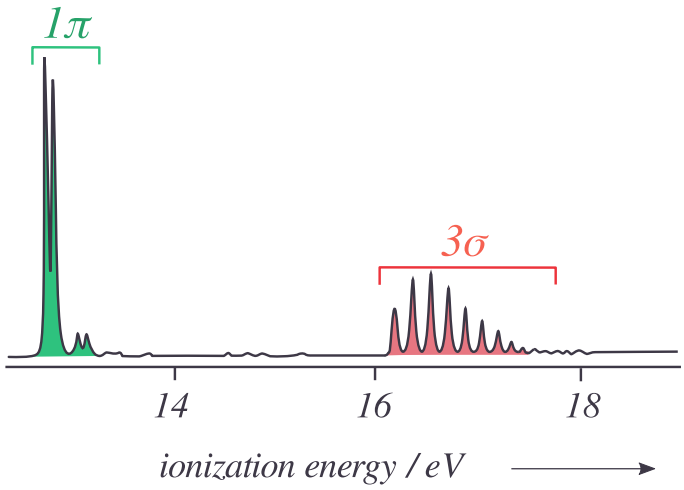


Figure 10.4.6: Photoelectron spectrum HCl. (CC BY 4.0; Ümit Kaya via LibreTexts)

The higher energy (more stabilized) core molecular orbitals are not observed since the incident photon energy $h\nu$ is below their ionization energies.

Water

In the simplified valence bond theory perspective of the water molecule, the oxygen atom form four sp^3 hybrid orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. Within the molecular orbital picture, the electronic configuration of the H_2O^+ molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ where the symbols a_1, b_2 and b_1 are orbital labels based on molecular symmetry that will be discussed later (Figure 10.4.7). Within Koopmans' theorem:

- The energy of the $1b_1$ HOMO corresponds to the ionization energy to form the H_2O^+ ion in its ground state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$.
- The energy of the second-highest molecular orbitals $3a_1$ refers to the ion in the excited state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

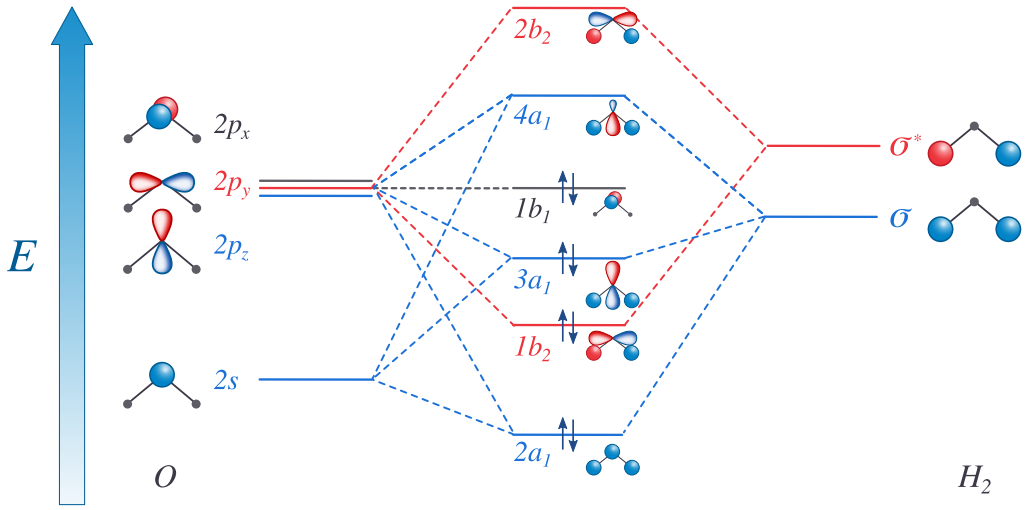


Figure 10.4.7: MO diagram for water. (CC BY 4.0; Ümit Kaya via LibreTexts)

The Hartree–Fock orbital energies (with sign changed) of these orbitals are tabulated below and compared to the experimental ionization energies.

Molecular orbital	Hartree–Fock orbital Energies (eV)	Experimental Ionization Energies (eV)
$2a_1$	36.7	32.2
$1b_2$	19.5	18.5
$3a_1$	15.9	14.7
$1b_1$	13.8	12.6

As explained above, the deviations between orbital energy and ionization energy is small and due to the effects of orbital relaxation as well as differences in electron correlation energy between the molecular and the various ionized states.

The molecular orbital perspective has the lone pair in different orbitals (one in a non-bonding orbital ($1b_1$ and one in the bonding orbitals). We tern to the photoelectron spectroscopy to help identify which theory is more accurate (i.e., describes reality better). The photoelectron spectrum of water in Figure 10.4.6 can be interpreted as having three major peaks with some fine structure arises from vibrational energy changes. The light source used in this experiment is not sufficiently energetic to ionize electrons from the lowest lying molecular orbitals.

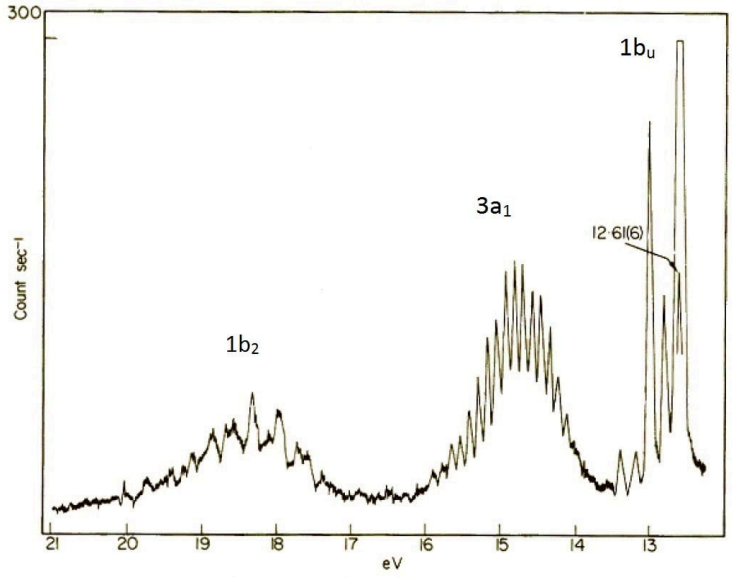


Figure 10.4.8: Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page. This spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

If water was formed two identical O-H bonds and two lone pairs on the oxygen atom line valence bond theory predicts, then the PES in Figure 10.4.8 would have two (degenerate) peaks, one for the two bonds and one for the two lone pairs. The photoelectron spectrum clearly shows three peaks in the positions expected for the molecular orbitals in Figure 10.4.8.

If the molecular orbitals in Figure 10.4.7 represent the real electronic structure, how do we view the bonding? These molecular orbitals are delocalized and bare little relationship to the familiar 2-center bonds used in valence bond theory. For example, the $2a_1$ $1b_1$ and $3a_1$ molecular orbitals all have contributions from all three atoms, they are really 3-centered molecular orbitals. The bonds however can be thought of as representing a build up of the total electron density which loosely put is a total of all the orbital contributions. Despite this, we keep the ideas of hybridization and 2-center bonds because they are useful NOT because they represent reality

Summary

A photoelecton spectrum can show the relative energies of occupied molecular orbitals by ionization. (i.e. ejection of an electron). A photoelectron spectrum can also be used to determine energy spacing between vibrational levels of a given electronic state. Each orbital energy band has a structure showing ionization to different vibrational levels.

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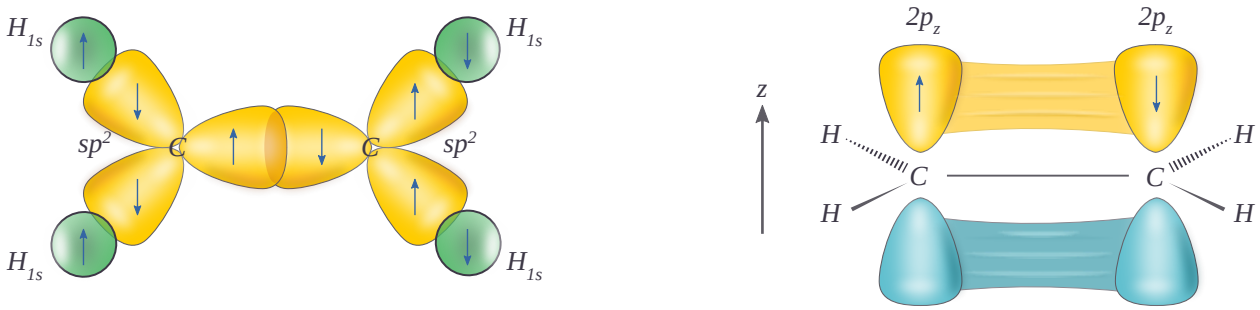
10.5: The pi-Electron Approximation of Conjugation (Hückel Theory)

Learning Objectives

- Demonstrate how Hückel's theory approximates the full molecular orbital picture of molecules by treating the σ-bonding and π-bonding networks independently.

Molecular orbital theory has been very successfully applied to large conjugated systems, especially those containing chains of carbon atoms with alternating single and double bonds. An approximation introduced by Hückel in 1931 considers only the delocalized *p* electrons moving in a framework of π-bonds. This is, in fact, a more sophisticated version of a free-electron model.

The simplest hydrocarbon to consider that exhibits π bonding is ethylene (ethene), which is made up of four hydrogen atoms and two carbon atoms. Experimentally, we know that the $\mathrm{H{-}C{-}H}$ and $\mathrm{H{-}C{-}C}$ angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + s) and one C–C (sp^2 + sp^2) (part a of Figure 10.5.1).



(a) C_2H_4 σ - bonded framework

(b) C_2H_4 π bonding

Figure 10.5.1 : (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.) (CC BY-NC; Ümit Kaya via LibreTexts)

The Hückel approximation is used to determine the energies and shapes of the π molecular orbitals in conjugated systems. Within the Hückel approximation, the covalent bonding in these hydrocarbones can be separated into two independent "frameworks": the σ-bonding framework and the the σ-bonding framework. The wavefunctions used to describe the bonding orbitals in each framework results from different combinations of atomic orbitals. The method limits itself to addressing conjugated hydrocarbons and specifically only π electron molecular orbitals are included because these determine the general properties of these molecules; the sigma electrons are ignored. This is referred to as *sigma-pi separability* and is justified by the orthogonality of σ and π orbitals in planar molecules. For this reason, the Hückel method is limited to planar systems. Hückel approximation assumes that the electrons in the π bonds “feel” an electrostatic potential due to the entire σ-bonding framework in the molecule (i.e. it focuses only on the formation of π bonds, given that the σ bonding framework has already been formed).

Conjugated Systems

A conjugated system has a region of overlapping p-orbitals, bridging the interjacent single bonds, that allow a *delocalization* of π electrons across all the adjacent aligned p-orbitals. These π electrons do not belong to a single bond or atom, but rather to a group of atoms.

Ethylene

Before considering the Hückel treatment for ethylene (C_2H_4), it is beneficial to review the general bonding picture of the molecule. Bonding in ethylene involves the sp^2 hybridization of the $2s$, $2p_x$, and $2p_y$ atomic orbitals on each carbon atom; leaving the $2p_z$ orbitals untouched (Figure 10.5.2).

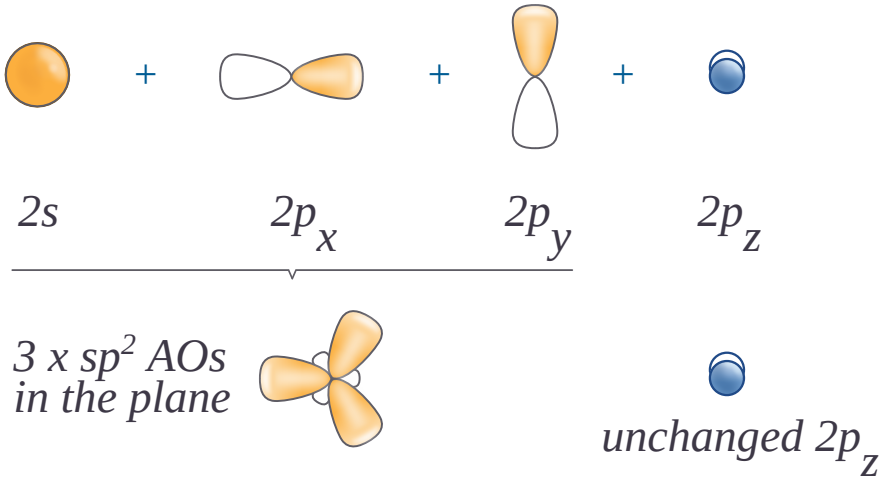


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

The use of hybrid orbitals in the molecular orbital approach describe here is merely a convenience and not invoking valence bond theory (directly). An identical description can be extracted using exclusively atomic orbitals on carbon, but the interpretation of the resulting wavefunctions is less intuitive. For example, the ith molecular orbital can be described via hybrid orbitals

$$|\psi_1\rangle = c_1|sp_1^2\rangle + c_2|1s_a\rangle$$

or via atomic orbitals.

$$|\psi_1\rangle = a_1|2s\rangle + a_1|2p_x\rangle + a_1|2p_y\rangle + a_4|1s_a\rangle$$

where $\{a_i\}$ and $\{c_i\}$ are coefficients of the expansion. Either describe will work and both are identical approaches since

$$|sp_1^2\rangle = b_1|2s\rangle + b_1|2p_x\rangle + b_1|2p_y\rangle$$

where $\{c_i\}$ are coefficients describing the hybridized orbital.

The bonding occurs via the mixing of the electrons in the sp^2 hybrid orbitals on carbon and the electrons in the $1s$ atomic orbitals of the four hydrogen atoms (Figure 10.5.1 ; left) resulting in the σ-bonding framework. The π-bonding framework results from the unhybridized $2p_z$ orbitals (Figure 10.5.2 ; right). The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram in Figure 10.5.3 ; Hückel theory is concerned only with describing the molecular orbitals and energies of the π bonding framework.

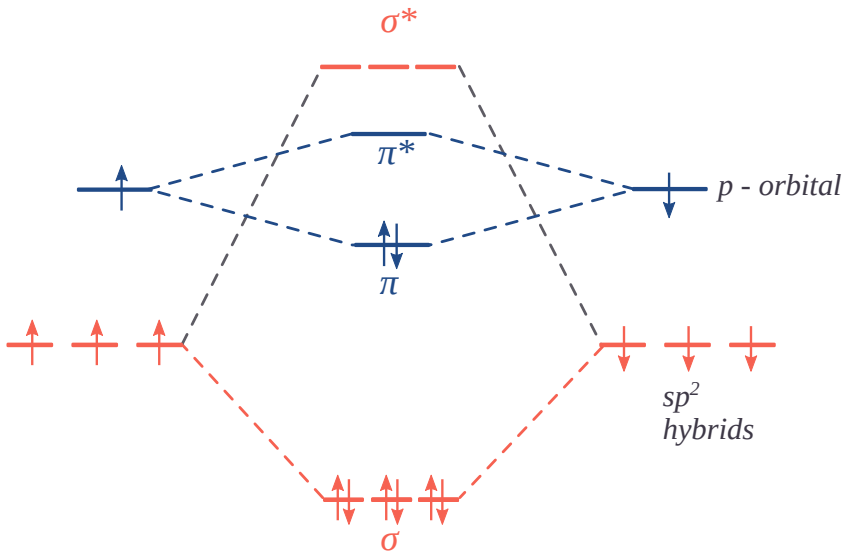


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the π-bonding framework (blue) and the σ-bonding frameworks (red) of ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

Hückel treatment is concerned only with describing the molecular orbitals and energies of the π bonding framework.

Since Hückel theory is a special consideration of molecular orbital theory, the molecular orbitals $|\psi_i\rangle$ can be described as a linear combination of the $2p_z$ atomic orbitals ϕ at carbon with their corresponding $\{c_i\}$ coefficients:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{10.5.1}$$

This equation is substituted in the Schrödinger equation:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

with $\hat{H}$ the Hamiltonian and E_i the energy corresponding to the molecular orbital to give:

$$\hat{H}c_1|\phi_1\rangle + \hat{H}c_2|\phi_2\rangle = Ec_1|\phi_1\rangle + Ec_2|\phi_2\rangle \tag{10.5.2}$$

If Equation 10.5.2 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{10.5.3}$$

where H_{ij} are the Hamiltonian matrix elements (see note below)

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i \phi_j \mathrm{d}v$$

If Equation 10.5.2 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{10.5.4}$$

Both Equations 10.5.3 and 10.5.4 can better represented in matrix notation,

$$\begin{bmatrix} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) \\ c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) \end{bmatrix} = 0$$

or more simply as a product of matrices.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.5}$$

All diagonal Hamiltonian integrals H_{ii} are called **Coulomb integrals** and those of type H_{ij} are called **resonance integrals**. Both integrals are negative and the resonance integrals determines the strength of the bonding interactions. The equations described by Equation 10.5.5 are called the ***secular equations*** and will also have the trivial solution of

$$c_1 = c_2 = 0$$

Within linear algebra, the secular equations in Equation 10.5.5 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{10.5.6}$$

or in shorthand notation

$$\det(H - ES) = 0$$

Everything in Equation 10.5.6 is a known number except E. Since the secular determinant for ethylene is a 2×2 matrix, finding E , requires solving a quadratic equation (after expanding the determinant)

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{21})(H_{12} - ES_{12}) = 0$$

There will be two values of E which satisfy this equation and they are the molecular orbital energies. For ethylene, one will be the bonding energy and the other the antibonding energy for the π-orbitals formed by the combination of the two carbon $2p_z$ orbitals (Equation 10.5.1). However, if more than two $|\phi\rangle$ atomic orbitals were used, e.g., in a bigger molecule, then more energies would be estimated by solving the secular determinant.

Solving the secular determinant is simplified within Hückel method via the following four assumptions:

1. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the $\pi -$ orbitals are directed perpendicular to the direction of their bonds (Figure 10.5.1). This assumption is often call neglect of differential overlap (NDO).
2. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.
3. All resonance integrals H_{ij} between neighboring atoms are equal and set to β.
4. All coulomb integrals H_{ii} are set equal to α.

These assumptions are mathematically expressed as

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

Assumptions 1 means that the overlap integral between the two atomic orbitals is 0

$$S_{11} = S_{22} = 1$$

$$S_{12} = S_{21} = 0$$

Matrix Representation of the Hamiltonian

The Coulomb integrals

$$H_{ii} = \langle \phi_i | H | \phi_i \rangle$$

and resonance integrals.

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \;\; (i \neq i)$$

are often described within the matrix representation of the Hamiltonian (specifically within the $|\phi\rangle$ basis):

$$\hat{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

or within the Hückel assumptions

$$\hat{H} = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix}$$

The Hückel assumptions reduces Equation 10.5.5 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.7}$$

if Equation 10.5.7 is divided by β:

$$\begin{bmatrix} \dfrac{\alpha - E}{\beta} & 1 \\ 1 & \dfrac{\alpha - E}{\beta} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

and then a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.5.8}$$

then Equation 10.5.7 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.9}$$

The trivial solution gives both wavefunction coefficients equal to zero and the other (non-trivial) solution is determined by solving the secular determinant

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

which when expanded is $x^2 - 1 = 0$ so $x = \pm 1$.

Knowing that $E = \alpha - x\beta$ from Equation 10.5.8, the energy levels can be found to be

$$E = \alpha - \pm 1 \times \beta$$

or

$$E = \alpha \mp \beta$$

Since β is negative, the two energies are ordered (Figure 10.5.4)

- For π_1: $E_1 = \alpha + \beta$
- For π_2: $E_2 = \alpha - \beta$

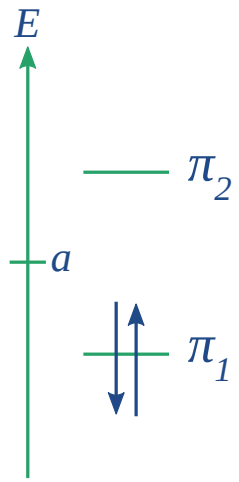


Figure 10.5.4 : π energies of ethylene with occupation. (CC BY-NC; Ümit Kaya via LibreTexts)

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 10.5.9). For the lower energy state ($x = -1$)

$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 10.5.1):

$$|\psi_1\rangle = N_1(\phi_1\rangle + |\phi_2\rangle) \tag{10.5.10}$$

where N_1 is the normalization constant for this molecular orbital; this is the **bonding** molecular orbital.

For the higher energy molecular orbital ($x = -1$) and then

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = -c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 10.5.1):

$$\psi_2\rangle = N_2(\phi_1\rangle - |\phi_2\rangle) \tag{10.5.11}$$

where N_2 is the normalization constant for this molecular orbital; this is the **anti-bonding** molecular orbital.

The normalization constants for both molecular orbitals can obtained via the standard normalization approach (i.e., $\langle\psi_i|\psi_i\rangle = 1$) to obtain

$$N_1 = N_2 = \frac{1}{\sqrt{2}}$$

These molecular orbitals form the π-bonding framework and since each carbon contributes one electron to this framework, only the lowest molecular orbital ($|\psi_1\rangle$) is occupied (Figure 10.5.5) in the ground state. The corresponding electron configuration is then π_1^2.

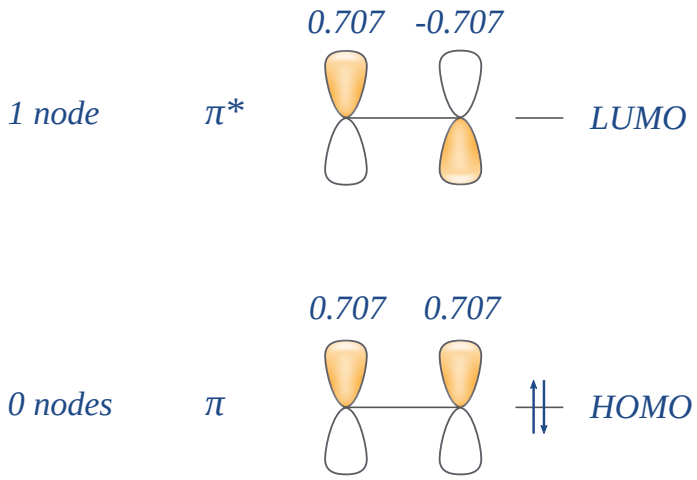


Figure 10.5.5 : Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy. (CC BY-NC; Ümit Kaya via LibreTexts)

HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively and are often referred to as frontier orbitals. The energy difference between the HOMO and LUMO is termed the HOMO–LUMO gap.

The 3-D calculated π molecular orbitals are shown in Figure 10.5.6 .

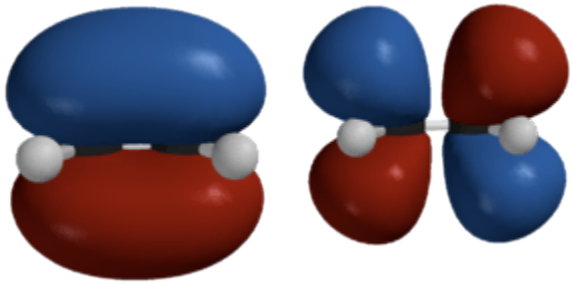


Figure 10.5.6 : Calculated π molecular orbitals for ethylene . (left) the bonding orbital (|\psi_1 \rangle\) and (right) the antibonding $(|\psi_2\rangle$ orbital.

Limitations of Hückel Theory

Hückel theory was developed in the 1930's when computers were unavailable and a simple mathematical approaches were very important for understanding experiment. Although the assumptions in Hückel theory are drastic they enabled the early calculations of molecular orbitals to be performed with mechanical calculators or by hand. Hückel Theory can be extended to address other types of atoms in conjugated molecules (e.g., nitrogen and oxygen). Moreover, it can be extended to also treat σ orbitals and this "Extended Hückel Theory" is still used today. Despite the utility of Hückel Theory, it is highly qualitative and we should remember the limitations of Hückel Theory:

- Hückel Theory is very approximate
- Hückel Theory cannot calculate energies accurately (electron-electron repulsion is not calculated)
- Hückel Theory typically overestimates predicted dipole moments

Hückel Theory is best used to provide simplified models for understanding chemistry and for a detailed understanding modern *ab initio* molecular methods discussed in Chapter 11 are needed.

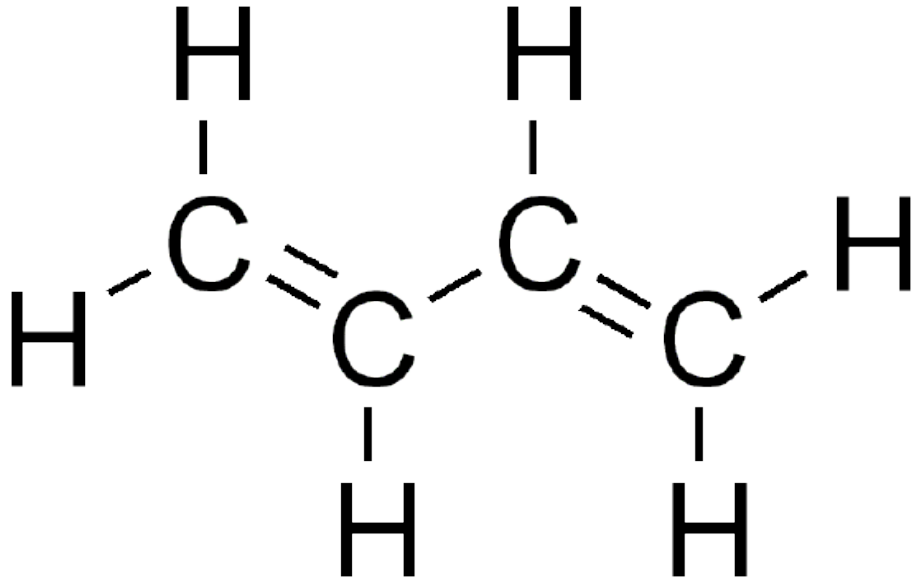
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10.6: Butadiene is Stabilized by a Delocalization Energy

Learning Objectives

- Apply Hückel theory to an extended π-bonding network
- Identify the origin of delocalization energy from Hückel theory and relate it to resonances structures in valence bond theory

1,3-Butadiene is a simple conjugated diene with the formula C_4H_6 and can be viewed structurally as two vinyl groups ($CH_2{=}CH_2$) joined together with a single bond. Butadiene can occupy either a cis or trans conformers and at room temperature, 96% of butadiene exists as the trans conformer, which is 2.3 kcal/mole more stable than the cis structure.



trans-1,3-Butadiene

For the simple application of applying Hückel theory for understanding the electronic structure of butadiene, we will ignore the energetic differences between the two conformers. As discussed previously, the molecular orbitals are linear combination of the four $|p\rangle$ atomic orbitals on the carbon atoms that are not participating in the σ bonding network:

$$|\psi_i\rangle = \sum_j^4 c_{ij}|p_i\rangle$$

or explicitly

$$|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}|p_2\rangle + c_{i3}|p_3\rangle + c_{i4}|p_4\rangle \tag{10.6.1}$$

for the ith molecular orbital $|\psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.2}$$

If the standard Hückel theory approximations were used

$$H_{ii} - ES_{ii} = \alpha$$

and

$$H_{ij} - ES_{ij} = \beta$$

when $i = j \pm 1$, otherwise

$$H_{ij} - ES_{ij} = 0$$

then the secular equations for butadiene in Equation 10.6.2 become

$$\begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.3}$$

Solving Equation 10.6.3 for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{10.6.4}$$

If both sides of Equation 10.6.4 were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.6.5}$$

then Equation 10.6.4 simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.6.6}$$

This is essentially the connection matrix for the butadiene molecule. Each pair of connected atoms is represented by 1, each non-connected pair by 0 and each diagonal element by x. Expansion of the determinant in Equation 10.6.6 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{10.6.7}$$

While solving 4th order equations typically require numerical estimation, Equation 10.6.7 can be further simplified by recognizing that it is a quadratic equation in terms of x^2. Therefore, the roots are

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

or $x = \pm\ 0.618$ and $x = \pm\ 1.618$. Since α and β are negative, these molecular orbital energies can ordered in terms of energy (from lowest to highest):

$$E_1 = \alpha + 1.618\beta \tag{10.6.8}$$

$$E_2 = \alpha + 0.618\beta \tag{10.6.9}$$

$$E_3 = \alpha - 0.618\beta \tag{10.6.10}$$

$$E_4 = \alpha - 1.618\beta \tag{10.6.11}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1 .

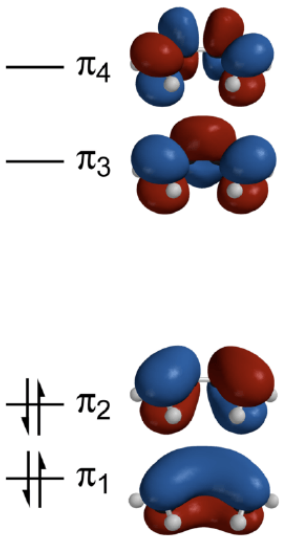


Figure 10.6.1 : The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

Each p atomic orbital of carbon contributes a single electron to the π manifold, so the ground-state occupation of the resulting four π electrons have a $\pi_1^2\pi_2^2$ configuration (Figure 10.6.1). The the total π-electron energy is then determined by adding up the energies in Equations 10.6.8-10.6.11 and scaling by their occupations to get

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_1 + 2\times E_2 + 0\times E_3 + 0\times E_4 \\ &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{10.6.12}$$

If the bonding of butadiene were described only as two localized double bond as in its dominant valence-bond structure (Figure 10.6.1), then its π-electron energy would be given by twice the E_π predicted for the ethlyene molecule:

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_\pi(\text{ethylene}) \\ &= 2\times 2(\alpha+\beta) \\ &= 4\alpha + 4\beta \end{aligned} \tag{10.6.13}$$

Comparing Equation 10.6.12 with Equation 10.6.12, the total π energy of butadiene lies lower than the total π energy of two double bonds by 0.48β (the σ bond does not contribute). This difference is known as the **delocalization energy**; a typical estimate of β is around -75 kJ/mol, which results in a *delocalization energy* for butadiene of -35 kJ/mol.

The delocalization energy is the extra stabilization resulting from the electrons extending over the whole molecule.

Delocalization Energy in Valence Bond Theory

Delocalization energy is intrinsic to molecular orbital theory, since it results from breaking the two-center bond concept with the molecular orbitals that spread over more that just one pair of atoms. However, within the two-center theory of valence bond theory, the delocalization energy results from a stabilization energy attributed to resonance. Several conventional valence bond resonance structures that can be written for 1,3-butadiene, four of which are shown in Figure 10.6.2 . However, while structure $2a$ dominates, the other resonance structures also contribute to describing the total molecule and hence predict a corresponding stabilization energy akin to the delocalization energy in molecular orbital theory.

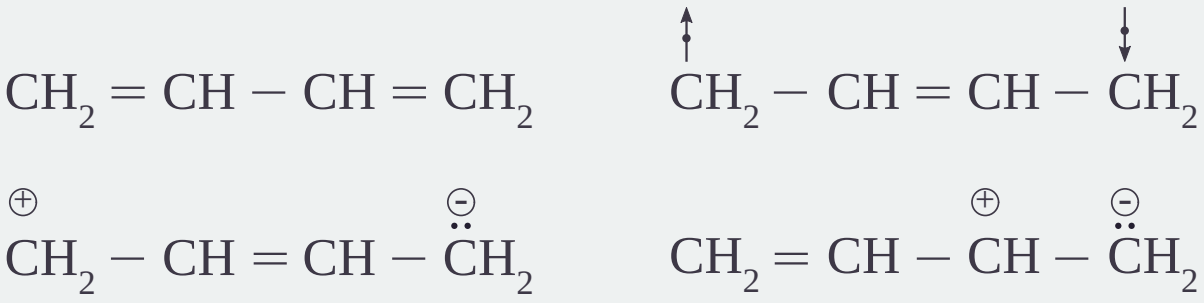


Figure 10.6.2 : Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (CC BY-NC; Ümit Kaya via LibreTexts)

In general, the true description of the bonding within the valence bond theory is a superposition of resonance structures with amplitudes that are determined via a variational optimization to find the lowest possible energy for the valence bond wavefunctions.

The solving the secular equations (Equation 10.6.2) gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 10.6.1 (not demonstrated):

$$|\psi_1\rangle = 0.37|p_1\rangle + 0.60|p_2\rangle + 0.60|p_3\rangle + 0.37|p_4\rangle \tag{10.6.14}$$

$$|\psi_3\rangle = 0.60|p_1\rangle + 0.37|p_2\rangle - 0.37|p_3\rangle - 0.60|p_4\rangle \tag{10.6.15}$$

$$|\psi_3\rangle = 0.60|p_1\rangle - 0.37|p_2\rangle - 0.37|p_3\rangle + 0.60|p_4\rangle \tag{10.6.16}$$

$$|\psi_4\rangle = 0.37|p_1\rangle - 0.60|p_2\rangle + 0.60|p_3\rangle - 0.37|p_4\rangle \tag{10.6.17}$$

These are depicted in Figure 10.6.3 .

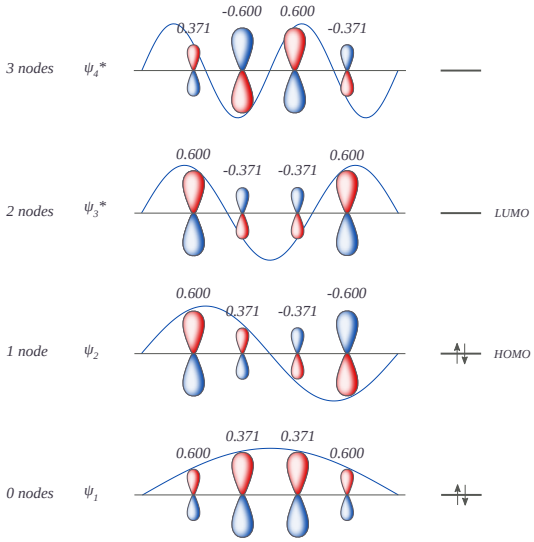


Figure 10.6.3 : Energy level diagram and decomposition of the π molecular orbitals of butadiene. This is view three-dimensionally in Figure 10.6.1 . (CC BY-NC; Ümit Kaya via LibreTexts)

Note the correlation of the energy of the π molecular orbitals of butadiene to the number of nodes in the wavefunction; this is the general trend observed in previous systems like the particle in the box and atomic orbitals. The four 3-D calculated molecular orbitals are contrasted in Figure 10.6.1 .

Exercise 10.6.1

What would Hückel theory predict for the energy levels and π molecular orbitals of cis-butadiene? Do you believe this approach adequately describes the energy levels of the cis-trans isomerization reaction of butadiene?

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10.7: Benzene and Aromaticity

Learning Objectives

- Apply Hückel theory to describing the pi bonding in cyclical conjugated system
- Identify the origin of aromaticity within Hückel theory to describe extra stabilization in certain cyclical conjugated systems

The previous sections addressed the π orbitals of linear conjugated system. Here we address conjugated systems of **cyclic conjugated hydrocarbons** with the general formula of $\mathrm{C}_n\mathrm{H}_n$ where n is the number of carbon atoms in the ring. The molecule from this important class of organic molecule that you are most familiar with is benzene ($\mathrm{C}_6\mathrm{H}_6$) with $n = 6$, although many other molecules exist like cyclobutadiene ($\mathrm{C}_4\mathrm{H}_4$) with $n = 4$ (Figure 10.7.1).

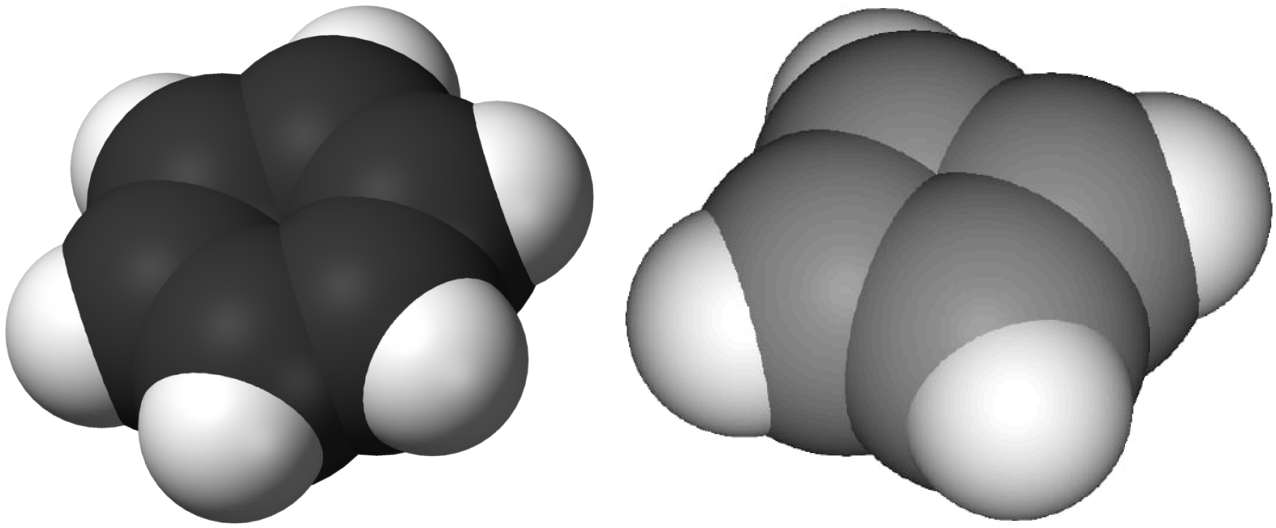


Figure 10.7.1 : Space-filling model of benzene (left) and cyclobutadiene (right). Carbon atoms are indicated in black, while hydrogen atoms are indicated in white. (Public domain; Benjah-bmm27 and Edgar181, respectively).

Structure of Benzene

The structure of benzene is an interesting historical topic. In 1865, the German chemist Friedrich August Kekulé published a paper suggesting that the structure of benzene contained a ring of six carbon atoms with alternating single and double bonds. Within this argument, two resonance structures can be formulated.

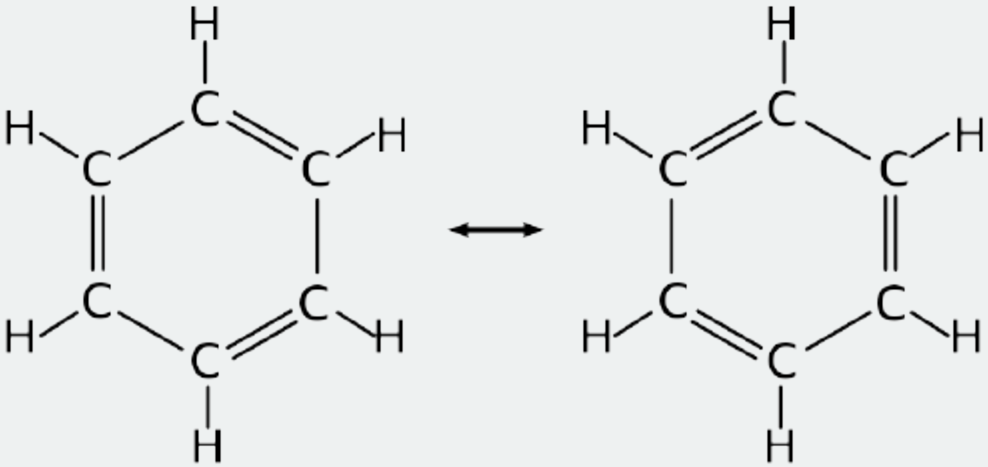


Figure 10.7.2 : Resonance structures of benzene.

However, X-ray diffraction shows that all six carbon-carbon bonds in benzene are of the same length, at 140 pm. The C–C bond lengths are greater than a double bond (135 pm), but shorter than a typical single bond (147 pm). This means that neither of the structures in Figure 10.7.2 are correct and the true 'structure' of benzene is a mixture of the two. As discussed previously, that such a valence bond perspective results in a **delocalization energy** within a molecular orbital approach.

Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular determinant

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.7.1}$$

with the six roots $x = \pm 2, \pm 1, \pm 1$. This corresponds to the following energies (ordered from most stable to least since $\beta < 0$):

- $E_1 = \alpha + 2\beta$
- $E_2 = \alpha + \beta$
- $E_3 = \alpha + \beta$
- $E_4 = \alpha - \beta$
- $E_5 = \alpha - \beta$
- $E_6 = \alpha - 2\beta$

The two pairs of $E = \alpha \pm \beta$ energy levels are two-fold degenerate (Figure 10.7.3).

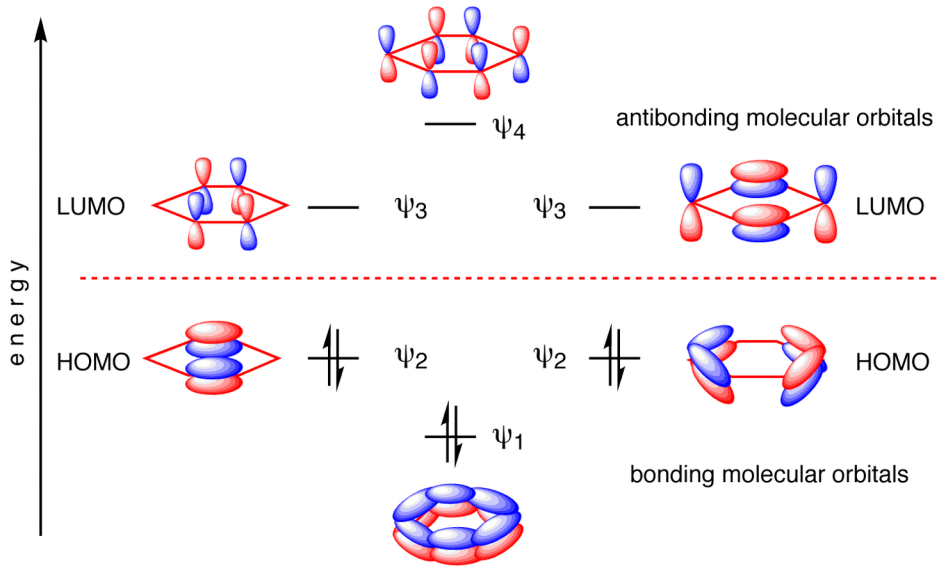


Figure 10.7.3 : The π molecular orbitals for benzene. The dashed lines represent the energy of an isolated p orbitals and all orbitals below this line are bonding. All orbitals above it are antibonding. (CC BY-NC-SA 4.0; Nick Greeves via ChemTube3D)

The resulting wavefunctions are below (expanded in terms of carbon $|2p\rangle$ atomic orbitals).

$$
\begin{aligned}
|\psi_1\rangle &= \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle\right] \\
|\psi_2\rangle &= \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle\right] \\
|\psi_3\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle\right] \\
|\psi_4\rangle &= \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle\right] \\
|\psi_5\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle\right] \\
|\psi_6\rangle &= \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle\right]
\end{aligned}
$$

Each of the carbons in benzene contributes one electron to the π-bonding framework (Figure 10.7.3). This means that all bonding molecular orbitals are fully occupied and benzene then has an electron configuration of $\pi_1^2\pi_2^2\pi_3^2$. With the three lowest molecular orbitals occupied, the total π-bonding energy is

$$
\begin{aligned}
E_{tot}(\text{benzene}) &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\
&= 6\alpha + 8\beta
\end{aligned}
\tag{10.7.2}
$$

Since the energy of a localized double bond is $2(\alpha + \beta)$, as determined from the analysis of ethylene, the delocalization energy of benzene is

$$
\begin{aligned}
\Delta E &= E_{tot}(\text{benzene}) - 3E_{tot}(\text{ethylene}) \\
&= (6\alpha + 8\beta) - 3 \times 2(\alpha + \beta) \\
&= 2\beta
\end{aligned}
$$

The experimental thermochemical value is -152 kJ mol^{-1}.

Aromaticity

In general, cyclic polyenes are only closed shell (i.e., each electron paired up) and extra stable for with $(4n + 2)\pi$ electrons (n=0,1,2...). These special molecules have the highest delocalization energies and are said to be “aromatic”. For benzene this is

2β (Equation 10.7.2), which is the energy by which the delocalized π electrons in benzene are more stable than those in three isolated double bonds.

Hückel's Rule

A stable, closed-shell conjugated cyclic structure is obtained for molecules with $(4n + 2)\pi$ electrons with n=2, 6, 10, ... electrons.

Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product.

$$\mathrm{C_6H_6 + 3\,H_2 \longrightarrow C_6H_{12}}$$

In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 11.9 kJ mol^{-1}. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 23.9 kJ mol^{-1} on complete hydrogenation, and 1,3,5-cyclohexatriene to release 35.9 kJ mol^{-1}. These heats of hydrogenation ΔH_{hyd} reflect the relative thermodynamic stability of the compounds (Figure 10.7.4).

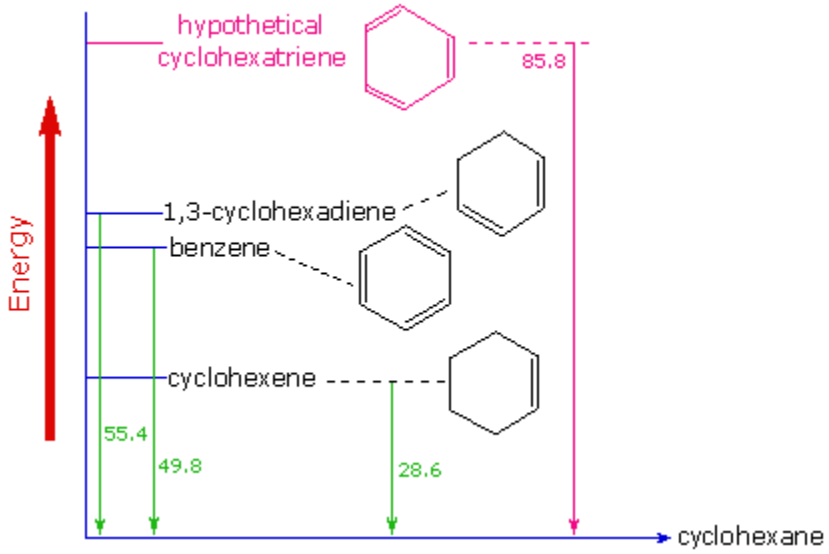


Figure 10.7.4 : Experimental evidence for aromatic stabilization energy in benzene from the heat of hydrogenation. Energies are in kcal/mol. (CC BY-NC-SA 4.0; William Resuch);

In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 8.1 kJ mol^{-1}, presumably due to conjugation of the double bonds. Benzene, however, is an extraordinary 15 kJ mol-1 more stable than expected. This additional stability is a characteristic of all aromatic compounds.

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10.E: Bonding in Polyatomic Molecules (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 10 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q10.8

Show that the four sp^3 orbitals are orthonormal.

S10.8

This means showing that each pair of $|sp^3\rangle$ hybrid orbitals meets the criteria: $\langle sp_i^3|sp_j^3\rangle = \delta_{ij}$

Designating the four sp^3 orbitals as:

$$|1\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)$$

$$|2\rangle = \frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)$$

$$|3\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle)$$

$$|4\rangle = \frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle)$$

Normality:

$$\langle 1|1\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| + \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{10.E.1}$$

$$= \frac{1}{4}\left(\langle s|s\rangle + \langle s|p_x\rangle + \langle s|p_y\rangle + \langle s|p_z\rangle + \langle p_x|s\rangle + \langle p_x|p_x\rangle + \langle p_x|p_y\rangle + \langle p_x|p_z\rangle + \langle p_y|s\rangle + \langle p_y|p_x\rangle + \langle p_y|p_y\rangle + \langle p_y|p_z\rangle + \langle p_z|s\rangle + \langle p_z\right.$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{10.E.3}$$

$$\langle 2|2\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| - \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{10.E.4}$$

$$= \frac{1}{4}\left(\langle s|s\rangle - \langle s|p_x\rangle - \langle s|p_y\rangle + \langle s|p_z\rangle - \langle p_x|s\rangle + \langle p_x|p_x\rangle + \langle p_x|p_y\rangle - \langle p_x|p_z\rangle - \langle p_y|s\rangle + \langle p_y|p_x\rangle + \langle p_y|p_y\rangle - \langle p_y|p_z\rangle + \langle p_z|s\rangle - \langle p_z\right.$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{10.E.6}$$

$$\langle 3|3\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle)\right) \tag{10.E.7}$$

$$= \frac{1}{4}\left(\langle s|s\rangle + \langle s|p_x\rangle - \langle s|p_y\rangle - \langle s|p_z\rangle + \langle p_x|s\rangle + \langle p_x|p_x\rangle - \langle p_x|p_y\rangle - \langle p_x|p_z\rangle - \langle p_y|s\rangle - \langle p_y|p_x\rangle + \langle p_y|p_y\rangle + \langle p_y|p_z\rangle - \langle p_z|s\rangle - \langle p_z\right.$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{10.E.9}$$

$$\langle 4|4\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle)\right) \tag{10.E.10}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle s|p_x\rangle + \langle s|p_y\rangle - \langle s|p_z\rangle - \langle p_x|s\rangle + \langle p_x|p_x\rangle - \langle p_x|p_y\rangle + \langle p_x|p_z\rangle + \langle p_y|s\rangle - \langle p_y|p_x\rangle + \langle p_y|p_y\rangle - \langle p_y|p_z\rangle - \langle p_z|s\rangle + \langle p$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{10.E.12}$$

Orthogonality:

For the longer wavefunctions, only surviving terms in the dot product are included:

$$\langle 1|2\rangle = \langle 2|1\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| - \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{10.E.13}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle - \langle p_y|p_y\rangle + \langle p_z|p_z\rangle) = \frac{1}{4}(1-1-1+1) = 0 \tag{10.E.14}$$

$$\langle 1|3\rangle = \langle 3|1\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{10.E.15}$$

$$= \frac{1}{4}(\langle s|s\rangle + \langle p_x|p_x\rangle - \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1+1-1-1) = 0 \tag{10.E.16}$$

$$\langle 1|4\rangle = \langle 4|1\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{10.E.17}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle + \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1-1+1-1) = 0 \tag{10.E.18}$$

$$\langle 2|3\rangle = \langle 3|2\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{10.E.19}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle + \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1-1+1-1) = 0 \tag{10.E.20}$$

$$\langle 2|4\rangle = \langle 4|2\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{10.E.21}$$

$$= \frac{1}{4}(\langle s|s\rangle + \langle p_x|p_x\rangle - \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1+1-1-1) = 0 \tag{10.E.22}$$

$$\langle 3|4\rangle = \langle 4|3\rangle = (\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|))(\frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle)) \tag{10.E.23}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle - \langle p_y|p_y\rangle + \langle p_z|p_z\rangle) = \frac{1}{4}(1-1-1+1) = 0 \tag{10.E.24}$$

Q10.9

The sp^3d^2 hybrid orbitals are given by:

$$\chi_1(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) - \frac{1}{\sqrt{2}}\psi_{3p_x}(r) - \frac{1}{\sqrt{12}}\psi_{3d_{z^2}} + \frac{1}{\sqrt{4}}\psi_{3d_{x^2-y^2}}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) + \frac{1}{\sqrt{2}}\psi_{3p_x}(r) - \frac{1}{\sqrt{12}}\psi_{3d_{z^2}} + \frac{1}{\sqrt{4}}\psi_{3d_{x^2-y^2}}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) - \frac{1}{\sqrt{2}}\psi_{3p_y}(r) - \frac{1}{\sqrt{12}}\psi_{3d_{z^2}} - \frac{1}{\sqrt{4}}\psi_{3d_{x^2-y^2}}$$

$$\chi_4(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) + \frac{1}{\sqrt{2}}\psi_{3p_y}(r) - \frac{1}{\sqrt{12}}\psi_{3d_{z^2}} - \frac{1}{\sqrt{4}}\psi_{3d_{x^2-y^2}}$$

$$\chi_5(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) - \frac{1}{\sqrt{2}}\psi_{3p_z}(r) + \frac{1}{\sqrt{12}}\psi_{3d_{z^2}}$$

$$\chi_6(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) + \frac{1}{\sqrt{2}}\psi_{3p_z}(r) + \frac{1}{\sqrt{12}}\psi_{3d_{z^2}}$$

Determine the angles of SF_6 using the vector approach (dot product formula).

S10.9

The s orbitals are spherical and therefor do not contribute to the directional vectors for this problem. The d_{z^2} orbital only has z directionality and the $d_{x^2-y^2}$ orbital has equal parts x and y directionality. The equations can be rewritten:

$$\psi_1 = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{4}}\right)\mathbf{i} + \frac{1}{\sqrt{4}}\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \qquad \psi_2 = \left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{4}}\right)\mathbf{i} + \frac{1}{\sqrt{4}}\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \tag{10.E.25}$$

$$\psi_3 = -\frac{1}{\sqrt{4}}\mathbf{i} + \left(-\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{4}}\right)\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \qquad \psi_4 = -\frac{1}{\sqrt{4}}\mathbf{i} + \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{4}}\right)\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \tag{10.E.26}$$

$$\psi_5 = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\mathbf{k} \qquad \psi_6 = \left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\mathbf{k} \tag{10.E.27}$$

For any two ψ the angel can be calculated using:

$$\left(\sqrt{A_x^2 + A_y^2 + A_z^2}\right)\left(\sqrt{B_x^2 + B_y^2 + B_z^2}\right) cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{10.E.28}$$

So, choosing ψ_5 and ψ_6 we get:

$$\left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right) cos\theta = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right) \tag{10.E.29}$$

$$-\frac{5}{12}cos\theta = -\frac{5}{12} \tag{10.E.30}$$

$$cos\theta = 0 \tag{10.E.31}$$

$$\theta = 90^\circ \tag{10.E.32}$$

Q10.10

Given

$$\xi_1 = \frac{1}{\sqrt{4}}2s + \sqrt{\frac{3}{4}}2p_z \tag{10.E.33}$$

$$\xi_2 = \frac{1}{\sqrt{4}}2s + \sqrt{\frac{2}{3}}2p_x - \frac{1}{\sqrt{12}}2p_z \tag{10.E.34}$$

what is the angle between ξ_1 and ξ_2?

What is the purpose of the square root constants before the orbitals?

S10.10

Since we know that

$$(\sqrt{A_x^2 + A_y^2 + A_z^2})(\sqrt{B_x^2 + B_y^2 + B_z^2})\cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{10.E.35}$$

When we plug in our constants in the x, y, and z directions for the two equations we get

$$(\sqrt{\frac{2}{3}+\frac{1}{12}})(\sqrt{\frac{3}{4}})\cos\theta = -\sqrt{\frac{1}{12}}\sqrt{\frac{3}{4}} \tag{10.E.36}$$

isolating the theta term we get

$$\theta = \arccos(-\sqrt{\frac{1}{12}}/\sqrt{\frac{12}{9}} \tag{10.E.37}$$

yielding

$$\theta = 109.47^{\circ} \tag{10.E.38}$$

The square root constants are the necessary normalization constants.

Q10.11

Given that

$$\psi_1 = 0.71j + 0.55k \tag{10.E.39}$$

and

$$\psi_2 = -0.71j + 0.55k \tag{10.E.40}$$

Find the bond angle between ψ_1 and ψ_2 using the vector approach.

S10.11

Using this equation below:

$$\left(\sqrt{A_x^2+A_y^2+A_z^2}\right)\left(\sqrt{B_x^2+B_y^2+B_z^2}\right)cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{10.E.41}$$

use to find the angle between the orbitals,

$$(0.71^2+0.55^2)^{0.5}(0.71^2+0.55^2)^{0.5}cos\theta = -0.71^2+0.55^2 \tag{10.E.42}$$

$$cos\theta = -0.25 \tag{10.E.43}$$

$$\theta = 104.5^{\circ} \tag{10.E.44}$$

Q10.12

Assuming a water molecule sits in the yz-plane, show that two bonding hybrid atomic orbitals on the oxygen atom can be expressed as

$$\psi_1 = N[\gamma 2s + (sin[\theta]2p_y + cos[\theta]2p_z] \tag{10.E.45}$$

and

$$\psi_2 = N[\gamma 2s - (sin[\theta]2p_y + cos[\theta]2p_z]. \tag{10.E.46}$$

Additionally, find γ assuming the bond angles to be 104.5 °.

S10.12

Because the molecules are in the yz plane, the p_x orbital can be neglected because it is completely orthogonal. The hybrid orbitals are a linear combination of the $2s,\ 2p_y,$ and $2p_z$ orbitals.

$$\psi_{bonding} = N[\gamma 2_s + c_1 2p_y + c_2 2p_z] \tag{10.E.47}$$

c_1 and c_2 can be found by thinking about how the bonds are oriented. The two bonds both have $cos[\theta]$ character in the z-direction and have $\pm sin[\theta]$ in the y-direction. The two functions can therefore be written as

$$\psi_1 = N[\gamma 2s + (sin[\theta]2p_y + cos[\theta]2p_z) \tag{10.E.48}$$

and

$$\psi_2 = N[\gamma 2s - (sin[\theta]2p_y + cos[\theta]2p_z) \tag{10.E.49}$$

when c_1 and c_2 are replaced with the sin and cos functions above.

The two functions when integrated will equal zero due to orthogonality.

$$\langle \psi_1 | \psi_2 \rangle = 0 \tag{10.E.50}$$

$$N^2(\gamma^2 + cos^2[\theta] - sin^2[\theta]) \tag{10.E.51}$$

$$\gamma^2 = sin^2[\theta] - cos^2[\theta] \tag{10.E.52}$$

The bond angles in water are 104.5° which can be substituted into θ.

$$\gamma = 0.5 \tag{10.E.53}$$

Q10.13

The lone pair wave functions of H2O can be described as:

$$\psi_{l1} = 0.54(2s) - 0.44(2pz) + 0.72(2px) \tag{10.E.54}$$

$$\psi_{l2} = 0.54(2s) - 0.44(2pz) - 0.72(2px) \tag{10.E.55}$$

Confirm the orthonormality of these wave functions.

S10.13

The two wave functions must be normalized and orthogonal to each other.

$$\int d\tau \psi_{l1}^* \psi_{l1} = 1 \tag{10.E.56}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) + (0.72)^2(2px) = 1 \tag{10.E.57}$$

$$\int d\tau \psi_{l2}^* \psi_{l2} = 1 \tag{10.E.58}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) + (-0.72)^2(2px) = 1 \tag{10.E.59}$$

$$\int d\tau \psi_{l1}^* \psi_{l2} = 0 \tag{10.E.60}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) - (0.72)^2(2px) = 0 \tag{10.E.61}$$

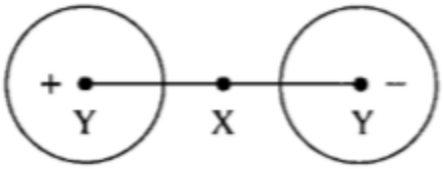
The atomic orbitals within the linear combination of the lone pair wave functions are normalized and orthogonal, zeroing out cross products and leaving only the squares of the coefficients.

10.14

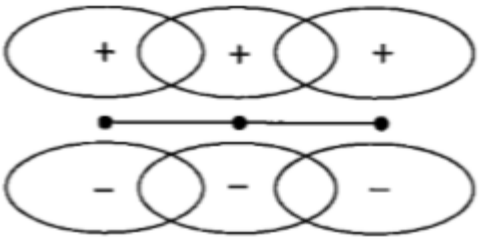
Molecular orbitals for a linear

$$XY_2 \tag{10.E.62}$$

molecule can be represented as



$2\sigma_u$



$1\pi_g$

Draw a schematic representation for the

$$3\sigma_g, 4\sigma_g, 1\pi_g, 2\sigma_g \tag{10.E.63}$$

orbitals

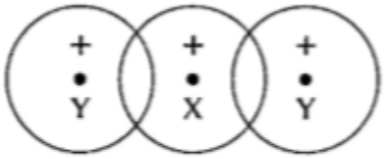
Which has the highest energy?

S10.14

$$3\sigma_g \tag{10.E.64}$$

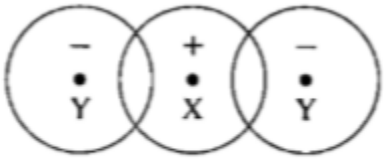
NOTE:

$$3\sigma_g \tag{10.E.65}$$



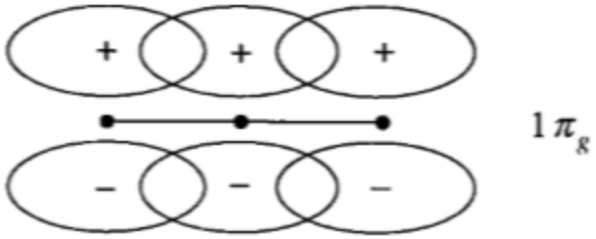
$3\sigma_g$

$$4\sigma_g \tag{10.E.66}$$



$4\sigma_g$

$$1\pi_g \tag{10.E.67}$$



$$2\sigma_g \tag{10.E.68}$$

$$4\sigma_g \tag{10.E.69}$$

has the highest energy

The

$$4\sigma_g \tag{10.E.70}$$

moleclar orbital has the highest energy; as expected since it more nodes.

Q10.18

Use the given Walsh diagram to predict the geometry of the following molecules:

a. H_2O
b. H_2S
c. H_2Be

Walshdiagramintro.gif

Walsh Diagram of an HAH molecule.Public Domain

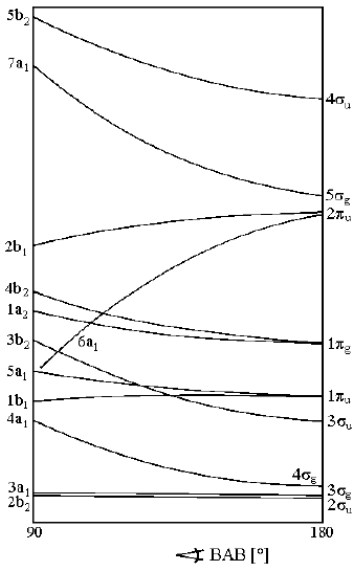
S10.18

The Walsh Diagram predicts the geometry of a molecule by assigning its valence electrons to the appropriate energy levels. In general, the lowest energy configuration is preferred.

a. H_2O has 8 valence electrons, which corresponds to the 4th highest orbital on the diagram. The **bent configuration** (90°) is lower in energy in this case.
b. H_2S has 8 valence electrons as well, because sulfur and oxygen are in the same periodic group. Therefore, the **bent configuration** will be favored.
c. H_2Be has 4 valence electrons, which corresponds to the 2nd highest orbital on the diagram. The **linear configuration** (180°) is lower in energy in this case.

Q10.19

Use the Walsh diagram for the valence electrons of a XY_2 molecule to predict whether the following molecules are linear or bent:



a. (CO_2) **b.** (CO_2^+) **c.** (CO_2^-) **d.** (SO_2^-) **b.** (CF_2^+)

S10.19

Valence Electrons	Geometry
2-16	linear
17-20	bent
21-24	linear

a. CO_2 16 valence electrons **Linear**
b. CO_2^+ 15 valence electrons **Linear**
c. CO_2^- 17 valence electrons **Bent**
d. SO_2^- 19 valence electrons **Bent**
e. CF_2^+ 18 valence electrons **Bent**

Q10.20

Walsh correlation diagrams can be used to predict the shapes of polyatomic molecules that contain more than three atoms. In this and the following three problems we consider molecules that have the general formula XH_3. We will restrict our discussion to XH_3 molecules, where all the H—X—H bond angles are the same. If the molecule is planar, then the H—X—H bond angle is 120°. A nonplanar XH_3 molecule, then, has an H—X—H bond angle that is less than 120°. Figure 10.26 shows the Walsh correlation diagram that describes how the energies of the molecular orbitals for an XH3 molecule change as a function of the H—X—H bond angle. Note that because XH_3 is not linear, the labels used to describe the orbitals on the two sides of the correlation diagram do not have designations such as and . We see that the lowest-energy molecular orbital is insensitive to the H—X—H bond angle. Which atomic orbital(s) contribute to the lowest-energy molecular orbital? Explain why the energy of this molecular orbital is insensitive to changes in the H—X—H bond angle.

S10.20

The lowest energy molecular orbital is the 1s orbital, which is a core atomic orbital instead of a bonding atomic orbital.

Q10.21

Consider the BH2 where the general Walsh diagram for a XH2 is shown below. What is the geometric preference of the molecule in ground and excited state?

S10.21

The BH2 molecule has the same geometric shape as water, it is bent where the HOMO is \({\pi_u}\). The first excited state relies on the degree of bending, and the $2a_1$ is unoccupied, and the next $1b_2$ is the highest occupied where the preferred geometry is linear, so at the first excited state will be linear.

BH_2 is a linear molecule. It has 4 valance electrons which fill 2 of the lines in the Walsh diagram. This second line has lower energy towards linear conformation and $1\sigma_u$.

Q10.24

Solve for ψ_π corresponding to the energy $E = \alpha + \beta$ for ethene.

S10.24

The bonding Huckel molecular orbitals is

$$\psi_\pi = c_1 2p_{z1} + c_2 2p_{z2} \tag{10.E.71}$$

the relationship of the coefficients can be defined as the following from the secular determinate:

$$c_1(\alpha - E) + c_2\beta = 0 \tag{10.E.72}$$

$$c_1\beta + c_2(\alpha - E) = 0 \tag{10.E.73}$$

Substituting $E = \alpha + \beta$ into these expressions and solving gives

$$-c_1\beta + c_2\beta = 0 \tag{10.E.74}$$

$$c_1 = c_2 \tag{10.E.75}$$

Then plugging back into the original equation gives

$$\psi_\pi = c_1(2p_{zA} + 2p_{zB}) \tag{10.E.76}$$

Now we can solve for c_1 by normalizing the wavefunction

$$c_1^2(1 + 2S + 1) = 1 \tag{10.E.77}$$

where S = 0 so solving yields

$$c_1 = \frac{1}{\sqrt{2}} \tag{10.E.78}$$

.

The final wave function can be written as

$$\psi_\pi = \frac{1}{\sqrt{2}}(2p_{z1} + 2p_{z2}) \tag{10.E.79}$$

Q10.25

Generalize the molecular orbital treatment of propene allyl cation. Find the energies and wave function of this molecule.

S10.25

The Huckel secular determinant for propene is

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{10.E.80}$$

making a substitution for $x = \frac{\alpha - E}{\beta}$ the secular determinant becomes

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{10.E.81}$$

Solving the determinant yields a cubic polynomial $x^3 - 2x = 0$ the roots of this polynomial are $x = 0, \pm\sqrt{2}$

Replacing x with the previous substitution made it is found that

$$E = \alpha \pm \sqrt{2}\beta \tag{10.E.82}$$

and

$$E = 0 \tag{10.E.83}$$

To find the wave function of propene you must find the constants

$$\begin{vmatrix} c_1(x) & c_2 & 0 \\ c_1 & c_2(x) & c_3 \\ 0 & c_2 & c_3(x) \end{vmatrix} = 0 \tag{10.E.84}$$

solving the determinant yields

$$c_1 = c_3 = \frac{1}{2} \tag{10.E.85}$$

$$c_2 = \frac{1}{\sqrt{2}} \tag{10.E.86}$$

therefore the wave function is

$$\psi = \frac{1}{2}1s + \frac{1}{\sqrt{2}}2s + \frac{1}{2}2p_z \tag{10.E.87}$$

Q10.26

Show that the six molecular orbitals for Benzene consturcted from the $2Pp_x$ atomic orbital on each of the six carbon atoms:

$$\psi_i = \sum_{j=1}^{6} c_{ij} 2p_{xj} \tag{10.E.88}$$

leads to a secular determinant.

S10.26

The above equation for benzene is :

$$\psi_i = c_{i1}2p_{z1} + c_{i2}2p_{z2} + c_{i3}2p_{z3} + c_{i4}2p_{z4} + c_{i5}2p_{z5} + c_{i6}2p_{z6} \tag{10.E.89}$$

The secular determinant for the benzene is :

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} & H_{15}-ES_{15} & H_{16}-ES_{16} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} & H_{25}-ES_{25} & H_{26}-ES_{26} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} & H_{35}-ES_{35} & H_{36}-ES_{36} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} & H_{45}-ES_{45} & H_{46}-ES_{46} \\ H_{15}-ES_{15} & H_{25}-ES_{25} & H_{35}-ES_{35} & H_{45}-ES_{45} & H_{55}-ES_{55} & H_{56}-ES_{56} \\ H_{16}-ES_{16} & H_{26}-ES_{26} & H_{36}-ES_{36} & H_{46}-ES_{46} & H_{56}-ES_{56} & H_{66}-ES_{66} \end{vmatrix} = 0 \tag{10.E.90}$$

$H_{11} = H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = \alpha$

$H_{12} = H_{23} = H_{34} = H_{45} = H_{56} = \beta$ The $H_{ij} = H_{ji}$ is a hermitian operator when i and j are neighbors

$H_{ij} = 0$ when i and j are not neighbors

$S_{11} = S_{22} = S_{33} = S_{44} = S_{55} = S_{66} = 1$

$S_{ij} = 0$

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10.S: Bonding in Polyatomic Molecules (Summary)

In this part of the text, we have discussed now how the basics of quantum mechanics apply to molecular systems. In particular we've found that no one knows how to solve the Schrödinger equation analytically for any molecule, but have introduced several approximations that help us get a handle on how chemical bonding and molecular structure come about. We've discussed brute-force ab-initio methods of solving the Schrödinger equation, and discussed some of the tradeoffs inherent in calculations. Finally, we talked about a couple approximate methods, hybridization and Hückel theory, that can give us quick ideas about structure and energetics in special cases, at the expense of accuracy and (sometimes) fidelity to reality. Armed with all of these tools, we now have a conceptual understanding of the electronic structure of molecules and how chemical bonding works. We have not yet looked at the internal degrees of freedom for molecules, so we don't know anything about molecular vibration or rotation in polyatomic molecules. We will study those later as we learn more about spectroscopy, because those topics are intimately linked. But first, we will take a look at the connection between symmetry and quantum mechanics, which will in turn lead naturally to spectroscopy.

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11: COMPUTATIONAL QUANTUM CHEMISTRY

Computational chemistry is the field of chemistry that uses mathematical approximations and computer programs to solve problems of chemical interest. Quantum chemistry is a subfield that addresses the equations and approximations derived from the postulates of quantum mechanics; specifically involving solving the Schrödinger equation for molecular systems. Quantum chemistry is typically separated into a*b initio,* which uses methods that do not include any empirical parameters or experimental data and semi-empirical which do.

11.1: Overview of Quantum Calculations

11.2: Gaussian Basis Sets

11.3: Extended Basis Sets

11.4: Orbital Polarization Terms in Basis Sets

11.E: Computational Quantum Chemistry (Exercises)

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11.1: Overview of Quantum Calculations

Multielectron Electronic Wavefunctions

We could symbolically write an approximate two-particle wavefunction as $\psi(r_1, r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_l) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_1, r_2)$. This new wavefunction must have the property that

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^* \psi(r_2, r_1) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.1.1}$$

Equation 11.1.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1, r_2) = e^{i\varphi} \psi(r_1, r_2)$$

so that

$$\left(e^{-i\varphi} \psi(r_1, r_2)^*\right) \left(e^{i\varphi} \psi(r_1, r_2)^*\right) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.1.2}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi} e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi} e^{i\varphi} = e^{i2\varphi} = 1$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature, but the behavior of elections is that the wavefunction be antisymmetric with respect to permutation ($e^{i\varphi} = -1$). A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\psi(r_2, r_1) = e^{i\varphi} \psi(r_1, r_2) = -\psi(r_1, r_2)$$

Blindly following the first statement of the Pauli Exclusion Principle, that each electron in a multi-electron atom **must** be described by a different spin-orbital, we try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) \tag{11.1.3}$$

After permutation of the electrons, this becomes

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1) \tag{11.1.4}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. However, an antisymmetric function must produce the same function multiplied by (–1) after permutation, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make a linear combination of functions. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 11.1.4 from the right-hand side of Equation 11.1.3 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1)]$$

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from

a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a Slater determinant.

The Slater determinant for the two-electron wavefunction for the ground state H_2 system (with the two electrons occupying the σ_{1s} molecular orbital)

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_{1s}(1)\alpha(1) & \sigma_{1s}(1)\beta(1) \\ \sigma_{1s}(2)\alpha(2) & \sigma_{1s}(2)\beta(2) \end{vmatrix}$$

We can introduce a shorthand notation for the arbitrary **spin-orbital**

$$\chi_{i\alpha}(\mathbf{r}) = \varphi_i\alpha$$

or

$$\chi_{i\beta}(\mathbf{r}) = \varphi_i\beta$$

as determined by the m_s quantum number. A shorthand notation for the determinant in Equation 8.6.4 is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = 2^{-\frac{1}{2}} Det|\chi_{1s\alpha}(\mathbf{r}_1)\alpha\chi_{1s\beta}(\mathbf{r}_2)\beta|$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is

$$(N!)^{-\frac{1}{2}}$$

for a system of N electrons.

The generalized Slater determinant for a multe-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{r}_1)\alpha & \chi_1(\mathbf{r}_1)\beta & \cdots & \chi_{N/2}(\mathbf{r}_1)\beta \\ \chi_1(\mathbf{r}_2)\alpha & \chi_2(\mathbf{r}_2)\beta & \cdots & \chi_{N/2}(\mathbf{r}_2)\beta \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_N)\alpha & \chi_2(\mathbf{r}_N)\beta & \cdots & \chi_{N/2}(\mathbf{r}_N)\beta \end{vmatrix} \tag{11.1.5}$$

In a modern *ab initio* electronic structure calculation on a closed shell molecule, the electronic Hamiltonian is used with a single determinant wavefunction. This wavefunction, Ψ, is constructed from molecular orbitals, ψ that are written as linear combinations of contracted Gaussian basis functions, φ

$$\varphi_j = \sum_k c_{jk}\psi_k \tag{11.1.6}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals. The exponential parameters in the STOs are optimized by calculations on small molecules using the nonlinear variational method and then those values are used with other molecules. The problem is to calculate the electronic energy from

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \tag{11.1.7}$$

or in bra-ket notation

$$E = \frac{\left\langle \Psi | \hat{H} | \Psi \right\rangle}{\langle \psi | \psi \rangle}$$

The the optimum coefficients c_{jk} for each molecular orbital in Equation 11.1.6 by using the Self Consistent Field Method and the Linear Variational Method to minimize the energy as was described previously for atoms.

The variational principle says an approximate energy is an upper bound to the exact energy, so the lowest energy that we calculate

is the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single determinant wavefunction (e.g., Equation 11.1.5). This limit is called the *Hartree-Fock limit*, the energy is the *Hartree-Fock energy*, the molecular orbitals producing this limit are called *Hartree-Fock orbitals*, and the determinant is the *Hartree-Fock wavefunction*.

Hartree-Fock Calculations

You may encounter the terms *restricted* and *unrestricted* Hartree-Fock. The above discussion pertains to a restricted HF calculation. In a restricted HF calculation, electrons with α spin are restricted or constrained to occupy the same spatial orbitals as electrons with β spin. This constraint is removed in an unrestricted calculation. For example, the spin orbital for electron 1 could be $\psi_A(r_1)\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(r_2)\beta(2)$, where both the spatial molecular orbital and the spin function differ for the two electrons. Such spin orbitals are called *unrestricted*. If both electrons are constrained to have the same spatial orbital, e.g. $\psi_A(r_1)\alpha(1)$ and $\psi_A(r_2)\beta(2)$, then the spin orbital is said to be *restricted*. While unrestricted spin orbitals can provide a better description of the electrons, twice as many spatial orbitals are needed, so the demands of the calculation are much higher. Using unrestricted orbitals is particular beneficial when a molecule contains an odd number of electrons because there are more electrons in one spin state than in the other.

Example 11.1.1 : Carbon Monoxide

It is well known that carbon monoxide is a poison that acts by binding to the iron in hemoglobin and preventing oxygen from binding. As a result, oxygen is not transported by the blood to cells. Which end of carbon monoxide, carbon or oxygen, do you think binds to iron by donating electrons? We all know that oxygen is more electron-rich than carbon (8 vs 6 electrons) and more electronegative. A reasonable answer to this question therefore is *oxygen*, but experimentally it is carbon that binds to iron.

A quantum mechanical calculation done by Winifred M. Huo, published in J. Chem. Phys. 43, 624 (1965), provides an explanation for this counter-intuitive result. The basis set used in the calculation consisted of 10 functions: the ls, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of C and O. Ten molecular orbitals (mo's) were defined as linear combinations of the ten atomic orbitals (Equation 11.1.6. The ground state wavefunction Ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 11.1.7 gives the energy of the ground state, where the denominator accounts for the normalization requirement. The coefficients C_{kj} in the linear combination are determined by the variational method to minimize the energy. The solution of this problem gives the following equations for the molecular orbitals. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

- $1s \approx 0.941s_o$. The 1 says this is the first σ orbital. The σ says it is symmetric with respect to reflection in the plane of the molecule. The large coefficient, 0.94, means this is essentially the 1s atomic orbital of oxygen. The oxygen 1s orbital should have a lower energy than that of carbon because the positive charge on the oxygen nucleus is greater.
- $2s \approx 0.921s_c$. This orbital is essentially the 1s atomic orbital of carbon. Both the 1σ and 2σ are "nonbonding" orbitals since they are localized on a particular atom and do not directly determine the charge density between atoms.
- $3s \approx (0.722s_o + 0.182p_{zo}) + (0.282s_c + 0.162p_{zc})$. This orbital is a "bonding" molecular orbital because the electrons are delocalized over C and O in a way that enhances the charge density between the atoms. The 3 means this is the third σ orbital. This orbital also illustrates the concept of hybridization. One can say the 2s and 2p orbitals on each atom are hybridized and the molecular orbital is formed from these hybrids although the calculation just obtains the linear combination of the four orbitals directly without the *à priori* introduction of hybridization. In other words, hybridization just falls out of the calculation. The hybridization in this bonding LCAO increases the amplitude of the function in the region of space between the two atoms and decreases it in the region of space outside of the bonding region of the atoms.
- $4s \approx (0.372s_c + 0.12p_{zc}) + (0.542p_{zo} - 0.432s_0)$. This molecular orbital also can be thought of as being a hybrid formed from atomic orbitals. The hybridization of oxygen atomic orbitals, because of the negative coefficient with $2s_O$, decreases the electron density between the nuclei and enhances electron density on the side of oxygen facing away from the carbon atom. If we follow how this function varies along the internuclear axis, we see that near carbon the function is positive whereas near oxygen it is negative or possibly small and positive. This change means there must be a node between the two nuclei or at the oxygen nucleus. Because of the node, the electron density between the two nuclei is

low so the electrons in this orbital do not serve to shield the two positive nuclei from each other. This orbital therefore is called an “antibonding” molecular orbital and the electrons assigned to it are called antibonding electrons. This orbital is the antibonding partner to the 3σ orbital.

- $1\pi \approx 0.322p_{xc} + 0.442p_{xo}\text{and}2\pi \approx 0.322p_{yc} + 0.442p_{yo}$. These two orbitals are degenerate and correspond to bonding orbitals made up from the p_x and p_y atomic orbitals from each atom. These orbitals are degenerate because the x and y directions are equivalent in this molecule. π tells us that these orbitals are antisymmetric with respect to reflection in a plane containing the nuclei.
- $5\sigma \approx 0.382_{sC} - 0.382_{pC} - 0.292p_{zO}$. This orbital is the sp hybrid of the carbon atomic orbitals. The negative coefficient for $2p_C$ puts the largest amplitude on the side of carbon away from oxygen. There is no node between the atoms. We conclude this is a nonbonding orbital with the nonbonding electrons on carbon. This is not a “bonding” orbital because the electron density between the nuclei is lowered by hybridization. It also is not an antibonding orbital because there is no node between the nuclei. When carbon monoxide binds to Fe in hemoglobin, the bond is made between the C and the Fe. This bond involves the donation of the 5σ nonbonding electrons on C to empty d orbitals on Fe. Thus molecular orbital theory allows us to understand why the C end of the molecule is involved in this electron donation when we might naively expect O to be more electron-rich and capable of donating electrons to iron.

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11.2: Gaussian Basis Sets

A basis set in theoretical and computational chemistry is a set of functions (called **basis functions**) which are combined in linear combinations (generally as part of a quantum chemical calculation) to create molecular orbitals. For convenience these functions are typically atomic orbitals centered on atoms, but can theoretically be any function; plane waves are frequently used in materials calculations.

The Variational Method and Basis Sets

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$\psi_i = \sum_j c_{ij}\varphi_j \tag{11.2.1}$$

The linear variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in chemical structure.

> Selecting the ab initio model for a chemical system is almost always involves a trade-off between accuracy and computational cost. More accurate methods and larger basis sets make jobs run longer.

In modern computational chemistry, quantum chemical calculations are typically performed using a finite set of basis functions. In these cases, the wavefunctions of the system in question are represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions in the basis set used.

The molecular spin-orbitals that are used in the Slater determinant usually are expressed as a linear combination of some chosen functions, which are called *basis functions*. This set of functions is called the *basis set*. The fact that one function can be represented by a linear combination of other functions is a general property. All that is necessary is that the basis functions *span-the-space*, which means that the functions must form a complete set and must be describing the same thing. For example, spherical harmonics cannot be used to describe a hydrogen atom radial function because they do not involve the distance r, but they can be used to describe the angular properties of anything in three-dimensional space.

This span-the-space property of functions is just like the corresponding property of vectors. The unit vectors $(\vec{x}, \vec{y}, \vec{z})$ describe points in space and form a complete set since any position in space can be specified by a linear combination of these three unit vectors. These unit vectors also could be called basis vectors.

Exercise 11.2.1 : "Spanning the Space"

Explain why the unit vectors $(\vec{x}, \vec{y})$ do not form a complete set to describe your (three-dimensional) classroom.

Just as we discussed for atoms, parameters in the basis functions and the coefficients in the linear combination can be optimized in accord with the Variational Principle to produce a self-consistent field (SCF) for the electrons. This optimization means that the

ground state energy calculated with the wavefunction is minimized with respect to variation of the parameters and coefficients defining the function. As a result, that ground state energy is larger than the exact energy, but is the best value that can be obtained with that wavefunction.

Slater Type Orbitals (STOs)

Intuitively one might select hydrogenic atomic orbitals as the basis set for molecular orbitals. After all, molecules are composed of atoms, and hydrogenic orbitals describe atoms exactly if the electron-electron interactions are neglected. At a better level of approximation, the nuclear charge that appears in these functions can be used as a variational parameter to account for the shielding effects due to the electron-electron interactions. Also, the use of atomic orbitals allows us to interpret molecular properties and charge distributions in terms of atomic properties and charges, which is very appealing since we picture molecules as composed of atoms. As described in the previous chapter, calculations with hydrogenic functions were not very efficient so other basis functions, **Slater-type atomic orbitals (STOs)**, were invented.

A minimal basis set of STOs for a molecule includes only those STOs that would be occupied by electrons in the atoms forming the molecule. As with most variational method calculations, a larger basis set improves the accuracy of the calculations by providing more variable parameters to produce a better approximate wavefunction. However, this is at the expense of increased computational time (i.e., calculation "cost" or "expense"). STOs have the following radial part (the spherical harmonic functions are used to describe the angular part)

$$R(r) = Nr^{n-1}e^{-\zeta r}$$

where

- n is a natural number that plays the role of principal quantum number, $n = 1,\ 2,\ ...,$
- N is a normalizing constant,
- r is the distance of the electron from the atomic nucleus, and ζ is a constant related to the effective charge of the nucleus, the nuclear charge being partly shielded by electrons. Historically, the effective nuclear charge was estimated by Slater's rules.

Double-zeta basis Sets

One can use more than one STO to represent one atomic orbital, as shown in Equation 11.2.2, and rather than doing a nonlinear variational calculation to optimize each ζ value, use two STOs with different ζ variables. The linear variation calculation then will produce the coefficients (C_1 and C_2) for these two functions in the linear combination that **best** describes the charge distribution in the molecule (for the ground state). The function with the large zeta accounts for charge near the nucleus, while the function with the smaller zeta accounts for the charge distribution at larger values of the distance from the nucleus. This expanded basis set is called a **double-zeta basis set**.

$$R_{2s}(r) = C_1 re^{-\zeta_1 r} + C_2 re^{-\zeta_2 r} \tag{11.2.2}$$

The use of double zeta functions in basis sets is especially important because without them orbitals of the same type are constrained to be identical even though in the molecule they may be chemically inequivalent. For example, in acetylene the p_z orbital along the internuclear axis is in a quite different chemical environment and is being used to account for quite different bonding than the p_x and p_y orbitals. With a double zeta basis set the p_z orbital is not constrained to be the same size as the p_x and p_y orbitals.

Example 11.2.1

Explain why the p_x, p_y, and p_z orbitals in a molecule might be constrained to be the same in a single-zeta basis set calculation, and how the use of a double-zeta basis set would allow the p_x, p_y, and p_z orbitals to differ.

Gaussian Orbitals

Although any basis set that sufficiently spans the space of electron distribution could be used, the concept of Molecular Orbitals as **Linear Combinations of Atomic Orbitals** **(LCAO)** suggests a very natural set of basis functions: AO-type functions centered on each nuclei. One obvious choice are the exact hydrogen AO's, known as **Slater-type orbitals (STO)** -describing the radial component of the functions. However, the computation of the integrals is greatly simplified by using **Gaussian-type orbitals (GTO)** for basis functions.

While the STO basis set was an improvement over hydrogenic orbitals in terms of computational efficiency, representing the STOs with Gaussian functions produced further improvements that were needed to accurately describe molecules. A Gaussian basis function has the form shown in Equation 11.2.3. Note that in all the basis sets, only the radial part of the orbital changes, and the spherical harmonic functions are used in all of them to describe the angular part of the orbital.

$$G_{nlm}(r,\theta,\psi) = N_n \underbrace{r^{n-1}e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta,\psi)}_{\text{angular part}} \tag{11.2.3}$$

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at $r = 0$, and they fall off more rapidly at large values of r (Figure 11.2.1).

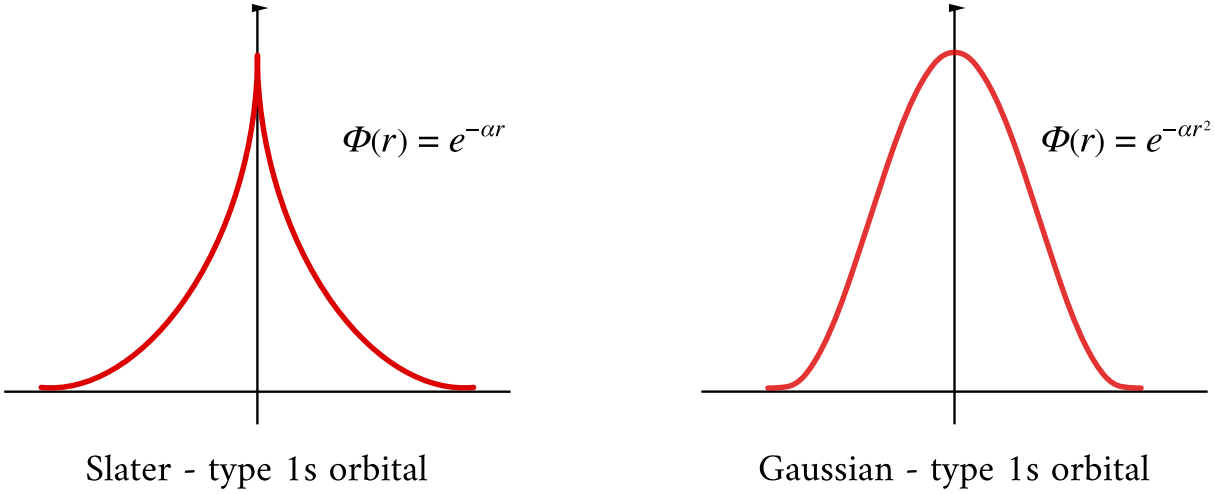


Figure 11.2.1 : Radial Dependence of Slater and Gaussian Basis Functions. (CC BY 4.0; Ümit Kaya via LibreTexts)

To compensate for this problem, each STO is replaced with a number of Gaussian functions with different values for the exponential parameter. These Gaussian functions form a *primitive Gaussian basis set*. Linear combinations of the primitive Gaussians are formed to approximate the radial part of an STO. This linear combination is not optimized further in the energy variational calculation, but rather is frozen and treated as a single function. The linear combination of **primitive Gaussian functions** is called a **contracted Gaussian function**. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials, so there is a net gain in the efficiency of the calculation.

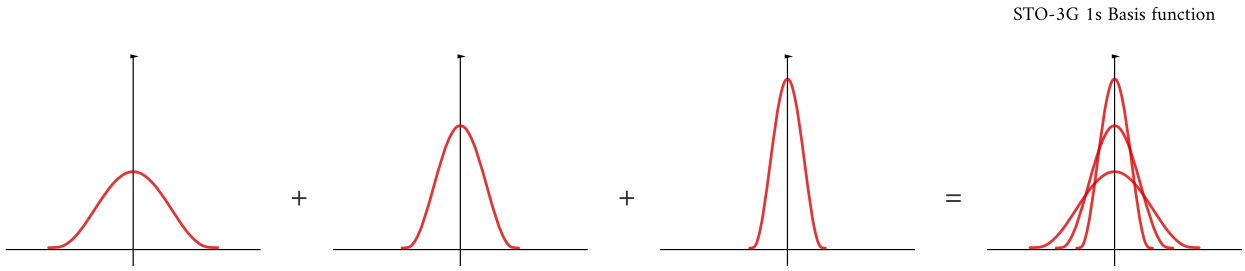


Figure 11.2.2 : To better represent the cusp in the electron density at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTOs (CGTO). The earliest CGTO basis sets, where constructed from N GTOs that best fit the desired STO. These are called STO-NG basis sets. (CC BY 4.0; Ümit Kaya via LibreTexts)

Gaussian basis sets are identified by abbreviations such as N-MPG*. N is the number of Gaussian primitives used for each inner-shell orbital. The hyphen indicates a split-basis set where the valence orbitals are double zeta. The M indicates the number of primitives that form the large zeta function (for the inner valence region), and P indicates the number that form the small zeta function (for the outer valence region). G identifies the set a being Gaussian. The addition of an asterisk to this notation means that a single set of Gaussian 3d polarization functions (discussed elsewhere) is included. A double asterisk means that a single set of Gaussian 2p functions is included for each hydrogen atom.

For example, 3G means each STO is represented by a linear combination of three primitive Gaussian functions. 6-31G means each inner shell (1s orbital) STO is a linear combination of 6 primitives and each valence shell STO is split into an inner and outer part (double zeta) using 3 and 1 primitive Gaussians, respectively (see Table 11.2.1 for other examples).

Table 11.2.1 : Different Gaussian Basis sets

Basis set	# functions		Basis set	# functions		Basis set	# functions
STO-3G	5		6-31G	9		6-311G	13
3-21G	9		6-31G*	15		6-311G*	18*
4-31G	9		6-31+G*	19		6-311+G*	22*

Example 11.2.2

The 1s Slater-type orbital $S_1(r) = \sqrt{4\zeta_1 e^{-\zeta_1 r}}$ with $\zeta_1 = 1.24$ is represented as a sum of three primitive Gaussian functions,

$$S_G(r) = \sum_{j=1}^{3} C_j e^{-\alpha_j r^2}$$

This sum is the contracted Gaussian function for the STO.

a. Make plots of the STO and the contracted Gaussian function on the same graph so they can be compared easily. All distances should be in units of the Bohr radius. Use the following values for the coefficients, C, and the exponential parameters, α.

index j	α_j	C_j
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

b. Change the values of the coefficients and exponential parameters to see if a better fit can be obtained.
c. Comment on the ability of a linear combination of Gaussian functions to accurately describe a STO.

Summary

When molecular calculations are performed, it is common to use a basis composed of a finite number of atomic orbitals (Equation 11.2.1), centered at each atomic nucleus within the molecule (linear combination of atomic orbitals ansatz). These atomic orbitals are well described with Slater-type orbitals (STOs), as STOs decay exponentially with distance from the nuclei, accurately describing the long-range overlap between atoms, and reach a maximum at zero, well describing the charge and spin at the nucleus. STOs are computationally difficult and it was later realized by Frank Boys that these Slater-type orbitals could in turn be approximated as linear combinations of Gaussian orbitals instead. Because it is easier to calculate overlap and other integrals with Gaussian basis functions, this led to huge computational savings

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11.3: Extended Basis Sets

Today, there are hundreds of basis sets composed of Gaussian Type Orbitals (GTOs). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain literally dozens to hundreds of basis functions on each atom.

Minimum Basis sets

A minimum basis set is one in which a **single** basis function is used for each orbital in a Hartree-Fock calculation on the atom. However, for atoms such as lithium, basis functions of p type are added to the basis functions corresponding to the 1s and 2s orbitals of each atom. For example, each atom in the first row of the periodic system (Li - Ne) would have a basis set of five functions (two s functions and three p functions).

> In a minimum basis set, a single basis function is used for each atomic orbital on each constituent atom in the system.

The most common minimal basis set is STO-nG, where n is an integer. This n value represents the number GTOs used to approximate the Slater Type orbital (STO) for both core and valence orbitals. Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper (less calculations requires) than the larger basis sets discussed below. Commonly used minimal basis sets of this type are: STO-3G, STO-4G, and STO-6G.

Two is Often Better than One

Minimal basis sets are not flexible enough for accurate representation of, which requires the use multiple functions to represent each atomic orbital. The distribution of the electron density of valence electrons is better represented by the sum of two orbitals with different "effective charges". This is a double-ζ basis sets and includes split-valence set (inner and valence) and linear combination of two orbitals of same type, but with different effective charges (i.e., ζ). This flexibility can be used to generate atomic orbital of adjustable sizes.

For example, the double-zeta basis set allows us to treat each orbital separately when we conduct the Hartree-Fock calculation.

$$\phi_i = a_1\phi_{2s}^{STO}(r,\zeta_1) + a_2\phi_{2s}^{STO}(r,\zeta_2) \tag{11.3.1}$$

The 2s atomic orbital approximated as a sum of two STOs. The two equations are the same except for the value of ζ which accounts for how large the orbital is. The constants a_1 and a_2 determines how much each STO contributes to the final atomic orbital, which will vary depending on the type of atom that the atomic orbit (i.e., hydrogen and lithium orbitals will have different a_1, a_2, ζ_1, and ζ_2 values).

Extended Basis Sets

The triple and quadruple-zeta basis sets work the same way, except use three and four STOs instead of two like in 11.3.1. The typical trade-off applies here as well, better accuracy, however with more expensive calculations. There are several different types of **extended basis sets** including: n split-valence, n polarized sets, n diffuse sets, and n correlation consistent sets. The notation of this sort of basis set (with a Gaussian basis) is

$$N-MPG$$

for describing split-valence basis set. N is the number of Gaussian functions describing inner-shell orbitals, while the hyphen denotes a split-valence set. M and P designate the number of Gaussian functions used to fit the two orbitals of the valence shell:

- M corresponds to number of Gaussian functions used to describe the smaller orbital
- P corresponds to number of Gaussian functions used to describe the larger orbital (e.g., 6-31G and 3-21G).

A minimal basis set is when one basis function for each atomic orbital in the atom, while a double-ζ, has two two basis functions for each atomic orbital. Correspondingly, a triple and quadruple-ζ set had three and four basis functions for each atomic orbital,

respectively. Higher order basis set have been constructed too, e.g., 5Z, 6Z,)..

There are hundreds of basis sets composed of Gaussian-type orbitals (Figure Figure 11.3.1). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain dozens to hundreds of basis functions on each atom.

Figure 11.3.1 : Commonly used split-valence basis sets

3-21G	3-21G	3-21G	3-21G* - Polarized	3-21+G - Diffuse functions	3-21+G* - With polarization and diffuse functions
4-21G	4-31G	4-31G	4-31G	4-31G	
6-21G	6-31G	6-31G*	6-31+G*	6-31G(3df, 3pd)	6-311G
6-311G	6-311G*	6-311+G*			

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11.4: Orbital Polarization Terms in Basis Sets

Polarization functions denoted in Pople's sets by an asterisk. Two asterisks, indicate that polarization functions are also added to light atoms (hydrogen and helium). n Polarization functions have one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1 s atomic orbital. When polarization is added to this basis set, a p -function is also added to the basis set. The 6-31G** is synonymous to 6-31 G(d,p).

The use of a minimal basis set with fixed zeta parameters severely limits how much the electronic charge can be changed from the atomic charge distribution to describe molecules and chemical bonds. This limitation is removed if STOs with larger n values and different spherical harmonic functions, the $Y_l^m(\theta, \varphi)$ in the definition of STO's are included. Adding such functions is another way to expand the basis set and obtain more accurate results. Such functions are called polarization functions because they allow for charge polarization away form the atomic distribution to occur.

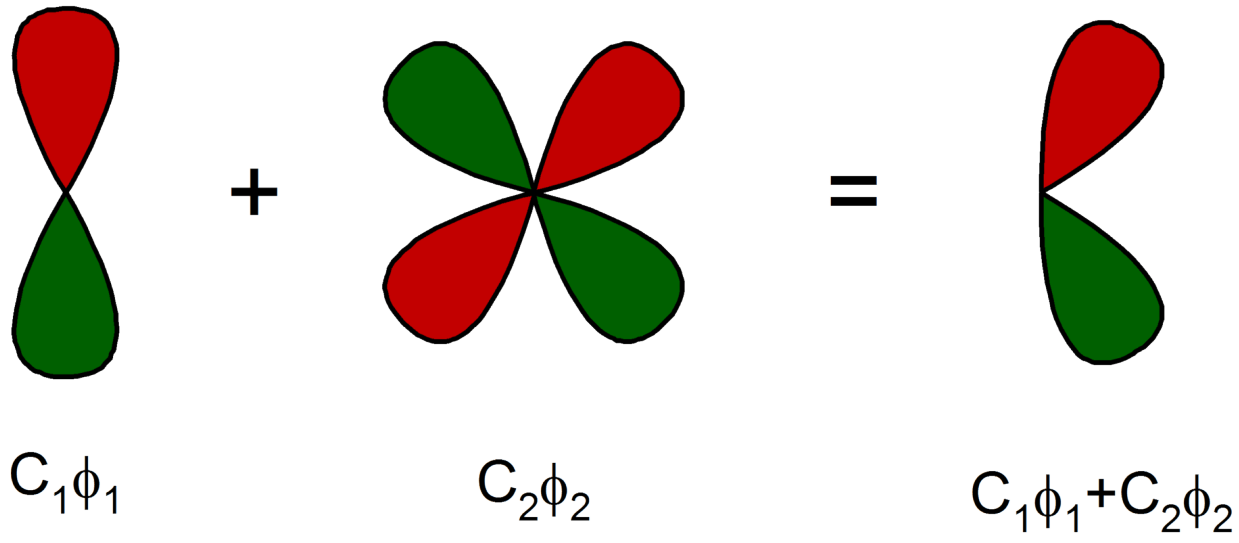


Figure 11.4.1 : A d-polarization function added to a p orbital. (CC-BY-SA-3.0; Rifleman 82)

The most common addition to minimal basis sets is probably the addition of polarization functions, denoted (in the names of basis sets developed by Pople) by an asterisk, *. Two asterisks, **, indicate that polarization functions are also added to light atoms (hydrogen and helium). These are auxiliary functions with one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1s atomic orbital. When polarization is added to this basis set, a p-function is also added to the basis set. This adds some additional needed flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen nucleus.

This is an important result when considering accurate representations of bonding between atoms, because the very presence of the bonded atom makes the energetic environment of the electrons spherically asymmetric. Similarly, d-type functions can be added to a basis set with valence p orbitals, and f-functions to a basis set with d-type orbitals, and so on. Another, more precise notation indicates exactly which and how many functions are added to the basis set, such as (d, p).

Diffuse Functions

Another common addition to basis sets is the addition of **diffuse functions**, denoted in Pople-type sets by a plus sign, +, and in Dunning-type sets by "aug" (from "augmented"). Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). These are very shallow Gaussian basis functions, which more accurately represent the "tail" portion of the atomic orbitals, which are distant from the atomic nuclei. These additional basis functions can be important when considering anions and other large, "soft" molecular systems.

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11.E: Computational Quantum Chemistry (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 11 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

What is meant by the expression ab initio calculation?
List all the terms in a complete molecular Hamiltonian.
Why are calculations on closed-shell systems more easily done than on open-shell systems?
How is it possible to reduce a multi-electron Hamiltonian operator to a single-electron Fock operator?
Why is the calculation with the Fock operator called a self-consistent field calculation?
What is the physical meaning of a SCF one-electron energy?
Why is the nonlinear variational method not used in every case to optimize basis functions, and what usually is done instead?
Why is it faster for a computer to use the variational principle to determine the coefficients in a linear combination of functions than to determine the parameters in the functions?
Identify the characteristics of hydrogenic, Slater, and Gaussian basis sets.
What is meant by the Hartree-Fock wavefunction and energy?
What is neglected that makes the Hartree-Fock energy necessarily greater than the exact energy?
What is meant by correlation energy?
What purpose is served by including configuration interaction in a calculation?

Q11.1

Prove that a three dimensional Gaussian function centered at r_1 = x_1i + y_1j + z_1k is a product of three one-dimensional Gaussian functions centered on x_1, y_1, z_1.

S11.1

$$e^{-a(r-r_0)^2} = e^{-a[(x-x_1)i+(y-y_1)j+(z-z_1)k]^2}$$

$$= e^{-a[(x-x_1)^2+(y-y_1)^2+(z-z_1)^2]}$$
$$= e^{-a(x-x_1)^2}\ e^{-a(y-y_1)^2}\ e^{-a(z-z_1)^2}$$

Q11.2

Show that

$$\int_0^\infty e^{-(x-x_0)^2}dx = \int_0^\infty e^{-x^2}dx = \frac{1}{2}\int_{-\infty}^\infty e^{-x^2}dx = \sqrt{\pi} \tag{11.E.1}$$

S11.2

The equalities are all equivalent since in the first integral x_0 is a constant and the second and third are even.

Q11.3

The Gaussian Integral

$$I_0 = \int_{-\infty}^\infty e^{-4x^2}dx \tag{11.E.2}$$

Convert the integration variables from Cartesian coordinates to polar coordinates and show that

$$I_0 = \frac{\sqrt{\pi}}{2} \tag{11.E.3}$$

S11.3

We first write

$$I_0^2 = \left(\int_{-\infty}^{\infty} e^{-4x^2} dx\right)^2 = \int_{-\infty}^{\infty} e^{-4x^2} dx \int_{-\infty}^{\infty} e^{-4y^2} dy \tag{11.E.4}$$

the product of two integrals can be expressed as a double integral

$$I_0^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-4(x^2+y^2)} dxdy \tag{11.E.5}$$

In polar coordinates $x^2 + y^2 = r^2$ and $dxdy = rdrd\theta$. The limits of integration in polar coordinates corresponding to the limits in Cartesian coordinates are $0 \leq r < \infty$ and $0 \leq \theta \leq 2\pi$.

The double integral becomes

$$I_0^2 = \int_0^{\infty} \int_0^{2\pi} e^{-4r^2} rdrd\theta = 2\pi \int_0^{\infty} e^{-4r^2} rdr. \tag{11.E.6}$$

The integration over θ gives a factor of 2π.The integral over r can be done using a **U substitution**, $u = 4r^2$ and $du = 8rdr$.

Therefore

$$\int_0^{\infty} e^{-4r^2} rdr = \frac{1}{8} \int_0^{\infty} e^{-u^2} du = \frac{1}{8} \tag{11.E.7}$$

meaning that $I^2 = 2\pi \times \frac{1}{8}$, so $I_0 = \frac{\sqrt{\pi}}{2}$.

Q11.4

Show that the integral

$$I_{2n} = \int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx$$

can be obtained from I_o

$$I_o = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

by differentiating n times with respect to a when I_o is

$$I_0 = \tfrac{1}{2}\left(\tfrac{\pi}{a}\right)^{\frac{1}{2}}$$

gives in a general form:

$$I_{2n} = \tfrac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n}\left(\tfrac{a}{2}\right)^{\frac{1}{2}}$$

S11.4

The first step is to take the derivative of I_o about 3 times with respect to a:

$$I_o = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

$$\frac{dI_o}{da} = \int_{-\infty}^{\infty} -x^2 e^{-ax^2} dx = -\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx$$

$$\frac{d^2 I_o}{da^2} = \int_{-\infty}^{\infty} -x^{2\cdot 2} e^{-ax^2} dx = \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx$$

solve the integrals for the first I_{2n} starting with I_o,

$$I_o = \int_{-\infty}^{\infty} e^{-ax^2} dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_2 = \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{dI_o}{da} = \frac{1}{4a}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_4 = \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx = \frac{d^2 I_o}{da^2} = -\frac{dI_2}{da} = \frac{3}{8a}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_6 = \int_{-\infty}^{\infty} x^6 e^{-ax^2} dx = -\frac{d^3 I_o}{da^3} = -\frac{dI_4}{da} = \frac{3\cdot 5}{16a}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

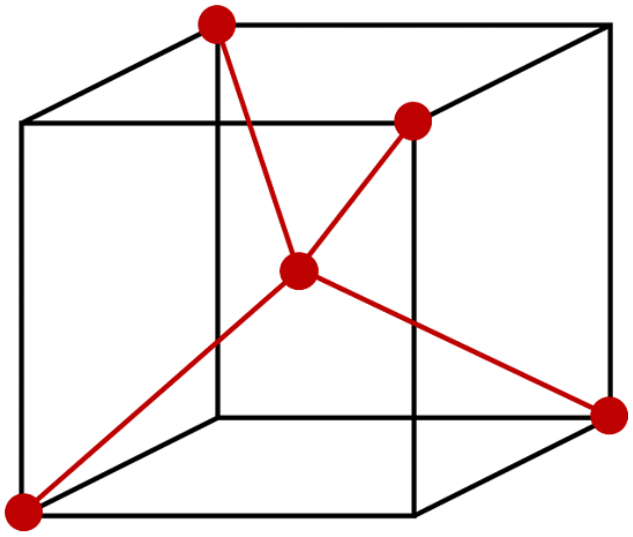
in general

$$I_{2n} = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\left(\frac{a}{2}\right)^{\frac{1}{2}}$$

(note: if you look at the equations sheet provided in the Gaussian integrals sections the limits of integration from -∞ to +∞ and from 0 to +∞ give the same end result with a minor difference in the exponent for the two in the denominator)

Q11.17

Using the Figure below, specify the coordinates of the atoms that comprise the molecule methane. Determine a set of Cartesian coordinates of the atoms in the molecule. The HCH bond angle is 110.0° and the C-H bond length is 109.1 pm.



S11.17

This figure can represent methane if and only if the central atom is carbon and the 4 atoms at the vertices are hydrogen atoms. We then must assign the origin of our coordinate system to be at the carbon atom. Considering the length of the edge of this cube is 2a, then the bond length from the vertices (hydrogen atoms) to the center (carbon atom) is $\sqrt{3}$ times the length of one edge of the cube, so

$$\frac{109.1\ pm}{\sqrt{3}} = 63\ pm = a \tag{11.E.8}$$

Diagonal of cube length 2a would be $2a\sqrt{(3)}$ - but we need half that.

Q11.18

Determine a rough set of Cartesian coordinates of the atoms in the molecule SiH_3F given the bond angle of $H-Si-H$ is 109.5° and the $Si-H$ and $Si-F$ bond lengths are 146.0 and $159.5\ pm$, respectively. (Hint: locate the origin at the Silicon.)

S11.18

For a simpler case of SiH_4, The four hydrogen would be equally far from the central atom (origin). The coordinates can be calculated as (a,a,a) ,$(-a,-a,a)$,$(a,-a,-a)$, and $(-a,-a,-a)$. The value of a can be determined by $a=\frac{l}{\sqrt{3}}$ where l is the bond length. For hydrogen:

$$a=\frac{146\,pm}{\sqrt{3}}=84.29\,pm \tag{11.E.9}$$

For florine:

$$a=\frac{159.5\,pm}{\sqrt{3}}=92.09\,pm \tag{11.E.10}$$

One set of solutions is:

	x/pm	y/pm	z/pm
C	0	0	0
H	84.29	84.29	84.29
H	-84.29	-84.29	84.29
H	84.29	-84.29	-84.29
F	-92.09	-92.09	-92.09

Q11.19

Molecule	Frequency [cm^{-1}]	R_e [pm]
H_2	4647	73.2
CO	2438	111.4
HCl	2886	130

Given the above table of calculated vibrational frequencies and bond lengths, calculate the vibrational force constant of each of the molecules. Do you expect that the calculated values are higher or lower than the experimental values? Are bond length calculations or vibrational-frequency calculations more accurate? Why?

S11.19

The relationship between wave number and harmonic force constant can be expressed as

$$\tilde{\nu}=(2c\pi)^{-1}\sqrt{\frac{k}{\mu}} \tag{11.E.11}$$

which can be rewritten as

$$k = 4\mu(\tilde{\nu}c\pi)^2. \tag{11.E.12}$$

The reduced masses can be found to be

$$\mu_{H_2} = 8.38 \times 10^{-28}\text{kg}, \mu_{CO} = 1.14 \times 10^{-26}\text{kg}, \text{and } \mu_{HCl} = 1.626 \times 10^{-27}\text{kg}.$$

Now we can find our force constants by plugging in the given values.

- $k_{H_2} = 642N/m$
- $k_{CO} = 2404N/m$
- $k_{HCl} = 481N/m$

We should expect that the values we found are higher than what is experimentally measured, as other forces are unaccounted for. Bond length calculations are more accurate because it requires a smaller basis set to calculate accurately.

Q11.20

Normalize the following Gaussian function:

$$\phi(r) = xe^{-\alpha r^2} \tag{11.E.13}$$

S11.20

We write $\phi(r)$ in spherical coordinates and then apply the normalization condition of the normalized function $A\phi(r)$

The normalization condition is

$$\int A^2x^2e^{-2\alpha r^2}d\tau = 1 \tag{11.E.14}$$

or in bra-ket notation

$$\langle\phi(r)|\phi(r)\rangle = 1.$$

where A is the normalization constant. In spherical coordinates,

$$1 = \int A^2r^2\sin^2\theta\cos^2\phi e^{-2\alpha r^2}d\tau \tag{11.E.15}$$

$$= A^2\int_0^\infty r^4e^{-2\alpha r^2}dr\int_0^\pi \sin^3\theta d\theta\int_0^{2\pi}\cos^2\phi d\phi \tag{11.E.16}$$

$$\frac{1}{A^2} = \frac{3}{8(2\alpha)^2}\left(\frac{\pi}{2\alpha}\right)^{1/2}\left(\frac{4}{3}\right)(\pi) \tag{11.E.17}$$

$$= \frac{\pi^{3/2}}{2^{7/2}\alpha^{5/2}} \tag{11.E.18}$$

Therefore, the nomalization constant will the inverse of this result:

$$A = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} \tag{11.E.19}$$

Q11.21

Which hydrogen atomic orbital corresponds to the following normalized Gaussian orbital?

$$G(x,y,z;\alpha) = \left(\frac{128\alpha^5}{\pi^3}\right)^{0.25} y e^{-\alpha r^2} \tag{11.E.20}$$

How many radial and angular nodes does the above function have? Is this result what you would expect for the corresponding hydrogen function?

S11.21

The typical form is:

$$G_{nlm}(r,\theta,\phi) = N_n r^{n-1} e^{-\alpha r^2} Y_l^m(\theta,\phi) \tag{11.E.21}$$

.

From this, we can see the function in the question shows n = 2 and l = 1. Because n = 2, there is 1 node and l = 1 tells us that there is 1 angular node. Therefore, there are no radial nodes.This is consistent with the $2p_y$ orbital in a hydrogenic function.

Q11-22

Slater type orbitals have the form,

$$\chi_{nlm} = R_n(r) Y_{lm}(\theta,\phi) \tag{11.E.22}$$

where the second term is the spherical harmonic given by

$$R_n(r) = \frac{(2\alpha)^{(n+1/2)}}{\sqrt{(2n)!}} r^{(n-1)} e^{(-\alpha r)} \tag{11.E.23}$$

Define the 1s-slater type orbital.

S11-22

For n=1, the slater-type orbital is

$$\phi_{nlm} = \frac{(2\zeta)^{(n+1/2)}}{\sqrt{(2n)!}} r^{(n-1)} e^{(-\zeta r)} Y_{lm}(\theta,\phi) \tag{11.E.24}$$

$$\phi_{1s}(r,\zeta) = S_{100}(r,\zeta) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r} \tag{11.E.25}$$

11.23

Consider the normalized functions

$$G_1(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})^(\frac{1}{4})x^2 e^(-\alpha r^2) \tag{11.E.26}$$

$$G_2(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})^(\frac{1}{4})y^2 e^(-\alpha r^2) \tag{11.E.27}$$

$$G_3(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})^(\frac{1}{4})z^2 e^(-\alpha r^2) \tag{11.E.28}$$

$$G_4(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})^(\frac{1}{4})(x^2-y^2) e^(-\alpha r^2) \tag{11.E.29}$$

Which hydrogen atomic orbital corresponds to the linear combination

$$G_3(x,y,z;\alpha) + G_1(x,y,z;\alpha)? \tag{11.E.30}$$

S11.23

$$G_3(x,y,z;\alpha) + G_1(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})^(\frac{1}{4})(z^2+x^2)e^(-\alpha r^2) \tag{11.E.31}$$

Corresponds to the

$$3d_{z^2+x^2} \tag{11.E.32}$$

hydrogen atomic orbital.

This is a good tricky question because usually people would think that

$$H_2 \tag{11.E.33}$$

only has two energy levels, but really there are more, just not occupied. Once you excite/add a good amount of energy, it could change to different orbitals.

(The math is right but Hydrogen has only five 3d orbitals and they are $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{y^2}$, and $3d_{(x^2-y^2)}$ so the $3d_{z^2+x^2}$ is not consistent . -RM)

Q11.27

Scientists are trying to theoretically predict the dipole moment of a CO molecule using the STO-3G and 6-31G* basis sets. When compared to their experimental data, the 6-31G* basis set provided a more accurate calculation than did the STO-3G basis set. Why is this?

S11.27

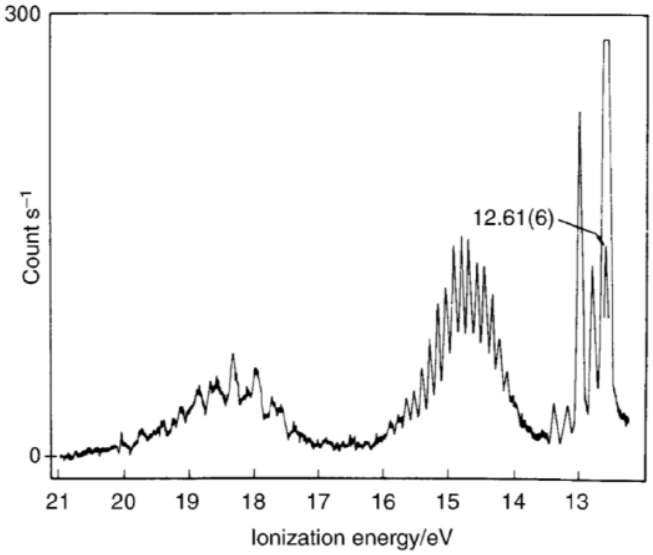
To calculate the dipole moment of a molecule, one needs an accurate description of the electron densities and molecular orbitals. This description becomes **more accurate when a larger basis set is used**, which is why the 6-31G* basis set gave more accurate calculations than did the STO-3G basis set.

Q11.28

The orbital energies calculated for formaldehyde using STO-3G an 3-21G basis sets are given below.

Orbital	energy/E_h	energy/E_h
$1a_1$	-20.3217	-20.4856
$2a_1$	-11.1250	-11.2866
$3a_1$	-1.3373	-1.4117
$4a_1$	-0.8079	-0.8661
$1b_2$	-0.6329	-0.6924
$5a_1$	-0.5455	-0.6345
$1b_1$	-0.4431	-0.5234
$2b_2$	-0.3545	-0.4330
$2b_1$	0.2819	0.1486
$6a_1$	0.6291	0.2718
$3b_2$	0.7346	0.3653
$7a_1$	0.9126	0.4512

Determine the ground-state electronic configuration of water. The photoelectron spectrum of water is shown below.



Assign the bands. Which calculated set of energies shows the best agreement with the photoelectron spectrum? Predict the ionization energy and electron affinity of water for each calculated set of energy levels. How do these compare with the experimental values?

S11.28

There are 8 electrons in water (2 from water and 6 from oxygen). This gives use the ground-state electronic configuration of

$$1a_1^2 2a_1^2\ 1b_2^2\ 3a_1^2\ 1b_1^2$$

The band at approx. 15 eV corresponds to the $1b_1^2$ electrons, the bands at 15.5 eV correspond to $1b_2^2\ 3a_1^2$ electrons. 18.5 ev = $1a_1^2 2a_1^2$.

IE = $-E_{2h2}$ = 0.6924*15 ev = 10.386 ev

EA = $-E_{2h1}$ = 0.5234*18.5 ev = 9.6829 ev

Q11.29

The units of dipole moment given by Gaussian 94 are called debyes (D), after the Dutch-American chemist, Peter Debye, who was awarded the Nobel Prize for chemistry in 1936 for his work on dipole moments. One dehye is equal to 10^{-18} esu•cm where esu (electrostatic units) is a non-SI unit for electric charge. Given that a 9v battery is 3.0 x 10^{-2} esu, show that the conversion factor between debyes and C • m (coulomb • meters) is 1 D = 5.34 x 10^-38 C•m.

S11.29

$$1D = 1 * 10^{-18} esu \bullet cm \left(\frac{1.6022 * 10^{-19}\, C}{4.803 * 10^{-10}\, esu} * \frac{1m}{100cm} \right) = 3.3407 * 10^{-30}\, C \bullet m \qquad (11.E.34)$$

Q11.30

Determine the dipole moment $SnCl_2$ by using the geometry and charges:

$$z = e \sum X_i r_i \tag{11.E.35}$$

S11.30

$$e((0.41sin(52.57)i + .041cos(52.75)j)94.7 * 10^{-12}m + (0.41sin(52.57)i + 0.41cos(52.75)j)94.7x10^{-12}m) \tag{11.E.36}$$

$$= 2.3D \tag{11.E.37}$$

Notes:

The equation I found for dipole moment is:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{11.E.38}$$

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12: GROUP THEORY - THE EXPLOITATION OF SYMMETRY

Symmetry can help resolve many chemistry problems and usually the first step is to determine the symmetry. If we know how to determine the symmetry of small molecules, we can determine symmetry of other targets which we are interested in. Usually, it is not only the symmetry of molecule but also the symmetries of some local atoms, molecular orbitals, rotations and vibrations of bonds, etc. that are important. For example, if the symmetries of molecular orbital wave functions are known, we can find out information about the binding. Also, by the selection rules that are associated with symmetries, we can explain whether the transition is forbidden or not and also we can predict and interpret the bands we can observe in Infrared or Raman spectrum. The qualitative properties of molecular orbitals can be obtained using symmetry from group theory (whereas their precise energetics and ordering have to be determined by a quantum chemical method). Group Theory is a branch of the mathematical field of algebra. In quantum chemistry, group theory can applied to *ab initio* or semi-empirical calculations to significantly reduce the computational cost. Symmetry operations and symmetry elements are two basic and important concepts in group theory. When we perform an operation to a molecule, if we cannot tell any difference before and after we do the operation, we call this operation a *symmetry operation*. This means that the molecule seems unchanged before and after a symmetry operation. As Cotton defines it in his book, when we do a symmetry operation to a molecule, every points of the molecule will be in an equivalent position.

12.1: The Exploitation of Symmetry Can Help Simplify Numerical Calculations

12.2: Symmetry Elements and Operations Define the Point Groups

12.3: Symmetry Operations Define Groups

12.4: Symmetry Operations as Matrices

12.5: Molecules can be Represented by Reducible Representations

12.6: Character Tables Summarize the Properties of a Point Group

12.7: Characters of Irreducible Representations

12.8: Using Symmetry to Solve Secular Determinants

12.9: Generating Operators

12.10: Molecular Motions of a Molecule can be Represented by a Reducible Reperesentation

12.11: Reducible Representations are Comprised of Irreducible Representations

12.12: Normal Modes of Vibrations Describe how Molecules Vibrate

12.13: Symmetry of Vibrations Describes their Spectroscopic Behavior

12.14: Symmetry Adapted Linear Combinations are the Sum over all Basis functions

12.15: Molecular Orbitals can be Constructed on the Basis of Symmetry

12.E: Group Theory - The Exploitation of Symmetry (Exercises)

12.S: Group Theory - The Exploitation of Symmetry (Summary)

12.T: Character Tables

12.T: Correlation Tables

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12.1: The Exploitation of Symmetry Can Help Simplify Numerical Calculations

To a fully understand the math behind group theory one needs to take a look at the theory portion of the Group Theory topic or refer to one of the reference text listed at the bottom of the page. Never the less as Chemist the object in question we are examining is usually a molecule. Though we live in the 21st century and much is known about the physical aspects that give rise to molecular and atomic properties. The number of high level calculations that need to be performed can be both time consuming and tedious. To most experimentalist this task is takes away time and is usually not the integral part of their work. When one thinks of group theory applications one doesn't necessarily associated it with everyday life or a simple toy like a Rubik's cube. A Rubik's cube is an a cube that has a 3×3 array of different colored tiles on each of its six surfaces, for a total of 54 tiles. Since the cube exist in 3D space, the three axis are x, y, z. Since the rubik's cube only allows rotation which are called operations, there are three such operations around each of the x, y, z axis.

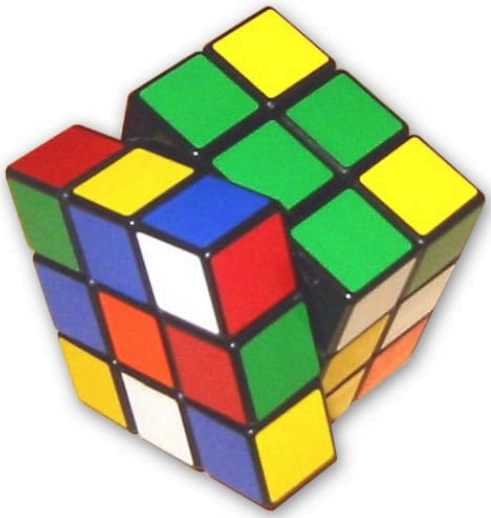


Figure: Reubik's cube. Use with permission from Wikipedia

Of course the ultimate challenge of a Rubik's cube is to place all six colors on each of the six faces. By performing a series of such operations on the Rubik's cube one can arrive at a solution (A link of a person solving a Rubik's cube[1] in 10.4s with operations performed noted, the operations performed will not translate to chemistry applications but it is a good example of how symmetry operations arrive at a solution). The operations shown in the Rubik's cube case are inherent to the make up of the cube, i.e., the only operations allowed are the rotations along the x, y, z axis. Therefore the Rubik's cube only has x,y,z rotation operations. Similarly the operations that are specific to a molecule are dependent on its symmetry.

Using group theory, we can exploit the symmetry of molecules to give us a rich amount of information on the molecular orbitals, rotations, and vibrations of bonds, to name a few. Making symmetry arguments, we can skip complicated quantum calculations to gain qualitatively accurate information.

In section 10.7, we used Hückel theory to explore the π bonding network of benzene by constructing linear combinations of $2p_x$ atomic orbitals on the carbon atoms. In doing so, the roots of the secular equations were found via solving the 6×6 secular determinant.

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{12.1.1}$$

Since the secular determinant is a 6×6 matrix, there are six solutions or values of x that can be determined after expanding the determinant into the resulting (6th-order) polynomial.

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{12.1.2}$$

Secular determinants are formulated in terms of a specific basis set; i.e., a set of functions that describe the wavefunctions. For the determinnat in Equation 12.1.1, that basis set is the the $\{|2p_z\rangle\}$ orbitals on the carbons. However, any basis set can be used to represent the determinant (long as it span the same space). For example, the following linear combination of $\{|2p_z\rangle\}$ orbitals could also be used:

$$\begin{aligned}
|\phi_1\rangle &= \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle\right] \\
|\phi_2\rangle &= \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle\right] \\
|\phi_3\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle\right] \\
|\phi_4\rangle &= \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle\right] \\
|\phi_5\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle\right] \\
|\phi_6\rangle &= \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle\right]
\end{aligned}$$

In this new basis set $\{\phi\rangle\}$, the secular determinant Equation 12.1.1 is represented as

$$\begin{vmatrix} x+2 & 0 & 0 & 0 & 0 & 0 \\ 0 & x-2 & 0 & 0 & 0 & 0 \\ 0 & 0 & x+1 & \frac{x+1}{2} & 0 & 0 \\ 0 & 0 & \frac{x+1}{2} & x+1 & 0 & 0 \\ 0 & 0 & 0 & 0 & x-1 & \frac{x-1}{2} \\ 0 & 0 & 0 & 0 & \frac{x-1}{2} & x-1 \end{vmatrix} = 0 \tag{12.1.3}$$

This is the determinant into a bock diagonal form; which can be expanded into a product of smaller determinants to give the polynomial

$$\frac{9}{16}(x+2)(x-2)(x+1)^2(x-1)^2 = 0$$

The roots to this equation are ± 2, ± 1 and ± 1. This is not surprising since these are the same roots obtained from expanding the determinant in the original basis set (Equation 12.1.2). You may remember that the selection of a specific basis set to represent a function does not change the fundamental nature of the function (e.g., a parabola in 2D space is the same curve if represented in terms of Cartesian coordinates (x and y) or polar coordinates (θ and r), which both span 2-D space).

As you recall, Hückel theory (irrespective of the basis set) was used to simplify the general secular determinant (e.g., for benzene)

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} & H_{15}-ES_{15} & H_{16}-ES_{16} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} & H_{25}-ES_{25} & H_{26}-ES_{26} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} & H_{35}-ES_{35} & H_{36}-ES_{36} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} & H_{45}-ES_{45} & H_{46}-ES_{46} \\ H_{51}-ES_{51} & H_{52}-ES_{52} & H_{53}-ES_{53} & H_{54}-ES_{54} & H_{55}-ES_{55} & H_{56}-ES_{56} \\ H_{61}-ES_{61} & H_{62}-ES_{62} & H_{63}-ES_{63} & H_{64}-ES_{64} & H_{65}-ES_{65} & H_{66}-ES_{6} \end{vmatrix} = 0 \tag{12.1.4}$$

where H_{ij} are the Hamiltonian matrix elements

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int \phi_i \phi_j \mathrm{d}v$$

In general, this involves solving 36 Hamiltonian matrix elements (H_{ij}) and 36 overlap integrals (S_{ij}), which can be a daunting task to do by hand without the assumptions of Hückel theory to help out. As with the application of Hückel theory, which was used to set most of these integrals to zero, solving for the energies from Equation 12.1.4 can be simplified by using the intrinsic symmetry of the benzene system to demonstrate (rigorously) that many of these integrals are zero. This is the subject of group theory. Group theory is used to exploit the symmetry of molecules to quickly gain insights into their properties, such as vibrations and molecular orbitals.

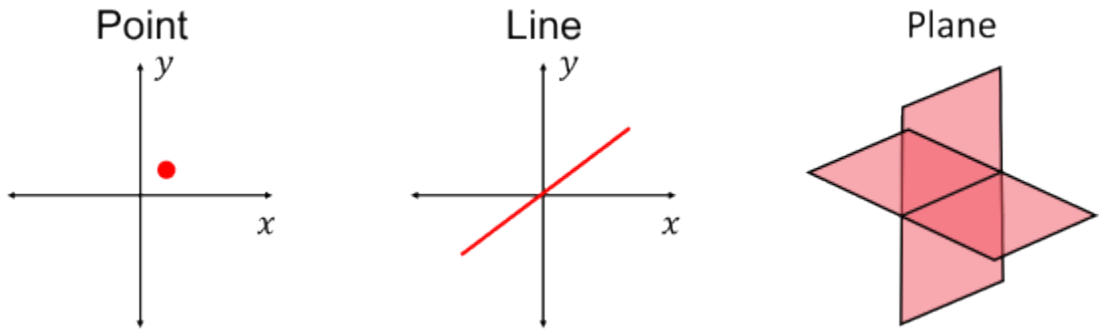
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12.2: Symmetry Elements and Operations Define the Point Groups

Symmetry Elements

A *symmetry operation* is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. Each symmetry operation has a corresponding *symmetry element*, which is the axis, plane (2-dimensional), line (1-dimensional) or point (0-dimensional) with respect to which the symmetry operation is carried out:



The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a *symmetry axis*; in a reflection the points that remain unchanged make up a *plane of symmetry*. The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. The symmetry elements that a molecule (and any other 3-D object) may possess are discussed below.

Symmetry Operations

The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. There are five types of operations:

1. Identity, E
2. Rotation, C_n
3. Reflection, σ
4. Inversion, i
5. Improper Rotation, S_n

Symmetry Operations

A symmetry operation is a permutation of atoms such that the molecule is transformed into a state **indistinguishable** from the starting state.

Identity Symmetry, E

The identity operator, E, consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule possesses at least this operation. For example, the $\mathrm{CHFClBr}$ molecule in Figure 12.2.1 . The identify symmetry operation is not indicated since all molecule exhibit this symmetry.

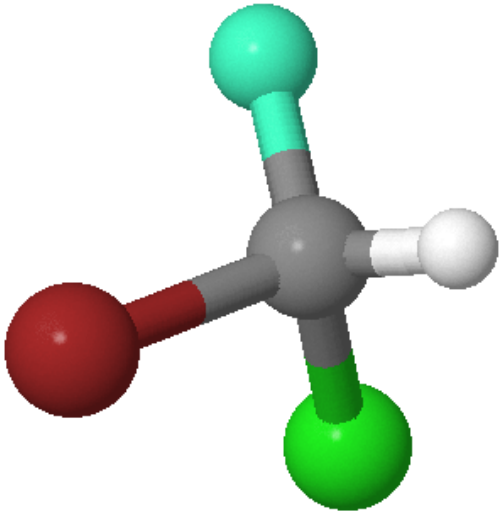


Figure 12.2.1 : Example of Identify Symmetry: The $\mathrm{CHFClBr}$ molecule contain no other symmetry other than identity. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

n-fold Axis of Rotation, C_n

The rotation operation (sometimes called proper rotation), C_n, rotates an object about an axis by $2\pi/n$ radians or $360^\circ/n$. Rotation by C_n leaves the molecule unchanged. The H_2O molecule has a C_2 axis (Figure 12.2.2). Molecules can have more than one C_n axis, in which case the one with the highest value of n is called the *principal axis*. In some high symmetry systems, there may be more than one principal axis. Note that by convention, rotations are *counterclockwise* about the axis. C_n rotations are indicated via vectors with labels as indicated below.

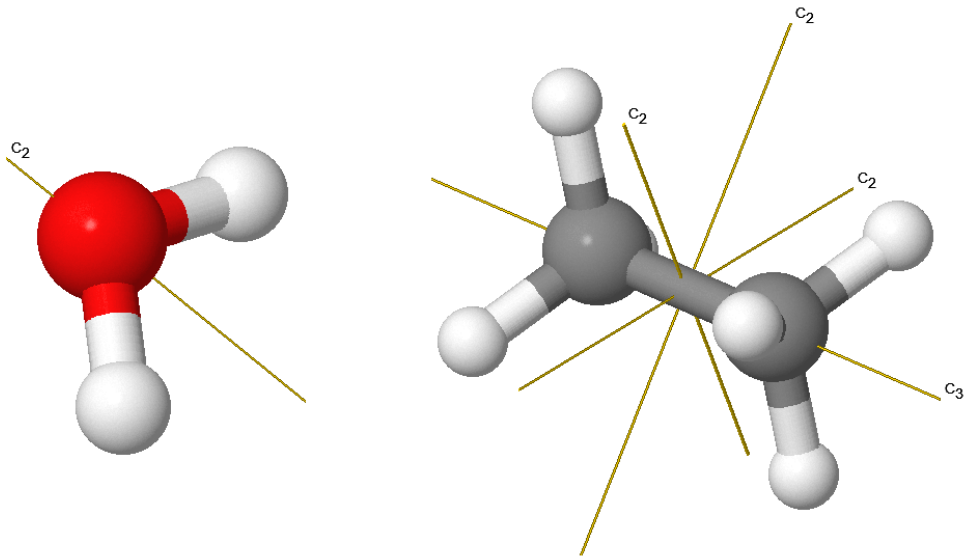


Figure 12.2.2 : Examples of n-fold Axis of Rotation: (left) The water molecule contains a C_2 axis. (right) Ethane contains both C_2 and C_3 axes. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

We always want to express rotations in their simplest equivalent fractions of m/n:

$$C_4^2 = C_2$$

$$C_6^4 = C_3^2$$

$$C_8^6 = C_4^3$$

Rotating an object n times brings the object back to the original object and is equivalent to the identity operation, E:

$$C_n^n = E$$

Linear molecules have a very high rotational symmetry: C_∞. Examples include diatomics such as CO, NO, and $\mathrm{CO_2}$.

Reflection, σ

Reflection, σ, defines the bilateral symmetry about a plane (mirror plane / reflection plane). Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labeled σ_v, while one perpendicular to the axis is called a horizontal mirror plane and is labeled σ_h. A vertical mirror plane that bisects the angle between two C_2 axes is called a dihedral mirror plane, σ_d. If no principal axis exist, σ_h is defined as the plane of the molecule. σ symmetry is indicated as a plane on molecules; since they often bisect atoms, which should be clearly indicated.

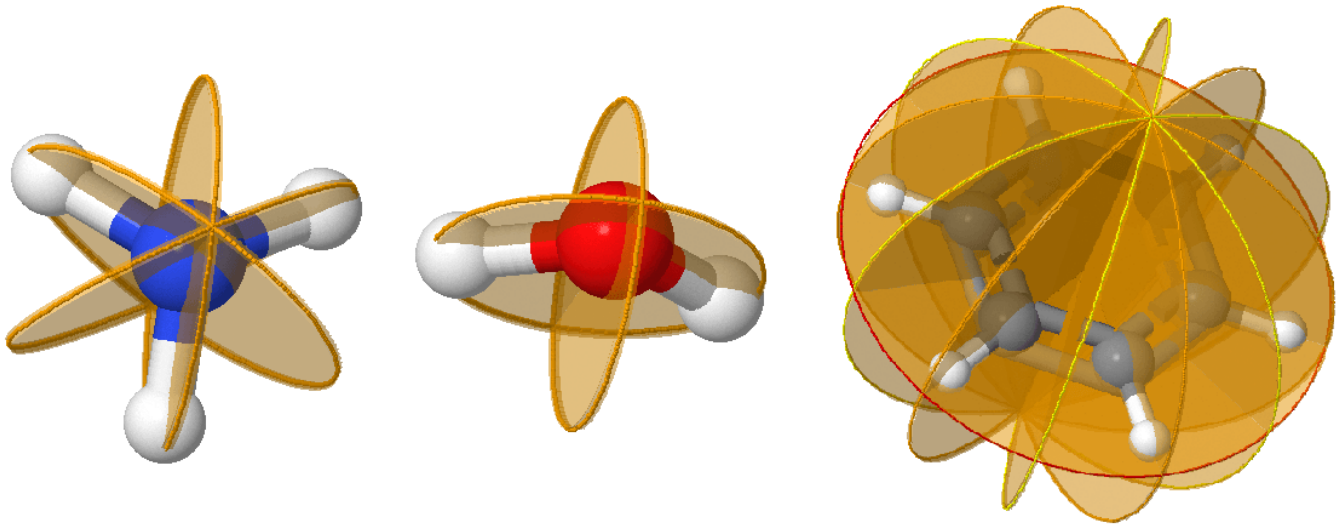


Figure 12.2.3 : Examples of reflection symmetry. (left) The ammonia molecule contains three identical reflection planes. All are designated as vertical symmetry planes (σ_v) because they contain the principle rotation axis.(middle) The water molecule contains two different reflection planes. (right) benzene contains a total of seven reflection planes, one horizontal plane (σ_h) and six vertical planes (σ_v and σ_d). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

For any mirror plane, performing two successive reflections about the same plane brings objects back to their original configuration:

$$\sigma\sigma = \sigma^2 = E$$

Inversion, i

Inversion, i, through the center of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the center of inversion and out to the same distance on the other side of the molecule. If inversion symmetry exists, a line drawn from any atom through the center will connect with an equivalent atom at an equivalent distance from the center. Examples of molecules with centers of inversion is shown in Figure 12.2.4 . Centers of inversion are indicated via a point, which may or may not overlap with an atoms. The inversion center is always located at the central point of the molecule and there can only be one inversion center in any system. The centers of inversion in the examples below do not overlap with atoms.

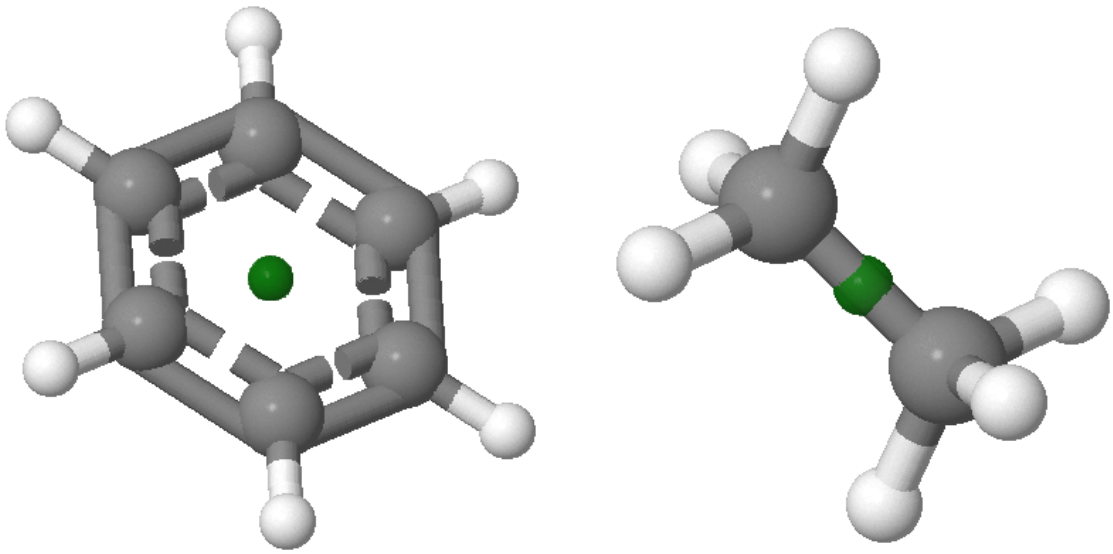


Figure 12.2.4 : Examples of Center of Inversion Symmetry. (left) Benzene and (right) staggard ethane have centers of inversion (green balls). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Performing inversion twice in succession brings every point back to its original position:

$$ii = i^2 = E$$

Molecules with no inversion symmetry are said to be centrosymmetric.

n-fold Axis of Improper Rotation, S_n

Improper rotations, S_n, are also called rotation-reflections. The rotation-reflection operation consists of rotating by C_n about an axis, followed by reflecting in a plane perpendicular to the same axis. Improper rotation symmetry is indicated with both an axis and a plan as demonstrated in the examples in Figure 12.2.5 .

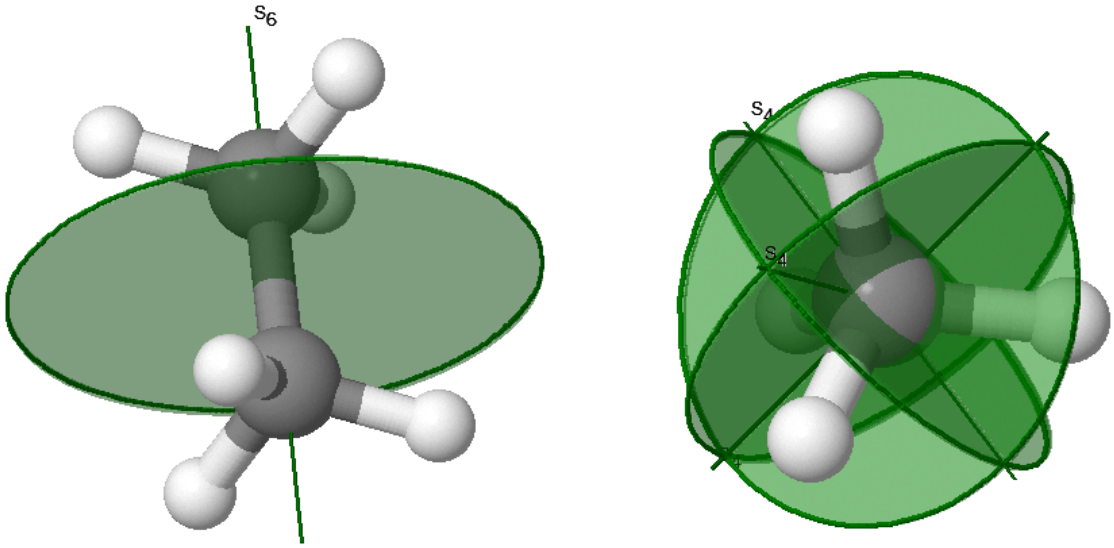


Figure 12.2.5 : Examples of Improper axis of rotation. (left) Staggered ethane contains an S_6 axis of improper rotation. (right) Methane contains three S_4 axes of improper rotation. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Note

S_1 is the same as reflection and S_2 is the same as inversion.

The lowest-order improper rotation that is not a simpler operation is S_3. The pattern of successive operations depends on if n is even or odd. The general relationships for S_n operations are:

- If n is even, $S_n^n = E$
  - Molecule returns to original orientation configuration after each full rotation
  - There are an even number of rotation operators and reflection operators
- If n is odd, $S_n^n = \sigma$ and $S_n^{2n} = E$
  - First full rotation:
    - Molecular does not return to original configuration after first rotation
    - There are an odd number of rotation operators and reflection operators
  - Second full rotation:
    - Molecule returns to original orientation configuration
    - There are an even number of rotation operators and reflection operators
- When m is even, there is always a corresponding proper rotation (C_n):
  - $S_n^m = C_n^m$ when $m < n$
  - $S_n^m = C_n^{m-n}$ when $m > n$ (2nd rotation)
- If S_n with even n exists, $C_{n/2}$ exists
- If S_n with odd n exists, then both C_n and σ perpendicular to C_n exist

Summary of Symmetry Operations

The identity E and rotations C_n are symmetry operations that could actually be carried out on a molecule. For this reason they are called *proper symmetry operations*. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed *improper symmetry operations*. These five symmetry operations are tabulated in Table 12.2.1 .

Table 12.2.1 : The five principal symmetry elements and their operators for 3D space

Symbol Elements	Description	Symbol Operator	Symbol
E	identity	$\hat{E}$	no change
C_n	n-fold axis of rotation	$\hat{C}_n$	Rotation by $360\,^\circ/n$ leaves the molecule unchanged
σ	plane of symmetry	$\hat{\sigma}$	Reflection in the plane leaves the molecule unchanged
i	center of symmetry.	$\hat{i}$	Inversion through the center of symmetry leaves the molecule unchanged.
S_n	n-fold improper rotation	$\hat{S}_n$	The rotary reflection operation consists of rotating through an angle $360\,^\circ/n$ about the axis, followed by reflecting in a plane perpendicular to the axis.

Defining the Coordinate System

Axis Definitions

Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

Generally, the following conventions are observed to define the coordinate system:

1. The origin of the coordinate system is located at the central atom or the center of the molecule.
2. The z-axis is collinear with the highest-order rotational axis (principal axis).
3. For planar molecules, if the z-axis is perpendicular to the molecular plane:
   - The x-axis lies in the plane of the molecule and passes through the greatest number of atoms.

   If the z-axis lies in the plane of the molecule:
   - The x-axis stands perpendicular to the plane
4. For non-planar molecules, once the z-axis has been defined, the x-axis is the usually chosen so that the xz plane contains as many atoms as possible.

Molecular Point Groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called *point groups* (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labeling symmetry groups, called the Schönflies and Hermann-Mauguin (or International) systems. Schönflies notation is used by chemists and spectroscopists, while Crystallographers prefer Hermann-Mauguin notation.The symmetry of individual molecules is usually described using the **Schönflies** notation, which is used below. The common point groups can be categorized into the following:

- Nonrotational groups
- Single-axis rotationa groups
- Dihedral groups
- Cubic groups

Shared Names

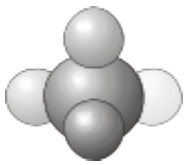
Some of the point groups share their names with symmetry operations, so be careful you do not mix up the two. It is usually clear from the context which one is being referred to.

Nonrotational groups

Nonrotational groups represent the lowest symmetry groups. They include:

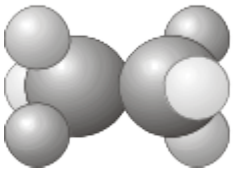
C_1 - Contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation, E). Molecules that belongs to the C_1 group have no symmetry and are therefore asymmetric.

- Example: CHDFCl

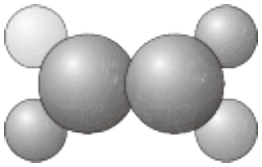


C_i - Contains the identity E and a center of inversion i.

- Example: $C_2H_2F_2Cl_2$



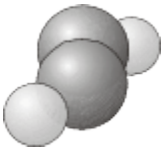
C_S - Contains the identity E and a plane of reflection σ.



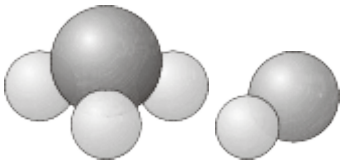
Single-axis rotation groups

Single-axis rotation groups are examples of cyclic groups. In cyclic groups, all of the operators commute (Abelian). In their multiplication tables, elements appear along right-to-left diagonals. Knowing this pattern makes it easy to construct multiplication tables! Single-axis rotational groups include:

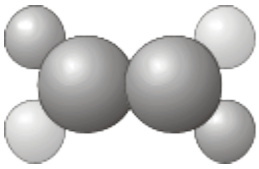
C_n - Contains the identity and an n-fold axis of rotation.



C_{nv} - Contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.



C_{nh} - Contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a center of inversion).



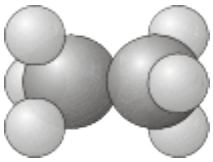
S_n - Contains the identity and *one* S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).

Dihedral groups

The dihedral groups have n two-fold axes perpendicular to the principal n-fold axis. These C_2 axis are called dihedral axes. Dihedral groups groups include:

D_n - Contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.

D_{nd} - Contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



D_{nh} - Contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.

- There are n-fold vertical mirror places (σ_v)
- Includes n-fold improper axis when $n > 2$
- They are centrosymmetric when n is even

$D_{\infty h}$ - Same as D_{nh}, except the principal rotational axis is an infinite-fold C_∞.

- This is the point group for all linear centrosymmetric linear molecules (e.g. H_2, CO_2)

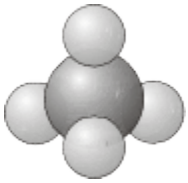


Cubic groups

The following groups are the cubic groups, which contain more than one principal axis. The cubic groups are associated with polyhedra that are geometrically related to the cube. All are characterized by the presence of multiple, intersecting, high-order rotational axes. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h).

T_d - Contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes e.g. $\mathrm{CH_4}$.

- Example: Methane, $\mathrm{C_4}$

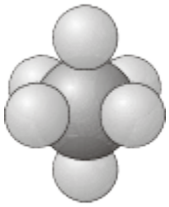


T - Same as for T_d but no planes of reflection.

T_h - Same as for T but contains a center of inversion.

O_h - The group of the regular octahedron.

- Example: Sulfur hexafluoride, $\mathrm{SF_6}$



O - Same as for O_h, but with no planes of reflection.

I_h - Icoshedral, a geometric shape with 20 faces.

- Example: Buckminsterfullerene, (C_{60})

Summary of groups

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics. However, we won't be treating it any further here.

Table 12.2.2 : Common Point Groups for Molecules

Nonaxial groups	C_1	C_s	C_i	-	-	-	-	-	-
C_n groups	C_2	C_3	C_4	C_5	C_6	C_7	C_8	-	-
D_n groups	D_2	D_3	D_4	D_5	D_6	D_7	D_8	-	-
C_{nv} groups	C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	C_{7v}	C_{8v}	-	-
C_{nh} groups	C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	-	-	-	-
D_{nh} groups	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}	-	-
D_{nd} groups	D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	D_{7d}	D_{8d}	-	-
S_n groups	S_2	-	S_4	-	S_6		S_8	S_{10}	S_{12}
Cubic groups	T	T_h	T_d	O	O_h	I	I_h	-	-
Linear groups	$C_{\infty v}$	$D_{\infty h}$	-	-	-	-	-	-	-

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.

alt

[1]Though the Hermann-Mauguin system can be used to label point groups, it is usually used in the discussion of crystal symmetry. In crystals, in addition to the symmetry elements described above, translational symmetry elements are very important. Translational symmetry operations leave no point unchanged, with the consequence that crystal symmetry is described in terms of *space groups* rather than *point groups*.

Symmetry and Physical Properties

Carrying out a symmetry operation on a molecule must not change any of its physical properties. It turns out that this has some interesting consequences, allowing us to predict whether or not a molecule may be chiral or polar on the basis of its point group.

For a molecule to have a permanent dipole moment, it must have an asymmetric charge distribution. The point group of the molecule not only determines whether the molecule may have a dipole moment, but also in which direction(s) it may point. If a molecule has a C_n axis with $n > 1$, it **cannot** have a dipole moment perpendicular to the axis of rotation (for example, a C_2 rotation would interchange the ends of such a dipole moment and reverse the polarity, which is not allowed – rotations with higher values of n would also change the direction in which the dipole points). Any dipole must lie parallel to a C_n axis.

Also, if the point group of the molecule contains any symmetry operation that would interchange the two ends of the molecule, such as a σ_h mirror plane or a C_2 rotation perpendicular to the principal axis, then there cannot be a dipole moment along the axis. The only groups compatible with a dipole moment are C_n, C_{nv} and C_s. In molecules belonging to C_n or C_{nv} the dipole must lie along the axis of rotation.

One example of symmetry in chemistry that you will already have come across is found in the isomeric pairs of molecules called enantiomers. Enantiomers are non-superimposable mirror images of each other, and one consequence of this symmetrical

relationship is that they rotate the plane of polarized light passing through them in opposite directions. Such molecules are said to be chiral,[2] meaning that they cannot be superimposed on their mirror image. Formally, the symmetry element that precludes a molecule from being chiral is a rotation-reflection axis S_n. Such an axis is often implied by other symmetry elements present in a group.

For example, a point group that has C_n and σ_h as elements will also have S_n. Similarly, a center of inversion is equivalent to S_2. As a rule of thumb, a molecule definitely cannot have be chiral if it has a center of inversion or a mirror plane of any type (σ_h, σ_v or σ_d), but if these symmetry elements are absent the molecule should be checked carefully for an S_n axis before it is assumed to be chiral.

Chirality

The word chiral has its origins in the Greek word for hand ($\chi\epsilon\rho\iota$, pronounced 'cheri' with a soft ch as in 'loch'). A pair of hands is also a pair of non-superimposable mirror images, and you will often hear chirality referred to as 'handedness' for this reason.

Summary

All molecules can be described in terms of their symmetry or lack thereof, which may contain symmetry elements (point, line, plane). Identity, rotation, reflection, and inversion are symmetry operations (movement of the molecules such that after the movement, all the atoms of the molecules is coincidental with equivalent atom of the molecule in original).

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12.3: Symmetry Operations Define Groups

Properties of Groups

Now that we have explored some of the properties of symmetry operations and elements and their behavior within point groups, we are ready to introduce the formal mathematical definition of a group. A mathematical group is defined as a set of elements (g_1, g_2, g_3...) together with a rule for forming combinations g_j. The number of elements h is called the **order** of the group. For our purposes, the elements are the symmetry operations of a molecule and the rule for combining them is the sequential application of symmetry operations investigated in the previous section. The elements of the group and the rule for combining them must satisfy the following criteria:

1. Identity
2. Closure
3. Associativity
4. Reciprocality

These criteria are explained below.

Identity

The group must include the **identity**, E. E commutes with any other elements of the group, g_i, such that:

$$Eg_i = g_iE = g_i \tag{12.3.1}$$

This requirement explains the need to define the symmetry operation of identity.

Closure

The elements must satisfy the group property of **closure**, meaning that the combination of any pair of elements is also an element of the group.

Closure is a mathematical definition. In mathematics, a group has closure under an operation if performance of that operation on members of the group always produces a member of the same group:

If A and B are elements of the group G, and if $AB = g_i$, then g_i is also in the group G

Reciprocality

To satisfy reciprocality, each element g_i must have an inverse g_i^{-1}, which is also an element of the group, such that:

$$g_ig_i^{-1} = g_i^{-1}g_i = E \tag{12.3.2}$$

Some symmetry operations are their own inverses:

- $C_2C_2 = E$
- $\sigma\sigma = E$
- $ii = E$
- $EE = E$

The inverse of each of these operations effectively 'undoes' the effect of the symmetry operation. Most other operations are not the inverse of themselves. For example, in C_{3v} the inverse of C_3 is C_3^{-1}.

Associativity

The **associative law** of combination states that all combinations of elements of a group must be associative:

$$(g_i g_j)(g_k) = g_i(g_j g_k) \tag{12.3.3}$$

The above definition **does not** require the elements to commute, which would require:

$$g_i g_k = g_k g_i \tag{12.3.4}$$

Group Multiplication

As we discovered in the C_{3v} example above, in many groups the outcome of consecutive application of two symmetry operations depends on the order in which the operations are applied.

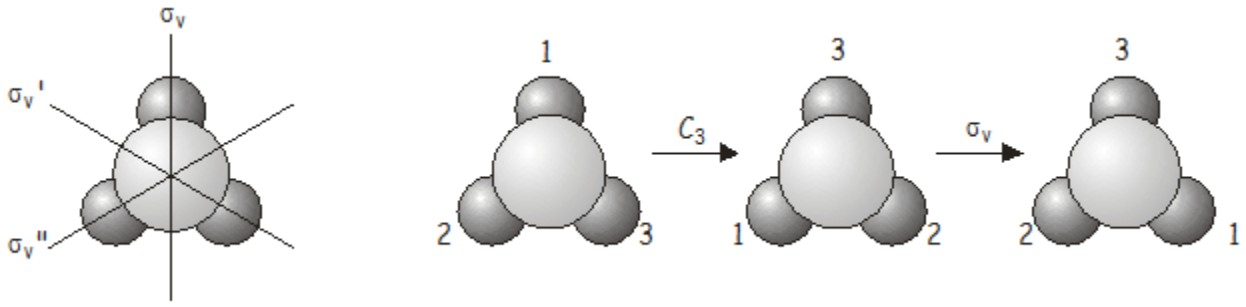
Commuting is not a Requirement of Group Elements

Groups for which the elements do not commute are called **non-Abelian** groups; those for which they elements do commute are *Abelian*.

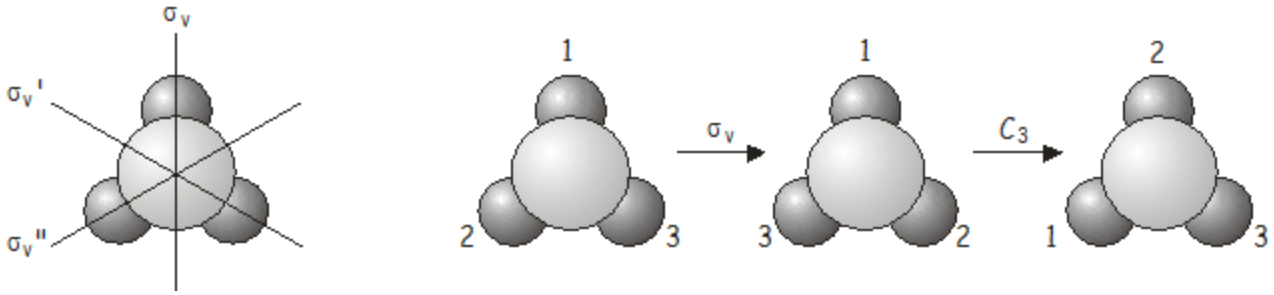
Group theory is an important area in mathematics, and luckily for chemists the mathematicians have already done most of the work for us. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems and learn about its consequences.

Many problems involving operators or operations (such as those found in quantum mechanics or group theory) may be reformulated in terms of matrices. Any of you who have come across transformation matrices before will know that symmetry operations such as rotations and reflections may be represented by matrices. It turns out that the set of matrices representing the symmetry operations in a group obey all the conditions laid out above in the mathematical definition of a group, and using matrix representations of symmetry operations simplifies carrying out calculations in group theory. Before we learn how to use matrices in group theory, it will probably be helpful to review some basic definitions and properties of matrices.

Now we will investigate what happens when we apply two symmetry operations in sequence. As an example, consider the NH_3 molecule, which belongs to the C_{3v} point group. Consider what happens if we apply a C_3rotation followed by a σ_v reflection. We write this combined operation $\sigma_v C_3$ (when written, symmetry operations operate on the thing directly to their right, just as operators do in quantum mechanics – we therefore have to work backwards from right to left from the notation to get the correct order in which the operators are applied). As we shall soon see, the order in which the operations are applied is important.



The combined operation $\sigma_v C_3$ is equivalent to σ_v'', which is also a symmetry operation of the C_{3v} point group. Now let's see what happens if we apply the operators in the reverse order i.e. $C_3\sigma_v$ (σ_v followed by C_3).



Again, the combined operation $C_3\sigma_v$ is equivalent to another operation of the point group, this time σ_v'.

There are two important points that are illustrated by this example:

1. The order in which two operations are applied is important. For two symmetry operations A and B, AB is not necessarily the same as BA, i.e. symmetry operations do not in general commute. In some groups the symmetry elements do commute; such groups are said to be *Abelian*.
2. If two operations from the same point group are applied in sequence, the result will be equivalent to another operation from the point group. Symmetry operations that are related to each other by other symmetry operations of the group are said to belong to the same *class*. In NH_3, the three mirror planes σ_v, σ_v' and σ_v'' belong to the same class (related to each other through a C_3 rotation), as do the rotations C_3^+ and C_3^- (anticlockwise and clockwise rotations about the principal axis, related to each other by a vertical mirror plane

The effects of applying two symmetry operations in sequence within a given point group are summarized in *group multiplication table*s. As an example, the complete group multiplication table for C_{3v} using the symmetry operations as defined in the figures above is shown below. The operations written along the first row of the table are carried out first, followed by those written in the first column (note that the table would change if we chose to name σ_v, σ_v' and σ_v'' in some different order).

$$\begin{array}{ccccccc}
C_{3v} & E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' \\
E & E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' \\
C_3^+ & C_3^+ & C_3^- & E & \sigma_v' & \sigma_v'' & \sigma_v \\
C_3^- & C_3^- & E & C_3^+ & \sigma_v'' & \sigma_v & \sigma_v' \\
\sigma_v & \sigma_v & \sigma_v'' & \sigma_v' & E & C_3^- & C_3^+ \\
\sigma_v' & \sigma_v' & \sigma_v & \sigma_v'' & C_3^+ & E & C_3^- \\
\sigma_v'' & \sigma_v'' & \sigma_v' & \sigma_v & C_3^- & C_3^+ & E
\end{array} \tag{12.3.5}$$

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- 1.5: Combining Symmetry Operations - 'Group Multiplication' by Claire Vallance is licensed CC BY 4.0. Original source: http://vallance.chem.ox.ac.uk/pdfs/SymmetryLectureNotes.pdf.

12.4: Symmetry Operations as Matrices

Matrices can be used to map one set of coordinates or functions onto another set. Matrices used for this purpose are called *transformation matrices*. The symmetry operations in a group may be represented by a set of transformation matrices $\Gamma(g)$, one for each symmetry element g. Each individual matrix is called a *representative* of the corresponding symmetry operation, and the complete set of matrices is called a *matrix representation* of the group. The matrix representatives act on some chosen *basis set* of functions, and the actual matrices making up a given representation will depend on the basis that has been chosen. The representation is then said to *span* the chosen basis. The basis we will use are unit vectors pointing in the x, y, and z directions.

The transformation matrix for any operation in a group has a form that is unique from the matrices of the other members of the same group; however, the character of the transformation matrix for a given operation is the same as that for any other operation in the same class. Each symmetry operation below will operate on an arbitrary vector, $\mathbf{u}$:

$$\mathbf{u} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The Identity Operation, E

The first rule is that the group must include the identity operation E (the 'do nothing' operation). The matrix representative of the identity operation is simply the identity matrix and leaves the vector unchanged:

$$E\mathbf{u} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{12.4.1}$$

Every matrix representation includes the appropriate identity matrix.

The Reflection Operation, σ

The reflection operation reflects the vector $\mathbf{u}$ over a plane. This can be the xy, xz, or yz plane. The matrix is similar to the identity matrix, with the exception that there is a sign change for the appropriate element. The reflect matrix in the xy plane is:

$$\sigma(xy)\mathbf{u} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ -z \end{pmatrix} \tag{12.4.2}$$

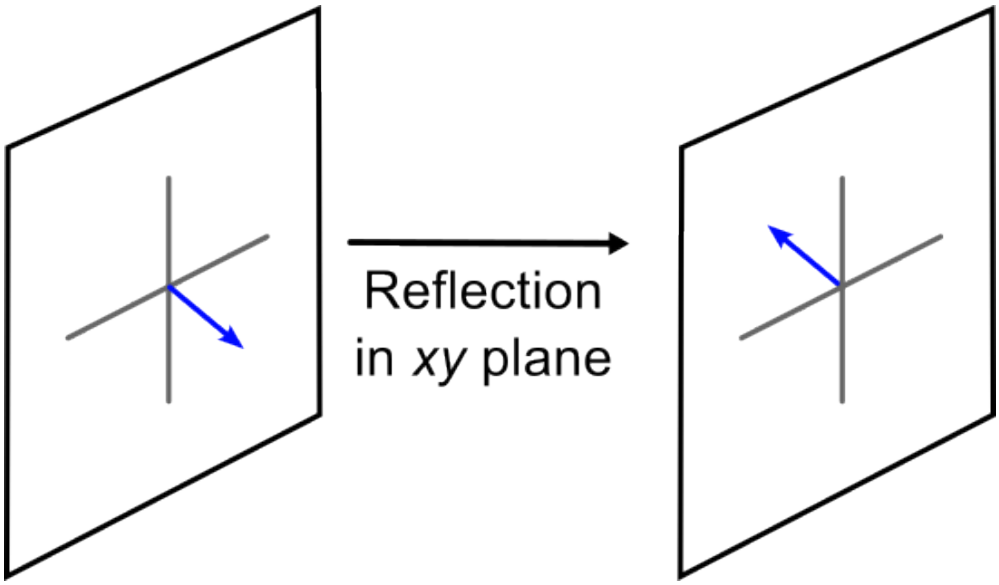


Figure 12.4.1 : Reflection in the xy plane.

Notice that the element for the dimension being reflected is the on that is negative. In the above case, since z is being reflected over the xy plane, the z element in the matrix is negative. If we were to reflect over the xz plane instead, the y element would be the one that is negative:

$$\sigma(xz)\mathbf{u} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

The n-fold Rotation Operation, C_n

The C_n operator rotates the molecule about an axis. The counterclockwise rotation of vector $\mathbf{u}$ about the z axis is:

$$C_n\mathbf{u} = \begin{pmatrix} \cos\frac{2\pi}{n} & -\sin\frac{2\pi}{n} & 0 \\ \sin\frac{2\pi}{n} & \cos\frac{2\pi}{n} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z \end{pmatrix}$$

For clockwise rotation, the sign on the $\sin\theta$ terms are reversed. This matrix simplifies dramatically for the C_2 rotation:

$$C_2\mathbf{u} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

Rotation matrices operating about the x, y and z axes are given by:

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \tag{12.4.3}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \tag{12.4.4}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{12.4.5}$$

The Inversion operation, I

The inversion operation inverts every point:

$$I\mathbf{u} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

C_{2v} Point Group

Now that we have seen the matrix form of our operators, we can see how the multiplication of each operator leads to another operations in the group. The C_{2v} multiplication table is:

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

For multiplication tables, the standard order of operation is the row elements (top) first, following by the column element (side). Every row or column includes every operation once and is different from any other row or column.

Let's look at $C_2\sigma_v$ multiplication, where σ_v is a reflection across the xz plane:

$$C_2\sigma_v = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma_v'$$

where σ_v' is the reflection across the yz plane.

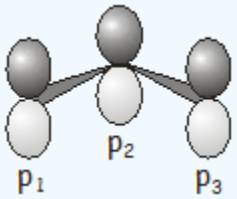
Matrix Representations and Groups

Before proceeding any further, we must check that a matrix representation of a group obeys all of the rules set out in the formal mathematical definition of a group.

1. **Identity**.The first rule is that the group must include the identity operation E (the 'do nothing' operation). We showed above that the matrix representative of the identity operation is simply the identity matrix. As a consequence, every matrix representation includes the appropriate identity matrix.
2. **Closure**. The second rule is that the combination of any pair of elements must also be an element of the group (the *group property*). If we multiply together any two matrix representatives, we should get a new matrix which is a representative of another symmetry operation of the group. In fact, matrix representatives multiply together to give new representatives in exactly the same way as symmetry operations combine according to the group multiplication table. For example, in the C_{2v} point group, we showed that the combined symmetry operation $C_2\sigma_v$ is equivalent to σ_v'. In a matrix representation of the group, if the matrix representatives of C_2 and σ_v are multiplied together, the result will be the representative of σ_v'.
3. **Associativity**. The third rule states that the rule of combination of symmetry elements in a group must be associative. This is automatically satisfied by the rules of matrix multiplication.
3. **Reciprocality**. The final rule states that every operation must have an inverse, which is also a member of the group. The combined effect of carrying out an operation and its inverse is the same as the identity operation. It is fairly easy to show that matrix representatives satisfy this criterion. For example, the inverse of a reflection is another reflection, identical to the first. In matrix terms we would therefore expect that a reflection matrix was its own inverse, and that two identical reflection matrices multiplied together would give the identity matrix. This turns out to be true, and can be verified using any of the reflection matrices in the examples above. The inverse of a rotation matrix is another rotation matrix corresponding to a rotation of the opposite sense to the first.

C_{2v} Example 12.4.1 : Matrix Representation of the Point Group (the allyl radical)

We often use sets of atomic orbitals as basis functions for matrix representations. In this example, we'll take as our basis a p orbital on each carbon atom (p_1, p_2, p_3).



Note that the p orbitals are *perpendicular* to the plane of the carbon atoms (this may seem obvious, but if you're visualizing the basis incorrectly it will shortly cause you a not inconsiderable amount of confusion). The symmetry operations in the C_{2v} point group, and their effect on the three p orbitals, are as follows:

$$
\begin{aligned}
E \quad & \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \rightarrow \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \\
C_2 \quad & \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \rightarrow \begin{pmatrix} -p_3 \\ -p_2 \\ -p_1 \end{pmatrix} \\
\sigma_v \quad & \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \rightarrow \begin{pmatrix} -p_1 \\ -p_2 \\ -p_3 \end{pmatrix} \\
\sigma_v' \quad & \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \rightarrow \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}
\end{aligned}
$$

The matrices that carry out the transformation are

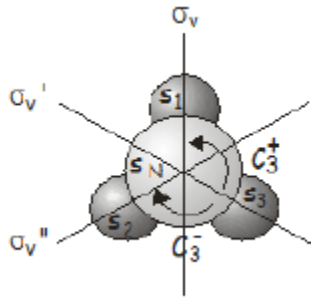
$$
\begin{aligned}
\Gamma(E) \quad & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \\
\Gamma(C_2) \quad & \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_3 \\ -p_2 \\ -p_1 \end{pmatrix} \\
\Gamma(\sigma_v) \quad & \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_1 \\ -p_2 \\ -p_3 \end{pmatrix} \\
\Gamma(\sigma_v') \quad & \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}
\end{aligned}
$$

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12.5: Molecules can be Represented by Reducible Representations

In addition to operators, we can define properties of molecules using a matrix representation. Before making the matrix, we need to carefully choose a basis set that defines the information we want to extract For example, let's say we want to know the symmetry of the valence s orbitals in ammonia, NH_3, which is in the C_{3v} point group. We will select a basis (s_N, s_1, s_2, s_3) that consists of the valence s orbitals on the nitrogen and the three hydrogen atoms. We need to consider what happens to this basis when it is acted on by each of the symmetry operations in the C_{3v} point group, and determine the matrices that would be required to produce the same effect. The basis set and the symmetry operations in the C_{3v} point group are summarized in the figure below.



The effects of the symmetry operations on our chosen basis are as follows:

$$\begin{array}{ll} E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\ C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\ C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\ \sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\ \sigma_v' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\ \sigma_v'' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \end{array} \tag{12.5.1}$$

By inspection, the matrices that carry out the same transformations are:

$$
\begin{aligned}
\Gamma(E) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_1, s_2, s_3) \\
\Gamma(C_3^+) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_2, s_3, s_1) \\
\Gamma(C_3^-) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_1, s_2) \\
\Gamma(\sigma_v) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_1, s_3, s_2) \\
\Gamma(\sigma_v') \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_2, s_1, s_3) \\
\Gamma(\sigma_v'') \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_2, s_1)
\end{aligned} \tag{12.5.2}
$$

These six matrices therefore form a **reducible representation** for the C_{3v} point group in the (s_N, s_1, s_2, s_3) basis as we will see in the next chapter that these matrices reduce down to the irreducible representations found in the character tables. These reducible representations multiply together according to the group multiplication table and satisfy all the requirements for a mathematical group.

We choose different basis sets to extract different properties of molecules. For example, we could include representations of the valence p orbitals in N in our basis set to obtain the structure and symmetry of the molecular orbitals for ammonia. To understand understand the molecular motions of ammonia (translates, rotates, and vibrates), we could place a x, y, and z unit vectors on each atom to represent the their motion, and then construct our matrices.

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12.6: Character Tables Summarize the Properties of a Point Group

Now that we've learned how to create a matrix representation of a point group within a given basis, we will move on to look at some of the properties that make these representations so powerful in the treatment of molecular symmetry.

Similarity Transforms

Suppose we have a basis set $(x_1, x_2, x_3, ...x_n)$, where x_i represents so position in x of each atom, and we have determined the matrix reducible representatives for the basis in a given point group. There is nothing particularly special about the basis set we have chosen, and we could equally well have used any set of linear combinations of the original functions (provided the combinations were linearly independent). Consider an additional basis set $(x'_1, x'_2, x'_3, ...x'_n)$, in which each basis function x'_i is a linear combination of our original basis $(x_1, x_2, x_3, ...x_n)$:

$$x'_j = \Sigma_i x_i c_{ji} = x_1 c_{j1} + x_2 c_{j2} + ... \tag{11.1}$$

The c_{ji} appearing in the sum are coefficients; c_{ji} is the coefficient multiplying the original basis function x_i in the new linear combination basis function x'_j. We could also represent this transformation in terms of a matrix equation $\mathbf{x'} = C\mathbf{x}$:

$$\begin{pmatrix} x'_1 \\ x'_2 \\ ... \\ x'_n \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & ... & c_{1n} \\ c_{21} & c_{22} & ... & c_{2n} \\ ... & ... & ... & ... \\ c_{n1} & c_{n2} & ... & c_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ ... \\ x_n \end{pmatrix} \tag{11.2}$$

where C is the transformation matrix. The matrix representatives for the two basis sets will certainly be different, but we would expect them to be related to each other in some way. As we shall show shortly, they are in fact related by a *similarity transform*. Now we look at what happens when we apply a symmetry operation g to our two basis sets. If $\Gamma(g)$ and $\Gamma'(g)$ are matrix representatives of the symmetry operation in the $\mathbf{x}$ and $\mathbf{x'}$ bases, then we have:

$$\begin{aligned} g\mathbf{x'} &= \mathbf{x'}\Gamma'(g) & & \\ g\mathbf{x}C &= \mathbf{x}C\Gamma'(g) & &\text{since } \mathbf{x'} = \mathbf{x}C \\ g\mathbf{x} &= \mathbf{x}C\Gamma'(g)C^{-1} &&\text{multiplying on the right by } C^{-1} \text{and using } CC^{-1} = I \\ &= \mathbf{x}\Gamma(g) & & \end{aligned} \tag{11.3}$$

We can therefore identify the similarity transform relating $\Gamma(g)$, the matrix representative in our original basis, to $\Gamma'(g)$, the representative in the transformed basis. The transform depends only on the matrix of coefficients used to transform the basis functions:

$$\Gamma(g) = C\Gamma'(g)C^{-1} \tag{11.4}$$

Also:

$$\Gamma'(g) = C^{-1}\Gamma(g)C \tag{11.5}$$

Characters of Representations

The trace of a matrix representative $\Gamma(g)$ is usually referred to as the *character* of the representation under the symmetry operation g. We will soon come to see that the characters of a matrix representation are often more useful than the matrix representatives themselves. Characters have several important properties.

1. The character of a symmetry operation is invariant under a similarity transform

2. Symmetry operations belonging to the same class have the same character in a given representation. Note that the character for a given class may be different in different representations, and that more than one class may have the same character.

Proofs of the above two statements are given in the Appendix.

Character Tables

A character table summarizes the behavior of all of the possible irreducible representations of a group under each of the symmetry operations of the group. The character table for C_{3v} is shown below. All operations in the character table are contained in the first row of the character table, in this case E, C_3, & σ_v, these are all of the operations that can be preformed on the molecule that return the original structure. The first column contains the three irreducible representations A_1, A_2 & E. The character of the irreducible representation denotes what the operation does. A value of 1 represents no change, -1 opposite change and 0 is a combination of 1 & -1 (0's are found in degenerate molecules. The final two columns Rotation and Translation represented by R_x, R_y, R_z & x, y, z respectively. Each R_x, R_y, R_z & x, y, z term is the irreducible symmetry of a rotation or translation operation. Like wise the final column the orbital symmetries relates the orbital wave function to a irreducible representation.

C_{3v}	E	$2C_3$	$3\sigma_v$	$h=6$
A_1	1	1	1	z, z^2, x^2+y^2
A_2	1	1	-1	R_z
E	2	-1	0	$(x,y), (xy, x^2-y^2), (xz, yz), (R_x, R_y)$

(12.6.1)

The various sections of the table are as follows:

i. The first element in the table gives the name of the point group, usually in both Schoenflies (C_{3v}) and Hermann-Mauguin ($3m$) notation.
ii. Along the first row are the symmetry operations of the group, E, $2C_3$ and $3\sigma_v$, followed by the order of the group. Because operations in the same class have the same character, symmetry operations are grouped into classes in the character table and not listed separately.
iii. In the first column are the irreducible representations of the group. In C_{3v} the irreducible representations are A_1, A_2 and E (the representation we considered above spans $2A_1$ + E).
iv. The characters of the irreducible representations under each symmetry operation are given in the bulk of the table.
v. The final column of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products (z^2, x^2+y^2, xy, yz), and the rotations (R_x, R_y, R_z).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y , T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. As we shall see later, the transformation properties of x, y, and z can also be used to determine whether or not a molecule can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

Character tables for common point groups are given in Appendix B.

A simple way to determine the characters of a representation

In many applications of group theory, we only need to know the characters of the representative matrices, rather than the matrices themselves. Luckily, when each basis function transforms as a 1D irreducible representation (which is true in many cases of interest) there is a simple shortcut to determining the characters without having to construct the entire matrix representation. All we have to do is to look at the way the individual basis functions transform under each symmetry operation. For a given operation, step through the basis functions as follows:

i. Add 1 to the character if the basis function is unchanged by the symmetry operation (i.e. the basis function is mapped onto itself);
ii. Add -1 to the character if the basis function changes sign under the symmetry operation (i.e the basis function is mapped onto minus itself);

iii. Add 0 to the character if the basis function moves when the symmetry operation is applied (i.e the basis function is mapped onto something different from itself).

Try this for the s orbital basis we have been using for the C_{3v} group. You should find you get the same characters as we obtained from the traces of the matrix representatives.

We can also work out the characters fairly easily when two basis functions transform together as a 2D irreducible representation. For example, in the C_{3v} point group x and y axes transform together as E. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. However, the new axes can each be written as a linear combination of our original x and y axes. Using the rotation matrices introduced in Section 9, we see that:

$$\begin{aligned} x' &= \cos\theta\, x + \sin\theta\, y \\ y' &= -\sin\theta\, x + \cos\theta\, y \end{aligned} \tag{12.6.2}$$

For one-dimensional irreducible representations we asked if a basis function/axis was mapped onto itself, minus itself, or something different. For two-dimensional irreducible representations we need to ask how much of the 'old' axis is contained in the new one. From the above we see that the x' axis contains a contribution $\cos\theta$ from the x axis, and the y' axis contains a contribution $\cos\theta$ from the y axis. The characters of the x and y axes under a rotation through θ are therefore $\cos\theta$, and the overall character of the E irreducible representation is therefore $\cos\theta + \cos\theta = 2\cos\theta$. For a C_3 rotation through 120 degrees, the character of the E irreducible representation is therefore $2\cos 120° = -1$.

In general, *when an axis is rotated by an angle θ by a symmetry operation, its contribution to the character for that operation is* $\cos\theta$.

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12.7: Characters of Irreducible Representations

Symbols of irreducible representations

The two one-dimensional irreducible representations spanned by s_N and s_1' are seen to be identical. This means that s_N and s_1' have the 'same symmetry', transforming in the same way under all of the symmetry operations of the point group and forming bases for the same matrix representation. As such, they are said to belong to the same *symmetry species*. There are a limited number of ways in which an arbitrary function can transform under the symmetry operations of a group, giving rise to a limited number of symmetry species. Any function that forms a basis for a matrix representation of a group must transform as one of the symmetry species of the group. The irreducible representations of a point group are labeled according to their symmetry species as follows:

A	Nondegenerate ($d_i = 1$) representation that is symmetric (character 1) with respect to rotation about the principal axis in finite-order ($h \neq \infty$) groups.
B	Nondegenerate ($d_i = 1$) representation that is antisymmetric (character -1) with respect to rotation about the principal axis in finite-order ($h \neq \infty$) groups.
E	Doubly-degenerate ($d_i = 2$) representation in finite-order ($h \neq \infty$) groups.
T	Triply-degenerate ($d_i = 3$) representation in finite-order ($h \neq \infty$) groups.
Σ	Nondegenerate ($d_i = 1$) representation in infinite-order ($h = \infty$) groups.
Π, Δ, Φ	Doubly-degenerate ($d_i = 2$) representation in infinite-order ($h = \infty$) groups.

1. In groups containing a center of inversion, g and u labels (from the German *gerade* and *ungerade*, meaning symmetric and antisymmetric) denote the character of the irreducible representation under inversion ($+1$ for g, -1 for u)
2. In groups with a horizontal mirror plane but no center of inversion, the irreducible representations are given prime and double prime labels to denote whether they are symmetric (character $+1$ or antisymmetric (character -1) under reflection in the plane.
3. If further distinction between irreducible representations is required, subscripts 1 and 2 are used to denote the character with respect to a C_2 rotation perpendicular to the principal axis, or with respect to a vertical reflection if there are no C_2 rotations.

The 1D irreducible representation in the C_{3v} point group is symmetric (has character $+1$) under all the symmetry operations of the group. It therefore belongs to the irreducible representation A_1. The 2D irreducible representation has character 2 under the identity operation, -1 under rotation, and 0 under reflection, and belongs to the irreducible representation E.

Sometimes there is confusion over the relationship between a function f and its irreducible representation, but it is quite important that you understand the connection. There are several different ways of stating the relationship. For example, the following statements all mean the same thing:

- "f has A_2 symmetry"
- "f transforms as A_2"
- "f has the same symmetry

Irreducible representations with complex characters

In many cases (see Appendix B), the characters for rotations C_n and improper rotations S_n are complex numbers, usually expressed in terms of the quantity $\epsilon = \exp(2\pi i/n)$. It is fairly straightforward to reconcile this with the fact that in chemistry we are generally using group theory to investigate physical problems in which all quantities are real. It turns out that whenever our basis spans an irreducible representation whose characters are complex, it will also span a second irreducible representation whose characters are the complex conjugates of the first irreducible representation i.e. complex irreducible representations occur in pairs. According to the strict mathematics of group theory, each irreducible representation in the pair should be considered as a separate representation. However, when applying such irreducible representations in physical problems, we add the characters

for the two irreducible representations together to get a single irreducible representation whose characters are real.

As an example, the 'correct' character table for the group C_3 takes the form:

$$\begin{array}{cccc} C_3 & E & C_3 & C_3^2 \\ A & 1 & 1 & 1 \\ E & \begin{Bmatrix} 1 & \epsilon & \epsilon* \\ 1 & \epsilon* & \epsilon \end{Bmatrix} \end{array} \tag{12.7.1}$$

Where ϵ = exp(2πi/3). However, as chemists we would usually combine the two parts of the E irreducible representation to give:

$$\begin{array}{cccc} C_3 & E & C_3 & C_3^2 \\ A & 1 & 1 & 1 \\ E & 2 & -1 & 1 \end{array} \tag{12.7.2}$$

Groups and subgroups have well-defined relationships as they descend or ascend in symmetry

Molecules can undergo structural changes through conformations or chemical reactions. Remember that the order of the subgroup must be an integer divisor from the order of the group. If the basic geometry of the molecule is preserved, the structure after the change may be a subgroup of the structure before the change, or vice versa. If the basic geometry does change, there may not be a relationship between the groups before and after. When point groups are related as group and subgroup, their irreducible representations are also related. A property that transforms as one representation in a group will transform as its correlated representation in a subgroup. **Correlation diagrams** show the relationships between subgroups and groups. Often, to or more bases of separate representations of a group yield the same set of $\chi(R)$ values for those operations that are carried over into the subgroup. In many cases, degenerate representations of a group (E or T) may become two or three distinguishable bases in a subgroup.

Reduce representations of infinite groups by approximating them as finite groups

We cannot use the tabular method for infinite-order groups since we cannot divide an infinite quantity by h. We will use group-subgroup relations to use the tabular method:

- Set up the reducible representation in any convenient subgroup
  - For $C_{\infty v}$, use C_{2v}
  - For $D_{\infty h}$, use D_{2h}
- Correlate the component irreducible representations with the species for the infinite-order group.

While somewhat limiting, this method is fairly effective.

The direct product of two irreducible representations give either a reducible or irreducible representation of the same group

The last column in the character table shows the direct product between any two linear vectors. Direct products can also be taken between any number of irreducible representations:

$$\Gamma_a \Gamma_b \Gamma_c = \Gamma_{abc}$$

The characters of the direct product representation Γ_{abc} for each operator R of the group are given by:

$$\chi_a(R)\chi_b(R)\chi_c(R) = \chi_{abc}(R)$$

The resulting representation may be reducible or irreducible. The dimension of the product, D_p, is the product of the dimensions

of all the component representations:

$$d_p = \prod_i d_i$$

These properties will become useful later, so we will reference them as needed. Briefly:

1. If all the combined irreducible representations are nondegenerate, then the product will be a nondegenerate representation too.
2. The product of a nondegenerate representation and a degenerate representation is a degenerate representation.
3. The direct product of any representation with the totally symmetric representation is the representation itself.
4. The direct product of degenerate representations is a reducible representation.
5. The direct product of an irreducible representation with itself is or contains the totally symmetry representation.
6. Only the direct product of a representation with itself is or contains the totally symmetric representation.

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12.8: Using Symmetry to Solve Secular Determinants

As we continue with this course, we will discover that there are many times when we would like to know whether a particular integral is necessarily zero, or whether there is a chance that it may be non-zero. We can often use group theory to differentiate these two cases.

You will have already used symmetry properties of functions to determine whether or not a one-dimensional integral is zero. For example, cos(x) is an 'even' function (symmetric with respect to reflection through the origin), and it follows from this that

$$\int_{-\infty}^{\infty} \cos(x) dx = 0$$

In general integral between these limits for any other even function will be also be zero.

In the general case we may have an integral of more than one dimension. The key to determining whether a general integral is necessarily zero lies in the fact that because an integral is just a number, it must be invariant to any symmetry operation. For example, bonding in a diatomic (see next section) depends on the presence of a non-zero overlap between atomic orbitals on adjacent atoms, which may be quantified by an *overlap integral*. You would not expect the bonding in a molecule to change if you rotated the molecule through some angle θ, so the integral must be invariant to rotation, and indeed to any other symmetry operation.

In group theoretical terms, for an integral to be non-zero, *the integrand must transform as the totally symmetric irreducible representation in the appropriate point group*. In practice, the integrand may not transform as a single irreducible representation, but it **must include** the totally symmetric irreducible representation. These ideas should become more clear in the next section.

> It should be noted that even when the irreducible representations spanned by the integrand do include the totally symmetric irreducible representation, it is still possible for the integral to be zero. All group theory allows us to do is identify integrals that are *necessarily* zero based on the symmetry (or lack thereof) of the integrand.

Secular Equations

As we have seen already, any set of linear equations may be rewritten as a matrix equation $A\mathbf{x} = \mathbf{b}$. Linear equations are classified as *simultaneous linear equations* or *homogeneous linear equations*, depending on whether the vector $\mathbf{b}$ is non-zero or zero. For a set of simultaneous linear equations (non-zero $\mathbf{b}$) it is fairly apparent that if a unique solution exists, it can be found by multiplying both sides by the inverse matrix A^{-1} (since $A^{-1}A$ on the left hand side is equal to the identity matrix, which has no effect on the vector $\mathbf{x}$)

$$\begin{aligned} A\mathbf{x} &= \mathbf{b} \\ A^{-1}A\mathbf{x} &= A^{-1}\mathbf{b} \\ \mathbf{x} &= A^{-1}\mathbf{b} \end{aligned} \tag{12.8.1}$$

In practice, there are easier matrix methods for solving simultaneous equations than finding the inverse matrix, but these need not concern us here. We previously argued that in order for a matrix to have an inverse, **it must have a non-zero determinant**. Since A^{-1} must exist in order for a set of simultaneous linear equations to have a solution, this means that the determinant of the matrix A must be non-zero for the equations to be solvable.

> For a matrix to have an inverse, it must have a non-zero determinant.

The reverse is true for homogeneous linear equations. In this case the set of equations only has a solution if the determinant of A *is* equal to zero. The secular equations we want to solve are homogeneous equations, and we will use this property of the determinant to determine the molecular orbital energies. An important property of homogeneous equations is that if a vector $\mathbf{x}$ is a solution, so is any multiple of $\mathbf{x}$, meaning that the solutions (the molecular orbitals) can be normalized without causing any problems.

Solving for the orbital energies and expansion coefficients

Recall the secular equations for the A_1 orbitals of NH_3 derived in the previous section

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{12.8.2}$$

where c_1 and c_2 are the coefficients in the linear combination of the SALCs $\phi_1 = s_N$ and $\phi_2 = \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3)$ used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{12.8.3}$$

In order for the equations to have a solution, the determinant of the matrix must be equal to zero. Writing out the determinant will give us a polynomial equation in E that we can solve to obtain the orbital energies in terms of the Hamiltonian matrix elements H_{ij} and overlap integrals S_{ij}. The number of energies obtained by 'solving the secular determinant' in this way is equal to the order of the matrix, in this case two.

The secular determinant for Equation (21.3) is (noting that S_{11} = $S_{22} = 1$ since the SALCs are normalized)

$$(H_{11} - E)(H_{22} - E) - (H_{12} - ES_{12})^2 = 0 \tag{12.8.4}$$

Expanding and collecting terms in E gives

$$E^2(1 - S_{12}^2) + E(2H_{12}S_{12} - H_{11} - H_{22}) + (H_{11}H_{22} - H_{12}^2) = 0 \tag{12.8.5}$$

which can be solved using the quadratic formula to give the energies of the two molecular orbitals.

$$E_{\pm} = \frac{-(2H_{12}S_{12} - H_{11} - H_{22}) \pm \sqrt{(2H_{12}S_{12} - H_{11} - H_{22})^2 - 4(1 - S_{12}^2)(H_{11}H_{22} - H_{12}^2)}}{2(1 - S_{12}^2)} \tag{12.8.6}$$

To obtain numerical values for the energies, we need to evaluate the integrals H_{11}, H_{22}, H_{12}, and S_{12}. This would be quite a challenge to do analytically, but luckily there are a number of computer programs that can be used to calculate the integrals. One such program gives the following values.

$$\begin{aligned} H_{11} &= -26.0000\ eV \\ H_{22} &= -22.2216\ eV \\ H_{12} &= -29.7670\ eV \\ S_{12} &= 0.8167\ eV \end{aligned} \tag{12.8.7}$$

When we substitute these into our equation for the energy levels, we get:

$$\begin{aligned} E_+ &= 29.8336\ eV \\ E_- &= -31.0063\ eV \end{aligned} \tag{12.8.8}$$

We now have the orbital energies and the next step is to find the orbital coefficients. The coefficients for an orbital of energy E are found by substituting the energy into the secular equations and solving for the coefficients c_i. Since the two secular equations are not linearly independent (i.e. they are effectively only one equation), when we solve them to find the coefficients what we will end up with is the *relative* values of the coefficients. This is true in general: in a system with N coefficients, solving the secular equations will allow all N of the coefficients c_i to be obtained in terms of, say, c_1. The absolute values of the coefficients are found by normalizing the wavefunction.

Since the secular equations for the orbitals of energy E_+ and E_- are not linearly independent, we can choose to solve either one of them to find the orbital coefficients. We will choose the first.

$$(H_{11} - E_{\pm})c_1 + (H_{12} - E_{\pm}S_{12})c_2 = 0 \tag{12.8.9}$$

For the orbital with energy E_- = -31.0063 eV, substituting numerical values into this equation gives

$$\begin{aligned} 5.0063c_1 - 4.4442c_2 &= 0 \\ c_2 &= 1.1265c_1 \end{aligned} \tag{12.8.10}$$

The molecular orbital is therefore

$$\Psi = c_1(\phi_1 + 1.1265\phi_2) \tag{12.8.11}$$

Normalizing to find the constant c_1 (by requiring $< \Psi | \Psi >$ = 1) gives

$$\begin{aligned} \Psi_1 &= 0.4933\phi_1 + 0.5557\phi_2 \\ &= 0.4933s_N + 0.3208(s_1 + s_2 + s_3) \quad \text{(substituting the SALCs for } \phi_1 \text{ and } \phi_2) \end{aligned} \tag{12.8.12}$$

For the second orbital, with energy E_+ = 29.8336 eV, the secular equation is

$$\begin{aligned} -55.8336c_1 - 54.1321c_2 &= 0 \\ c_2 &= -1.0314c_1 \end{aligned} \tag{12.8.13}$$

giving

$$\begin{aligned} \Psi_2 &= c_1(\phi_1 - 1.0314\phi_2) \\ &= 1.6242\phi_1 - 1.6752\phi_2 \qquad \text{(after normalization)} \\ &= 1.6242s_N - 0.9672(s_1 + s_2 + s_3) \end{aligned} \tag{12.8.14}$$

These two A_1 molecular orbitals Ψ_1 and Ψ_2, one bonding and one antibonding, are shown below.



The remaining two SALCs arising from the s orbitals of NH_3 ($\phi_3 = \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3)$ and $\phi_4 = \frac{1}{\sqrt{2}}(s_2 - s_3)$), form an orthogonal pair of molecular orbitals of E symmetry. We can show this by solving the secular determinant to find the orbital energies. The secular equations in this case are:

$$\begin{aligned} c_1(H_{33} - ES_{33}) + c_2(H_{34} - ES_{34}) &= 0 \\ c_1(H_{34} - ES_{34}) + c_2(H_{44} - ES_{44}) &= 0 \end{aligned} \tag{12.8.15}$$

Solving the secular determinant gives

$$E_\pm = \frac{-(2H_{34}S_{34} - H_{33} - H_{44}) \pm \sqrt{(2H_{34}S_{34} - H_{33} - H_{44})^2 - 4(1 - S_{34}^2)(H_{33}H_{44} - H_{34}^2)}}{2(1 - S_{34}^2)} \tag{12.8.16}$$

The integrals required are

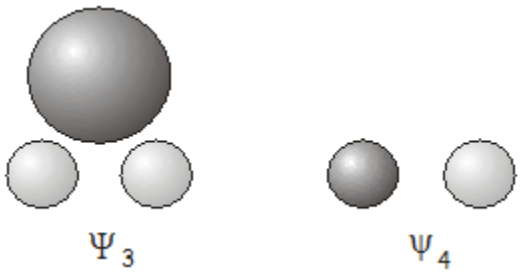
$$\begin{aligned} H_{33} &= -9.2892\, eV \\ H_{44} &= -9.2892\, eV \\ H_{34} &= 0 \\ S_{34} &= 0 \end{aligned} \tag{12.8.17}$$

Using the fact that H_{34} = $S_{34} = 0$, the expression for the energies reduces to

$$E_\pm = \frac{(H_{33} + H_{44}) \pm (H_{33} - H_{44})}{2} \tag{12.8.18}$$

giving E_+ = H_{33} = -9.2892 eV and E_- = H_{44} = -9.2892 eV. Each SALC therefore forms a molecular orbital by itself, and the two

orbitals have the same energy; the two SALCs form an orthogonal pair of degenerate orbitals. These two molecular orbitals of E symmetry are shown below.



Summary of the steps involved in constructing molecular orbitals

1. Choose a basis set of functions f_i consisting of the valence atomic orbitals on each atom in the system, or some chosen subset of these orbitals.
2. With the help of the appropriate character table, determine which irreducible representations are spanned by the basis set using Equation (15.20) to determine the number of times a_k that the k^{th} irreducible representation appears in the representation.

$$a_k = \frac{1}{h}\sum_C n_C \chi(g)\chi_k(g) \tag{12.8.19}$$

3. Construct the SALCs ϕ_i that transform as each irreducible representation using Equation 16.1

$$\phi_i = \sum_g \chi_k(g) g f_i \tag{12.8.20}$$

4. Write down expressions for the molecular orbitals by taking linear combinations of all the irreducible representations of the same symmetry species.
5. Write down the secular equations for the system.
6. Solve the secular determinant to obtain the energies of the molecular orbitals.
7. Substitute each energy in turn back into the secular equations and solve to obtain the coefficients appearing in your molecular orbital expressions in step 4.
8. Normalize the orbitals.

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12.9: Generating Operators

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12.10: Molecular Motions of a Molecule can be Represented by a Reducible Reperesentation

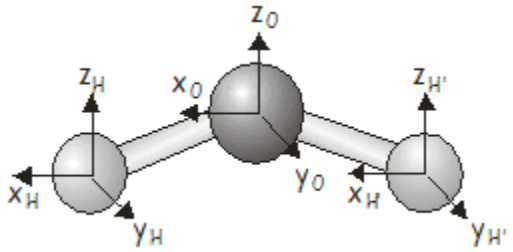
Determining the Symmetries of Molecular Motions

We mentioned above that the procedure for determining the normal vibrational modes of a polyatomic molecule is very similar to that used in previous sections to construct molecular orbitals. In fact, virtually the only difference between these two applications of group theory is the choice of basis set.

As we have already established, the motions of a molecule may be described in terms of the motions of each atom along the x , y and z axis. Consequently, it probably won't come as too much of a surprise to discover that a very useful basis for describing molecular motions comprises a set of (x, y, z) axes centered on each atom. This basis is usually known as the $3N$ *Cartesian* basis since there are $3N$ Cartesian axes, 3 axes for each of the N atoms in the molecule. In other words, each atom as 3 degrees of freedom. **Degrees of freedom** are the number of independent ways a molecule can move. An atom has 3 degrees of freedom as it can move in x, y, and z, but cannot rotate or vibrate. Note that each molecule will have a different $3N$ Cartesian basis, just as every molecule has a different atomic orbital basis.

Our first task in investigating motions of a particular molecule is to determine the characters of the matrix representatives for the $3N$ Cartesian basis under each of the symmetry operations in the molecular point group. We will use the H_2O molecule, which has C_{2v} symmetry, as an example.

H_2O has three atoms, so the $3N$ Cartesian basis will have 9 elements. The basis vectors are shown in the diagram below.



One way of determining the characters would be to construct all of the matrix representatives and take their traces. While you are more than welcome to try this approach if you want some practice at constructing matrix representatives, there is an easier way. Recall that we can also determine the character of a matrix representative under a particular symmetry operation by stepping through the basis functions and applying the following rules:

i. Add 1 to the character if the basis function is unchanged by the symmetry operation;
ii. Add -1 to the character if the basis function changes sign under the symmetry operation;
iii. Add 0 to the character if the basis function moves when the symmetry operation is applied.

For H_2O, this gives us the following characters for the $3N$ Cartesian basis (check that you can obtain this result using the rules above and the basis vectors as drawn in the figure):

$$\begin{array}{lcccc} \text{Operation:} & E & C_2 & \sigma_v(xz) & \sigma_v'(yz) \\ \chi_{3N}: & 9 & -1 & 3 & 1 \end{array} \tag{24.1}$$

There is an even quicker way to work out the characters of the $3N$ Cartesian basis if you have a character table in front of you. The character for the *Cartesian* basis is simply the sum of the characters for the x, y, and z (or T_x, T_y, and T_z) functions listed in the character table. To get the character for the $3N$ *Cartesian* basis, simply multiply this by the number of atoms in the molecule that are unshifted by the symmetry operation.

The C_{2v} character table is shown below.

C_{2v}	E	C_2	σ_v	σ_v'	$h=4$
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	−1	−1	xy, R_z
B_1	1	−1	1	−1	x, xz, R_y
B_2	1	−1	−1	1	y, yz, R_x

(24.2)

x transforms as B_1, y as B_2, and z as A_1, so the characters for the Cartesian basis are

Operation:	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
χ_{3N} :	3	−1	1	1

(24.3)

We multiply each of these by the number of unshifted atoms (3 for the identity operation, 1 for C_2, 3 for σ_v and 1 for σ_v') to obtain the characters for the $3N$ Cartesian basis.

$$\chi_{3N}: \quad 9 \quad -1 \quad 3 \quad 1 \tag{24.4}$$

Reassuringly, we obtain the same characters as we did previously. Which of the three methods you use to get to this point is up to you.

We now have the characters for the molecular motions (described by the $3N$ Cartesian basis) under each symmetry operation. At this point, we want to separate these characters into contributions from translation, rotation, and vibration. This turns out to be a very straightforward task. We can read the characters for the translational and rotational modes directly from the character table, and we obtain the characters for the vibrations simply by subtracting these from the $3N$ Cartesian characters we've just determined. The characters for the translations are the same as those for χ_{Cart}. We find the characters for the rotations by adding together the characters for R_x, R_y, and R_z from the character table (or just R_x and R_y if the molecule is linear). For H_2O, we have:

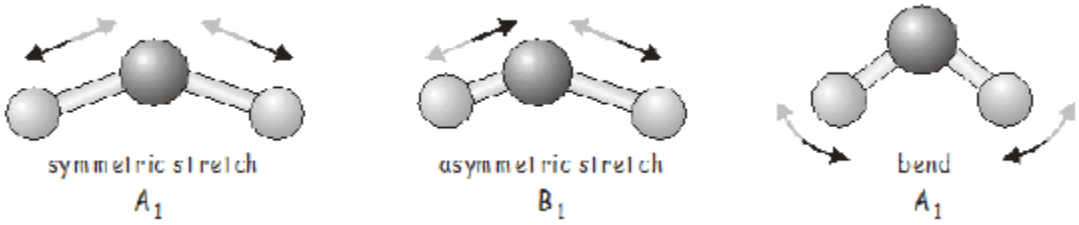
Operation:	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
χ_{3N} :	9	−1	3	1
χ_{Trans} :	3	−1	1	1
χ_{Rot} :	3	−1	−1	−1
$\chi_{\text{Vib}} = \chi_{3N} - \chi_{\text{Trans}} - \chi_{\text{Rot}}$:	3	1	3	1

(24.5)

The characters in the final row are the sums of the characters for all of the molecular vibrations. We can find out the symmetries of the individual vibrations by using the reduction equation (Equation (15.20)) to determine the contribution from each irreducible representation.

In many cases you won't even need to use the equation, and can work out which irreducible representations are contributing just by inspection of the character table. In the present case, the only combination of irreducible representations that can give the required values for χ_{Vib} is $2A_1 + B_1$. As an exercise, you should make sure you are also able to obtain this result using the reduction equation.

So far this may all seem a little abstract, and you probably want to know is what the vibrations of H_2O actually look like. For a molecule with only three atoms, it is fairly easy to identify the possible vibrational modes and to assign them to the appropriate irreducible representation.



For a larger molecule, the problem may become much more complex, and in that case we can generate the SALCs of the $3N$ Cartesian basis, which will tell us the atomic displacements associated with each vibrational mode. We will do this now for H_2O.

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12.11: Reducible Representations are Comprised of Irreducible Representations

As we saw in the previous section, the complete motion (translations, rotations, and vibrations) of ammonia (NH_3) can be represented by the following reducible representation:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	12	0	2

We want to relate the reducible form representation to the irreducible representation. To do this, we use the tabular method. First, create a new table:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	12	0	2
A_1			
A_2			
E			

We will need the C_{3v} character table for ammonia:

A_1	A	A'
A_2	A	A''
E	E	$A' + A''$

Fill in each number in our table by using the following equation:

$$g_c \chi_i X_r$$

g_e	Number of operations (order) in the class
χ_i	Character of the irreducible representation from the character table
χ_r	Character of the reducible representation from Γ

For example, the top-left value would be:

$$1 \times 1 \times 12 = 12$$

Where:

- 1 is the number of operations in the E class
- 1 is the character of the irreducible representation
- 9 is the character of the reducible representation

The table becomes:

C_{3v}	E	$2C_3$	$3\sigma_v$

Γ	12	0	2
A_1	12	0	6
A_2	12	0	-6
E	24	0	0

Sum up each row:

C_{3v}	E	$2C_3$	$3\sigma_v$	$\sum$
Γ	12	0	2	
A_1	12	0	6	18
A_2	12	0	-6	6
E	24	0	0	24

Now divide the summed values by the order of the group to obtain the number of times the irreducible representation appears (n_i). Ammonia has order $h = 6$:

C_{3v}	E	$2C_3$	$3\sigma_v$	$\sum$	$n_i = \frac{\sum}{h}$
Γ	12	0	2		
A_1	12	0	6	18	3
A_2	12	0	-6	6	1
E	24	0	0	24	4

The reducible representation can be broken down to its irreducible forms:

$$\Gamma = 3A_1 + A_2 + 4E$$

Now that we have the irreducible representations for the motion of ammonia, we can determine which are associated with rotations, vibrations, and translations. To start, we turn to the C_{3v} character table:

C_{3v}	**E**	**2C$_3$**	**3σ$_v$**		
A$_1$	1	1	1	z	x^2+y^2, z^2
A$_2$	1	1	-1	R$_z$	
E	2	-1	0	(R$_x$, R$_y$), (x,y)	(xz, yz) (x^2-y^2, xy)

The first column to the right of the characters includes to the terms x, y, z, R_x, R_y, and R_z. The rows with x, y, and z represent the irreducible representations for the translational modes in those directions:

$$\Gamma_{\text{trans}} = A_1 + E$$

The rows with R_x, R_y, and R_z represent the irreducible representations for the rotational modes about those axes:

$$\Gamma_{\text{rot}} = A_2 + E$$

We can subtract the translational and rotational irreducible representations from our \Gamma to get the irreducible representations for the normal vibrational modes:

$$\Gamma_{\text{vib}} = \Gamma - \Gamma_{\text{trans}} - \Gamma_{\text{rot}}$$

Doing this, we obtains:

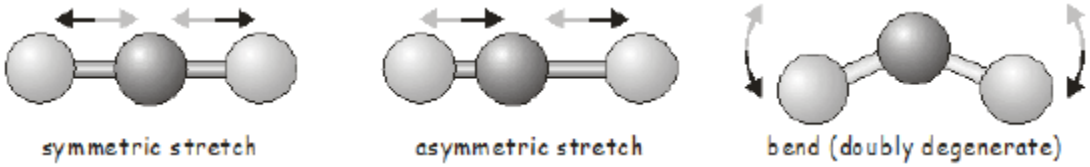
$$\Gamma_{\text{vib}} = 2A_1 + 2E$$

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12.12: Normal Modes of Vibrations Describe how Molecules Vibrate

Normal modes of vibration

All molecules vibrate. The simplest vibration is the one that takes place between two atoms in a diatomic molecule. Vibrational motion in diatomic molecules is often discussed within the context of the simple harmonic oscillator in quantum mechanics. A diatomic molecule has only a single bond that can vibrate; we say it has a single *vibrational mode*. As you may expect, the vibrational motions of polyatomic molecules are much more complicated than those of a diatomic. First, there are more bonds that can vibrate; and secondly, in addition to stretching vibrations, the only type of vibration possible in a diatomic, we can also have bending and torsional vibrational modes. Since changing one bond length in a polyatomic will often affect the length of nearby bonds, we cannot consider the vibrational motion of each bond in isolation; instead we talk of **normal modes of vibration** involving the concerted motion of groups of bonds. As a simple example, the normal modes of a linear triatomic molecule are shown below.



Once we know the symmetry of a molecule at its equilibrium structure, group theory allows us to predict the vibrational motions it will undergo using exactly the same tools we used above to investigate molecular orbitals. Each vibrational mode transforms as one of the irreducible representations of the molecule's point group. Before moving on to an example, we will quickly review how to determine the number of vibrational modes in a molecule.

Molecular degrees of freedom – determining the number of normal vibrational modes

An atom can undergo only translational motion, and therefore has three degrees of freedom corresponding to motion along the x, y, and z Cartesian axes. Translational motion in any arbitrary direction can always be expressed in terms of components along these three axes. When atoms combine to form molecules, each atom still has three degrees of freedom, so the molecule as a whole has $3N$ degrees of freedom, where N is the number of atoms in the molecule. However, the fact that each atom in a molecule is bonded to one or more neighboring atoms severely hinders its translational motion, and also ties its motion to that of the atoms to which it is attached. For these reasons, while it is entirely possible to describe molecular motions in terms of the translational motions of individual atoms (we will come back to this in the next section), we are often more interested in the motions of the molecule as a whole. These may be divided into three types: translational; rotational and vibrational.

Just as for an individual atom, the molecule as a whole has three degrees of translational freedom, leaving $3N-3$ degrees of freedom in rotation and vibration.

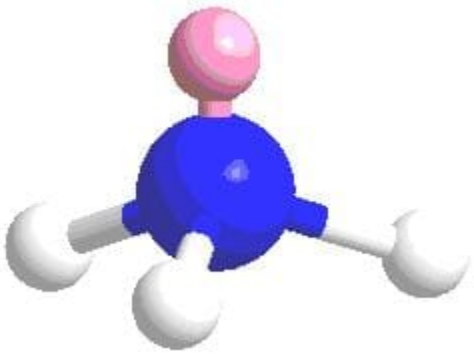
The number of rotational degrees of freedom depends on the structure of the molecule. In general, there are three possible rotational degrees of freedom, corresponding to rotation about the x, y, and z Cartesian axes. A non-linear polyatomic molecule does indeed have three rotational degrees of freedom, leaving $3N-6$ degrees of freedom in vibration (i.e $3N-6$ vibrational modes). In a linear molecule, the situation is a little different. It is generally accepted that to be classified as a true rotation, a motion must change the position of one or more of the atoms. If we define the z axis as the molecular axis, we see that spinning the molecule about the axis does not move any of the atoms from their original position, so this motion is not truly a rotation. Consequently, a linear molecule has only two degrees of rotational freedom, corresponding to rotations about the x and y axis. This type of molecule has $3N-5$ degrees of freedom left for vibration, or $3N-5$ vibrational modes.

In summary:

- A linear molecule has $3N-5$ vibrational modes
- A non-linear molecule has $3N-6$ vibrational modes.

Symmetry

Let's work through an example: Ammonia (NH_3) with a C_{3v} symmetry. Consequently, all of the properties contained in the C_{3v} character table above are pertinent to the ammonia molecule.



The principle axis is the axis that the highest order rotation can be preformed. In this case the z-axis pass through the lone pairs (pink sphere), which contains a C_3 axis. The ?'s or mirror planes (σ_v parallel to z-axis & σ_h perpendicular to the z-axis). In ammonia there is no σ_h only three σ_v's. The combination of C_3 & σ_v leads to C_{3v} point group, which leads to the C3v character table.

The number of transitions is dictated by 3N-6 for non-linear molecules, so in the case of Ammonia, there will be $3(4)-6=6$ vibrational modes. This can be confirmed by working through the vibrations of the molecule. This work is shown in the table below.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{xyz}	3	0	1
Unmoved Atoms	4	1	1
Γ_{total}	12	0	1

Γ_{total} is the total reducible form for the motions of ammonia. Using the character table for C_{3v}, we can subtract the 3 translation motions defined by x, y, and z, as well as the rotation motions defined by R_x, R_y, and R_z:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{total}	12	0	1
$\Gamma_{\text{translational}}$	3	0	1
$\Gamma_{\text{rotational}}$	3	0	-1
$\Gamma_{\text{vibrational}}$	6	0	1
	$2A_1+2E$		

This gives us the reducible representation for the vibrational motion of ammonia ($\Gamma_{\text{vibrational}}$), which we can reduce down to there irreducible representations of $2A_1$ and $2E$. E is doubly degenerate, meaning two vibration modes each, totalling 6 vibrations. This calculation was done by using the character table to find out the rotation and translation values and what atoms move during each operation. Using the character table we can characterize the A_1 vibration as IR active along the z-axis and raman active as well. The E vibration is IR active along both the x & y axis and is Raman active as well. From the character table the IR symmetries correspond to the x, y & z translations. Where the Raman active vibrations correspond to the symmetries of the d-orbitals.

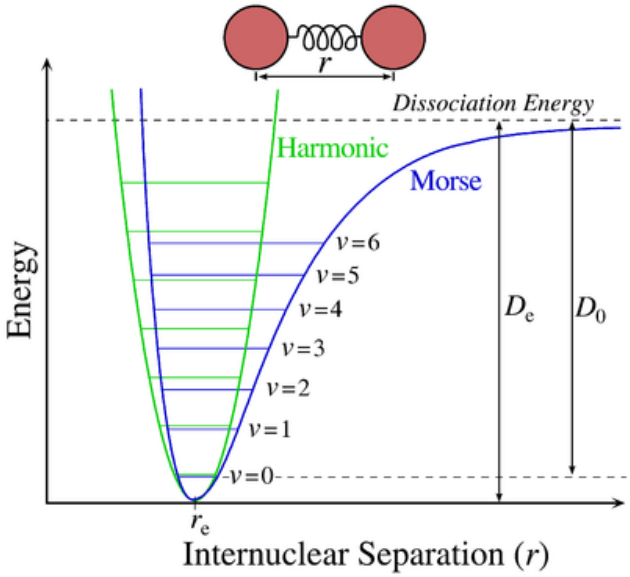
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12.13: Symmetry of Vibrations Describes their Spectroscopic Behavior

Vibrational transitions in molecules

The potential energy surface (electronic state), often approximated as a Morse potential, describes the energy of the eigenstate as a function of the interatomic distance. When an electron is excited form one eigenstate to another within the electronic state there is a change in interatomic distance, this result in a vibration occurring.



Vibrational transitions oftne occur when a molecule absorbs or emits infrared light, though, as we will see later, there are other processes that can cause vibrational transitions. During the vibrational transition, the electrons remains in the same electronic state, but that vibrational state changes from one eigenstate to another. In the case of the Morse diagram above, the vibrational eigenstates are denoted as ν. As you can see from the diagram the eigenstate is a function of energy versus interatomic distance. To predict whether a vibrational transition will occur, or for that matter a transition of any kind, we use the transition moment integral:

$$\int \Psi_i * \mu \Psi_f d\tau = \langle \Psi_i | \mu | \Psi_f \rangle$$

The transition moment integral is written here in standard integral format, but this is equivalent to Bra & Ket format which is standard in most chemistry quantum mechanical text (The $\langle \Psi_i |$ is the Bra portion, $| \Psi_f \rangle$ is the Ket portion). The transition moment operator μ is the operator the couples the initial state Ψ_i to the final state Ψ_f, which is derived from the time independent Schrödinger equation. However using group theory we can ignore the detailed mathematical methods. We can use the Γ_{ir} of the vibrational energy levels and the symmetry of the transition moment operator to find out if the transition is allowed by selection rules. The selection rules for vibrations or any transition is that is allowed, for it to by allowed by group theory the answer **must contain the totally symmetric** Γ_{ir}, which is always the first Γ_{ir} in the character table for the molecule in question.

Infrared Spectroscopy

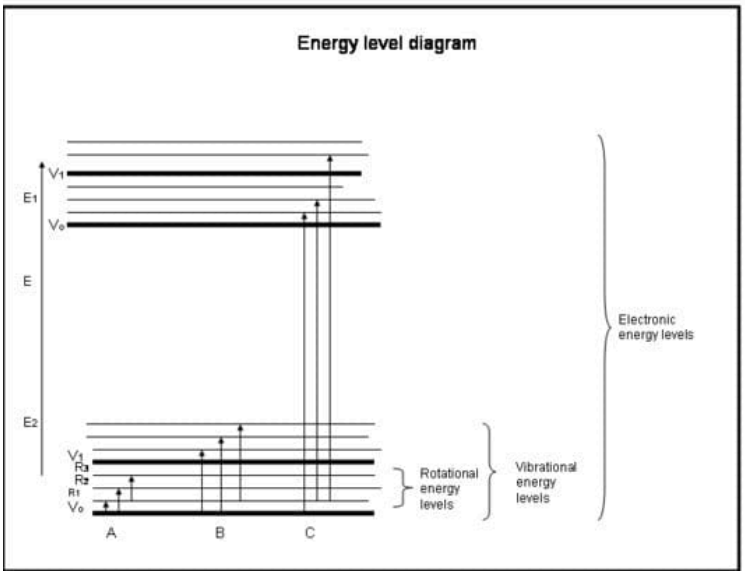
Infrared Spectroscopy (IR) measures the vibrations that occur within a single electronic state, such as the one shown above. Because the transition occurs within a single electronic state there is a variation in interatomic distance. The dipole moment is dictate by the equation.

$$\vec{\mu} = \alpha \vec{E}$$

Where $\vec{\mu}$ is the magnitude of dipole moment; α is the polarizability constant (actually a tensor) & E is the magnitude of the electric field which can be described as the electronegitivity.[3] Therefore when a vibration occurs within a single electronic state there is a change in the dipole moment, which is the definition of an active IR transition.

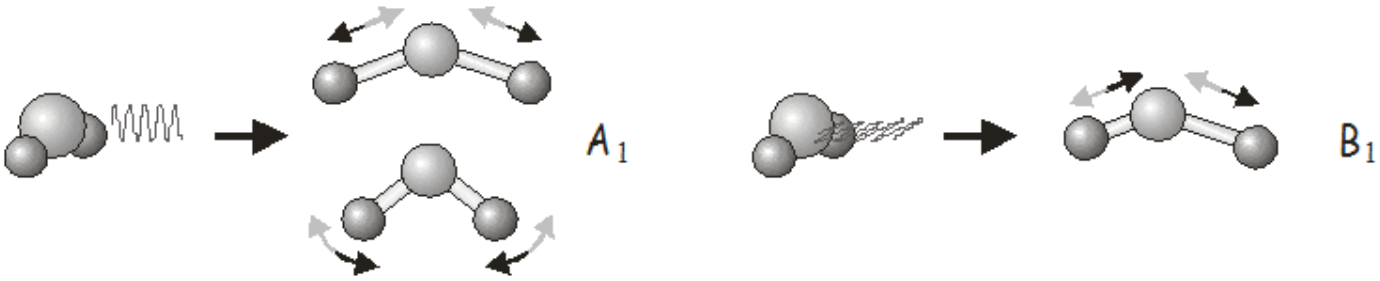
$$\left(\frac{\mathrm{d}\mu}{\mathrm{d}q}\right)_{eq} \neq 0$$

In terms of group theory a change in the dipole is a change from one vibrational state to another, as shown by the equation above. A picture of the vibrational states with respect ot the rotational states and electronic states is given below. In IR spectroscopy the transition occurs only from on vibrational state to another all within the same electronic state, shown below as B.



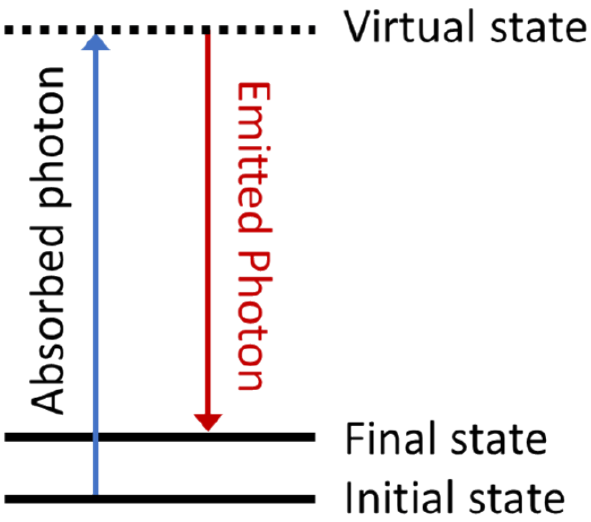
Light polarized along the x, y, and z axes of the molecule may be used to excite vibrations with the same symmetry as the x, y and z functions listed in the character table.

For example, in the C_{2v} point group, x-polarized light (light polarized in the x direction) may be used to excite vibrations of B_1 symmetry, y-polarized light to excite vibrations of B_2 symmetry, and z-polarized light to excite vibrations of A_1 symmetry. In H_2O, we would use z-polarized light to excite the symmetric stretch and bending modes, and x-polarized light to excite the asymmetric stretch. Shining y-polarized light onto a molecule of H_2O would not excite any vibrational motion.



Raman Scattering

If there are vibrational modes in the molecule that may not be accessed using a single photon, it may still be possible to excite them using a two-photon process known as Raman scattering. An energy level diagram for Raman scattering is shown below.



The first photon excites the molecule to some high-lying intermediate state, known as a *virtual state*. Virtual states are not true stationary states of the molecule (i.e. they are not eigenfunctions of the molecular Hamiltonian), but they can be thought of as stationary states of the 'photon + molecule' system. These types of states are extremely short lived, and will quickly emit a photon to return the system to a stable molecular state, which may be different from the original state. Since there are two photons (one absorbed and one emitted) involved in Raman scattering, which may have different polarizations, the transition dipole for a Raman transition transforms as one of the Cartesian products x^2, y^2, z^2, xy, xz, yz listed in the character tables.

Vibrational modes that transform as one of the Cartesian products may be excited by a Raman transition, in much the same way as modes that transform as x, y, or z may be excited by a **one-photon** vibrational transition.

In H_2O, all of the vibrational modes are accessible by ordinary one-photon vibrational transitions. However, they may also be accessed by Raman transitions. The Cartesian products transform as follows in the C_{2v} point group.

$$\begin{array}{llll} A_1 & x^2, y^2, z^2 & B_1 & xz \\ A_2 & sy & B_2 & yz \end{array} \tag{27.5}$$

The symmetric stretch and the bending vibration of water, both of A_1 symmetry, may therefore be excited by any Raman scattering process involving two photons of the same polarization (x-, y- or z-polarized). The asymmetric stretch, which has B_1 symmetry, may be excited in a Raman process in which one photon is x-polarized and the other z-polarized.

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12.14: Symmetry Adapted Linear Combinations are the Sum over all Basis functions

The construction of linear combinations of the basis of atomic movements allows the vibrations belonging to irreducible representations to be investigated. The wavefunction of these symmetry equivalent orbitals is referred to as **Symmetry Adapted Linear Combinations**, or SALCs. SALCs (Symmetry Adapted Linear Combinations) are the linear combinations of basis sets composed of the stretching vectors of the molecule. The SALCs of a molecule can help determine binding schemes and symmetries. The procedure used to determine the SALCs of a molecule is also used to determine the LCAO of a molecule. The LCAO, Linear Combination of Atomic Orbitals, uses the basis set of atomic orbitals instead of stretching vectors. The LCAO of a molecule provides a detailed description of the molecular orbitals, including the number of nodes and relative energy levels.

Symmetry adapted linear combinations are the sum over all the basis functions:

$$\phi_i = \sum_j c_{ij} b_j \tag{12.14.1}$$

ϕ_i is the i^{th} SALC function, bj is the j^{th} basis function, and c_{ij} is a coefficient which controls how much of b_j appears in ϕ_i. In method two, the projection operator is used to obtain the coefficients consistent with each irreducible representation.[1]

The SALCs of a molecule may be constructed in **two** ways. The first method uses a basis set composed of the irreducible representation of the stretching modes of the molecule. On the other hand, the second method uses a projection operator on each stretching vector. When determining the irreducible representations of the stretching modes, the reducible representations for all the vibrational modes must first be determined. Basis vectors are assigned characters and are treated as individual objects. A

Background

In order to understand and construct SALCs, a background in group theory is required. The identification of the point group of the molecule is essential for understanding how the application of operations affects the molecule. This allows for the determination of the nature of the stretching modes. As a review, let's first determine the stretching modes of water together. Water has the point group C_{2v}. Table 1 is the character table for the C_{2v} point group.

Table 12.14.1*: C_{2v} Character Table*

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	xy
B_1	1	–1	1	–1	x, R_y	xz
B_2	1	–1	–1	1	y, R_x	yz

The first step in determining stretching modes of a molecule is to add the characters contained in the x, y, and z rows to obtain the total reducible representation of the xyz coordinates, Γ_{XYZ}. Γ_{XYZ} can also be found by applying the symmetry operations to the three vectors (x, y, and z) of the coordinate system of the molecule. The next step involves the investigation of the atoms that remain unchanged when an operation is applied, Γ_{UMA}. This step refers to the unmoved atoms (UMA). Multiplying Γ_{XYZ} and Γ_{UMA} gives the reducible representation for the molecule referred to as Γ_{TOTAL}. The Γ_{TOTAL} is the reducible representation for all the modes of the molecule (vibrational, rotational, and translational) and can also be determined by applying the symmetry operations to each coordinate vector (x, y, and z) on each atom.

Table 12.14.2*: C_{2v} Reducible Representation for H2O*

C_{2v}	E	C_2	σ_v(xz)	σ_v'(yz)
Γ_{XYZ}	3	-1	1	1
Γ_{UMA}	3	1	1	3
Γ_{TOTAL}	9	-1	1	3

Γ_{TOTAL} is then reduced to later give the stretching modes that are unique to the molecule. First, the reduction formula is applied to decompose the reducible representation:

$$a_i = \frac{1}{h}\sum_R (X^R X_i^R C^R) \tag{12.14.2}$$

Here, a_i is the number of times the irreducible representation will appear in the initial reducible representation. The order of the point group is represented by *h; R* is an operation of the group; X^R is a character of the operation *R* in the reducible representation; X_i^R is a character of the operation *R* in the irreducible representation, and C^R is the number of members in the class to which *R* belongs. Applying this formula and subtracting the representations obtained from the basis functions x, y, z, R_x, R_y, and R_z (for the translations and rotations of the molecule) gives the irreducible representation that corresponds to the vibrational states of the molecule:

$$\Gamma_{Vibration} = 2a_1 + b_2$$

A simple check can be performed to determine that the right number of modes was obtained. For linear molecules (3N-5) gives the correct number of normal modes. For molecules with any other shape otherwise known as non-linear molecules, the formula is (3N-6). *N* represents the number of atoms in a molecule. Let's double check the above water example:

$$(3N-6)N = 3 \tag{12.14.3}$$

$$[3(3)-6] = 3$$

Water should have three vibrational modes. When the irreducible representation was obtained, it was seen that water has two a_1 modes and a $b_2$mode for a total of three.

When double checking that you have the correct number of normal modes for other molecules, remember that the irreducible representation E is doubly degenerate and counts as two normal modes. T is triply degenerate and counts for three normal modes, etc.

Constructing SALCs

Method 1

There are multiple ways of constructing the SALCs of a molecule. The first method uses the known symmetries of the stretching modes of the molecule. To investigate this method, the construction of the SALCs of water is examined. Water has three vibrational states, $2a_1$+b_2. Two of these vibrations are stretching modes. One is symmetric with the symmetry A_1, and the other is antisymmetric with the symmetry B_2. While looking for the SALC of a molecule, one uses vectors represented by b_j as the basis set. The vectors demonstrate the irreducible representations of molecular vibrations.

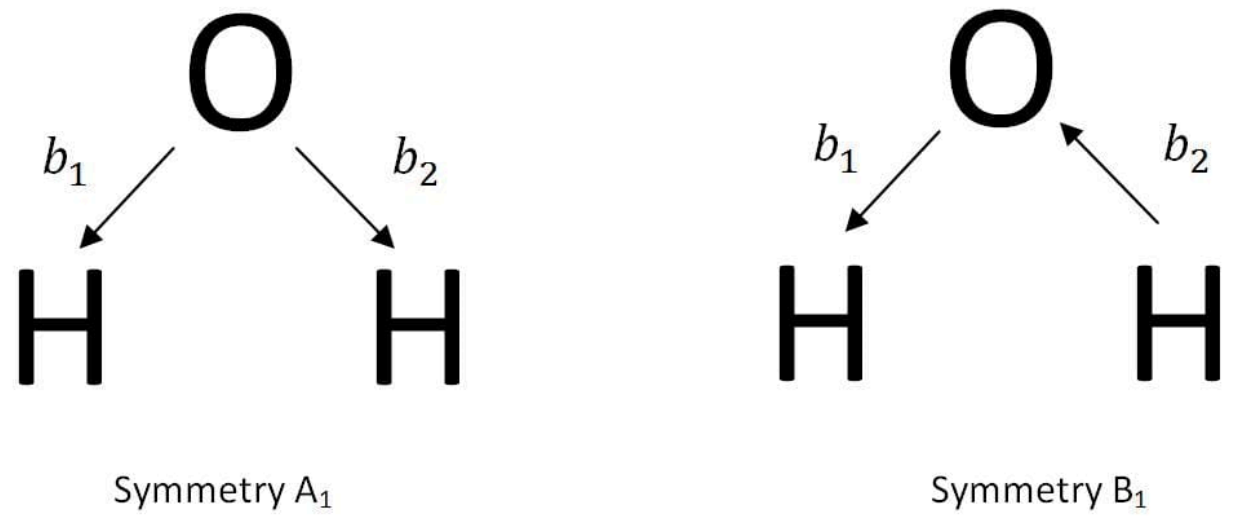


Figure 12.14.1: The stretching modes of H_2O.

The SALCs of water can be composed by creating a linear combination of the stretching vectors.

$$\phi(A_1) = b_1 + b_2$$

and

$$\phi(B_1) = b_1 - b_2 \tag{12.14.4}$$

Normalization

The final step in constructing the SALCs of water is to normalize expressions. To normalize the SALC, multiply the entire expression by the normalization constant that is the inverse of the square root of the sum of the squares of the coefficients within the expression.

$$\phi_i = N \sum_j c_{ij} b_j \tag{12.14.5}$$

$$N = \frac{1}{\sqrt{\sum_{j=1}^{n} c_{ij}^2}} \tag{12.14.6}$$

$$\phi(A_1) = \frac{1}{\sqrt{2}}(b_1 + b_2)$$

and

$$\phi(B_1) = \frac{1}{\sqrt{2}}(b_1 - b_2)$$

Normalizing the SALCs ensures that the magnitude of the SALC is unity, and therefore the dot product of any SALC with itself will equal one.

Method 2

The other method for constructing SALCs is the projection operator method. The SALC of a molecule can be constructed in the same manner as the LCAO, Linear Combination of Atomic Orbitals, however the basis set differs. While looking for the SALCs of a molecule, one uses vectors represented by b_j, on the other hand, while looking for the LCAO of a molecule, one uses atomic

orbitals as the basis set. The vectors demonstrate the possible vibration of the molecule. While constructing SALCs, the basis vectors can be treated as individual vectors.

Example 12.14.1: Water

Let's take a look at how to construct the SALC for water. The first step in constructing the SALC is to label all vectors in the basis set. Below are the bond vectors of water that will be used as the basis set for the SALCs of the molecule.

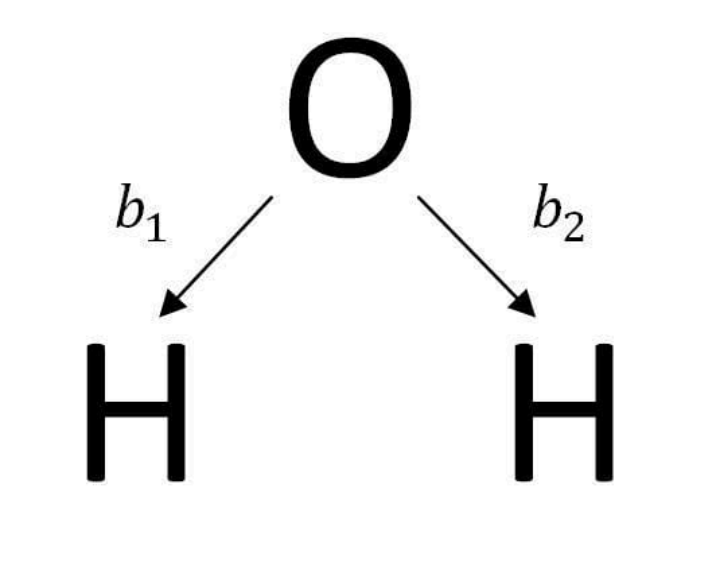


Figure 12.14.2: Labeled vectors of H_2O.

Next, the basis vector, *v*, is transformed by T_j, the *j*th symmetry operation of the molecule's point group. As the vector of the basis set is transformed, record the vector that takes its place. Water is a member of the point group C_{2V}. The Symmetry elements of the C_{2V} point group are E, C_2, σ_v, $\sigma_{v'}$.

The i^{th} SALC function, $\phi_i$is shown below using the vector $v=b_1$.

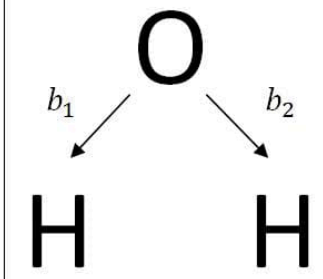
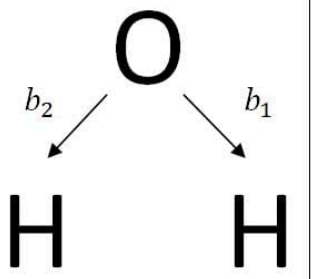
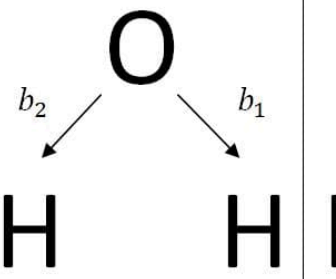
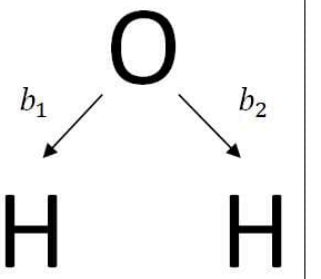
E	C_2	σ_V	$\sigma_{V'}$
			
b_1 will remain b_1	b_2 will take the place of b_1	b_2 will take the place of b_1	b_1 will remain b_1

Figure 12.14.3: The transformations of the basis vectors of H_2O.

Once the transformations have been determined, the SALC can be constructed by taking the sum of the products of each character of a representation within the point group and the corresponding transformation. The SALCs functions are the collective transformations of the basis sets represented by $\phi_i$where $X_i(j)$ is the character of the ith irreducible representation and the jth symmetry operation.

$$\phi_i = \sum_j X_i(j) T_j \nu \tag{12.14.7}$$

	E	C_2	σ_v	$\sigma_{v'}$	SUM
$T_j b_1$	b_1	b_2	b_2	b_1	
$A_1 T_j b_1$	$b_1(1)$	$b_2(1)$	$b_2(1)$	$b_1(1)$	$=2b_1 + 2b_2$
$A_2 T_j b_1$	$b_1(1)$	$b_2(1)$	$b_2(-1)$	$b_1(-1)$	$=0$
$B_1 T_j b_1$	$b_1(1)$	$b_2(-1)$	$b_2(1)$	$b_1(-1)$	$=0$
$B_2 T_j b_1$	$b_1(1)$	$b_2(-1)$	$b_2(-1)$	$b_1(1)$	$=2b_1 - 2b_2$

Table 12.14.3**:** Projection Operator method for C_{2v}

The final step in constructing the SALCs of water is to normalize expressions.

$A_1 T_j b_1$	$=2b_1 + 2b_2$	$=\frac{1}{\sqrt{2}}(b_1 + b_2)$
$A_2 T_j b_1$	$=0$	$=0$
$B_1 T_j b_1$	$=0$	$=0$
$B_2 T_j b_1$	$=2b_1 - 2b_2$	$=\frac{1}{\sqrt{2}}(b_1 - b_2)$

Table 12.14.4***:*** *Normalized SALCs of H_2O*

There are two SALCs for the water molecule, $\phi_1(A_1)$ and $\phi_1(B_2)$. This demonstrates that water has two stretching modes, one is a totally symmetric stretch with the symmetry, A_1, and the other is an antisymmetric stretch with the symmetry B_2.

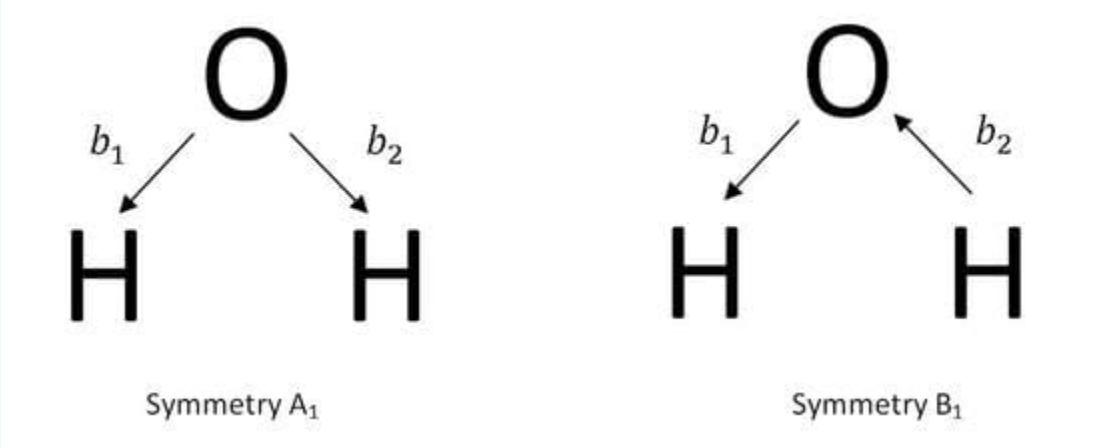


Figure 12.14.4: The stretching modes of H_2O resulting from Method 2.

Interpreting SALCs

Both methods of construction result in the same SALCs. Only irreducible representations corresponding to the symmetries of the stretching modes of the molecule will produce a SALC that is non-zero. Method 1 only utilized the known symmetries of the vibrational modes. All irreducible representations of the point group were used, but the representations that were not vibrational modes resulted in SALCs equal to zero.

Therefore, with the SALCs of a molecule given, all the symmetries of the stretching modes are identified. This allows for a clearer understanding of the spectroscopy of the molecule. Even though vibrational modes can be observed in both infrared and Raman spectroscopy, the SALCs of a molecule cannot identify the magnitude or frequency of the peak in the spectra. The normalized SALCs can, however, help to determine the relative magnitude of the stretching vectors. The magnitude can be determined by the equation below.

$$a \cdot b = |a||b|cos\theta \tag{12.14.8}$$

The resulting A_1 and B_1 symmetries for the above water example are each active in both Raman and IR spectroscopies, according to the C_{2v} character table. If the vibrational mode allows for a change in the dipole moment, the mode can be observed through infrared spectroscopy. If the vibrational mode allows for a change in the polarization of the molecule, the mode can be observed through Raman spectroscopy. Both stretching and bending modes are seen in the spectra, however only stretching modes are expressed in the SALCs.

Example 12.14.2: Difluorobenzene

The SALCs of a molecule can also provide insight to the geometry of a molecule. For example, SALCs can aid in determining the differences between para-difluorobenzene and ortho-difluorobenzene. The SALCs for these two molecules are given below.

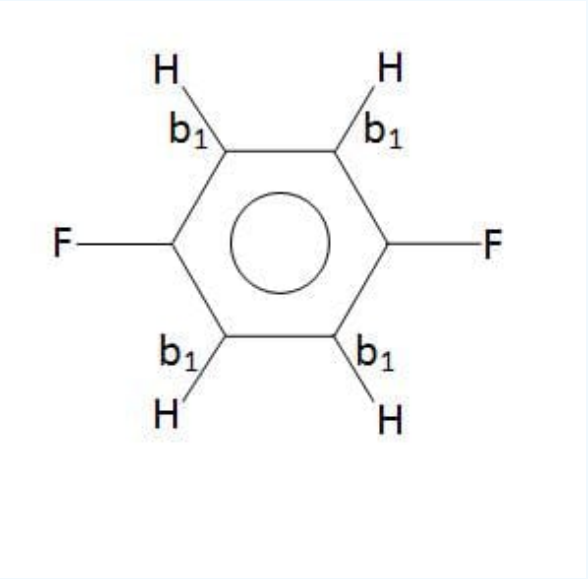


Figure 12.14.5: para-difluorobenzene

$$\phi(A_g) = \frac{1}{2}(b_1 + b_2 + b_3 + b_4)$$

$$\phi(B_{1g}) = \frac{1}{2}(b_1 - b_2 + b_3 - b_4)$$

$$\phi(B_{2u}) = \frac{1}{2}(b_1 - b_2 - b_3 + b_4)$$

$$\phi(B_{3u}) = \frac{1}{2}(b_1 + b_2 - b_3 - b_4)$$

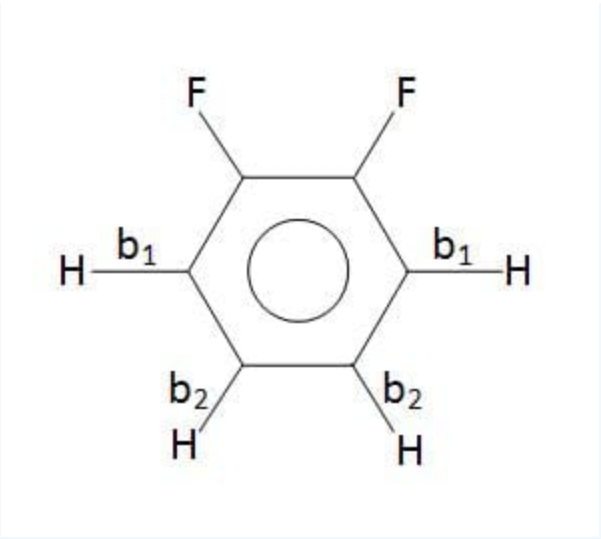


Figure 12.14.6: ortho-difluorobenzene

$$\phi_1(A_1) = \frac{1}{\sqrt{2}}(b_1 + b_2 + b_3 + b_4)$$

$$\phi_2(A_1) = \frac{1}{\sqrt{2}}(b_1 - b_2 + b_3 - b_4)$$

$$\phi_1(B_1) = \frac{1}{\sqrt{2}}(b_1 - b_2 - b_3 + b_4)$$

$$\phi_2(B_1) = \frac{1}{\sqrt{2}}(b_1 + b_2 - b_3 - b_4)$$

From the SALCs, it is seen that para-difluorobenzene has four stretching modes and ortho-difluorobenzene has only two. Therefore, it is no surprise that the vibrational spectroscopy of the para-difluorobenzene shows more peaks than the ortho-difluorobenzene.

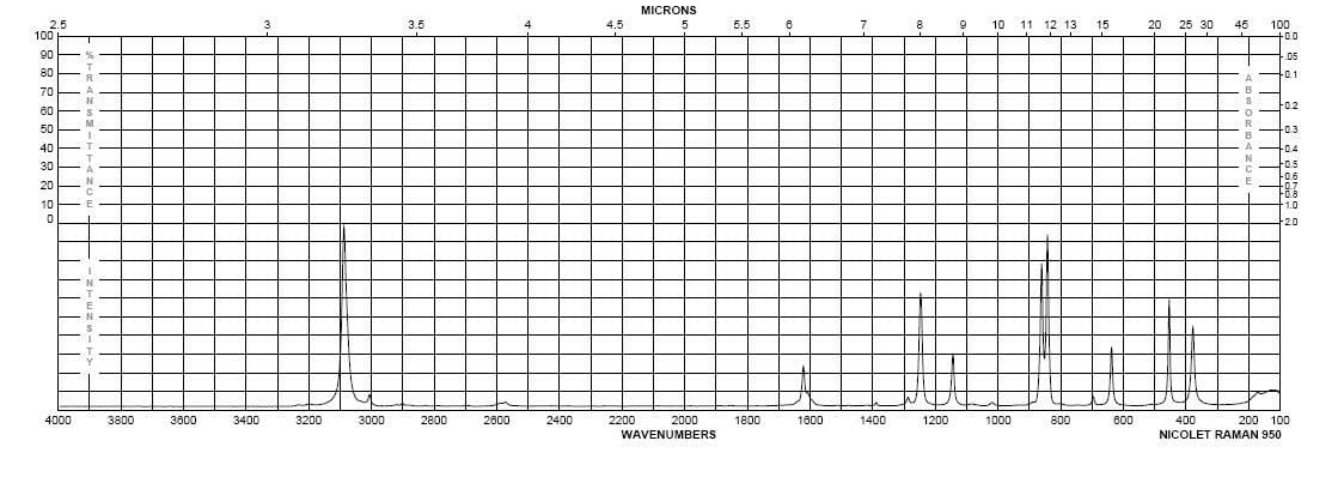


Figure 12.14.7: FT-IR Raman Spectrum of para-difluorobenzene[4]

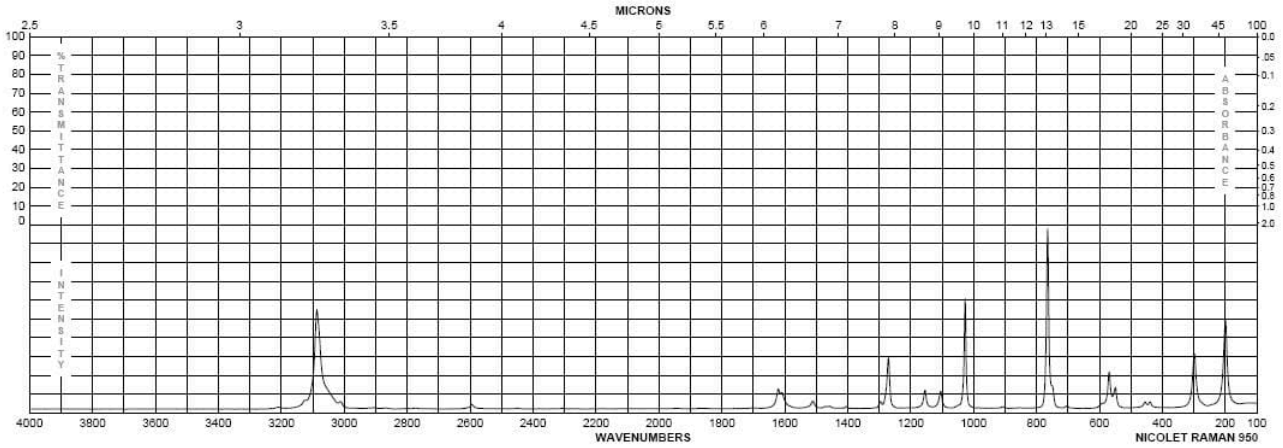


Figure 12.14.8: FT-IR Raman Spectrum of ortho-difluorobenzene[5]

Applications

The SALCs of a molecule can be used to understand the stretching modes and binding schemes of a molecule. More information can also be interpreted when applying the projection operator used in SALCs on the atomic orbitals of the molecule. This results in the determination of the linear combination of atomic orbitals (LCAO), which gives information on the molecular orbitals of the molecule. The molecular orbitals (MO) of a molecule are often constructed as LCAOs. Each MO is a solution to the Schrödinger equation and is an eigenfunction of the Hamiltonian operator. The LCAOs can be determined in the same manner as the SALCs of a molecule, with the use of a projection operator. The difference is that the basis set is no longer stretching vectors, but instead the atomic orbitals of the molecule. Hydrogen only has s orbitals, but oxygen has s and p orbitals, where the p_x, p_y, and p_z all transform differently and therefore must be treated differently.

Once the LCAOs of the molecule have been determined, the expressions can be interpreted into images of the orbitals bonding. If two orbitals are of the same sign in the expression, the electrons in the orbitals are in phase with each other and are bonding. If two orbitals are of the opposite sign in the expression, the electrons in the orbitals are out of phase with each other and are antibonding. The image below shows the atomic orbitals' phases (or signs) as red or blue lobes.

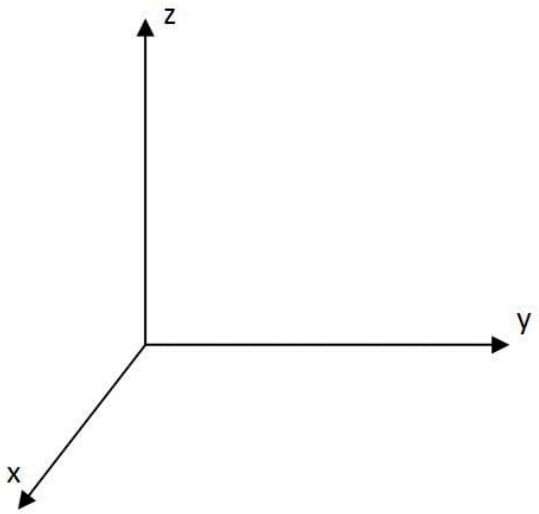


Figure 12.14.9: Atomic Orbitals of H_2O.

Any separation between two antibonding atomic orbitals is a planar node. As the number of nodes increases, so does the level

of antibonding. This allows for the LCAO to place the molecular orbitals in order of increasing energy, which can be used in constructing the molecular orbital (MO) diagram of the molecule. The irreducible representation used to construct the LCAO is used to describe the MOs. The LCAOs for water are shown below with red dotted lines showing the nodes. Notice the nodes for the p_x orbitals are in a different plane than the s orbitals of the hydrogens, so these are degenerate and nonbonding.

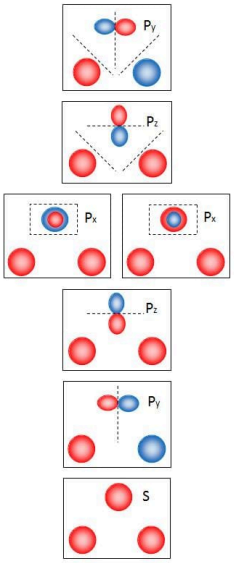


Figure 12.14.10: Molecular Orbital diagram for H_2O in order of increasing energy.

Information from the LCAO of water can also be used to analyze and anticipate the adsorption of water onto various surfaces. Evarestov and Bandura used this technique to identify the water adsorption on Y-doped $BaZrO_3$ and $TiO2$ (Rutile) respectively.[2,3]

2

Applying a combination of Methods 1 and 2, the SALCs for CBr_2H_2 can be determined. The point group of this molecule is C_{2v}, making it similar to the determination of SALCs for water.

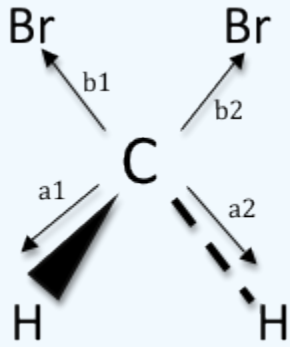


Figure 12.14.11: CBr_2H_2, point group C_{2v}.

However, the central carbon contains more than one type of attached atom; therefore, the stretching analysis must be performed in pieces. First, the C-H stretches are examined, followed by the C-Br stretches:

Table 5: Irreducible Representations for C-H and C-Br stretches in CBr2H2.

C_{2V}	E	C_2	σ_V	$\sigma_{V'}$	Irreducible Representation
Γ_{C-H}	2	0	0	2	$\Gamma_{C-H} = A_1 + B_2$
Γ_{C-Br}	2	0	2	0	$\Gamma_{C-Br} = A_1 + B_1$

Applying the projection operator method to C-Br and C-H stretches individually, the SALCs are obtained in the same fashion as before.

Table 6: SALCs for CBr2H2.

Γ_{C-Br}	E	C_2	σ_V	$\sigma_{V'}$	SUM
$A_1T_j(b_1)$	b_1	b_2	b_1	b_2	$2(b_1 + b_2)$
$B_1T_j(b_1)$	b_1	$-b_2$	b_1	$-b_2$	$2(b_1 - b_2)$

Table 7: SALCs for CBr2H2.

Γ_{C-H}	E	C_2	σ_V	$\sigma_{V'}$	SUM
$A_1T_j(a_1)$	a_1	a_2	a_2	a_1	$2(a_1 + a_2)$
$B_2T_j(a_1)$	a_1	$-a_2$	$-a_2$	a_1	$2(a_1 - a_2)$

The results are normalized and the following SALCs are obtained for the C_{2V} molecule CBr_2H_2:

$$\phi CBr(A_1) = \frac{1}{\sqrt{2}}(b_1 + b_2)$$

$$\phi CBr(B_1) = \frac{1}{\sqrt{2}}(b_1 - b_2)$$

$$\phi CH(A_1) = \frac{1}{\sqrt{2}}(a_1 + a_2)$$

$$\phi CH(B_2) = \frac{1}{\sqrt{2}}(a_1 - a_2)$$

4

To obtain the SALCs for $PtCl_4$, the same general method is applied.

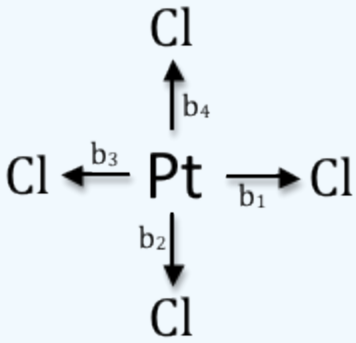


Figure 12.14.12: $PtCl_4$, point group D_{4h}.

However, even though the point group of the molecule is D_{4h}, the cyclic subgroup C_4 may be used (this is a more simplified character table used for spherically symmetrical molecules). Some manipulation is required in order to use this cyclic subgroup and will be discussed. Below is the C_4 cyclic character table.

Table 12.14.8: C4 cyclic character table.

C_4	E	C_4^1	C_4^2	C_4^3
A	1	1	1	1
B	1	-1	1	-1
E^1 E^2	1 1	i -i	-1 -1	-i i

Notice, there are two rows for E, each singly degenerate. To solve for the characters of E, one must take the sum and difference of the two rows. Then, a reduction can be applied to obtain the easiest possible characters by dividing each row by a common factor (removing the common factor is not necessary, but it does simplify the problem as well as remove any imaginary terms):

Sum = [(1+1) (i-i) (-1-1) (-i+i)] = (2 0 -2 0) ÷ 2 = E^1 (1 0 -1 0)

Difference = [(1-1) (i+i) (-1+1) (-i-i)] = (0 2i 0 -2i) ÷ 2i = E^2 (0 1 0 -1)

Using the above cyclic group, and the newly obtained characters for *E*, the projection operator can be applied using Method 2 for the construction of SALCs.

Table 12.14.9: SALCs for PtCl4 using Method 2.

C_4	E	C_4^1	C_4^2	C_4^3	SUM
$AT_j(b_1)$	b_1	b_2	b_3	b_4	$b_1 + b_2 + b_3 + b_4$
$BT_j(b_1)$	b_1	$-b_2$	b_3	$-b_4$	$b_1 - b_2 + b_3 - b_4$
$E^1T_j(b_1)$	b_1	0	$-b_3$	0	$b_1 - b_3$
$E^2T_j(b_1)$	0	b_2	0	$-b_4$	$b_2 - b_4$

Normalizing the sum as mentioned in Method 1, the following SALCs are obtained for the D_{4h} molecule $PtCl_4$:

$$\phi(A) = \frac{1}{2}(b_1 + b_2 + b_3 + b_4)$$

$$\phi(B) = \frac{1}{2}(b_1 - b_2 + b_3 - b_4)$$

$$\phi(E^1) = \frac{1}{\sqrt{2}}(b_1 - b_3)$$

$$\phi(E^2) = \frac{1}{\sqrt{2}}(b_2 - b_4)$$

3

Applying a combination of Methods 1 and 2, the SALCs for the C-H stretches of PF_2H_3 can be determined. The point group of this molecule is C_s. The central carbon contains more than one type of attached hydrogen; therefore, the stretching analysis must be performed in pieces. First, the C-H_A stretches are examined, followed by the C-H_B stretches:

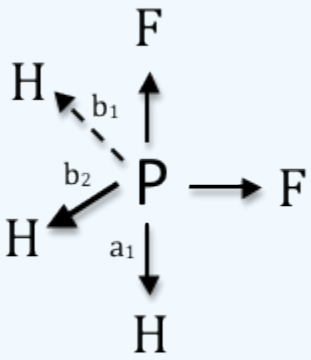


Figure 12.14.13: PF_2H_3, point group C_s.

Table 12.14.10: Irreducible Representations for C-Ha and C-Hb stretches in PF2H3.

C_s	E	σ_h	Irreducible Representation
$\Gamma_{C\text{-}Ha}$	2	0	$\Gamma_{C\text{-}Ha}$ = A' + A"
$\Gamma_{C\text{-}Hb}$	1	1	$\Gamma_{C\text{-}Hb}$ = A'

Applying the projection operator method to C-H_A and C-H_B stretches individually, the SALCs are obtained in the same fashion as before.

Table 12.14.11: SALCs for PF2H3 using Method 2.

$\Gamma_{C\text{-}HB}$	E	σ_h	SUM
A' $Tj(b_1)$	b_1	b_2	$b_1 + b_2$
A" $Tj(b_1)$	b_1	$-b_2$	$b_1 - b_2$
A' $T_j(a_1)$	a_1	a_1	$a_1 + a_1$

Table 12.14.12: SALCs for PF2H3 using Method 2.

$\Gamma_{C\text{-}HA}$	E	C_2	σ_V	$\sigma_{V'}$	SUM
$A_1T_j(a_1)$	a_1	a_2	a_2	a_1	$2(a_1 + a_2)$
$B_2T_j(a_1)$	a_1	$-a_2$	$-a_2$	a_1	$2(a_1 - a_2)$

The results are normalized and the following SALCs are obtained for the C_s molecule PF_2H_3:

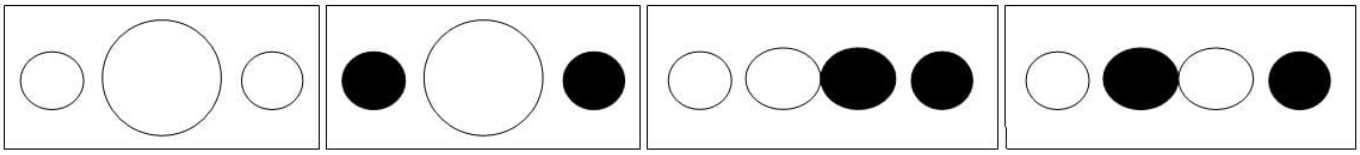
$$\phi_1 A' = \frac{1}{\sqrt{2}}(b_1 + b_2) + a_1 = \frac{1}{sqrt3}(b_1 + b_2 + a_1)$$

$$\phi_2 A' = \frac{1}{\sqrt{2}}(b_1 + b_2) - a_1 = \frac{1}{sqrt3}(b_1 + b_2 - a_1)$$

$$\phi A'' = \frac{1}{\sqrt{2}}(b_1 - b_2)$$

Problems

1. Construct the SALCs for C-H stretches of ortho-difluorobenzene.
2. Construct the SALCs for ammonia.
3. Draw the nodes for the MOs of BeH_2 (determined by used of LCAOs) and rank the MOs in order of increasing energy.



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3. A. V. Bandura,, D. G. Sykes,, V. Shapovalov,, T. N. Troung,, J. D. Kubicki,' and, R. A. Evarestov. Adsorption of Water on the TiO_2 (Rutile) (110) Surface: A Comparison of Periodic and Embedded Cluster Calculations. *The Journal of Physical Chemistry B* **2004** *108* (23), 7844-7853.
4. "1,4-Difluorobenzene" Sigma Aldrich. www.sigmaaldrich.com/catalog/...0&QS=ON&F=SPEC. 14 March, 2011.
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Solutions to Practice Problems

1. $A_1T_j(b_1)$= \frac{1}{\sqrt{2}} (b_{1} +b_{2})\)

   $B_2T_j(b_1)$= \frac{1}{\sqrt{2}} (b_{1} -b_{2})\)

   $A_1T_j(b_3)$= \frac{1}{\sqrt{2}} (b_{3} +b_{4})\)

   $B_2T_j(b_3)$= \frac{1}{\sqrt{2}} (b_{3} -b_{4})\)

   Then add and subtract (for in phase and out of phase) the individual linear combinations found by the projection operator to give the SALCs.

   $\phi_1(A_1)$ = \frac{1}{2} (b_{1} +b_{2} +b_{3} +b_{4})\)

   $\phi_2(A_1)$ = \frac{1}{2} (b_{1} +b_{2} -b_{3} -b_{4})\)

   $\phi_1(B_2)$ = \frac{1}{2} (b_{1} -b_{2} +b_{3} -b_{4})\)

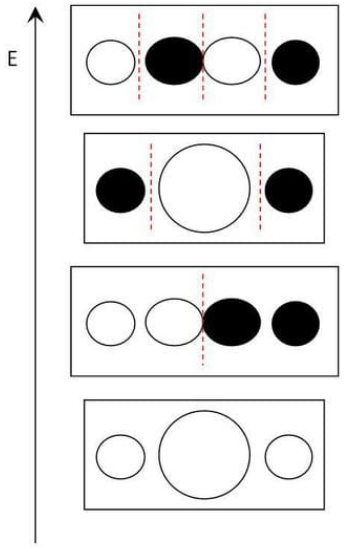
   $\phi_2(B_2)$ = \frac{1}{2} (b_{1} -b_{2} -b_{3} +b_{4})\).

2. $AT_j(b_1)= \frac{1}{\sqrt{3}} (b_{1} +b_{2} +b_{3})\)

$E_1T_j(b_1)= \frac{1}{\sqrt{6}} (2b_{1} -b_{2} -b_{3})\)

$E_2T_j(b_1)= \frac{1}{\sqrt{2}} (b_{2} -b_{3})\)

3.

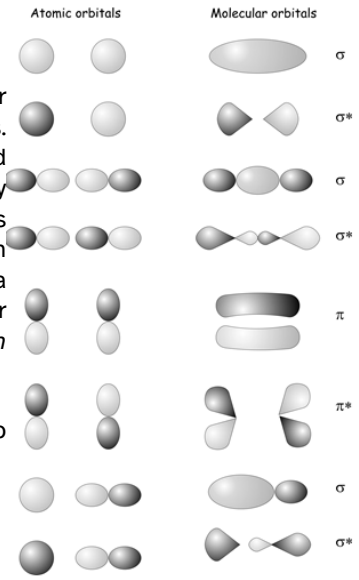


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12.15: Molecular Orbitals can be Constructed on the Basis of Symmetry

Bonding in Diatomics



You will already be familiar with the idea of constructing molecular orbitals from linear combinations of atomic orbitals from previous courses covering bonding in diatomic molecules. By considering the symmetries of s and p orbitals on two atoms, we can form **bonding** and **antibonding** combinations labeled as having either σ or π symmetry depending on whether they resemble s or p orbitals when viewed along the bond axis (see diagram below). In all of the cases shown, only atomic orbitals that have the same symmetry when viewed along the bond axis z can form a chemical bond e.g. two s orbitals, two p_z orbitals , or an s and a p_z can form a bond, but a p_z and a p_x or an s and a p_x or a p_y cannot. It turns out that the rule that determines whether or not two atomic orbitals can bond is that *they must belong to the same symmetry species within the point group of the molecule*.

We can prove this mathematically for two atomic orbitals ϕ_i and ϕ_j by looking at the overlap integral between the two orbitals.

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int \phi_i^* \phi_j d\tau \qquad (18.1)$$

In order for bonding to be possible, this integral must be non-zero. The product of the two functions ϕ_1 and ϕ_2 transforms as the direct product of their symmetry species i.e. $\Gamma_{12} = \Gamma_1 \otimes \Gamma_2$. As explained above, for the overlap integral to be non-zero, Γ_{12} must contain the totally symmetric irreducible representation (A_{1g} for a homonuclear diatomic, which belongs to the point group $D_{\infty h}$). As it happens, this is only possible if ϕ_1 andϕ_2 belong to the same irreducible representation. These ideas are summarized for a diatomic in the table below.

First Atomic Orbital	Second Atomic Orbital	$\Gamma_1 \otimes \Gamma_2$	Overlap Integral	Bonding?
$s\ (A_{1g})$	$s\ (A_{1g})$	A_{1g}	Non-zero	Yes
$s\ (A_{1g})$	$p_x\ (E_{1u})$	E_{1u}	Zero	No
$s\ (A_{1g})$	$p_z\ (A_{1u})$	A_{1u}	Zero	No
$p_x\ (E_{1u})$	$p_x\ (E_{1u})$	$A_{1g} + A_{2g} + E_{2g}$	Non-zero	Yes
$p_X\ (E_{1u})$	$p_z\ (A_{1u})$	E_{1g}	Zero	No
$p_z\ (A_{1u})$	$p_z\ (A_{1u})$	A_{1g}	Non-zero	Yes

(18.2)

Bonding in Polyatomics- Constructing Molecular Orbitals from SALCs

In the previous section we showed how to use symmetry to determine whether two atomic orbitals can form a chemical bond. How do we carry out the same procedure for a polyatomic molecule, in which many atomic orbitals may combine to form a bond? Any SALCs of the same symmetry could potentially form a bond, so all we need to do to construct a molecular orbital is take a linear combination of all the SALCs of the same symmetry species. The general procedure is:

1. Use a basis set consisting of valence atomic orbitals on each atom in the system.
2. Determine which irreducible representations are spanned by the basis set and construct the SALCs that transform as each irreducible representation.
3. Take linear combinations of irreducible representations of the same symmetry species to form the molecular orbitals. E.g. in our NH_3 example we could form a molecular orbital of A_1 symmetry from the two SALCs that transform as A_1,

$$\begin{aligned}\Psi(A_1) &= c_1\phi_1 + c_2\phi_2 \\ &= c_1 s_N + c_2\frac{1}{\sqrt{3}}(s_1 + s_2 + s_3)\end{aligned} \tag{19.1}$$

Unfortunately, this is as far as group theory can take us. It can give us the functional form of the molecular orbitals but it cannot determine the coefficients c_1 and c_2. To go further and obtain the expansion coefficients and orbital energies, we must turn to quantum mechanics. The material we are about to cover will be repeated in greater detail in later courses on quantum mechanics and valence, but they are included here to provide you with a complete reference on how to construct molecular orbitals and determine their energies.

Summary of the Steps Involved in Constructing Molecular Orbitals

1. Choose a basis set of functions f_i consisting of the valence atomic orbitals on each atom in the system, or some chosen subset of these orbitals.
2. With the help of the appropriate character table, determine which irreducible representations are spanned by the basis set using Equation (15.20) to determine the number of times a_k that the k^{th} irreducible representation appears in the representation.

$$a_k = \frac{1}{h}\sum_C n_C\chi(g)\chi_k(g) \tag{12.15.1}$$

3. Construct the SALCs ϕ_i that transform as each irreducible representation using Equation 16.1

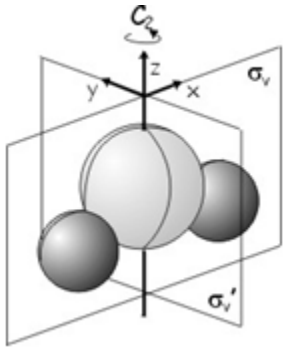
$$\phi_i = \sum_g \chi_k(g) g f_i \tag{12.15.2}$$

4. Write down expressions for the molecular orbitals by taking linear combinations of all the irreducible representations of the same symmetry species.
5. Write down the secular equations for the system.
6. Solve the secular determinant to obtain the energies of the molecular orbitals.
7. Substitute each energy in turn back into the secular equations and solve to obtain the coefficients appearing in your molecular orbital expressions in step 4.
8. Normalize the orbitals.

A more complicated bonding example

As another example, we will use group theory to construct the molecular orbitals of H_2O (point group C_{2v}) using a basis set consisting of all the valence orbitals. The valence orbitals are a $1s$ orbital on each hydrogen, which we will label s_H and s'_H, and a $2s$ and three $2p$ orbitals on the oxygen, which we will label s_O, p_x, p_y, p_z giving a complete basis $(s_H, s'_H, s_O, p_x, p_y, p_z)$.

The first thing to do is to determine how each orbital transforms under the symmetry operations of the C_{2v} point group (E, C_2, σ_v and σ'_v), construct a matrix representation and determine the characters of each operation. The symmetry operations and axis system we will be using are shown below.



The orbitals transform in the following way

$$\begin{array}{lllll} E & (s_H, s'_H, s_O, p_x, p_y, p_z) & \rightarrow & (s_H, s'_H, s_O, p_x, p_y, p_z) \\ C_2 & (s_H, s'_H, s_O, p_x, p_y, p_z) & \rightarrow & (s'_H, s_H, s_O, -p_x, -p_y, p_z) \\ \sigma_v(xz) & (s_H, s'_H, s_O, p_x, p_y, p_z) & \rightarrow & (s_H, s'_H, s_O, p_x, -p_y, p_z) \\ \sigma'_v(yz) & (s_H, s'_H, s_O, p_x, p_y, p_z) & \rightarrow & (s'_H, s_H, s_O, -p_x, p_y, p_z) \end{array} \tag{12.15.3}$$

A short aside on constructing matrix representatives

After a little practice, you will probably be able to write matrix representatives straight away just by looking at the effect of the symmetry operations on the basis. However, if you are struggling a little the following procedure might help.

Remember that the matrix representatives are just the matrices we would have to multiply the left hand side of the above equations by to give the right hand side. In most cases they are very easy to work out. Probably the most straightforward way to think about it is that each column of the matrix shows where one of the original basis functions ends up. For example, the first column transforms the basis function s_H to its new position. The first column of the matrix can be found by taking the result on the right hand side of the above expressions, replacing every function that *isn't* s_H with a zero, putting the coefficient of s_H (1 or -1 in this example) in the position at which it occurs, and taking the transpose to give a column vector.

Rotation

Consider the representative for the C_2 operation. The original basis $(s_H, s'_H, s_O, p_x, p_y, p_z)$ transforms into $(s'_H, s_H, s_O, -p_x, -p_y, p_z)$. The first column of the matrix therefore transforms s_H into s'_H. Taking the result and replacing all the other functions with zeroes gives $(0, s_H, 0, 0, 0, 0)$. The coefficient of s_H is 1, so the first column of the C_2 matrix representative is

$$\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{12.15.4}$$

Matrix representation, characters and SALCs

The matrix representatives and their characters are

$$\begin{array}{cccc} E & C_2 & \sigma_v & \sigma'_v \\ \begin{pmatrix} 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&1&0&0 \\ 0&0&0&0&1&0 \\ 0&0&0&0&0&1 \end{pmatrix} & \begin{pmatrix} 0&1&0&0&0&0 \\ 1&0&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&-1&0&0 \\ 0&0&0&0&-1&0 \\ 0&0&0&0&0&1 \end{pmatrix} & \begin{pmatrix} 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&1&0&0 \\ 0&0&0&0&-1&0 \\ 0&0&0&0&0&1 \end{pmatrix} & \begin{pmatrix} 0&1&0&0&0&0 \\ 1&0&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&-1&0&0 \\ 0&0&0&0&1&0 \\ 0&0&0&0&0&1 \end{pmatrix} \\ \chi(E) = 6 & \chi(C_2) = 0 & \chi(\sigma_v) = 4 & \chi(\sigma'_v) = 2 \end{array} \tag{12.15.5}$$

Now we are ready to work out which irreducible representations are spanned by the basis we have chosen. The character table for C_{2v} is:

C_{2v}	E	C_2	σ_v	σ'_v	$h = 4$
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	−1	−1	xy, R_z
B_1	1	−1	1	−1	x, xz, R_y
B_2	1	−1	−1	1	y, yz, R_x

As before, we use Equation (15.20) to find out the number of times each irreducible representation appears.

$$a_k = \frac{1}{h}\sum_C n_C \chi(g)\chi_k(g) \tag{12.15.6}$$

We have

$$\begin{aligned} a(A_1) &= \frac{1}{4}(1\times 6\times 1+1\times 0\times 1+1\times 4\times 1+1\times 2\times 1) &= 3\\ a(A_2) &= \frac{1}{4}(1\times 6\times 1+1\times 0\times 1+1\times 4\times -1+1\times 2\times -1) &= 0\\ a(B_1) &= \frac{1}{4}(1\times 6\times 1+1\times 0\times -1+1\times 4\times 1+1\times 2\times -1) &= 2\\ a(B_2) &= \frac{1}{4}(1\times 6\times 1+1\times 0\times -1+1\times 4\times -1+1\times 2\times 1) &= 1 \end{aligned} \tag{12.15.7}$$

so the basis spans $3A_1 + 2B_1 + B_2$. Now we use the projection operators applied to each basis function f_i in turn to determine the SALCs $\phi_i = \Sigma_g \chi_k(g) g f_i$

The SALCs of A_1 symmetry are:

$$\begin{aligned} \phi(s_H) &= s_H + s'_H + s_H + s'_H &= 2(s_H + s'_H)\\ \phi(s'_H) &= s'_H + s_H + s'_H + s_H &= 2(s_H + s'_H)\\ \phi(s_O) &= s_O + s_O + s_O + s_O &= 4s_O\\ \phi(p_x) &= p_x - p_x + p_x - p_x &= 0\\ \phi(p_y) &= p_y - p_y + p_y - p_y &= 0\\ \phi(p_z) &= p_z + p_z + p_z + p_z &= 4p_z \end{aligned} \tag{12.15.8}$$

The SALCs of B_1 symmetry are:

$$\begin{aligned} \phi(s_H) &= s_H - s'_H + s_H - s'_H &= 2(s_H - s'_H)\\ \phi(s'_H) &= s'_H - s_H + s'_H - s_H &= 2(s'_H - s_H)\\ \phi(s_O) &= s_O - s_O + s_O - s_O &= 0\\ \phi(p_x) &= p_x + p_x + p_x + p_x &= 4p_x\\ \phi(p_y) &= p_y + p_y - p_y - p_y &= 0\\ \phi(p_z) &= p_z - p_z + p_z - p_z &= 0 \end{aligned} \tag{12.15.9}$$

The SALCs of B_2 symmetry are:

$$\begin{aligned} \phi(s_H) &= s_H - s'_H - s_H = s'_H &= 0\\ \phi(s'_H) &= s'_H - s_H - s'_H + s_H &= 0\\ \phi(s_O) &= s_O - s_O - s_O + s_O &= 0\\ \phi(p_x) &= p_x + p_x - p_x - p_x &= 0\\ \phi(p_y) &= p_y + p_y + p_y + p_y &= 4p_y\\ \phi(p_z) &= p_z - p_z - p_z + p_z &= 0 \end{aligned} \tag{12.15.10}$$

After normalization, our SALCs are therefore:

A_1 symmetry

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{2}}(s_H + s'_H)\\ \phi_2 &= s_O\\ \phi_3 &= p_z \end{aligned} \tag{12.15.11}$$

B_1 symmetry

$$\begin{aligned} \phi_4 &= \frac{1}{\sqrt{2}}(s_H - s'_H)\\ \phi_5 &= p_x \end{aligned} \tag{12.15.12}$$

B_2 symmetry

$$\phi_6 = p_y \tag{12.15.13}$$

Note that we only take one of the first two SALCs generated by the B_1 projection operator since one is a simple multiple of the other (i.e. they are not linearly independent). We can therefore construct three molecular orbitals of A_1 symmetry, with the general form

$$\begin{aligned} \Psi(A_1) &= c_1\phi_1 + c_2\phi_2 + c_3\phi_3 \\ &= c_1'(s_H + s_H') + c_2 s_O + c_3 p_z \quad \text{where } c_1' = \frac{c_1}{\sqrt{2}} \end{aligned} \tag{12.15.14}$$

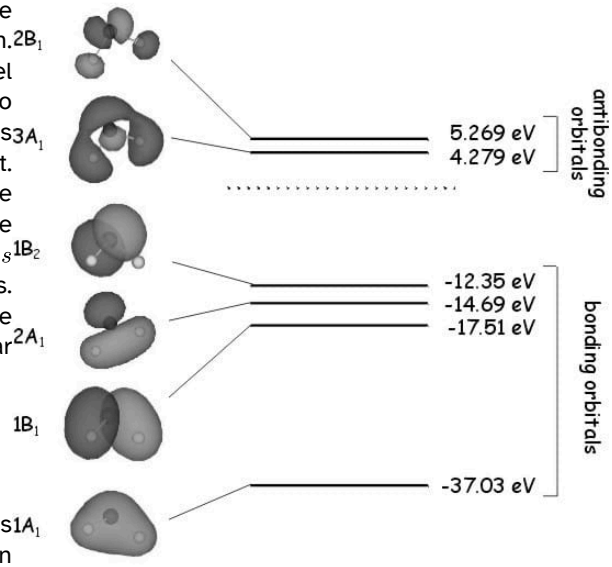
two molecular orbitals of B_1 symmetry, of the form

$$\begin{aligned} \Psi(B_1) &= c_4\phi_4 + c_5\phi_5 \\ &= c_4'(s_H - s_H') + c_5 p_z \end{aligned} \tag{12.15.15}$$

and one molecular orbital of B_2 symmetry

$$\begin{aligned} \Psi(B_2) &= \phi_6 \\ &= p_y \end{aligned} \tag{12.15.16}$$

To work out the coefficients c_1 - c_5 and determine the orbital energies, we would have to solve the secular equations for each set of orbitals in turn. We are not dealing with a conjugated p system, so in this case Hückel theory cannot be used and the various H_{ij} and S_{ij} integrals would have to be calculated numerically and substituted into the secular equations. This involves a lot of tedious algebra, which we will leave out for the moment. The LCAO orbitals determined above are an approximation of the true molecular orbitals of water, which are shown on the right. As we have shown using group theory, the A_1 molecular orbitals involve the oxygen $2s$ and $2p_z$ atomic orbitals and the sum $s_H + s_H'$ of the hydrogen $1s$ orbitals. The B_1 molecular orbitals involve the oxygen $2p_x$ orbital and the difference $s_H - s_H'$ of the two hydrogen $1s$ orbitals, and the B_2 molecular orbital is essentially an oxygen $2p_y$ atomic orbital.



Electronic transitions in molecules

When an electron is excited from one electronic state to another, this is what is called an electronic transition. A clear example of this is part C in the energy level diagram shown above. Just as in a vibrational transition the selection rules for electronic transitions are dictated by the transition moment integral. However we now must consider both the electronic state symmetries and the vibration state symmetries since the electron will still be coupled between two vibrational states that are between two electronic states. This gives us this modified transition moment integral:

Transition Moment Integral, electronic.JPG

Where you can see that the symmetry of the initial electronic state & vibrational state are in the Bra and the final electronic and vibrational states are in the Ket. Though this appears to be a modified version of the transition moment integral, the same equation holds true for a vibrational transition. The only difference would be the electronic state would be the same in both the initial and final states. Which the dot product of yields the totally symmetric representation, making the electronic state irrelevant for purely vibrational spectroscopy.

Raman

In Resonance Raman spectroscopy transition that occurs is the excitation from one electronic state to another and the selection rules are dictated by the transition moment integral discussed in the electronic spectroscopy segment. However mechanically Raman does produce a vibration like IR, but the selection rules for Raman state there must be a change in the polarization, that is

the volume occupied by the molecule must change. But as far as group theory to determine whether or not a transition is allowed one can use the transition moment integral presented in the electronic transition portion. Where one enters the starting electronic state symmetry and vibrational symmetry and final electronic state symmetry and vibrational state, perform the direct product with the different M's or polarizing operators For more information about this topic please explore the Raman spectroscopy portion of the Chemwiki

Fluorescence

For the purposes of Group Theory Raman and Fluorescence are indistinguishable. They can be treated as the same process and in reality they are quantum mechanically but differ only in how Raman photons scatter versus those of fluorescence.

Phosphorescence

Phosphorescence is the same as fluorescence except upon excitation to a singlet state there is an interconversion step that converts the initial singlet state to a triplet state upon relaxation. This process is longer than fluorescence and can last microseconds to several minutes. However despite the singlet to triplet conversion the transition moment integral still holds true and the symmetry of ground state and final state still need to contain the totally symmetric representation.

Symmetry

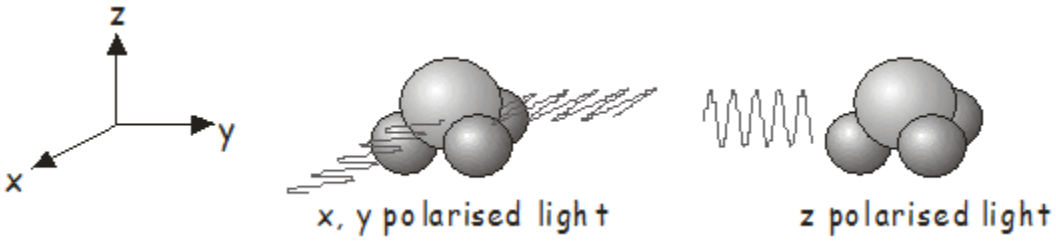
Assume that we have a molecule in some initial state Ψ_i. We want to determine which final states Ψ_f can be accessed by absorption of a photon. Recall that for an integral to be non-zero, the representation for the integrand must contain the totally symmetric irreducible representation. The integral we want to evaluate is

$$\hat{\boldsymbol{\mu}}_{fi} = \int \Psi_f^* \hat{\boldsymbol{\mu}} \Psi_i d\tau \tag{27.4}$$

so we need to determine the symmetry of the function $\Psi_f^* \hat{\boldsymbol{\mu}} \Psi_i$. As we learned in Section 18, the product of two functions transforms as the direct product of their symmetry species, so all we need to do to see if a transition between two chosen states is allowed is work out the symmetry species of Ψ_f, $\hat{\boldsymbol{\mu}}$ and Ψ_i , take their direct product, and see if it contains the totally symmetric irreducible representation for the point group of interest. Equivalently (as explained in Section 18), we can take the direct product of the irreducible representations for $\hat{\boldsymbol{\mu}}$ and Ψ_i and see if it contains the irreducible representation for Ψ_f. This is best illustrated using a couple of examples.

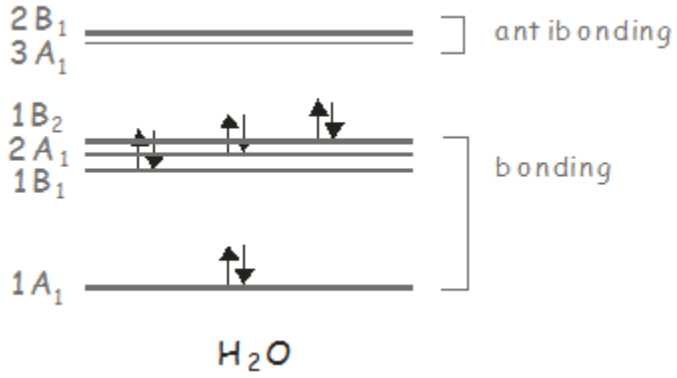
Earlier in the course, we learned how to determine the symmetry molecular orbitals. The symmetry of an electronic state is found by identifying any unpaired electrons and taking the direct product of the irreducible representations of the molecular orbitals in which they are located. The ground state of a closed-shell molecule, in which all electrons are paired, always belongs to the totally symmetric irreducible representation[7]. As an example, the electronic ground state of NH_3, which belongs to the C_{3v} point group, has A_1 symmetry. To find out which electronic states may be accessed by absorption of a photon, we need to determine the irreducible representations for the electric dipole operator $\hat{\mu}$. Light that is linearly polarized along the x, y, and z axes transforms in the same way as the functions x, y, and z in the character table[8]. From the C_{3v} character table, we see that x- and y-polarized light transforms as E, while z-polarized light transforms as A_1. Therefore:

i. For x- or y-polarized light, $\Gamma_{\hat{\mu}} \otimes \Gamma_{\Psi 1}$ transforms as $E \otimes A_1 = E$. This means that absorption of x- or y-polarized light by ground-state NH_3 (see figure below left) will excite the molecule to a state of E symmetry.
ii. For z-polarized light, $\Gamma_{\hat{\mu}} \otimes \Gamma_{\Psi 1}$ transforms as $A_1 \otimes A_1 = A_1$. Absorption of z-polarized light by ground state NH_3 (see figure below right) will excite the molecule to a state of A_1 symmetry.



Of course, the photons must also have the appropriate energy, in addition to having the correct polarization to induce a transition.

We can carry out the same analysis for H_2O, which belongs to the C_{2v} point group. We showed previously that H_2O has three molecular orbitals of A_1 symmetry, two of B_1 symmetry, and one of B_2 symmetry, with the ground state having A_1 symmetry. In the C_{2v} point group, x-polarized light has B_1 symmetry, and can therefore be used to excite electronic states of this symmetry; y-polarized light has B_2 symmetry, and may be used to access the B_2 excited state; and z-polarized light has A_1 symmetry, and may be used to access higher lying A_1 states. Consider our previous molecular orbital diagram for H_2O.



The electronic ground state has two electrons in a B_2 orbital, giving a state of A_1 symmetry ($B_2 \otimes B_2 = A_1$). The first excited electronic state has the configuration $(1B_2)^1(3A_1)^1$ and its symmetry is $B_2 \otimes A_1 = B_2$. It may be accessed from the ground state by a y-polarized photon. The second excited state is accessed from the ground state by exciting an electron to the $2B_1$ orbital. It has the configuration $(1B_2)^1(2B_1)^1$, its symmetry is $B_2 \otimes B_1 = A_2$. Since neither x-, y- or z-polarized light transforms as A_2, this state may not be excited from the ground state by absorption of a single photon.

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12.E: Group Theory - The Exploitation of Symmetry (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 12 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q12.1

Normalize the following equation:

$$\psi(x) = Zxe^{-kx^2} \tag{12.E.1}$$

S12.1

$$\int_{-\infty}^{\infty} \psi(x)^* \psi(x) dx \tag{12.E.2}$$

$$1 = Z^2 \frac{1}{4} \sqrt{\frac{\pi}{2}} \alpha^{\frac{-3}{2}} \tag{12.E.3}$$

$$Z^2 = 4\sqrt{\frac{2}{\pi}} (\frac{m\omega}{2\hbar})^{3/2} \tag{12.E.4}$$

notes:

When I integrated $(xe^{-kx^2})^2$ the answer had an erf term in it. I think that the normalization of this specific function is more complex than was intended

Q12.3

List the symmetry elements for the bent molecule H_2O.

S12.3

Identity element E, two reflection planes σ_{xz} and σ_{yz}, one 2-fold rotation axis C_2, and it belongs to the point group C_2v.

Q12.4

Verify that an ethene molecule has the symmetry elements given in Table 12.2.

S12.4

The point group of ethene is D_{2h}. The identity of element is given. There are three C_2 axes and three vertical axes.

Q12.5

Verify that a water molecule has the symmetry elements given in Table 12.2.

S12.5

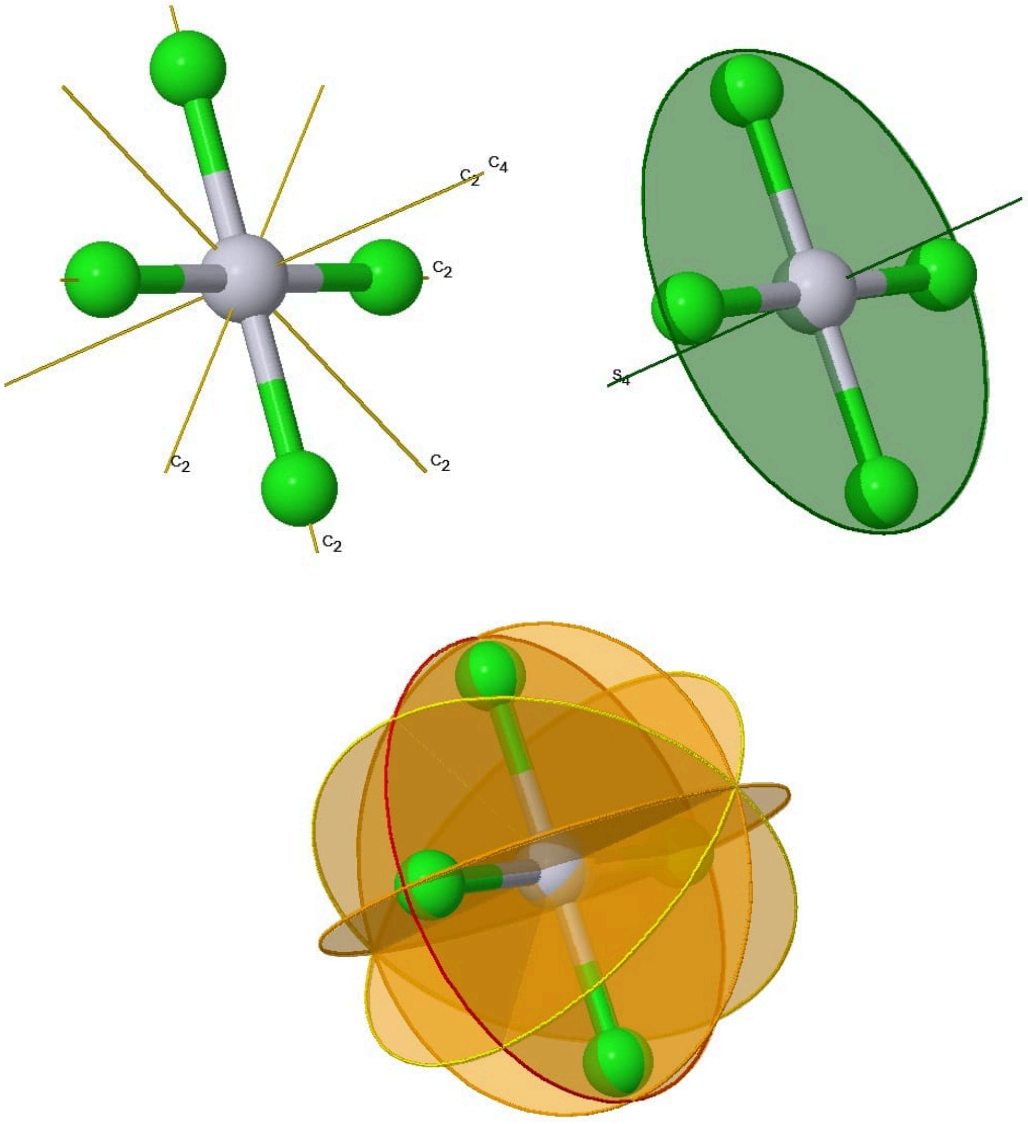
The point group of water is C_{2v}. A water molecule contains the symmetry elements E, C_2, and $2\sigma_v$. Water contains a two- fold C_2 axis through the oxygen molecule located directly on the Z axis. Water also contains two vertical planes of symmetry. The first mirror plane cuts vertically through all three molecules, H-O-H. The second mirror plane cuts through the water molecule perpendicular to the other vertical plane. The C_2 axis lies along the intersection of the two σ planes.

Q12.6

What is the point group of tetrachlropalladate $[PdCl_4]^{2-}$ and show the symmetry elements.

S12.6

The symmetry elements for tetrachlropalladate are $E, i, C_4, 4C_2, S_4, \sigma_h, 2\sigma_v, 2\sigma_d$.



(left): proper rotations (C_2 and C_4), (center) improper S_4 rotation, (right) relection planes (σ_h σ_d and σ_h)

Q12.31

Considering the allyl anion, $CH_2CHCH_2^-$, which belongs to the C_{2v} point group, calculate the Huckel secular determinant using $|\psi_1\rangle$, $|\psi_2\rangle$, and $|\psi_3\rangle$ (2_{pz} on each carbon atom). Then find the reducible representation for the allyl anion using $|\psi_j\rangle$ as the basis.

Show that the reducible representation $\Gamma = A_2 + 2B_1$. What does this say about the expected secular determinant? Now, use the generating operator (Equation 13.2) to derive three symmetry orbitals for the allyl anion. Normalize them and calculate the Huckel secular determinant equation and solve for the π electron energies.

S12.31

Applying the Huckel theory to the allyl anion yields the secular determinant given as

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{12.E.5}$$

Dividing the matrix by β and using the variable $x = \dfrac{\alpha - E}{\beta}$, we can solve a determinant of the form:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{12.E.6}$$

Expanding this determinant gives the equation

$$x^3 - 2x = 0 \tag{12.E.7}$$

Solving this equation gives $x = 0, \pm\sqrt{2}$.

The reducible representation can be found by looking at the four operators in the C_{2v} point group, which are $E, C_2, \sigma_v, \sigma_v'$. The operator E leaves all three orbitals unchanged (reducible representation of 3). The C_{2v} operator inverts just one of the orbitals (a reducible representation of -1). The σ_v operator leaves just one of the orbitals unchanged but does not invert any (reducible representation of 1). Lastly, the σ_v' operator inverts all three orbitals (reducible representation of -3). Thus, the reducible representation of the C_{2v} point group is

$$\Gamma = 3 \quad -1 \quad 1 \quad -3$$

Using equation 12.23, we find the irreducible representations to be

$$a_{A_1} = \frac{1}{4}(3 - 1 + 1 - 3) = 0 \tag{12.E.8}$$

$$a_{A_2} = \frac{1}{4}(3 - 1 - 1 + 3) = 1 \tag{12.E.9}$$

$$a_{B_1} = \frac{1}{4}(3 + 1 + 1 + 3) = 2 \tag{12.E.10}$$

$$a_{B_2} = \frac{1}{4}(3 + 1 - 1 - 3) = 0 \tag{12.E.11}$$

We therefore yield the reducible representation $\Gamma = A_2 + 2B_1$. This result shows us that the secular determinant can be written in either a 1 x 1 or 2 x 2 block diagonal form corresponding to the A_2 or B_1 representation, respectively. The three symmetry orbitals are found by

$$P_{A_2}\psi_1 = \frac{1}{4}(\psi_1 - \psi_3 - \psi_3 + \psi_1) \propto \psi_1 - \psi_3 \tag{12.E.12}$$

$$P_{B_1}\psi_1 = \frac{1}{4}(\psi_1 + \psi_3 + \psi_3 + \psi_1) \propto \psi_1 + \psi_3 \tag{12.E.13}$$

$$P_{B_1}\psi_2 = \frac{1}{4}(\psi_2 + \psi_2 + \psi_2 + \psi_2) = \psi_2 \tag{12.E.14}$$

using generating operators for A_2 and B_1.

The three normalized symmetry orbitals are

$$\Phi_1 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_3) \tag{12.E.15}$$

$$\Phi_2 = \psi_2 \tag{12.E.16}$$

$$\Phi_3 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_3) \tag{12.E.17}$$

Thus, these three orbitals give the symmetry elements below.

$$H_{11} = \frac{1}{2}(2\alpha) = \alpha \tag{12.E.18}$$

$$H_{22} = \alpha \tag{12.E.19}$$

$$H_{33} = \frac{1}{2}(2\alpha) = \alpha \tag{12.E.20}$$

$$H_{12} = \frac{1}{2}(\beta - \beta) = 0 \tag{12.E.21}$$

$$H_{13} = \frac{1}{2}(\alpha - \alpha) = 0 \tag{12.E.22}$$

$$H_{23} = \frac{1}{\sqrt{2}}(2\beta) = \sqrt{2}\beta \tag{12.E.23}$$

$$S_{11} = S_{22} = S_{33} = 1 \tag{12.E.24}$$

$$S_{12} = S_{13} = S_{23} = 0 \tag{12.E.25}$$

This gives the secular determinant

$$\begin{vmatrix} \alpha - E & 0 & 0 \\ 0 & \alpha - E & \sqrt{2}\beta \\ 0 & \sqrt{2}\beta & \alpha - E \end{vmatrix} = 0 \tag{12.E.26}$$

Dividing the matrix by β and using the variable $x = \dfrac{\alpha - E}{\beta}$, we can solve a determinant of the form:

$$\begin{vmatrix} x & 0 & 0 \\ 0 & x & \sqrt{2} \\ 0 & \sqrt{2} & x \end{vmatrix} = 0 \tag{12.E.27}$$

which gives roots $x = 0, \pm\sqrt{2}$. Using the substitution that $x = \dfrac{\alpha - E}{\beta}$, we get the energies to be

$$E_1 = \alpha - \sqrt{2}\beta \tag{12.E.28}$$

$$E_2 = \alpha \tag{12.E.29}$$

$$E_3 = \alpha + \sqrt{2}\beta \tag{12.E.30}$$

Q12.32

How will the secular determinant for SF_6 look if we use group theory to generate symmetry orbitals?

S12.32

The reducible representation for an octahedral is

$$\begin{array}{cccccccccc} O_h & E & 8C_3 & 6C_2 & 6C_4 & 3C_2 & i & 6S_4 & 8S_6 & 3\sigma_h & 6\sigma_d \\ \Gamma & 6 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & 4 & 2 \end{array} \tag{12.E.31}$$

Use this equation:

$$a_i = \frac{1}{h}\sum \chi(\hat{R})\chi_i(\hat{R}) \tag{12.E.32}$$

to get:

$$a_E = \frac{1}{10}\big(6+2+2+4+2\big) \tag{12.E.33}$$

However, the reducible representation is better represented in a table format:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

Q12.33

Apply the *Great Orthogonality Theorem,*

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{nm}\Gamma_{ij}(\hat{R})_{n'm'} = \frac{h}{d_i}\delta_{ij}\delta_{mm'}\delta_{nn'} \tag{12.E.34}$$

,

to C_{3v} point group given in which

$$\Gamma_E = [E_1E_2E_3E_4E_5E_6] \tag{12.E.35}$$

where

$$E_1 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{12.E.36}$$

$$E_2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \tag{12.E.37}$$

$$E_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \tag{12.E.38}$$

$$E_4 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{12.E.39}$$

$$E_5 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix} \tag{12.E.40}$$

$$E_6 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix} \tag{12.E.41}$$

(h is the number of elements of Γ_i and d_i is the length of the diagonal of the matrix element of Γ_i)

S12.33

If we assume that $i = j = E_i$ and that $m = m', n = n'$, the general equation looks like

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{nm}]^2 \tag{12.E.42}$$

we must to pick the same element of each matrix, square it, and add them all together. All of them should equal $/frachl = 3$.

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{11}]^2 = 1 + 1/4 + 1/4 + 1 + 1/4 + 1/4 = 3 \tag{12.E.43}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{12}]^2 = 0 + 3/4 + 3/4 + 0 + 3/4 + 3/4 = 3 \tag{12.E.44}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{21}]^2 = 0 + 3/4 + 3/4 + 0 + 3/4 + 3/4 = 3 \tag{12.E.45}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{22}]^2 = 1 + 1/4 + 1/4 + 1 + 1/4 + 1/4 = 3 \tag{12.E.46}$$

for unequal cases,($m \neq m'$ and $n \neq n'$) we can use the products of the elements and they should sum to zero.

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{11}\Gamma_E(\hat{R})_{12} = 0 + \sqrt{3}/4 - \sqrt{3}/4 + 0 - \sqrt{3}/4 + \sqrt{3}/4 = 0 \tag{12.E.47}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{11}\Gamma_E(\hat{R})_{21} = 0 - \sqrt{3}/4 + \sqrt{3}/4 + 0 - \sqrt{3}/4 + \sqrt{3}/4 = 0 \tag{12.E.48}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{12}\Gamma_E(\hat{R})_{21} = 0 - 3/4 - 3/4 + 0 + 3/4 + 3/4 = 0 \tag{12.E.49}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{12}\Gamma_E(\hat{R})_{22} = 1 + 1/4 + 1/4 - 1 - 1/4 - 1/4 = 0 \tag{12.E.50}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{21}\Gamma_E(\hat{R})_{22} = 0 - \sqrt{3}/4 + \sqrt{3}/4 + 0 + \sqrt{3}/4 - \sqrt{3}/4 = 0 \tag{12.E.51}$$

Q12.34

Using the Great Orthogonality Theorem, let *i* = *j*, *m* = *n*, and *m*' = *n*' and sum over *n* and n' to show that

$$\sum_{\hat{R}} [\chi_j(\hat{R}]^2 = h \tag{12.E.52}$$

.

S12.34

Recall that $\chi_j(\hat{R})$ is defined as the character of the *j*th irreducible representation of $\hat{R}$, which in terms of matrix elements, is given by

$$\chi_i(\hat{R}) = \sum_m \Gamma_i(\hat{R})_{mm} \tag{12.E.53}$$

We now use the **great orthogonality theorem** to find the summed equation:

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{mn}\Gamma_j(\hat{R})_{m'n'} = \frac{h}{l_i}\delta_{ij}\delta_{mm'}\delta_{nn'} \tag{12.E.54}$$

Let *i* = *j*, *m* = *n*, and *m*' = *n*'. Then

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{nn} \Gamma_i(\hat{R})_{n'n'} = \frac{h}{l_i} \delta_{nn'} \tag{12.E.55}$$

$$\sum_{\hat{R}} \sum_{n} \Gamma_i(\hat{R})_{nn} \sum_{n'} \Gamma_i(\hat{R})_{n'n'} = \frac{h}{l_i} \delta_{nn'} \tag{12.E.56}$$

$$\sum_{\hat{R}} [\chi_i(\hat{R})]^2 = \frac{h}{l_i} = h \tag{12.E.57}$$

Q12.35

Determine the character table for C_i which has the symmetry elements E and *i*.

S12.35

Because there are two symmetry elements, there are two rows to the character table also to have a 2x2. The first row is completely symmetric to both operations while the second is antisymmetric with respect to the inversion center. Therefore, the character table is as shown below.

Q12-36

The C_i point group character table is given by

Ci	E	i
Ag	+1	+1
Au	+1	-1

Show that the basis for this point group are the even and odd functions over an interval (-a,a). Evaluate the integrals of this basis set using group theory in order to establish symmetry principles.

S12-36

Applying the inversion operator to a function,

$$i f_{even} = f_{even} \tag{12.E.58}$$

$$i f_{odd} = -f_{odd} \tag{12.E.59}$$

This demonstrates that f(even) belongs to Ag and f(odd) belongs to Au. As a result these functions are a basis of the C_i point group.

$$S_{ij} = \int \phi_i{}^* \phi_j d\tau \tag{12.E.60}$$

$$RS_{ij} = \int R\phi_i{}^* R\phi_j d\tau = S_{ij} = \int \phi_i{}^* \phi_j d\tau \tag{12.E.61}$$

with the value of Sij unchanged by the symmetry operation of the point group.

$$S_{ij} = \int_{-a}^{a} f_{even}(x) f_{even}(x) dx \tag{12.E.62}$$

$$iS_{ij} = \int_{-a}^{a} if_{even}(x) if_{even}(x) dx = \int_{-a}^{a} f_{even}(x) f_{even}(x) dx = 1 \tag{12.E.63}$$

$$S_{ij} = \int_{-a}^{a} f_{odd}(x) f_{odd}(x) dx \tag{12.E.64}$$

$$iS_{ij} = \int_{-a}^{a} if_{odd}(x) if_{odd}(x) dx = \int_{-a}^{a} -f_{odd}(x) - f_{odd}(x) dx = 1 \tag{12.E.65}$$

$$S_{ij} = \int_{-a}^{a} f_{even}(x) f_{odd}(x) dx \tag{12.E.66}$$

$$iS_{ij} = \int_{-a}^{a} if_{even}(x) if_{odd}(x) dx = -\int_{-a}^{a} f_{even}(x) f_{odd}(x) dx = 0 \tag{12.E.67}$$

12.37

Derive the symmetry orbitals for the pi- orbitals of butadiene by applying the generating operator

$$P_j = \frac{d_j}{h} \sum_R \chi_j(R) R \tag{12.E.68}$$

to the atomic 2pz orbital on each carbon atom. Identify the irreducible representation to which each resulting symmetry orbital belong. Derive the Huckel secular determinant.

S12.37

Butadiene belongs to the C2h point-group. Denote the 2pz orbital on

$$C_i \tag{12.E.69}$$

by

$$\psi_i \tag{12.E.70}$$

$$P\psi_1 = \frac{1}{4} \sum_R \chi(R) R \tag{12.E.71}$$

$$= \frac{1}{4}[(1)E\psi_1 + (1)C_2\psi_1 + (1)i\psi_1 + (1)\sigma\psi_1] \tag{12.E.72}$$

$$= \frac{1}{4}(\psi_1 + \psi_4 - \psi_4 + \psi_2) = 0 \tag{12.E.73}$$

Similarly,

$$P\psi_2 = \frac{1}{4}(\psi_2 + \psi_3 - \psi_3 - \psi_2) = 0 \tag{12.E.74}$$

$$P\psi_2 = \frac{1}{4}(\psi_2 + \psi_3 - \psi_3 - \psi_2) = 0 \tag{12.E.75}$$

Using Psi 1 and 2 (things get very confusing after this line, especially the part of the equation "=0 $\alpha\psi_1 - \psi_4$? -RM)

$$P\psi_1 = \frac{1}{4}(\psi_1 - \psi_4 - \psi_4 + \psi_1) = 0\alpha\psi_1 - \psi_4 \tag{12.E.76}$$

$$P\psi_2 = \frac{1}{4}(\psi_2 - \psi_3 - \psi_3 + \psi_2) = 0\alpha\psi_2 - \psi_3 \tag{12.E.77}$$

$$P\psi_3 = \frac{1}{4}(\psi_1 + \psi_4 + \psi_4 + \psi_1) = 0\alpha\psi_1 + \psi_4 \tag{12.E.78}$$

$$P\psi_4 = \frac{1}{4}(\psi_2 + \psi_3 + \psi_3 + \psi_2) = 0\alpha\psi_2 + \psi_3 \tag{12.E.79}$$

$$P\psi_1 = \widehat{P}\psi_2 = 0 \tag{12.E.80}$$

The process isnt very clear as to how you got to the solution...perhaps explain a little better how the math works.

Q12.41

An arbitrary tetrahedral molecule (AB_4) belonging to the T_d point group has the reducible representation: Γ = 4 1 0 0 2. Show that:

a. the symmetry elements of the point group give this representation, and
b. it can be reduced as $\Gamma = A_1 + T_2$.

Finally, prove that an **sp^3** orbital with **T_d** symmetry can be formed.

S12.41

a.) Applying the symmetry elements, we see that:

- $\hat{E}$ leaves all 4 bonds unmoved
- $\hat{C}_3$ leaves 1 bond unmoved
- $\hat{C}_2$ leaves 0 bonds unmoved
- $\hat{S}_4$ leaves 0 bonds unmoved
- $\hat{\sigma}_d$ leaves 2 bonds unmoved

The result is the reducible representation Γ = 4 1 0 0 2.

b.) Rewriting the symmetry elements in terms of the irreducible representations, we see that:

- $\alpha_{A_1} = \frac{1}{24}(4 + 8 + 0 + 0 + 12) = 1$
- $\alpha_{A_2} = \frac{1}{24}(4 + 8 + 0 + 0 - 12) = 0$
- $\alpha_E = \frac{1}{24}(8 - 8 + 0 + 0 + 0) = 0$
- $\alpha_{T_1} = \frac{1}{24}(12 + 0 + 0 + 0 - 12) = 0$
- $\alpha_{T_2} = \frac{1}{24}(12 + 0 + 0 + 0 + 12) = 1$

Using α as a coefficient and taking the sum of these 5 equations, we can rewrite the reducible representation as $\Gamma = A_1 + T_2$.

c.) The 2 p orbitals all have T_2 symmetry for a T_d molecule, so they can combine to form a hybrid T_2 orbital. All s orbitals are totally symmetric due to their spherical shape, making them A_1. Summing the 3 p orbitals and an s orbital will give a hybrid orbital of the desired $A_1 + T_2$ symmetry.

-Interesting question. I like the explanation on how an Sp3 orbital with T_2 symmetry can be formed

Q12.42

Consider an octahedral molecule XY6 whose point group is O_h. Prove the irreducible representation of O_h is Γ = A_{1g} + E_g + T_{1u}.

S12.43

$$(12.E.81)$$

$$a_{A_{1g}} = \frac{1}{48}(6+0+0+12+6+0+0+0+12+12) = 1$$
$$a_{A_{2g}} = \frac{1}{48}(6+0+0-12+6+0+0+0+12-12) = 0$$
$$a_{E_g} = \frac{1}{48}(12+0+0+0+12+0+0+0+24+0) = 1$$
$$a_{T_{1g}} = \frac{1}{48}(18+0+0+12-6+0+0+0-12-12) = 0$$
$$a_{T_{2g}} = \frac{1}{48}(18+0+0-12-6+0+0+0-12+12) = 0$$
$$a_{A_{1u}} = \frac{1}{48}(6+0+0+12+6+0+0+0-12-12) = 0$$
$$a_{A_{2u}} = \frac{1}{48}(6+0+0-12+6+0+0+0-12+12) = 0$$
$$a_{E_u} = \frac{1}{48}(12+0+0+0+12+0+0+0-24+0) = 0$$
$$a_{T_{1u}} = \frac{1}{48}(18+0+0+12-6+0+0+0+12+12) = 1$$
$$a_{T_{2u}} = \frac{1}{48}(18+0+0-12-6+0+0+0+12-12) = 0$$

= Γ = A_{1g} + E_g + T_{1u}.

Q12.43

Consider an octahedral molecule XY6 whose point group is O_h. Prove the irreducible representation of O_h is Γ = A_{1g} + E_g + T_{1u}.

S12.43

$$(12.E.82)$$

$$a_{A_{1g}} = \frac{1}{48}(6+0+0+12+6+0+0+0+12+12) = 1$$
$$a_{A_{2g}} = \frac{1}{48}(6+0+0-12+6+0+0+0+12-12) = 0$$
$$a_{E_g} = \frac{1}{48}(12+0+0+0+12+0+0+0+24+0) = 1$$
$$a_{T_{1g}} = \frac{1}{48}(18+0+0+12-6+0+0+0-12-12) = 0$$
$$a_{T_{2g}} = \frac{1}{48}(18+0+0-12-6+0+0+0-12+12) = 0$$
$$a_{A_{1u}} = \frac{1}{48}(6+0+0+12+6+0+0+0-12-12) = 0$$
$$a_{A_{2u}} = \frac{1}{48}(6+0+0-12+6+0+0+0-12+12) = 1$$
$$a_{E_u} = \frac{1}{48}(12+0+0+0+12+0+0+0-24+0) = 0$$
$$a_{T_{1u}} = \frac{1}{48}(18+0+0+12-6+0+0+0+12+12) = 1$$
$$a_{T_{2u}} = \frac{1}{48}(18+0+0-12-6+0+0+0+12-12) = 0$$

Therefore, the irreducible representation becomes $\Gamma = A_1 + A_2 + E$

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12.S: Group Theory - The Exploitation of Symmetry (Summary)

Learning Objectives

By the end of this chapter, you should know the following:

- The four defining properties of a mathematical group
- What the elements, classes, and order of a group are
- What a Cayley table is
- What a representation is
- What a character table is
- The great orthogonality theorem
- The vanishing integral rule
- The difference between a reducible representation and an irreducible representation
- What a symmetry element a
- The implications for the solutions to the Schrödinger equation when the Hamiltonian is invariant under symmetry operations
- What a point group is
- The effect of SALCs on the molecular Hamiltonian matrix

Skill goals (what you should be able to do/calculate):

- Determine whether a set constitutes a group
- Given a partial character table, how to complete it
- How to calculate a group multiplication table
- How to determine the dimensionality of a representation
- How to decompose an arbitrary representation into its irreducible components
- How to determine the point group of a molecule
- How to compute symmetry-adapted linear combinations (SALCs)

In this chapter, we will discuss how to make use of the symmetry of molecules to simplify quantum-mechanical calculations. In essence, symmetry can give a quick answer to the question: “Is this integral zero or nonzero?” Many times, quite a large number of integrals turn out to be zero, so screening those out not only provides for faster computer calculations, but it also helps our qualitative understanding of which quantum-mechanical interactions are important in a molecule and which are not. And as we will discuss further in the next chapter, symmetry allows us to determine which spectroscopic transitions are allowed and which are forbidden for a molecule.

The formal mathematics of symmetry arise from the properties of mathematical structures called groups, and so we must learn about group theory in order to make use of symmetry. Group theory is a type of abstract algebra, and many, many theorems can be proved about the relationships that come out of objects in groups. We do not have time to derive and prove all of the relationships we will make use of. They are all very simple and straightforward, though clever, and are actually very beautiful, mathematically speaking. Most groups we’ll be interested in for molecular applications contain just a handful of elements (usually less than 20), and the calculations involving these elements boil down to basic arithmetic on integers. However, there are two challenges people face when trying to learn and understand group theory:

In chemistry courses, we use what are called spatial point groups, which are groups of operations in three-dimensional space (rotations, reflections, inversions). Typically, people who do not have great spatial intuition struggle with “seeing” the symmetry operations, and this creates a problem with understanding the basic properties of groups. We will attempt to get around this by introducing the principles of group theory with permutation groups, which are much easier to visualize and manipulate.

Mathematically, the notation gets very complex, because mathematicians like to make their equations very general. There will be a ton of summations over various indices, and terms with multiple subscripts and superscripts. It is very important not to get overwhelmed by the notation. Almost every equation turns out to be extremely simple to use.

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12.T: Character Tables

Nonaxial Groups

These groups are characterized by a lack of a proper rotation axis.

A	1

C_s	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A"	1	-1	z, R_x, R_y	yz, xz

C_i	E	i		
Ag	1	1	R_x, R_y, R_z	x^2, y^2, z^2, xy, yz, zx
A_u	1	-1	x,y,z	

Cyclic C_n Groups

These groups are characterized by an *n*-fold proper rotation axis C_n.

C_2	E	C_2		
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	-1	x, y, R_x, Ry	yz,xz

C_3	E	C_3	C_3^2		ε=exp(2π/3)
A	1	1	1	z, R_z	x^2+y^2, z^2
E	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}\}$	(x,y),(R_x,R_y)	(x^2-y^2, xy), (xz, yz)

C_4	E	C_4	C_2	C_4^3		
A	1	1	1	1	z, R_z	x^2+y^2, z^2
B	1	-1	1	-1		x^2-y^2, xy
E	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}\}$	(x,y), (R_x,R_y)	(xz, yz)

C_5	E	C_5	C_5^2	C_5^3	C_5^4		ε=exp(i2π/5)
A	1	1	1	1	1	Z, R_z	x^2+y^2, z^2
E_1	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^2\\\epsilon^{*2}\end{matrix}$	$\begin{matrix}\epsilon^{*2}\\\epsilon^2\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}\}$	(x, y), (R_x,R_y)	(xz, yz)

E_2	$\begin{Bmatrix}1\\1\end{Bmatrix}$	ϵ^2 ϵ^{*2}	ϵ^* ϵ	ϵ ϵ^*	$\begin{Bmatrix}\epsilon^{*2}\\\epsilon^2\end{Bmatrix}$		$(x^2\text{-}y^2, xy)$

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5		ε=exp(i2π/6)
A	1	1	1	1	1	1	z, R_z	x^2+y^2, z^2
B	1	-1	1	-1	1	-1		
E_1	$\begin{Bmatrix}1\\1\end{Bmatrix}$	ϵ ϵ^*	$-\epsilon^*$ $-\epsilon$	-1 -1	$-\epsilon$ $-\epsilon^*$	$\begin{Bmatrix}\epsilon^*\\\epsilon\end{Bmatrix}$	(R_x,R_y), (x,y)	(xz, yz)
E_2	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$-\epsilon^*$ $-\epsilon$	$-\epsilon$ $-\epsilon^*$	1 1	$-\epsilon^*$ $-\epsilon$	$\begin{Bmatrix}-\epsilon\\-\epsilon^*\end{Bmatrix}$		$(x^2\text{-}y^2, xy)$

C_7	E	C_7	C_7^2	C_7^3	C_7^4	C_7^5	C_7^6		ε=exp(i2π/7)
A	1	1	1	1	1	1	1	z, R_z	x^2+y^2, z^2
E_1	$\begin{Bmatrix}1\\1\end{Bmatrix}$	ϵ ϵ^*	ϵ^2 ϵ^{*2}	ϵ^3 ϵ^{*3}	ϵ^{*3} ϵ^3	ϵ^{*2} ϵ^2	$\begin{Bmatrix}\epsilon^*\\\epsilon\end{Bmatrix}$	(R_x,R_y), (x,y)	(xz, yz)
E_2	$\begin{Bmatrix}1\\1\end{Bmatrix}$	ϵ^2 ϵ^{*2}	ϵ^{*3} ϵ^3	ϵ^* ϵ	ϵ ϵ^*	ϵ^3 ϵ^{*3}	$\begin{Bmatrix}\epsilon^{*2}\\\epsilon^2\end{Bmatrix}$		$(x^2\text{-}y^2, xy)$
E_3	$\begin{Bmatrix}1\\1\end{Bmatrix}$	ϵ^3 ϵ^{*3}	ϵ^* ϵ	ϵ^2 ϵ^{*2}	ϵ^{*2} ϵ^2	ϵ ϵ^*	$\begin{Bmatrix}\epsilon^{*3}\\\epsilon^3\end{Bmatrix}$		

C_8	E	C_8	C_4	C_8^3	C_2	C_8^5	C_4^3	C_8^7		ε=exp(i2π/8)
A	1	1	1	1	1	1	1	1	z, R_z	x^2+y^2, z^2
B	1	-1	1	-1	1	-1	1	-1		
E_1	$\begin{Bmatrix}1\\1\end{Bmatrix}$	ϵ ϵ^*	i $-i$	$-\epsilon^*$ $-\epsilon$	-1 -1	$-\epsilon$ $-\epsilon^*$	$-i$ i	$\begin{Bmatrix}\epsilon^*\\\epsilon\end{Bmatrix}$	(R_x,R_y), (x,y)	(xz, yz)
E_2	$\begin{Bmatrix}1\\1\end{Bmatrix}$	i $-i$	-1 -1	$-i$ i	1 1	i $-i$	-1 -1	$\begin{Bmatrix}-i\\i\end{Bmatrix}$		$(x^2\text{-}y^2, xy)$
E_3	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$-\epsilon$ $-\epsilon^*$	i $-i$	ϵ^* ϵ	-1 -1	ϵ ϵ^*	$-i$ i	$\begin{Bmatrix}-\epsilon^*\\-\epsilon\end{Bmatrix}$		

Pyramidal C_{nv} Groups

These groups are characterized by an *n*-fold proper rotation axis C_n and n mirror planes σ_v which contain C_n

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	

E	2	-1	0	$(R_x, R_y), (x,y)$	(xz, yz) (x^2-y^2, xy)

C_{4v}	**E**	**2C4**	**C2**	**2σv**	**2σd**		
A1	1	1	1	1	1	z	x^2+y^2, z^2
A2	1	1	1	-1	-1	R_z	
B1	1	-1	1	1	-1		x^2-y^2
B2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(R_x, R_y), (x,y)$	(xz, yz)

C_{5v}	**E**	**2C5**	**2C5²**	**5σv**		
A1	1	1	1	1	z	x^2+y^2, z^2
A2	1	1	1	-1	R_z	
E1	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	$(R_x, R_y), (x,y)$	(xz, yz)
E2	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0		(x^2-y^2, xy)

C_{6v}	**E**	**2C6**	**2C3**	**C2**	**3σv**	**3σd**		
A1	1	1	1	1	1	1	z	x^2+y^2, z^2
A2	1	1	1	1	-1	-1	R_z	
B1	1	-1	1	-1	1	-1		
B2	1	-1	1	-1	-1	1		
E1	2	1	-1	-2	0	0	$(R_x, R_y), (x,y)$	(xz, yz)
E2	2	-1	-1	2	0	0		(x^2-y^2, xy)

C∞v	**E**	**2C∞**	**…**	**∞σv**		
A1	1	1	…	1	z	x^2+y^2, z^2
A2	1	1	…	-1	R_z	
E1	2	$2\cos\phi$	…	0	$(x,y), (R_x, R_y)$	(xz, yz)
E2	2	$2\cos 2\phi$	…	0		(x^2-y^2, xy)
E3	2	$2\cos 3\phi$	…	0		
…	…	…	…	…		

Reflection C_{nh} Groups

These groups are characterized by an *n*-fold proper rotation axis C_n and a mirror plane σ_h *normal* to C_n.

C_{2h}	**E**	**C2**	**i**	**σh**		
Ag	1	1	1	1	R_z	x^2, y^2, z^2
Bg	1	-1	1	-1	R_x, R_y	xz, yz

A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x,y	

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5		ε=exp(i2π/3)
A'	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E'	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	(x,y)	(x^2-y^2, xy)
A"	1	1	1	-1	-1	-1	z	
E"	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	(R_x, R_y)	(xz, yz)

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B_g	1	-1	1	-1	1	-1	1	-1		x^2-y^2, xy
E_g	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	(R_x, R_y)	(xz, yz)
A_u	1	1	1	1	-1	-1	-1	-1	z	
B_u	1	-1	1	-1	-1	1	-1	1		
E_u	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	(x,y)	

C_{5h}	E	C_5	C_5^2	C_5^3	C_5^4	σ_h	S_5	S_5^7	S_5^3	S_5^9		ε=exp(i2π/5)
A'	1	1	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E_1'	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^2\\\epsilon^{*2}\end{matrix}$	$\begin{matrix}\epsilon^{*2}\\\epsilon^2\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^2\\\epsilon^{*2}\end{matrix}$	$\begin{matrix}\epsilon^{*2}\\\epsilon^2\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	(x, y)	
E_2'	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon^2\\\epsilon^{*2}\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^{*2}\\\epsilon^2\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\epsilon^2\\\epsilon^{*2}\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^{*2}\\\epsilon^2\end{matrix}$		(x^2-y^2, xy)
A"	1	1	1	1	1	-1	-1	-1	-1	-1	z	
$E_1"$	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^2\\\epsilon^{*2}\end{matrix}$	$\begin{matrix}\epsilon^{*2}\\\epsilon^2\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}-\epsilon^2\\-\epsilon^{*2}\end{matrix}$	$\begin{matrix}-\epsilon^{*2}\\-\epsilon^2\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	(R_x, R_y)	(xz, yz)
$E_2"$	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon^2\\\epsilon^{*2}\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^{*2}\\\epsilon^2\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon^2\\-\epsilon^{*2}\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}-\epsilon^{*2}\\-\epsilon^2\end{matrix}$		

C_{6h}	E	C_6	C_3	C_2	C_3^2	C_6^5	i	S_3^5	S_6^5	σ_h	S_6	S_3		ε=exp(i2π/6)
A_g	1	1	1	1	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B_g	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
E_{1g}	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	(R_x, R_y)	(xz, yz)
E_{2g}	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$		(x^2-y^2, xy)
A_u	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	z	
B_u	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		

E_{1u}	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}\right\}$	(x, y)	
E_{2u}	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}\right\}$		

Dihedral D_n Groups

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		x^2, y^2, z^2
B_1	1	1	-1	-1	z, R_z	xy
B_2	1	-1	1	-1	y, R_y	zx
B_3	1	-1	-1	1	x, R_x	yz

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z, R_z	
E	2	-1	0	(R_x, R_y), (x,y)	(x^2-y^2, xy) (xz, yz)

D_4	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	z, R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(R_x, R_y), (x,y)	(xz, yz)

D_5	E	$2C_5$	$2C_5^2$	$5C_2$		
A_1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	z, R_z	
E_1	2	$2\cos 72^\circ$	$2\cos 144^\circ$		(R_x, R_y), (x,y)	(xz, yz)
E_2	2	$2\cos 144^\circ$	$2\cos 72^\circ$			(x^2-y^2, xy)

D_6	E	$2C_6$	$2C_3$	C_2	$2C_2'$	$3C_2''$		
A_1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	-1	-1	z, R_z	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	(R_x, R_y), (x,y)	(xz, yz)
E_2	2	-1	-1	2	0	0		(x^2-y^2, xy)

Prismatic D_{nh} Groups

These groups are characterized by

i. an *n*-fold proper rotation axis C_n
ii. *n* 2-fold proper rotation axes C_2 normal to C_n
iii. a mirror plane σ_h normal to C_n and containing the C_2 axes.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ(xy)	σ(xz)	σ(yz)		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E"	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x,y)	

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$		

A_1'	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	1	-1	1	1	1	-1	R_z	
E_1'	2	$2\cos 72°$	$2\cos 144°$	0	2	$2\cos 72°$	$2\cos 144°$		(x,y)	
E_2'	2	$2\cos 144°$	$2\cos 72°$	0	2	$2\cos 144°$	$2\cos 72°$			(x^2-y^2, xy)
A_1''	1	1	1	1	-1	-1	-1	-1		
A_2''	1	1	1	-1	-1	-1	-1	1	z	
E_1''	2	$2\cos 72°$	$2\cos 144°$	0	-2	$-2\cos 72°$	$-2\cos 144°$	0	(R_x, R_y)	(xz, yz)
E_2''	2	$2\cos 144°$	$2\cos 72°$	0	-2	$-2\cos 144°$	$-2\cos 72°$	0		

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x,y)	
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

D_{8h}	E	$2C_8$	$2C^3{}_8$	$2C_4$	C_2	$4C_2'$	$4C_2''$	i	$2S_8$	$2S^3{}_8$	$2S_4$	σ_h	$4\sigma_d$	$4\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	1	-1	-1	1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	-1	1	1	1	-1	1	-1	-1	1	1	1	-1		
B_{2g}	1	-1	-1	1	1	-1	1	1	-1	-1	1	1	-1	1		
E_{1g}	2	$-\sqrt{2}$	$\sqrt{2}$	0	-2	0	0	2	$-\sqrt{2}$	$\sqrt{2}$	0	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	0	0	-2	2	0	0	2	0	0	-2	2	0	0		(x^2-y^2, xy)
E_{3g}	2	$\sqrt{2}$	$-\sqrt{2}$	0	-2	0	0	2	$\sqrt{2}$	$-\sqrt{2}$	0	-2	0	0		
A_{1u}	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	-1	1	1	1	-1	-1	1	1	-1	-1	-1	-1	1	
B_{2u}	1	-1	-1	1	1	-1	1	-1	1	1	-1	-1	1	-1		
E_{1u}	2	$-\sqrt{2}$	$\sqrt{2}$	0	-2	0	0	-2	$\sqrt{2}$	$-\sqrt{2}$	0	2	0	0	(x,y)	

E_{2u}	2	0	0	-2	2	0	0	-2	0	0	2	-2	0	0		
E_{1u}	2	$\sqrt{2}$	$-\sqrt{2}$	0	-2	0	0	-2	$-\sqrt{2}$	$\sqrt{2}$	0	2	0	0		

$D_{\infty h}$	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	∞ C_2		
S_g^+	1	1	...	1	1	1	...	1		x^2+y^2, z^2
S_g^-	1	1	...	-1	1	1	...	-1	R_z	
π_g	2	$2\cos\phi$	...	0	2	$-2\cos\phi$	...	0	(R_x, R_y)	(xz, yz)
D_g	2	$2\cos 2\phi$	...	0	2	$2\cos 2\phi$	...	0		(x^2-y^2, xy)
...	...	...	...	.....	...	...	...	...		
S_u^+	1	1	...	1	-1	-1	...	-1	z	
S_u^-	1	1	...	-1	-1	-1	...	1		
π_u	2	$2\cos\phi$	...	0	-2	$2\cos\phi$	...	0	(x, y)	
D_u	2	$2\cos 2\phi$	...	0	-2	$-2\cos 2\phi$	...	0		
...	...	...	...	...	...	...	...	...		

Antiprismatic D_{nd} Groups

These groups are characterized by

i. an *n*-fold proper rotation axis C_n
ii. *n* 2-fold proper rotation axes C_2 normal to C_n
iii. *n* mirror planes σ_d which contain C_n.

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1	z	xy
E	2	0	-2	0	0	(x, y), (R_x, R_y)	(xz, yz)

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	-1	1	1	-1	R_z	
E_g	2	-1	0	2	-1	0	(R_x, R_y)	$(x^2-y^2, xy),(xz, yz)$
A_{1u}	1	1	1	-1	-1	-1		
A_{2u}	1	1	-1	-1	-1	1	z	
E_u	2	-1	0	-2	1	0	(x, y)	

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		

A_1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1	-1	1	z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(x, y)	
E_2	2	0	-2	0	2	0	0		(x^2-y^2, xy)
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0	(R_x, R_y)	(xz, yz)

D_{5d}	E	$2C_5$	$2C_5^2$	$5C_2$	i	$2S_{10}^3$	$2S_{10}$	$5\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	1	1	1	-1	R_z	
E_{1g}	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	1	-1	1	z	
E_{1u}	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	-2	$-2\cos 72^\circ$	$-2\cos 144^\circ$	0	(x, y)	
E_{2u}	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0	-2	$-2\cos 144^\circ$	$-2\cos 72^\circ$	0		

D_{6d}	E	$2S_{12}$	$2C_6$	$2S_4$	$2C_3$	$2S_{12}^5$	C_2	$6C_2'$	$6\sigma_d$		
A_1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1	-1	1	-1	1	z	
E_1	2	$\sqrt{3}$	1	0	-1	$-\sqrt{3}$	-2	0	0	(x, y)	
E_2	2	1	-1	-2	-1	1	2	0	0		(x^2-y^2, xy)
E_3	2	0	-2	0	2	0	-2	0	0		
E_4	2	-1	-1	2	-1	-1	2	0	0		
E_5	2	$-\sqrt{3}$	1	0	-1	$\sqrt{3}$	-2	0	0	(R_x, R_y)	(xz, yz)

Improper Rotation S_n Groups

These groups are characterized by an *n*-fold improper rotation axis S_n, where n is necessarily even

S_4	E	S_4	C_2	S_4^3		
A	1	1	1	1	R_z	x^2+y^2, z^2
B	1	-1	1	-1	z	x^2-y^2, xy

E	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{Bmatrix}-i\\i\end{Bmatrix}$	(x, y); (R_x, R_y)	(xz, yz)

S_6	E	C_3	C_3^2	i	S_6^5	S_6		
A_g	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E_g	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{Bmatrix}\epsilon^*\\\epsilon\end{Bmatrix}$	(R_x, R_y)	(x^2-y^2, xy), (xz, yz)
A_u	1	1	1	-1	-1	-1	z	
E_u	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{Bmatrix}-\epsilon^*\\-\epsilon\end{Bmatrix}$	(x, y)	

S_8	E	S_8	C_4	S_8^3	C_2	S_8^5	C_4^3	S_8^7		ε=exp(i2π/8)
A	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B	1	-1	1	-1	1	-1	1	-1	z	
E_1	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{Bmatrix}\epsilon^*\\\epsilon\end{Bmatrix}$	(R_x, R_y), (x, y)	
E_2	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{Bmatrix}-i\\i\end{Bmatrix}$		(x^2-y^2, xy)
E_3	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{Bmatrix}-\epsilon\\-\epsilon^*\end{Bmatrix}$		(xz, yz)

Cubic Groups

These polyhedral groups are characterized by not having a C_5 proper rotation axis.

T	E	$4C_3$	$4C_3^2$	$3C_2$		
A	1	1	1	1		$x^2+y^2+z^2$
E	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{Bmatrix}1\\1\end{Bmatrix}$		($2z^2$-x^2-y^2, x^2-y^2)
T	3	0	0		(R_x, R_y, R_z), (x, y, z)	(xz, yz, xy)

T_h	E	$4C_3$	$4C_3^2$	$3C_2$	i	$4S_6$	$4S_6^5$	$3\sigma_h$		ε=exp(i2π/3)
A_g	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
E_g	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{Bmatrix}1\\1\end{Bmatrix}$		($2z^2$-x^2-y^2, x^2-y^2)
T_g	3	0	0	-1	1	0	0	-1	(R_x, R_y, R_z)	(xz, yz, xy)
A_u	1	1	1	1	-1	-1	-1	-1		
E_u	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\begin{matrix}\epsilon^*\\\epsilon\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\epsilon\\-\epsilon^*\end{matrix}$	$\begin{matrix}-\epsilon^*\\-\epsilon\end{matrix}$	$\begin{Bmatrix}-1\\-1\end{Bmatrix}$		
T_u	3	0	0	-1	-1	0	0	1	(x, y, z)	

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		

A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xz, yz, xy)

O	**E**	**$8C_3$**	**$3C_2$**	**$6C_4$**	**$6C_2$**		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z), (x, y, z)	
T_2	3	0	-1	-1	1		(xz, yz, xy)

O_h	**E**	**$8C_2$**	**$6C_2$**	**$6C_4$**	**$3C_2(C_4^2)$**	**i**	**$6S_4$**	**$8S_6$**	**$3\sigma_h$**	**$6\sigma_d$**		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

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12.T: Correlation Tables

A_1	A	A'	A'
A_2	A	A''	A''
B_1	B	A'	A''
B_2	B	A''	A'

A_1	A	A'
A_2	A	A''
E	E	$A' + A''$

A_1	A	A_1	A_1	A	A'	A'
A_2	A	A_2	A_2	A	A''	A''
B_1	B	A_1	A_2	A	A'	A''
B_2	B	A_2	A_1'	A	A''	A'
E	E	$B_1 + B_2$	$B_1 + B_2$	$2B$	$A' + A''$	$A' + A''$

A_1	A	A'
A_2	A	A''
E_1	$\{E_1\}$	$A' + A''$
E_2	$\{E_2\}$	$A' + A''$

A_1	A	A_1	A_1	A_1	A	A	A'	A'
A_2	A	A_2	A_2	A_2	A	A	A''	A''
B_1	B	A_1	A_2	B_1	A	B	A'	A''
B_2	B	A_2	A_1'	B_2	A'	B	A''	A'
E_1	$\{E_1\}$	E	E	$B_1 + B_2$	$\{E\}$	$2B$	$A' + A''$	$A' + A''$
E_2	$\{E_2\}$	E	E	$A_1 + A_2$	$\{E\}$	$2A$	$A' + A''$	$A' + A''$

Σ^+	A_1
Σ^-	A_2
Π	$B_1 + B_2$

Δ	$A_1 + A_2$

Σ_g^+	A_g
Σ_g^-	B_{1g}
Π_g	$B_{2g} + B_{3g}$
Δ_g	$A_g + B_{1g}$
Σ_u^+	B_{1u}
Σ_u^-	A_u
Π_u	$B_{2u} + B_{3u}$
Δ_u	$A_u + B_{1u}$

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13: MOLECULAR SPECTROSCOPY

Spectroscopy generally is defined as the area of science concerned with the absorption, emission, and scattering of electromagnetic radiation by atoms and molecules, which may be in the gas, liquid, or solid phase. Visible electromagnetic radiation is called light, although the terms light, radiation, and electromagnetic radiation can be used interchangeably. Spectroscopy played a key role in the development of quantum mechanics and is essential to understanding molecular properties and the results of spectroscopic experiments. It is used as a “stepping stone” to take us to the concepts of quantum mechanics and the quantum mechanical description of molecular properties in order to make the discussion more concrete and less abstract and mathematical.

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13.2: Rotations Accompany Vibrational Transitions

13.3: Unequal Spacings in Vibration-Rotation Spectra

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13.5: Vibrational Overtones

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13.1: The Electromagnetic Spectrum

An important aspect of studying Physical Chemistry is to be able to recognize the interaction of molecules to the surroundings. Molecular Spectroscopy provides a clear image of how diatomic and polyatomic molecules interact by looking at the Frequency, Wavelength, Wave number, Energy, and molecular process. We will also be able to see the absorption properties of molecules in various regions from the electromagnetic spectrum.

Electromagnetic Radiation

Electromagnetic radiation—light—is a form of energy whose behavior is described by the properties of both waves and particles. Some properties of electromagnetic radiation, such as its refraction when it passes from one medium to another are explained best by describing light as a wave. Other properties, such as absorption and emission, are better described by treating light as a particle. The exact nature of electromagnetic radiation remains unclear, as it has since the development of quantum mechanics in the first quarter of the 20th century. Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. In a vacuum electromagnetic radiation travels at the speed of light, c, which is $2.99792 \times 10^8\ m/s$. When electromagnetic radiation moves through a medium other than a vacuum its velocity, v, is less than the speed of light in a vacuum. The difference between v and c is sufficiently small (<0.1%) that the speed of light to three significant figures, $3.00 \times 10^8\ m/s$, is accurate enough for most purposes.

The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation. Figure 13.1.1 shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

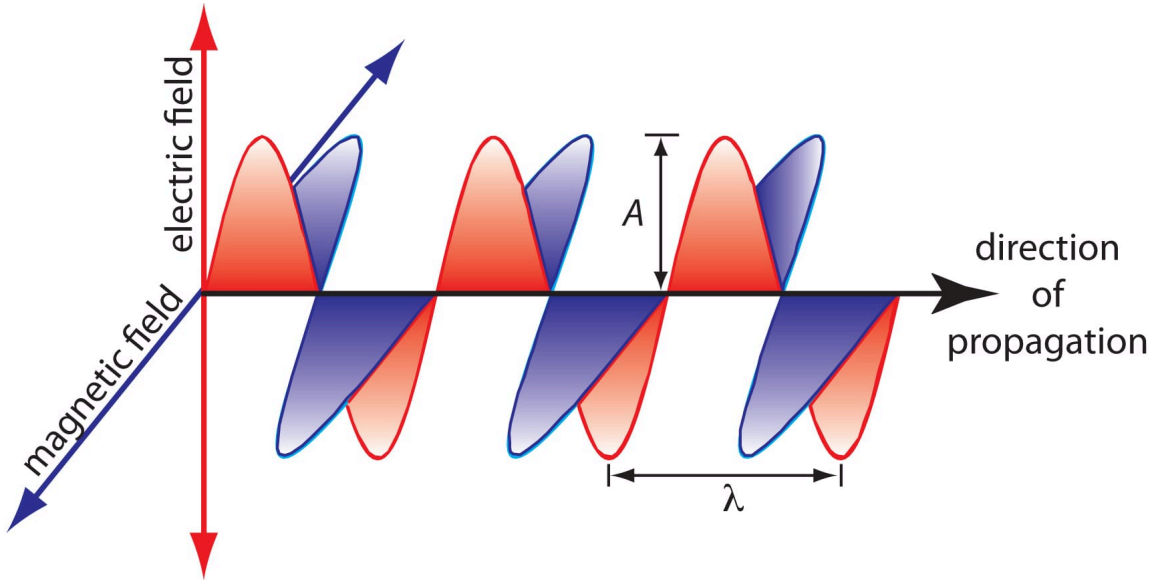


Figure 13.1.1 : Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi)$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_\mathrm{t} = A_\mathrm{m} \sin(2\pi\nu t + \phi)$$

where A_m is the magnetic field's maximum amplitude.

The frequency and wavelength of electromagnetic radiation vary over many orders of magnitude. For convenience, we divide electromagnetic radiation into different regions—the **electromagnetic spectrum**—based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons (Figure 13.1.2). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

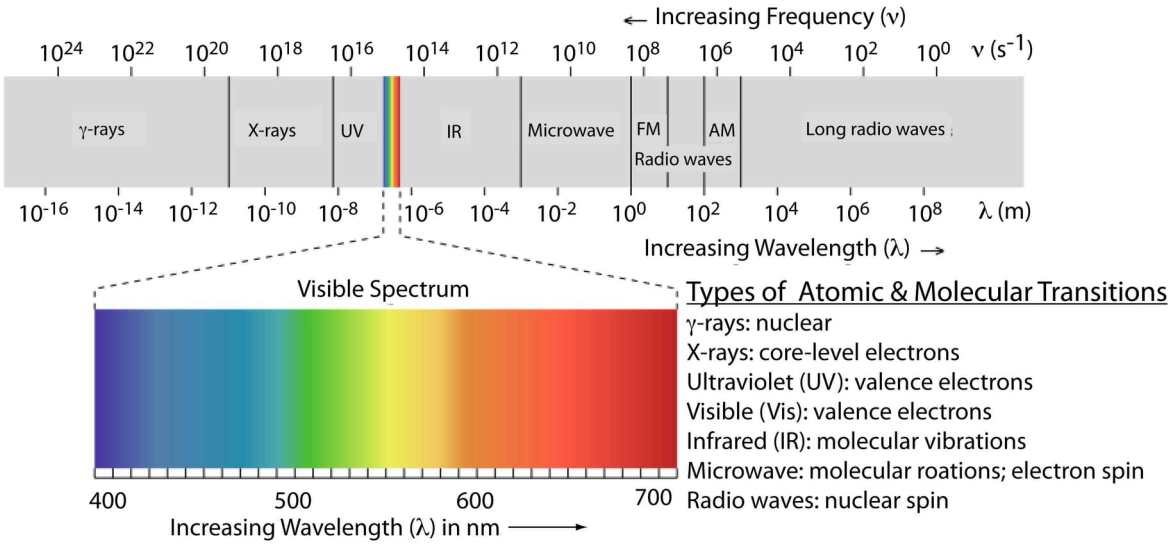


Figure 13.1.2 : The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

Other Units

Other properties also are useful for characterizing the wave behavior of electromagnetic radiation. The **wavelength**, λ, is defined as the distance between successive maxima (Figure 13.1.1). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

$$\lambda = \frac{c}{\nu}$$

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

$$\tilde{\nu} = \frac{1}{\lambda}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Example 13.1.1

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{589 \times 10^{-9}\ \text{m}} = 5.09 \times 10^{14}\ \text{s}^{-1}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9}\ \text{m}} \times \frac{1\ \text{m}}{100\ \text{cm}} = 1.70 \times 10^{4}\ \text{cm}^{-1}$$

Exercise 13.1.1

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Above, we defined several characteristic properties of electromagnetic radiation, including its energy, velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties. We can divide spectroscopy into two broad classes of techniques. In one class of techniques there is a transfer of energy between the photon and the sample. Table 13.1.1 provides a list of several representative examples.

Table 13.1.1 : Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Technique
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	UV/Vis spectroscopy atomic absorption spectroscopy
	IR	infrared spectroscopy raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	atomic emission spectroscopy
photoluminescence	X-ray	X-ray fluorescence

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Technique
	UV/Vis	fluorescence spectroscopy phosphorescence spectroscopy atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

Electromagnetic spectrum provides clearly information of molecules if they are rotational transitions, vibrational transitions, or electronic transitions. A molecule or a set of molecules can be read by the absorption of microwave radiation which provides transitions between rotational energy levels. In addition, if the molecules absorbs infrared radiation provides the transitions between vibrational levels follows by transitions between rotational energy levels. Finally, when molecules absorbs visible and ultraviolet radiation gives transitions between electronic energy levels follows by simultaneous transitions between vibrational and rotational levels.

When given the energy level of the molecules along with wavelength, we can easily figure the frequency of the molecules where they fall in the electromagnetic spectrum regions:

$$\Delta E = E_u - E_l = h\nu$$

The above equation describes the energy change between upper state and lower state of energy.

- Frequency falls between 10^9 - 10^{11} which is in the microwave range correlates to the rotation of polyatomic molecules.
- Frequency falls between 10^{11} - 10^{13} which is in the far infrared range correlates to the rotation of small molecules.
- Frequency falls between 10^{13} - 10^{14} which is in the infrared range correlates to the vibrations of flexible bonds.
- Frequency falls between 10^{14} - 10^{16} which is in the visible and ultraviolet range correlates to the electronic transitions.

The powerful technique of figuring out the the frequency of the molecules can help us determine the bond length, temperature, probability distribution as you will learn later on from the degree of freedoms and how the process is undergo in specific a reaction.

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13.2: Rotations Accompany Vibrational Transitions

Each of the modes of vibration of diatomic molecules in the gas phase also contains closely-spaced (1-10 cm^{-1} difference) energy states attributable to rotational transitions that accompany the vibrational transitions. A molecule's rotation can be affected by its vibrational transition because there is a change in bond length, so these rotational transitions are expected to occur. Since vibrational energy states are on the order of 1000 cm^{-1}, the rotational energy states can be superimposed upon the vibrational energy states.

Selection Rules

Rotational and Vibration transitions (also known as rigid rotor and harmonic oscillator) of molecules help us identify how molecules interact with each other, their bond length as mentioned in previous section. In order to know each transitions, we have to consider other terms like wavenumber, force constant, quantum number, etc. There are rotational energy levels associated with all vibrational levels. From this, vibrational transitions can couple with rotational transitions to give **rovibrational spectra**. Rovibrational spectra can be analyzed to determine average bond length.

We treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete levels and given by

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

Where v is the vibrational quantum number and can have integer values 0, 1, 2..., and ν is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{13.2.1}$$

We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_r = \frac{h^2}{8\pi^2 I}J(J+1)$$

In which I is the moment of inertia, given by

$$I = \mu r^2$$

where μ is the reduced mass (Equation 13.2.1) and r is the equilibrium bond length.

Experimentally, frequencies or wavenumbers are measured rather than energies, and dividing by h or hc gives more commonly seen term symbols, $F(J)$ using the rotational quantum number J and the rotational constant B in either frequency

$$F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I}J(J+1) = BJ(J+1)$$

or wavenumbers

$$\tilde{F}(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = \tilde{B}J(J+1)$$

It is important to note in which units one is working since the rotational constant is always represented as B, whether in frequency or wavenumbers.

- **Vibrational Transition Selection Rules**: At room temperature, typically only the lowest energy vibrational state v= 0 is populated, so typically v_0 = 0 and Δv = +1. The full selection rule is technically that Δv = ±1, however here we assume energy can only go upwards because of the lack of population in the upper vibrational states.
- **Rotational Transition Selection Rules**: At room temperature, states with J≠0 can be populated since they represent the fine structure of vibrational states and have smaller energy differences than successive vibrational levels. Additionally, ΔJ = ±1 since a photon contains one quantum **of angular momentum** and we abide by the principle of **conservation of energy**. This is also the selection rule for rotational transitions.

These two selection rules mean that the transition ΔJ = 0 (i.e. J" = 0 and J' = 0, but $\nu_0 \neq 0$ is forbidden and the pure vibrational transition is not observed in most cases. The rotational selection rule gives rise to an R-branch (when ΔJ = +1) and a P-branch (when ΔJ = -1). Each line of the branch is labeled R(J) or P(J), where J represents the value of the lower state Figure 13.2.1).

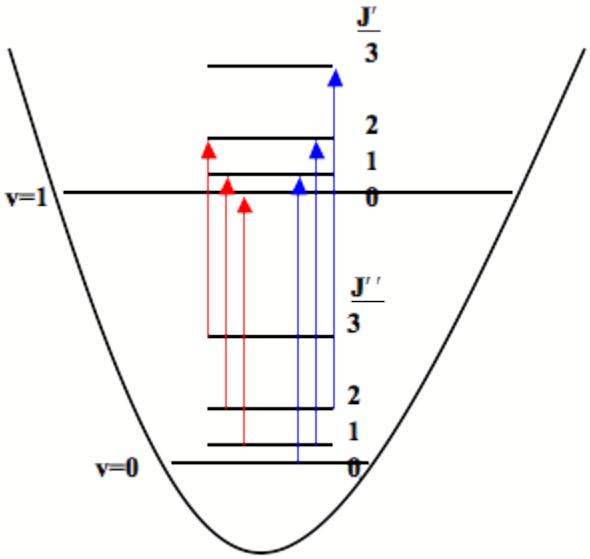


Figure 13.2.1 : Rotation-Vibration Transitions. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.

R-branch

When ΔJ = +1, i.e. the rotational quantum number in the ground state is one more than the rotational quantum number in the excited state – R branch (in French, *riche* or rich). To find the energy of a line of the R-branch:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{13.2.2}$$
$$= h\nu_0 + hB\left[(J+1)(J+2) - J(J+1)\right] \tag{13.2.3}$$
$$= h\nu_0 + 2hB(J+1) \tag{13.2.4}$$

P-branch

When ΔJ = -1, i.e. the rotational quantum number in the ground state is one less than the rotational quantum number in the excited state – P branch (in French, *pauvre* or poor). To find the energy of a line of the P-branch:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{13.2.5}$$
$$= h\nu_0 + hB\left[J(J-1) - J(J+1)\right] \tag{13.2.6}$$
$$= h\nu_0 - 2hBJ \tag{13.2.7}$$

Q-branch

When ΔJ = 0, i.e. the rotational quantum number in the ground state is the same as the rotational quantum number in the excited state – Q branch (simple, the letter between P and R). To find the energy of a line of the Q-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{13.2.8}$$

$$= h\nu_0 \tag{13.2.9}$$

The Q-branch can be observed in polyatomic molecules and diatomic molecules with electronic angular momentum in the ground electronic state, e.g. nitric oxide, NO. Most diatomics, such as O_2, have a small moment of inertia and thus very small angular momentum and yield no Q-branch.

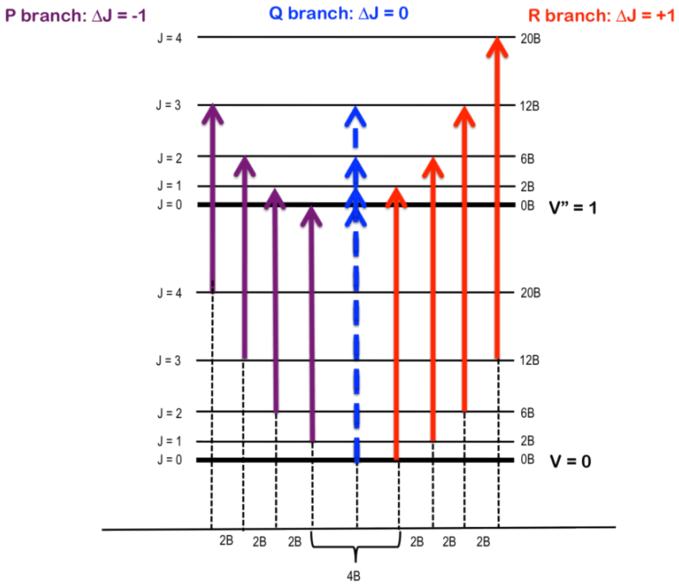


Figure 13.2.3 : Cartoon depiction of rotational energy levels, J, imposed on vibrational energy levels, v. The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.

As seen in Figure 13.2.2 , the lines of the P-branch (represented by purple arrows) and R-branch (represented by red arrows) are separated by specific multiples of B (i.e, $2B$), thus the bond length can be deduced without the need for pure rotational spectroscopy.

The total nuclear energy of the combined rotation-vibration terms, $S(v, J)$, can be written as the sum of the vibrational energy and the rotational energy

$$S(v, J) = G(v) + F(J)$$

where $G(v)$ represents the energy of the harmonic oscillator, ignoring anharmonic components and $S(J)$ represents the energy of a rigid rotor, ignoring centrifugal distortion.

From this, we can derive

$$S(v, J) = \nu_0 \left(v + \frac{1}{2}\right) + BJ(J+1)$$

The spectrum we expect, based on the conditions described above, consists of lines equidistant in energy from one another, separated by a value of $2B$. The *relative* intensity of the lines is a function of the rotational populations of the ground states, i.e. the intensity is proportional to the number of molecules that have made the transition. The *overall* intensity of the lines depends on the vibrational transition dipole moment.

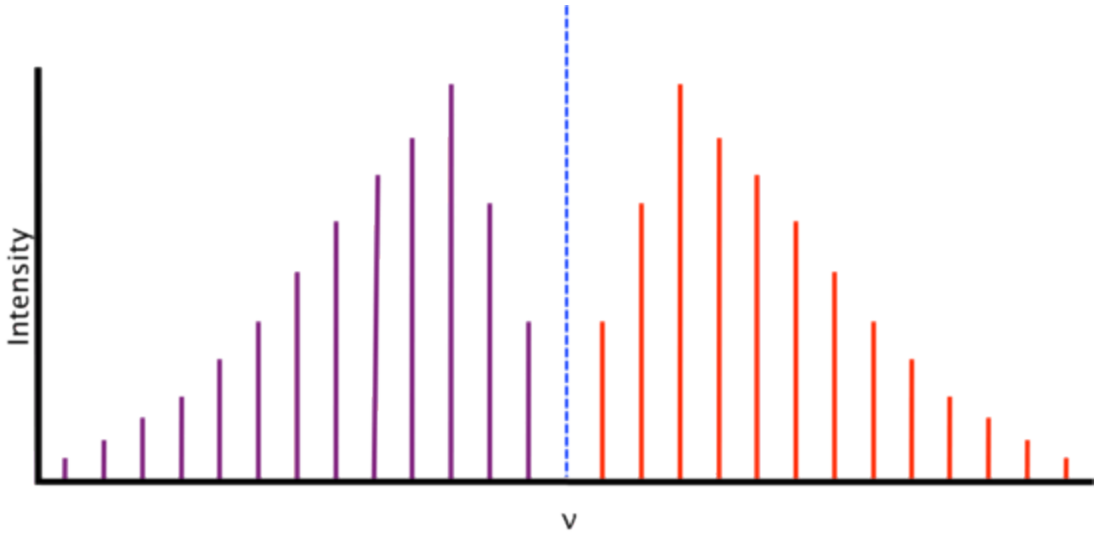


Figure 13.2.3 : A cartoon depiction of an ideal rovibrational spectrum.

In Figure 13.2.2 , between $P(1)$ and $R(0)$ lies the zero gap, where the the first lines of both the P- and R-branch are separated by $4B$, assuming that the rotational constant B is equal for both energy levels. The zero gap is also where we would expect the Q-branch, depicted as the dotted line, if it is allowed.

Advanced Concept: Occupations (Peak Intensities)

The relative intensity of the P- and R-branch lines depends on the thermal distribution of electrons; more specifically, they depend on the population of the lower J state. If we represent the population of the Jth upper level as N_J and the population of the lower state as N_0, we can find the population of the upper state relative to the lower state using the Boltzmann distribution:

$$\frac{N_J}{N_0} = (2J+1)e^{\left(-\frac{E_r}{kT}\right)}$$

(2J+1) gives the degeneracy of the Jth upper level arising from the allowed values of M_J (+J to –J). As J increases, the degeneracy factor increases and the exponential factor decreases until at high J, the exponential factor wins out and N_J/N_0 approaches zero at a certain level, J_{max}. Thus, when

$$\frac{d}{dJ}\left(\frac{N_J}{N_0}\right) = 0$$

by differentiation, we obtain

$$J_{max} = \left(\frac{kT}{2hB}\right)^{\frac{1}{2}} - \frac{1}{2}$$

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 13.2.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

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13.3: Unequal Spacings in Vibration-Rotation Spectra

We find that real rovibrational spectra do not exhibit the equal spacing expectations from the treatment in the previous section and look more like the idealized spectrum in Figure 13.3.1 . As energy increases, the R-branch lines become increasingly similar in energy (i.e., the lines move closer together) and as energy decreases, the P-branch lines become increasingly dissimilar in energy (i.e. the lines move farther apart). This is attributable to two phenomena: *rotational-vibrational coupling* and *centrifugal distortion*.

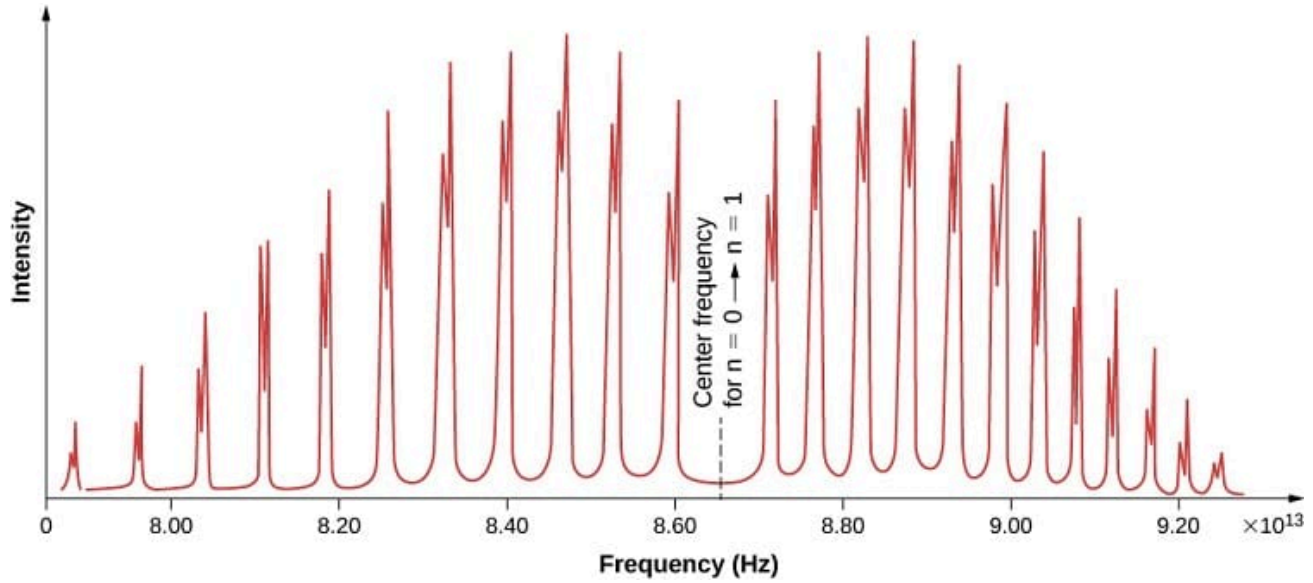


Figure 13.3.1 : Absorption spectrum of hydrogen chloride (HCl) from the $n = 0$ to $n = 1$ vibrational levels. The discrete peaks indicate a quantization of the angular momentum of the molecule. The bands to the left indicate a decrease in angular momentum, whereas those to the right indicate an increase in angular momentum. (CC-SA; OpenStax).

Experimental data shows that the P branch has closer spaces between the lines as the frequencies decrease while R branch has further spaces between the lines as the frequencies increase. On the spectrum, R region is on the left and P region is on the right separated by a large gap in between. There are other graphs show differently, but the regions can be labeled using their spacing characteristic discussed below.

Vibration-Rotation Interaction

Consider the rotational constant for a rigid rotator $\tilde{B} = h/8\pi^2 c\mu R_e^2$ where $\tilde{B}$ is the rotational constant, and R_e^2 is the bond length. It is clear from the equation that $\tilde{B}$ depends on R_e^2 in a inverse manner, so $\tilde{B}$ will decrease as R_e^2 increase, and vice versa.

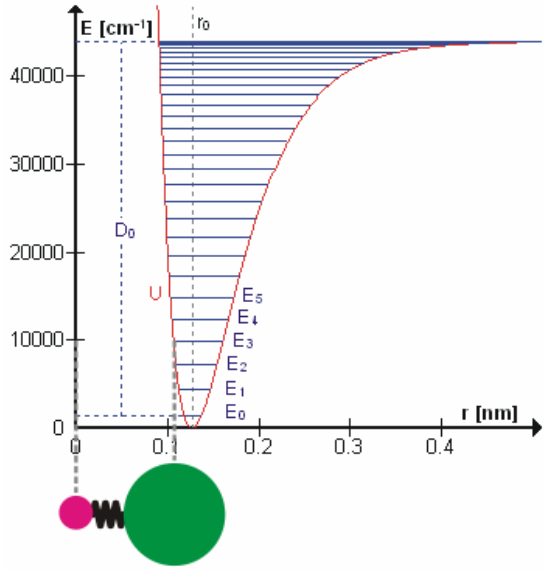


Figure 13.3.2 : Anharmonic Oscillator and Bond Length. Figure used with permission from Wikipedia.

Vibrational state and the bond length also possess a relationship, and that is bond length, R_e^2, will increase as the vibrational state, v increases. High vibrational states have large vibrational amplitudes (the amplitude can be visualized as the distance from one side to the other on the harmonic-oscillator parabola, and higher states has greater distance). On a potential graph, imagine a diatomic molecule with one of the atom fixed at the origin, the bond is along the x-axis, and the molecule vibrate toward and away from the origin along x-axis. The range at how much the bond can stretch or squeeze depend on the vibrational amplitude. So, at high vibrational state (thus high amplitude), the bond can squeeze in and stretch out more (just a little more) on the regular harmonic-oscillator potential, but it can stretch out greatly on an anharmonic oscillator. That's why bond length increase with vibrational state.

Note

The two relationship established above

- $\tilde{B} \propto R_e^2$ (inversely proportional)

and

- $R_e^2 \propto v$ (directly proportional)

Therefore,

- $\tilde{B} \propto v$ (inversely proportional)

The rotational constant dependent on the vibrational state is denoted as $\tilde{B}_v$, and the dependence of $\tilde{B}$ on v is the vibrational-rotational interaction.

Let's calculate the frequencies of R and P Branches with vibrational dependent rotational constants. The energies of the rigid rotator-harmonic oscillator is

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}J(J+1)$$

or in term of $\tilde{B}_v$

$$\tilde{E}_{v,J} = \tilde{\nu}\left(v + \frac{1}{2}\right) + \tilde{B}_v J(J+1)$$

According to the vibration-rotation interaction, $\tilde{B}_1 < \tilde{B}_0$ because $R_e^2(v=1) > R_e^2(v=0)$. Hence, the frequencies of rovibrational transitions from $v = 0 \rightarrow 1$ can be calculated as the following:

For R branch, allowed $J = 0, 1, 2, ...$

$$\tilde{\nu}_R(\Delta J = +1) = \tilde{E}_{1,J+1} - \tilde{E}_{0,J}$$

$$= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

For P branch, allowed $J = 1, 2, 3, ...$

$$\tilde{\nu}_P(\Delta J = -1) = \tilde{E}_{1,J-1} - \tilde{E}_{0,J}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

Decrease in Spacing of Lines in the R Branch with Increasing J

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$ +(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$ −(smaller and smaller value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

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13.4: Unequal Spacings in Pure Rotational Spectra

Vibrational energy which is a consequence of the oscillations/ vibrations of the nuclei along inter nuclear axis, is possible only when the distance between the nuclei is not fixed/ rigid; that means the separation between the two nuclei is flexible/ elastic (non-rigid rotator). Consequently, centrifugal force, when the molecule is rotating, tends to fly the reduced mass μ away from the axis of rotation. To keep the mass rotating about the axis, there must be some restoring force to counter balance the centrifugal force. The work done to supply this force is stored as potential energy. Therefore, unlike the case of rigid rotator, total energy of rotation in a molecule comprises of kinetic and the potential energy corresponding to centrifugal force of rotation.

Let r_e is the distance between the nuclei when the separation is taken to be rigid and r_c under the action of the centrifugal force. According to Hook's law, restoring force is proportional to change in internuclear distance $(r_c - r_e)$, or $= k(r_c - r_e)$ which in turn, will be equal to the centrifugal force.

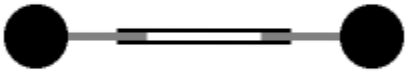


Figure 13.4.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{13.4.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{13.4.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{13.4.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 13.4.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{13.4.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{13.4.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 13.4.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1+\Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{13.4.6}$$

$$= \frac{L^2(1-2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{13.4.7}$$

using

$$(1+\Delta r/r_e)^{-2} \approx (1-2\Delta r/r_e) \tag{13.4.8}$$

$$E_r = \frac{L^2}{2\mu\, {r_e}^2} - \frac{L^4}{k\mu^2\, {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{13.4.9}$$

$$= \frac{L^2}{2\mu\, {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2\, {r_e}^6} \tag{13.4.10}$$

$$= \frac{\hbar^2\ J(J+1)}{2\mu\, {r_e}^2} - \frac{\hbar^4\ J^2(J+1)^2}{2k\mu^2\, {r_e}^6} \tag{13.4.11}$$

Use of Equation 13.4.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\ \sqrt{J(J+1)} \tag{13.4.12}$$

has been made to obtain relation in Equation 13.4.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{13.4.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{13.4.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{13.4.15}$$

First term in the Equation 13.4.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 13.4.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 13.4.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 13.4.2.

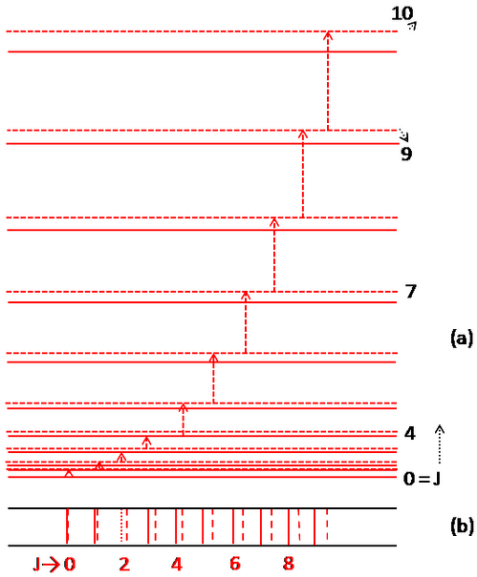


Figure 13.4.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational lines decreases with increase in J , as shown in the Figure 13.4.2. It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4 \quad cm^{-1}$ and $D \sim 0.0004 \ cm^{-1}$. Usually, D is ignored in the calculations. Figure 13.4.2 exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

Contributors and Attributions

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13.5: Vibrational Overtones

Although the harmonic oscillator proves useful for modeling lower energy levels, like $v = 0, 1$, it fails at higher numbers of v. It not only fails to properly model atomic bonds and dissociations, but also is unable to match spectra showing additional lines that are not accounted for in the harmonic oscillator model.

Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to a transition of $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure $13.5.1$). For example, the parabolic potential of the Harmonic Oscillator approximation means that the vibrations can hold any amount of energy and bonds can stretch to any length, while in real molecules if the atoms are too far apart the bond will dissociate.

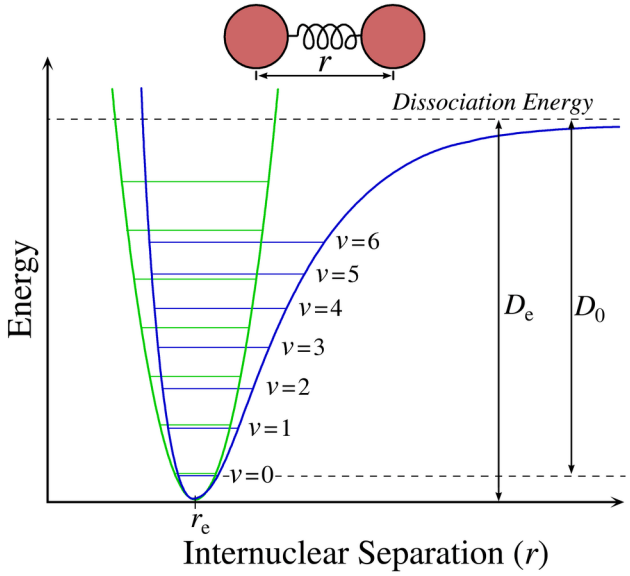


Figure $13.5.1$: Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure $13.5.1$, the harmonic oscillator potential well (in green) only roughly fits over the more accurate anharmonic oscillator well (in blue). The blue curve accounts for dissociation at large R values, which the green curve does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \tag{13.5.1}$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant, ignoring the absolute energy term($V(R_e)$) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 13.5.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{13.5.2}$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and
- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

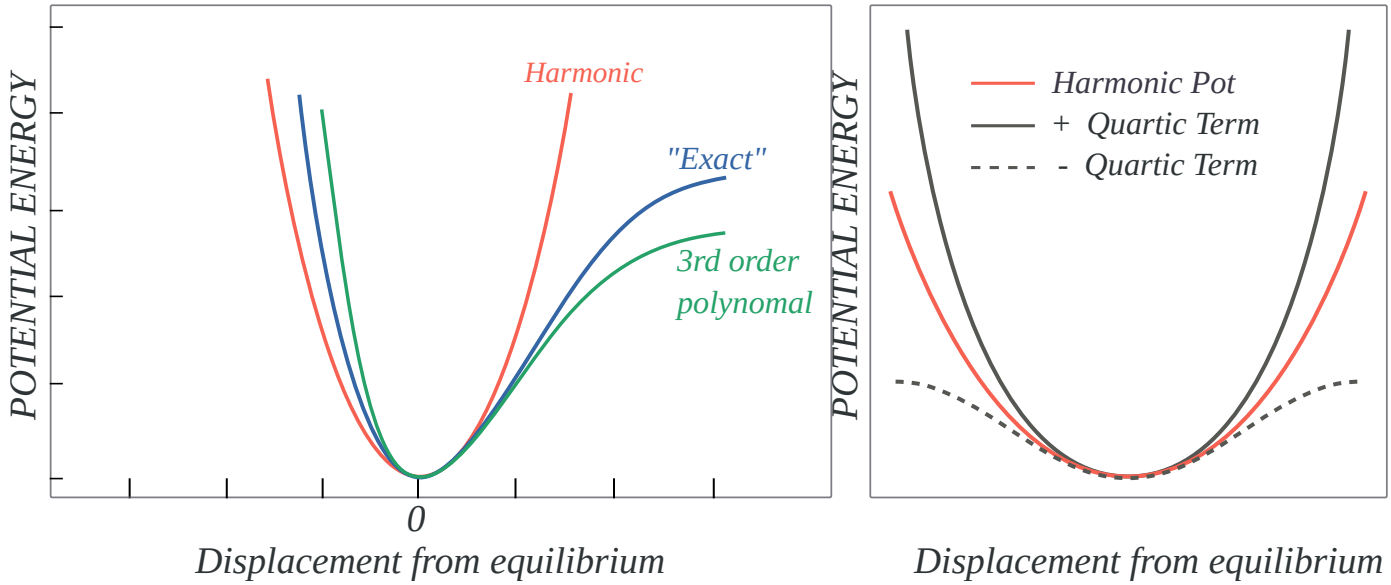


Figure 13.5.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation gives by the following energies:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right)$$

When the cubic term in the expansion (Equation 13.5.2) is included, and the Schrödinger equation is solved using perturbation theory this gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although E_v technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 13.5.1.

Overtones

The Harmonic Oscillator approximation predicts that there will be only one line in the spectrum of a diatomic molecule, while experimental data shows there is in fact one dominant line--**the fundamental**--and other weaker lines. How can we account for

these extra lines?

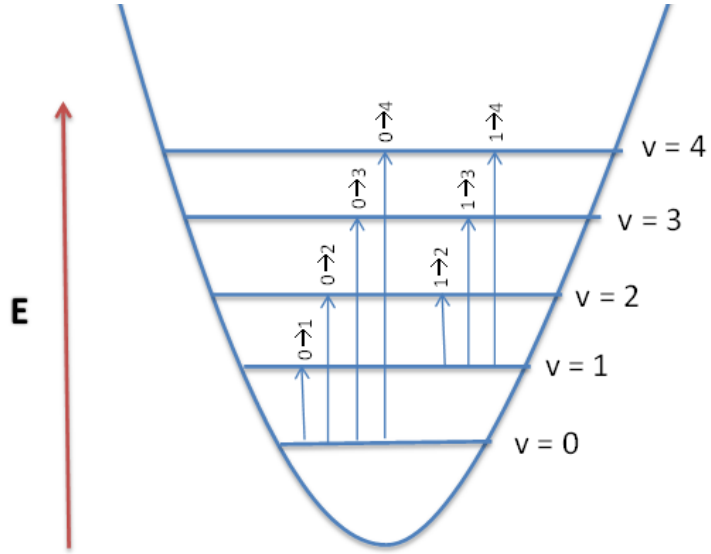


Figure 13.5.3 : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n > 1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 0 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

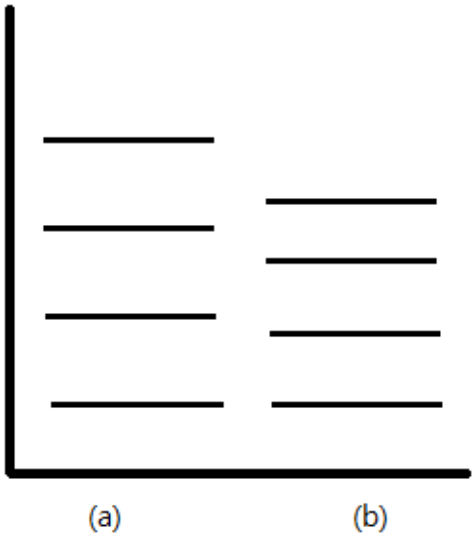


Figure 13.5.4 : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, as implied by Figure 13.5.4. Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \text{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapidly decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

Table $13.5.1$ *: HCl vibrational spectrum.*

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table $13.5.1$ that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi}_e$.

Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

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13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information

Molecules can also undergo changes in electronic transitions during microwave and infrared absorptions. The energy level differences are usually high enough that it falls into the visible to UV range; in fact, most emissions in this range can be attributed to electronic transitions.

Electron Transitions are not Purely Electronic

We have thus far studied *rovibrational transitions*--that is, transitions involving both the vibrational and rotational states. Similarly, electronic transitions tend to accompany both rotational and vibrational transitions. These are often portrayed as an electronic potential energy cure with the vibrational level drawn on each curve. Additionally, each vibrational level has a set of rotational levels associated with it.

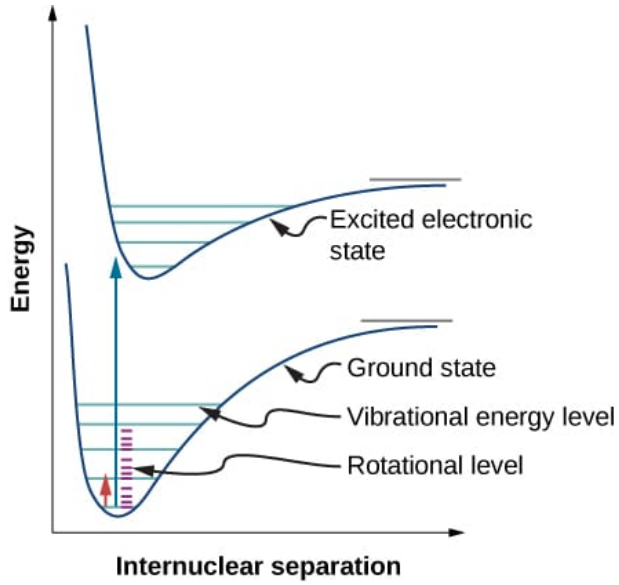


Figure 13.6.1: Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

Recall that in the Born-Oppenheimer approximation, nuclear kinetic energies can be ignored (e.g., fixed) to solve for electronic wavefunctions and energies, which are much faster than rotation or vibration. As such, it is important to note that unlike rovibrational transitions, electronic transitions aren't dependent on rotational or transitional terms and are assumed to be separate. Therefore, when using an anharmonic oscillator-nonrigid rotator approximation (and excluding translation energy), the total energy of a diatomic is:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{13.6.1}$$

where $\tilde{\nu}_{el}$ is the electronic transition energy change in wavenumbers, $G(n)$ is the vibrational energy with energy level v (assuming anharmonic oscillator), and $F(J)$ is the rotational energy, assuming a nonrigid rotor. Equation 13.6.1 can be expanded accordingly:

$$\tilde{E}_{total} = \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{13.6.2}$$

Notice that both the vibration constant ($\tilde{\nu}_e$) and anharmonic constant ($\tilde{\chi}_e$) are electronic state dependent (and hence the rotational constants would be too, but are ignored here). Since rotational energies tend to be so small compared to electronic, their effects are minimal and are typically ignored when we do calculations and are referred to as *vibronic* transitions.

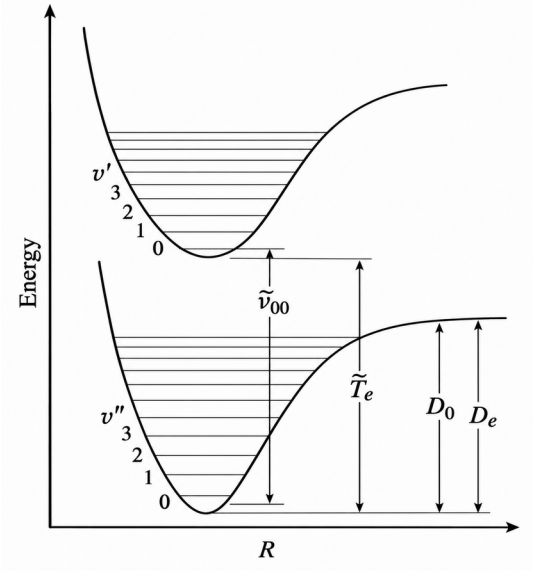


Figure 13.6.2: As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded. (CC BY 4.0; LibreTexts)

The eigenstate-to-eigenstate transitions (e.g., $1 \rightarrow 2$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{13.6.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 13.6.3 is

$$\tilde{\nu}_{obs} = E''\tilde{(}v'') - E'\tilde{(}v')$$

Also important to note that typically vibronic transitions are usually the result of the vibrational $v' = 0$ vibratonal state. Within this assumption and excluding the rotational contributions (due to their low energies), Equation 13.6.2 can be used with Equation 13.6.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{13.6.4}$$

A common transition of importance is the $\tilde{\nu}_{00}$, which is the $0 \rightarrow 0$ transition and include no vibrational change. For this case, equation 13.6.4 is then

$$\tilde{\nu}_{00} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right)$$

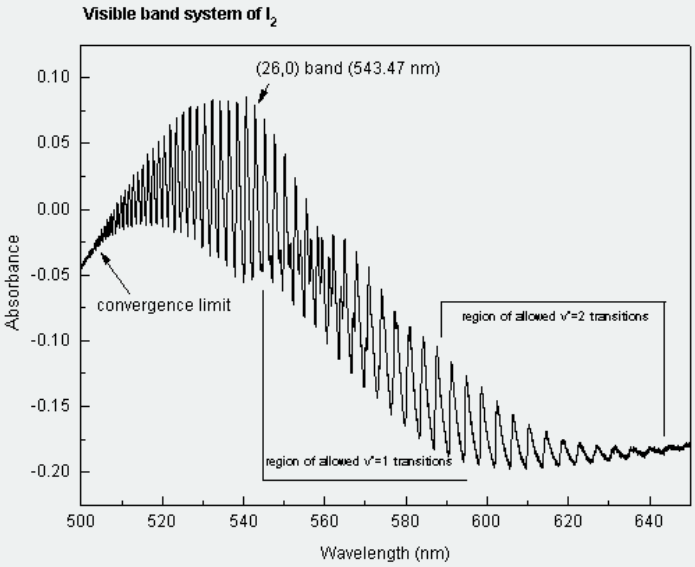
This is the lowest energy possible to observe in an electronic transition although it may be of low intensity as discussed in the following section.

Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 13.6.4 depends primarily on excited state parameters). In this experiment you will characterize the excited state well by extracting values for the following excited state parameters.

Recall that as v' increases, the vibrational energy spacing decreases. At the upper edge of the well, the vibrational energy spacing decreases to 0, which means that the energies form a continuum rather than being quantized. It is at this limit that **bond dissociation occurs**. The energy required to dissociate the bond is actually D'_o rather than D'_e because the molecule cannot have less than **the zero point energy**.

The vibrational-electronic spectrum of I_2 in the region from 500-650 nm displays a large number of well-defined bands which, for the most part, correspond to v'<-- 0 transitions connecting the v" = 0 vibrational level of the ground electronic state (denoted as $X^1\Sigma^+$) to many different vibrational levels v' of the excited $B^3\Pi$ electronic state. Under the conditions of this experiment (i.e., low resolution), the rotational lines within each band are not resolved. However, the peaks may be identified as R-branch band heads (1). For a molecule as heavy as I_2, the position of each band head is within a few tenths of one cm^{-1} of the band origin (2), and for the purposes of this experiment, the distinction between the two may be ignored. The general features of the absorption spectrum are shown below:



Each small bump, or peak, such as the (26,0) band labelled on the spectrum, corresponds to a transition between two vibrational levels and is called a *band*. Each band is comprised of several hundred *lines*, each of which involves different upper and lower rotational quantum numbers; as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the *band head*. The set of all of these bands is referred to as the *visible band system* of I_2.

If the sample is hot, then excited vibrational levels of the ground state may be populated, and these also will absorb light. The *hot bands* arising from absorption from v"=1 and v"=2 are shown very approximately on the absorption spectrum above.

At a point called the *convergence limit*, the spacing between bands decreases to zero. Beyond this convergence limit, the spectrum is continuous because the excited state of the I_2 molecule is not bound. One of the purposes of this experiment is to identify this convergence limit accurately.

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13.7: The Franck-Condon Principle

Learning Objectives

- To explain the vibrational fine structure in electronic spectroscopy for bound excited states in terms of the Franck-Condon approximation
- To calculate the vibrational progressions (Franck-Condon factors) in a single displaced harmonic oscillator vibronic system.

The **Franck-Condon Principle** describes the intensities of vibronic transitions, or the absorption or emission of a photon. It states that when a molecule is undergoing an electronic transition, such as ionization, the nuclear configuration of the molecule experiences no significant change. This is due in fact that nuclei are much more massive than electrons and the electronic transition takes place faster than the nuclei can respond. When the nucleus realigns itself with the new electronic configuration, the theory states that it must undergo a vibration.

If we picture the vertical transition from ground to excited electronic state as occurring from a vibrational wavefunction that gives a probability distribution of finding the nuclei in a give region of space we can determine the probability of a given vibrational level from the overlap integral $S_{v',v}$ which gives the overlap of the vibrational wavefunction in the ground and excited state. The v' quantum numbers refer to the ground state and the v quantum numbers refer to the excited state. The transition probability can be separated into electronic and nuclear parts using the Condon approximation.

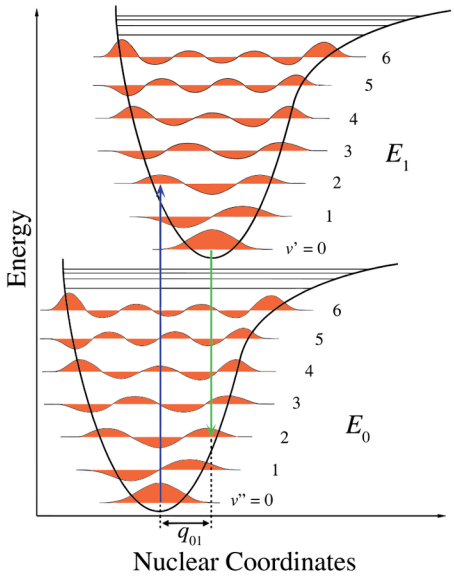


Figure 13.7.1 : Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure 13.7.1 , the nuclear axis shows a consequence of the internuclear separation and the vibronic transition is indicated by the blue and green vertical arrows. This figure demonstrates three things:

1. An absorption leads to a higher energy state,
2. fluorescence leads to a lower energy state, and
3. the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential. The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

The Classical Condon approximation

Condon approximation is the assumption that the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

This change in vibration is maintained during a state termed the **rapid electronic excitation**. The resulting Coulombic forces produce an equilibrium as shown in the figure for the nuclei termed a turning point. The turning point can be mapped by drawing a vertical line from the minimum of the lower curve to the intersection of the higher electronic state. This procedure is termed a **vertical transition** and was discussed before in the context of photoelectron spectroscopy (another electronic spectroscoy).

The Franck-Condon Principle explains the relative intensities of vibronic transitions by relating the probability of a vibrational transition to the overlap of the vibrational wavefunctions. It states that the probability of a vibrational transition occurring is weighted by the Franck-Condon overlap integral:

$$\begin{aligned} {}_{i\rightarrow f} &= |\langle \psi^*_{final}|\boldsymbol{\mu}|\psi_{initial}\rangle|^2 \\ &= \left|\int \psi^*_{final}\boldsymbol{\mu}\psi_{initial}d\tau\right|^2 \end{aligned}$$

Within the Franck-Condon approximation, the nuclei are considered "fixed" during electronic transitions. Thus, electronic transitions can be considered vertical transitions on electronic potential energy curves (vierical transitions in Figure $13.7.1$).

The Quantum Franck-Condon Principle

The Franck-Condon Principle has both a Classical and Quantum application. Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic q and nuclear Q wavefunctions given the total wavefunction.

$$|\psi_{total}(Q,q) = |\psi_{nuc}(Q)\rangle\psi_{el}(Q;q)\rangle$$

Since the transition operator, $\hat{\mu}(q)$, is dependent only on the electronic component, the nuclear components can be separated from the transition moment integral that dictates the probability of the transition occurring:

$$\langle\psi^*_{total,f}|\hat{\mu}|\psi_{total,i}\rangle = \langle\psi^*_{nuc,f}|\langle\psi^*_{el,f}|\boldsymbol{\mu}|\psi_{el,i}\rangle|\psi_{nuc,i}\rangle \tag{13.7.1}$$

$$= \underbrace{\langle\psi^*_{nuc,f}|\psi_{nuc,i}\rangle}_{\text{nuclear overlap}}\langle\psi^*_{el,f}|\boldsymbol{\mu}|\psi_{el,i}\rangle \tag{13.7.2}$$

If the nuclear overlap integral is zero for this transition, then the transition will not be observed, irrespective of the magnitude of the electronic factor.

S_{00} Transition Evaluated within Harmonic Oscillator Model

The nuclear overlap for the zero-zero transition S_{00} can be calculated quite simply using the definition of the Gaussian form of the harmonic oscillator wavefunctions.

The zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = |\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2}\rangle$$

The zero-point wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \Big| \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-Q_e)^2/2} \Big\rangle$$

where

- $\alpha = \dfrac{\sqrt{mk}}{\hbar}$
- R_e is the equilibrium bond length in the ground electronic state
- Q_e is the equilibrium bond length in the excited electronic state

The nuclear overlap integral is

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{13.7.3}$$

The exponent in Equation 13.7.3 can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{13.7.4}$$

and we use

$$(R_e + Q_e)^2 = R_e^2 + Q_e^2 + 2R_eQ_e$$

and

$$(R_e - Q_e)^2 = R_e^2 + Q_e^2 - 2R_eQ_e$$

to substitute and complete the square inside the integral. We can express

$$R_e^2 + Q_e^2 = \frac{1}{2}[(R_e + Q_e)^2 + (R_e - Q_e)^2].$$

Thus, the integral in Equation 13.7.4 is

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} e^{-\alpha\{R - 1/2(R_e + Q_e)\}^2} dR$$

The integral is a **Gaussian integral**. You can show that if we let $z = \sqrt{\alpha}\{R - 1/2(R_e + Q_e)\}$ then $dz = \sqrt{\alpha} dR$ and the integral becomes

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{13.7.5}$$

this integral has been solved already, from a table of integrals, Equation 13.7.5 becomes

$$S_{00} = e^{-\alpha(R_e - Q_e)^2/4}$$

We would follow the same procedure to calculate that overlap of the zeroth level vibration in the ground to the first excited vibrational level of the excited state: S_{01}.

S_{01} Transition Evaluated within Harmonic Oscillator Model

To calculate the overlap of zeroth ground state level ($v = 0$) with the first excited state level ($v' = 1$) we use the Hermite polynomial $H_1(x) = 2x$ for describing the excited state wavefunction (see here for a review on harmonic oscillator wavefunctions). Here $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{13.7.6}$$

with the zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = \left| \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2} \right\rangle$$

The first excited-state wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \left| \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{\alpha} 2(R-Q_e) e^{-\alpha(R-Q_e)^2/2} \right\rangle$$

The overlap of zeroth ground state level with the first excited state level (Equation 13.7.6) is then

$$S_{01} = \frac{1}{\sqrt{2}} \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} \sqrt{\alpha} 2(R-Q_e) e^{-\alpha(R-Q_e)^2/2}$$

and

$$S_{01} = \sqrt{\frac{2\alpha^2}{\pi}} e^{-\alpha(R_e-Q_e)^2/4} \int_{-\infty}^{\infty} (R-Q_e) e^{-\alpha\{R-1/2(R_e+Q_e)^2\}}$$

The same substitutions can be made as above so that the integral can be written as (not shown and to be demonstrated in a homework exercises) and the final result is

$$S_{01} = \sqrt{\frac{\alpha^2}{2}} (R_e - Q_e) e^{-\alpha(R_e-Q_e)^2/4}$$

We could continue and calculate that overlap of the zeroth level in the ground state with all the higher light vibrational levels: S_{02} , S_{03}, etc. Each term corresponds to a transition with a different energy since the vibrational levels have different energies. The absorption band then has the appearance of a progression (a Franck-Condon progression) of transitions between different levels each with its own probability.

Franck-Condon Progressions

To understand the significance of the above formula for the FC factor, let us examine a ground and excited state potential energy surface at $T = 0$ Kelvin. Shown below are two states separated by 8,000 cm^{-1} in energy. This is energy separation between the bottoms of their potential wells, but also between the respective zero-point energy levels. Let us assume that the wavenumber of the vibrational mode is 1,000 cm^{-1} and that the bond length is increased due to the fact that an electron is removed from a bonding orbital and placed in an anti-bonding orbital upon electronic excitation.

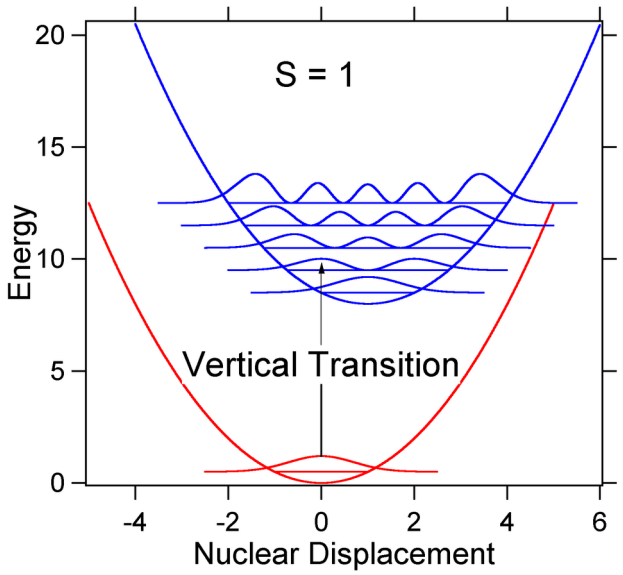


Figure 13.7.2 : Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure 13.7.3) where each vibrational transition is infinitely narrow and transition can only occur when $E = h\nu$ exactly. For example, the potential energy surfaces were given for S = 1 and the transition probability at each level is given by the sticks (black) in the figure below.

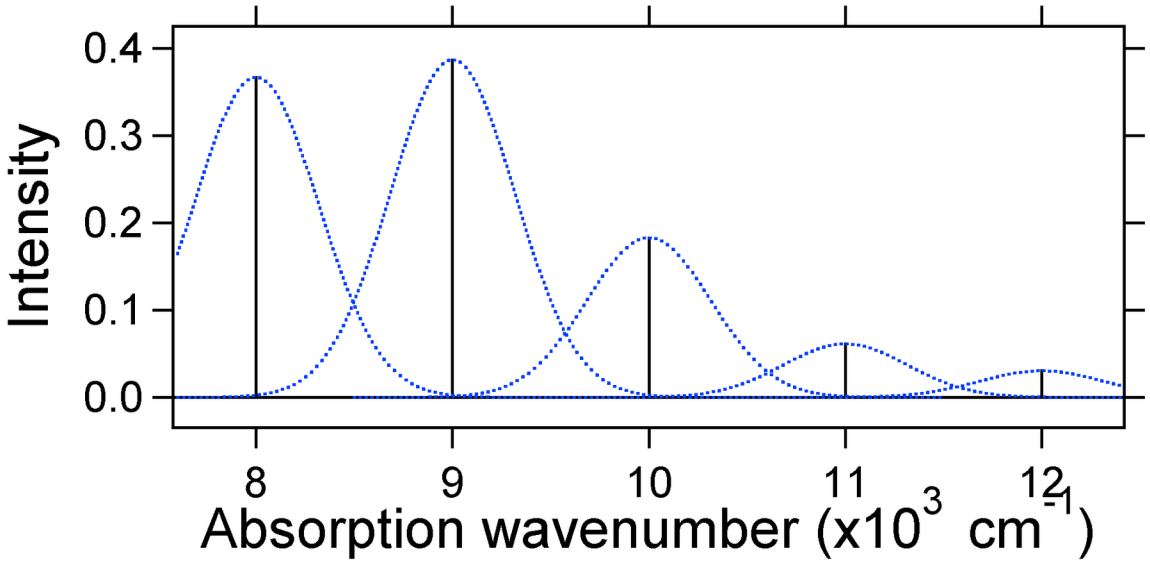


Figure 13.7.3 : Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure 13.7.2 .

The dotted Gaussians that surround each stick give a more realistic picture of what the absorption spectrum should look like. In this first place each energy level (stick) will be given some width by the fact that the state has a finite lifetime. Such broadening is called homogeneous broadening since it affects all of the molecules in the ensemble in a similar fashion. There is also broadening due to small differences in the environment of each molecule. This type of broadening is called inhomogeneous broadening. Regardless of origin the model above was created using a Gaussian broadening

The nuclear displacement between the ground and excited state determines the shape of the absorption spectrum. Let us examine both a smaller and a large excited state displacement. If $S = ½$ and the potential energy surfaces in this case are:

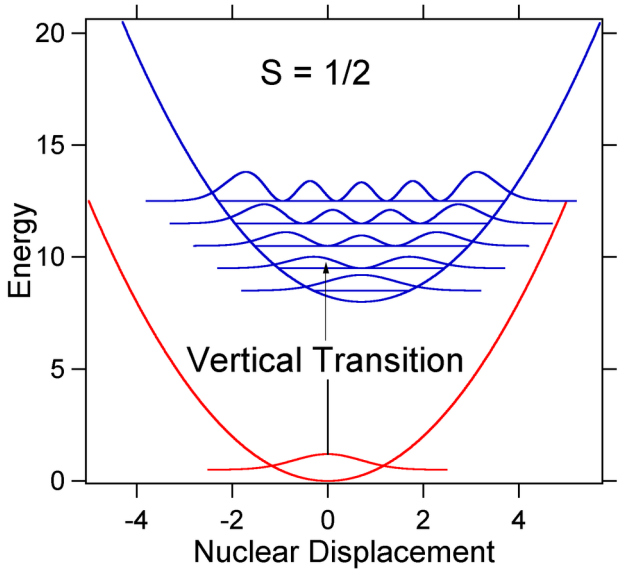


Figure 13.7.4 : Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure 13.7.5

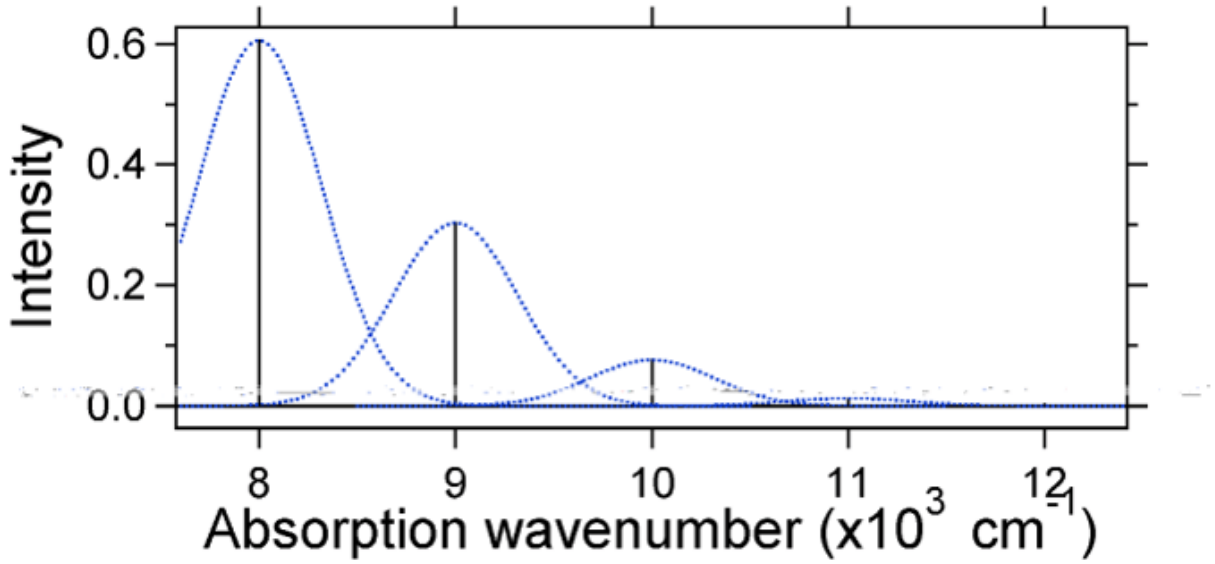


Figure 13.7.5 : Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure 13.7.4.

Note that the zero-zero or $S_{0,0}$ vibrational transition is much large in the case where the displacement is small.

> As a general rule of thumb the S constant gives the ratio of the intensity of the $v = 2$ transition to the $v = 1$ transition. In this case since $S = 0.5$, the $v = 2$ transition is 0.5 the intensity of $v = 1$ transition.

As an example of a larger displacement the disposition of the potential energy surfaces for S = 2 is shown below.

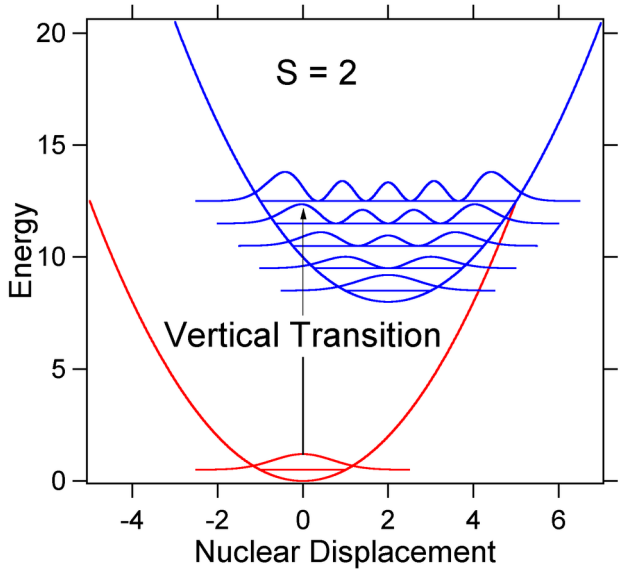


Figure 13.7.6 : Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

The larger displacement results in decreased overlap of the ground state level with the v = 0 level of the excited state. The maximum intensity will be achieved in higher vibrational levels as shown in the stick spectrum.

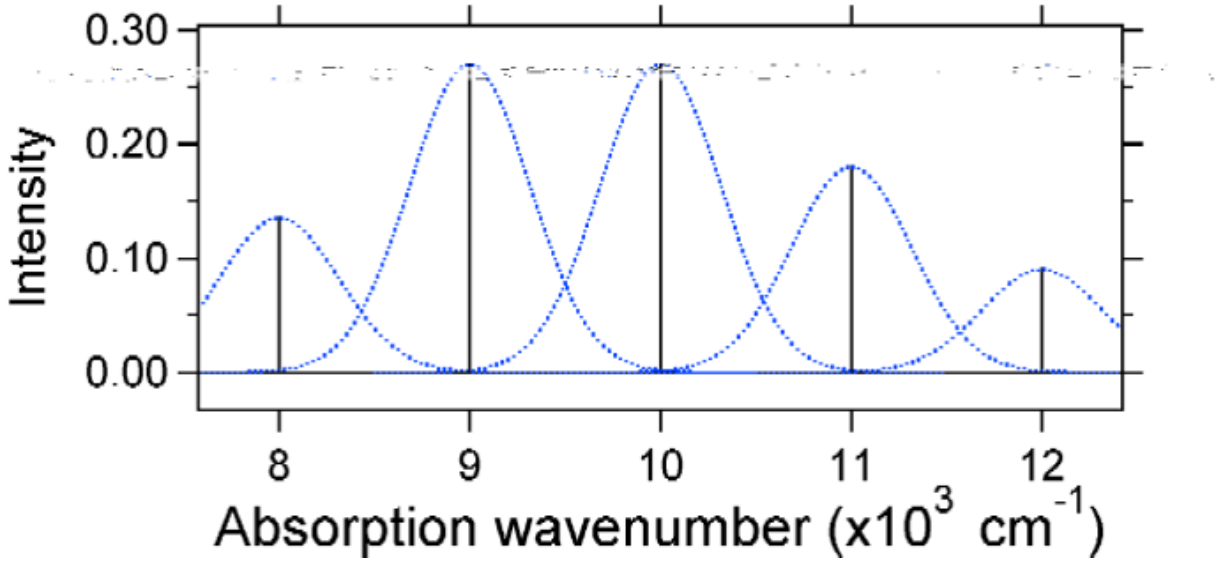


Figure 13.7.7 : Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure 13.7.6.

The absorption spectra plotted below all have the same integrated intensity, however their shapes are altered because of the differing extent of displacement of the excited state potential energy surface.

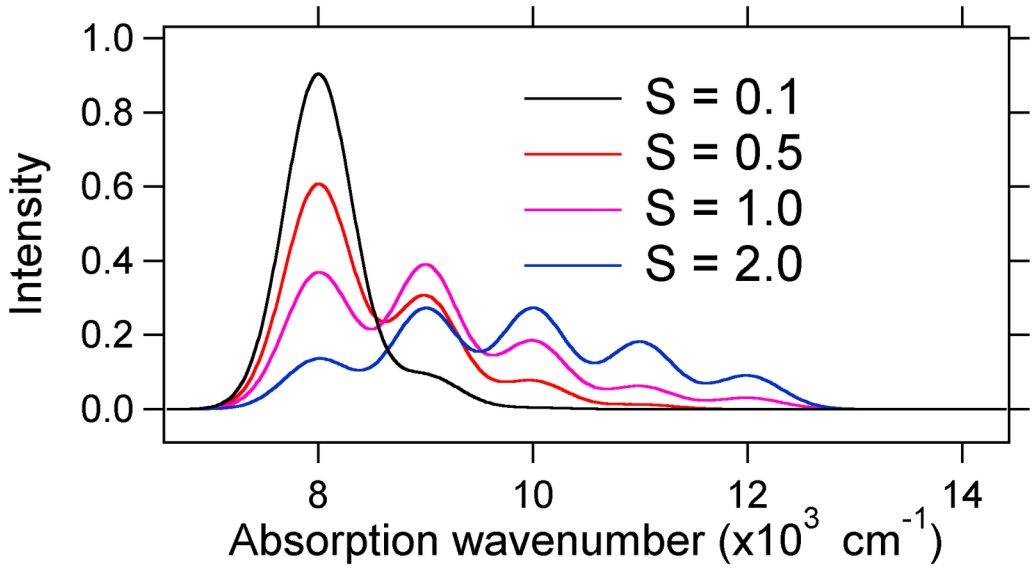


Figure 13.7.8 : Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

So the nature of the relative vibronic band intensities can tell us whether there is a displacement of the equilibrium nuclear coordinate that accompanied a transition. When will there be an increase in bond length (i.e., $Q_e > R_e$)? This occurs when an electron is promoted from a bonding molecular orbital to a non-bonding or anti-bonding molecular orbitals (i.e., when the bond order is less in the excited state than the ground state).

- Non-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ non-bonding molecular orbital

In short, when the bond order is lower in the excited state than in the ground state, then $Q_e > R_e$; an increase in bond length will occur when this happens.

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13.8: Rotational Spectra of Polyatomic Molecules

Quick Review of Diatomic Rotation

As discussed previously, the Schrödinger equation for the angular motion of a rigid (i.e., having fixed bond length R) diatomic molecule is

$$\frac{\hbar^2}{2\mu}\left[\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\psi\rangle = E|\psi\rangle$$

or

$$\frac{L^2}{2\mu R^2}|\psi\rangle = E|\psi\rangle$$

The Hamiltonian in this problem contains only the kinetic energy of rotation; no potential energy is present because the molecule is undergoing unhindered "free rotation". The angles θ and φ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The eigenvalues corresponding to each eigenfunction are straightforward to find because H_{rot} is proportional to the L^2 operator whose eigenvalues have already been determined. The resultant rotational energies are given as:

$$E_J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = BJ(J+1) \tag{13.8.1}$$

and are independent of M. B is the rotational constant. Thus each energy level is labeled by J and is $2J+1$-fold degenerate (because M ranges from $-J$ to J). The rotational energy in Equation 13.8.1 can be expressed in terms of the moment of inertia I

$$I = \sum_i m_i R_i^2 \tag{13.8.2}$$

where m_i is the mass of the i^{th} atom and R is its distance from the center of mass of the molecule. This moment of inertia replaces μR^2 in the denominator of Equation 13.8.1:

$$E_J = \frac{\hbar^2 J(J+1)}{2I} = BJ(J+1) \tag{13.8.3}$$

Rotation of Polyatomic Molecules

In contrast to diatomic molecules (Equation 13.8.2), the rotational motions of polyatomic molecules in three dimensions are characterized by multiple moments of inertia. typically reflected in an 3×3 inertia tensor. It is common in rigid body mechanics to express in these moments of inertia in *lab-based Cartesian coordinates* via a notation that explicitly identifies the x, y, and z axes such as I_{xx} and I_{xy}, for the components of the inertia tensor.

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \tag{13.8.4}$$

The components of this tensor can be assembled into a matrix given by

$$I_{xx} = \sum_{k=1}^{N} m_k (y_k^2 + z_k^2)$$

$$I_{yy} = \sum_{k=1}^{N} m_k (x_k^2 + z_k^2)$$

$$I_{zz} = \sum_{k=1}^{N} m_k (x_k^2 + y_k^2)$$

$$I_{yx} = I_{xy} = -\sum_{k=1}^{N} m_k x_k y_k$$

$$I_{zx} = I_{xz} = -\sum_{k=1}^{N} m_k x_k z_k$$

$$I_{zy} = I_{yz} = -\sum_{k=1}^{N} m_k y_k z_k.$$

The rotational motions of polyatomic molecules are characterized by moments of inertia that are defined in a *molecule based coordinates* with axes that are labeled a, b, and c. Measured in the body frame the inertia matrix (Equation 13.8.4) is a constant real symmetric matrix, which can be decomposed into a diagonal matrix, given by

$$I = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}$$

These labels are assigned so that I_c is the **largest** principal moment of inertia with an order of the three moments set as

$$I_a < I_b < I_c$$

The rotational kinetic energy operator for a rigid non-linear polyatomic molecule is then expressed as

$$H_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \tag{13.8.5}$$

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \sin\chi \frac{\partial}{\partial\theta} \tag{13.8.6}$$

$$J_b = i\hbar \sin\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \cos\chi \frac{\partial}{\partial\theta} \tag{13.8.7}$$

$$J_c = -\frac{ih\partial}{\partial\chi} \tag{13.8.8}$$

The angles θ, φ, and χ are the **Euler angles** needed to specify the orientation of the rigid molecule relative to a laboratory-fixed coordinate system. The corresponding square of the total angular momentum operator J^2 can be obtained as

$$J^2 = J_a^2 + J_b^2 + J_c^2 \tag{13.8.9}$$

$$= -\frac{\partial^2}{\partial\theta^2} - \cot\theta \frac{\partial}{\partial\theta} - \left(\frac{1}{\sin\theta} \right) \left(\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\chi^2} - 2\cos\theta \frac{\partial^2}{\partial\varphi\partial\chi} \right) \tag{13.8.10}$$

and the component along the lab-fixed Z axis is

$$J_Z = -ih \frac{\partial}{\partial\varphi}.$$

Spherical Tops

When the three principal moment of inertia values are identical, the molecule is termed a spherical top. In this case, the total rotational energy Equation 13.8.5 can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = \frac{J^2}{2I}$$

As a result, the eigenfunctions of H_{rot} are those of J^2 (and J_a as well as J_Z both of which commute with J_2 and with one another; J_Z is the component of J along the lab-fixed Z-axis and commutes with J_a because

$$J_Z = -ih\frac{\partial}{\partial\varphi}$$

and

$$J_a = -ih\frac{\partial}{\partial\chi}$$

act on different angles. The energies associated with such eigenfunctions are

$$E(J,K,M) = \frac{\hbar^2 J(J+1)}{2I^2}$$

for all K (i.e., J a quantum numbers) ranging from -J to J in unit steps and for all M (i.e., J Z quantum numbers) ranging from -J to J. Each energy level is therefore $(2J+1)^2$ degenarate because there are $2J+1$ possible K values and $2J+1$ possible M values for each J. The eigenfunctions of J^2, J_Z and J_a, $|J,M,K>$ are given in terms of the set of rotation matrices $D_{J,M,K}$:

$$|J,M,K\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^*_{J,M,K}(\theta,\varphi,\chi)$$

which obey

$$J^2|J,M,K\rangle = \hbar^2 J(J+1)|J,M,K\rangle$$

$$J_a|J,M,K\rangle = \hbar K|J,M,K\rangle$$

$$J_Z|J,M,K\rangle = \hbar M|J,M,K\rangle$$

Symmetric Tops

Symmetrical tops are molecules with two rotational axes that have the same inertia and one unique rotational axis with a different inertia. Symmetrical tops can be divided into two categories based on the relationship between the inertia of the unique axis and the inertia of the two axes with equivalent inertia. If the unique rotational axis has a greater inertia than the degenerate axes the molecule is called an **oblate symmetrical top** (Figure 13.8.1). If the unique rotational axis has a lower inertia than the degenerate axes the molecule is called a **prolate symmetrical top**. For simplification think of these two categories as either frisbees for oblate tops or footballs for prolate tops.

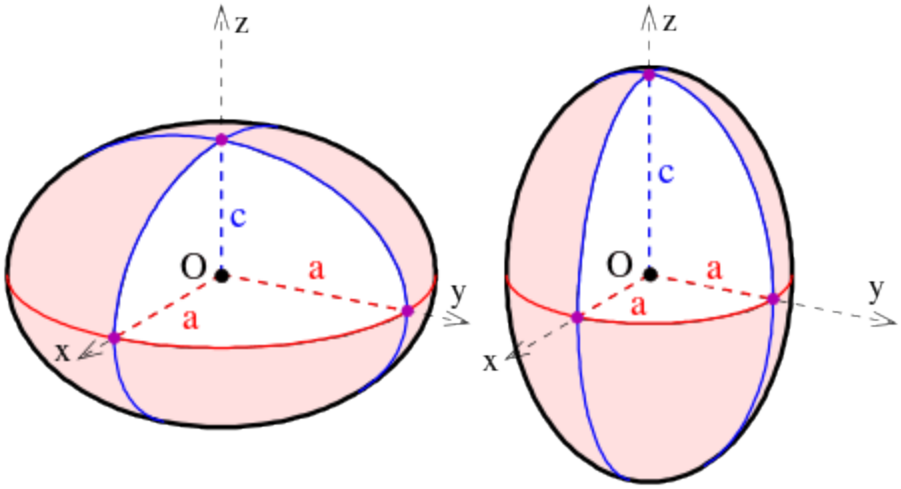


Figure 13.8.1 : The assignment of semi-axes on a spheroid. It is oblate if $c < a$ (left) and prolate if $c > a$ (right). (CC BY-SA 4.0; Ag2gaeh)

Again, the rotational kinetic energy, which is the full rotational Hamiltonian, can be written in terms of the total rotational angular momentum operator J^2 and the component of angular momentum along the axis with the unique principal moment of inertia.

For prolate tops, Equation 13.8.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_a^2 \left(\frac{1}{2I_a} - \frac{1}{2I} \right)$$

For oblate tops, Equation 13.8.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_c^2 \left(\frac{1}{2I_c} - \frac{1}{2I} \right)$$

As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a or J_c (and of J_Z), and the corresponding energy levels.

The energies for prolate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I^2} + h^2 K^2 \left(\frac{1}{2I_a} - \frac{1}{2I} \right)$$

and the energies for oblate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I2} + h^2 K^2 \left(\frac{1}{2I_c} - \frac{1}{2I} \right)$$

again for K and M (i.e., J_a or J_c and J_Z quantum numbers, respectively) ranging from $-J$ to J in unit steps. Since the energy now depends on K, these levels are only $2J+1$ degenerate due to the $2J+1$ different M values that arise for each J value. The eigenfunctions $|J,M,K>$ are the same rotation matrix functions as arise for the spherical-top case.

Asymmetric Tops

The rotational eigenfunctions and energy levels of a molecule for which all three principal moments of inertia are distinct (a **asymmetric top**) can not easily be expressed in terms of the angular momentum eigenstates and the J, M, and K quantum numbers. However, given the three principal moments of inertia I_a, I_b, and I_c, a matrix representation of each of the three contributions to the general rotational Hamiltonian in Equation 13.8.5 can be formed within a basis set of the $\{|J,M,K\rangle\}$ rotation matrix functions. This matrix will **not** be diagonal because the $|J,M,K\rangle$ functions are not eigenfunctions of the asymmetric top H_{rot}. However, the matrix can be formed in this basis and subsequently brought to diagonal form by finding its eigenvectors {C n, J,M,K } and its eigenvalues $\{E_n\}$. The vector coefficients express the asymmetric top eigenstates as

$$\psi_n(\theta,\varphi,\chi) = \sum_{J,M,K} C_{n,J,M,K} |J,M,K\rangle$$

Because the total angular momentum J^2 still commutes with H_{rot}, each such eigenstate will contain only one J-value, and hence Ψ_n can also be labeled by a J quantum number:

$$\psi_{n,J}(\theta,\varphi,\chi) = \sum_{M,K} C_{n,J,M,K}|J,M,K\rangle$$

To form the only non-zero matrix elements of H_{rot} within the $|J,M,K\rangle$ basis, one can use the following properties of the rotation-matrix functions:

$$\langle j,\rangle = \langle j,\rangle = 1/2 < j,\rangle = h2[J(J+1) - K2],$$

$$\langle j,\rangle = h^2K^2$$

$$\langle j\rangle = -\langle j\rangle = h^2[J(J+1) - K(K\pm1)]1/2[J(J+1) - (K\pm1)(K\pm2)]1/2\langle j\rangle = 0$$

Each of the elements of J_c^2, J_a^2, and J_b^2 must, of course, be multiplied, respectively, by $1/2I_c$, $1/2I_a$, and $1/2I_b$ and summed together to form the matrix representation of H_{rot}. The diagonalization of this matrix then provides the asymmetric top energies and wavefunctions.

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13.9: Normal Modes in Polyatomic Molecules

Normal modes are used to describe the different vibrational motions in molecules. Each mode can be characterized by a different type of motion and each mode has a certain symmetry associated with it. Group theory is a useful tool in order to determine what symmetries the normal modes contain and predict if these modes are IR and/or Raman active. Consequently, IR and Raman spectroscopy is often used for vibrational spectra.

Degrees of Freedom

In general, a normal mode is an independent motion of atoms in a molecule that occurs without causing movement to any of the other modes. Normal modes, as implied by their name, are orthogonal to each other. In order to discuss the quantum-mechanical equations that govern molecular vibrations it is convenient to convert Cartesian coordinates into so called normal coordinates. Vibrations in polyatomic molecules are represented by these normal coordinates.

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into three categories.

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Table 13.9.1 : Overview of degrees of freedom

	Total Degrees of Freedom	Translational degrees of freedom	Rotational degrees of freedom	Vibrational degrees of freedom
Nonlinear Molecules	3N	3	3	3N -**6**
Linear Molecules	3N	3	2	3N - 5

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Example 13.9.1 : Ethane vs. Carbon Dioxide

Ethane, C_2H_6 has eight atoms ($N = 8$) and is a nonlinear molecule so of the $3N = 24$ degrees of freedom, three are translational and three are rotational. The remaining 18 degrees of freedom are internal (vibrational). This is consistent with:

$$3N - 6 = 3(8) - 6 = 18$$

Carbon Dioxide, CO_2 has three atoms ($N = 3$ and is a linear molecule so of the $3N = 9$ degrees of freedom, three are translational and two are rotational. The remaining 4 degrees of freedom are vibrational. This is consistent with:

$$3N - 5 = 3(3) - 5 = 4$$

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

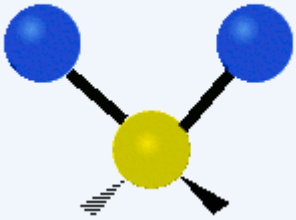
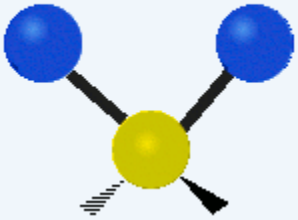
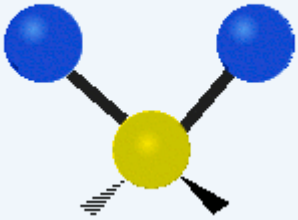
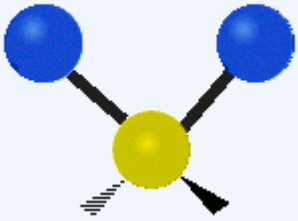
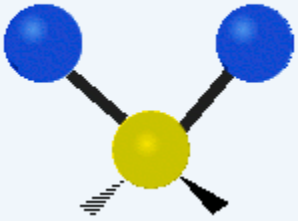
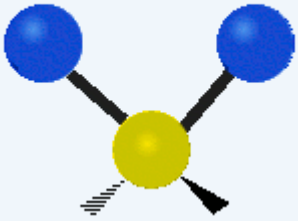
Symmetricical Stretching	Asymmetrical Stretching	Wagging
		
Twisting	**Scissoring**	**Rocking**
		

Figure 13.9.1 : *Six types of Vibrational Modes. Taken from publisher en.Wikipedia.org/wiki/Infrared_spectroscopy with permission from copyright holder.*

Normal Modes

If there is no external field present, the energy of a molecule does not depend on its orientation in space (its translational degrees of freedom) nor its center of mass (its rotational degrees of freedom). The potential energy of the molecule is therefore made up of its vibrational degrees of freedom only of $3N - 6$ (or $3N - 5$ for linear molecules). The difference in potential energy is given by:

$$\Delta V = V(q_1, q_2, q_3, ..., q_n) - V(0, 0, 0, ..., 0) \tag{13.9.1}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{vib}} \sum_{j=1}^{N_{vib}} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j \tag{13.9.2}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{vib}} \sum_{j=1}^{N_{vib}} f_{ij} q_i q_j \tag{13.9.3}$$

where q represents the equilibrium displacement and N_{vib} the number of vibrational degrees of freedom.

For simplicity, the *anharmonic* terms are neglected in this equation (i.e., higher order terms are ignore). A theorem of classical mechanics states that the cross terms can be eliminated from the above equation (the details of the theorem are very complex and will not be discussed in detail). By using matrix algebra a new set of coordinates {Qj} can be found such that

$$\Delta V = \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{13.9.4}$$

Note that there are no cross terms in this new expression. These new coordinates are called **normal coordinates** or **normal**

modes. With these new normal coordinates in hand, the Hamiltonian operator for vibrations can be written as follows:

$$\hat{H}_{vib} = -\sum_{j=1}^{N_{vib}} \frac{\hbar^2}{2\mu_i} \frac{d^2}{dQ_j^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{13.9.5}$$

The total wavefunction is a product of the individual wavefunctions and the energy is the sum of independent energies. This leads to:

$$\hat{H}_{vib} = \sum_{j=1}^{N_{vib}} \hat{H}_{vib,j} = \sum_{j=1}^{N_{vib}} \left(\frac{-\hbar^2}{2\mu_j} \frac{d^2}{dQ_i^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \right) \tag{13.9.6}$$

and the wavefunction is then

$$\begin{aligned} \psi_{vib} &= Q_1, Q_2, Q_3 ..., Q_{vib} \\ &= \psi_{vib,1}(Q_1)\psi_{vib,2}(Q_2)\psi_{vib,3}(Q_3), ..., \psi_{vib,N_{vib}}(Q_{N_{vib}}) \end{aligned}$$

and the total vibrational energy of the molecule is

$$E_{vib} = \sum_{j=1}^{N_{vin}} h\nu_j \left(v_j + \frac{1}{2} \right) \tag{13.9.7}$$

where $v_j = 0, 1, 2, 3....$

The consequence of the result stated in the above equations is that each vibrational mode can be treated as a harmonic oscillator approximation. There are N_{vib} harmonic oscillators corresponding to the total number of vibrational modes present in the molecule.

Pictorial description of normal coordinates using CO

The normal coordinate q is used to follow the path of a normal mode of vibration. As shown in Figure 13.9.2 the displacement of the C atom, denoted by $\Delta r_o(\mathrm{C})$, and the displacement of the O atom, denoted by $\Delta r_o(\mathrm{O})$, occur at the same frequency. The displacement of atoms is measured from the equilibrium distance in ground vibrational state, r_o.

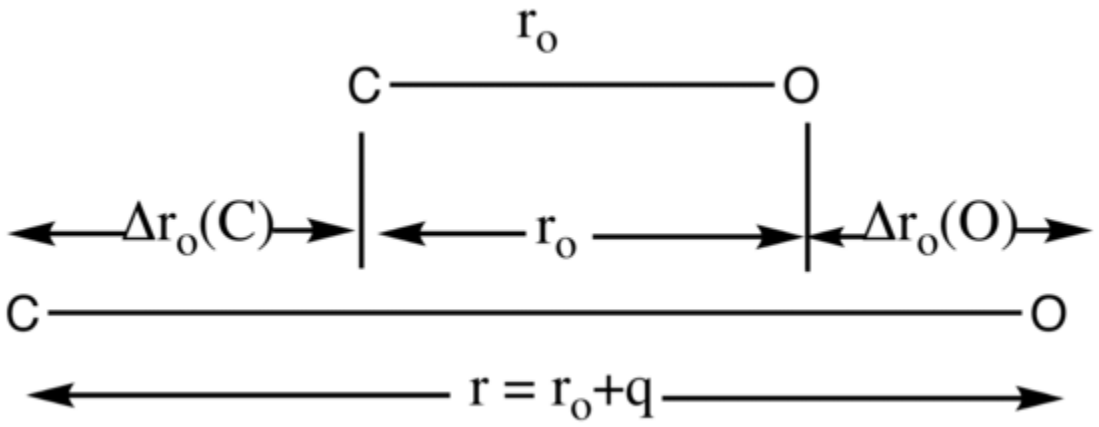


Figure 13.9.2 : The Normal coordinate for CO is equation to $\Delta r(C) + \Delta r(O)$

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13.10: Irreducible Representation of Point Groups

There exists an important fact about normal coordinates. Each of these coordinates belongs to an irreducible representation of the point the molecule under investigation. Vibrational wavefunctions associated with vibrational energy levels share this property as well. The normal coordinates and the vibration wavefunction can be categorized further according to the point group they belong to. From the character table predictions can be made for which symmetries can exist. The irreducible representation offers insight into the IR and/or Raman activity of the molecule in question.

Symmetry of normal modes

It is important to realize that every normal mode has a certain type of symmetry associated with it. Identifying the point group of the molecule is therefore an important step. With this in mind it is not surprising that every normal mode forms a basis set for an irreducible representation of the point group the molecule belongs to. For a molecule such as water, having a structure of XY_2, three normal coordinates can be determined. The two stretching modes are equivalent in symmetry and energy. The figure below shows the three normal modes for the water molecule:

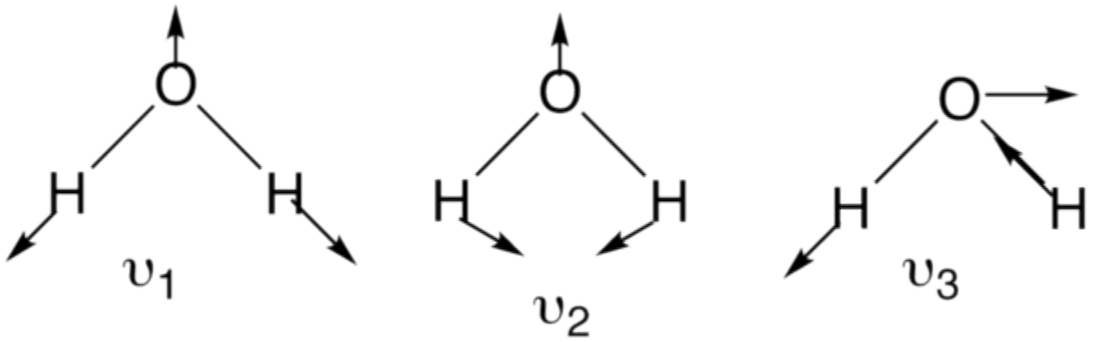


Figure 13.10.1 : Three normal modes of water

By convention, with nonlinear molecules, the symmetric stretch is denoted v_1 whereas the asymmetric stretch is denoted v_2. Bending motions are v_3. With linear molecules, the bending motion is ν_2 whereas asymmetric stretch is v_3.

The water molecule has C_{2v} symmetry and its symmetry elements are E, C_2, σ(xz) and σ(yz). To determine the symmetries of the three vibrations and how they each transform, symmetry operations will be performed. As an example, performing C_2 operations using the two normal mode v_2 and v_3 gives the following transformation:

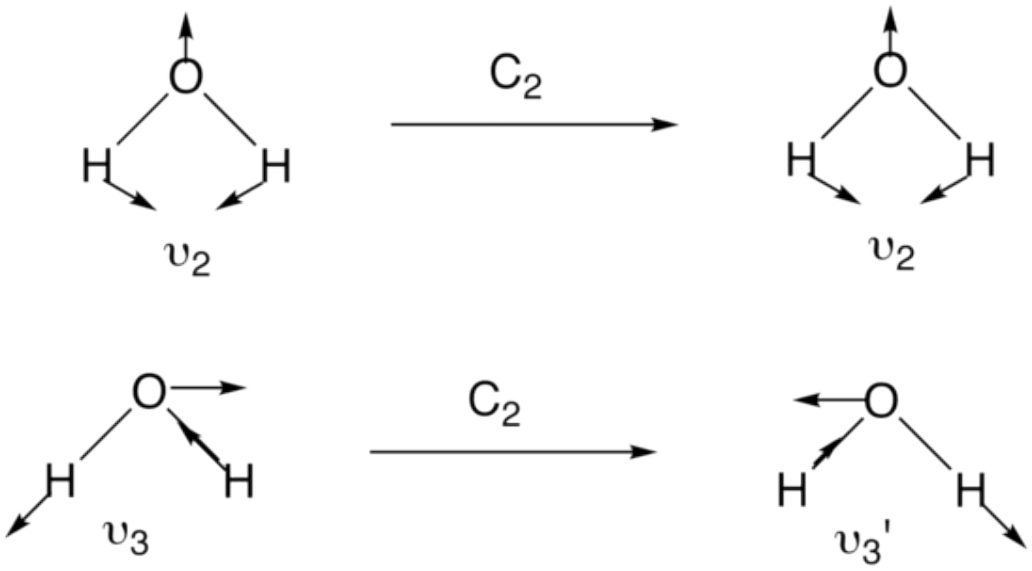


Figure 13.10.2 : Symmetry operations on the symmetric and asymmetric stretches of water

Once all the symmetry operations have been performed in a systematic manner for each modes the symmetry can be assigned to the normal mode using the character table for C_{2v}:

Table 13.10.2 : Character table for the C_{2v} point group

C_{2v}	E	C2	σ (xz)	σ (yz)	
ν_1	1	1	1	1	**= a_1**
ν_2	1	1	1	1	**= a_1**
ν_3	1	-1	-1	1	**= b_2**

Water has three normal modes that can be grouped together as the reducible representation

$$\Gamma_{vib} = 2a_1 + b_2.$$

Determination of normal modes becomes quite complex as the number of atoms in the molecule increases. Nowadays, computer programs that simulate molecular vibrations can be used to perform these calculations. The example of $[PtCl_4]^{2-}$ shows the increasing complexity (Figure 13.10.2). The molecule has five atoms and therefore 15 degrees of freedom, 9 of these are vibrational degrees of freedom. The nine normal modes are exemplified below along with the irreducible representation the normal mode belongs to (D_{4h} point group).

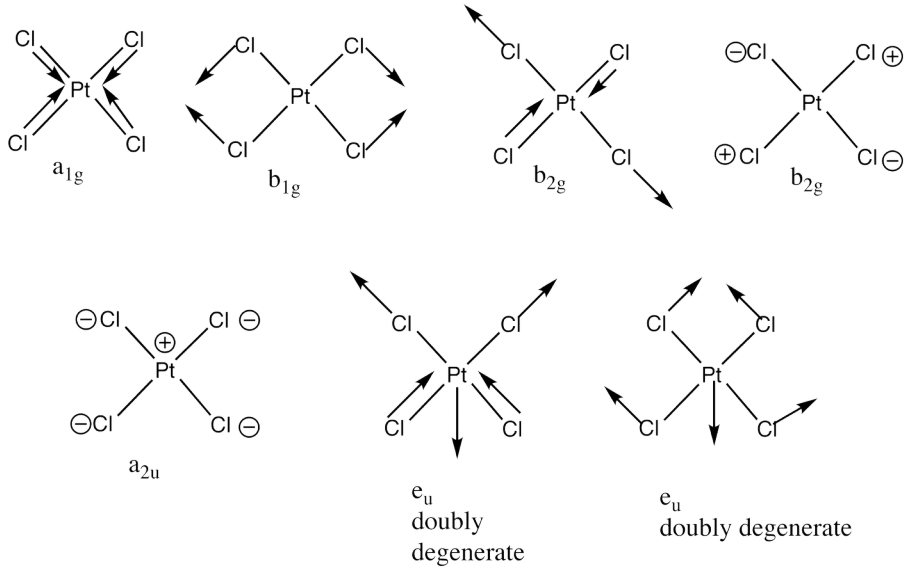


Figure 13.10.3 : A_{1g}, b_{1g} and e_u are stretching vibrations whereas b_{2g}, a_{2u}, b_{2u} and e_u are bending vibrations.

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13.11: Time-Dependent Perturbation Theory

Time-independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics. In time-independent perturbation theory, the perturbation Hamiltonian is **static** (i.e., possesses no time dependence). Time-dependent perturbation theory, developed by Paul Dirac, studies the effect of a time-dependent perturbation $V(t)$ applied to a **time-independent Hamiltonian** H_0. Since the perturbed Hamiltonian is time-dependent, so are its energy levels and eigenstates. Thus, the goals of time-dependent perturbation theory are slightly different from time-independent perturbation theory, where one may be interested in the following quantities:

- The time-dependent expectation value of some observable A, for a given initial state.
- The time-dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.

The first quantity is important because it gives rise to the classical result of a measurement performed on a macroscopic number of copies of the perturbed system. The second quantity looks at the time-dependent probability of occupation for each eigenstate. This is particularly useful in laser physics, where one is interested in the populations of different atomic states in a gas when a time-dependent electric field is applied. We will briefly examine the method behind Dirac's formulation of time-dependent perturbation theory. Choose an energy basis $|n\rangle$ for the unperturbed system. (We drop the (0) superscripts for the eigenstates, because it is not useful to speak of energy levels and eigenstates for the perturbed system.)

If the unperturbed system is in eigenstate $|j\rangle$ at time $t = 0$, its state at subsequent times varies only by a phase (this is the Schrödinger picture, where state vectors evolve in time and operators are constant)

$$|j(t)\rangle = e^{-iE_j t/\hbar}|j\rangle$$

Now, introduce a time-dependent perturbing Hamiltonian $H_1(t)$. The Hamiltonian of the perturbed system is

$$H = H_0 + H_1(t)$$

Let $|\psi(t)\rangle$ denote the quantum state of the perturbed system at time t and obeys the time-dependent Schrödinger equation,

$$H|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

The quantum state at each instant can be expressed as a linear combination of the complete eigenbasis of $|n\rangle$:

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}|n\rangle$$

where the $c_n(t)$ coefficients are to be determined complex functions of *t* which we will refer to as **amplitudes**

We have explicitly extracted the exponential phase factors $\exp(-iE_n t/\hbar)$ on the right hand side. This is only a matter of convention, and may be done without loss of generality. The reason we go to this trouble is that when the system starts in the state $|j\rangle$ and no perturbation is present, the amplitudes have the convenient property that, for all t, $c_j(t) = 1$ and $c_n(t) = 0$ if $n \neq j$.

The square of the absolute amplitude $c_n(t)$ is the probability that the system is in state n at time t, since

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}|n\rangle$$

Plugging into the Schrödinger equation and using the fact that $\partial/\partial t$ acts by a chain rule, one obtains

$$\sum_n \left(i\hbar\frac{\partial c_n}{\partial t} - c_n(t)V(t)\right)e^{-iE_n t/\hbar}|n\rangle = 0\ .$$

By resolving the identity in front of *V*, this can be reduced to a set of partial differential equations for the amplitudes,

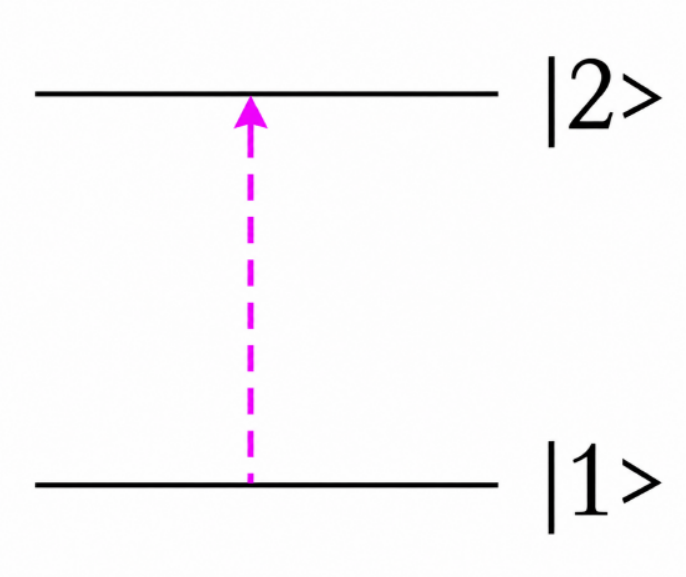
$$\frac{\partial c_n}{\partial t} = \frac{-i}{\hbar}\sum_k \langle n|H_1(t)|k\rangle\, c_k(t)\, e^{-i(E_k - E_n)t/\hbar}\ .$$

The matrix elements of H_1 play a similar role as in time-independent perturbation theory, being proportional to the rate at which amplitudes are shifted between states. Note, however, that the direction of the shift is modified by the exponential phase factor. Over times much longer than the energy difference $E_k - E_n$, the phase winds around 0 several times. If the time-dependence of H_1 is sufficiently slow, this may cause the state amplitudes to oscillate (e.g., such oscillations are useful for managing radiative transitions in a laser).

Two-Level System

Consider the two level system (i.e. $n = 1, 2$)

$$|\psi\rangle = \sum_{n=1,2} c_n(t)|n\rangle_o$$



Solution of time-dependent perturbation for two level system:

$$i\hbar\frac{\partial c_1(t)}{\partial t} = c_1(t)H_{11}(t) + c_2 e^{-i\omega_o t}H_{12}(t)$$

$$i\hbar\frac{\partial c_2(t)}{\partial t} = c_2(t)H_{22}(t) + c_1 e^{+i\omega_o t}H_{21}(t)$$

where the matrix elements of the permutation (in terms of the eigenstates of $H(0)$) are

$$\langle m|H_1(t)|n\rangle = H_{mn}(t)$$

Assume initial state is $n = 1$, and $H_{11} = H_{22} = 0$

$$|\psi(t = 0)\rangle = |1\rangle$$

Probability of particle at $n = 2$ at time t after the perturbation is turned on (i.e., incident light):

$$c_2(t) = \frac{-i}{\hbar}\int_o^t e^{i\omega_o t}dt' H_{21}(t') \tag{13.11.1}$$

where

$$H_1(t) = \cos(\omega t)V(r)$$

$V(r)$ is an amplitude of polarization vector, which we can ignore for now.

If we assume incident frequency of incident light ω is comparable to the natural frequency of oscillation from ω_o

$$\omega \approx \omega_o$$

then Equation 13.11.1 can be simplified to

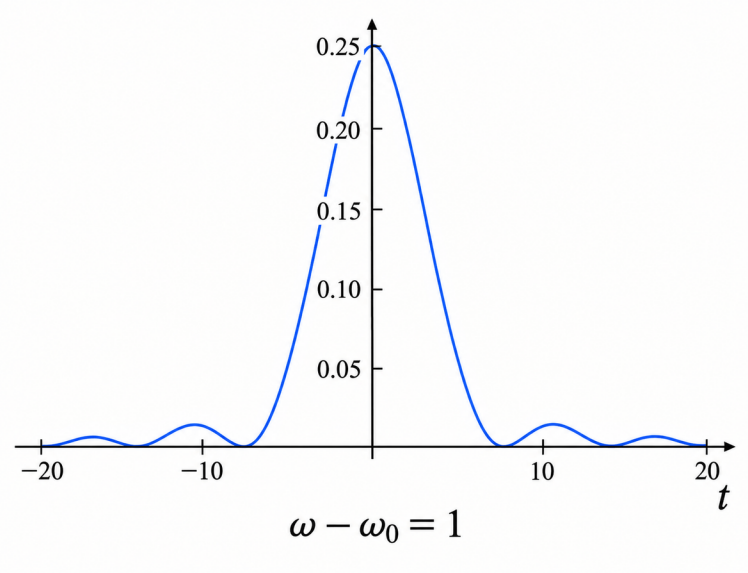
$$c_2(t) = -\frac{2i}{\hbar}\frac{\sin(\omega-\omega_o)t/2}{(\omega-\omega_o)t}e^{i(\omega_0-\omega)t/2}H_{21}$$

Transition Probability

Assume initial state is $n = 1$, and probability of transition from $n = 1$ state to $n = 2$ state is:

$$P_{12}(t) = |c_2(t)|^2 = \frac{4}{\hbar^2}\left|\frac{\sin(\omega-\omega_o)t/2}{(\omega-\omega_o)t}\right|^2 |H_{21}|^2$$

What does this mean? Strangely, it means that the probability of making a transition is actually oscillating sinusoidally (squared)! If you want to cause a transition, should turn off perturbation after time $\pi/|\omega-\omega_o|$or some odd multiple, when the system is in upper state with maximum probability.



$P_{12}(t)$ is peaked at $\omega-\omega_o = 0$. The height of $|H_{12}t/2\hbar|^2$ and width of $4\pi/t$ gets higher and narrower as time goes on. Recall this is perturbative treatment, however, and $P_{12}(t)$ cannot get bigger than 1, so perturbation theory breaks down eventually.

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13.12: The Selection Rule for the Rigid Rotor

A **selection rule** describes how the probability of transitioning from one level to another cannot be **zero**. It has two sub-pieces: a **gross selection rule** and a **specific selection rule**. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. Incident electromagnetic radiation presents an oscillating electric field $E_0 \cos(\omega t)$ that interacts with a transition dipole. The dipole operator is $\mu = e \cdot r$ where r is a vector pointing in a direction of space.

A dipole moment of a given state is

$$\mu_z = \int \Psi_1{}^* \mu_z \Psi_1 \, d\tau$$

A transition dipole moment is a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule

$$(\mu_z)_{12} = \int \Psi_1{}^* \mu_z \Psi_2 \, d\tau$$

In an experiment we present an electric field along the z axis (in the laboratory frame) and we may consider specifically the interaction between the transition dipole along the x, y, or z axis of the molecule with this radiation. If μ_z is zero then a transition is forbidden. The selection rule is a statement of when μ_z is non-zero.

> The selection rule is a statement of when μ_z is non-zero.

Rotational transitions

We can use the definition of the transition moment and the spherical harmonics to derive selection rules for a rigid rotator. Once again we assume that radiation is along the z axis.

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta,\phi) \mu_z Y_J^M(\theta,\phi) \sin\theta \, d\phi, d\theta$$

Notice that m must be non-zero in order for the transition moment to be non-zero. This proves that a molecule must have a permanent dipole moment in order to have a rotational spectrum. The spherical harmonics can be written as

$$Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi}$$

where N_{JM} is a normalization constant. Using the standard substitution of $x = \cos q$ we can express the rotational transition moment as

$$(\mu_z)_{J,M,J',M'} = \mu N_{JM} N_{J'M'} \int_0^{2\pi} e^{I(M-M')\phi} \, d\phi \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

The integral over f is zero unless M = M' so $\Delta M = 0$ is part of the rigid rotator selection rule. Integration over ϕ for $M = M'$ gives 2π so we have

$$(\mu_z)_{J,M,J',M'} = 2\pi\mu N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

We can evaluate this integral using the identity

$$(2J+1)x \, P_J^{|M|}(x) = (J - |M| + 1) P_{J+1}^{|M|}(x) + (J - |M|) P_{J-1}^{|M|}(x)$$

Substituting into the integral one obtains an integral which will vanish unless $J' = J + 1$ or $J' = J - 1$.

$$\int_{-1}^{1} P_{J'}^{|M'|}(x)\left(\frac{(J-|M|+1)}{(2J+1)}P_{J+1}^{|M|}(x)+\frac{(J-|M|)}{(2J+1)}P_{J-1}^{|M|}(x)\right)dx$$

This leads to the selection rule $\Delta J = \pm 1$ for absorptive rotational transitions. Keep in mind the physical interpretation of the quantum numbers J and M as the total angular momentum and z-component of angular momentum, respectively. As stated above in the section on electronic transitions, these selection rules also apply to the orbital angular momentum ($\Delta l = \pm 1$, $\Delta m = 0$).

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13.13: The Harmonic Oscillator Selection Rule

Selection rules are a very important concept in spectroscopy and physical chemistry, as they directly complement the concept that systems on the atomic level are quantized. Quantization tells us how electrons, neutrons, and protons are set up, and selection rules tell us how, energetically speaking, they may move about. For example, the principal quantum number, n, determines the energy state of particles in the Particle in a Box model. With respect to real systems, the quantum number n describes electronic transitions, such as the excitation of an electron. There are other transitions, such as the rotational transition, which applies to the rigid rotator model and occurs where there are spherical harmonics. Vibrational transitions occur where there is a system that can be visualized as two masses connected by a spring, such as a diatomic molecule.

Selection rules can be very useful in spectroscopy for obtaining information about an unknown substance; any given substance has properties and behaviors that operate within the selection rules and determine the wavelengths of electromagnetic radiation (light) that cause transitions. By tracking these properties, chemists can use techniques like IR spectroscopy to determine the chemical structure of a molecule. For example, a selection rule might govern how a quantum number changes during a transition. That quantum number appears in equations that determine the energy transition based on the mass and other structural properties of a molecule. Thus, if one knows the selection rules and the energy transition, he or she can determine other properties about the molecule, such as its mass or its bond strength.

Example: Evaluating vibrational transitions using a transition moment integral.

Vibrational systems are described by the harmonic oscillator wavefunctions, which look like

$$\Psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

A transition dipole moment can be written to describe a transition along the z-axis.

$$\mu_z = \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}\mu_z(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

μ is the dipole moment, so we pull it out of the integral.

$$\mu_z = \mu_z \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

Using the idea that the transition moment μ_z changes on x, we express it as a derivative.

$$\mu_z = \frac{d\mu}{dx} \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

To evaluate the integral, we take advantage of a special Hermite relationship: $\sqrt{\alpha}xH_v(\sqrt{\alpha}x) = vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)$

$$\mu_z = \frac{N_v N_{v+1}}{\sqrt{\alpha}}\left(\frac{d\mu}{dx}\right) \int_{-\infty}^{\infty} H_{v+1}(\sqrt{\alpha}x)e^(-\alpha x^2/2)[vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)]dx$$

By inspection, it is clear that the integral only allows transitions of $\Delta v = \pm 1$, because for any other value, the integral will be zero.

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13.14: Group Theory Determines Infrared Activity

Determining if a Normal Modes is IR or Raman Active

A transition from $v \rightarrow v'$ is IR active if the **transition moment integral** contains the totally symmetric irreducible representation of the point group the molecule belongs to. The transition moment integral is derived from the one-dimensional harmonic oscillator. Using the definition of electric dipole moment μ, the integral is:

$$M(v \rightarrow v') = \langle \text{final wavefunction} | \vec{\mu} | \text{initial wavefunction} \rangle$$

or in terms of vibrational wavefunctions for a specific normal mode $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \vec{\mu} | \phi(v = 0) \rangle \tag{13.14.1}$$

assuming the transition from the $v = 0$ wavefunction to the $v' \neq 0$ wavefunction.

Now, consider the case that $\vec{\mu}$, is a constant and therefore independent of the vibration (i.e., the electric dipole moment does not change during the vibration). This it could be taken outside the integral in Equation 13.14.1 becomes

$$M(v \rightarrow v') = \vec{\mu} \langle \phi(v' \neq 0) | \phi(v = 0) \rangle \tag{13.14.2}$$

Since $|\phi(v = 0)\rangle$ and $|\phi(v =\neq 0)\rangle$ are mutually orthogonal to each other, the integral in Equation 13.14.1 will equal zero and the transition will **not** be allowed (i.e., it is forbidden). For the M to be nonzero, $\vec{\mu}$ must change during a vibration. This selection rule explains why homonuclear diatomic molecules do not produce an IR spectrum. There is no change in dipole moment resulting in a transition moment integral of zero and a transition that is forbidden.

For a transition to be Raman active, the same rules apply. The transition moment integral must contain the totally symmetric irreducible representation of the point group. The integral contains the polarizability tensor α (usually represented by a square matrix):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \alpha | \phi(v = 0) \rangle \tag{13.14.3}$$

Following a similar argument as above, α must be nonzero for the transition to be allowed and exhibits Raman scattering.

Character Table

For a molecule to be IR active the dipole moment has to change during the vibration. For a molecule to be Raman active the polarizability of the molecule has to change during the vibration. The reducible representation $\mathbf{\Gamma_{vib}}$ can also be found by determining the reducible representation of the 3N degrees of freedom of H_2O, Γ_{tot}. By applying Group Theory it is straightforward to find $\mathbf{\Gamma_{x,y,z}}$ as well as UMA (number of unmoved atoms). Again, using water as an example with C_{2v} symmetry where 3N = 9, $\mathbf{\Gamma_{tot}}$ can be determined:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\mathbf{T_{x,y,z}}$	3	-1	1	1	
UMA	3	1	1	3	
$\mathbf{\Gamma_{tot}}$	**9**	**-1**	**1**	**3**	$\mathbf{=3a_1 + a_2 + 2b_1 + 3b_2}$
Note that Γ_{tot} contains nine degrees of freedom consistent with 3N = 9.					

Γ_{tot} contains $\Gamma_{translational}$, $\Gamma_{rotational}$ as well as $\Gamma_{vibrational}$. Γ_{trans} can be obtained by finding the irreducible representations corresponding to x,y and z in the right side of the character table, Γ_{rot} by finding the ones corresponding to R_x, R_y and R_z. Γ_{vib} can be obtained by Γ_{tot} - Γ_{trans} - Γ_{rot}.

$$\Gamma_{vib}(H_2O) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2$$

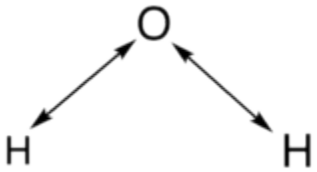
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation Γ_{vib} is necessary. If they contain the same irreducible representation, the mode is IR active.

For H_2O, z transforms as a_1, x as b_1 and y as b_2. The modes a1 and b2 are IR active since Γvib contains $2a_1 + b_2$.

In order to determine which modes are Raman active, the irreducible representation that corresponds to z^2, x^2-y^2, xy, xz and yz is used and again cross checked with Γvib. For H_2O, z^2 and x^2-y^2 transform as a_1, xy as a_2, xz as b_1 and yz as b_2.The modes a_1 and b_2 are also Raman active since Γ_{vib} contains both these modes.

The IR spectrum of H2O does indeed have three bands as predicted by Group Theory. The two symmetric stretches v1 and v2 occur at 3756 and 3657 cm-1 whereas the bending v3 motion occurs at 1595 cm-1.

In order to determine which normal modes are stretching vibrations and which one are bending vibrations, a stretching analysis can be performed. Then the stretching vibrations can be deducted from the total vibrations in order to obtain the bending vibrations. A double-headed arrow is drawn between the atom as depicted below:



Then a determination of how the arrows transform under each symmetry operation in C2v symmetry will yield the following results:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\Gamma_{stretch}$	2	0	0	2	**= a_1 + b_2**

$$\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} = 2a_1 + b_2 - a_1 - b_2 = a_1$$

H_2O has two stretching vibrations as well as one bending vibration. This concept can be expanded to complex molecules such as $PtCl4^-$. Four double headed arrows can be drawn between the atoms of the molecule and determine how these transform in D_{4h} symmetry. Once the irreducible representation for $\Gamma_{stretch}$ has been worked out, Γ_{bend} can be determined by $\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch}$.

Most molecules are in their zero point energy at room temperature. Therefore, most transitions do originate from the v=0 state. Some molecules do have a significant population of the v=1 state at room temperature and transitions from this thermally excited state are called **hot** bands.

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13.E: Molecular Spectroscopy (Exercises)

These are homework exercises to accompany Chapter 13 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q13.1

1. Calculate the energy difference for radiation wavenumber of, $\nu = 1.00 cm^{-1}$ including the type of molecular process that absorbs of this radiation corresponding to.
2. Given the wavelength of 3.4 x 10^{-4}, which molecular process does it fall into?
3. What are other advantages of knowing the spectroscopy of molecules?
4. Do you think the spectroscopy and molecular processes of the molecules have relationship to temperature? Explain.
5. What is other form that you can express in above equation?

Q13.20

The vibrational term of a diatomic molecule is

$$G(v) = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2 \chi_e \nu_e \tag{13.E.1}$$

Show that the spacing between adjacent levels is given by

$$\Delta G = G(v+1) - G(v) = \nu_e - 2\chi_e \nu_e (v+1)$$

Show that the maximum vibrational quantum number, v_{max} is given by

$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{13.E.2}$$

Use this result to show that the dissociation energy of the diatomic molecule can be written as

$$D_e = \frac{\nu_e - \nu_e \chi_e^2}{4\chi_e} \approx \frac{\nu_e}{4\chi_e} \tag{13.E.3}$$

Explain how the constants ν_e and χ_e can be evaluated from a plot of ΔG versus $v + 1$, called a Birge-Sponer plot. After finding these constants, determine the dissociation energy of the molecule. Use the following experimental data of H_2 to determine the dissociation energy of the molecule.

v	G(v) / cm^{-1}
0	4161.12
1	8087.11
2	11782.35
3	15250.36
4	18497.92
5	21505.65
6	24287.83
7	26830.97
8	29123.93
9	31150.19

v	G(v) / cm^{-1}
10	32886.65
11	34301.83
12	35351.01
13	35972.97

Explain why your plot is not linear for high values of v. How does this dissocation energy differ with the experimental value of $38269.48cm^{-1}$.

S13.20

$$\Delta G = G(v+1) - G(v) = \left(v+\frac{3}{2}\right)\nu_e - \left(v+\frac{3}{2}\right)^2 \chi_e\nu_e - \left(v+\frac{1}{2}\right)\nu_e + \left(v+\frac{1}{2}\right)^2 \chi_e\nu_e = \nu_e - \chi_e\nu_e(2v+2) = \nu_e - 2\chi_e\nu_e(v+1)$$

In the limit that $\Delta G \to 0, v \to v_{max}$, solving for v_{max} gives

$$0 = \nu_e - 2\chi_e\nu_e(v_{max}+1) \tag{13.E.4}$$

$$2\chi_e(v_{max}+1) = 1 \tag{13.E.5}$$

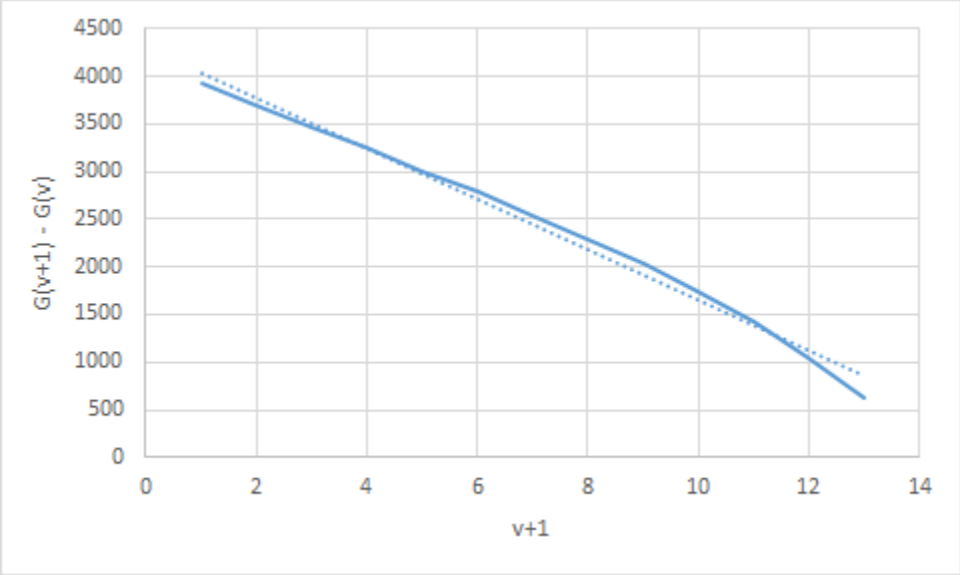
$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{13.E.6}$$

The molecule dissociates in the limit $\Delta G \to 0$, so the dissociation energy is given by

$$D_e = G(v_{max}) = (\frac{1}{2\chi_e} - \frac{1}{2})\nu_e - (\frac{1}{2\chi_e} - \frac{1}{2})^2\chi_e\nu_e = \frac{\nu_e}{2\chi_e}(1-\chi_e) - \frac{\nu_e}{4\chi_e}(1-\chi_e)^2 = \frac{\nu_e}{4\chi_e}(2-2\chi_e-1+2\chi_e-\chi_e^2) = \frac{\nu_e}{4\chi_e}(1$$

The final step can be made if we assume χ_e to be very small.

Looking at the equation for ΔG, we conclude that a plot of ΔG versus $v+1$ will have an intercept of ν_e and a slope of $-2\chi_e\nu_e$. The experimental data points for H_2 can be plotted as such:



If we use a best linear fit, we determine that the intercept is $\nu_e = 4164.4cm^{-1}$ and the slope is $-2\chi_e\nu_e = -232.01cm^{-1}$. Thus, $\chi_e = 0.0279$. Then, the dissociation energy is

$$D_e = \frac{\nu_e}{4\chi_e} = 37400cm^{-1} \tag{13.E.8}$$

The plot is not linear for large values of v because the potential curve is not well described by the anharmonic potential energy function.

Q13.21

An analysis of the vibrational spectrum of the ground-state homonuclear diatomic molecule Na_2 gives $\tilde{\nu}_e = 159.125\ \ cm^{-1}$ and $\tilde{\nu}_e\tilde{x}_e = 0.7255\ \ cm^{-1}$. Suggest an experimental method that can be used to determine there spectroscopic parameters. Use $\nu_{max} = \dfrac{1}{2\tilde{x}_e} - 1$ to determine the number of bound vibrational levels for ground state of Na_2.

S13.21

First solve for $\tilde{x}$:

$$\tilde{x} = \frac{0.7255\ cm^{-1}}{159.125\ cm^{-1}} = 4.5593 \times 10^{-3}\ cm^{-1} \tag{13.E.9}$$

Then plug it in to the equation:

$$\nu_{max} = \frac{1}{2 \times 4.5593 \times 10^{-3}\ cm^{-1}} - 1 = 109.67\ cm^{-1} \tag{13.E.10}$$

There are 109 bound vibrational levels for the ground state of Ne_2.

Q13.22

A Morse potential is a decent representation of internuclear potential and is modeled by

$$U(q) = D_e(1 - e^{-/betaq})^2 \tag{13.E.11}$$

where $q = R - R_e$. Prove the force constant for the Morse Potential is evaluated

$$k = 2D_e\beta^2 \tag{13.E.12}$$

If $D_e = 6.23 \times 10^{-19} J \cdot Molecule^{-1}$ and $\beta = 1.37 \times 10^{10} m^{-1}$ for a given compound, calculate the force constant for that compound.

S13.22

Using a Maclaurin series expansion of the Morse potential, the formula can be rewritten

$$U(q) = D_e(1 - e^{-\beta q})^2 = D_e(1 - (1 - \beta q + \frac{\beta^2 q^2}{2} O(q)^3))^2 = D_e(\beta^2 q^2 + O(q)^3) \tag{13.E.13}$$

We know that

$$U(q) = \frac{kq^2}{2} \tag{13.E.14}$$

assuming that $O(q)^3$ approaches zero, we get

$$\frac{kq^2}{2} = D_e(\beta^2 q^2 + O(q)^3) \implies k = 2D_e\beta^2 \tag{13.E.15}$$

Plugging in our given values, we get

$$l = 2(6.23 \times 10^{-19} J \cdot Molecule^{-1})(1.37 \times 10^{10})^2 = 234N \cdot m^{-1} \tag{13.E.16}$$

Q13.23

Given that $D_e = 7.33 \times 10^{-19} J \cdot molecule^{-1}, \tilde{v}_e = 1580.0 cm^{-1}, and R_e = 121 pm$, find k and β for $^{16}O_2$.

S13.23

Assuming a a harmonic oscillator model, we can use the equation:

$$\tilde{v}_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{13.E.17}$$

We can find k from the parameters given in the problem. Solving for k gives

$$k = (2\pi c \tilde{v}_e)^2 \mu \tag{13.E.18}$$

$$= [2\pi(3 \times 10^{10} cm \cdot s^{-1})(1580.0 cm^{-1})]^2 (7.9975 amu)(1.661 x 10^{-27} kg \cdot amu^{-1}) \tag{13.E.19}$$

$$= 1176.3 N \cdot m^{-1} \tag{13.E.20}$$

Using the equation:

$$\beta = \left(\frac{k}{2D_e}\right)^{1/2} \tag{13.E.21}$$

We can solve for β using the information above

$$\beta = \left[\frac{1176.3 N \cdot m^{-1}}{2(7.33 \times 10^{-19} J)}\right]^{1/2} \tag{13.E.22}$$

$$= 2.84 \times 10^{10} m^{-1} \tag{13.E.23}$$

Q13.24

The fundamental line in the IR spectrum of $^{12}C^{16}O\ cm^{-1}$, and the first overtone occurs at 4260.0 cm^{-1}. Find $\tilde{v}_e$ and $\tilde{x}_e\tilde{v}_e$ for $^{12}C^{16}O$.

S13.24

The equations for the fundamental frequency and the overtone are

$$\tilde{v} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e \tag{13.E.24}$$

and

$$\tilde{v} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e, \tag{13.E.25}$$

respectively.

We can set the fundamental frequency equal to $2143.0\ cm^{-1}$ and the first overtone equal to $4260.0\ cm^{-1}$ which is given from the problem statement. Then, we want to solve for $\tilde{x}_e\tilde{v}_e$.

Multiply the fundamental frequency by 3 and subtract the overtone.

$$\tilde{v}_e = [3(2143.0) - 4260.0] cm^{-1} = 2169.0 cm^{-1} \tag{13.E.26}$$

Then multiply the fundamental frequency by 2 and subtract from the overtone.

$$\tilde{x}_e\tilde{v}_e = 13.0 cm^{-1} \tag{13.E.27}$$

Q13.24

Which of the following molecules exhibit a microwave rotational absorption spectrum: BF_2,SO_2,C_2F_2,NO_3^-

S13.24

SO_2

notes: microwave rotational absorption correlates to the rotation of polyatomic molecules. Would BF_2 and NO_3^- also fall in this range?

Q13-25 Slightly Incorrect

Calculate the fundamental and the first two overtones of

$$H^{35}Cl \tag{13.E.28}$$

given

$$\tilde{v_e} = 2990.946 cm^{-1} \tag{13.E.29}$$

$$\tilde{x_e}\tilde{v_e} = 52.819 cm^{-1} \tag{13.E.30}$$

S13-25

Use equation,

$$\tilde{v_{obs}} = \tilde{v_e}\nu - \tilde{x_e}\tilde{v_e}\nu(\nu+1) \tag{13.E.31}$$

with v =1,2...

The fundamental frequency is given by v=1 and the first two overtones are given by v=2 and v=3.

Fundamental:

$$\tilde{v_{obs}} = \tilde{v_e} - 2\tilde{x_e}\tilde{v_e} = 2990.946 cm^{-1} - 2(52.819 cm^{-1}) = 2885.308 cm^{-1} \tag{13.E.32}$$

First overtone:

$$\tilde{v_{obs}} = 2\tilde{v_e} - 6\tilde{x_e}\tilde{v_e} = 2990.946 cm^{-1} - 6(52.819 cm^{-1}) = 5664.978 cm^{-1} \tag{13.E.33}$$

Second overtone:

$$\tilde{v_{obs}} = 3\tilde{v_e} - 12\tilde{x_e}\tilde{v_e} = 3(2990.946 cm^{-1}) - 12(52.819 cm^{-1}) = 8339.01 cm^{-1} \tag{13.E.34}$$

Q13.26

Plot the

$$\frac{\nu_{obs}}{\nu} \tag{13.E.35}$$

versus

$$(\nu+1) \tag{13.E.36}$$

for the anharmonic oscillator approximation and use it to determine the values of

$$\nu_e \tag{13.E.37}$$

and

$$x_e\nu_e \tag{13.E.38}$$

for

$$H^{3}5Cl \tag{13.E.39}$$

. Use the information in Table13.4.

S13.26

$$\nu_{obs} = \nu_{obs}\nu - x_e\nu_e\nu(\nu+1) \tag{13.E.40}$$

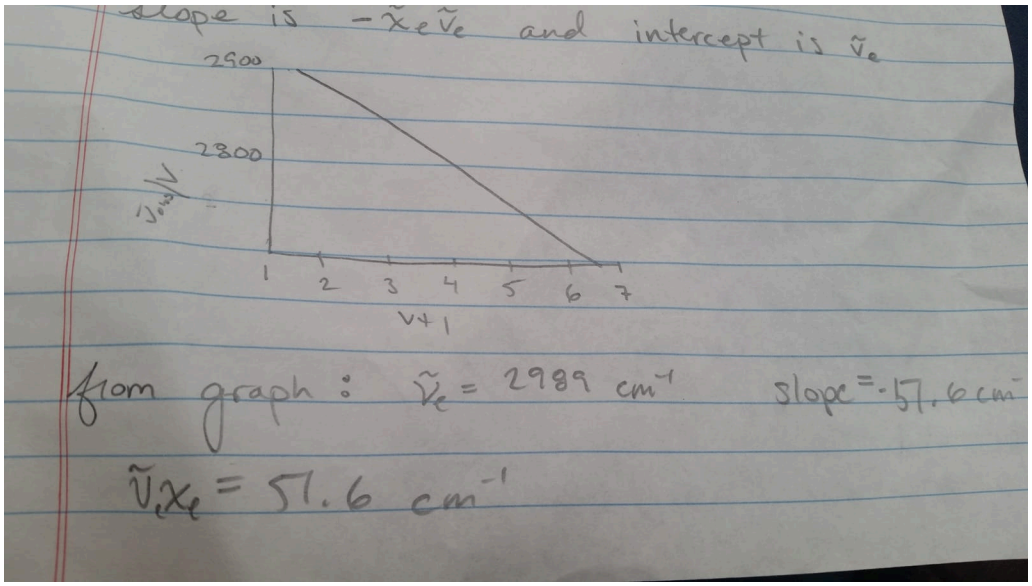
$$\frac{\nu_{obs}}{\nu} = \nu_e - x_e\nu_e(\nu+1) \tag{13.E.41}$$

The slope is

$$-x_e\nu_e \tag{13.E.42}$$

and the intercept is

$$\nu_e \tag{13.E.43}$$



The problem is nice and straight forward. It would be great for an explanation of why the slope is negative for an insight of the graph

Q13.31

Phosphorus nitride (PN) is a heteronuclear diatomic molecule that is a similar to N_2 with a triple bond, although is substantially weaker because P is a larger atomic radius than N. Using the following data, calculate $\tilde{\nu_e}'$ and $\tilde{\chi_e}'\ \tilde{\nu_e}'$ for PN.

IR Transition	$\nu_{\tilde{abs}}$ [cm^{-1}]
$0 \rightarrow 0$	39,699.10
$0 \rightarrow 1$	40,786.80
$0 \rightarrow 2$	41,858.90

S13.31

We will use the following equation:

$$\nu_{\tilde{abs}} = \nu_{\tilde{0,0}}' + \tilde{\nu_e}'\tilde{\nu}' - \tilde{\chi_e}'\tilde{\nu_e}'\tilde{\nu}'(\nu'+1) \tag{13.E.44}$$

Plugging in the appropriate values of ν', we get:

According to your table $\tilde{\nu_{0,0}}'$ should be 39,699.10 not 29,699.10.

- $\nu' = 0$:

$$\tilde{\nu_{0,0}}' = 29,699.10\ cm^{-1} \tag{1}$$

- $\nu' = 1$:

$$\tilde{\nu_{0,0}}' + \tilde{\nu_e}' - 2\tilde{\chi_e}'\tilde{\nu_e}' = 40,786.80\ cm^{-1} \tag{2}$$

- $\nu' = 2$:

$$\tilde{\nu_{0,0}}' + 2\tilde{\nu_e}' - 6\tilde{\chi_e}'\tilde{\nu_e}' = 41,858.90\ cm^{-1} \tag{3}$$

Solving as a system of equations, we subtract:

(2) - (1) = (4), (3) - (1) = (5), and finally (5) - 2x(4) = (6)

Equation (6) can be solved for $\tilde{\chi_e}'\tilde{\nu_e}'$, and then plugged back in to equation (4) or equation (5) to solve for $\tilde{\nu_e}'$. The answer is:

$$\tilde{\chi_e}'\tilde{\nu_e}' = 1103.3\ cm^{-1} \tag{13.E.45}$$

and

$$\tilde{\nu_e}' = 7.80\ cm^{-1} \tag{13.E.46}$$

from my calculations $\tilde{\nu_e}' = 1103.3$ and $\tilde{\chi_e}'\tilde{\nu_e}' = 7.80$ it looks like you had them switched

Q13.32

The frequencies of the first few vibronic transitions to an excited state of NaCl* are as follows:

Vibronic Transitions	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$
$\tilde{v}_{obs}/cm^{-}1$	12376	89706	15219

*not accurate values for NaCl

Use these data to calculate the values of $\tilde{v}_e$ and $\tilde{v}_e\tilde{x}_e$ for the excited state of NaCl

S13.32

$A = \tilde{v}'_e, B = \tilde{v}'_e\tilde{x}'_e$

$12376 = \tilde{v}_0, 0$

$89706 = \tilde{v}_0, 0 + \tilde{v}'_e - 2\tilde{v}'_e\tilde{x}'_e - 12376 = \tilde{v}_0, 0 = 77330 = +\tilde{v}'_e - 2\tilde{v}'_e\tilde{x}'_e$ (1)

$15219 = \tilde{v}_0, 0 + 2\tilde{v}'_e - 6\tilde{v}'_e\tilde{x}'_e - 12376 = \tilde{v}_0, 0 = 2843 = 2\tilde{v}'_e - 6\tilde{v}'_e\tilde{x}'_e$ (2)

77330 + 2B = A (1a)

2843 = 2A - 6B (2a)

77330+2B = A

2843 - 154660 = -2B

B = 75908.5 cm^{-1} = $\tilde{v}'_e$

A = 229147 cm^{-1} = $\tilde{v}'_e\tilde{x}'_e$

Q13.33

Determine the number of translational, rotational, and vibrational degrees of freedom in

a. Xe
b. HCl
c. CS_2
d. hemoglobin containing 9272 molecules

The total number of degrees of freedom is 3N, where N is the number of atoms in the molecule. All molecules have three translational degrees of freedom. A nonlinear molecule has three rotational degrees of freedom and a linear molecule has two rotational degrees of freedom. A linear molecule has $3N-5$ vibrational degrees of freedom and a nonlinear molecule has 3N — 6 vibrational degrees of freedom.

S13.33

The number of translational degrees of freedom is 3, the number of rotational degrees of freedom is 2 for linear molecules and 3 for non-linear molecules. Therefore, the remaining degrees of freedom, which is equal to 3N-5 for linear molecules or 3N-6 for non-linear molecules, is equal to the number of vibrational degrees of freedom.

	Translation	Rotation	Vibration	Total
Xe	3	0	0	3
HCl	3	2	1	6
CS_2	3	2	4	9
hemoglobin	3	3	27810	27816

Q13.36

Classify each of the following molecules as either a prolate or an oblate symmetric top: XeF_4, $ClCH_3$, NH_3, and C_6H_6.

S13.36

- XeF_4 :oblate
- $ClCH_3$:prolate
- NH_3:prolate
- C_6H_6:oblate

Q13.37

Solve for the components of the moment of inertia of a trigonal planar molecule if all the masses are m, the bond lengths are unit length, and all bond angles are 120°.

S13.37

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(sin^2 30^\circ) = \frac{3}{2}m \tag{13.E.47}$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(cos^2 30^\circ) = \frac{3}{2}m \tag{13.E.48}$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m \tag{13.E.49}$$

Q13.38

This problem illustrates how the principal moments of inertia can be obtained as an eigenvalue problem. Consider a molecule where all the masses are unit masses and the long and short bond lengths are 2 and 1, respectively.

Show that

$$I_{xx} = 2\cos^2\theta + 8\sin^2\theta \tag{13.E.50}$$

$$I_{yy} = 8\cos^2\theta + 2\sin^2\theta \tag{13.E.51}$$

$$I_{xy} = -6\cos\theta\sin\theta \tag{13.E.52}$$

Solve the secular determinant equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0 \tag{13.E.53}$$

and compare the result with the values of I_{xx} and I_{yy} that you would obtain if you align the "molecule" and coordinate system such that $\theta = 180^\circ$. What does this comparison tell you? What are the values of I_{xx} and I_{yy} if $\theta = 90$?

S13.38

We use trigonometric functions to find the x and y components

$$I_{xx} = \sum m_i y_i^2 = 2(1)(2\sin\theta)^2 + 2(1)\left[\sin\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\sin^2\theta + 2\cos^2\theta \tag{13.E.54}$$

$$I_{yy} = \sum m_i x_i^2 = 2(1)(2\cos\theta)^2 + 2(1)\left[\cos\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\cos^2\theta + 2\sin^2\theta \tag{13.E.55}$$

$$I_{xy} = -\sum m_i x_i y_i = -(2\cos\theta)(2\sin\theta) - 2\left[\cos(\pi) + \theta\right]\left[\sin(\pi) + \theta\right] - \left[\sin\left(\frac{\pi}{2}\right) - \theta\right]\left[\cos\left(\frac{\pi}{2}\right) - \theta\right] - \left[\cos\left(\frac{\pi}{2}\right) + \theta\right]\left[\sin\left(\frac{\pi}{2}\right.\right.$$

$$= -6\cos\theta\sin\theta$$

The secular determinantal equation becomes

$$\begin{vmatrix} 8\sin^2\theta + 2\cos^2\theta - \lambda & -6\cos\theta\sin\theta \\ -6\cos\theta\sin\theta & 8\cos^2\theta + 2\sin^2\theta - \lambda \end{vmatrix} = 0 \tag{13.E.57}$$

Expanding the determinant gives

$$0 = \lambda^2 - \lambda(10)(\sin\theta^2 + \cos\theta^2) + 16(\sin\theta^2 + \cos\theta^2)^2 \tag{13.E.58}$$

$$0 = \lambda^2 - 10\lambda + 16 \tag{13.E.59}$$

$$\lambda = 5 \pm 3 \tag{13.E.60}$$

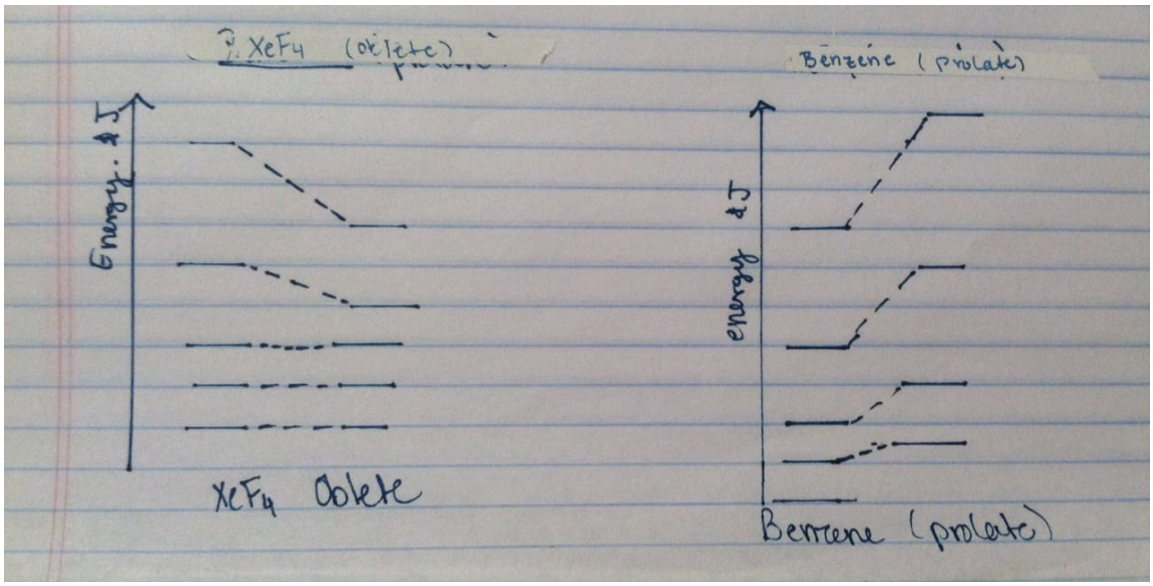
If $\theta = 180^\circ$ then $I_{xx} = 2, I_{yy} = 8, and I_{xy} = 0$. If $\theta = 90^\circ$ then $I_{xx} = 8, I_{yy} = 2, and I_{xy} = 0$. This tells us that the coordinate system does not affect the values of the principal momentum of inertia.

Q13.39

Sketch the energy level diagram of NH_3 (a prolate symmetric top molecule) and XeF_4 (an oblate symmetric top). How do they differ?

S13.39

The energies increase as the J levels increases for the prolate symmetry and the energies decrease as J increases for the oblate symmetry



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13.S: Molecular Spectroscopy (Summary)

In this chapter, we talk about what happens when light (expressed as an oscillating electric field) interacts with a quantum system, especially focusing on molecules. This requires use of time-dependent Schrödinger equation. What we will see is that a transition between two quantum states can take place when two conditions are met: first, the frequency of the electric field oscillation must be nearly equal to the energy difference between the two states, and second, the "transition dipole moment" between the states must be nonzero. Then, we will talk about the complete molecular Hamiltonian (instead of just the electronic Hamiltonian we've been discussing previously), and show how in many cases, we can separate it into an electronic part, a vibrational part, and a rotational part. We'll conclude by looking at a variety of types of spectroscopic processes in a general sense, as indicated by a Jablonski diagram.

Learning Objectives

By the end of this chapter, you should know the following:

- Solutions to the time-dependent Schrödinger equation
- Why light can cause a transition to occur between stationary states
- The significance of the transition dipole moment integral
- The resonance condition for absorption and emission
- How the nuclear Hamiltonian depends on the electronic Hamiltonian
- Nuclear degrees of freedom
- Which regions of the electromagnetic spectrum correspond to which types of molecular transitions
- How Jablonski diagrams illustrate types and energies of spectroscopic transitions
- Zero-point vibrational energy

Skill goals (what you should be able to do/calculate):

- Determine the time-dependent behavior of a stationary state
- Identify the degrees of freedom of a molecule (both the number and their types)
- Draw and label Jablonski diagrams, use them to calculate transition energies
- Compute frequencies and wavelengths of spectroscopic transitions in a variety of units
- Use simple approximations for electronic and vibrational structure to estimate transition energies
- Define zero-point vibrational energy, know where it comes from, and indicate it on a Jablonski diagram

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14: NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) is a physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation. This energy is at a specific resonance frequency which depends on the strength of the magnetic field and the magnetic properties of the isotope of the atoms. Many scientific techniques exploit NMR phenomena to study molecular physics, crystals, and non-crystalline materials through nuclear magnetic resonance spectroscopy. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

14.1: Nuclei Have Intrinsic Spin Angular Momenta

14.2: Magnetic Moments Interact with Magnetic Fields

14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz

14.4: The Magnetic Field Acting upon Nuclei in Molecules is Shielded

14.5: Chemical Shifts Depend upon the Chemical Environment of the Nucleus

14.6: Spin-Spin Coupling Can Lead to Multiplets in NMR Spectra

14.7: Spin-Spin Coupling Between Chemically Equivalent Protons is Not Observed

14.8: The n+1 Rule Applies Only to First-Order Spectra

14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

14.E: Nuclear Magnetic Resonance Spectroscopy (Exercises)

14.S: Nuclear Magnetic Resonance Spectroscopy (Summary)

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14.1: Nuclei Have Intrinsic Spin Angular Momenta

The electron, as well as certain other fundamental particles, possesses an intrinsic angular momentum or *spin*, in addition to its orbital angular momentum. These two types of angular momentum are analogous to the daily and annual motions, respectively, of the Earth around the Sun. To distinguish the spin angular momentum from the orbital, we designate the quantum numbers as s and m_s, in place of ℓ and *m*. For the electron, the quantum number s always has the value $\frac{1}{2}$, while m_s can have one of two values,$\pm\frac{1}{2}$. The electron is said to be an elementary particle of spin $\frac{1}{2}$. The proton and neutron also have spin $\frac{1}{2}$ and belong to the classification of particles called *fermions*, which are governed by the Pauli exclusion principle. Other particles, including the photon, have integer values of spin and are classified as *bosons*. These do *not* obey the Pauli principle, so that an arbitrary number can occupy the same quantum state. A complete theory of spin requires relativistic quantum mechanics. For our purposes, it is sufficient to recognize the two possible internal states of the electron, which can be called `spin up' and `spin down.' These are designated, respectively, by α and β as factors in the electron wavefunction. Spins play an essential role in determining the possible electronic states of atoms and molecules.

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14.2: Magnetic Moments Interact with Magnetic Fields

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.2.1}$$

You can see from Equation 14.2.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

Exercise 14.2.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

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14.4: The Magnetic Field Acting upon Nuclei in Molecules is Shielded

An isolated nucleus in an external magnetic field experiences the external magnetic field. However, a nucleus in a molecule, when the molecule is placed in an external magnetic field, does not experience the external magnetic field, due to interference by the magnetic field generated by the surrounding electrons. The magnetic field experienced by the nucleus is either slightly lower than the external magnetic field or slightly higher. If the magnetic field experienced by the nucleus is lower than the external magnetic field, the nucleus is said to be shielded; if it is higher, the nucleus is said to be deshielded.

- B_x = the external magnetic field
- B_y = the magnetic field experienced by the nucleus

If $B_y < B_x$, the nucleus is shielded. If $B_y > B_x$, the nucleus is deshielded

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14.5: Chemical Shifts Depend upon the Chemical Environment of the Nucleus

The chemical shift in NMR is extremely important, as it gives vital information about the local structure surrounding the nucleus of interest. For a majority of scientists, the chemical shift is used exlusivley to determine structure, especially in organic systems. Additional information may be gained by examining the anisotropy of the chemical shift. This section will be devoted to looking at chemical shift from a mathematical standpoint including a full treatment of the chemical shift tensor and the relation to the NMR lineshape.

The Chemical Shift

The local magnetic field is the field felt by a particular nucleus, where the applied field B induces currents in the electrons surrounding the nucleus give rise to a shielding. The shielding constant is σ. The local magnetic field is reduced by shielding by a factor $1-\sigma$.

$$B_{loc} = B + \delta B = (1–\sigma)B$$

The chemical shift is the difference between the resonance frequency of a nucleus and that of a standard.

The Larmor frequency of a shielded nucleus is:

$$\nu_L = \frac{\gamma B_{loc}}{2\pi}$$

Chemical shifts are reported on the δ-scale.

$$\delta = \frac{\nu–\nu_0}{\nu_0} \times 10^6$$

The resonance frequency of the standard is ν_0.

The shielding constant is the sum of three contributions.

$$\sigma = \sigma(local) + \sigma(molecule) + \sigma(solvent)$$

The local contribution is due to electrons on the atom that contains the nucleus. The molecular contribution is from the rest of the molecule. The solvent contribution is from surrounding solvent molecules.

The Local Contribution

The local contribution is a sum of both diamagnetic σ_d and paramagnetic σ_p parts. The diamagnetic part arises from circulation of the electrons in response to B. The Lamb formula gives the magnitude of σ_d,

$$\sigma_d = \frac{e^2 \mu_0}{3m_e} \int_o^\infty \rho(r) r \, dr$$

where ρ is the electron probability density $|\Psi^2|$. σ_d is inversely proportional to the **Bohr radius**. The magnetic moment of a current loop is proportional to a_o^2 and the magnetic field generated at the nucleus is proportional $\frac{1}{a_o^3}$.

The Molecular Contribution

The applied magnetic field generates currents in neighboring groups proportional to the magnetic susceptibility χ of a group. The induced magnetic moment gives rise to a magnetic field that is inversely proportional to the cube of the distance from the nucleus.

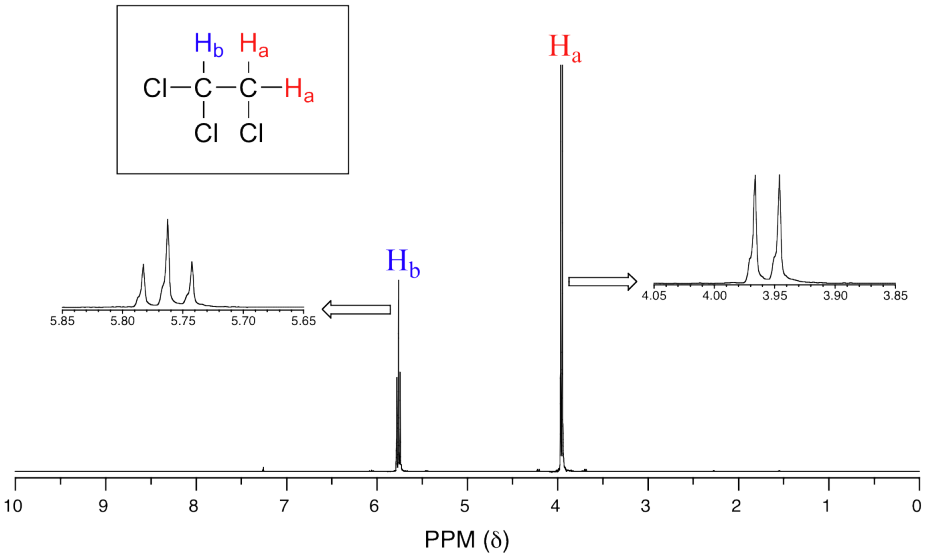
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14.6: Spin-Spin Coupling Can Lead to Multiplets in NMR Spectra

5.5A: The source of spin-spin coupling

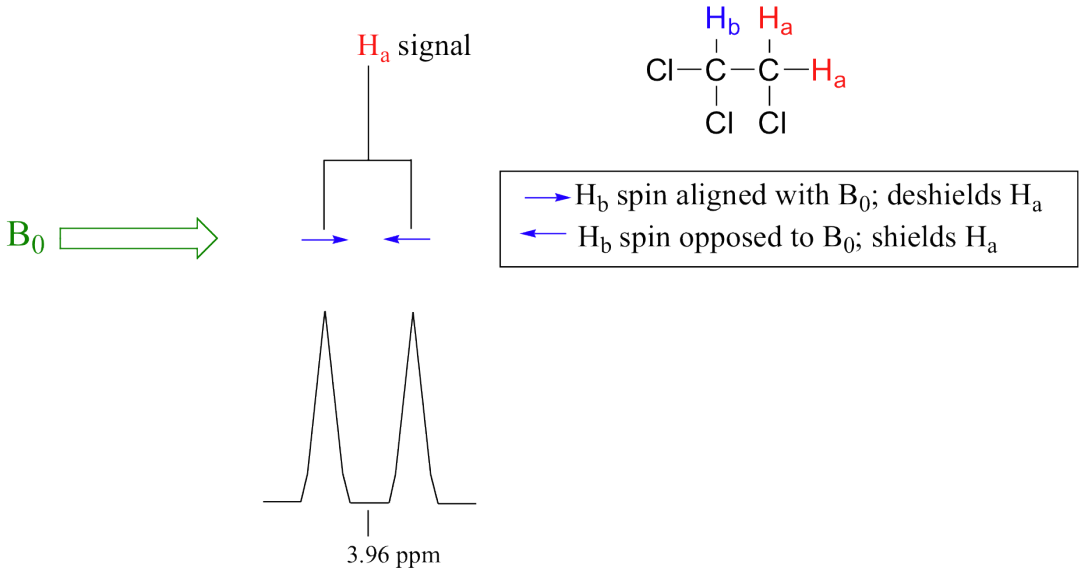
The ^{1}H-NMR spectra that we have seen so far (of methyl acetate and *para*-xylene) are somewhat unusual in the sense that in both of these molecules, each set of protons generates a single NMR signal. In fact, the ^{1}H-NMR spectra of most organic molecules contain proton signals that are 'split' into two or more sub-peaks. Rather than being a complication, however, this splitting behavior actually provides us with more information about our sample molecule.

Consider the spectrum for 1,1,2-trichloroethane. In this and in many spectra to follow, we show enlargements of individual signals so that the signal splitting patterns are recognizable.

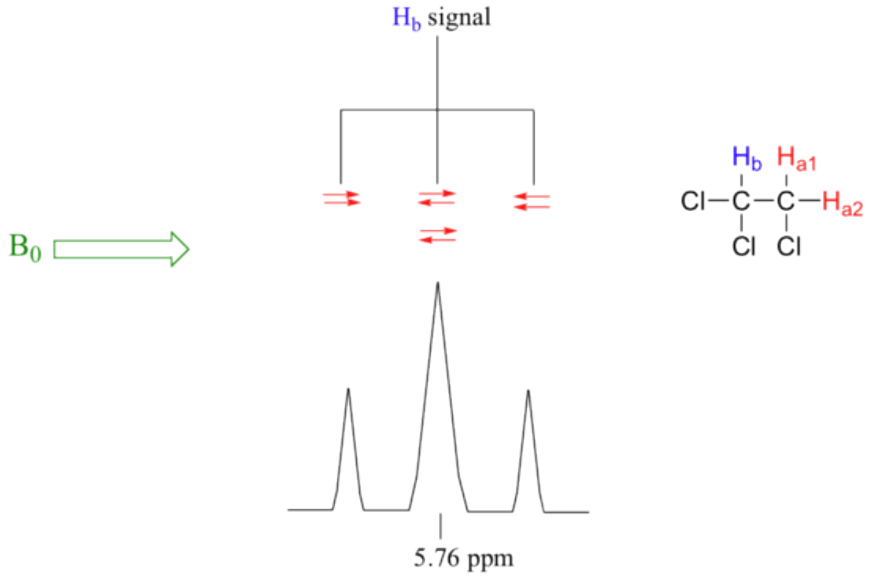


The signal at 3.96 ppm, corresponding to the two H_a protons, is split into two subpeaks of equal height (and area) – this is referred to as a **doublet**. The H_b signal at 5.76 ppm, on the other hand, is split into three sub-peaks, with the middle peak higher than the two outside peaks - if we were to integrate each subpeak, we would see that the area under the middle peak is twice that of each of the outside peaks. This is called a **triplet**.

The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, non-equivalent NMR-active nuclei. In our 1,1,2 trichloromethane example, the H_a and H_b protons are spin-coupled to each other. Here's how it works, looking first at the H_a signal: in addition to being shielded by nearby valence electrons, each of the H_a protons is also influenced by the small magnetic field generated by H_b next door (remember, each spinning proton is like a tiny magnet). The magnetic moment of H_b will be aligned *with* B_0 in (slightly more than) half of the molecules in the sample, while in the remaining half of the molecules it will be opposed to B_0. The B_{eff} 'felt' by H_a is a slightly weaker if H_b is aligned against B_0, or slightly stronger if H_b is aligned with B_0. In other words, in half of the molecules H_a is *shielded* by H_b (thus the NMR signal is shifted slightly upfield) and in the other half H_a is *deshielded* by H_b(and the NMR signal shifted slightly downfield). What would otherwise be a single H_a peak has been split into two sub-peaks (a doublet), one upfield and one downfield of the original signal. These ideas an be illustrated by a **splitting diagram**, as shown below.

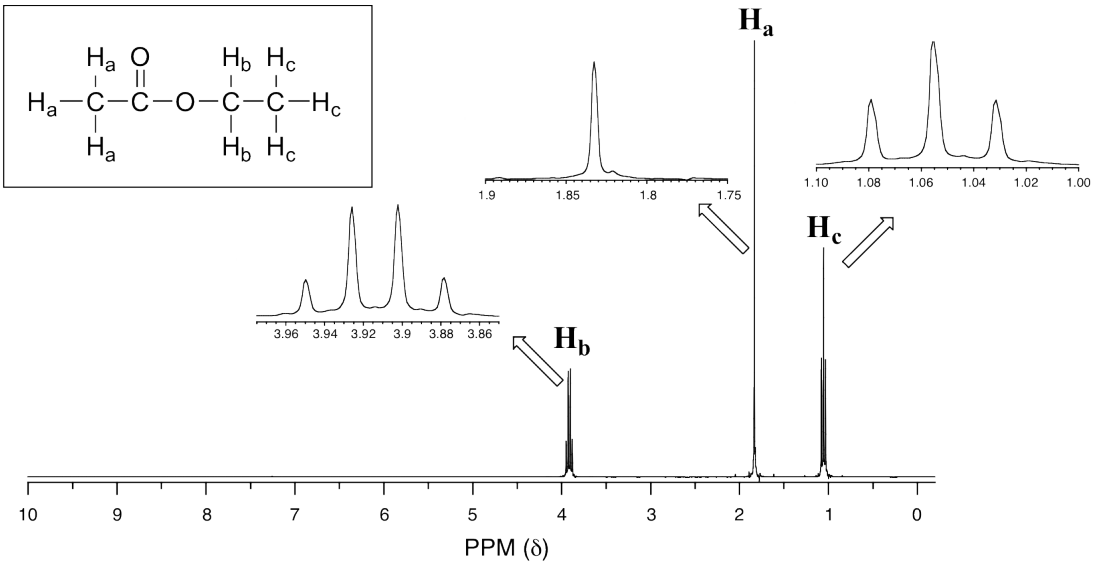


Now, let's think about the $H_b$signal. The magnetic environment experienced by H_b is influenced by the fields of both neighboring H_a protons, which we will call H_{a1} and H_{a2}. There are four possibilities here, each of which is equally probable. First, the magnetic fields of both H_{a1} and H_{a2} could be aligned with B_0, which would deshield H_b, shifting its NMR signal slightly downfield. Second, both the H_{a1} and H_{a2} magnetic fields could be aligned opposed to B_0, which would shield H_b, shifting its resonance signal slightly upfield. Third and fourth, H_{a1} could be with B_0 and H_{a2} opposed, or H_{a1}opposed to B_0 and H_{a2} with B_0. In each of the last two cases, the shielding effect of one H_a proton would cancel the deshielding effect of the other, and the chemical shift of H_b would be unchanged.



So in the end, the signal for H_b is a **triplet**, with the middle peak twice as large as the two outer peaks because there are *two* ways that H_{a1} and H_{a2} can cancel each other out.

Now, consider the spectrum for ethyl acetate:



We see an unsplit **'singlet'** peak at 1.833 ppm that corresponds to the acetyl (H_a) hydrogens – this is similar to the signal for the acetate hydrogens in methyl acetate that we considered earlier. This signal is unsplit because there are no adjacent hydrogens on the molecule. The signal at 1.055 ppm for the H_c hydrogens is split into a triplet by the two H_b hydrogens next door. The explanation here is the same as the explanation for the triplet peak we saw previously for 1,1,2-trichloroethane.

The $H_b$hydrogens give rise to a **quartet** signal at 3.915 ppm – notice that the two middle peaks are taller then the two outside peaks. This splitting pattern results from the spin-coupling effect of the *three* H_c hydrogens next door, and can be explained by an analysis similar to that which we used to explain the doublet and triplet patterns.

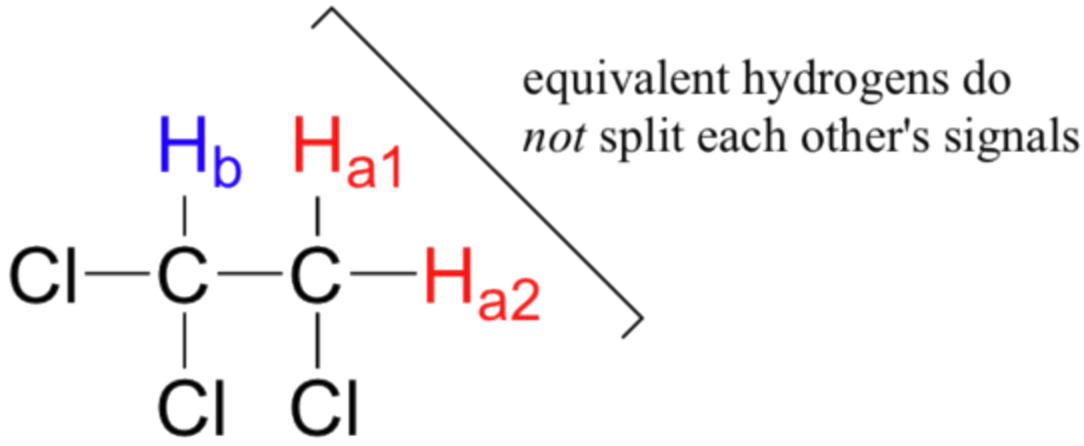
Example 5.6

a. Explain, using left and right arrows to illustrate the possible combinations of nuclear spin states for the H_c hydrogens, why the H_b signal in ethyl acetate is split into a quartet.
b. The integration ratio of doublets is 1:1, and of triplets is 1:2:1. What is the integration ratio of the H_b quartet in ethyl acetate? (Hint – use the illustration that you drew in part a to answer this question.)

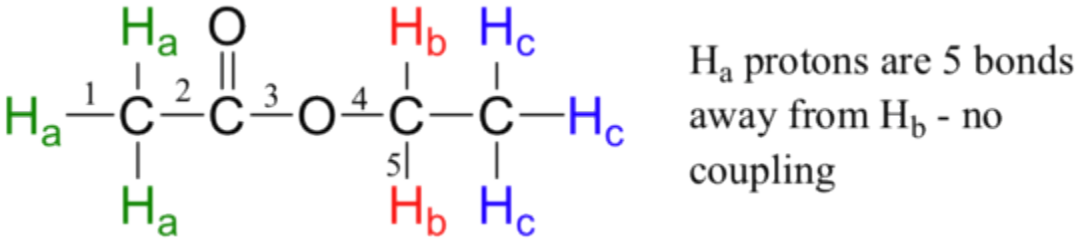
Solution

By now, you probably have recognized the pattern which is usually referred to as the ***n* + 1 rule**: if a set of hydrogens has *n* neighboring, non-equivalent hydrogens, it will be split into *n* + 1 subpeaks. Thus the two H_b hydrogens in ethyl acetate split the H_c signal into a triplet, and the three H_c hydrogens split the H_b signal into a quartet. This is very useful information if we are trying to determine the structure of an unknown molecule: if we see a triplet signal, we know that the corresponding hydrogen or set of hydrogens has two `neighbors`. When we begin to determine structures of unknown compounds using ^{1}H-NMR spectral data, it will become more apparent how this kind of information can be used.

Three important points need to be emphasized here. First, signal splitting only occurs between non-equivalent hydrogens – in other words, H_{a1} in 1,1,2-trichloroethane is *not* split by H_{a2}, and vice-versa.

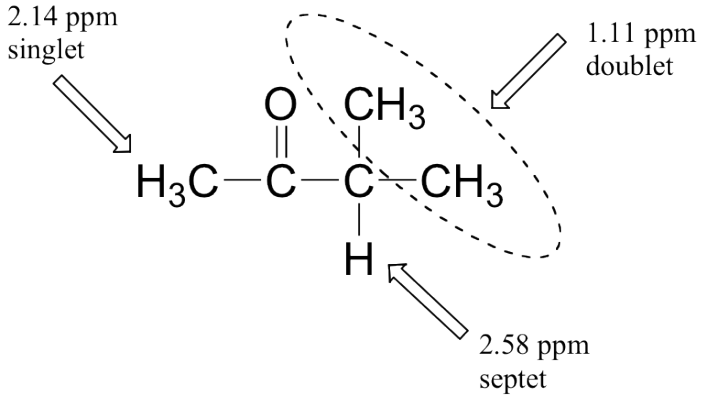


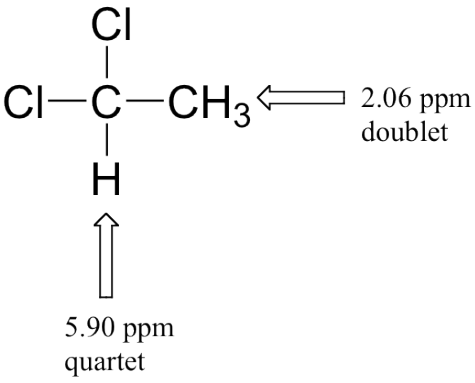
Second, splitting occurs primarily between hydrogens that are separated by three bonds. This is why the H_a hydrogens in ethyl acetate form a singlet– the nearest hydrogen neighbors are five bonds away, too far for coupling to occur.

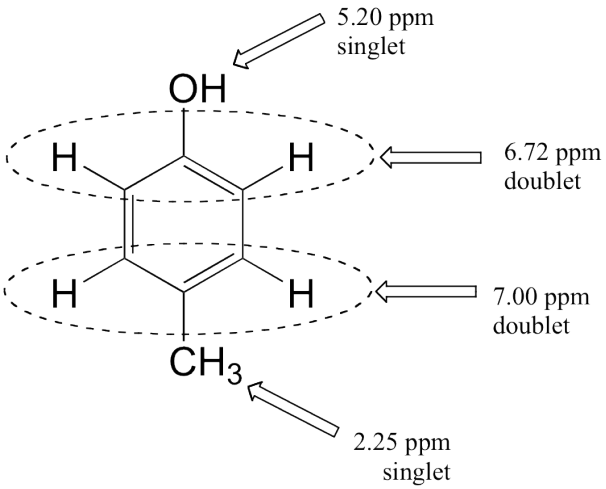


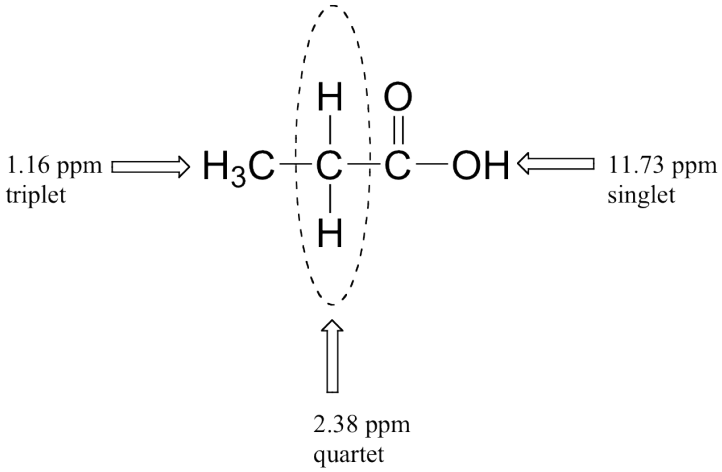
Occasionally we will see four-bond and even 5-bond splitting, but in these cases the magnetic influence of one set of hydrogens on the other set is much more subtle than what we typically see in three-bond splitting (more details about how we quantify coupling interactions is provided in section 5.5B). Finally, splitting is most noticeable with hydrogens bonded to carbon. Hydrogens that are bonded to heteroatoms (alcohol or amino hydrogens, for example) are coupled weakly - or not at all - to their neighbors. This has to do with the fact that these protons exchange rapidly with solvent or other sample molecules.

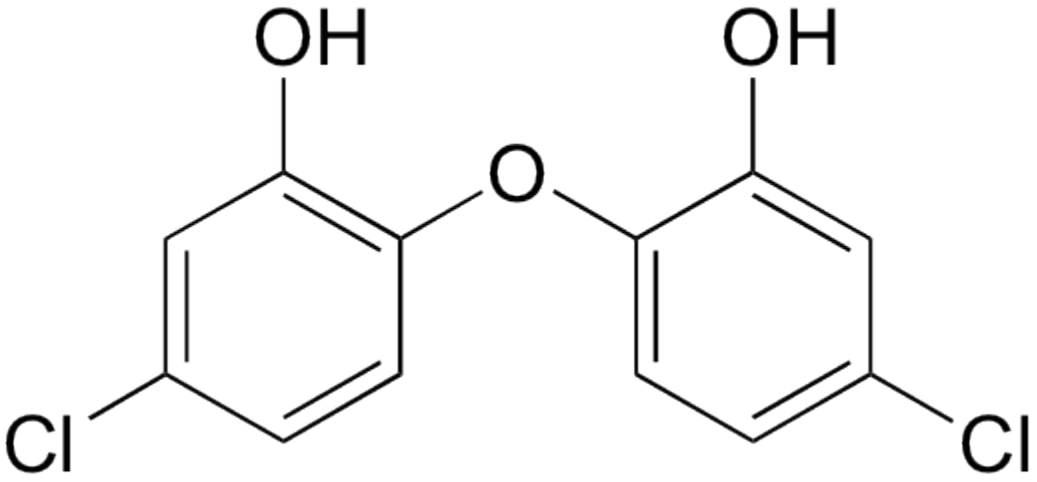
Below are a few more examples of chemical shift and splitting pattern information for some relatively simple organic molecules.











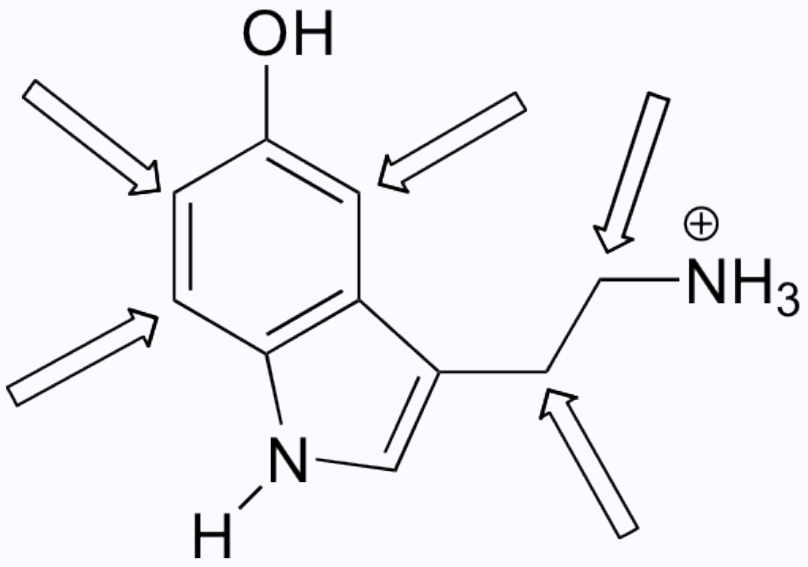
Example 5.7

a. How many proton signals would you expect to see in the ^{1}H-NMR spectrum of triclosan (a common antimicrobial agent found in detergents)? For each of the proton signals, predict the splitting pattern. Assume that you see only 3-bond coupling.

Solution

Example 5.8

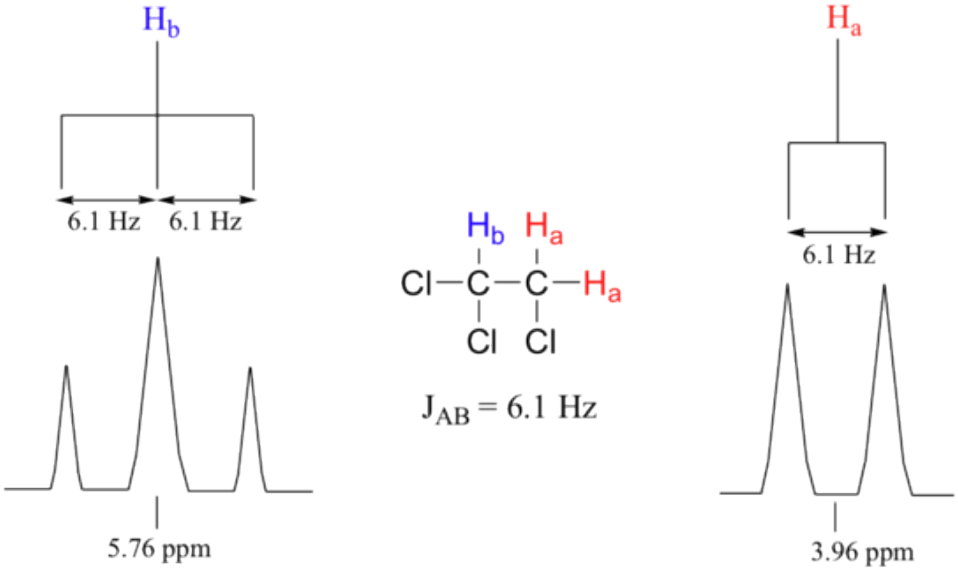
Predict the splitting pattern for the ^{1}H-NMR signals corresponding to the protons at the locations indicated by arrows (the structure is that of the neurotransmitter serotonin).



Solution

5.5B: Coupling constants

Chemists quantify the spin-spin coupling effect using something called the **coupling constant**, which is abbreviated with the capital letter *J*. The coupling constant is simply the difference, expressed in Hz, between two adjacent sub-peaks in a split signal. For our doublet in the 1,1,2-trichloroethane spectrum, for example, the two subpeaks are separated by 6.1 Hz, and thus we write $^{3}J_{a\text{-}b}$ = 6.1 Hz.

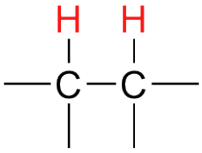


The superscript 3 tells us that this is a three-bond coupling interaction, and the a-b subscript tells us that we are talking about coupling between H_a and H_b. Unlike the chemical shift value, *the coupling constant, expressed in Hz, is the same regardless of the applied field strength of the NMR magnet*. This is because the strength of the magnetic moment of a neighboring proton, which is the source of the spin-spin coupling phenomenon, does *not* depend on the applied field strength.

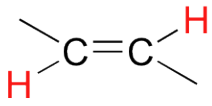
When we look closely at the triplet signal in 1,1,2-trichloroethane, we see that the coupling constant - the `gap` between subpeaks - is 6.1 Hz, the same as for the doublet. This is an important concept! The coupling constant $^{3}J_{a\text{-}b}$ quantifies the magnetic

interaction between the H_a and H_b hydrogen sets, and *this interaction is of the same magnitude in either direction*. In other words, H_a influences H_b to the same extent that H_b influences H_a. When looking at more complex NMR spectra, this idea of **reciprocal coupling constants** can be very helpful in identifying the coupling relationships between proton sets.

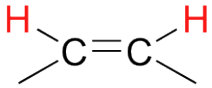
Coupling constants between proton sets on neighboring sp^3-hybridized carbons is typically in the region of 6-8 Hz. With protons bound to sp^2-hybridized carbons, coupling constants can range from 0 Hz (no coupling at all) to 18 Hz, depending on the bonding arrangement.



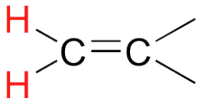
^3J = 6-8 Hz



vinylic *trans*:
^3J = 11-18 Hz

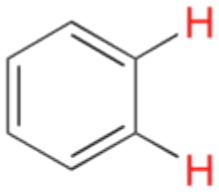


vinylic *cis*:
^3J = 6-15 Hz

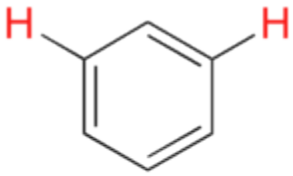


vinylic *gem*:
^2J = 0-5 Hz

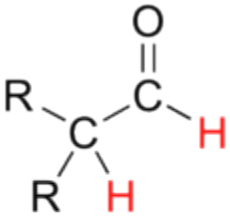
For vinylic hydrogens in a *trans* configuration, we see coupling constants in the range of ^3J = 11-18 Hz, while *cis* hydrogens couple in the ^3J = 6-15 Hz range. The 2-bond coupling between hydrogens bound to the same alkene carbon (referred to as geminal hydrogens) is very fine, generally 5 Hz or lower. *Ortho* hydrogens on a benzene ring couple at 6-10 Hz, while 4-bond coupling of up to 4 Hz is sometimes seen between *meta* hydrogens.



ortho-benzylic:
^3J = 6-10 Hz



meta-benzylic:
^4J = 0-4 Hz

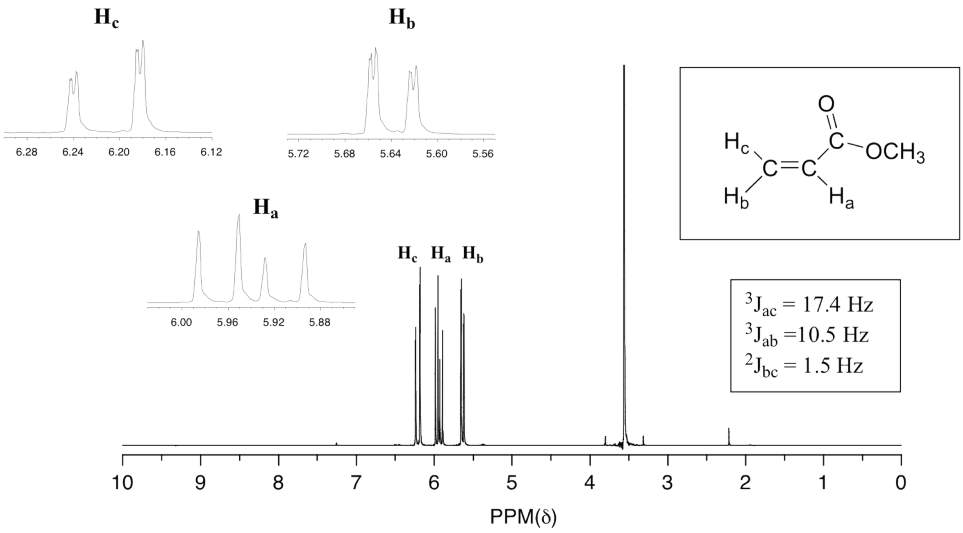


aldehyde:
^3J = 2-3 Hz

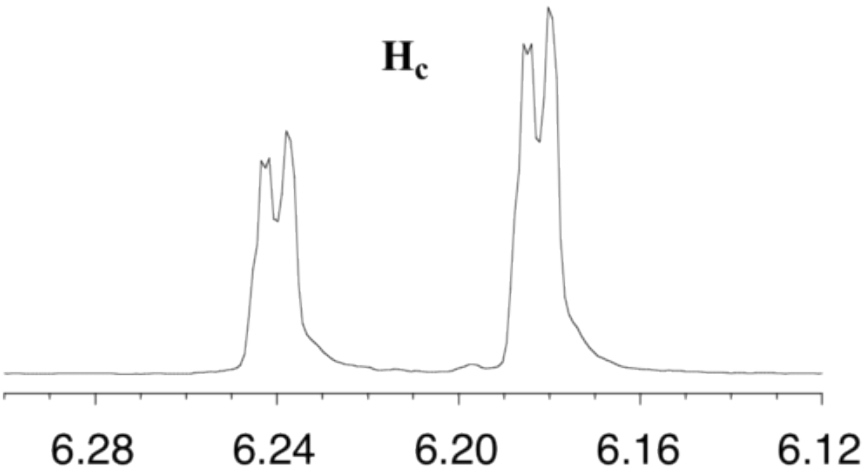
Fine (2-3 Hz) coupling is often seen between an aldehyde proton and a three-bond neighbor. Table 4 lists typical constant values.

5.5C: Complex coupling

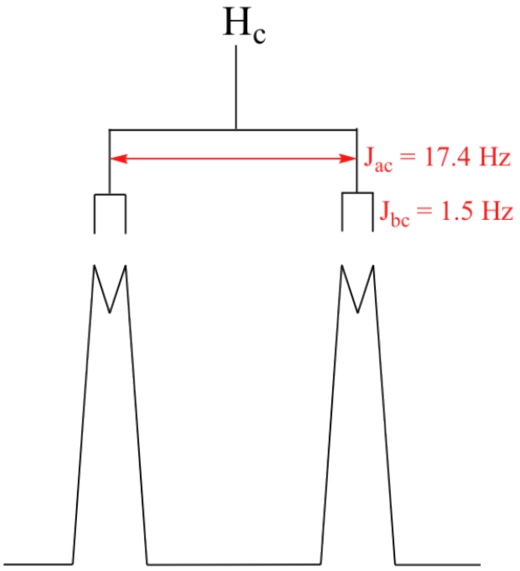
In all of the examples of spin-spin coupling that we have seen so far, the observed splitting has resulted from the coupling of one set of hydrogens to *just one* neighboring set of hydrogens. When a set of hydrogens is coupled to *two or more* sets of nonequivalent neighbors, the result is a phenomenon called **complex coupling**. A good illustration is provided by the ^{1}H-NMR spectrum of methyl acrylate:



First, let's first consider the H_c signal, which is centered at 6.21 ppm. Here is a closer look:

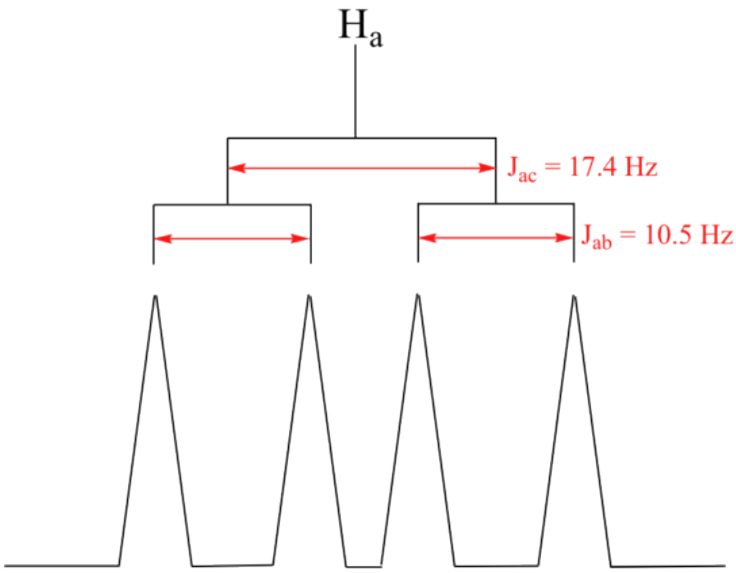


With this enlargement, it becomes evident that the Hc signal is actually composed of four sub-peaks. Why is this? H_c is coupled to both H_a and H_b , but with *two different coupling constants*. Once again, a splitting diagram can help us to understand what we are seeing. H_a is *trans* to H_c across the double bond, and splits the H_c signal into a doublet with a coupling constant of $^3J_{ac}$ = 17.4 Hz. In addition, each of these H_c doublet sub-peaks is split again by H_b (*geminal* coupling) into two more doublets, each with a much smaller coupling constant of $^2J_{bc}$ = 1.5 Hz.

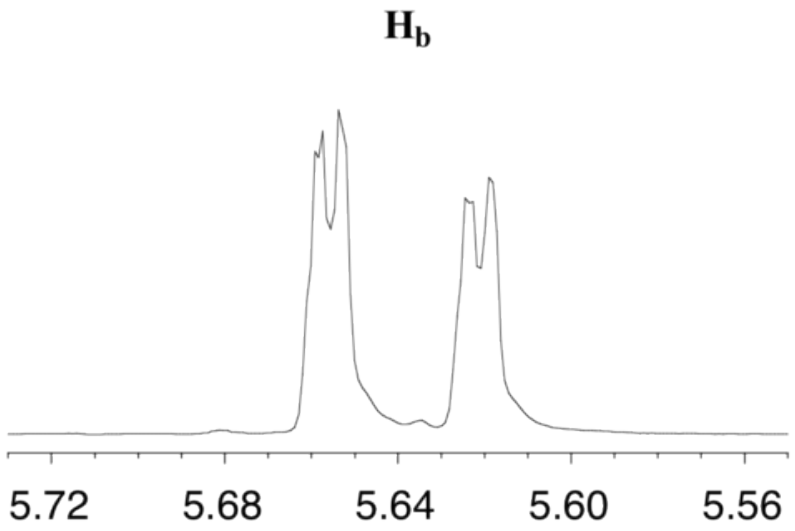


The result of this `double splitting` is a pattern referred to as a **doublet of doublets**, abbreviated `**dd**`.

The signal for H_a at 5.95 ppm is also a doublet of doublets, with coupling constants $^3J_{ac}$= 17.4 Hz and $^3J_{ab}$ = 10.5 Hz.



The signal for H_b at 5.64 ppm is split into a doublet by H_a, a *cis* coupling with $^3J_{ab}$ = 10.4 Hz. Each of the resulting sub-peaks is split again by H_c, with the same *geminal* coupling constant $^2J_{bc}$ = 1.5 Hz that we saw previously when we looked at the H_c signal. The overall result is again a doublet of doublets, this time with the two `sub-doublets` spaced slightly closer due to the smaller coupling constant for the *cis* interaction. Here is a blow-up of the actual $H_b$signal:



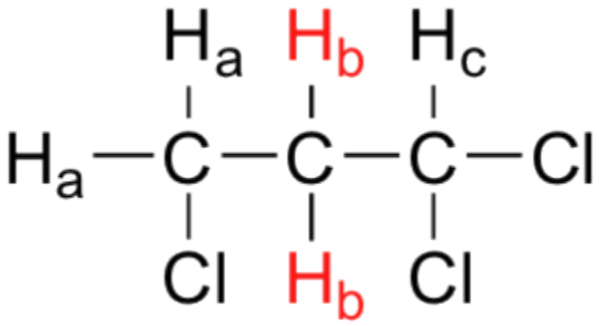
Example 5.9

Construct a splitting diagram for the H_b signal in the ^{1}H-NMR spectrum of methyl acrylate. Show the chemical shift value for each sub-peak, expressed in Hz (assume that the resonance frequency of TMS is exactly 300 MHz).

Solution

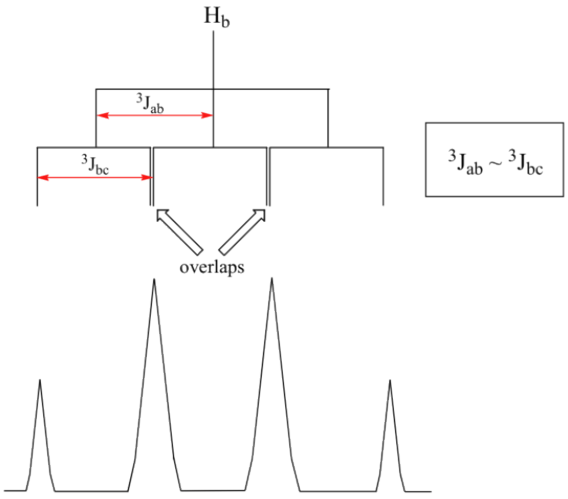
When constructing a splitting diagram to analyze complex coupling patterns, it is usually easier to show the larger splitting first, followed by the finer splitting (although the reverse would give the same end result).

When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the simple `*n* + 1 rule` of non-complex splitting. In the spectrum of 1,1,3-trichloropropane, for example, we would expect the signal for H_b to be split into a triplet by H_a, and again into doublets by H_c, resulting in a 'triplet of doublets'.



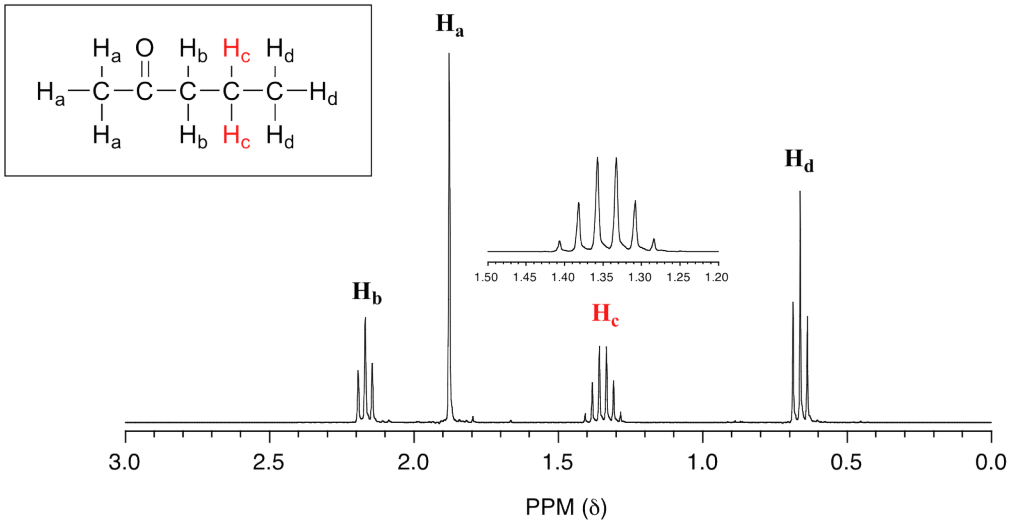
$$^3J_{ab} \sim {}^3J_{bc}$$

H_a and H_c are not equivalent (their chemical shifts are different), but it turns out that $^3J_{ab}$ is very close to $^3J_{bc}$. If we perform a splitting diagram analysis for H_b, we see that, due to the overlap of sub-peaks, the signal appears to be a quartet, and for all intents and purposes follows the *n* + 1 rule.



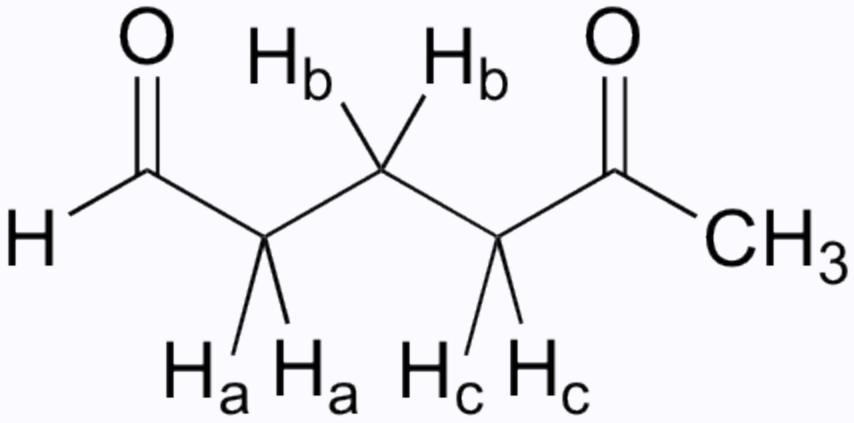
triplet of doublets becomes a quartet
when coupling constants are close

For similar reasons, the H_c peak in the spectrum of 2-pentanone appears as a sextet, split by the five combined H_b and H_d protons. Technically, this 'sextet' could be considered to be a 'triplet of quartets' with overlapping sub-peaks.



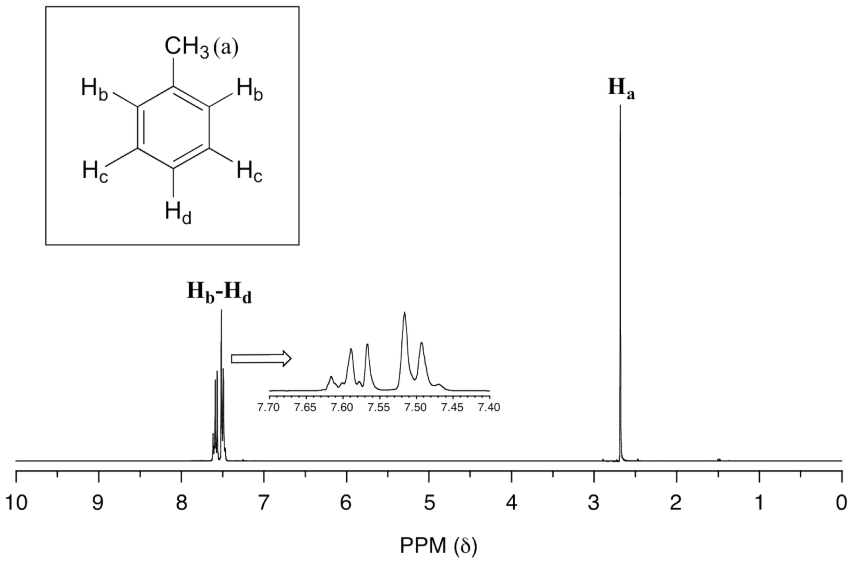
Example 5.10

What splitting pattern would you expect for the signal coresponding to H_b in the molecule below? Assume that J_{ab} ~ J_{bc}. Draw a splitting diagram for this signal, and determine the relative integration values of each subpeak.



Solution

In many cases, it is difficult to fully analyze a complex splitting pattern. In the spectrum of toluene, for example, if we consider only 3-bond coupling we would expect the signal for H_b to be a doublet, H_d a triplet, and H_c a triplet.



In practice, however, all three aromatic proton groups have very similar chemical shifts and their signals overlap substantially, making such detailed analysis difficult. In this case, we would refer to the aromatic part of the spectrum as a **multiplet**.

When we start trying to analyze complex splitting patterns in larger molecules, we gain an appreciation for why scientists are willing to pay large sums of money (hundreds of thousands of dollars) for higher-field NMR instruments. Quite simply, the stronger our magnet is, the more resolution we get in our spectrum. In a 100 MHz instrument (with a magnet of approximately 2.4 Tesla field strength), the 12 ppm frequency 'window' in which we can observe proton signals is 1200 Hz wide. In a 500 MHz (~12 Tesla) instrument, however, the window is 6000 Hz - five times wider. In this sense, NMR instruments are like digital cameras and HDTVs: better resolution means more information and clearer pictures (and higher price tags!)

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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14.7: Spin-Spin Coupling Between Chemically Equivalent Protons is Not Observed

When doing NMR spectroscopy, it is an observed fact that equivalent hydrogens do not split one another. Why don't equivalent hydrogens split each other's signals? For example, why is the NMR spectrum for ethane a singlet instead of a quartet or even a dodecuplet (due to the hydrogens on the same carbon)? What is so special about hydrogens being equivalent to one another that causes no splitting to be observed?

Finding the states between which transitions occur

The Hamiltonian for two coupled spins is

$$\hat{H} = \omega_1 \hat{I}_{1z} + \omega_2 \hat{I}_{2z} + \frac{2\pi J_{12}}{\hbar}(\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) \tag{14.7.1}$$

where ω_1 and ω_2 are the Larmor frequencies[2] of the two nuclei and J_{12} is the coupling constant (in Hz) between the two nuclei. (The factor of $2\pi/\hbar$ is simply there to bring it into energy units.) $\hat{I}_i$ is the operator for the spin angular momentum of nucleus i and $\hat{I}_{iz}$ is the operator for its projection along the z-axis.

However, in NMR, it is customary to work in frequency units instead of energy units. Since $E = h\nu$, we simply need to divide through by h. Bearing in mind that $\omega = 2\pi\nu$ and $h = 2\pi\hbar$, we get:

$$\hat{H}_{\text{freq}} = \frac{\nu_1}{\hbar}\hat{I}_{1z} + \frac{\nu_2}{\hbar}\hat{I}_{2z} + \frac{J_{12}}{\hbar^2}(\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) \tag{14.7.2}$$

On top of that, to make the math easier, it is also quite common to set $\hbar = 1$. Therefore, we have

$$\hat{H}_{\text{freq}} = \nu_1 \hat{I}_{1z} + \nu_2 \hat{I}_{2z} + J_{12}(\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) \tag{14.7.3}$$

We will deal with two spin-$1/2$ nuclei here, where $|\alpha\rangle$ and $|\beta\rangle$ represent the "up" and "down" spins (recall we set $\hbar = 1$ so it doesn't appear in the eigenvalues):

$$\hat{I}_{iz}|\alpha_i\rangle = \frac{1}{2}|\alpha_i\rangle \qquad \hat{I}_{iz}|\beta_i\rangle = -\frac{1}{2}|\beta_i\rangle \qquad (i = 1, 2)$$

Furthermore since we are dealing with equivalent nuclei we can simply set $\nu_1 = \nu_2 = \nu$ and drop the subscript in J_{12} just to make it a bit cleaner:

$$\hat{H} = \nu(\hat{I}_{1z} + \hat{I}_{2z}) + J(\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) \tag{14.7.4}$$

Now, we need to find the eigenstates and eigenvalues of $\hat{H}$. To do so, we will adopt the basis set of product functions $(|\alpha_1\alpha_2\rangle, |\alpha_1\beta_2\rangle, |\beta_1\alpha_2\rangle, |\beta_1\beta_2\rangle)$. From equation (4) we have

Multiple \label

The action of the scalar product $\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2$ is more complicated. We need to introduce the *shift operators* (or *ladder operators*).

$$\hat{I}_{i+} = \hat{I}_{ix} + \mathrm{i}\hat{I}_{iy} \qquad \hat{I}_{i-} = \hat{I}_{ix} - \mathrm{i}\hat{I}_{iy}$$

from which we can obtain

$$\hat{I}_{ix} = \frac{\hat{I}_{i+} + \hat{I}_{i-}}{2} \qquad \hat{I}_{iy} = \frac{\hat{I}_{i+} - \hat{I}_{i-}}{2\mathrm{i}}$$

So, finally, we can write

Multiple \label

where in going from (12) to (13) one simply substitutes in (11) and does a fair bit of algebraic manipulation. The action of the shift operators are

$$\hat{I}_{i+}|\alpha_i\rangle = 0 \qquad \hat{I}_{i+}|\beta_i\rangle = |\alpha_i\rangle \tag{14}$$
$$\hat{I}_{i-}|\alpha_i\rangle = |\beta_i\rangle \qquad \hat{I}_{i-}|\beta_i\rangle = 0 \tag{14}$$

This allows you to work out the effect of $\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2$ on our basis states. The actual math is left to the reader and I will simply quote the results:

Multiple \label

Therefore in this basis the Hamiltonian matrix is

$$\mathbf{H} = \begin{pmatrix} \nu + J/4 & 0 & 0 & 0 \\ 0 & -J/4 & J/2 & 0 \\ 0 & J/2 & -J/4 & 0 \\ 0 & 0 & 0 & -\nu + J/4 \end{pmatrix} \tag{14.7.5}$$

Finding the eigenvectors and eigenvalues of this matrix is again left to the reader (it is not a difficult task) and they are (eigenvalues denoted \(E_i$)

Multiple \label

The form of the eigenstates should be familiar: they are simply the triplet and singlet states of two spin-$1/2\) particles. These states arise from the coupling of two sources of angular momenta, I_1 and I_2, to form one overall angular momentum denoted I.

$$\vec{I} = \vec{I}_1 + \vec{I}_2 \tag{14.7.6}$$

The allowed values of I are determined by the **Clebsch-Gordan series**:

$$I = I_1 + I_2, I_1 + I_2 - 1, \cdots, |I_1 - I_2| \tag{14.7.7}$$

Since $I_1 = I_2 = 1/2$, I can take the values 1 and 0. The values of M_I, the projection of the total angular momentum along the \(z$-axis, are as usual

$$M_I = I, I-1, \cdots, -I \tag{14.7.8}$$

so the states with $I = 1$ ("triplet") have $M_I = 1, 0, -1$ and the state with $I = 0$ ("singlet") has $M_I = 0$. One can use more quantum mechanics to work out which state is associated with which quantum numbers, but I will not do it here. They are:

State	I	M_I
$\|1\rangle$	1	1
$\|2\rangle$	1	0
$\|3\rangle$	0	0
$\|4\rangle$	1	-1

Selection rules

We have four different states, which leads to $\binom{4}{2} = 6$ different possible transitions. However, not all of these transitions are allowed.

The intensity of the transition is proportional to the square of the matrix element $\langle\psi_\mathrm{f}|\hat{H}'|\psi_\mathrm{i}\rangle$ (the so-called "transition dipole moment"), where $\hat{H}'$ is the Hamiltonian for the process that induces the transition. In the case of NMR transitions, the transition arises due to a magnetic field aligned along the \(x$-axis.[3] The corresponding Hamiltonian is therefore

$$\hat{H}' = \omega'(\hat{I}_{1x} + \hat{I}_{2x}) = \omega'\hat{I}_x \tag{14.7.9}$$

Exactly what ω' represents is not important here because we are only really concerned about whether the transition dipole moment is zero or not.[4] Making use of the relations established in equations ??? and ???,[5] one can find that the selection rules are

$$\Delta I = 0; \Delta M_I = \pm 1 \tag{14.7.10}$$

which means that the allowed transitions are $|4\rangle \leftrightarrow |2\rangle$ and $|2\rangle \leftrightarrow |1\rangle$. Transitions to and from the singlet state $|3\rangle$ are forbidden. The energies of the transitions are

Multiple \label

i.e. the two transitions are degenerate and only one line in the spectrum at frequency ν is observed. This is exactly what is depicted in the diagrams posted in the other answers.

the two transitions are degenerate and only one line in the spectrum at frequency ν is observed.

Notes and references

[1] I am assuming the reader has some knowledge of the quantum mechanical treatment of angular momentum, which is a topic that is treated thoroughly in most quantum mechanics textbooks. See, for example, chapter 4 of Atkins's *Molecular Quantum Mechanic*s (5th ed.).

[2] The Larmor frequency is given by $\omega = -\gamma B_0$, where γ is the magnetogyric ratio of the nucleus in question and B_0 is the strength of the external magnetic field. It represents the frequency with which a magnetic moment precesses about a magnetic field. See any textbook on magnetism for further details.

[3] I am glossing over some details here. The so-called magnetic field in the $x$$ $-axisisacomponentoftheradiofrequencypulseappliedinthe\(xy$-plane. If you are interested please consult a textbook on the vector model of NMR. In particular I recommend Keeler's *Understanding NMR Spectroscopy* (2nd ed.).

[4] It is related to the strength of the magnetic field in the x-axis, B_1, by $w' = |\gamma| B_1$. The usual symbol is ω_1, but I chose not to use this here to avoid potential confusion. Again, please consult a textbook on the vector model of NMR if you wish to find out more.

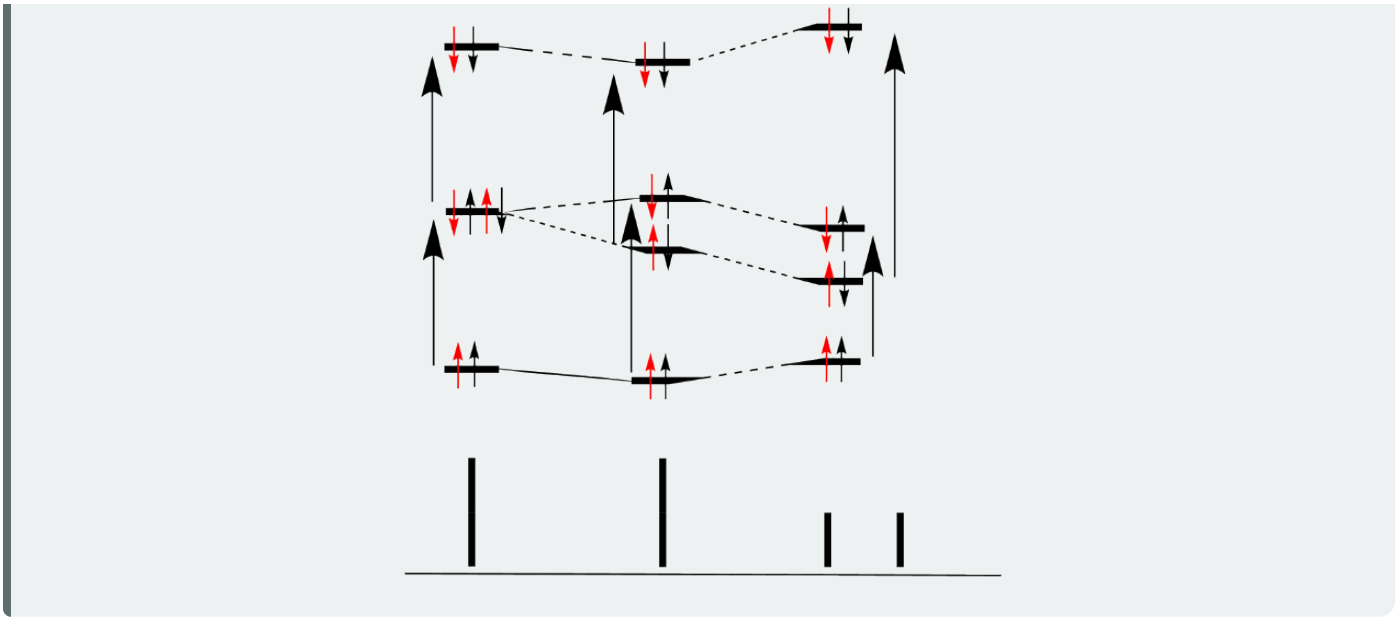
[5] A full proof can be found in *J. Chem. Educ.* **1982,** *59* (10), 819. There is also some discussion of the selection rules in Gunther's *NMR Spectroscopy* (3rd ed.), p 156 onwards.

Note

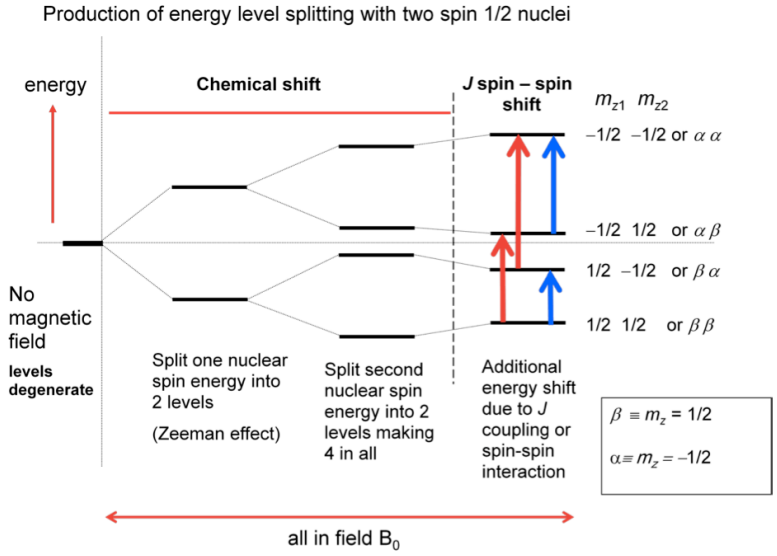
The first important point to note is that *magnetically* equivalent nuclei do in fact couple to each other, however no splitting is *observed* in the spectrum. The second point is that *chemically equivalent, but magnetically non-equivalent*, nuclei couple to each other, and this coupling *is* observable in the NMR spectrum.

Spin coupling comes from a magnetic interaction between nuclear spins transmitted through the bonding electrons. Signals observed in the NMR spectrum are a transition between energy levels of allowed spin states. When two nuclei 'couple', the energy levels are stabilised or destabilsed slightly based on the relative orientations of the nuclear moments, so that (for a doublet) one transition is now δ+J/2, and the other transition is δ-J/2. These two transitions constitute the two lines of the doublet signal. When two equivalent nuclei couple, transitions between energy levels do not change because the interactions between the nuclear moments are the same, as are all other contributing factors such as the Fermi contact. As long as the transitions remain the same, all possible transitions will be equivalent.

The diagram below hopefully explains it a little clearer. The middle energy levels are for two non-coupled spins. Spin A (shown in red) has two possible transitions, both of which are equivalent. When the two spins are coupled, the energy levels are stabilised/destabilised as shown on the right. The transitions for spin A are now no longer equivalent, and they will appear as two lines (doublet). On the left, the equivalent nuclei have an overall change in energy level, but the transition between the levels remains the same, hence the observed line is still a singlet.

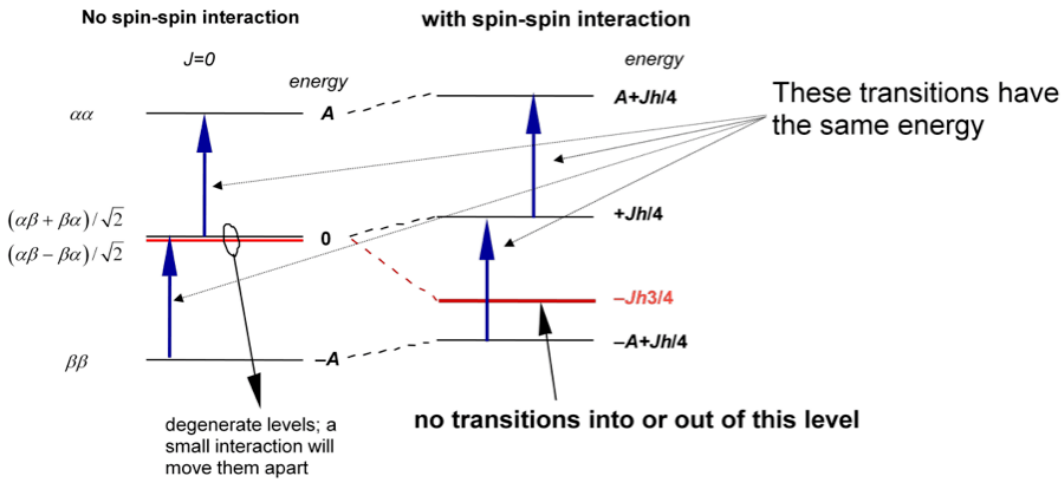


When there are two distinct nuclei (The AX case) and there is spin-spin interaction (J coupling) between them (in addition to chemical shift) then fine structure can be observed in the nmr spectrum. The first diagram shows the energy levels and how they interact. Note how the J coupling moves the levels up and down in addition to chemical shift.



Now there are selection rules that allow the radio frequency radiation to couple different levels together and so produce a spectrum. The rule is that the m_z quantum number (variously called magnetic, or azimuthal or projection quantum number) has to change by $+1$ or -1. This means that in the first diagram only levels in which one alpha changes to beta or vice versa, as shown by the vertical arrows, are allowed transitions. (The selection rule occurs because the photon (even if at radio frequency) has one unit of angular momentum and total angular momentum is conserved.)

In the equivalent nuclei case (called A2) the interaction between spins is still present but because of the magnetically identical nuclei the spin states are not either symmetrical or anti symmetrical to exchange of nuclei and a linear combination has to be made. This is shown on the left of the figure below. The reason that the splitting in energy levels is not observed is that selection rules make the transitions unobservable



Advanced: Liouville–von Neumann Equation

An alternative answer using the product operator formalism:

The fundamental equation describing NMR quantum mechanically (neglecting relaxation) is the **Liouville–von Neumann Equation** (in frequency units, i.e. setting $\hbar = 1$):

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho} = -\mathrm{i}[\hat{H}, \hat{\rho}]$$

For a 2-spin system with identical chemical shifts and a coupling

$$\hat{H} = \Omega\hat{I}_{1z} + \Omega\hat{I}_{2z} + J(\vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2)$$

After a 90 degree pulse on both nuclei the density matrix $\hat{\rho}$ is of the form $\hat{I}_{1\chi} + \hat{I}_{2\chi}$, where $\chi = x$ or y. Now it is a bit lengthy but easy to show that

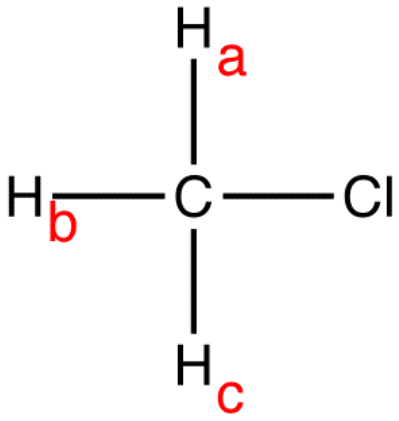
$$[\hat{I}_{1\chi} + \hat{I}_{2\chi}, J(\vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2)] = 0, \quad \text{with } \chi = x, y, z$$

meaning that the coupling Hamiltonian does not influence the signal after a 90 degree pulse, as $[\hat{H}_{\text{coupling}}, \hat{\rho}] = 0$.

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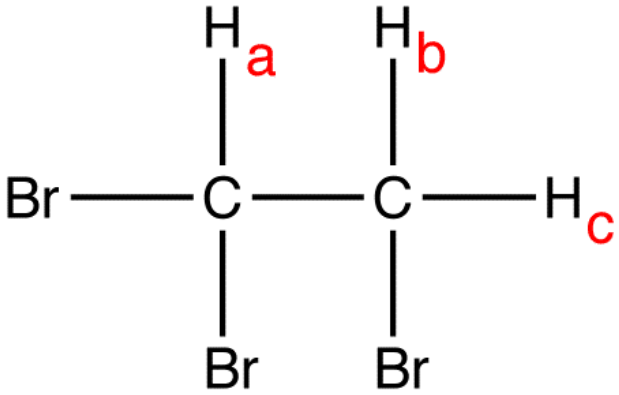
14.8: The n+1 Rule Applies Only to First-Order Spectra

The (n+1) Rule, an empirical rule used to predict the multiplicity and, in conjunction with Pascal's triangle, splitting pattern of peaks in ^{1}H and ^{13}C NMR spectra, states that if a given nucleus is coupled (see spin coupling) to n number of nuclei that are equivalent (see equivalent ligands), the multiplicity of the peak is n+1. eg. 1:



1

The three hydrogen nuclei in 1, H_a, H_b, and H_c, are equivalent. Thus, 1H NMR spectrum of 1 H_as only one peak. H_a, H_b, and H_c are coupled to no hydrogen nuclei. Thus, for H_a, H_b, and H_c, n=0; (n+1) = (0+1) = 1. The multiplicity of the peak of H_a, H_b, and H_c is one. The peak H_as one line; it is a singlet. eg. 2:



2

There are two sets of equivalent hydrogen nuclei in 2:

- Set 1: H_a
- Set 2: H_b, H_c

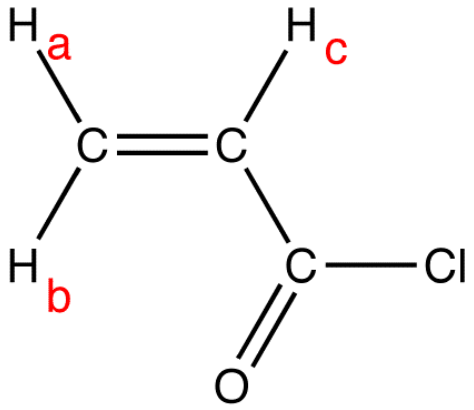
Thus, the 1H NMR spectrum of 2 H_as two peaks, one due to H_a and the other to H_b and H_c.

The peak of H_a: There are two vicinal hydrogens to H_a: H_b and H_c. H_b and H_c are equivalent to each other but not to H_a. Thus, for H_a, n=2; (n+1) = (2+1) = 3. The multiplicity of the peak of H_a is three. The peak H_as three lines; from the Pascal's triangle, it is a triplet.

The peak of H_b and H_c: There is only one vicinal hydrogen to H_b and H_c: H_a. H_a is not equivalent to H_b and H_c. Thus, for H_b and H_c, n=1; (n+1) = (1+1) = 2. The multiplicity of the peak of H_b and H_c is two. The peak H_as two lines, from the Pascal's triangle, it is a doublet.

To determine the multiplicity of a peak of a nucleus coupled to more than one set of equivalent nuclei, apply the (n+1) Rule independently to each other.

eg:



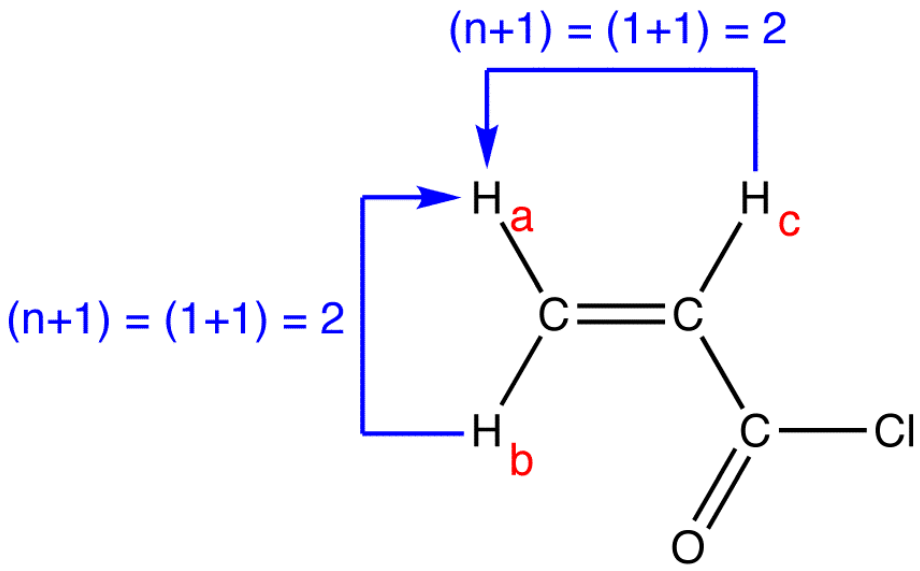
3

There are three set of equivalent hydrogen nuclei in 3:

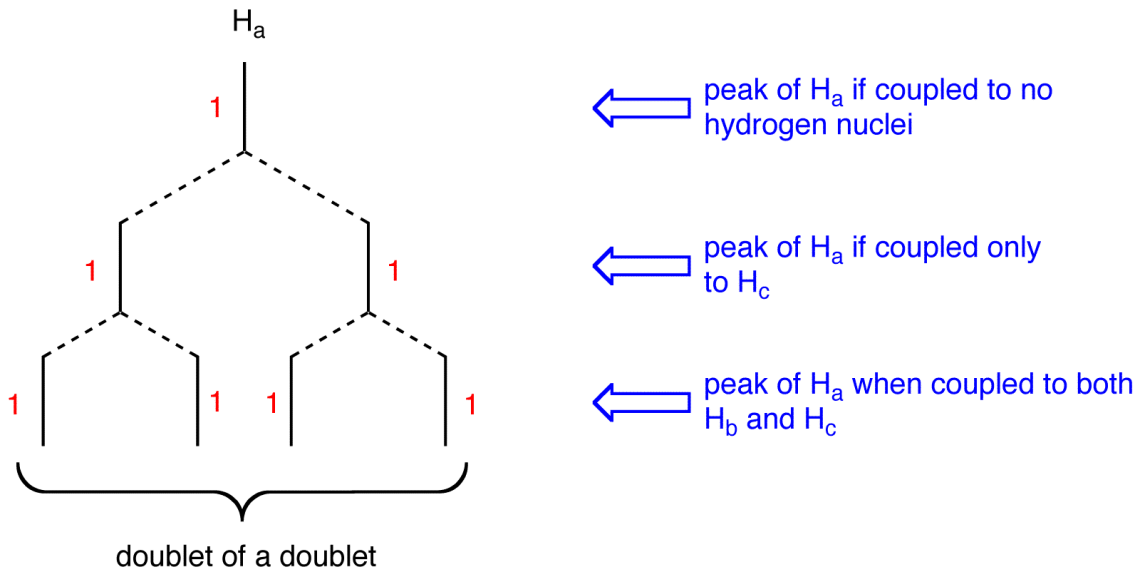
- Set 1: H_a
- Set 2: H_b
- Set 3: H_c

	H_a	H_b	H_c
H_a		geminal; coupling occurs	vicinal; coupling occurs
H_b	geminal; coupling occurs		vicinal; coupling occurs
H_c	vicinal; coupling occurs	vicinal; coupling occurs	

peak of H_a:

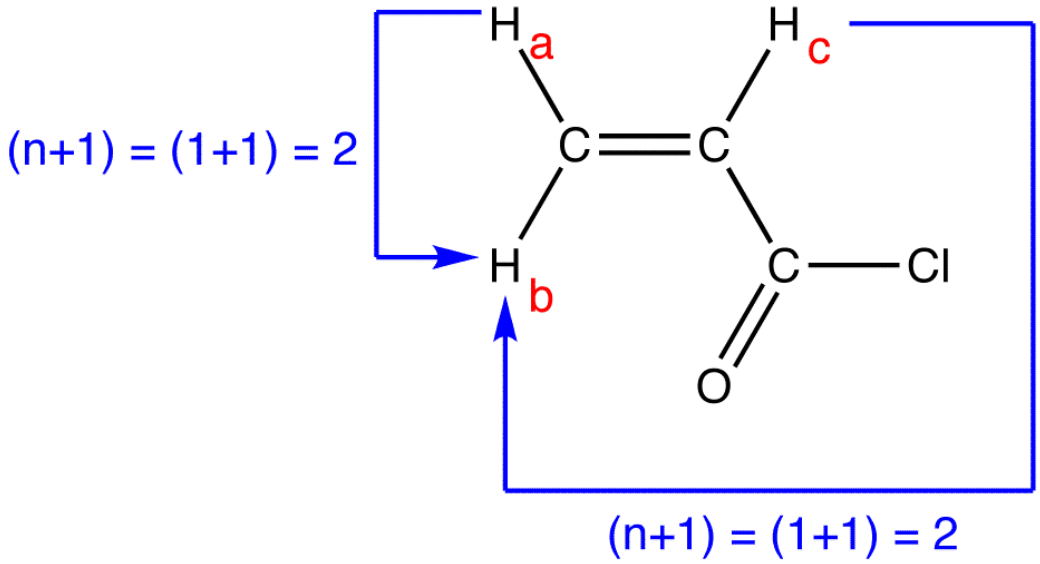


multiplicity of the peak of $H_a = 2 \times 2 = 4$. To determine the splitting pattern of the peak of H_a, use the Pascal's triangle, based on the observation that, for alkenyl hydrogens, $J_{cis} > J_{gem}$.

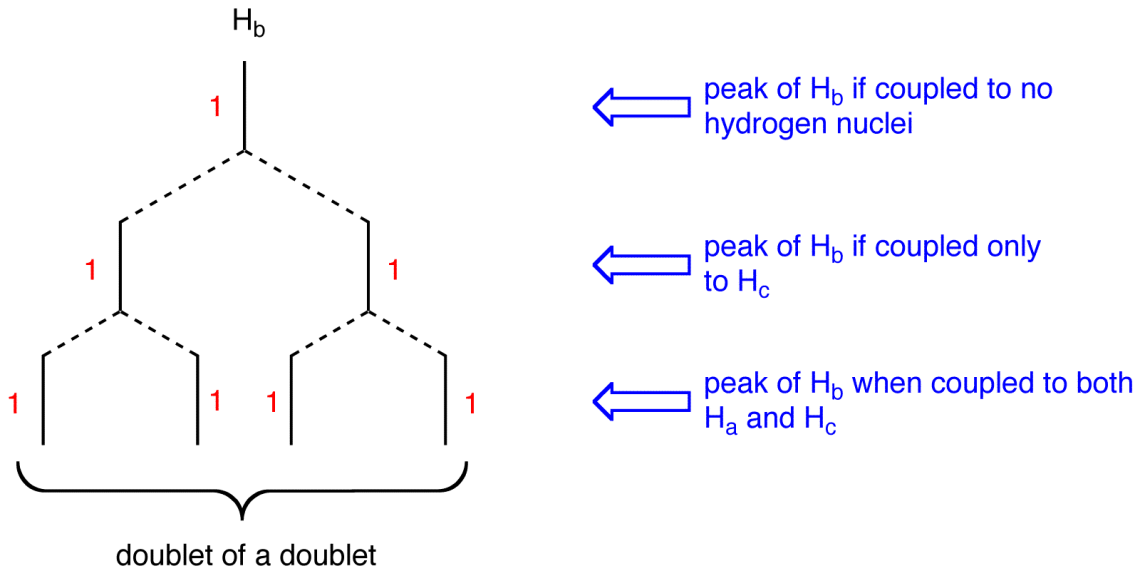


The peak of H_a is a doublet of a doublet.

peak of H_b:

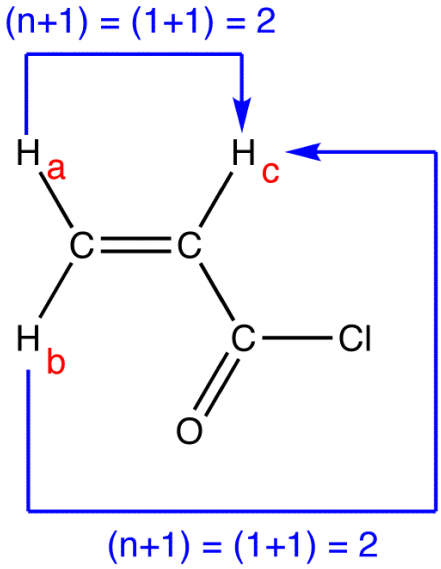


multiplicity of the peak of $H_b = 2 \times 2 = 4$. To determine the splitting pattern of the peak of H_b, use the Pascal's triangle, based on the observation that, for alkenyl hydrogens, $J_{trans} > J_{gem}$.

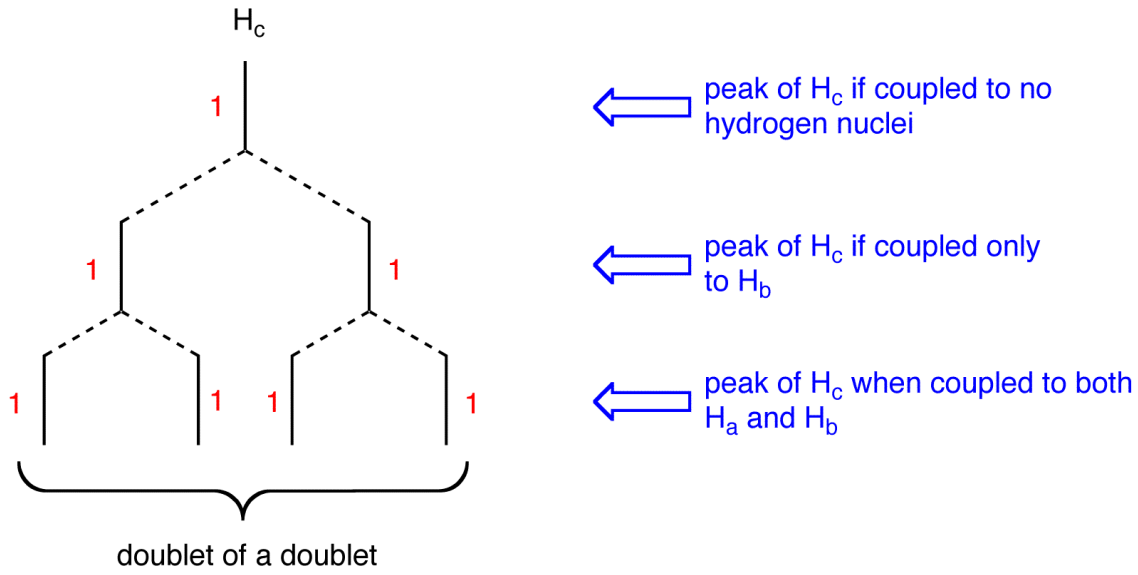


The peak of H_b is a doublet of a doublet.

peak of H_c:



multiplicity of the peak of $H_c = 2 \times 2 = 4$. To determine the splitting pattern of the peak of H_c, use the Pascal's triangle based on the observation that, for alkenyl hydrogens, $J_{trans} > J_{cis}$.



The peak of H_c is a doublet of a doublet.

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14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

under development

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14.E: Nuclear Magnetic Resonance Spectroscopy (Exercises)

These are homework exercises to accompany Chapter 14 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q14.1

Write the equation for a magnetic dipole in the angular momentum form starting from $\mu = \frac{q(\mathbf{r}\ x\ \mathbf{v})}{2}$.

S14.1

μ can be expressed in terms of angular momentum by using the fact $\mathbf{L} = \mathbf{r}$ x $\mathbf{p}$ and that $\mathbf{p} = m\mathbf{v}$.

By substituting $\mathbf{p} = m\mathbf{v}$ in to $\mathbf{L}$ gives :

$$\mathbf{L} = \mathbf{r}\ \mathrm{x}\ m\mathbf{v}$$

by dividing out the m becuse it is a scalar μ becomes:

$$\mu = \frac{q}{2m}\mathrm{L}.$$

Q14.3

Show that the frequency from $\nu_{1\to3}$ given in Table 14.6 reduces to Equation 14.66 when $J \ll \nu_0(\sigma_1 - \sigma_2)$

S14.35

$$\nu_{1\to3} = \frac{\nu_0}{2}(2 - \sigma_1 - \sigma_2) - \frac{J}{2} + \frac{1}{2}\left[\nu_0^2(\sigma_1 - \sigma_2)^2 + J^2\right]^{\frac{1}{2}}$$

$$= \frac{\nu_0}{2}(2 - \sigma_1 - \sigma_2) - \frac{J}{2} + \frac{\nu_0(\sigma_1 - \sigma_2)}{2}\left[1 + \frac{J^2}{\nu_0^2(\sigma_1 - \sigma_2)^2}\right]^{\frac{1}{2}}$$

Since $J \ll \nu_0(\sigma_1 - \sigma_2)$, we can use a Taylor expansion and keeping only the terms that are linear in J gives

$$\frac{\nu_0}{2}(2 - \sigma_1 - \sigma_2) - \frac{J}{2} + \frac{\nu_0(\sigma_1 - \sigma_2)}{2} - O(J^2)$$

$$= \nu_0(1 - \sigma_2) - \frac{J}{2}$$

Q14.18

Nuclear spin operators I_x, I_y, I_z all obey the commutation relations, that

$$[I_x, I_y] = ihI_z$$

$$[I_y, I_z] = ihI_x$$

$$[I_z, I_x] = ihI_y$$

Show that

$$I_zI_+ = I_+I_z + hI_+ \qquad and \qquad I_zI_- = I_-I_z - hI_-$$

S14.18

We know that the commutation relations are as follows:

$$I_xI_y - I_yI_x = ihI_z$$

$$I_yI_z - I_zI_y = ihI_x$$

$$I_zI_x - I_xI_z = ihI_y$$

Therefore,

$$I_zI_+ = I_z(I_x + iI_y) = ihI_y + I_xI_z + iI_zI_y = ihI_y + I_xI_z + i(I_yI_z - ihI_x) = I_xI_z + iI_yI_z + hI_x + ihI_y = I_+I_z + hI_+$$

and

$$I_zI_- = I_z(I_x - iI_y) = ihI_y + I_xI_z - iI_zI_y = ihI_y + I_xI_z - i(I_yI_z - ihI_x) = I_xI_z - iI_yI_z - hI_x + ihI_y = I_-I_z - hI_-$$

Q14.19

Given:

$$\hat{I}_+\hat{I}_- = \hat{I}_x^2 + i\hat{I}_x\hat{I}_y - i\hat{I}_x\hat{I}_y + \hat{I}_y^2$$

and

$$\hat{I}^2 = \hat{I}_x^2 + \hat{I}_y^2 + \hat{I}_z^2$$

Show:

$$\hat{I}_+\hat{I}_- = \hat{I}^2 - \hat{I}_z^2 + \hbar\hat{I}_z$$

and

$$\hat{I}_-\hat{I}_+ = \hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z$$

S14.19

$\hat{I}^2 - \hat{I}_z^2 = \hat{I}_x^2 + \hat{I}_y^2$, so

$$\hat{I}_+\hat{I}_- = \hat{I}^2 - \hat{I}_z^2 + i\hat{I}_y\hat{I}_x - i\hat{I}_x\hat{I}_y$$

$$= \hat{I}^2 - \hat{I}_z^2 - i(i\hbar\hat{I}_z)$$

$$= \hat{I}^2 - \hat{I}_z^2 + \hbar\hat{I}_z$$

and

$$\hat{I}_-\hat{I}_+ = \hat{I}_x^2 + \hat{I}_y^2 + i\hat{I}_x\hat{I}_y - i\hat{I}_y\hat{I}_x$$

$$= \hat{I}^2 - \hat{I}_z^2 + i(i\hbar\hat{I}_z)$$

$$= \hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z$$

Q14.20

Using

$$\hat{I}_z\hat{I}_+ = \hat{I}_+\hat{I}_z + \hbar\hat{I}_+$$

$$\hat{I}_z\beta = -\frac{\hbar}{2}\beta$$

$$\hat{I}_+\beta = \hbar\alpha$$

and $c = \hbar$,
derive $\hat{I}_x\alpha$, $\hat{I}_y\alpha$, $\hat{I}_x\beta$, and $\hat{I}_y\beta$ in terms of $\alpha, \beta, \hbar$.

S14.20

We know

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y \text{ and } \hat{I}_- = \hat{I}_x - i\hat{I}_y$$

So we can show that

$$\hat{I}_+\alpha = \hat{I}_x\alpha + i\hat{I}_y\alpha = 0 \text{ and } \hat{I}_-\alpha = \hat{I}_x\alpha - i\hat{I}_y\alpha = \hbar\beta$$

by adding the equations we can show that

$$\hat{I}_x\alpha = \frac{\hbar}{2}\beta \text{ and } \hat{I}_y\alpha = \frac{i\hbar}{2}\beta$$

if we apply the same methodology as above but with \(\beta)\ we can see that

$$\hat{I}_x\beta = \frac{\hbar}{2}\alpha \text{ and } \hat{I}_y\beta = \frac{i\hbar}{2}\alpha$$

Q14.21

This problem shows that the proportionality constant c in

$$\hat{I}_+\beta = c\alpha \; or \; \hat{I}_-\alpha = c\beta$$

is equal to $\hbar$. Start with

$$\int \alpha^*\alpha d\tau = 1 = \frac{1}{c^2}\int (\hat{I}_+\beta)^*(\hat{I}_+\beta)d\tau$$

Let $\hat{I}_+ = \hat{I}_x + i\hat{I}_y$ in the second factor in the above integral and use the fact that $\hat{I}_x$ and $\hat{I}_y$ are Hermitian to get

$$\int (\hat{I}_x\hat{I}_+\beta)^*\beta d\tau + i\int (\hat{I}_y\hat{I}_+\beta)^*\beta d\tau = c^2$$

Now take the complex conjugate of both sides to get

$$\int \beta^*\hat{I}_x\hat{I}_+\beta d\tau - i\int \beta^*\hat{I}_y\hat{I}_+\beta d\tau = c^2 = \int \beta^*\hat{I}_-\hat{I}_+\beta d\tau$$

Using the given equation:

$$\hat{I}_-\hat{I}_+ = \hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z$$

Show that:

$$c^2 = \int \beta^* \hat{I}_- \hat{I}_+ \beta d\tau = \int \beta^* (\hat{I}^2 - \hat{I}_z^2 - \hbar \hat{I}_z) \beta d\tau = \int \beta^* \left(\frac{3}{4}\hbar^2 - \frac{1}{4}\hbar^2 + \frac{\hbar^2}{2} \right) \beta d\tau = \hbar^2$$

or that $c = \hbar$

S14.21

Recall that for a Hermitian operator $\hat{A}$,

$$\int f^*(x) \hat{A} g(x) dx = \int g(x) \hat{A}^* f^*(x) dx$$

Begin with the expression

$$\int \alpha^* \alpha d\tau = 1 = \frac{1}{c^2} \int (\hat{I}_+ \beta)^* (\hat{I}_+ \beta) d\tau$$

Solving for c^2 gives

$$c^2 = \int (\hat{I}_+ \beta)^* (\hat{I}_+ \beta) d\tau = \int (\hat{I}_+ \beta)^* (\hat{I}_x \beta + i \hat{I}_y \beta) d\tau = \int (\hat{I}_+ \beta)^* (\hat{I}_+ \beta d\tau + i \int (\hat{I}_+ \beta)^* \hat{I}_y \beta d\tau$$

We can use the fact that $\hat{I}_x$ and $\hat{I}_y$ are Hermitian to write this as

$$c^2 = \int \beta \hat{I}_+^* (\hat{I}_+ \beta)^* d\tau + i \int \beta \hat{I}_y^* (\hat{I}_+ \beta)^* d\tau$$

Take the complex conjugate of both sides of the last equation to find

$$c^2 = \int \beta^* \hat{I}_x \hat{I}_+ \beta d\tau - i \int \beta^* \hat{I}_y \hat{I}_+ \beta d\tau = \int \beta^* (\hat{I}_x - i \hat{I}_y) \hat{I}_+ \beta d\tau = \int \beta^* \hat{I}_- \hat{I}_+ \beta d\tau$$

Substituting $\hat{I}_- \hat{I}_+ = \hat{I}^2 - \hat{I}_z^2 - \hbar \hat{I}_z$, we obtain

$$c^2 = \int \beta^* \hat{I}_- \hat{I}_+ \beta d\tau = \int \beta^* (\hat{I}^2 - \hat{I}_z^2 - \hbar \hat{I}_z) \beta d\tau = \int \beta^* \left(\frac{3\hbar^2}{4} - \frac{1\hbar^2}{4} + \frac{\hbar^2}{2} \right) \beta d\tau = \hbar^2$$

where we have used the given equation to evaluate the various terms involving $\hat{I}^2$ and $\hat{I}_z$.

Taking the squareroot of both sides of the final equation proves that $c = \hbar$.

Q14.22

Show that $H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \hat{I}_{y1} \hat{I}_{y2} \alpha(1) \alpha(2) = 0$.

S14.22

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \hat{I}_{y1} \hat{I}_{y2} \alpha(1) \alpha(2)$$

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) [\hat{I}_{y1} \alpha(1)] [\hat{I}_{y2} \alpha(2)]$$

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \left[\frac{i\bar{h}}{2} \beta(1) \right] \left[\frac{i\bar{h}}{2} \beta(2) \right]$$

$$= -\frac{hJ_{12}}{4} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \beta(1) \beta(2) = 0$$

Orthogonality of spin functions is used so that the equation equates to zero.

Q14-23 Nice work! Correct

The energy levels of a two-spin system can be calculated using first-order perturbation theory. Show this for the first energy level.

S14-23

$$E_j = E_j^{(0)} + \int d\tau_1 d\tau_2 \psi_j^* H^{(1)} \psi_j \tag{14.E.1}$$

$$H^{(0)}\psi_j = E_j^{(0)}\psi_j \tag{14.E.2}$$

$$E_j = E_j^{(0)} + H_{xjj}^{(1)} + H_{yjj}^{(1)} + H_{zjj}^{(1)} \tag{14.E.3}$$

The unperturbed first-order energy is calculated using

$$I_{zj}\alpha(j) = \frac{\hbar}{2}\alpha(j) \tag{14.E.4}$$

$$H^{(0)}\psi_1 = H^{(0)}\alpha(1)\alpha(2) \tag{14.E.5}$$

$$= -\gamma B_0(1-\sigma_1)I_{z1}\alpha(1)\alpha(2) - \gamma B_0(1-\sigma_2)I_{z2}\alpha(1)\alpha(2) \tag{14.E.6}$$

$$E_1^{(0)}\alpha(1)\alpha(2) = E_1^{(0)}\psi_1 \tag{14.E.7}$$

$$E_1^{(0)} = -\hbar\gamma B_0(1 - \frac{\sigma_1+\sigma_2}{2}) \tag{14.E.8}$$

The first-order correction is defined as

$$H_{ii} = \frac{hJ_{12}}{\hbar^2}\int d\tau_1 d\tau_2 \psi_i^* I_1 I_2 \psi_i \tag{14.E.9}$$

with the x and y terms in I1 and I2 not contributing to the first-order energy.

Considering the unperturbed wave function for a two-spin system

$$\psi_1 = \alpha(1)\alpha(2) \tag{14.E.10}$$

$$I_{z1}I_{z2}\alpha(1)\alpha(2) = \frac{\hbar^2}{4}\alpha(1)\alpha(2) \tag{14.E.11}$$

Furthermore, the perturbation to the first-order energy becomes

$$H_{z,11} = \frac{hJ_{12}}{\hbar^2}\int d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2) I_{z1}I_{z2}\alpha(1)\alpha(2) = \frac{hJ_{12}}{4} \tag{14.E.12}$$

As a result the first order energy energy can be represented by

$$E_1 = -h\nu_0(1 - \frac{\sigma_1+\sigma_2}{2}) + \frac{hJ_{12}}{4} \tag{14.E.13}$$

.

Q14.24

Derive the frequencies associated with the allowed transitions between nuclear spin up to n = 4.

S14.24

(its good that you started from the beginning to derive the frequencies good job--RM)

$$E = h\nu \tag{14.E.14}$$

$$E_{1=>2} = E_2 - E_1 \tag{14.E.15}$$

$$= \frac{h\nu}{2}(\sigma_2 - \sigma_1) - \frac{hJ_{12}}{4} + h\nu_0(1 - \frac{\sigma_1 + \sigma_2}{2}) - \frac{hJ_{12}}{4} \tag{14.E.16}$$

$$= h\nu_0(1 - \sigma_1) - \frac{hJ_{12}}{2} \tag{14.E.17}$$

$$\nu_{1=>2} = \nu_0(1 - \sigma_1) - \frac{hJ_{12}}{2} \tag{14.E.18}$$

$$E_{1=>3} = E_3 - E_1 \tag{14.E.19}$$

$$= \frac{h\nu}{2}(\sigma_1 - \sigma_2) - \frac{hJ_{12}}{4} + h\nu_0(1 - \frac{\sigma_1 + \sigma_2}{2}) - \frac{hJ_{12}}{4} \tag{14.E.20}$$

$$= h\nu_0(1 - \sigma_3) - \frac{hJ_{12}}{2} \tag{14.E.21}$$

$$\nu_{1=>3} = \nu_0(1 - \sigma_2) - \frac{hJ_{12}}{2} \tag{14.E.22}$$

$$E_{2=>4} = E_4 - E_2 \tag{14.E.23}$$

$$= h\nu(\sigma_1 + \sigma_2) - \frac{hJ_{12}}{4} - \frac{h\nu_0}{2}(\sigma_2 - \sigma_1) + \frac{hJ_{12}}{4} \tag{14.E.24}$$

$$= h\nu_0(1 - \sigma_2) + \frac{hJ_{12}}{2} \tag{14.E.25}$$

$$\nu_{2=>4} = \nu_0(1 - \sigma_2) + \frac{hJ_{12}}{2} \tag{14.E.26}$$

$$E_{3=>4} = E_4 - E_3 \tag{14.E.27}$$

$$= h\nu(1 - \frac{\sigma_1 + \sigma_2}{2}) + \frac{hJ_{12}}{4} - \frac{h\nu_0}{2}(\sigma_1 - \sigma_2) + \frac{hJ_{12}}{4} \tag{14.E.28}$$

$$= h\nu_0(1 - \sigma_1) + \frac{hJ_{12}}{2} \tag{14.E.29}$$

$$\nu_{2=>4} = \nu_0(1 - \sigma_1) + \frac{hJ_{12}}{2} \tag{14.E.30}$$

Q14.28

Using the Hamiltonian for an H_2 molecule with 2 nonequivalent hydrogen atoms, prove that $H_{13} = \iint d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\hat{H}\beta(1)\alpha(2) = 0$.

S14.28

The necessary Hamiltonian is:

$$\hat{H} = -\gamma B_0(1 - \sigma_1)\hat{I}_1 - \gamma B_0(1 - \sigma_2)\hat{I}_2 + \frac{hJ_{12}}{\hbar^2}\hat{I}_1 \cdot \hat{I}_2.$$

We can then plug in the Hamiltonian and write the second half of the equation as:

$$\hat{H}\beta(1)\beta(2) = -\gamma B_0(1 - \sigma_1)(-\frac{\hbar}{2})\beta(1)\alpha(2) - \gamma\beta_0(1 - \sigma_2)(\frac{\hbar}{2})\beta(1)\beta(2) + \frac{hJ_{23}}{\hbar^2}[\frac{\hbar^2}{4}\alpha(1)\beta(2) + \frac{\hbar^2}{4}\alpha(1)\beta(2) - \frac{\hbar^2}{4}\beta(1)\alpha(2)]$$

$$= \frac{\hbar}{2}\gamma B_0\beta(1)\alpha(2)[(1 - \sigma_1) - (1 - \sigma_2)] + \frac{hJ_{12}}{4}[2\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Doing some algebra, we get that:

$$H_{13} = \iint d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\left[\frac{\hbar}{2}\gamma B_0 \beta(1)\alpha(2)[(1-\sigma_1)-(1-\sigma_2)] + \frac{hJ_{12}}{4}[2\alpha(1)\beta(2)-\beta(1)\alpha(2)]\right]$$

Because α and β are orthonormal, **the integral goes to zero**. Therefore, we have proved that $H_{13} = 0$.

Q14.29

Prove that

$$H_{44} = \iint d\tau_(1) d\tau_(2) \beta^*(1)\beta^*(2)\hat{H}\beta(1)\beta(2)$$

$$= -\frac{1}{2}h\nu_0(1-\sigma_1) - \frac{1}{2}h\nu_0(1-\sigma_2) + \frac{hJ_12}{4}$$

with

$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_1 - \gamma B_0(1-\sigma_2)\hat{I}_2 + \frac{hJ_{12}}{\hbar^2}\hat{I}_1 \cdot \hat{I}_2.$$

S14.29

$$\hat{H}\beta(1)\beta(2) = -\gamma B_0(1-\sigma_1)(\frac{\hbar}{2})\beta(1)\beta(2) - \gamma\beta_0(1-\sigma_2)(\frac{\hbar}{2})\beta(1)\beta(2) + \frac{hJ_{12}}{\hbar^2}[\frac{\hbar^2}{4}\beta(1)\beta(2) - \frac{h^2}{4}\beta(1)\beta(2) + \frac{\hbar^2}{4}\alpha(1)\alpha(2)]$$

$$= \left[\frac{-\hbar\gamma B_0}{2}(1-\sigma_1) - \frac{-\hbar\gamma B_0}{2}(1-\sigma_2) + \frac{hJ_{12}}{4}][2\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\beta(1)\beta(2)$$

Calculated with matlab,

$$H_{44} = \iint d\tau_1 d\tau_2 \left[\frac{-\hbar\gamma B_0}{2}(1-\sigma_1) - \frac{-\hbar\gamma B_0}{2}(1-\sigma_2) + \frac{hJ_{12}}{4}][2\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\beta(1)\beta(2)$$

$$= \frac{1}{2}h\nu_0(1-sigma_1) - \frac{1}{2}h\nu_0(1-\sigma_2) + h\frac{J_{12}}{4}$$

Q14.30

Using Equation 14.58, prove that

$$H_{44} = -\frac{1}{2}hv_0(1-\sigma_1) + \frac{1}{2}h_v0(1-\sigma_2) + \frac{hJ_{12}}{4}$$

S14.30

To find this matrix element, you must complete the integral given by $\langle\psi_4|H|\psi_4\rangle$. By using the relationships in Table 14.4 to evaluate parts of the integral, Equation 14.45 and Equation 14.58, algebra, and calculus, this integral can be solved to give the final answer above.

Q14.31

Given the following matrix, expand the determinants to solve for the energies:

$$\begin{pmatrix} \alpha-E & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha-E \end{pmatrix}$$

S14.31

\[x_{i} = \frac{\alpha E}{\beta}\nonumber \]

$$E_j = \alpha - \beta x_j$$

$$x_j = -2cos(\frac{j\pi}{n_c+1})$$

$$E_j = \alpha + 2\beta * cos(\frac{j\pi}{n_c} + 1)$$

$$E_1 = \alpha + 2\beta * cos(\frac{\pi}{6+1}) = \alpha + 1.8\beta$$

$$E_2 = \alpha + 2\beta * cos(\frac{2\pi}{6+1}) = \alpha + 1.24\beta$$

$$E_3 = \alpha + 2\beta * cos(\frac{3\pi}{6+1}) = \alpha + 0.44\beta$$

$$E_4 = \alpha + 2\beta * cos(\frac{4\pi}{6+1}) = \alpha - 0.44\beta$$

$$E_5 = \alpha + 2\beta * cos(\frac{5\pi}{6+1}) = a - 1.25\beta$$

$$E_6 = \alpha + 2\beta * cos(\frac{6\pi}{6+1}) = \alpha - 1.8\beta$$

Q14.33

Show that a two-spin system with $J = 0$ consists of only two peaks with frequencies $v_0(1 - \sigma_1)$ and $v_0(1 - \sigma_2)$.

S14.33

The resonance frequencies is given by

$$v_1 \rightarrow_2 = \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) - \frac{J}{2} - \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2 + J^2]^{\frac{1}{2}}$$

with J = 0, this leads to

$$v_1 \rightarrow_2 = \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) - \frac{0}{2} - \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2 + 0^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) - \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2]^{\frac{1}{2}}$$
$$= v_0(1 - \sigma_1)$$

Similarly, for the other transitions:

$$v_1 \rightarrow_3 = \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) - \frac{J}{2} + \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2 + J^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) - \frac{0}{2} + \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2 + 0^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) + \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2]^{\frac{1}{2}}$$
$$= v_0(1 - \sigma_2)$$

$$v_2 \rightarrow_4 = \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) + \frac{J}{2} + \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2 + J^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) + \frac{0}{2} + \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2 + 0^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\ (2 - \sigma_1 - \sigma_2) + \frac{1}{2}\ [v_0^2(\sigma_1 - \sigma_2)^2]^{\frac{1}{2}}$$

$$= v_0(1-\sigma_2)$$

$$v_3 \rightarrow_4 = \tfrac{v_0}{2}\ (2-\sigma_1-\sigma_2) + \tfrac{J}{2}\text{-}\tfrac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2+J^2]^{\frac{1}{2}}$$

$$= \tfrac{v_0}{2}\ (2-\sigma_1-\sigma_2) + \tfrac{0}{2}\text{-}\tfrac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2+0^2]^{\frac{1}{2}}$$

$$= \tfrac{v_0}{2}\ (2-\sigma_1-\sigma_2) \text{-}\tfrac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2]^{\frac{1}{2}}$$
$$= v_0(1-\sigma_1)$$

Q14.34

Show that

$$\nu_{2\rightarrow 4} = \frac{\nu_0}{2}(2-\sigma_1-\sigma_2)+\frac{J}{2}) + \frac{1}{2}[\nu_0^2()\sigma_1-\sigma_2)^2+J^2]^{1/2}$$

for a general two-spin system.

S14.34

$$E_4-E_2 = [h\nu_0(1-\frac{\sigma_1+\sigma_2}{2})+\frac{hJ}{4}] - [-\frac{hJ}{4}-\frac{h}{2}[\nu_0^2(\sigma_1-\sigma_2)^2+J^2]^{1/2}]$$

$$= h\nu_0(1-\frac{\sigma_1+\sigma_2}{2})+\frac{hJ}{2}-\frac{h}{2}[\nu_0^2(\sigma_1-\sigma_2)^2+J^2]^{1/2}$$

$$\frac{E_4-E_2}{2} = \frac{\nu_0}{2}(2-\sigma_1-\sigma_2)+\frac{J}{2}) + \frac{1}{2}[\nu_0^2()\sigma_1-\sigma_2)^2+J^2]^{1/2}$$

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14.S: Nuclear Magnetic Resonance Spectroscopy (Summary)

Up until this point, we've been looking at spectroscopic transitions that can occur when the internal states of a molecule interact with the electric component of electromagnetic radiation. In general, these are the strongest and most readily observed spectroscopic transitions for a molecule in free space, but there are a number of other types of spectroscopic transitions that are observable. In this section, we will look at nuclear magnetic resonance spectroscopy: nuclear spin transitions that are observable when a molecule is placed in a magnetic field. Nuclear spin angular momentum is perfectly analogous to electron spin angular momentum: some nuclei possess intrinsic quantum angular momentum that cannot be explained classically; the eigenstates for a nucleus with angular momentum I are $|I, m_I\rangle$, where m_I, the projection of the angular momentum onto an axis, has values ranging from $I, I-1, \ldots, -I$. In free space, these states are all degenerate, but in the presence of a strong magnetic field, each state adopts a different energy. NMR requires first placing a molecule in a strong magnetic field to lift the nuclear spin degeneracies, then uses the magnetic component of light to induce nuclear spin flips, resulting in absorption of the radiation.

NMR spectroscopy, and particularly NMR, is widely used as a tool for determining the structures of organic molecules. The reasons for this are threefold:

1. Any molecule possessing hydrogen atoms will have an NMR signature, and the magnetogyric ratio of a proton is one of the largest for any nucleus.
2. The exact absorption frequency for a proton depends on the electronic structure near the atom, meaning that the frequencies are sensitive nearby functional groups.
3. The spins of protons bound to adjacent carbon atoms couple, leading to spectral patterns that give structural information about how the hydrogen atoms in a molecule are distributed.

From a physical chemistry standpoint, NMR spectroscopy is the quintessential spectroscopic technique that involves magnetism, and the energy levels and spectral splittings observed in NMR spectra can be explained rather easily using simple quantum mechanical tools.

Learning Objectives

By the end of this chapter, you should know the following:

- How quantum mechanical spin is different than normal angular momentum.
- The commutation relationships among the spin operators $\op I^2$, $\op I_x$, $\op I_y$, and $\op I_z$, and how they act on spin functions
- How the frequency of a NMR spectrometer is related to the magnetic field.
- Chemical shift and why it is used in NMR spectroscopy
- Shielding and how it relates to electron density and chemical shift
- Spin-spin coupling and its effect have on a NMR spectrum
- The $n+1$ rule
- The effect of chemically equivalent protons on an NMR spectrum
- How and why second-order spectra differ from first-order spectra

Skill goals (what you should be able to do/calculate):

- List the complete set of spin functions for a particle.
- Compute the energy levels for a nucleus in a given magnetic field.
- Convert between raw frequency and chemical shift.
- Use shielding constants to calculate chemical shifts.
- Use first-order perturbation theory to calculate energy levels and frequencies of coupled protons.
- Use the Rayleigh-Ritz variational method to calculate the frequencies in a second-order spectrum.

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15: LASERS, LASER SPECTROSCOPY, AND PHOTOCHEMISTRY

The word 'laser' is an acronym for "light amplification by stimulated emission of radiation." The use of lasers in science and in society has rapidly expanded since their development in the early 1960s. Lasers provides chemists with a powerful and versatile tool for probing the nature of and dynamics of species and chemical reactions. This chapter will discuss the foundations of lasers and the interaction of their output toward understanding atomic and molecular properties. We will describe the generation of laser light from electronically excited atoms using the rate-equation model developed by Einstein. Modern laser designs and applications will then be discussed.

15.1: Electronically Excited Molecules can Relax by a Number of Processes

15.2: The Dynamics of Transitions can be Modeled by Rate Equations

15.3: A Two-Level System Cannot Achieve a Population Inversion

15.4: Population Inversion can be Achieved in a Three-Level System

15.5: What is Inside a Laser?

15.6: The Helium-Neon Laser

15.7: Modern Applications of Laser Spectroscopy

15.8: Pulsed Lasers Can by Used to Measure the Dynamics of Photochemical Processes

15.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises)

15.S: Lasers, Laser Spectroscopy, and Photochemistry (Summary)

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15.1: Electronically Excited Molecules can Relax by a Number of Processes

To understand how lasers work we must first describe how a molecule in an excited state can relax back to the ground state because the light emitted by a laser is influenced by these relaxation processes. The two radiative decay pathways for an excited molecule are fluorescence and phosphorescence. Fluorescence differs from phosphorescence in that the energy transition that is responsible for fluorescence does not involve a change in electron spin multiplicity. Thus fluorescence lifetimes are short (10^{-9} - 10^{-6} s). In phosphorescence, there is a change in electron spin multiplicity, resulting in a longer lifetime of the excited state (second to minutes). A description of electron spin and the differences between singlet and triplet states will clarify the difference between fluorescence and phosphorescence.

Spin Multiplicity - Singlet and Triplet Excited States

The Pauli Exclusion principle states that two electrons in an atom cannot have the same four quantum numbers (n, l, m_l, m_s). Therefore, because two electrons can occupy each orbital, these two electrons must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules are diamagnetic, and are not attracted or repelled by an external magnetic or electric field. Molecules that contain unpaired electrons (free radicals) do have magnetic moments that are attracted to an external magnetic or electric field.

A molecule is said to be in a singlet state when all the electron spins are paired in the molecular electronic state, and the electronic energy levels do not split when the molecule is exposed to a magnetic field. A doublet state occurs when there is an unpaired electron that gives two possible orientations when exposed to a magnetic field and imparts different energies to the system. A singlet or a triplet state can form when one electron is excited to a higher energy level. In an excited singlet state, the promoted electron retains the spin orientation it had in the ground state (i.e., paired). In a triplet excited state, the promoted electron undergoes a change in spin, and so has the same spin orientation (parallel) to the unpaired electron that remains in the ground state orbital. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure 15.1.1. The terms singlet, doublet and triplet are derived using the equation for multiplicity, 2S+1, where S is the total spin angular momentum (sum of all the electron spins). Individual spins are denoted as spin up (s = +1/2) or spin down (s = -1/2). If we were to calculate the multiplicity for the singlet ground state or the singlet excited state, the equation would be

$$2(+1/2 + -1/2) + 1 = 2(0) + 1 = 1$$

In a similar fashion, the spin multiplicity for the triplet excited state can be calculated as

$$2(+1/2 + +1/2) + 1 = 2(1) + 1 = 3$$

which gives a triplet state as expected.

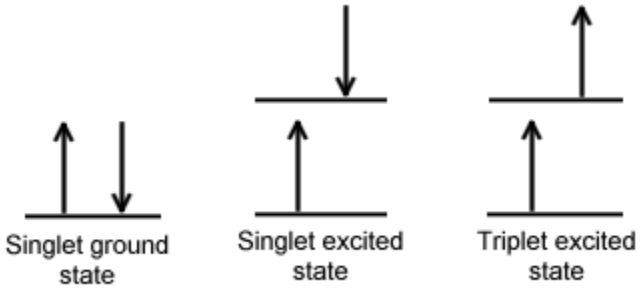


Figure 15.1.1: Spin in the ground and excited states (Tyler Matthews - Paint Shop Pro, Public Domain, https://commons.wikimedia.org/w/inde...curid=64926546)

The difference between a molecule in the ground and the triplet excited state is that the molecule is diamagnetic in the ground state and paramagnetic in the triplet excited state. This difference in spin state makes the transition from singlet to triplet (or

triplet to singlet) less likely than the singlet-to-singlet transitions. For this reason, the lifetime of the triplet state is longer than the lifetime of the singlet state by a factor of roughly 10^4 seconds. The transition from ground to excited triplet state has a low probability of occurring, thus these absorption bands are less intense than singlet-singlet state absorption bands. However, an excited triplet state can be populated from an excited singlet state of certain molecules. Jablonski diagrams can be used to explain transitions such as this that occur in photoluminescence molecules.

Jablonski Diagrams

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. He developed a graphic representation that shows the possible consequences of applying photons from the visible spectrum of light to a particular molecule. These schematics are referred to as Jablonski diagrams.

A Jablonski diagram is an energy diagram, arranged with energy on a vertical axis. The energy levels can be quantitatively denoted, but most of these diagrams use energy levels schematically. The rest of the diagram is arranged into columns. Every column usually represents a specific spin multiplicity for a particular species. However, some diagrams divide energy levels within the same spin multiplicity into different columns. Within each column, horizontal lines represent eigenstates for that particular molecule. Bold horizontal lines are representations of the limits of electronic energy states. Within each electronic energy state are multiple vibrational energy states that may be coupled with the electronic state. Usually only a portion of these vibrational eigenstates are represented due to the massive number of possible vibrations in a molecule. Each of these vibrational energy states can be subdivided even further into rotational energy levels; however, typical Jablonski diagrams omit such intense levels of detail.

Through the use of straight and wavy lines, these figures show transitions between eigenstates that occur from the exposure of a molecule to a particular wavelength of light. Straight lines show the conversion between a photon of light and the energy of an electron. Wavy lines show nonradiative transitions of electrons. Within a Jablonski diagram several different pathways show how an electron may accept and then dissipate the energy from a photon. Thus, most diagrams start with arrows originating from the ground electronic state and finish with arrows returning to the ground electronic state.

The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of a photoluminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as S_o. At room temperature, a majority of the molecules are in this state. The thicker lines on the left labeled S_1, S_2 , and S_3 represent the excited electronic states for the molecule in the singlet state. The thicker lines on the right labeled T_1, T_2, and T_3 represent excited triplet states.

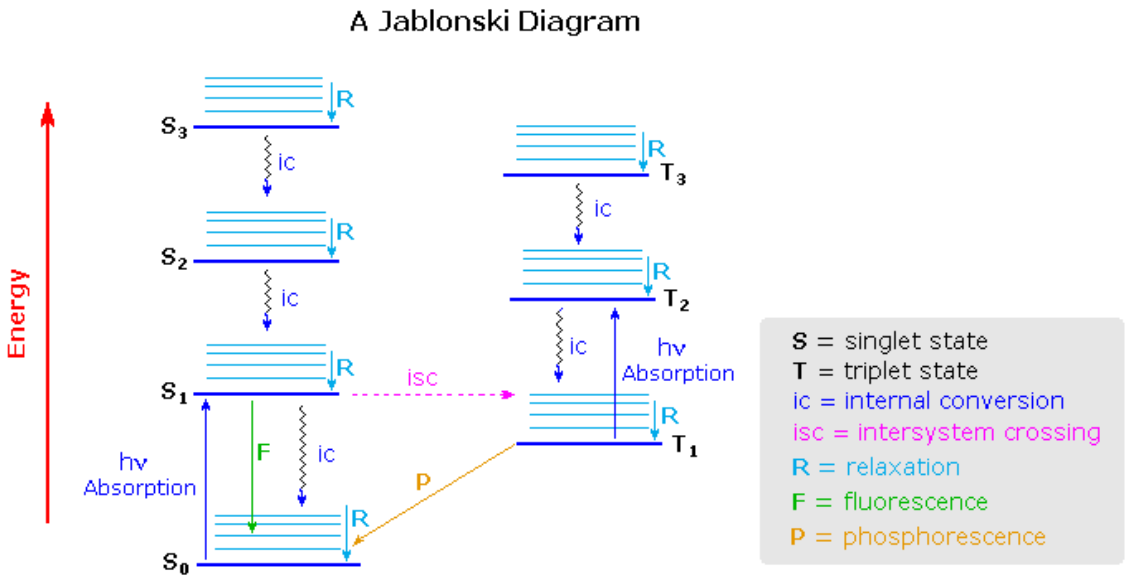


Figure 15.1.2: Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. (Bill Reusch, Michigan State University).

Deactivation Processes

A molecule that is excited can return to the ground state by several combinations of mechanical steps that will be described below and shown in Figure 15.1.2.The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrow in Figure 15.1.2. The wiggly arrows in Figure 15.1.2 are deactivation processes without the use of radiation. The favored deactivation process is the route that is most rapid and spends the least time in the excited state. If the rate constant for relaxation is more favorable in the radiationless path, the fluorescence will be less intense or absent.

Relaxation and Fluorescence

Often, when an excited state species relaxes, giving off a photon, the wavelength of the photon is different from the one that initially led to excitation. When this happens, the photon is invariably red-shifted; its wavelength is longer than the initial one. This situation is called "fluorescence" (Figure 15.1.3).

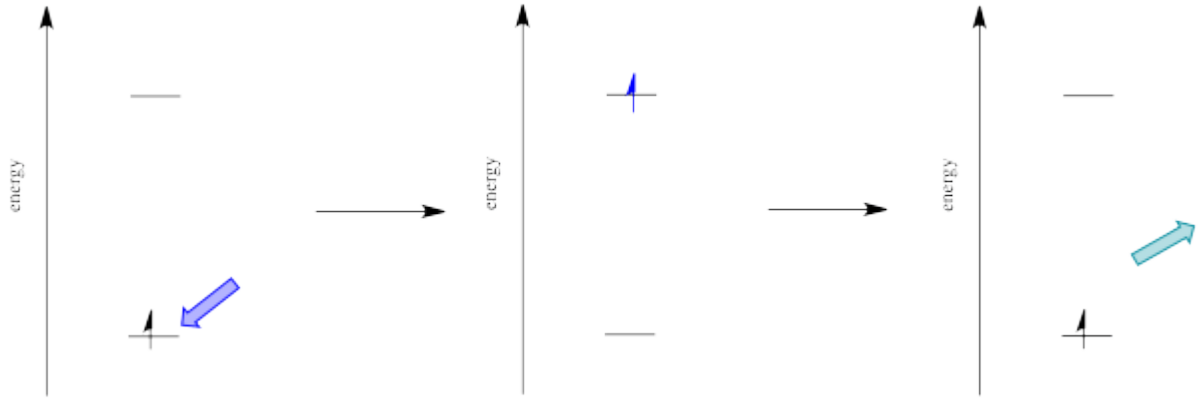


Figure 15.1.3: The absorption of purple light by a ground state particle, leading to the creation of an excited state particle. This excited state particle then emits blue light as it returns to the ground state.

How can that be? Isn't energy quantized? How is the molecule suddenly losing some of the energy that the original photon brought with it? This energy discrepancy is related to the Franck-Condon principle from the previous page. When an electron is promoted to an electronic excited state, it often ends up in an excited vibrational state as well (Figure 15.1.4). Vibrational energy, however, is not exchanged exclusively by means of photons. It can be gained or lost through molecular collisions and heat transfer.

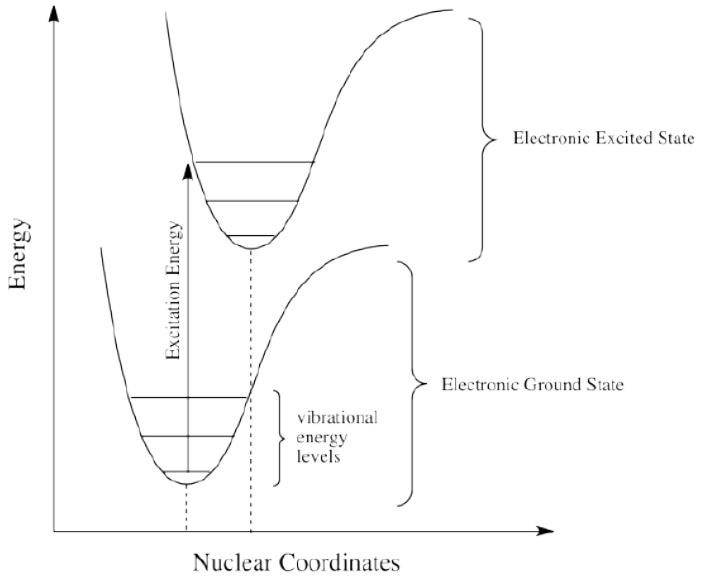


Figure 15.1.4: Transition from the ground state to an excited vibrational state within the excited electronic state.

Thus, an excited state molecule with an electron in a high-energy vibrational level within an excited electronic state might simply re-emit a photon of exactly the same wavelength as the one that was absorbed. But the excited electron is much more likely to relax into the lowest vibrational state within the excited electronic state, losing some of that initial excitation energy as heat. When the electron relaxes to this lower vibrational state, the energy gap between this excited state and the ground state is a little smaller. The photon that is emitted upon fluorescence will have lower energy and longer wavelength than a photon emitted from the original, higher vibrational level, excited state. See Figure 15.1.5.

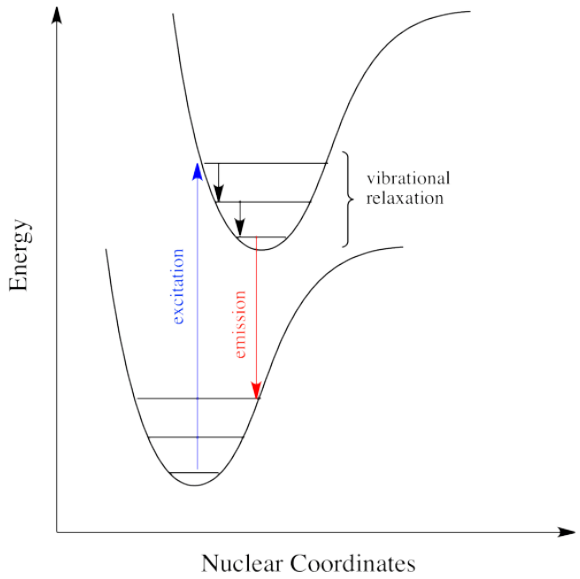


Figure 15.1.5: Excitation, followed by vibrational relaxation, and then emission.

Figure 15.1.6 shows the fluorescence transitions of a hypothetical diatomic molecule in which the equilibrium bond length of the ground state and the first singlet excited state are identical. In this molecule all absorptions involve transitions from the lowest vibrational level of the electronic ground state ($v'' = 0$) to various vibrational levels in the excited electronic state. Because vibrational relaxation occurs more rapidly than fluorescence, the fluorescence spectrum is composed of lines showing transitions from the lowest vibrational level of the excited state ($v' = 0$) to various vibrational levels in the electronic ground state.

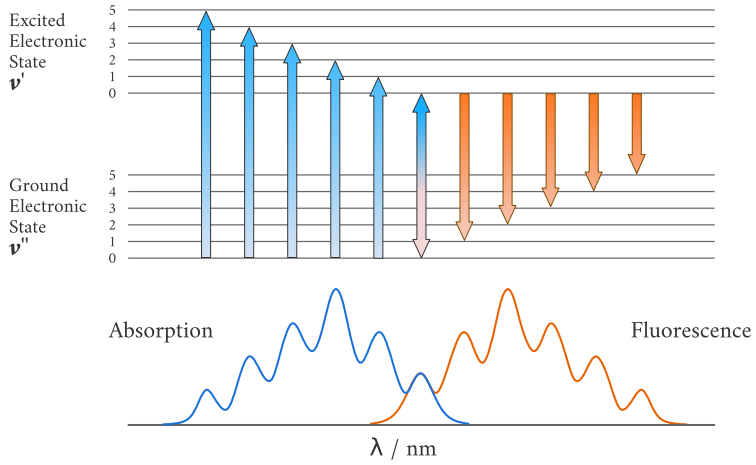


Figure 15.1.6: Absorption and fluorescence transitions in a hypothetical diatomic molecule in which the equilibrium bond length of the ground state is equal to the equilibrium bond length of the excited state. (CC BY-NC; Ümit Kaya, via LibreTexts)

Just how does a molecule undergo vibrational relaxation? Vibrational energy is the energy used to lengthen or shorten bonds, or to widen or squeeze bond angles. Given a big enough molecule, some of this vibrational energy could be transferred into bond lengths and angles further away from the electronic transition. Otherwise, if the molecule is small, it may transfer some of its

energy in collisions with other molecules. In molecules, as one molecule drops to a lower vibrational state, the other will hop up to a higher vibrational state with the energy it gains. In Figure 15.1.7 below, the red molecule is in an electronic excited and vibrational state. In a collision, it transfers some of its vibrational energy to the blue molecule.

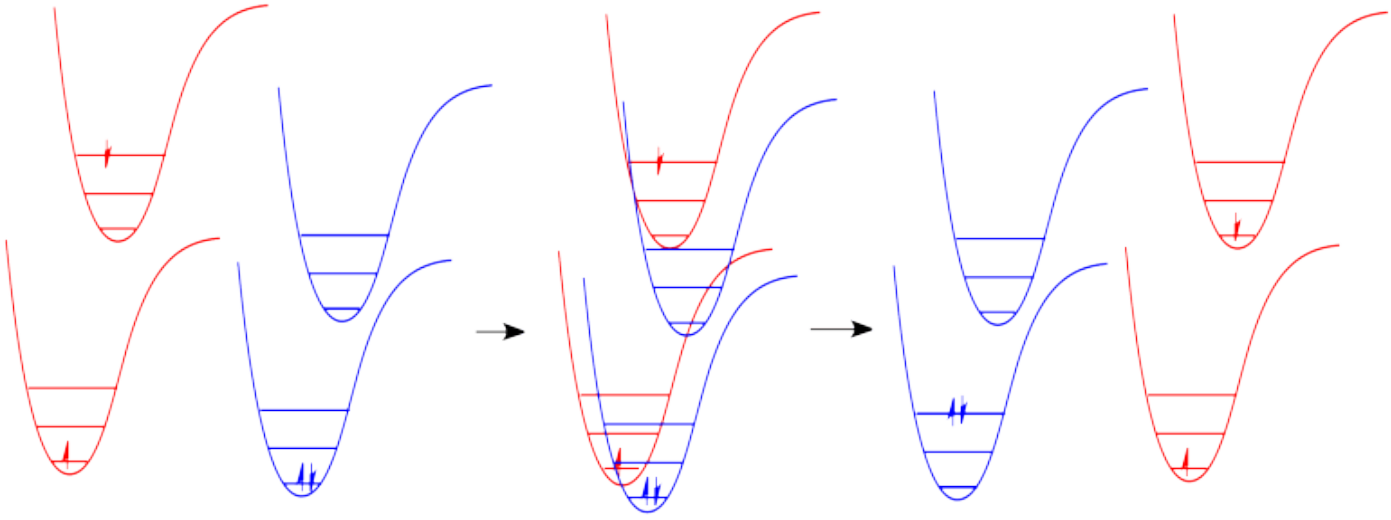


Figure 15.1.7: The transfer of vibrational energy (heat) through a collision.

Note

There are many examples of energy being transferred this way in everyday life. In a game of pool, one billiard ball can transfer its energy to another, sending it toward the pocket. Barry Bonds can transfer a considerable amount of energy through his bat into a baseball, sending it out of the park, just as Serena Williams can send a whole lot of energy whizzing back at her sister.

Exercise 15.1.1

How does the energy of an electronic absorption compare to other processes? To find out, you might consider the excitation of an entire mole of molecules, rather than a single molecule absorbing a single photon. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 180 nm (ultraviolet)
b. absorbance at 476 nm (blue)
c. absorbance at 645 nm (red)

Answer available at the end of this section.

Exercise 15.1.2

How does the energy of an excitation between vibrational states compare to that of an electronic excitation? Typically, infrared absorptions are reported in cm^{-1}, which is simply what it looks like: the reciprocal of the wavelength in cm. Because wavelength and frequency are inversely related, wavenumbers are considered a frequency unit. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 3105 cm^{-1}
b. absorbance at 1695 cm^{-1}
c. absorbance at 963 cm^{-1}

Answer available at the end of this section.

Internal Conversion

If electrons can get to a lower energy state, and give off a little energy at a time, relaxing to lower and lower vibrational levels, do they need to give off a photon at all? Maybe they can relax all the way down to the ground state via vibrational relaxation. That is certainly the case. Given many vibrational energy levels, and an excited state that is low enough in energy so that some of its lower vibrational levels overlap with some of the higher vibrational levels of the ground state, an electron can relax from an excited electronic state back to the ground state without releasing a photon (Figure \({15{.}1{.}\eatSpaces{8} \endSpaces}).

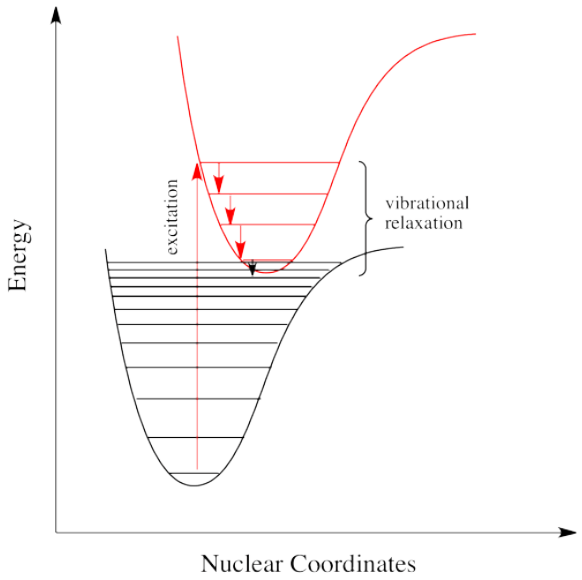


Figure 15.1.8: Relaxation of an excited state particle to the ground state through the nonradiative process of internal conversion.

This event is called a "radiationless transition", because it occurs without release of a photon. The electron simply slides over from a low vibrational state of the excited electronic state to a high vibrational state of the electronic ground state. If the electron simply keeps dropping a vibrational level at a time back to the ground state, the process is called **"internal conversion"**.

Internal conversion has an important consequence. Because the absorption of UV and visible light can result in energy transfer into vibrational states, much of the energy that is absorbed from these sources is converted into heat. That can be a good thing if you happen to be a marine iguana trying to warm up in the sun after a plunge in the icy Pacific. It can also be a tricky thing if you are a process chemist trying to scale up a photochemical reaction for commercial production of a pharmaceutical, because you have to make sure the system has adequate cooling available.

Intersystem Crossing

Intersystem crossing is a process that leads to the electron getting caught between the excited state and the ground state. Just as, little by little, vibrational relaxation can lead the electron back onto the ground state energy surface, it can also lead the electron into states that are intermediate in energy in which the spin multiplicity has changed.

For example, suppose an organic molecule undergoes electronic excitation. Generally, organic molecules have no unpaired electrons. Their ground states are singlet states. According to one of the selection rules for electronic excitation, the excited state must also have no unpaired electrons. In other words, the spin on the electron that gets excited is the same after excitation as it was before excitation.

However, that's not the lowest possible energy state for that electron. When we think about atomic orbital filling, there is a rule that governs the spin on the electrons in degenerate orbitals: in the lowest energy state, **spin is maximized** (Hund's rule). In other words, when we draw a picture of the valence electron configuration of nitrogen, we show nitrogen's three p electrons each in its own orbital, with their spins parallel.



Figure 15.1.9: The diagram on the left shows the energetically stable quartet spin state. The diagram on the right shows the less stable doublet spin state.

In Figure 15.1.9, the diagram on the left, with three unpaired electrons, all with parallel spins, shows a nitrogen in the quartet spin state. This is the most stable state. Having one of those spins point the other way would result in a different, higher energy spin state. The diagram on the right shows a different a different spin state, in which one pair of electrons in the p level is spin-paired, one up and one down, even though they are in different p orbitals. That would leave one electron without an opposite partner, so the nitrogen would be in a doublet spin state. The spin state on the left is **lower** in energy than the state on the right. That's just one of the rules of quantum mechanics (**Hund's rule**): maximize spin when degenerate orbitals are singly occupied.

A similar argument can be made for a molecule with the triplet state lower in energy than the singlet state, as shown in Figure 15.1.10. Why didn't the electron get excited to the triplet state in the first place? That is a forbidden (unlikely) electronic transition. But sliding down vibrationally onto the triplet state from the singlet excited state is not, because it doesn't involve absorption or emission of a photon.

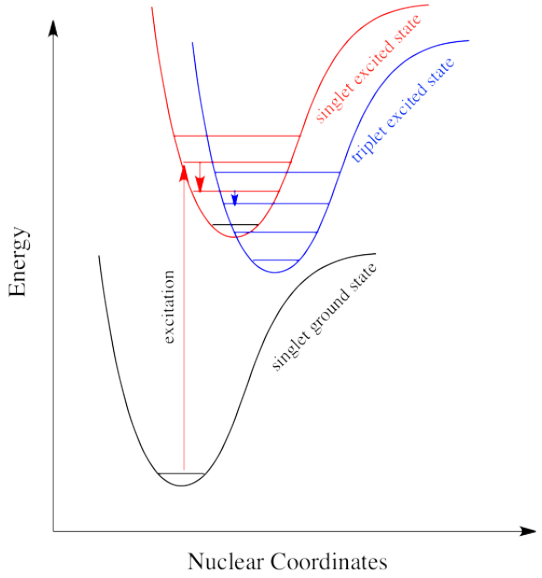


Figure 15.1.10: Intersystem crossing from a singlet excited state to a triplet excited state.

Intersystem crossing can have important consequences in reaction chemistry because it allows access to triplet states that are not normally available in many molecules. Because triplet states feature unpaired electrons, their reactivity is often typified by radical processes. That means an added suite of reactions can be accessed via this process.

Phosphorescence: A Radiationless Transition Followed by Emission

Intersystem crossing is one way a system can end up in a triplet excited state. Even though this state is lower in energy than a singlet excited state, it cannot be accessed directly via electronic excitation because that would violate the spin selection rule (\Delta S=0\). Once intersystem crossing has occurred, the process of reattaining the ground state slows down dramatically. The quick way back to ground state is to emit a photon. But because that would involve a change in spin state, it is not allowed. Realistically speaking, that means it takes a long time. By "a long time", we might mean a few seconds, several minutes, or possibly even hours. Eventually, the electron can drop back down, accompanied by the emission of a photon. This situation is called "phosphorescence" (Figure \({15{.}1{.}\eatSpaces{11} \endSpaces}).

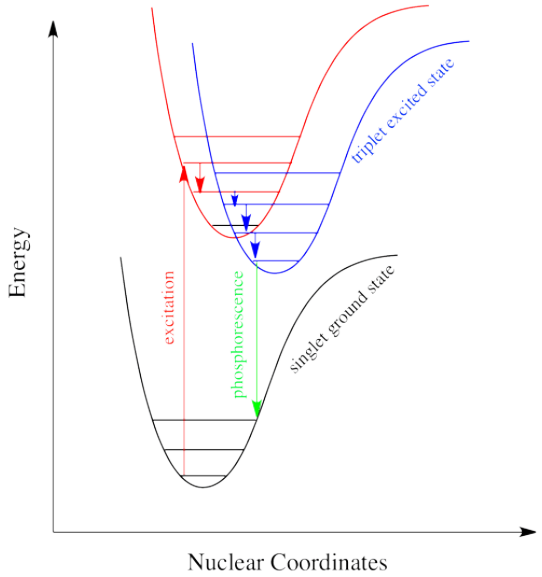


Figure 15.1.11: The process of phosphorescence - excitation, followed by vibrational relaxation, intersystem crossing, and phosphorescence.

Many plants and animals use phosphorescence as a means of signaling. Molecules that display phosphorescence are also often incorporated into toys and shirts so that they will glow in the dark.

External Conversion

Deactivation of the excited electronic state may also involve the interaction and energy transfer between the excited state and the solvent or solute in a process called **external conversion.** Low temperature and high viscosity lead to enhanced fluorescence because they reduce the number of collision between molecules, thus slowing down this type of deactivation process.

Absorption and Emission Rates

The table below compares the absorption and emission rates of fluorescence and phosphorescence. The rate of photon absorption is very rapid. Fluorescence emission occurs at a slower rate. Since the triplet to singlet (or reverse) is a forbidden transition, meaning it is less likely to occur than the singlet-to-singlet transition, the rate of triplet to singlet is typically slower. Therefore, phosphorescence emission requires more time than fluorescence.

Table 15.1.1 : Rates of Absorption and Emission comparison.

Process	Radiative Process?	Transition	Timescale (sec)
Light Absorption (Excitation)	yes	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	no	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	no	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	no	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	yes	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	yes	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay to Ground State (Internal Conversion)	no	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

References

1. D. A. Skoog, et al. "Principles of Instrumental Analysis" 6th Edition, Thomson Brooks/Cole. 2007
2. D. C. Harris and M.D. Bertolucci "Symmetry and Spectroscopy, An Introduction to Vibrational and Electronic Spectroscopy" Dover Publications, Inc., New York. 1989.

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Answers

Exercise 15.1.1

One method to carry out this calculation: $\frac{1}{x\text{nm}} \times \frac{1\,\text{nm}}{1x10^{-9}\,\text{m}} \times 6.626x10^{-34}\text{Js} \times \frac{3.000x10^{8}\text{m}}{\text{s}} \times \frac{6.022x10^{23}\text{photons}}{1.000\text{mole}} \times \frac{1\text{kJ}}{1000\text{J}}$

a. 665.0 kJ/mol
b. 251.5 kJ/mol
c. 185.6 kJ/mol

Exercise 15.1.2

One method to carry out this calculation: $x\text{cm}^{-1} \times \frac{100\,\text{cm}}{1\,\text{m}} \times 6.626x10^{-34}\text{Js} \times \frac{3.000x10^{8}\text{m}}{\text{s}} \times \frac{6.022x10^{23}\text{photons}}{1.000\text{mole}} \times \frac{1\text{kJ}}{1000\text{J}}$

a. 37.14 kJ/mol
b. 20.27 kJ/mol
c. 11.52 kJ/mol

By comparing these answers with those from Exercise 15.1.1, we can see that the energy difference between vibrational states is an order of magnitude less than the energy difference between electronic states.

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15.2: The Dynamics of Transitions can be Modeled by Rate Equations

The Interaction of Light with Atoms

In 1916, Albert Einstein proposed that there are three processes occurring in the formation of an atomic spectral line. The three processes are referred to as spontaneous emission, stimulated emission, and absorption (figure 15.2.1).

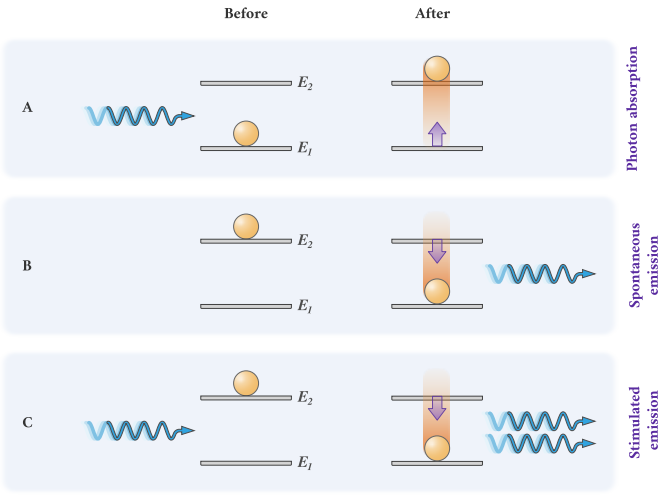


Figure 15.2.1: The three processes that can occur during the formation of a spectral line. A) Absorption of a photon, leading to the promotion of an electron to a higher electronic energy level. B) The spontaneous emission of a photon created by the relaxation of an electron back to the ground state. C) The stimulated emission of a photon created by the influence of a passing photon, accompanied by the relaxation of an electron back to the ground state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For now, let's make our discussion as simple as possible, by assuming we are talking about the interaction of light with an atom that has only two energy levels. There is a collection of these atoms present, and they are in an assortment of states, some in the ground state, and some in "the" excited state. Our discussion of photon emission to this point has generally centered around *spontaneous emission*, the triggering of which we attributed to a perturbation in the hamiltonian that comes from (if nothing else) vacuum fluctuations.

Suppose some of these atoms spontaneously emit photons, and now the collection of atoms is not sitting in a total vacuum, but is in the presence of many photons as well. We now consider what effects these present photons can have on the atoms. The answer depends upon which state the atom is in when it encounters the photon. If the atom is in the ground state, then it can absorb the photon and go to the excited state. If the atom is in its excited state, it can't absorb the photon, but the time-varying EM fields of the photon present a nice perturbation to the electron's hamiltonian (at just the right frequency!) to induce the emission of a photon. This is called *stimulated emission*. The photon that induces the emission is unaffected by the interaction, and continues on its merry way. The emitted photon naturally has the same frequency as the passing photon (the energy gap assured this), but it also emerges moving in the same direction as, *and in phase with* the stimulating photon. This completes the acronym - **L**ight **A**mplification by the **S**timulated **E**mission of **R**adiation.

It turns out that if a photon happens by two of these atoms, the first in the ground state and the second in the excited state, the probability that it will be absorbed by the first is equal to the probability that it will stimulate emission in the other – neither of these results is preferred over the other. Now consider a collection of these atoms in a state of some fixed total energy. This total energy comes from the number of atoms in the ground state multiplied by the energy of that state, plus the number of atoms in the excited state multiplied by the number of atoms in that state. As we will discuss in a future chapter, the populations of these two states subject to the constraint of the total energy can be shown to be a function that depends upon the energy difference of

the two states and the temperature of the collection of atoms. Specifically, if N_1 is the number of atoms in the ground state, N_2 is the number of atoms in the excited state, and the energy difference is ΔE, then the following relation holds:

$$N_1 = N_2\, e^{\frac{\Delta E}{k_B T}}$$

where T is the temperature and k_B is Boltzmann's constant. Clearly N_1 is greater than N_2, but how much greater? We can do a very quick calculation of this using an approximation that at room temperature, the constant $k_B T$ is about 1/40 eV. Let's assume that the energy difference between two energy states of an atom is on the order of 1eV. Then the number of ground state atoms would exceed the number of excited state atoms by a factor of $e^{40} = 2.4\times10^{17}$!

Thus, a photon passing through this collection has an equal probability of being absorbed or stimulating emission if it happens by an atom prepared for one of those actions. But there are so many more atoms available to absorb the photon, that this has a much greater chance of happening. While waiting for a photon to stimulate emission, an atom in an excited state will impatiently emit a photon spontaneously, which will then be much more likely to be absorbed than stimulate emission, and things continue like this, with some atoms spontaneously sending out photons while others absorb them... no laser.

Einstein Coefficients

Einstein proposed a separate rate equation for each of the three processes described above. The rate of each process is proportional to the number of particles in either the ground state (absorption) or the excited state (emission). Each rate is also proportional to the spectral radiant energy density, ρ_ν, which is a measure of the radiant energy density (ρ) per unit frequency of the light associated with the transition. Thus, $\rho_\nu = \frac{d\rho}{d\nu}$, and has units of $\frac{J \cdot s}{m^3}$. With each process there is also an associated Einstein coefficient, which is a proportionality constant.

Photon absorption

Absorption is the process by which a photon is absorbed by the atom, causing an electron to jump from a lower energy level to a higher one (figure $15.2.1a$). The process is described by the Einstein coefficient $B_{12}\left(\frac{m^3}{J \cdot s^2}\right)$, which gives the probability per unit time per unit spectral radiance of the radiation field that an electron in state 1 with energy E_1 will absorb a photon with an energy $E_2 - E_1 = h\nu_{12}$ and jump to state 2 with energy E_2. If $N_1(t)$ is the number density of atoms in state 1, then the change in the number density of atoms in state 1 per unit time due to absorption will be

$$-\frac{dN_1(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t)$$

If only absorption occurred, the increase of the excited state population as a function of time is equal to the decrease of the ground state population as a function of time.

Spontaneous emission

Spontaneous emission is the process by which an electron "spontaneously" (i.e. without any outside influence) decays from a higher energy level to a lower one (figure $15.2.1b$). The process is described by the Einstein coefficient $A_{21}(s^{-1})$, which gives the probability per unit time that an electron in state 2 with energy E_2 will decay spontaneously to state 1 with energy E_1, emitting a photon with an energy $E_2 - E_1 = h\nu_{21}$. Due to the energy-time uncertainty principle, the transition actually produces photons within a narrow range of frequencies called the spectral linewidth. If $N_2(t)$ is the number density of atoms in state 2, then the change in the number density of atoms in state 2 per unit time due to spontaneous emission will be

$$-\frac{dN_2(t)}{dt} = A_{21}N_2(t)$$

The same process results in increasing of the population of the state 1:

$$\frac{dN_1(t)}{dt} = A_{21}N_2(t)$$

Stimulated emission

Stimulated emission (also known as induced emission) is the process by which an electron is induced to jump from a higher energy level to a lower one by the presence of electromagnetic radiation at (or near) the frequency of the transition (figure $15.2.1c$). From the thermodynamic viewpoint, this process must be regarded as negative absorption. The process is described by the Einstein coefficient $B_{21}\left(\frac{m^3}{J\cdot s^2}\right)$, which gives the probability per unit time per unit spectral radiance of the radiation field that an electron in state 2 with energy E_2will decay to state 1 with energy E_1, emitting a photon with an energy $E_2 - E_1 = h\nu_{21}$. The change in the number density of atoms in state 1 per unit time due to induced emission will be

$$\frac{dN_1(t)}{dt} = B_{21}\rho_\nu(\nu_{21})N_2(t)$$

The Relationship between A_{21}, B_{12}, and B_{21}

In 1900, Max Planck derived a formula for the energy density per unit bandwidth of a blackbody radiator by making the assumption that only discrete energies are allowed. His work agreed with known experimental data, and it is one of the fundamental ideas of quantum mechanics. More specifically, the spectral energy density per unit bandwidth, $\rho_\nu(\nu_{12})$ in units $\frac{J\cdot s}{m^3}$, is given by

$$\rho_\nu(\nu_{12}) = \frac{8\pi h}{c^3}\frac{\nu_{12}^3}{e^{(h\nu_{12})/(k_BT)}-1} \tag{15.2.1}$$

In a given sample of atoms exposed to radiation of the correct frequency all three processes will be occurring simultaneously. Thus the rate of change of the populations of the two states will be

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_\nu(\nu_{21})N_2(t) \tag{15.2.2}$$

If we assume that the two energy states are in thermal equilibrium, then N_1 and N_2 are constant, and thus

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_\nu(\nu_{21})N_2(t) = 0 \tag{15.2.3}$$

Upon solving for $\rho_\nu(\nu_{12})$, we get

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{(N_1(t)/N_2(t))B_{12} - B_{21}} \tag{15.2.4}$$

Recall that in this equation N_1/N_2 represents the electron density in the lower energy state divided by the electron density in the upper state at equilibrium. This quantity is a function of temperature. Assuming many allowed energy states, the number of occupied states decreases exponentially with temperature, as per Boltzmann statistics.

$$N_2/N_1 = \frac{g_2}{g_1}e^{(-h\nu_{12})/(k_BT)} \tag{15.2.5}$$

The quantity $\frac{g_2}{g_1}$ represents the degeneracy level, which is the number of allowed electrons in the upper state over the number of allowed electrons in the lower state. In this expression, g_1 and $g2$ are unitless measures of the number of ways electrons can occupy an energy states. Upon rearrangement, equation 15.2.5 becomes

$$N_1/N_2 = \frac{g_1}{g_2}e^{(h\nu_{12})/(k_BT)} \tag{15.2.6}$$

Equations 15.2.6 and 15.2.4 can be combined to get

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{\left(\frac{g_1}{g_2}e^{(h\nu_{12})/(k_BT)}\right)B_{12} - B_{21}} \tag{15.2.7}$$

which can be rearranged to

$$\rho_\nu(\nu_{12}) = \frac{\frac{A_{21}}{B_{21}}}{\left(\frac{g_1 B_{12}}{g_2 B_{21}} e^{(h\nu_{12})/(k_B T)}\right) - 1} \tag{15.2.8}$$

One expression for the energy density per unit bandwidth of this system is given by Equation 15.2.1. Equation 15.2.8 gives a second expression for the energy density per unit bandwidth, and it was found by considering the relative rates of absorption, spontaneous emission, and stimulated emission. These equations can be combined to relate the rates of the different processes.

$$\frac{8\pi h}{c^3} \frac{\nu_{12}^3}{e^{(h\nu_{12})/(k_B T)} - 1} = \frac{\frac{A_{21}}{B_{21}}}{\left(\frac{g_1 B_{12}}{g_2 B_{21}} e^{(h\nu_{12})/(k_B T)}\right) - 1} \tag{15.2.9}$$

The above equation is true for the conditions

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h \nu_{12}^3}{c^3} \tag{15.2.10}$$

and

$$\frac{g_1 B_{12}}{g_2 B_{21}} = 1 \tag{15.2.11}$$

If we know one of the Einstein coefficients, we can quickly calculate the other two Einstein coefficients using equations 15.2.10 and 15.2.11.

These equations also provide further insight into the operation of lasers and other devices based on stimulated emission. The overall nonequilibrium upper state population rate is given by

$$\frac{dN_2(t)}{dt} = -A_{21} N_2 - B_{21} \rho_\nu(\nu_{21}) N_2 + B_{21} \frac{g_2}{g_1} \rho_\nu(\nu_{12}) N_1 \tag{15.2.12}$$

which can be simplified with some algebra.

$$\frac{dN_2(t)}{dt} = -A_{21} N_2 - B_{21} \rho_\nu(\nu_{12}) \left(N_2 - \frac{g_2}{g_1} N_1\right) \tag{15.2.13}$$

The term in parenthesis is the net upper state population. Optical amplification and lasing can only occur when the term in parenthesis is positive. The condition

$$N_2 - \frac{g_2}{g_1} N_1 > 0 \tag{15.2.14}$$

is called a population inversion. It only occurs when enough energy is being supplied to the system, by optical, electrical, or thermal means, so that there are more electrons in the upper energy level than the lower energy level. This situation cannot be achieved for a two-level system, as will be shown in the next section. However, in section 15.4, it will be shown that this situation can be achieved if the system has more than two levels.

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15.3: A Two-Level System Cannot Achieve a Population Inversion

Lasing in Two-Level Systems

For the sake of our studies, let's first consider a laser medium whose atoms have only two energy states: a ground state and one excited state. In such an idealized atom the only possible transitions are excitation from the ground state to the excited state and de-excitation from the excited state back into ground state. Could such an atom be used to make a laser?

There are several important conditions that our laser must satisfy. First of all, the light that it produces must be coherent. That is to say, it must emit photons that are in-phase with one another. Secondly, it should emit monochromatic light, i.e. photons of the same frequency (or wavelength). Thirdly, it would be desirable if our laser's output were collimated, producing a sharply defined "pencil-like" beam of light (this is not crucial, but clearly a desirable condition). Lastly, it would also be desirable for our laser to be efficient, i.e. the higher the ratio of output energy - to - input energy, the better.

Let us begin by examining the requirements for our first condition for lasing, coherence. This condition is satisfied only when the lasing transition occurs through stimulated emission. As we have already seen, stimulated emission produces identical photons that are of equal energy and phase and travel in the same direction. But for stimulated emission to take place a "passer-by" photon whose energy is just equal to the de-excitation energy must approach the excited atom before it de-excites via spontaneous emission. Typically, a photon emitted by the spontaneous emission serves as the seed to trigger a collection of stimulated emissions. Still, if the lifetime of the excited state is too short, then there will not be enough excited atoms around to undergo stimulated emission. So, the first criteria that we need to satisfy is that the upper lasing state must have a relatively long lifetime, otherwise known as a meta-stable state, with typical lifetimes in the milliseconds range. In addition to the requirement of a long lifetime, we need to ensure that the likelihood of absorption of the "passer-by" photons is minimized. This likelihood is directly related to the ratio of the atoms in their ground state versus those in the excited state. The smaller this ratio, the more likely that the "passer-by" photon will cause a stimulated emission rather than get absorbed. So, to satisfy this requirement, we need to produce a **population inversion**: create more atoms in the excited state than those in the ground state.

Another way of stating the above set of conditions is that the rate of absorption must be less than the rate of stimulated emission

$$\underbrace{B_{21}\rho_\nu(\nu_{21})N_2}_{\text{rate of stimulated emission}} > \underbrace{B_{12}\rho_\nu(\nu_{12})N_1}_{\text{rate of absorption}} \tag{15.3.1}$$

As shown in the previous section, $B_{21} = B_{12}$ and $\rho_\nu(\nu_{12}) = \rho_\nu(\nu_{21})$, thus Equation 15.3.1 becomes

$$N_2 > N_1.$$

Hence, if $N_2 > N_1$ then there is a population inversion.

Achieving population inversion in a two-level atom is not very practical. Such a task would require a very strong pumping transition that would send any decaying atom back into its excited state. This would be similar to reversing the flow of water in a waterfall. It can be done but is very energy costly and inefficient. In a sense, the pumping transition would have to work against the lasing transition.

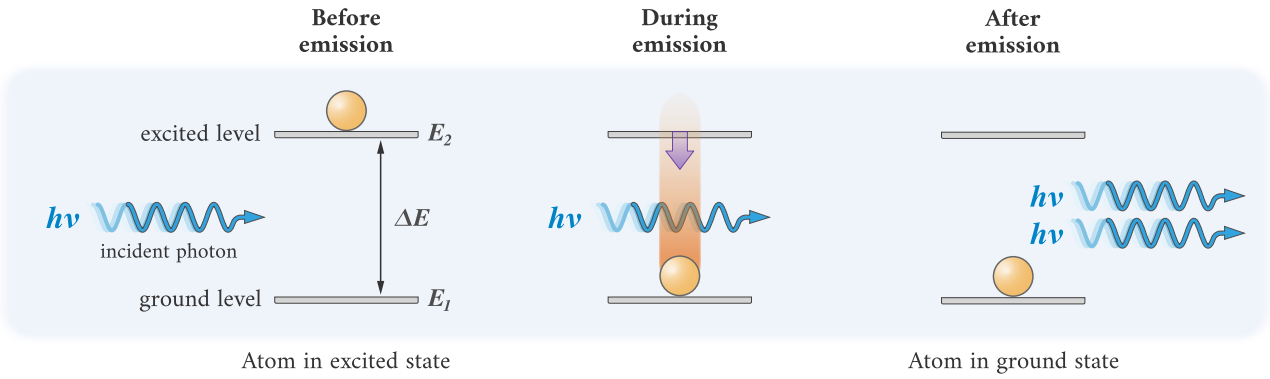


Figure 15.3.1: A two-level lasing system. (CC BY-NC; Ümit Kaya via LibreTexts)

It is clear, from figure 15.3.1, that in the two-level atom the pump is, in a way, the laser itself! Such a two-level laser would work only in jolts. That is to say, once the population inversion is achieved the laser would lase. But immediately it would end up with more atoms in the lower level. Such two-level lasers involve a more complicated process. We will see, in later material, examples of these in the context of excimer lasers, which are pulsed lasers. For continuous lasing action, we need to consider other possibilities, such as a three-level atom.

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15.4: Population Inversion can be Achieved in a Three-Level System

Optical pumping will at most achieve only an equal population in a two-level system. This is because the probabilities for raising an electron to the upper level and inducing the decay of an electron to the lower level (stimulated emission) are exactly the same! In other words, when both levels are equally populated, the numbers of electrons "going up" and "down" will be the same, so you cannot achieve population inversion which is required for lasers. The solution is to involve a third, metastable level of intermediate energy. The pumping will occur between the two levels with the greatest energy difference, creating a highly populated upper energy level. Two lasing processes are possible once this situation has been obtained. Lasing occurs between the upper level and the intermediate level if the electrons in the upper energy level decay slowly to the intermediate, metastable level, and if the electrons in the intermediate level decay rapidly to the ground state. However, if the electrons in the upper energy level quickly decay into the intermediate level, and the transition from the intermediate level to the ground level is slow, then lasing occurs between the intermediate level and the ground state. In both cases, the lasing frequency has a frequency different than that of the pumping frequency between the ground level and the upper level, so the pumping is off-resonant to the laser transition and will not trigger stimulated emission.

Lasing in Three-Level Systems

The first laser that was demonstrated to operate was a three-level laser, known as **Maiman's ruby laser**.

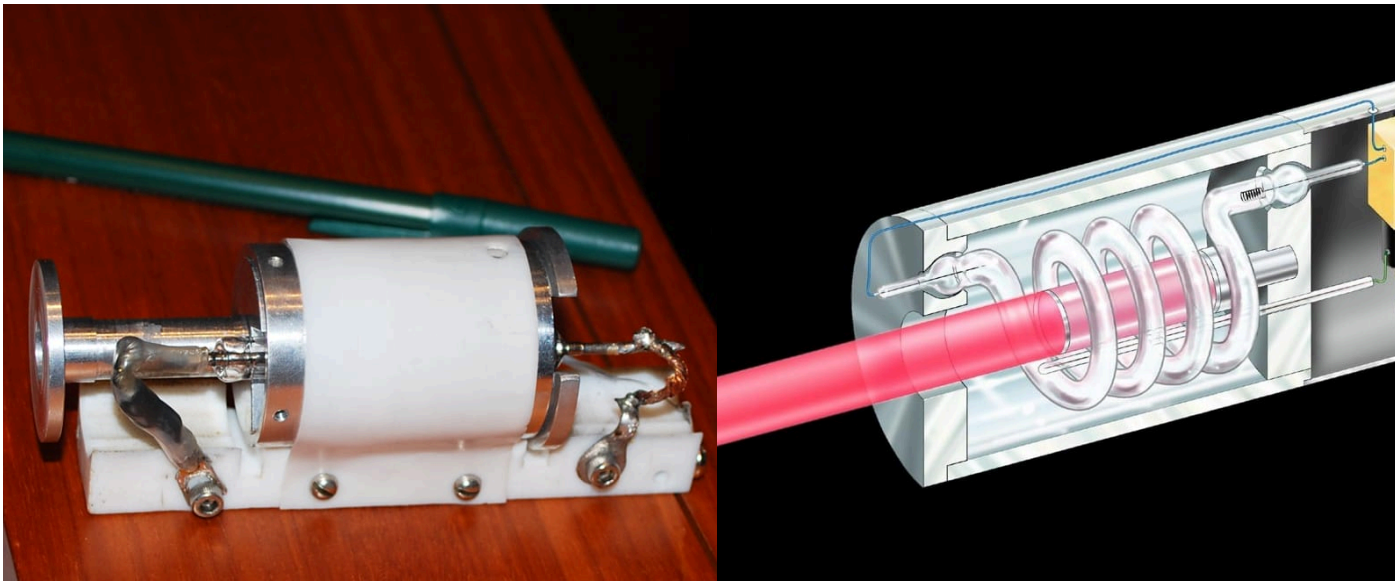


Figure 15.4.1: (left) A copy of a Maiman laser (CC 0; Guy Immega) (right) Internal view of a Maiman laser (https://commons.wikimedia.org/w/inde...ldid=42317741)

Figure 15.4.1 shows the outside and inside of a three-level laser. A pump causes an excitation from the ground state to the second excited state. This state is a rather short-lived state so that the atom quickly decays into the first excited level. (Atoms in the second excited state may also decay directly back to the ground state, but these atoms can be pumped back to the second excited state again.) The first excited state is a long-lived (i.e. metastable) state which allows the atom to "wait" for the "passer-by" photon while building up a large population of atoms in this state. The lasing transition, in this laser, is due to the decay of the atom from this first excited metastable state to the ground state. If the number of atoms in the ground state exceeds the number of atoms that are pumped into the excited state, then there is a high likelihood that the "lasing photon" will be absorbed and we will not get sustained laser light. The fact that the lower lasing transition is the ground state makes it rather difficult to achieve efficient population inversion. In a ruby laser, this task is accomplished by providing the ruby crystal with a very strong pulsating light source, called a flash lamp. The flash lamp produces a very strong pulse of light that is designed to excite the atoms from their ground state into a short-lived upper level. In this way, the ground state is depopulated and population inversion is achieved until a pulse of laser light is emitted. In the ruby laser, the flash lamp light lasts for about 1/1000 of a second (1 ms) and can

be repeated about every second. The duration of the laser pulse is shorter than this, typically 0.1 ms. In some pulsed lasers, the pulse duration can be tailored using special methods to be much shorter than this, down to about 10 fs (where 1 fs = 10^{-15} s or one thousandth of a millionth of a millionth of a second). So, the output of a three-level laser is not continuous but consists of pulses of laser light.

Transition Rates in Three-level Systems

In a three-level system, there are nine (9) events that can occur (Figure 15.4.2):

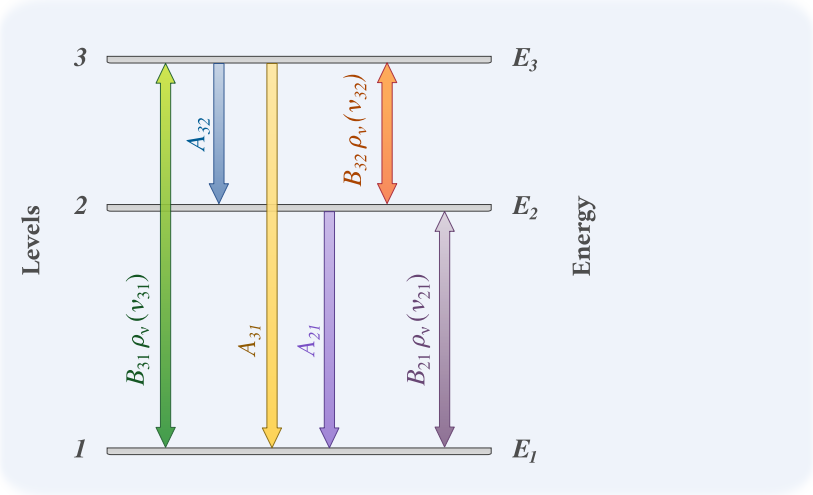


Figure 15.4.2: The nine possible events in a three-level system. (CC BY-NC; Ümit Kaya via LibreTexts)

a. absorption from level 1 to level 3, as described by $\rho_\nu(\nu_{13})B_{13}N_1$
b. spontaneous emission from level 3 to level 1, as described by $A_{31}N_3$
c. stimulated emission from level 3 to level 1, as described by $\rho_\nu(\nu_{31})B_{31}N_3$
d. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
e. stimulated emission from level 3 to level 2 (possible lasing), as described by $\rho_\nu(\nu_{32})B_{32}N_3$
f. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{23})B_{23}N_2$
g. absorption from level 1 to level 2, as described by $\rho_\nu(\nu_{12})B_{12}N_1$
h. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$
i. stimulated emission from level 2 to level 1 (possible lasing), as described by $\rho_\nu(\nu_{21})B_{21}N_2$

In most three-level lasers, neither the spontaneous emission from level 3 to level 1, nor the stimulated emission from level 3 to level 1 occur to any significant extent, and so these events are ignored in terms of the kinetics of the lasing process. It is also true that there is no excitation source to cause absorption from level 1 to level 2 other than the possible reabsorption of light emitted from a level 2 to level 1 transition, but this event is unlikely because most atoms in the ground state are pumped up to level 3. Because the pump will be used to drive the absorption from level 1 to level 3, this event is essentially under the control of the experimenter. This leaves a maximum of five events that we need to take into consideration when studying the lasing process.

A Ruby Laser

In a three-level system ruby laser such as that described above, the flash lamp will serve as the pump to repeatedly excite most of the atoms from the ground state to the second excited state. In this laser, lasing occurs due to the stimulated emission from level 2 to level 1 (Figure 15.4.3.)

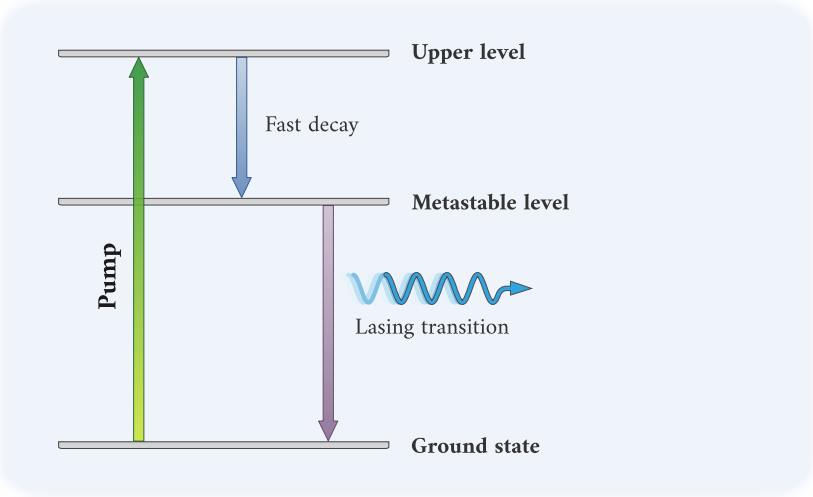


Figure 15.4.3: Lasing from level 2 to level 1 in a three-level laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Because the lasing will occur from the intermediate, metastable energy level 2, we will focus on the five events that affect its population:

a. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{32})B_{32}N_2$
b. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
c. stimulated emission from level 3 to level 2, as described by $\rho_\nu(\nu_{32})B_{32}N_3$
d. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$
e. stimulated emission from level 2 to level 1 (lasing), as described by $\rho_\nu(\nu_{21})B_{21}N_2$

In this system, the rate of spontaneous emission from level 3 to level 2 is much more rapid than the rate of absorption from level 2 to level 3, and also much more rapid than the rate of stimulated emission from level 3 to level 2. Thus, any electrons pumped into the upper level are most likely to transition between level 2 and level 3 by spontaneous emission. This means that N_2 is greater than N_1 and thus, population inversion between states 2 and 1 can be achieved. A system of atoms that are able to attain such a population inversion is called a gain medium, and can lase.

A Copper Vapor Laser

In this three-level system, the flash lamp will again, serve as the pump to repeatedly excite most of the atoms from the ground state to the second excited state. However, in this laser, lasing occurs due to the stimulated emission from level 3 to level 2 (Figure 15.4.4).

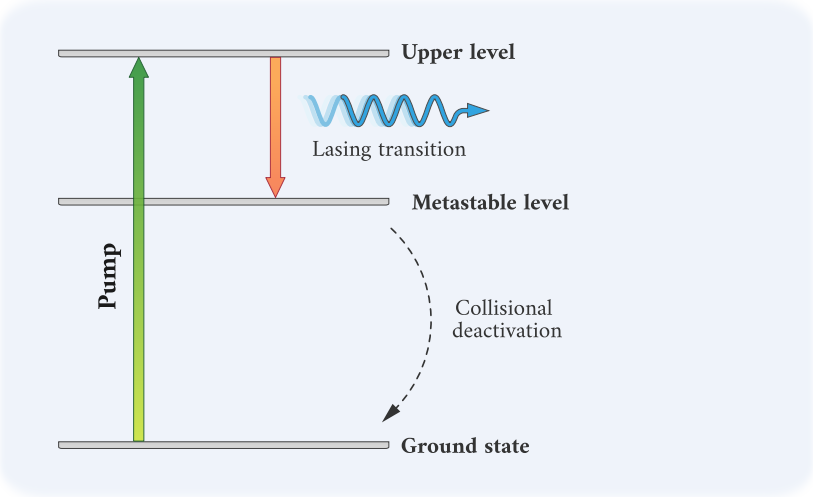


Figure 15.4.4: Lasing from level 3 to level 2 in a three-level laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Because the lasing will occur from the higher energy excited state, we focus on the four events that affect the population ratio between level 3 and level 2:

a. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{32})B_{32}N_2$
b. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
c. stimulated emission from level 3 to level 2 (lasing), as described by $\rho_\nu(\nu_{32})B_{32}N_3$
d. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$

If we assume that the atoms in the total population will be distributed between the three energy levels, then

$$N_1(t) + N_2(t) + N_3(t) = N_{total}$$

At equilibrium, the population of each level will remain constant, and so

$$0 = \frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = \frac{dN_3(t)}{dt}.$$

Thus,

$$\frac{N_2(t)}{dt} = -\rho_\nu(\nu_{32})B_{32}N_2 + A_{32}N_3 - A_{21}N_2 + \rho_\nu(\nu_{32})B_{32}N_3 = 0 \tag{15.4.1}$$

Rearranging Equation 15.4.1 gives

$$N_2(A_{21} + \rho_\nu(\nu_{32})B_{32}) = N_3(A_{32} + \rho_\nu(\nu_{32})B_{32}) \tag{15.4.2}$$

which rearranges to

$$\frac{N_3}{N_2} = \frac{A_{21} + \rho_\nu(\nu_{32})B_{32}}{A_{32} + \rho_\nu(\nu_{32})B_{32}} \tag{15.4.3}$$

From Equation 15.4.3 we can see that if A_{21} is greater than A_{32}, then N_3 can be greater than N_2. If N_3 is greater than N_2, then population inversion between states 3 and 2 can be achieved. In other words, if atoms in state 2 decay to the ground state more rapidly than atoms in state 3 decay to state 2, there will be a population inversion between states 3 and 2, and the system can lase.

Four-Level Lasers

There are also lasers based on transitions between four energy levels. These lasers can be more efficiently pumped, because the

lower level of the lasing transition is not the ground state. Only four-level lasers can provide a continuous lasing output. He-Ne and Nd:YAG lasers are common four-level lasers and will be described in section 15.6.

References

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15.5: What is Inside a Laser?

Most lasers consist of three basic components:

1. the gain medium from which light of a specific frequency is emitted
2. the pump source which provides energy to the gain medium to create the light
3. the laser optical cavity in which the light is amplified by repeatedly passing through the gain medium

The Gain Medium

The gain medium, or active medium, is a collection of atoms or molecules that can undergo stimulated emission. The active medium can be in a gaseous, liquid, or solid form. It can be a pure substance or a solution. Because the emitted light of a laser is created by the transition between two quantized states of the gain medium, laser light is always monochromatic. Laser light is also always coherent, meaning that the light waves emitted by the laser are all in phase.

Solids

The first laser, Maiman's ruby laser, described in section 15.4, used a solid rod of synthetic ruby as the gain medium (Figure 15.5.1).

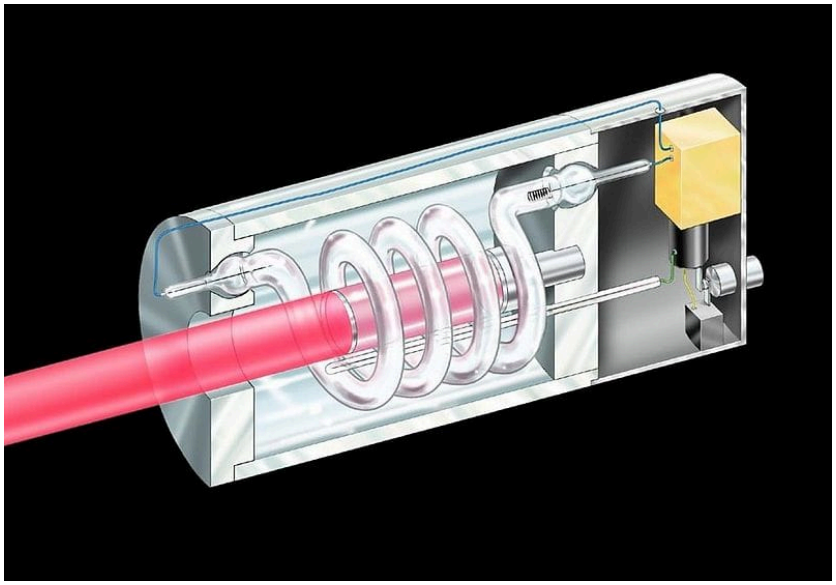


Figure 15.5.1: Internal view of a Maiman laser (Public Domain; United States Department of Energy via Wikipedia)

Ruby is a gem variety of the mineral corundum, Al_2O_3, in which Cr^{3+} ions replace roughly 0.05% (by mass) of the Al^{3+} ions. The electronic structure of the Cr^{3+} impurities enables to ruby to act as a gain medium. However, synthetic ruby must be used because natural rubies have too many crystal defects. Other solid-state gain media are shown in Table 15.5.1.

Table 15.5.1: Solid-phase gain media

Solid-state Host	Active Ion	Wavelength (nm)	Output	Lifetime
Al_2O_3	Ti^{3+}	780	continuous and pulsed	10 fs - 5 ps
Al_2O_3	Cr^{3+}	694.3	pulsed	10 ps
Glass (SiO_2)	Nd^{3+}	1059	pulsed	1 ps

Solid-state Host	Active Ion	Wavelength (nm)	Output	Lifetime
YAG $Y_3Al_5O_{15}$	Nd^{3+}	1064.1	continuous and pulsed	10-150 ps
YLF Y_3LixFy	Nd^{3+}	1054.3	continuous and pulsed	10-100 ps

Gases

A basic He-Ne laser is shown in figure 15.5.2. The gain medium is the gas mixture through which the laser beam passes.

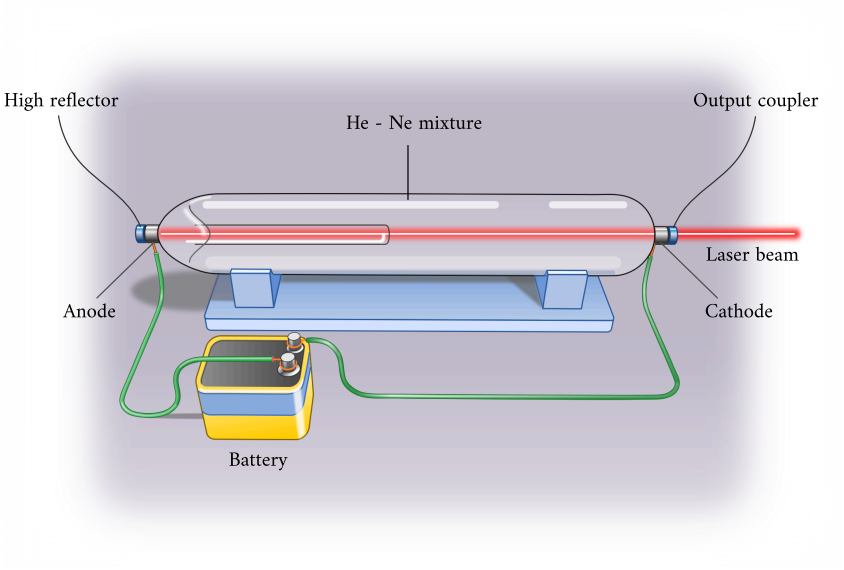


Figure 15.5.2: Internal view of a He-Ne laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Other common gas-phase media include noble gases and molecules, but also metal cations, and metal atoms as shown in Table 15.5.2.

Table 15.5.2: Gas-phase gain media

Gaseous Gain Medium	Wavelength (nm)	Output	Pulse Duration
N_2	337	pulsed	1 ns
Cu	510	pulsed	30 ns
CO_2, He, N_2	tunable near 10,000	pulsed	> 100 ns
He, Ne	3391, 1152, 632, 544	continuous	continuous
He, Cd	441, 325	continuous	continuous
Ar^+	488, 515	continuous	continuous
K^+	647	continuous	continuous.

Exciplex Lasers

Exciplex lasers involve the formation of an exciplex, a gaseous species that forms and exists only in an excited state. Because only the upper, excited state can exist, there is no population in the lower, dissociated state, thus a population inversion is obtained. The lasing transition occurs as the excited state exciplex emits its excitation energy and simultaneously falls apart. Two common exciplex lasers are XeCl* (308 nm) and KrF* ((249 nm). These lasers are often referred to as excimer laser, but the term "excimer" refers to an excited dimer, AA*, and so should not be used to describe an exciplex, AB*.

Liquid Solutions

Many dye lasers use an organic dye, usually dissolved in a solution, as the gain medium. One advantage of using a dye solution as the gain medium is that it can create a tunable laser, which allows for continuous tuning over a wide range of wavelengths. For example, rhodamine 6G is a dye that can be tuned from 635 nm to 560 nm. The dye solution enters the laser cavity by passing through a cell or by streaming through the air using a dye jet. (Figure 15.5.3).

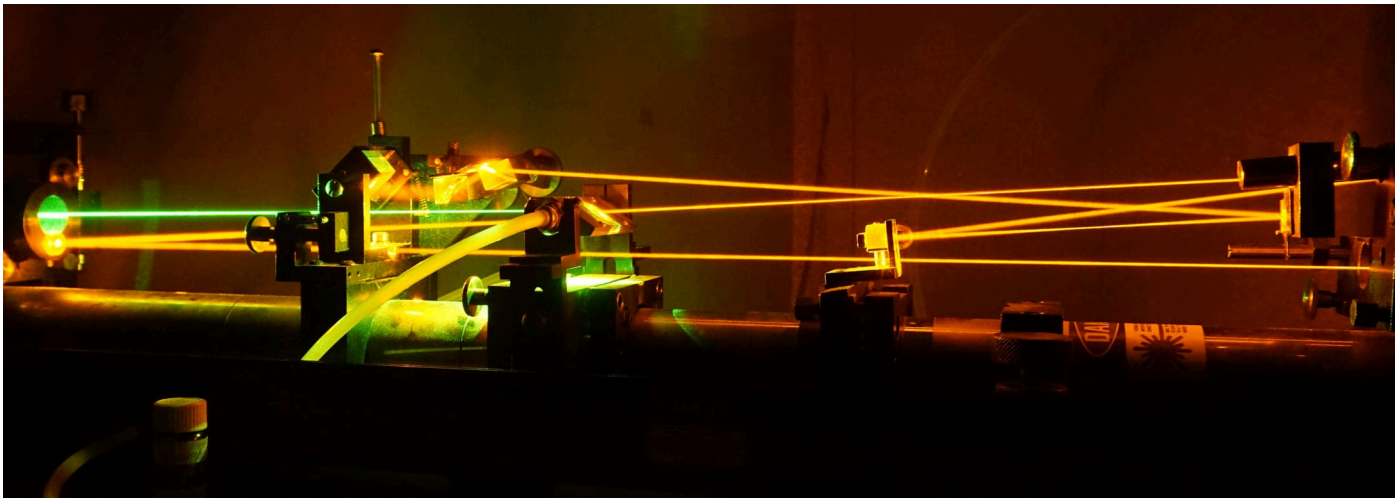


Figure 15.5.3: A dye laser in use. The dye is entering the dye cell through the yellow tube in the left foreground. (CC BY-SA 4.0, By Zaereth - Own work, https://commons.wikimedia.org/w/inde...curid=55762750)

Some common laser dyes other than rhodamine 6G and the rhodamines, include various coumarins, stilbenes, and fluorescein. There are solid state dye lasers (SSDL), in which the dye is dispersed uniformly within a solid polymer matrix.

The Pump Source

For lasing to take place, the gain medium must be pumped into an *excited state* capable of undergoing stimulated emission. The energy required for excitation is often supplied by an electric current or an intense light source, such as a flashlamp or an excitation laser. Diode lasers, excimer lasers, and YAG lasers have all been used as pump sources.

Lasers are categorized as having either a continuous beam or a pulsed beam. In theory, any laser could be run as a pulsed beam laser if the pump source is set to deliver the excitation energy in regularly repeated bursts. Not all lasers can operate as continuous-wave (CW) lasers, though, because there are gain media in which it is not possible to maintain a continuous population inversion. The ruby laser is an example of a laser that cannot produce a continuous wave.

The Laser Optical Cavity

Figure 15.5.4 shows the main components of a generic laser optical (or resonator) cavity. The optical cavity is formed by a pair of mirrors that surround the gain medium and enable feedback of light into the medium. This feedback is critical to the operation of a laser because it is where the amplification of the signal occurs. The gain medium is excited by an external pump source, such as a flash lamp, electric current, or another laser. The output coupler is a partially reflective mirror that allows a portion of the laser radiation to leave the cavity but reflects a majority of the light back through the gain medium. The light trapped between the mirrors forms standing wave structures called modes. Although beyond the scope of this discussion, the reader interested in cavity modes can consult the “Laser Radiation Properties” module.

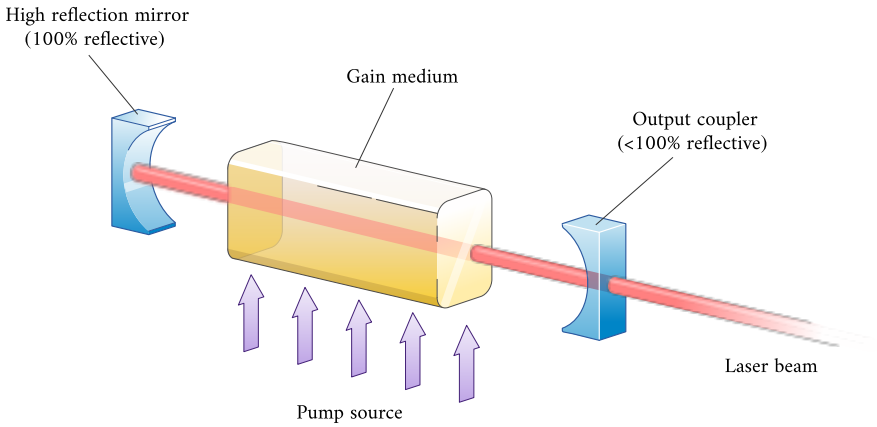


Figure 15.5.4: A schematic of a generic laser cavity. (CC BY-NC; Ümit Kaya via LibreTexts)

Figure 15.5.5 shows the laser cavity of a tunable dye laser. The laser is tunable because the pump source provides several excitation energies, which result in the creation of several possible energies for the lasing beam. The user chooses the desired lasing energy by means of a tuning element, which is often a movable diffraction grating.

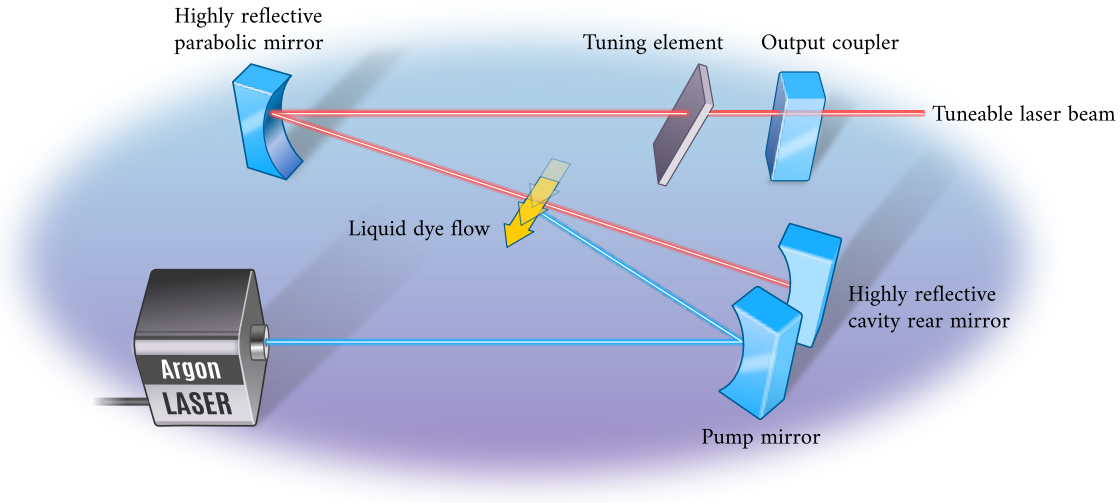


Figure 15.5.5: A schematic of a dye laser cavity with a dye jet. (CC BY-NC; Ümit Kaya via LibreTexts)

Diode Lasers

Diode lasers do not lase in the same manner as the lasers described above. There is no laser optical cavity, and thus there is no stimulated emission. Diodes made of materials such as GaAs emit light when the recombination of an electron and a hole in a semiconductor releases energy in the form of photons. A population inversion is maintained by rapidly removing the electrons that are falling into the holes of the p-type semiconductor. A pseudo-optical cavity is formed because the semiconductor materials generally have a very high refractive index, causing the photons to be trapped in the crystal of the semiconductor due to the large and abrupt difference in the refractive indices at the surfaces of the crystal. GaAs emits infrared light, but it can be doped to create a material that emits at another wavelength. For example, $GaAs_{0.6}P_{0.4}$ emits red light.

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15.6: The Helium-Neon Laser

The He-Ne laser was the first continuous-wave (cw) laser invented. A few months after Maiman announced his invention of the pulsed ruby laser, Ali Javan and his associates W. R. Bennet and D. R. Herriott announced their creation of a cw He-Ne laser. This gas laser is a four-level laser that uses helium atoms to excite neon atoms. The atomic transitions in the neon produce the laser light. The most commonly used neon transition in these lasers produces red light at 632.8 nm. These lasers can also produce green and yellow light in the visible region, as well as several UV and IR wavelengths (Javan's first He-Ne operated in the IR at 1152.3 nm). By using highly reflective mirrors designed for one of these many possible lasing transitions, a given He-Ne's output is made to operate at a single wavelength.

He-Ne lasers are not sources of high-power laser light, typically producing a few to tens of mW (milli-Watt, or 10^{-3} W) of power. Probably one of the most important features of these lasers is that they are highly stable, both in terms of their wavelength (mode stability) and intensity of their output light (low jitter in power level). For these reasons, He-Ne lasers are often used to stabilize other lasers. They are also used in applications, such as holography, where mode stability is important. Until the mid-1990's, He-Ne lasers were the dominant type of lasers produced for low-power applications - from range finding to scanning to optical transmission, to laser pointers, etc. Recently, however, other types of lasers, most notably the semiconductor lasers, seem to have won the competition because of reduced costs.

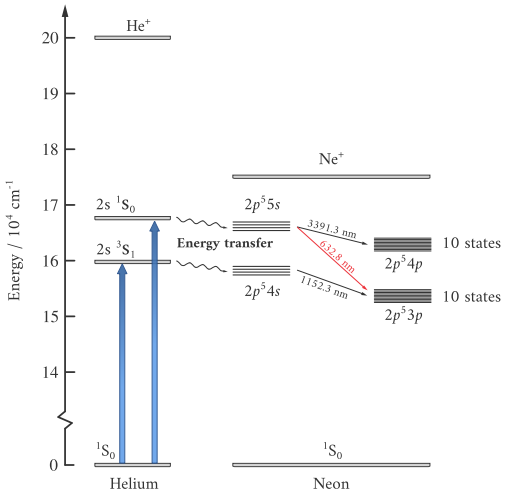


Figure 15.6.1: An energy level diagram for He and Ne in a He-Ne laser. The pumping creates helium atoms in two excited states. These excited states have energies similar to two sets of four excited states in the Ne atoms. Thus, collisions between the excited He atoms and Ne atoms can lead to nonradiative energy transfer. The excited state Ne atoms have lifetimes that enable a population inversion and lasing. (CC BY-NC; Ümit Kaya via LibreTexts)

The energy level diagram in figure 15.6.1 shows the two excited states of a helium atom, the 2 ^{3}S and 2 ^{1}S, that get populated as a result of electromagnetic pumping. Both of these states are metastable and do not allow de-excitations via radiative transitions. Instead, the helium atoms give off their energy to neon atoms through collisional excitation. In this way, the 4s and 5s levels in neon get populated.

$$He^*(2s^3\,S_1) + Ne(g) \rightarrow He(g) + Ne^*(2p^5 4s)$$

$$He^*(2s^1\,S_0) + Ne(g) \rightarrow He(g) + Ne^*(2p^5 5s)$$

These are the two upper lasing levels, each for a separate set of lasing transitions. Each of these upper lasing levels contains 4 states ($^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$). Radiative decay from the 5s to the 4s levels is forbidden. So, ten states associated with the 4p and 3p levels serve as the lower lasing levels and rapidly decay into the metastable 3s level. In this way, population inversion is easily achieved in the He-Ne mixture. The 632.8 nm laser transition, for example, involves the 5s and 3p levels, as shown above. Table 15.6.1 lists parameters of several of the Ne transitions.

Table 15.6.1: Several Lasing Transitions for an Excited State Ne Atom

Transition	λ (nm)	Einstein Coefficient A (s^{-1})	Relative Intensity
$5s^1\ P_1 \rightarrow 3p^3\ P_1$	640.1	0.60×10^6	100
$5s^1\ P_1 \rightarrow 3p^3\ P0$	635.2	0.70×10^6	100
$5s^1\ P_1 \rightarrow 3p^3\ P2$	632.8	6.56×10^6	300
$5s^1\ P_1 \rightarrow 3p^1\ P_1$	629.4	1.35×10^6	100
$5s^1\ P_1 \rightarrow 3p^1\ D_2$	611.8	1.28×10^6	100

In most He-Ne lasers the gas, a mixture of 5 parts helium to 1 part neon, is contained in a sealed glass tube with a narrow (2 to 3 mm diameter) bore as shown above in figure 15.6.2. Typically the laser's optical cavity mirrors, the high reflector and the output coupler form the two sealing caps for the narrow bore tube. High voltage electrodes create a narrow electric discharge along the length of this tube, which then leads to the narrow beam of laser light.

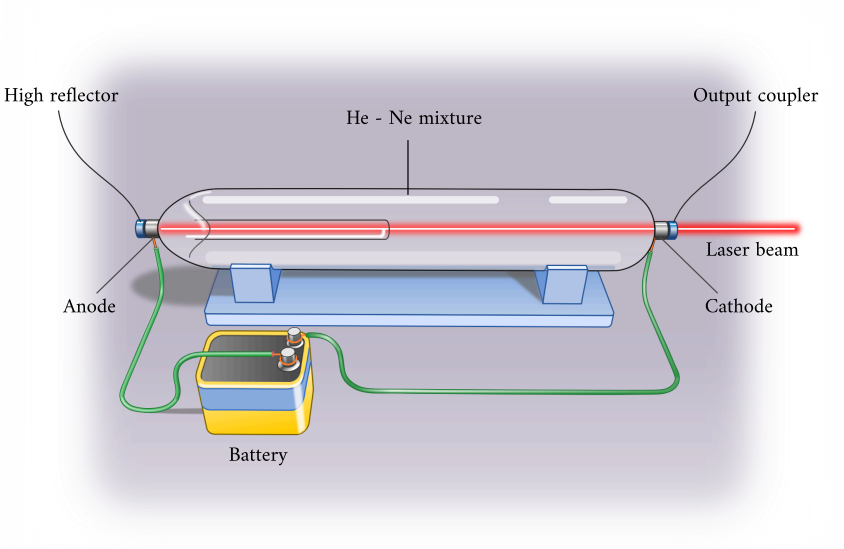


Figure 15.6.2: A He-Ne laser cavity. (CC BY-NC; Ümit Kaya via LibreTexts)

Many He-Ne lasers also contain a ballast which serves to maintain the desired gas mixture. Since some of the atoms may get embedded in the glass and/or the electrodes as they accelerate within the discharge, in the absence of a ballast the lasing mixture would not last very long. To further prolong the useable life of the laser, some of these lasers also use "getters", often metals such as titanium, that absorb impurities in the gas. Figure 15.6.3 below shows a He-Ne laser with a ballast.

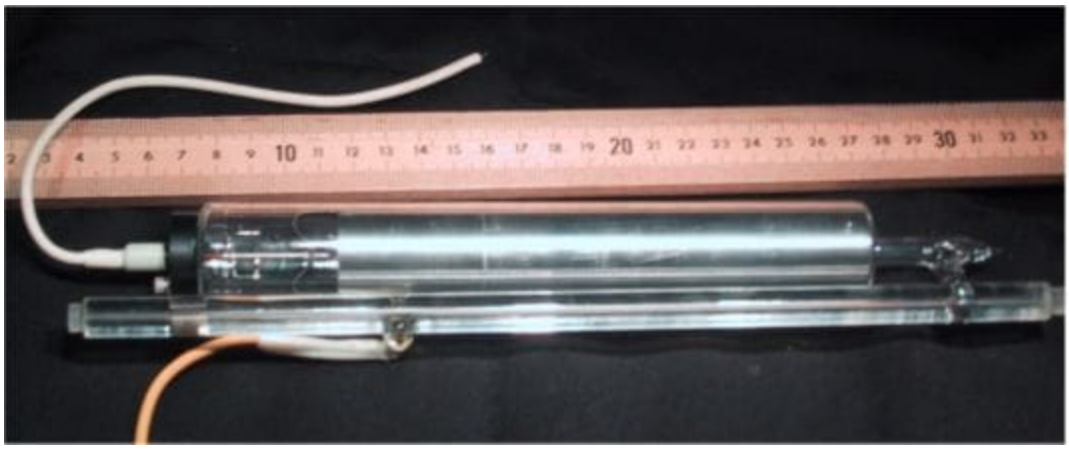


Figure 15.6.3: A commercial He-Ne tube. The thicker cylinder closest to the meter-stick (shown for scale) is the ballast. The thinner tube houses the resonant cavity where the lasing occurs. Notice the two mirrors that seal the two ends of the bore. For mode stability reasons, these mirrors are concave; they serve as the output coupler and the high reflector. (Copyright; author via source)

A typical commercially available He-Ne produces about a few mW of 632.8 nm light with a beam width of a few millimeters at an overall efficiency of near 0.1%. This means that for every 1 Watt of input power from the power supply, 1 mW of laser light is produced. Still, because of their long operating lifetime of 20,000 hours or more and their relatively low manufacturing cost, He-Ne lasers are among the most popular gas lasers.

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15.7: Modern Applications of Laser Spectroscopy

A Quick Overview

Laser light offers valuable tools to researchers who wish to use the interaction of light with matter to interrogate atomic and molecular systems. Most laser light is characterized by its near monochromaticity (relative to light from other sources), directionality, and coherence [1]. Those characteristics are used in modern laser spectroscopy. The monochromaticity of laser light allows it to be used to probe specific energy changes in atoms and molecules. This ability to select specific wavelengths allows scientists to focus on chosen components in mixtures, including complex reaction mixtures. For example, Park et. al. tracked the dynamics of the reaction of ground state oxygen with ethyl radical by using a 355 nm laser beam to track one of the products of this reaction [2]. Parsons et. al. used near monochromatic laser light sources to achieve state-selective ionization for the study of the products of a photodissociation reaction of atmospheric relevance [3]. Laser monochromaticity can be used to quantify the amount of greenhouse gases in the atmosphere [4]. Even when the samples are not mixtures, monochromaticity allows researchers to gather detailed information about atomic and/or molecular structure. Applications of this type are extremely numerous, including detailed studies of atomic systems [5], semiconductor materials [6], single molecules [7], and biological molecules [8]. Lasers find research applications in art and archeology, where the property of monochromaticity allows specific energies to be probed and laser beam directionality and small spot size curtail destruction of samples [9,10].

Other laser applications focus on the ability of pulsed lasers to provide short pulses. Short-pulsed lasers offer myriad tools for exploring chemical kinetics at a range of timescales, including very short ones. Short-pulse lasers open the opportunity for time-resolved studies of molecular processes such as reaction processes [2,11] and biological processes [12 - 15], and the properties of excited states [16]. Some research applications take advantage of the ability of certain lasers to produce high intensity light. One such application is laser-induced break down spectroscopy (LIBS), in which the high intensity of the laser creates a plasma from solid or liquid samples; that plasma can subsequently be probed [17]. Other techniques that exploit high laser intensities are the nonlinear spectroscopies, where the high intensities of some lasers can produce behaviors in samples that lower-power sources cannot sufficiently stimulate [18,19]. Although most lasers are monochromatic and coherent, some researchers have modified laser light to obtain information from broadband, incoherent laser light [20 – 22], which allows them to probe the response of samples to light that more resembles sunlight (incoherent) than do traditional laser sources [22, 23]. Another possibility is to probe multiple wavelengths with broadband laser sources that are coherent [24].

Conclusion

This brief overview has only skimmed the surface of the vast field of laser spectroscopy. The examples given here are a very small, somewhat arbitrary, and significantly biased subset of the enormous library of published laser-based experiments. References have been chosen to give examples of the topics covered here and have not been extensively reviewed by the author.

Overall, lasers are especially useful as light sources when one or more of the following properties are desired for light in an experiment:

1. A high degree of monochromaticity
2. A well-known central wavelength for a light source
3. A tunable light source
4. Spatial coherence
5. Phase coherence
6. Directionality
7. High intensity
8. Tight focus
9. Short pulses

A particular laser type will not necessarily have all the properties in the list above; however, the menu of available laser types allows a researcher to choose a laser system or systems with the characteristics needed for a particular experiment. New applications of laser spectroscopy and new spectroscopic techniques employing laser light continue to be invented.

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15.8: Pulsed Lasers Can by Used to Measure the Dynamics of Photochemical Processes

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15.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises)

These are homework exercises to accompany Chapter 15 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q15.9

The Einstein coefficient of a ground and excited state with a degeneracy of g_1 and g_2 is given by

$$A = \frac{16\pi^3 v^3 g_1}{3\epsilon_0 h c^3 g_2} |\mu|^2$$

where $|\mu|$ is the transition dipole moment. Consider the 1s --> 2p absorption of H(g), which is observed at 121.8 nm. The radiative lifetime of the triply degenerate excited 2p state of H(g) is 1.6 x 10^{-9} s. Determine the value of the transition dipole moment of this transition.

S15.9

Using the expression given in the problem, we can isolate $|\mu|$ to be given as

$$|\mu| = \sqrt{\frac{3A\epsilon_0 h c^3 g_2}{16\pi^3 v^3 g_1}} \tag{15.E.1}$$

Since we know the wavelength and the radiative lifetime, we can find frequency (v) and amplitude (A) with the following equations, respectively.

$$v = \frac{c}{\lambda} = 2.46 \times 10^{15} s^{-1} \tag{15.E.2}$$

$$A = \frac{1}{\tau} = 6.25 \times 10^{8} s^{-1} \tag{15.E.3}$$

where τ represents radiative lifetime.

The 2p orbital is threefold degenerate $g_2 = 3$ and the 1s orbital is signly degenerate $g_1 = 1$. Therefore, we can plug the corresponding numbers into the equation below in order to yield the transition dipole moment, which would be

$$|\mu| = \sqrt{\frac{3A\epsilon_0 h c^3 g_2}{16\pi^3 v^3 g_1}} \tag{15.E.4}$$

$$|\mu| = 1.1 \times 10^{-29} C * m \tag{15.E.5}$$

Q15.10

$$A = \frac{16\pi^3 \nu^3 g_1}{3\varepsilon_0 h c^3 g_2} |\mu|^2 \tag{15.E.6}$$

$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3} B_{21} \tag{15.E.7}$$

Use the equations above to derive the quantum mechanical expression for the Einstein B coefficient. Consider the $5s^1P_1 \rightarrow 3p^1S_0$ transition of neon at $730.0\ nm$. Einstein A coefficient is $0.48 \times 10^6 s^{-1}$. Determine the values of the Einstein B coefficient and the transition moment dipole for this transition.

S15.10

$$\mu = \frac{h\nu}{4\pi} n_2 A_{21} \tag{15.E.8}$$

$$A = \frac{32h\pi^3\nu^7}{c^3\varepsilon_0} n_2 B_{21} \tag{15.E.9}$$

$$B_{21} = \frac{c^3\varepsilon_0}{n_2 A 32h\pi^3\nu^7} \tag{15.E.10}$$

$$730nm = 7.3 * 10^{-7}m \tag{15.E.11}$$

λ = $7.3 * 10^{-7}m$ and thus ν = $c\lambda$ = $2.189 * 10^{16}s^{-1}$

$$B_{21} = \frac{c^3\varepsilon_0}{n_2 A 32h\pi^3\nu^7} \tag{15.E.12}$$

$$B_{21} = \frac{c^3 A}{8h\pi\nu^3} \tag{15.E.13}$$

$$B_{21} = \frac{(2.998 * 10^8 m * s^{-1})^3 * (0.48 * 10^6 s^{-1})}{8h\pi(2.189 * 10^{16})^3} \tag{15.E.14}$$

$$B_{21} = 7.420 * 10^{13} kg^{-1} m \tag{15.E.15}$$

Q15.11

Given

$$N_{total} = N_1(t) + N_2(t) + N_3(t) \tag{15.E.16}$$

find the rate equation for each N_i.

S15.11

For each one we must look at the excitation energy, and the stimulated and spontaneous emissions energies.

For example, the excitation from 1 to 3, stimulated emission from 3 to 1 and the spontaneous emission from 3 to 1 and 2 to 1.

$$\frac{dN_1}{dt} = -B_{31}\rho_v\nu_{31}N_1 + B_{31}\rho_v\nu_{31}N_3 + A_{31}N_3 + A_21N_2 \tag{15.E.17}$$

the others follow as

$$\frac{dN_2}{dt} = -B_{32}\rho_v\nu_{32}N_2 + B_{32}\rho_v\nu_{32}N_3 + A_{32}N_3 - A_21N_2 \tag{15.E.18}$$

and

$$\frac{dN_3}{dt} = -B_{31}\rho_v\nu_{31}N_1 + -B_{31}\rho_v\nu_{31}N_3 - A_{32}N_3 - A_31N_3 - B_{32}\rho_v\nu_{32}N_3 + B_{32}\rho_v\nu_{32}N_2 \tag{15.E.19}$$

where we estimate the emission from level 3 to level 2.

Q15.12

Consider a nondegenerate 3-level system. Suppose that an incident light beam of energy $h\nu = E_3 - E_1$ is turned on for a while and then turned off. Show that the subsequent decay of the E_3 is given by

$$N_3(t) = N_3^0 e^{-(A_{32}+A_{31})t} \tag{15.E.20}$$

Where N_3^0 is the number of atoms in state 3 at the instant the light source is turned off. What will be the observed radiative lifetime of this excited state?

S15.12

After the light is turned off, no stimulated processes will occur and the rate equation of N_3 becomes:

$$N_3 = Ce^{-(A_{32}+A_{31})t} \tag{15.E.21}$$

At t = 0 (when the light is turned off), $N_3(t) = N_3^0 = C$, so

$$N_3(t) = N_3^0 e^{-(A_{32}+A_{31})t} \tag{15.E.22}$$

The observed radiative lifetime will be $(A_{32} + A_{31})^{-1}$. (The radiative lifetime is the reciprocal of the coefficient of the t in the exponential term.)

Q15-14

An excited state of Lithium has the electron configuration,

$$1s^2 2p^1 \tag{15.E.23}$$

Define the lowest energy term symbol.

S15-14

Construct a micro state table with spin (M(S)) across the top and angular momentum (M(L)) down the left side.

	-1/2	1/2
-1	-1(-)	-1(+)
0	0(-)	0(+)
1	1(-)	1(+)

The highest spin value is +1/2, while the highest angular momentum value is 1. As a result, J can range from 3/2 (L+S) to 1/2 (L-S). Because the p-orbital is less than half-full, the term symbol with the lowest J value will be lower in energy.

Term symbol:

$$^2P_{1/2} \tag{15.E.24}$$

Q15.15

The ground state energy of the He atom is -2.904 hartrees. Use this value to determine the energy of He^+

S15.15

(good job however you could have shown more steps as it us unclear how you made the jumps from energy to He^+ and then that the energy was 0.904, it took me some time to fiddle with what you gave me as a solution to arrive to that number so more in between steps are need --RM)

$$E = \frac{-Z^2}{2n^2} \tag{15.E.25}$$

$$He^+ = -2E_h \tag{15.E.26}$$

Therefore the energy of He+ is 0.904 hartrees above that of He.

There isn't too many steps in solving the problem. It would have been great to compare it to another method or the actual energy of an H+ hydrogen, such as, using the Rydberg formula to evaluate the energy....

Q15.19

A laser operating at 640 nm produces pulses at a rate of 85 MHz. Calculate the radiant power of each pulse if the pulses last 15 fs each and the average radiant power of the laser is 2.6 W. How many photons are produced by the laser per second?

S15.19

We can first calculate the amount of energy per pulse:

$$\frac{2.6W}{85\frac{pulses}{MHz}} = \frac{2.6\frac{J}{s}}{85\cdot 10^{6}\frac{pulses}{s}} = 3.059\cdot 10^{-8}\frac{J}{pulse} \tag{15.E.27}$$

Using this, we can then calculate the radiant energy of each laser pulse:

$$\frac{3.059\cdot 10^{-8}\frac{J}{pulse}}{15\cdot 10^{-15}s} = 2039.216\frac{kW}{pulse} \tag{15.E.28}$$

Finally, we can calculate the radiant energy of a single photon:

$$E_{photon} = \frac{hc}{\lambda} = \frac{(6.626\cdot 10^{-34}J\cdot s)(2.988\cdot 10^{8}\frac{m}{s})}{640\cdot 10^{-9}m} = 3.094\cdot 10^{-19}J \tag{15.E.29}$$

Using this energy, we can calculate the the number of photons produced per second by the laser:

$$\frac{E_{laser}}{E_{photon}} = \frac{2.6\frac{J}{s}}{3.094\cdot 10^{-19}\frac{J}{photon}} = 8.40\cdot 10^{18}\frac{photons}{second} \tag{15.E.30}$$

Q15.21

Which laser pulse contains more photons, a 945 ns, 9.45 mJ pulse at 945 nm or a 23 ns, 2.30 mJ at 230 nm? Does the speed of the pulse effect the number of photons?

S15.21

- $\mathbf{E}$ = energy per photon
- $\mathbf{h}$ = plancks constant = $6.626 * 10^{-34} J\cdot s$
- $\mathbf{c}$ = speed of light = $3.00 * 10^{8}\frac{m}{s}$
- λ = wavelength = 945 nm or 230 nm = $540 * 10^{-9}m \ or \ 230 * 10^{-9}m$

$$E_{photon} = \frac{(6.626 * 10^{-34} J\cdot s) * (3.00 * 10^{8}\ \frac{m}{s})}{945 * 10^{-9}\, m} = 2.104x10^{-19}\ J/photon$$

$$E_{pulse} = 9.45\ mJ = 9.45 * 10^{-3} J$$

$$\#_{photon} = \frac{E_{pulse}}{E_{photon}} = \frac{9.45 * 10^{-3} J}{2.104 * 10^{-19}\, J/photon} = \mathbf{4.493 * 10^{16}\ photons}$$

$$E_{photon} = \frac{(6.626 * 10^{-34} J \cdot s) * (3.00 * 10^{8} \frac{m}{s})}{230 * 10^{-9} m} = 8.64 * 10^{-19} J$$

$$E_{pulse} = 2.30\ mJ = 2.30 * 10^{-3} J$$

$$\#_{photon} = \frac{E_{pulse}}{E_{photon}} = \frac{2.30 * 10^{-3} J}{8.64 * 10^{-19}\ J/photon} = \mathbf{2.66 * 10^{15}\ photons}$$

First and foremost, the speed of the laser DOES NOT effect the number of photons! The 9.45 mJ at 945 nm laser pulse has more photons than the 2.30 mJ at 230 nm pulse.

The pulse duration does not affect the number of photons a laser pulse contains. Energies of both laser pulses are equivalent. Energy per pulse is propotional to the number of photons and inversely proportional to the wavelength of the emitted photons. Therefore, the 945 pulse contains more photons.

Q15.22

Given the following laser pulses: a $10 \times 10^{-9} s$, $1.6 \times 10^{6} J$ pulse at $76 \times 10^{-10} m$ or a $5 \times 10^{8} s$, $1.6 \times 10^{6} J$ pulse at 5.32×10^{-11}, which one has the most photons?

S15.22

For 10-ns, 1.60-mJ pulse at 760 nm:

$$Q_p = \frac{hc}{\lambda} \tag{15.E.31}$$

$$= \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{760 \times 10^{-9}} \tag{15.E.32}$$

$$= 2.62 \times 10^{-19} \tag{15.E.33}$$

Number of photon in 1.6 mJ pulse is:

$$N_1 = \frac{Q}{Q_p} = 6.12 \times 10^{15} \tag{15.E.34}$$

For 500-ms, 1.60-mJ pulse at 5320 nm:

$$Q_p = 3.75 \times 10^{-18} \tag{15.E.35}$$

Number of photon in 1.6 mJ pulse is:

$$N_2 = \frac{Q}{Q_p} = 0.4 \times 10^{15} \tag{15.E.36}$$

Thus, 10-ns, 1.60-mJ pulse at 760 nm contain more photon.

Q15.24

A CO_2 laser operating at 9.0 μm uses an electrical power of 5.20 kW. If this laser produces 100-ns pulses at a repetition rate of 20Hz and has an efficiency of 29%, how many photons are in each laser pulses?

S15.24

The pump energy per pulse is:

$$\frac{5200J * s^{-1}}{20s^{-1}} = 260J * pulse^{-1}$$

Given that the laser is 29% effcient, the radiant per pulse is $(260J)(0.29) = 67.6J$.

The number of photons per pulse, n is

$$n = \frac{E\lambda}{hc},$$

by plugging in the values into this equation, we have

$$n = \frac{(260J)(0.29)(9.0 * 10^{-6}m)}{(6.626 * 10^{-34}J * s)(2.998 * 10^{8}m * s^{-1})}$$

$= 3.42 * 10^{37}$ photons

My calculation reveals the final answer to be 3.42×10^{21} photons (Aaron Choi)/ I believe you accidentally calculated using the speed of light as $2.998 \times 10^{-8}\frac{m}{s}$

Q15.25

Figure 15.10 displays the energy levels of the CO_2 laser. Given the following spectroscopic data for $CO_2(g)$, calculate the spacing between the $J' = 3 \rightarrow 2$ laser lines for the $001 \rightarrow 100$ vibrational transition.

$$Fundamental frequency (J' = 0 \rightarrow 0) 100 \rightarrow 001 = 960.80cm^{-1} \tag{15.E.37}$$

$$\tilde{B}(001) = 0.3871cm^{-1} \tilde{B}(100) = 0.3902cm^{-1} \tag{15.E.38}$$

The fundamental frequency is \(960.80cm^{-1}

S15.25

Using the following equation F(J) for J = 2 and J = 3 can calculated:

$$F(J) = \tilde{B}J(J+1) \tag{15.E.39}$$

$$F_{001}(3) = (0.3871cm^{-1})(3)(3+1) = 4.645cm^{-1} \tag{15.E.40}$$

$$F_{100}(2) = (0.3902cm^{-1})(2)(2+1) = 2.341cm^{-1} \tag{15.E.41}$$

Therefore the spacing is

$$960.80cm^{-1} + 4.645cm^{-1} - 2.341cm^{-1} = 963.10cm^{-1} \tag{15.E.42}$$

Q15.26

The upper level of the $H_2(g)$ laser is the lowest excited state of the molecule, the $B^1 \sum_u^+$ state, and the lower level is the $X^1 \sum_g^+$ ground state.The lasting occurs between the $v^{'} = 6$ level of the excited state and the $v^{''} = 13$ level of the ground state. Use the following spectroscopic data to determine the wavelength of the laser light from $H_2(g)$ laser.

State	$\tilde{T}_e/cm^{-1}$	$\tilde{\nu}_e/cm^{-1}$	$\tilde{\nu}_e\tilde{x}_e/cm^{-1}$
$B^1 \sum_u^+$	91,689.9	1356.9	19.93
$X^1 \sum_g^+$	0	4401.2	121.34

A 3.0 ns pulse can be generated with a pulse radiant power of 200kW. Calculate the radiant energy of such a laser pulse. How

many photons are there in this pulse?

S15.26

To calculate the energy of the upper and lower lasing levels the following equation is used:

$$G(v) = \tilde{\nu}_e \left(v + \frac{1}{2}\right) - \tilde{x}_e \tilde{\nu}_e \left(v + \frac{1}{2}\right)^2 \tag{15.E.43}$$

$$G^{''}(13) = (4401.2cm^{-1})(13.5) - (121.34cm^{-1})(13.5)^2 = 37,301.98cm^{-1} \tag{15.E.44}$$

$$G^{''}(6) = (1356.9cm^{-1})(6.5) - (19.93cm^{-1})(6.5)^2 = 7,977.81cm^{-1} \tag{15.E.45}$$

the transition is as follows

$$\tilde{\nu} = \tilde{T}_e + G^{''}(6) - G^{''}(13) \tag{15.E.46}$$

$$= 91,689.9cm^{-1} + 7,977.81cm^{-1} - 37,301.98cm^{-1} = 62,365.73cm^{-1} \tag{15.E.47}$$

therefore

$$\lambda = 160.34nm \tag{15.E.48}$$

The radiant energy of the laser pulse is found using dimensional analysis

$$\left(200\frac{kJ}{s}\right)\left(2 \times 10^{-9}s\right) = 1x10^{-4}J \tag{15.E.49}$$

the number of photons per pulse is determined using $E = nhv = 8.06 \times 10^{13}$ photons.

Q15.27

Determine the excited-state rotational quantum number for $X \rightarrow A$ adsorption bands of H_2(g). The transition is from the $v'' = 0$of the X state to the excited vibrational level of the A state $v^{'} = 3$. To accurately calculate the vibrational term $G(v)$ for the excited state A, a second-order anharmonic correction is made to account for the shape of the potential curve, while first-order corrections are sufficient for the ground level electron state.

$$G(v) = \tilde{v}_e(v + \frac{1}{2}) - \tilde{v}_e\tilde{x}_e(v + \frac{1}{2})^2 + \tilde{v}_e\tilde{y}_e(v + \frac{1}{2})^3$$

The need spectroscopic constants are tabulated below for the ground state X and the excited state A of H_2(g).

State	$\tilde{T}_e/cm^{-1}$	$\tilde{v}_e/cm^{-1}$	$\tilde{v}_e\tilde{x}_e/cm^{-1}$	$\tilde{v}_e\tilde{y}_e/cm^{-1}$	$\tilde{B}_e/cm^{-1}$	$\tilde{\alpha}_e/cm^{-1}$
A	120952	2321.4	62.8	0	29.9	1.24
X	0	2291.7	62.4			

These values are from the NIST website for the H_2

Determine the value of $\tilde{v}$ corresponding to the transition $X(v'' = 0, j'' = 0) \rightarrow A(v^{'} = 3, j^{'} = 0)$. Given that the ground state levels are $v'' = 0, j'' = 1$ of the X state and that the rotational term for this level is $F(1) = 1.057cm^{-1}$, determine the closest value of $J^{'}$, the rotational number of the $v'' = 3$ level of the excited A state.

S15.27

For the ground state, the $G(v)$ value is :

$$G''(0) = (\frac{1}{2})(2291cm^{-1}) - (\frac{1}{2})^2 62.4cm^{-1}$$

$$G''(0) = 1129.9cm^{-1}$$

For the excited state $G(v)$ value is :

$$G''(3) = (2321.4cm^{-1})(3+\frac{1}{2}) - (62.8cm^{-1})(3+\frac{1}{2})^2$$

$$G''(32) = 7354cm^{-1}$$

$\tilde{T}_e$is the difference in the minima of the electronic potential energy curve in wave numbers, so the transition will have the energy

$$\tilde{v}_e = \tilde{T}_e + G^{'}(32) - G''(0)$$

$$\tilde{v}_e = 120952cm^{-1} + 7354cm^{-1} - 1129.9cm{-}1$$

$$\tilde{v}_e = 127176.1cm^{-1}$$

$\tilde{B}_v$ can be found for A state, $v = 3$ with this equation:

$$\tilde{B}_{32} = \tilde{B}_e - \tilde{\alpha}_e(v+\frac{1}{2})$$

$$\tilde{B}_{32} = 29.9cm^{-1} - (1.24cm^{-1})(3+\frac{1}{2}) = 25.56cm{-}1.$$

the observed lines are in between 35714.29 cm^{-1} and 3448.28 cm_{-1} recalling that $\tilde{E}_{v,j} = G(v) - F(j)$;

$$35717.29cm^{-1} = 127176.1cm^{-1} - 1.057cm{-}1 + F^{'}(j)$$

$$35717.29cm^{-1} = 127175.043cm^{-1} + F^{'}(j)$$

Therefore 91461 $\approx F^{'}(j)$ so j would be around 10 or higher.

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15.S: Lasers, Laser Spectroscopy, and Photochemistry (Summary)

Lasers are a type of light source that are widely used in scientific and commercial applications today. The word itself is an acronym for light amplification by stimulated emission of radiation. We can understand the operating principles of lasers with a little knowledge of quantum mechanics, electronic relaxation pathways, and rate equations, and we will see how a laser is built. Finally, we will see that the light these devices produce is extremely useful for spectroscopy and for interrogating molecular dynamics.

Learning Objectives

By the end of this chapter, you should know the following:

- Einstein coefficients and their relationships to one another
- Population inversion and its relationship to lasing
- In what types of quantum systems population inversion can be achieved
- The principal components of a laser and their functions
- The differences between cw and pulsed lasers
- Spectral and temporal resolution
- Why cw lasers are advantageous for high-resolution spectroscopy
- Why pulsed lasers are used in photodissociation studies
- What quantum yield is

Skill goals (what you should be able to do/calculate):

- Write the rate equations for the populations of a given set of states including absorption, spontaneous emission, and stimulated emission
- Describe how a laser works
- Calculate the efficiency of a laser
- Compute photon energies, radiant energy densities, duty cycle, average power, and peak power for laser systems.
- Calculate quantum yields of photodissociation processes.

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16: THE PROPERTIES OF GASES

In this chapter, we look at the properties of real gases to see how interactions between molecules cause deviations from the ideal gas law. As the simplest equation of state, the ideal gas law is often used to get a good approximation for the pressure, density, and temperature for a gaseous sample, and at high temperatures and low pressures, it is an very good approximation, A “perfect” gas consists of noninteracting particles that individually have no volume: there are no collisions between gas particles because they take up no space. However, as the gas density/pressure increases, or as the temperature decreases, deviations from ideal behavior are observed– atoms and molecules do experience attractive and repulsive forces.

16.1: All Dilute Gases Behave Ideally

16.2: van der Waals and Redlich-Kwong Equations of State

16.3: A Cubic Equation of State

16.4: The Law of Corresponding States

16.5: The Second Virial Coefficient

16.6: The Repulsive Term in the Lennard-Jones Potential

16.7: Van der Waals Constants in Terms of Molecular Parameters

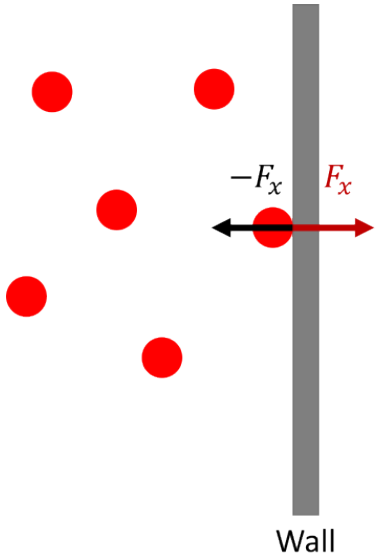
16.E: The Properties of Gases (Exercises)

16.S: The Properties of Gases (Summary)

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16.1: All Dilute Gases Behave Ideally

Ideal gases have no interactions between the particles, hence, the particles do not exert forces on each other. However, particles do experience a force when they collide with the walls of the container. Let us assume that each collision with a wall is elastic. Let us assume that the gas is in a cubic box of length a and that two of the walls are located at $x = 0$ and at $x = a$. Thus, a particle moving along the x direction will eventually collide with one of these walls and will exert a force on the wall when it strikes it, which we will denote as F_x. Since every action has an equal and opposite reaction, the wall exerts a force $-F_x$ on the particle.



According to Newton's second law, the force $-F_x$ on the particle in this direction gives rise to an acceleration via

$$-F_x = ma_x = m\frac{\Delta v_x}{\Delta t} \tag{16.1.1}$$

Here, t represents the time interval between collisions with the same wall of the box. In an elastic collision, all that happens to the velocity is that it changes sign. Thus, if v_x is the velocity in the x direction before the collision, then $-v_x$ is the velocity after, and $\Delta v_x = -v_x - v_x = -2v_x$, so that

$$-F_x = -2m\frac{v_x}{\Delta t} \tag{16.1.2}$$

Since the particles have no forces acting upon them, except for when they collide iwht the wall container, the particles move at constant speed. Thus, a collision between a particle and, say, the wall at $x = 0$ will not change the particle's speed. Before it strikes this wall again, it will proceed to the wall at $x = a$ first, bounce off that wall, and then return to the wall at $x = 0$. The total distance in the x direction traversed is $2a$, and since the speed in the x direction is always v_x, the interval $\Delta t = \dfrac{2a}{v_x}$. Consequently, the force is:

$$-F_x = -\frac{mv_x^2}{a} \tag{16.1.3}$$

Thus, the force that the particle exerts on the wall is:

$$F_x = \frac{mv_x^2}{a} \tag{16.1.4}$$

The mechanical definition of pressure is the average force over area:

$$P = \frac{\langle F \rangle}{A} \tag{16.1.5}$$

where $\langle F \rangle$ is the average force exerted by all N particles on a wall of the box of area A. Here $A = a^2$. If we use the wall at $x = 0$ we have been considering, then

$$P = \frac{N\langle F_x \rangle}{a^2} \tag{16.1.6}$$

because we have N particles hitting the wall. Hence:

$$P = \frac{Nm\langle v_x^2 \rangle}{a^3} \tag{16.1.7}$$

from our study of the Maxwell-Boltzmann distribution, we found that:

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \tag{16.1.8}$$

Hence, since $a^3 = V$:

$$\begin{aligned} P &= \frac{Nk_B T}{V} \\ &= \frac{nRT}{V} \end{aligned} \tag{16.1.9}$$

which is the ideal gas law. It relates the pressure, volume, and temperature of an ideal gas and is referred to as an equation of state. An equation of state is a relation between variables and describes the state of matter under a set of given physical conditions. One way to visualize any equation of state is to plot *isotherms*, which are graphs of P vs. V at fixed values of T . For the ideal-gas equation of state, some of the isotherms are shown in the figure below (left panel): If we plot P vs. T at fixed volume (called the *isochores*), we obtain the plot in the right panel. What is important to note, here, is that an ideal gas can exist *only* as a gas. It is not possible for an ideal gas to condense into some kind of "ideal liquid". In other words, a phase transition from gas to liquid can be modeled only if interparticle interactions are properly accounted for.

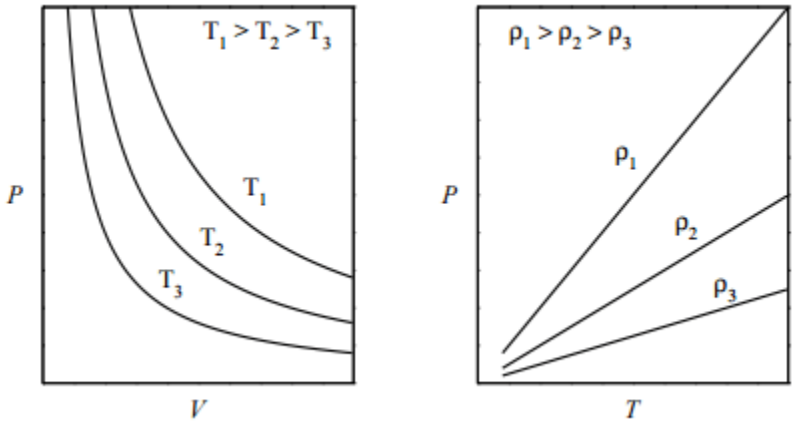


Figure 16.1.1 : (Left) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (Right) Pressure vs. temperature for different densities $\rho = N/V$.

We can rearrange the ideal gas equation of state to put all the constants and variables on one side:

$$\frac{PV}{nRT} = 1 = Z \tag{16.1.10}$$

Z is called the *compressibility* of the gas. In an ideal gas, if we compress the gas by increasing P , the volume decreases as well so as to keep $Z = 1$. For a real gas, Z, therefore, gives us a measure of how much the gas deviates from ideal-gas behavior.

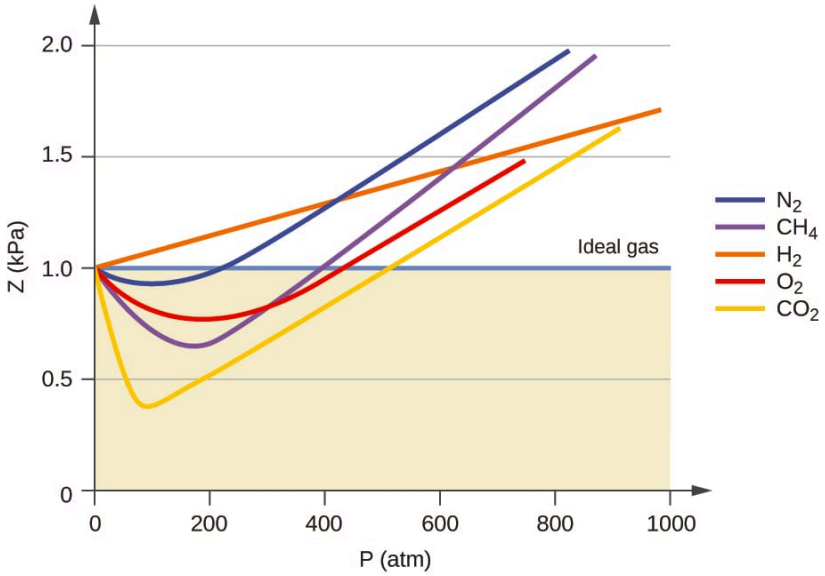


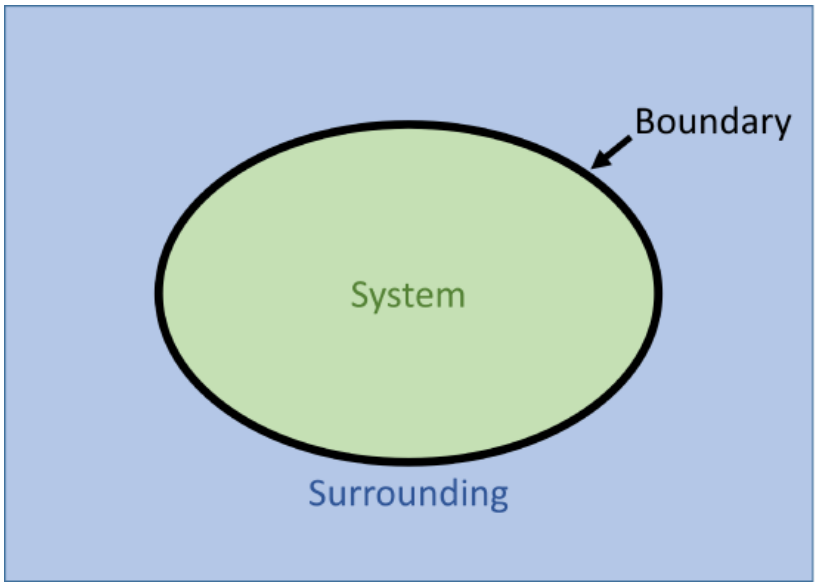
Figure 16.1.2 : A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law. from Openstax (CC-BY)

Figure 16.1.2 shows a plot of Z vs. P for several real gases and for an ideal gas. The plot shows that for sufficiently low pressures (hence, low densities), each gas approaches ideal-gas behavior, as expected.

Extensive and Intensive Properties in Thermodynamics

Before we discuss ensembles and how we construct them, we need to introduce an important distinction between different types of thermodynamic properties that are used to characterize the ensemble. This distinction is *extensive* and *intensive* properties.

Thermodynamics always divides the universe into a *system* and its *surroundings* with a *boundary* between them. The unity of all three of these is the thermodynamic *universe*.



Now suppose we allow the system to grow in such a way that both the number of particles and the volume grow with the ratio N/V remaining constant. Any property that increases as we grow the system in this way is called an *extensive* property. Any property that remains the same as we grow the system in this way is called *intensive*.

The ideal gas equation of state can be written in an extensive form:

$$\begin{aligned} PV &= nRT \\ P\bar{V} &= RT \\ P &= \rho RT \end{aligned} \tag{16.1.11}$$

where $\bar{V} = V/n$ is called the molar volume and $\rho = N/V$ is called density. Unlike V , which increases as the number of moles increases (an *extensive* quantity, $\bar{V}$ and ρ do not exhibit this dependence and, therefore, are called *intensive*. Compressibility can also be written in an intensive form:

$$\begin{aligned} Z &= \frac{PV}{nRT} \\ &= \frac{P\bar{V}}{RT} \\ &= \frac{P}{\rho RT} \end{aligned}$$

Some examples of intensive and extensive properties include:

- Extensive: number of particles (N), moles (n), volume (V), mass (m), energy, free energy
- Intensive: pressure (P), density (ρ), molar heat capacity (C), temperature (T)

Contributors and Attributions

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16.2: van der Waals and Redlich-Kwong Equations of State

The ideal gas law is valid for low pressures, where the finite volume of particles and intermolecular attractions do not have a large impact. At higher pressures, we must account for these factors. The van der Waals and Redlich-Kwong equations of states are equations of state that attempt to account for real gas behavior by modifying the ideal gas law with two additional parameters.

The Van der Waals Equation of State

The van der Waals Equation of State is an equation relating the density of gases and liquids to the pressure, volume, and temperature conditions (i.e., it is a thermodynamic equation of state). It can be viewed as an adjustment to the ideal gas law that takes into account the non-zero volume of gas molecules and inter-particle attraction using correction terms a and b. It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel Prize in 1910 for this work. The van der Waals equation of state is:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{16.2.1}$$

Equation 16.2.1 can also be rewritten as

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

If the correction terms a and b go to zero, the equation reduces to the ideal gas equation of state:

$$PV = nRT$$

Let's first look first at the correction term b, which represents the volumes of the particles and assumes a hard-wall potential, $u_o(r)$. This potential energy term describes a system of hard sphere “billiard balls” of diameter σ. Figure 16.2.1 shows two of these billiard ball type particles at the point of contact (i.e, the distance of closest approach). At this point, they undergo a collision and separate, so they cannot be closer than that distance.

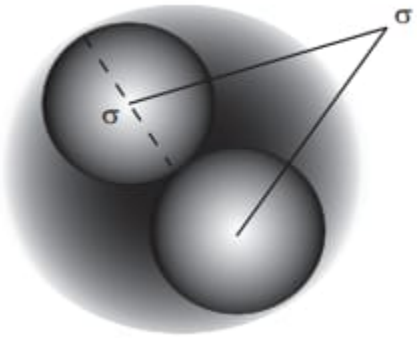


Figure 16.2.1 : Two hard spheres of diameter σ at closest contact. The distance between their centers is also σ. A sphere of radius σ just containing the two particles is shown in cross-section.

The distance between their centers is also σ. Because of this distance of closest approach, the total volume available to the particles is not the volume of the container, V, but some volume less than V. This reduction in volume can be calculated. Figure 16.2.1 shows a shaded sphere that just contains the pair of billiard ball particles. The volume of this sphere is the volume excluded from any two particles. The radius of the sphere is σ and the excluded volume for the two particles is $4\pi\sigma^3/3$, which is the volume of the shaded sphere. From this, we see that the excluded volume for any *one* particle is just half of this or $\frac{2}{3}\pi\sigma^3$. The excluded volume for a mole of such particles is the parameter b:

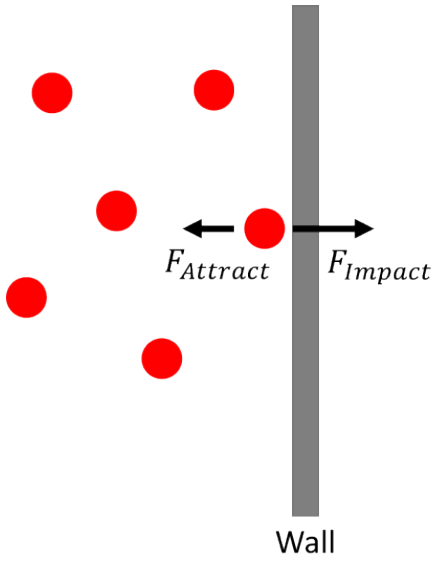
$$b = \frac{2}{3}\pi\sigma^3 N_0$$

Given n moles of gas, the total excluded volume is then nb, so that the total *available* volume is $V - nb$.

Let's turn our attention the a, which represents the intermolecular attractions of the particles. Molecular attractions tend to make the P exerted by the gas less than that predicted by the ideal gas law at low pressures. P is force over area:

$$P = \frac{F}{A}$$

Pressure is proportion to the net force on the wall of the container:



The net force is the force of the molecules impacting the container wall minus the intermolecular attraction of the molecules:

$$\bar{F}_{Net} = \bar{F}_{Impact} - \bar{F}_{Attract}$$

Therefore, the pressure will be less for the real gas than the ideal gas. We can add a correction term to pressure to account for intermolecular attractions:

$$P_{VDW} = P_{Real} + a\,(?)$$

V does influence the amount of intermolecular attraction because P is reduced as V is increased:

$$P \propto \frac{1}{V}$$

And pressure is proportional to the number of attractive interactions:

# of molecular interactions $\propto P^2$

# of molecular interactions $\propto \frac{1}{V^2}$

We now have an expression for the van der Waals P:

$$P = P_{Real} + \frac{an^2}{V^2}$$

The constants a and b depend on the substance. Some typical values are:[1]

Molecule	a $\left(\frac{\text{L}^2 \cdot \text{bar}}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mole}}\right)$
H_2O	5.536	0.03049

N_2	1.43	0.03913
CH_4	2.283	0.04278
C_2H_6	5.562	0.0638

1. *R. C. Weast (1972). Handbook of Chemistry and Physics 53rd Edition. Chemical Rubber Pub.*

Redlich-Kwong Equation of State

The van der Waals Equation of State had to wait almost 100 years before a real, successful improvement was introduced to it. This progress occurred once researchers committed themselves to finding the empirical temperature dependency of the attraction parameter a proposed by van der Waals. In contrast, very little attention has been paid to modifying the parameter b for co-volume. It makes a lot of sense that b would not be modified by temperature, because it represents the *volume* of the molecules, which should not be affected by their kinetic energy (measured in terms of temperature). The very first noteworthy successful modification to the attraction parameter came with the publication of the equation of state of Redlich-Kwong in 1949.

The Redlich–Kwong equation of state is an empirical, algebraic equation that relates temperature, pressure, and volume of gases. It is generally more accurate than the van der Waals and the ideal gas equations of state at temperatures above the critical temperature. It was formulated by Otto Redlich and Joseph Neng Shun Kwong in 1949, who showed that a simple two-parameter equation of state could well reflect reality in many situations. Redlich and Kwong revised the van der Waals Equation of State (Equation 16.2.1) and proposed the following expressions:

$$\left(P+\frac{a}{\sqrt{T}\bar{V}(\bar{V}+b)}\right)(\bar{V}-b)=RT \tag{16.2.2}$$

The fundamental change they introduced was to the functional form of $\partial P_{\text{attraction}}$. Additionally, they introduced the co-volume b into the denominator of this functional form. The important concept here is that the attraction parameter a of van der Waals needed to be made a function of temperature to do a better job of quantitatively matching experimental data. This was a realization that van der Waals had suggested, but no actual functional dependency had been introduced until the Redlich-Kwong equation.

We know what follows at this point. To come up with an expression for a and b of Equation 16.2.2, we apply the criticality conditions to this equation of state. As we recall, imposing the criticality conditions allows us to relate the coefficients a and b to the critical properties (P_c, T_c) of the substance. Once we have done that, we obtain the definition of a and b for the Redlich-Kwong equation of state:

$$a=0.42780\frac{R^2T_c^{2.5}}{P_c} \tag{16.2.3}$$

$$b=0.086640\frac{RT_c}{P_c} \tag{16.2.4}$$

The Redlich-Kwong equation of state radically improved, in a quantitative sense, the predictions of the van der Waals equation of state. We now recall that van der Waals-type equations are cubic because they are cubic polynomials in molar volume and compressibility factor. It comes as no surprise then, that we can transform Equation 16.2.2 into:

$$\bar{v}^3-\left(\frac{RT}{P}\right)\bar{v}^2+\frac{1}{P}\left(\frac{1}{T^{0.5}}-bRT-Pb^2\right)\bar{v}-\frac{ab}{PT^{0.5}}=0 \tag{16.2.5}$$

and, by defining the following parameters:

$$A=\frac{aP}{R^2T^{2.5}} \tag{16.2.6}$$

$$B=\frac{bP}{RT} \tag{16.2.7}$$

and introducing the compressibility factor definition:

$$Z = \frac{P\bar{v}}{RT}$$

we get:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{16.2.8}$$

We may also verify the two-parameter corresponding state theory by introducing Equations 16.2.3, 16.2.4, and 16.2.5 into Equation 16.2.8:

$$Z^3 - Z^2 + \frac{P_r}{T_r}\left(\frac{0.42748}{T_r^{1.5}} - 0.08664 - 0.007506\frac{P_r}{T_r}\right)Z - 0.03704\frac{P_r^2}{T_r^{3.5}} = 0 \tag{16.2.9}$$

Where:

$$P_r = \frac{P}{P_c}$$

$$T_r = \frac{T}{T_c}$$

P_r and T_r are the pressure and temperature at the reduced state. See Section 16.4 for more information on reduced states. In Equation 16.2.9, we can observe the same thing that we saw with the van der Waals equation of state: gases at corresponding states have the same properties. Equation 16.2.9 is particularly clear about it: any two different gases at the same P_r, T_r condition have the same compressibility factor.

Just as any other cubic equation of state, Equations 16.2.2 through 16.2.9, as they stand, are to be applied to pure substances. For mixtures, however, we apply *the same equation,* but we impose certain mixing rules to obtain a and b, which are functions of the properties of the pure components. Strictly speaking, we create a new "pseudo" pure substance that has the average properties of the mixture. Redlich-Kwong preserved the same mixing rules that van der Waals proposed for his eqution of state:

$$a_m = \sum_i \sum_j y_i y_j a_{ij}$$

with

$$a_{ij} = \sqrt{a_i a_j}$$

and

$$b_m = \sum_i y_i b_i$$

Naturally, Redlich and Kwong did not have the last word on possible improvements to the van der Waals equation of state. The Redlich-Kwong equation of state, as shown here, is no longer used in practical applications. Research continued and brought with it new attempts to improve the Redlich-Kwong equation of state. After more than two decades, a modified Redlich-Kwong equation of state with very good potential was developed.

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16.3: A Cubic Equation of State

Isotherms

Isotherms are plots of the pressure of a gas as a function of volume at a fixed constant temperature. The isotherms for an ideal gas are hypberbolas:

$$P = \frac{RT}{\bar{V}}$$

where $\bar{V}$ is the molar volume V/n. We know that at sufficiently low temperatures, any real gas, when compressed, must undergo a transition from gas to liquid. The signature of such a transition is a discontinuous change in the volume, signifying the condensation of the gas into a liquid that occupies a significantly lower volume.

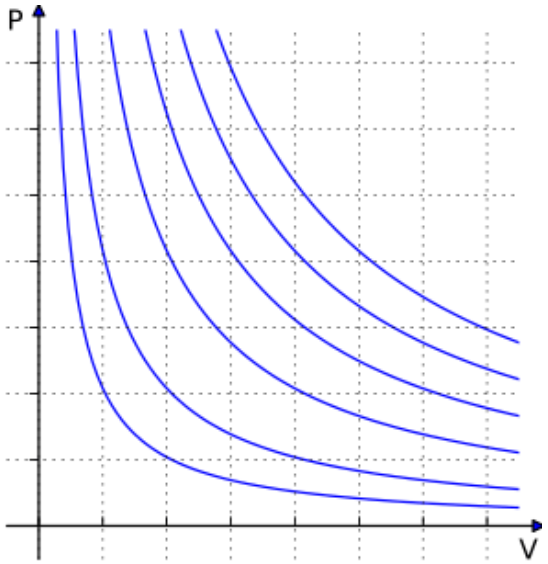


Figure 16.3.1 : Ideal gas isotherms for one mole of the gas and at select temperatures. (public domain).

CO_2 isotherms for the van der Waals Equation of state are shown in Figure 16.3.2 . At sufficiently high temperatures, the isotherms approach those of an ideal gas. At lower temperatures, the fluid obeys approximately the ideal gas law $PV = nRT$ at large volumes when the pressures are low. If we decrease the volume (go to the left in the figure along an isotherm), the pressure rises. Consider the (blue) isotherm of 10 °C, which is below the critical temperature. Decrease the volume until we reach the point B , where condensation (formation of liquid CO_2) starts. At this point the van der Waals curve is no longer physical (excluding the possibility of the occurrence of an oversaturated, metastable gas) because P and V increase together. It should be clear that many approximations and assumptions go into the derivation of the van der Waals equation so that some of the important physics is missing from the model. Hence, we should not be surprised if the van der Waals equation has some unphysical behavior buried in it. In reality, the pressure stays constant between the region A and B and the real physical behavior is given by the dashed blue line, called the *tie line*. This lines represents the gas-liquid coexistence and the pressure is equal to the vapor pressure of the liquid.

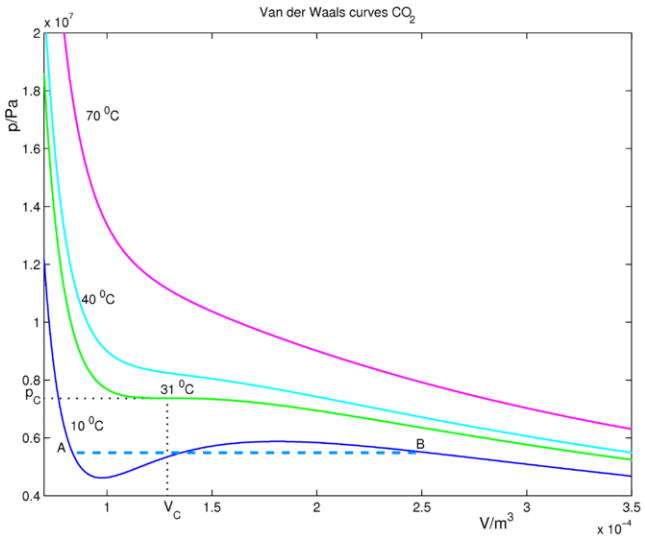


Figure 16.3.2 : Different isotherms (curves of constant temperature) of the van der Waals equation of state using parameters a and b computed for carbon dioxide. The dashed line from A to B is drawn in accordance with Maxwell's equal area rule. The carbon dioxide molecule (CO_2) has p_C = 7.37 MPa and T_C = 304.1 K = 31 ˚C , which gives a = 0.366 m^6 Pa and b = 42.9 10^{-6} m^3. The critical pressure is at 73.7 bar = 7370 kPa.

The tie line must be added in *ad hoc* by drawing a horizontal line through the isotherm (Figure 16.3.2). The vertical position of the line is chosen so that the area above the line (between the line and the isotherm) and below the line (again between the line and the isotherm) is exactly the same. This is known as *Maxwell*'s *construction*. In this way, we entirely remove the artifact of the unphysical increase of P with V when we compute the compressional work on the gas from $\int P(V)\ dV$, to be discussed in our section on thermodynamics. Although the van der Waals curves have regions where they are not physical, the equation for these curves, derived by van der Waals in 1873, was a great scientific achievement.

Note

Even today it is not possible to give a *single* equation that describes correctly the gas-liquid phase transition.

Critical Point

Looking to the left of point A on the 10 °C isotherm (blue curve), the system is in the liquid state. Increasing the volume to point A leads to a rapid drop in the pressure of the system because the compressibility of a liquid is considerable smaller than that of a gas. The system is still in the liquid state at point A, but as we increase the volume further, we enter the gas-liquid coexistence line and the liquid begins to transition to gas. As we move along this line to the right, there is less liquid and more gas in the system until we reach point B, at which point the system will be completely in the gas phase. The areas, bounded by the 10 °C isotherm (blue curve) below and above the coexistence line are equal. Any further increase in the volume will lead to an expansion of the gas.There is exactly one isotherm along which the van der Waals equation correctly predicts the gas-to-liquid phase transition. If one follows the 31 °C isotherm (green curve in Figure 16.3.2) of critical temperature, the volume discontinuity captured by the tie line is shrunken down to a single point (so that there is no possibility of an increase of P with V!). This point is called the critical point and it exists at only one temperature, called the **critical temperature**, denoted T_c. The critical isotherm at the critical temperature corresponds to the highest possible temperature at which a gas-liquid transition can occur. Isotherms at higher temperatures have no liquid-gas phase transitions. Along those isotherms, the higher pressure fluid, called a supercritical fluid, resembles a liquid, while at lower pressures the fluid is more gas-like.

The critical point exists at an inflection where the first and second derivatives of P with respect to V are zero:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

Substituting the van der Waals equation into these two conditions, we find the following:

$$-\frac{nRT_c}{(V_c - nb)^2} + \frac{2an^2}{V_c^3} = 0$$
$$\frac{2nRT_c}{(V_c - nb)^3} - \frac{6an^2}{V_c^4} = 0$$

Hence, we have two equations in two unknowns V_c and T_c for the critical temperature and critical volume. Once these are determined, the van der Waals equation, itself, allows us to determine the critical pressure, P_c. To solve the equations, first divide one by the other. This gives us a simple condition for the volume:

$$\frac{V_c - nb}{2} = \frac{V_c}{3}$$
$$3V_c - 3nb = 2V_c$$
$$V_c = 3nb$$

This is the **critical volume**. Now use either of the two conditions to obtain the critical temperature, T_c. If we use the first one, we find:

$$\frac{nRT_c}{(V_c - nb)^2} = \frac{2an^2}{V_c^3}$$
$$\frac{nRT_c}{(3nb - nb)^2} = \frac{2an^2}{(3nb)^3}$$
$$\frac{nRT_c}{4n^2b^2} = \frac{2an^2}{27n^3b^3}$$
$$RT_c = \frac{8a}{27b}$$

Finally, plugging the critical temperature and volume into the van der Waals equation, we obtain the critical pressure:

$$P_c = \frac{nRT_c}{V_c - nb} - \frac{an^2}{V_c^2}$$
$$= \frac{8an/27b}{3nb - nb} - \frac{an^2}{(3nb)^2}$$
$$= \frac{a}{27b^2}$$

It comes as no surprise that cubic equations of state like the van der Waals (and Redlich-Kwong) equations of state yield three different roots for volume and compressibility factor. This is simply because they are algebraic equations, and any nth order algebraic equation will always yield “n” roots. However, those “n” roots are not required to be distinct, and that is not all: they are not required be real numbers, either. A quadratic expression (n = 2) may have zero real roots (e.g., $x^2 + 1 = 0$); this is because those roots are complex numbers. In the case of cubic expressions (n = 3), we will either have one or three real roots; this is because complex roots always show up in pairs (i.e., once you have a complex root, its conjugate must also be a solution). In our case, and because we are dealing with physical quantities (densities, volumes, compressibility factors), only real roots are of interest. More specifically, we look for real, positive roots such that $\bar{V} > b$ in the case of molar volume and $Z > \frac{Pb}{RT}$ in the case of compressibility factor.

In a cubic equation of state, the possibility of three real roots is restricted to the case of sub-critical conditions ($T < T_c$), because the S-shaped behavior, which represents the vapor-liquid transition, takes place only at temperatures below critical. This restriction is mathematically imposed by the criticality conditions. Anywhere else, beyond the S-shaped curve, we will only get one real root of the type $\bar{V} > b$. Figure 16.3.3 illustrates this point.

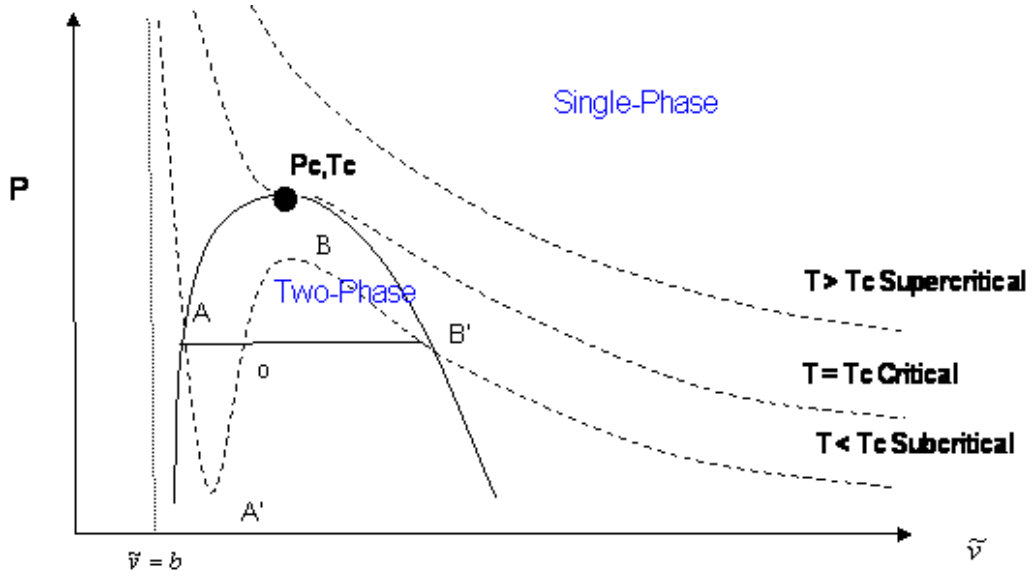


Figure 16.3.3 : Multiple Roots in Cubic EOS

The shape of the critical isotherm at the critical point allows us to determine the exact temperature, pressure, and volume at which the phase transitions from gas to liquid will occur. If we draw a curve through the isotherms joining all points of these isotherms at which the tie lines begin, continue the curve up to the critical isotherm, and down the other side where the tie lines end, this curve reaches a maximum at the critical point. The region inside this curve is when the gas and liquid phases coexist.

Let us summarize the three cases presented in Figure 16.3.3 :

1. Supercritical isotherms ($T > T_c$: At temperatures beyond critical, the cubic equation will have only one real root (the other two are imaginary complex conjugates). In this case, there is no ambiguity in the assignment of the volume root since we have single-phase conditions. The occurrence of a unique real root remains valid at any pressure: any horizontal (isobaric) line cuts the supercritical isotherm just once in Figure 16.3.3 .
2. Critical isotherm ($T = T_c$): At the critical point ($P = P_c$), vapor and liquid properties are the same. Consequently, the cubic equation predicts three real and equal roots at this special and particular point. However, for any other pressure along the critical isotherm ($P < P_c$ or $P > P_c$,) the cubic equation gives a unique real root with two complex conjugates.
3. Subcritical isotherm ($T < T_c$): Predictions for pressures within the pressure range for metastability ($P'_A < P < P'_B$) or for the saturation condition ($P = P^{sat}$) will always yield three real, different roots. In fact, this is the only region where an isobar cuts the same isotherm more than once. The smallest root is taken as the specific volume of the liquid phase; the largest is the specific volume of the vapor phase; the intermediate root is not computed as it is physically meaningless. However, do not get carried away. Subcritical conditions will not always yield three real roots of the type $\bar{\nu} > b$. If the pressure is higher than the maximum of the S-shaped curve, P_B, we will only have one (liquid) real root that satisfies $\bar{\nu} > b$. By the same token, pressures between $0 < P < P'_A$ yield only one (vapor) root. In the case of P'_A being a negative number, three real roots are to be found even for very low pressures when the ideal gas law applies. The largest root is always the correct choice for the gas phase molar volume of pure components.

Most of these considerations apply to the cubic equation of state in Z (compressibility factor). The most common graphical representation of compressibility factor is the well-known chart of Standing and Katz, where compressibility, Z, is plotted against pressure (Figure 16.3.4). Standing and Katz presented their chart for the compressibility factor of sweet natural gases in 1942. This chart was based on experimental data. Graphical determination of properties was widespread until the advent of computers, and thus the Standing and Katz Z-chart became very popular in the natural gas industry. Typical Standing and Katz charts are given for high temperature conditions ($T > T_c$ or $T_r > 1$).

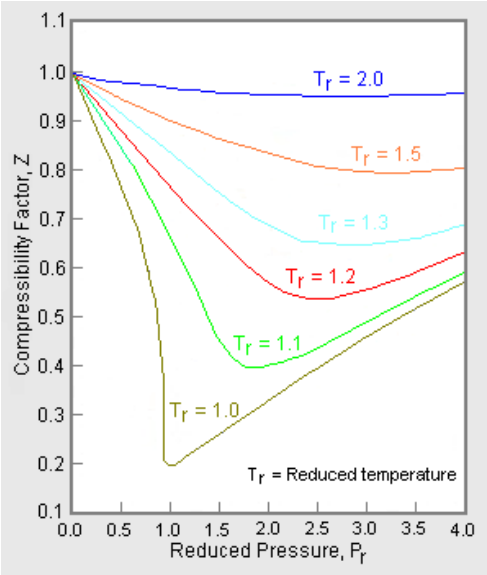


Figure 16.3.4 : Compressibility Factor versus Pressure

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16.4: The Law of Corresponding States

Johannes Diderik van der Waals modified the ideal gas law to better describe the behavior of real gases by introducing corrections to account for the finite size of molecules and the intermolecular forces between them, leading to the well-known van der Waals equation.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \tag{16.4.1}$$

This expression for the van der Waal gas involves two phenomenological constants, a and b. Van der Waals postulated that all real gases at corresponding states should behave similarly and he focused on applying Equation 16.4.1 at the critical point of difference gases—the unique temperature, pressure, and volume at which the distinction between liquid and gas disappears.

The corresponding state that van der Waals chose to use is called the **reduced state**, which is based on the deviation of the conditions of a substance from its own critical conditions. We can define reduced quantities:

$$P_r = \frac{P}{P_c}$$
$$V_r = \frac{V}{V_c}$$
$$T_r = \frac{T}{T_c}$$

By substitution into Equation 16.4.1, the Van der Waal equations can be expressed differently

$$\left(P_r + \frac{3}{\bar{V}_r^2}\right)\left(\bar{V}_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{16.4.2}$$

Equation 16.4.2 means the critical parameters for a gas can be expressed in terms of a and b parameters:

$$V_c = 3b$$
$$P_c = \frac{a}{27b^2}$$
$$T_c = \frac{8a}{27bR}$$

Hence, when gases are expressed in terms of their **reduced variables**, the van der Waals equation takes on a universal form (Equation 16.4.2) that applies to all gases, regardless of their chemical identity. This discovery led van der Waals to formulate the **Law of Corresponding State**s, which states that different gases at the same reduced temperature and reduced pressure will exhibit similar thermodynamic behavior. This principle provided a unifying framework for understanding real-gas behavior and laid the foundation for generalized equations of state and compressibility charts used in modern thermodynamics.

Although the actual pressures and volumes may differ, two gases are said to be in corresponding states if their reduced pressure, volume, and temperature are the same. What it says is that the behavior of all gases (and liquids!!) is pretty much the same, except for a scaling factor that is related to the critical point of the substance. The compressibility value (Z) of 3/8 at the critical point for the van der Waals equation is actually not in such good agreement with measurement. This is why the more complicated Redlich-Kwong and Peng-Robertson expressions are better, although the idea is the same. Hence, all one needs to know to describe any fluid's behavior is its critical point. For example, argon behaves much the same at 300 K as ethane does at 600 K because these temperatures correspond to twice their respective critical temperatures (150.72 K and 305.4 K, respectively) so $T_r = 2.0$.

Compressibility

The Compressibility provides a useful way to compare the behavior of real gases with that predicted by the ideal gas law, and it connects directly to the critical ratios first introduced by van der Waals.

$$Z = \frac{PV}{RT}$$

Over the past 150 years, researchers have collected extensive experimental data on a wide variety of fluids, allowing the Law of Corresponding States to be tested and validated. When the pressure, temperature, and volume of different fluids are expressed in terms of their reduced values, their measurements can be superimposed on the same compressibility chart (Figure 16.4.1). This overlap shows that most "normal" fluids, despite having different molecular structures, follow a common pattern of behavior when scaled by their critical properties.

We can rewrite the universal expression for compressibility Z using reduced variables and plot measured values of Z versus the reduced pressure, P_r (Figure 16.4.1). As you can see, very different gases/liquids like nitrogen and water can be made to coincide if their properties are plotted relative to there critical points rather than in absolute terms. The compressibility factor Z can also be cast into the form of corresponding states showing that Z also can be expressed as a universal function of V_r and T_r or any other two reduced quantities:

$$Z = \frac{\bar{V}_r}{\bar{V}_r - \frac{1}{3}} - \frac{9}{8\bar{V}_r T_r}$$

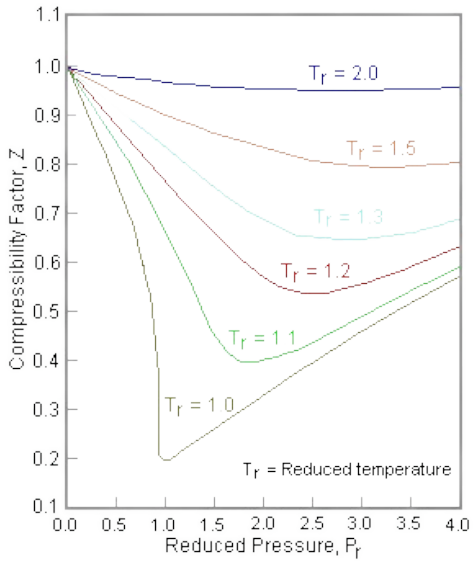


Figure 16.4.1: Example of a generalized compressibility factor graph (Public domain; Milton Beychok)

These charts show that most "normal" fluids, such as simple hydrocarbons, noble gases, and diatomic molecules, conform closely to the predictions of the Law of Corresponding States. Deviations occur mainly in more complex or strongly associating fluids—such as water, ammonia, or hydrogen fluoride—where strong polarity or hydrogen bonding introduces additional interactions not accounted for by van der Waals' simple model. Nevertheless, the overall success of the law demonstrates its power: by scaling thermodynamic variables to the critical constants, we can describe the behavior of a wide variety of substances with a single framework. This insight not only validated van der Waals' pioneering theory but also provided a foundation for modern equations of state and practical tools in chemical engineering and physical chemistry.

Van der Waals did not stop here. He went on to describe the root cause of condensation of gases into liquids at lower temperatures: the attractive interactions between the molecules.

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16.5: The Second Virial Coefficient

The second virial coefficient describes the contribution of the pair-wise potential to the pressure of the gas. The third virial coefficient depends on interactions between three molecules, and so on and so forth.

Introduction

As the density is increased the interactions between gas molecules become non-negligible. Deviations from the ideal gas law have been described in a large number of equations of state. The *virial equation of state* expresses the deviation from ideality in terms of a power series in the density:

$$\frac{P}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \ldots$$

- $B_2(T)$ is the second virial coefficient,
- $B_3(T)$ is called the third virial coefficient, etc.

The jth virial coefficient can be calculated in terms of the interaction of j molecules in a volume V. The second and third virial coefficients give most of the deviation from ideal (P/rkT) up to 100 atm.

The **second virial coefficient** is usually written as B or as B_2. The second virial coefficient represents the initial departure from ideal-gas behavior. The second virial coefficient, in three dimensions, is given by:

$$B_2(T) = -\frac{1}{2}\int \left(\exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right) - 1\right) 4\pi r^2 dr$$

where $\Phi_{12}(\mathbf{r})$ is the intermolecular pair potential, T is the temperature, and k_B is the Boltzmann constant. Notice that the expression within the parenthesis of the integral is the *Mayer f-function*. In practice, the integral is often *very hard* to integrate analytically for anything other than, say, the hard sphere model, thus one numerically evaluates:

$$B_2(T) = -\frac{1}{2}\int \left(\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right)\right\rangle - 1\right) 4\pi r^2 dr$$

calculating:

$$\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right)\right\rangle$$

for each r using the numerical integration scheme proposed by Harold Conroy [1][2].

Calculation of virial coefficients

The configuration integrals for Z_1, Z_2, and Z_3 are:

- $Z_1 = \int dr_1 = V$
- $Z_2 = \int e^{-U_2/kT} dr_1 \;\; dr_2$
- $Z_3 = \int e^{-U_3/kT} dr_1 \;\; dr_2 \;\; dr_3$

The series method allows the calculation of a number of virial coefficients. Recall that the second and third virial coefficient can account for the properties of gases up to hundreds of atmospheres. We will discuss the calculation of the second virial coefficient for a monatomic gas to illustrate the procedure. To calculate $B_2(T)$ we need U_2. For monatomic particles it is reasonable to assume that the potential depends only on the separation of the two particles so $U_2 = u(r_{12})$, where $r_{12} = |r_2 - r_1|$. Using a change of variables we can write this integral $r_{12} = r_2 - r_1$ and after integration over r_1 we can transform variables from dr_{12} to $4\pi r^2 dr$. The result is:

$$B_2(T) = -2\pi \int [e^{-\beta u(r)} - 1] r^2 \, dr$$

This expression can be used to obtain parameters from experiment. The second virial coefficient is tabulated for a number of gases. For a hard-sphere potential there is an infinite repulsive wall at a particle radius σ. There is no attractive part.

$$B_2(T) = -2\pi \int_0^\sigma [-1] r^2 \, dr$$
$$= \frac{2\pi\sigma^3}{3}$$

The Lennard-Jones potential cannot be calculated analytically, but the integral can be computed numerically. The second virial coefficient was a useful starting point for obtaining Lennard-Jones parameters that were used in simulations.

Isihara-Hadwiger Formula

The Isihara-Hadwiger formula was discovered simultaneously and independently by Isihara and the Swiss mathematician Hadwiger in 1950. The second virial coefficient for any hard convex body is given by the exact relation:

$$B_2 = RS + V$$

or:

$$\frac{B_2}{V} = 1 + 3\alpha$$

where:

$$\alpha = \frac{RS}{3V}$$

where V is the volume, S, the surface area, and R the mean radius of curvature.

Hard spheres

For the hard sphere model one has:[9]

$$B_2(T) = -\frac{1}{2} \int_0^\sigma \left(\langle 0 \rangle - 1 \right) 4\pi r^2 dr$$

leading to

$$B_2 = \frac{2\pi\sigma^3}{3}$$

Note that B_2 for the hard sphere is independent of temperature.

Van der Waals equation of state

For the Van der Waals equation of state one has:

$$B_2(T) = b - \frac{a}{RT}$$

Excluded volume

The second virial coefficient can be computed from the expression:

$$B_2 = \frac{1}{2} \iint v_{\text{excluded}}(\Omega, \Omega') f(\Omega) f(\Omega') \, \mathrm{d}\Omega \mathrm{d}\Omega'$$

where v_{excluded} is the excluded volume.

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Related reading

- W. H. Stockmayer "Second Virial Coefficients of Polar Gases", Journal of Chemical Physics **9** pp. 398- (1941)
- G. A. Vliegenthart and H. N. W. Lekkerkerker "Predicting the gas–liquid critical point from the second virial coefficient", Journal of Chemical Physics **112** pp. 5364-5369 (2000)

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16.6: The Repulsive Term in the Lennard-Jones Potential

Proposed by Sir John Edward Lennard-Jones, the Lennard-Jones potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation. The potential equation accounts for the difference between attractive forces (dipole-dipole, dipole-induced dipole, and London interactions) and repulsive forces.

Introduction

Imagine two rubber balls separated by a large distance. Both objects are far enough apart that they are not interacting. The two balls can be brought closer together with minimal energy, allowing interaction. The balls can continuously be brought closer together until they are touching. At this point, it becomes difficult to further decrease the distance between the two balls. To bring the balls any closer together, increasing amounts of energy must be added. This is because eventually, as the balls begin to invade each other's space, they repel each other; the force of repulsion is far greater than the force of attraction.

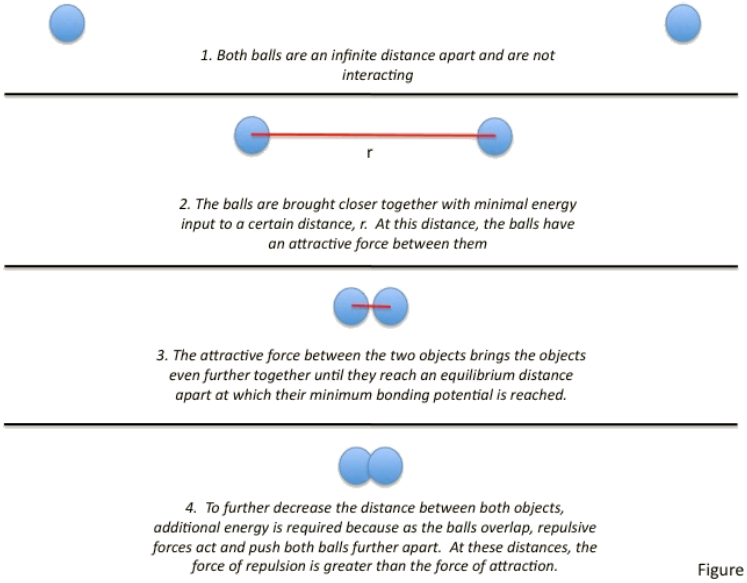


Figure A

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by the **Lennard-Jones potential**.

The Lennard-Jones Potential

The Lennard-Jones model consists of two 'parts'; a steep repulsive term, and smoother attractive term, representing the London dispersion forces. Apart from being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. It is worth mentioning that the 12-6 Lennard-Jones model is not the most faithful representation of the potential energy surface, but rather its use is widespread due to its computational expediency. The Lennard-Jones Potential is given by the following equation:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{16.6.1}$$

or is sometimes expressed as:

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} \tag{16.6.2}$$

where

- V is the intermolecular potential between the two atoms or molecules.
- ϵ is the well depth and a measure of how strongly the two particles attract each other.
- σ is the distance at which the intermolecular potential between the two particles is zero (Figure $16.6.1$). σ gives a measurement of how close two nonbonding particles can get and is thus referred to as the *van der Waals radius*. It is equal to one-half of the internuclear distance between nonbonding particles.
- r is the distance of separation between both particles (measured from the center of one particle to the center of the other particle).
- $A = 4\epsilon\sigma^{12}$, $B = 4\epsilon\sigma^{6}$
- Minimum value of $\Phi_{12}(r)$ at $r = r_{min}$.

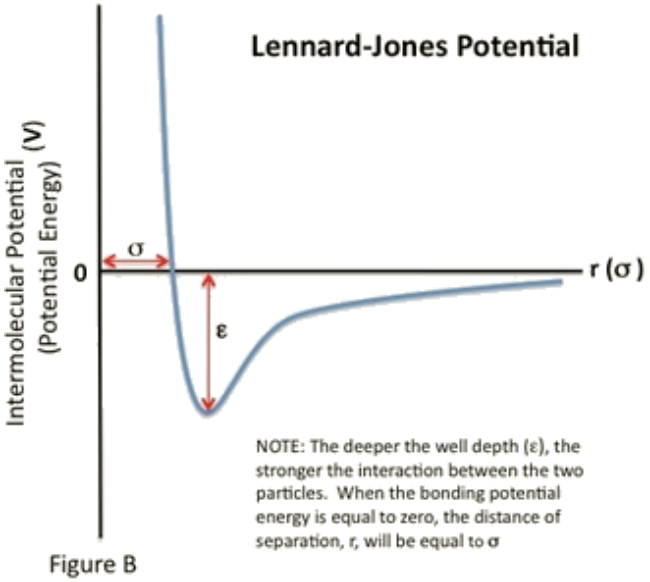


Figure $16.6.1$: The Lennard-Jones potential describes both the attraction and repulsion between nonionic particles. The first part of the equation, the short-ranged $\sigma/r)^{12}$ term describes the repulsive forces between particles while the latter part of the equation and the longer-ranged σ/r^{6} term denotes the attraction.

Example $16.6.1$: The van der Waals Radius

The ϵ and σ values for Xenon (Xe) are found to be 1.77 kJ/mol and 4.10 Angstroms, respectively. Determine the van der Waals radius for the Xenon atom.

Solution

Recall that the van der Waals radius is equal to one-half of the internuclear distance between nonbonding particles. Because σ gives a measure of how close two non-bonding particles can be, the van der Waals radius for Xenon (Xe) is given by:

r = σ/2 = 4.10 Angstroms/2 = 2.05 Angstroms

Bonding Potential

The Lennard-Jones potential is a function of the distance between the centers of two particles. When two non-bonding particles are an infinite distance apart, the possibility of them coming together and interacting is minimal. For simplicity's sake, their bonding potential energy is considered zero. However, as the distance of separation decreases, the probability of interaction increases. The particles come closer together until they reach a region of separation where the two particles become bound; their bonding potential energy decreases from zero to a negative quantity. While the particles are bound, the distance between their centers continue to decrease until the particles reach an equilibrium, specified by the separation distance at which the minimum potential energy is reached.

If the two bound particles are further pressed together, past their equilibrium distance, repulsion begins to occur: the particles are so close together that their electrons are forced to occupy each other's orbitals. Repulsion occurs as each particle attempts

to retain the space in their respective orbitals. Despite the repulsive force between both particles, their bonding potential energy increases rapidly as the distance of separation decreases.

Example 16.6.2

Calculate the intermolecular potential between two Argon (Ar) atoms separated by a distance of 4.0 Angstroms (use ϵ=0.997 kJ/mol and σ=3.40 Angstroms).

Solution

To solve for the intermolecular potential between the two Argon atoms, we use equation 2.1 where V is the intermolecular potential between two non-bonding particles.

$$V = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The data given are:

- $\epsilon = 0.997\ \text{kJ/mol}$,
- $\sigma = 3.40\ \text{Angstroms}$, and
- the distance of separation, $r = 4.0\ \text{Angstroms}$.

We plug these values into Equation 16.6.1 and solve as follows:

$$\begin{aligned} V &= 4(0.997\ \text{kJ/mol})\left[\left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{12} - \left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{6}\right] \\ &= 3.988(0.14 - 0.38) \\ &= 3.988(-0.24) \\ &= -0.96kJ/mol \end{aligned}$$

Stability and Force of Interactions

Like the bonding potential energy, the stability of an arrangement of atoms is a function of the Lennard-Jones separation distance. As the separation distance decreases below equilibrium, the potential energy becomes increasingly positive (indicating a repulsive force). Such a large potential energy is energetically unfavorable, as it indicates an overlapping of atomic orbitals. However, at long separation distances, the potential energy is negative and approaches zero as the separation distance increases to infinity (indicating an attractive force). This indicates that at long-range distances, the pair of atoms or molecules experiences a small stabilizing force. Lastly, as the separation between the two particles reaches a distance slightly greater than σ, the potential energy reaches a minimum value (indicating zero force). At this point, the pair of particles is most stable and will remain in that orientation until an external force is exerted upon it.

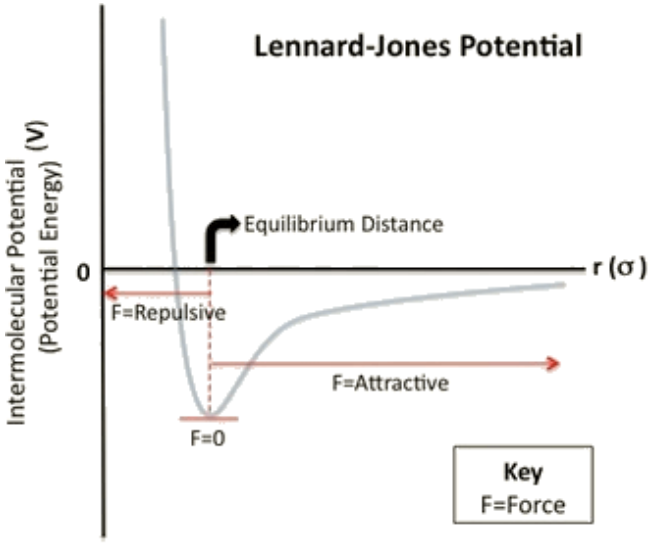


Figure C

Example 16.6.3

Two molecules, separated by a distance of 3.0 angstroms, are found to have a σ value of 4.10 angstroms. By decreasing the separation distance between both molecules to 2.0 angstroms, the intermolecular potential between the molecules becomes more negative. Do these molecules follow the Lennard-Jones potential? Why or why not?

Solution

Recall that σ is the distance at which the bonding potential between two particles is zero. On a graph of the Lennard-Jones potential, then, this value gives the x-intersection of the graph. According to the Lennard-Jones potential, any value of r greater than σ should yield a negative bonding potential and any value of r smaller than σ should yield a positive bonding potential. In this scenario, as the separation between the two molecules decreases from 3.0 angstroms to 2.0 angstroms, the bonding potential is becomes more negative. In essence however, because the starting separation (3.0 angstroms) is already less than σ (4.0 angstroms), decreasing the separation even further (2.0 angstroms) should result in a more positive bonding potential. Therefore, these molecules do not follow the Lennard-Jones potential.

Exercise 16.6.1

The second part of the Lennard-Jones equation is $(\sigma/r)^6$ and denotes attraction. Name at least three types of intermolecular interactions that represent attraction.

Answer available at the end of this section.

Exercise 16.6.2

At what separation distance in the Lennard-Jones potential does a species have a repulsive force acting on it? An attractive force? No force?

Answer available at the end of this section.

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Answers

Exercise 16.6.1

From section 2.1, dipole-dipole, dipole-induced dipole, and London interactions are all attractive forces.

Exercise 16.6.2

See Figure C. A species will have a repulsive force acting on it when r is less than the equilibrium distance between the particles. A species will have an attractive force acting on it when r is greater than the equilibrium distance between the particles. Lastly, when r is equal to t↑he equilibrium distance between both particles, the species will have no force acting upon it.

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16.7: Van der Waals Constants in Terms of Molecular Parameters

The van der Waals equation can be written as:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

Using the binomial expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots$$

We can write the van der Waals equation of state as:

$$\begin{aligned} P &= \frac{RT}{\bar{V}}\left[1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots\right] - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} + (RTb - a)\frac{1}{\bar{V}^2} + \frac{RTb^2}{\bar{V}^3} + \cdot \end{aligned}$$

Rearranging in terms of compressibility, Z:

$$Z = \frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots$$

Comparing to the Viral equation of state, we can see that the second Viral coefficient is related to the van der Waals coefficients:

$$B_{2V}(T) = b - \frac{a}{RT}$$

Using a combination of the hard sphere model and the Lennard-Jones potential, we obtain:

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\dfrac{C_6}{r^6} & r > \sigma \end{cases} \tag{16.7.1}$$

We can write the second Virial coefficient as

$$B_2(T) = \frac{2}{3}\pi N_0 \sigma^3 \left[1 - \frac{C_6}{3k_B T \sigma^6}\right] \tag{16.7.2}$$

Let us introduce to simplifying variables

$$b = \frac{2}{3}\pi N_0 \sigma^3 \tag{16.7.3}$$

$$a = \frac{2\pi N_0^2 C_6}{9\sigma^3} \tag{16.7.4}$$

In which the second Virial coefficient becomes:

$$B_2(T) = b - \frac{a}{RT} \tag{16.7.5}$$

From these equations, we can see that a is directly proportional to c_6, the intermolecular attraction between particles with a force proportional to r^{-6}. Likewise, b is equivalent to four times the volume of the particle. In other words, the van der Waals equations assumes the hard sphere model at small distances and weak interactions (attractive forces) at larger distances.

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16.E: The Properties of Gases (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 16 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q16.10

One liter of N_2 (g) at 2.1 bar and two liters of Ar(g) at 3.4 bar are mixed in a 4.0-L flask to form an ideal-gas mixture. Calculate the value of the final pressure of the mixture if the initial and final temperature of the gases are the same. Then, repeat this calculation if the initial temperatures of the N_2 (g) and Ar(g) are 304 K and 402 K, respectively, and the final temperature of the mixture is 377 K. (Assume ideal-gas behavior.)

S16.10

Using the ideal gas law, we can find the number of moles of each gas.

$$n_{N_2} = \frac{P_{N_2}V_{N_2}}{RT} = \frac{(2.1x10^5 Pa) * (1x10^{-3}m^3)}{RT} = \frac{210Pa * m^3}{RT}$$

$$n_{Ar} = \frac{P_{Ar}V_{Ar}}{RT} = \frac{(3.4x10^5 Pa) * (2x10^{-3}m^3)}{RT} = \frac{680Pa * m^3}{RT}$$

The total moles of gas in the final mixture is the sum of the moles of each gas in the mixture, which is

$$\frac{210Pa * m^3}{RT} + \frac{680Pa * m^3}{RT} = \frac{890Pa * m^3}{RT}$$

Therefore,

$$P = \frac{nRT}{V} = \frac{890Pa * m^3}{0.0040m^3} = 2.2x10^5 Pa = 2.2bar$$

Now, considering the initial temperatures of the gases are different from each other and from the final temperature of the mixture, we calculate the total number of moles to be

$$n_{total} = n_{N_2} + n_{Ar} = \frac{210Pa * m^3}{R * (304K)} + \frac{680Pa * m^3}{R * (402K)}$$

Substituting this into the ideal gas law, we get the final pressure to be

$$P = [\frac{210Pa * m^3}{R * (304K)} + \frac{680Pa * m^3}{R * (402K)}] * \frac{R * (377K)}{0.0040m^3} = 2.2x10^5 Pa = 2.2bar$$

Q16.12

What is the molar Gas Constant in units of cm^3 torr K^{-1} mol^{-1}.

S16.12

We know $R = 0.082058L \cdot atm \cdot mol^{-1}K^{-1}$

using dimensional analysis:

$$R = 0.082058 L \cdot atm \cdot mol^{-1} K^{-1} \times \frac{760 torr}{1 atm} \times \frac{1 dm^3}{1 L} \times \frac{1 dm^3}{1000 cm^3} \tag{16.E.1}$$

$$R = 0.0623639 cm^3 \cdot atm \cdot mol^{-1} K^{-1} \tag{16.E.2}$$

Q16.13

Use the van der Waals equation to plot the compressibility factor, Z, against P for methane for T = 180 K, 189 K, 190 K, 200 K, and 250 K.

S16.13

First, calculate Z as a function of $\bar{V}$ and P as a function of $\bar{V}$ and plot Z versus P

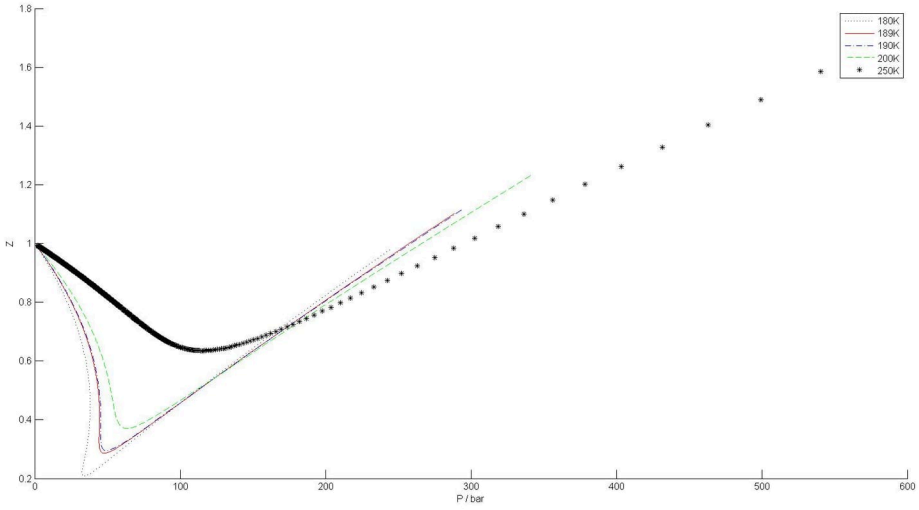
For methane, a = 2.3026 $dm^6 \cdot bar \cdot mol^{-2}$ and b = 0.043067 $dm^3 \cdot mol^{-1}$

$$Z = \frac{P\bar{V}}{RT} \tag{16.E.3}$$

and the van der Waals equation of state is:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \tag{16.E.4}$$

Then create a parametric plot of Z versus P for the suggested temperatures as shown below.



Q16-15

Define the equation that could be solved by using the Netwon-Raphson method to find the molar volume of O2 at 300K and 200atm. Use the van der Waals anf Redlich-Kwong equations.

Constants:

- van der Waals:

$$a = 1.3820 dm^6 * bar * mol, b = 0.031860 dm^3 * mol^{-1} \tag{16.E.5}$$

- Redlich-Kwong:

$$A = 17.411 dm^6 * bar * mol^{-2} * K^{1/2}, B = 0.022082 dm^3 * mol^{-1} \tag{16.E.6}$$

S16.15

Solving van der Waals equation for volume produces:

$$\bar{V}^{3} - (b + \dfrac{RT}{P})\bar{V}^{2} + \dfrac{a}{P}\bar{V} - \dfrac{ab}{P}=0\]

Plugging in constants gives:

$$\bar{V}^{3} - 0.15486\bar{V}^{2} + 0.00691\bar{V} - 0.00022015=0\]

which can be solved numerically to find molar volume.

The Redlich-Kwong equation can be written as a cubic in volume:

$$\bar{V}^{3} - \dfrac{RT}{P}\bar{V}^{2} - \left(B^{2} + \dfrac{BRT}{P} - \dfrac{A}{T^{1/2}P}\right)\bar{V} - \dfrac{AB}{T^{1/2}P} = 0\]

Plugging in constants gives:

$$\bar{V}^{3} - 0.123\bar{V}^{2} + 0.001822\bar{V} - 0.00011099 = 0\]

which can be solved numerically to find molar volume.

Q16.16

Compare the Redlich-Kwong and the van der Waals equations for ethane. Take the molar volume to be 0.09416 .

S16.16

van der Waals:

$$P = \dfrac{RT}{\bar{V}-b}-\dfrac{a}{(\bar{V})^2}\]

Reference Table 16.3 for a, b

$$P = \dfrac{0.083145*400}{.09416-0.065144}-\dfrac{5.5818}{(0.09416)^2}\]

Redlich-Kwong equation of state improved the accuracy of the van der Waals equation by adding a temperature dependence for the attractive term:

$$P = \dfrac{RT}{\bar{V}-B} - \dfrac{A}{T^(\dfrac{1}{2})\bar{V}(\bar{V}+B)}\]

Reference Table 16.4 for A, B

$$P = \dfrac{0.083145*400}{0.09416-0.045153} - \dfrac{98.831}{400^(\dfrac{1}{2})0.09416*(0.09416+0.62723)}\]

Q16.17

$$p = \frac{RT}{\frac{V}{n} - b} - \frac{a}{\sqrt{T}\frac{V}{n}\left(\frac{V}{n} + b\right)} \tag{16.E.7}$$

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{16.E.8}$$

Use the equations above to calculate the temperature of a system with $1.5\ mol$ of methane at $300\ K$ confined to a volume of $100\ cm^3$. Compare the two calculated pressures.

S16.17

$R = 82.057338 \frac{cm^2\ atm}{K\ mol}$

Redlich-Kwong constants: $a = 31.59 \times 10^6\ (atm)(K^{\frac{1}{2}})\left(\frac{cm^3}{mol}\right)^2$ and $b = 29.6\ \frac{cm^3}{mol}$

Van der Waals constants: $a = 2.25 \times 10^6\ (atm)\left(\frac{cm^3}{mol}\right)^2$ and $b = 42.8\ \frac{cm^3}{mol}$

Redlich-Kwong equation: $p = \frac{82.057338 \frac{cm^2\ atm}{K\ mol}\ 300\ K}{\frac{100\ cm^3}{1.5\ mol} - 29.6\ \frac{cm^3}{mol}} - \frac{31.59 \times 10^6\ (atm)(K^{\frac{1}{2}})\left(\frac{cm^3}{mol}\right)^2}{\sqrt{300\ K}\frac{100\ cm^3}{1.5\ mol}\left(\frac{100\ cm^3}{1.5\ mol} + 29.6\ \frac{cm^3}{mol}\right)} = 379.95\ atm$

Van der Waals equation: $p = \frac{(1.5\ mol)(82.057338 \frac{cm^2\ atm}{K\ mol})(300\ K)}{(100\ cm^3) - (1.5\ mol)(42.8\ \frac{cm^3}{mol})} - \frac{(1.5\ mol)^2(2.25 \times 10^6\ (atm)\left(\frac{cm^3}{mol}\right)^2)}{(100\ cm^3)^2} = 525.2\ atm$

There is a $145.25\ atm$ difference in the calculated pressures.

Q16.20

The following equation can be used to relate the pressure of propane to its density at temperatures below 400 K:

$$P = 33.258\rho - 7.5884\rho^2 + 1.0306\rho^3 - 0.058757\rho^4 - 0.0033566\rho^5 + 0.00060696\rho^6 \tag{16.E.9}$$

where the pressure (P) is in bar and the density (ρ) is in $\frac{mol}{L}$ and ranges from $0 \frac{mol}{L} \leq \rho \leq 12.3 \frac{mol}{L}$.

Calculate and plot the pressure for the given density range using:

a. the equation given above
b. the Van der Waals equation of state
c. the Redlich-Kwong equation of state

Compare your results from the above parts.

S16.20

a.) Straight forward to calculate.

Even though straight forward, should still put solution for students.

graph plotted using matlab.

b.) The following constants were used in the equation below:

$$a = 9.3919 \frac{L^2 bar}{mol^2} \text{ and } b = 0.09049 \frac{L}{mol}$$

$$P_{VDW} = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \tag{16.E.10}$$

c.) The following constants were used in the equation below:

$$a = 183.01 \frac{L^2 bar}{mol^2} \text{ and } b = 0.06272 \frac{L}{mol}$$

$$P_{RK} = \frac{RT}{\overline{V} - b} - \frac{a}{\sqrt{T}\overline{V}(\overline{V} + b)} \tag{16.E.11}$$

As can be seen by the plot, the Van der Waals equation of state deviates greatly from the empirical fit at higher densities. The Redlich-Kwong equation provides a reasonable approximation to the empirical data. (All calculations were done in MATLAB, and the above plot was produced by me)

Q16.21

Use the data below to evaluate the van der waals and Redlich Kwong constants for benzene.

Species	T_c/K	P_c/bar	P_c/atm	V_{nc}/L mol^{-1}*	P_cV_{nc}/RT_c
Benzene	561.75	48.758	48.120	0.256	0.26724

*n to indicate molar volume

Van Der Waals

$$a = \frac{27(RT_c)^2}{64P_c} \; and \; b = \frac{RT_c}{8P_c}$$

Redlich-Kwong

$$A = 0.42748 \frac{R^2 T_c^{\frac{5}{2}}}{P_c} \; and \; B = 0.08664 \frac{RT_c}{P_c}$$

S16.21

Van Der Waals

$$\text{a} = \frac{27 * (0.083145 dm^3 \cdot bar \cdot mol^{-1} K^{-1})^2 * (561.75K)^2}{64 * 48.758 bar} = \mathbf{18.8754\,dm^6 \cdot atm \cdot mol^{-2}}$$

$$\text{b} = \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1} K^{-1})^2 * (561.75K)^2}{8 * 48.758 bar} = \mathbf{5.5927\,dm^3 \cdot mol^{-1}}$$

Redlich-Kwong

$$A = 0.42748 * \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1} K^{-1})^2 * (561.75K)^{\frac{5}{2}}}{48.758 bar} = \mathbf{453.315\,dm^6 \cdot atm \cdot mol^{-2} \cdot K^{\frac{1}{2}}}$$

$$B = 0.42748 * \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1} K^{-1})^2 * (561.75K)^2}{48.758 bar} = \mathbf{19.126\,dm^3 \cdot mol^{-1}}$$

Q16.22

Show that the van der Waals equation for argon at T = 142.69 K and P = 35.00 atm can be written as

$$\overline{V}^3 - 0.3664\overline{V}^2 + 0.001210 = 0 \tag{16.E.12}$$

where, for convenience, we have suppressed the units in the coefficients. Use the Newton-Raphson method (MathChapter G) to

find the three roots to this equation, and calculate the values of the density of liquid and vapor in equilibrium with each other under these conditions.

S16.22

Using Table 16.3, we can get the values of a and b for argon to use in Van der Waals equation of state.

By doing this, you can isolate $\overline{V}$ in van der Waals equation of state. Next, by applying the Newton-Raphson method to the function given by van der Waals equation (which is only dependent on $\overline{V}$), and the derivative of the function, we find the roots to the equation. On the case here, the smallest root represents the molar volume of liquid argon, and the largest root represents the molar volume of vapor argon.

Q16.23

Calculate the Volume occupied by $50\ kg$ of propane at $50^{\circ}C$ and $35\ bar$, using the Redlich-Kwong equation of state and the Peng-Robinson equation of state.

S16.23

Redlich-Kwong equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{16.E.13}$$

v is volume of gas per mole.

we have $T = 50^{\circ}C = 323\ K$, $P = 35\ bar = 35 \times (10^5)Pa$

For propane, we have $P_c = 42.4924\ bar = 42.4924 \times 10^5 Pa$ and $T_c = 369.522\ K$

so we have $a = \frac{0.42748 R^2 T_c^{2.5}}{P_c T^{0.5}}$;

$b = \frac{0.08664 * R * T_c}{P_c}$

so, $a = \frac{0.42748(8.314^2)369.522^{2.5}}{42.4924\times10^5(323^{0.5})} = 1.015603$

$b = \frac{(0.08664)(8.314)(369.522)}{42.4924\times10^5} = 6.2640829 \times 10^{-5}$

so, $P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$

$(35 * (10^5)) = \frac{(8.314)(323)}{v-(6.2640829\times10^{-5})} - \frac{1.015603}{v(v+6.2640829\times10^{-5})}$

The only real solution is

$v = 0.00010933 \frac{m^3}{mol}$

so In $50\ Kg$ propane, number of moles = $\frac{50*1000}{44.10} = 1133.78684$

total volume occupied by $50\ Kg$ propane at the specified conditions = $(1133.78684)(0.00010933) = 0.1239569 m^3 = 123.9569$ Liters is the answer.

Peng - Robinson's equation of state:

$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$

$a = 0.45724 R^2 * T_c^2 * \frac{\alpha}{P_c}$

$b = 0.0778R\frac{T_c}{P_c}$

$\alpha = 1 + S(1 - \sqrt{T_r})$

$S = 0.37464 + 1.54226w - 0.26992w^2$

$T_r = \frac{T}{T_c}$

we have $P = 35 \times 10^5 Pa$ and $T = 323\ K$

$P_c = 42.4924\ bar = 42.4924 \times 10^5 Pa$ and $T_c = 369.522\ K$

we have accentric factor = $w = 0.152$.

$T_r = \frac{T}{T_c} = \frac{323}{369.522} = 0.87410$

$S = 0.37464 + (1.54226)(0.152) - (0.26992)(0.152^2) = 0.602827$

$\alpha = 1 + 0.602827 * (1 - \sqrt{0.87410}) = 1.0392240523$

$a = (0.45724)(8.314^2)(369.522^2)\frac{1.0392240523}{42.4924 \times 10^5} = 1.055462444$

$b = (0.0778)(8.314)\frac{369.522}{42.4924 \times 10^5} = 0.0000562494$

so, by the equation of state:

$(35 \times 10^5) = \frac{(8.314)(323)}{v - 0.0000562494} - \frac{1.055462444}{v(v + 0.0000562494 + 0.0000562494(v - 0.0000562494)}$

$v = 0.0000988504\frac{m^3}{mol}$

so In $50\ Kg$ propane, number of moles = $\frac{(50)(1000)}{44.10} = 1133.78684$

total volume occupied by $50\ Kg$ propane at the specified conditions = $(1133.78684)(0.0000988504) = 0.1120752 m^3 = 112.0752$ Liters is the answer.

Q16.25

A way to obtain the expressions for the van der Waals constants is to make $(\frac{\partial P}{\partial \bar{V}})_T$ and $(\frac{\partial^2 P}{\partial \bar{V}^2})_T$ zero at the critical point, but why do they equal to zero at critical point? Obtain the equation $\bar{V}_c$ = $3b$from this procedure.

S16.25

$$(\frac{\partial P}{\partial \bar{V}})_T = 0$$

$$(\frac{\partial^2 P}{\partial \bar{V}^2})_T = 0$$

$$(\frac{\partial P}{\partial \bar{V}})_T = \frac{\partial}{\partial \bar{V}}\ (\frac{RT}{\bar{V} - b} - \frac{a}{\bar{T}^2})_T$$

$$= RT\ (-\frac{1}{(\bar{V} - b)^2})\ -\ a\ (\frac{-2}{\bar{V}^3})$$

$$= -\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3}$$

At critical point,

$\frac{RT_c}{(\bar{V}_c - b)^2} = \frac{2a}{\bar{V}_c^3}$ by equating $(\frac{\partial P}{\partial \bar{V}})_T = 0$.

By differentiating the equation $RT\ (-\frac{1}{(\bar{V}-b)^2})$ - $a\ (\frac{-2}{\bar{V}^3})$ with respect to $\bar{V}$,

$$(\frac{\partial^2 P}{\partial \bar{V}^2})_T = \frac{\partial}{\partial \bar{V}}\ (-\frac{RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3})_T$$

$$= RT\ (-\frac{2}{(\bar{V}-b)^3}) + 2a\ (\frac{-3}{\bar{V}^4})$$

$$= \frac{2RT}{(\bar{V}-b)^3} - \frac{6a}{\bar{V}^4}$$

At critical point,

$\frac{2RT_c}{(\bar{V}_c-b)^3} = \frac{6a}{\bar{V}_c^4}$ by equating $(\frac{\partial^2 P}{\partial \bar{V}^2})_T = 0$.

Now,

$$\frac{\frac{2a}{\bar{V}_c^3}}{\frac{6a}{\bar{V}_c^4}} = \frac{\frac{RT_c}{(\bar{V}_c-b)^2}}{\frac{2RT_c}{(\bar{V}_c-b)^3}}$$

$$\frac{\bar{V}_c}{3} = \frac{(\bar{V}_c-b)}{2}$$

$$\bar{V}_c = 3b$$

Q16.26

Show that the Redlich-Kwong equation can be rewritten in the following form:

$$\overline{(V)}^3 - \frac{RT}{P}\bar{V}^2 - (B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}})\bar{V} - \frac{AB}{PT^{1/2}} = 0 \tag{16.E.14}$$

S16.26

Starting with the Redlich-Kwong equation and manipulating it we get the following:

$$P = \frac{RT}{\bar{V}-B} - \frac{A}{T^{1/2}\bar{V}(\bar{V}+B)} \tag{16.E.15}$$

$$P(\bar{V}-B)T^{1/2}\bar{V}(\bar{V}+B) = RT^{3/2}\bar{V}(\bar{V}+B) - A(\bar{V}-B) \tag{16.E.16}$$

$$PT^{1/2}\bar{V}(\bar{V}^2-B^2) = RT^{3/2}\bar{V}^2 + RT^{3/2}\bar{V}B - A\bar{V} + AB \tag{16.E.17}$$

$$\overline{(V)}^3 - \frac{RT}{P}\bar{V}^2 - (B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}})\bar{V} - \frac{AB}{PT^{1/2}} = 0 \tag{16.E.18}$$

Q16.27

Use the results of the previous question, Q16.26, to derive Equations 16.14.

$(a)\bar{V}_c = 3.8473B$, $(b)P_c = .029894\frac{A^{2/3}R^{1/3}}{B^{5/3}}$, and $(c)T_c = .34504\left(\frac{A}{BR}\right)^{2/3}$

The following are solved from Q16.26 and are necessary to solve for Equation 16.14:

$$1)B = .25992\bar{V}_c \tag{16.E.19}$$

$$2)A = 0.42748\frac{R^2T_c^{5/2}}{P_c} \tag{16.E.20}$$

$$3)\frac{P_c\bar{V}_C}{RT_c} = \frac{1}{3} \tag{16.E.21}$$

S16.27

From equation (1) we see that solving for $\bar{V}_c$ yields the first equation

$$\bar{V}_c = 3.8473B \tag{16.E.22}$$

.

From equation (2) we can rewrite the expression with some manipulation as

$$A = .42748RT_c^{3/2}\left(\frac{RT_c}{P_c\bar{V}_c}\right)\bar{V}_c \tag{16.E.23}$$

Substituting equation (3) and 16.14a into the previous equation gives the expression

$$A = 3(.42748)RT_c^{3/2}(3.8473B) \tag{16.E.24}$$

Lastly, solving for T_c gives the equation for 16.14c

$$T_c = .34504\left(\frac{A}{BR}\right)^{2/3} \tag{16.E.25}$$

Finally, solving for equation 16.14b we must substitute the previously solved 16.14c into equation (2),solving for P_c

$$P_c = 0.42748\frac{R^2T_c^{5/2}}{A} = \left(\frac{.42748}{A}\right)R^2\left[.34504\left(\frac{A}{BR}\right)^{2/3}\right]^{5/2} = .029894\frac{A^{2/3}R^{1/3}}{B^{5/3}} \tag{16.E.26}$$

which is equation 16.14b.

Q16.28

Derive the Van der Waals cubic equation of state from

$$\left(P + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT \tag{16.E.27}$$

S16.28

The Van der Waal equation can be rewritten in terms of Z:

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}} \tag{16.E.28}$$

solving for $\bar{V}$

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0 \tag{16.E.29}$$

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16.S: The Properties of Gases (Summary)

We will begin by looking at various empirical equations of state that account for deviations from ideality using equations that are cubic in molar volume. Such equations can crudely account for the gas-liquid phase transition, which is one of the most readily observable consequences of intermolecular forces. We will see that by analyzing the behavior of these equations, a more fundamental relationship arises: the law of corresponding states, which shows that there is one universal equation of state that all gases/liquids obey (though regrettably, there is no analytical functional form for it).

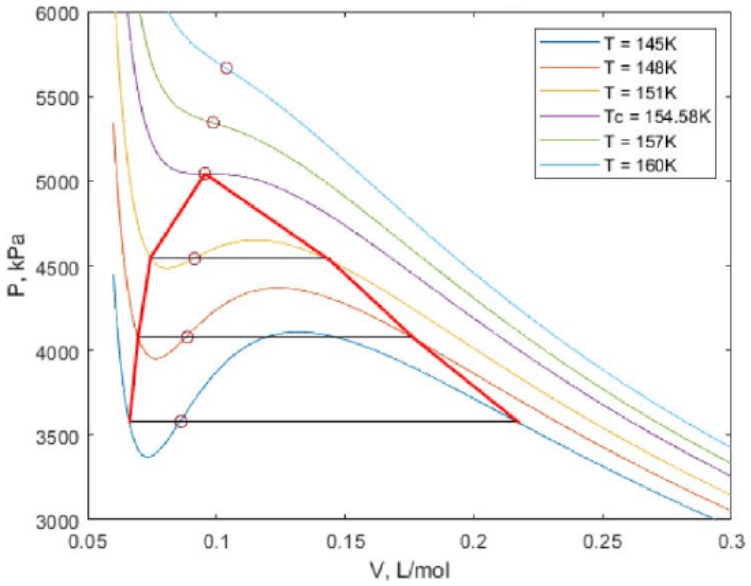


Figure 7.1: Pressure/molar volume isotherm for O_2 using the van der Waals equation of state. The red parabola is a rough approximation of the liquid/gas phase change region. Figure by John Davis, Jamie Ng, and Brendan Russ (2019W).

After working with these equations of state, we will explore in detail how intermolecular forces give rise to nonideality. Using a virial expansion, we can concentrate on the potential energy between two particles, between 3 particles, and so on. The two-body interaction is embodies by the “second virial coefficient,” which gives a first-order correction to the molar volume calculated from the ideal gas law. We examine the two-body interactions by looking at several effective intermolecular potentials and analyze the attracive forces between molecules that arise from the interaction of molecular dipole moments and from electron correlation (i.e., London dispersion forces). The repulsive forces are not well-grounded theoretically, but we find that the behavior of gases is largely insensitive to the exact functional form of the repulsive potential, so we can use a number of effective repulsive potentials to obtain similar results. We find that we can relate the attractive forces to atomic/molecular parameters such as their dipole moments, polarizabilities, and ionization energies; these parameters are the most important contributors to the nonideality of a gas at low temperature and/or moderate density.

Learning Objectives

By the end of this chapter, you should know the following:

- The compressibility factor and how can it be used as a measure of nonideality
- How equations of state that are cubic in molar volume account for phase transitions
- The definitions of critical points and critical constants
- The law of corresponding states
- How intermolecular forces connect quantum mechanical properties of isolated properties to bulk properties of materials
- Virial expansion, and virial coefficients relate to n-body interactions
- The relationship between the second virial coefficient and compressibility
- How the second virial coefficient relates to intermolecular forces
- Explain the physical justification for the Lennard-Jones potential

Skill goals (what you should be able to do/calculate):

- Use the van der Waals equation calculate state variables of real gases
- Use the law of corresponding states to calculate the state of a real gas
- Read compressibility charts, phase diagrams, and other visualizations of physical data pertaining to real gases
- Classify the types of intermolecular forces between atoms and molecules
- Use the Lennard-Jones equation to calculate an intermolecular potential, and use molecular parameters to calculate the c_6 coefficient
- Use the hard-sphere and square-well potentials to calculate virial coefficients

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17: BOLTZMANN FACTOR AND PARTITION FUNCTIONS

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc. Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties – spectra, rate constants, etc., using time correlation functions. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice, be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

17.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System

17.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution

17.3: The Average Ensemble Energy is Equal to the Observed Energy of a System

17.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature

17.5: Pressure can be Expressed in Terms of the Canonical Partition Function

17.6: The Partition Function of Distinguishable, Independent Molecules is the Product of the Molecular Partition Functions

17.7: Partition Functions of Indistinguishable Molecules Must Avoid Over Counting States

17.8: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom

17.E: Boltzmann Factor and Partition Functions (Exercises)

17.S: Boltzmann Factor and Partition Functions (Summary)

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17.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

The Microscopic Laws of Motion

Consider a system of N classical particles. The particles are confined to a particular region of space by a container of volume V . In classical mechanics, the state of each particle is specified by giving its position and its velocity, i.e., by telling where it is and where it is going. The position of particle i is simply a vector of three coordinates $r_i = (x_i, y_i, z_i)$, and its velocity $\mathbf{v}_i$ is also a vector $(v_{x_i}, v_{y_i}, v_{z_i})$ of the three velocity components. Thus, if we specify, at any instant in time, these six numbers, we know everything there is to know about the state of particle i.

The particles in our system have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)$, and the velocities at t are related to the positions by differentiation:

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{17.1.1}$$

In order to determine the positions and velocities as function of time, we need the classical laws of motion, particularly, Newton's second law. Newton's second law states that the particles move under the action of the forces the particles exert on each other and under any forces present due to external fields. Let these forces be denoted $\mathbf{F}_1, \mathbf{F}_2, \ldots, \mathbf{F}_N$. Note that these forces are functions of the particle positions:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{17.1.2}$$

which is known as a force field (because it is a function of positions). Given these forces, the time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

where $\mathbf{F}_1, \ldots, \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivatives, $\{\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), \ldots, \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

The Ensemble Concept (Heuristic Definition)

For a typical macroscopic system, the total number of particles is $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we content ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ gigabytes which is also 10^2 yottabytes! The largest computers we have today have perhaps 10^6 gigabytes of memory, so we are off by 11 orders of magnitude just to specify 1 classical state.

Fortunately, we do not need all of this detail. There are enormous numbers of microscopic states that give rise to the same macroscopic observable. Let us again return to the connection between temperature and kinetic energy:

$$\frac{3}{2}NkT = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \tag{17.1.3}$$

which can be solved to give:

$$T = \frac{2}{3k}\left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m_i\mathbf{v}_i^2\right) \tag{17.1.4}$$

Here we see that T is related to the average kinetic energy of all of the particles. We can imagine many ways of choosing the particle velocities so that we obtain the same average. One is to take a set of velocities and simply assign them in different ways to the N particles, which can be done in $N!$ ways. Apart from this, there will be many different choices of the velocities, themselves, all of which give the same average.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procedure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Consider a large number of systems each described by the same set of microscopic forces and sharing a common set of macroscopic thermodynamic variables (e.g. the same total energy, number of moles, and volume). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time.

The questions that naturally arise are:

1. How do we construct an ensemble?
2. How do we perform averages over an ensemble?
3. How do we determine which thermodynamic properties characterize an ensemble?
4. How many different types of ensembles can we construct, and what distinguishes them?

These questions will be addresses in the sections ahead.

Thermal energy

A confined monatomic gas can be seen as a box with a whole bunch of atoms in it. Each of these particles can be in one of the states given by the last formula. If all of them have large n values there is obviously a lot of kinetic energy in the system. The lowest energy is when all atoms have 1,1,1 as quantum numbers. Boltzmann realized that this should relate to temperature. When we add energy to the system (by heating it up without changing the volume of the box), the temperature goes up. At higher temperatures we would expect higher quantum numbers, and at lower T, lower ones. But how exactly are the atoms distributed over the various states?

This is a good example of a problem involving a discrete probability distribution. The probability that a certain level (e.g., $n = (n_1, n_2, n_3)$ with energy E_i) is occupied should be a function of temperature: $P_i(T)$. Boltzmann postulated that you could look at temperature as a form of energy. The thermal energy of a system is directly proportional to an absolute temperature.

$$E_{thermal} = kT$$

The proportionality constant k (or k_B) is named after him: the Boltzmann constant. It plays a central role in all statistical thermodynamics. The Boltzmann factor is used to approximate the fraction of particles in a large system. The Boltzmann factor is given by:

$$e^{-\beta E_i} \tag{17.1.5}$$

where:

- E_i is the energy in the state i,
- T is the kelvin temperature, and
- k is Boltzmann constant.

As the following section demonstrates, the term β in Equation 17.1.5 is expressed as:

$$\beta = \frac{1}{kT}$$

The rates of many physical processes are also determined by the Boltzmann factor. For a random particle, its thermal energy of a particle is a small multiple of the energy kT. An increase in temperature results in more particles crossing the energy barrier characteristic of activation processes. If this is to occur, particles need to carry sufficient energy. This energy is needed for the particles to successfully cross the energy barrier and is usually called activation energy. The fraction of molecules that have sufficient energy to escape the original material surface is approximately proportional to the Boltzmann factor.

References

1. Hakala, R.W. (1961). A new derivation of the Boltzmann distribution law. *Journal of Chemical Education*. **doi:** 10.1021/ed038p33.
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Problems

1. How are temperature and the average energy per particle for a system related?
2. What does the Boltzmann factor tell you? Why is it important?
3. When is it possible for particles to get extra energy?
4. Give three examples of activation processes.
5. What do "separate arrangements" mean? What are the differences between these arrangements?

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17.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution

Consider a N-particle ensemble. The particles are not necessarily indistinguishable and possibly have mutual potential energy. Since this is a large system, there are many different ways to arrange its particles and yet yield the same thermodynamic state. Only one arrangement can occur at a time. The sum of the probabilities of each separate arrangement equals the total number of separate arrangements. Then the probability of a system is:

$$p_N = W_N p_i$$

where p_N is the probability of the system, W_N is the total number of different possible arrangements of the N particles in the system, and p_i is the probability of each separate arrangement. Heisenberg's uncertainty principle states that it is impossible to simultaneously know the momentum and the position of an object with complete precision. In agreement with the uncertainty principle, the total possible number of combinations can be defined as the total number of distinguishable rearrangements of the N particles.

The most practical ensemble is the canonical ensemble with N, V, and T fixed. We can imagine a collection of boxes with equal volumes and number of particles with the entire collection kept in thermal equilibrium. Based on the Boltzmann factor, we know that for a system that has states with energies e_1, e_2, e_3..., the probability p_j that the system will be in the state j with energy E_j is exponentially proportional to the energy of state j. The partition functions of the state places a very important role in calculating the properties of a system, for example, it can be used to calculate the probability, as well as the energy, heat capacity, and pressure.

The Boltzmann Distribution

We are ultimately interested in the probability that a given distribution will occur. The reason for this is that we must have this information in order to obtain useful thermodynamic averages. Let's consider an ensemble of A systems. We will define a_j as the number of systems in the ensemble that are in the quantum state j. For example, a_1 represents the number of systems in the quantum state 1. The total number of possible microstates is:

$$W(a_1, a_2, ...) = \frac{A!}{a_1! a_2! ...}$$

The overall probability that P_j that a system is in the jth quantum state is obtained by averaging a_j/A over all the allowed distributions. Thus, P_j is given by:

$$\begin{aligned} P_j &= \frac{\langle a_j \rangle}{A} \\ &= \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)} \end{aligned}$$

where the angle brackets indicate an ensemble average. Using this definition we can calculate any average property (i.e. any thermodynamic property):

$$\langle M \rangle = \sum_j M_j P_j \tag{17.2.1}$$

The method of the most probable distribution is based on the idea that the average over P_j is **identical** to the most probable distribution. Physically, this results from the fact that we have so many particles in a typical system that the fluctuations from the mean are extremely (immeasurably) small. The equivalence of the average probability of an occupation number and the most probable distribution is expressed as follows:

$$P_j = \frac{\langle a_j \rangle}{A} = \frac{a_j}{A}$$

The probability function is subject to the following constraints:

- Constraint 1: Conservation of energy requires:

$$E_{total} = \sum_j a_j e_j \tag{17.2.2}$$

  where e_j is the energy of the jth quantum state.
- Constraint 2: Conservation of mass requires:

$$A = \sum_j a_j \tag{17.2.3}$$

  which says only that the total number of all of the systems in the ensemble is A.

As we will learn in later chapters, the system will tend towards the distribution of a_j that maximizes the total number of microstates. This can be expressed as:

$$\sum_j \left(\frac{\partial \ln W}{\partial a_j} \right) = 0$$

Our constraints becomes:

$$\sum_j e_j da_j = 0$$

$$\sum_j da_j = 0$$

The method of Lagrange multipliers (named after Joseph Louis Lagrange is a strategy for finding the local maxima and minima of a function subject to equality constraints. Using the method of LaGrange undetermined multipliers we have:

$$\sum_j \left[\left(\frac{\partial \ln W}{\partial a_j} \right) da_j + \alpha da_j - \beta e_j da_j \right] = 0$$

We can use Stirling's approximation:

$$\ln x! \approx x \ln x – x$$

to evaluate:

$$\left(\frac{\partial \ln W}{\partial a_j} \right)$$

to get:

$$\left(\frac{\partial A!}{\partial a_j} \right) - \sum_i \left(\frac{\partial \ln a_i}{\partial a_j} \right) = 0$$

as outlined below.

Application of Stirling's Approximation

First step is to note that:

$$\ln W = \ln A! - \sum_j \ln a_j ! a \approx A \ln A – A - \sum_j a_j \ln a_j - \sum_j a_j$$

Since (from Equation 17.2.3):

$$A = \sum_j a_j$$

these two cancel to give:

$$\ln W = A \ln A - \sum_j a_j \ln a_j$$

The derivative is:

$$\left(\frac{\partial \ln W}{\partial a_j}\right) = \frac{\partial A \ln A}{\partial a_j} - \sum_i \frac{\partial a_i \ln a_i}{\partial a_j}$$

Therefore we have:

$$\left(\frac{\partial A \ln A}{\partial a_j}\right) = \frac{\partial A}{\partial a_j} \ln A - \frac{\partial A}{\partial a_j} = \ln A - 1$$

$$\left(\frac{\partial a_i \ln a_i}{\partial a_j}\right) = \frac{\partial a_i}{\partial a_j} \ln a_i - \frac{\partial a_i}{\partial a_j} = \ln a_j + 1$$

These latter derivatives result from the fact that:

$$\left(\frac{\partial a_i}{\partial a_i}\right) = 1$$

$$\left(\frac{\partial a_j}{\partial a_i}\right) = 0$$

The simple expression that results from these manipulations is:

$$-\ln\left(\frac{a_j}{A}\right) + \alpha - \beta e_j = 0$$

The most probable distribution is:

$$\frac{a_j}{A} = e^a \sum_j e^{-\beta e_j} \tag{17.2.4}$$

Now we need to find the undetermined multipliers α and β.

The left hand side of Equation 17.2.4 is 1. Thus, we have:

$$P_j = \frac{a_j}{A} = \frac{e^{-\beta e_j}}{\sum_j e^{-\beta e_j}}$$

This determines a and defines the Boltzmann distribution. We will show that β from the optimization procedure of method of Lagrange multipliers is:

$$\beta = \frac{1}{kT}$$

This identification will show the importance of temperature in the Boltzmann distribution. The distribution represents a thermally equilibrated most probable distribution over all energy levels (Figure 17.2.1).

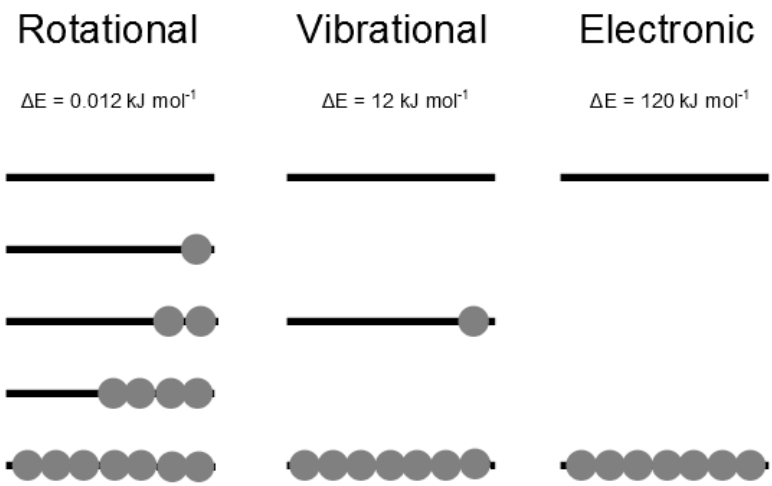


Figure 17.2.1 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. k_BT 2.5 $kJ\ mol^{-1}$ at 300 K. (CC SA-BY 3.0; Mysterioso via Wikiversity).

Boltzmann Distribution

The Boltzmann distribution represents a thermally equilibrated **most probable** distribution over all energy levels. There is always a **higher** population in a state of lower energy than in one of higher energy.

Once we know the probability distribution for energy, we can calculate thermodynamic properties like the energy, entropy, free energies and heat capacities, which are all average quantities (Equation 17.2.1). To calculate P_j, we need the energy levels of a system (i.e., $\{e_i\}$). The energy ("levels") of a system can be built up from the quantum energy levels

> It must always be remembered that no matter how large the energy spacing is, there is always a non-zero probability of the upper level being populated. The only exception is a system that is at absolute zero. This situation is however hypothetical as absolute zero can be approached but not reached.

Partition Function

The sum over all factors $e^{-\beta e_j}$ is given a name. It is called the molecular partition function, q:

$$q = \sum_j e^{-\beta e_j}$$

The molecular partition function q gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number. Larger the value of q, larger the number of states which are available for the molecular system to occupy (Figure 17.2.2).

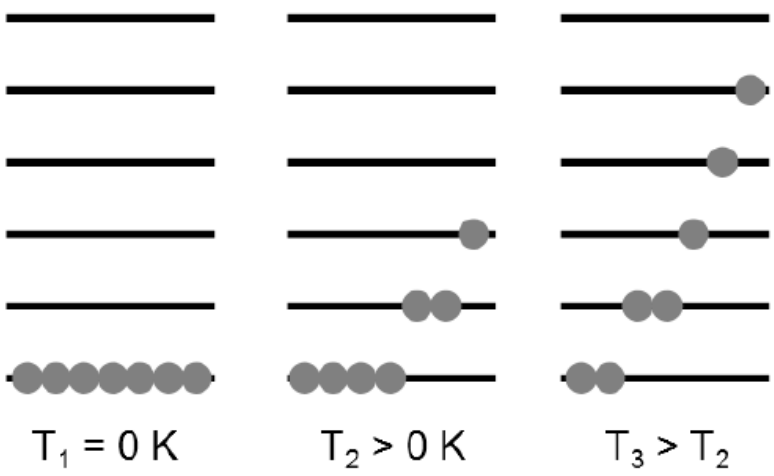


Figure 17.2.2 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. (CC SA-BY 3.0; Mysterioso via Wikiversity).

We distinguish here between the partition function of the ensemble, Q and that of an individual molecule, q. Since Q represents a sum over all states accessible to the system it can written as:

$$Q(N,V,T) = \sum_{i,j,k...} e^{-\beta(e_i+e_j+e_k...)}$$

where the indices $i,\ j,\ k$ represent energy levels of **different** particles.

Regardless of the type of particle the molecular partition function, q represents the energy levels of one individual molecule. We can rewrite the above sum as:

$$Q = q_i q_j q_k \ldots$$

or:

$$Q = q^N$$

for N particles. Note that q_i means a sum over states or energy levels accessible to molecule i and q_j means the same for molecule j. The molecular partition function, q counts the energy levels accessible to molecule i only. Q counts not only the states of all of the molecules, but all of the possible combinations of occupations of those states. However, if the particles are not distinguishable then we will have counted $N!$ states too many. The factor of $N!$ is exactly how many times we can swap the indices in $Q(N,V,T)$ and get the same value (again provided that the particles are not distinguishable). See this video for more information.

References

1. Hakala, R.W. (1967). Simple justification of the form of Boltzmann's distribution law. *Journal of Chemical Education. 44(11), 657.* **doi:** 10.1021/ed044p657
2. Grigorenko, I, Garcia, M.E. (2002). Calculation of the partition function using quantum genetic algorithms. Physica A: Satistical Mechanics and its Applications. 313. 463-470. Retrieved from http://www.sciencedirect.com/science...784371020009883

Problems

1. Complete the justification of Boltzmann's distribution law by computing the proportionality constant a.
2. A system contains two energy levels E_1, E_2. Using Boltzmann statistics, express the average energy of the system in terms of

E_1, E_2.

3. Consider a system contains N energy levels. Redo problem #2.
4. Use the property of exponential function, derive equation (17.9).
5. What are the uses of partition functions?

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17.3: The Average Ensemble Energy is Equal to the Observed Energy of a System

We will be restricting ourselves to the canonical ensemble (constant temperature and constant pressure). Consider a collection of N molecules. The probability of finding a molecule with energy E_i is equal to the fraction of the molecules with energy E_i. That is, in a collection of N molecules, the probability of the molecules having energy E_i:

$$P_i = \frac{n_i}{N}$$

This is the directly obtained from the Boltzmann distribution, where the fraction of molecules n_i/N having energy E_i is:

$$P_i = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{Q} \tag{17.3.1}$$

The average energy is obtained by multiplying E_i with its probability and summing over all i:

$$\langle E \rangle = \sum_i E_i P_i \tag{17.3.2}$$

> Equation 17.3.2 is the standard average over a distribution commonly found in quantum mechanics as expectation values. The quantum mechanical version of this Equation is
>
> $$\langle \psi | \hat{H} | \psi \rangle$$
>
> where Ψ^2 is the distribution function that the Hamiltonian operator (e.g., energy) is averaged over; this equation is also the starting point in the Variational method approximation.

Equation 17.3.2 can be solved by plugging in the Boltzmann distribution (Equation 17.3.1):

$$\langle E \rangle = \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{17.3.3}$$

Where Q is the partition function:

$$Q = \sum_i e^{-\frac{E_i}{kT}}$$

We can take the derivative of $\ln Q$ with respect to temperature, T:

$$\left(\frac{\partial \ln Q}{\partial T}\right) = \frac{1}{kT^2} \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{17.3.4}$$

Comparing Equation 17.3.3 with 17.3.4, we obtain:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)$$

It is common to write these equations in terms of β, where:

$$\beta = \frac{1}{kT}$$

The partition function becomes:

$$Q = \sum_i e^{-\beta E_i}$$

We can take the derivative of $\ln Q$ with respect to β:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right) = -\sum_i \frac{E_i e^{-\beta E_i}}{Q}$$

And obtain:

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

Replacing $1/kT$ with β often simplifies the math and is easier to use.

> It is not uncommon to find the notation changes: Z instead of Q and $\bar{E}$ instead of $\langle E \rangle$.

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17.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature

The heat capacity at constant volume (C_V) is defined to be the change in internal energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{17.4.1}$$

Since:

$$E = -\frac{\partial \ln Q(N,V,\beta)}{\partial \beta} \tag{17.4.2}$$

We see that:

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} \\ &= \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} \\ &= \frac{1}{kT^2}\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \\ &= k\beta^2\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \end{aligned} \tag{17.4.3}$$

where k is the Boltzmann constant. Energy can be stored in materials/gases via populating the specific degrees of freedom that exist in the sample. Understanding how this occurs requires the usage of Quantum Mechanics.

Dulong-Petit Law on the Heat Capacities of Solids

Pierre Louis Dulong and Alexis Thèrèse Petit conducted experiments in 1819 on three dimensional solid crystals to determine the heat capacities of a variety of these solids (Heat capacity is the solids ability to absorb and retain heat). Dulong and Petit discovered that all investigated solids had a heat capacity of approximately 2.49 x 10^4 J kilomole^{-1} K^{-1} at around 298 K or room temperature. The result from their experiment was explained by considering every atom inside the solid as an oscillator with six degrees of freedom (an oscillator can be thought of as a spring connecting all the atoms in the solid lattice). These springs extend into three dimensional space. The more energy that is added to the solid the more these springs vibrate. Each atom has an energy of $\frac{1}{2}kT$, where k is the Boltzmann constant and T is the absolute temperature. Thus,

$$C_V = \frac{6R}{2} = 3R \qquad \text{(Dulong-Petit Law)}$$

The number 6 in this equation is the number of degrees of freedom for the molecule. Petit and Dulong suggested that these results supported their foundation for the heat capacity of solids. The explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased as temperature approached absolute zero. The degrees of freedom do not slow down or cease to move when the solid reaches a sufficiently cold temperature. An additional model was proposed to explain this deviance. Two main theories were developed to explain this puzzling deviance in the heat capacity experiments. The first was constructed by Einstein and the second was authored by Debye.

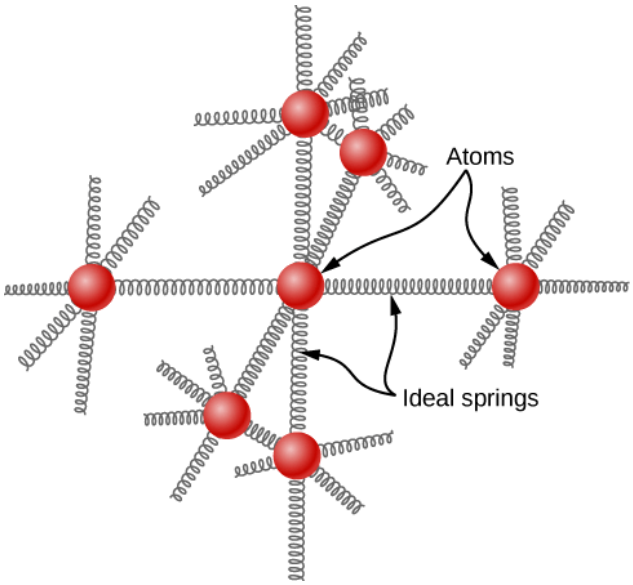


Figure 17.4.1 : In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. (CC BY-SA 4.0; OpenStax).

Einstein's Theory on the Heat Capacities of Solids

Einstein assumed three things when he investigated the heat capacity of solids. First, he assumed that each solid was composed of a lattice structure consisting of N atoms. Each atom was treated as moving independently in three dimensions within the lattice (3 degrees of freedom). This meant that the entire lattice's vibrational motion could be described by a total of $3N$ motions, or degrees of freedom. Secondly, he assumed that the atoms inside the solid lattice did not interact with each other and thirdly, all of the atoms inside the solid vibrated at the same frequency. The third point highlights the main difference in Einstein's and Debye's two models.

Einstein's first point is accurate because the experimental data supported his hypothesis, however his second point is not because if atoms inside a solid could not interact, sound could not propagate through it. For example, a tuning fork's atoms, when struck, interact with one another to create sound which travels through air to the listener's ear. Atoms also interact in a solid when they are heated. Take for example a frying pan. If the pan is heated on one side, the heat transfers throughout the metal effectively warming the entire pan. Molecules that make up the frying pan interact to transfer heat. Much in the same way the oscillators in a solid interact when energy is added to the system. The extent of these interactions lead to the physically observed heat capacity.

The heat capacity of a solid at a constant volume is

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= 3Nk\left(\frac{\theta_E}{T}\right)^2 \\ &= \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\frac{\theta_E}{T}-1\right)^2} \end{aligned}$$

where

- $\theta_E = \dfrac{h\nu}{k}$ is the **Einstein temperature**,
- h is Planck's constant,
- k is Boltzmann's constant, and
- ν is the oscillator frequency of the atoms inside the solid.

The Einstein temperature's accessibility of the vibrational energy inside of a solid molecule determines the heat capacity of that solid. The greater the accessibility the greater the heat capacity. If the vibrational energy is easily accessible the collisions in the molecule have a greater probability of exciting the atom into an upper vibrational level. This is displayed below.

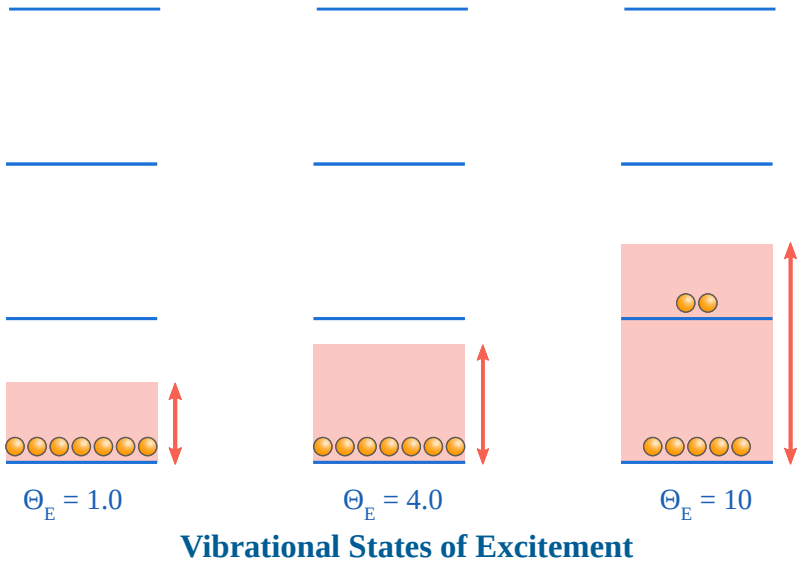


Figure 17.4.2 : This Figure illustrates the effect of the Einstein temperature on the likelihood of an oscillator absorbing energy from a collision and transferring that energy into stored heat or heat capacity. As the Einstein temperature increases, the greater the probability of an oscillator being excited to the next vibrational state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

So the Einstein temperature specifically indicates the probability that a molecule has in its degrees of freedom to store energy in its atomic oscillators (or bonds). Comparing the Einstein temperature to the traditional classical values of Heat capacity will illustrate the differences the specific strengths (high temperature) and weaknesses (low temperature) of the Einstein model.

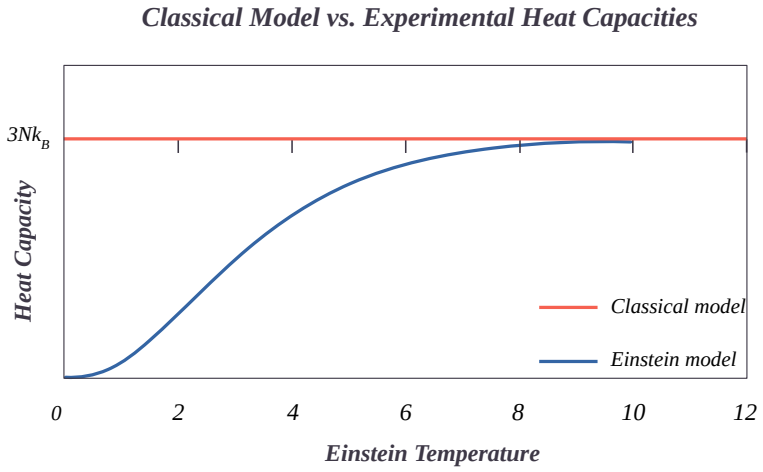


Figure 17.4.3 :This graph shows the accuracy of the of the Einstein temperature at low temperatures. The classical model is effective at temperatures above 10 Einstein Temperatures. (Cc BY-NC; Ümit Kaya via LibreTexts)

Thus, in the high temperature limit ($\frac{\theta_E}{T} \ll 1$) (i.e., the temperature is very large compared to the Einstein temperature) then

$$C_V \approx 3Nk = 3nR. \tag{17.4.4}$$

Einstein's model reveals the accuracy of the Petit and Dulong model and models high temperatures accurately. However, just as Petit and Dulong's model decreased in accuracy as the temperature decreased, so followed Einstein's.

When examining the extremely low temperature limit: $\frac{\theta_E}{T} \gg 1$, it can be seen:

$$C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 e^{\frac{-\theta_E}{T}} \tag{17.4.5}$$

As temperature (T) goes to zero, the exponential portion of the above equation goes to zero and therefore C_V also approaches zero. This supports the experimental values as temperature approaches zero the heat capacity of the solid likewise decreases to zero.

Einstein's theory also explains solids that exhibit a low heat capacity even at relatively high temperatures. An example of such a solid is diamond. The heat capacity of diamond approaches $3Nk$ as temperature greatly increases. Einstein's model supports this through the definition of an Einstein temperature. As the Einstein temperature increases, ν must increase likewise. This is the equivalent of each atom possessing more energy and therefore vibrating more rapidly within the solid itself. The oscillator frequency, ν, can be written as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \tag{17.4.6}$$

where κ is the force constant and μ is the reduced mass. This formula better predicts solids with high force constants or low reduced masses. This corrects deviations from the Petit and Dulong model.

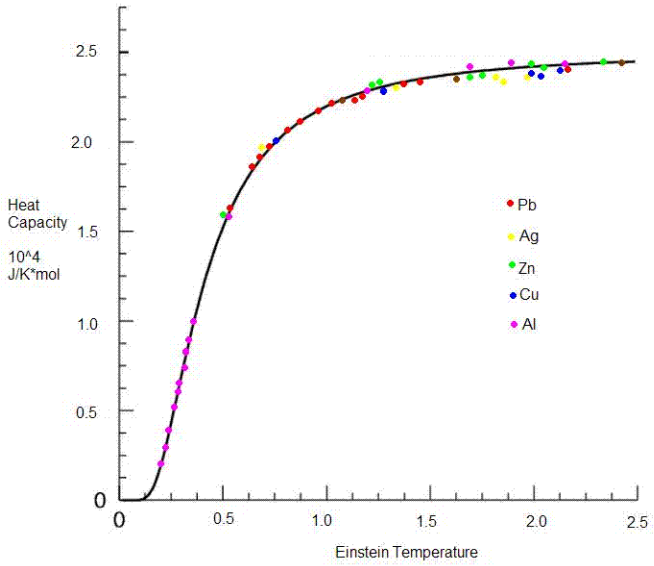


Figure 17.4.4 . This graph indicates the heat capacity of several solid metals as a function of the Einstein temperature: $\theta_E = \frac{hv}{k_B}$.

Essentially the Einstein temperature allows for the heat capacity equation and the vibrational frequencies in the solid to change as the temperature changes. This effectively adjusts for the deviations seen in the Petit/Dulong model. As the temperature increases or decreases, the Einstein temperature increases or decreases likewise to mirror the actual physical activity within the solid.

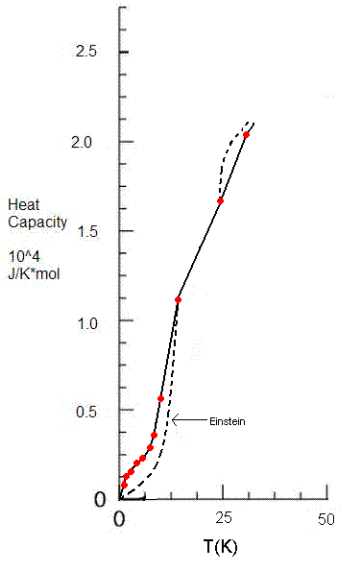


Figure 17.4.5 . This plot shows the heat capacity of lead compared to the expected values calculated from Einstein's model.

Einstein's model predicts relatively low temperatures well. However, when decreasing from approximately 15 K, Einstein's model deviates from experimental values. Also, this can be observed, although not as dramatically, for temperatures from 25 K to 30 K. Clearly a term or correction is still missing from Einstein's model to increase its accuracy.

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17.5: Pressure can be Expressed in Terms of the Canonical Partition Function

Pressure can also be derived from the canonical partition function. The average pressure is the sum of the probability times the pressure:

$$\langle P \rangle = \sum_i P_i(N,V,T) P_i(N,V)$$

The pressure of a macroscopic system is:

$$P(N,V) = -\left(\frac{\partial E_i}{\partial V}\right)_N$$

So we can write the average pressure as:

$$\begin{aligned}\langle P \rangle &= \sum_i P_i(N,V,\beta)\left(-\frac{\partial E_i}{\partial V}\right)_N \\ &= \sum_i \left(-\frac{\partial E_i}{\partial V}\right)_N \frac{e^{-E_i(N,V)/kT}}{Q(N,V,T)}\end{aligned}$$

In a few steps we can show that the temperature can be expressed in terms of the partition function:

$$Q(N,V,T) = \sum_i e^{-E_i(N,V)/kT}$$

Writing in terms of β instead of temperature:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_i(N,V)}$$

The derivative of the partition function with respect to volume is:

$$\left(\frac{\partial Q}{\partial V}\right)_{N,\beta} = -\beta \sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i(N,V)}$$

The average pressure can then be written as:

$$\langle P \rangle = \frac{kT}{Q(N,V,\beta}\left(\frac{\partial Q}{\partial V}\right)_{N,\beta}$$

Which shows that the pressure can be expressed solely terms of the partition function:

$$\langle P \rangle = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

We can use this result to derive the ideal gas law. For N particles of an ideal gas:

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!}$$

where:

$$q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

is the translational partition function. The utility of expressing the pressure as a logarithm is clear from the fact that we can write:

$$\begin{aligned}\ln Q &= N\ln q - \ln N! \\ &= -\frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N\ln V - \ln N!\end{aligned}$$

We have used the property of logarithms that $\ln(AB) = \ln(A) + \ln(B)$ and $\ln(X^Y) = Y\ln(X)$. Only one term in the ln Q depends on V. Taking the derivative of $N\ln V$ with respect to V gives:

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V}$$

Substituting this into the above equation for the pressure gives:

$$P = \frac{NkT}{V}$$

which is the ideal gas law. Recall that $Nk = nR$ where N is the number of molecules and n is the number of moles. R is the universal gas constant (8.314 J/mol-K) which is nothing more than k multiplied by Avagadro's number. $N_A k = R$ converts the constant from a "per molecule" to a "per mole" basis.

Gas Compressed by a Piston

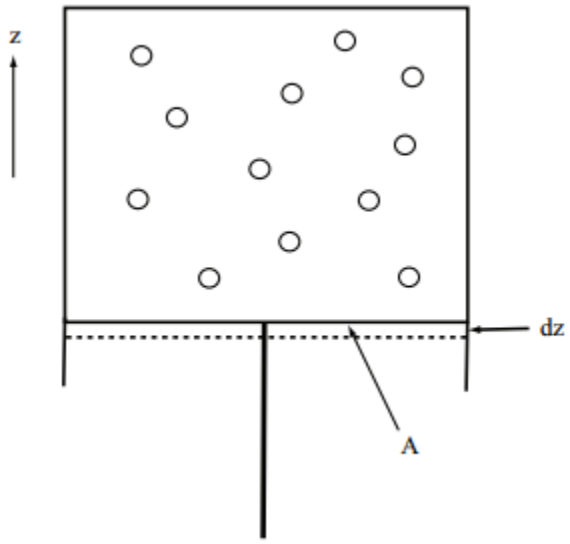


Figure 17.5.1 : Illustration of a thought experiment in which a system is compressed via a piston pushed into the system along the positive z axis.

Let us consider a simple thought experiment, which is illustrated in the figure above: A system of N particles is compressed by a piston pushing in the positive z direction. Since this is a classical thought experiment, we think in terms of forces. The piston exerts a constant force of magnitude F on the system. The direction of the force is purely in the positive z direction, so that we can write the force vector $\mathbf{F}$ as $\mathbf{F} = (0, 0, F)$. At equilibrium (the piston is not moving), the system exerts an equal and opposite force on the piston of the form $(0, 0, -F)$. If the energy of the system is E, then the force exerted by the system on the piston will be given by the negative change in E with respect to z:

$$-F = -\frac{dE}{dz} \tag{17.5.1}$$

or:

$$F = \frac{dE}{dz} \tag{17.5.2}$$

The force exerted by the system on the piston is manifest as an observable pressure P equal to the force F divided by the area A of the piston, $P = F/A$. Given this, the observed pressure is just:

$$P = \frac{dE}{Adz} \tag{17.5.3}$$

Since the volume decreases when the system is compressed, we see that $Adz = -dV$. Hence, we can write the pressure as $P = -dE/dV$.

Of course, the relation $P = -dE/dV$ is a thermodynamic one, but we need a function of x that we can average over the ensemble. The most natural choice is:

$$p(x) = -\frac{d\mathcal{E}(x)}{dV} \tag{17.5.4}$$

so that $P = \langle p(x) \rangle$. Setting up the average, we obtain:

$$P = -\frac{C_N}{Q(N,V,T)} \int \frac{\partial \mathcal{E}}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{17.5.5}$$

$$= \frac{C_N}{Q(N,V,T)} \frac{1}{\beta} \int \frac{\partial}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{17.5.6}$$

$$= \frac{kT}{Q(N,V,T} \frac{\partial}{\partial V} C_N \int e^{-\beta \mathcal{E}(x)} \tag{17.5.7}$$

$$= kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right) \tag{17.5.8}$$

Ideal Gas in the Canonical Ensemble

Recall that the mechanical energy for an ideal gas is:

$$\mathcal{E}(x) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{17.5.9}$$

where all particles are identical and have mass m. Thus, the expression for the canonical partition function $Q(N,V,T)$ is:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} \int dx \, e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2 / 2m}$$

Note that this can be expressed as:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} V^N \left[\int dp \, e^{-\beta p^2 / 2m} \right]^{3N}$$

Evaluating the Gaussian integral gives us the final result immediately:

$$Q(N,V,T) = \frac{1}{N!} \left[\frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right]^N$$

The expressions for the energy:

$$E = -\frac{\partial}{\partial \beta} \ln Q(N,V,T)$$

which gives:

$$E = \frac{3}{2} NkT = \frac{3}{2} nRT \tag{17.5.10}$$

and pressure:

$$P = kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right)$$

giving:

$$P = \frac{NkT}{V} = \frac{nRT}{V} \tag{17.5.11}$$

which is the ideal gas law.

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17.6: The Partition Function of Distinguishable, Independent Molecules is the Product of the Molecular Partition Functions

A system, such as a container of gas, can consist of a large number of subsystems. How is the partition function of the system built up from those of the subsystems? This depends on whether the subsystems are distinguishable or indistinguishable. Let's start with energy. Energy is additive so that:

$$E_{\text{tot}}(N,V) = \epsilon_1(V) + \epsilon_2(V) + \epsilon_3(V) + \cdots$$

Each of the molecules can have their energy distributed over their respective energy states (e.g., vibrations, rotations, etc.). This means that each ϵ_i is already a summation over the states of the molecule. Let us assume that we can somehow distinguish all the molecules as: a, b, c, d... and denote the energy state they are in by i, j, k:

$$E_l(N,V) = \epsilon_i^a(V) + \epsilon_j^b(V) + \epsilon_k^c(V) + \cdots$$

A good example would be the molecules in a molecular crystal. They only move around a fixed site and so we can distinguish by how far molecule 'a' is from a given corner of the crystal. The systems partition function becomes:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_l} = \sum_{i,j,k,\ldots} e^{-\beta(\epsilon_i^a + \epsilon_j^b + \epsilon_k^c)}$$

So far, we have done little effort to distinguish between the partition function of a molecular system q and the whole ensemble Q (e.g. the gas). If the entities that we called systems are **distinguishable** and independent, the whole ensemble partition function is the product of the molecular system partition functions. We get:

$$Q(N,V,\beta) = \prod_i q_i$$

for N distinguishable systems. We can split up the summation into a product of molecular partition functions:

$$Q(N,V,\beta) = \prod_i^N q_i(V,\beta) = q_a(V,\beta)q_b(V,\beta)q_c(V,\beta)\cdots$$

This results in each molecular system partition function being summed over independently:

$$Q(N,V,\beta) = \sum_i e^{-\beta\epsilon_i^a} \sum_j e^{-\beta\epsilon_i^b} \sum_k e^{-\beta\epsilon_i^c} \cdots$$

If the energy states of all the particles are the same, then the equation simplifies to:

$$Q(N,V,\beta) = [q(V,\beta)]^N$$

We can do this if, for example, the particles are embedded in a crystal where we can distinguish them by their location. We will see in the next chapter that for indistinguishable particles, such as those in a gas, we get a different result.

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17.7: Partition Functions of Indistinguishable Molecules Must Avoid Over Counting States

In the previous section, the definition of the the partition function involves a sum of state formulism:

$$Q = \sum_i e^{-\beta E_i}. \tag{17.7.1}$$

However, under most conditions, full knowledge of each member of an ensemble is missing and hence we have to operate with a more reduced knowledge. This is demonstrated via a simple model of two particles in a two-energy level system in Figure 17.7.1 . Each particle (red or blue) can occupy either the $E_1 = 0$ energy level or the $E_2 = \epsilon$ energy level resulting in four possible states that describe the system. The corresponding partition function for this system is then (via Equation 17.7.1):

$$Q_{\text{distinguishable}} = e^0 + e^{-\beta\epsilon} + e^{-\beta\epsilon} + e^{-2\beta\epsilon} = q^2 \tag{17.7.2}$$

and is just the molecular partition function (q) squared.

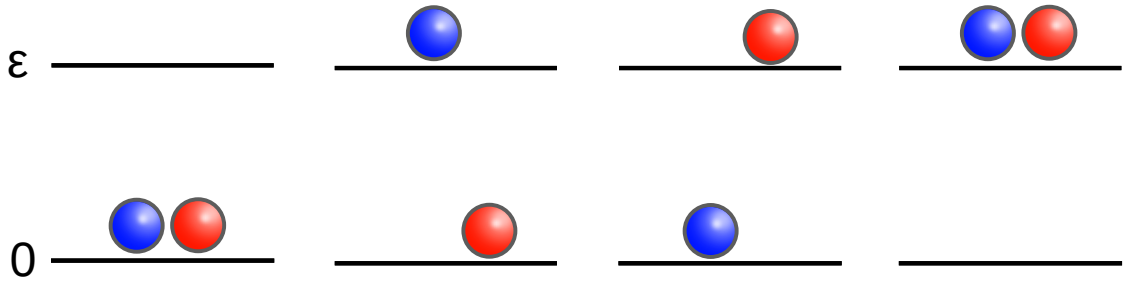


Figure 17.7.1: Four different states can exist for a two-level system with two distinguishable particles (red and blue balls). (CC BY 4.0; Delmar Larsen via LibreTexts)

However, if the two particles are indistinguishable (e.g., both the same color as in Figure 17.7.2) then while four different combinations can be generated like in Figure 17.7.1, there is no discernible way to separate the two middle states. Hence, there are effectively only three states observable for this system.

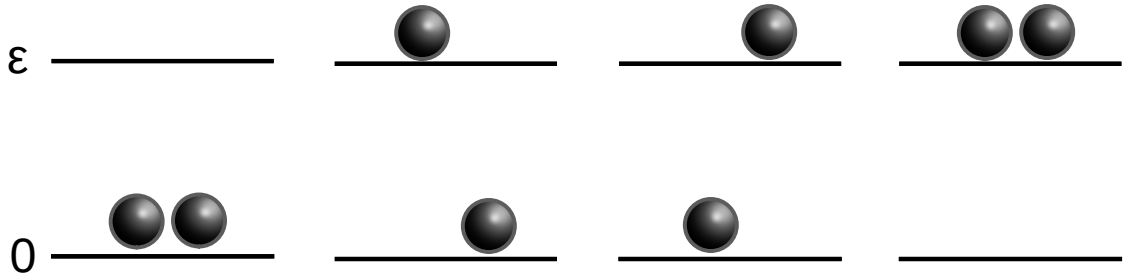


Figure 17.7.2: Three different states can exist for a two-level system with two indistinguishable particles (black balls). The two middle states are indescernable and represent a single state with one particle exited and the other in the ground state. (CC BY 4.0; Delmar Larsen via LibreTexts)

The corresponding partition function for this system (again using Equation 17.7.1) can be constructed:

$$Q(N, V, \beta) = e^0 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} \neq q^2 \tag{17.7.3}$$

and this is not equal to the square of the molecular partition function. If Equation 17.7.2 were used to describe the indistinguishable particle case, then it would overestimate the number of observable states. From combinatorics, using q^N for a large N-particle system of indistinguishable particles will overestimate the number of states by a factor of $N!$. Therefore Equation 17.7.1 requires a slight modification to account for this over counting.

$$Q(N,V,\beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{17.7.4}$$

If we have N molecules, we can perform $N!$ permutations that should not affect the outcome. To avoid over counting (making sure we do not count each state more than once), the partition function becomes:

$$Q(N,V,\beta) = \frac{q(V,\beta)^N}{N!}$$

Note

As you may have noticed, using Equation 17.7.4 to estimate of Q for the two-indistinguishable particle discussed case above with $N = 2$ is incorrect (i.e., Equation 17.7.4 is not equal to Equation 17.7.3). That is because the $N!$ factor is only applicable for large N.

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17.8: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom

From the previous sections, the partition function for a system of N indistinguishable and independent molecules is:

$$Q(N,V,\beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{17.8.1}$$

And the average energy of the system is:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \tag{17.8.2}$$

We can combine these two equations to obtain:

$$\begin{aligned} \langle E \rangle &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \\ &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= N \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{q(V,T)} \end{aligned} \tag{17.8.3}$$

The average energy is equal to:

$$\langle E \rangle = N \langle \epsilon \rangle \tag{17.8.4}$$

where $\langle \epsilon \rangle$ is the average energy of a single particle. If we compare Equation 17.8.2 with Equation 17.8.2, we can see:

$$\langle \epsilon \rangle = \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{q(V,T)}$$

The probability that a particle is in state i, π_i, is given by:

$$\langle \epsilon \rangle = \frac{e^{-\epsilon_i/kT}}{q(V,T)} = \frac{e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}$$

The energy of a particle is a sum of the energy of each degree of freedom for that particle. In the case of a molecule, the energy is:

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}$$

The molecular partition function is the product of the degree of freedom partition functions:

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

The partition function for each degree of freedom follows the same is related to the Boltzmann distribution. For example, the vibrational partition function is:

$$q_{\text{vib}} = \sum_i e^{-\epsilon_i/kT}$$

The average energy of each degree of freedom follows the same pattern as before. For example, the average vibrational energy is:

$$\langle \epsilon_{\text{vib}} \rangle = kT^2 \frac{\partial \ln q_{\text{vib}}}{\partial t} = -\frac{\partial \ln q_{\text{vib}}}{\partial \beta}$$

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17.E: Boltzmann Factor and Partition Functions (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 17 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q17.9

In Section 17-3, we derived an expression for the expectation value of energy, $\langle E \rangle$, by applying Equation 17.20 to $Q(N,V,T)$ given by Equation 17.22. Now, apply Equation 17.21 to $Q(N,V,T)$ to give the same result, except with β replaced by $\frac{1}{k_b T}$.

S17.9

Beginning with Equation 17.21

$$\langle E \rangle = k_b T^2 (\frac{\partial ln Q}{\partial T})_{N,V}$$

We can use the partition function in the problem to find $(\frac{\partial ln Q}{\partial T})_{N,V}$:

$$Q(N,V,T) = \frac{V^N}{N!}(\frac{2\pi m k_b}{h^2})^{\frac{3N}{2}} T^{\frac{3N}{2}}$$

$$ln Q = \frac{3N}{2} ln T$$

$$(\frac{\partial_{lnQ}}{\partial T})_{N,V} = \frac{3N}{2T}$$

Substituting this last result into Equation 17.21 yields

$$\langle E \rangle = k_b T^2 \frac{3N}{2T} = \frac{3}{2}(N k_b T)$$

Q17.10

A gas absorbed on a surface can sometimes be modeled as a two-dimensional ideal gas. We will learn in that the partition function of a two-dimensional ideal gas is:

$$Q(N,A,T) = \frac{1}{N!}\Big(\frac{2\pi m k_B T}{h^2}\Big)^N A^N \tag{17.E.1}$$

where A is the area of the surface. Derive an expression for $\bar{C}_V$.

S17.10

$$\bar{C}_V = \Big(\frac{\partial U}{\partial T}\Big)_{N,A} \text{ and } U = K_b T^2 \Big(\frac{\partial ln(Q)}{\partial T}\Big)_{N,A}$$

Addition:

$$\bar{C}_V = \left(\frac{\partial U}{\partial T}\right)_{N,A}$$

and

$$U = K_b T^2 \left(\frac{\partial ln(Q)}{\partial T}\right)_{N,A}$$

where

$$U = K_b T^2 * \frac{N}{T}$$

and thus

$$U = N K_b T.$$

Q17.11

Given the partition function of a monatomic can der Waals gas:

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}(V - Nb)^N e^{\frac{aN^2}{Vk_bT}} \tag{17.E.2}$$

what is the average energy of this gas?

S17.11

The average energy of a gas is given by

$$< E >= k_b T^2 \left(\frac{\partial lnQ}{\partial T}\right)_{N,V} \tag{17.E.3}$$

taking the natural log of the partition function gives us

$$lnQ = \frac{3N}{2} ln\left(\frac{2\pi m k_B T}{h^2}\right) + \frac{aN^2}{Vk_bT} + \frac{1}{N!} N ln(V - Nb) \tag{17.E.4}$$

Now we take the partial derivative with respect to T while holding N and V constant.

This yields

$$\left(\frac{\partial lnQ}{\partial T}\right)_{N,V} = \frac{3Nh^2 2\pi m k_b}{4\pi m k_b T} - \frac{aN^2}{Vk_bT^2} = \frac{3nh^2}{2T} - \frac{aN^2}{Vk_bT^2} \tag{17.E.5}$$

Substituting this value into the Average Energy equation, we get

$$< E >= \frac{3Nk_bT}{2} - \frac{aN^2}{V} \tag{17.E.6}$$

.

Q17.12

Given the following equation:

$$Q(N,V,T) = \frac{(V)^N}{N!}\left(\frac{2\pi m k_B}{h^2}\right)^{3N/2} T^{3N/2} \tag{17.E.7}$$

An approximate partition function for a gas of hard spheres can be obtained from the partition function of a monatomic gas by replacing V in the given equation with $V - b$, where b is related to the volume of the N hard spheres. Derive expressions for the energy and the pressure of this system.

S17.12

We can use the partition function specified in the problem to find

$$Q(N,V,T) = \frac{(V-b)^N}{N!}\Big(\frac{2\pi m k_B}{h^2}\Big)^{3N/2} T^{3N/2} \tag{17.E.8}$$

$$lnQ = \frac{3N}{2} lnT + terms\ not\ involving\ T \tag{17.E.9}$$

After substitution into the given equation, we find that the energy (E) is the same as that for a monatomic ideal gas: $3Nk_BT/2$. We can use the partition function specified in the problem to find

$$Q(N,V,T) = \frac{1}{N!}\Big(\frac{2\pi m k_B T}{h^2}\Big)^{3N/2} (V-b)^N \tag{17.E.10}$$

$$lnQ = Nln(V-b) + terms\ not\ involving\ V \tag{17.E.11}$$

Similar substitution allows us to find

$$\langle P\rangle = k_BT\Big(\frac{\partial lnQ}{\partial V}\Big)_{N,B} = \frac{Nk_BT}{V-b} \tag{17.E.12}$$

Q17.13

Using the partition function

$$Q(N,\ ,A\ ,T) = \frac{1}{N!}\Big(\frac{2\pi m k_B T}{h^2}\Big)^N A^N \tag{17.E.13}$$

,

calculate the heat capacity of a two-dimensional ideal gas.

S17.13

First, the energy must be found. This can be done by finding $\Big(\frac{\partial lnQ}{\partial T}\Big)_{N,\,V}$.

$$ln[Q] = Nln[T] + ... \tag{17.E.14}$$

where the ... refers to terms that do not depend on T. Because they do not depend on T, the partial with respect to those terms are 0.

The partial derivative is

$$\Big(\frac{\partial lnQ}{\partial T}\Big)_{N,\,V} = \frac{N}{T} \tag{17.E.15}$$

.

The energy can be expressed as

$$E = \Big(\frac{\partial lnQ}{\partial T}\Big)_{N,\,V} * k_BT^2 \tag{17.E.16}$$

$$E = \frac{Nk_BT^2}{T} \tag{17.E.17}$$

$$E = Nk_BT \tag{17.E.18}$$

In the case of our two-dimensional ideal gas,

$$E = U \tag{17.E.19}$$

,

so we can use the relationship

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{17.E.20}$$

$$C_v = Nk_B \tag{17.E.21}$$

Q17-14 This is correct, but show algebra for better understanding of the topic.

How is the energy of a monatomic van der Waals gas related to the capacity of a monatomic van der Waals gas?

S17-14

The heat capacity, Cv is a measure of how energy changes with temperature (given a constant amount and volume).

$$C_v = (\frac{\partial < E >}{\partial T})_{N,V} = (\frac{\partial U}{\partial T})_{N,V} \tag{17.E.22}$$

because <E>=U.

Q17.15

The partition function of the rigid rotator-harmonic oscillator model of an ideal diatomic gas is given by

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!} \tag{17.E.23}$$

where

$$q(V,\beta) = (\frac{2\pi m}{h^2\beta})^(\frac{3}{2}) * V * \frac{8\pi^2 I}{h^2\beta} * \frac{e^(-\beta h\nu/2)}{1-e^(-\beta h\nu/2)} \tag{17.E.24}$$

Find the expression for the pressure of an ideal atomic gas.

S17.15

(There needs to be way more details how you arrived from the first equation to the last. -- RM)

$$Q(N,V,\beta) = \frac{1}{N!}(\frac{2\pi m}{h^2\beta})^N * V^N * \frac{8\pi^2 I}{h^2\beta}^N * \frac{e^(-\beta h\nu/2)}{1-e^(-\beta h\nu/2)}^N \tag{17.E.25}$$

$$lnQ = NlnV \tag{17.E.26}$$

$$\frac{dlnQ}{dV} = \frac{N}{V} \tag{17.E.27}$$

$$\langle P \rangle = \frac{Nk_BT}{V} \tag{17.E.28}$$

which is the ideal gas law.

It would be useful to show the intermediate step in how you got to the end solution...I feel that the more detail it is, the clearer the solution will be.

Q17.19

a.) Prove that a simplified form of the molar heat capacity of system of independent particles can be written as:

$$\overline{C_V} = R(\beta\varepsilon)^2 \frac{e^{-\beta\varepsilon}}{(1+e^{-\beta\varepsilon})^2} \tag{17.E.29}$$

b.) Verify by plotting $\overline{C_V}$ versus $\beta\varepsilon$ that the maximum value occurs when $\beta\varepsilon = 2.40$.

S17.19

a.) We can write the partition function of the system as:

$$q = e^{-\frac{\varepsilon_0}{k_B T}} + e^{-\frac{\varepsilon_1}{k_B T}} \tag{17.E.30}$$

If we assume that the ground quantum state, ε_0 is equal to zero, we get:

$$q = e^{-\frac{0}{k_B T}} + e^{-\frac{\varepsilon_1}{k_B T}} = 1 + e^{-\frac{\varepsilon_1}{k_B T}} \tag{17.E.31}$$

We can then write the average energy of the system in terms of q:

$$\langle E \rangle = RT^2 \left(\frac{\partial ln(q)}{\partial T}\right)_V = RT^2 \left(\frac{\partial ln\left(1+e^{-\frac{\varepsilon_1}{k_B T}}\right)}{\partial T}\right)_V = RT^2 \frac{1}{1+e^{-\frac{\varepsilon_1}{k_B T}}} \left(-\frac{\varepsilon_1}{k_B}\right)\left(-\frac{1}{T^2}\right) e^{-\frac{\varepsilon_1}{k_B T}} = R\left(\frac{\varepsilon_1}{k_B}\right) \frac{e^{-\frac{\varepsilon}{k_B}}}{1+e^{-\frac{}{}}}$$

Using the definition of molar heat capacity, we can then plug in our expression for $\langle E \rangle$:

$$\overline{C_V} = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V = \left(\frac{\partial\left(R\left(\frac{\varepsilon_1}{k_B}\right)\frac{e^{-\frac{\varepsilon_1}{k_B T}}}{1+e^{-\frac{\varepsilon_1}{k_B T}}}\right)}{\partial T}\right)_V \tag{17.E.33}$$

$$= R\left(\frac{\varepsilon_1}{k_B}\right)\left(-\frac{\varepsilon_1}{k_B}\right)\left(-\frac{1}{T^2}\right) e^{-\frac{\varepsilon_1}{k_B T}} \left(1+e^{-\frac{\varepsilon_1}{k_B T}}\right)^{-2} = R\left(\frac{\varepsilon_1}{k_B T}\right)^2 \frac{e^{-\frac{\varepsilon_1}{k_B T}}}{\left(1+e^{-\frac{\varepsilon_1}{k_B T}}\right)^2} \tag{17.E.34}$$

If we define $\varepsilon_1 = \varepsilon$ and $\frac{1}{k_B T} = \beta$, we can simplify the above expression for the molar heat capacity as:

$$\overline{C_V} = R(\beta\varepsilon)^2 \frac{e^{-\beta\varepsilon}}{(1+e^{-\beta\varepsilon})^2} \tag{17.E.35}$$

which is what the original problem asked us to show.

b.) Plotting $\overline{C_V}$ versus $\beta\varepsilon$ results in the following graph, with the maximum at $\beta\varepsilon = 2.40$ verified. (All calculations and graphs were done in MATLAB and produced by me)

Q17.20

Each of the N atoms of the crystal is assumed to vibrate independently about its lattice position, so that the crstal is pictures as

N independent harmonic oscillators, each vibrating in three directions. The partition function of a harmonic oscillator is

$$q_{ho}(T) = \sum_{\nu=0}^{\infty} e^{-\beta(\nu+\frac{1}{2})hv} \tag{17.E.36}$$

$$e^{-\beta h\nu/2} \sum_{\nu=0}^{\infty} e^{\beta\nu hv} \tag{17.E.37}$$

This summation is easy to evaluate if you recognize it as the so-called geometric series

$$\sum_{\nu=0}^{\infty} x^{\nu} = \frac{1}{1-x} \tag{17.E.38}$$

Show that

$$q_{ho}(T) = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}} \tag{17.E.39}$$

and that

$$Q = e^{\beta U_0}\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^3 N \tag{17.E.40}$$

where U_0 simply represents the zero-of-energy, where all N atoms are infinitely separated.

S17.20

let $x = e^{-\beta h\nu} then \sum_{\nu=0}^{\infty} e^{-\beta h\nu} = \frac{1}{1-e^{-\beta h\nu}}$

$$Q = q^N = (q_{vib}q_{elec})^N$$

\[q_{elec}=e^{-\beta U_0 /N}+q_{vib} = (q_{ho}^3)]

$$Q = e^{-\beta U_0}\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^{3N} \tag{17.E.41}$$

Q17.21

Evaluate

$$S = \sum_{i=0}^{2}\sum_{j=0}^{1} x^{i+j} = x(1+y) + x^2(1+y) = (x+x^2)(1+y) \tag{17.E.42}$$

by summing over j first then over i. Now obtain the same result by writing S as a product of two separate summations.

S17.21

By evaluating the formula given in the problem, S can be written as a product of two separate summations, given by

$$S = \sum_{i=0}^{2}\sum_{j=0}^{1} = (x+x^2)(y+1) \tag{17.E.43}$$

Q17.22

Evaluate:

$$S = \sum_{i=0}^{4} \sum_{j=1}^{i} 5 + j \tag{17.E.44}$$

S17.22

$$(1+5) + [(1+5) + (2+5)] + [(1+5) + (2+5) + (3+5)] + [(1+5) + (2+5) + (3+5) + (4+5)] = 6 + 13 + 21 + 30 = 70$$

Q17.24

Consider a system of two noninteracting identical femions, each has energy states of ε_1, ε_2 and ε_3. How many terms are there in the unrestriced evaluation of Q(2,V,T)?

S17.24

$$\text{Q(2,V,T)} = \Sigma e^{-\beta(\varepsilon_i + \varepsilon_j)}$$

Total terms = 9. From these 9 terms that will appear in the unrestricted evaluation of Q, only 3 of them will be allowed for 2 identical femions:

$$\varepsilon_1 + \varepsilon_2$$

$$\varepsilon_1 + \varepsilon_3$$

$$\varepsilon_2 + \varepsilon_3$$

The 6 terms that are not allowed by the fermion restriction would be (Aaron Choi):

$$\varepsilon_1 + \varepsilon_3 = \varepsilon_3 + \varepsilon_1 \tag{17.E.46}$$

$$\varepsilon_1 + \varepsilon_2 = \varepsilon_2 + \varepsilon_1 \tag{17.E.47}$$

$$\varepsilon_2 + \varepsilon_3 = \varepsilon_3 + \varepsilon_2 \tag{17.E.48}$$

Q17.25

Looking at problem 17.24, how many allowed terms are there in the case of bosons instead of fermions?

S17.25

There are six allowable terms, three that were found in Q17.24 and an additional three, they are as follows:

$$\epsilon_1 + \epsilon_3 \tag{17.E.49}$$

$$\epsilon_1 + \epsilon_2 \tag{17.E.50}$$

$$\epsilon_2 + \epsilon_3 \tag{17.E.51}$$

$$\epsilon_1 + \epsilon_1 \tag{17.E.52}$$

$$\epsilon_2 + \epsilon_2 \tag{17.E.53}$$

$$\epsilon_3 + \epsilon_3 \tag{17.E.54}$$

Q17.26

Consider a system of three noninteracting identical bosons, each of which has states with energies ε_1, ε_2, and ε_3. How many terms are there in the unrestricted evaluation of $Q(3, V, T)$? How many terms occur in $Q(3, V, T)$ when the boson restriction is taken into

account? Enumerate the allowed total energies in the summation of Equation 17.37:

$$Q(N,V,T)=\sum_{i,j,k..} e^{-\beta(\varepsilon_i+\varepsilon_j+\varepsilon_k...)} \tag{17.E.55}$$

S17.26

There are ten allowed terms, given by the total energies

$$1.\varepsilon_1+\varepsilon_2+\varepsilon_3 \tag{17.E.56}$$

$$2.\varepsilon_1+\varepsilon_1+\varepsilon_3 \tag{17.E.57}$$

$$3.\varepsilon_2+\varepsilon_2+\varepsilon_3 \tag{17.E.58}$$

$$4.\varepsilon_2+\varepsilon_2+\varepsilon_1 \tag{17.E.59}$$

$$5.\varepsilon_2+\varepsilon_2+\varepsilon_2 \tag{17.E.60}$$

$$6.\varepsilon_2+\varepsilon_2+\varepsilon_3 \tag{17.E.61}$$

$$7.\varepsilon_1+\varepsilon_3+\varepsilon_3 \tag{17.E.62}$$

$$8.\varepsilon_3+\varepsilon_2+\varepsilon_3 \tag{17.E.63}$$

$$9.\varepsilon_1+\varepsilon_1+\varepsilon_1 \tag{17.E.64}$$

$$10.\varepsilon_3+\varepsilon_3+\varepsilon_3 \tag{17.E.65}$$

Q17.26

Consider a system of 2 noninteracting bosons, each having a state with energy $\epsilon_1,\epsilon_2,\epsilon_3,\epsilon_4$. How many terms are in the unrestricted evaluation $Q\left(2,V,T\right)$ Write the allowed energies in the summation form?.

S17.26

There are 10 allowed terms, given by the total energies

$$\epsilon_1+\epsilon_2\ \epsilon_2+\epsilon_2$$

$$\epsilon_1+\epsilon_3\ \epsilon_2+\epsilon_3$$

$$\epsilon_1+\epsilon_4\ \epsilon_2+\epsilon_4$$

$$\epsilon_1+\epsilon_1\ \epsilon_3+\epsilon_4$$

$$\epsilon_4+\epsilon_4\ \epsilon_3+\epsilon_3$$

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17.S: Boltzmann Factor and Partition Functions (Summary)

This chapter covers statistical thermodynamics: the link between the microscopic properties and bulk properties of matter. At its heart, the foundational principle of statistical thermodynamics is that any observable thermodynamic or mechanical property of a system is the time average of its instantaneous value at equilibrium. By considering all the possible configurations of a system that are consistent with the overall state of the system, we can find that the most likely configuration is consistent with a Boltzmann distribution, and that the quantity that serves as a "thermodynamic wavefunction" for that distribution is the partition function. If the partition function for a system is known, then all mechanical and thermodynamic properties can be calculated, and it is possible to determine how the particles that make up the system are statistically distributed among the system's quantum states.

We will begin by deriving the Boltzmann distribution from considering quantum states with equal *a priori* probabilities. After deriving the Boltzmann distribution, we will derive partition functions for general systems, and for systems consisting of independent particles. We will see that the overall partition function of a system can be expressed in terms of a product of molecular partition functions, and that the molecular partition function can in turn be expressed as a product of partition functions for each degree of freedom of the molecule. As we go along, we will show how to derive several mechanical and thermodynamic quantities from the partition functions of these systems. We will make connections between statistical thermodynamics and the relative intensities of spectroscopic transitions to show how spectroscopy can be used to measure temperatures and abundances of molecules in a thermal environment.

Learning Objectives

By the end of this chapter, you should know the following:

- The principle of equal *a priori* probabilities
- The configuration of a system of N particles in k states
- How the Boltzmann distribution relates to the weights of configurations
- The physical interpretation of the molecular partition function
- The difference between the molecular partition function q and the system partition function Q
- When it is possible to calculate Q from q
- How Bose-Einstein and Fermi-Dirac statistics impact the relationship between Q and q
- How the molecular partition function can be used to describe the various degrees of freedom of a molecule

Skill goals (what you should be able to do/calculate):

- Calculate the weight of a configuration.
- Given a set of states and their energies (or levels, degeneracies, and energies), calculate the molecular partition function
- Use the Boltzmann distribution to calculate the probability that a system or molecule will be found with a given energy at a given temperature
- Use simple models for the energies of an ideal diatomic gas to calculate state populations
- Use partition functions to calculate total energy, heat capacity, pressure, and entropy
- Use the relative intensities of a molecular spectrum to calculate temperature and number density

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18: PARTITION FUNCTIONS AND IDEAL GASES

In chemistry, we are typically concerned with a collection of molecules. However, if the molecules are reasonably far apart as in the case of a dilute gas, we can approximately treat the system as an ideal gas system and ignore the intermolecular forces. The present chapter deals with systems in which intermolecular interactions are ignored. In ensemble theory, we are concerned with the ensemble probability density, i.e., the fraction of members of the ensemble possessing certain characteristics such as a total energy E, volume V, number of particles N or a given chemical potential μ and so on. The molecular partition function enables us to calculate the probability of finding a collection of molecules with a given energy in a system. The equivalence of the ensemble approach and a molecular approach may be easily realized if we treat part of the molecular system to be in equilibrium with the rest of it and consider the probability distribution of molecules in this subsystem (which is actually quite large compared to systems containing a small number of molecules of the order of tens or hundreds).

18.1: Translational Partition Functions of Monotonic Gases

18.2: Most Atoms are in the Ground Electronic State

18.3: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms

18.4: Most Molecules are in the Ground Vibrational State

18.5: Most Molecules are Rotationally Excited at Ordinary Temperatures

18.6: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number

18.7: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate

18.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule

18.9: Molar Heat Capacities

18.10: Ortho and Para Hydrogen

18.11: The Equipartition Principle

18.E: Partition Functions and Ideal Gases (Exercises)

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18.1: Translational Partition Functions of Monotonic Gases

Let us consider the translational partition function of a monatomic gas particle confined to a cubic box of length L. The particle inside the box has translational energy levels given by:

$$E_{\text{trans}} = \frac{h^2\left(n_x^2 + n_y^2 + n_z^2\right)}{8mL^2}$$

where n_x, n_y and n_z are the quantum numbers in the three directions. The translational partition function is given by:

$$q_{\text{trans}} = \sum_i e^{-\epsilon_i/kT}$$

which is the product of translational partition functions in the three dimensions. We can write the translation partition function as the product of the translation partition function for each direction:

$$q_{\text{trans}} = q_x q_y q_z \tag{18.1.1}$$

$$= \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/kT} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/kT} \tag{18.1.2}$$

Since the levels are very closely spaced (continuous), we can replace each sum in Equation 18.1.2 with an integral. For example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{18.1.3}$$

$$\approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{18.1.4}$$

and after substituting the energy for the relevant dimension:

$$\epsilon_x = \frac{h^2 n_x^2}{8mL^2}$$

we can extend the lower limit of integration in the approximation of Equation 18.1.4:

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 kT}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 kT}}$$

We then use the following solved Gaussian integral:

$$\int_o^{\infty} e^{-an^2} dn = \sqrt{\frac{\pi}{4a}}$$

with the following substitution:

$$a = \frac{h^2}{8mL^2 kT}$$

we get:

$$q_x = \frac{1}{2}\sqrt{\frac{\pi}{a}} = \frac{1}{2}\sqrt{\frac{\pi 8mkT}{h^2}}L$$

or more commonly presented as:

$$q_x = \frac{L}{\Lambda}$$

where Λ is the **de Broglie wavelength** and is given by

$$\Lambda = \frac{h}{\sqrt{2\pi 8mkT}}$$

Multiplying the expressions for q_x, q_y and q_z (Equation 18.1.1) and using V as the volume of the box L^3, we arrive at:

$$q_{\text{trans}} = \left(\frac{\sqrt{2\pi 8mkT}}{h}\right)^{3/2} V = \frac{V}{\Lambda^3} \tag{18.1.5}$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for small molecular masses. This means that such a large number of translational states are accessible and available for occupation by the molecules of a gas. This result is very similar to the result of the classical kinetic gas theory that said that the observed energy of an ideal gas is:

$$U = \frac{3}{2}nRT$$

We postulate therefore that the observed energy of a macroscopic system should equal the statistical average over the partition function as shown above. In other words: if you know the particles your system is composed of and their energy states you can use statistics to calculate what you should observe on the whole ensemble.

Example

Calculate the translational partition function of an I_2 molecule at 300K. Assume V to be 1 liter.

Solution

Mass of I_2 is $2 \times 127 \times 1.6606 \times 10^{-27} kg$

$$\begin{aligned} 2\pi mkT &= 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27}\, kg) \times 1.3807 \times 10^{-23}\, J/K \times 300K \\ &= 1.0969 \times 10^{-44}\, J\, kg \end{aligned}$$

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi mkT}} \\ &= \frac{6.6262 \times 10^{-34}\, J\, s}{\sqrt{1.0969 \times 10^{-44}\, J\, kg}} = 6.326 \times 10^{-12}\, m \end{aligned}$$

The via Equation 18.1.5

$$q_{\text{trans}} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} m^3}{(6.326 \times 10^{-12}\, m)^3} = 3.95 \times 10^{30}$$

This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

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18.2: Most Atoms are in the Ground Electronic State

Writing the electronic energies as $E_1, E_2, E_3, ...$ with corresponding degeneracies $g_1, g_2, g_3, ...$ The electronic partition function is then given by the following summation:

$$q_{el}(T) = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{18.2.1}$$

Usually, the differences in electronic energies are significantly greater than thermal energy kT:

$$kT \ll E_1 < E_2 < E_3$$

If we treat the lowest energy electronic state E_1 as the reference value of zero of energy, the electronic partition function (Equation 18.2.1) can be approximated as:

$$q_{elec}(T) = g_1 + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{18.2.2}$$

Typically electronic states are tens of thousands of wave numbers above the ground state. For example, the first excited electronic state of nitric oxide (NO) is ~40,000 cm^{-1}. Using this value:

$$\frac{E_2}{kT} = \frac{40000 \text{ cm}^{-1}}{kT} = \frac{10^4 \text{ K}}{T}$$

That means, that even at 1,000 K, the value of the second term in {\reference{3.24}} is:

$$g_2 e^{-10} = g_2 4.5 \times 10^{-5}$$

The result is that the higher electronic states are not accessible under ordinary temperatures. There are some cases, however, where the first excited state lies much closer to the ground state, but these are the exception rather than the rule.

Example 18.2.1

Find the electronic partition of H_2 at 300 K.

Solution

The lowest electronic energy level of H_2 is near $-32 \ eV$ and the next level is about $5 \ eV$ higher. Taking -32 eV as the zero (or reference value of energy), then

$$q_{el} = e_0 + e^{-5eV/kT} + ...$$

At 300 K, T = 0.02\; eV and

$$q_{el} = 1 + e^{-200} + ...$$
$$\approx 1.0$$

Where all terms other than the first are essentially 0. This implies that $q_{el} = 1$.

The physical meaning of the result from Example 18.2.1 is that only the ground electronic state is generally thermally accessible at room temperature.

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18.3: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms

A monatomic gas has three degrees of freedom per molecule, all of them translational:

1. movement in x-direction
2. movement in y-direction
3. movement in z-direction

A polyatomic gas, including diatomic molecules, has other levels that you can 'stuff' energy into. Polyatomic molecules can rotate and vibrate, and if enough energy is available you could also excite the electrons involved in the σ and π bonds. A reasonable approximation of the partition function of the molecule would become:

$$q_{\text{tot}}(V,T) = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$

The partition function of a molecular idea gas is then:

$$Q(N,V,T) = \frac{(q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}})^N}{N!}$$

The total energy of the molecule is then the sum of the translation, vibrational, rotational, and electronic energies:

$$E_{tot} = E_{\text{trans}} E_{\text{vib}} E_{\text{rot}} E_{\text{elec}}$$

We will only scratch the surface of the additional degrees of freedom and their partition functions.

Electronic

At room temperature the system is usually in its ground electronic state. This means that the **electronic partition function** $q_{\text{elec}} = 1$. Usually we do not have to worry about these degrees of freedom. If we do, there are usually just a few levels to worry about. This includes their **degeneracy g**. If there is a single state at a certain energy ($g = 1$), two states ($g = 2$), or more states, we must multiply the Boltzmann factor by this degeneracy number.

If there are more than one state to worry about, we could follow the same procedure as we did for the translational states:

1. Define the energy states and their degeneracies
2. Compose the partition function q for the molecule and Q for the gas
3. Use the (β or T) derivative of $\ln Q$ to determine $\langle E \rangle$
4. Use the T derivative of $U \approx \langle E \rangle$ to find the contribution to the heat capacity

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18.4: Most Molecules are in the Ground Vibrational State

The vibrational energy levels of a diatomic are given by:

$$E_v = (v + 1/2)h\nu$$

where is ν the vibrational frequency and v is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below:

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} \\ &= e^{-h\nu/2kT}\left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + ...\right) \end{aligned}$$

or rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(1 + x + x^2 + x^3 + ...\right) \tag{18.4.1}$$

where $x = e^{-h\nu/kT}$. Given the following power series expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ...$$

Equation 18.4.1 can be rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(\frac{1}{1-x}\right)$$

or:

$$q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \tag{18.4.2}$$

If the zero of energy scale is at $h\nu/2kT$, then Equation 18.4.2 can be rewritten as:

$$q_{\text{vib}} \approx \frac{1}{1 - e^{-h\nu/kT}} \tag{18.4.3}$$

A vibrational temperature Θ_{vib} may be defined as:

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k}$$

where $\tilde{\nu}$ is the vibrational frequency in cm^{-1}. Θ_{vib} is a good way to express the *stiffness* of the vibrating bond in units of the Boltzmann constant. Because the stiffness obviously depends on what bond your are talking about, this is a good way to do the same thing we did for the critical temperature of the non-ideal gases.

Table 18.4.1 *: Representative molecular data for a few diatomics*

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/ mol)
H_2	1	0.7474	4400	6332	60.9	87.6	5.749	103.2
D_2	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
N_2	1	1.097	2358	3393	2.001	2.99	22.94	225.1
O_2	3	1.207	1580	2274	1.446	2.08	11.76	118.0
Cl_2	1	1.987	560	805	0.244	0.351	3.2	57.0

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/ mol)
CO	1	1.128	2170	3122	1.931	2.78	19.03	255.8
NO	2	1.15	190	2719	1.695	2.45	15.7	150.0
HCl	1	1.275	2938	4227	10.44	15.02	4.9	102.2
HI	1	1.609	2270	3266	6.46	9.06	3.0	70.5
Na_2	1	3.096	159	229	0.154	0.221	0.17	17.3
K_2	1	3.979	92.3	133	0.0561	0.081	0.10	11.8

Example 18.4.1

The vibrational frequency of of I_2 is $214.57\ \ cm^{-1}$. Calculate the vibrational partition function of I_2 at 300 K.

Solution:

$$\frac{h\nu}{kT} = \frac{214.57}{209.7} = 1.0232$$

so

$$e^{-h\nu/kT} = 0.3595$$

and

$$q_{vib} = \frac{1}{1-0.3595} = 1.561$$

This implies, as before, that very few vibrational states are accessible and much less than rotation states and many orders less than translation states.

Vibrational Heat Capacity

The vibrational energy is given by the above expression and the molar heat capacity at constant volume, $\bar{C}_V$ is given by:

$$\bar{C}_V = \left(\frac{\partial E}{\partial T}\right)_V$$

We have:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} \tag{18.4.4}$$

$$= \frac{-1}{kT^2}\frac{\partial}{\partial \beta} \tag{18.4.5}$$

$$= (-k\beta^2)\left(\frac{\partial}{\partial \beta}\right) \tag{18.4.6}$$

Therefore:

$$\bar{C}_V = (-k\beta^2)\left(\frac{\partial \varepsilon_{vib}}{\partial \beta}\right)$$

and when the vibrational partition function (Equation 18.4.3) is introduced:

$$q_{\text{vib}} = -k\beta^2 \frac{\left[(1-e^{-hc\nu/kT})(-hc\tilde{\nu}) - e^{-hc\nu/kT}(+hc\tilde{\nu})\right] e^{-hc\nu/kT}}{(1-e^{-hc\nu/kT})^2} hv\tilde{\nu} \tag{18.4.7}$$

$$= k\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1-e^{-\Theta_{\text{vib}}/T}\right)^2} \tag{18.4.8}$$

For large T, the $\bar{C}_V$ becomes:

$$N_A k = R$$

and for small T, $\bar{C}_V$ goes to zero as demonstrated in Figure 18.4.1 .

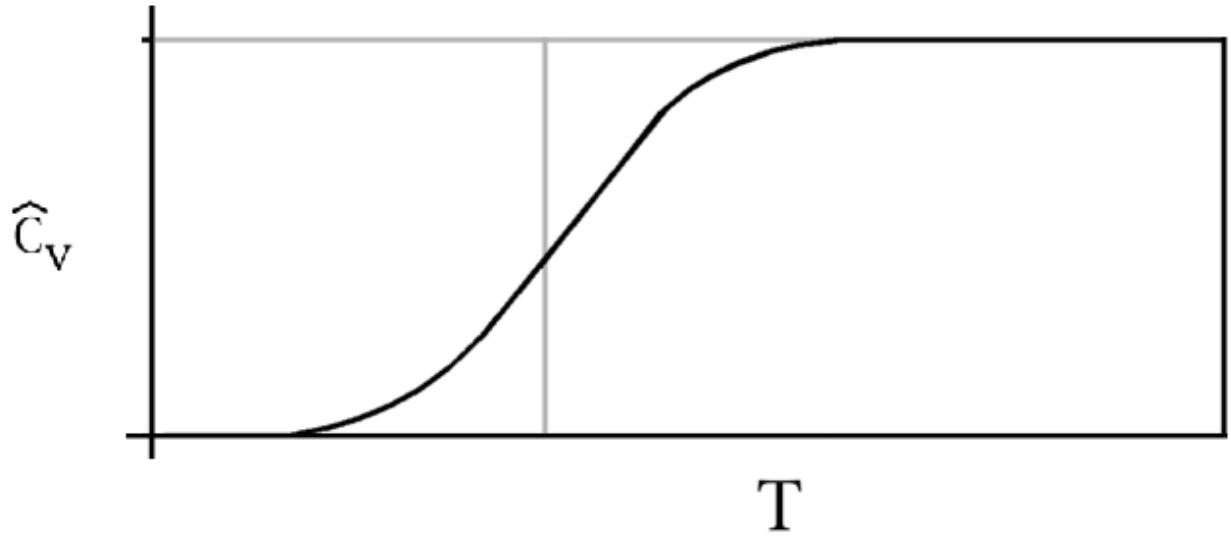


Figure 18.4.1 : Vibrational heat capacity of a diatomic

The vibrational heat capacity is shown as function of the reduced temperature T/Θ to get a general picture valid for all diatomic gases. Compare the parameters on Table 18.4.1 to see on what different absolute scales we have to think for different gases. Clearly the vibrational contribution to the heat capacity *depends on temperature*. For many molecules (especially light ones), the vibrational contribution only kicks in at quite high temperatures.

The value of Θ_{vib} is determined mostly by

1. the strength of a bond (the stronger the higher Θ_{vib})
2. the (effective) mass of the molecule (the lighter the higher Θ_{vib})

Molecules with low Θ_{vib} often dissociate at lower temperatures, although the *harmonic* oscillator model is not sufficient to describe that phenomenon.

Vibrational Populations

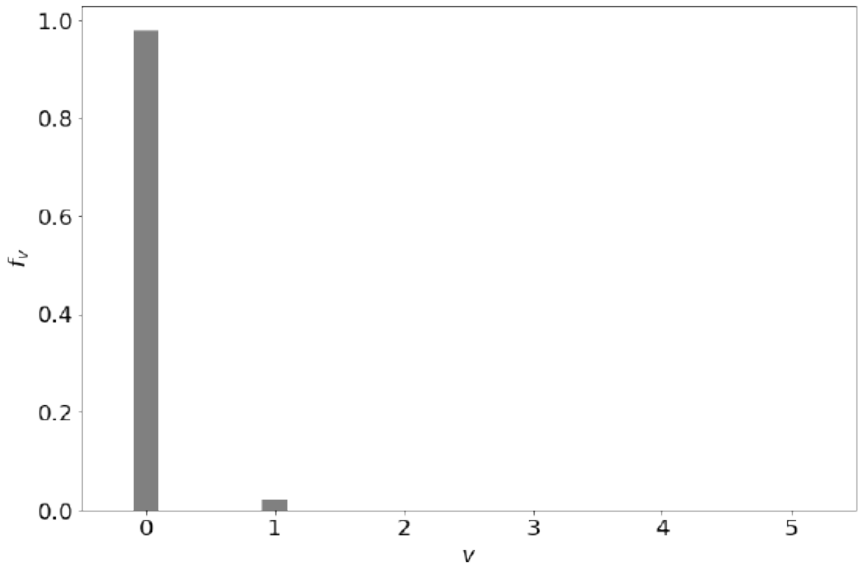
We can calculate the fraction of molecules in each vibrational state. The fraction of molecules in the vth vibrational state is given by:

$$f_v = \frac{e^{-h\nu(v+\frac{1}{2})/kT}}{q_{\text{vib}}}$$

Substituting in Equation 18.4.2, we get:

$$\begin{aligned} f_v &= \left(1-e^{-h\nu/kT}\right) e^{-h\nu v/kT} \\ &= \left(1-e^{-\Theta_{\text{vib}}/T}\right) e^{-\Theta_{\text{vib}} v/T} \end{aligned} \tag{18.4.9}$$

We can plot the fraction molecules in each vibrational state.



The vibrational population of Cl_2 at 300 K. Most of the molecules are in the ground vibrational state, $v = 0$.

From the figure, we can see that most of the Cl_2 molecules are in the ground vibrational state at room temperature (300 K). This is true for most molecules. Only molecules with very weak bonds and low vibrational temperatures will populate a significant fraction of molecules in excited vibrational states.

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18.5: Most Molecules are Rotationally Excited at Ordinary Temperatures

The rotational quantum number is J and the energy of the rotations is:

$$E(J) = \tilde{B}J(J+1)$$

Where $\tilde{B}$ is in units of cm^{-1} and is equivalent to:

$$\frac{h}{8\pi^2 Ic}$$

Where c is the speed of light in units of cm^{-1}. However, with the exception of the ground state (i.e., $J = 0$), multiple eigenstates exist for a given value of J. This is a form of **degeneracy**, (g), and the number of levels per energy goes as 1, 3, 5, 7, 9 etc or:

$$g(J) = 2J + 1$$

Therefore, the summation to find the partition function $q_{\text{rot}}(T)$ contains an extra factor $g = 2J + 1$. This factor is mathematically very handy, because it is the derivative of:

$$g(J) = J(J+1)$$

This makes it possible to change variables to $X = J(J+1)$ and the integration becomes very easy. Notice that just like in the translation partition function, we approximate the summation with an integral. However, because we are dealing with far fewer levels, this is less justified in the rotational case. How justified it is depends on the gas and the temperature we consider. Roughly speaking we should be at a temperature $T >> \Theta_{\text{rot}}$.

Exercise 18.5.1

Look at table 18.2. When do we need to actually work out the (discrete) summation instead of making a (continuous) integration out of it?

Answer available at the end of this section.

The rotational constant B is directly linked to the moment of inertia:

$$I = \mu r^2$$

Where μ is the reduced mass of the molecule:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

and r is the bond length. Again we can scale the behavior of different systems to one and the same picture by introducing a characteristic temperature:

$$\Theta_{rot} = \frac{hb}{k} = \frac{\hbar^2}{2Ik_b}$$

As we did for the translations, we can calculate the moment $\langle\epsilon\rangle$. For vibrations we get a relatively complicated function of temperature. However, for rotations, the moment is simply equal to NkT and this means that the rotational contribution to the molar C_v of a diatomic is simply R. As the vibrational and electronic contributions to the heat capacity are typically negligible at room temperature, we get:

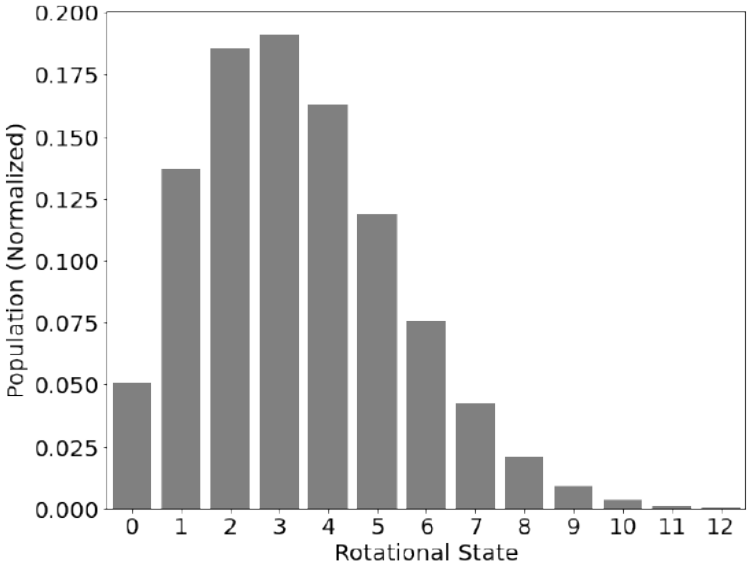
- monatomic gas

$$C_v = C_v^{trans} = \frac{3}{2}nR$$

- diatomic

$$C_v = C_v^{trans} + C_v^{rot} \tag{18.5.1}$$
$$= \frac{3}{2}nR + nR \tag{18.5.2}$$
$$= \frac{5}{2}nR \tag{18.5.3}$$

Rotational energies are less than vibrational and electronic energies and, at room temperature, many rotational states will be populated.



The normalized rotational population of HCl at room temperature.

Answers

Only for the lightest gases like He and $\mathrm{H_2}$ do we need to worry and then only at pretty low cryogenic circumstances. At room temperature, we can take the rotational levels as a continuous set and use an integral. Notice that the vibrational Θ values are much larger! At $T = 300\ \mathrm{K}$, usually only a single level is occupied and we are in the discrete limit. On the surface of the sun that would be a different matter of course.

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18.6: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number

The rotational energy levels of a **diatomic molecule** are given by:

$$E_{\text{rot}}(J) = \tilde{B}J(J+1) \tag{18.6.1}$$

where:

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

Here, $\tilde{B}$ is the rotational constant expressed in cm^{-1}. The rotational energy levels are given by:

$$E_j = \frac{J(J+1)h^2}{8\pi I}$$

where I is the moment of inertia of the molecule given by μr^2 for a diatomic, and μ is the reduced mass, and r the bond length (assuming rigid rotor approximation). The energies can be also expressed in terms of the rotational temperature, Θ_{rot}, defined as:

$$\Theta_{\text{rot}} = \frac{r^2}{8\pi^2 Ik} \tag{18.6.2}$$

The interpretation of θ_{rot} is as an estimate of the temperature at which thermal energy ($\approx kT$) is comparable to the spacing between rotational energy levels. At about this temperature the population of excited rotational levels becomes important. See Table 1.

Table 1: Select Rotational Temperatures. In each case the value refers to the most common isotopic species.

Molecule	H_2	N_2	O_2	F_2	HF	HCl	CO_2	HBr	CO
Θ_{rot}	87.6	2.88	2.08	1.27	30.2	15.2	0.561	12.2	2.78

In the summation for the expression for rotational partition function (q_{rot}), Equation 18.6.3, we can do an explicit summation:

$$q_{\text{rot}} = \sum_{j=0}(2J+1)e^{-E_J/kT} \tag{18.6.3}$$

if only a finite number of terms contribute. The factor $(2J+1)$ for each term in the expansion accounts for the degeneracy of a rotational state J. For each allowed energy E_J from Equation 18.6.1 there are $(2J+1)$ eigenstates. The Boltzmann factor must be multiplied by $(2J+1)$ to properly account for the degeneracy these states:

$$(2J+1)e^{-E_J/kT}$$

If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} previously to get:

$$q_{\text{rot}} = \int_0^\infty (2J+1)R^{-\tilde{B}J(J+1)/kT}dJ$$

This integration can easily be done by substituting $x = J(J+1)$ and $dx = (2J+1)dJ$:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}} \tag{18.6.4}$$

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is *indistinguishable* from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ, which is called the **symmetry number** and is equal to the distinct number of ways by which a

molecule can be brought into identical configurations by rotations. The rotational partition function becomes:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}\sigma} \tag{18.6.5}$$

or commonly expressed in terms of Θ_{rot}:

$$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}\sigma} \tag{18.6.6}$$

Example 18.6.1

What is the rotational partition function of H_2 at 300 K?

Solution

The value of $\tilde{B}$ for H_2 is 60.864 cm^{-1}. The value of kT in cm^{-1} can be obtained by dividing it by hc, i.e., which is $kT/hc = 209.7\ cm^{-1}$ at 300 K. $\sigma = 2$ for a homonuclear molecule. Therefore from Equation 18.6.5,

$$\begin{aligned} q_{\text{rot}} &= \frac{kT}{\tilde{B}\sigma} \\ &= \frac{209.7\ cm^{-1}}{(2)(60.864\ cm^{-1})} \\ &= 1.723 \end{aligned}$$

Since the rotational frequency of H_2 is quite large, only the first few rotational states are accessible at 300 K

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18.7: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate

As with diatomic molecules, the energies of polyatomic molecules can be approximated by the sum of its individual degrees of freedom. Therefore, we can write the partition function as:

$$Q(N,V,T) = \frac{[q(V,T)]^2}{N!}$$

We can write the polyatomic analog to diatomic molecules:

$$Q(N,V,T) = \frac{(q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}})^N}{N!}$$

When derived for diatomic molecules, we assumed the rigid rotor model for rotations and the harmonic oscillator for vibrations. This allowed us to separate the rotational motion from the vibrational motion of the molecule. Polyatomic molecules are a bit more complicated, but we will still make use of these approximations.

The number of translational states available to any given molecule is far greater than the number of molecules in the system. q_{trans} is given by:

$$q_{\text{trans}} = \left[\frac{2\pi MkT}{h^2}\right]^{3/2} V$$

where M is the mass of the particle. Moving to the electronic partition function:

$$q_{\text{elec}} = \sum_i g_i e^{-E_i/kT}$$

where E_i is the energy of the electronic state i and {g_i} is its degeneracy. Electronic states are typically spaced far apart from each other. The probability of the system being in any state but the ground state is extremely small. We can therefore simplify the electronic partition function to include only the ground electronic state:

$$q_{\text{elec}} = g_{e1}e^{D_e/kT}$$

where $-D_e$ is the energy of the ground electronic state. To complete the polyatomic partition function, we still need q_{vib} and q_{rot}. We will finish this section with q_{vib} and talk about q_{rot} in the next.

The vibrational motion of diatomic molecules can be expressed as a set of independent harmonic oscillators. For polyatomic molecules, the independent vibrational motions are referred to as normal modes of vibration. The vibrational energy is then the sum of the energies for each normal mode:

$$E_{\text{vib}} = \sum_i^{\alpha} \left(v_i + \frac{1}{2}\right) h\nu$$

where ν_i is the vibrational frequency for the ith normal mode and α is the number of vibration degrees of freedom. A linear molecule has $3n-5$ vibrational degrees of freedom and a nonlinear molecule has $3n-6$ vibrational degrees of freedom. Because the normal modes are independent of each other, we can take out results from previous sections:

$$q_{\text{vib}} = \prod_i^{\alpha} \frac{e^{-\theta_{\text{vib},i}/2T}}{1-e^{-\theta_{\text{vib},i}/T}}$$

$$E_{\text{vib}} = Nk\sum_i^{\alpha}\left(\frac{\theta_{\text{vib},i}}{2} + \theta_{\text{vib},i}\frac{e^{-\theta_{\text{vib},i}/T}}{1-e^{-\theta_{\text{vib},i}/T}}\right)$$

$$C_{V,\text{vib}} = Nk\sum_i^{\alpha}\left(\left(\frac{\theta_{\text{vib},i}}{2}\right)^2 + \frac{e^{-\theta_{\text{vib},i}/T}}{(1-e^{-\theta_{\text{vib},i}/T})^2}\right)$$

where $\theta_{\text{vib},i}$ is the characteristic vibrational temperature defined by:

$$\theta_{\text{vib},i} = \frac{h\nu_i}{k}$$

Vibrational Entropy

There is a great deal of utility for thermodynamic functions calculated from the vibrational normal modes of a molecule. The vibrational energy and entropy depend on the shape a multidimensional potential energy surface. If one performs a conformational search of macromolecule it is one obtains energies and structures but little direct information concerning the shape of the potential energy surface for each conformation. The vibrational entropy gives a means determining whether there are significant entropic differences in the structures and therefore whether certain conformations will be favored based on the entropy.

However, it is possible to take appropriate linear combinations of the coordinates so that the cross terms are eliminated and the classical Hamiltonian as well as the operator corresponding to it contains no cross terms and in terms of the new coordinates, the Hamiltonian can be written as,

$$H = \sum_{i=1}^{f} \frac{h^2}{2\mu_i} \frac{\partial}{\partial q_i^2} + \sum_{i=1}^{f} \frac{k_i}{2} q_i^2 \tag{18.7.1}$$

Here, the degrees of freedom f is $3N-5$ for a linear molecule and $3N-6$ for a nonlinear molecule. Here, k_i is the force constant and μ_i is the reduced mass for that particular vibrational mode which is referred to as a **normal mode**.

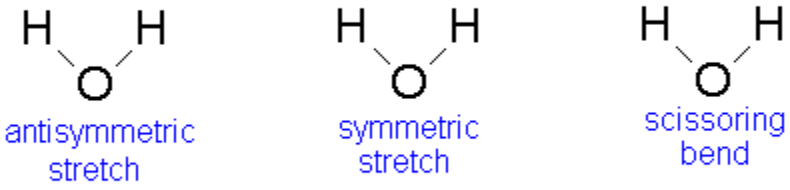


Figure 18.7.1 : The three vibrational modes of water, the symmetric stretch (3656.7 cm^{-1}, 5160 K), the asymmetric stretch (3755.8 cm^{-1} , 5360 K) and the bending mode (1594.8 cm^{-1} ,2290 K) are shown. The vibrational frequencies and the characteristic temperature for each mode are shown in parenthesis. Although not shown in the animation, the oxygen atom also moves with each of these normal modes.

The Equation 18.7.1 represents f linearly independent harmonic oscillators and the total energy for such a system is

$$\epsilon_{vib} = \sum_{i=1}^{f} \left(v_i + \frac{1}{2} \right) h\nu_i$$

The vibrational frequencies are given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}$$

The vibrational partition function is given by the product of f vibrational functions for each frequency.

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}} \tag{18.7.2}$$

with

$$\Theta_{vib,i} = \frac{h\nu_i}{k_B}$$

As with the previous discussion regarding simple diatomics, $\Theta_{vib,i}$ is called the **characteristic vibrational temperature**. The molar energies and the heat capacities are given by

$$\langle E_{vib} \rangle = Nk \sum_{i=1}^{f} \left[\frac{\Theta_{vib,i}}{2} + \frac{\Theta_{vib,i} e^{-\Theta_{vib,i}/T}}{1 - e^{-\Theta_{vib,i}/T}} \right]$$

and

$$\bar{C}_V = Nk_B \sum_{i=1}^{f} \left(\frac{\Theta_{vib,i}}{T} \right)^2 \frac{e^{-\Theta_{vib,i}/T}}{\left(1 - e^{-\Theta_{vib,i}/T}\right)^2}$$

NO_2 Exam

The three characteristic vibrational temperatures for NO_2 are 1900 K, 1980 K and 2330 K. Calculate the vibrational partition function at 300 K.

Solution

The vibrational partition is (Equation 18.7.2)

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}}$$

If we calculate q_{vib} by taking the zero point energies as the reference points with respect to which the other energies are measured

$$\begin{aligned} q_{vib} &= \prod_{i=1}^{f} \frac{1}{1 - e^{-\Theta_{vib,i}/T}} = \left(\frac{1}{1 - e^{-1900/300}} \right) \left(\frac{1}{1 - e^{-1980/300}} \right) \left(\frac{1}{1 - e^{-2330/300}} \right) \\ &= (1.0018)(1.0014)(1.0004) = 1.0035 \end{aligned}$$

The implication is that very few vibrational states of NO_2 (other than the ground vibrational state) are accessible at 300 K. This is standard of the vibrations of most molecules.

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18.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule

For a polyatomic molecule containing N atoms, the total number of degrees of freedom is $3N$. Out of these, three degrees of freedom are taken up for the translational motion of the molecule as a whole. For nonlinear molecules, there are three rotational degrees of freedom and the $3N–6$ vibrational degrees. For linear molecules, the rotational motion along the molecular axis is quantum mechanically not meaningful as the rotated configuration is indistinguishable from the original configuration. Therefore, linear molecules have two rotational degrees of freedom and $3N–5$ vibrational degrees of freedom.

To investigate the rotational motion, we need to fix the center of mass of the molecule and calculate the three principal moments of inertia I_A, I_B, and I_C of the ellipsoid of inertia. The center of mass is defined as the point for which the following identities hold:

$$\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i$$

The inertia products are defined by:

$$I_{xx} = \sum_i m_i \left(y_i^2 + z_i^2\right)$$

$$I_{xy} = \sum_i m_i \left(x_i y_i\right)$$

The other components I_{yy}, I_{xz},.. are defined analogously. To find the direction cosines $\alpha_i, \beta_o, \gamma_i$ of the three principle moments of inertia, we need to solve the following matrix equations:

$$\alpha(I_{xx} - \eta) - \beta I_{xy} - \gamma I_{xz} = 0$$

$$\alpha I_{xy} - \beta(I_{yy} - \eta) - \gamma I_{yz} = 0$$

$$-\alpha I_{xz} - \beta I_{yz} + \gamma(I_{zz} - \eta) = 0$$

If the off diagonal terms I_{xy} are zero in the above equations, then the x, y, z axis will be the principal axis. The energy of a rotor with the three moments of inertia I_A, I_B. and I_C is given by:

$$\begin{aligned}\epsilon &= \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 \\ &= \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C}\end{aligned}$$

Each of the rotational degrees of freedom will have a characteristic rotational temperature in terms of the moment of inertia:

$$\Theta_{rot,i} = \frac{hbar^2}{2I_i k} \qquad i = A, B, C$$

There are many different shapes of molecules and these shapes affect the rotational behavior of the molecules. Molecules are therefore classified according to symmetry into different groups called tops. The three different tops are:

$$\begin{aligned}&\text{Spherical top} && \Theta_{rot,A} = \Theta_{rot,B} = \Theta_{rot,C} \\ &\text{Symmetric top} && \Theta_{rot,A} = \Theta_{rot,B} \neq \Theta_{rot,C} \\ &\text{Asymmetric top} && \Theta_{rot,A} \neq \Theta_{rot,B} \neq \Theta_{rot,C}\end{aligned}$$

Spherical Tops

The spherical top can be solved exactly to give:

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

$$g_J = (2J + 1^2) \qquad J = 0, 1, 2, ...$$

The rotational partition function is:

$$\begin{aligned} q_{\text{rot}} &= \sum_{J=0}^{\infty} (2J+1)^2 e^{h^2 J(J+1)/2IkT} \\ &= \sum_{J=0}^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T} \end{aligned}$$

For almost all spherical top molecules:

$$\Theta_{\text{rot}} \gg T$$

Therefore, we can convert the sum to an integral:

$$q_{\text{rot}} = \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

where we have now included the symmetry term, σ. Solving for this integral, we get:

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{q_{\text{rot}}} \right)^{3/2}$$

Symmetric Tops

Here, ω_A, ω_B, and ω_C are the three angular speeds and L_A, L_B, and L_C are the three angular momenta. For a symmetric top molecule such as ammonia, or chloromethane, two components of the moments of inertia are equal, i.e., $I_B = I_C$. The rotational energy levels of such a molecule are specified by two quantum numbers J and K. The total angular momentum is determined by J and the component of this angular momentum along the unique molecular axis is determined by K. The energy levels are given by:

$$\epsilon_{J,K} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$$

with rotational constants in units of wavenumbers:

$$\tilde{B} = \frac{h}{8\pi^2 c I_B}$$

and:

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}$$

where

- J takes on values $0, 1, 2, ...\infty$ and
- $K = -J, -J+1, -J+2, ...0, 1, 2, ...J$.

The rotational partition function is given by:

$$q_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\tilde{B}J(J+1)/kT} \sum_{K=-J}^{J} (2J+1) e^{\tilde{A}-\tilde{B})K^2/kT}$$

This can be converted to an integral and the result is:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi I_B kT}{h^2}\right)\left(\frac{8\pi I_A kT}{h^2}\right)^{1/2}$$

Asymmetric Tops

For asymmetric tops, the expressions for rotational energies are more complex and the conversions to integrations are not easy. One can actually calculate the sum of terms using a computer. An intuitive answer can be obtained by integrating over the angular momenta L_A, L_B and L_C as:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{H(p,q)/kT}\, dL_A\, dL_B\, dL_C = \sqrt{2\pi I_A kT}\sqrt{2\pi I_B kT}\sqrt{2\pi I_C kT}$$

And then multiplying by a factor of $8\pi^2/\sigma h^3$, we get the rotational partition function. The factor of $8\pi^2$ accounts for the angular integration. For any axis chosen in a molecule, a complete rotation contributes a factor of 2π. Integration over all possible orientations of this axis contribute another factor of 4π. The factor of h^3 is for the conversion from the classical phase space to the quantum mechanical phase space.

Symmetry Number

As discussed previously, the **symmetry number** σ corrects for overcounting of rotational configurations. If the molecule has no center of symmetry (e.g. HCN) $\sigma = 1$ whereas if the molecule has a center of symmetry (e.g. $\mathrm{CO_2}$) then $\sigma = 2$.

The final result is:

$$q_{rot} = \frac{\pi^2}{\sigma}\sqrt{\frac{8\pi I_A kT}{h^2}}\sqrt{\frac{8\pi I_B kT}{h^2}}\sqrt{\frac{8\pi I_C kT}{h^2}} \tag{18.8.1}$$

Classical Derivation (Optional)

We can explicitly obtain the classical rotational partition function of an asymmetric top by writing the classical expression for the rotational energy in terms of the Euler angles. The orientation of a rigid rotor can be specified by there Euler angles θ, φ, and ψ with the ranges of angles 0 to π, 0 to 2π and 0 to 2π respectively. The rotational Hamiltonian for the kinetic energy can be written in terms of the angles and their conjugate momenta (p_θ, p_ϕ, p_ψ)

$$H = \frac{\sin^2\psi}{2I_A}\left(p_\theta - \frac{\cos\psi}{\sin\theta\sin\psi}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{\cos^2\psi}{2I_B}\left(p_\theta - \frac{\sin\psi}{\cos\theta\cos\psi}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2I_C}p_\psi^2$$

The classical rotational partition function is given by

$$q_{rot} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\frac{1}{h^3}e^{-H(p,q)/kT}dp_\theta\, dp_\phi\, dp_\psi\, d\theta\, d\phi\, d\psi$$

The integrations can be simplified by rewriting $H(p,q)/kT$ as

$$\frac{H}{kT} = \frac{1}{2I_A kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)\left(p_\theta + \left(\frac{1}{I_B} - \frac{1}{I_A}\right)\frac{\sin\psi\cos\psi}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{1}{2kTI_AI_B\sin^2\theta}\left(\frac{1}{\sin\theta\left(\frac{\sin^{\psi}}{I_A}+\frac{\cos^2\psi}{I_B}\right)}(p_\phi-\cos\theta p_\psi)\right)^2+\frac{1}{2KTI_c}p_\psi^2$$

Using the following integral,

$$\int_{-\infty}^{\infty}e^{-a(x+b)^2}dx=\int_{-\infty}^{\infty}e^{-ax^2}dx=\sqrt{\frac{\pi}{a}}$$

Integration over p_θ gives using the above expression

$$\sqrt{2\pi kT}\left(\frac{\sin^2\psi}{I_A}+\frac{\cos^2\psi}{I_B}\right)^{-1/2} \tag{18.8.2}$$

Integration over p_φ gives the factor,

$$\sqrt{2\pi kTI_AI_B}\sin\theta\left(\frac{\sin^2\psi}{I_A}+\frac{\cos^2\psi}{I_B}\right)^{1/2}$$

This cancels partly the second square root in Equation 18.8.2. Integration over p_ψ gives the factor

$$\sqrt{2\pi kTI_c}$$

Integration over θ, φ and ψ gives a factor of $8\pi^2$.

$$\int_0^{\pi}\sin\theta\,d\theta=2$$

$$\int_0^{2\pi}d\phi=2\pi$$

$$\int_0^{2\pi}d\psi=2\pi$$

Combining all the integrals, we finally get Equation 18.8.1 after reintroduced the symmetry number σ as before with diatomic molecular rotation.

We can simplify calculations by defining **characteristic rotational temperatures** for each axis of rotational:

$$\Theta_A=\frac{h^2}{8\pi^2I_Ak}$$

$$\Theta_B=\frac{h^2}{8\pi^2I_Bk}$$

$$\Theta_C=\frac{h^2}{8\pi^2I_Ck}$$

The polyatomic rotational partition function expressed in Equation 18.8.1 can then be re-expressed as:

$$q_{rot}=\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}} \tag{18.8.3}$$

or alternatively:

$$\ln q_{rot}=\frac{1}{2}\ln\frac{\pi T}{\Theta_A\Theta_B\Theta_C\sigma^2}$$

Example: Nitrogen Dioxide

The three characteristic rotational temperatures for NO_2 are $111.5\ K$, $0.624\ K$ and $0.590\ K$. Calculate the rotational partition function at 300 K.

Solution

The rotational temperature is given by Equation 18.8.3:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}$$

The rotational partition function becomes,

$$q_{rot} = \frac{1.772}{2}\sqrt{\frac{300\ K}{(11.5\ K)(0.624\,K)(22.55\ K)}} = 2242.4$$

Thermodynamics Properties

The molar thermodynamic functions can be readily calculated including average rotation energy and molar heat capacity:

$$E_{rot} = \frac{3}{2}RT$$

and:

$$\bar{C_V} = \frac{3}{2}R$$

Improvements over the classical approximation for the rotational partition function derived above have been obtained. One of the improved versions (with no derivation) is:

$$q_{rot} = q^0_{rot}\left[1 + \frac{h^2}{96\pi^2 kT}\left(\frac{2}{I_A} + \frac{2}{I_C} + \frac{2}{I_C} + \frac{I_C}{I_B I_B} - \frac{I_A}{I_B I_C} - \frac{I_B}{I_A I_C}\right)\right]$$

where q^0_{rot} is the classical approximation in Equation 18.8.1.

Comparing this result with the vibrational partition function calculation before ($q_{vib} = 1.0035$), give the implication that while multiple rotational states are accessible at room temperature, very few vibrational states (other than the ground vibrational state) are accessible.

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18.9: Molar Heat Capacities

Learning Objectives

- **Goal**: Specific heat capacity data for a wide range of elements are used to assess the accuracy and limitations of the Dulong-Petit Law.
- **Prerequisites**: An introductory knowledge of statistical thermodynamics including the derivation of the vibrational (harmonic oscillator) contributions to the heat capacity are recommended.
- **Resources you will need**: This exercise should be carried out within a data analysis software environment which is capable of graphing and generating a best-fit line for an x-y data set.

The heat capacity (C) of a substance is a measure of how much heat is required to raise the temperature of that substance by one degree Kelvin. For a simple molecular gas, the molecules can simultaneously store kinetic energy in the translational, vibrational, and rotational motions associated with the individual molecules. In this case, the heat capacity of the substance can be broken down into translational, vibrational, and rotational contributions;

$$C = C_{trans} + C_{vib} + C_{rot} \tag{18.9.1}$$

Monoatomic crystalline solids represent a much simpler case. Einstein proposed a simple model for such substances whereby the atoms only have vibrational energy (each atom can vibrate in three perpendicular directions around its lattice position). Specifically, the 'Einstein Solid Model' assumes that the atoms act like three-dimensional harmonic oscillators (with the vibrational motion of each atom in each perpendicular dimension entirely independent). Statistical mechanics provides a relatively simple expression for the constant volume molar heat capacity ($C_{V,m}$) of a one-dimensional harmonic oscillator

$$C_{V,m}^{1-D} = R\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{18.9.2}$$

where R is the universal gas constant, T is absolute temperature, and Θ_v is called the 'characteristic vibrational temperature' of the oscillator and depends on the vibrational frequency (ν) according to

$$\Theta_v = \frac{hv}{k} \tag{18.9.3}$$

with h representing Plank's constant and k representing Boltzmann's constant.

Since the vibrations in each dimension are assumed to be independent, the expression for the constant volume molar heat capacity of a 'three-dimensional' Einstein Solid is obtained by simply multiplying Equation 18.9.2 by three;

$$C_{V,m}^{3-D} = 3R\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{18.9.4}$$

The temperature variation of the heat capacity of most metallic solids is well described by Equation 18.9.4. Furthermore, plots of Equation 18.9.4 as a function of temperature for metals with widely varying vibrational frequencies reveal that the heat capacity always approaches the same asymptotic limit of $3R$ at high temperatures. Stated another way, at high temperatures

$$\lim_{T\to\infty}\left[\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2\right] = 1 \tag{18.9.5}$$

and Equation 18.9.4 reduces to

$$\lim_{T\to\infty}\left[C_{V,m}^{3D}\right] = 3R \tag{18.9.6}$$

(You will be asked to verify this result in the exercise below). According to Equation 18.9.6, the molar heat capacities of metallic solids should approach 24.9 J/(K mol) at high temperatures, regardless of the identity of the metal.

The vibrational frequencies of most metallic solids are usually small enough so that Θ_v lies considerably below room temperature ($\Theta_v \ll 298\ K$). For these substances, the limits implied by Equations 18.9.5 and 18.9.6 are well approximated even at room temperature, leading to the result that $C_{v,m} = 24.9\ J/(K \cdot mol)$ for most metals at room temperature.

In the early 1800s, two French scientists by the names of Pierre Louis Dulong and Alexis Therese Petit empirically discovered the same remarkable result. The Dulong-Petit Law is normally expressed in terms of the specific heat capacity (C_s) and the molar mass (M) of the metal

$$C_s M = C_{V,m} \approx 25(J\,K^{-1}\,mol^{-1}) \tag{18.9.7}$$

where C_s represents how much heat is required to raise the temperature of 'one gram' of that substance by one degree Kelvin. Dulong and Petit, as well as other scientists of their time, used this famous relationship as a means of establishing more accurate values for the atomic weight of metallic elements (by instead measuring the specific heat capacity of the element and using the Dulong-Petit relationship, which is a relatively simple method of establishing weights in comparison to the more disputable gravimetric methods that were being used at the time to establish the equivalent weights of elements).

In the exercise below, you will look up the specific heat capacities of a number of elements that exist as simple monoatomic solids at room temperature and assess the accuracy of the Dulong-Petit law.

Experimental Data

Consult the CRC Handbook of Chemistry and Physics (CRC Press: Boca Raton, FL) and compile a table of specific heat capacities for a large number of elements that are known to exist as monoatomic solids at room temperature. Also look up and record the molar mass of these elements. The elements that you consider should be restricted to those appearing in groups 1-14 of the periodic table. Make sure you generate a fairly large list which includes a number of elements that are normally considered as metallic in character (such as copper, iron, sodium, lithium, gold, platinum, barium, and aluminum), but also some non-metallic elements that are nonetheless monoatomic isotropic solids (such as carbon-diamond, beryllium, boron, and silicon). Heat capacities that are usually reported in the literature are not actual constant volume heat capacities (C_v), but are instead constant pressure heat capacities (C_p). Fortunately, C_p and C_v are essentially equal for simple solids (within the level of precision that we consider in this exercise), and you can assume that the values from the CRC Handbook represent C_s.

Exercises

1. Enter the element name, the specific heat capacity, and the molar mass of each element in a spreadsheet. Calculate the product of specific heat and molar mass for each element and calculate how much this product differs from the Dulong-Petit prediction (express your result as a percent difference relative to $3R$).
2. Assess the generality of the Dulong-Petit law in an alternate way by generating a plot of specific heat as a function of reciprocal Molar Mass (C_s versus $1/M$), which should be linear with a slope equal to 3R if the data behave according to Equation 18.9.7.
3. Inspect your results from 1 and 2 above and identify any elements that significantly deviate from the Dulong-Petit law. When they occur, do deviations tend to be smaller or larger than 3R? Does the degree of deviation from the Dulong-Petit law seem to correlate with periodic trends in metallic (or covalent) bonding for these elements? Do deviations tend to occur more readily for elements of smaller or higher atomic weight? Explain how the type of bonding and the magnitude of the atomic weight can lead to deviations from the arguments made in Equations 18.9.5-18.9.7 above.
4. Use the plotting method that you employed in step 2 above as a means of determining a value for the universal gas constant (R) - but make sure you throw-out any specific heat data for elements that you suspect do not fall within the limit $\Theta_v \ll 298\ K$. Calculate the percent error in the value of R that you determine.
5. Verify that the limit expressed in Equation 18.9.5 above is true (HINT: expand each of the exponential terms in a power series and note that higher-order terms are negligible in the limit $T \gg \Theta_v$).

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18.10: Ortho and Para Hydrogen

The molecules of hydrogen can exist in two forms depending on the spins on the two hydrogen nuclei. If both the nuclear spins are parallel, the molecule is called ortho and if the spins are antiparallel, it is referred to as para (in disubstituted benzene, **para** refers to the two groups at two opposite ends, while in **ortho**, they are adjacent or "parallel" to each other). The spin on the hydrogen nucleus has a magnitude of ½$\hbar$. The presence of nuclear spins leads to very interesting consequences for the populations of the rotational states and on a macroscopic scale, has consequences on measured entropies and heat capacities as well. The total partition function of H_2 can be written as:

$$q_{\mathrm{tot}} = q_{\mathrm{elec}} q_{\mathrm{vib}} q_{\mathrm{rot}} q_{\mathrm{trans}} q_{\mathrm{nuc}}$$

where, the subscripts refer to the respective motions. After "half" a rotation, the nuclei are superimposed on each other. Since a proton is a spin half nucleus, the total wave function must be antisymmetic with respect to the exchange of the particles. i.e.:

$$\psi(1,2) = -\psi(2,1)$$

The translational motion refers to the motion of the molecular center of mass and has no influence on the symmetry of the nuclear wave function. Vibrational motion depends on the magnitude of the internuclear distance and has no effect on the particle exchange. The electronic motion also has no effect on the symmetry properties of the nuclear wave function. Therefore, the product of the nuclear spin and rotational wave functions must be antisymmetric with respect to the particle exchange. For the nuclear spin functions, there are four combinations. One combination is a singlet:

$$|\psi_{\nu,s}\rangle = \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

And the other three combinations are the three states of a triplet:

$$|\psi_{\nu,s}\rangle = \alpha(1)\alpha(2)$$
$$|\psi_{\nu,s}\rangle = \alpha(1)\beta(2) + \alpha(2)\beta(1)$$
$$|\psi_{\nu,s}\rangle = \beta(1)\beta(2)$$

The rotational wavefunctions (ψ_r) are given in terms of the associated Legendre polynomials $P_l^{|m|}(x)$ where $x = \cos\theta$:

$$|\psi_r\rangle = e^{im\phi} P_l^{|m|}(\cos\theta) \tag{18.10.1}$$

with:

$$P_l^{(m)}(x) = \left(1 - x^2\right)^{|m/2} \frac{d^{|m|} P_l(x)}{dx^{m|}} \tag{18.10.2}$$

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l \left(x^2 - 1\right)^l}{dx^l} \tag{18.10.3}$$

When the nuclei are interchanged, θ becomes $\pi - \theta$ and φ is changed to $\varphi + \pi$. The polynomials change as:

$$P_l(-x) = (-1)' P_l(x); \quad P_l^{|m|}(-x) = (-1)^{l-|m|||} P_l^{|m|}(x) \tag{18.10.4}$$

The exponential function changes as:

$$e^{im(\phi+\pi)} = e^{im\pi} e^{im\varphi} = (-1)^{|m|} e^{im\varphi} \tag{18.10.5}$$

Therefore, the rotational wave function changes as:

$$P_l(-x) = (-1)^l P_l(x) \tag{18.10.6}$$

$$P_l^{|m|}(-x) = (-1)^{l-|m|} P_l^{|m|}(x) \tag{18.10.7}$$

- $|\psi_r\rangle$ is symmetrical for even J, and
- $|\psi_r\rangle$ is antisymmetrical for odd J

Combining the nuclear spin and the rotational parts, we see that, the product ψ_r, ψ_m must be antisymmetrical (with respect to the exchange of nuclei) for half integral nuclear spins and symmetrical for integral spins. To accomplish this, the singlet nuclear states (para) must be combined with the even rotational functions and the triplet nuclear states must be combined with the odd rotational states. The rotational partition functions for ortho and para hydrogens are, thus:

$$q_{\text{ortho}} = q_{\nu,t} q_{r,\text{odd}} = 3 \sum_{J=1,3,5,\ldots} (2J+1) e^{-J(J+1)\Theta_R/T} \tag{18.10.8}$$

and:

$$q_{\text{para}} = q_{\nu,\,\text{s}}\, q_{r,\text{even}} = 1 \sum_{J=0,2,4,\ldots} (2J+1) e^{-J(J+1)\Theta_R/T} \tag{18.10.9}$$

where Θ_R is the rotational temperature defined previously. The total partition function consisting both ortho and para hydrogens is given by:

$$q_{\text{rot},nu} = 1 \sum_{j=0.2.4} (2J+1) e^{-J(J+1)\Theta_k/T} + 3 \sum_{j=1,3,5,n} (2J+1) e^{-J(J+1)\Theta_R/T} \tag{18.10.10}$$

The ratio of ortho to para hydrogens at thermal equilibrium is given by:

$$\frac{N_o}{N_p} = \frac{3 \sum_{j=1,2,3\ldots} (2J+1) e^{-J(J+1)\Theta_R/T}}{\sum_{j=0} 2(2J+1) e^{-J(J+1)\Theta_R/T}} \tag{18.10.11}$$

At high temperature, the two summations become equal and therefore, the high temperature limit of N_o/N_p is 3. At low temperature, the ratio becomes:

$$\frac{N_o}{N_p} = \frac{3\left(3e^{-2\Theta_k/T} + \ldots\ldots\right)}{1\left(1 + 5e^{-5\Theta_n/T} + \ldots\right)} \to 0, \text{ as } T \to 0 \tag{18.10.12}$$

A good experimental verification of the above analysis is a comparison between the calculated rotational heat capacities at constant volume (C_V) rot, nu (calculated from:

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

where:

$$\langle E \rangle = \frac{\partial \ln q_{\text{rot},\nu}}{\partial \beta}$$

The heat capacities are shown as a function of temperature in Figure 18.10.1 .

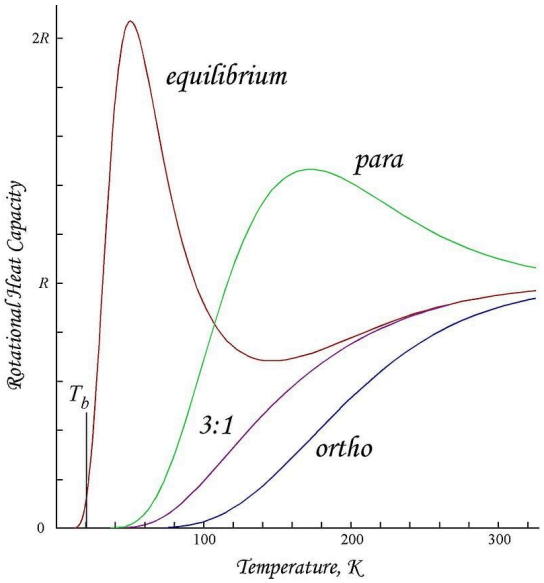


Figure 18.10.1 : The heat capacities of o- and p- hydrogens as a function of temperature. The curve marked Exp depicts the experimental data, the curve eq represents the data for an equilibrated mixture of o- and p- at a given temperature and the curves o- and p-represent the heat capacities of pure o- and pure p- hydrogens. (CC-SA-BY 3.0; Gadolinist).

The purple curve marked 3:1 gives the experimental data, the curve eq represents the data for an equilibrated mixture of o- and p- at a given temperature. The curves o- and p- represent the heat capacities of pure o- and pure p- hydrogens calculated from the o- and p- partition functions given by Equations 18.10.8 and 18.10.9 respectively. Initially it was a puzzle as to why the experimental data differs from the calculated values. In fact, the experimental data seemed to agree very well with the following equation:

$$(C_V)_{\mathrm{rot},\nu} = \frac{3}{4}(C_V)_{\mathrm{rot},\nu}(\mathrm{ortho}) + \frac{1}{4}(C_V)_{\mathrm{rot},\nu}(\mathrm{para}) \tag{18.10.13}$$

The reason for this is that, when $\mathrm{H_2}$ is cooled down from a higher temperature, the ortho:para ratio continues to remain 0.75 / 0.25 (the high temperature value) because the $\mathrm{ortho} \rightarrow \mathrm{para}$ interconversion rate is very very small and we do not reach the equilibrium composition unless a catalyst such as activated charcoal is added to the gas mixture. Equation 18.10.13 corresponds to a “frozen high temperature mixture” of ortho:para hydrogens. In the presence of the catalyst, the experiments also give the curve labeled as eq in the graph. This in indeed a very nice case where the experiments support not only the methods of statistical thermodynamics but also of the antisymmetry principle for bosons and fermions. If we consider the case of $^{16}\mathrm{O_2}$, where the nuclear spins are zero, the rotational wave function has to be symmetric as only symmetric wave functions are permitted for bosons. Thus, only even rotational states contribute to the partition function:

$$q_{\mathrm{rot},V}(^{16}\mathrm{O_2}) = \sum_{J=0,2,4,\ldots} (2J+1)e^{-J(J+1)\theta_R/T}$$

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18.11: The Equipartition Principle

The equipartition theorem, also known as the law of equipartition, equipartition of energy or simply equipartition, states that every degree of freedom that appears only quadratically in the total energy has an average energy of $½k_BT$ in thermal equilibrium and contributes $½k_B$ to the system's heat capacity. Here, k_B is the Boltzmann constant, and T is the temperature in Kelvin. The law of equipartition of energy states that each quadratic term in the classical expression for the energy contributes ½kBT to the average energy. For instance, the motion of an atom has three degrees of freedom (number of ways of absorbing energy), corresponding to the x, y and z components of its momentum. Since these momenta appear quadratically in the kinetic energy, every atom has an average kinetic energy of $3/2k_BT$ in thermal equilibrium. The number of degrees of freedom of a polyatomic gas molecule is $3N$ where N is the number of atoms in the molecule. This is equal to number of coordinates for the system; e.g. for two atoms you would have x, y, z for each atom.

Translations

The translational contribution to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{trans}\rangle = -\frac{1}{q_{trans}}\frac{\partial q_{trans}}{\partial \beta} \tag{18.11.1}$$

Introducing the translational partition function derived earlier, Equation 18.11.1 becomes

$$= -\frac{\Lambda^3}{V}\frac{\partial}{\partial\beta}\frac{V}{\Lambda^3} = -\frac{3}{\Lambda}\frac{\partial\Lambda}{\partial\beta} = \frac{3}{2}k_BT$$

Thus, the three translational degrees of freedom in three dimensions satisfy the equipartition theorem with each translational degree providing $½k_BT$ of energy.

Rotations

Consider the molecular partition functions. The average rotational energy to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{rot}\rangle = -\frac{1}{q_{rot}}\frac{\partial q_{rot}}{\partial \beta} \tag{18.11.2}$$

which when you introduce the rotational partition function, Equation 18.11.2 becomes

$$\langle E_{rot}\rangle = -\sigma\beta\tilde{B}\frac{1}{\sigma\tilde{B}}\frac{\partial}{\partial\beta}\frac{1}{\beta} = \frac{1}{\beta} = k_BT$$

The classical expression for the rotational energy of a diatomic molecule is

$$E_{rot}^{(classical)} = \frac{1}{2}I(\omega_x^2+\omega_y^2)$$

where I is the moment of inertia and ω_x and ω_y are the angular velocities in the x and y directions. The rotation along the molecular axis (the z axis here) has no meaning in quantum mechanics because the rotations along the molecular axis lead to configurations which are indistinguishable from the original configuration. The two rotational degrees of freedom have thus given a value of kT with with each rotational degree providing $½k_BT$ of energy.

Vibrations

Consider vibrational motions. The average vibrational energy to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{vib} \rangle = -\frac{1}{q_{vib}} \frac{\partial q_{vib}}{\partial \beta} \tag{18.11.3}$$

which when you introduce the partition function for vibration, Equation 18.11.3 becomes

$$\langle E_{vib} \rangle = \frac{-1}{q_{vib}} \left(-hc\tilde{\nu} \frac{e^{-hc\tilde{\nu}/k_BT}}{(1-e^{-hc\tilde{\nu}/k_BT})^2} \right) = hc\tilde{\nu} \frac{e^{-hc\tilde{\nu}/k_BT}}{(1-e^{-hc\tilde{\nu}/k_BT})} \tag{18.11.4}$$

This can be simplified by dividing both numerator and denominator of Equation 18.11.4 by $e^{-hc\tilde{\nu}/k_BT}$

$$\langle E_{vib} \rangle = hc\tilde{\nu} \left(\frac{1}{e^{hc\tilde{\nu}/k_BT} - 1} \right) \tag{18.11.5}$$

Equation 18.11.5 is applicable at all temperatures, but if $hc\tilde{\nu}/k_BT \ll 1$ (i.e., the high temperature limit), then the exponential in the denominator can be expanded

$$e^{hc\tilde{\nu}/k_BT} - 1 \approx 1 + hc\tilde{\nu}/k_BT - 1 = hc\tilde{\nu}/k_BT \tag{18.11.6}$$

and Equation 18.11.5 becomes

$$\langle E_{vib} \rangle \approx \cancel{hc\nu} \left(\frac{1}{\cancel{hc\nu}/k_BT} \right)$$

$$\langle E_{vib} \rangle \approx k_BT \tag{18.11.7}$$

with each vibrational degree providing k_BT of energy (since there ar two quadratic terms in the Hamiltonian for a harmonic oscillator (kinetics energy and potential energy).

Compare Equation 18.11.7 with the classical expression for the vibrational energy

$$E_{vib}^{(classical)} = ½kx^2 + ½\mu v_x^2$$

At high temperature the equipartition theorem is valid, but at low temperature, the expansion in Equation 18.11.6 fails (or more terms are required). In this case, only a few vibrational states are occupied and the equipartition principle is not typically applicable.

Heat Capacity

Heat capacity at constant volume C_v, is defined as

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

The equipartition theorem requires that each degree of freedom that appears only quadratically in the total energy has an average energy of ½k_BT in thermal equilibrium and, thus, contributes ½kB to the system's heat capacity. Thus the three translational degrees of freedom each contribute ½R to (3/2 R). The contribution of rotational kinetic energy will be R for the linear, and 3/2R for the nonlinear molecules. For the vibration, an oscillator has quadratic kinetic and potential terms, making the contribution of each vibrational mode R. However, k_BT has to be much greater than the spacing between the quantum energy levels. If this is not satisfied, the heat capacity will be reduced and which drop to zero at low temperatures. The corresponding degree of freedom is said to be **frozen out**; this is the situation for the vibrational degrees of freedom at room temperature and that is why the usual assumption is that they will not contribute.

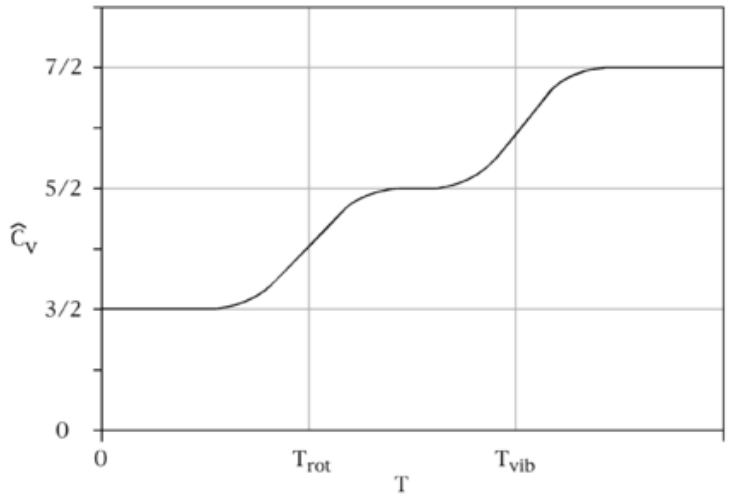


Figure 18.11.1 : Idealized plot of the molar specific heat of a diatomic gas against temperature. It agrees with the value (7/2)R predicted by equipartition at high temperatures (where R is the gas constant), but decreases to (5/2)R and then (3/2)R at lower temperatures, as the vibrational and rotational modes of motion are "frozen out". The failure of the equipartition theorem led to a paradox that was only resolved by quantum mechanics. For most molecules, the transitional temperature T_{rot} is much less than room temperature, whereas T_{vib} can be ten times larger or more. A typical example is carbon monoxide, CO, for which T_{rot} ≈ 2.8 K and T_{vib} ≈ 3103 K. For molecules with very large or weakly bound atoms, T_{vib} can be close to room temperature (about 300 K); for example, T_{vib} ≈ 308 K for iodine gas, I_2. (Public domain; PD-Self)

22Example: CO vs. NO

For comparing the molar heat capacities of nitrogen dioxide and carbon dioxide at constant volume (at room temperature), let us use the law of equipartition and assume the vibrations to be frozen out at room temperature. The predicted molar for the linear CO_2 (with three translational and two rotational degrees of freedom) is $5/2R$ $20.8\ JK^{-1}mo'^{-1}$).

The estimated molar for NO_2 (a bent molecule, with three translational and three rotational degrees of freedom) is $3R$ $(25.0\ JK^{-1}mol^{-1})$. These estimations are close to the experimental values:

- 30.1 JK^{-1} mol^{-1} for CO_2
- 29.5 JK^{-1} mol^{-1} for NO_2

Especially for CO_2, the deviation is significant. This suggests that, although not all vibrational degrees of freedom are available, they cannot be totally ignored. The bigger deviation in the prediction of molar heat capacities is probably due to the existence of the lower frequency-bending vibration in carbon dioxide.

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18.E: Partition Functions and Ideal Gases (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 18 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

1) If the nucleus has a spin of s_n, then its spin degeneracy $g_n = 2s_n + 1$. The diatomic molecule formed from such a nucleus will have g n 2 spin functions which have to be combined to form symmetric and antisymmetric functions. Carry out an analysis similar to that of H 2 for D 2 where the deuterium nucleus has a spin of 1.

2) Derive the thermodynamic functions from the polyatomic rotational partition function. 3) Carry out the integration for the rotational partition function of the symmetric top.

4) Calculate the total partition function and the thermodynamic functions of water at 1000K. The three moments of inertia of water are 1.02, 1.91 and 2.92 in 10 - 47 kg m 2 . The symmetry number is 2. The vibrational data in given in Fig. 3.5. Assume a non- degenerate electronic ground state.

5) Verify that the symmetry numbers for methane, benzene and SF 6 are 12, 12 and 24 respectively.

6) The ground state of Na is a doublet (two states with the same energy). Assuming this to be the zero of energy and assuming that the next energy level to be 2 eV higher than the ground state, calculate q el .

7) The bond length r_{eq} of O_2 is 1.2 Å. The moment of inertia I is $mr_{eq}^2/2$ where m of O is $16X1.66times10^{-27}\ kg$. Calculate $\tilde{B}$ and the rotational partition function of O_2 at 300 K.

8) The vibrational frequency ν of ICl is 384 cm -1 . What is its vibrational partition function at 300 K? What is the fraction of molecules in the ground state (n = 0) and the first excited state n = 1? 9) Calculate the translational partition function of N 2 at 300 K. For volume, use the molar volume at 300 K.

10) An isotope exchange reaction between isotopes of bromine is 79 79 81 81 79 81 2 Br Br Br Br Br Br +

The fundamental vibrational frequency of 79 81 Br Br 323.33 cm -1 . All the molecules can be assumed to have the same bond length and have a singlet ground electronic state. Calculate the equilibrium constant at 300K and 1000K.

11) For the reaction I 2 ↔ 2I, calculate the equilibrium constant at 1000K. The relevant data are as follows. The ground electronic state of I is 2 3/ 2 P whose degeneracy is 4. The rotational and vibrational frequencies of I 2 are 0.0373 cm -1 and 214.36 cm -1 respectively. The dissociation energy of I 2 is 1.5422 eV.

12) The representative molecular data for a few molecules is given in table 3.1. Using the relevant data, calculate the equilibrium constant for the reaction H 2 + Cl 2 I HCl at 1000K. What is the value of the equilibrium constant as T → ∞?

13) Eq. (3.50) is related to the Giauque function. Estimate the total molar Giauque function for molecules that behave as harmonic oscillators-rigid rotors.

14) The energy of a molecule in the rigid rotor – harmonic oscillator approximation is E vib, rot is (n +1/2) hν + B J (J+1) Real molecules deviate from this behaviour due to the existence of anharmonicity (anharmonicity constant x e), centrifugal distortion (centrifugal distortion constant D) and the interaction between vibration and rotation (α is the coupling constant between the vibrational and rotational modes). The expression for the energy when these affects are included is 2 2 2 1 1 1 2 2 2 , ( ) (1) ( ) (1) ( ) (1) vib rot e E n h BJ J x n h DJ J n J J ν ν α = + + + – + + + – + + Here, the third term is due to anharmonicity, the fourth term is due to centrifugal distortion and the last term is due to the interaction between vibration and rotation. Calculate the q vib, rot which includes the effects of these distortions.

Q18.4

Using the data in Table 8.6, calculate the fraction of sodium atoms in the first excited state at temperatures 300 K, 1000 K, and 2000 K.

S18.4

Using Equation 18.10, we can calculate the fraction of sodium atoms in the first excited state, with $g_{e1} = 2, g_{e2} = 2, g_{e3} = 4, g_{e4} = 2$:

$$f_2 = \frac{2e^{-\beta\epsilon_{e2}}}{2 + 2e^{-\beta\epsilon_{e2}} + 4e^{-\beta\epsilon_{e3}} + 2e^{-\beta\epsilon_{e4}} + ...} \tag{18.E.1}$$

Using the data in Table 8.6, the numerator of this fraction becomes

$$2exp[-\frac{16956.183cm^{-1}}{(0.6950cm^{-1}K^{-1})T}] \tag{18.E.2}$$

and the denominator becomes

$$2 + 2exp[-\frac{16956.183cm^{-1}}{(0.6950cm^{-1}K^{-1})T}] + 4exp[-\frac{16973.379cm^{-1}}{(0.6950cm^{-1}K^{-1})T}] + 2exp[-\frac{25739.86cm^{-1}}{(0.6950cm^{-1}K^{-1})T}] + ...$$

Using these values, we can find the values of f_2 at the different temperatures.

$$f_2(T = 300K) = 4.8x10^{-36}$$

$$f_2(T = 1000K) = 2.5x10^{-11}$$

$$f_2(T = 2000K) = 5.0x10^{-6}$$

Q18.5

Using the data in the table, calculate the fraction of hydrogen atoms in the first excited state at $400\ K$, $1800\ K$, and $2100\ K$.

Electronic Configuration	Term Symbol	Degeneracy $g_e = 2J + 1$	energy/cm^{-1}
$1s$	$^2S_{1/2}$	2	0
$2p$	$^2P_{1/2}$	2	82 258.907
$2s$	$^2S_{1/2}$	2	82 258.942
$2p$	$^2P_{3/2}$	4	82 259.272

S18.5

Use the equation:

$$f_2 = \frac{g_{e2} e^{-\beta \varepsilon_{e2}}}{g_{e1} + g_{e2} e^{-\beta \varepsilon_{e2}} + g_{e3} e^{-\beta \varepsilon_{e3}} + \cdots} \tag{18.E.3}$$

and

$$\beta \approx \frac{1}{T \; 0.6950 \; cm^{-1} K^{-1}} \tag{18.E.4}$$

to get:

$$f_2 = \frac{2e^{-\frac{82\;258.907\;cm}{T\;0.6950\;cm^{-1}K^{-1}}}}{2 + 2e^{-\frac{82\;258.907\;cm}{T\;0.6950\;cm^{-1}K^{-1}}} + 2e^{-\frac{82\;258.942\;cm}{T\;0.6950\;cm^{-1}K^{-1}}} + 4e^{-\frac{82\;259.272\;cm}{T\;0.6950\;cm^{-1}K^{-1}}}} \tag{18.E.5}$$

$$f_2(400\;K) = 0.2498$$

$$f_2(900\;K) = 0.2499$$

$$f_2(2100\;K) = 0.2500$$

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19: THE FIRST LAW OF THERMODYNAMICS

19.1: Overview of Classical Thermodynamics

19.2: Pressure-Volume Work

19.3: Work and Heat are not State Functions

19.4: Energy is a State Function

19.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred

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19.7: Work and Heat Have a Simple Molecular Interpretation

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19.13: The Temperature Dependence of ΔH

19.14: Enthalpy is a State Function

19.E: The First Law of Thermodynamics (Exercises)

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19.1: Overview of Classical Thermodynamics

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19.2: Pressure-Volume Work

Work in general is defined as a product of a force $\mathbf{F}$ and a path element $\mathbf{ds}$. Both are vectors and work is computed by integrating over their inner product:

$$w = \int \mathbf{F}\cdot\mathbf{ds}$$

Moving an object against the force of friction as done in the above dissipation experiment is but one example of work:

$$w_{friction} = \int \mathbf{F}_{\text{friction}}\cdot\mathbf{ds}$$

We could also think of *electrical* work. In that case we would be moving a charge *e* (e.g. the negative charge of an electron) against an electrical (vector) field $\mathbf{E}$. The work would be:

$$w_{electical} = \int e\mathbf{E}\cdot\mathbf{ds}$$

Other examples are the stretching of a rubber band against the elastic force or moving a magnet in a magnetic field etc, etc.

Pressure-volume (PV) work

In the case of a cylinder with a piston, the pressure of gas molecules on the inside of the cylinder, P, and the gas molecules external to the piston, P_{ext} both exert a force against each other. Pressure, (\P\), is the force, F, being exerted by the particles per area, A:

$$P = \frac{F}{A}$$

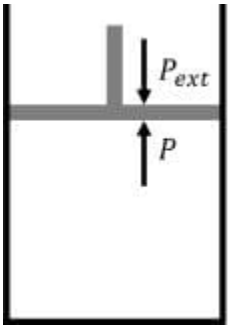


Figure 19.2.1 : A piston with internal pressure P and external pressure P_{ext}.

We can assume that all the forces generated by the pressure of the particles operate parallel to the direction of motion of the piston. That is, the force moves the piston up or down as the movement of the piston is constrained to one direction. The piston moves as the molecules of the gas rapidly equilibrate to the applied pressure such that the internal and external pressures are the same. The result of this motion is work:

$$w_{volume} = \int \left(\frac{F}{A}\right)(A\,ds) = \int P\,dV \tag{19.2.1}$$

This particular form of work is called **pressure-volume (PV) work** and will play an important role in the development of our theory. Notice however that volume work is only ***one form*** of work.

Sign Conventions

It is important to create a sign convention at this point: positive heat, positive work is always energy you put in into the system. If the system decides to remove energy by giving off heat or work, that gets a minus sign.

In other words: ***you pay the bill***.

To comply with this convention we need to rewrite volume work (Equation 19.2.1) as

$$w_{PV} = -\int \left(\frac{F}{A}\right)(A\,ds) = -\int P\,dV$$

Hence, to decrease the volume of the gas (ΔV is negative), we must put in (positive) work.

Thermodynamics would not have come very far without cylinders to hold gases, in particular steam. The following figure shows when the external pressure, P_{ext}, is greater than and less than the internal pressure, P, of the piston.

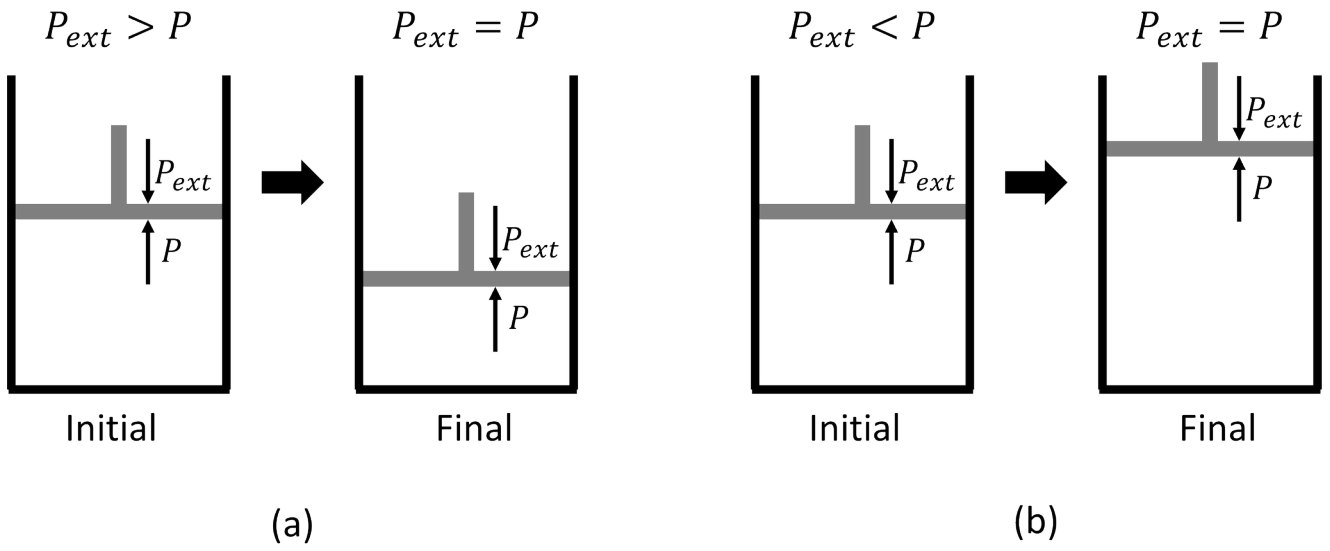


Figure 19.2.2 : Pistons showing a compression (left) and an expansion (right).

If the pressure, P_{ext}, being exerted on the system is constant, then the integral becomes:

$$w = -P_{\text{ext}} \int_{V_{initial}}^{V_{final}} dV = -P_{\text{ext}} \Delta V \tag{19.2.2}$$

Since the system pressure (inside the piston) is not the same as the pressure exerted on the system, the system is not in a state of equilibrium and cannot be shown directly on and PV diagram. This type of process is called an irreversible process. For a system that undergoes irreversible work at constant external pressure, we can show the amount of work being done on a PV diagram despite not being able to show the process itself.

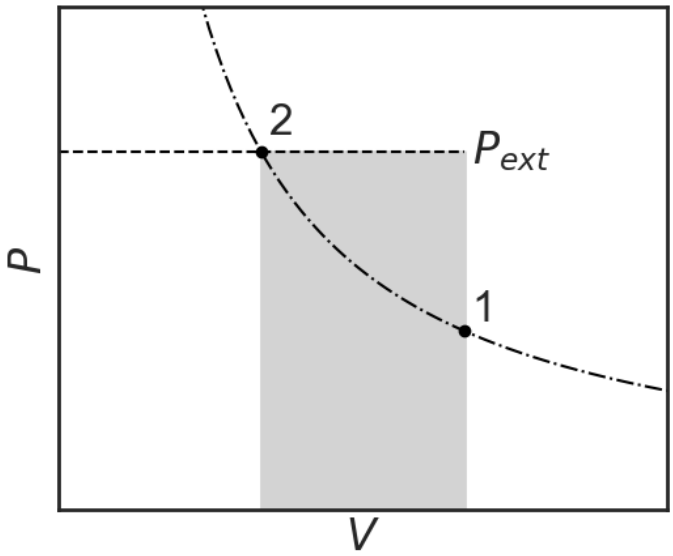


Figure 19.2.3 : A system is compressed under constant external pressure, P_{ext}, from state 1 to state 2. The shaded area shows the amount of work being done for the compression. The dash-dot line is an isotherm, a path of constant temperature, showing that the initial and final temperature of the irreversible compression are the same.

Note that the external pressure, P_{ext}, exerted on the system is constant. If the external pressure changes during the compression, we must *integrate* over the whole range:

$$w = -\int_{V_{initial}}^{V_{final}} P_{\text{ext}}(V)\, dV$$

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19.3: Work and Heat are not State Functions

Heat and work are path functions

Heat (q) and work (w) are path functions, not state functions:

1. They are path dependent.
2. They are energy transfer → they are not intrinsic to the system.

Path Functons

Functions that depend on the path taken, such as work (w) and heat (q), are referred to as **path functions**.

Reversible versus irreversible

Let's consider a piston that is being compressed at constant temperature (isothermal) to half of its initial volume:

1. Start with cylinder 1 liter, both external and internal pressure 1 bar.
2. ***Peg*** the piston in a fixed position.
3. Put cylinder in a pressure chamber with $P_{ext} = 2$ bar.
4. Suddenly pull the peg.

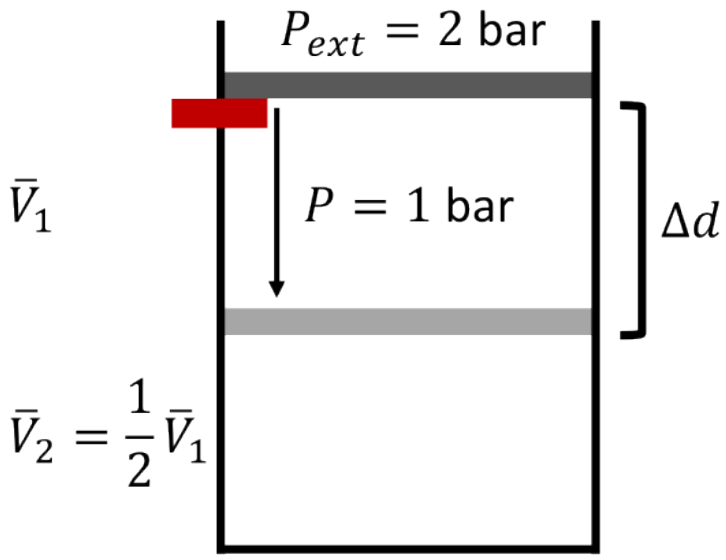


Figure 19.3.1 : A piston is being irreversibly and isothermally compressed under constant external pressure from state 1 to state 2.

The piston will shoot down till the internal and external pressures balance out again and the volume is 1/2 L. Notice that the external pressure was ***maintained*** constant at 2 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time. In a $P-V$ diagram of an ideal gas, P is a hyperbolic function of V under constant temperature (isothermal), but this refers to the *internal* pressure of the gas. It is the external one that counts when computing work and they are not necessarily the same. As long as $P_{external}$ is constant, work is represented by a rectangle.

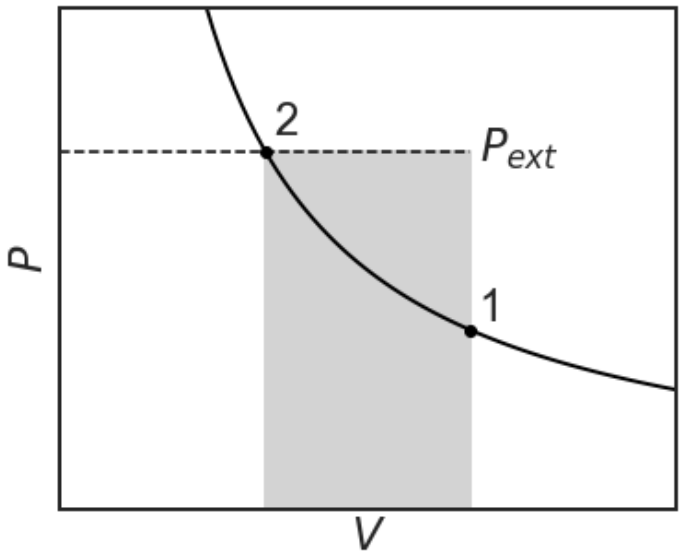


Figure 19.3.1 : The system is being irreversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area.

The amount of work being done is equal to the shaded region and in equation:

$$w = -\int_{V_1}^{V_2} PdV = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the maximum amount of work that can be done for an isothermal compression. Work is being done on the system, so the overall work being done is positive. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$:

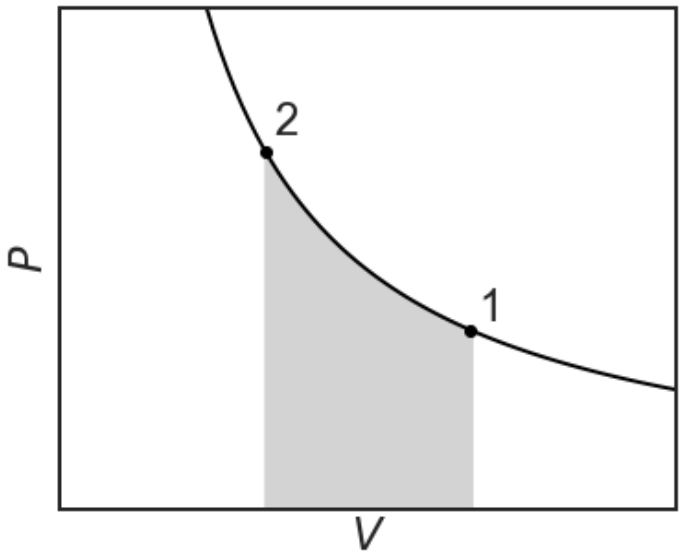


Figure 19.3.1 : The system is being reversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area. Note that for a compression, a reversible process does less work than an irreversible process.

For an ideal gas, the amount of work being done along the reversible compression is:

$$w = -\int_{V_1}^{V_2} PdV = -nRT\int_{V_1}^{V_2} \frac{1}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

The amount of work being done to the two systems are not the same in the two diagrams (see the gray areas). Work is not a state, but a path function, as it depends on the path taken. You may say, what's the big difference. In both cases, the system is compressed from state 1 to state 2. The key is the word ***suddenly***. By pegging the position in place for the first compression, we have created a situation where the external pressure is higher than the internal pressure ($P_{ext} > P$). Because work is done suddenly by pulling the peg out, the internal pressure is struggling to catch up with the external one. During the second compression, we have $P_{ext} = P$ at all times. It's a bit like falling off a cliff versus gently sliding down a hill. Path one is called an irreversible path, the second a reversible path.

Reversible vs. Irreversible Processes

A reversible path is a path that follows a series of states at rest (i.e., the forces are allowed to balance at all times). In an irreversible one the forces only balance at the very end of the process.

Notice that less work is being done on the reversible isothermal compression than the one-step irreversible isothermal compression. In fact, the minimum amount of work that can be done during a compression always occurs along the reversible path.

Isothermal Expansion

Let's consider a piston that is being expanded at constant temperature (isothermal) to twice of its initial volume:

1. Start with cylinder 1 liter in a pressure chamber with both an external and internal pressure of 2 bar.
2. ***Peg*** the piston in a fixed position.
3. Take the cylinder out of the pressure chamber with P_{ext}= 1 bar.
4. Suddenly pull the peg.

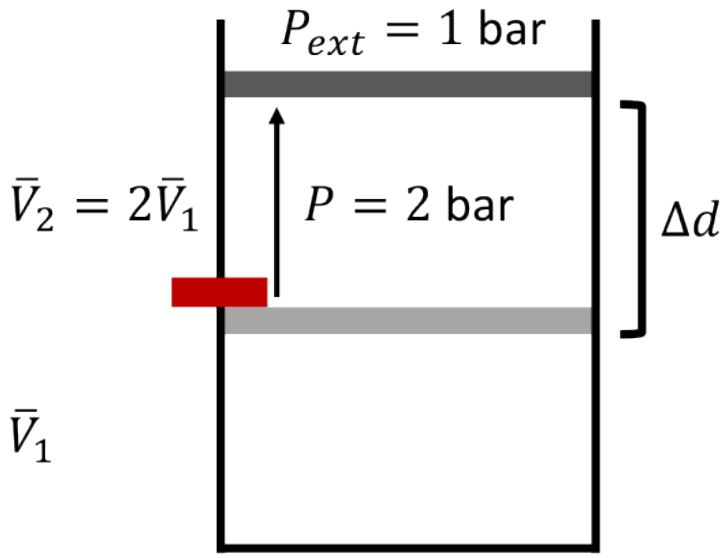


Figure 19.3.1 : A piston is being irreversibly and isothermally expanded under constant external pressure from state 1 to state 2.

The piston will shoot up till the internal and external pressures balance out again and the volume is 2 L. Notice that the external pressure was ***maintained*** constant at 1 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time.

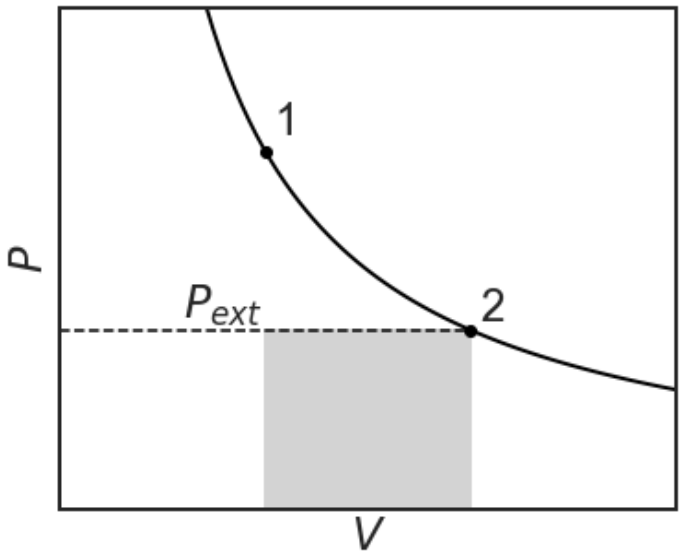


Figure 19.3.1 : The system is being irreversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area.

The amount of irreversible work being done is again equal to the shaded region and the equation:

$$w = -P\Delta V = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the minimum amount of work that can be done for an isothermal expansion. Work is being done on the system, so the overall work being done is negative. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$:

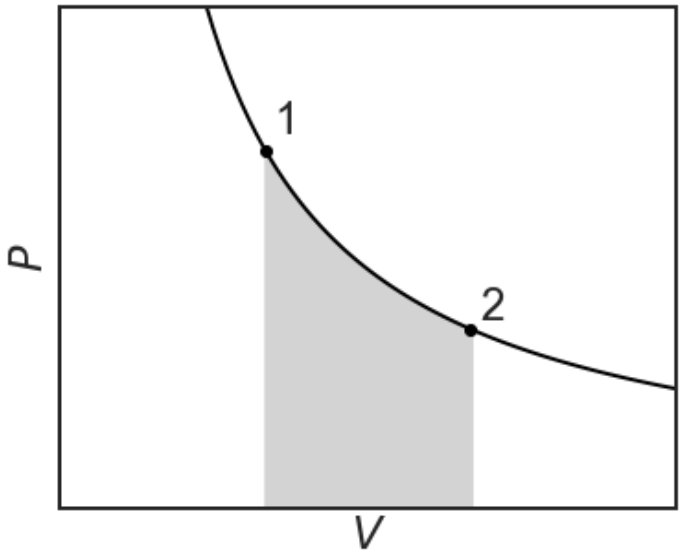


Figure 19.3.1 : The system is being reversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area. Note that for an expansion, a reversible process does more work than an irreversible process.

Notice that not only is more work is being done than the one-step irreversible isothermal expansion, but it is the same amount of work being done as the reversible isothermal compression. This is the maximum amount of work that can be done during an expansion.

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19.4: Energy is a State Function

Work and heat are not state functions

A Better Definition of the First law of thermodynamics

The change in internal energy of a system is the sum of w and q, which is a state function.

The realization that work and heat are both forms of energy transfer undergoes quite an extension by saying that internal energy is a state function. It means that although heat and work can be produced and destroyed (and transformed into each other), energy is conserved. This allows us to do some serious bookkeeping! We can write the law as:

$$\Delta U = w + q$$

But the (important!) bit about the state function is better represented if we talk about small changes of the energy:

$$dU = \delta w + \delta q$$

We write a straight Latin d for U to indicate when the change in a state function, where as the changes in work and heat are path-dependent. This is indicated by the 'crooked' δ. We can represent changes as integrals, but only for U can we say that regardless of path we get $\Delta U = U_2 - U_1$ if we go from state one to state two. (I.e. it only depends on the end points, not the path).

Notice that when we write dU or δq, we always mean infinitesimally small changes, i.e. we are implicitly taking a limit for the change approaching zero. To arrive at a macroscopic difference like ΔU or a macroscopic (finite) amount of heat q or work w **we need to integrate**.

We will now invoke the **first law of thermodynamics**:

- $dU = \delta q + \delta w$
- $\oint dU = 0$
- Internal energy is conserved

These are all ways of saying that internal energy is a state function.

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19.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred

Isothermal expansion of an ideal gas

For a monatomic ideal gas we have seen that energy $\langle E \rangle$ observed as $U = 3/2nRT$. This means that energy is only dependent on temperature and if a gas is compressed **isothermally**, then the internal energy does not change:

$$\Delta U_{isothermal-idealgas} = 0$$

This means that the reversible work must ***cancel*** the reversible heat:

$$\Delta U_{rev} = w_{rev} + q_{rev} = 0$$

Therefore

$$w_{rev} = -q_{rev}$$

so from the expression of the reversible work for expansion in the last section

$$q_{rev} = nRT \ln \frac{V_2}{V_1}$$

If $V_2 > V_1$ (expansion), then you (or the environment) **must** put heat into the system because this is a positive number.

Adiabatic expansion of an ideal gas

Now suppose you make sure that no heat can enter the cylinder. (Put it in styrofoam or so). Then the path can still be reversible (slow pulling) but the process is then adiabatic.

> This bat- part comes from a Greek verb *βαινω* (baino) that means walking, compare acro**bat**, someone who goes high places (acro-). The *δια* (dia) part means 'through' (cf. diagram, diorama, diagonal etc.) and the prefix *α*- (a-) denies it all (compare *atypical* versus *typical*).

So the styrofoam prevents the heat from walking through the wall. When expanding the gas from V_1 to V_2 it still does reversible work but where does that come from? It can only come from the internal energy itself. So in this case any energy change should consist of work (adiabatic means: $\delta q = 0$).

$$dU = \delta w_{rev}$$

This implies that the temperature must drop, because if U changes, then T must change.

The change of energy with temperature at constant volume is known as the heat capacity (at constant volume) C_v

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V$$

For an ideal gas U only changes with temperature, so that

Image:CH431_Image61.gif

or:

Image:CH431_Image62.gif

We can now compare two paths to go from state P_1, V_1, T_1 to state P_2, V_2, T_1:

1. Reversible isothermal expansion A
2. Reversible adiabatic expansion B followed by reversible isochoric heating C

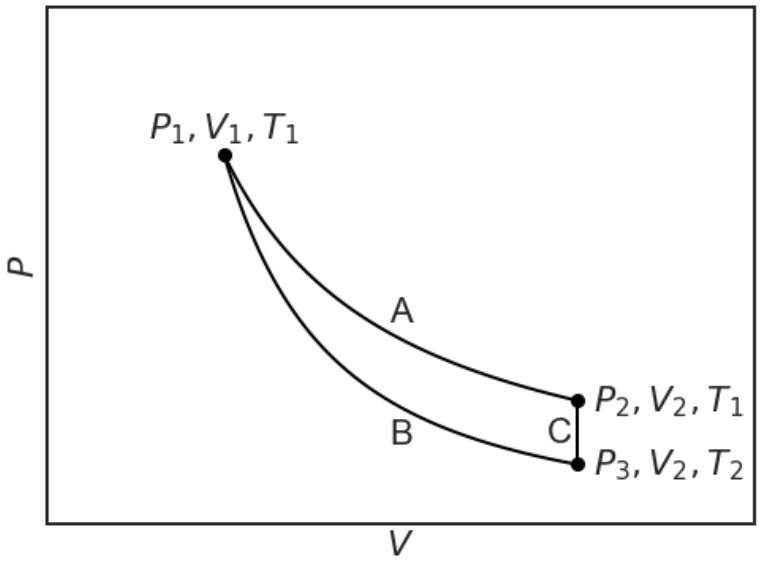


Figure __:

Notice that the temperature remains T_1 for path A (isotherm!), but that it drops to T_2 on the adiabat B, so that the cylinder has to be isochorically warmed up, C, to regain the same temperature.

ΔU_{tot} should be the same for both path A and the combined path B+C, because the end points are the same (U is a state function!). As the and points are at the same temperature and U only depends on T:

$$\Delta U_{tot} = 0$$

Along adiabat B:

$$q_{rev} = 0$$

Along isochoric heating C, there is no volume work because the volume is kept constant, so that:

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This is the only reversible heat involved in path B+C. However, we know that ΔU_{tot} for path A is zero (isothermal!). This means that the volume work along B must cancel the heat along C:

The book keeping looks as follows, all paths are reversible:

$$\Delta U_{B+C} = \Delta U_A = 0 = q_B + w_B + q_C + w_C$$

We know that $q_B = 0$ since it is an adiabat and $w_C = 0$ since it is an isochore:

$$\Delta U_{B+C} = \Delta U_A = 0 = 0 + w_B + q_C + 0$$

Therefore:

$$w_B = -q_C$$

We had already seen before that along the isotherm A:

$$w_A = -q_A = -nRT \ln \frac{V_1}{V_2}$$

As you can see \w_A\) and w_B are ***not*** the same. Work is a path function, even if reversible. As we are working with an ideal gas

we can be more precise about w_B and q_c as well. The term w_B along the adiabat is reversible volume work. Since there is no heat along B we can write a straight d instead of δ for the work contributions (It is the only contribution and must be identical to the state function dU):

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19.6: The Temperature of a Gas Decreases in a Reversible Adiabatic Expansion

We can make the same argument for the heat along C. If we do the three processes A and B+C only to a tiny extent we can write:

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And now we can integrate from V_1 to V_2 over the reversible adiabatic work along B and from T_1 to T_2 for the reversible isochoric heat along C. To separate the variables we do need to bring the temperature to the right side of the equation.:

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The latter expression is valid for a reversible adiabatic expansion of a monatomic ideal gas (say Argon) because we used the C_v expression for such a system. We can use the gas law $PV = nRT$ to translate this expression in one that relates pressure and volume see Eq 19.23

We can mathematically show that the temperature of a gas decreases during an adiabatic expansion. Assuming an ideal gas, the internal energy along an adiabatic path is:

$$\begin{aligned} d\bar{U} &= \delta q + \delta w \\ &= 0 - Pd\bar{V} \\ &= -Pd\bar{V} \end{aligned}$$

The constant volume heat capacity is defined as:

$$\bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V$$

We can rewrite this for internal energy:

$$d\bar{U} = \bar{C}_V dT$$

Combining these two expressions for internal energy, we obtain:

$$\bar{C}_V dT = -Pd\bar{V}$$

Using the ideal gas law for pressure of an ideal gas:

$$\bar{C}_V dT = -\frac{RT}{\bar{V}} d\bar{V}$$

Separating variables:

$$\frac{\bar{C}_V}{T} dT = -\frac{R}{\bar{V}} d\bar{V}$$

This is an expression for an ideal path along a reversible, adiabatic path that relates temperature to volume. To find our path along a PV surface for an ideal gas, we can start in TV surface and convert to a PV surface. Let's go from (T_1, V_1) to (T_2, V_2).

$$\int_{T1}^{T_2} \frac{\bar{C}_V}{T} dT = -\int_{\bar{V}_1}^{\bar{V}_2} \frac{R}{\bar{V}} d\bar{V}$$

$$\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) = R \ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{\bar{C}_V}\ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\frac{R}{\bar{C}_V}}$$

We know that:

$$R = \bar{C}_P - \bar{C}_V$$

$$\frac{R}{\bar{C}_V} = \frac{\bar{C}_P - \bar{C}_V}{\bar{C}_V} = \frac{\bar{C}_P}{\bar{C}_V} - 1$$

$$\frac{R}{\bar{C}_V} = \gamma - 1$$

Therefore:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\gamma-1}$$

This expression shows that volume and temperature are inversely related. That is, as the volume increase from V_1 to V_2, the temperature must decrease from T_1 to T_2.

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19.7: Work and Heat Have a Simple Molecular Interpretation

Statistical interpretation

We can use what we know about the statistical side of thermodynamics to give a simple interpretation to a change dU:

we see that because $\delta w_{rev} = -PdV$

Image:CH431_Image67.gif

Image:CH431_Image68.gif

See also section 17-5 :In this section it is shown that we can manipulate the partition function to find the pressure of a system by calculating the above moment of the distribution. Again we take the derivative of the logarithm of the partition function Q, this time versus V and show that the result resembles the last equation pretty closely (apart from a factor). Thus we get:

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Image:CH431_Image70.gif

Once again we can find an important quantity of our system by manipulating the partition function Q**.**

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19.8: Pressure-Volume Work

Enthalpy

An important point is that pressure-volume work $-PdV$ is only one kind of work. It is the important one for gases but for most other systems we are interested in other kinds of work (e.g. electrical work in a battery).

A good way to measure ΔU's is to make sure there are no work terms at all. If so:

$$\Delta U_{nowork} = q + w = q + 0 = q$$

However, this means that the $-PdV$ volume work term should also be zero and this implies we must keep volumes the same. That can actually be hard. Therefore we define at new state function ENTHALPY

$$H \equiv U + PV$$

(The $\equiv$ symbol is used to show that this equality is actually a definition.)

If we differentiate we get:

$$dH = dU + d(PV) = dU + PdV + VdP$$

We know that under reversible conditions we have

$$dU = \delta w + \delta q = -PdV + \delta q$$

(+ other work terms that we assume zero)

Thus,

$$dH = -PdV + \delta q + PdV + VdP$$

$$dH = \delta q + VdP$$

That means that as long as there is no other work and we keep the pressure constant:

$$\Delta H = q_P$$

instead of

$$\Delta U = q_V$$

Working at constant P is a lot easier to do than at constant V. This means that the enthalpy is a much easier state function to deal with than the energy U.

For example when we melt ice volumes change whether we like or not, but at long as the weather does not change too much pressure is constant. So if we measure how much heat we need to add to melt a mole of ice we get the molar heat of fusion:

Image:CH431 Image71.gif

Such enthalpies are measured and tabulated.

In this case the volume change is actually quite small, as it usually is for condensed matter. Only if we are dealing with gases is the difference between enthalpy and energy really important

So, U H for condensed matter, but U and H differ for gases.

A good example of this is the difference between the heat capacity at constant V and at constant P. For most materials there is

not much of a difference, but for an ideal gas we have

$$C_p = C - V + nR$$

Needless to say that the heat capacity is a path function: it depends on what you keep constant.

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19.9: Heat Capacity is a Path Function

Determining enthalpies from heat capacities.

The functions H and C_p are related by differentiation:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

This means that we can:

1. measure C_p as a function of temperature
2. integrate this function and find $H(T)$

However, there are problems with this approach:

1. Reference point: we have to deal with the lower limit of integration.
   Ideally we start at zero Kelvin (but we cannot get there), but how do we compare one compound to the other?
2. At temperatures where there is a phase transition there is a sudden jump in enthalpy. E.g. when ice melts we have to first add the heat of fusion until all ice is gone before the temperature can go up again (assuming all is done under reversible well-equilibrated conditions).
3. At the jumps in H, the C_p is infinite.

It should be stressed that there **are no absolute enthalpies**.

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19.10: Relative Enthalpies Can Be Determined from Heat Capacity Data and Heats of Transition

It should be stressed that there **are no absolute enthalpies**. All that is properly defined are differences in enthalpy ΔH and these are only defined for ***processes***

When dealing with enthalpies

Define the Process

For example for the process of:

Process 1: ***heating ice from -20°C to -0°C***

We could write $\Delta H_1 = \int C_{P,ice}$. dT from T=253K to T=273K = H(273) -H(253). But before moving beyond the melting point first a different process needs to take place, that of

Process 2: ***melting***

This gives us $\Delta_{fus}H = H_{liquid} - H_{solid}$ (both at 273K!). When we heat the liquid water further to say +20°C we would have to integrate over the heat capacity of the liquid.

Process 3: ***heating water from 0°C to +20°C***

We could write

$$\Delta H_3 = \int C_{P,water} dT$$

from T=273K to T=293K = H(293)-H(273).

The total change in enthalpy between -20 and +20 would be the sum of the three enthalpy changes.

$$\Delta H_{totalprocess} = \Delta H_1 + \Delta_{fus}H + \Delta H_3$$

Of course we could consider doing the same calculation for any temperature between -20 and +20 and summarize all our results in a graph. The three processes can thus schematically be shown in Figure 19.10.1 .

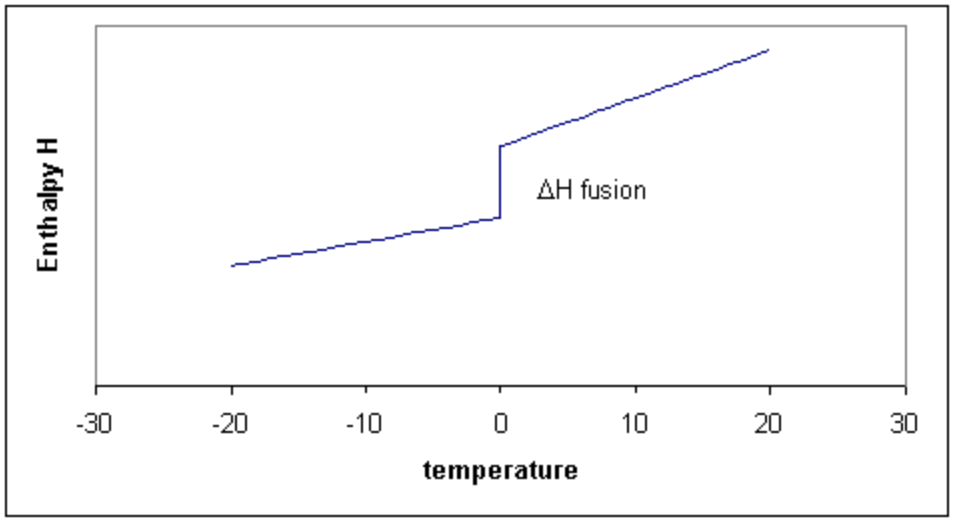


Figure 19.10.1 *: Schematic enthalpy function showing the jump at the melting point*

Notice that the slopes (i.e. the heat capacities!) before and after the melting point differ. The slope for the liquid is a little steeper because the liquid has more degrees of freedom and therefore the heat capacity of the liquid tends to be higher than of the solid. In the figure the enthlapy curves are shown as straight lines. This would be the case if the heat capacities are *constant* over the temperature interval. Although C_p is typically a 'slow' or 'weak' function of temperature it usually does change a bit, which means that the straight lines for H become curves.

Although C_p is typically a 'slow' or 'weak' function of temperature and is well approximated as a constant.

Notice that for process two, the temperature is constant, that means that ΔT or dT is zero, but ΔH is finite, consequently ΔH/ΔT is infinitly large. Taking the limit for ΔT going to zero, we get a derivative:

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

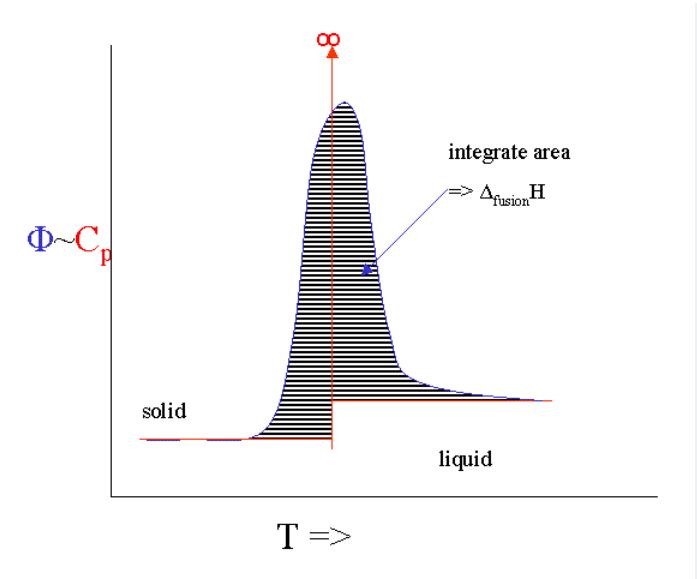
This derivative, the heat capacity must undergo a singularity: the slope is infinitely large (i.e, the H curve goes straight up). When there are more phase transitions, more discontinuities in H and singularities in C_p result (Figure 19.10.1). Note that $H(T) - H(0)$, not $H(T)$ is plotted to avoid the question what the absolute enthalpy is.

Scanningcalorimetry

There is technique that allows us to measure the heat capacity as a function of temperature fairly directly. It is called Differential Scanning Calorimetry (DSC). You put a sample in a little pan and put the pan plus an empty reference pan in the calorimeter. The instrument heats up both pans with a constant heating rate. Both pans get hotter by ***conduction***, but the heat capacity of the filled pan is obviously bigger. This means that the heat flow into the sample pan must be a bit bigger than into the empty one. This differential heat flow induces a tiny temperature difference ΔT between the two pans that can be measured. This temperature difference is proportional to the heat flow difference which is proportional to the heat capacity difference.

$$\Delta T\ \Delta\Phi\ \Delta_{betweenpans} C_p = C_p^{sample}\ (if the pans cancel)$$

However, there are number of serious broadening issues with the technique. If you melt something you will never get to see the infinite singularity of the heat capacity. Instead it broadens out into a peak. If you integrate the peak you get the Δ_{fusion}H and the onset is calibrated to give you the melting point.



The ideal heat capacity signal and its broadened DSC signal

It is even possible to heat the sample with a rate that fluctuates with a little sine wave. This "Modulated DSC" version can even give you the (small) difference in C_p before and after the melting event.

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19.11: Enthalpy Changes for Chemical Equations are Additive

Hess's law

As enthalpy and energy are state functions we should expect ***additivity*** of U and H when we study chemical reactions. This additivity is expressed in **Hess's Law**. The additivity has important consequences and the law finds wide spread application in the prediction of heats of reaction.

1. The reverse reaction has the negative enthalpy of the forward one.
2. If we can do a reaction in two steps we can calculate the enthalpy of the combined reaction by adding up:

Reaction	Enthalpy
$C_{(s)}$ + ½ $O_{2(g)}$ -> $CO_{(g)}$	$\Delta_r H$ = -110.5 kJ
$CO_{(g)}$ + ½ $O_{2(g)}$ -> $CO_{2(g)}$	$\Delta_r H$ = -283.0 kJ
This means that	----------+
$C_{(s)}$ + O2(g) -> CO2(g)	$\Delta_r H$ = -393.5 kJ

By this mechanism it is often possible to calculate the heat of a reaction even if this reaction is hard to carry out. E.g. we could burn both graphite and diamond and measure the heats of combustion for both. The difference would give us the heat of the transformation reaction from graphite to diamond.

Reaction-as-written convention (caution!)

The enthalpy is for the ***reaction-as-written***. That means that if we write:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

with $\Delta_r H$ = -221 kJ (***not***: -110.5 kJ)

Reverse reactions

Because H is a state function the reverse reaction has the same enthalpy but with opposite sign

$$2CO(g) \rightarrow 2C(s) + O_2(g)$$

with $\Delta_r H$ = +221 kJ

Combining values

It is quite possible that you cannot really do a certain reaction in practice. For many reactions we can arrive at enthalpy values by doing some bookkeeping. For example, we can calculate the enthalpy for the reaction of PCl_3 with chlorine if we know the two reactions that the elements phosphorous and chlorine can undergo.

> You do have to make sure you balance your equations properly!

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19.12: Heats of Reactions Can Be Calculated from Tabulated Heats of Formation

Reaction enthalpies are important, but difficult to tabulate. However, because enthalpy is a state function, it is possible to use **Hess' Law** to simplify the tabulation of reaction enthalpies. Hess' Law is based on the addition of reactions. By knowing the reaction enthalpy for constituent reactions, the enthalpy of a reaction that can be expressed as the sum of the constituent reactions can be calculated. The key lies in the canceling of reactants and products that °Ccur in the "data" reactions but not in the "target reaction.

Example 19.12.1:

Find ΔH_{rxn} for the reaction

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Given

$$C(gr) + ½O_2(g) \rightarrow CO(g)$$

with $\Delta H_1 = -110.53\ kJ$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_2 = -393.51\ kJ$

Solution

The target reaction can be generated from the data reactions.

$$2\times\ [CO(g) \rightarrow C(gr) + O_2(g)]$$

plus

$$2\times\ [C(gr) + 2O_2(g) \rightarrow 2CO_2(g)]$$

equals

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

so

$$2\times\Delta H_1 = -787.02\,kJ$$

$$2\times\Delta H_2 = 221.06\,kJ$$

$$2\times\Delta H_1 + 2\times\Delta H_2 = -565.96\,kJ$$

Standard Enthalpy of Formation

One of the difficulties with many thermodynamic state variables (such as enthalpy) is that while it is possible to measure changes, it is impossible to measure an absolute value of the variable itself. In these cases, it is necessary to define a zero to the scale defining the variable. For enthalpy, the definition of a zero is that the standard enthalpy of formation of a pure element in its standard state is zero. All other enthalpy changes are defined relative to this standard. Thus it is essential to very carefully define a standard state.

Definition: the Standard State

The standard state of a substance is the most stable form of that substance at 1 atmosphere pressure and the specified temperature.

Using this definition, a convenient reaction for which enthalpies can be measured and tabulated is the **standard formation reaction**. This is a reaction which forms one mole of the substance of interest in its standard state from elements in their standard states. The enthalpy of a standard formation reaction is the **standard enthalpy of formation** (ΔH_{f^o}). Some examples are

- $NaCl(s)$:

  $$Na(s) + ½Cl_2(g) \rightarrow NaCl(s)$$

  with $\Delta H_f^o = -411.2\ kJ/mol$
- $C_3H_8(g)$:

  $$3C(gr) + 4H_2(g) \rightarrow C_3H_8(g)$$

  with $\Delta H_f^o = -103.8\ kJ/mol$

It is important to note that the standard state of a substance is **temperature dependent**. For example, the standard state of water at -10 °C is solid, whereas the standard state at room temperature is liquid. Once these values are tabulated, calculating reaction enthalpies becomes a snap. Consider the heat combustion (ΔH_c) of methane (at 25 °C) as an example.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The reaction can expressed as a sum of a combination of the following standard formation reactions.

$$C(gr) + 2H_2(g) \rightarrow CH_4(g)$$

with $\Delta H_f^o = -74.6\ kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\ kJ/mol$

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$$

with $\Delta H_f^o = -285.8\ kJ/mol$

The target reaction can be generated from the following combination of reactions

$$-1\times [C(gr) + 2H_2(g) \rightarrow CH_4(g)]$$

$$CH_4(g) \rightarrow C(gr) + 2H_2(g)$$

with $\Delta H_f^o = -1\times [-74.6\,kJ/mol] = 74.6\ kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\ kJ/mol$

$$2\times [H_2(g) + ½O_2(g) \rightarrow H_2O(l)]$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

with $\Delta H_f^o = 2\times [-285.8\,kJ/mol] = -571.6\ kJ/mol.$

$$CH_4(g) + 2O_2(g) \rightarrow CO2_(g) + 2H_2O(l)$$

with $\Delta H_c^o = -890.5\ kJ/mol$

Alternately, the reaction enthalpy could be calculated from the following relationship

$$\Delta H_{rxn} = \sum_{products} \nu \cdot \Delta H_f^o - \sum_{reactants} \nu \cdot \Delta H_f^o$$

where ν is the stoichiometric coefficient of a species in the balanced chemical reaction. For the combustion of methane, this calculation is

$$\begin{aligned} \Delta_{rxn} &= (1\,mol)\left(\Delta H_f^o(CO_2)\right) + (2\,mol)\left(\Delta H_f^o(H_2O)\right) - (1\,mol)\left(\Delta H_f^o(CH_4)\right) && (19.12.1)\\ &= (1\,mol)(-393.5\,kJ/mol) + (2\,mol)\,(-285.8\,kJ/mol) - (1\,mol)\,(-74.6\,kJ/mol) && (19.12.2)\\ &= -890.5\,kJ/mol && (19.12.3) \end{aligned}$$

A note about units is in order. Note that reaction enthalpies have units of kJ, whereas enthalpies of formation have units of kJ/mol. The reason for the difference is that enthalpies of formation (or for that matter enthalpies of combustion, sublimation, vaporization, fusion, etc.) refer to specific substances and/or specific processes involving those substances. As such, the total enthalpy change is scaled by the amount of substance used. General reactions, on the other hand, have to be interpreted in a very specific way. When examining a reaction like the combustion of methane

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

with $\Delta H_{rxn} = -890.5\ kJ$. The correct interpretation is that the reaction of one mole of CH_4(g) with two moles of O_2(g) to form one mole of CO_2(g) and two moles of H_2O(l) releases 890.5 kJ at 25 °C.

Ionization Reactions

Ionized species appear throughout chemistry. The energy changes involved in the formation of ions can be measured and tabulated for several substances. In the case of the formation of positive ions, the enthalpy change to remove a single electron at 0 K is defined as the **ionization potential**.

$$M(g) \rightarrow M^+(g) + e^-$$

with $\Delta H(0K) \equiv 1^{st}\ \text{ionization potential (IP)}$

The removal of subsequent electrons requires energies called the 2nd Ionization potential, 3rd ionization potential, and so on.

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

with $\Delta H(0K) \equiv 2^{nd} IP$

$$M^{2+}(g) \rightarrow M^{3+}(g) + e^-$$

with $\Delta H(0K) \equiv 3^{rd} IP$

An atom can have as many ionization potentials as it has electrons, although since very highly charged ions are rare, only the first few are important for most atoms.

Similarly, the **electron affinity** can be defined for the formation of negative ions. In this case, the first electron affinity is defined by

$$X(g) + e^- \rightarrow X^-(g)$$

with $-\Delta H(0K) \equiv 1^{st}\ \text{electron affinity (EA)}$

The minus sign is included in the definition in order to make electron affinities mostly positive. Some atoms (such as noble gases) will have negative electron affinities since the formation of a negative ion is very unfavorable for these species. Just as in the case of ionization potentials, an atom can have several electron affinities.

$$X^-(g) + e^- \rightarrow X^{2-}(g)$$

with $-\Delta H(0K) \equiv 2^{nd} EA$.

$$X^{2-}(g) + e^- \rightarrow X^{3-}(g)$$

with $-\Delta H(0K) \equiv 3^{rd} EA$.

Average Bond Enthalpies

In the absence of standard formation enthalpies, reaction enthalpies can be estimated using average bond enthalpies. This method is not perfect, but it can be used to get ball-park estimates when more detailed data is not available. A **bond dissociation energy** D is defined by

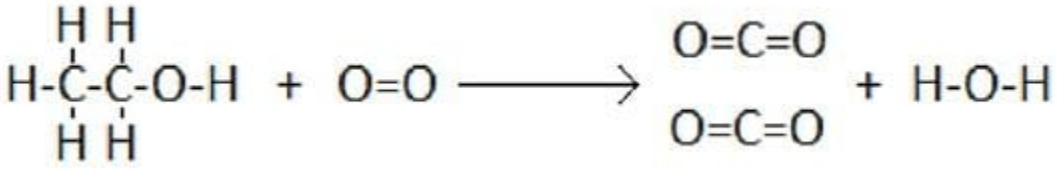
$$XY(g) \rightarrow X(g) + Y(g)$$

with $\Delta H \equiv D(X-Y)$

In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\Delta H_{rxn} = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

As an example, consider the combustion of ethanol:



In this reaction, five C-H bonds, one C-C bond, and one C-O bond, and one O=O bond must be broken. Also, four C=O bonds, and one O-H bond are formed.

Bond	Average Bond Energy (kJ/mol)
C-H	413
C-C	348
C-O	358
O=O	495
C=O	799
O-H	463

The reaction enthalpy is then given by

$$\begin{aligned} \Delta H_c &= 5(413\,kJ/mol) + 1(348\,kJ/mol) + 1(358\,kJ/mol) \\ &\quad + 1(495\,kJ/mol) - 4(799\,kJ/mol) - 2(463\,kJ/mol) \\ &= -856\,kJ/mol \end{aligned} \tag{19.12.4}$$

Because the bond energies are defined for gas-phase reactants and products, this method does not account for the enthalpy change of condensation to form liquids or solids, and so the result may be off systematically due to these differences. Also, since the bond enthalpies are averaged over a large number of molecules containing the particular type of bond, the results may deviate due to the variance in the actual bond enthalpy in the specific molecule under consideration. Typically, reaction enthalpies derived by this method are only reliable to within ± 5-10%.

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19.13: The Temperature Dependence of ΔH

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

$$dH = C_p\, dT$$

And so for a temperature change from T_1 to T_2

$$\Delta H = \int_{T_2}^{T_2} C_p\, dT \tag{19.13.1}$$

Equation 19.13.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p\, \Delta T \tag{19.13.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 19.13.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{19.13.3}$$

After combining Equations 19.13.3 and 19.13.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) dT \tag{19.13.4}$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2}T^2 - \frac{c}{T}\right]_{T_1}^{T_2} \tag{19.13.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{19.13.6}$$

This expression can then be used with experimentally determined values of a, b, and c, some of which are shown in the following table.

Table 19.13.1: Empirical Parameters for the temperature dependence of C_p

Substance	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-2})	c (J mol^{-1} K)
C(gr)	16.86	4.77 x 10^{-3}	-8.54 x 10^{5}
CO_2(g)	44.22	8.79 x 10^{-3}	-8.62 x 10^{5}
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77 x 10^{-3}	-5.0 x 10^{4}
Pb(s)	22.13	1.172 x 10^{-2}	9.6 x 10^{4}

Example 19.13.1: Heating Lead

What is the molar enthalpy change for a temperature increase from 273 K to 353 K for Pb(s)?

Solution

The enthalpy change is given by Equation 19.13.1 with a temperature dependence C_p given by Equation 19.13.1 using the parameters in Table 19.13.1. This results in the integral form (Equation 19.13.6):

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

when substituted with the relevant parameters of Pb(s) from Table 19.13.1.

$$\begin{aligned}\Delta H =& (22.14\,\frac{J}{mol\,K}(353\,K - 273\,K) \\ &+ \frac{1.172 \times 10^{-2}\frac{J}{mol\,K^2}}{2}\left((353\,K)^2 - (273\,K)^2\right) \\ &- 9.6 \times 10^4\,\frac{J\,K}{mol}\left(\frac{1}{(353\,K)} - \frac{1}{(273\,K)}\right) \\ \Delta H =& 1770.4\,\frac{J}{mol} + 295.5\,\frac{J}{mol} + 470.5\,\frac{J}{mol} \\ =& 2534.4\,\frac{J}{mol}\end{aligned}$$

For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

$$\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \int_{T_1}^{T_2} \Delta C_p \Delta T$$

Example 19.13.2: Enthalpy of Formation

The enthalpy of formation of NH_3(g) is -46.11 kJ/mol at 25 °C. Calculate the enthalpy of formation at 100 °C.

Solution

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightleftharpoons \mathrm{2\,NH_3\,(g)}$$

with $\Delta H\ (298\ K) = -46.11\ kJ/mol$

Compound	Cp (J mol^{-1} K^{-1})
N_2(g)	29.12
H_2(g)	28.82
NH_3(g)	35.06

$$\begin{aligned}\Delta H(373\,K) &= \Delta H(298\,K) + \Delta C_p \Delta T \\ &= -46110 + \frac{J}{mol}\left[2\left(35.06\frac{J}{mol\,K}\right) - \left(29.12\,\frac{J}{mol\,K}\right) - 3\left(28.82\,\frac{J}{mol\,K}\right)\right](373\,K - 298\,K) \\ &= -49.5\,\frac{kJ}{mol}\end{aligned}$$

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19.14: Enthalpy is a State Function

Our expression for internal energy at constant pressure:

$$\Delta U = q_P + w = q_P - P\Delta V$$

Rearrange:

$$q_P = \Delta U + P\Delta V = U_2 - U_1 + P(V_2 - V_1)$$
$$q_P = (U_2 + PV_2) - (U_1 + PV_1)$$

We can define this term as enthalpy:

$$H \equiv U + PV$$

This is a new state function.

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19.E: The First Law of Thermodynamics (Exercises)

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{19.E.1}$$

You can see from Equation 19.E.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

Exercise 19.E.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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20: ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

20.1: Energy Does not Determine Spontaneity

20.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Energy Dispersal

20.3: Unlike heat, Entropy is a State Function

20.4: The Second Law of Thermodynamics

20.5: The Famous Equation of Statistical Thermodynamics is S=k ln W

20.6: We Must Always Devise a Reversible Process to Calculate Entropy Changes

20.7: Thermodynamics Provides Insight into the Conversion of Heat into Work

20.8: Entropy Can Be Expressed in Terms of a Partition Function

20.9: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition

20.E: Entropy and The Second Law of Thermodynamics (Exercises)

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20.1: Energy Does not Determine Spontaneity

There are many spontaneous events in nature. If you open the valve in both cases a spontaneous event occurs. In the first case the gas fills the evacuated chamber, in the second the gases will mix. The state functions U and H do not give us a clue what will happen. You might think that only those events are spontaneous that produce heat.

Not so:

- If you dissolve $\mathrm{KNO_3}$ in water, it does so spontaneously, but the solution gets ***cold***.
- If you dissolve KOH in water, it does so spontaneously, but the solution gets ***hot***.

Clearly the first law is not enough to describe nature.

Two items left on our wish list

The development of the new state function entropy has brought us much closer to a complete understanding of how heat and work are related:

1. the spontaneity problem
   we now have a criterion for spontaneity for isolated systems

2. the asymmetry between work->heat (dissipation) and heat->work (power generation)
   at least we can use the new state law to predict the limitations on the latter.

Two problems remain:

1. we would like a spontaneity criterion *for all systems* (not just isolated ones)
2. we have a new state function S, but what is it?

Entropy on a microscopic scale

Let us start with the latter. Yes we can use S to explain the odd paradox between w and q both being forms energy on the one hand, but the conversion being easier in one direction than the other, but we have introduced the concept *entropy* purely as a phenomenon on iis own. Scientifically there is nothing wrong with such a phenomenological theory except that experience tells us that if you can understand the phenomenon itself better your theory becomes more powerful.

To understand entropy better we need to leave the macroscopic world and look at what happens on a molecular level and do statistics over many molecules. First, let us do a bit more statistics of the kind we will need.

Permutations

If we have n distinguishable objects, say playing cards we can arrange them in a large number of ways. For the first object in our series we have n choices, for number two we have $n-1$ choices (the first one being spoken for) etc. This means that in total we have

$$W = n(n-1)(n-2)\ldots.4.3.2.1 = n! \text{ choices.}$$

The quantity W is usually called the number of realizations in thermodynamics.

The above is true if the objects are all distinguishable. If they fall in groups within which they are not distinguishable we have to correct for all the swaps within these groups that do not produce a distinguishably new arrangement. This means that W becomes $\frac{n!}{a!b!c!\ldots z!}$ where a,b, c to z stands for the size of the groups. (Obviously $a+b+c+..+z=n$)

In thermodynamincs our 'group of objects' is typically an ensemble of systems, think of size N_{av} and so the factorial become horribly large. This makes it necessary to work with logarithms. Fortunately there is a good approximation (by Stirling) for a

logarithmic factorial:

$$\ln N! \approx N \ln N - N$$

Causality vs. Correlation

In Europe nosey little children who are curious to find out where their newborn little brother or sister came from, often get told that the stork brought it during the night. When you look at the number of breeding pairs of this beautiful bird in e.g. Germany since 1960 you see a long decline to about 1980 when the bird almost got extinct. After that the numbers go up again due to breeding programs mostly. The human birth rate in the country follows a pretty much identical curve and the correlation between the two is very high (>0.98 or so). (Dr H. Sies in Nature (volume 332 page 495; 1988). Does this prove that storks indeed bring babies?



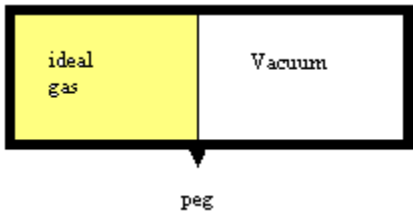
An adult White Stork. from Wikipedia (credit: Frank Vassen).

Answer:

No, it does ***not*** show causality, just a correlation due a common underlying factor. In this case that is the choices made by the German people. First they concentrated on working real hard and having few children to get themselves out of the poverty WWII had left behind and neglected the environment, then they turned to protect the environment and opened the doors to immigration of people, mostly from Muslim countries like Turkey or Morocco, that usually have larger families. The lesson from this is that you can only conclude causality ***if*** you are sure that there are no other intervening factors.

Changing the size of the box with the particles in it

The expansion of an ideal gas against vacuum is really a wonderful *model experiment*, because *nothing else happens* but a spontaneous expansion and a change in entropy. No energy change, no heat, no work, no change in mass, no interactions, nothing. In fact, it does not even matter whether we consider it an isolated process or not. We might as well do so.

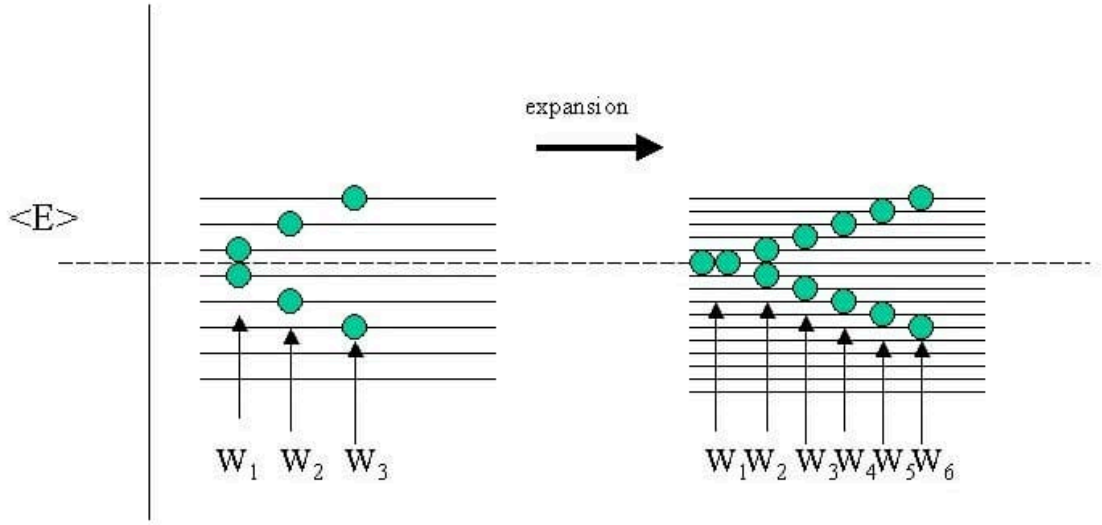


Physicists and Physical Chemists love to find such experiments that allows them to retrace *causality*. All this means that if we look at what happens at the atomic level, we should be able to retrace the ***cause*** of the entropy change. As we have seen before, the available energy states of particles in a box depend on the size of the box.

$$E_{kin} = \frac{h^2}{8ma^2}\left[n_1^2 + n_2^2 + n_2^2\right]$$

Clearly if the side (a and therefore the volume of the box changes, the energy spacing between the states will become smaller.

Therefore during our expansion against vacuum, the energy states inside the box are changing. Because U does not change the *average* energy $\langle E \rangle$ is constant. Of course this average is taken over a great number of molecules (*systems*) in the gas (the *ensemble*), but let's look at just two of them and for simplicity let us assume that the energy of the states are equidistant (rather than quadratic in the quantum numbers n).



As you can see there is more than one way to skin a cat, or in this case to *realize* the same average $\langle E \rangle$ of the complete ensemble (of only two particles admittedly). Before expansion I have shown three realizations W_1, W_2, W_3 that add up to the same $\langle E \rangle$. After expansion however, there are more energy states available and the schematic figure shows twice as many realizations W in the same energy interval.

Boltzmann was the first to postulate that this is what is at the root of the entropy function, not so much the (total) energy itself (that stays the same!), but the number of ways the energy can be distributed in the ensemble. Note that because the ensemble average (or total) energy is identical, we could also say that the various realizations W represent the degree of *degeneracy* Ω of the ensemble.

Boltzmann considered a much larger (*canonical*) ensemble consisting of a great number of identical *systems* (e.g. molecules, but it could also be planets or so). If each of our systems already has a large number of energy states the systems can all have the same (total) energy but distributed in rather different ways. This means that two systems within the ensemble can either have the same distribution or a different one. Thus we can divide the ensemble A in subgroups a_j having the same energy distribution and calculate the number of ways to distribute energy in the ensemble A as

$$W = \frac{A!}{a1!a2!\ldots}.$$

Boltzmann postulated that entropy was directly related to the number of realizations W, that is the number of ways the same energy can be distributed in the ensemble. This leads immediately to the concept of order versus disorder, e.g, if the number of realizations is $W = 1$, all systems must be in the same state (W=A! / A!0!0!0!...) which is a very orderly arrangement of energies.

If we were to add two ensembles to each other the total number of possible arrangements W_{tot} becomes the product W_1W_2 but the entropies should be additive. As logarithms transform products into additions Boltzmann assumed that the relation between W and S should be logarithmic and wrote:

$$S = k \ln W$$

Again, if we consider a very ordered state, e.g. where all systems are in the ground state the number of realizations A!/A!= 1 so that the entropy is zero. If we have a very messy system where the number of ways to distribute energy over the many many different states is very large S becomes very large. Thus entropy is very large.

This immediately gives us the driving force for the expansion of a gas into vacuum or the mixing of two gases. We simply get

more energy states to play with, this increases W. This means an increase in S. This leads to a spontaneous process.

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20.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Energy Dispersal

In spontaneous processes for an isolated system, there is a competition between minimizing the energy of the system and increasing the dispersal of energy within the system. If energy is constant, then the system will evolve to maximize energy dispersal. If energy dispersal is not a factor, the system will evolve to minimize its energy. We already have a quantitative basis for the energy of a system and we need to do the same for energy dispersal. Suppose we have a small reversible change dU in the energy of an ideal gas. We know that U only depends on temperature:

$$dU = C_v dT$$

We also know that any reversible work would be volume work.

$$\delta w_{rev} = -PdV$$

This means that we can write:

$$\begin{aligned} \delta q_{rev} &= dU - \delta w_{rev} \\ &= C_v dT + PdV \end{aligned}$$

Let us examine if this represents an **exact differential**. If δq were an exact differential, we could write the total differential:

$$\delta q_{rev} = \left(\frac{\partial q}{dT}\right)_V dT + \left(\frac{\partial q}{dV}\right)_T dV$$

And the following would be true:

$$\frac{\partial^2 q_{rev}}{\partial T \partial V} = \frac{\partial^2 q_{rev}}{\partial V \partial T}$$

From our equation above, we know that:

$$\frac{\partial q_{rev}}{\partial T} = C_V$$

$$\frac{\partial q_{rev}}{\partial V} = P$$

Therefore, the following should be true:

$$\frac{\partial C_V}{\partial V} = \frac{\partial P}{\partial T}$$

However,

$$\frac{\partial C_v}{\partial V} = 0$$

Because C_v does not depend on volume (only T, just like U: it is its derivative). And:

$$\frac{\partial P}{\partial T} = \frac{\partial nRT}{\partial T} = \frac{nR}{V}$$

Which is not zero!! Clearly, δq_{rev} is **not a state function**, but look what happens if we multiply everything with an 'integration factor' $1/T$:

$$\frac{\delta q_{rev}}{T} = \frac{C_v}{T} dT + \frac{P}{T} dV$$

$$\frac{\partial C_v/T}{\partial V} = 0$$

Because $\frac{C_v}{T}$ does not depend on volume. However,

$$\frac{\partial (P/T)}{\partial T} = \frac{\partial (nR/V)}{\partial T} = 0$$

Thus, the quantity $dS = \frac{\delta q_{rev}}{T}$ is an exact differential, so S is a state function and it is called **entropy**. Entropy is the dispersal of energy, or equivalently, the measure of the number of possible microstates of a system.

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20.3: Unlike heat, Entropy is a State Function

Circular integrals

Because entropy is a state function, it integrates to zero over any circular path going back to initial conditions, just like U and H:

$$\oint dS = 0$$

$$\oint dH = 0$$

$$\oint dU = 0$$

As discussed previously, we can use this fact to revisit the isotherm + isochore + adiabat circular path (Figure 20.3.1).

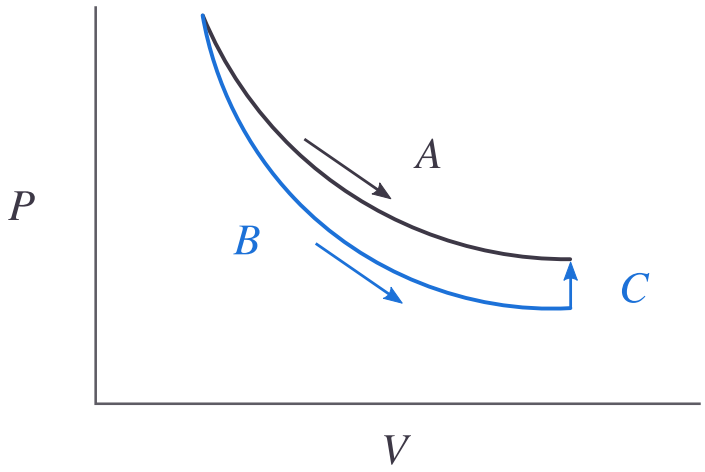


Figure 20.3.1 : A: isothermal expansion, B:adiabat, C:isochore (CC BY-NC; Ümit Kaya via LibreTexts)

Along adiabat B and isochore C:

- There is no heat transfer along adiabat B:

$$q_{rev,B} = 0$$

- There is no work along isochore C:

$$\delta w = 0$$

- But the temperature changes from T_2 back to T_1. This requires heat:

$$q_{rev,C} = C_V \Delta T$$

Along the isotherm A:

- We have seen that

$$q_{rev,A} = nRT \ln \frac{V_2}{V_1}$$

The quantities $q_{rev,A}$, $q_{rev,B}$, and $q_{rev,C}$ are ***not*** the same, which once again underlines that heat is a path function. How about entropy?

First, consider the combined paths of B and C:

$$q_{rev,B+C} = \int_{T_2}^{T_1} C_v dT$$

$$\int dS_{B+C} = \int \frac{dq_{rev,B+C}}{T} = \int_{T_2}^{T_1} \frac{C_v}{T} dT$$

We had seen this integral before from Section 19-6, albeit from T_1 to T_2:

$$\Delta S_{B+C} = nR \ln \frac{V_2}{V_1} \tag{20.3.1}$$

(Notice sign in Equation 20.3.1 is positive)

Along the isotherm A:

$$q_{rev,A} = nRT \ln \frac{V_2}{V_1}$$

T is a constant so we can just divide $q_{rec,A}$ by T to get ΔS_A:

$$\Delta S_A = nR \ln \frac{V_2}{V_1}$$

We took two different paths to get start and end at the same points. Both paths had the same change in entropy. Clearly entropy is a *state function* while q_{rev} is not.

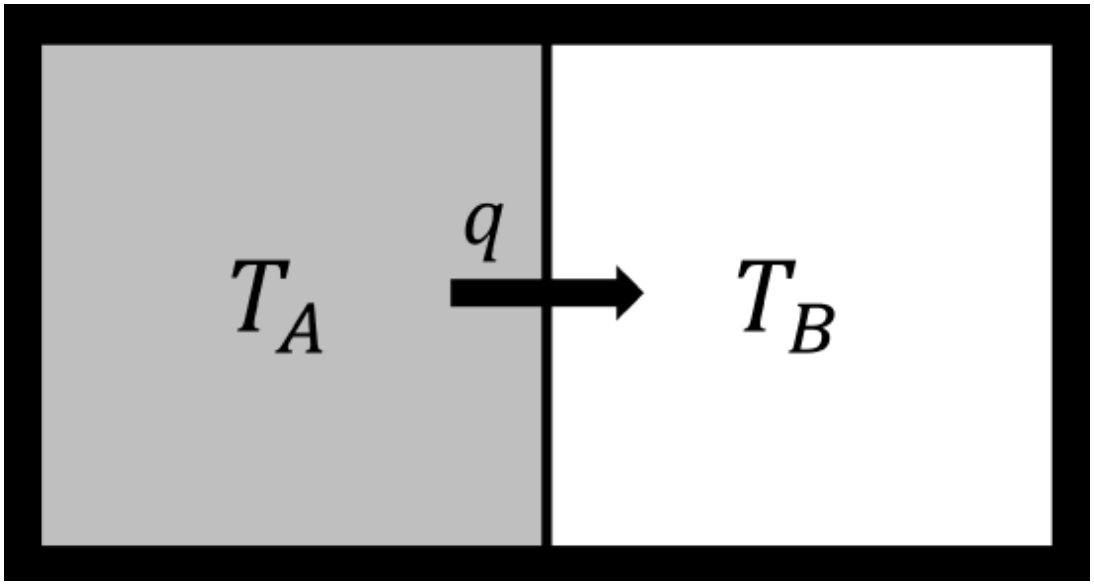
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20.4: The Second Law of Thermodynamics

Spontaneity of an isolated system

> An **isolated system** is a little more than just adiabatic. In the latter heat cannot get in or out. In an isolated system *nothing* gets in or out, neither heat nor mass nor even any radiation, such as light. The isolated system is like a little universe all to itself.

Let us consider a zero law process. We have two identical blocks of metal, say aluminum. They are each at thermal equilibrium, but at different temperatures. They are brought into contact with each other but isolated from the rest of the universe.



- ***Zeroth law***: *Heat will flow from hot to cold*
- ***First law***: *There is no change in total energy*

so:

$$dU_A = -dU_B$$

There is also no work so:

$$dU_A = \delta q_A + 0$$

Because U is a state function this makes q a state function as well, otherwise this equality does not hold. As there is only one term on the right there is only one path (along q). So we could write:

$$dU_A = dq_A$$

This implies that we do not need to worry about reversible and irreversible paths as there is only one path. Since:

$$dS = \frac{\delta q_{rev}}{T}$$

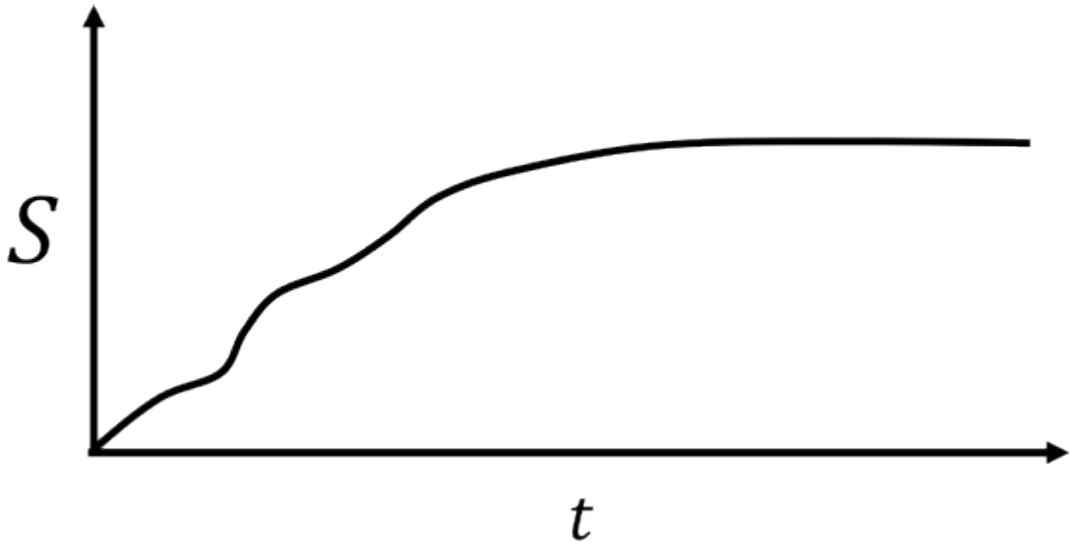
In this particular case:

$$TdS = \delta q_{rev} = dU$$

Thus we get:

$$dS = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} = \frac{dU_A}{T_A} - \frac{dU_A}{T_B} = dU_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right)$$

Clearly as long as the two temperatures are not the same dS is not zero and entropy is not conserved. Instead it is **increasing**. Over time, the temperatures will become the same (if the blocks are identical, the final temperature is the average of T_A and T_B) and the entropy will reach a maximum.



For our two identical blocks of metal (with same heat capacity, C_V), we can, in fact, derive that the entropy change:

$$\Delta S = C_V \ln \left[\frac{T_A^2 + T_B^2}{4 T_A T_B} \right].$$

This is indeed a positive quantity. In general, we can say for an isolated system:

$$dS \geq 0$$

Thus if we are dealing with a spontaneous (and isolated) process $dS > 0$ and ***entropy is being produced***. This gives us a ***criterion for spontaneity***.

Entropy exchange of an open system

In an isolated system dS represents the produced entropy dS_{prod} and this is a good criterion for spontaneity. Of course the requirement that the system is isolated is very restrictive and makes the criterion as good as useless... What happens in a system that can exchange heat with the rest of the universe? We do have entropy changes in that case, but part of them may have nothing to do with production, because we also have to consider the heat that is exchanged.

$$dS = dS_{prod} + dS_{exchange}$$

If the process is reversible (that is completely non-spontaneous) we are dealing with δq_{rev} so that $dS_{exchange} = \delta q_{rev}/T$, but that is also what dS_{tot} is equal to (by definition). This leaves no room for entropy production.

So we have:

Isolated: $dS = dS_{prod} + 0$

Reversible $dS = 0 + \delta q_{rev}/T$

Notice that this demonstrates that for non-isolated systems entropy change is *not* a good criterion for spontaneity at all... In the case the heat exchange is ***irreversible*** *part* of the entropy is entropy production by the system:

Irreversible: $dS = dS_{prod} + \delta q_{irrev}/T$

$dS > \delta q_{irrev}/T$ in this case.

Generalizing the isolated, irreversible and reversible cases we may say:

$$dS \geq \frac{\delta q}{T}$$

This is the ***Clausius inequality***.

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20.5: The Famous Equation of Statistical Thermodynamics is S=k ln W

A common interpretation of entropy is that it is somehow a measure of chaos or randomness. There is some utility in that concept. Given that entropy is a measure of the dispersal of energy in a system, the more chaotic a system is, the greater the dispersal of energy will be, and thus the greater the entropy will be. Ludwig Boltzmann (1844 – 1906) (O'Connor & Robertson, 1998) understood this concept well, and used it to derive a statistical approach to calculating entropy. Boltzmann proposed a method for calculating the entropy of a system based on the number of energetically equivalent ways a system can be constructed.

Boltzmann proposed an expression, which in its modern form is:

$$S = k_b \ln(W) \tag{20.5.1}$$

W is the number of available microstates in a macrostate (ensemble of systems) and can be taken as the quantitative measure of energy dispersal in a macrostate:

$$W = \frac{A!}{\prod_j a_j!}$$

Where a_j is the number of systems in the ensemble that are in state j and A represents the total number of systems in the ensemble:

$$A = \sum_j a_j$$

Equation 20.5.1 is a rather famous equation etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics (Figure $20.5.1$).



Figure $20.5.1$: Ludwig Boltzmann (1844 - 1906)

Example $20.5.1$:

Calculate the entropy of a carbon monoxide crystal, containing 1.00 mol of CO, and assuming that the molecules are randomly oriented in one of two equivalent orientations.

Solution:

Using the Boltzmann formula (Equation 20.5.1):

$$S = nK\ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$\begin{aligned} S &= \left(1.00\,mol\cot\frac{6.022\times10^{23}}{1\,mol}\right)(1.38\times10^{-23}J/K)\ln 2 \\ &= 5.76\,J/K \end{aligned}$$

Contributors and Attributions

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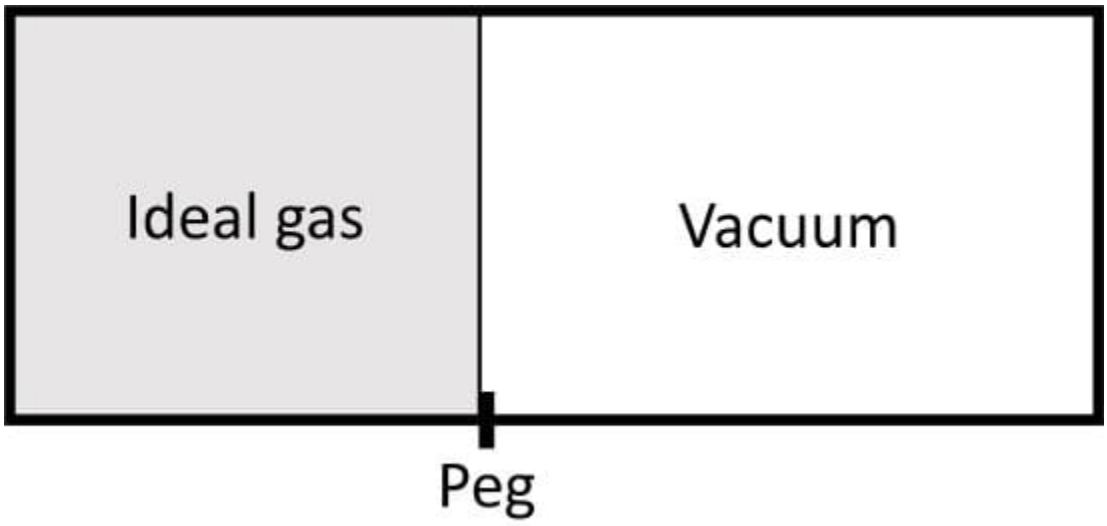
20.6: We Must Always Devise a Reversible Process to Calculate Entropy Changes

The second law of thermodynamics can be formulated in many ways, but in one way or another they are all related to the fact that the state function entropy, S, tends to increase over time in isolated systems. For a long time, people have looked at the entire universe as an example of an isolated system and concluded that its entropy must be steadily increasing until $\delta S_{universe}$ becomes zero. As we will see below, the second law has important consequences for the question of how we can use heat to do useful work.

> Of late, cosmologists like the late Richard Hawkins have begun to question the assumption that the entropy of the universe is steadily increasing. The key problem is the role that gravity and relativity play in creating black holes.

Vacuum Expansion

Let's compare two expansions from V_1 to V_2 for an ideal gas, both are isothermal. The first is an irreversible one, where we pull a peg an let the piston move against vacuum:



The second one is a reversible isothermal expansion from V_1 to V_2 (and P_1 to P_2) that we have examined before. In both cases, the is no change in internal energy since T does not change. During the irreversible expansion, however, there is also no volume work because the piston is expanding against a vacuum and the following integral:

$$\int -P_{ext} dV = 0$$

integrates to zero. The piston has nothing to perform work against until it slams into the right hand wall. At this point $V = V_2$ and then dV becomes zero. This is not true for the reversible isothermal expansion as the external pressure must always equal the internal pressure.

> No energy and no work means no heat!

Clearly the zero heat is irreversible heat ($q_{irr} = 0$) and this makes it hard to calculate the entropy of this spontaneous process. But then this process ends in the same final state as the reversible expansion from V_1 to V_2. We know that dU is still zero, but now $\delta w_{rev} = -\delta q_{rev}$ is nonzero. We calculated its value before:

$$q_{rev} = nRT \ln\left(\frac{V_2}{V_1}\right) \tag{20.6.1}$$

The Claussius definition of entropy change can be used to find ΔS (under constant temperature).

$$\Delta S = \frac{q_{rev}}{T} \tag{20.6.2}$$

Substituting Equation 20.6.1 into Equation 20.6.2 results in

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

As S is a state function this equation also holds for the irreversible expansion against vacuum.

> Always calculate the entropy difference between two points along a **reversible** path.

For the irreversible expansion into vacuum we see that

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR \ln\left(\frac{V_2}{V_1}\right) + 0 \\ &= nR \ln\left(\frac{V_2}{V_1}\right)\end{aligned}$$

For the reversible expansion, heat is transferred to the system while the system does work on the surroundings in order to keep the process isothermal:

$$\Delta S_{\text{sys}} = nR \ln\left(\frac{V_2}{V_1}\right)$$

The entropy change for the surrounding is the opposite of the system:

$$\Delta S_{\text{surr}} = -nR \ln\left(\frac{V_2}{V_1}\right)$$

This is because the amount of heat transferred to the system is the same as the heat transferred from the surroundings and this process is reversible so the system and surroundings are at the same temperature (equilibrium). Heat is related to entropy by the following equation:

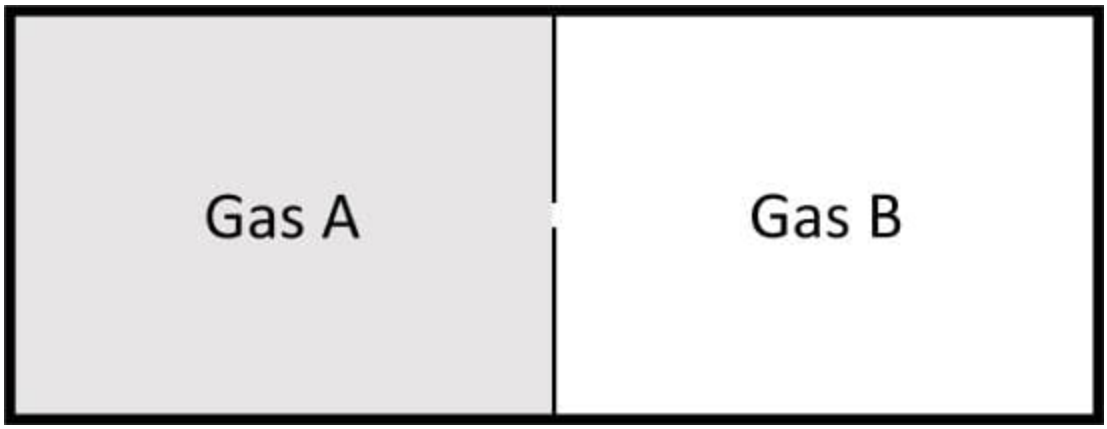
$$dS = \frac{\delta q}{T}$$

Therefore, the total entropy change for the reversible process is zero:

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR \ln\left(\frac{V_2}{V_1}\right) - nR \ln\left(\frac{V_2}{V_1}\right) \\ &= 0\end{aligned}$$

The Mixing of Two Gases

Consider two ideal gases at same pressure separated by a thin wall that is punctured. Both gases behave as if the other one is not there and again we get a spontaneous process, mixing in this case.



If the pressure is the same the number of moles of each gas should be proportional to the original volumes, V_A and V_B, and the total number of moles to the total volume V_{tot}.

For gas A we can write:

$$\Delta S_A = n_A R \ln \frac{V_{tot}}{V_A} = n_A R \ln \frac{n_{tot}}{n_A}$$

and similarly for gas B we can write:

$$\Delta S_B = n_B R \ln \frac{V_{tot}}{V_B} = n_B R \ln \frac{n_{tot}}{n_B}$$

The total entropy change is therefore the sum of constituent entropy changes:

$$\Delta S = \Delta S_A + \Delta S_B$$

and the entropy change total per mole of gas is:

$$\frac{\Delta S}{n_{tot}} = R \frac{\left[n_B \ln \frac{n_{tot}}{n_B} + n_A \ln \frac{n_{tot}}{n_A} \right]}{n_{tot}} \tag{20.6.3}$$

Equation 20.6.3 can be simplified using mole fractions:

$$\chi_A = \frac{n_A}{n_{tot}}$$

and the mathematical relationship of logarithms that:

$$\ln \left(\frac{x}{y} \right) = - \ln \left(\frac{y}{x} \right)$$

to:

$$\Delta \bar{S} = -R \left[\chi_A \ln \chi_A + \chi_B \ln \chi_B \right] \tag{20.6.4}$$

In the case of mixing of more than two gases, Equation 20.6.4 can be expressed as:

$$\Delta \bar{S} = -R \sum \chi_i \ln \chi_i \tag{20.6.5}$$

This entropy expressed in Equations 20.6.4 and 20.6.5 is known as the **entropy of mixing**; its existence is the major reason why there is such a thing as diffusion and mixing when gases, and also solutions (even solid ones), are brought into contact with each other.

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20.7: Thermodynamics Provides Insight into the Conversion of Heat into Work

Heat and work are both forms of transferring energy, and under the right circumstance, one form may be transformed into the other. However, the second law of thermodynamics puts a limitation on this. To go from work to heat is called dissipation and there is no limitation on this at all. In fact it was through dissipation (by friction) that we discovered that heat and work were both forms of energy. There is, however, a limitation on converting heat to work.

The Carnot Cycle

Let's consider a circular, reversible path of an ideal gas on a PV diagram in Figure $20.7.1$:

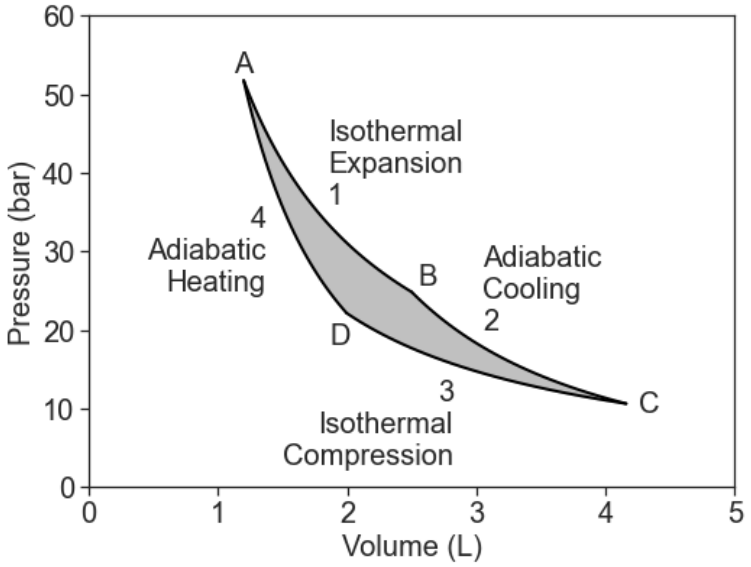


Figure $20.7.1$: A circular, reversible path of a Carnot cycle as an ideal gas on a PV diagram. (CC BY 4.0; Jerry LaRue via LibreTexts)

This cycle forms the 4-stage Carnot cycle heat engine. A heat engine converts heat energy into work. The cycle consists of:

1. Isothermal expansion at the hot temperature, T_h:
$$\Delta U_1 = w_1 + q_h = 0$$
2. Adiabatic cooling from T_h to T_c:
$$\Delta U_2 = w_2$$
3. Isothermal compression at the cold temperature, T_c:
$$\Delta U_3 = w_3 + q_c = 0$$
4. Adiabatic heating from T_c to T_h:
$$\Delta U_4 = w_4$$

The total four-step process produces work because $w_{hot} > w_{cold}$. The work is the integral under the upper isotherm minus the one under the lower curve, i.e. the surface *area in between*.

Sadi Carnot

Sadi Carnot was a French engineer at the beginning of the 19th century. He considered a cyclic process involving a cylinder filled with gas. This cycle the Carnot cycle contributed greatly to the development of thermodynamics and the improvement of the steam engine. Carnot demonstrated that the cold temperature on the right is as important as the heat source on the left in defining the possible efficiency of a heat engine

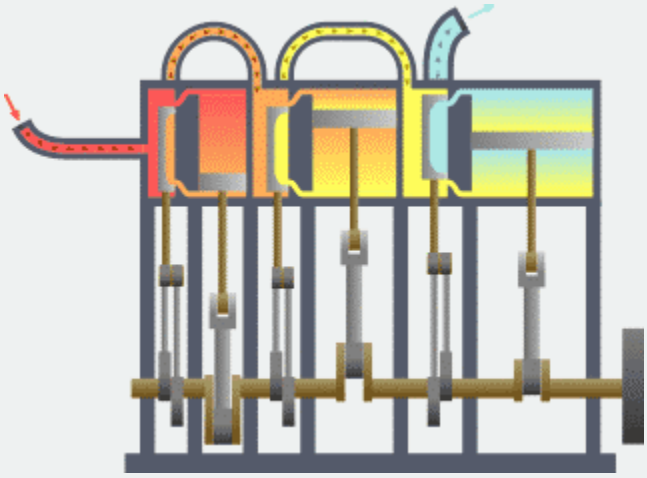


Figure 20.7.2: Animation of a typical vertical triple-expansion engine. (CC SA-BY 2.5; Emoscopes)

Efficiency

Of course we spend good money on the fuel to start the cycle by heating things up. So how much work do we get for the heat we put in? In other words, we want to know how efficient our heat engine is. The efficiency, η of a heat engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

To get the work of the cycle, we can make use of internal energy as a state function. As the path is circular the circular integrals for U is zero:

$$\begin{aligned} \oint dU &= \Delta U_{\text{cycle}} \\ &= \sum \Delta U_i \\ &= w_1 + q_h + w_2 + w_3 + q_c + w_4 \\ &= 0 \end{aligned}$$

Rearranging:

$$\begin{aligned} q_h + q_c &= -w_1 - w_2 - w_3 - w_4 \\ &= -w_{\text{cycle}} \end{aligned}$$

An ideal engine would take $q_h \to q_c$ with 100% efficiency. The work of the cycle will be equivalent to the heat transfer. For ideal gases:

1. $w_1 = -RT_h \ln\left(\frac{V_B}{V_A}\right) = -q_h$
2. $dU = \delta w = \bar{C}_V dT \to w_2 = \bar{C}_V (T_c - T_h)$
3. $w_3 = -RT_c \ln\left(\frac{V_D}{V_C}\right) = -q_c$
4. $w_4 = \bar{C}_V (T_h - T_c)$

Finding an expression for w_{cycle}:

$$w_{\text{cycle}} = -RT_h \ln\left(\frac{V_B}{V_A}\right) + \bar{C}_V\left(T_c - T_h\right) - RT_c \ln\left(\frac{V_D}{V_C}\right) + \bar{C}_V\left(T_h - T_c\right)$$
$$= -RT_h \ln\left(\frac{V_B}{V_A}\right) - RT_c \ln\left(\frac{V_D}{V_C}\right) = -R(T_h - T_c)\ln\left(\frac{V_B}{V_A}\right)$$

We have an expression for work, so we can evaluate the efficiency, η. The efficiency of the Carnot engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{R\left(T_h - T_c\right)\ln\left(\frac{V_B}{V_A}\right)}{RT_h \ln\left(\frac{V_B}{V_A}\right)} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$

Paths (2) and (4) are adiabats, so we can also use entropy, S, to get the same solution:

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

Therefore:

$$\frac{q_c}{q_h} = -\frac{T_c}{T_h}$$

And we get that:

$$\eta = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \tag{20.7.1}$$

As you see we can only get full efficiency if T_{cold} is 0 K, which is never (i.e., we always waste energy). Another implication is that if $T_c = T_h$ then **no work** can be obtained, no matter how much energy is available in the from of heat. Or in other words, if one dissipates work into heat isothermally, *none* of it can be retrieved. Equation 20.7.1 is not very forgiving at all. Just imaging that you have a heat source of say 400 K (a superheated pool of water, e.g. a geyser) and you are dumping in the river at room temperature 300 K. The best efficiency you'll ever get is:

$$\eta = 1 - \frac{300}{400} = 24\%$$

Sadly, you'd be dumping three quarters of your energy as heat in the river (and that is best case scenario as there are always more losses, e.g. due to friction). The arrow saying Q_C in Figure 20.7.3 should then be three times as fat as the one that says w.

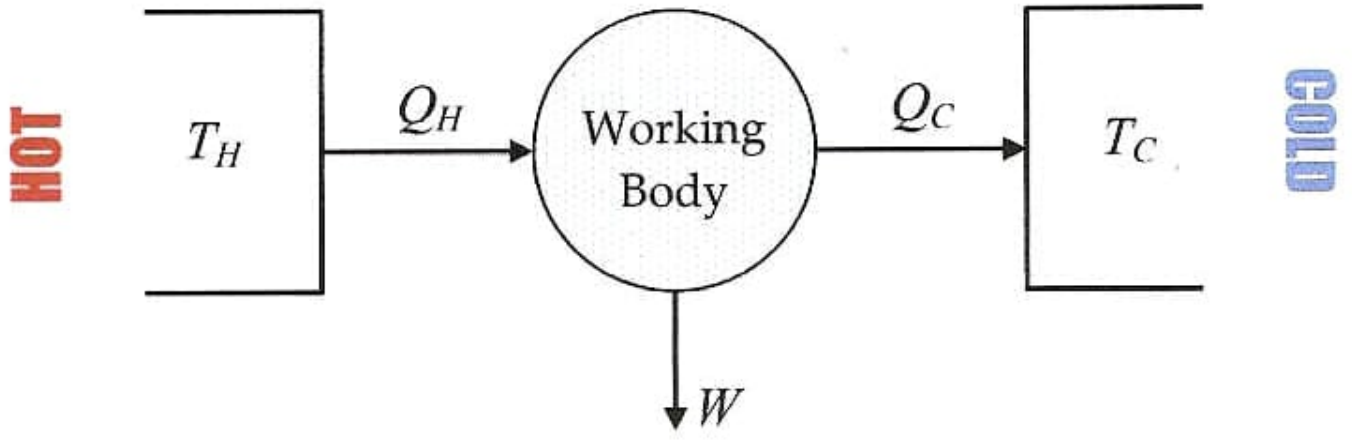


Figure 20.7.3: Carnot engine diagram (modern) - where an amount of heat Q_H flows from a high temperature $T_H$furnace through the fluid of the "working body" (working substance) and the remaining heat Q_C flows into the cold sink T_C, thus forcing the working substance to do mechanical work W on the surroundings, via cycles of contractions and expansions. (Public Domain; Eric Gaba)

Heat pumps

So getting our work from heat is hard and always less than 100% successful. The other way around should be easy. After all, we

can dissipate work into heat freely even under isothermal conditions!

What happens if we let the heat engine run backwards? Consider reversing all the flows in the above diagram. Obviously we must *put in work* to make the cycle run in reverse. The heat will now flow from cold to hot, say from your cold garden into your nice and warm apartment. The amount of heat you get in your humble abode will be the sum of all the work (say 100 Joules) you dissipate *plus* the heat you pumped out of the garden (say 300 Joules). Thus if you are willing to pay for the energy you dissipate (100 Joules), you may well end up with a total of 400 Joules of heat in your apartment! Obviously if it is heat you after this is a better deal than just dissipating the work in your apartment (by burning some oil). Then you'd only get 100 J for your precious buck.

Dissipating it as electrical heating is even worse because you would

1. first burn (a lot more!) oil to generate heat
2. use this heat to produce electrical work at great expense because a lot of the heats gets dumped at the low temperature side (the river or so)
3. dissipate the work again in your apartment (without using it to pump any heat out of the garden)

Refrigerators are also heat pumps. They heat the kitchen by pumping heat from its innards to the kitchen. If I keep the door open, however, all it does is dissipate precious electrical work, because the pumped heat will flow back into its innards and spoil the milk.

Stirling Engine

Let's consider another type of heat engine, the Stirling engine. The Stirling engine uses a circular reversible path in an ideal PV diagram in Figure 20.7.4:

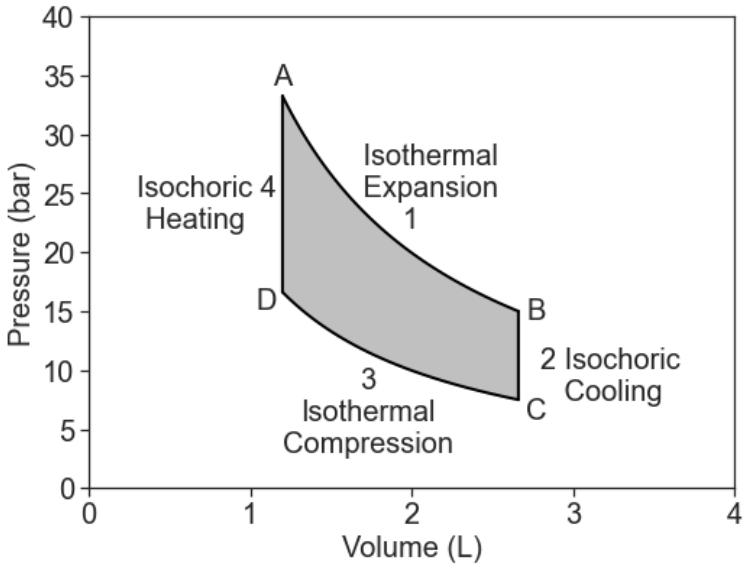


Figure 20.7.4: an ideal PV diagram of the Stirling engine. (CC BY 4.0; Jerry LaRue via LibreTexts)

The path consists of four steps:

1. *Isothermal* expansion at the hot temperature T_h:

   $$q_1 = q_h = -w$$

   and we get work **out** (i.e., negative work):

   $$w_h = -RT_h \ln\left(\frac{V_B}{V_A}\right)$$

2. *Isochoric* heating from T_c to T_h (with constant C_V):

   $$q_2 = \frac{C_V}{\Delta T} \tag{20.7.2}$$

3. *Isothermal* compression at the cold temperature T_c:

$$q_3 = q_c = -w$$

and we must put work **in** (i.e., positive work):

$$w_c = -RT_c \ln\left(\frac{V_D}{V_C}\right) = RT_c \ln\left(\frac{V_B}{V_A}\right)$$

4. *Isochoric* cooling from T_h to T_c (with constant C_V):

$$q_4 = -\frac{C_V}{\Delta T} \tag{20.7.3}$$

Notice that this gray area *vanishes* if $T_h = T_c$. Obviously how cold the cold side is of great importance! The amount of work is also equal to the difference in the heat picked up at high temperature q_h and dumped at low temperature q_c. The isochoric heats cancel. The problem is that q_c is only zero if the cold temperature is 0 K. That means that we can never get all the heat we pick up at high temperatures to come out as work.

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20.8: Entropy Can Be Expressed in Terms of a Partition Function

We have seen that the partition function of a system gives us the key to calculate thermodynamic functions like energy or pressure as a moment of the energy distribution. We can extend this formulism to calculate the entropy of a system once its Q is known. We can start with Boltzmann's (statistical) definition of entropy:

$$S = k \ln(W) \tag{20.8.1}$$

with

$$W = \frac{A!}{\prod_j a_j!}$$

Combining these equations, we obtain:

$$S_{ensemble} = k \ln \frac{A!}{\prod_j a_j!}$$

Rearranging:

$$S_{ensemble} = k \ln A! - k \sum_j \ln a_j!$$

Using Sterling's approximation:

$$\begin{aligned} S_{ensemble} &= kA \ln A - kA - k \sum_j a_j \ln a_j + k \sum_j a_j \\ &= kA \ln A - k \sum_j a_j \ln a_j \end{aligned}$$

Since:

$$\sum_j a_j = A$$

The probability of finding the system in state a_j is:

$$p_j = \frac{a_j}{A}$$

Rearranging:

$$a_j = p_j A$$

Plugging in:

$$S_{ensemble} = kA \ln A - k \sum_j p_j A \ln p_j A$$

Rearranging:

$$S_{ensemble} = kA \ln A - k \sum_j p_j A \ln p_j - k \sum_j p_j A \ln A$$

If A is constant, then:

$$k \sum_j p_j A \ln A = kA \ln A \sum_j p_j$$

Since:

$$\sum_j p_j = 1$$

We get:

$$S_{ensemble} = kA \ln A - k \sum_j p_j A \ln p_j - kA \ln A$$

The first and last term cancel out:

$$S_{ensemble} = -k \sum_j p_j A \ln p_j$$

We can divide by A to get the entropy of the system:

$$S_{system} = -k \sum_j p_j \ln p_j \tag{20.8.2}$$

If all the p_j are zero except for the for one, then the system is perfectly ordered and the entropy of the system is zero. The probability of being in state j is

$$p_j = \frac{e^{-\beta E_j}}{Q} \tag{20.8.3}$$

Plugging Equation 20.8.3 into Equation 20.8.2 results in

$$\begin{aligned} S &= -k \sum_j \frac{e^{-\beta E_j}}{Q} \ln \frac{e^{-\beta E_j}}{Q} \\ &= -k \sum_j \frac{e^{-\beta E_j}}{Q} \left(-\beta E_j - \ln Q\right) \\ &= -\beta k \sum_j \frac{E_j e^{-\beta E_j}}{Q} + \frac{k \ln Q}{Q} \sum_j e^{-\beta E_j} \end{aligned}$$

Making use of:

$$\beta k = \frac{1}{T}$$

And:

$$\sum \frac{e^{-\beta E_j}}{Q} = \sum p_j = 1$$

We obtain:

$$S = \frac{U}{T} + k \ln Q \tag{20.8.4}$$

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20.9: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition

The laws of thermodynamics can be understood in two ways: by looking at large-scale properties like temperature and pressure, or by examining how countless tiny atoms move and interact. Both perspectives lead to the same laws, even though the reasoning behind them is quite different.

We learned earlier that entropy, S, is related to the number of microstates, W, in an ensemble with A systems:

$$S_{ensemble} = k_B \ln W \tag{20.9.1}$$

and

$$W = \frac{A!}{\prod_j a_j!} \tag{20.9.2}$$

Combining Equations 20.9.1 and 20.9.2 to get:

$$\begin{aligned} S_{ensemble} &= k_B \ln \frac{A!}{\prod_j a_j!} \\ &= k_B \ln A! - k_B \sum_j \ln a_j! \end{aligned}$$

Using Sterling's approximation:

$$\ln A! \approx A \ln A - A$$

We obtain:

$$S_{ensemble} = k_B A \ln A - k_B A - k_B \sum_j a_j \ln a_j + k_B \sum a_j$$

Since:

$$A = \sum a_j$$

The expression simplifies to:

$$S_{ensemble} = k_B A \ln A - k_B \sum_j a_j \ln a_j$$

We can make use of the fact that the number of microstates in state j is equal to the total number of microstates multiplied by the probability of finding the system in state j, p_j:

$$a_j = p_j A$$

Plugging in, we obtain

$$\begin{aligned} S_{ensemble} &= k_B A \ln A - k_B \sum_j p_j A \ln p_j A \\ &= k_B A \ln A - k_B \sum_j p_j A \ln p_j - k_B \sum_j p_j A \ln A \end{aligned}$$

Since A is a constant and the sum of the probabilities of finding the system in state j is always 1:

$$\sum p_j = 1$$

The first and last term cancel out:

$$S_{ensemble} = -k_B A \sum_j p_j \ln p_j$$

We can use that the entropy of the system is the entropy of the ensemble divided by the number of systems:

$$S_{system} = S_{ensemble}/A$$

Dividing by A, we obtain:

$$S_{system} = -k_B \sum_j p_j \ln p_j$$

We can differentiate this equation and dropping the subscript:

$$dS = -k_B \sum_j (dp_j + \ln p_j dp_j)$$

Since $\sum_j p_j = 1$, the derivative $\sum_j dp_j = 0$:

$$dS = -k_B \sum_j \ln p_j dp_j$$

In short:

$$\sum_j \ln p_j dp_j = -\frac{\delta q_{rev}}{k_B T}$$

Plugging in:

$$dS = \frac{\delta q_{rev}}{T} \tag{20.9.3}$$

The thermodynamic definition of entropy comes from macroscopic observations. In classical thermodynamics, entropy is defined as the measure of energy dispersal in a system (Equation 20.9.3). It tells us how much heat is spread out or distributed in a system at temperature. This definition is practical and works well at the bulk level but does not say why entropy behaves this way.

The statistical definition of entropy in Equation 20.9.1, developed by Boltzmann, defines entropy in terms of the number of possible microstates that correspond to the same overall macroscopic state (macrostate). This shows that entropy measures the degree of microscopic disorder or multiplicity of arrangements consistent with what we see at the macroscopic level.

Both definitions describe the same underlying concept:

- The thermodynamic view says entropy measures the spread of energy in terms of heat and temperature.
- The statistical view says entropy measures the spread of possible microstates that energy can occupy.

They are equivalent because a system with more accessible microstates (higher disorder) will also tend to have greater energy dispersal, and thus higher entropy. In fact, the statistical definition explains why the thermodynamic definition works: macroscopic energy dispersal arises from the overwhelming number of microscopic ways energy can be arranged.

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20.E: Entropy and The Second Law of Thermodynamics (Exercises)

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21: ENTROPY AND THE THIRD LAW OF THERMODYNAMICS

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21.2: The 3rd Law of Thermodynamics Puts Entropy on an Absolute Scale

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21.E: Entropy and the Third Law of Thermodynamics (Exercises)

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21.1: Entropy Increases with Increasing Temperature

Learning Objectives

- Define entropy and its relation to energy flow.

Entropy versus temperature

We can put together the first and the second law for a reversible process with no other work than volume (PV) work and obtain:

$$dU = \delta q_{rev} + \delta w_{rev}$$

Entropy is the dispersal of energy and is related to heat:

$$\delta q_{rev} = TdS$$

Work is related to the change in volume:

$$\delta w_{rev} = -PdV$$

Plugging these into our expression for dU for reversible changes:

$$dU = TdS - PdV$$

We no longer have any path functions in the expression, as U, S and V are ***all state functions***. This means this expression must be an exact differential. We can generalize the expression to hold for irreversible processes, but then the expression becomes an inequality:

$$dU \leq TdS - PdV$$

This equality expresses U as a function of two variables, entropy and volume: $U(S,V)$. S and V are the ***natural variables*** of U.

Entropy and heat capacity

At constant volume, dU becomes:

$$dU = TdS$$

Recall that internal energy is related to constant volume heat capacity, C_V:

$$C_V = \left(\frac{dU}{dT}\right)_V$$

Combining these two expressions, we obtain:

$$dS = \frac{C_V}{T}dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T}dT$$

If we know how C_V changes with temperature, we can calculate the change in entropy, ΔS. Since heat capacity is always a positive value, entropy must increase as the temperature increases. There is nothing to stop us from expressing U in ***other*** variables, e.g.

T and V. In fact, we can derive some interesting relationships if we do.

Example 21.1.1

1. Write U as a function of T and V.
2. Write U as a function of its natural variables.
3. Rearrange (2) to find an expression for dS.
4. Substitute (1) into (3) and rearrange. This is the definition of C_V.
5. Write out S as a function of T and V.

We can also derive an expression for the change in entropy as a function of constant pressure heat capacity, C_P. To start, we need to change from internal energy, U, to enthalpy, H:

$$\begin{aligned} H &= U + PV \\ dH &= dU + d(PV) \\ &= dU + PdV + VdP \end{aligned}$$

For reversible processes:

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= TdS - PdV + PdV + VP \\ &= TdS + VdP \end{aligned}$$

The natural variables of the enthalpy are S and P (not: V). A similar derivation as above shows that the temperature change of entropy is related to the constant pressure heat capacity:

$$dH = TdS + VdP$$

At constant pressure:

$$dH = TdS + VdP$$

Recall that:

$$C_P = \frac{dH}{dT}$$

Combining, we obtain:

$$dS = \frac{C_P}{T} dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

This means that if we know the heat capacities as a function of temperature we can calculate how the entropy changes with temperature. Usually it is easier to obtain data under constant P conditions than for constant V, so that the route with C_p is the more common one.

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21.2: The 3rd Law of Thermodynamics Puts Entropy on an Absolute Scale

Learning Objectives

- Recall the third law of thermodynamics.

In the unlikely case that we have C_p data all the way from 0 K we could write:

$$S(T) = S(0) + \int_0^T C_p(T)\ dT$$

It is tempting to set the $S(0)$ to zero and make the entropy thus an absolute quantity. As we have seen with enthalpy, it was not really possible set $H(0)$ to zero. All we did was define ΔH for a particular process, although if C_p data are available we could construct an enthalpy function (albeit with a floating zero point) by integration of C_P (instead of C_p/T!). The situation is different for entropy S than for H. Here we can actually put things on an ***absolute*** scale. Both Nernst and Planck have proposed to do so. Nernst postulated that for a pure and perfect crystal S should indeed to go to zero as T goes to zero (Figure 21.2.1).

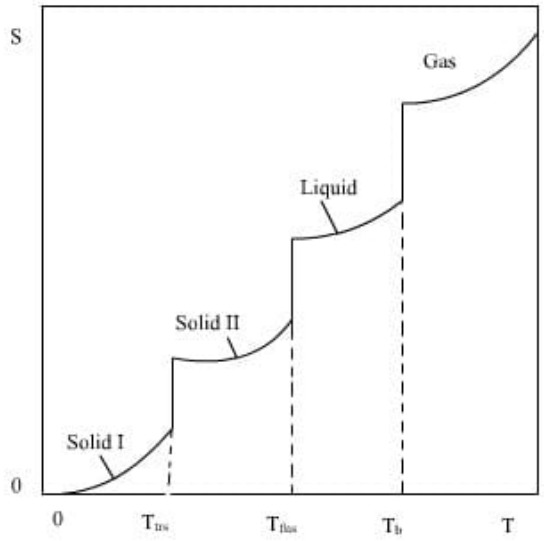


Figure 21.2.1: Entropy as a Function of Temperature. The entropy (S) of a substance (compound or element) as a function of temperature (T). Note that there are three phase transitions in this system with evolution through two solid phases. These result in positive jumps in the entropy.

Example 21.2.1: Sulfur

Sulfur has two solid crystal structure, rhombic and monoclinic. At 368.5 K, the entropy of the phase transition from rhombic to monoclinic, $S_{(rh)} \rightarrow S_{(mono)}$, is:

$$\Delta_{\text{trs}} S(368.5\ \text{K}) = 1.09\ \frac{\text{J} \cdot \text{mol}}{\text{K}}$$

As the temperature is lowered to 0 K, the entropy of the phase transition approaches zero:

$$\lim_{T \to 0} \Delta_r S = 0$$

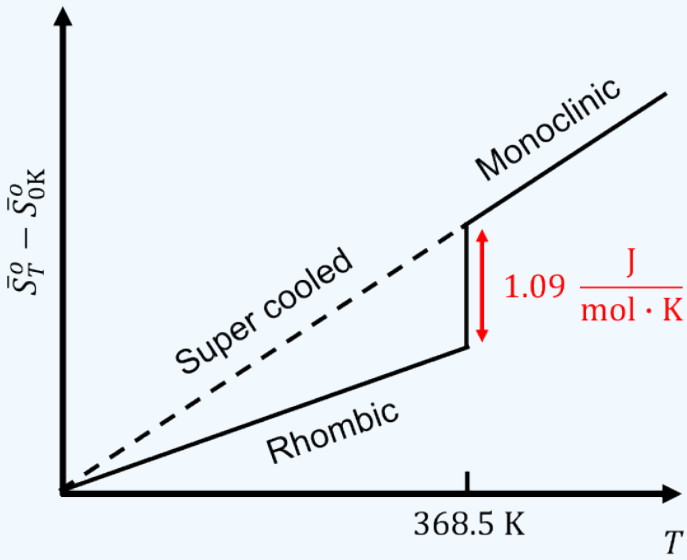


Figure 21.2.2: Schematic showing the entropy of the rhombic and monoclinic structures of sulfur as a function of temperature.

This shows that the entropy of the two crystalline forms are the same. The only way is if all species have the same absolute entropy at 0 K. For energy dispersal at 0 K:

1. Energy is as concentrated as it can be.
2. Only the very lowest energy states can be occupied.

For a pure, perfect crystalline solid at 0 K, there is only one energetic arrangement to represent its lowest energy state. We can use this to define a natural zero, giving entropy an absolute scale. The **third Law of Thermodynamics** states that the entropy of a pure substance in a perfect crystalline form is 0 $\frac{J}{mol \cdot K}$ at 0 K:

$$\bar{S}^\circ_{0\text{ K}} = 0$$

This is consistent with our molecular formula for entropy:

$$S = k \ln W$$

For a perfect crystal at 0 K, the number of ways the total energy of a system can be distributed is one ($W = 1$). The $\ln W$ term goes to zero, resulting in the perfect crystal at 0 K having zero entropy (Figure $21.2.3a$).

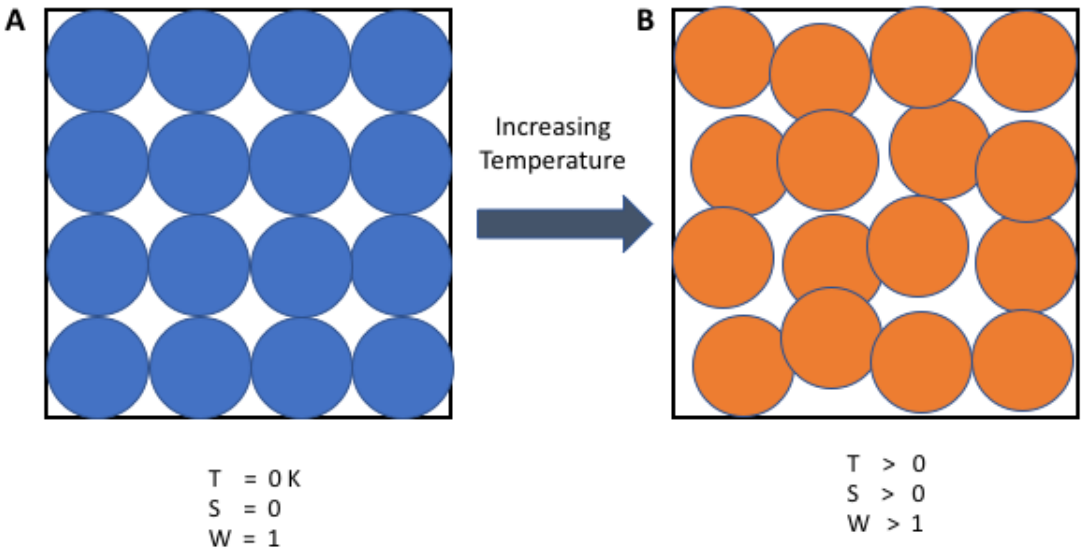


Figure 21.2.3: (a) Single possible configuration for a system at absolute zero, i.e., only one microstate is accessible. Thus $S = k \ln W = 0$. (b) At temperatures greater than absolute zero, multiple microstates are accessible due to atomic dislocation (exaggerated in the figure). Since the number of accessible microstates is greater than 1, $S = k \ln W > 0$. (CC BY-SA 4.0; BlyumJ via Wikipedia)

It is certainly true that for the great majority of materials we end up with a crystalline material at sufficiently low materials (although there are odd exceptions like liquid helium). However, it should be mentioned that a completely *perfect* crystal can only be grown at zero Kelvin! It is not possible to grow anything at 0 K however. At any finite temperature the crystal always incorporates defects, more so if grown at higher temperatures. When cooled down very slowly the defects tend to be ejected from the lattice for the crystal to reach a new equilibrium with less defects. This tendency towards less and less disorder upon cooling is what the third law is all about.

However, the ordering process often becomes impossibly slow, certainly when approaching absolute zero. This means that real crystals always have *some* frozen in imperfections. Thus there is always *some* residual entropy. Fortunately, the effect is often too small to be measured. This is what allows us to ignore it in many cases (but not all). We could state the Third law of thermodynamics as follows:

Definition: Third law of thermodynamics

The entropy of a perfect crystal approaches zero when T approaches zero (but perfect crystals do not exist).

$$\lim_{T \to 0} S^{\circ}(T) = 0 \tag{21.2.1}$$

Another complication arises when the system undergoes a phase transition, e.g. the melting of ice. As we can write:

$$\Delta_{fus} H = q_P$$

If ice and water are in equilibrium with each other the process is quite reversible and so we have:

$$\Delta_{fus} S = \frac{q_{rev}}{T} = \frac{\Delta_{fus} H}{T}$$

This means that at the melting point the curve for S makes a sudden jump by this amount because all this happens at one an the same temperature. Entropies are typically calculated from calorimetric data (e.g., C_P measurements) and tabulated in standard molar form.

There are some clear trends in the entropy values of elements and molecules, e.g. when the noble gas gets heavier this induces more entropy. This is a direct consequence of the particle in the box formula. It has mass in the denominator and therefore the energy levels get more crowded together when m increases: more energy levels, more entropy.

The energy levels get more crowded together when m increases: more energy levels, more entropy

There are tables for $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(0)$ as a function of temperature for numerous substances. As we discussed before the plimsoll defines are standard state in terms of pressure (1 bar) and of concentration reference states, if applicable, but temperature is the one of interest.

Residual Entropy in Carbon Monoxide

For most substances, the assumption made in Equation 21.2.1 regarding the Third Law is generally valid; however, there are notable exceptions, such as carbon monoxide. In its solid state, carbon monoxide molecules would ideally be fully ordered at absolute zero. However, due to the similar sizes of carbon and oxygen atoms and the molecule's weak dipole, it is possible for some molecules to be positioned "upside down"—with oxygen occupying a carbon site and vice versa (i.e., the $\mathrm{C{\equiv}O}$ and $\mathrm{O{\equiv}C}$ orientations are nearly isoenergetic in the lattice). When the crystal forms at higher temperatures, this disorder increases entropy, thereby lowering the Gibbs energy (G). Essentially, if each molecule can be placed into the lattice in two different orientations, the total number of possible configurations (W_{disorder}) for N molecules is 2^N.

This leads to an additional contribution to the entropy of

$$S_{disorder} = k\,\ln W_{disorder} = k\,\ln 2^N = Nk\ln 2 = 5.7\,\mathrm{J/(mol\ K)}$$

At lower temperatures, the entropy term in $\Delta G = \Delta H - T\Delta S$ diminishes in significance, and the crystal should theoretically transition to a more ordered state with lower entropy. However, in practice, the kinetics of this process are extremely slow, preventing the ordering from occurring. As a result, solid CO retains **a nonzero entropy** even as it approaches absolute zero (Equation 21.2.1).

In principle *all* crystalline materials have this effect to some extent, but CO is unusual because the concentration of 'wrongly aligned' entities is of the order of 50% rather than say 1 in 10^{13} (a typical defect concentration in say single crystal silicon). The experimental residual entropy of CO is approximately 4.4 J/(mol K); this indicates that the two orientations of CO are not exactly identical in energy (i.e., equal probability of forming), which would give a residulate entropy of 5.7 J/(mol K).

Exercise 21.2.1

The entropy of a crystal composed of one mole of identical molecules is measured to be 9.134 J/K at 0 K. Determine the number of possible orientations each molecule can adopt within the crystal. Additionally, illustrate a molecule that would be expected to exhibit this behavior.

Summary

Residual entropy quantifies the remaining disorder or randomness in a system even at absolute zero temperature (0 K). According to the Third Law of Thermodynamics, the entropy of a perfect crystal approaches zero as the temperature nears absolute zero. However, some systems retain a nonzero entropy at 0 K, exhibiting residual entropy. This phenomenon represents an exception to the Third Law rather than a contradiction. The law assumes a perfect crystal with a singular, unique ground state, whereas systems with residual entropy, such as carbon monoxide, possess multiple degenerate ground states.

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21.3: The Entropy of a Phase Transition can be Calculated from the Enthalpy of the Phase Transition

Phase transitions (e.g. melting) often occur under equilibrium conditions. We have seen that both the H and the S curves undergo a discontinuity at constant temperature during melting, because there is an enthalpy of fusion to overcome. For a general phase transition at equilibrium at constant T and P, we can say that:

$$\begin{aligned}\Delta_{trs}G &= \Delta_{trs}H - T_{trs}\Delta_{trs}S \\ &= 0 \\ \Delta_{trs}H &= T_{trs}\Delta_{trs}S \\ \frac{\Delta_{trs}H}{T_{trs}} &= \Delta_{trs}S\end{aligned}$$

For melting of a crystalline solid, we now see *why* there is a sudden jump in enthalpy. The reason is that the solid has a much more ordered structure than the crystalline solid. The decrease in order implies a finite $\Delta_{trs}S$. We should stress at this point that we are talking about ***first order*** transitions here. The reason for this terminology is that the discontinuity is in a function like S, that is a first order derivative of G (or A):

$$\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

Second order derivatives (e.g. the heat capacity) will display a singularity (+∞) at the transition point.

Every phase transition will have a change in entropy associated with it. The different types of phase transitions that can occur are:

$l \rightarrow g$	Vaporization / boiling
$g \rightarrow l$	Condensation
$s \rightarrow l$	Fusion / melting
$l \rightarrow s$	Freezing
$s \rightarrow g$	Sublimation
$g \rightarrow s$	Deposition
$s \rightarrow s$	Solid to solid phase transition

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21.4: The Debye Function is Used to Calculate the Heat Capacity at Low Temperatures

The Debye function is a mathematical expression used in solid-state physics to calculate the heat capacity of solids at low temperatures. Unlike the classical Dulong–Petit law, which assumes that each atom contributes a constant amount of heat capacity, the Debye model incorporates quantum mechanics by considering the vibrational modes of a crystal lattice as quantized phonons. At low temperatures, only the low-frequency vibrational modes are thermally accessible, causing the heat capacity to decrease sharply rather than remain constant. The Debye function provides a way to describe this temperature dependence, predicting the characteristic behavior at very low temperatures and approaching the classical limit at higher temperatures:

$$C_P = aT^3 \tag{21.4.1}$$

Using quantum mechanics, Debye showed that the vibrational energy of a crystal lattice could be modeled as a collection of quantized normal modes, or phonons, leading to a temperature-dependent heat capacity that accurately describes low-temperature behavior in Equation 21.4.1.

However, for metallic crystals, the situation is slightly more complex. In addition to lattice vibrations, the conduction electrons contribute to the heat capacity, resulting in a modified equation at low temperatures. The total heat capacity $C(T)$ for metals is often expressed as:

$$C_P = aT + bT^3 \tag{21.4.2}$$

where a and b are constants.

The aT term in Equation 21.4.2 represents the linear contribution from conduction electrons, while the bT^3 term arises from the lattice vibrations described by the Debye model (form Equation 21.4.1. This combination allows for an accurate prediction of the low-temperature heat capacity of metals.

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21.5: Practical Absolute Entropies Can Be Determined Calorimetrically

Practical absolute entropies can also be determined experimentally using calorimetry, based on the Third Law of Thermodynamics. The Third Law states that a perfect crystalline substance has zero entropy at absolute zero (0 K). From this reference point, the entropy at any higher temperature can be obtained by measuring the heat capacity of the substance as it is warmed from 0 K up to the temperature of interest (often 298 K for standard entropies).

From section 21.1, we learned that the entropy at constant pressure changes with temperature by:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT \tag{21.5.1}$$

where C_p is the molar heat capacity at constant pressure.

Equation 21.5.1 accounts for the continuous increase in entropy as the substance absorbs heat with rising temperature but does not address the increase in entropy if the substances undergoes a phase transition. From section 21.3, we learned that the entropy of a phase transition (e.g., melting or vaporization) is:

$$\Delta S_{trs} = \frac{\Delta H_{trs}}{T_{trs}} \tag{21.5.2}$$

Note that third law of thermodynamics can be used to set the entropy at absolute zero ($T_1 = 0K$) to zero in the integral in Equation 21.5.1 and the expression in Equation 21.5.2 applies to all possible phase transitions. These aspects combined with Equations 21.5.1 and 21.5.2 results in an expression for the absolute entropy of a substance at temperature T:

$$S(T) = \int_0^T \frac{C_p(T)}{T} dT + \sum \frac{\Delta H_{\text{trs}}}{T_{\text{trs}}} \tag{21.5.3}$$

The summation term adds contributions from multiple possible phase transitions, where entropy changes abruptly due to latent heats (ΔH) at specific transition temperatures.

The values of C_p, ΔH_{trs}, and T can be experimentally determined using calorimetry. We can calculate the practical absolute entropy of a substance for any temperature.

Example 21.5.1

What is the absolute entropy of CO_2 gas at 300 K?

Solution

The entropy of CO_2 gas at 300 K can be calculated by:

$$S(T) = \int_{0K}^{T_{sub}} \frac{C_P(T)}{T} dT + \frac{\Delta H_{sub}}{T_{sub}} + \int_{T_{sub}}^{300\text{ K}} \frac{C_P^g(T)}{T} dT$$

where the temperature of sublimation (T_{sub}) is 194.7 K.

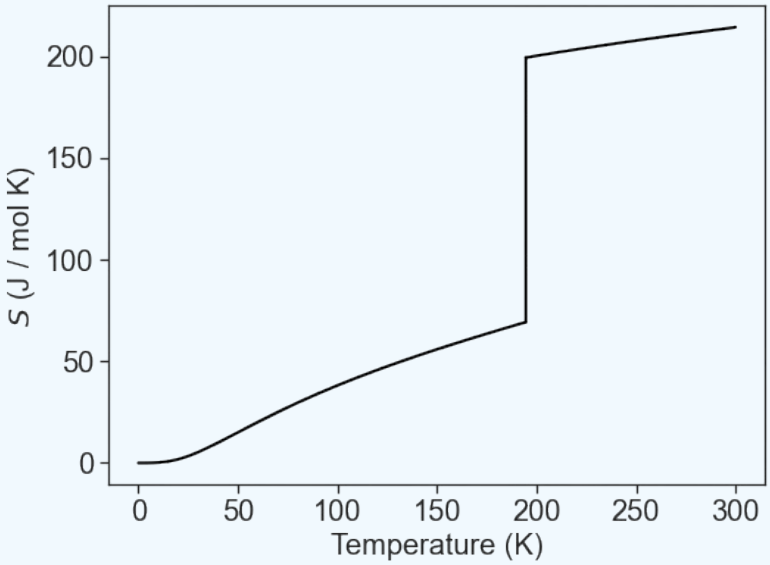


Figure 21.5.1. The molar entropy of CO_2 from 0 K to 300 K.

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21.6: Practical Absolute Entropies of Gases Can Be Calculated from Partition Functions

Recall that the entropy of a system, S, can be calculated if the partition function, Q, is known:

$$S = \frac{U}{T} + k_B \ln Q$$

where Q is:

$$Q = \sum_j e^{-\frac{E_j}{kT}}$$

The internal energy of the system can also be calculated from the partition function:

$$U = k_B T^2 \left(\frac{\delta \ln Q}{\delta T} \right)$$

Combining these equations, we obtain:

$$S = k_B \ln Q + k_B T \left(\frac{\delta \ln Q}{\delta T} \right)$$

The third law of thermodynamics states that entropy of a perfect crystal at absolute zero is zero. We can show that our equation for entropy in terms of the partition function is consistent with the third law. Plugging in our equation for the partition function into our equation for entropy, we obtain:

$$S = k_B \ln \sum_j e^{-\frac{E_j}{kT}} + k_B T \left(\frac{\delta \ln \sum_j e^{-\frac{E_j}{kT}}}{\delta T} \right)$$

As T goes to zero, all the states will be in their lowest energy configuration. If the ground state is n degenerate, then n states will be in the ground state:

$$E_1 = E_2 = ... = E_m$$

This is true for all the next states. For example, if the next state is m degenerate, then:

$$E_{n+1} = E_{n+2} = ... = E_{n+m}$$

This gives us the result:

$$\sum_j e^{-\frac{E_j}{kT}} = ne^{-\frac{E_1}{kT}} + me^{-\frac{E_{n+1}}{kT}} + ...$$

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21.7: Standard Entropies Depend Upon Molecular Mass and Structure

Entropy is related to the number of microstates a collection of particles can occupy. As both the molecular mass and molecular structure of the particles will affect the number of available microstates, they also affect the entropy of the collection of particles. So why does S° depend on molecular mass and molecular structure?

Standard molar entropies depend strongly on both molecular mass and molecular structure. Heavier molecules generally have higher entropies because their greater mass leads to more accessible translational and vibrational energy states at a given temperature. Molecular complexity also plays a key role: larger or more structurally intricate molecules have more ways to store energy through rotations and vibrations, giving rise to a greater number of microstates. For example, methane $(\mathrm{CH_4})$ has a higher standard entropy than carbon dioxide $(\mathrm{CO_2})$ because it possesses more rotational and vibrational modes, while oxygen $(\mathrm{O_2})$ has a higher entropy than nitrogen $(\mathrm{N_2})$ due to its larger molecular mass. In essence, both increased mass and increased structural complexity expand the possible distributions of molecular energy, leading to higher entropy values.

From quantum theory, we know that increasing the molecular mass of a particle decreases the energy spacing between states. For a given temperature, more states are available to be occupied, increasing the number of available microstates the system may occupy, and hence the entropy of the system. Heavier molecules have more closely spaced translational and vibrational energy levels, so at room temperature a larger number of these quantum states can be populated, giving rise to higher entropy. Molecular structure also determines how many distinct types of motion are possible: nonlinear and polyatomic molecules possess more rotational and vibrational modes than simpler, linear, or diatomic molecules. Each additional degree of freedom increases the total number of accessible quantum states. Thus, as molecular mass increases or as structure becomes more complex, the system gains a vastly greater multiplicity of microstates, and the entropy correspondingly increases.

The table below shows the molar entropies for the noble gases. As the mass of increases, so does the molar entropy.

Table: Molar entropies for the noble gases

Noble Gas	He	Ne	Ar	Kr	Xe	Rn
Mass $\left(\frac{\mathrm{g}}{\mathrm{mol}}\right)$	4.0	20.2	39.9	84.8	131.3	222.0
$S^\circ_{g,1\ \mathrm{bar}}$ $\left(\frac{\mathrm{J}}{\mathrm{mol\cdot K}}\right)$	126.15^1	146.33^1	154.84^1	164.08^1	169.68^1	176.2^1

The same is true for the number of atoms in a molecule. A molecule with more atoms will, in general, have a more degrees of freedom to take up energy, increasing its number of available microstates and entropy.

References

1. Chase, M.W., Jr., *NIST-JANAF Themochemical Tables, Fourth Edition*, **J. Phys. Chem. Ref. Data, Monograph 9**, 1998, 1-1951.

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21.8: Spectroscopic Entropies sometimes disgree with Calorimetric Entropies

The entropy of gases can be experimentally measured using calorimetry (S°_{exp}) or calculated using spectroscopic methods (S°_{calc}). For most molecules, the experiment and calculated values are in a good agreement, however, this is not true for all molecules. The discrepancy is referred to as residual entropy:

$$\bar{S}_{\text{calc}} - \bar{S}_{\text{exp}}$$

Residual entropy arises from a material that can have many different states a 0 K. The third law of thermodynamics states that at zero kelvin, a substance will have an entropy of zero. In substances, such as glass, ice, and carbon monoxide, the substance can exist in many different configurations; it is not a perfect crystal, but must still have zero entropy according to third law. The material has residual entropy.

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21.9: Standard Entropies Can Be Used to Calculate Entropy Changes of Chemical Reactions

Entropy is a state function, so we can calculate values for a process using any path. This allows us to calculate the entropy change of a chemical reaction using standard entropies. Specifically, we sum the entropies of the products and subtract the entropies of the reactions:

$$\Delta_{rxn}S^\circ = \sum_{\text{Products}} v_i S_i^\circ - \sum_{\text{Reactants}} v_i S_i^\circ$$

Where v_i is the stoichiometric coefficient. Let's look at the combustion of methane:

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow 2\mathrm{H_2O} + \mathrm{CO_2}\,(g)$$

The standard entropies are:

Molecule	Entropy $\left(\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right)$
$\mathrm{CH_4}$	186.25[1]
$\mathrm{O_2}$	205.15[1]
$\mathrm{H_2O}$	188.84[1]
$\mathrm{CO_2}$	213.79[1]

The entropy for the combustion of methane is:

$$\Delta S^\circ = [2\,(188.84) + 1\,(213.70)] - [1\,(186.25) + 2\,(205.15)] = -5.17\,\frac{\mathrm{J}}{\mathrm{mol \cdot K}}$$

References

1. Chase, M.W., Jr., *NIST-JANAF Themochemical Tables, Fourth Edition*, **J. Phys. Chem. Ref. Data, Monograph 9**, 1998, 1-1951.

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21.E: Entropy and the Third Law of Thermodynamics (Exercises)

Problem 1

Liquid water has a nearly constant molar heat capacity of $\bar{C}_P = 75.4.\ \mathrm{J \cdot mol^{-1} K^{-1}}$. What is the change in entropy as 200. g of water are cooled from 70.0°C to 20.0°C?

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22: HELMHOLTZ AND GIBBS ENERGIES

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22.1: Helmholtz Energy

We have answered the question: what is entropy, but we still do not have a general criterion for spontaneity, just one that works in an isolated system. We will consider what happens when we hold volume and temperature constant. As discussed previously, the expression for the change in internal energy:

$$dU = TdS - PdV$$

is only valid for *reversible* changes. Let us consider a spontaneous change. If we assume constant volume, the $-PdV$ work term drops out. From the *Clausius inequality* $dS > \frac{\delta q}{T}$ we get:

$$\underset{\text{constant V}}{dU \leq TdS}$$

$$\underset{\text{constant V}}{dU - TdS \leq 0}$$

Consider a new state function, **Helmholtz energy**, **A**:

$$A \equiv U - TS$$

$$dA = dU - TdS - SdT \tag{22.1.1}$$

If we also set T constant, we see that Equation 22.1.1 becomes

$$\underset{\text{constant V and T}}{dA = dU - TdS \leq 0}$$

This means that the Helmholtz energy, A, is a ***decreasing quantity*** for spontaneous processes (regardless of isolation!) when T and V are held constant. A becomes constant once a reversible equilibrium is reached.

Example 22.1.1 : What A stands for

A good example is the case of the mixing of two gases. Let's assume isothermal conditions and keep the total volume constant. For this process, ΔU is zero (isothermal, ideal) but the

$$\Delta S_{molar} = -y_1 R \ln y_1 - y_2 R \ln y_2$$

This means that

$$\Delta A_{molar} = RT(y_1 \ln y_1 + y_2 \ln y_2).$$

This is a negative quantity because the mole ratios are smaller than unity. So yes this spontaneous process has a negative ΔA. If we look at $\Delta A = \Delta U - T\Delta S$ we should see that the latter term is the same thing as $-q_{rev}$ So we have :

$$\Delta A = \Delta U - q_{rev} = w_{rev}$$

This is however the *maximal work that a system is able to produce* and so the Helmholtz energy is a direct measure of how much work one can get out of a system. A is therefore often called the Helmholtz ***free*** energy. Interestingly this work **cannot** be volume work as volume is constant. so it stands for the maximal ***other*** work (e.g. electrical work) that can be obtained under the unlikely condition that volume is constant.

Natural variables of A

Because $A \equiv U - TS$ we can write

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= TdS - PdV - TdS - SdT \\ &= -PdV - SdT \end{aligned}$$

The natural variables of A are volume V and temperature T.

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22.2: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature

The Helmholtz energy A is developed for isochoric changes and as we have often said before it is much easier to deal with isobaric ones where $P =$ constant. We can therefore repeat the above treatment for the enthalpy and introduce another state function the Gibbs energy

$$\begin{aligned} G &\equiv H - TS \\ &= U + PV - TS \\ &= A + PV \end{aligned}$$

If we take both T and P constant we get

$$\begin{aligned} dU - TdS + PdV &\leq 0 \\ dG &\leq 0 \end{aligned}$$

G either decreases (spontaneously) or is constant (at equilibrium). Calculating the state function between two end points we get:

$$\Delta G = \Delta H - T\Delta S \leq 0 (T, P \text{ constant})$$

This quantity is key to the question of spontaneity under the conditions we usually work under. If for a process ΔG is positive it does not occur spontaneous and can only be made to occur if it is 'pumped', i.e. coupled with a process that has a negative ΔG. The latter is spontaneous.

> If $\Delta G = 0$ then the system is as ***equilibrium***.

Direction of the spontaneous change

Because the ΔS term contains the temperature T as coefficient the spontaneous direction of a process, e.g. a chemical reaction can **change** with temperature depending on the values of the enthalpy and the entropy change ΔH and ΔS. This is true for the melting process, e.g. for water below 0^{o}C we get water=>ice, above this temperature ice melts to water, but it also goes for chemical reactions.

Example

Consider

$$\mathrm{NH_3\,(g) + HCl\,(g) \rightleftharpoons NH_4Cl\,(s)}$$

$\Delta_r H$ at 298K / 1 bar is -176.2 kJ. The change in entropy is -0.285 kJ/K so that at 298K ΔG is -91.21 kJ. Clearly this is a reaction that will proceed to the depletion of whatever is the limiting reagent on the left.

However at 618 K this is a different story. Above this temperature ΔG is positive! (assuming enthalpy and entropy have remained the same, which is almost but not completely true) The reaction will not proceed. Instead the *reverse* reaction would proceed spontaneously. The salt on the right would decompose in the two gases -base and acid- on the left.

Meaning of the ΔG term

As we have seen, ΔA can be related to the maximal amount of work that a system can perform at constant V and T. We can hold

an analogous argument for ΔG except that V is not constant so that we have to consider volume work (zero at constant volume) .

$$dG = d(U + PV - TS) = dU - TdS - SdT - PdV + VdP$$

As $dU = TdS + \delta w_{rev}$

$$dG = \delta w_{rev} - SdT + VdP + PdV$$

As the later term is $-\delta w_{volume}$

$$dG = \delta w_{rev} - SdT + VdP - \delta w_{volume}$$

At constant T and P the two middle terms drop out

$$dG = \delta w_{rev} - \delta w_{volume} = \delta w_{otherusefulwork}$$

Note

ΔG stands for the (maximal) reversible, isobaric isothermal non-PV work that a certain spontaneous change can perform. The volume work may not be zero, but is corrected for.

Natural variables of G

Because $G \equiv H - TS$, we can write

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned}$$

The natural variables of G are pressure P and temperature T. This is what makes this function the most useful of the four U, H, A , and G: these are the natural variables of most of your laboratory experiments!

Summary

We now have developed the basic set of concepts and functions that together form the framework of thermodynamics. Let's summarize four very basic state functions:

state function	natural variables
$dU = -PdV + TdS$	$U(V,S)$
$dH = +VdP + TdS$	$H(P,S)$
$dA = -PdV - SdT$	$A(V,T)$
$dG = +VdP - SdT$	$G(P,T)$

Note:

1. The replacement of δq by TdS was based on *reversible* heat. This means that in the irreversible case the expressions for dU and dH become inequalities
2. We only include *volume* work in the above expressions. If other work (elastic, electrical e.g.) is involved extra terms need to be added: $dU = TdS - PdV + xdX$ etc.

We are now ready to begin applying thermodynamics to a number of very diverse situations, but we will first develop some useful partial differential machinery.

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22.3: The Maxwell Relations

Modeling the dependence of the Gibbs and Helmholtz functions behave with varying temperature, pressure, and volume is fundamentally useful. But in order to do that, a little bit more development is necessary. To see the power and utility of these functions, it is useful to combine the First and Second Laws into a single mathematical statement. In order to do that, one notes that since

$$dS = \frac{dq}{T}$$

for a reversible change, it follows that

$$dq = TdS$$

And since

$$dw = TdS - pdV$$

for a reversible expansion in which only p-V works is done, it also follows that (since $dU = dq + dw$):

$$dU = TdS - pdV \tag{22.3.1}$$

This is an extraordinarily powerful result. This differential for dU can be used to simplify the differentials for H, A, and G. But even more useful are the constraints it places on the variables T, S, p, and V due to the mathematics of exact differentials!

Maxwell Relations

The above result suggests that the natural variables of internal energy are S and V (or the function can be considered as $U(S,V)$). So the total differential (dU) in Equation 22.3.1 can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{22.3.2}$$

Also, by inspection (comparing the two expressions for dU in Equations 22.3.1 and 22.3.2) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{22.3.3}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{22.3.4}$$

But the value does not stop there! Since dU is an exact differential, the Euler relation must hold that

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

By substituting Equations 22.3.3 and 22.3.4, we see that

$$\left[\frac{\partial}{\partial V}(T)_V\right]_S = \left[\frac{\partial}{\partial S}(-p)_S\right]_V$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

This is an example of a **Maxwell Relation**. These are very powerful relationship that allows one to substitute partial derivatives

when one is more convenient (perhaps it can be expressed entirely in terms of α and/or κ_T for example.)

A similar result can be derived based on the definition of H.

$$H \equiv U + pV$$

Differentiating (and using the chain rule on $d(pV)$) yields

$$dH = dU + pdV + Vdp$$

Making the substitution using the combined first and second laws ($dU = TdS – pdV$) for a reversible change involving on expansion (p-V) work

$$dH = TdS – \cancel{pdV} + \cancel{pdV} + Vdp$$

This expression can be simplified by canceling the pdV terms.

$$dH = TdS + Vdp \tag{22.3.5}$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{22.3.6}$$

Comparing Equations 22.3.5 and 22.3.6 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{22.3.7}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{22.3.8}$$

It is worth noting at this point that both Equation 22.3.3

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and Equation 22.3.7

$$\left(\frac{\partial H}{\partial S}\right)_p$$

are equal to T. So they are equation to each other

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

Moreover, the Euler Relation must also hold

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p$$

so

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

This is the Maxwell relation on H. Maxwell relations can also be developed based on A and G. The results of those derivations are summarized in Table 22.3.1.

Table 22.3.1: Maxwell Relations

Function	Differential	Natural Variables	Maxwell Relation
U	$dU = TdS - pdV$	$S,\ V$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
H	$dH = TdS + Vdp$	$S,\ p$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
A	$dA = -pdV - SdT$	$V,\ T$	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
G	$dG = Vdp - SdT$	$p,\ T$	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

The Maxwell relations are extraordinarily useful in deriving the dependence of thermodynamic variables on the state variables of p, T, and V.

Example 22.3.1

Show that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

Solution

Start with the combined first and second laws:

$$dU = TdS - pdV$$

Divide both sides by dV and constraint to constant T:

$$\left.\frac{dU}{dV}\right|_T = \left.\frac{TdS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

Noting that

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$\left.\frac{TdS}{dV}\right|_T = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left.\frac{dV}{dV}\right|_T = 1$$

The result is

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Now, employ the Maxwell relation on A (Table 6.2.1)

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

to get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

It is apparent that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

Note: How cool is that? This result was given without proof in Chapter 4, but can now be proven analytically using the Maxwell Relations!

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- 6.2: Combining the First and Second Laws - Maxwell's Relations by Patrick Fleming is licensed CC BY-NC-SA 4.0.

22.4: The Enthalpy of an Ideal Gas is Independent of Pressure

How does pressure affect enthalpy H? As we showed above we have the following relations of first and second order for G

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = -V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

We also know that by definition:

$$G = H - TS \tag{22.4.1}$$

Consider an isothermal change in pressure, so taking the partial derivative of each side of Equation 22.4.1, we get:

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{22.4.2}$$

For an ideal gas

$$\frac{\partial V}{\partial T} = \frac{nR}{P}$$

so Equation 22.4.2 becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{nR}{P}\right) = 0$$

As we can see for an ideal gas, there is no dependence of H on P.

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22.5: Thermodynamic Functions have Natural Variables

The fundamental thermodynamic equations follow from five primary thermodynamic definitions and describe internal energy, enthalpy, Helmholtz energy, and Gibbs energy in terms of their natural variables. Here they will be presented in their differential forms.

Introduction

The fundamental thermodynamic equations describe the thermodynamic quantities U, H, G, and A in terms of their natural variables. The term "natural variable" simply denotes a variable that is one of the convenient variables to describe U, H, G, or A. When considered as a whole, the four fundamental equations demonstrate how four important thermodynamic quantities depend on variables that can be controlled and measured experimentally. Thus, they are essentially equations of state, and using the fundamental equations, experimental data can be used to determine sought-after quantities like G or H.

First Law of Thermodynamics

The first law of thermodynamics is represented below in its differential form

$$dU = đq + đw$$

where

- U is the internal energy of the system,
- q is heat flow of the system, and
- w is the work of the system.

The "đ" symbol represent **inexact differentials** and indicates that both q and w are path functions. Recall that U is a state function. The first law states that internal energy changes occur only as a result of heat flow and work done.

It is assumed that w refers only to PV work, where

$$w = -\int pdV$$

The fundamental thermodynamic equation for internal energy follows directly from the first law and the principle of Clausius:

$$dU = đq + đw$$
$$dS = \frac{\delta q_{rev}}{T}$$

we have

$$dU = TdS + \delta w$$

Since only PV work is performed,

$$dU = TdS - pdV \tag{22.5.1}$$

The above equation is the fundamental equation for U with natural variables of entropy S and volume$V$.

Principle of Clausius

The *Principle of Clausius* states that the entropy change of a system is equal to the ratio of heat flow in a reversible process to the temperature at which the process occurs. Mathematically this is written as

$$dS = \frac{\delta q_{rev}}{T}$$

where

- S is the entropy of the system,
- q_{rev} is the heat flow of a reversible process, and
- T is the temperature in Kelvin.

Enthalpy

Mathematically, enthalpy is defined as

$$H = U + pV \tag{22.5.2}$$

where H is enthalpy of the system, p is pressure, and V is volume. The fundamental thermodynamic equation for enthalpy follows directly from it deffinition (Equation 22.5.2) and the fundamental equation for internal energy (Equation 22.5.1) :

$$\begin{aligned} dH &= dU + d(pV) \\ &= dU + pdV + VdP \\ dU &= TdS - pdV \\ dH &= TdS - pdV + pdV + Vdp \\ dH &= TdS + Vdp \end{aligned}$$

The above equation is the fundamental equation for H. The natural variables of enthalpy are S and p, entropy and pressure.

Gibbs Energy

The mathematical description of Gibbs energy is as follows

$$\begin{aligned} G &= U + pV - TS \\ &= H - TS \end{aligned} \tag{22.5.3}$$

where G is the Gibbs energy of the system. The fundamental thermodynamic equation for Gibbs Energy follows directly from its definition 22.5.3 and the fundamental equation for enthalpy 22.5.2:

$$\begin{aligned} dG &= dH - d(TS) \\ & dH - TdS - SdT \end{aligned}$$

Since

$$\begin{aligned} dH &= TdS + VdP \\ dG &= TdS + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned} \tag{22.5.4}$$

The above equation is the fundamental equation for G. The natural variables of Gibbs energy are P and T.

Helmholtz Energy

Mathematically, Helmholtz energy is defined as

$$A = U - TS \tag{22.5.5}$$

where A is the Helmholtz energy of the system, which is often written as the symbol F. The fundamental thermodynamic equation for Helmholtz energy follows directly from its definition (Equation 22.5.5) and the fundamental equation for internal energy (Equation 22.5.1):

$$\begin{aligned} dA &= dU - d(TS) \\ &= dU - TdS - SdT \end{aligned}$$

Since

$$\begin{aligned} dU &= TdS - pdV \\ dA &= TdS - pdV - TdS - SdT \\ &= -pdV - SdT \end{aligned} \tag{22.5.6}$$

Equation 22.5.6 is the fundamental equation for A with natural variables of V and T. For the definitions to hold, it is assumed that **only** PV work is done and that **only reversible** processes are used. These assumptions are required for the first law and the principle of Clausius to remain valid. Also, these equations do not account include n, the number of moles, as a variable. When n is included, the equations appear different, but the essence of their meaning is captured without including the n-dependence.

Chemical Potential

The fundamental equations derived above were not dependent on changes in the amounts of species in the system. Below the n-dependent forms are presented[1,4].

$$dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

$$dG = -SdT + Vdp + \sum_{i=1}^{N} \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

where μ_i is the chemical potential of species i and dn_i is the change in number of moles of substance i.

Importance/Relevance of Fundamental Equations

The differential fundamental equations describe U, H, G, and A in terms of their natural variables. The natural variables become useful in understanding not only how thermodynamic quantities are related to each other, but also in analyzing relationships between measurable quantities (i.e. P, V, T) in order to learn about the thermodynamics of a system. Below is a table summarizing the natural variables for U, H, G, and A:

Thermodynamic Quantity	Natural Variables
U (internal energy)	S, V
H (enthalpy)	S, P
G (Gibbs energy)	T, P
A (Helmholtz energy)	T, V

Maxwell Relations

The fundamental thermodynamic equations are the means by which the Maxwell relations are derived[1,4]. The Maxwell Relations can, in turn, be used to group thermodynamic functions and relations into more general "families"[2,3].

As we said dA is an **exact differential**. Let's write is out in its natural variables (Equation 22.5.6) and take a cross derivative. The dA expression in natural variables is

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

The partial derivatives of A of first order can already be quite interesting we see e.g. in step 2 that the first partial of A versus V (at T constant) is the negative of the pressure.

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Likewise we find the (isochoric) slope with temperature gives us the negative of the entropy. Thus entropy is one of the ***first order derivatives*** of A.

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

When we apply a cross derivative

$$\left(\frac{\partial^2 A}{\partial V \partial T}\right) = \left(\frac{\partial(-S)}{\partial V}\right)_T + \left(\frac{\partial(-P)}{\partial T}\right)_V$$

we get what is known as a ***Maxwell relation***:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

Exercise

What does Equation three mean for the heat capacity? answer

A similar treatment of dG (Equation 22.5.4 gives:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

and another Maxwell relation

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Exercise 22.5.1

If the assumptions made in the derivations above were not made, what would effect would that have? Try to think of examples were these assumptions would be violated. Could the definitions, principles, and laws used to derive the fundamental equations still be used? Why or why not?

Answer available at the end of this section.

Exercise 22.5.2

For what kind of system does the number of moles not change? This said, do the fundamental equations without n-dependence apply to a wide range of processes and systems?

Answer available at the end of this section.

Exercise 22.5.3

Derive the Maxwell Relations.

Answer available at the end of this section.

Exercise 22.5.4

1. Derive the expression

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V$$

Then apply this equation to an ideal gas. Does the result seem reasonable?

Answer available at the end of this section.

Exercise 22.5.5

Using the definition of Gibbs energy and the conditions observed at phase equilibria, derive the Clapeyron equation.

Answer available at the end of this section.

References

1. DOI: 10.1063/1.1749582
2. DOI: 10.1063/1.1749549
3. DOI:10.1103/PhysRev.3.273
4. *A Treatise on Physical Chemistry,* 3rd ed.; Taylor, H. S. and Glasstone, S., Eds.; D. Van Nostrand Company: New York, 1942; Vol. 1; p 454-485.

Answers

Exercise 22.5.1

If it was not assumed that PV-work was the only work done, then the work term in the second law of thermodynamics equation would include other terms (e.g. for electrical work, mechanical work). If reversible processes were not assumed, the Principle of Clausius could not be used. One example of such situations could the movement of charged particles towards a region of like charge (electrical work) or an irreversible process like combustion of hydrocarbons or friction.

Exercise 22.5.2

In general, a closed system of non-reacting components would fit this description. For example, the number of moles would not change for a closed system in which a gas is sealed (to prevent leaks) in a container and allowed to expand/is contracted.

Exercise 22.5.3

See the Maxwell Relations section.

Exercise 22.5.4

$(\frac{\partial H}{\partial P})_{T,n} = 0$ for an ideal gas. Since there are no interactions between ideal gas molecules, changing the pressure will not involve the formation or breaking of any intermolecular interactions or bonds.

Exercise 22.5.5

See the third outside link.

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22.6: The Standard State for a Gas is an Ideal Gas at 1 Bar

Tabulated data are expressed in terms of a pure ideal gas (no mixing) at 1 bar, known as standard state conditions (SSC). Standard states are indicated with the ◦ symbol. These values are tabulated at a specific temperature, but that temperature can vary and is not included in the definition of SSC. No real gas has perfectly ideal behavior, but this definition of the standard state allows corrections for non-ideality to be made consistently for all the different gases.

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22.7: The Gibbs-Helmholtz Equation

Ideal gas

For a mole of ideal gas we can use the gas law to integrate volume over pressure and we get

$$\Delta G_{molar} = RT \ln\left(\frac{P_2}{P_1}\right)$$

It is customary to identify one of the pressures (P_1} with the *standard state* of **1 bar** and use the plimsoll to indicate the fact that we are referring to a standard state by writing:

$$G_{molar}(P) = G^o_{molar} + RT \ln\left(\frac{P}{1}\right) = G^o_{molar} + RT \ln[P]$$

The fact that we are making the function intensive (per mole) is usually indicated by putting a bar over the G symbol, although this is often omitted for $G^{\ominus}_{molar}$

Solids

For solids the volume does not change very much with pressure (the *isothermal compressibility* κ is small), so can assume it more or less constant:

$$G(P_{final}) = G(P_{initial}) + \int V dP(\text{from init to final}) \approx G(P_{initial}) + V \int dP(\text{from init to final}) = G(P_{initial}) + V\Delta P$$

The Gibbs-Helmholtz Expression

$$\frac{G}{T} = \frac{H}{T} - S$$

Take the derivative under constant pressure of each side to get

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

We make use of the relationship between C_p and H and C_p and S

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{\cancel{C_P}}{\cancel{T}} - \frac{\cancel{C_P}}{\cancel{T}} \tag{22.7.1}$$

$$= -\frac{H}{T^2} \tag{22.7.2}$$

We said before that S is a first order derivative of G. As you can see from this derivation the enthalpy H is also a first order derivative, albeit not of G itself, but of G/T.

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = -\frac{\triangle H}{T^2}$$

The last step in the derivation simply takes the step before twice -say for the G and H at the begin and end of a *process*- and subtracts the two identical equations leading to a Δ symbol. In this differential form the Gibbs-Helmholtz equation can be applied to any process.

Gibbs Energy as a Function of Temperature

If heat capacities are know from 0 K we could determine both enthalpy and entropy by integration:

$$S(T) = S(0) + \int_0^T \frac{C_p}{T} dT$$

$$H(T) = H(0) + \int_0^T C_p \, dT$$

As we have seen we must be careful at phase transitions such as melting or vaporization. At these points the curves are *discontinuous* and the derivative C_p is undefined.

$$H(T) = H(0) + \int_0^{T_{fus}} C_p(T)_{solid} dT + \Delta H_{fus} + \int_{T_{fus}}^{T_{boil}} C_p(T)_{liquid} dT + \Delta H_{vap} + etc. \tag{22.7.3}$$

$$S(T) = S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \Delta S_{fus} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \Delta S_{vap} + etc. \tag{22.7.4}$$

$$= S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + etc. \tag{22.7.5}$$

with $H(T = 0) = \text{undefined}$ and $S(T = 0) = 0$ from the third law of thermodynamics.

> We also discussed the fact that the third law allows us to define $S(0)$ as zero in most cases. For the enthalpy we cannot do that so that our curve is with respect to an undefined zero point. We really should plot $H(T) - H(0)$ and leave $H(0)$ undefined.

Because the Gibbs free energy $G = H - TS$ we can also construct a curve for G as a function of temperature, simply by combining the H and the S curves (Equations 22.7.3 and 22.7.5):

$$G(T) = H(T) - TS(T)$$

Interestingly, if we do so, the **discontinuties** at the phase transition points will **drop out** for G because at these points $\Delta_{trs}H = T_{trs}\Delta_{trs}S$. Therefore, G is **always** continuous.

The $H(0)$ problem does not disappear so that once again our curve is subject to an arbitrary offset in the y-direction. The best thing we can do is plot the quantity $G(T) - H(0)$ and leave the offset $H(0)$ undefined.

We have seen above that the derivative of G with temperature is $-S$. As entropy is always positive, this means that the G-curve is always *descending* with temperature. It also means that although the curve is *continuous* even at the phase transitions, the slope of the G curve is not, because the derivative $-S$ makes a jump there. Fig. 22.7 in the book shows an example of such a curve for benzene. Note the kinks in the curve at the mp and the boiling point.

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22.8: Fugacity Measures Nonideality of a Gas

We have seen that, for a closed system, the Gibbs energy is related to pressure and temperature as follows:

$$dG = VdP - SdT$$

For a constant temperature process:

$$dG = VdP \tag{22.8.1}$$

Equation 22.8.1 can be evaluated for an ideal gas:

$$d\bar{G} = \frac{RT}{P}dP$$

At constant temperature, T:

$$d\bar{G} = RT\ d\ln P$$

This expression by itself is strictly applicable to ideal gases. However, Lewis, in 1905, suggested extending the applicability of this expression to all substances by defining a new thermodynamic property called **fugacity**, f, such that:

$$d\bar{G} = RT\ d\ln f$$

This definition implies that for ideal gases, f must be equal to P. For non ideal gases, f is not equal to P. The ratio between fugacity and pressure is:

$$\phi = \frac{f}{P}$$

where ϕ is the fugacity coefficient. The fugacity coefficient takes a value of unity when the substance behaves like an ideal gas. Therefore, the fugacity coefficient is also regarded as a *measure of non-ideality*; the closer the value of the fugacity coefficient is to unity, the closer we are to the ideal state. In the zero-pressure limit, fugacity approaches ideal gas behavior:

$$\lim_{P\to 0} d\bar{G} = RT\ d\ln P$$

For mixtures, this expression is written as:

$$d\bar{G}_i = RT\ d\ln f_i$$

where $\bar{G}_i$ and f_i are the partial molar Gibbs energy and fugacity of the i-th component, respectively. Fugacity can be readily related to chemical potential because of the one-to-one relationship of Gibbs energy to chemical potential, which we have discussed previously. Therefore, the definition of fugacity in terms of chemical potential becomes:

$$d\bar{\mu}_i = RT\ d\ln f_i$$

Even though the concept of thermodynamic equilibrium is given in terms of chemical potentials, the above definitions allow us to restate the same principle in terms of fugacity. To do this, previous expressions can be integrated to obtain:

$$\bar{\mu} = \bar{\mu}^\circ + RT\ln\frac{f}{P^\circ}$$

At equilibrium:

$$0 = \bar{\mu}^\circ + RT\ln\frac{f}{P^\circ}$$

$$\bar{\mu}^\circ = -RT\ln\frac{f}{P^\circ}$$

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23: PHASE EQUILIBRIA

Phase equilibria is the term used to describe with two or more phases co-exist (in equilibrium). The stability of phases can be predicted by the chemical potential, in that the most stable form of the substance will have the minimum chemical potential at the given temperature and pressure. A key tool in exploring phase equilibria is a phase diagram which is used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium.

23.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

23.2: Gibbs Energies and Phase Diagrams

23.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

23.4: The Clausius-Clapeyron Equation

23.5: Chemical Potential Can be Evaluated From a Partition Function

23.E: Phase Equilibria (Exercises)

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23.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

A good map will take you to your destination with ease, provided you know how to read it. A map is an example of a *diagram*, a pictorial representation of a body of knowledge. In science they play a considerable role. Next to plots and tables *diagrams* are an important means of making information and/or theoretical knowledge accessible.

Constructing them takes quite a bit of thought. You want to represent as much of what you know and give as accurate a picture of it without conveying anything incorrect. If the drawing can be made to scale that makes it quite a bit more powerful, but this is not strictly necessary. A remark like *not to scale* or *schematically* does need to be given if applicable. A good caption or description is essential.

Thermodynamic Stability and Fluctuations

There are different kinds of equilibrium, besides the ***stable*** equilibrium that represents an absolute minimum in the G function. Of course G is potentially a function of a great number of variables, but let us look at a *diagram* in which G is shown as a function of only one unspecified variable. You could think of the density, the mole fraction of one of the components of a mixture or an applied electrical field or whatever, but the argument is general.

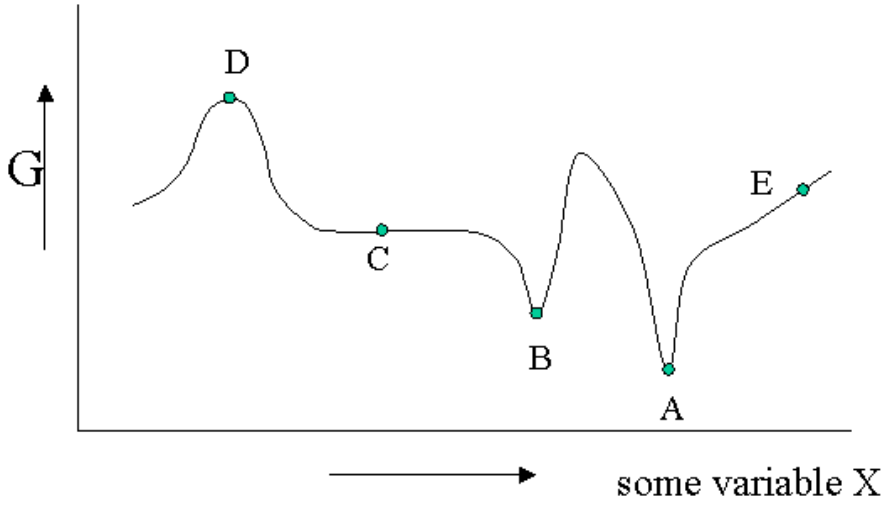


Figure 23.1.1 : A schematic G curve showing various Points of stability. Due to statistical fluctuations the value of G is not quite constant over time, because less likely realizations of the ensemble (having a slightly less favorable value of G) do occur from time to time. After all, the Boltzmann distribution is simply the most likely one, not the only one possible. The fluctuations have drastically different consequences depending on whether the system is in an unstable (E), labile (D) , indifferent (C), metastable (B) or stable (A) state. Notice that A and B just wobble around a bit. C fluctuates wildly in the value of X, while both E and D eventually vanish because the system transits to a more favorable state. For E this starts immediately, for D it starts once fluctuation has caused it to move from its peak sufficiently.

Figure 23.1.1 is helpful to point out that besides a stable equilibrium (A) there can also be an ***metastable*** equilibrium (B) or an ***indifferent*** equilibrium (C). The local derivatives of G (versus *all* variables of which we only show one) are zero in all three cases, which means that changes in the variables are *not* s*pontaneous*. For a ***labile*** equilibrium (D) the opposite is true. Any small deviation will make the system role down hill. (Note that the second derivative has the opposite sign compared to cas A) and B)) A labile equilibrium is seldom or never observed except in a circus where artists delight in balancing objects on their heads (because you pay for it).. This usually requires continuous small corrections to maintain the precarious balance. All other points in our diagram represent state of ***instability*** because locally dG is not zero and a spontaneous process can take place.

The fact that $dG = 0$ in the equilibrium points does not mean small deviations from the minimum cannot happen at times. We have seen e.g. that the Boltzmann distribution was simply *the most likely* distribution. The most likely one is the one that has the

highest number of realizations W. Another way of saying that is that it is the one with the highest entropy S. A slightly less likely distribution may occur from time to time by chance. It will have a little less entropy, but the same $\langle E \rangle$. That means it will have a slightly higher G ($G = H - TS$). From time to time therefore G will fluctuate a bit. Such fluctuations are very small for large systems, but they are of greater relative importance for small systems (like a nanoparticle). (Statistical averaging works best on large ensembles.)

The fluctuations in G mean that small fluctuations in its variables like density etc. can also occur. They are usually kept in check, because dG is no longer zero when moving away from the equilibrium state. This drives the system back to the minimum spontaneously. You could picture the system wobbling a bit around in its G-well. This holds for stable and metastable equilibria alike.

In the indifferent case (C) however the derivative is zero (or very close to zero) for a *range* of neighboring values of some variable. In contrast to A and B also the *second derivative* is zero. This means that there is little penalty to much larger deviations in the variable. If this variable is the density the system becomes milky and shows *opalescence* a strong scattering of light because the refractive index depends on the strongly fluctuating density. This is observed near critical points and is called *critical opalescence*.

Unary Phase Diagrams

A unary phase diagram summarizes the equilibrium states of a single pure substance. We will see that we can also look at mixtures of two components (binary diagrams) or more (ternary, quaternary, quinary, senary etc.). Usually a phase diagram only maps out stable equilibria, but occasionally metastable ones may be given too (e.g., with a dashed line).

Liquid-Vapor Equilibrium Curve

We have seen that the Gibbs function G depends strongly (logarithmically) on pressure for a gas, but only slightly (and linearly) for a liquid. The two curves intersect in a point representing the *equilibrium vapor pressure* of the liquid. At lower pressures the vapor is more stable, at higher ones the liquid. (For a solid the same holds as for the liquid). This means that except at the intersection point we only will observe one phase.

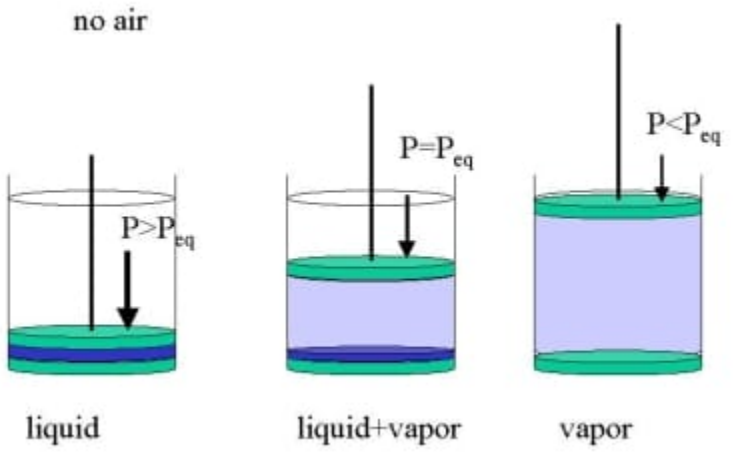


Figure 23.1.2 *: A cylinder with one substance*

It is important to stress that this holds *in the absence of other matter*, e.g., when we put only water into an evacuated cylinder (Figure 23.1.2). We may get three cases:

- we compress the cylinder until it only contains the liquid under hydrostatic pressure ($P > P_{eq}$)
- we expand the cylinder until all water has vaporized ($P < p_{eq}$)>
- we let part of the water evaporate, just enough so that the space above the liquid is filled with an equilibrium vapor pressure ($P = P_{eq}$)

At room temperature P_{eq} for water is only about 15 Torr. If we apply 1 bar -or let the atmosphere do the job- we will only have liquid water. If other gases are present, e.g., air, we must distinguish between the total pressure (e.g., 1 bar) and the equilibrium vapor pressure which will now be the *partial* pressure. In a cylinder with water and one bar of air just enough water will evaporate to establish equilibrium. The evaporation will be limited to the gas-liquid interface unless the partial pressure equals the total pressure. Then the liquid will *boil*.

(Do allow the volume to expand, though., why? If the volume is constant the pressure builds up and boiling will stop.

If we consider the set of equilibrium pressures as a function of temperature and plot that in a P vs. T diagram we have one component of our phase diagram.

Gas-solid Equilibrium Curve

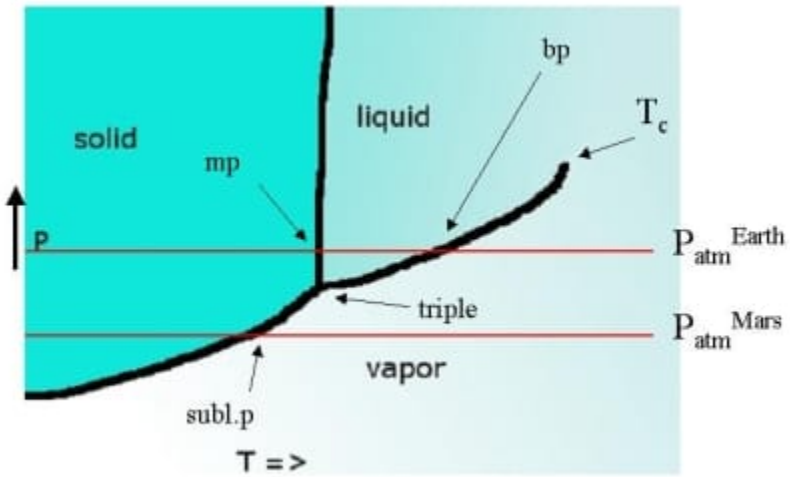
For solids the situation is similar as the $G(P)$ curve is once again an almost flat straight line. The intersection with the logarithmic curve for the gas will define an equilibrium pressure for gas-solid co-existence. Generally vapor pressures above solids are quite small, but not negligible. As for liquids we can construct a line representing the equilibrium pressures for sublimation as function of temperature and add it to the phase diagram.

Liquid-solid Equilibrium Curve

The $\mathrm{solid} \rightleftharpoons \mathrm{liquid}$ equilibrium is known as **melting** or **freezing** is not very dependent on pressure. Usually melting points increase a little bit with pressure, although water is a peculiar exception. It expands upon freezing and the melting point goes down (a bit) with pressure. In our diagram this will represent an almost vertical line leaning a little forwards for most substances, but backwards for water and a few others.

Putting the Curve Together

The three lines come together in the *triple point*, the only point where all three phases are at equilibrium with each other. For water, its temperature is only 0.01 K different from the normal melting point (273.16 K) and its pressure is only 4.58 Torr. The intersection points with a line representing atmospheric pressure give the melting and boiling points at that pressure.



A typical unary diagram

If the triple point lies above the line that represents atmospheric pressure this implies that a liquid is never observed. On earth CO_2 is such a substance. The intersection of the solid-vapor equilibrium line with the 1 bar line represents a state where the solid will '*boil*' (evaporate from inside out). This is known as the *sublimation point*. The melting points at P=1 bar are known as the *standard melting point*, the only slightly different one at 760 Torr = 1 atm is called *normal melting point*. The same goes for boiling and sublimation points.

There is *nothing magical* about $P = 1\ bar$. It just happens to be the pressure of our home planet. On a planet with higher atmospheric pressures CO_2 may well be a liquid and on such a planet, all boiling points will be quite different (higher than on earth). The melting points will also differ, but only slightly so. On Mars where atmospheric pressure is much lower water can not occur in liquid form, much like carbon dioxide on earth - it sublimes.

We should also realize that in a *closed container* (glass ampoule, hermetically sealed DSC pan), we can observe melting points at only very slightly different temperature values, but we will ***not*** see a boiling effect. Why?

To see a boiling point the container must be open to the (*constant!*) 1 bar pressure of the earths atmosphere that ***defines*** it and causes the boiling phenomenon. If the ampoule is sealed it will generate its *own* (autogenous) pressure, depending on what you put in, how much of it in relation to the volume, how volatile it is and the temperature. The autogenous pressure does not interfere with the melting point much (the melting line is almost vertical), but as P changes with temperature you may never reach boiling conditions.

In DSC experiments it is possible to observe boiling points only if the pan has been carefully *perforated* with a hole of known size. It must be big enough that the pressure inside the pan does not build up above atmospheric, but small enough that it does not cause premature loss of mass during the run. The latter spoils the calculation of the intensive value (per mole, per gram) of the heat of vaporization.

The liquid evaporation line ends in a point that we have encountered before: the critical point T_C. As temperature increases the liquid and vapor phases in equilibrium with each other start to resemble each other more and more and at T_c they coalesce. At this point the liquid-gas equilibrium becomes indifferent with respect to density and large fluctuations occur leading to critical opalescence.

Notice that there is a relationship of dimensionality between the objects in the diagram and the number of phases present:

- 2 D planes: one phase
- 1 D curves: two phases
- 0 D point: three phases

As you see the sum is always three.

Number of moles

So far we have typically considered one substance at the time, but for chemists it is imperative to deal with more than one because we are typically changing one into the other in our reactions. This means that the number of moles n, that we often simply set equal to one now becomes an important variable in its own right. Besides we will actually have two (or more) of them: the number of moles of component one and the one for the other component. This makes n a much less trivial variable.

This is already the case at a simple melting point, say when ice melts, because we are dealing with changing quantities of ice and water:

$$n_{ice} + n_{water} = n_{total}$$

If all we do is turn water into ice or vice versa, we have $dn_{total} = 0$, so that:

$$dn_{ice} = -dn_{water}$$

To deal with changing n's, we need to expand our mathematical notation a bit.

Partial variables

So far we have simply divided our thermodynamic functions if they were extensive by the number of moles and arrived at intensive molar values:

$$G_{molar} = \frac{G}{n}$$

$$V_{molar} = \frac{V}{n}$$

We have written such intensive molar values by writing a bar over the symbol G or V. We should note that scaling the function this way departs from the assumption that the function G depends on the variable n as a straight line that passes through the origin.

If we have the same pure compound in two phases, like ice and water we can still apply this principle and write:

$$G^{ice}_{molar} = \frac{G^{ice}}{n^{ice}}$$

$$V^{ice}_{molar} = \frac{V^{ice}}{n^{ice}}$$

$$G^{water}_{molar} = \frac{G^{water}}{n^{water}}$$

$$V^{water}_{molar} = \frac{V^{water}}{n^{water}}$$

If we have a ***mixture*** of two substances present as n_1 and n_2 moles the dependency need not be linear on either if the two substances interact with each other. This is also true for function like the volume of a liquid mixture. In the presence of interactions volumes do *not* have to be linearly additive. We can define a partial molar value of e.g. for the volume:

$$V_{partialmolar,1} = \frac{\partial V}{\partial n_1}$$

at n_2 = constant

$$V_{partialmolar,2} = \frac{\partial V}{\partial n_2}$$

at n_1 = constant

The notation of putting a bar over the V symbol is used for these partial quantities as well. Partial molar volumes have been measured for many binary systems. They are functions of the composition (mole fraction) as well as the temperature and to a lesser extent the pressure.

The partial molar Gibbs free energy

The partial molar Gibbs free energy ($\left(\frac{\partial G}{\partial n_i}\right)_{P,T}$, all other n's) is denoted with μ and is called the thermodynamic potential.

When numbers of moles can change we can write the corresponding change in G as:

$$dG = -SdT + VdP + \sum_i^N \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_{j\neq i}} dn_i$$

$$dG = -SdT + VdP + \sum_i^N \mu_i dn_i$$

over N phases in the system. As you can see we are adding a set of conjugate variables $\mu_i n_i$ for each phase i. If we are considering a *pure* component (but in different modifications, like ice and steam), we can still write:

$$\mu_i = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_{j\neq i}} = \frac{G_i}{n_i}$$

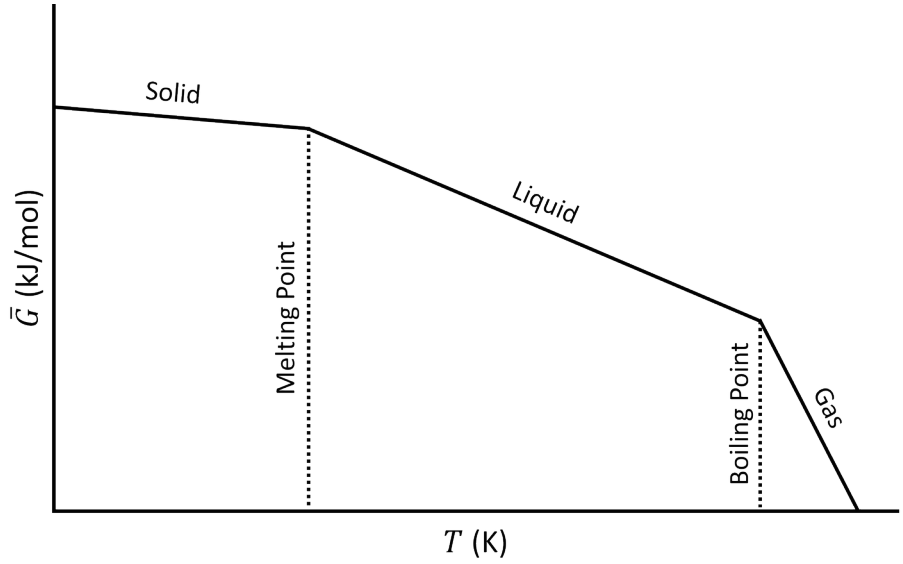
As soon as we are dealing with mixtures we really do have derivatives.

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23.2: Gibbs Energies and Phase Diagrams

First Order Transitions

The following plot shows the Gibbs energy as a function of temperature, including phase changes from solid to liquid (melting) and liquid to gas (boiling).



Gibbs energy ($\bar{G}$) as a function of temperature (T).

Although the G curve is continuous, its first order derivatives ($-S$) is discontinuous at the phase changes. This is why this transition it called a *first order transition*. We could say that:

- G is continuous but has a kink
- The first order derivatives (H,S,..) are discontinuous (have a jump)
- The second order derivatives (C_P, ..) have a singularity (go to ∞)

Second Order Transitions

More subtle transitions where G is continuous, H and S are also continuous but have a kink and the discontinuity is only found in the second order derivatives (such as C_P) also exist. They are called *second order transitions*. In such a case:

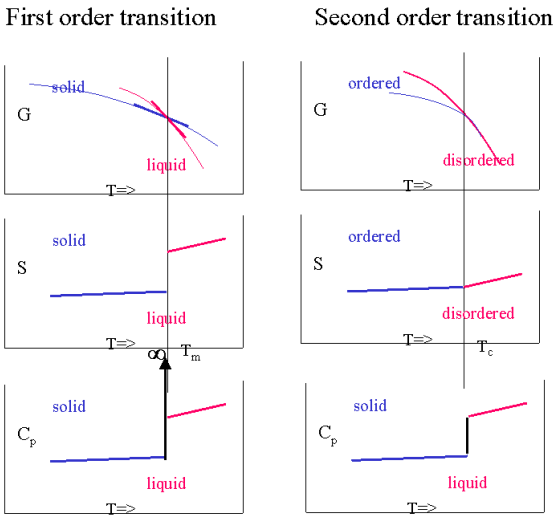
- G is continuous and has no kink
- The first order derivatives (H,S,..) are continuous (but have a kink)
- The second order derivatives (C_P, ..) are discontinuous (have a jump)

Table 23.2.1: Properties of Phase Transitions

Transition Order	Function	1st Order	2nd Order
0	G,A	kink	smooth
1	H,S,V,..	jump	kink
2	CP,CV,α,κ	sing. ∞	jump

This classification goes back to Ehrenfest. Obviously it based on the question: what order derivative is the first to go

discontinuous? Of course we could extend this principle and define *third order transitions* but there are reasons to be doubtful that such things exist. Another problem is that it is assumed that the order must be integer: 1,2, etc. Is it possible to have a transition of intermediate non-integer order, say 1.3? Although derivatives of fractional order are beyond the scope of the chemistry curriculum the mathematics does exist (Liouville).



Schematic comparison of G, S and C_P for 1st and 2nd order transitions

The Gibbs free energy is a particularly important function in the study of phases and phase transitions. The behavior of $G(N, P, T)$, particularly as a function of P and T, can signify a phase transition and can tell us some of the thermodynamic properties of different phases.

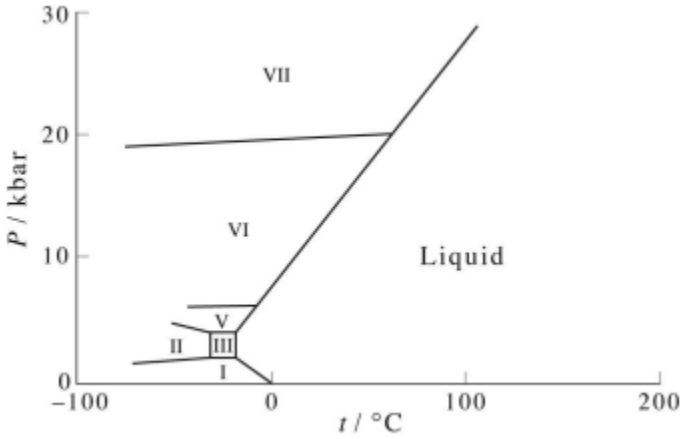


Figure 13.4: Some of the ice polymorphs.

Consider, first, the behavior of G vs. T between the solid and liquid phases of benzene: We immediately notice several things. First, although the free energy is continuous across the phase transition, its first derivative, $\partial G/\partial T$ is not: The slope of $G(T)$ in the solid region is different from the slope in the liquid region. When the first derivative of the free energy with respect to one of its dependent thermodynamic variables is discontinuous across a phase transition, this is an example of what is called a *first order phase transition*. The solid-liquid-gas phase transition of most substances is first order. When the free energy exhibits continuous first derivatives but discontinuous second derivatives, the phase transition is called *second order*. Examples of this type of phase transition are the order-disorder transition in paramagnetic materials.

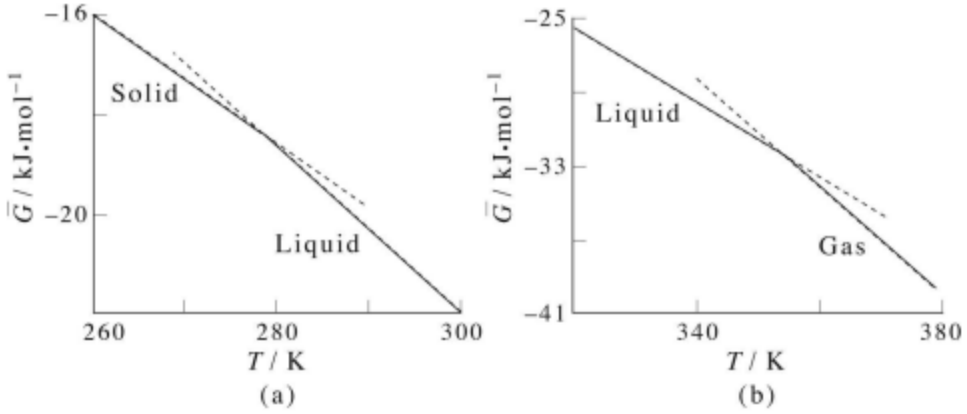


Figure 13.5: Behavior of the Gibbs free energy across the solid-liquid phase (left) and liquid-gas (right) transitions for benzene.

Now, recall that

$$S = -\frac{\partial G}{\partial T} \tag{23.2.1}$$

Consider the slopes in the solid and liquid parts of the graph:

$$\frac{\partial G^{(\text{solid})}}{\partial T} = -S^{(\text{solid})}, \qquad \frac{\partial G^{(\text{liquid})}}{\partial T} = -S^{(\text{liquid})} \tag{23.2.2}$$

However, since

$$\frac{\partial G^{(\text{liquid})}}{\partial T} < \frac{\partial G^{(\text{solid})}}{\partial T} \tag{23.2.3}$$

(*note that the slopes are all negative, and the slope of the liquid line is more negative than that of the solid line*), it follows that $-S^{(\text{liquid})} < -S^{(\text{solid})}$ or $S^{(\text{liquid})} > S^{(\text{solid})}$. This is what we might expect considering that the liquid phase is higher in entropy than the solid phase. The same argument can be made with regards to the gaseous phase.

Similarly, if we consider the dependence of G on pressure, we obtain a curve like that shown in the figure below:

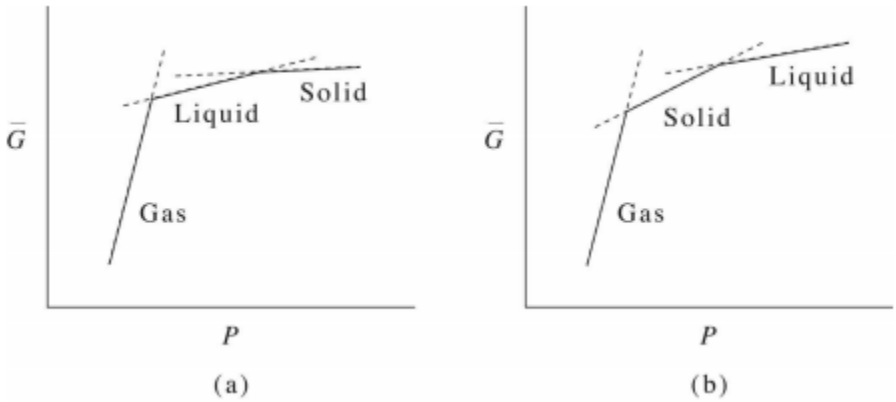


Figure 13.6: Dependence of the Gibbs free energy as a function of pressure for benzene (left) and water (right). For benzene, the temperature is above the triple point, whereas for water, it is set below triple point.

As noted previously, here again, we see that the first derivative of $\bar{G}(P)$ is discontinuous, signifying a first-order phase transition. Recalling that the average molar volume is

$$\bar{V} = \frac{\partial \bar{G}}{\partial P} \tag{23.2.4}$$

From the graph, we see that the slopes obey

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{liquid})} > \bar{V}^{(\text{solid})} \tag{23.2.5}$$

as one might expect for a normal substance like benzene at a temperature above its triple point. Because the temperature is above the triple point, the free energy follows a continuous path (even though it is not everywhere differentiable) from gas to liquid to solid.

On the other hand, for water, we see something a bit different, namely, that

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{solid})} > \bar{V}^{(\text{liquid})} \tag{23.2.6}$$

at a temperature below the triple point. This, again, indicates, the unusual property of water that its solid phase is less dense than its liquid phase in the coexistence region.

Interestingly, if we look at how the plot of $G(P)$ changes with T, we obtain a plot like that shown below: Below the triple point, it is easy to see from the benzene phase diagram that the system proceeds directly from solid to gas. There is a liquid curve on this plot that is completely disconnected from the gas-solid curve, suggesting that, below the triple point, the liquid state can exist metastably if at all. AT the triple point, the solid can transition into the liquid or gas phases depending on the value of the free energy. Near the critical temperature, we see the liquid-gas transition line, while the solid line is disconnected. Above the critical temperature, the system exists as a supercritical fluid, which is shown on the lower line, and this line now shows derivative discontinuity.

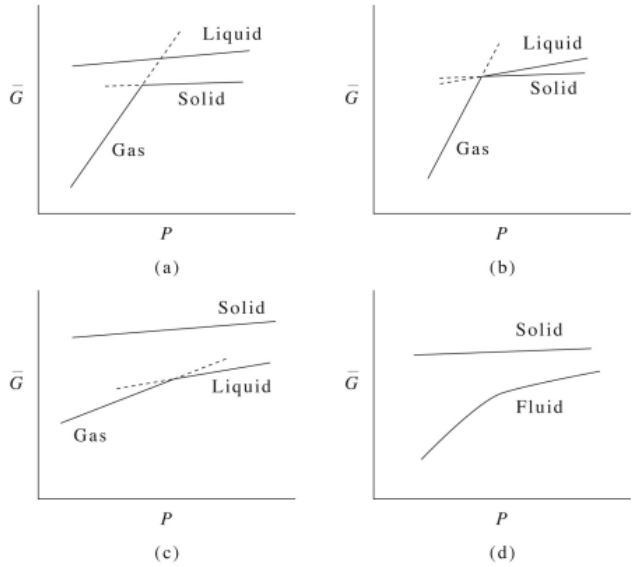


Figure 13.7: Behavior of the Gibbs free energy as a function of P across different phases at different temperatures for benzene. (a): Temperature is less than the triple point; (b): Temperature is equal to the triple point; (c): Temperature is just below the critical temperature; (d): Temperature is greater than the critical temperature.

Conjugate Variables

As discussed before there are many other forms of work possible, such as electrical work, magnetic work or elastic work. These they are commonly incorporated in the formalism of thermodynamics by adding other terms, e.g:

$$dG = -SdT + VdP + \mathscr{E}de + MdH + FdL + \gamma dA$$

1. $\mathscr{E}de$ stands for the electromotoric force $\mathscr{E}$ and *de* the amount of charge transported against it.
2. *MdH* stand for magnetization and (change in) magnetic field.
3. *F* stands for the elastic force of e.g. a rubber band *dL* for the length it is stretched
4. *y* stands for the surface tension (e.g. of a soap bubble), *A* for its surafce area.

The terms always appear in a pair of what is known as conjugate variables. That is even clearer if we write out the state function rather than its differential form:

$$G = U + PV - TS + \mathscr{E}e + MH + FL + \gamma A + ...$$

The PV term can also be generalized -and needs to be so- for a viscous fluid to a stress-strain conjugate pair. It then involves a stress tensor. We will soon encounter another conjugate pair: μdn that deals with changes in composition (n) and the thermodynamic potential μ.

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23.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

Chemical Potential of Two Phases in Equilibrium

Equilibrium between two phases, e.g. water ice (ice) and liquid water ($water$), is at constant T and P. Therefore:

$$dG = \cancel{-SdT + VdP} + \mu_{ice}dn_{ice} + \mu_{water}dn_{water}$$

There is a relationship between the amount of ice and water:

$$dn_{ice} = -dn_{water}$$

From this, we get:

$$0 = [\mu_{ice} - \mu_{water}]dn_{water} = \Delta\mu \; dn_{water}$$

As dn_{water} is not zero, this means that $\Delta\mu$ must be zero! This must hold true for any set of points where ice and water are in equilibrium. The statement is not just for liquid and solid water, but for any two phases in equilibrium. That is, any two phases in equilbrium will always have the same chemical potential.

The Clapeyron Equation

That is the almost vertical line in the diagram. Its points are not at the same P and T, but we can find out where they should be by considering the thermodynamic potential μ as a *function* of T and P:

$$d\mu = \left(\frac{\partial\mu}{\partial P}\right)_T dT + \left(\frac{\partial\mu}{\partial T}\right)_P dP$$

Because $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \bar{G}$, it is not hard to identify the partial derivatives:

$$\left(\frac{\partial\mu}{\partial P}\right) = \left(\frac{\partial\bar{G}}{\partial P}\right) = \bar{V}$$

$$\left(\frac{\partial\mu}{\partial T}\right) = \left(\frac{\partial\bar{G}}{\partial T}\right) = -\bar{S}$$

This is true for both water and ice, or any two phases in equilibrium. As the $\Delta\mu = 0$, we can equate the $d\mu$ expressions for both water and ice:

$$\left(\frac{\partial\mu_{ice}}{\partial P}\right)_T dT + \left(\frac{\partial\mu_{ice}}{\partial T}\right)_P dP = \left(\frac{\partial\mu_{water}}{\partial P}\right)_T dT + \left(\frac{\partial\mu_{water}}{\partial T}\right)_P dP$$

Rearranging and identifying the partials gives:

$$\bar{V}_{ice}dP - \bar{S}_{ice}dT = \bar{V}_{water}dP - \bar{S}_{water}dT$$

Solving for dP/dT we get:

$$\frac{dP}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

As $\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S} = 0$, we have:

$$\Delta \bar{S} = \frac{\Delta \bar{H}}{T_m}$$

So:

$$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T \Delta \bar{V}}$$

This expression should be valid for all points along a phase boundary, such as the melt line. In fact, it tells use that the phase boundary is **defined** by $\Delta \bar{H}/T\Delta \bar{V}$. For water and ice, we immediately see why the melt line runs a little to the left: exceptionally $\Delta \bar{V}$ is negative for ice, because water is actually a little denser that ice.

The above expression(s) are named after ***Clapeyron.*** The values of $\Delta \bar{H}$ and $\Delta \bar{V}$ do not change much with pressure and can often be considered *constants* for the melting line. When gases are involved that is not really true.

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23.4: The Clausius-Clapeyron Equation

Evaporation

In Section 23.3, the Clapeyron Equation was derived for melting points.

$$\frac{dP}{dT} = \frac{\Delta H_{molar}}{T\Delta V_{molar}}$$

However, our argument is actually quite general and should hold for vapor equilibria as well. The only problem is that the molar volume of gases are by no means so nicely constant as they are for condensed phases. (i. e., for condenses phases, both α and κ are pretty small).

We can write:

$$\frac{dP}{dT} = \frac{\Delta H_{molar}}{T\Delta V_{molar}} = \frac{\Delta H_{molar}}{T}\left[V_{molar}^{gas} - V_{molar}^{liquid}\right]$$

as

$$V_{molar}^{gas} \gg V_{molar}^{liquid}$$

we can approximate

$$V_{molar}^{gas} - V_{molar}^{liquid}$$

by just taking V_{molar}^{gas}. Further more if the vapor is considered an ideal gas, then

$$V_{molar}^{gas} = \frac{RT}{P}$$

We get

$$\frac{1}{P}\cdot\frac{dP}{dT} = \frac{d\ln P}{dT} = \frac{\Delta H_{molar}^{vap}}{RT^2} \tag{23.4.1}$$

Equation 23.4.1 is known as the **Clausius-Clapeyron** equation. We can further work our the integration and find the how the equilibrium vapor pressure changes with temperature:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{molar}^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Thus if we know the molar enthalpy of vaporization we can predict the vapor lines in the diagram. Of course the approximations made are likely to lead to deviations if the vapor is not ideal or very dense (e.g., approaching the critical point).

The Clapeyron Equation

The Clapeyron attempts to answer the question of what the shape of a two-phase coexistence line is. In the $P-T$ plane, we see the a function $P(T)$, which gives us the dependence of P on T along a coexistence curve.

Consider two phases, denoted α and β, in equilibrium with each other. These could be solid and liquid, liquid and gas, solid and gas, two solid phases, et. Let $\mu_\alpha(P,T)$ and $\mu_\beta(P,T)$ be the chemical potentials of the two phases. We have just seen that

$$\mu_\alpha(P,T) = \mu_\beta(P,T) \tag{23.4.2}$$

Next, suppose that the pressure and temperature are changed by dP and dT. The changes in the chemical potentials of each phase are

$$d\mu_\alpha(P,T) = d\mu_\beta(P,T) \tag{23.4.3}$$

$$\left(\frac{\partial \mu_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \mu_\beta}{\partial P}\right)_T dP + \left(\frac{\partial \mu_\beta}{\partial T}\right)_P dT \tag{23.4.4}$$

However, since $G(n,P,T) = n\mu(P,T)$, the *molar* free energy $\bar{G}(P,T)$, which is $G(n,P,T)/n$, is also just equal to the chemical potential

$$\bar{G}(P,T) = \frac{G(n,P,T)}{n} = \mu(P,T) \tag{23.4.5}$$

Moreover, the derivatives of $\bar{G}$ are

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}, \qquad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S} \tag{23.4.6}$$

Applying these results to the chemical potential condition in Equation 23.4.4, we obtain

$$\left(\frac{\partial \bar{G}_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \bar{G}_\beta}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\beta}{\partial T}\right)_P dT \tag{23.4.7}$$

$$\bar{V}_\alpha dP - \bar{S}_\alpha dT = \bar{V}_\beta dP - \bar{S}_\beta dT \tag{23.4.8}$$

Dividing through by dT, we obtain

$$\bar{V}_\alpha \frac{\partial P}{\partial T} - \bar{S}_\alpha = \bar{V}_\beta \frac{\partial P}{\partial T} - \bar{S}_\beta \tag{23.4.9}$$

$$(\bar{V}_\alpha - \bar{V}_\beta)\frac{\partial P}{\partial T} = \bar{S}_\alpha - \bar{S}_\beta \tag{23.4.10}$$

$$\frac{dP}{dT} = \frac{\bar{S}_\alpha - \bar{S}_\beta}{\bar{V}_\alpha - \bar{V}_\beta} \tag{23.4.11}$$

The importance of the quantity dP/dT is that is represents the slope of the coexistence curve on the phase diagram between the two phases. Now, in equilibrium $dG = 0$, and since $G = H - TS$, it follows that $dH = T\ dS$ at fixed T. In the narrow temperature range in which the two phases are in equilibrium, we can assume that H is independent of T, hence, we can write $S = H/T$. Consequently, we can write the molar entropy difference as

$$\bar{S}_\alpha - \bar{S}_\beta = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T} \tag{23.4.12}$$

and the pressure derivative dP/dT becomes

$$\frac{dP}{dT} = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T(\bar{V}_\alpha - \bar{V}_\beta)} = \frac{\Delta_{\alpha\beta}\bar{H}}{T\Delta_{\alpha\beta}\bar{V}} \tag{23.4.13}$$

a result known as the **Clapeyron equation**, which tells us that the slope of the coexistence curve is related to the ratio of the molar enthalpy between the phases to the change in the molar volume between the phases. If the phase equilibrium is between the solid and liquid phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{fus}}$ and $\Delta\bar{V}_{\text{fus}}$, respectively. If the phase equilibrium is between the liquid and gas phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{vap}}$ and $\Delta\bar{V}_{\text{vap}}$, respectively.

For the liquid-gas equilibrium, some interesting approximations can be made in the use of the Clapeyron equation. For this equilibrium, Equation 23.4.13 becomes

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{T(\bar{V}_g - \bar{V}_l)} \tag{23.4.14}$$

In this case, $\bar{V}_g \gg \bar{V}_l$, and we can approximate Equation 23.4.14 as

$$\frac{dP}{dT} \approx \frac{\Delta \bar{H}_{\text{vap}}}{T\bar{V}_g} \tag{23.4.15}$$

Suppose that we can treat the vapor phase as an ideal gas. Certainly, this is not a good approximation so close to the vaporization point, but it leads to an example we can integrate. Since $PV_g = nRT$, $P\bar{V}_g = RT$, Equation 23.4.15 becomes

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}} P}{RT^2} \tag{23.4.16}$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} \tag{23.4.17}$$

$$\frac{d \ln P}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} \tag{23.4.18}$$

which is called the ***Clausius-Clapeyron equation***. We now integrate both sides, which yields

$$\ln P = -\frac{\Delta \bar{H}_{\text{vap}}}{RT} + C$$

where C is a constant of integration. Exponentiating both sides, we find

$$P(T) = C' e^{-\Delta \bar{H}_{\text{vap}}/RT}$$

which actually has the wrong curvature for large T, but since the liquid-vapor coexistence line terminates in a critical point, as long as T is not too large, the approximation leading to the above expression is not that bad.

If we, instead, integrate both sides, the left from P_1 to P_2, and the right from T_1 to T_2, we find

$$\int_{P_1}^{P_2} d \ln P = \int_{T_1}^{T_2} \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} dT \tag{23.4.19}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{23.4.20}$$

$$= \frac{\Delta \bar{H}_{\text{vap}}}{R}\left(\frac{T_1 - T_1}{T_1 T_2}\right) \tag{23.4.21}$$

assuming that $\Delta \bar{H}_{\text{vap}}$ is independent of T. Here P_1 is the pressure of the liquid phase, and P_2 is the pressure of the vapor phase. Suppose we know P_2 at a temperature T_2, and we want to know P_3 at another temperature T_3. The above result can be written as

$$\ln\left(\frac{P_3}{P_1}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \tag{23.4.22}$$

Subtracting the two results, we obtain

$$\ln\left(\frac{P_2}{P_3}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_3}\right) \tag{23.4.23}$$

so that we can determine the vapor pressure at any temperature if it is known as one temperature.

In order to illustrate the use of this result, consider the following example:

Example 23.4.1

At $1\ \text{bar}$, the boiling point of water is $373\ \text{K}$. At what pressure does water boil at $473\ \text{K}$? Take the heat of vaporization of water to be $40.65\ \text{kJ/mol}$.

Solution

Let $P_1 = 1\ \text{bar}$ and $T_1 = 373\ \text{K}$. Take $T_2 = 473\ \text{K}$, and we need to calculate P_2. Substituting in the numbers, we find

$$\ln P_2(\text{bar}) = -\frac{(40.65\ \text{kJ/mol})(1000\ \text{J/kJ})}{8.3145\ \text{J/mol}\cdot\text{K}}\left(\frac{1}{473\ \text{K}} - \frac{1}{373\ \text{K}}\right) = 2.77 \tag{23.4.24}$$

$$P_2(\text{bar}) = (1\ \text{bar})\, e^{2.77} = 16\ \text{bar} \tag{23.4.25}$$

Learning Objectives

- Apply the Clausius-Clapeyron equation to estimate the vapor pressure at any temperature.
- Estimate the heat of phase transition from the vapor pressures measured at two temperatures.

The *vaporization curves* of most liquids have similar shapes with the vapor pressure steadily increasing as the temperature increases (Figure 23.4.1).

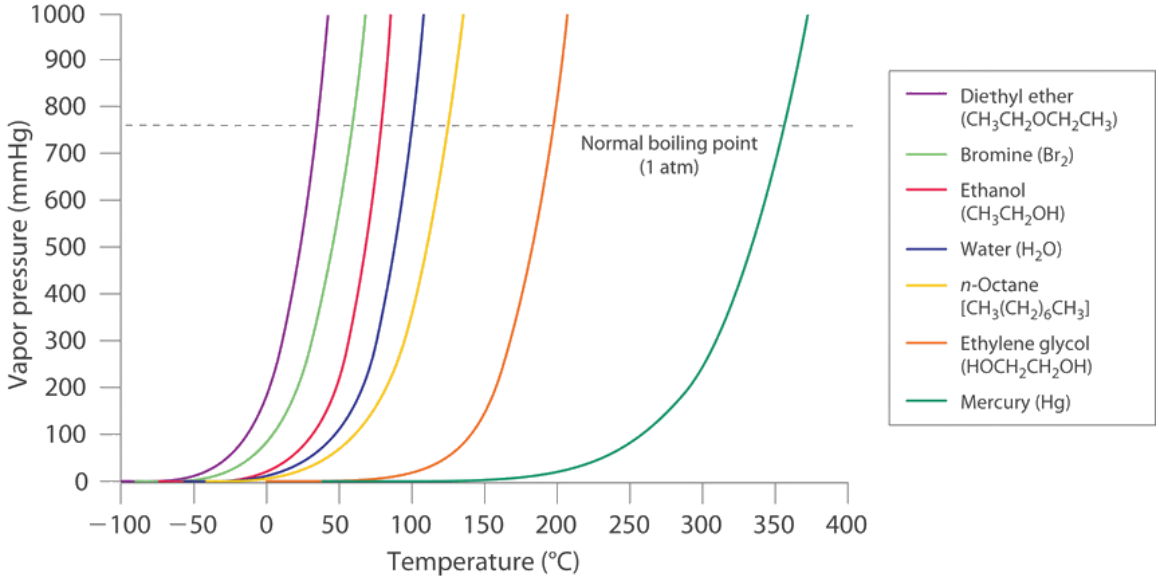


Figure 23.4.1: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the *P* = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC 3.0; Anonymous)

A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the vapor pressure P and temperature T are related,

$$P \propto \exp\left(-\frac{\Delta H_{vap}}{RT}\right) \tag{23.4.26}$$

where ΔH_{vap} is the Enthalpy (heat) of Vaporization and R is the gas constant (8.3145 J mol^{-1} K^{-1}).

A simple relationship can be found by integrating Equation 23.4.26 between two pressure-temperature endpoints:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{23.4.27}$$

where P_1 and P_2 are the vapor pressures at two temperatures T_1 and T_2. Equation 23.4.27 is known as the **Clausius-Clapeyron Equation** and allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

Alternative Formulation

The order of the temperatures in Equation 23.4.27 matters as the Clausius-Clapeyron Equation is sometimes written with a negative sign (and switched order of temperatures):

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{23.4.28}$$

Example 23.4.1: Vapor Pressure of Water

The vapor pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol^{-1}. Estimate the vapor pressure at temperature 363 and 383 K respectively.

Solution

Using the Clausius-Clapeyron equation (Equation 23.4.28), we have:

$$\begin{aligned} P_{363} &= 1.0\exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{363\ K} - \frac{1}{373\ K}\right)\right] \\ &= 0.697\ \text{atm} \end{aligned}$$

$$\begin{aligned} P_{383} &= 1.0\exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{383\ K} - \frac{1}{373\ K}\right)\right] \\ &= 1.409\ \text{atm} \end{aligned}$$

Note that the increase in vapor pressure from 363 K to 373 K is 0.303 atm, but the increase from 373 to 383 K is 0.409 atm. The increase in vapor pressure is not a linear process.

Discussion

We can use the Clausius-Clapeyron equation to construct the entire vaporization curve. There is a deviation from experimental value, that is because the enthalpy of vaporization varies slightly with temperature.

The Clausius-Clapeyron equation can be also applied to sublimation; the following example shows its application in estimating the heat of sublimation.

Example 23.4.2: Sublimation of Ice

The vapor pressures of ice at 268 K and 273 K are 2.965 and 4.560 torr respectively. Estimate the heat of sublimation of ice.

Solution

The enthalpy of sublimation is ΔH_{sub}. Use a piece of paper and derive the Clausius-Clapeyron equation so that you can get the form:

$$\begin{aligned} \Delta H_{sub} &= \frac{R\ln\left(\frac{P_{273}}{P_{268}}\right)}{\frac{1}{268\ K} - \frac{1}{273\ K}} \\ &= \frac{8.3145\ln\left(\frac{4.560}{2.965}\right)}{\frac{1}{268\ \text{K}} - \frac{1}{273\ \text{K}}} \\ &= 52,370\ \text{J mol}^{-1} \end{aligned}$$

Note that the heat of sublimation is the sum of heat of melting (6,006 J/mol at 0°C and 101 kPa) and the heat of vaporization (45,051 J/mol at 0 °C).

Exercise 23.4.2

Show that the vapor pressure of ice at 274 K is higher than that of water at the same temperature. Note the curve of vaporization is also called the curve of vaporization.

Example 23.4.3: Vaporization of Ethanol

Calculate ΔH_{vap} for ethanol, given vapor pressure at 40 °C = 150 torr. The normal boiling point for ethanol is 78 °C.

Solution

Recognize that we have TWO sets of (P, T) data:

- Set 1: (150 torr at 40+273K)
- Set 2: (760 torr at 78+273K)

We then directly use these data in Equation 23.4.28

$$\ln\left(\frac{150}{760}\right) = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$\ln 150 - \ln 760 = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$-1.623 = \frac{-\Delta H_{vap}}{8.314}\left[0.0032 - 0.0028\right]$$

Then solving for ΔH_{vap}

$$\Delta H_{vap} = 3.90 \times 10^4 \text{ J/mol}$$
$$= 39.0 \text{ kJ/mol}$$

Advanced Note

It is important to not use the Clausius-Clapeyron equation for the solid to liquid transition. That requires the use of the more general **Clapeyron equation**

$$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T\Delta \bar{V}}$$

where $\Delta \bar{H}$ and $\Delta \bar{V}$ is the molar change in enthalpy (the enthalpy of fusion in this case) and volume respectively between the two phases in the transition.

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23.5: Chemical Potential Can be Evaluated From a Partition Function

The chemical potential can be given in terms of a partition function. Internal energy can be defined as:

$$U = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{n,V}$$

And entropy can be defined as:

$$S = RT \left(\frac{\partial \ln Q}{\partial T} \right)_{n,V} + R \ln Q$$

We know that Helmholtz energy is:

$$A = U - TS$$

Using our two equations above, we obtain:

$$A = -RT \ln Q$$

Now, let's change gears a bit to show how Helmholtz energy is related to chemical potential. The total differential for Helmholtz energy is:

$$dA = \left(\frac{\partial A}{\partial T} \right)_{n,V} + \left(\frac{\partial A}{\partial V} \right)_{n,T} + \left(\frac{\partial A}{\partial n} \right)_{V,T}$$

And the fundamental equation is:

$$dA = -SdT - PdV + \left(\frac{\partial A}{\partial n} \right)_{V,T} dn$$

Using the relationship between Helmholtz energy and Gibbs energy:

$$G = A + PV$$

We obtain:

$$\begin{aligned} dG &= dA + d(PV) \\ &= -SdT + VdP + \left(\frac{\partial A}{\partial n} \right)_{V,T} dn \end{aligned}$$

We know that the change in Gibbs energy is:

$$\begin{aligned} dG &= -SdT + VdP + \left(\frac{\partial G}{\partial n} \right)_{P,T} dn \\ &= -SdT + VdP + \mu dn \end{aligned}$$

Inspecting these equations, we see that:

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{P,T} = \left(\frac{\partial A}{\partial n} \right)_{V,T}$$

This shows us that, as long as the natural variables for each thermodynamic potential are held constant, the partial derivatives of Gibbs energy and Helmholtz energy with respect to the number of moles, n are equal to the chemical potential. We can now plug in our expression above for Helmholtz energy in terms of the partition function:

$$\mu = -RT \left(\frac{\partial \ln Q}{\partial n} \right)_{V,T}$$

We now have chemical potential written in terms of the partition function, Q.

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23.E: Phase Equilibria (Exercises)

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24: SOLUTIONS I - VOLATILE SOLUTES

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24.1: A Mixture is a Combination of Two or More Substances

So far, we have only discussed systems that are comprised of one component. Because a lot of chemistry occurs in mixtures or produces a mixture, chemists need to consider the thermodynamics of mixtures. A mixture can consist of many different components, however, for the sake of simplicity, we will restrict ourselves for now to two-component mixtures. Two-component mixtures can consist of two gases, two liquids, two solids, or even a liquid and a gas.

Partial Quantities and Scaling

Let's consider a two-component system where the volume and number of moles are changing. For example, we could have a system of a certain size of 1 and reduce its size stepwise in successive steps by taking half of it and throwing the other half away. The number of moles of each component, n_1 and n_2, will change as the volume of the system, V, changes:

$$dn_1 = n_1 dV$$

$$dn_2 = n_2 dV$$

The extensive Gibbs free energy will be affected the same way:

$$dG = GdV$$

At constant T and P we can write:

$$dG = \cancel{-SdT} + \cancel{VdP} + \mu_1 dn_1 + \mu_2 dn_2$$

So:

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$GdV = \mu_1 n_1 dV + \mu_2 n_2 dV$$

If we integrate this from the original size, 1, down to 0 (or 0 to 1, it does not matter). We get:

$$\int_0^1 GdV = \int_0^1 \mu_1 n_1 dV + \int_0^1 \mu_2 n_2 dV$$

$$G\int_0^1 dV = \mu_1 n_1 \int_0^1 dV + \mu_2 n_2 \int_0^1 dV$$

$$G = \mu_1 n_1 + \mu_2 n_2$$

By the same argument we have:

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

where $\bar{V}_i$ is the partial molar volume for component i. These partial molar volumes are generally a function of composition (and P, T) and have been tabulated for a number of liquid systems. They allow us to calculate the real volume of a binary mixture. Volumes are generally speaking ***not strictly additive***. This fact is typically ignored in volumetric analysis and the use of molarities. Fortunately the deviations are often negligible in dilute solutions.

For phase diagrams, molarity (moles per liter) is not a very suitable quantity to use for concentration due to its volume dependence. Usually we work with mole fractions or molalities (moles per kilogram), where there are no volume dependencies.

Gaseous Mixtures

Gases can always mix in any ratio and mixtures typically act close to ideal unless heavily compressed or brought to low temperatures. The only exception is if the gases react (e.g, HCl and NH_3). Gas molecules experience little interaction with

each other and, therefore, it does not matter much whether the molecules are different or the same. The total pressure can be computed by adding the partial pressures of the two components (Dalton's Law of Partial Pressures):

$$P_{total} = P_1 + P_2 \tag{24.1.1}$$

Liquid Mixtures

There are binary liquid systems that are fully miscible and are said to act as *ideal solutions*. Liquid molecules typically experience *strong* interactions with their neighbors. For the solution to be ideal, the interactions must remain *equally strong* even when the neighboring substance is different. This means they must be chemically similar. For this reason, liquid binaries are often *not* ideal. The next nearest thing are **regular solutions**. Even these systems can display phase segregation and limited mutual solubilities at low temperatures. Many liquid-liquid binaries diverge from ideality even more than the regular solutions and many of them are hardly miscible at all.

Table 24.1.1: Solutions

Solution/mixture	Interactions	Miscibility
Ideal gas	none	complete
Ideal liquid	strong but similar	complete
Regular liquid	strong, modestly dissimilar	not always complete
Real liquid	often strongly dissimilar	partial or none

Solid Mixtures

Solid binaries tend to be even less miscible than liquid binaries to the point that immiscibility is the rule and miscibility is the exception. Even totally miscible systems like electrum (the alloys of silver and gold) are far from ideal.



Figure 24.1.1: Electrum coin of the Byzantine Emperor Alexius I Comnenus. (CC-BY-SA-3.0; Classical Numismatic Group, Inc. http://www.cngcoins.com)

Another point of practical (kinetic rather than thermodynamic) importance is that even if two compounds are able to form a homogeneous solid solution, it usually takes heating for prolonged periods to get them to mix because solid diffusion is typically very slow. Nevertheless, solid solubility is an important issue for many systems, particularly for metal alloys. Two molecular solid substances that differ vastly in shape, size, polarity and or hydrogen bonding (e.g. organic compounds) typically have *negligible* mutual solid solubility. The latter fact is frequently exploited in organic chemistry to purify compounds through recrystallization.

Note

Solid solutions are relatively infrequent and never ideal.

Ideal liquid/Ideal Gas Phase Diagrams

Let's mix two liquids together. Liquids typically have different boiling points, with one being more volatile than the other. The vapor pressure of a component scales simply with the equilibrium vapor pressure of the pure component. In the gas phase, ***Dalton's law*** is applicable:

$$y_i = \frac{P_i}{P_{total}} \tag{24.1.2}$$

This is a consequence of the fact that ideal gases do not interact. The latter implies that the total pressure is simply the sum of the partial ones:

$$P_{total} = \sum_i^N P_i$$

If the liquid solution is ideal, then the vapor pressure of both components follow ***Raoult's law***, which states that the equilibrium vapor pressure above the mixture is the equilibrium pressure of the pure component times the mole fraction:

$$P_i = \chi_i P_i^\circ \tag{24.1.3}$$

- P_i is the vapor pressure of component i in the mixture
- P_i° is equilibrium vapor pressure of the pure component i.
- χ_i is the mole fraction of i^{th} component in the liquid phase.

Note that values for pure components are typically indicated by adding an asterisk $^\circ$ superscript.

The idea behind Raoult's law is that if the interactions are similar, it is a matter of random chance which component sits at the interface at any given moment. The equilibrium vapor pressure has to do with the probability that a molecule escapes from the interface into the gas phase and is dependent on both the substances volatility and the number that cover the surface. This leads to Raoult's Law, where we must multiply the vapor pressure of the pure liquid (volatility) by the mole fraction (number on the surface).

Note: Applicability of Raoult's Law

Raoult's law seldom holds completely, which is more applicable if the two components are almost chemically identical like two isomers, e.g., 1-propanol and 2-propanol.

The Pressure Phase Diagram

If we assume that temperature is constant, we can plot the total pressure for both Dalton and Raoult's laws versus composition (of gas: y_1 and liquid: χ_1 on the same axis).

Liquid Phase:

$$\begin{aligned} P_{total} &= P_1 + P_2 \\ &= \chi_1 P_1^\circ + \chi_2 P_2^\circ \\ &= \chi_1 P_1^\circ + (1-\chi_1) P_2^\circ \\ &= P_2^\circ - \chi_1 (P_2^\circ - P_1^\circ) \end{aligned} \tag{24.1.4}$$

Clearly this is a straight line going from P_2° at $x = 0$ to P_1° at $x = 1$.

However the composition of the vapor in equilibrium with a liquid at a given mole fraction χ is *different* than that of the liquid. So y is not χ. If we take Dalton's law (Equation 24.1.2) and substitute Raoult's Law (Equation 24.1.3) in the numerator and the straight line in the denominator we get:

$$y_1 = \frac{\chi_1 P_1^\circ}{P_2^\circ - \chi_1(P_2^\circ - P_1^\circ)} \tag{24.1.5}$$

Exercise

Suppose $P_1^\circ = 50$ Torr and $P_2^\circ = 25$ Torr. If $\chi_1 = 0.6$ what is the composition of the vapor?

We can rearrange Equations 24.1.4 and 24.1.5 to plot the total pressure as function of y_1:

$$P_{total} = \frac{P_1^\circ P_2^\circ}{P_1^\circ + (P_2^\circ - P_1^\circ)y_1} \tag{24.1.6}$$

This is *not* a straight line.

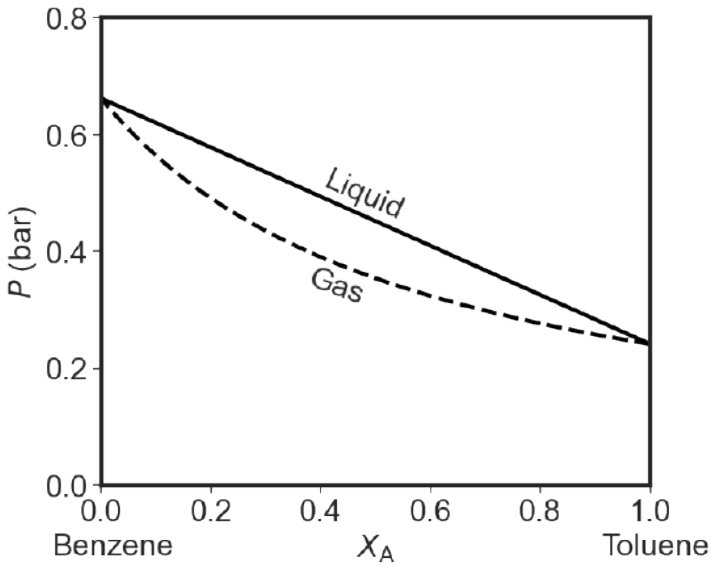


Figure 24.1.1: an ideal-ideal phase diagram for the binary system of toluene (A) and benzene (B). The curves are calculated from Equations 24.1.4 and 24.1.6.

As you can see when we plot both lines we get a diagram with three regions. At high pressures we just have a liquid. At low pressures we just have a gas. In between we have a ***phase gap*** or ***two phase region***. Points inside this region represent states that the system cannot achieve homogeneously. The horizontal ***tie-line*** shows which *two* phases coexists. I used the same 25 and 50 Torr values for the pure equilibrium pressures as in the question above. If you try to make a system with *overall* composition x and impose a pressure that falls in the forbidden zone you get two phases: a gaseous one that is richer in the more volatile component and a liquid one that is poorer in the volatile component than the overall composition would indicate.

The Temperature Phase Diagram

Note that the question: *what phase do we have when?* is really a function of ***both*** P ***and*** T, so that if we want to represent *all* our knowledge in a diagram we should make it a three dimensional picture. This is not so easy to draw and not easy to comprehend visually either. This is why we usually look at a 2D cross section of the 3D space.

The above diagram is *isothermal*: we vary P, keeping T constant. It is, however, more usual (and easier) to do it the other way around. We keep pressure constant (say 1 bar, that's easy) and start heating things up isobarically.

The boiling points of our mixtures can also be plotted against x (the liquid composition) and y (the gaseous one) on the same horizontal axis. Again because in general y is not equal x we get two different curves. Neither of them are straight lines in this case and we end up with a lens-shaped two phase region:

binary T-X diagram showing the lever rule

binary T-X diagram showing the lever rule

What happens to a mixture with a given overall composition x(=x_1) when it is brought to a temperature where it boils can be seen at the intersection of a vertical line (an isopleth) at $x_{overall}$ and a horizontal one (an isotherm) at T_{boil}. If the intersection points in inside the two phase region a vapor phase and a liquid phase result that have a different composition from the overall one. The vapor phase is always richer in the more volatile component (the one with the lowest boiling point, on the left in the diagram). The liquid phase is enriched in the less volatile one.

The Lever Rule

How much of each phase is present is represented by the arrows in the diagram. The amount of liquid is proportional to the left arrow, the amount of gas to the right one (i.e. it works crosswise). The composition of the liquid in equilibrium with the vapor is:

$$x_2 = \frac{n_2^{liq}}{n_{1+2}^{liq}}$$

$$x_2^* n_{1+2}^{liq} = n_2^{liq}$$

The composition of the vapor is:

$$y_2 = \frac{n_2^{gas}}{n_{1+2}^{gas}}$$

$$y_2^* n_{1+2}^{gas} = n_2^{gas}$$

The overall composition is:

$$x_{all} = \frac{n_2^{liq+gas}}{n_{1+2}^{liq+gas}}$$

$$x_{all}^* n_{1+2}^{liq+gas} = n_2^{gas} + n_2^{liq}$$

$$x_{all}^* n_{1+2}^{liq+gas} = y_2^* n_{1+2}^{gas} + x_2^* n_{1+2}^{liq}$$

$$x_{all}^* n_{1+2}^{gas} + x_{all}^* n_{1+2}^{liq} = y_2^* n_{1+2}^{gas} + x_2^* n_{1+2}^{liq}$$

Thus:

$$\frac{n_{1+2}^{liq}}{n_{1+2}^{gas}} = \frac{y_2 - x_{all}}{x_{all} - x_2}$$

Distillation

The difference in composition between the gas and the liquid can be exploited to separate the two components, at least partially. We could trap the vapor and cool it down to form a liquid with a different composition. We could then boil it again and repeat the process. Each time the vapor will be more enriched in the volatile phase whereas the residual liquid is more enriched in the less volatile one. This process is known as ***distillation***. In practice the process is done one a fractionation column which makes it possible to have a series of vapor-liquid equilibria at once.

A good degree of purity can be reached this way, although 100% purity would take an infinite number of distillation steps.

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24.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium

At **equilibrium**, there is no change in chemical potential for the system:

$$\sum_i n_i d\mu_i = 0 \tag{24.2.1}$$

This is the Gibbs-Duhem relationship and it places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i. And as with other partial molar quantities:

$$G_{\text{tot}} = \sum_i n_i \mu_i$$

Taking the derivative of both sides yields:

$$dG_{\text{tot}} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

But dG can also be expressed as:

$$dG = Vdp - sdT + \sum_i \mu_i dn_i$$

Setting these two expressions equal to one another:

$$\sum_i n_i d\mu_i + \cancel{\sum_i \mu_i dn_i} = Vdp - sdT + \cancel{\sum_i \mu_i dn_i}$$

And after canceling terms, one gets:

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{24.2.2}$$

For a system at constant temperature and pressure:

$$V\ dp - s\ dT = 0 \tag{24.2.3}$$

Substituting Equation 24.2.3 into 24.2.2 results in the **Gibbs-Duhem equation** (Equation 24.2.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium.

Gibbs-Duhem for Binary Systems

For a binary system consisting of components two components, A and B:

$$n_B d\mu_B + n_A d\mu_A = 0$$

Rearranging:

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

Consider a Gibbs free energy that only includes μ_n conjugate variables as we obtained it from our scaling experiment at T and P constant:

$$G = \mu_A n_A + \mu_B n_B$$

Consider a change in G:

$$\begin{aligned} dG &= d(\mu_A n_A) + d(\mu_B n_B) \\ &= n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B \end{aligned}$$

However, if we simply write out a change in G due to the number of moles we have:

$$dG = \mu_A dn_A + \mu_B dn_B$$

Consequently the other terms must add up to zero:

$$0 = n_A d\mu_A + n_B d\mu_B$$

$$d\mu_A = -\frac{n_B}{n_A} d\mu_B$$

$$d\mu_A = -\frac{\chi_B}{\chi_A} d\mu_B$$

In the last step we have simply divided both denominator and numerator by the total number of moles. This expression is the Gibbs-Duhem equation for a 2-component system. It relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).

> The Gibbs-Duhem equation relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).

Gibbs-Duhem in the Ideal Case

In the ideal case we have:

$$\mu_B = \mu_B^* + RT \ln x_B$$

Gibbs-Duhem gives:

$$d\mu_A = -\frac{\chi_B}{\chi_A} d\mu_B$$

As:

$$d\mu_B = 0 + \frac{RT}{\chi_B}$$

with x_B being the only active variable at constant temperature, we get:

$$d\mu_A = -\frac{\chi_B}{\chi_A} \frac{RT}{\chi_B} = \frac{RT}{\chi_A}$$

If we now wish to find μ_A we need to integrate $d\mu_A$, e.g. form pure 1 to χ_A. This produces:

$$\mu_A = \mu_A^* + RT \ln \chi_A$$

This demonstrates that Raoult's law can only hold over the whole range for one component ***if*** it also holds for the other over the whole range.

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24.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound i in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i} \tag{24.3.1}$$

The partial molar function is of particular importance and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. Since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function and reach equilibrium. In general, the total change in the Gibbs function (dG) can be calculated from:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_j \neq i} dn_i$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives:

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

But as it turns out, the chemical potential can be defined as the partial molar quantity of any of the four major thermodynamic functions U, H, A, or G:

Table 24.3.1*: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions*

$dU = TdS - PdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq i}$
$dH = TdS - VdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq i}$
$dA = -PdV - TdS + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_j \neq i}$
$dG = VdP - SdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i}$

The last definition, in which the chemical potential is defined as the partial molar Gibbs function, is the most commonly used, and perhaps the most useful (Equation 24.3.1). As the partial most Gibbs function, it is easy to show that:

$$d\mu = VdP - SdT$$

where V is the molar volume, and S is the molar entropy. Using this expression, it is easy to show that:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V$$

and so at constant temperature:

$$\int_{\mu^o}^{\mu} d\mu = \int_{P^o}^{P} V\, dP \tag{24.3.2}$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (i. e., κ_T is very small), therefore Equation 24.3.2 becomes:

$$\int_{\mu^o}^{\mu} d\mu = V \int_{P^o}^{P} dP$$

$$\mu - \mu^o = V(P - P^o)$$

or:

$$\mu = \mu^o + V(P - P^o)$$

Where P^o is the standard state pressure (1 bar) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas:

$$V = \frac{RT}{P}$$

So at constant temperature, Equation 24.3.2 then becomes:

$$\int_{\mu^o}^{\mu} d\mu = RTint_{P^o}^{P} \frac{dP}{P} \tag{24.3.3}$$

or:

$$\mu = \mu^o + RT \ln\left(\frac{P}{P^o}\right)$$

A lot of chemistry takes place in solution and therefore this topic is of prime interest for chemistry.

Thermodynamic potentials of solutions

The Gibbs free energy of an ideal gas depends logarithmically on pressure:

$$G = G^o + RT \ln \frac{P}{P^o}$$

$P^{\ominus}$ is *is often dropped out of the formula.* and we write:

$$G = G^o + RT \ln P$$

> Notice however that although P and P/P^o have the same numerical value, the dimensions are different. P usually has dimensions of bar, but P/P^o is *dimensionless*.

If we have a gas mixture we can hold the same logarithmic argument for each partial pressure as the gases do not notice each other. We do need to take into account the number of moles of each and work with (partial) molar values, i.e. the thermodynamic potential:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{24.3.4}$$

If we are dealing with an equilibrium over an ideal liquid solution the situation in the gas phase gives us a probe for the situation in the liquid. The equilibrium must hold for each of *all* components j (say two in binary mixture). That means that for each of them the thermodynamic potential in the liquid and in the gas must be equal:

$$\mu_j^{sln} = \mu_j^{gas}$$

for all j. Consider what happens to a pure component, e.g. $j = 1$ in equilibrium with its vapor. We can write:

$$\mu_1^{pure\ liq} = \mu_1^{pure\ vapor} = \mu_1^o + RT \ln \frac{P_1^*}{P^o}$$

The asterisk in P_1^* denotes the equilibrium vapor pressure of pure component 1 and we will use that to indicate the thermodynamic potential of pure compounds too:

$$\mu_1^{*liq} = \mu_1^o + RT \ln \frac{P_1^*}{P^o} \tag{24.3.5}$$

Combining Equations 24.3.5 and 24.3.4 we find a relationship between the solution and the pure liquid:

$$\mu_j^{sln} = \mu_j^* + RT \ln \frac{P_j}{P_j^*}$$

Notice that the *gas* and its pressure is used to link the mixture and the pure compound.

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24.4: Ideal Solutions obey Raoult's Law

Liquids tend to be volatile, and as such will enter the vapor phase when the temperature is increased to a high enough value, provided they do not decompose first. A volatile liquid is one that has an appreciable vapor pressure at the specified temperature. An ideal mixture containing at least one volatile liquid can be described using **Raoult's Law:**

$$P_j = x_j P_j^*$$

Raoult's law can be used to predict the total vapor pressure above a mixture of two volatile liquids. As it turns out, the composition of the vapor will be different than that of the two liquids, with the more volatile compound having a larger mole fraction in the vapor phase than in the liquid phase. This is summarized in the following diagram for an ideal mixture of two compounds, water and ethanol at 75 °C. At this temperature, water a pure vapor pressure of 384 Torr and ethanol has a pure vapor pressure of 945 Torr. In Figure 24.4.1, the composition of the liquid phase is represented by the solid line and the composition of the vapor phase is represented by the dashed line.

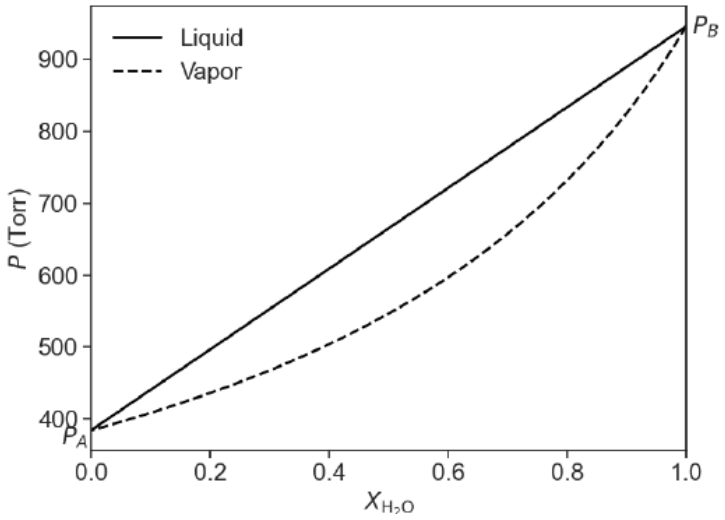


Figure 24.4.1: The composition of the liquid phase (solid line) and the vapor phase (dashed lined) as a function of mole fraction according to Raoult's law. The solution is a mixture of water and ethanol. P_A is the vapor pressure of pure water and P_B is the vapor pressure of pure ethanol at 75 °C

Often, it is desirable to depict the phase diagram at a single pressure so that temperature and composition are the variables included in the graphical representation. In such a diagram, the vapor, which exists at higher temperatures) is indicated at the top of the diagram, while the liquid is at the bottom. A typical temperature vs. composition diagram is depicted in Figure 24.4.2 for an ideal mixture of two volatile liquids.

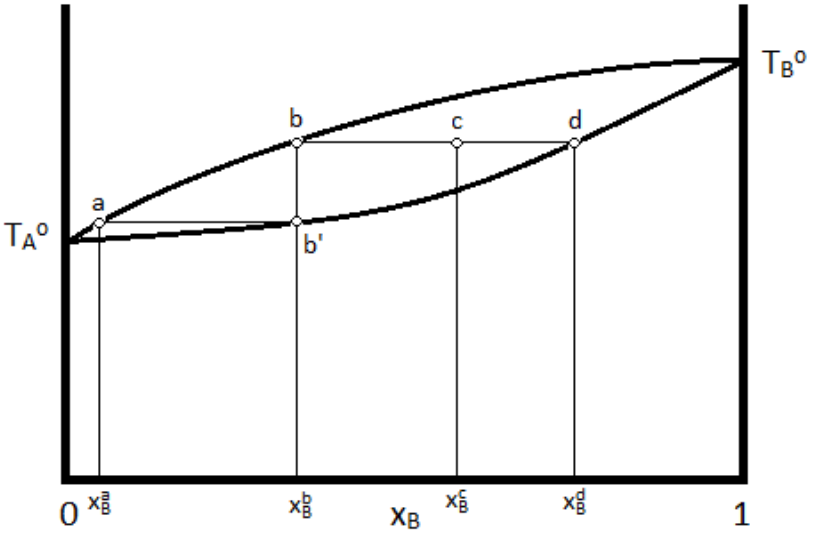


Figure 24.4.2: A typical temperature vs. composition diagram.

In this diagram, T_A and T_B represent the boiling points of pure compounds A and B. If a system having the composition indicated by χ_B^c has its temperature increased to that indicated by point c, The system will consist of two phases, a liquid phase, with a composition indicated by χ_B^d and a vapor phase indicated with a composition indicated by χ_B^b. The relative amounts of material in each phase can be described by the lever rule, as described previously.

Further, if the vapor with composition χ_B^b is condensed (the temperature is lowered to that indicated by point b') and re-vaporized, the new vapor will have the composition consistent with χ_B^a. This demonstrates how the more volatile liquid (the one with the lower boiling temperature, which is A in the case of the above diagram) can be purified from the mixture by collecting and re-evaporating fractions of the vapor. If the liquid was the desired product, one would collect fractions of the residual liquid to achieve the desired result. This process is known as distillation.

The Gibbs energy of mixing is always negative

When we add n_A moles of component A and n_B moles of component B to form an ideal liquid solution, this is generally a spontaneous process. Let us consider the Gibbs free energy change of that process:

$$\Delta_{mix}G = n_1\mu_1^{sln} + n_2\mu_2^{sln} - (n_1\mu_1^* + n_2\mu_2^*)$$

Using:

$$\mu_i^{sln} \equiv \mu_i^* + nRTx_i \ln x_i$$

his expression simplifies to:

$$\Delta_{mix}G = nRTx_A \ln x_A + nRTx_B \ln x_B$$

where n is the total moles. Mole fraction, x_i, is always less than one, so the Gibbs energy of mixing is always negative; mixing is always spontaneous. We can generalize this to mixtures with more than two components:

$$\Delta_{mix}G = nRT \sum_i x_i \ln x_i$$

This expression looks suspiciously familiar. Apart from a factor of $-T$, it is just like the **entropy of mixing**:

$$\Delta_{mix}S = -nR \sum_i x_i \ln x_i$$

Recalling the relationship between Gibbs energy and entropy:

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$$

This leaves no room at all for an enthalpy effect:

$$\Delta_{mix}H = 0$$

Even though there are strong interactions between neighboring particles in liquids, there is no enthalpy change. This implies that it does not matter what the neighboring molecules are. If we represent the average interaction energy between molecule i and j by U_{ij}, we are assuming that U_{ij} is always the same. In practice, this is *seldom* the case. It usually does matter and then the enthalpy term is not zero. As this affects the thermodynamics of the liquid solution, it should also affect the vapor pressures that are in equilibrium with it.

In the ideal case, volumes are additive

From the change of G in its natural variables, we know that:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

This means that if we take

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V_{mix}$$

In the ideal case we get:

$$\left(\frac{\partial \Delta G^{ideal}}{\partial P}\right)_T = \Delta V_{mix}^{ideal}$$

$$\left(\frac{\partial RT(n_1 \ln x_1 + n_2 \ln x_2)}{\partial P}\right)_T = \Delta V_{mix}^{ideal} = 0$$

In the ideal case, volumes are *additive* and we need not worry about how the partial molar volumes change with composition.

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24.5: Most Solutions are Not Ideal

If we plot the partial pressure of one component, P_1, above a mixture with a mole fraction x_1, we should get a straight line with a slope of P_1^* (Raoult's law). Above non-ideal solutions the graph will no longer be a straight line but a curve. However towards $x_1 = 1$ the curve typically approaches the Raoult line. On the other extreme, there often is a more or less linear region as well, ***but with a different slope*** (Figure 24.5.1). This means that we can identify two *limiting* laws:

- For $x \to 0$: **Henry's law**:

$$P_1 = K_H x_1$$

- For $x \to 1$: **Raoult's law**:

$$P_1 = P_1^* x_1$$

This implies that the straight line that indicates the Henry expression will intersect the y-axis at $x = 1$ (pure compound) at a ***different*** point than P^*. For $x \to 0$ (low concentrations) we can speak of component 1 being the *solute* (the minority component). At the other end $x \to 1$ it plays the role of the *solvent* (majority component).

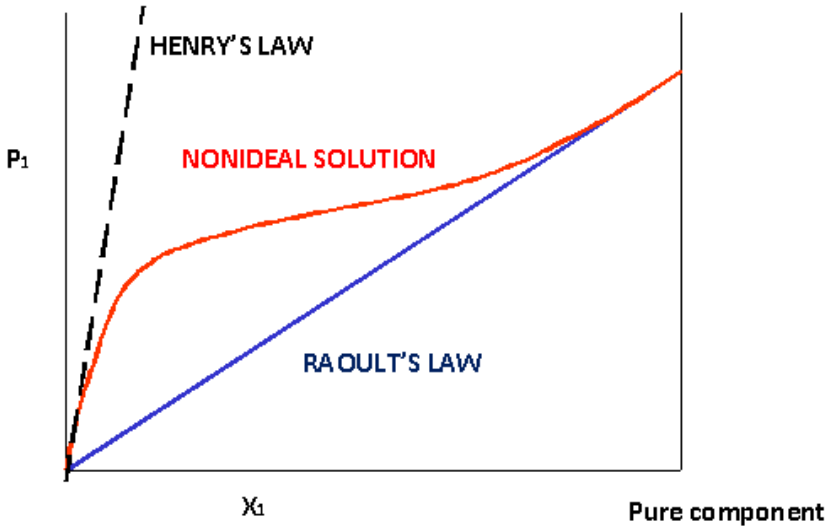


Figure 24.5.1 : Vapor pressure above an ideal and a non-ideal solution

> Another thing to note is that P^* is a property of *one pure component*, the value of K_H by contrast is a property of the *combination of two components*, so it needs to be measured for each solute-solvent combination.

As you can see we have a description for both the high and the low end, but not in the middle. In general, the more modest the deviations from ideality the larger the range of validity of the two limiting laws. The way to determine K_H would be to actually determine vapor pressures. How about the other component? Do we need to measure them too? Fortunately we can use thermodynamics to answer this question with no. There is a handy expression that saves us the trouble.

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24.6: Vapor Pressures of Volatile Binary Solutions

The behaviors of ideal solutions of volatile compounds follow Raoult's Law. Henry's Law can be used to describe the deviations from ideality. Henry's law states:

$$P_B = k_H P_B^o$$

For which the Henry's Law constant (k_H) is determined for the specific compound. Henry's Law is often used to describe the solubilities of gases in liquids. The relationship to Raoult's Law is summarized in Figure 24.6.1.

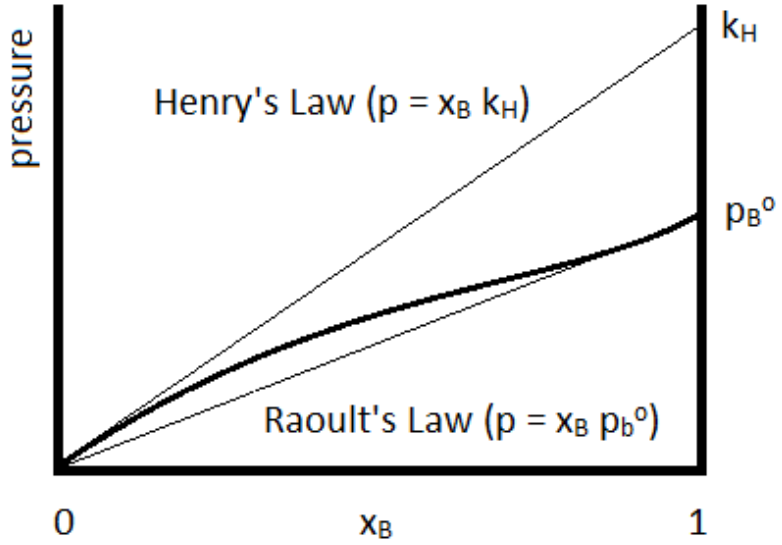


Figure 24.6.1: The relationship between Raoult's Law and Henry's Law for a binary mixture.

Henry's Law is depicted by the upper straight line and Raoult's Law by the lower.

Example 24.6.1: Solubility of Carbon Dioxide in Water

The solubility of $CO_2(g)$ in water at 25 °C is 3.32 x 10^{-2} M with a partial pressure of CO_2 over the solution of 1 bar. Assuming the density of a saturated solution to be 1 kg/L, calculate the Henry's Law constant for CO_2.

Solution:

In one L of solution, there is 1000 g of water (assuming the mass of CO_2 dissolved is negligible.)

$$(1000\,g)\left(\frac{1\,mol}{18.02\,g}\right) = 55\,mol\,H_2O$$

The solubility of CO_2 can be used to find the number of moles of CO_2 dissolved in 1 L of solution also:

$$\frac{3.32\times10^{-2}mol}{L}\cdot 1\,L = 3.32\times10^{-2}mol\,CO_2$$

and so the mol fraction of CO_2 is

$$\chi_b = \frac{3.32\times10^{-2}mol}{55.5\,mol} = 5.98\times10^{-4}$$

And so

$$10^5\ Pa = 5.98 \times 10^{-4} k_H$$

or

$$k_H = 1.67 \times 10^9\ Pa$$

Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

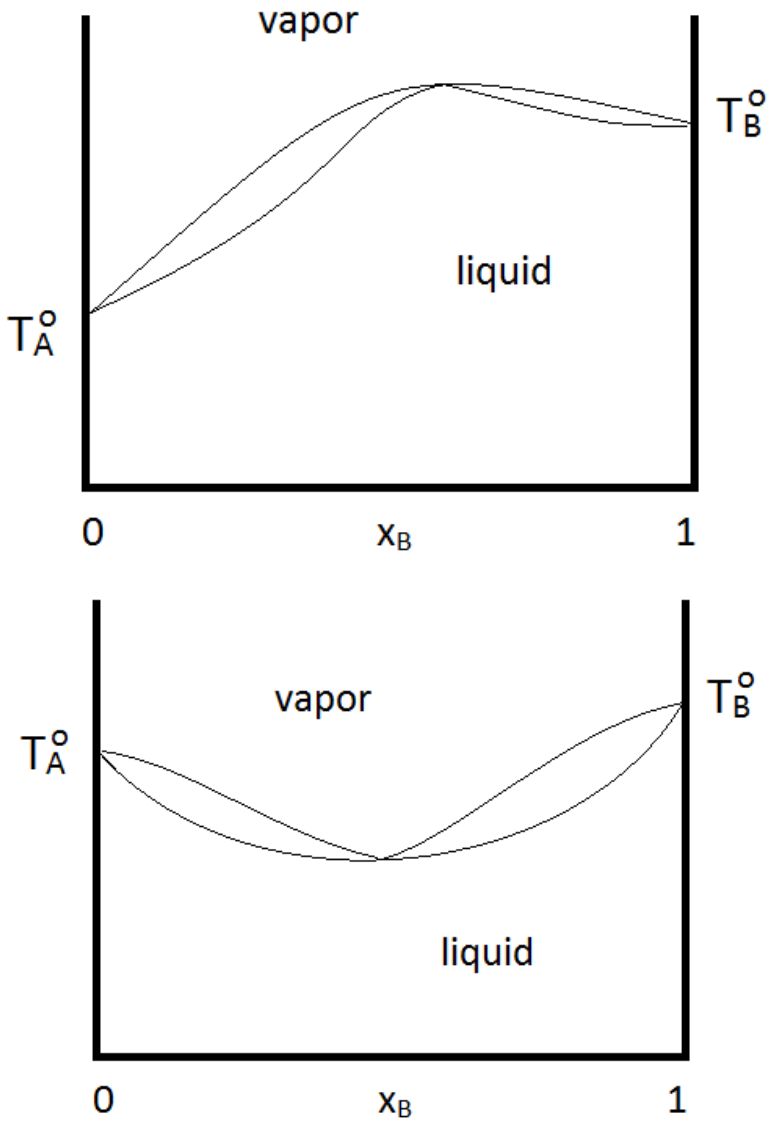


Figure $24.6.2$: Phase diagrams for (left) a maximum boiling point azeotrope and (right) Ta maximum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as show in Figure $24.6.2; left$. Regardless, distillation cannot purify past the azeotrope point, since the vapor and the liquid phases have the same composition. If a system forms a minimum boiling azeotrope and has a range of compositions and temperatures at which two liquid phases exist, the phase diagram might look like Figure $24.6.2; right$:

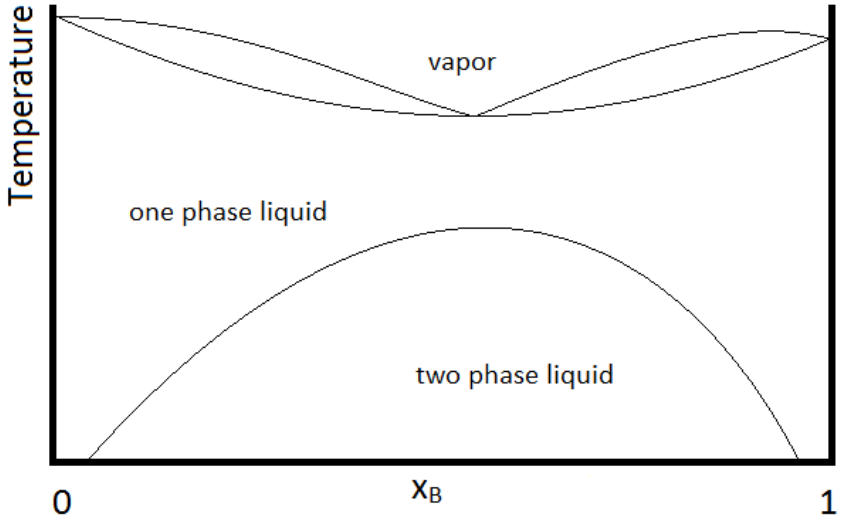
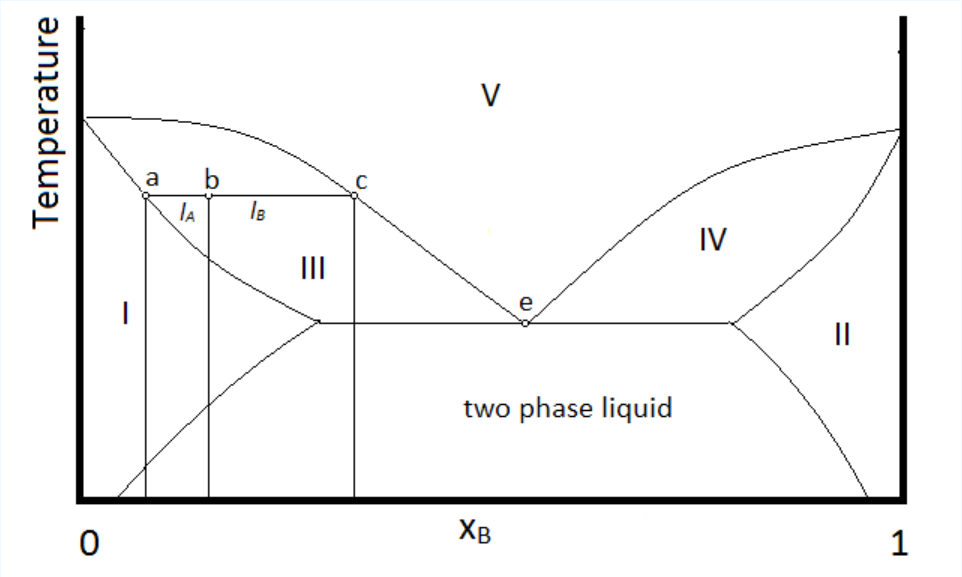


Figure 24.6.3: *Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher that when components are miscible (single phase).*

Another possibility that is common is for two substances to form a two-phase liquid, form a minimum boiling azeotrope, but for the azeotrope to boil at a temperature below which the two liquid phases become miscible. In this case, the phase diagram will look like Figure 24.6.3.

Example 24.6.1:

In the diagram, make up of a system in each region is summarized below the diagram. The point e indicates the azeotrope composition and boiling temperature.



I. Single phase liquid (mostly compound A)
II. Single phase liquid (mostly compound B)
III. Single phase liquid (mostly A) and vapor
IV. Single phase liquid (mostly B) and vapor
V. Vapor (miscible at all mole fractions since it is a gas)

Solution

Within each two-phase region (III, IV, and the two-phase liquid region, the lever rule will apply to describe the composition of each phase present. So, for example, the system with the composition and temperature represented by point b (a single-phase liquid which is mostly compound A, designated by the composition at point a, and vapor with a composition designated by that at point c), will be described by the lever rule using the lengths of tie lines l_A and l_B.

Gibbs-Duhem and Henry's law

What happens when Raoult does *not* hold over the whole range? Recall that in a gas:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{24.6.1}$$

or

$$\mu_j = \mu_j^o + RT \ln P_j$$

after dropping $P^o = 1 \ \ bar$ out of the notation. Note that numerically this does not matter, since P_j is now *assumed* to be dimensionless.

Let's consider $d\mu_1$ at constant temperature:

$$d\mu_1 = RT \left(\frac{\partial \ln P_1}{\partial x_1} \right) dx_1$$

likewise:

$$d\mu_2 = RT \left(\frac{\partial \ln P_2}{\partial x_2} \right) dx_2$$

If we substitute into the Gibbs-Duhem expression we get:

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right) dx_1 + x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right) dx_2 = 0$$

Because $dx_1 = -dx_2$:

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right) = x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)$$

(This is an alternative way of writing Gibbs-Duhem).

If in the limit for $x_1 \to 1$ Raoult Law holds then

$$P_1 \to x_1 P_1^*$$

Thus:

$$\frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_1}$$

and

$$\frac{x_1}{x_1} = x_2 \frac{\partial \ln P_2}{\partial x_2}$$

$$1 = x_2 \frac{\partial \ln P_2}{\partial x_2}$$

$$\frac{1}{x_2} = \frac{\partial \ln P_2}{\partial x_2} \tag{24.6.2}$$

We can integrate Equation 24.6.2 to form a logarithmic impression, but it will have an integration constant:

$$\ln P_2 = \ln x_2 + constant$$

This constant of integration can be folded into the logarithm as a multiplicative constant, K

$$\ln P_2 = \ln (K x_2)$$

So for $x_1 \to 1$ (i.e., $x_2 \to 0$), we get that

$$P_2 = K x_2$$

where K is s*ome* constant, but not necessarily P^*. What this shows is that when one component follows Raoult the other *must* follow Henry and vice versa. (Note that the ideal case is a subset of this case, in that the value of K then becomes P^* and the linearity must hold over the whole range.)

Margules Functions

Of course a big drawback of the Henry law is that it only describes what happens at the two extremes of the phase diagram and not in the middle. In cases of moderate non-ideality, it is possible to describe the whole range (at least in good approximation) using a **Margules function**:

$$P_1 = (x_1 P_1^*)\, f_{Mar}$$

The function f_{Mar} has the shape:

$$f_{Mar} = \exp\left[\alpha x_2^2 + \beta x_2^3 + \delta x_2^3 + ...\right]$$

Notice that the Margules function involves the mole fraction of the *opposite* component. It is an exponential with a series expansion. with the constant and linear term missing. As you can see the function has a number of parameters α, β, δ etc. that need to be determined by experiment. In general, the more the system diverges from ideality, the more parameters you need. Using Gibbs-Duhem is is possible to translate the expression for P_1 into the corresponding one for P_2.

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24.7: Activities of Nonideal Solutions

The bulk of the discussion in this chapter dealt with ideal solutions. However, real solutions will deviate from this kind of behavior. So much as in the case of gases, where fugacity was introduced to allow us to use the ideal models, **activity** is used to allow for the deviation of real solutes from limiting ideal behavior. The activity of a solute is related to its concentration by

$$a_B = \gamma \frac{m_B}{m^o}$$

where γ is the **activity coefficient**, m_B is the molaliy of the solute, and m^o is unit molality. The activity coefficient is unitless in this definition, and so the activity itself is also unitless. Furthermore, the activity coefficient approaches unity as the molality of the solute approaches zero, insuring that dilute solutions behave ideally. The use of activity to describe the solute allows us to use the simple model for chemical potential by inserting the activity of a solute in place of its mole fraction:

$$\mu_B = \mu_B^o + RT \ln a_B$$

The problem that then remains is the measurement of the activity coefficients themselves, which may depend on temperature, pressure, and even concentration.

Activity Coefficients for Ionic Solutes

For an ionic substance that dissociates upon dissolving

$$MX(s) \rightarrow M^+(aq) + X^-(aq)$$

the chemical potential of the cation can be denoted μ_+ and that of the anion as μ_-. For a solution, the total molar Gibbs function of the solutes is given by

$$G = \mu_+ + \mu_-$$

where

$$\mu = \mu^* + RT \ln a$$

where \(\mu^*\) denotes the chemical potential of an ideal solution, and a is the activity of the solute. Substituting his into the above relationship yields

$$G = \mu_+^* + RT \ln a_+ + \mu_-^* + RT \ln a_-$$

Using a molal definition for the activity coefficient

$$a_i = \gamma_i m_i$$

The expression for the total molar Gibbs function of the solutes becomes

$$G = \mu_+^* + RT \ln \gamma_+ m_+ + \mu_-^* + RT \ln \gamma_- m_-$$

This expression can be rearranged to yield

$$G = \mu_+^* + \mu_-^* + RT \ln m_+ m_- + RT \ln \gamma_+ \gamma_-$$

where all of the deviation from ideal behavior comes from the last term. Unfortunately, it impossible to experimentally deconvolute the term into the specific contributions of the two ions. So instead, we use a geometric average to define the **mean activity coefficient**, $\gamma_\pm$.

$$\gamma_\pm = \sqrt{\gamma_+ \gamma_-}$$

For a substance that dissociates according to the general process

$$M_xX_y(s) \rightarrow xM^{y+}(aq) + yX^{x-}(aq)$$

the expression for the mean activity coefficient is given by

$$\gamma_{\pm} = (\gamma_+^x \gamma_-^y)^{1/x+y}$$

Debeye-Hückel Law

In 1923, Debeye and Hückel (Debye & Hückel, 1923) suggested a means of calculating the mean activity coefficients from experimental data. Briefly, they suggest that

$$\log_{10} \gamma_{\pm} = \frac{1.824 \times 10^6}{(\epsilon T)^{3/2}} |z_+ + z_-| \sqrt{I}$$

where ϵ is the dielectric constant of the solvent, T is the temperature in K, z_+ and z_- are the charges on the ions, and I is the **ionic strength** of the solution. I is given by

$$I = \frac{1}{2} \frac{m_+ z_+^2 + m_- z_-^2}{m^o}$$

For a solution in water at 25 ^{o}C,

As seen before activities are a way to account for deviation from ideal behavior while still keeping the formulism for the ideal case intact. For example in a ideal solution we have:

$$\mu^{sln} = \mu^* + RT \ln x_i$$

is replaced by

$$\mu^{sln} = \mu^* + RT \ln a_i$$

The relationship between a_i and x_i is often written using an activity coefficient γ:

$$a_i = \gamma_i x_i$$

Raoult versus Henry

Implicitly we have made use of Raoult's law here because we originally used

$$x_i = \frac{P_i}{P_i^*}$$

In the case of a solvent this makes sense because Raoult's law is still valid in the limiting case, but for the solute it would make more sense to use Henry's law as a basis for the definition of activity:

$$a_{solute,H} \equiv \frac{P_{solute}}{K_{x,H}}$$

This does mean that the μ^* now becomes a μ^{*Henry} because the extrapolation of the Henry law all the way to the other side of the diagram where $x_{solute} = 1$ points to a point that is not the equilibrium vapor pressure of this component. In fact it represents a virtual state of the system that cannot be realized. This however does not affect the usefulness of the convention.

Various concentration units

The subscript X was added to the K value because we are still using mole fractions. However Henry's law is often used with other concentration measures. The most important are:

- molarity

- molality
- mole fraction

Both the numerical values and the dimensions of K will differ depending on which concentration measure is used. In addition the pressure units can differ. For example for oxygen in water we have:

$K_{x,H}$= 4.259 10^{4} atm

$K_{cp,H}$= 1.3 10^{-3} mol/lit.atm

$K_{pc,H}$= 769.23 lit.atm/mol

As you can see $K_{cp,H}$ is simply $1/K_{pc,H}$, both conventions are used..

Note that in this case a choice based on Raoult is really not feasible. At room temperature we are far above the critical point of oxygen which make the equilibrium vapor pressure a non-existent entity. Returning to activities we could use each of the versions of K as a basis for the activity definition. This means that when using activities it must be specified what scale we are using. Activities and Henry coefficients of dissolved gases in water (both fresh and salt) are quite important in geochemistry, environmental chemistry etc.

Non-volatile solutes

A special case arises if the vapor pressure of a solute is negligible. For example if we dissolve sucrose in water. In that case we can still use the Henry based definition

$$a_{solute,H} \equiv \frac{P_{solute}}{K_{x,H}}$$

Even though both K and P will be exceedingly small their ratio is still finite. However how do we determine either?

The answer lies in the solvent. Even if the vapor pressure of sucrose is immeasurably small, the water vapor pressure above the solution can be measured. The Gibbs-Duhem equation can then be used to translate one into the other. We can use Raoult Law to define the activity of the solvent:

$$a_1 = \frac{P_1}{P_1^*}$$

We can measure the pressures as a function of the solute concentrations. At low concentrations

$$\ln a_1 \ln x - 1 \approx -x - 2$$

At higher concentrations we will get deviations, we can write:

$$\ln \frac{P_1}{P_1^*} = \ln a_1 \approx -x_2 \varphi$$

The 'fudge factor' φ is known as the *osmotic coefficient* and can thus be determined as a function of the solute concentration from the pressure data. What we are really interested in is a_2, not a_1:

$$a_2 = \gamma_2 x_2$$

Using Gibbs-Duhem we can convert φ into γ_2. Usually this is done in terms of molalities rather than mole fractions and it leads to this integral:

$$\ln \gamma_{2,m} = \varphi - 1 + \int_{m'=0}^{m} \frac{\varphi - 1}{m'} dm'$$

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24.8: Activities are Calculated with Respect to Standard States

Need to define a new variable. The thermodynamic activity, a, is the effective concentration of a species in a mixture. It is a dimensionless quantity that are calculated with respect to standard states. For a gas, this would be related to the fugacity and for a solution, to the concentration. The activity for a real gas:

$$a_i = \frac{f_i}{P^\circ} = \frac{\phi_i P_i}{P^\circ} = \frac{\phi_i (y_i P)}{P^\circ}$$

For systems where we treat the gases as ideal:

$$\phi_i = 1$$

$$a_i = \frac{P_i}{P^\circ} = y_i \frac{P}{P^\circ}$$

The activity for a solution:

$$a_i = \gamma i \frac{[\mathrm{A}]}{1\ \underline{\mathrm{M}}}$$

General chemistry and organic chemistry use ideal reactants where $\gamma_i = 1$:

$$a_i = \frac{[\mathrm{A}]}{1\ \underline{\mathrm{M}}}$$

The activity for a solid or liquid:

$$a_i = 1$$

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24.9: Gibbs Energy of Mixing of Binary Solutions in Terms of the Activity Coefficient

Activity and activity coefficients

In the ideal case, we have seen that the thermodynamic potential for species i can be written as:

$$\mu_i^{sln} = \mu_i^o + RT \ln\, x_i = \mu_2^o + RT \ln \left(\frac{P_i}{P^o} \right)$$

One approach to non-ideality is to simply ***redefine*** the problem and say:

$$\mu_i^{sln} \equiv \mu_i^o + RT \ln\, a_i$$

≡ indicates this is actually a definition. The newly defined variable a_2 is known as the **activity**. Alternatively we can define it as:

$$[a_i] \equiv \frac{P_i}{P^o}$$

As at high enough values of the mole fraction we know that we can still apply Raoult law. So a_i must approach x_i in this limit, but for other concentrations this will no longer hold. Often this is expressed in terms of an ***activity coefficient*** γ:

$$[a_i] = \gamma_i x_i$$

For high values of x_i, γ_i will approach unity. If we model the non-ideality with a Margules function we see that:

$$P_i = x_i P^o f_{Mar}$$

$$[a_i] = \left[\frac{P_i}{P^0} \right] = \left[\frac{x_i P^0 f_{Mar}}{P^0} \right] = [x_i f_{Mar}]$$

The activity coefficient and the Margules function are the same thing in this description.

Regular solutions

A special and simplest case of a Margules function is the case where all but one Margules parameters (a) can be neglected. Such a system is called a ***regular solution***. In this case, we can write:

$$a_1 = x_1 e^{a x_2^2}$$

We can use Gibbs-Duhem to show that this *implies*:

$$a_2 = x_2 e^{a x_1^2}$$

Gibbs free energy of regular solutions

Consider the change in Gibbs free energy when we mix two components to form a regular solution:

$$\Delta G_{mix} = n_1 \mu_1^{sln} + n_2 \mu_2^{sln} - (n_1 \mu_1^* + n_2 \mu_2^*)$$

Dividing by the total number of moles, we get:

$$\Delta_{mix} G = x_1 \mu_1^{sln} + x_2 \mu_2^{sln} - (x_1 \mu_1^* + x_2 \mu_2^*)$$

Using:

$$\mu_i^{sln} \equiv \mu_i^* + RT \ln a_i$$

and:

$$[a_i] = \gamma_i x_i$$

We get:

$$\frac{\Delta_{mix}G}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

For a regular solution:

$$\ln \gamma_1 = \ln f_{Mar} = a x_2^2$$

$$\ln \gamma_2 = \ln f_{Mar} = a x_1^2$$

This gives:

$$\begin{aligned} \frac{\Delta_{mix}G}{RT} &= x_1 \ln x_1 + x_2 \ln x_2 + x_1 a x_2^2 + x_2 a x_1^2 \\ &= x_1 \ln x_1 + x_2 \ln x_2 + a[x_1 + x_2] x_1 x_2 \\ &= x_1 \ln x_1 + x_2 \ln x_2 + a x_1 x_2 \end{aligned}$$

Since:

$$x_1 + x_2 = 1$$

In this expression we see that we have an additional term to the entropy of mixing term we had seen before. Its coefficient a is dimensionless but represents the fact that the (strong!) interactions between the molecules are different depending on who is the neighbor. In general. a can be written as W/RT, where W represents an energy (enthalpy) that brings the difference in interaction energies into account. W does not depend strongly on temperature. We could look at W as the difference in average interaction energies:

$$W = 2U_{12} - U_{11} - U_{22}$$

Rearranging we get:

$$\frac{\Delta_{mix}G}{W} = \frac{RT}{W}[x_1 \ln X_1 + x_2 \ln x_2] + x_1 x_2$$

The two terms will ***compete*** as a function of temperature. The mixing entropy will be more important at high temperatures, the interaction enthalpy at low temperatures. The entropy term has a *minimum* at x_1=0.5, the enthalpy term a *maximum* if W is positive. So, one tends to favor mixing, the other segregation and we will get a compromise between the two. Depending on the value of RT/W (read: temperature), we can either get one or two minima. This means that at low temperatures there will be a solubility limit of 1 into 2 and *vice versa*. At higher temperatures the two components can mix completely. At the transition between these two regimes we will have ***critical or consolute point***.

Notice that even though we used the vapor pressures of the gas to develop our theory, they are conspicuously absent from the final result. The same thing we said about melting points hold true here. Because we are dealing with the miscibility behavior of two condensed phases, the outcome should not depend very strongly on the total pressure of our experiment.

Although in regular solutions the consolute point is predicted to be a maximum in temperature, we can find them as minima as well in practice. The nicotine-water system even has two consolute points, an upper and a lower one. When heating up a mixture of these we first observe mixing, then segregation and then mixing again. Obviously this behavior is far more complicated than we can describe with just one Margules parameter.

Partial molar volumes

What we said above about volumes simply being additive in the ideal case is no longer true here.

$$\left(\frac{\partial \Delta G_{mix}}{\partial P}\right)_T = \Delta V_{\text{regular}}$$

$$\left(\frac{\partial \Delta H_{mix} + RT(n_1 \ln [x_1] + n_2 \ln [x_2])}{\partial P}\right)_T = \Delta V_{\text{mix}}$$

$$\left(\frac{\partial \Delta H_{mix}}{\partial P}\right)_T = \Delta V_{\text{mix}}$$

In general the enthalpy of mixing does depend on pressure as it is related to the interactions between the molecules in solution. (W depends on the distance between them). This means that partial molar volumes now become a function of composition and volume is no longer simply additive.

Real solutions

Notice that the curves are *symmetrical* around $x = 0.5$. This implies that it is as easy (or not) dissolving A into B as vice versa. In many cases this is not realistic. Many systems diverge more seriously from ideal behavior that the regular one. Up to a point we can model that by adding more terms to the Margules function. For example, adding a β-term undoes the symmetry (see example 24-7). However, many systems are so non-ideal that the Margules expression become unwieldy with too many parameters.

Boiling non-ideal solutions

Azeotropes

For ideal solutions we have seen that there is a lense shaped two-phase region between the gas and the liquid phase. For non-ideal systems the two-phase region can attain different shapes. In many cases there is either a minimum or a maximum. As such a point the phase gap closes to a point that is known as an *azeotrope*. It represents a composition of the liquid that boils *congruently*. That means that the vapor and the liquid have the same composition for a change. Azeotropes impose an important limitation unto distillation: they represent the end point of a distillation beyond which we can not purify by this method.

Eutectics

Another point to be made is that in the diagram with the consolute point we are assuming the pressure to be constant. If we lower the pressure this would affect the boiling points strongly: the whole gas-liquid gap would come down in temperature (see animation). The mixing behavior is only weakly affected. (The reason is that one involves the volume term of the gas, the other only of the liquid(s)). At lower pressures it is possible therefore that the consolute point is *above* the gas-liquid gap. In other words: the mixtures will boil before they get a chance to mix. The boiling points will be lower there than for the pure compounds. There will be a composition for which the boiling point is at a minimum and where the mixture boils congruently (i.e. to a vapor with the same (overall) composition).

The mutual solubility limits increase as temperature increases, just as happens in the critical mixing case, but that due to the competition from the vapor phase this process comes to an end at the eutectic temperature. At this temperature one liquid boils always completely, the other one in part. At the eutectic composition they both boil away simultaneously.

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24.E: Solutions I- Liquid-Liquid Solutions (Exercises)

TBA

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25: SOLUTIONS II - NONVOLATILE SOLUTES

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25.2: The Activities of Nonvolatile Solutes

25.3: Colligative Properties Depend only on Number Density

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25.1: Standard State of Nonvolatile Solutions

The activity is a relative measure as it measures equilibrium relative to a standard state. The standard state is defined by the International Union of Pure and Applied Chemistry (IUPAC) and followed systematically by chemists around the globe. The standard state for a solution is defined in terms of the infinite-dilution behavior. This is in contrast to the standard state concentration of 1 mol/L. This can be reconciled by considering that the standard state is a hypothetical solution of 1 mol/L in which the solute has infinite-dilution properties, e.g. solute particles do not interact with each other. This means that the activity coefficient describes all non-ideal behavior when the value is not equal to 1.

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25.2: The Activities of Nonvolatile Solutes

For non-ideal gases, we introduced in chapter 11 the concept of *fugacity* as an *effective pressure* that accounts for non-ideal behavior. If we extend this concept to non-ideal solution, we can introduce the *activity* of a liquid or a solid, a, as:

$$\mu_{\text{non-ideal}} = \mu^{-\ominus} + RT \ln a, \tag{25.2.1}$$

where μ is the chemical potential of the substance or the mixture, and $\mu^{-\ominus}$ is the chemical potential at standard state. Comparing this definition to Equation 11.4.2, it is clear that the activity is equal to the fugacity for a non-ideal gas (which, in turn, is equal to the pressure for an ideal gas). However, for a liquid and a liquid mixture, it depends on the chemical potential at standard state. This means that the activity is not an absolute quantity, but rather a relative term describing how "active" a compound is compared to standard state conditions. The choice of the standard state is, in principle, arbitrary, but conventions are often chosen out of mathematical or experimental convenience. We already discussed the convention that standard state for a gas is at $P^{-\ominus} = 1 \text{ bar}$, so the activity is equal to the fugacity. The standard state for a component in a solution is the pure component at the temperature and pressure of the solution. This definition is equivalent to setting the activity of a pure component, i, at $a_i = 1$.

For a component in a solution we can use Equation 11.4.2 to write the chemical potential in the gas phase as:

$$\mu_i^{\text{vapor}} = \mu_i^{-\ominus} + RT \ln \frac{P_i}{P^{-\ominus}}. \tag{25.2.2}$$

If the gas phase is in equilibrium with the liquid solution, then:

$$\mu_i^{\text{solution}} = \mu_i^{\text{vapor}} = \mu_i^*, \tag{25.2.3}$$

where μ_i^* is the chemical potential of the pure element. Subtracting Equation 25.2.3 from Equation 25.2.2, we obtain:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \frac{P_i}{P_i^*}. \tag{25.2.4}$$

For an ideal solution, we can use Raoult's law, Equation 13.1.1, to rewrite Equation 25.2.4 as:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln x_i, \tag{25.2.5}$$

which relates the chemical potential of a component in an ideal solution to the chemical potential of the pure liquid and its mole fraction in the solution. For a non-ideal solution, the partial pressure in Equation 25.2.4 is either larger (positive deviation) or smaller (negative deviation) than the pressure calculated using Raoult's law. The chemical potential of a component in the mixture is then calculated using:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \left(\gamma_i x_i\right), \tag{25.2.6}$$

where γ_i is a positive coefficient that accounts for deviations from ideality. This coefficient is either larger than one (for positive deviations), or smaller than one (for negative deviations). The activity of component i can be calculated as an *effective mole fraction*, using:

$$a_i = \gamma_i x_i, \tag{25.2.7}$$

where γ_i is defined as the **activity coefficient**. The partial pressure of the component can then be related to its vapor pressure, using:

$$P_i = a_i P_i^*. \tag{25.2.8}$$

Comparing Equation 25.2.8 with Raoult's law, we can calculate the activity coefficient as:

$$\gamma_i = \frac{P_i}{x_i P_i^*} = \frac{P_i}{P_i^{\text{R}}}, \tag{25.2.9}$$

where P_i^{R} is the partial pressure calculated using Raoult's law. This result also proves that for an ideal solution, $\gamma = 1$. Equation 25.2.9 can also be used experimentally to obtain the activity coefficient from the phase diagram of the non-ideal solution. This

is achieved by measuring the value of the partial pressure of the vapor of a non-ideal solution. Examples of this procedure are reported for both positive and negative deviations in Figure 25.2.1.

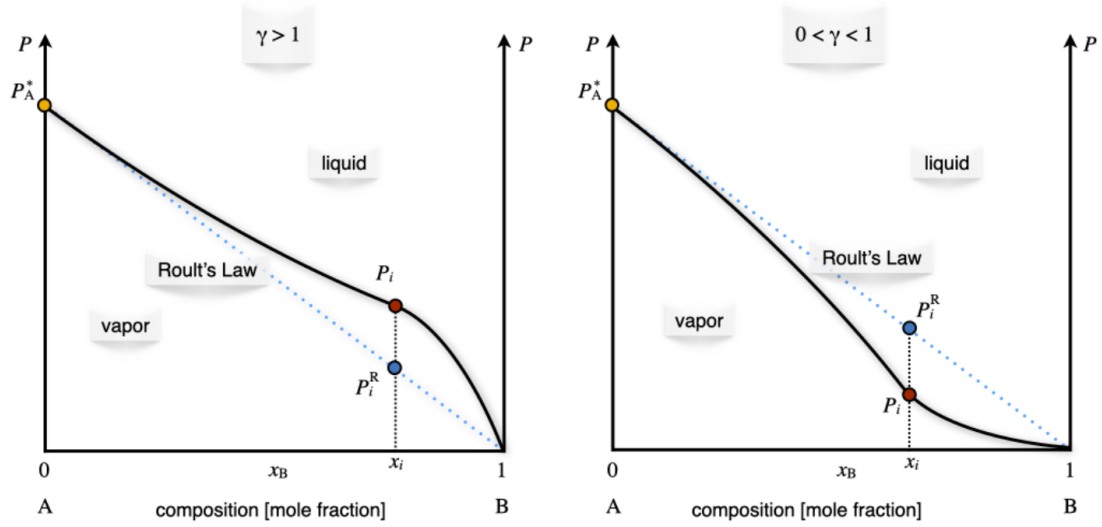


Figure 25.2.1: Positive and Negative Deviation from Raoult's Law in the Pressure–Composition Phase Diagram of Non-Ideal Solutions at Constant Temperature.

- As we already discussed in chapter 10, the activity is the most general quantity that we can use to define the equilibrium constant of a reaction (or the reaction quotient). The advantage of using the activity is that it's defined for ideal and non-ideal gases and mixtures of gases, as well as for ideal and non-ideal solutions in both the liquid and the solid phase.[1]

---

1. Notice that, since the activity is a relative measure, the equilibrium constant expressed in terms of the activities is also a relative concept. In other words, it measures equilibrium relative to a standard state. This fact, however, should not surprise us, since the equilibrium constant is also related to $\Delta_{rxn}G^{-\ominus}$ using Gibbs' relation. This is why the definition of a universally agreed-upon standard state is such an essential concept in chemistry, and why it is defined by the International Union of Pure and Applied Chemistry (IUPAC) and followed systematically by chemists around the globe.

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25.3: Colligative Properties Depend only on Number Density

Colligative properties are properties that depend on the *number* of particles rather than their total mass. This implies that these properties can be used to measure molar mass. Colligative properties include:

- melting point depression
- boiling point elevation
- osmotic pressure

Melting Point Depression

When we freeze a dilute solution the resulting frozen solvent is often quite a bit purer than the original solution. Let us consider this problem and make the following rather opposite assumptions about the solvent component:

1. In the liquid state it can be considered to follow Raoult's law over a sufficient concentration range
2. In the solid state, the solubility is nil

Under these two assumptions, we can consider the thermodynamic potentials of the solvent component (1) at the freezing point. They should be equal once equilibrium has been reached:

$$\mu_1^s = \mu_1^{sln}$$

$$\mu_1^s = \mu_1^{liq*} + RT \ln\, a_1$$

$$\frac{\mu_1^s - \mu_1^{liq*}}{RT} = \ln\, a_1$$

$$\frac{-\Delta\mu_1}{RT} = \ln\, a_1$$

We can now apply *Gibbs-Helmholtz relations* by differentiation with respect to temperature:

$$\frac{\partial}{\partial\, T}\frac{\Delta\mu_1}{T} = \frac{-\Delta_{fus}H_{molar,1}}{T^2}$$

$$\frac{\partial[\ln\, a_1}{\partial T} = \frac{\Delta_{fus}H_{molar,1}}{RT^2}$$

This means that we can actually use the quantity $\Delta_{fus}H_{molar,1}/RT^2$ to determine activities by integration, but usually Raoult Law is assumed valid:

$$\ln a_1 \ln x_1 \approx -x_2$$

If we integrate $\Delta_{fus}H_{molar,1}/RT^2$ from the melting point of the pure solvent T_m^* to the actual melting point of the solution T_m we get:

$$-x_2 = \frac{\Delta_{fus}H_{molar,1}}{R}\left(\frac{1}{T_m^*} - \frac{1}{T_m}\right) = \frac{\Delta_{fus}H_{molar,1}}{R}\left(\frac{T_m - T_m^*}{T_m^* T_m}\right) \approx \frac{\Delta_{fus}H_{molar,1}}{R}\left(\frac{-\Delta T}{T_m^{*2}}\right)$$

This is often rewritten in terms of molality as:

$$\Delta T = K_f.m$$

If K_f is known for the solvent we can add a number of grams of an unknown compound to the solvent measure the temperature depression, this tells us the molality. From molality and weight we can then calculate molar mass. Boiling point elevation is quite similar.

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25.4: Osmotic Pressure can Determine Molecular Masses

Some membrane materials are permeable for some molecules, but not for others. This is often a matter of the *size* of the molecules, but it can also be a question of *solubility* of the molecule in the barrier material. Many biological membranes have semipermeable properties and osmosis is therefore an important biological process. Figure 25.4.1 shows a simple osmotic cell. Both compartments contain water, but the one on the right also contains a solute whose molecules (represented by green circles) are too large to pass through the membrane. Many artificial and natural substances are capable of acting as semi-permeable membranes. For example, the walls of most plant and animal cells fall into this category.

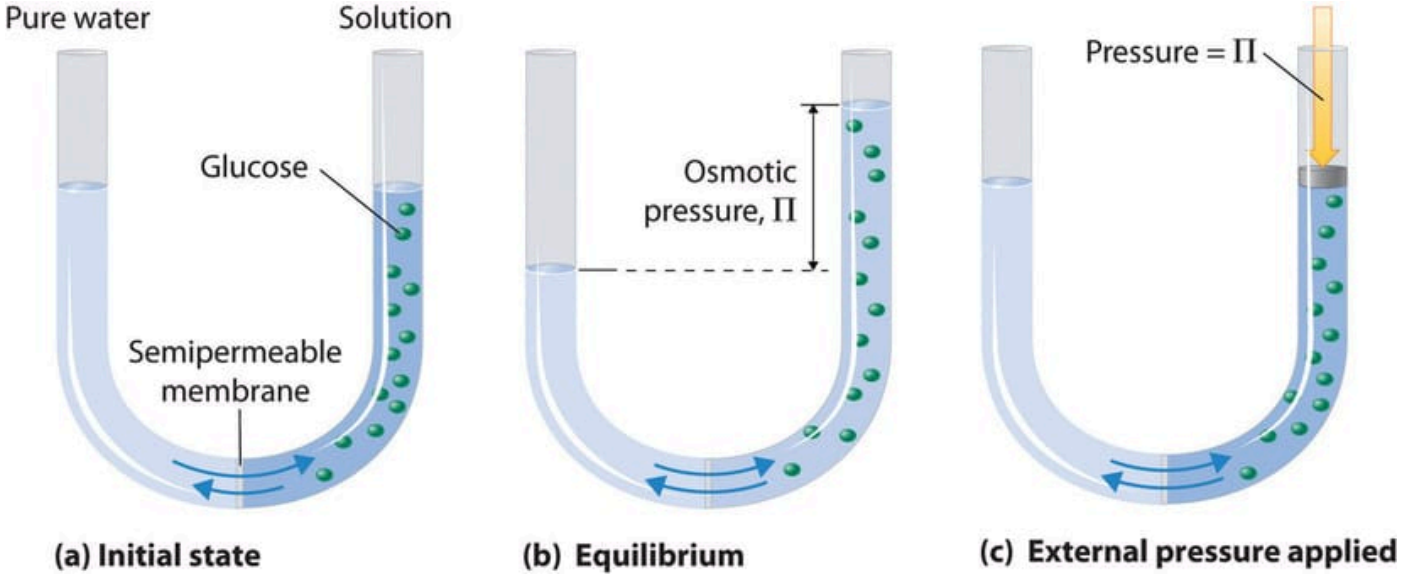


Figure 25.4.1 : Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

If solvent molecules can pass through the membrane, but solute molecules (or ions) cannot, solvent molecules will spontaneously migrate across the membrane to increase the solution's volume and thus reduce its concentration. If the solution is ideal, this process is in many ways analogous to the spontaneous increase in volume of a gas allowed to expand against vacuum. Of course the volume of the 'solute-gas' is limited by the availability of solvent and, if done under gravity in a U-shaped tube, by the build up of hydrostatic pressure. This pressure is known as the *osmotic pressure* Π. At equilibrium we can write:

$$\mu^*(T,P) = \mu^{sln}(T, P+\Pi, a_1)$$

$$\mu^*(T,P) = \mu^*(T, P+\Pi) + RT\ln a_1$$

From Gibbs energy (dG) in its natural variables (P, T) we know that:

$$\left(\frac{\partial G}{\partial P}\right)_{T,x} = V$$

Taking the partial versus x_1 we get:

$$\left(\frac{\partial \mu^*}{\partial P}\right)_{T,x_j} = \bar{V}_1^*$$

This means we can integrate over the molar volume to convert $\mu^*(T, P+\Pi)$ to a different pressure:

$$\mu^*(T, P + \Pi) = \mu^*(T, P) + \int_P^{P+\Pi} \bar{V}_1^* dP$$

Thus we get:

$$\mu^*(T, P) = \mu^*(T, P + \Pi) + RT \ln a_1$$

$$\mu^*(T, P) = \mu^*(T, P) + \Pi \bar{V}_1^* + RT \ln a_1$$

Once again using the ideal approximation:

$$\ln a_1 \ln x_1 \approx -x_2$$

we get:

$$RTx_2 = \Pi \bar{V}_1^*$$

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

The combination gives an expression involving the molarity:

$$\Pi = RTc$$

Where c is the molar concentration. Osmosis can be used in reverse, if we apply about 30 bar to sea water we can obtain fresh water on the other side of a suitable membrane. This process is used in some places, but better membranes would be desirable and they easily get clogged. The resulting water is not completely salt-free and this means that if used for agriculture the salt may accumulate on the field over time.

Determining Molar Masses

Both melting point depression and boiling point elevation only facilitate the determination of relatively *small* molar weights. The need for such measurements is no longer felt because we now have good techniques to determine the structure of most small to medium size molecules. For polymers this is a different matter. They usually have a molecular weight (mass) *distribution* and determining it is an important topic of polymer science.

Osmometry is still of some practical usefulness. It is also colligative and able to measure up to about 8000 daltons. Many polymers are much bigger than that. Their mass distribution is usually determined by different means. The polymers is dissolved and led over a chromatographic column usually based on size-exclusion. The effluent is then probed as function of the elution time by a combination of techniques:

1. UV absorption (determine the monomer concentration)
2. Low Angle Laser Light Scattering (LALLS) and/or Viscometry

The latter two provide information on the molar mass distribution but they give a different moment of that distribution. The combination of techniques gives an idea not only of how much material there is of a given molar mass but also of the linearity or degree of branching of the chains.

Purity analysis

Nevertheless melting point depression is still used in a somewhat different application. When a slightly impure solid is melted its melting point in depressed. Also the melting process is not sudden but takes place over the whole trajectory from typically a lower eutectic temperature up to the depressed melting point (the liquid line in the phase diagram). In organic synthesis the melting behavior is often used as a first convenient indication of purity. In a differential scanning calorimetry (DSC) experiment the melting peak becomes progressively skewed towards lower temperatures at higher impurity levels. The shape of the curve can be modeled with a modified version of the melting point depression expression. This yields a value for the total impurity level in the solid. This technique is used in the pharmaceutical industry for quality control purposes.

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25.5: Electrolytes Solutions are Nonideal at Low Concentrations

A solution with a strong electrolyte, such as NaCl in water, is perhaps one of the most obvious systems to consider but, unfortunately, is also one of the more difficult ones. The reason is that the electrolyte produces two ***charged*** solutes, Na^+ and Cl^+ (both in hydrated form), in solution. We need to consider the dissociation process and stoichiometry as we are bringing more than one solute species into solution. We also need to consider electrostatic interactions between solutes. The charges introduce a strong interaction that falls off with r^{-1}, as opposed to ~r^{-6} if only neutral species are present. This causes a very serious divergence from ideality even at very low concentrations. Consider a salt going into solution:

$$C_{\nu_+}A_{\nu_-} \rightarrow \nu_+ C^{z+} + \nu_- A^{z-} \tag{25.5.1}$$

where ν_+ and ν_- are the ***stoichiometric coefficients*** and z_+ and z_- are the formal charges of the cation and anion, respectively. As we shall see, the stoichiometric coefficients involved in the dissociation process are important for a proper description of the thermodynamics of strong electrolytes. Charge neutrality demands:

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{25.5.2}$$

Thermodynamic potentials versus the dissociation

For the salt, we can write:

$$\mu_2 = \mu_2^o + RT \ln a_2 \tag{25.5.3}$$

However, we need to take into account the dissociation of the salt. To do so, we write:

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_- \tag{25.5.4}$$

This implies:

$$\mu_2^o = \nu_+ \mu_+^o + \nu_- \mu_-^o \tag{25.5.5}$$

where

$$\mu_+ = \mu_-^o + RT \ln a_+ \tag{25.5.6}$$

$$\mu_- = \mu_-^o + RT \ln a_- \tag{25.5.7}$$

Usually Henry's law is taken as standard state for both type of ions. However, we cannot measure the activities of the ions separately as it is impossible to add one without adding the other. Nevertheless, we can derive a useful formalism that takes into account the dissociation process. If we substitute the last two equations in the ones above we get:

$$\nu_+ \ln a_+ + \nu_- \ln a_- = \ln a_2 \tag{25.5.8}$$

Taking the exponent of either side of Equation 25.5.8, we get:

$$a_2 = a_+^{\nu_+} a_-^{\nu_-} \tag{25.5.9}$$

Notice that the stoichiometric coefficients (Equation 25.5.1) are *exponents* in Equation 25.5.9. We now introduce the sum of the stoichiometric coefficients:

$$\nu_+ + \nu_- = \nu \tag{25.5.10}$$

and *define* the ***mean ionic activity*** $a_\pm$ as:

$$a_\pm^\nu \equiv a_2 = a_+^{\nu_+} a_-^{\nu_-}$$

Note

The mean ionic activity $a_{\pm}$ and the activity of the salt are closely related but the relationship involves *exponents* due to stoichiometric coefficients involved in the dissociation process. For example:

- For Na_1Cl_1: ν= 1+1 = **2**: $a_{\pm}^{\ 2} = a_{NaCl}$
- For $Al_2(SO_4)_3$: ν= 2+3 = **5**: $a_{\pm}^{\ 5} = a_{Al_2(SO_4)_3}$

Activity coefficients

All this remains a formality unless we find a way to relate it back to the concentration of the salt. Usually *molality* is used as a convenient concentration measure rather than molarity because we are dealing with pretty strong deviations from ideal behavior and that implies that volume may not be an additive quantity. Molality does not involve volume in contrast to molarity. Working with molalities, we can define activity coefficients for both ions, even though we have no hope to determine them separately:

$$a_+ = \gamma_+ m_+ \tag{25.5.11}$$

$$a_- = \gamma_- m_- \tag{25.5.12}$$

Stoichiometry dictates the molalities of the individual ions must be related to the ***molality of the salt*** m by:

$$m_- = \nu_- m \tag{25.5.13}$$

$$m_+ = \nu_+ m \tag{25.5.14}$$

Note

We cannot measure the activities of the ions separately because it is impossible to add one without adding the other

Analogous to the mean ionic activity, we can define a **mean ionic molality** as:

$$m_{\pm}^{\nu} \equiv m_+^{\nu+} m_-^{\nu-} \tag{25.5.15}$$

We can do the same for the **mean ionic activity coefficient**:

$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu+} \gamma_-^{\nu-} \tag{25.5.16}$$

Using this definitions we can rewrite:

$$a_2 = a_{\pm}^{\nu} = a_+^{\nu+} a_-^{\nu-} \tag{25.5.17}$$

as:

$$a_2 = a_{\pm}^{\nu} = \gamma_{\pm}^{\nu} m_{\pm}^{\nu} \tag{25.5.18}$$

Note

Note that when preparing a salt solution of molality m, we should ***substitute***:

$$m_- = \nu_- m$$

$$m_+ = \nu_+ m$$

into:

$$m_{\pm}^{\nu} \equiv m_{+}^{\nu+} m_{-}^{\nu-}$$

Example 25.5.1: Aluminum Sulfate

For $Al_2(SO_4)_3$ we get:

- $\nu = 2+3 = \mathbf{5}$
- $a_{\pm}{}^{\mathbf{5}} = a_{Al_2(SO_4)_3}$
- $m_{-}=3m$
- $m_{+}=2m$

So:

Answer available at the end of this section.

Answer available at the end of this section.

As you can see the stoichiometry enter *both* into the exponents *and* into the calculation of the molality. Notice that the activity of the salt now goes as the fifth power of its overall molality (on top of the dependency of $\gamma_{\pm}$ of $\exp(\sqrt{m})$ as shown below).

Measuring mean ionic activity coefficients

In contrast to the individual coefficients, the ***mean ionic activity coefficient*** $\gamma_{\pm}$ is a quantity that ***can be determined***. In fact we can use the same Gibbs-Duhem trick we did for the sucrose problem to do so. We simply measure the water vapor pressure above the salt solution and use:

$$\ln \gamma_{\pm} = \varphi - 1 + \int_{m'=0}^{m} [\varphi - 1] m' \, dm'$$

The fact that the salt itself has a negligible vapor pressure does not matter. Particularly for ions with high charges, the deviations from ideality are very strong even at tiny concentrations. Admittedly doing these vapor pressure measurements in pretty tedious, there are some other procedures involving electrochemical potentials. However, they too are tedious.

Answers

$m_{\pm}{}^{\nu} = m_{+}{}^{\nu_+} m_{-}{}^{\nu_-} = (2m)^2 (3m)^3 = \mathbf{108} m^{\mathbf{5}}$

$m_{\pm}{}^{\nu} = m_{+}{}^{\nu_+} m_{-}{}^{\nu_-} = (2m)^2 (3m)^3 = \mathbf{108} m^{\mathbf{5}}$

$a_{Al_2(SO_4)_3} = a_{\pm}{}^{\mathbf{5}} = \mathbf{108} m^{\mathbf{5}} \gamma_{\pm}{}^{5}$

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25.6: The Debye-Hückel Theory

As ionic solutions are very common in chemistry, having to measure all activity coefficients ($\gamma_{\pm}$) for all possible solute-solvent combinations is a pretty daunting task, even though in times past extensive tabulation has taken place. We should be grateful for the rich legacy that our predecessors have left us in this respect (it would be hard to get any funding to do such tedious work today). Of course, it would be very desirable to be able to *calculate* $\gamma_{\pm}$ values from first principles or if that fails by semi-empirical means. Fortunately, considerable progress has been made on this front as well. We can only scratch the surface of that topic in this course and will briefly discuss the simplest approach due to Debye and Hückel

Debye and Hückel came up with a theoretical expression that makes is possible to predict mean ionic activity coefficients as *sufficiently* dilute concentrations. The theory considers the vicinity of each ion as an atmosphere-like cloud of charges of opposite sign that cancels out the charge of the central ion (Figure $25.6.1$). From a distance the cloud looks neutral. The quantity $1/\kappa$ is a measure for the size of this cloud and κ is the ***Debye-length***. Its size depends on the concentration of all other ions.

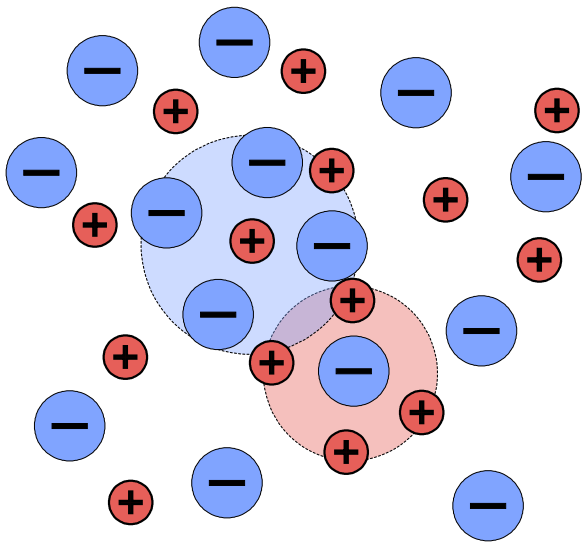


Figure $25.6.1$: An idealized representation of a solution of a 1:1 electrolyte. (CC BY-SA 3.0 unported; Roland1952 via Wikipedia)

Ionic Strength

To take the effect from all other ions into account, it is useful to define the ***ionic strength*** (I) as:

$$I = \frac{1}{2}\sum m_i z_i^2$$

where m_i is the molality of ion i and z_i is its charge coefficient. Note that highly charged ions (e.g. $z = 3+$) contribute strongly (nine times more than +1 ions), but the formula is *linear* in the molality. Using the ionic strength the Debye-length becomes:

$$\kappa^2 = constant\, I$$

The constant contains kT and $\varepsilon_r\varepsilon_o$ in the denominator and the number of Avogadro N_A and the square of the charge of the electron e in the numerator:

$$constant = 2000\frac{e^2 N_A}{\varepsilon_r\varepsilon_o kT}$$

The Debye length and the logarithmic mean ionic activity coefficient are proportional:

$$\ln\gamma_{\pm} \propto \kappa$$

Again there are a number of factors in the proportionality constant:

$$\ln \gamma_{\pm} = -|q_{+}q_{-}| \frac{\kappa}{8\pi\varepsilon_r\varepsilon_o kT}$$

Note

The factors ε_r and ε_o are the relative permittivity of the medium and the permittivity of vacuum, respectively. Note that the factor $8\pi\varepsilon_r\varepsilon_o$ is *specific* to the SI system of units. In cgs units the expression would look different, because the permittivities are defined differently in that system

If there is only one salt being dissolved, the ionic strength depends linearly on its concentration, the Debye length κ and $\ln \gamma_{\pm}$, therefore, go as the *square root of concentration* (usually molality):

$$\ln \gamma_{\pm} \propto \sqrt{m}$$

If there are other ions present the ionic strength involves *all* of them. This fact is sometimes used to keep ionic strength constant while changing the concentration of one particular ion. Say we wish to lower the concentration of Cu^{2+} in a redox reaction but we want to keep activity coefficients the same as much as possible. We could then *replace* it by an ion of the same charge say Zn^{2+} that does not partake in the reaction. A good way to do that is to dilute the copper solution with a zinc solution of the same concentration instead of with just solvent. The mean activity coefficient is given by the logarithm of this quantity as follows:

$$\log_{10} \gamma_{\pm} = -Az_j^2 \frac{\sqrt{I}}{1 + Ba_0\sqrt{I}} \tag{25.6.1}$$

with:

$$A = \frac{e^2 B}{2.303 \times 8\pi\epsilon_0\epsilon_r k_{\mathrm{B}} T}$$

$$B = \left(\frac{2e^2 N}{\epsilon_0\epsilon_r k_{\mathrm{B}} T} \right)^{1/2}$$

where I is the ionic strength and a_0 is a parameter that represents the distance of closest approach of ions. For aqueous solutions at 25 °C $A = 0.51\ mol^{-1}/2dm^{3/2}$ and $B = 3.29nm^{-1}mol^{-1}/2dm^{3/2}$.

Unfortunately this theory only works at very low concentrations and is therefore also known as the **Debye limiting law** (Figure $25.6.2$). There are a number of refinements that aim at extending the range of validity of the theory to be able to work at somewhat higher concentrations. These are discussed in the next section.

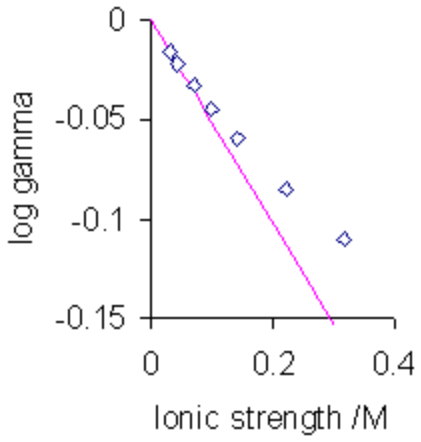


Figure 25.6.2: Experimental $\log \gamma_{\pm}$ values for KBr at 25°C (points) and Debye–Hückel limiting law (coloured line) (Public Domain; Petergans via Wikipedia)

The most significant aspect of Equation 25.6.1 is the prediction that the mean activity coefficient is a function of *ionic strength* rather than the electrolyte concentration. For very low values of the ionic strength the value of the denominator in the expression above becomes nearly equal to one. In this situation the mean activity coefficient is proportional to the square root of the ionic strength.

Importance for Colloids

When a solid is formed by a reaction from solution it is sometimes possible that it remains dispersed as very small particles in the solvent. The sizes typically range in the nanometers This is why it has become fashionable to call them *nanoparticles*, although they had been known as *colloidal particles* since the mid nineteenth century. They are smaller than the wavelength of the visible reason. This causes liquids that contain them to remain *clear*, although they can at times be beautifully colored.

A good example is the reduction of $AuCl_4^-$ with citrate to metallic gold. This produces clear wine red solutions, even at tiny gold concentrations.

$$2n\,\mathrm{AuCl_4(aq)^-} + \mathrm{n\ citrate^{3-}(aq)} + 2\,\mathrm{n\ H_2O\,(l)} \rightarrow$$
$$2\,\mathrm{n\ Au(colloid)} + 3\,\mathrm{n\ CH_2O\,(aq)} + 3\,\mathrm{n\ CO_2\,(g)} + 8\,\mathrm{n\ Cl^-(aq)} + 3\,\mathrm{n\ H^+(aq)}$$

The reason the gold does not precipitate completely is typically that the nanoparticle (AuNP) formed during the reaction are *charged* by the attachment of some of the ionic species in solution to its surface. This results in an charged particle with an atmosphere with a certain Debye length around it (Figure 25.6.3). This charged cloud prevents the particle form coalescing with other particles by electrostatic repulsion.

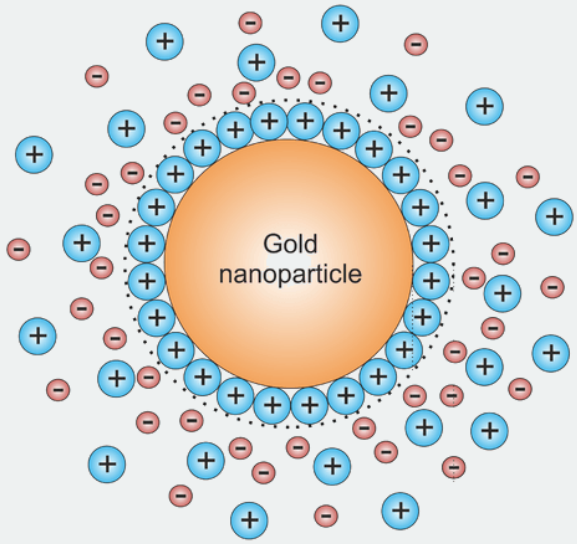


Figure 25.6.3: Potential difference as a function of distance from gold nanoparticle surface. (CC-SA-BY-3.0; Larryisgood)

Such a system is called a ***colloid.*** Of course these systems are ***metastable***. Often they have a pretty small threshold to crashing to a real precipitate under influence of the strong van der Waals interactions that the particles experience once they manage to get in close contact. Under the right conditions colloids can survive for a long time. Some gold colloids prepared by Faraday in the 1850's are still stable today.

It will be clear from the above that addition of a salt -particularly containing highly charged ions like 3+ or 3-- may destabilize the colloid because the ionic strength will changed drastically and this will affect the Debye length.

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25.7: Extending Debye-Hückel Theory to Higher Concentrations

The equation for $\log \gamma_{\pm}$ predicted from Debye–Hückel limiting law is:

$$\log_{10} \gamma_{\pm} = -Az_j^2 \frac{\sqrt{I}}{1 + Ba_0\sqrt{I}} \tag{25.7.1}$$

It gives satisfactory agreement with experimental measurements for low electrolyte concentrations, typically less than $10^{-3} mol/L$. Deviations from the theory occur at higher concentrations and with electrolytes that produce ions of higher charges, particularly asymmetrical electrolytes. These deviations occur because the model is oversimplified, so there is little to be gained by making small adjustments to the model. Instead, we must challenge the individual assumptions of the model:

- **Ions do not interact with each other**. Ion association may take place, particularly with ions of higher charge. This was followed up in detail by Niels Bjerrum. The Bjerrum length is the separation at which the electrostatic interaction between two ions is comparable in magnitude to kT.
- **Complete dissociation**. A weak electrolyte is one that is not fully dissociated. As such it has a dissociation constant. The dissociation constant can be used to calculate the extent of dissociation and hence, make the necessary correction needed to calculate activity coefficients.
- **Ions are spherical point charges that cannot be polarizable**. Ions, as all other atoms and molecules, have a finite size. Many ions, such as the nitrate ion NO_3^-, are not spherical. Polyatomic ions are polarizable.
- **The solvent composition does not matter**. The solvent is not a structureless medium but is made up of molecules. The water molecules in aqueous solution are both dipolar and polarizable. Both cations and anions have a strong primary solvation shell and a weaker secondary solvation shell. Ion–solvent interactions are ignored in Debye–Hückel theory.
- **Ionic radius is negligible**. At higher concentrations, the ionic radius becomes comparable to the radius of the ionic atmosphere.

Most extensions to the Debye–Hückel theory are empirical in nature. They usually allow the Debye–Hückel equation to be followed at low concentration and add further terms in some power of the ionic strength to fit experimental observations. Several approaches have been proposed to extend the validity of the Debye–Hückel theory.

Extended Debye-Hückel Equation

One such approach is the Extended Debye-Hückel Equation:

$$-\log(\gamma) = \frac{A|z_+z_-|\sqrt{I}}{1 + Ba\sqrt{I}}$$

where γ is the activity coefficient, z is the integer charge of the ion μ is the ionic strength of the aqueous solution, and a, is the size or effective diameter of the ion in angstrom. The effective hydrated radius of the ion, a is the radius of the ion and its closely bound water molecules. Large ions and less highly charged ions bind water less tightly and have smaller hydrated radii than smaller, more highly charged ions. Typical values are 3 Å for ions such as H+,Cl-,CN-, and HCOO-. The effective diameter for the hydronium ion is 9 Å. \ (A\) and B are constants with values of respectively 0.5085 and 0.3281 at 25°C in water.

Other approaches include the Davies equation, Pitzer equations and specific ion interaction theory.

Davis Equation

The Davies equation is an empirical extension of Debye–Hückel theory which can be used to calculate activity coefficients of electrolyte solutions at relatively high concentrations at 25 °C. The equation, originally published in 1938, was refined by fitting to experimental data. The final form of the equation gives the mean molal activity coefficient f± of an electrolyte that dissociates into ions having charges z1 and z2 as a function of ionic strength I:

$$-\log f_{\pm} = 0.5 z_1 z_2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.30 I \right).$$

The second term, 0.30 I, goes to zero as the ionic strength goes to zero, so the equation reduces to the Debye–Hückel equation at low concentration. However, as concentration increases, the second term becomes increasingly important, so the Davies equation can be used for solutions too concentrated to allow the use of the Debye–Hückel equation. For 1:1 electrolytes the difference between measured values and those calculated with this equation is about 2% of the value for 0.1 M solutions. The calculations become less precise for electrolytes that dissociate into ions with higher charges. Further discrepancies will arise if there is association between the ions, with the formation of ion pairs, such as $\mathrm{Mg^{2+}SO_4^{2-}}$.

Plot of activity coefficients calculated using the Davies equation.

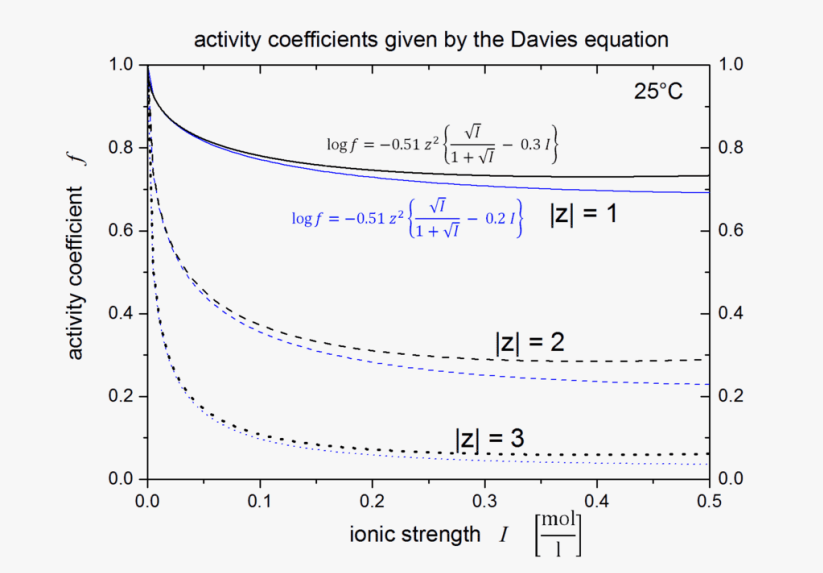


Figure 25.7.1: Semi-log plot of activity coefficients calculated using the Davies equation. (CC BY-SA 4.0; PChemiker via Wikipedia)

Pitzer Equations

Pitzer equations are important for the understanding of the behaviour of ions dissolved in natural waters such as rivers, lakes and sea-water. They were first described by physical chemist Kenneth Pitzer. The parameters of the Pitzer equations are linear combinations of parameters, of a virial expansion of the excess Gibbs free energy, which characterize interactions amongst ions and solvent. The derivation is thermodynamically rigorous at a given level of expansion. The parameters may be derived from various experimental data such as the osmotic coefficient, mixed ion activity coefficients, and salt solubility. They can be used to calculate mixed ion activity coefficients and water activities in solutions of high ionic strength for which the Debye–Hückel theory is no longer adequate.

An expression is obtained for the mean activity coefficient.

$$\ln \gamma_{\pm} = \frac{p \ln \gamma_M + q \ln \gamma_X}{p+q}$$

$$\ln \gamma_{\pm} = |z^+ z^-| f^{\gamma} + m \left(\frac{2pq}{p+q} \right) B^{\gamma}_{MX} + m^2 \left[2 \frac{(pq)^{3/2}}{p+q} \right] C^{\gamma}_{MX}$$

These equations were applied to an extensive range of experimental data at 25 °C with excellent agreement to about 6 mol kg–1 for various types of electrolyte. The treatment can be extended to mixed electrolytes and to include association equilibria. Values for the parameters β(0), β(1) and C for inorganic and organic acids, bases and salts have been tabulated. Temperature and pressure variation is also discussed.

Specific ion interaction theory

Specific ion Interaction Theory (SIT theory) is a theory used to estimate single-ion activity coefficients in electrolyte solutions at relatively high concentrations. It does so by taking into consideration interaction coefficients between the various ions present in solution. Interaction coefficients are determined from equilibrium constant values obtained with solutions at various ionic strengths. The determination of SIT interaction coefficients also yields the value of the equilibrium constant at infinite dilution.

The activity coefficient of the jth ion in solution is written as γ_j when concentrations are on the molal concentration scale and as yj when concentrations are on the molar concentration scale. (The molality scale is preferred in thermodynamics because molal concentrations are independent of temperature). The basic idea of SIT theory is that the activity coefficient can be expressed as

$$\log \gamma_j = -z_j^2 \frac{0.51\sqrt{I}}{1+1.5\sqrt{I}} + \sum_k \epsilon_{jk} m_k$$

where z is the electrical charge on the ion, I is the ionic strength, ε and b are interaction coefficients and m are concentrations. The summation extends over the other ions present in solution, which includes the ions produced by the background electrolyte. The first term in these expressions comes from Debye-Hückel theory. The second term shows how the contributions from "interaction" are dependent on concentration. Thus, the interaction coefficients are used as corrections to Debye-Hückel theory when concentrations are higher than the region of validity of that theory.

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25.8: Homework Problems

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{25.8.1}$$

You can see from Equation 25.8.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

Exercise 25.8.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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26: CHEMICAL EQUILIBRIUM

26.1: Equilibrium Results when Gibbs Energy is Minimized

26.2: An Equilibrium Constant is a Function of Temperature Only

26.3: Standard Gibbs Energies of Formation Can Be Used to Calculate Equilibrium Constants

26.4: Gibbs Energy of a Reaction vs. Extent of Reaction is a Minimum at Equilibrium

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26.1: Equilibrium Results when Gibbs Energy is Minimized

Many important chemical reactions -if not *most*- are performed in *solution* rather than between solids or gases. Solid state reactions are often very slow and not all chemical species can be put in the vapor phase because they decompose before evaporating.

Often we are not concerned with the temporal aspects of a reaction. That can be technologically very important but it is the domain of *kinetics* - a different branch of Physical Chemistry - rather than classical thermodynamics.. The latter is more concerned with the endpoint. This is the thermodynamically speaking the (stable) equilibrium, but chemically it can either represent a *completed* reaction or a *chemical equilibrium*.

Unfortunately, of the three main aggregation states: gas – liquid – solid, the structure of liquids is least understood and one of the most complex liquids is also one of the most extensively used ones: water. It is vital to many branches of chemistry varying from geochemistry to environmental chemistry to biochemistry. We shall make just a small inroad into its complexity.

Extent of reaction

To describe the progress of a reaction we define the **extent of reaction**. It is usually denoted by the Greek letter ξ.

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

Using stoichiometry we can define the extent by considering how the number of moles (or molar amounts) of each species changes during the reaction:

reactants

- $n_A = n_{A,0} - v_A \xi$
- $n_B = n_{B,0} - v_B \xi$

products

- $n_Y = n_{Y,0} + v_Y \xi$
- $n_Z = n_{Z,0} + v_Z \xi$

The dimension of ξ is [mol] because the stoichiometric coefficients v_i are dimensionless integers. If the reaction goes to completion for one of the reactants -the *limiting reactant*- $n_{A \text{ or } B}$=n_{limiting} will go to zero. If we start with $n_{limiting} = v_{limiting}$ moles, the value of ξ starts at 0 (no products) and goes to 1 at completion (limiting reactant depleted). When approaching an equilibrium ξ will not go beyond ξ_{eq}.

Measuring ξ

The extent of reaction is what is the central subject of reaction kinetics. Its value is typically measured as a function of time indirectly by measuring a quantity q that is *linearly dependent* on ξ(t):

$$q(\xi) = a\xi + b$$

Consider the situation at the extremes $\xi = 0$ and $\xi = 1$:

$$q_0 = a.0 + b = b$$

$$q_1 = a.1 + b = a + b$$

$$q_1 - q_0 = a$$

Thus, ξ can be found from

$$\frac{q(t)-q0}{q_1-q_0}=\frac{q(t)-b}{a}$$

The nature of q can vary widely from UV/Vis absorption, conductivity, gravimetric to caloric data.

In practice, q_0 at $\xi=0$ is often hard to observe because it takes time to mix the reactants, particularly in solutions, and q_1 at ξ=1 may never be reached if the reaction goes to equilibrium. Nevertheless the values of a and b can often be found from the available data by fitting techniques.

In (equilibrium, static) thermodynamics we are only concerned with the endpoint:

- $\xi=1$: the reaction runs to completion
- $\xi=\xi_{eq}$: the react ion goes to a state of chemical equilibrium

Thermodynamic Potentials

As we have seen we can write any change in the Gibbs free energy due to changes in the molar amounts of the species involved in the reaction (at T, P constant) as:

$$dG=\sum\frac{\partial G}{\partial n_i}dn_i=\sum\mu_i dn_i$$

where μ is the *thermodynamic potential*, often called *chemical potential* when dealing with reactions. From the definition of ξ we can see by differentiation that

- $dn_A=-v_A d\xi$
- $dn_B=-v_A d\xi$
- $dn_Y=v_Y d\xi$
- $dn_Z=v_Z d\xi$

This allows us to *unify the changes* in the molar amount of all the species into *one single variable* $d\xi$. We get:

$$dG=\left[\sum -v_{i,reactants}\mu_{i,reactants}+\sum +v_{i,products}\mu_{j,products}\right]d\xi$$

or

$$\left(\frac{\partial G}{\partial\xi}\right)_{T,P}=-\sum v_{i,r}\mu_{i,r}+\sum v_{i,p}\mu_{j,p}$$

This quantity is also written as:

$$\left(\frac{\partial G}{\partial\xi}\right)_{T,P}=\Delta_r G$$

This quantity gives the change in Gibbs free energy for the reaction (as written!!) for Δξ=1 mole. (Units are [J/mol] therefore). This is the change in Gibbs energy (the slope of G vs ξ) when the extent of reaction changes by one mole with a fixed composition. Equilibrium results when Gibbs energy is at a minimum with respect to the extent of reaction.

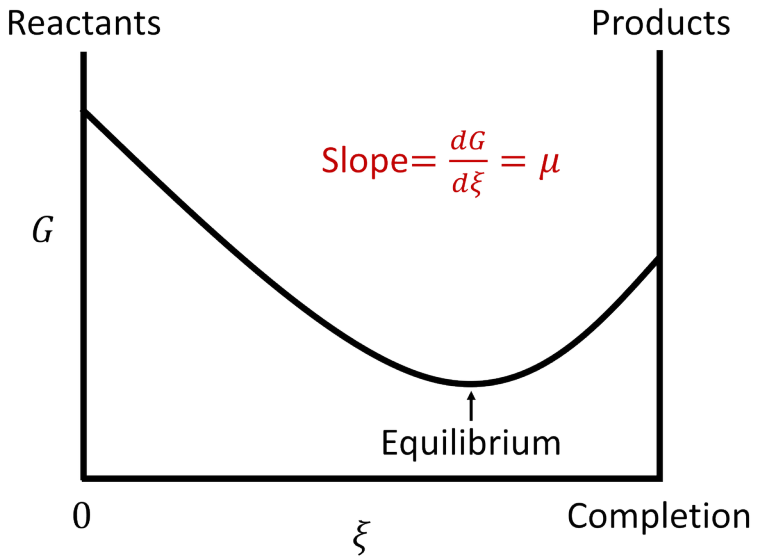


Figure 1. Gibbs energy plotted as a function of the extent of reaction. Equilibrium results when the Gibbs energy is minimized.

Gas Reactions

Let us assume that our reaction is entirely between gas species and that the gas is sufficiently dilute that we can use the ideal gas law. Then we can write for each species:

$$\mu_i = \mu_i^o + RT \ln \frac{P_i}{P_i^o}$$

We can then split up the Δ_rG expression in two parts:

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

The standard potentials:

$$\Delta_r G^o = -\sum v_{i,r}\, \mu_{i,r}^o + \sum v_{i,p} \mu_{j,p}^o$$

and the logarithmic terms:

$$RT \ln Q = -v_A RT \ln \left(\frac{P_A}{P_A^o} \right) - v_B RT \ln \left(\frac{P_B}{P_B^o} \right) + v_Y RT \ln \left(\frac{P_Y}{P_Y^o} \right) + v_Z RT \ln \left(\frac{P_Z}{P_Z^o} \right)$$

We can combine all the logarithmic terms into Q, called the ***reaction quotient***. The stoichiometric coefficients become exponents and the reactants' factors will be 'upside down' compared to the products, because of the properties of logarithms:

$$a \ln x = \ln x^a$$

$$-a \ln x = \ln \left(\frac{1}{x^a} \right)$$

We have kept the standard pressures P_i^o in the expression, but often they are omitted. They are usually all 1 bar, but in principle we could choose 1 bar for A 1 Torr for B an 1 psi for the products. It creates a valid (though ridiculous) definition of what $^{\ominus}$ stands for. (Of course the value of $\Delta_r G^o$ does *depend* on that choice!).

We could write

$$RT \ln Q = RT \ln \frac{Q_P}{Q^o}$$

Q^o is typically unity in magnitude but it *cancels the dimensions* of Q_P. That means that Q and Q_P are equal in magnitude and

we can get Q from Q_P by simply dropping the dimensions. Q is dimensionless but Q_P usually is not. Often this fine distinction is simply not made and Q^o is *omitted*, we get:

$$\Delta_r G = \Delta_r G^o + RT \ln \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}}$$

Notice the difference between $\Delta_r G$ which denotes the conditions (e.g. pressures) of *your reaction* and $\Delta_r G^o$ denotes standard conditions.

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26.2: An Equilibrium Constant is a Function of Temperature Only

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

When the reaction reaches equilibrium, the Gibbs energy of reaction, $\Delta_r G$, goes to zero. In this case, the reaction quotient, Q, is usually rewritten as the **equilibrium constant**, K, and we get:

$$\Delta_r G = \Delta_r G^o + RT \ln K = 0$$

$$\Delta_r G^o = -RT \ln K$$

where

$$K = \frac{P_{eq,Y}^{vY} P_{eq,Z}^{vZ}}{P_{eq,A}^{vA} P_{eq,B}^{vB}}$$

Note

As you see $\Delta_r G^o$ is ***not*** zero, because the standard state does ***not*** represent an equilibrium state (typically).

We can calculate the temperature dependence of K. Rather than look at:

$$\left(\frac{\partial K}{\partial T}\right)_P$$

We will look at:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P$$

Starting with Gibbs energy:

$$\Delta_r G^\circ = -RT \ln K$$

$$\therefore \ln K = -\frac{\Delta r G^\circ}{RT}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = -\frac{1}{R}\left[\frac{\partial (\Delta_r G^\circ / T)}{\partial T}\right]_P$$

We need to take the Gibbs-Helmholtz equation:

$$\Delta \bar{H} = -T^2 \left[\frac{\partial (\Delta \bar{G}/T)}{\partial T}\right]_P$$

We can also write it as:

$$\left[\frac{\partial \left(\Delta \bar{G}/T\right)}{\partial T}\right]_P = -\frac{\Delta \bar{H}}{T^2}$$

Plugging the Gibbs-Helmholtz equation into our earlier equation, we obtain the Van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_r H^\circ}{RT^2}$$

The temperature dependence of the equilibrium constant depends on enthalpy of reaction. Rearranging:

$$d(\ln K) = \frac{\Delta_r H^\circ(T)}{RT^2} dT$$

This is the Van't Hoff equation. We can use it to find K at other temperatures. Assuming enthalpy is independent of temperature, the integrated form becomes:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Le Chatelier's Principle

In the ideal gas reaction case, K **only** depends on temperature, T, (just like U) not on the total pressure, P. This leads to the well-known principle of Le Chatelier. Consider a gas reaction like:

\[A \rightleftharpoons B + C \nonumber \nonumber \]

e.g.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

In pressures, the equilibrium constant becomes:

$$K = \frac{P_B P_C}{P_A}$$

If initially n_A =1 we have at an extent ξ:

n_A = 1- ξ

n_B= ξ

n_C= ξ

n_{Total} = 1+ ξ

The partial pressures are given by Dalton's law:

P_A= [1- ξ /1+ ξ] P

P_B [ξ / 1+ ξ] P

P_C [ξ /1+ ξ] P

The equilibrium constant becomes:

$$K = P\frac{\xi_{eq}^2}{1-\xi_{eq}^2}$$

Even though the total pressure, P, does occur in this equation, K is *not* dependent on P. If the total pressure is changed (e.g. by compression of the gas) the value of ξ_{eq} will change (the equilibrium shifts) in response. It will go to the side with the fewer molecules. This fact is known as le Chatelier's principle

If the system is not ideal we will also get a Chatelier shift, but the value of K may change a little because the value of the activity coefficients (or fugacity) is a little dependent on the pressure too. In solution the same thing holds. In ideal solutions K is only T dependent, but as we saw these systems are rare. Particularly in ionic solutions equilibrium constants will be effected

by other things than just temperature, e.g. changes in the ionic strength and we need to find the activity coefficients to make any predictions.

Example

Consider the reaction of ammonia decomposition:

$$2NH_3\,(g) \leftrightharpoons N_2\,(g) + 3H_2\,(g)$$

$$\Delta_f H^\circ(NH_3, g) = -45.90 \text{ kJ/mol}$$

The reaction is initially at equilibrium. For each of the stresses, use your General Chemistry knowledge to decide if equilibrium will be unaffected, or if it will shift towards reactants or products.

Process	Shifts towards
Isothermal removal of H_2 gas	
Isothermal addition of N_2 gas	
Isothermal decrease of container volume	
Isothermal and isochoric addition of argon gas	
Isobaric increase of temperature	

Write the equilibrium constant expression for the above chemical reaction in terms of gas-phase mole fractions.

Concentration

The gas law contains a hidden definition of concentration:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = cRT$$

$$c = \frac{P}{RT} \tag{26.2.1}$$

Here c stands for the molar amount per unit volume or ***molarity***. For gaseous mixtures we do not use this fact much, but it provides the link to the more important liquid solution as a reaction medium. We can rewrite the equilibrium constant as

$$K = \frac{c_{eq,Y}^{\upsilon_Y} c_{eq,Z}^{\upsilon_Z}}{c_{eq,A}^{\upsilon_A} c_{eq,B}^{\upsilon_B}} \tag{26.2.2}$$

However, c (Equation 26.2.1) is substituted into K (Equation 26.2.2), then not all the factors of RT cancel. The missing term g. ln[RT] depends on the stoichiometric coefficients:

$$g = \upsilon_Y + \upsilon_Z - \upsilon_A - \upsilon_B$$

The term is generally *incorporated* in $\Delta_r G^\ominus$ so that the latter now refers to a new standard state of 1 mole per liter of each species rather than 1 bar of each (or so).

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26.3: Standard Gibbs Energies of Formation Can Be Used to Calculate Equilibrium Constants

The relation $K = e^{-\frac{\Delta_r G^\circ}{RT}}$ gives us a way to evaluate the thermodynamic equilibrium constant K of a reaction at a given temperature from the value of the standard molar reaction Gibbs energy $\Delta_r G^\circ$ at that temperature. If we know the value of $\Delta_r G^\circ$, we can calculate the value of K.

One method is to calculate $\Delta_r G^\circ$ from values of the **standard molar Gibbs energy of formation** $\Delta_f G^\circ$ of each reactant and product. These values are the standard molar reaction Gibbs energies for the formation reactions of the substances. To relate $\Delta_f G^\circ$ to measurable quantities, we make the substitution $\mu_i = H_i - TS_i$ (Eq. 9.2.46) in $\Delta_r G = \sum_i \nu_i \mu_i$ to give $\Delta_r G = \sum_i \nu_i H_i - T \sum_i \nu_i S_i$, or

$$\Delta_r G = \Delta_r H - T \Delta_r S \tag{11.8.20}$$

When we apply this equation to a reaction with each reactant and product in its standard state, it becomes

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \tag{11.8.21}$$

where the standard molar reaction entropy is given by

$$\Delta_r S^\circ = \sum_i \nu_i S_i^\circ \tag{11.8.22}$$

If the reaction is the *formation* reaction of a substance, we have

$$\Delta_f G^\circ = \Delta_f H^\circ - T \sum_i \nu_i S_i^\circ \tag{11.8.23}$$

where the sum over i is for the reactants and product of the formation reaction. We can evaluate the standard molar Gibbs energy of formation of a substance, then, from its standard molar enthalpy of formation and the standard molar entropies of the reactants and product.

Extensive tables are available of values of $\Delta_f G^\circ$ for substances and ions. An abbreviated version at the single temperature $298.15\,\mathrm{K}$ is given in Appendix H. For a reaction of interest, the tabulated values enable us to evaluate $\Delta_r G^\circ$, and then K, from the expression (analogous to Hess's law)

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ(i) \tag{11.8.24}$$

The sum over i is for the reactants and products of the reaction of interest.

Recall that the standard molar enthalpies of formation needed in Eq. 11.8.23 can be evaluated by calorimetric methods (Sec. 11.3.2). The absolute molar entropy values S_i° come from heat capacity data or statistical mechanical theory by methods discussed in Sec. 6.2. Thus, it is entirely feasible to use nothing but calorimetry to evaluate an equilibrium constant, a goal sought by thermodynamicists during the first half of the 20th century. (Another method, for a reaction that can be carried out reversibly in a galvanic cell, is described in Sec. 14.3.3.)

For *ions in aqueous solution*, the values of S_m° and $\Delta_f G^\circ$ found in Appendix H are based on the reference values $S_m^\circ = 0$ and $\Delta_f G^\circ = 0$ for H^+(aq) at all temperatures, similar to the convention for $\Delta_f H^\circ$ values discussed in Sec. 11.3.2. For a reaction with aqueous ions as reactants or products, these values correctly give $\Delta_r S^\circ$ using Eq. 11.8.22, or $\Delta_r G^\circ$ using Eq. 11.8.24.

Note that the values of S_m° in Appendix H for some ions, unlike the values for substances, are *negative*; this simply means that the standard molar entropies of these ions are less than that of H^+(aq).

The relation of Eq. 11.8.23 does not apply to an ion, because we cannot write a formation reaction for a single ion. Instead, the relation between $\Delta_f G^\circ$, $\Delta_f H^\circ$ and S_m° is more complicated.

Consider first a hypothetical reaction in which hydrogen ions and one or more elements form H_2 and a cation M^{z+} with charge number z_+:

$$z_+ \mathrm{H}^+(\mathrm{aq}) + \text{elements} \rightarrow (z_+/2)\mathrm{H}_2(\mathrm{g}) + \mathrm{M}^{z+}(\mathrm{aq})$$

For this reaction, using the convention that $\Delta_f H^\circ$, S°_m, and $\Delta_f G^\circ$ are zero for the aqueous H^+ ion and the fact that $\Delta_f H^\circ$ and $\Delta_f G^\circ$ are zero for the elements, we can write the following expressions for standard molar reaction quantities:

$$\Delta_r H^\circ = \Delta_f H^\circ(M^{z+}) \tag{11.8.25}$$

$$\Delta_r S^\circ = (z_+/2)S^\circ_m(H_2) + S^\circ_m(M^{z+}) - \sum_{\text{elements}} S^\circ_i \tag{11.8.26}$$

$$\Delta_r G^\circ = \Delta_f G^\circ(M^{z+}) \tag{11.8.27}$$

Then, from $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, we find

$$\Delta_f G^\circ(M^{z+}) = \Delta_f H^\circ(M^{z+}) \quad - T\left[S^\circ_m(M^{z+}) - \sum_{\text{elements}} S^\circ_i + (z_+/2)S^\circ_m(H_2)\right] \tag{11.8.28}$$

For example, the standard molar Gibbs energy of the aqueous mercury(I) ion is found from

$$\Delta_f G^\circ({Hg_2}^{2+}) = \Delta_f H^\circ({Hg_2}^{2+}) - TS^\circ_m({Hg_2}^{2+}) + 2TS^\circ_m(Hg) - \tfrac{2}{2}TS^\circ_m(H_2) \tag{11.8.29}$$

For an anion X^{z-} with negative charge number z_-, using the hypothetical reaction

$$|z_-/2|H_2(g) + \text{elements} \rightarrow |z_-|H^+(aq) + X^{z-}(aq)$$

we find by the same method

$$\Delta_f G^\circ(X^{z-}) = \Delta_f H^\circ(X^{z-}) - T\left[S^\circ_m(X^{z-}) - \sum_{\text{elements}} S^\circ_i - |z_-/2|S^\circ_m(H_2)\right] \tag{11.8.30}$$

For example, the calculation for the nitrate ion is

$$\Delta_f G^\circ({NO_3}^-) = \Delta_f H^\circ({NO_3}^-) - TS^\circ_m({NO_3}^-) + \tfrac{1}{2}TS^\circ_m(N_2) + \tfrac{3}{2}TS^\circ_m(O_2) + \tfrac{1}{2}TS^\circ_m(H_2) \tag{11.8.31}$$

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26.4: Gibbs Energy of a Reaction vs. Extent of Reaction is a Minimum at Equilibrium

As discussed in Section 26.4, we defined the extent of the reaction (ξ) as a quantitative measure of how far along the reaction has evolved. For simple reactions like $\mathrm{A} \rightleftharpoons \mathrm{B}$, the extent of reaction is easy to define and is simply the number of moles of A that has been converted to B. Since $d\xi$ has the same value as dn, we can write that

$$\begin{aligned} dG &= \mu_A dn_A + \mu_B dn_B \\ &= -\mu_A d\xi + \mu_B d\xi. \end{aligned}$$

The minus sign comes from the fact that when the reaction goes in the left to right direction, the amount of A is decreasing, while the amount of B is increasing. Looking at these equations, it is reasonable to suggest that:

$$\left(\frac{\partial G}{\partial \xi}\right)_{PT} = \mu_B - \mu_A$$

This is the slope of the free energy with respect to the extent of the reaction. This relationship will have a region where the sign is negative, one point where the value is zero and a region where the value is positive (Figure $26.4.1$). If we look at a plot of G as a function of ξ, we can see that the point where is the minimum of the curve:

$$\left(\frac{\partial G}{\partial \xi}\right)_{PT} = 0$$

This is the point where μ_A and μ_B are the same. On one side of the minimum, the slope is negative and on the other side, the slope is positive. In both cases, the reaction is spontaneous (i.e, $dG < 0$) as long as the reaction is evolving towards the minimum, which will be called the **equilibrium position**. Hence, all reactions spontaneously move towards equilibrium; the immediate question is what value of ξ corresponds to the equilibrium position of a reaction?

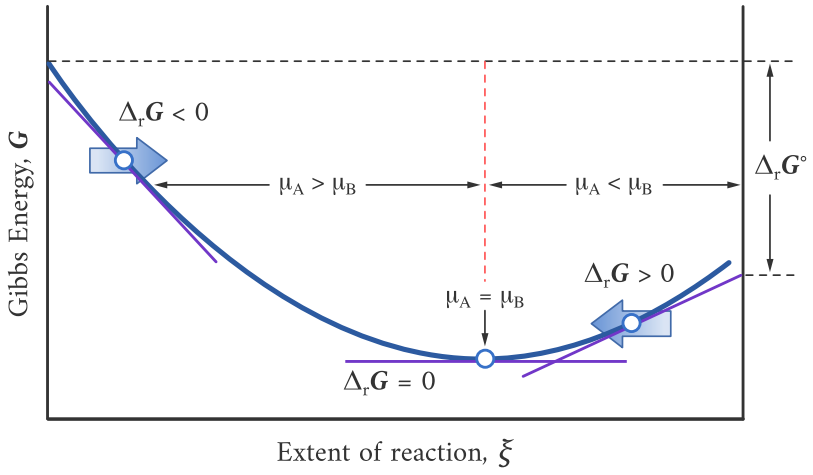


Figure $26.4.1$: Reactive Gibbs Energy and Equilibria. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Terminology

- A reaction for which $\Delta_r G < 0$ is called **exergonic**.
- A reaction for which $\Delta_r G > 0$ is called **endergonic**.
- $\Delta_r G < 0$, the forward reaction is spontaneous.

- $\Delta_r G > 0$, the reverse reaction is spontaneous.
- $\Delta_r G = 0$, the reaction is at equilibrium.

Ideal Gas Equilibrium

To understand how we can find the minimum and what the Gibbs free energy of a reaction depends on, let's first start with a reaction that converts one ideal gas into another.

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

Let's assume the reaction enthalpy is zero and hence the only thing that determines what the ratio of product to reactant should be is the entropy term (the mixing term), which is the most favorable when the mixture is half and half.

$$\Delta G_{\text{mix}} = nRT\left(\chi_A \ln \chi_A + \chi_B \ln \chi_B\right) \tag{26.4.1}$$

Remember that the Gibbs free energy of mixing is not a molar quantity and depends on n (unlike the reaction Gibbs free energy). Also, the Gibbs free energy of mixing is defined relative to pure A and B. The free energy of mixing in Equation 26.4.1 is at a minimum when the amounts of A equal B.

Thus, if we have a reaction $\mathrm{A} \rightleftharpoons \mathrm{B}$ and there is no enthalpy term (and no change in the inherent entropy of A vs. B), we would expect the system to have the minimum Gibbs free energy when the mole fraction of A and B are each 0.5.

Think about it

If A can form B and B can form A and there is no other forces involved (no heat/enthalpy) that would favor one product over the other, probability would just state that eventually you will have statistically the same amount of both A and B present -- this is the lowest free energy state. (This, of course, will not be true if the enthalpy for the reaction is not zero or if A and B have different inherent entropies). Usually there are additional terms for the reaction.

Lets work through this for an ideal gas reaction:

$$\begin{aligned}\Delta_r G &= \mu_B - \mu_A \\ &= \mu_B^o + RT\ln\frac{P_B}{P^\theta} - \mu_A^o - RT\ln\frac{P_A}{P^\theta} \\ &= \mu_B^o - \mu_A^o + RT\ln\frac{P_B}{P_A}\end{aligned}$$

What we normally do at this point is to give the first two terms a special name. Since it is the difference between the chemical potentials at standard conditions, we refer to it as the Gibbs free energy of reaction at standard conditions or the **standard Gibbs free energy of reaction**.

$$\begin{aligned}\Delta_r G^o &= \mu_B^o - \mu_A^o \\ \Delta_r G &= \Delta_r G^o + RT\ln\frac{P_B}{P_A}\end{aligned} \tag{26.4.2}$$

There are two parts to Equation 26.4.2. The first term ($\Delta_r G^o$) is the Gibbs free energy for converting one mole of A to B under standard conditions (1 bar of both A and B). The second term is the mixing term that is minimized when the amounts of A and B are equal to one another (Figure 26.4.2). The first term you look up in a reference book and is specific for a specific reaction. The second term is calculated knowing the partial pressures of A and B in the gas.

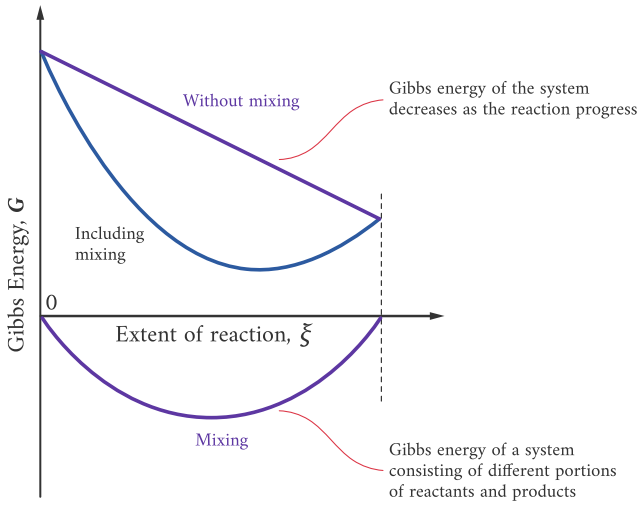


Figure 26.4.2: Molecular interpretation of the minimum in the reaction Gibbs energy Gibbs energy of the system decreases as the reaction progress Gibbs energy of a system consisting of different portions of reactants and products. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Now the minimum absolute Gibbs free energy will occur at the bottom of the curve where the slope is zero. Thus, the lowest free energy will occur when the reaction free energy (i.e., the slope of that curve in Figure 26.4.1) is equal to zero. The chemical potentials of A and B are equal.

$$\mu_A = \mu_B$$

At this point, the reaction will neither go forwards or backwards and we call this equilibrium. Hence, at equilibrium:

$$\begin{aligned}\Delta_r G &= \Delta_r G^o + RT \ln \frac{P_B}{P_A} \\ &= 0\end{aligned}$$

and the specific ratio of P_A and P_B necessary to ensure $\Delta_r G = 0$ is characteristic of the reaction and is called the **equilibrium constant** for that reaction.

$$K_{eq} = \frac{P_B}{P_A}$$

We can now relate thermodynamic quantities to concentrations of molecules at equilibrium. We can also see that at equilibrium:

$$\begin{aligned}0 &= \Delta_r G^o + RT \ln K_{eq} \\ \Delta_r G^o &= -RT \ln K_{eq} \\ K_{eq} &= e^{-\frac{\Delta_r G^o}{RT}}\end{aligned}$$

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26.5: Reaction Quotient and Equilibrium Constant Ratio Determines Reaction Direction

The Gibbs free energy function was constructed to be able to predict which changes could occur spontaneously. If we start with a set of initial concentrations we can write them in a reaction quotient

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

if we subtract the equilibrium version of this expression:

$$0 = \Delta_r G^o + RT \ln K$$

we get

$$\Delta_r G = RT \ln \left(\frac{Q}{K} \right)$$

That gives us the sign of $\Delta_r G$. If this is negative the reaction will spontaneously proceed from left to right as written, if positive it will run in reverse. In both case the value of Q will change until $Q = K$ and equilibrium has been reached.

The main difference between K and Q is that K describes a reaction that is at equilibrium, whereas Q describes a reaction that is not at equilibrium. To determine Q, the concentrations of the reactants and products must be known. For a given general chemical equation:

$$aA + bB \rightleftharpoons cC + dD \tag{26.5.1}$$

the Q equation is written by multiplying the activities for the species of the products and dividing by the activities of the reactants. If any component in the reaction has a coefficient, indicated above with lower case letters, the concentration is raised to the power of the coefficient. Q for the above equation is therefore:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{26.5.2}$$

Note

A comparison of Q with K indicates which way the reaction shifts and which side of the reaction is favored:

- If $Q > K$, then the reaction favors the reactants. This means that in the Q equation, the ratio of the numerator (the concentration or pressure of the products) to the denominator (the concentration or pressure of the reactants) is larger than that for K, indicating that more products are present than there would be at equilibrium. Because reactions always tend toward equilibrium (Le Châtelier's Principle), the reaction produces more reactants from the excess products, therefore causing the system to shift to the **LEFT.** This allows the system to reach equilibrium.
- If $Q < K$, then the reaction favors the products. The ratio of products to reactants is less than that for the system at equilibrium—the concentration or the pressure of the reactants is greater than the concentration or pressure of the products. Because the reaction tends toward reach equilibrium, the system shifts to the **RIGHT** to make more products.
- If $Q = K$, then the reaction is already at equilibrium. There is no tendency to form more reactants or more products at this point. No side is favored and no shift occurs.

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26.6: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity

It is important to distinguish between the Gibbs energy of reaction, $\Delta_r G$ and the standard state Gibbs energy of reaction, $\Delta_r G^\circ$. The $^\circ$ refers to standard state conditions. That is, each reactant and product has a partial pressure of 1 bar if a gas, a concentration of 1 M if a solution, and they are all unmixed from each other. Such idealized conditions, while convenient for serving as a reference state, do not actually represent real reaction conditions. Consider the reaction of nitrogen with hydrogen to form ammonia:

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

$$\Delta_r G^\circ = -32.9\ \frac{\text{kJ}}{\text{mol K}}$$

If the reaction was run under standard state conditions (1 bar partial pressure of each gas), the reaction would shift towards the products since $\Delta_r G^\circ < 0$. That is, the partial pressures of N_2 and O_2 will decrease and the partial pressure of NH_3 will increase until equilibrium is reached. The Gibbs energy of reaction is dependent on the composition:

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q = \Delta_r G^\circ + RT \ln \left(\frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} \right)$$

At equilibrium, the minimum Gibbs energy of reaction will be reached:

$$\Delta_r G = 0\ \frac{\text{kJ}}{\text{mol K}}$$

And the reaction quotient will equal the equilibrium constant:

$$Q = K$$

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26.7: The van 't Hoff Equation

We can use Gibbs-Helmholtz to get the temperature dependence of K

$$\left(\frac{\partial[\Delta G^o/T]}{\partial T}\right)_P = \frac{-\Delta H^o}{T^2}$$

At equilibrium, we can equate ΔG^o to $-RT\ln K$ so we get:

$$\left(\frac{\partial[\ln K]}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2}$$

We see that whether K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative. If temperature is changed little enough that ΔH^o can be considered constant, we can translate a K value at one temperature into another by integrating the above expression, we get a similar derivation as with melting point depression:

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

If more precision is required we could correct for the temperature changes of ΔH^o by using heat capacity data.

How K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative.

The expression for K is a rather sensitive function of temperature given its exponential dependence on the difference of stoichiometric coefficients One way to see the sensitive temperature dependence of equilibrium constants is to recall that

$$K = e^{-\Delta_r G^o/RT} \tag{26.7.1}$$

However, since under constant pressure and temperature

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Equation 26.7.1 becomes

$$K = e^{-\Delta H^o/RT} e^{\Delta S^o/R} \tag{26.7.2}$$

Taking the natural log of both sides, we obtain a linear relation between $\ln K$and the standard enthalpies and entropies:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \tag{26.7.3}$$

which is known as the van 't Hoff equation. It shows that a plot of $\ln K$ vs. $1/T$ should be a line with slope $-\Delta_r H^o/R$ and intercept $\Delta_r S^o/R$.

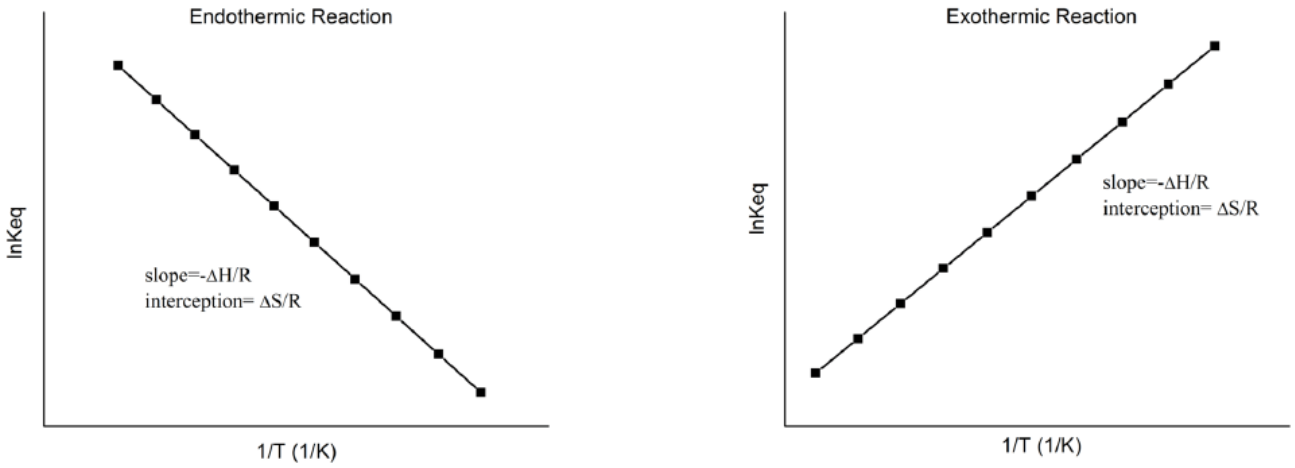


Figure 26.7.1 : Endothermic Reaction (left) and Exothermic Reaction van 't Hoff Plots (right). Figures used with permission of Wikipedia

Hence, these quantities can be determined from the $\ln K$ vs. $1/T$ data without doing calorimetry. Of course, the main assumption here is that $\Delta_r H^o$ and $\Delta_r S^o$ are only very weakly dependent on T, which is usually valid.

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26.8: Equilibrium Constants in Terms of Partition Functions

Consider the general gas phase chemical reaction represented by

$$\nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B} \rightleftharpoons \nu_{\mathrm{C}}\mathrm{C} + \nu_{\mathrm{D}}\mathrm{D} \tag{26.8.1}$$

where A, B, C and D are the reactants and products of the reaction, and ν_A is the stoichiometric coefficient of chemical A, ν_B is the stoichiometric coefficient of chemical B, and so on. Each of the gases involved in the reaction will eventually reach an equilibrium concentration when the forward and reverse reaction rates become equal. The distribution of reactants to products at the equilibrium point is represented by the equilibrium constant (K_c):

$$K_c = \frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}}$$

If the system is not at equilibrium, a shift in the number of reactants and products will occur to lower the overall energy of the system. The difference in the energy of the system at this non-equilibrated point and the energy of the system at equilibrium for any particular species is termed chemical potential. When both temperature and volume are constant for both points aforementioned, the chemical potential μ of species i is expressed by the equation

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq 1}} \tag{26.8.2}$$

where A is the Helmholtz energy, and N_i is the number of molecules of species i. The Helmholtz energy can be determined as a function of the total partition function, Q:

$$A = -k_B T \ln Q$$

where k_B is the Boltzmann constant and T is the temperature of the system. The total partition function is given by

$$Q = \frac{q_i(V,T)^{Ni}}{N_i!}$$

where q_i is the molecular partition function of chemical species i. Substituting the molecular partition function into the equation for Helmholtz energy yields:

$$A = -k_B T \ln\left(\frac{q_i(V,T)^{N_i}}{N_i!}\right)$$

and then further substituting this equation into the definition of chemical potential (Equation 26.8.2) yields:

$$\mu_i = \left(\frac{\partial - k_B T \ln\left(\frac{q_i(V,T)^{Ni}}{N_i!}\right)}{\partial N_i}\right)_{T,V,N_{j\neq 1}}$$

rearranging this equation the following derivative can be set-up:

$$\mu_i = -k_B T\left[\left(\frac{\partial N_i \ln\left(q_i(V,T)\right)}{\partial N_i}\right) - \left(\frac{\partial \ln\left(N_i!\right)}{\partial N_i}\right)\right]_{T,V,N_{j\neq 1}}$$

From this point Sterling's approximation

$$\ln N! = N \ln N - N$$

can be substituted into the derivative to yield:

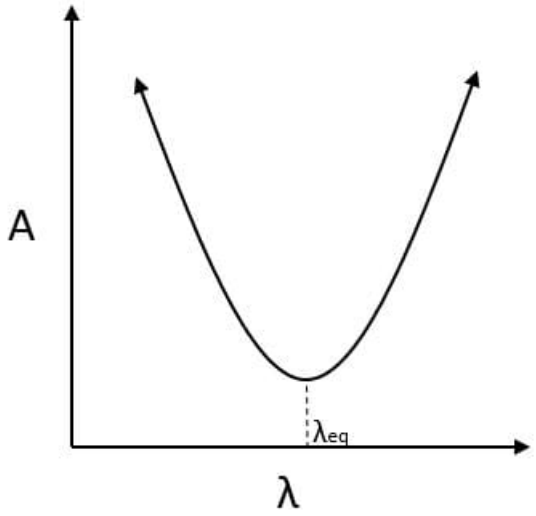
$$\mu_i = -k_B T\left[\left(\frac{\partial N_i \ln\left(q_i(V,T)\right)}{\partial N_i}\right) - \left(\frac{\partial\left(N_i \ln N_i - N_i\right)}{\partial N_i}\right)\right]_{T,V,N_{j\neq 1}}$$

From here the derivative can be rearranged and solved:

$$\begin{aligned}\mu_i &= -k_B T\left[\ln\left(q_i(V,T)\right)\frac{\partial N_i}{\partial N_i} + N_i\frac{\partial \ln\left(q_i(V,T)\right)}{\partial N_i} - \ln\left(N_i\right)\frac{\partial N_i}{\partial N_i} - N_i\frac{\partial \ln\left(N_i\right)}{\partial N_i} + \frac{\partial N_i}{\partial N_i}\right]_{T,V,N_{j\neq 1}} \\ &= -k_B T\left(\ln\left(q_i(V,T)\right) + 0 - \ln\left(N_i\right) - N_i\frac{1}{N_i} + 1\right) \\ &= -k_B T\left(\ln\left(q_i(V,T)\right) - \ln\left(N_i\right)\right) \\ &= -k_B T \ln\left(\frac{q_i(V,T)}{N_i}\right)\end{aligned} \tag{26.8.3}$$

A variable, λ, is then defined such that $dN_j = \nu_j d\lambda$, where j = A, B, C or D and ν_j is taken to be positive for products and negative for reactants. A change in λ therefore corresponds to a change in the concentrations of the reactants and products. Thus, at equilibrium,

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,V} = 0$$



Helmholtz Energy with respect to Equilibrium Shifts

From Classical thermodynamics, the total differential of A is:

$$dA = -SdT - pdV + \sum_j \mu_j dN_j$$

For a reaction at a fixed volume and temperature (such as in the canonical ensemble), dT and dV equal 0. Therefore,

$$\begin{aligned}dA &= \sum_j \mu_j dN_j \\ &= \sum_j \mu_j \nu_j d\lambda \\ &= d\lambda \sum_j \mu_j \nu_j\end{aligned}$$

with

$$\sum_j \mu_j \nu_j = 0$$

Substituting the expanded form of chemical potential (Equation 26.8.3):

$$-k_B T \sum_j \ln\left(\frac{q_i}{N_i}\right)\nu_j = 0$$

$$\sum_j \ln\left(\frac{q_i}{N_i}\right)\nu_j = 0$$

$$\sum_j \nu_j[\ln(q_j) - \ln(N_j)] = 0$$

For the reaction in Equation 26.8.1:

$$[\nu_C \ln(q_C) - \nu_C \ln(N_C)] + [\nu_D \ln(q_D) - \nu_D \ln(N_D)] - [\nu_A \ln(q_A) - \nu_A \ln(N_A)] - [\nu_B \ln(q_B) - \nu_B \ln(N_B)] = 0$$

This equation simplifies to

$$\frac{(q_C)^{\nu_C}(q_D)^{\nu_D}}{(q_A)^{\nu_A}(q_B)^{\nu_B}} = \frac{(N_C)^{\nu_C}(N_D)^{\nu_D}}{(N_A)^{\nu_A}(N_B)^{\nu_B}}$$

By dividing all terms by volume, and noting the relationship $\frac{N_A}{V} = \frac{\#molecules}{volume} = \rho_A = [A]$ where ρ is referred to a number density, the following equation is obtained:

$$K_c = \frac{\rho_C^{\nu_C}\rho_D^{\nu_D}}{\rho_A^{\nu_A}\rho_B^{\nu_B}} = \frac{(q_C/V)^{\nu_C}(q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A}(q_B/V)^{\nu_B}} \tag{26.8.4}$$

Hence, knowledge of the molecular partition function for all species in the reaction will ensure the calculation of the equilibrium constant.

Example 26.8.1: Reacting Diatomic Molecules

Calculate the equilibrium constant (K_c) for the reaction of $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$ at 650 K.

$$\mathrm{H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2\,HCl\,(g)}$$

Solution

We will use Equation 26.8.4 that uses Molecular Partition Functions to evaluate K_c.

$$K_c(T) = \frac{\left(\frac{q_{\mathrm{HCl}}}{V}\right)^2}{\left(\frac{q_{\mathrm{H_2}}}{V}\right)\left(\frac{q_{\mathrm{Cl_2}}}{V}\right)} \tag{26.8.5}$$

This equation is expanded into the rotational, vibrational, translational and electronic molecular partition functions of each species.

$$K_c(T) = \frac{\left(\frac{q_{\mathrm{trans\ HCl}}q_{rot\mathrm{HCl}}q_{vib\mathrm{HCl}}q_{elec\mathrm{HCl}}}{V}\right)^2}{\left(\frac{q_{\mathrm{trans H_2}}q_{\mathrm{rot\ H_2}}q_{vib\mathrm{H_2}}q_{elec\mathrm{H_2}}}{V}\right)\left(\frac{q_{\mathrm{trans Cl_2}}q_{\mathrm{rot\ Cl_2}}q_{vib\mathrm{Cl_2}}q_{elec\mathrm{Cl_2}}}{V}\right)}$$

A simple problem solving strategy for finding equilibrium constants via statistical mechanics is to separate the equation into the molecular partition functions of each of the reactant and product species, solve for each one, and recombine them to arrive at a final answer (e.g., for HCl.

$$\frac{q_{\mathrm{HCl}}}{V} = \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}_{\text{translation}} \times \underbrace{\frac{2k_B T \mu r_e^2}{\sigma \hbar^2}}_{\text{rotation}} \times \underbrace{\frac{1}{1-\exp\left(\frac{-h\nu}{k_B T}\right)}}_{\text{vibration}} \times \underbrace{g_1 \exp\left(\frac{D_0}{k_B T}\right)}_{\text{electronic}}$$

To simplify the calculations of molecular partition functions, the characteristic temperature of rotation (Θ_r) and vibration (Θ_ν) are used.

$$\frac{q_{\mathrm{HCl}}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \times \frac{T}{\sigma \Theta_r} \times \frac{1}{1-\exp\left(\frac{-\Theta_\nu}{T}\right)} \times g_1 \exp\left(\frac{D_0}{RT}\right) \tag{26.8.6}$$

These values are constants that incorporate the physical constants found in the rotational and vibrational partition functions of the molecules. Tabulated values of Θ_r and Θ_ν for select molecules can be found here.

Species	Θ_ν (K)	Θ_r (K)	D_0 (kJ mol^{-1})
$Cl_2\,(g)$	6125	0.351	239.0
$H_2\,(g)$	808	87.6	431.9
$HCl\,(g)$	4303	15.2	427.7

We need to evaluate Equation 26.8.6 for each species then then evaluate Equation 26.8.5 directly.

For HCl:

$$\frac{q_{\mathrm{HCl}}}{V} = \left(\frac{2\pi\left(2.1957\times10^{-24}\ \mathrm{kg}\right)\left(1.38065\times10^{-23}\mathrm{JK}^{-1}\right)(650K)}{\left(6.62607\times10^{-34}\mathrm{Js}\right)^2}\right)^{3/2} \times \frac{650\ \mathrm{K}}{(1)(15.2\ \mathrm{K})} \times \frac{1}{1-\exp\left(\frac{-4303\ \mathrm{K}}{650\ \mathrm{K}}\right)} \times (1)\exp\left(\frac{427}{(8.3145\ \mathrm{J}}\right.$$

$$\frac{q_{\mathrm{HCl}}}{V} = \left(1.4975\times10^{35}\ \mathrm{m}^{-3}\right)(42.76)(1.0013)\left(2.3419\times10^{34}\right)$$

For H_2:

$$\frac{q_{\mathrm{H_2}}}{V} = \left(\frac{2\pi\left(1.2140\times10^{-25}\ \mathrm{kg}\right)\left(1.38065\times10^{-23}\mathrm{JK}^{-1}\right)(650\ \mathrm{K})}{\left(6.62607\times10^{-34}\mathrm{Js}\right)^2}\right)^{3/2} \times \frac{650\ \mathrm{K}}{(2)(87.6\ \mathrm{K})} \times \frac{1}{1-\exp\left(\frac{-808\ \mathrm{K}}{650\ \mathrm{K}}\right)} \times (1)\exp\left(\frac{431,}{(8.3145\ \mathrm{J}}\right.$$

$$\frac{q_{\mathrm{H_2}}}{V} = \left(1.9468\times10^{33}\ \mathrm{m}^{-3}\right)(3.71)(1.41)\left(5.0942\times10^{34}\right)$$

For Cl_2:

$$\frac{q_{\mathrm{Cl_2}}}{V} = \left(\frac{2\pi\left(4.2700\times10^{-24}\ \mathrm{kg}\right)\left(1.38065\times10^{-23}\mathrm{JK}^{-1}\right)(650K)}{\left(6.62607\times10^{-34}\mathrm{Js}^2\right.}\right)^{3/2} \times \frac{650\ \mathrm{K}}{(2)(0.351\ \mathrm{K})} \times \frac{1}{1-\exp\left(\frac{-6125\ \mathrm{K}}{650\ \mathrm{K}}\right)} \times (1)\exp\left(\frac{2}{(8.3145}\right.$$

$$\frac{q_{\mathrm{Cl_2}}}{V} = \left(5.4839\times10^{35}\ \mathrm{m}^{-3}\right)(925.9)(1.00)\left(1.606\times10^{19}\right)$$

Combining the terms from each species, the following expression is obtained:

$$\begin{aligned} K_c &= \frac{\left(1.9468\times10^{33}\ \mathrm{m}^{-3}\right)^2}{\left(1.9468\times10^{33}\ \mathrm{m}^{-3}\right)\left(5.4839\times10^{35}\ \mathrm{m}^{-3}\right)} \times \frac{(42.76)^2}{(3.71)(925.9)} \times \frac{(1.0013)^2}{(1.41)(1.00)} \times \frac{\left(2.3419\times10^{34}\right)^2}{\left(1.606\times10^{19}\right)\left(5.0942\times10^{34}\right)} \\ &= (0.003550)(0.1333)(0.711)\left(6.7037\times10^{14}\right) \\ &= \left(2.26\times10^{11}\right) \end{aligned}$$

At 650 K, the reaction between $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$ proceeds spontaneously towards the products. From a statistical mechanics point of view, the product $\mathrm{HCl\,(g)}$ molecule has more states accessible to it than the reactant species. The spontaneity of this reaction is largely due to the electronic partition function: two very strong H—Cl bonds are formed at the expense of a very strong H—H bond and a relatively weak Cl—Cl bond.

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26.9: Molecular Partition Functions and Related Thermodynamic Data Are Extensively Tabulated

Real molecules can be significantly more complicated than the simple models that we often use to approximate them. To obtain a high degree of accuracy, calculations include complex corrections that can significantly decrease the efficiency of the calculations. For this reason, numerical tables of partition functions and other thermodynamical data are extensively tabulated. By placing these data in tables, they become readily accessible. The tables include experimental data combined with theoretical calculations that represent a collection of thermodynamic properties of substances.

The tabulated thermochemical properties of a substance are often given in JANAF (joint, army, navy, air force) tables. NIST contains are a large database of JANAF tables for many substances. Consider the JANAF table for methane (CH_4). The table contains the constant pressure heat capacity (C_P), standard state entropy (S°), standard state Gibbs energy (G°), standard state enthalpy (H°), standard state enthalpy of formation ($\Delta_f H^\circ$), standard state Gibbs energy of formation ($\Delta_f H^\circ$), equilibrium constant of formation expressed as a log value ($\log(K_f)$). G° and H° are expressed relative to the standard molar enthalpy at 298.15 K, $H^\circ(298.15\ \mathrm{K})$.

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26.10: Real Gases Are Expressed in Terms of Partial Fugacities

The relationship for chemical potential

$$\mu = \mu^o + RT \ln \left(\frac{p}{p^o} \right)$$

was derived assuming **ideal gas** behavior. But for real gases that deviate widely from ideal behavior, the expression has only limited applicability. In order to use the simple expression on real gases, a “fudge” factor is introduced called **fugacity**. Using fugacity instead of pressure, the chemical potential expression becomes

$$\mu = \mu^o + RT \ln \left(\frac{f}{f^o} \right)$$

where f is the fugacity. Fugacity is related to pressure, but contains all of the deviations from ideality within it. To see how it is related to pressure, consider that a change in chemical potential for a single component system can be expressed as

$$d\mu - V dp - S dT$$

and so

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V \tag{26.10.1}$$

Differentiating the expression for chemical potential above with respect to pressure at constant volume results in

$$\left(\frac{\partial \mu}{\partial p} \right)_T = \left\{ \frac{\partial}{\partial p} \left[\mu^o + RT \ln \left(\frac{f}{f^o} \right) \right] \right\}$$

which simplifies to

$$\left(\frac{\partial \mu}{\partial p} \right)_T = RT \left[\frac{\partial \ln(f)}{\partial p} \right]_T = V$$

Multiplying both sides by p/RT gives

$$\left[\frac{\partial \ln(f)}{\partial p} \right]_T = \frac{pV}{RT} = Z$$

where Z is the compression factor as discussed previously. Now, we can use the expression above to obtain the **fugacity coefficient** γ, as defined by

$$f = \gamma p$$

Taking the natural logarithm of both sides yields

$$\ln f = \ln \gamma + \ln p$$

or

$$\ln \gamma = \ln f - \ln p$$

Using some calculus and substitutions from above,

$$\int \left(\frac{\partial \ln \gamma}{\partial p} \right)_T dp = \int \left(\frac{\partial \ln f}{\partial p} - \frac{\partial \ln p}{\partial p} \right)_T dp$$

$$= \int \left(\frac{Z}{\partial p} - \frac{1}{\partial p} \right)_T dp$$

Finally, integrating from 0 to p yields

$$\ln \gamma = \int_0^p \left(\frac{Z-1}{p} \right)_T dp$$

If the gas behaves ideally, $\gamma = 1$. In general, this will be the limiting value as $p \to 0$ since all gases behave ideal as the pressure approaches 0. The advantage to using the fugacity in this manner is that it allows one to use the expression

$$\mu = \mu^o + RT \ln \left(\frac{f}{f^o} \right)$$

to calculate the chemical potential, insuring that Equation 26.10.1 holds even for gases that deviate from ideal behavior!

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- 7.5: Non-ideality in Gases - Fugacity by Patrick Fleming is licensed CC BY-NC-SA 4.0.

26.11: Thermodynamic Equilibrium Constants Are Expressed in Terms of Activities

The above is a general principle that can be extended to other concentration units and to liquid solutions, ideal or not. In non-ideal systems we could replace

$$\mu_i = \mu_i^{\ominus} + RT \ln P_i/P_i^{\ominus}$$

by:

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i$$

and follow the same procedure as above. In stead of an expression for K involving pressures or concentrations it now read in ***activities***:

$$K = [a_{eq,Y}^{\nu_Y} a_{eq,Z}^{\nu_Z} / a_{eq,A}^{\nu_A} a_{eq,B}^{\nu_B}]$$

For each species we could write the activity as:

$$a_i = \gamma_i c_i / c_i^{\ominus}$$

Here $c_i^{\ominus}$ is unity in whatever concentration measure we wish to choose. Again its function is to cancel the dimension of c_i.

With this split in three factors we can write K as three factors as well:

$$K = K_\gamma K_c / K_{c^{\ominus}}$$

$$K_\gamma = [\gamma_{eq,Y}^{\nu_Y} \gamma_{eq,Z}^{\nu_Z} / \gamma_{eq,A}^{\nu_A} \gamma_{eq,B}^{\nu_B}]$$

$$K_c = [c_{eq,Y}^{\nu_Y} c_{eq,Z}^{\nu_Z} / c_{eq,A}^{\nu_A} c_{eq,B}^{\nu_B}]$$

$$K_{c^{\ominus}} = [c_{\ominus}^{\nu_Y} c_{\ominus}^{\nu_Z} / c_{\ominus}^{\nu_A} c_{\ominus}^{\nu_B}]$$

The last factor is unity, it cancels the dimensions of K_c and is often *omitted*. The factor K_γ is unity *if the solution is ideal*. Obviously, for ionic solutions that is seldom the case.

activities of pure condensed phases

Sometimes one of the reactants or products is a pure solid (precipitate) or liquid (more solvent e.g.). What activity should we assign in such a case?

We start by choosing a suitable standard state, say the pure compound at 1 bar and temperature of interest, we then have:

$$\mu = \mu^{\ominus}$$

but also:

$$\mu = \mu^{\ominus} + RT \ln a$$

So a=1 at standard conditions

Any change can be written as

$$d\mu = RTdlna$$

We can study the pressure dependence by considering:

$$\partial \mu / \partial P |_T = V_{partial\ molar} (V_{bar})$$

For a solid or liquid V_{bar} is a relatively small and constant value. Thus we can write:

$$d\mu = V_{bar}dP$$

$$RTdlna = V_{bar}dP$$

$$dlna = V_{bar}dP/RT$$

Upon integration to a different pressure P' we find

$$lna' = (P'-1)\ V_{bar}/RT$$

S&McQ
10.3

Example 26-12 shows that for graphite the activity is only 1.01 at 100 bars, so the activity is *not* very pressure dependent. Mostly if pure condensed compounds are involved in reactions the activity can taken as **unity**.

This is also in line with what we said previously about the solvent following Raoult's law. In the limit of the solvent going to pure solvent we have that its P goes to P*. As the activity is defined as P/P* this converges to unity. If a reaction produces more solvent molecules we can usually consider their activity equal to one in very good approximation for dilute solutions, even if they are already non-ideal.

The fact that a=1 for pure condensed phases has an important consequence for reactions (in general: processes) that only involve such phases. If all activities are unity, Q=1 and lnQ=0 which means that $\Delta_rG = \Delta_rG^{\ominus} + 0$. Thus Δ_rG can only be zero -i.e. an equilibrium achieved- ***if*** $\Delta_rG^{\ominus}$ happens to be zero, which is generally not the case. In fact there can only be an equilbrium at one specific temperature:

$$\Delta_rG^{\ominus} = 0$$

$$\Delta_rH^{\ominus}-T\Delta_rS^{\ominus}$$

$$T_{equilibrium}= \Delta_rH^{\ominus}/\Delta_rS^{\ominus}$$

If the process is the transformation from a solid to a liquid this is the well-known *melting point*. At temperature other than 0^oC only one phase can exist: either ice or water. If the other is present, that is an unstable condition and it will transform *entirely* to the stable form. In other words the process will go to completion, *not* equilbirium. Only *at* 0^oC can the two coexist in equilibrium. This holds for all melting points but it also holds for e.g. a solid-solid chemical reactions only producing, say, another solid.

Another way of expressing the above is to say that in order to have equilibrium at a *series* of temperatures, one needs at least one species involved for which activity depends on composition, e.g. a dilute solute or a gas.

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26.12: Activities are Important for Ionic Species

Weak electrolytes

We have seen that strong electrolytes are non-ideal even at tiny concentrations and that even the Debye-Hückel theory only allowed us to work at very small concentrations of strong electrolytes. The same problems are encountered with weak electrolytes but they are compounded by the equilibrium that is inherent to their solutions. Take acetic acid as in household vinegar:

$$HAc + H_2O \rightleftharpoons Ac^- + H_3O^+$$

We can write the equilibrium constant as:

$$K = \frac{a_{Ac^-} a_{H_3O^+}}{a_{HAc} a_{H_2O}}$$

As

$$a_{H2O} = 1$$

$$K = \frac{a_{Ac^-} a_{H_3O^+}}{a_{HAc}}$$

At an initial concentration of say 0.1 mol/l the activity coefficient for HAc (being a *neutral* species) is essentially one, but for the other species we should write:

$$(a_{Ac^-} a_{H_3O^+}) = [Ac^-][H_3O^+]\gamma_{\pm}^2$$

The value of $\gamma_{\pm}^2$ is *not* unity and this will affect the equilibrium. In first approximation we will ignore that fact and write:

$$K = \frac{[Ac^-][H_3O^+]}{[HAc]} = 1.74 \times 10^{-5}$$

(We can either write [mol.l] as dimensions or drop them, depending on whether we are talking about K or K_c)

At equilibrium we would get:

$$K = \frac{x^2}{0.1 - x} = 1.74 \times 10^{-5}$$

which yields

$$x = 1.31 \times 10^{-3} mol/l$$

We can now use Debye-Hückel theory to estimate the means ionic activity coefficient but the concentrations are already to high for that. Instead we will use one of its extensions:

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \frac{\sqrt{I}}{1 + \sqrt{I}}$$

The ionic strength is ½ ($[Ac^-]+[H_3O^+]$) =x

Although we do not know x precisely the value we have is at least a starting point. We can use it to calculate a first approximation for $\gamma_{\pm}^2$. We find a value of 0.921. We then divide the value of K by this value and recalculate x. It changes from x=1.31 10^{-3} mol/l to x=1.365 10^{-3} mol/l. Now we can repeat this process until the value of x does not change appreciably anymore (*converges*). This process is called ***iteration***. The final value is about x=1.37 10^{-3} mol/l.

As can be seen the non-ideality does change the values from the ones you would have calculated before entering this course, but

the difference is not staggering, at least if no other solutes are present.

Question: does the equilibrium change if we add 0.5 mol/l NaCl to the solution?

Solubility products

For solubility products the differences can be more important. Take BaF_2 in water K= 1.7 10^{-6}.

$$K = \gamma_{\pm}^{3}[Ba^{2+}][F^{-}]2$$

Let's start by assuming ideality and say that $\gamma_{\pm}^{3}$=1 and say that :$[Ba^{2+}]$=x

$$[F^{-}] = 2x$$

Thus K= x ($4x^2$) so x= 7.52 10^{-3} mol/lit

The ionic strength is

$$I = \frac{1}{2}(+2)^2 x + (-1)^2 x = 3x$$

The extended Debye-Hückel theory gives $\gamma_{\pm}$ =0.736 this raises x to 0.0102. Repeating the process a few times we find x=0.011. This means an increase of about 30% due to non-ideal behavior for this sparingly soluble salt. Again the presence of other solutes may induce larger effects because they add to the ionic strength.

Exercise

Even pure water contains OH^- and H_3O^+ ions. The K for this equilibrium is 10^{-14}. How does the pH change if we add 0.5 m/lit of a strong electrolyte M^{2+} X^{2-}? CH 431/Lecture 17/answer2

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26.13: Homework Problems

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{26.13.1}$$

You can see from Equation 26.13.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

Exercise 26.13.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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27: THE KINETIC THEORY OF GASES

27.1: The Average Translational Kinetic Energy of a Gas
27.2: The Gaussian Distribution of One Component of the Molecular Velocity
27.3: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution
27.4: The Frequency of Collisions with a Wall
27.5: The Maxwell-Boltzmann Distribution Has Been Verified Experimentally
27.6: Mean Free Path
27.7: Rates of Gas-Phase Chemical Reactions
27.E: The Kinetic Theory of Gases (Exercises)

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27.1: The Average Translational Kinetic Energy of a Gas

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

One key property of the individual particles is their velocity. However, in a sample of many gas particles, the particles will likely have various velocities. Rather than list the velocity of each individual gas molecule, we can combine these individual velocities in several ways to obtain "collective" velocities that describe the sample as a whole.

Table 27.1.1: Kinetic Properties of a Thermalized Ensemble (i.e., follows Maxwell-Boltzmann Distribution)

Property	Speed	Kinetic Energy
Most probable	$\sqrt{\frac{2k_bT}{m}}$	k_BT
Average	$\sqrt{\frac{8k_bT}{\pi m}}$	$\frac{4k_BT}{\pi}$
Root-mean-square	$\sqrt{\frac{3k_bT}{m}}$	$\frac{3}{2}k_BT$

In the following example, these three collective velocities are defined and calculated for a sample of gas consisting of only eight molecules.

Example 27.1.1 : A Gas Sample with Few Molecules

The speeds of eight molecules were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{avg}) root mean square speed (v_{rms}), and most probable speed (v_{mp}).

Solution

Start with definitions:

- **average speed** (v_{avg}) = the sum of all the speeds divided by the number of molecules
- **root-mean square speed** (v_{rms}) = the square root of the sum of the squared speeds divided by the number of molecules
- **most probable speed** (v_{mp}) = the speed at which the greatest number of molecules is moving

The average speed:

$$\begin{aligned} v_{\text{avg}} &= \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} \\ &= 5.6\ m/s \end{aligned}$$

The root-mean square speed:

$$\begin{aligned} v_{\text{rms}} &= \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} \\ &= 6.2\ m/s \end{aligned}$$

The most probable speed:

Of the eight molecules, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three molecules have different speeds. Hence

$$v_{\text{mp}} = 6.0\,m/s.$$

Using expressions for v_{mp}, v_{ave}, or v_{rms}, it is fairly simple to derive expressions for kinetic energy from the expression

$$E_{kin} = \frac{1}{2}mv^2$$

It is important to remember that there will be a full distribution of molecular speeds in a thermalized sample of gas. Some molecules will be traveling faster and some more slowly. It is also important to recognize that the most probable, average, and RMS kinetic energy terms that can be derived from the kinetic molecular theory do not depend on the mass of the molecules (Table 27.1.1). As such, it can be concluded that the average kinetic energy of the molecules in a thermalized sample of gas depends only on the temperature. However, the average speed depends on the molecular mass. So, for a given temperature, light molecules will travel faster on average than heavier molecules.

The calculations carried out in Example 27.1.1 become cumbersome as the number of molecules in the sample of gas increases. Thus, a more efficient way to determine the various collective velocities for a gas sample containing a large number of molecules is required.

A Molecular Description of Pressure and Molecular Speed

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Scotsman James Clerk Maxwell (1831–1879), this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

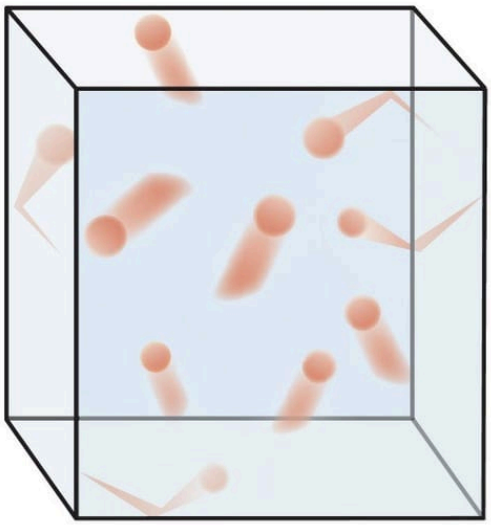


Figure 27.1.1 : Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In Topic 1C, we explain how this theory must be modified to account for the behavior of real gases.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 27.1.2).

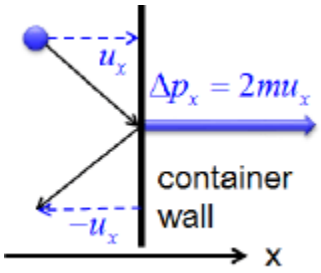


Figure 27.1.2 : Note: In this figure, the symbol u is used to represent velocity. In the rest of this text, velocity will be represented with the symbol v. Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. Momentum transfer ($\Delta\rho_x$) for an elastic collision is equal to mΔv_x, where m is the mass of the molecule and Δv_x is the change in the x component of the molecular velocity ($v_{x_{final}} - v_{x_{initial}}$).The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction, and Δv_x equals $2v_x$.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity v_x in the x direction hits is expressed as:

$$\text{momentum transfer}_\text{x} = \Delta\rho_\text{x} = \text{m}\Delta\text{v}_\text{x} = 2\text{mv}_\text{x} \tag{27.1.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (v_x) \times \left(\frac{N}{V}\right) \tag{27.1.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mv_x) \times (v_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mv_x^2 \tag{27.1.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace v_x^2 in the expression above with the average value of v_x^2, which is denoted by $\bar{v_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\bar{v_x^2} \tag{27.1.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that $\bar{v_x^2} = \bar{v_y^2} = \bar{v_z^2} = \frac{1}{3}\bar{v^2}$. Here the quantity $\bar{v^2}$ is called the **mean-square speed** defined as the average value of square-speed (v^2) over all molecules. Since $v^2 = v_x^2 + v_y^2 + v_z^2$ for each molecule, $\bar{v^2} = \bar{v_x^2} + \bar{v_y^2} + \bar{v_z^2}$. By substituting $\frac{1}{3}\bar{v^2}$ for $\bar{v_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\bar{v^2} \tag{27.1.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas,

$$\epsilon = m\bar{v^2}/2 \tag{27.1.6}$$

By rearranging equation 27.1.5 and substituting in equation 27.1.6, we obtain

$$PV = \frac{1}{3}Nm\bar{v^2} = \frac{2}{3}N\epsilon \tag{27.1.7}$$

The 2/3 factor in the proportionality reflects the fact that velocity components in each of the three directions contributes ½ *kT* to the kinetic energy of the particle. The average translational kinetic energy is directly proportional to temperature:

$$\epsilon = \frac{3}{2}kT \tag{27.1.8}$$

in which the proportionality constant k is known as the *Boltzmann constant*. Substituting Equation 27.1.8 into Equation 27.1.7 yields

$$PV = \left(\frac{2}{3}N\right)\left(\frac{3}{2}kT\right) = NkT \tag{27.1.9}$$

The Boltzmann constant k is just the gas constant per molecule, so if N is chosen as Avogadro's number, N_A, then $N_A k$ is R, the gas constant per mole. Thus, for *n* moles of particles, the Equation 27.1.9 becomes

$$PV = nRT \tag{27.1.10}$$

which is the ideal gas law.

As noted in Example 27.1.1 , the root-mean square speed (v_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\bar{v^2}} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots v_N^2}{N}} \tag{27.1.11}$$

where N is the number of particles and v_i is the speed of particle i.

The v_{rms} for a sample containing a large number of molecules can be obtained by combining equations 27.1.7 and 27.1.8 in a slightly different fashion than that used to obtain equation 27.1.10:

$$PV = \frac{1}{3}Nm\bar{v^2} = \frac{2}{3}N\epsilon \tag{27.1.10}$$

$$\epsilon = \frac{3}{2}kT \tag{27.1.11}$$

$$\frac{1}{3}Nm\bar{v^2} = \left(\frac{2}{3}\right)\left(\frac{3}{2}\right)NkT \tag{27.1.12}$$

$$\frac{1}{3}Nm\bar{v^2} = NkT \tag{27.1.13}$$

$$Nm\bar{v^2} = 3NkT \tag{27.1.14}$$

If N is chosen to be Avogadro's number, N_A, then $N_Am = M$, the molar mass, and $N_Ak = R$, the gas constant per mole,

$$\bar{v^2} = \frac{3RT}{M} \tag{27.1.15}$$

$$v_{\text{rms}} = \sqrt{\bar{v^2}} = \sqrt{\frac{3RT}{M}} \tag{27.1.16}$$

In Equation 27.1.16, v_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 27.1.16 shows that v_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

Example 27.1.2 :

What is the root mean-square speed for O_2 molecules at 25°C?

Given: Temperature in °C, type of molecules, ideal gas gas constant

Asked for: v_{rms}, the root mean-square speed

Strategy:

Convert temperature to kelvins:

$$\text{T (in kelvin)} = (25\ ^{\circ}\text{C} + 273\ ^{\circ}\text{C})\frac{1\ \text{K}}{1\ ^{\circ}\text{C}} = 298\ \text{K}$$

Convert molar mass of O_2 molecules to kg per mole:

$$\text{M (in } \frac{\text{kg}}{\text{mole}}\text{)} = 32.00\frac{\text{g}}{\text{mole}}\text{x}\frac{1\ \text{kg}}{1000\ \text{g}} = 0.03200\frac{\text{kg}}{\text{mole}}$$

Use equation 27.1.16 to calculate the rms speed.

Solution

$$v_{\text{rms}_{O_2}} = \sqrt{\frac{3(8.3145\frac{\text{J}}{\text{K}\cdot\text{mole}})(298.15\ \text{K})}{0.03200\frac{\text{kg}}{\text{mole}}}} = 482\frac{m}{s}$$

Exercise 27.1.2

What is the root mean-square speed for $\mathrm{Cl_2}$ molecules at 25°C?

$v_{\mathrm{rms}_{\mathrm{Cl_2}}} = 324 \frac{m}{s}$

Many molecules, many velocities

At temperatures above absolute zero, all molecules are in motion. In the case of a gas, this motion consists of straight-line jumps whose lengths are quite great compared to the dimensions of the molecule. Although we can never predict the velocity of a particular *individual* molecule, the fact that we are usually dealing with a huge number of them allows us to know what fraction of the molecules have kinetic energies (and hence velocities) that lie within any given range.

The trajectory of an individual gas molecule consists of a series of straight-line paths interrupted by collisions. What happens when two molecules collide depends on their relative kinetic energies; in general, a faster or heavier molecule will impart some of its kinetic energy to a slower or lighter one. Two molecules having identical masses and moving in opposite directions at the same speed will momentarily remain motionless after their collision.

If we could measure the instantaneous velocities of all the molecules in a sample of a gas at some fixed temperature, we would obtain a wide range of values. A few would be zero, and a few would be very high velocities, but the majority would fall into a more or less well-defined range. We might be tempted to define an average velocity for a collection of molecules, but here we would need to be careful: molecules moving in opposite directions have velocities of opposite signs. Because the molecules are in a gas are in random thermal motion, there will be just about as many molecules moving in one direction as in the opposite direction, so the velocity vectors of opposite signs would all cancel and the average velocity would come out to zero. Since this answer is not very useful, we need to do our averaging in a slightly different way.

The proper treatment is to average the *squares* of the velocities, and then take the square root of this value to obtain the root-mean-square velocity (v_{rms}), which is what we developed above. This velocity describes the gas sample as a whole, but it does not tell us about the range of velocities possible, nor does it tell us the distribution of velocities. To obtain a more complete description of how many gas molecules are likely to be traveling at a given velocity range we need to make use of the Maxwell-Boltzmann distribution law.

Contributors and Attributions

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27.2: The Gaussian Distribution of One Component of the Molecular Velocity

As was shown in section 27.1, the pressure of an ideal gas is given as the total force exerted per unit area

$$P = \frac{F_{tot}}{A} = N_{tot}\left(\frac{mv_x^2}{V}\right) = \frac{N_{tot}m}{V}v_x^2$$

The question then becomes how to deal with the velocity term. Initially, it was assumed that all of the molecules had the same velocity, and so the magnitude of the velocity in the x-direction was merely a function of the trajectory. However, real samples of gases comprise molecules with an entire distribution of molecular speeds and trajectories. To deal with this distribution of values, we replaced (v_x^2) with the squared average of velocity in the x direction $\langle v_x \rangle^2$.

$$P = \frac{N_{tot}m}{V}\langle v_x \rangle^2$$

The distribution function for velocities in the x direction, known as the **Maxwell-Boltzmann distribution**, is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}} \tag{27.2.1}$$

This function has two parts: a **normalization constant** and an exponential term. The normalization constant is derived by noting that

$$\int_{-\infty}^{\infty} f(v_x)dv_x = 1 \tag{27.2.2}$$

Normalizing the Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution has to be normalized because it is a continuous probability distribution. As such, the sum of the probabilities for all possible values of v_x **must** be unity. And since v_x can take any value between -∞ and ∞, then Equation 27.2.2 must be true. So if the form of $f(v_x)$ is assumed to be

$$f(v_x) = N\exp\left(\frac{-mv_x^2}{2k_B T}\right)$$

The normalization constant N can be found from

$$\int_{-\infty}^{\infty} f(v_x)dv_x = \int_{-\infty}^{\infty} N\exp\left(\frac{-mv_x^2}{2k_B T}\right)dv_x = 1$$

The expression can be simplified by letting $\alpha = m/2k_B T$:

$$N\int_{-\infty}^{\infty} \exp\left(-\alpha v_x^2\right)dv_x = 1$$

A table of definite integrals says that

$$\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

So

$$N\sqrt{\frac{\pi}{\alpha}} = 1$$

Thus,

$$N = \sqrt{\frac{\alpha}{\pi}} = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

And thus the normalized distribution function is given by

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m v_x^2}{2k_B T}\right) \tag{27.2.3}$$

Calculating an Average from a Probability Distribution

Calculating an average for a finite set of data is fairly easy. The average is calculated by

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$$

But how does one proceed when the set of data is infinite? Or how does one proceed when all one knows are the probabilities for each possible measured outcome? It turns out that that is fairly simple too!

$$\bar{x} = \sum_{i=1}^{N} x_i P_i$$

where P_i is the probability of measuring the value x_i. This can also be extended to problems where the measurable properties are not discrete (like the numbers that result from rolling a pair of dice) but rather come from a continuous parent population. In this case, if the probability is of measuring a specific outcome, the average value can then be determined by

$$\bar{x} = \int x P(x) dx$$

where $P(x)$ is the function describing the probability distribution, and with the integration taking place across all possible values that x can take.

Calculating the average velocity in the x direction

A value that is useful (and will be used in further developments) is the average velocity in the x direction. This can be derived using the probability distribution, as shown in the mathematical development box above. The average value of v_x is given by

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dx$$

This integral will, by necessity, be zero. This must be the case as the distribution is symmetric, so that half of the molecules are traveling in the +x direction, and half in the –x direction. These motions will have to cancel. So, a more satisfying result will be given by considering the magnitude of v_x, which gives the speed in the x direction. Since this cannot be negative, and given the symmetry of the distribution, the problem becomes

$$\langle |v_x| \rangle = 2\int_{0}^{\infty} v_x f(v_x) dx$$

In other words, we will consider only half of the distribution, and then double the result to account for the half we ignored.

For simplicity, we will write the distribution function as

$$f(v_x) = N\exp(-\alpha v_x^2)$$

where

$$N = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

and

$$\alpha = \frac{m}{2k_B T}.$$

A table of definite integrals shows

$$\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a}$$

so

$$\langle v_x \rangle = 2N\left(\frac{1}{2\alpha}\right) = \frac{N}{\alpha}$$

Substituting our definitions for N and α produces

$$\langle v_x \rangle = \left(\frac{m}{2\pi k_B T}\right)^{1/2}\left(\frac{2k_B T}{m}\right) = \left(\frac{2k_B T}{\pi m}\right)^{1/2}$$

This expression indicates the average speed for motion in one direction.

It is important to note that equation 27.2.1 describes the distribution function for one component of the molecular ***velocity***. Because a molecule is able to move in a positive or a negative direction, the range of one component of the molecular velocity (v_x in this case) is $-\infty$ to ∞. This distribution of velocities is a Gaussian distribution of velocities, as shown in Figure 27.2.1 .

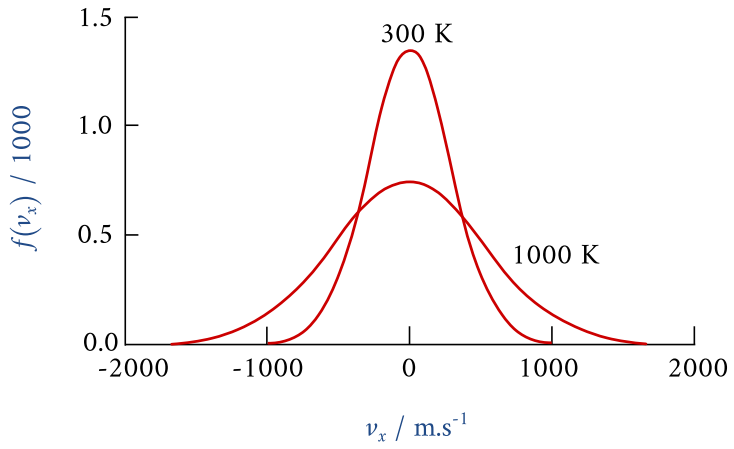


Figure 27.2.1 : Distribution of the x component of the velocity of a nitrogen molecule at 300 K and 1000 K. (CC BY-NC; Ümit Kaya via LibreTexts)

We will find in section 27.3 that the distribution of molecular ***speeds*** is not a Gaussian distribution.

Contributors and Attributions

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27.3: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution

The Boltzmann Distribution

If we were to plot the number of molecules whose velocities fall within a series of narrow ranges, we would obtain a slightly asymmetric curve known as a *velocity distribution*. The peak of this curve would correspond to the *most probable* velocity. This velocity distribution curve is known as the *Maxwell-Boltzmann distribution*, but is frequently referred to only by Boltzmann's name. The **Maxwell-Boltzmann distribution law** was first worked out around 1860 by the great Scottish physicist, **James Clerk Maxwell** (1831-1879), who is better known for discovering the laws of electromagnetic radiation. Later, the Austrian physicist **Ludwig Boltzmann** (1844-1906) put the relation on a sounder theoretical basis and simplified the mathematics somewhat. Boltzmann pioneered the application of statistics to the physics and thermodynamics of matter and was an ardent supporter of the atomic theory of matter at a time when it was still not accepted by many of his contemporaries.

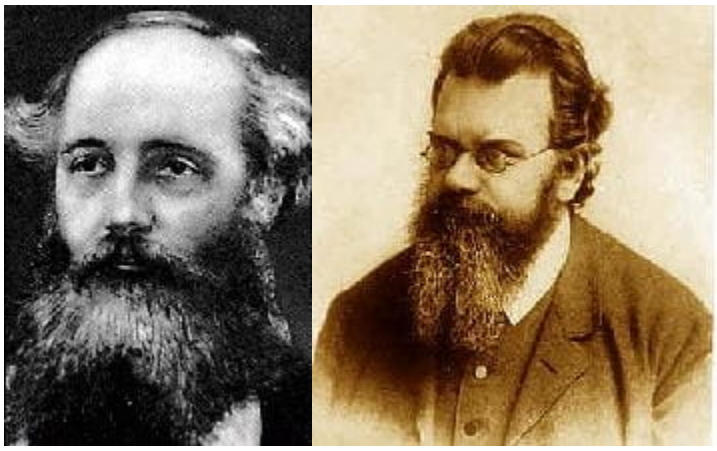


Figure 27.3.1 : Maxwell (left) and Boltzmann (right) are responsible for describing the velocity distribution of gas molecules

In section 27.2 we saw that the distribution function for molecular speeds in the x direction is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}}$$

However, real gas samples have molecules not only with a distribution of molecular speeds and but also a random distribution of directions. Using normal vector magnitude properties (or simply using the Pythagorean Theorem), it can be seen that

$$\langle v \rangle^2 = \langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2$$

Since the direction of travel is random, the velocity can have any component in x, y, or z directions with equal probability. As such, the average value of the x, y, or z components of velocity should be the same. And so

$$\langle v \rangle^2 = 3\langle v_x \rangle^2$$

Substituting this into the expression for pressure yields

$$p = \frac{N_{tot} m}{3V} \langle v \rangle^2$$

All that remains is to determine the form of the distribution of velocity magnitudes the gas molecules can take. In his 1860 paper (Illustrations of the dynamical theory of gases. Part 1. On the motions and collisions of perfectly elastic spheres, 1860), Maxwell proposed a form for this distribution of speeds which proved to be consistent with observed properties of gases (such as their

viscosities). He derived this expression based on a transformation of coordinate system from Cartesian coordinates (x, y, z) to spherical polar coordinates (v, θ, ϕ). In this new coordinate system, v represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles θ and ϕ. The infinitesimal volume unit becomes

$$dx\,dy\,dz = v^2 \sin(\theta)\,dv\,d\theta\,d\phi$$

Applying this transformation of coordinates **Maxwell's distribution** took the following form

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \tag{27.3.1}$$

The Distribution of Speed over all Directions

The Distribution of Kinetic Energy in Three Dimensions

As noted above, the distribution function of molecular energies for one dimension is

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-mv_x^2}{2k_B T}\right)$$

To obtain a three-dimensional probability distribution, you multiply the distribution function for each of the three dimensions so that

$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

given

$$\langle v \rangle^2 = \langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2$$

The Conversion of Energy Distribution to Speed Distribution

To convert the three-dimensional energy distribution to a speed distribution over all space, the energy distribution must be summed over all directions. This sum is usually described by imagining a "velocity space" in spherical polar coordinates. As noted above, in this new coordinate system, v represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles θ and ϕ. The infinitesimal volume unit becomes

$$dx\,dy\,dz = v^2 \sin(\theta)\,dv\,d\theta\,d\phi$$

You integrate over θ and ϕ to sum over all space, thus

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \underbrace{\int_0^{\pi}\int_0^{2\pi} v^2 \sin\theta d\phi d\theta}_{=4\pi v^2}$$

This equation is rearranged to give

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

This function can be thought of as having three basic parts to it: **a normalization constant** (N), a velocity dependence (v^2), and an exponential term that contains the kinetic energy ($\frac{1}{2}mv^2$).

Because the function represents the fraction of molecules with the speed v, the sum of the fractions for all possible velocities must be unity. This sum can be calculated as an integral. The normalization constant ensures that

$$\int_0^{\infty} f(v)dv = 1$$

Thus the normalization constant is

$$N = 4\pi\sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}$$

Velocity distributions depend on temperature and mass

Higher temperatures allow a larger fraction of molecules to acquire greater amounts of kinetic energy, causing the Boltzmann plots to spread out. Figure 27.3.2 shows how the Maxwell-Boltzmann distribution is affected by temperature. At lower temperatures, the molecules have less energy. Therefore, the speeds of the molecules are lower and the distribution has a smaller range. As the temperature of the molecules increases, the distribution flattens out. Because the molecules have greater energy at higher temperature, the molecules are moving faster.

Notice how the left ends of the plots are anchored at zero velocity (there will always be a few molecules that happen to be at rest.) As a consequence, the curves flatten out as the higher temperatures make additional higher-velocity states of motion more accessible. The area under each plot is the same for a constant number of molecules.

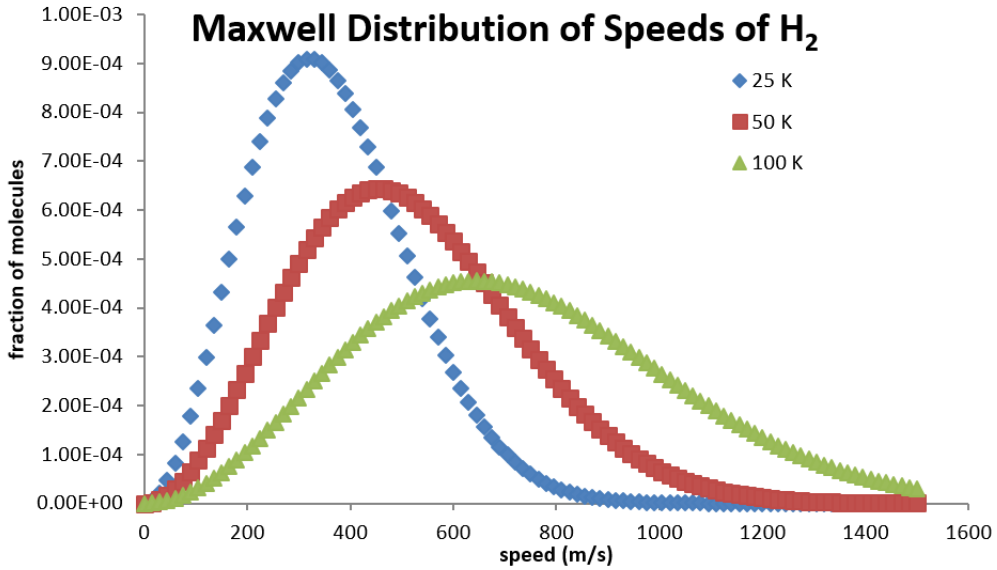


Figure 27.3.2: Maxwell Distribution of speeds for hydrogen molecules at differing temperatures.

Calculating the Average Speed

Using the Maxwell distribution as a distribution of probabilities, the average molecular speed in a sample of gas molecules can be determined.

$$\begin{aligned}\langle v\rangle &= \int_{-\infty}^{\infty} v\, f(v)dv \\ &= \int_{-\infty}^{\infty} v\, 4\pi\sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv \\ &= 4\pi\sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}\int_{-\infty}^{\infty} v^3 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv\end{aligned}$$

The following can be found in a table of integrals:

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

So

$$\langle v \rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1}{2\left(\frac{m}{2k_B T}\right)^2}\right]$$

Which simplifies to

$$\langle v \rangle = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

Note: the value of $\langle v \rangle$ is twice that of $\langle v_x \rangle$ which was derived in an earlier example!

$$\langle v \rangle = 2\langle v_x \rangle$$

Example 27.3.1 :

What is the average value of the squared speed according to the Maxwell distribution law?

Solution:

$$\begin{aligned}\langle v^2 \rangle &= \int_{-\infty}^{\infty} v^2 f(v) dv \\ &= \int_{-\infty}^{\infty} v^2 \, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right) \, dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^4 \exp\left(\frac{-mv^2}{2k_B T}\right) \, dv\end{aligned}$$

A table of integrals indicates that

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$

Substitution (noting that $n = 2$) yields

$$\langle v^2 \rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1 \cdot 3}{2^3 \left(\frac{m}{2k_B T}\right)^2} \sqrt{\frac{\pi}{\left(\frac{m}{2k_B T}\right)}}\right]$$

which simplifies to

$$\langle v^2 \rangle = \frac{3k_B T}{m}$$

Note: The square root of this average squared speed is called the **root mean square** (RMS) speed, and has the value

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \left(\frac{3k_B T}{m}\right)^{1/2}$$

All molecules have the same kinetic energy ($\frac{1}{2}mv^2$) at the same temperature, so the fraction of molecules with higher velocities will increase as *m*, and thus the molecular weight, decreases. Figure 27.3.3 shows the dependence of the Maxwell-Boltzmann distribution on molecule mass. On average, heavier molecules move more slowly than lighter molecules. Therefore, heavier molecules will have a smaller speed distribution, while lighter molecules will have a speed distribution that is more spread out.

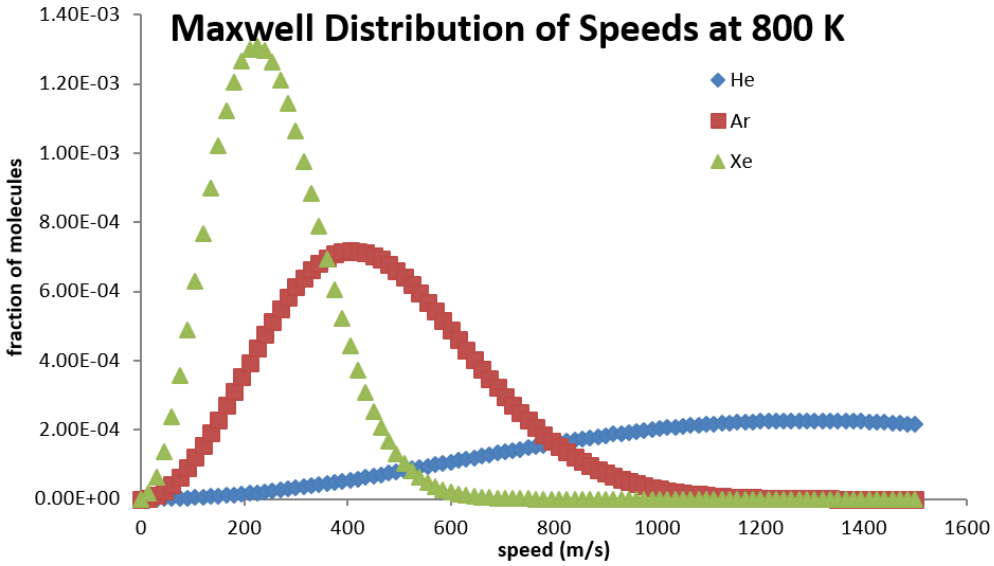


Figure 27.3.3: Maxwell Distribution of speeds at 800 K for different gasses of differing molecular masses.

Related Speed Expressions

Usually, we are more interested in the speeds of molecules rather than their component velocities. The Maxwell–Boltzmann distribution for the speed follows immediately from the distribution of the velocity vector, above. Note that the speed of an individual gas particle is:

$$v = \sqrt{v_x^2 + v_y^2 = v_z^2}$$

Three speed expressions can be derived from the Maxwell-Boltzmann distribution:

- the most probable speed,
- the average speed, and
- the root-mean-square speed.

The **most probable speed** is the maximum value on the distribution plot (Figure 27.3.4). This is established by finding the velocity when the derivative of Equation 27.3.1 is zero

$$\frac{df(v)}{dv} = 0$$

which is

$$v_{mp} = \sqrt{\frac{2RT}{M}} \tag{27.3.2}$$

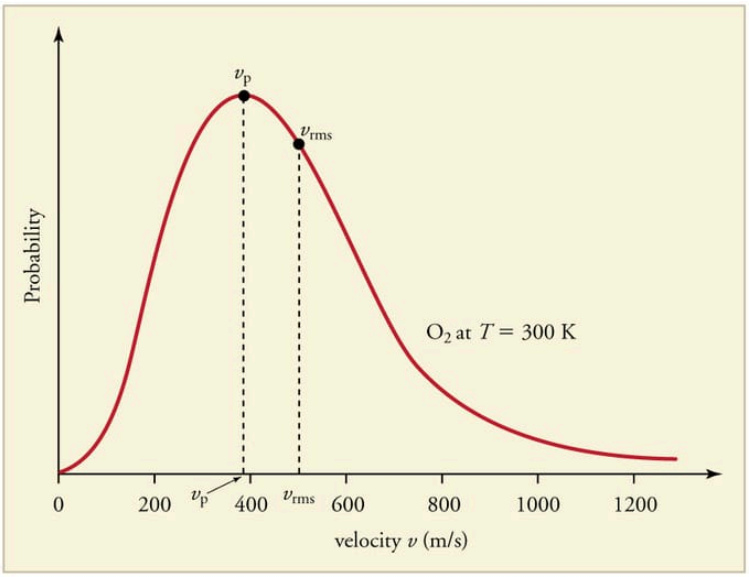


Figure 27.3.4 : The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures. from OpenStax. The speed at the top of the curve is called the most probable speed because the largest number of molecules have that speed.

The **average speed** is the sum of the speeds of all the molecules divided by the number of molecules.

$$v_{avg} = \bar{v} = \int_0^\infty v f(v) dv = \sqrt{\frac{8RT}{\pi M}}$$

The **root-mean-square speed** is square root of the average speed-squared.

$$v_{rms} = \bar{v^2} = \sqrt{\frac{3RT}{M}}$$

where

- R is the gas constant,
- T is the absolute temperature and
- M is the molar mass of the gas.

It *always* follows that for gases that follow the Maxwell-Boltzmann distribution:

$$v_{mp} < v_{avg} < v_{rms}$$

Problems

1. Using the Maxwell-Boltzman function, calculate the fraction of argon gas molecules with a speed of 305 m/s at 500 K.
2. If the system in problem 1 has 0.46 moles of argon gas, how many molecules have the speed of 305 m/s?
3. Calculate the values of C_{mp}, C_{avg}, and C_{rms} for xenon gas at 298 K.
4. From the values calculated above, label the Boltzmann distribution plot with the approximate locations of (C_{mp}\), C_{avg}, and C_{rms}.
5. What will have a larger speed distribution, helium at 500 K or argon at 300 K? Helium at 300 K or argon at 500 K? Argon at 400 K or argon at 1000 K?

Answers

1. 0.00141
2. 3.92×10^{20} argon molecules
3. c_{mp} = 194.27 m/s, c_{avg} = 219.21 m/s, c_{rms} = 237.93 m/s

4. As stated above, C_{mp} is the most probable speed, thus it will be at the top of the distribution curve. To the right of the most probable speed will be the average speed, followed by the root-mean-square speed.
5. Hint: Use the related speed expressions to determine the distribution of the gas molecules: helium at 500 K. helium at at 300 K. argon at 1000 K.

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Contributors and Attributions

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27.4: The Frequency of Collisions with a Wall

In the derivation of an expression for the pressure of a gas, it is useful to consider the frequency with which gas molecules collide with the walls of the container. To derive this expression, consider the expression for the "collision volume".

$$V_{col} = v_x \Delta t \ \cdot A$$

in which the product of the velocity v_x and a time interval Δt is multiplied by A, the area of the wall with which the molecules collide.

All of the molecules within this volume, and with a velocity such that the x-component exceeds v_x (and is positive) will collide with the wall. That fraction of molecules is given by

$$N_{col} = \frac{N}{V} \frac{\langle v_x \rangle \Delta t \cdot A}{2}$$

and the frequency of collisions with the wall per unit area per unit time is given by

$$z_w = \frac{N}{V} \frac{\langle v_x \rangle}{2}$$

In order to expand this model into a more useful form, one must consider motion in all three dimensions. Considering that

$$\langle v \rangle = \sqrt{\langle v_x \rangle + \langle v_y \rangle + \langle v_z \rangle}$$

and that

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle$$

it can be shown that

$$\langle v \rangle = 2 \langle v_x \rangle$$

or

$$\langle v_x \rangle = \frac{1}{2} \langle v \rangle$$

and so

$$z_w = \frac{1}{4} \frac{N}{V} \langle v \rangle$$

A different approach to determining z_w is to consider a collision cylinder that will enclose all of the molecules that will strike an area of the wall at an angle θ and with a speed v in the time interval dt. The volume of this collision cylinder is the product of its base area (A) times its vertical height $(v \cos \theta dt)$, as shown in figure $27.4.1$.

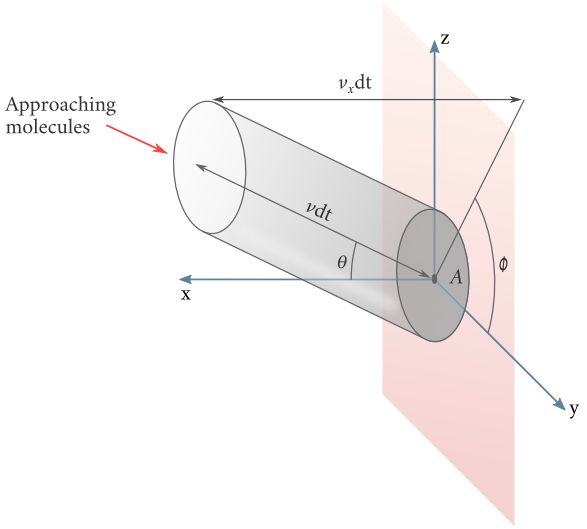


Figure 27.4.1: The collision cylinder for determining the number of collisions of gas molecules with a wall. (CC BY-NC; Ümit Kaya)

The number of molecules in this cylinder is $\rho \cdot A \cdot v \cdot \cos\theta dt$, where ρ is the number density $\frac{N}{V}$. The fraction of molecules that are traveling at a speed between v and $v + dv$ is $F(v)dv$. The fraction of molecules traveling within the solid angle bounded by θ and $\theta + d\theta$ and between ϕ and $\phi + d\phi$ is $\frac{\sin\theta d\theta d\phi}{4\pi}$. Multiplying these three terms together results in the number of molecules colliding with the area A from the specified direction during the time interval dt

$$dN_w = \rho \cdot A \cdot v \cdot \cos\theta\, dt \;\cdot\; F(v)dv \;\cdot\; \frac{\sin\theta d\theta d\phi}{4\pi}$$

This equation can be rearranged to obtain

$$\frac{1}{A}\frac{dN_w}{dt} = \frac{\rho}{4\pi} vF(v)dv \cdot \cos\theta \sin\theta\, d\theta d\phi = dz_w$$

Integrating this equation over all possible speeds and directions (on the front side of the wall only), we get

$$z_w = \frac{\rho}{4\pi}\int_0^\infty vF(v)dv \cdot \int_0^{\pi/2} \cos\theta \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

The result is that

$$z_w = \frac{1}{A}\frac{dN_w}{dt} = \frac{1}{4}\frac{N}{V}\langle v\rangle = \rho\frac{\langle v\rangle}{4} \tag{27.4.1}$$

Example 27.4.1

Calculate the collision frequency per unit area (Z_w) for oxygen at 25.00°C and 1.000 bar using equation 27.4.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Solution

N molecules = N_A x n, so that

$$\frac{N}{V} = \frac{(N_A)\cdot n}{V} = \frac{(N_A)\cdot P}{R\cdot T}$$

$$\frac{(6.022x10^{23}\,mole^{-1})(1.00\,bar)}{(0.08319\,L\cdot bar\cdot mole^{-1}\cdot K^{-1})(298\,K)} = 2.43\times10^{22}\,L^{-1} = 2.43\times10^{25}\,m^{-3}$$

and

$$\langle v\rangle = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8(8.314J\cdot K^{-1}\cdot mol^{-1})(298K)}{\pi\cdot(0.031999\,kg)}\right)^{\frac{1}{2}} = 444\,m\cdot s^{-1}$$

Thus

$$z_w = \frac{1}{4}(2.43\times10^{25}m^{-3})(444\,m\cdot s^{-1})\left(\frac{1\,m}{100\,cm}\right)^2 = 2.70\times10^{23}s^{-1}\cdot cm^{-2}$$

The factor of N/V is often referred to as the “number density” as it gives the number of molecules per unit volume. At 1 atm pressure and 298 K, the number density for an ideal gas is approximately 2.43 x 10^{19} molecule/cm^3. (This value is easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm^3.

Exercise 27.4.1

Calculate the collision frequency per unit area (Z_w) for hydrogen at 25.00°C and 1.000 bar using equation 27.4.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Answer available at the end of this section.

Contributors and Attributions

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)
- Tom Neils, Grand Rapids Community College

Answers

$$\langle v\rangle = 1770\,m\cdot s^{-1}$$

and

$$Z_w = 1.08\times10^{24}s^{-1}\cdot cm^{-2}$$

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27.5: The Maxwell-Boltzmann Distribution Has Been Verified Experimentally

The Maxwell-Boltzman distruction distribution has been verified experimentally by a device called a velocity selector, which is essentially a series of spinning wheels with a hole through which the gas is effused. This ensures that only gas particles with a certain velocity will pass through all the holes as the wheels are spun at various rates. Thus it is possible to count the number of particles with various velocities and show that, indeed they do satisfy the Maxwell-Boltzmann distribution.

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27.6: Mean Free Path

Collision energy

Consider two particles A and B in a system. The kinetic energy of these two particles is

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} \tag{27.6.1}$$

We can describe kinetic energy in terms of center-of-mass $(\mathbf{P})$ and relative momentum $(\mathbf{p})$, which are given by

$$\mathbf{P} = \mathbf{p}_A + \mathbf{p}_B$$

and

$$\begin{aligned} \mathbf{p} &= \text{relative velocity} \times \mu \\ &= (\mathbf{v}_A - \mathbf{v}_B) \times \left(\frac{m_A m_B}{m_A + m_B} \right) \\ &= \frac{m_B \mathbf{p}_A - m_A \mathbf{p}_B}{M} \end{aligned}$$

where

$$M = m_A + m_B$$

is the total mass of the two particles, and

$$\mu = \frac{m_A m_B}{M}$$

is the **reduced mass** of the two particles.

Substituting these terms into equation 27.6.1, we find

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu}$$

Note that the kinetic energy separates into a sum of a center-of-mass term and a relative momentum term.

Now the relative position of the two particles is $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$ so that the relative velocity is $\dot{\mathbf{r}} = \dot{\mathbf{r}}_A - \dot{\mathbf{r}}_B$ or $\mathbf{v} = \mathbf{v}_A - \mathbf{v}_B$. Thus, if the two particles are approaching each other such that $\mathbf{v}_A = -\mathbf{v}_B$, then $\mathbf{v} = 2\mathbf{v}_A$. However, by equipartitioning the relative kinetic energy, which is mass independent, we get

$$\left\langle \frac{\mathbf{p}^2}{2\mu} \right\rangle = \frac{3}{2} k_B T$$

which is called the *collision energy*

Collision cross-section

Consider two molecules in a system. The probability that they will collide increases with the effective “size” of each particle. However, the size measure that is relevant is the apparent cross-section area of each particle. For simplicity, suppose the particles are spherical, which is not a bad approximation for small molecules. If we are looking at a sphere, what we perceive as the size of the sphere is the cross section area of a great circle. Recall that each spherical particle has an associated “collision sphere” that just encloses two particles at closest contact, i.e., at the moment of a collision, and that this sphere is a radius d, where d is the diameter of each spherical particle. The cross-section of this collision sphere represents an effective cross section for each

particle inside which a collision is imminent. The cross-section of the collision sphere is the area of a great circle, which is πd^2. We denote this apparent cross section area σ. Thus, for spherical particles A and B with diameters d_A and d_B, the individual cross sections are

$$\sigma_A = \pi d_A^2, \quad \sigma_B = \pi d_B^2$$

The *collision cross section*, σ_{AB} is determined by an effective diameter d_{AB} characteristic of both particles. The collision probability increases of both particles have large diameters and decreases if one of them has a smaller diameter than the other. Hence, a simple measure sensitive to this is the arithmetic average

$$d_{AB} = \frac{1}{2}(d_A + d_B)$$

and the resulting collision cross section becomes

$$\begin{aligned}
\sigma_{AB} &= \pi d_{AB}^2 \\
&= \pi \left(\frac{d_A + d_B}{2} \right)^2 \\
&= \frac{\pi}{4} \left(d_A^2 + 2 d_A d_B + d_B^2 \right) \\
&= \frac{1}{4} \left(\sigma_A + 2\sqrt{\sigma_A \sigma_B} + \sigma_B \right) \\
&= \frac{1}{2} \left[\left(\frac{\sigma_A + \sigma_B}{2} \right) + \sqrt{\sigma_A \sigma_B} \right]
\end{aligned}$$

which, interestingly, is an average of the two types of averages of the two individual cross sections, the arithmetic and geometric averages!

Average collision Frequency

Consider a system of particles with individual cross sections σ. A particle of cross section σ that moves a distance l in a time Δt will sweep out a cylindrical volume (ignoring the spherical caps) of volume σl (Figure 27.6.1). If the system has a number density ρ, then the number of collisions that will occur is

$$N_{\text{coll}} = \rho \sigma l$$

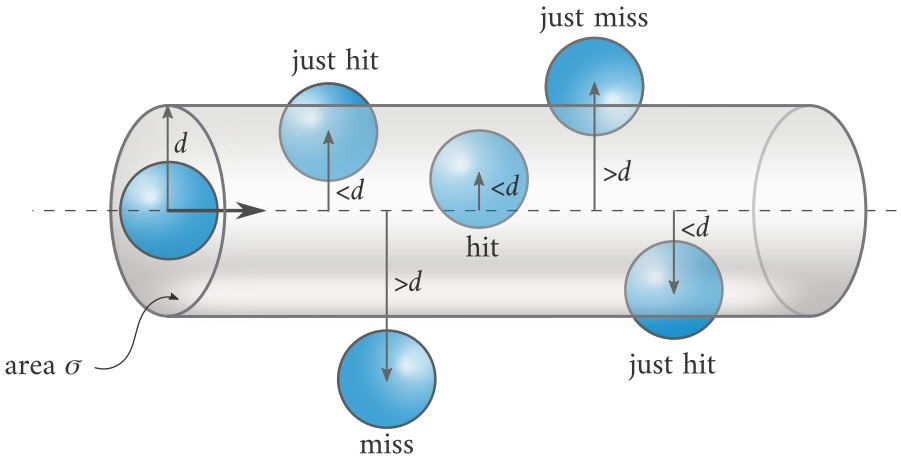


Figure 27.6.1 : Collision cylinder. Any particle that partially overlaps with this volume will experience a collision with a test particle tracing out this volume. (CC BY-NC; Ümit Kaya)

We define the collision frequency for a single molecule, z_A, also known as the average collision rate as $N_{\text{coll}}/\Delta t$, i.e.,

$$z_A = \frac{N_{\text{coll}}}{\Delta t} = \frac{\rho\sigma l}{\Delta t} = \rho\sigma\langle v\rangle \tag{27.6.2}$$

where $\langle v\rangle$ is the average speed of a particle

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m_A}}$$

Equation 27.6.2 is not quite correct because it is based on the assumption that only the molecule of interest is moving. If we take into account the fact that all of the particles are moving relative to one another, and assume that all of the particles are of the same type (say, type A), then performing the average over a Maxwell-Boltzmann speed distribution gives

$$\langle v_r\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

where $\mu = m_A/2$ is the reduced mass.

Thus,

$$\langle v_r\rangle = \sqrt{2}\langle v\rangle$$

and

$$z_A = \sqrt{2}\rho\sigma\langle v\rangle \ = \rho\sigma\langle v_r\rangle$$

The reciprocal of z_A is a measure of the average time between collisions for a single molecule.

Mean Free Path

The mean free path is the distance a particle will travel, on average, before experiencing a collision event. This is defined as the product of the average speed of a particle and the time between collisions. The former is $\langle v\rangle$, while the latter is $1/z_A$. Hence, we have

$$\lambda = \frac{\langle v\rangle}{\sqrt{2}\rho\sigma\langle v\rangle} = \frac{1}{\sqrt{2}\rho\sigma}$$

The mean free path can also be described using terms from the ideal gas law, because $\rho = \dfrac{P\cdot N_A}{R\cdot T}$:

$$\lambda = \frac{R\cdot T}{\sqrt{2}\cdot N_A\cdot\sigma\cdot P}$$

Random Walks

In any system, a particle undergoing frequent collisions will have the direction of its motion changed with each collision and will trace out a path that appears to be random. In fact, if we treat the process as statistical, then, we are, in fact, treating each collision event as a random event, and the particle will change its direction at random times in random ways! Such a path might appear as shown in Figure 27.6.2. Such a path is often referred to as a *random walk path*.

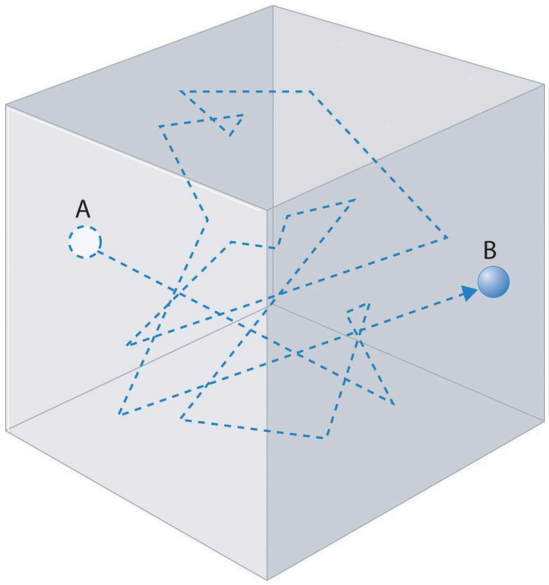


Figure 27.6.2: Random walk path. The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

In order to analyze such paths, let us consider a random walk in one dimension. We'll assume that the particle move a mean-free path length λ between collisions and that each collision changes the direction of the particles motion, which in one dimension, means that the particle moves either to the right or to the left after each event. This can be mapped onto a metaphoric "coin toss" that can come up heads "H" or tails "T", with "H" causing motion to the right, and "T" causing motion to the left. Let there be N such coin tosses, let i be the number of times "H" comes up and j denote the number of times "T" comes up. Thus, the progress of the particle, which we define as net motion to the right, is given by $(i-j)\lambda$. Letting $k = i - j$, this is just $k\lambda$. Thus, we need to know what the probability is for obtaining a particular value of k in a very large number N of coin tosses. Denote this $P(k)$.

In N coin tosses, the total number of possible sequences of "H" and "T" is 2^N. However, the number of ways we can obtain i heads and \)j\) tails, with $i + j = N$ is a binomial coefficient $N!/i!j!$. Now

$$j = N - i = N - (j + k) = N - j - k$$

so that $j = (N - k)/2$. Similarly,

$$i = N - j = N - (i - k) = N - i + k$$

so that $i = (N + k)/2$. Thus, the probability $P(k)$ is

$$P(k) = \frac{N!}{2^N i!j!} = \frac{1}{2^N} \frac{N!}{\left(\frac{N+k}{2}\right)!\left(\frac{N-k}{2}\right)!}$$

We now take the logarithm of both sides:

$$\ln P(k) = \ln N! - \ln 2^N - \ln \left(\frac{N+k}{2}\right)! - \ln \left(\frac{N-k}{2}\right)!$$

and use Stirling's approximation:

$$\ln N! \approx N \ln N - N$$

and write $\ln\ P(k)$ as

$$\begin{aligned}\ln P(k) &\approx N\ln N - N - N\ln 2 - \frac{1}{2}(N+k)\ln\frac{1}{2}(N+k) + \frac{1}{2}(N+k) - \frac{1}{2}(N-k)\ln\frac{1}{2}(N-k) + \frac{1}{2}(N-k)\\ &= N\ln N - N\ln 2 + \frac{1}{2}(N+k)\ln\frac{1}{2} - \frac{1}{2}(N+k)\ln(N+k) - \frac{1}{2}(N-k)\ln\frac{1}{2} - \frac{1}{2}(N-k)\ln(N-k)\\ &= N\ln N - N\ln 2 + \frac{1}{2}(N+k)\ln 2 - \frac{1}{2}(N+k)\ln(N+k) + \frac{1}{2}(N-k)\ln 2 - \frac{1}{2}(N-k)\ln(N-k)\\ &= N\ln N - \frac{1}{2}\left[(N+k)\ln(N+k) + (N-k)\ln(N-k)\right]\end{aligned}$$

Now, write

$$\ln(N+k) = \ln N\left(1+\frac{k}{N}\right) = \ln N + \ln\left(1+\frac{k}{N}\right)$$

and

$$\ln(N-k) = \ln N\left(1-\frac{k}{N}\right) = \ln N + \ln\left(1-\frac{k}{N}\right)$$

We now use the expansions

$$\begin{aligned}\ln\left(1+\frac{k}{N}\right) &= \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots\\ \ln\left(1-\frac{k}{N}\right) &= -\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots\end{aligned}$$

If we stop at the second-order term, then

$$\begin{aligned}\ln P(k) &= N\ln N - \frac{1}{2}(N+k)\left[\ln N + \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] - \frac{1}{2}(N-k)\left[\ln N - \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right]\\ &= -\frac{1}{2}(N+k)\left[\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] + \frac{1}{2}(N-k)\left[\left(\frac{k}{N}\right) + \frac{1}{2}\left(\frac{k}{N}\right)^2\right]\\ &= \frac{1}{2}N\left(\frac{k}{N}\right)^2 - k\left(\frac{k}{N}\right)\\ &= \frac{k^2}{2N} - \frac{k^2}{N} = -\frac{k^2}{2N}\end{aligned}$$

so that

$$P(k) = e^{-k^2/2N}$$

Now, if we let $x = k\lambda$ and $L = \sqrt{N}\lambda$, and if we let x be a continuous random variable, then the corresponding probability distribution $P(x)$ becomes

$$P(x) = \frac{1}{L\sqrt{2\pi}}\,e^{-x^2/2L^2} = \frac{1}{\sqrt{2\pi N\lambda^2}}\,e^{-x^2/2N\lambda^2} \tag{27.6.3}$$

which is a simple Gaussian distribution. Now, N is the number of collisions, which is given by $z_A t$, so we can write the probability distribution for the particle to diffuse a distance x in time t as

$$P(x,t) = \frac{1}{\sqrt{2\pi z_A t\lambda^2}}\,e^{-x^2/2z_A t\lambda^2}$$

Define $D = z_A\lambda^2/2$ as the *diffusion constant,* which has units of (length)^2/time. The distribution then becomes

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\,e^{-x^2/4Dt}$$

Note that this distribution satisfies the following equation:

$$\frac{\partial}{\partial t}P(x,t) = D\frac{\partial^2}{\partial x^2}P(x,t)$$

which is called the diffusion equation. The diffusion equation is, in fact, more general than the Gaussian distribution in Equation 27.6.3. It is capable of predicting the distribution in any one-dimensional geometry subject to any initial distribution $P(x,0)$ and any imposed boundary conditions.

In three dimensions, we consider the three spatial directions to be independent, hence, the probability distribution for a particle to diffuse to a location $\mathbf{r} = (x,y,z)$ is just a product of the three one-dimensional distributions:

$$\mathcal{P}(\mathbf{r}) = P(x)\,P(y)\,P(z) = \frac{1}{(4\pi Dt)^{3/2}}\,e^{-(x^2+y^2+z^2)/4Dt}$$

and if we are only interested in diffusion over a distance r, we can introduce spherical coordinates, integrate over the angles, and we find that

$$P(r,t) = \frac{4\pi}{(4\pi Dt)^{3/2}}\,e^{-r^2/4Dt}$$

Total collision frequency per unit volume

In equation 27.6.18, z_A represents the collision frequency for one specific molecule in a gas sample. If we wish to calculate the total collision frequency per unit volume, the number density of the molecules, ρ, must be taken into account. The total collision frequency in a sample that contains only A molecules, Z_{AA}, is

$$Z_{AA} = \frac{1}{2}\rho z_A = \frac{1}{2}\sigma\langle v_r\rangle\rho^2 = \frac{\sigma\langle v\rangle\rho^2}{\sqrt{2}}$$

The factor of $\frac{1}{2}$ must be included to avoid double counting collisions between similar molecules. (This is identical reasoning to the fact that there is only one way to roll double 3 with two dice.)

If you have a gas sample that contains A molecules and B molecules, then

$$Z_{AB} = \sigma_{AB}\langle v_r\rangle\rho_A\rho_B \tag{27.6.4}$$

where

$$\sigma_{AB} = \pi\left(\frac{d_A + d_B}{2}\right)^2 \text{ and } \langle v_r\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

Example 27.6.1

Calculate the frequency of hydrogen-hydrogen collisions in a 1.00 cubic centimeter container at 1.00 bar and 298 K.

Solution

The collisional frquency requires knowledge of (1) the number denisty, the average speed (Equation 27.6.4).

The value of σ_{H_2} is 2.30 x 10^{-19} m^2.

The number density:

$$\rho = \left(\frac{N_A P_{H_2}}{RT}\right) = \left(\frac{(6.022x10^{23}mole^{-1})(1.00\text{ bar})}{(0.08314L\cdot bar\cdot mol^{-1}\cdot K^{-1})(298K)}\right) = 2.43\times10^{22}L^{-1} = 2.43\times10^{25}m^{-3}$$

The average speed:

$$\langle \mathrm{v}\rangle = \sqrt{\frac{8\mathrm{R\ T}}{\pi \mathrm{M}}} = \sqrt{\left(\frac{8(8.314J\cdot K^{-1})(298K)}{\pi(0.002016kg)}\right)} = 1770\frac{m}{s}$$

These are substituted into Equation 27.6.4 to get the collisional frequency

$$\begin{aligned} Z_{H_2,H_2} &= \frac{(2.30x10^{-19}m^2)(1770\frac{m}{s})(2.43x10^{25}m^{-3})^2}{\sqrt{2}} \\ &= 1.7x10^{35}s^{-1}m^{-3} \\ &= 1.7 \times 10^{29}s^{-1}cm^{-3} \end{aligned}$$

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27.7: Rates of Gas-Phase Chemical Reactions

Now that we have a description of how often gas molecules will collide with one another, we can make an initial attempt to describe how the collision of gas molecules can lead to reactions between the molecules. This topic will be covered in much more detail in Chapter 30.

Collision Frequency, Collision Energy, and Effective Collisions

In example 27.6.1, we calculated that the number of collision between H_2 molecules at one bar and 25°C is around $10^8 \ \frac{\text{moles}}{\text{dm}\cdot\text{s}}$. Consider the elementary reaction

$$\text{A} + \text{B} \longrightarrow \text{C}$$

If all of the collisions between A and B resulted in a reaction, then the rate of the reaction would be about $10^8 \ \frac{\text{moles}}{\text{dm}\cdot\text{s}}$. We know from experiment that most chemical reactions do not occur this quickly. It must be true, then, that not all collisions result in a reaction. It is intuitive that molecules traveling at faster speeds should be more likely to react because they have sufficient energy to overcome electronic repulsions, and to break existing bonds.

One way to approach this estimate is to use a modified version of the equation for the collision frequency with a wall. The reason for starting with this equation is that it is reasonable to assume that the faster a molecule is traveling, the more likely it is to hit the wall. If this is so, then the faster a molecule is traveling, the more likely it is to collide with other molecules so as to react.

Recall equation 26.4.1

$$z_w = \frac{1}{4}\frac{N}{V}\langle v \rangle$$

which can be rewritten for the molecular level by substituting ρ for $\frac{N}{V}$

$$z_w = \frac{1}{4}\rho\langle v \rangle$$

This equation was obtained by carrying out the integration

$$z_w = \frac{\rho}{4\pi}\int_0^\infty vF(v)dv \int_0^{\pi/2} \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi \tag{27.7.1}$$

which takes into account the fact that molecules will only hit the wall from one direction.

Recall from equation 27.3.1, the Maxwell-Boltzmann distribution of speeds

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

that $f(v)$ has a factor of v^2. Thus, equation 27.7.1 has a factor of v^3, meaning that the molecules colliding with the wall are traveling faster than the molecule in the bulk of the sample. The assumption is that the faster molecules are more likely to hit the wall in a given amount of time.

We must modify equation 27.7.1 to take into account the collision of molecules with each other, rather than with the wall. This is done by replacing the mass of a single molecule m with the reduced mass of the two colliding molecules μ. The resulting speed is the relative average speed v_r. The result of these assumptions is that the collision frequency of molecules A and B per unit volume in which the molecules collide with a relative speed between v_r and $v_r + dv_r$ is

$$dZ_{AB} = Av_r^3 e^{-\mu v_r^2/2k_B T} dv_r \tag{27.7.2}$$

where A is a proportionality constant.

If we require the integral of this equation over all relative speeds to be equal to Z_{AB}, then

$$Z_{AB} = \sigma_{AB}\rho_A\rho_B \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = A\int_0^\infty v_r^3 e^{-\mu v_r^2/2k_BT} dv_r$$

$$Z_{AB} = \sigma_{AB}\rho_A\rho_B \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = 2A\left(\frac{k_BT}{\mu}\right)^2$$

Rearranging to solve for A gives

$$A = \sigma_{AB}\rho_A\rho_B \left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} \tag{27.7.3}$$

Substituting equation 27.7.3 into equation 27.7.2 gives

$$dZ_{AB} = \sigma_{AB}\rho_A\rho_B \left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2/2k_BT} dv_r$$

With this equation, we can describe the collision frequency per unit volume between A molecules and B molecules with relative speeds in the range of v_r and $v_r + dv_r$. In this equation, the portion

$$\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2/2k_BT} dv_r$$

which is $v_r f(v_r) dv_r$, is the probability that the relative speed of the molecules will fall between v_r and $v_r + dv_r$.

Contributors and Attributions

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27.E: The Kinetic Theory of Gases (Exercises)

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28: CHEMICAL KINETICS I - RATE LAWS

28.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law
28.2: Rate Laws Must Be Determined Experimentally
28.3: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time
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28.7: Rate Constants Are Usually Strongly Temperature Dependent
28.8: Transition-State Theory Can Be Used to Estimate Reaction Rate Constants
28.E: Chemical Kinetics I - Rate Laws (Exercises)

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28.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

The Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction

$$aA + bB \rightarrow cC + dD$$

the reaction rate can be defined by any of the ratios

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{dt} = -\frac{1}{b}\frac{\Delta[B]}{dt} = +\frac{1}{c}\frac{\Delta[C]}{dt} = +\frac{1}{d}\frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[C]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Example 28.1.1:

Under a certain set of conditions, the rate of the reaction

$$\mathrm{N_2} + 3\,\mathrm{H_2} \rightarrow 2\,\mathrm{NH_3}$$

the reaction rate is $6.0 \times 10^{-4}\ M/s$. Calculate the time-rate of change for the concentrations of N_2, H_2, and NH_3.

Solution:

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

so

$$\frac{d[N_2]}{dt} = -6.0 \times 10^{-4}\,M/s$$
$$\frac{d[H_2]}{dt} = -2.0 \times 10^{-4}\,M/s$$
$$\frac{d[NH_3]}{dt} = 3.0 \times 10^{-4}\,M/s$$

Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

The Rate Law

As shown above, the rate of the reaction can be followed experimentally by measuring the rate of the loss of a reactant or the rate

of the production of a product. The rate of the reaction is often related to the concentration of some or all of the chemical species present at a given time. An equation called the *rate law* is used to show this relationship. The rate law **cannot** be predicted by looking at the balanced chemical reaction but must be determined by experiment. For example, the rate law for the reaction

$$\mathrm{Cl_2\,(g) + CO\,(g) \longrightarrow Cl_2CO\,(g)}$$

was experimentally determined to be

$$\mathrm{rate} = k[Cl_2]^{3/2}[CO]$$

In this equation, k is the rate constant, and $[\mathrm{Cl_2}]$ and $[\mathrm{CO}]$ are the molar concentrations of Cl_2 and of CO. Each exponent is called the *order* of the given species. Thus, the rate law is second order in Cl_2 and first order in CO. The sum of the individual reactant orders is called the **reaction order**. This reaction has a reaction order of two and a half.

In the next section, we will discuss methods to experimentally determine the rate law.

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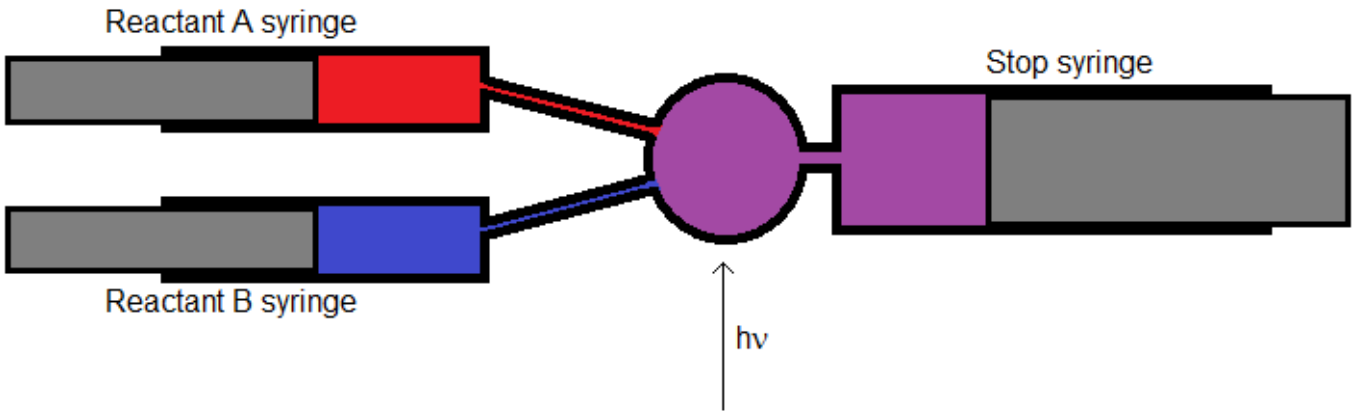
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28.2: Rate Laws Must Be Determined Experimentally

There are several methods that can be used to measure chemical reactions rates. A common method is to use spectrophotometry to monitor the concentration of a species that will absorb light. If it is possible, it is preferable to measure the appearance of a product rather than the disappearance of a reactant, due to the low background interference of the measurement. However, high-quality kinetic data can be obtained either way.

The Stopped-Flow Method

The **stopped-flow method** involves using flow control (which can be provided by syringes or other valves) to control the flow of reactants into a mixing chamber where the reaction takes place. The reaction mixture can then be probed spectrophotometrically. Stopped-flow methods are commonly used in physical chemistry laboratory courses (Progodich, 2014).



Some methods depend on measuring the initial rate of a reaction, which can be subject to a great deal of experimental uncertainty due to fluctuations in instrumentation or conditions. Other methods require a broad range of time and concentration data. These methods tend to produce more reliable results as they can make use of the broad range of data to smooth over random fluctuations that may affect measurements. Both approaches (initial rates and full concentration profile data methods) will be discussed below.

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28.3: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

A first order rate law would take the form

$$\frac{d[A]}{dt} = k[A]$$

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

$$\frac{d[A]}{[A]} = -k\,dt$$

This expression is also easily integrated as before

$$\int_{[A]=0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_o = kt$$

or

$$\ln[A] = \ln[A]_o - kt \tag{28.3.1}$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of ln[A] as a function of time should produce a linear plot, the slope of which is -k, and the intercept of which is $\ln[A]_0$.

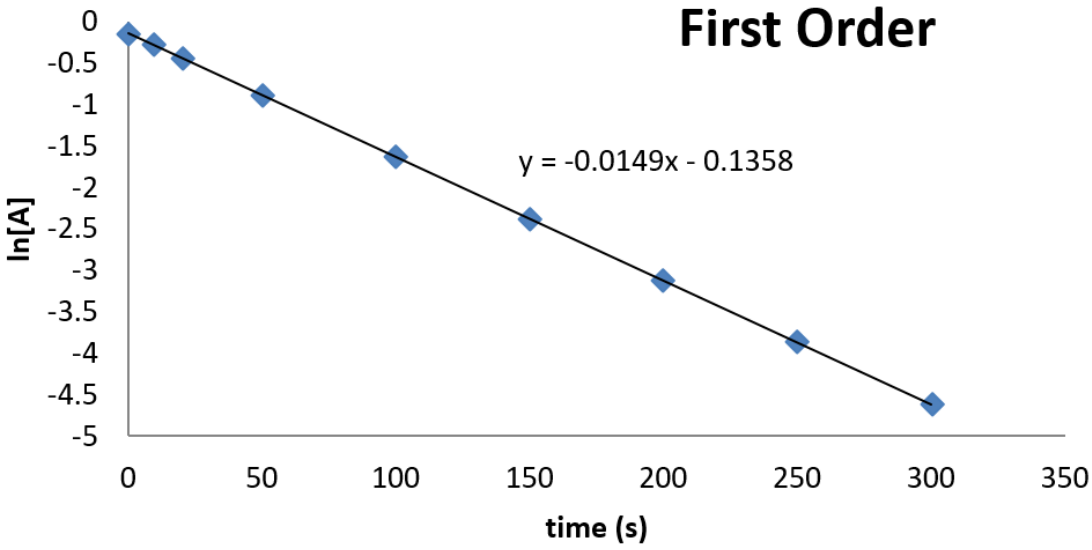
Example 28.3.1:

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

Time (s)	0	10	20	50	100	150	200	250	300
[A] (M)	0.873	0.752	0.648	0.414	0.196	0.093	0.044	0.021	0.010

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law (Equation 28.3.1) can be expressed in exponential form:

$$[A] = [A]_o e^{-kt}$$

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

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28.4: Different Rate Laws Predict Different Kinetics

Difference rate laws predict different kinetics

Zero-order Kinetics

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

$$-\frac{d[A]}{dt} = k$$

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A] = -k\,dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time t = 0, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_o}^{[A]} d[A] = -k\int_{t_o}^{t} dt$$

which yields

$$[A] - [A]_o = -kt$$

or

$$[A] = [A]_o - kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is –k, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0^{th} order kinetics. If they are not, other possibilities must be considered.

Second Order Kinetics

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2 \tag{28.4.1}$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2} = k\,dt$$

The integration then becomes

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} k\,dt \tag{28.4.2}$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result of integration Equation 28.4.2 is

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

or

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k, and the intercept of which is $1/[A]_0$.

Other 2nd order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type

$$A + B \rightarrow P$$

That has rate laws given by

$$-\frac{d[A]}{dt} = k[A][B]$$

and

$$-\frac{d[B]}{dt} = k[A][B]$$

the integration will depend on the decrease of [A] and [B] (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product [P].

$$[A] = [A]_o - [P] \tag{28.4.3}$$

and

$$[B] = [B]_o - [P] \tag{28.4.4}$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

$$\frac{d[P]}{dt} = k[A][B] \tag{28.4.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 28.4.3 and 28.4.4) into the rate law expression (Equation 28.4.5) yields

$$\frac{d[P]}{dt} = k([A]_o - [P])([B] = [B]_o - [P]) \tag{28.4.6}$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_o - [P])([B] = [B]_o - [P])} = k\,dt$$

Noting that at time $t = 0$, $[P] = 0$, the integrated form of the rate law can be generated by solving the integral

$$\int_{[A]_o}^{[A]} \frac{d[P]}{([A]_o - [P])([B]_o - [P])} = \int_{t=0}^{t} k\,dt$$

Consulting a table of integrals reveals that for $a \neq b$[1],

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a} \ln\left(\frac{b-x}{a-x}\right)$$

Applying the definite integral (as long as $[A]_0 \neq [B]_0$) results in

$$\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B]_0-[P]}{[A]_0-[P]}\right)\Bigg|_0^{[A]} = k\,t|_0^t$$

$$\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B]_0-[P]}{[A]_0-[P]}\right)-\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B]_0}{[A]_0}\right)=k\,t \tag{28.4.7}$$

Substituting Equations 28.4.3 and 28.4.4 into Equation 28.4.7 and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0-[A]_0}\ln\left(\frac{[B][A]_o}{[A][B]_o}\right)=kt$$

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is

$$m=([B]_0-[A]_0)k.$$

In the limit at $[A]_0=[B]_0$, then $[A]=[B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

$$\text{rate}=k[A]^2$$

and integrate direct like in Equation 28.4.1 and the integrated rate law is (as before)

$$\frac{1}{[A]}=\frac{1}{[A]_o}+kt$$

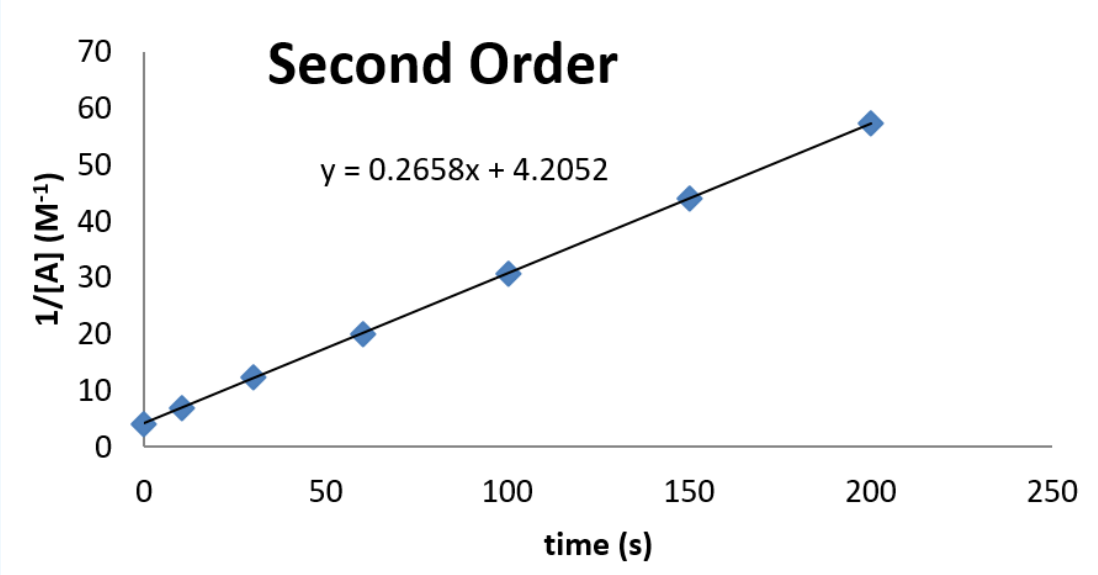
Example 28.4.2: Confirming Second Order Kinetics

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are second order, determine the value of the rate constant for the reaction.

time (s)	0	10	30	60	100	150	200
[A] (M)	0.238	0.161	0.098	0.062	0.041	0.029	0.023

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.2658 M^{-1} s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

---

[1] This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

Example 28.4.3

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:

$$2N_2O_5\,(soln) \rightarrow 4NO_2\,(soln) + O_2\,(g)$$

This reaction is carried out in a CCl_4 solution at 45°C. The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
0	0.0365	−3.310	27.4
600	0.0274	−3.597	36.5
1200	0.0206	−3.882	48.5
1800	0.0157	−4.154	63.7
2400	0.0117	−4.448	85.5
3000	0.00860	−4.756	116
3600	0.00640	−5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

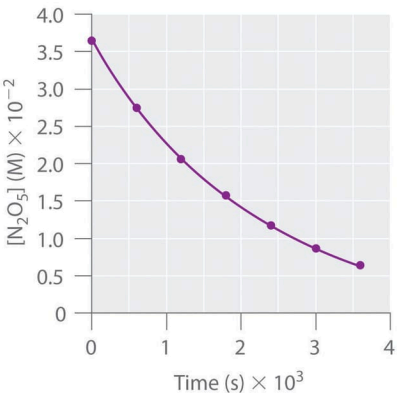
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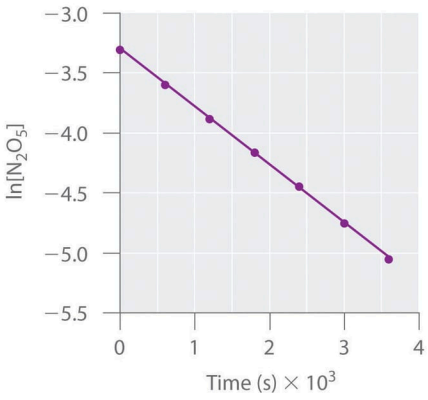
A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 13.4.2 to determine the reaction order.

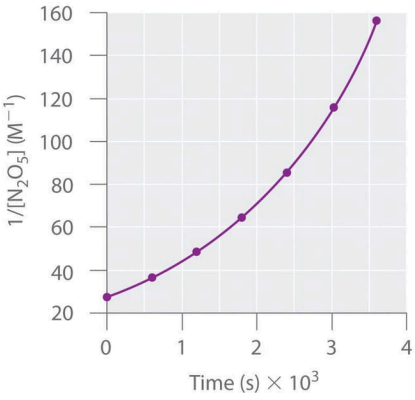
B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution:

A Here are plots of $[N_2O_5]$ versus *t*, $\ln[N_2O_5]$ versus *t*, and $1/[N_2O_5]$ versus *t*:







The plot of ln$[N_2O_5]$ versus *t* gives a straight line, whereas the plots of $[N_2O_5]$ versus *t* and 1/$[N_2O_5]$ versus *t* do not. This means that the decomposition of N_2O_5 is first order in $[N_2O_5]$.

B The rate law for the reaction is therefore

$$rate = k\,[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus *t* for a first-order reaction is *–k*. We can calculate the slope using any two points that lie on the line in the plot of ln$[N_2O_5]$ versus *t*. Using the points for *t* = 0 and 3000 s,

$$slope = \frac{ln\,[N_2O_5]_{3000} - ln\,[N_2O_5]_0}{3000\ s - 0\ s} = \frac{[-4.756] - [-3.310]}{3000\ s} = 4.820 \times 10^{-4}\ \ s^{-1}$$

Thus $k = 4.820 \times 10^{-4}$ s^{-1}.

Contributors

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28.5: Reactions can also be Reversible

Reversible and irreversible reactions are prevalent in nature and are responsible for reactions such as the breakdown of ammonia.

Introduction

It was believed that all chemical reactions were irreversible until 1803, when French chemist Claude Louis Berthollet introduced the concept of reversible reactions. Initially he observed that sodium carbonate and calcium chloride react to yield calcium carbonate and sodium chloride; however, after observing sodium carbonate formation around the edges of salt lakes, he realized that large amount of salts in the evaporating water reacted with calcium carbonate to form sodium carbonate, indicating that the reverse reaction was occurring.

Chemical reactions are represented by chemical equations. These equations typically have a unidirectional arrow ($\rightarrow$) to represent irreversible reactions. Other chemical equations may have a bidirectional harpoons ($\rightleftharpoons$) that represent reversible reactions (not to be confused with the double arrows $\leftrightarrow$ used to indicate resonance structures). To review the fundamentals of chemical reactions, click here: Chemical Reactions

Irreversible Reactions

A fundamental concept of chemistry is that chemical reactions occurred when reactants reacted with each other to form products. These unidirectional reactions are known as irreversible reactions, reactions in which the reactants convert to products and where the products *cannot* convert back to the reactants. These reactions are essentially like baking. The ingredients, acting as the reactants, are mixed and baked together to form a cake, which acts as the product. This cake cannot be converted back to the reactants (the eggs, flour, etc.), just as the products in an irreversible reaction cannot convert back into the reactants.

An example of an irreversible reaction is combustion. Combustion involves burning an organic compound—such as a hydrocarbon—and oxygen to produce carbon dioxide and water. Because water and carbon dioxide are stable, they do not react with each other to form the reactants. Combustion reactions take the following form:

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O \tag{28.5.1}$$

Reversible Reactions

In reversible reactions, the reactants and products are never fully consumed; they are each constantly reacting and being produced. A reversible reaction can take the following summarized form:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \tag{28.5.2}$$

This reversible reaction can be broken into two reactions.

Reaction 1:

$$A + B \xrightarrow{k_1} C + D \tag{28.5.3}$$

Reaction 2:

$$C + D \xrightarrow{k_{-1}} A + B \tag{28.5.4}$$

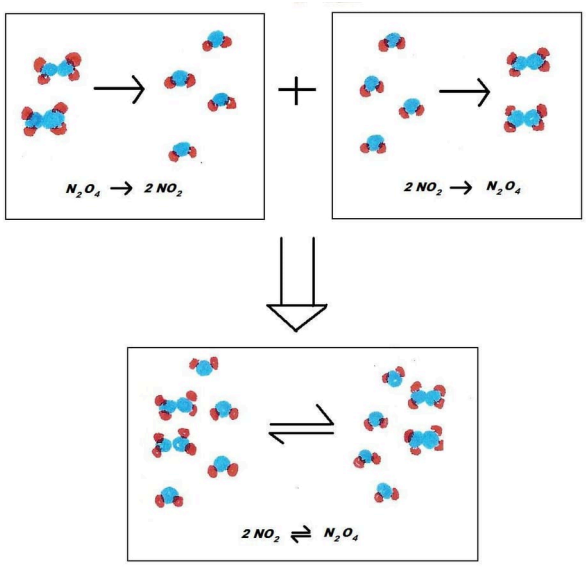
These two reactions are occurring ***simultaneously***, which means that the reactants are reacting to yield the products, as the products are reacting to produce the reactants. Collisions of the reacting molecules cause chemical reactions in a closed system. After products are formed, the bonds between these products are broken when the molecules collide with each other, producing sufficient energy needed to break the bonds of the product and reactant molecules.

Below is an example of the summarized form of a reversible reaction and a breakdown of the reversible reaction $N_2O_4 \leftrightarrow 2NO_2$

Reaction 1 and Reaction 2 happen at the same time because they are in a closed system.

Blue: Nitrogen Red: Oxygen

Reaction 1 Reaction 2



Imagine a ballroom. Let reactant A be 10 girls and reactant B be 10 boys. As each girl and boy goes to the dance floor, they pair up to become a product. Once five girls and five boys are on the dance floor, one of the five pairs breaks up and moves to the sidelines, becoming reactants again. As this pair leaves the dance floor, another boy and girl on the sidelines pair up to form a product once more. This process continues over and over again, representing a reversible reaction.

Unlike irreversible reactions, reversible reactions lead to equilibrium: in reversible reactions, the reaction proceeds in both directions whereas in irreversible reactions the reaction proceeds in only one direction. To learn more about this phenomenon, click here: Chemical Equilibrium

If the reactants are formed at the same rate as the products, a dynamic equilibrium exists. For example, if a water tank is being filled with water at the same rate as water is leaving the tank (through a hypothetical hole), the amount of water remaining in the tank remains consistent.

Connection to Biology

There are four binding sites on a hemoglobin protein. Hemoglobin molecules can either bind to carbon dioxide or oxygen. As blood travels through the alveoli of the lungs, hemoglobin molecules pick up oxygen-rich molecules and bind to the oxygen. As the hemoglobin travels through the rest of the body, it drops off oxygen at the capillaries for the organ system to use oxygen. After expelling the oxygen, it picks up carbon dioxide. Because this process is constantly carried out through the body, there are always hemoglobin molecules picking or expelling oxygen and other hemoglobin molecules that are picking up or expelling carbon dioxide. Therefore, the hemoglobin molecules, oxygen, and carbon dioxide are reactants while the hemoglobin molecules with oxygen or carbon dioxide bound to them are the products. In this closed system, some reactants convert into products as some products are changing into reactants, making it similar to a reversible reaction.

Contributors and Attributions

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28.6: The Rate Constants of a Reversible Reaction Can Be Determined Using Relaxation Techniques

The traditional experimental methods described above all assume the possibility of following the reaction after its components have combined into a homogeneous mixture of known concentrations. But what can be done if the time required to complete the mixing process is comparable to or greater than the time needed for the reaction to run to completion?

Flow methods

Flow instruments are a rapid mixing devices used to study the chemical kinetics of fast reactions in solution. There are different flavors that can be implement depending on the nature of the reaction as discussed below.

Continuous Flow Approach

For reactions that take place in milliseconds, the standard approach since the 1950s has been to employ a flow technique of some kind. An early example was used to study fast gas-phase reactions in which one of the reactants is a free radical such as OH that can be produced by an intense microwave discharge acting on a suitable source gas mixture. This gas, along with the other reactant being investigated, is made to flow through a narrow tube at a known velocity.

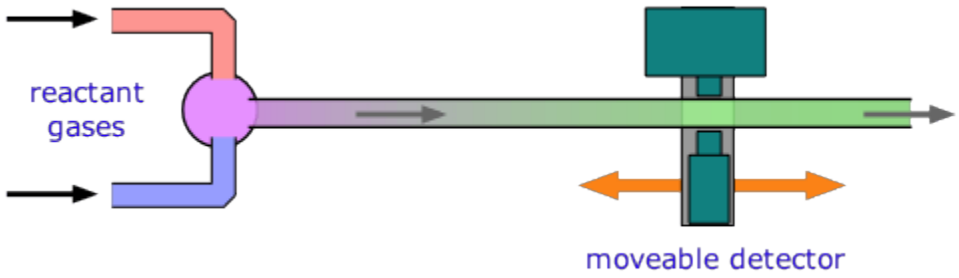


Figure 28.6.1: A continuous flow fast kinetic system.

If the distance between the point at which the reaction is initiated and the product detector is known, then the time interval can be found from the flow rate. By varying this distance, the time required to obtain the maximum yield can then be determined. Although this method is very simple in principle, it can be complicated in practice.

Stopped Flow Approach

Owing to the rather large volumes required, continuous flow method is more practical for the study of gas-phase reactions than for solutions, for which the stopped-flow method described below is generally preferred. These are by far the most common means of studying fast solution-phase reactions over time intervals of down to a fraction of a millisecond. The use of reasonably simple devices is now practical even in student laboratory experiments. These techniques make it possible to follow not only changes in the concentrations of reactants and products, but also the buildup and decay of reaction intermediates.

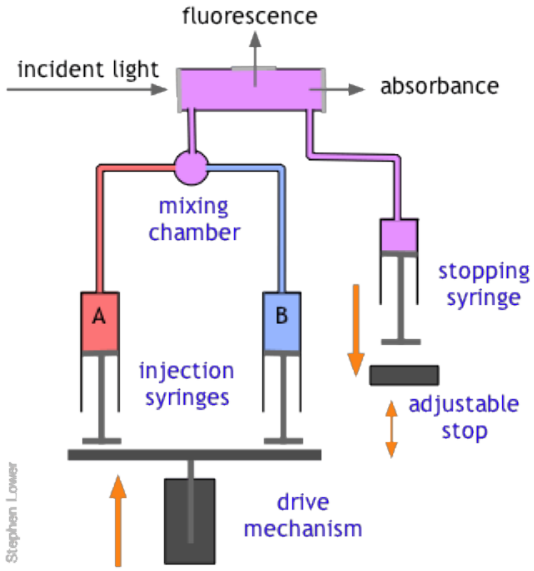


Figure 28.6.2: A stop flow fast kinetic system.

The basic stopped-flow apparatus consists of two or more coupled syringes that rapidly inject the reactants into a small mixing chamber and then through an observation cell that can be coupled to instruments that measure absorption, fluorescence, light scattering, or other optical or electrical properties of the solution. As the solution flows through the cell, it empties into a stopping syringe that, when filled, strikes a backstop that abruptly stops the flow. The volume that the stopping syringe can accept is adjusted so that the mixture in the cell has just become uniform and has reached a steady state; at this point, recording of the cell measurement begins and its change is followed.

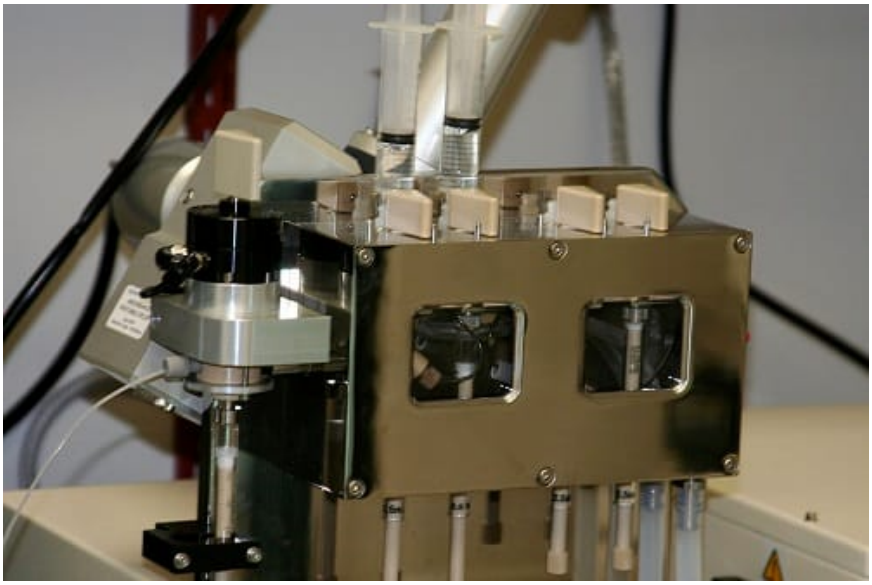


Figure 28.6.3: Stop-flow equipment at a biochemistry research laboratory for measuring rapid reactions and properties such as enzyme kinetics. from Wladimir Labeikovsky.

Quenched Flow Approach

In a quenched-flow instrument, the reaction is stopped after a certain amount of time has passed after mixing. The stopping of the reaction is called quenching and it can be achieved by various means, for example by mixing with another solution, which stops the reaction (chemical quenching), quickly lowering the temperature (freeze quenching) or even by exposing the sample to light of a certain wavelength (optical quenching).

Of course, there are many reactions that cannot be followed by changes in light absorption or other physical properties that are

conveniently monitored. In such cases, it is often practical to *quench* (stop) the reaction after a desired interval by adding an appropriate quenching agent. For example, an enzyme-catalyzed reaction can be stopped by adding an acid, base, or salt solution that denatures (destroys the activity of) the protein enzyme. Once the reaction has been stopped, the mixture is withdrawn and analyzed in an appropriate manner.

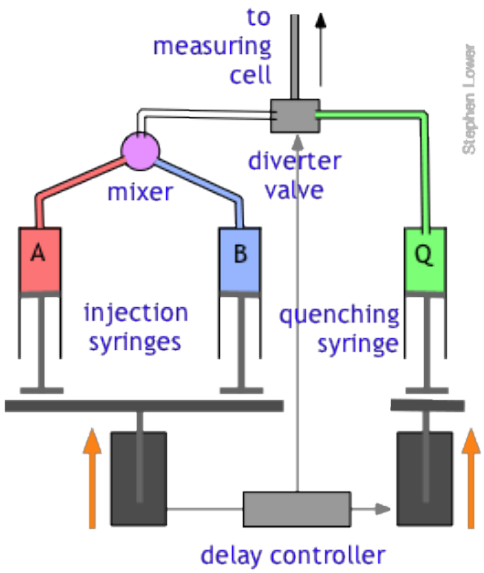


Figure 28.6.4: A quench flow fast kinetic system.

The quenched-flow technique works something like the stopped-flow method described above, with a slightly altered plumbing arrangement. The reactants A and B are mixed and fed directly through the diverter valve to the measuring cell, which is not shown in this diagram. After a set interval that can vary from a few milliseconds to 200 sec or more, the controller activates the quenching syringe and diverter valve, flooding the cell with the quenching solution.

Relaxation Methods

To investigate reactions that are complete in less than a millisecond, one can start with a pre-mixed sample in which one of active reactants is generated *in situ*. Alternatively, a rapid change in pressure or temperature can alter the composition of a reaction that has already achieved equilibrium.

Flash Photolysis

Many reactions are known which do not take place without light of wavelength sufficiently short to supply the activation energy needed to break a bond, often leading to the creation of a highly reactive radical. A good example is the combination of gaseous Cl_2 with H_2, which proceeds explosively when the system is illuminated with visible light. In *flash photolysis*, a short pulse of light is used to initiate a reaction whose progress can be observed by optical or other means.

Photolysis refers to the use of light to decompose a molecule into simpler units, often ions or free radicals. In contrast to *thermolysis* (decomposition induced by high temperature), photolysis is able to inject energy into a molecule almost instantaneously and can be much "cleaner," meaning that there are fewer side reactions that often lead to complex mixtures of products. Photolysis can also be highly *specific*; the wavelength of the light that triggers the reaction can often be adjusted to

activate one particular kind of molecule without affecting others that might be present.

Norrish and Porter

All this had been known for a very long time, but until the mid-1940's there was no practical way of studying the kinetics of the reactions involving the highly reactive species produced by photolysis. In 1945, Ronald Norrish of Cambridge University and his graduate student George Porter conceived the idea of using a short-duration flash lamp to generate gas-phase CH_2 radicals, and then following the progress of the reaction of these radicals with other species by means of absorption spectroscopy.

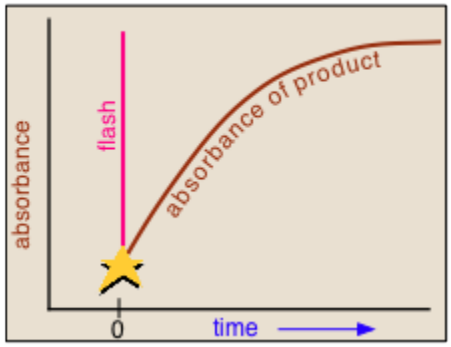


Figure 28.6.5: Basic principle of a flash-photolysis relaxation experiment where an excitation pulse purturbed a system at equilibrium and the subsequent dynamics are resolved in time.

In a flash photolysis experiment, recording of the absorbance of the sample cell contents is timed to follow the flash by an interval that can be varied in order to capture the effects produced by the product or intermediate as it is formed or decays. Norrish and Porter shared the 1967 Nobel Prize in Chemistry for this work.

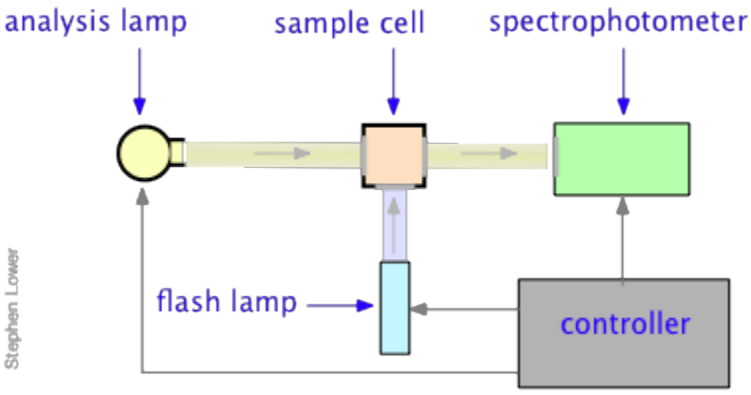


Figure 28.6.6: A flash-photolysis relaxation experiment

Many reactions, especially those that take place in solution, occur too rapidly to follow by flow techniques, and can therefore only be observed when they are already at equilibrium. The classical examples of such reactions are two of the fastest ones ever observed, the dissociation of water

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{28.6.1}$$

and the formation of the triiodide ion in aqueous solution

$$I^- + I_2 \rightarrow I_3^- \tag{28.6.2}$$

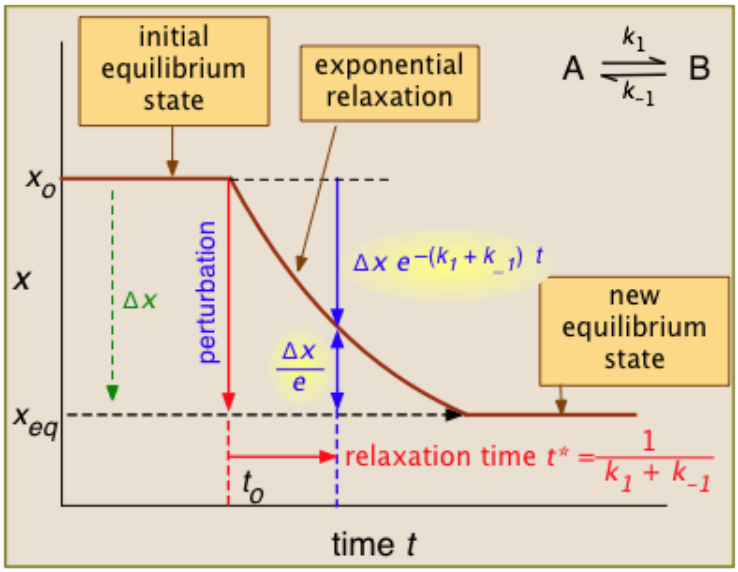
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

Temperature Jumps

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured. For example, if the reaction

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{28.6.3}$$

is endothermic, then according to the Le Chatelier principle, subjecting the system to a rapid jump in temperature will shift the equilibrium state to one in which the product B has a higher concentration. The composition of the system will than begin to shift toward the new equilibrium composition at a rate determined by the kinetics of the process.



For the general case illustrated here, the quantity "*x*" being plotted is a measurable quantity such as light absorption or electrical conductivity that varies linearly with the composition of the system. **In a first-order process**, *x* will vary with time according to

$$x_t = x_o e^{-kt} \tag{28.6.4}$$

After the abrupt perturbation at time t_o, the relaxation time t^* is defined as the half-time for the return to equilibrium — that is, as the time required for x_o to decrease by \(Δx/e = Δx/2.718\). The derivation of t^* and the relations highlighted in yellow can be found in most standard kinetics textbooks. Temperature jumps are likely most commonly used.

The rate law for the reversible reaction in Equation 28.6.3 can be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\,[\mathrm{A}] - k_{-1}\,[\mathrm{B}] \tag{28.6.5}$$

Consider a system comprising A and B that is allowed to achieve equilibrium concentrations at a temperature, T_1. After equilibrium is achieved, the temperature of the system is instantaneously lowered to T_2 and the system is allowed to achieve new equilibrium concentrations of A and B, $[\mathrm{A}]_{\mathrm{eq},2}$ and $[\mathrm{B}]_{\mathrm{eq},2}$. During the transition time from the first equilibrium state to the second equilibrium state, we can write the instantaneous concentration of A as

$$[\mathrm{A}] = [\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}] \tag{28.6.6}$$

The rate of change of species B can then be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\left([\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}]\right) - k_{-1}\,[\mathrm{B}] = k_1\,[\mathrm{B}]_{\mathrm{eq},1} - (k_1 + k_{-1})\,[\mathrm{B}] \tag{28.6.7}$$

At equilibrium, $d\left[\mathrm{B}\right]/dt = 0$ and $\left[\mathrm{B}\right] = \left[\mathrm{B}\right]_{\mathrm{eq},2}$, allowing us to write

$$k_1 \left[\mathrm{B}\right]_{\mathrm{eq},1} = \left(k_1 + k_{-1}\right) \left[\mathrm{B}\right]_{\mathrm{eq},2} \tag{28.6.8}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathrm{B}}{\left(\left[\mathrm{B}\right]_{\mathrm{eq},2} - \left[\mathrm{B}\right]\right)} = \left(k_1 + k_{-1}\right) dt \tag{28.6.9}$$

Integrating yields

$$-\ln\left(\left[\mathrm{B}\right] - \left[\mathrm{B}\right]_{\mathrm{eq},2}\right) = -\left(k_1 + k_{-1}\right) t + C \tag{28.6.10}$$

We can rearrange the above equation in terms of B

$$\left[\mathrm{B}\right] = Ce^{-(k_1+k_{-1})t} + \left[\mathrm{B}\right]_{\mathrm{eq},2} \tag{28.6.11}$$

At $t = 0$, $\left[\mathrm{B}\right] = \left[\mathrm{B}\right]_{\mathrm{eq},1}$, so $C = \left[\mathrm{B}\right]_{\mathrm{eq},1} - \left[\mathrm{B}\right]_{\mathrm{eq},2}$. Plugging the the value of C, we arrive at

$$\left[\mathrm{B}\right] - \left[\mathrm{B}\right]_{\mathrm{eq},2} = \left(\left[\mathrm{B}\right]_{\mathrm{eq},1} - \left[\mathrm{B}\right]_{\mathrm{eq},2}\right) e^{-(k_1+k_{-1})t} \tag{28.6.12}$$

which can also be expressed as

$$\Delta\left[\mathrm{B}\right] = \Delta\left[\mathrm{B}\right]_0 e^{-(k_1+k_{-1})t} = \Delta\left[\mathrm{B}\right]_0 e^{-t/\tau} \tag{28.6.13}$$

where $\Delta\left[\mathrm{B}\right]$ is the difference in the concentration of B from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln\left(\Delta\left[\mathrm{B}\right]/\Delta\left[\mathrm{B}\right]_0\right)$ versus t will be linear with a slope of $-\left(k_1 + k_{-1}\right)$, where k_1 and k_{-1} are the rate constants at temperature, T_2.

Contributors and Attributions

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28.7: Rate Constants Are Usually Strongly Temperature Dependent

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28.8: Transition-State Theory Can Be Used to Estimate Reaction Rate Constants

Transition State Theory

In Figure 28.8.1 , the point at which we evaluate or measure E_a serves as a dividing line (also called a *dividing surface*) between reactants and products. At this point, we do not have $\mathrm{A}+\mathrm{B}$, and we do not have C. Rather, what we have is an activated complex of some kind called a *transition state* between reactants and products. The value of the reaction coordinate at the transition state is denoted $q^{\ddagger}$. Recall our notation x for the complete set of coordinates and momenta of all of the atoms in the system. Generally, the reaction coordinate q is a function $q(\mathrm{x})$ of all of the coordinates and momenta, although typically, $q(\mathrm{x})$ is a function of a subset of the coordinates and, possibly, the momenta.

As an example, let us consider two atoms A and B undergoing a collision. An appropriate reaction coordinate could simply be the distance r between A and B. This distance is a function of the positions $\mathbf{r}_{\mathrm{A}}$ and $\mathbf{r}_{\mathrm{B}}$ of the two atoms, in that

$$q=r=\left|\mathbf{r}_{\mathrm{A}}-\mathbf{r}_{\mathrm{B}}\right| \tag{28.8.1}$$

When A and B are molecules, such as proteins, $q(\mathrm{x})$ is a much more complicated function of x.

Now, recall that the mechanical energy $\mathcal{E}(\mathrm{x})$ is given by

$$\mathcal{E}(\mathrm{x})=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_1}+U\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right) \tag{28.8.2}$$

and is a sum of kinetic and potential energies. Transition state theory assumes the following:

1. The system is classical, and the time dependence of the coordinates and momenta is determined by Newton's laws of motion
$$m_i\ddot{\mathbf{r}}_i=\mathbf{F}_i \tag{28.8.3}$$
2. We start a trajectory obeying this equation of motion with an initial condition x that makes $q(\mathrm{x})=q^{\ddagger}$ and such that $\dot{q}(\mathrm{x})>0$ so that the reaction coordinate proceeds initial to the right, i.e., toward products.
3. We follow the motion x_t of the coordinates and momenta in time starting from this initial condition x, which gives us a unique function $\mathrm{x}_t(\mathrm{x})$.
4. If $q\left(\mathrm{x}_t(\mathrm{x})\right)>q^{\ddagger}$ at time t, then the trajectory is designated as "reactive" and contributes to the reaction rate.

Define a function $\theta(y)$, which is 1 if $y\geq 0$ and 0 if $y<0$. The function $\theta(y)$ is known as a *step function*.

We now define a *flux* of reactive trajectories $k(t)$ using statistical mechanics

$$k(t)=\frac{1}{hQ_r}\int_{q(\mathrm{x})=q^{\ddagger}}d\mathrm{x}\,e^{-\beta\mathcal{E}(\mathrm{x})}\left|\dot{q}(\mathrm{x})\right|\theta\left(q\left(\mathrm{x}_t(\mathrm{x})\right)-q^{\ddagger}\right) \tag{28.8.4}$$

where h is Planck's constant. Here Q_r is the partition function of the reactants

$$Q_r=\int d\mathrm{x}\,e^{-\beta\mathcal{E}(\mathrm{x})}\theta\left(q^{\ddagger}-q(\mathrm{x})\right) \tag{28.8.5}$$

The meaning of Equation 28.8.4 is an ensemble average over a canonical ensemble of the product $\left|\dot{q}(\mathrm{x})\right|$ and $\theta\left(q\left(\mathrm{x}_t(\mathrm{x})\right)-q^{\ddagger}\right)$. The first factor in this product $\left|\dot{q}(\mathrm{x})\right|$ forces the initial velocity of the reaction coordinate to be positive, i.e., toward products, and the step function $\theta\left(q\left(\mathrm{x}_t(\mathrm{x})\right)-q^{\ddagger}\right)$ requires that the trajectory of $q\left(\mathrm{x}_t(\mathrm{x})\right)$ be reactive, otherwise, the step function will give no contribution to the flux. The function $k(t)$ in Equation 28.8.4 is known as the *reactive flux*. In the definition of Q_r the step function $\theta\left(q^{\ddagger}-q(\mathrm{x})\right)$ measures the total number of microscopic states on the reactive side of the energy profile.

A plot of some examples of reactive flux functions $k(t)$ is shown in Figure 28.8.2 . These functions are discussed in greater detail in *J. Chem. Phys.* **95**, 5809 (1991). These examples all show that $k(t)$ decays at first but then finally reaches a plateau value. This

plateau value is taken to be the true rate of the reaction under the assumption that eventually, all trajectories that will become reactive will have done so after a sufficiently long time. Thus,

$$k = \lim_{t\to\infty} k\left(t\right) \tag{28.8.6}$$

gives the true rate constant. On the other hand, a common approximation is to take the value $k\left(0\right)$ as an estimate of the rate constant, and this is known as the transition *state theory approximation* to k, i.e.,

$$k^{(\mathrm{TST})} = k\left(0\right) \tag{28.8.7}$$

$$= \frac{1}{Q_r}\int_{q(\mathrm{x})=q^{\ddagger}} d\mathrm{x}\, e^{-\beta\mathcal{E}(\mathrm{x})}\left|\dot{q}\left(\mathrm{x}\right)\right|\theta\left(q\left(\mathrm{x}\right)-q^{\ddagger}\right) \tag{28.8.8}$$

However, note that since we require $\dot{q}\left(\mathrm{x}\right)$ to initially be toward products, then by definition, at $t=0$, $q\left(\mathrm{x}\right)\geq q^{\ddagger}$, and the step function in the above expression is redundant. In addition, if $\dot{q}\left(\mathrm{x}\right)$ only depends on momenta (or velocities) and not actually on coordinates, which will be true if $q\left(\mathrm{x}\right)$ is not curvilinear (and is true for some curvilinear coordinates $q\left(\mathrm{x}\right)$), and if $q\left(\mathrm{x}\right)$ only depends on coordinates, then Equation ??? reduces to

$$k^{(\mathrm{TST})} = \frac{1}{hQ_r}\int d\mathrm{x}_{\mathbf{p}} e^{-\beta\sum_{i=1}^{N}\mathbf{p}_i^2/2m_i}\left|\dot{q}\left(\mathbf{p}_1,\ldots,\mathbf{p}_N\right)\right|\int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^{\ddagger}} d\mathrm{x}_{\mathbf{r}} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{28.8.9}$$

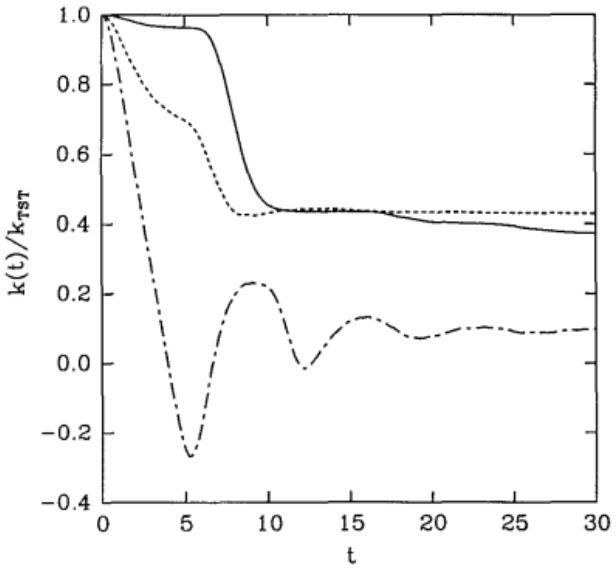


Figure 28.8.2 : Examples of the reactive flux $k\left(t\right)$.

The integral

$$Z^{\ddagger} = \int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^{\ddagger}} d\mathrm{x}_{\mathbf{r}} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

counts the number of microscopic states consistent with the condition $q\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right)=q^{\ddagger}$ and is, therefore, a kind of partition function, and is denoted $Q^{\ddagger}$. On the other hand, because it is a partition function, we can derive a free energy $\Delta F^{\ddagger}$ from it

$$F^{\ddagger} \propto -k_B T\ln Z^{\ddagger} \tag{28.8.10}$$

Similarly, if we divide Q_r into its ideal-gas and configurational contributions

$$Q_r = Q_r^{(\mathrm{ideal})} Z_r \tag{28.8.11}$$

then we can take

$$Z_r = e^{-\beta F_r} \tag{28.8.12}$$

where F_r is the free energy of the reactants. Finally, setting $\dot{q}=p/\mu$, where μ is the associated mass, and p is the corresponding

momentum of the reaction coordinate, then, canceling most of the momentum integrals between the numerator and $Q_r^{(\text{ideal})}$, the momentum integral we need is

$$\int_0^\infty e^{-\beta p^2/2\mu} \frac{p}{\mu} = k_B T \tag{28.8.13}$$

which gives the final expression for the transition state theory rate constant

$$k^{(\text{TST})} = \frac{k_B T}{h} e^{-\beta(F^\ddagger - F_r)} = \frac{k_B T}{h} e^{-\beta \Delta F^\ddagger} \tag{28.8.14}$$

Figure 28.8.2 actually shows $k(t)/k^{(\text{TST})}$, which must start at 1. As the figure shows, in addition, for $t > 0$, $k(t) < k^{(\text{TST})}$. Hence, $k^{(\text{TST})}$ is always an upper bound to the true rate constant. Transition state theory assumes that any trajectory that initially moves toward products will be a reactive trajectory. For this reason, it overestimates the reaction rate. In reality, trajectories can cross the dividing surface several or many times before eventually proceeding either toward products *or* back toward reactants.

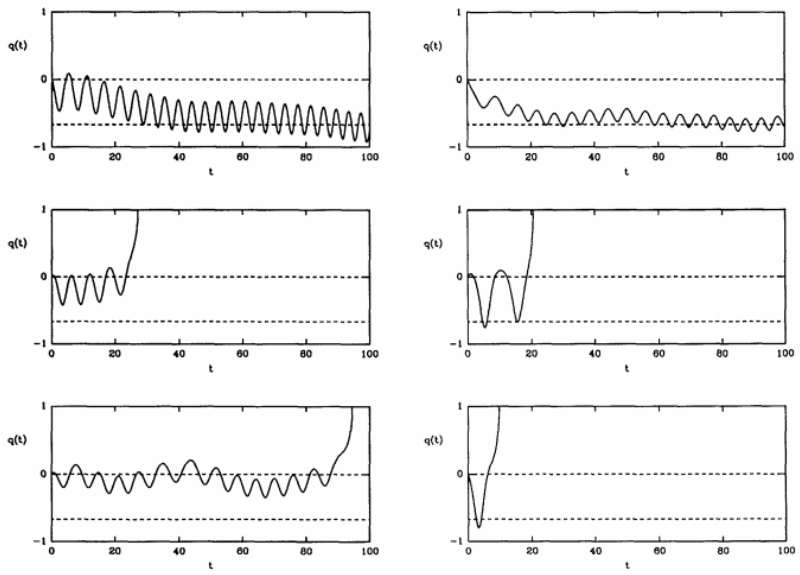


Figure 28.8.3 : Examples of the trajectories in a typical system, some of which are reactive but some of which return to reactants.

Figure 28.8.3 shows that one can obtain trajectories of both types. Here, the dividing surface lies at $q = 0$. Left, toward $q = -1$ is the reactant side, and right, toward $q = 1$ is the product side. Because some trajectories return to reactants and never become products, the true rate is always less than $k^{(\text{TST})}$, and we can write

$$k = \kappa k^{(\text{TST})} \tag{28.8.15}$$

where the factor $\kappa < 1$ is known as the *transmission factor*. This factor accounts for multiple recrossings of the dividing surface and the fact that some trajectories do not become reactive ones.

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28.E: Chemical Kinetics I - Rate Laws (Exercises)

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29: CHEMICAL KINETICS II- REACTION MECHANISMS

29.1: A Mechanism is a Sequence of Elementary Reactions
29.2: The Principle of Detailed Balance
29.3: Multiple Mechanisms are often Indistinguishable
29.4: The Steady-State Approximation
29.5: Rate Laws Do Not Imply Unique Mechanism
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29.8: A Catalyst Affects the Mechanism and Activation Energy
29.9: The Michaelis-Menten Mechanism for Enzyme Catalysis
29.E: Chemical Kinetics II- Reaction Mechanisms (Exercises)

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29.1: A Mechanism is a Sequence of Elementary Reactions

The mechanism of a reaction is a series of steps leading from the starting materials to the products. After each step, an intermediate is formed. The intermediate is short-lived, because it quickly undergoes another step to form the next intermediate. These simple steps are called elementary reactions. Because an overall reaction is composed of a series of elementary reaction, the overall rate of the reaction is somehow dependent on the rates of those smaller reactions. But how are the two related? Let's look at two cases. We'll keep it simple and both cases will be two-step reactions.

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29.2: The Principle of Detailed Balance

The principle of **detailed balance** is formulated for kinetic systems which are decomposed into elementary processes (collisions, or steps, or elementary reactions): *At equilibrium, each elementary process should be equilibrated by its reverse process*. Lewis put forward this general principle in 1925:

> *Corresponding to every individual process there is a reverse process, and in a state of equilibrium the average rate of every process is equal to the average rate of its reverse process.*[1]

According to Ter Haar, [2] the essence of the detailed balance is:

> *...at equilibrium the number of processes destroying situation A and creating situation B will be equal to the number of processes producing A and destroying B*

The principle of detailed balance was explicitly introduced for collisions by Ludwig Boltzmann. In 1872, he proved his H-theorem using this principle. The arguments in favor of this property are founded upon microscopic reversibility. In 1901, R. Wegscheider introduced the principle of detailed balance for chemical kinetics. In particular, he demonstrated that the irreversible cycles

$$A \to B \to C ... Y \to Z \tag{29.2.1}$$

are impossible and found explicitly the relations between kinetic constants that follow from the principle of detailed balance. This system is more accurately described thusly:

$$A \rightleftharpoons B \rightleftharpoons C ... Y \rightleftharpoons Z \tag{29.2.2}$$

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29.3: Multiple Mechanisms are often Indistinguishable

The great value of chemical kinetics is that it can give us insights into the actual reaction pathways (mechanisms) that reactants take to form the products of reactions. Analyzing a reaction mechanism to determine the type of rate law that is consistent (or not consistent) with the specific mechanism can give us significant insight. For example, the reaction

$$A + B \rightarrow C$$

might be proposed to follow one of two mechanistic pathways:

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{step 1}}$$

$$\underbrace{A_2 + B \xrightarrow{k_2} C}_{\text{step 2}}$$

or

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{step 1}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{step 2}}$$

The first rate law will predict that the reaction should be second order in A, whereas the second mechanism predicts that it should be first order in A (in the limit that the steady state approximation, discussed in the following sections, can be applied to A_2 and A^*). Based on the observed rate law being first or second order in A, one can rule out one of the rate laws. Unfortunately, this kind of analysis cannot confirm a specific mechanism. Other evidence is needed to draw such conclusions, such as the spectroscopic observation of a particular reaction intermediate that can only be formed by a specific mechanism.

In order analyze mechanisms and predict rate laws, we need to build a toolbox of methods and techniques that are useful in certain limits. The next few sections will discuss this kind of analysis, specifically focusing on

- the **Rate Determining Step** approximation,
- the **Steady State** approximation, and
- the **Equilibrium** approximation.

Each type of approximation is important in certain limits, and they are oftentimes used in conjunction with one another to predict the final forms of rate laws.

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29.4: The Steady-State Approximation

One of the most commonly used and most attractive approximations is the **steady state approximation**. This approximation can be applied to the rate of change of concentration of a highly reactive (short lived) intermediate that holds a constant value over a long period of time. The advantage here is that for such an intermediate (I),

$$\frac{d[I]}{dt} = 0$$

So long as one can write an expression for the rate of change of the concentration of the intermediate I, the steady state approximation allows one to solve for its constant concentration. For example, if the reaction

$$A + B \rightarrow C \tag{29.4.1}$$

is proposed to follow the mechanism

$$A + A \xrightarrow{k_1} A_2 \tag{29.4.2}$$

$$A_2 + B \xrightarrow{k_2} C + A \tag{29.4.3}$$

The time-rate of change of the concentration of the intermediate A_2 can be written as

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B]$$

In the limit that the steady state approximation can be applied to A_2

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B] \approx 0$$

or

$$[A_2] \approx \frac{k_1[A]^2}{k_2[B]}$$

So if the rate of the overall reaction is expressed as the rate of formation of the product C,

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

the above expression for $[A_2]$ can be substituted

$$\frac{d[C]}{dt} = k_2\left(\frac{k_1[A]^2}{k_2[B]}\right)[B]$$

of

$$\frac{d[C]}{dt} = k_1[A]^2$$

and the reaction is predicted to be second order in $[A]$.

Alternatively, if the mechanism for Equation 29.4.1 is proposed to be

$$A \xrightarrow{k_1} A^* \tag{29.4.4}$$

$$A^* + B \xrightarrow{k_2} C \tag{29.4.5}$$

then the rate of change of the concentration of A^* is

$$\frac{[A^*]}{dt} = k_1[A] - k_2[A^*][B]$$

And if the steady state approximation holds, then

$$[A^*] \approx \frac{k_1[A]}{k_2[B]}$$

So the rate of production of C is

$$\frac{d[C]}{dt} = k_2[A^*][B] \tag{29.4.6}$$

$$= \cancel{k_2}\left(\frac{k_1[A]}{\cancel{k_2}\,\cancel{[B]}}\right)\cancel{[B]} \tag{29.4.7}$$

or

$$\frac{d[C]}{dt} = k_1[A]$$

and the rate law is predicted to be first order in A. In this manner, the plausibility of either of the two reaction mechanisms is easily deduced by comparing the predicted rate law to that which is observed. If the prediction cannot be reconciled with observation, then the scientific method eliminates that mechanism from consideration.

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29.5: Rate Laws Do Not Imply Unique Mechanism

Because a proposed mechanism can only be valid if it is consistent with the rate law found experimentally, the rate law plays a central role in the investigation of chemical reaction mechanisms. The discussion above introduces the problems and methods associated with collecting rate data and with finding an empirical rate law that fits experimental concentration-*versus*-time data. We turn now to finding the rate laws that are consistent with a particular proposed mechanism. For simplicity, we consider reactions in closed constant-volume systems.

In principle, numerical integration can be used to predict the concentration at any time of each of the species in any proposed reaction mechanism. This prediction can be compared to experimental observations to see whether they are consistent with the proposed mechanism. To do the numerical integration, it is necessary to know the initial concentrations of all of the chemical species and to know, or assume, values of all of the rate constants. The initial concentrations are known from the procedure used to initiate the reaction. However, the rate constants must be determined by some iterative procedure in which initial estimates of the rate constants are used to predict concentration-*versus*-time data that can be compared to the experimental results to produce refined estimates.

In practice, we tailor our choice of reaction conditions so that we can use various approximations to test whether a proposed mechanism can explain the data. We now consider the most generally useful of these approximations.

In this discussion, we assume that the overall reaction goes to completion; that is, at equilibrium the concentration of the reactant whose concentration is limiting has become essentially zero. If the overall reaction involves more than one elementary step, then an intermediate compound is involved. A valid mechanism must include this intermediate, and more than one differential equation may be needed to characterize the time rate of change of all of the species involved in the reaction. We focus on conditions and approximations under which the rate of appearance of the final products in a multi-step reaction mechanism can be described by a single differential equation, the rate law.

We examine the application of these approximations to a particular reaction mechanism. When we understand the application of these approximations to this mechanism, the ways in which they can be used in other situations are clear.

Consider the following sequence of elementary steps

$$\mathrm{A} + \mathrm{B} \underset{\mathrm{k_2}}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{C} \xrightarrow{\mathrm{k_3}} \mathrm{D}$$

whose kinetics are described by the following simultaneous differential equations:

$$\begin{aligned} \frac{d[A]}{dt} = \frac{d[B]}{dt} &= -k_1[A][B] + k_2\,[C] \\ \frac{d\,[C]}{dt} &= k_1[A][B] - k_2\,[C] - k_3\,[C] \\ \frac{d\,[D]}{dt} &= k_3\,[C] \end{aligned}$$

The general analytical solution for this system of coupled differential equations can be obtained, but it is rather complex, because $[C]$ increases early in the reaction, passes through a maximum, and then decreases at long times. In principle, experimental data could be fit to these equations. The numerical approach requires that we select values for k_1, k_2, k_3, $[A]_0$, $[B]_0$, $[C]_0$, and $[D]_0$, and then numerically integrate to get $[A]$, $[B]$, $[C]$, and $[D]$ as functions of time. In principle, we could refine our estimates of k_1, k_2, and k_3 by comparing the calculated values of one or more concentrations to the experimental ones. In practice, the approximate treatments we consider next are more expedient.

When we begin a kinetic study, we normally have a working hypothesis about the reaction mechanism, and we design our experiments to simplify the differential equations that apply to it. For the present example, we will assume that we always arrange the experiment so that $[C]_0 = 0$ and $[D]_0 = 0$. In consequence, at all times:

$$[A]_0 = [A] + [C] + [D]\,.$$

Also, we restrict our considerations to experiments in which $[B]_0 \gg [A]_0$. This exemplifies the use of **flooding**. The practical effect

is that the concentration of B remains effectively constant at its initial value throughout the entire reaction, which simplifies the differential equations significantly. In the present instance, setting $[B]_0 \gg [A]_0$ means that the rate-law term $k_1[A][B]$ can be replaced, to a good approximation, by $k_{obs}[A]$, where $k_{obs} = k_1[B]_0$.

Once we have decided upon the reaction conditions we are going to use, whether the resulting concentration-*versus*-time data can be described by a single differential equation depends on the relative magnitudes of the rate constants in the several steps of the overall reaction. Particular combinations of relationships that lead to simplifications are often referred to by particular names; we talk about a combination that has a ***rate-determining step***, or one that involves a ***prior equilibrium***, or one in which a ***steady-state approximation*** is applicable. To see what we mean by these terms, let us consider some particular relationships that can exist among the rate constants in the mechanism above.

Case I

Suppose that $k_1[A][B] \gg k_2[C]$ and $k_3 \gg k_2$. We often describe this situation by saying, rather imprecisely, that the reaction to convert C to D is very fast and that the reaction to convert C back to A and B is very slow—compared to the reaction that forms C from A and B. When C is produced in these circumstances, it is converted to D so rapidly that we never observe a significant concentration of C in the reaction mixture. The formation of a molecule of C is tantamount to the formation of a molecule of D , and the reaction produces D at essentially the same rate that it consumes A or B. We say that the first step, $A + B \rightarrow C$, is the rate-determining step in the reaction. We have

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} \approx \frac{d[D]}{dt}$$

The assumption that $k_1[A][B] \gg k_2[C]$ means that we can neglect the smaller term in the equation for $d[A]/dt$, giving the approximation

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[D]}{dt} = -k_1[A][B]$$

Letting $[D] = x$ and recognizing that our assumptions make $[C] \approx 0$, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Choosing $[B]_0 \gg [A]_0$ means that $k_1[B] \approx k_1[B]_0 = k_{I,obs}$. The rate equation becomes first-order:

$$\frac{dx}{dt} = k_{I,obs}\,(\,[A]_0 - x)$$

Since $k_{I,obs}$ is not strictly constant, it is a pseudo-first-order rate constant. The disappearance of A is said to follow a pseudo-first-order rate equation.

The concept of a rate-determining step step is an **approximation**. In general, the consequence we have in mind when we invoke this approximation is that no intermediate species can accumulate to a significant concentration if it is produced by the rate-determining step or by a step that occurs after the rate-determining step. We do not intend to exclude the accumulation of a species that is at equilibrium with another product. Thus, in the mechanism

$$\mathrm{A} \xrightarrow{\mathrm{k}} \mathrm{B} \rightleftharpoons \mathrm{C}$$

we suppose that the conversion of A to B is rate-determining and that the interconversion of B and C is so rapid that their concentrations always satisfy the equilibrium relationship

$$K = \frac{[C]}{[B]}.$$

For the purpose at hand, we do not consider B to be an intermediate; B is a product that happens to be at equilibrium with the co-product, C.

Case II

Suppose that $k_1[A][B] \gg k_3[C]$. In this case $A + B \rightarrow C$ is fast compared to the rate at which C is converted to D, and we say that $C \rightarrow D$ is the rate-determining step. We can now distinguish three sub-cases depending upon the way $[C]$ behaves during the course of the reaction.

Case IIa: Suppose that $k_1[A][B] \gg k_3[C]$ and $k_3 \gg k_2$. Then $A + B \rightarrow C$ is rapid and essentially quantitative. That is, within a short time of initiating the reaction, all of the stoichiometrically limiting reactant is converted to C. Letting $[D] = x$ and recognizing that our assumptions make $[A] \approx 0$, the mass-balance condition,

$$[A]_0 = [A] + [C] + [D]$$

becomes

$$[C] = [A]_0 - x.$$

After a short time, the rate at which D is formed becomes

$$\frac{d[D]}{dt} = k_3[C]$$

or

$$\frac{dx}{dt} = k_3([A]_0 - x)$$

The disappearance of C and the formation of D follow a first-order rate law.

Case IIb: If the forward and reverse reactions in the first elementary process are rapid, then this process may be effectively at equilibrium during the entire time that D is being formed. (This is the case that $k_1[A][B] \gg k_3[C]$ and $k_2 \gg k_3$.) Then, throughout the course of the reaction, we have

$$K_{eq} = [C]/[A][B]$$

Letting $[D] = x$ and making the further assumption that $[A] \gg [C] \approx 0$ throughout the reaction, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Substituting into the equilibrium-constant expression, we find

$$[C] = K_{eq}[B]_0\ ([A]_0 - x)$$

Substituting into $d[D]/dt = k_3[C]$ we have

$$\frac{dx}{dt} = k_3K_{eq}[B]_0\ ([A]_0 - x) = k_{IIa,obs}([A]_0 - x)$$

where $k_{IIa,obs} = k_3K_{eq}[B]_0$. The disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is a composite quantity that is directly proportional to $[B]_0$.

Case IIc: If we suppose that the first step is effectively at equilibrium during the entire time that D is being produced (as in case IIb) but that $[C]$ is not negligibly small compared to $[A]$, we again have $K_{eq} = [C]/[A][B]$. With $[D] = x$, the mass-balance condition becomes $[A] = [A]_0 - [C] - x$. Eliminating $[A]$ between the mass-balance and equilibrium-constant equations gives

$$[C] = \frac{K_{eq}[B]_0([A]_0 - x)}{1 + K_{eq}[B]_0}$$

so that $d[D]/dt = k_3[C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_3K_{eq}[B]_0}{1 + K_{eq}[B]_0}\right)([A]_0 - x) = k_{IIc,obs}([A]_0 - x)$$

The formation of D follows a pseudo-first-order rate equation. (The disappearance of A is also pseudo-first-order, but the pseudo-first-order rate constant is different.) As in Case IIb, the pseudo-first-order rate constant, $k_{IIc,obs}$, is a composite quantity, but now its dependence on $[B]_0$ is more complex. The result for Case IIc reduces to that for Case IIb if $K_{eq}[B]_0 \ll 1$.

Case III

In the cases above, we have assumed that one or more reactions are intrinsically much slower than others are. The differential equations for this mechanism can also become much simpler if all three reactions proceed at similar rates, but do so in such a way that the concentration of the intermediate is always very small, $[C] \approx 0$. If the concentration of C is always very small, then we

expect the graph of $[C]$ versus time to have a slope, $d\,[C]/dt$, that is approximately zero. In this case, we have

$$\frac{d\,[C]}{dt} = k_1[A][B] - k_2\,[C] - k_3\,[C] \approx 0$$

so that

$$[C] = \frac{k_1[A][B]}{k_2 + k_3}$$

With $[D] = x$, $d\,[D]/dt = k_3\,[C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_1 k_3 [B]_0}{k_2 + k_3}\right)([A]_0 - x) = k_{III,obs}\,([A]_0 - x)$$

As in the previous cases, the disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is again a composite quantity, which depends on $[B]_0$ and the values of all of the rate constants.

Case III illustrates the ***steady-state approximation***, in which we assume that the concentration of an intermediate species is much smaller than the concentrations of other species that affect the reaction rate. Under these circumstances, we can be confident that the time-derivative of the intermediate's concentration is negligible compared to the reaction rate, so that it is a good approximation to set it equal to zero. The idea is simply that, if the concentration is always small, its time-derivative must also be small. If the graph of the intermediate's concentration versus time is always much lower than that of other participating species, then its slope will be much less.

Equating the time derivative of the steady-state intermediate's concentration to zero produces an algebraic expression that involves the intermediate's concentration. Solving this expression for the concentration of the steady-state intermediate makes it possible to greatly simplify the set of simultaneous differential equations that is predicted by the mechanism. When there are multiple intermediates to which the approximation is applicable, remarkable simplifications can result. This often happens when the mechanism involves free-radical intermediates.

The name "steady-state approximation" is traditional. When we use it, we do so on the understanding that the "state" which is approximately "steady" is the concentration of the intermediate, not the state of the system. Since a net reaction is occurring, the state of the system is distinctly not constant.

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29.6: The Lindemann Mechanism

The Lindemann mechanism, sometimes called the Lindemann-Hinshelwood mechanism, is a schematic reaction mechanism. Frederick Lindemann discovered the concept in 1921 and Cyril Hinshelwood developed it. It breaks down a stepwise reaction into two or more elementary steps, then it gives a rate constant for each elementary step. The rate law and rate equation for the entire reaction can be derived from this information. Lindemann mechanisms have been used to model gas phase decomposition reactions. Although the net formula for a decomposition may appear to be first-order (unimolecular) in the reactant, a Lindemann mechanism may show that the reaction is actually second-order (bimolecular).

A Lindemann mechanism typically includes an activated reaction intermediate, labeled A* (where A can be any element or compound). The activated intermediate is produced from the reactants only after a sufficient activation energy is applied. It then either deactivates from A* back to A, or reacts with another (dis)similar reagent to produce yet another reaction intermediate or the final product.

General Mechanism

The schematic reaction $A + M \rightarrow P$ is assumed to consist of two elementary steps:

STEP 1: Bimolecular activation of A

$$A + M \rightleftharpoons A^* + M \tag{29.6.1}$$

with

- forward activation reaction rate: k_1
- reverse deactivation reaction rate: k_{-1}

STEP 2: Unimolecular reaction of $A*$

$$A^* \overset{k_2}{\rightarrow} P \tag{29.6.2}$$

with

- forward reaction rate: k_2

Assuming that the concentration of intermediate A^* is held constant according to the quasi steady-state approximation, what is the rate of formation of product P?

Solution

First, find the rates of production and consumption of intermediate A^*. The rate of production of A^* in the first elementary step (Equation 29.6.1) and A^* is consumed both in the reverse first step and in the forward second step. The respective rates of consumption of A^* are:

$$\frac{d[A^*]}{dt} = \underset{\text{(forward first step)}}{k_1[A][M]} - \underset{\text{(reverse first step)}}{k_{-1}[A^*][M]} - \underset{\text{(forward second step)}}{k_2[A^*]} \tag{29.6.3}$$

According to the steady-state approximation,

$$\frac{d[A^*]}{dt} \approx 0 \tag{29.6.4}$$

Therefore the rate of production of A^* (first term in Equation 29.6.3) equals the rate of consumption (second and third terms in Equation 29.6.3):

$$k_1[A][M] = k_{-1}[A^*][M] + k_2[A^*] \tag{29.6.5}$$

Solving for $[A^*]$, it is found that

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2} \tag{29.6.6}$$

The overall reaction rate is (Equation 29.6.2)

$$\frac{d[P]}{dt} = k_2[A^*] \tag{29.6.7}$$

Now, by substituting the calculated value for $[A^*]$ (Equation 29.6.6 into Equation 29.6.7), the overall reaction rate can be expressed in terms of the original reactants A and M as follows:

$$\frac{d[P]}{dt} = \frac{k_1 k_2[A][M]}{k_{-1}[M] + k_2} \tag{29.6.8}$$

The rate law for the Lindemann mechanism is not a simple first or second order reaction. However, under certain conditions (discussed below), Equation 29.6.8 can be simplified.

Three Principles of the Lindemann Mechanism

1. Energy is transferred by collision (forward reaction of Equation 29.6.1)
2. There is a time delay Δt between collision and reaction (Equation 29.6.2)
3. Molecules may be de-activated by another collision during Δt (reverse reaction of Equation 29.6.1)

Example 29.6.1 : Dissociation of N_2O_5

The decomposition of dinitrogen pentoxide to nitrogen dioxide and nitrogen trioxide

$$N_2O_5 \rightarrow NO_2 + NO_3$$

is postulated to take place via two elementary steps, which are similar in form to the schematic example given above:

1. $N_2O_5 + N_2O_5 \rightleftharpoons N_2O_5^* + N_2O_5$
2. $N_2O_5^* \rightarrow NO_2 + NO_3$

Using the quasi steady-state approximation soluioten (Equation 9) with $[M] = [N_2O_5]$, then rate equation is:

$$\text{Rate} = k_2[N_2O_5]^* = \frac{k_1 k_2[N_2O_5]^2}{k_{-1}[N_2O_5] + k_2}$$

Experiment has shown that the rate is observed as first-order in the original concentration of N_2O_5 sometimes, and second order at other times.

- If $k_2 >> k_{-1}$, then the rate equation may be simplified by assuming that $k_{-1} \approx 0$. Then the rate equation is

  $$\text{Rate} = k_1[N_2O_5]^2$$

  which is *second order*.
- If $k_2 << k_{-1}$, then the rate equation may be simplified by assuming $k_2 \approx 0$. Then the rate equation is

  $$\text{Rate} = \frac{k_1 k_2[N_2O_5]}{k_{-1}} = k_{obs}[N_2O_5]$$

  which is *first order* with

  $$k_{obs} = \frac{k_2 k_2}{k_{-1}}.$$

Exercise 29.6.1

The following first order rate constants for the gas phase decomposition of N_2O_5 have been obtained as a function of number density at 298 K.

$k_{obs}(s^{-1})$	7.81×10^{-3}	12.5×10^{-3}	15.6×10^{-3}
$[N_2O_5](mol/m^{-3})$	10	25	50

Confirm that these data are consistent with the Lindemann mechanism and derive a rate constant and a ratio of two rate constants for elementary reactions in the mechanism. What are the units of the two quantities.

Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN$$

If the isomerization is a unimolecular elementary reaction, we should expect to see 1^{st} order rate kinetics. Experimentally, however, 1^{st} order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2^{nd} order rate law:

$$\frac{d\left[CH_3NC\right]}{dt} = -k\left[CH_3NC\right]^2 \tag{29.6.9}$$

To explain this observation, J.A. Christiansen and F.A. Lindemann proposed that gas molecules first need to be energized via intermolecular collisions before undergoing an isomerization reaction. The reaction mechanism can be expressed as the following two elementary reactions

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{29.6.10}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{B} \tag{29.6.11}$$

where M can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of A^* is small, or $k_1 \ll k_2 + k_{-1}$, we can use a steady-state approximation to solve for the concentration profile of species B with time:

$$\frac{d\left[\mathrm{A}^*\right]}{dt} = k_1\left[\mathrm{A}\right]\left[\mathrm{M}\right] - k_{-1}\left[\mathrm{A}^*\right]_{ss}\left[\mathrm{M}\right] - k_2\left[\mathrm{A}^*\right]_{ss} \approx 0 \tag{29.6.12}$$

Solving for $[\mathrm{A}^*]$,

$$\left[\mathrm{A}^*\right] = \frac{k_1\left[\mathrm{M}\right]\left[\mathrm{A}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} \tag{29.6.13}$$

The reaction rates of species A and B can be written as

$$-\frac{d\left[\mathrm{A}\right]}{dt} = \frac{d\left[\mathrm{B}\right]}{dt} = k_2\left[\mathrm{A}^*\right] = \frac{k_1 k_2\left[\mathrm{M}\right]\left[\mathrm{A}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} = k_{\mathrm{obs}}\left[\mathrm{A}\right] \tag{29.6.14}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2\left[\mathrm{M}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} \tag{29.6.15}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}\left[\mathrm{M}\right] \gg k_2$. Equation 29.6.14 then becomes

$$-\frac{d\left[\mathrm{A}\right]}{dt}=\frac{k_1k_2}{k_{-1}}\left[\mathrm{A}\right] \tag{29.6.16}$$

which follows 1^{st} order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}\left[\mathrm{M}\right]\ll k_2$. In this scenario, Equation 29.6.14 becomes

$$-\frac{d\left[\mathrm{A}\right]}{dt}=k_1\left[\mathrm{A}\right]\left[\mathrm{M}\right] \tag{29.6.17}$$

which follows second order rate kinetics, consistent with experimental observations.

References

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29.7: Some Reaction Mechanisms Involve Chain Reactions

A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

- **initiation step** – a step that creates the intermediates from stable species
- **propagation step** – a step that consumes an intermediate, but creates a new one
- **termination step** – a step that consumes intermediates without creating new ones

These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

The observed rate law for this reaction is

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \tag{29.7.1}$$

A proposed mechanism is

$$Br_2 \underset{\blacksquare}{\overset{k_1}{\rightleftharpoons}} 2Br^{\cdot} \tag{29.7.2}$$

$$2Br^{\cdot} + H_2 \underset{\blacksquare}{\overset{k_2}{\rightleftharpoons}} HBr + H^{\cdot} \tag{29.7.3}$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot} \tag{29.7.4}$$

Based on this mechanism, the rate of change of concentrations for the intermediates ($H^{\cdot}$ and $Br^{\cdot}$) can be written, and the steady state approximation applied.

$$\frac{d[H^{\cdot}]}{dt} = k_2[Br^{\cdot}][H_2] - k_{-2}[HBr][H^{\cdot}] - k_3[H^{\cdot}][Br_2] = 0$$

$$\frac{d[Br^{\cdot}]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 - k_2[Br^{\cdot}][H_2] + k_{-2}[HBr][H^{\cdot}] + k_3[H^{\cdot}][Br_2] = 0$$

Adding these two expressions cancels the terms involving k_2, k_{-2}, and k_3. The result is

$$2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 = 0$$

Solving for $Br^{\cdot}$

$$Br^{\cdot} = \sqrt{\frac{k_1[Br_2]}{k_{-1}}}$$

This can be substituted into an expression for the $H^{\cdot}$ that is generated by solving the steady state expression for $d[H^{\cdot}]/dt$.

$$[H^{\cdot}] = \frac{k_2[Br^{\cdot}][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

so

$$[H^{\cdot}] = \frac{k_2\sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for $H^{\cdot}$ and $Br^{\cdot}$, we can substitute them into an expression for the rate of production of the product

HBr:

$$\frac{d[HBr]}{dt} = k_2[Br^{\cdot}][H_2] + k_3[H^{\cdot}][Br_2] - k_{-2}[H^{\cdot}][HBr]$$

After substitution and simplification, the result is

$$\frac{d[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}}{1 + \frac{k_{-1}}{k_3}\frac{[HBr]}{[Br_2]}}$$

Multiplying the top and bottom expressions on the right by $[Br_2]$ produces

$$\frac{d[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2] + \frac{k_{-1}}{k_3}[HBr]}$$

which matches the form of the rate law found experimentally (Equation 29.7.1)! In this case,

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$

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29.8: A Catalyst Affects the Mechanism and Activation Energy

As can be seen from the Arrhenius equation, the magnitude of the activation energy, E_a, determines the value of the rate constant, k, at a given temperature and thus the overall reaction rate. Catalysts provide a means of reducing E_a and increasing the reaction rate. Catalysts are defined as substances that participate in a chemical reaction but are not changed or consumed. Instead they provide a new mechanism for a reaction to occur which has a lower activation energy than that of the reaction without the catalyst.

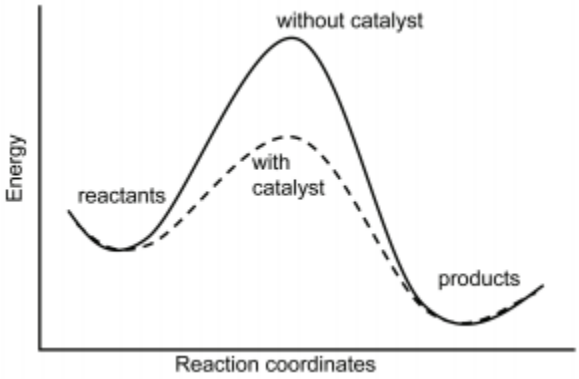


Figure 29.8.1 : Comparison of energy profiles with and without catalyst present.

Homogeneous catalysis refers to reactions in which the catalyst is in solution with at least one of the reactants whereas *heterogeneous catalysis* refers to reactions in which the catalyst is present in a different phase, usually as a solid, than the reactants. Figure 29.8.1 shows a comparison of energy profiles of a reaction in the absence and presence of a catalyst.

Consider a non-catalyzed elementary reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{P}$$

which proceeds at rate k at a certain temperature. The reaction rate can be expressed as

$$\frac{d\left[\mathrm{A}\right]}{dt} = -k\left[\mathrm{A}\right]$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_{\mathrm{cat}}} \mathrm{P} + \mathrm{C}$$

and the reaction rate as

$$\frac{d\left[\mathrm{A}\right]}{dt} = -k\left[\mathrm{A}\right] - k_{\mathrm{cat}}\left[\mathrm{A}\right]\left[\mathrm{C}\right]$$

where the first term represents the uncatalyzed reaction and the second term represents the catalyzed reaction. Because the reaction rate of the catalyzed reaction is often magnitudes larger than that of the uncatalyzed reaction (i.e. $k_{\mathrm{cat}} \gg k$), the first term can often be ignored.

Example of Homogenous Catalysis: Acid Catalysis

A common example of homogeneous catalysts are acids and bases. For example, given an overall reaction is $\mathrm{S} \rightarrow \mathrm{P}$. If k is the rate, then

$$\frac{d\left[\mathrm{P}\right]}{dt} = k\left[\mathrm{S}\right]$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S} + \mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^+ + \mathrm{A}^- \tag{29.8.1}$$

$$\mathrm{S}H^+ + H_2O \xrightarrow{k_2} \mathrm{P} + H_3O^+ \tag{29.8.2}$$

$$H_3O^+ + \mathrm{A}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H + H_2O \tag{29.8.3}$$

The full set of kinetic equations is

$$\frac{d\left[\mathrm{S}\right]}{dt} = -k_1\left[\mathrm{S}\right]\left[\mathrm{A}H\right] + k_{-1}\left[\mathrm{S}H^+\right]\left[\mathrm{A}^-\right] \tag{29.8.4}$$

$$\frac{d\left[\mathrm{A}H\right]}{dt} = -k_1\left[\mathrm{S}\right]\left[\mathrm{A}H\right] + k_{-1}\left[\mathrm{S}H^+\right]\left[\mathrm{A}^-\right] - k_{-3}\left[\mathrm{A}H\right] + k_3\left[H_3O^+\right]\left[\mathrm{A}^-\right] \tag{29.8.5}$$

$$\frac{d\left[\mathrm{S}H^+\right]}{dt} = k_1\left[\mathrm{S}\right]\left[\mathrm{A}H\right] - k_{-1}\left[\mathrm{S}H^+\right]\left[\mathrm{A}^-\right] - k_2\left[\mathrm{S}H^+\right] \tag{29.8.6}$$

$$\frac{d\left[\mathrm{A}^-\right]}{dt} = k_1\left[\mathrm{S}\right]\left[\mathrm{A}H\right] - k_{-1}\left[\mathrm{S}H^+\right]\left[\mathrm{A}^-\right] - k_2\left[\mathrm{A}^-\right]\left[H_3O^+\right] + k_{-3}\left[\mathrm{A}H\right] \tag{29.8.7}$$

$$\frac{d\left[\mathrm{P}\right]}{dt} = k_2\left[\mathrm{S}H^+\right] \tag{29.8.8}$$

$$\frac{d\left[H_3O^+\right]}{dt} = -k_2\left[\mathrm{S}H^+\right] - k_3\left[H_3O^+\right]\left[\mathrm{A}^-\right] + k_{-3}\left[\mathrm{A}H\right] \tag{29.8.9}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}\left[\mathrm{A}^-\right]$ and $k_2 \ll k_{-1}\left[\mathrm{A}^-\right]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d\left[\mathrm{S}H^+\right]}{dt} = k_1\left[\mathrm{S}\right]\left[\mathrm{A}H\right] - k_{-1}\left[\mathrm{A}^-\right]\left[\mathrm{S}H^+\right] - k_2\left[\mathrm{S}H^+\right] = 0$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$\left[\mathrm{S}H^+\right] = \frac{k_1\left[\mathrm{S}\right]\left[\mathrm{A}H\right]}{k_{-1}\left[\mathrm{A}^-\right] + k_2}$$

and the rate of production of P can be written as

$$\frac{d\left[\mathrm{P}\right]}{dt} = k_2\left[\mathrm{S}H^+\right] = \frac{k_1k_2\left[\mathrm{S}\right]\left[\mathrm{A}H\right]}{k_{-1}\left[\mathrm{A}^-\right] + k_2}$$

In the case where $k_2 \gg k_{-1}\left[\mathrm{A}^-\right]$, Equation 29.8.17 can be written as

$$\frac{d\left[\mathrm{P}\right]}{dt} = k_1\left[\mathrm{S}\right]\left[\mathrm{A}H\right]$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}\left[\mathrm{A}^-\right]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d\left[\mathrm{P}\right]}{dt} = \frac{k_1k_2\left[\mathrm{S}\right]\left[\mathrm{A}H\right]}{k_{-1}\left[\mathrm{A}^-\right]} = \frac{k_1k_2}{k_{-1}K}\left[\mathrm{S}\right]\left[H^+\right]$$

where K is the acid dissociation constant:

$$K = \frac{\left[\mathrm{A}^-\right]\left[H^+\right]}{\left[\mathrm{A}H\right]}$$

In this case, the reaction is hydrogen ion-catalyzed.

Example of Heterogeneous Catalysis: Surface Catalysis of Gas-Phase Reactions

Many gas-phase reactions are catalyzed on a solid surface. For a first-order, unimolecular reaction, the reaction mechanism can be written as

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{AS}\,(s) \overset{k_2}{\rightarrow} \mathrm{P}\,(g) + \mathrm{S}\,(g)$$

where the first step is reversible adsorption of the gas molecule, A, onto active sites on the catalyst surface, S, to form a transition state, AS, and the second step is the conversion of adsorbed A molecules to species P. Applying the steady-state approximation to species AS, we can write

$$\frac{d\,[\mathrm{AS}]}{dt} = k_1\,[\mathrm{A}]\,[\mathrm{S}] - k_{-1}\,[\mathrm{AS}]_{ss} - k_2\,[\mathrm{AS}]_{ss} = 0$$

Because the concentration of total active sites on the catalyst surface is fixed at $[\mathrm{S}]_0$, the concentration of adsorbed species on the catalyst surface, $[\mathrm{AS}]$ can be written as

$$[\mathrm{AS}] = \theta\,[\mathrm{S}]_0$$

and $[\mathrm{S}]$ can be written as

$$[\mathrm{S}] = (1-\theta)\,[\mathrm{S}]_0$$

where θ is the fractional surface coverage of species A on the catalyst surface. We can now write Equation 29.8.23 as

$$k_1\,[\mathrm{A}]\,(1-\theta)\,[\mathrm{S}]_0 - (k_{-1}+k_2)\,\theta\,[\mathrm{S}]_0 = 0$$

Rearranging the above equation in terms of θ yields

$$\theta = \frac{k_1\,[\mathrm{A}]}{k_1\,[\mathrm{A}] + k_{-1} + k_2}$$

The rate of production of P can be written as

$$\frac{d\,[\mathrm{P}]}{dt} = k_2\,[\mathrm{AS}]_{ss} = k_2\theta\,[\mathrm{S}]_0 = \frac{k_1 k_2}{k_1\,[\mathrm{A}] + k_{-1} + k_2}\,[\mathrm{A}]\,[\mathrm{S}]_0$$

From the above equation, we can observe the importance of having high surface areas for catalytic reactions.

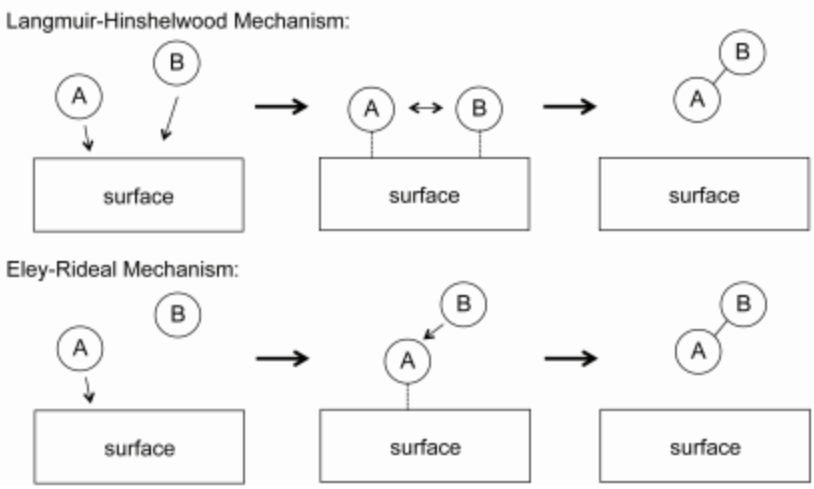


Figure 29.8.2 : Illustrations of the Langmuir-Hinshelwood and Eley-Rideal mechanisms for heterogeneous catalysis of bimolecular gas-phase reactions.

For bimolecular gas-phase reactions, two generally-used mechanisms to explain reactions kinetics are the Langmuir-Hinshelwood and Eley-Rideal mechanisms, shown in Figure 29.8.2 . In the Langmuir-Hinshelwood mechanism, A and B both adsorb onto the catalyst surface, at which they react to form a product. The reaction mechanism is

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{B}\,(g) + \mathrm{S}\,(s) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{BS}\,(s)$$

$$\mathrm{AS}\,(s) + \mathrm{BS}\,(s) \overset{k_3}{\rightarrow} \mathrm{P}$$

The rate law for the Langmuir-Hinshelwood mechanism can be derived in a similar manner to that for unimolecular catalytic reactions by assuming that the total number of active sites on the catalyst surface is fixed. In the Eley-Rideal mechanism, only one species adsorbs onto the catalyst surface. An example of such a reaction is the partial oxidation of ethylene into ethylene oxide, as shown in Figure 29.8.3 . In this reaction, diatomic oxygen adsorbs onto the catalytic surface where it reacts with ethylene molecules in the gas phase.

The reactions for the Eley-Rideal mechanism can be written as

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{AS}\,(s) + \mathrm{B}\,(g) \overset{k_2}{\rightarrow} \mathrm{P}\,(g) + \mathrm{S}\,(s)$$

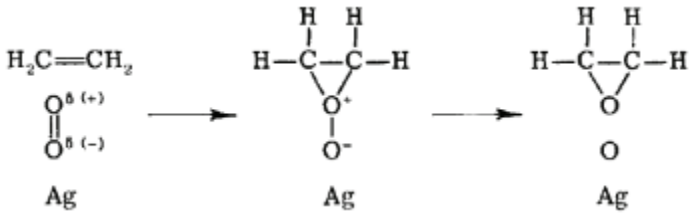


Figure 29.8.3 : Illustrations of the reaction mechanism for the partial oxidation of ethylene to ethylene oxide. [Reproduced from Kilty, PA and WMH Sacthler. Catal. Rev., 10, 1]

Assuming that $k_{-1} \gg k_1$, we can apply a steady-state approximation to species AS:

$$\frac{d\,[\mathrm{AS}]}{dt} = 0 = k_1\,[\mathrm{A}]\,[\mathrm{S}] - k_{-1}\,[\mathrm{AS}]_{ss} - k_2\,[\mathrm{AS}]_{ss}\,[\mathrm{B}]$$

As in the case of unimolecular catalyzed reactions, we can express the concentrations of AS and S in terms of a fraction of the total number of active sites, S_0 and rewrite the above equation as

$$0 = k_1 [\mathrm{A}] (1 - \theta) [\mathrm{S}]_0 - k_{-1} [\mathrm{S}]_0 - k_2 \theta [\mathrm{S}]_0 [\mathrm{B}]$$

Solving for θ yields

$$\theta = \frac{k_1 [\mathrm{A}]}{k_1 [\mathrm{A}] + k_{-1} + k_2 [\mathrm{B}]}$$

Furthermore, if $k_2 \ll k_1$ and k_{-1}, we can simplify θ to

$$\theta = \frac{k_1 [\mathrm{A}]}{k_1 [\mathrm{A}] + k_{-1}}$$

The rate of production of P can be expressed as

$$\frac{d [\mathrm{P}]}{dt} = k_2 [\mathrm{AS}]_{ss} [\mathrm{B}] = k_2 \theta [\mathrm{S}]_0 [\mathrm{B}] = \frac{k_1 k_2 [\mathrm{A}]}{k_1 [\mathrm{A}] + k_{-1}} [\mathrm{S}]_0 [\mathrm{B}]$$

We can also write the above expression in terms of the equilibrium constant, K, which is equal to k_1 / k_{-1}

$$\frac{d [\mathrm{P}]}{dt} = K k_2 [\mathrm{B}] \frac{K [\mathrm{A}]}{K [\mathrm{A}] + 1}$$

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29.9: The Michaelis-Menten Mechanism for Enzyme Catalysis

Enzymes are biological catalysts and functional proteins. Enzymes contain specificity in its protein structure in order to have its specialized function. It usually contains more than one subunit and they are critical to sustain life. Enzymes can increase the chemical reactions in living cells. However, enzymes are not consumed in the reaction and their main function is to assist in bringing the substrates together so they can undergo normal reaction faster.

The first enzyme was found in the process of fermentation in milk and alcohol during the nineteenth century. Later in the early 1830s, the term enzyme was used to replace the term ferment. Some scientists believe that ferments must contain living cells and some think ferments could be non-living cells. Finally, in the 1920s, Sumner purified the structure of enzyme and then properties of enzyme then was more clearly understood. Until today, enzymes are still the popular research field that many people are subject to study.

Michaelis-Menten Kinetics

In biological systems, enzymes act as catalysts and play a critical role in accelerating reactions, anywhere from 10^3 to 10^{17} times faster than the reaction would normally proceed. Enzymes are high-molecular weight proteins that act on a substrate, or reactant molecule, to form one or more products. In 1913, Leonor Michaelis and Maude Menten proposed the following reaction mechanism for enzymatic reactions:

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \overset{k_2}{\rightarrow} \mathrm{E} + \mathrm{P}$$

where E is the enzyme, ES is the enzyme-substrate complex, and P is the product. In the first step, the substrate binds to the active site of the enzyme. In the second step, the substrate is converted into the product and released from the substrate. For this mechanism, we can assume that the concentration of the enzyme-substrate complex, ES, is small and employ a steady-state approximation:

$$\frac{d\left[\mathrm{ES}\right]}{dt} = k_1\left[\mathrm{E}\right]\left[\mathrm{S}\right] - k_{-1}\left[\mathrm{ES}\right]_{ss} - k_2\left[\mathrm{ES}\right]_{ss} \approx 0 \tag{29.9.1}$$

Furthermore, because the enzyme is unchanged throughout the reaction, we express the total enzyme concentration as a sum of enzyme and enzyme-substrate complex:

$$\left[\mathrm{E}\right]_0 = \left[\mathrm{ES}\right] + \left[\mathrm{E}\right] \tag{29.9.2}$$

Plugging Equation 29.9.2 into Equation 29.9.1, we obtain

$$0 = k_1\left(\left[\mathrm{E}\right]_0 - \left[\mathrm{ES}\right]_{ss}\right)\left[\mathrm{S}\right] - k_{-1}\left[\mathrm{ES}\right]_{ss} + k_2\left[\mathrm{ES}\right]_{ss} \tag{29.9.3}$$

Solving for $\left[\mathrm{ES}\right]_{ss}$

$$\left[\mathrm{ES}\right]_{ss} = \frac{k_1\left[\mathrm{E}\right]_0\left[\mathrm{S}\right]}{k_1\left[\mathrm{S}\right] + k_{-1} + k_2} = \frac{\left[\mathrm{E}\right]_0\left[\mathrm{S}\right]}{\left[\mathrm{S}\right] + \dfrac{k_{-1} + k_2}{k_1}} \tag{29.9.4}$$

We can then write the reaction rate of the product as

$$\frac{d\left[\mathrm{P}\right]}{dt} = k_2\left[\mathrm{ES}\right]_{ss} = \frac{k_2\left[\mathrm{E}\right]_0\left[\mathrm{S}\right]}{\left[\mathrm{S}\right] + \dfrac{k_{-1} + k_2}{k_1}} = \frac{k_2\left[\mathrm{E}\right]_0\left[\mathrm{S}\right]}{\left[\mathrm{S}\right] + K_M} \tag{29.9.5}$$

where K_M is the Michaelis constant. Equation 29.9.5 is known as the Michaelis-Menten equation. The result for Michaelis-Menten kinetics equivalent to that for a unimolecular gas phase reaction catalyzed on a solid surface. In the limit where there is a large amount of substrate present $(\left[\mathrm{S}\right] \gg K_M)$ Equation 29.9.5 reduces to

$$\frac{d\,[\mathrm{P}]}{dt} = r_{\max} = k_2\,[\mathrm{E}]_0 \tag{29.9.6}$$

which is a 0^{th} order reaction, since $[\mathrm{E}]_0$ is a constant. The value $k_2\,[\mathrm{E}]_0$ represents the maximum rate, $r_{\max}$, at which the enzymatic reaction can proceed. The rate constant, k_2, is also known as the *turnover number*, which is the number of substrate molecules converted to product in a given time when all the active sites on the enzyme are occupied. Figure 29.9.4 displays the dependence of the reaction rate on the substrate concentration, $[\mathrm{S}]$. This plot is known as the Michaelis-Menten plot. Examining the figure, we can see that the reaction rate reaches a maximum value of $k_2\,[\mathrm{E}]_0$ at large values of $[\mathrm{S}]$.

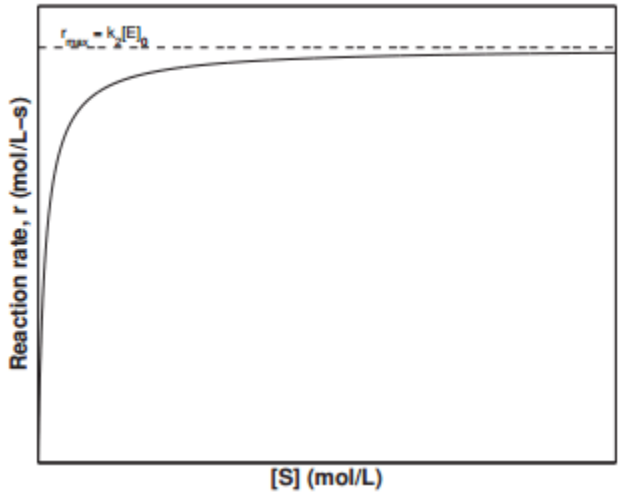


Figure 29.9.4 : Rate dependence on substrate concentration for an enzymatic reaction.

Another commonly-used plot in examining enzyme kinetics is the **Lineweaver-Burk plot**, in with the inverse of the reaction rate, $1/r$, is plotted against the inverse of the substrate concentration $1/\,[\mathrm{S}]$. Rearranging Equation 29.9.5,

$$\frac{1}{r} = \frac{K_M + [\mathrm{S}]}{k_2\,[\mathrm{E}]_0\,[\mathrm{S}]} = \frac{K_M}{k_2\,[\mathrm{E}]_0}\,\frac{1}{[\mathrm{S}]} + \frac{1}{k_2\,[\mathrm{E}]_0} \tag{29.9.7}$$

The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M/k_2\,[\mathrm{E}]_0$ and y-intercept equal to $1/k_2\,[\mathrm{E}]_0$.

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29.E: Chemical Kinetics II- Reaction Mechanisms (Exercises)

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30: GAS-PHASE REACTION DYNAMICS

30.1: The Rate of Bimolecular Gas-Phase Reaction Can Be Estimated Using Hard-Sphere Collision Theory and an Energy-Dependent Reaction Cross Section

30.2: A Reaction Cross Section Depends Upon the Impact Parameter

30.3: The Rate Constant for a Gas-Phase Chemical Reaction May Depend on the Orientations of the Colliding Molecules

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30.10: The Potential-Energy Surface Can Be Calculated Using Quantum Mechanics

30.E: Gas-Phase Reaction Dynamics (Exercises)

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30.1: The Rate of Bimolecular Gas-Phase Reaction Can Be Estimated Using Hard-Sphere Collision Theory and an Energy-Dependent Reaction Cross Section

Collision Frequency using the Hard Sphere Model

For the bimolecular gas-phase reaction

$$\mathrm{Q\,(g)} \;+\; \mathrm{B\,(g)} \;\rightarrow \text{products}$$

the reaction rate is

$$\text{rate} = -\frac{d[Q]}{dt} = k[Q][B]$$

If it is assumed that every collision between Q and B particles results in products, the rate at which molecules collide is equal to the frequency of collisions per unit volume, Z_{QB} (Equation 27.6.4)

$$\text{rate} = Z_{QB} = \sigma_{QB}\langle v_r\rangle \rho_Q \rho_B \tag{30.1.1}$$

Also known as the collision frequency, Z_{QB}, has units of molecules per volume per time, molecules·m^{-3}·s^{-1}. It is possible to obtain a rough estimate of the value of the rate constant, k, from the collision frequency.

Equation 30.1.1 shows the rate on a molecular scale. Generally, Z_{QB} is divided by Avogadro's number, N_0, to obtain the collision frequency on a molar scale

$$\text{rate} = -\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = \frac{\sigma_{QB}\langle v_r\rangle}{N_0}\rho_Q \rho_B$$

To convert the number densities to molar concentrations, we need to realize that

$$\frac{\rho_Q}{N_0} = [Q]$$

then

$$-\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = \frac{\sigma_{QB}\langle v_r\rangle}{N_0}(N_0[Q])(N_0[B])$$

$$-\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = N_0\sigma_{QB}\langle v_r\rangle [Q][B]$$

$$-\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = N_0\sigma_{QB}\sqrt{\frac{8k_BT}{\pi\mu_{QB}}}[Q][B]$$

Thus

$$Z_{QB} = N_0^2\sigma_{QB}\sqrt{\frac{8k_BT}{\pi\mu_{QB}}}[Q][B]$$

and

$$k = N_0\sigma_{QB}\sqrt{\frac{8k_BT}{\pi\mu_{QB}}}$$

where:

- $\langle v_r \rangle$ is the mean relative speed of molecules, which is equal to $\sqrt{\frac{8k_BT}{\pi\mu_{QB}}}$
- ρ_Q and ρ_B are the number densities of Q molecules and B molecules
- N_Q and NB are the numbers of Q molecules and B molecules
- σ_{QB} is the averaged sum of the collision cross sections of molecules Q and B, $\sigma_{QB} = \pi\left(\frac{d_Q + d_B}{2}\right)^2$. The collision cross section represents the collision region presented by one molecule to another. σ_{QB} is often written as πd_{QB}^2.

The units of σ are m^2, the units of N_0 are mole^{-1}, and the units of $\langle v_r \rangle$ are $\frac{m}{s}$. Thus, the units of k are $\frac{m^3}{\text{mole} \cdot s}$

As noted earlier, using this hard-sphere collision theory value for the rate constant is a rough estimate, mainly because the temperature dependence of k is improperly represented in the hard-sphere collision theory prediction. The next sections will describe an initial attempt to correct that error.

Successful Collisions

For a successful collision to occur, the reactant molecules must collide with enough kinetic energy to overcome the repulsions of the electron clouds and to break the existing bonds. To take the energy dependence of a successful collision into account, we will introduce a new reaction cross-section, $\sigma_r(v_r)$, which takes into account the speed of the reactants. Thus

$$k(v_r) = v_r \sigma_r(v_r)$$

The rate constant can be calculated by averaging over a distribution of all speeds, $f(v_r)$

$$k = \int_0^\infty k(v_r) f(v_r) dv_r = \int_0^\infty v_r f(v_r) dv_r \sigma_r(v_r) \tag{30.1.2}$$

From equation 27.7.4, we know that $v_r f(v_r) dv_r$ is

$$v_r f(v_r) dv_r = \left(\frac{\mu}{k_B T}\right)^{3/2} \left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2 / 2k_B T} dv_r \tag{30.1.3}$$

Equation 30.1.3 presents the rate constant as a function of speed. If we want to compare this version of k with the common, Arrhenius form of k, the dependent variable must be changed from relative speed to relative kinetic energy, E_r. The relationship is

$$E_r = \frac{1}{2}\mu v_r^2 \text{ which rearranges to } v_r = \left(\frac{2E_r}{\mu}\right)^{1/2}$$

Thus,

$$dv_r = \left(\frac{1}{2\mu E_r}\right)^{1/2} dE_r$$

Substituting v_r and dv_r into equation 30.1.3 gives

$$v_r f(v_r) dv_r = \left(\frac{\mu}{k_B T}\right)^{3/2} \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{2E_r}{\mu}\right)^{3/2} e^{-E_r/k_B T} \left(\frac{1}{2\mu E_r}\right)^{1/2} dE_r$$

Substituting this equation into equation 30.1.2 and simplifying gives

$$k = \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} \int_0^\infty dE_r E_r e^{-E_r/k_B T} \sigma_r(E_r) \tag{30.1.4}$$

We can then assume that the energy dependent reaction cross section $\sigma_r(E_r)$ will include only those molecules which undergo effective collisions with a kinetic energy that is greater than or equal to a minimum sufficient energy, E_0. Thus $\sigma_r(E_r)$ is equal to

0 if $E_r < E_0$ and is equal to σ_{QB} if $E_r \geq E_0$.

Thus we integrate from E_0 to ∞ using the known integral $\int xe^{ax}dx = a^{-2}e^{ax}(ax-1)$,

$$k = \left(\frac{2}{k_B T}\right)^{3/2}\left(\frac{1}{\mu\pi}\right)^{1/2}\int_{E_0}^{\infty} dE_r E_r e^{-E_r/k_B T}\sigma_{QB}$$

$$= \left(\frac{8k_B T}{\mu\pi}\right)^{1/2}\sigma_{QB}e^{-E_0/k_B T}\left(1+\frac{E_0}{k_B T}\right)$$

$$= \langle v_r\rangle\sigma_{QB}e^{-E_0/k_B T}\left(1+\frac{E_0}{k_B T}\right)$$

This model results in a value for k that takes into account the temperature and a minimum energy requirement to determine the fraction of successful collisions. However, it is not yet equivalent to the Arrhenius equation, in which k is proportional to $e^{-E_0/k_B T}$ and not $e^{-E_0/k_B T}\left(1+\frac{E_0}{k_B T}\right)$.

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30.2: A Reaction Cross Section Depends Upon the Impact Parameter

In the previous section, it was assumed that all collisions with sufficient energy would lead to a reaction between the Q and B particles. This is an unrealistic assumption because not all collisions occur with a proper alignment of the particles as shown in Figure 30.2.1.

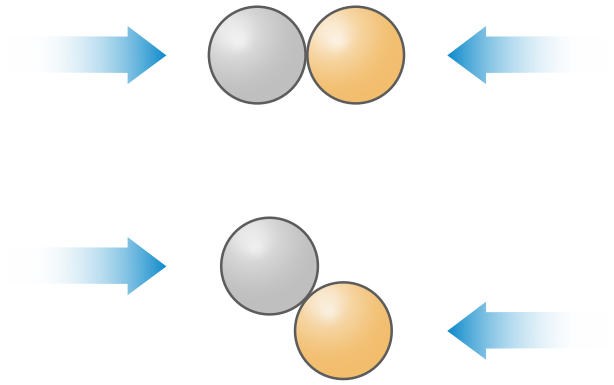


Figure 30.2.1 In the top collision, the particles collide head-on, and thus all of the kinetic energy can be used to overcome electron-electron repulsion and to break bonds. In the bottom collision, the particles collide with a glancing blow so that only part of the kinetic energy is contributed to the reaction process. With collisions involving larger, more complex molecules, there is often a specific molecular orientation required for an effective collision. (CC BY-NC; Ümit Kaya via LibreTexts)

Thus, the energy-dependent reaction cross-section,$\sigma_r(E_r)$, introduced previously is inaccurate and must be modified to take into account the inefficient collisions. One modification is to employ the *line-of-centers* (loc) model for $\sigma_r(E_r)$. This model incorporates the angle of collision relative to the line drawn between the centers of the two colliding particles, as shown in Figure 30.2.2.

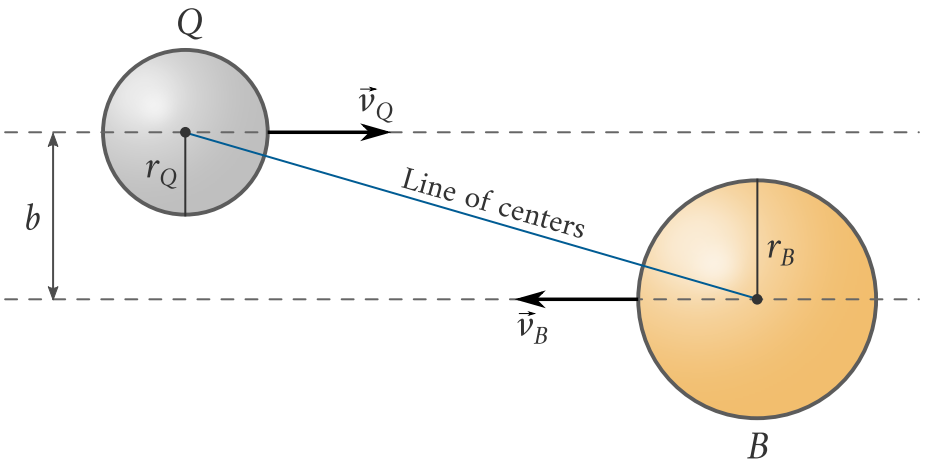


Figure 30.2.2: This figure shows the geometry of the collision between two particles. The particle velocities are $\vec{v}_Q$ and $\vec{v}_B$. The distance between the paths traveled by the two particle centers is b. (CC BY-NC; Ümit Kaya via LibreTexts)

In this model, and effective collision occurs when $E_{loc} > E_0$ where E_{loc} takes into account the fact that all particle collisions are not head-on collisions. If we define v_r as the relative velocity of approach of particles Q and B, then $v_r = \vec{v}_Q - \vec{v}_B$. The relative kinetic energy, E_r, is then $\frac{1}{2}\mu v_r^2$. From Figure 30.2.2 we can see that the fraction of E_r that can be applied to the collision, (E_{loc}), is dependent upon b, the impact parameter, which is the perpendicular distance between the extrapolated paths traveled by the centers of the particles before the collision occurs. If b is 0, then $E_{loc} = E_r$, but for any other value of b, $E_{loc} < E_r$. If b is greater than the sum of the radii of Q and B, the particles will not collide, and $E_{loc} = 0$. The calculation for determining the exact relationship between the $\sigma_r(E_r)$ and E_r for this line of center model rather complicated, but the result is that $\sigma_r(E_r)$ is equal to 0 if $E_r < E_0$ and is equal to $\sigma_{QB}\left(1 - \frac{E_0}{E_r}\right)$ if $E_r \geq E_0$.

When compared to the simple hard-sphere collision theory, we see that

$$\sigma_r(E_r) = \sigma_{QB} \text{ if } E_r \geq E_0 \text{ (hard-sphere theory)} \tag{30.2.1}$$

$$\sigma_r(E_r) = \sigma_{QB}\left(1 - \frac{E_0}{E_r}\right) \text{ if } E_r \geq E_0 \text{ (line of centers theory)} \tag{30.2.2}$$

If we substitute Equation 30.2.2 into Equation 30.1.4 we get

$$\begin{aligned} k &= \left(\frac{2}{k_B T}\right)^{3/2}\left(\frac{1}{\mu\pi}\right)^{1/2}\int_{E_0}^{\infty} dE_r E_r e^{-E_r/k_B T}\sigma_{QB}\left(1 - \frac{E_0}{E_r}\right) \\ &= \left(\frac{8k_B T}{\mu\pi}\right)^{1/2}\sigma_{QB}e^{-E_r/k_B T} \\ &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_B T} \end{aligned}$$

When compared to the simple hard-sphere collision theory, we see that

$$\begin{aligned} k &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_B T}\left(1 + \frac{E_0}{k_B T}\right) \text{ (hard-sphere theory)} \\ &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_B T} \text{ (line of centers theory)} \end{aligned}$$

The line of centers theory expresses k in the same terms as the Arrhenius equation, yet experimental values of k still differ from those predicted by the line of centers model. The errors come about because $\sigma_r(E_r)$ is not accurately described by $\sigma_{QB}\left(1 - \frac{E_0}{E_r}\right)$. More work needs to be done to improve the model for describing A, the Arrhenius factor.

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30.3: The Rate Constant for a Gas-Phase Chemical Reaction May Depend on the Orientations of the Colliding Molecules

In the previous section, the simple hard-sphere model for collisions was modified to take into account the fact that not every collision of particles occurred with sufficient energy to result in a reaction. The line of centers model assumed that all colliding particles were spheres, yet we know that this is definitely not the case. Thus, we need to modify the collision model to factor in the orientation of non-spherical particles. Figure 30.3.1 shows an example of properly oriented particles and an example of improperly oriented molecules.

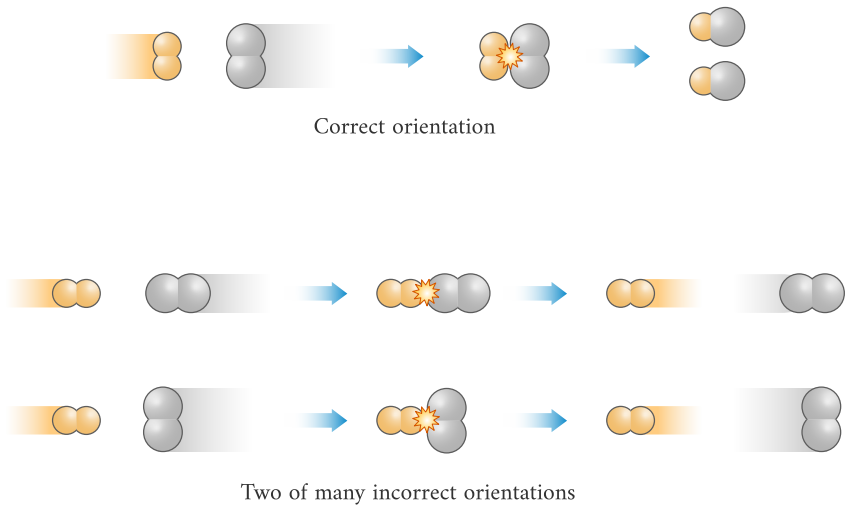


Figure 30.3.1: (top) Molecules colliding with the correct orientation that leads to a successful reaction. (bottom) Molecules colliding in two of the many incorrect orientations that do not lead to a reaction. (CC BY-NC; Ümit Kaya via LibreTexts)

Because proper orientation of colliding molecules is necessary, the hard-sphere collision model overestimates the number of effective collisions. This is one of the factors that leads an incorrect value for A estimated by the hard-sphere collision model.

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30.4: The Internal Energy of the Reactants Can Affect the Cross Section of a Reaction

A further modification of our collision model involves including the internal energy of the colliding gas particles. Recall that the internal energy for a polyatomic gas particle includes electronic, vibrational, and, possibly, rotational energy. It is possible for polyatomic molecules to be in a high enough vibrational state that their vibrational energy alone is greater than E_0. Such molecules would not require any additional translational energy to react. Thus, for a constant total energy, the value of σ_r depends on the vibrational and, to a smaller extent, rotational state of the particle. During a collision between reacting particles, energy can be exchanged between the different degrees of freedom of the particle, so we will need to modify our model to take into account these energy exchanges that occur during a collision. We will see in section 30.5 that using a center-of-mass coordinate system to describe the reaction collision will allow us to incorporate internal energy into our model.

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30.5: A Reactive Collision Can Be Described in a Center-of-Mass Coordinate System

We will apply a center-of-mass coordinate system to the bimolecular reaction of ideal gases

$$\mathrm{B\,(g) + Q\,(g) \longrightarrow F\,(g) + G\,(g)}$$

to develop an improved model for reaction kinetics that produces theoretical values that more closely represent experimental results. In this model, the reactant molecules will travel at velocities $\vec{v}_B$ and $\vec{v}_Q$ before the collision. The product molecules will travel at velocities $\vec{v}_F$ and $\vec{v}_G$ after the collision.

The Velocity and Kinetic Energy of the Center of Mass

The center of mass of two objects must lie along a straight line drawn between the centers of the two objects. Because the two molecules are heading toward each other, the line between them will be changing in size and can be best represented with the vector, $\vec{r}$, where $\vec{r} = \vec{r}_B - \vec{r}_Q$. The pre-reaction center of mass, $\mathbf{R}$ is defined as

$$\mathbf{R} = \frac{m_B \mathbf{r}_B + m_Q \mathbf{r}_Q}{M}$$

where m_B and m_Q are the masses of the individual reactants, and M is the total mass, $m_B + m_Q$.

Velocity is $\frac{d\vec{r}}{dt}$, and so the velocity of the center of mass, $\vec{v}_{cm}$ is

$$\vec{v}_{cm} = \frac{m_B \vec{v}_B + m_Q \vec{v}_Q}{M}$$

The kinetic energy of the reacting system is

$$\mathrm{KE}_{react} = \frac{1}{2} m_B v_B^2 + \frac{1}{2} m_Q v_Q^2$$

This equation can be rewritten as

$$\mathrm{KE}_{react} = \frac{1}{2} M v_{cm}^2 + \frac{1}{2} \mu v_r^2 \tag{30.5.1}$$

Here, μ is the reduced mass and the realtive speed of the colliding particles is $v_r = |\vec{v}_r| = |\vec{v}_B| - |\vec{v}_Q|$. Because we are assuming we have ideal gases, KE_{react} is a constant for the center of mass.

The Reaction

As shown in equation 30.5.1, the kinetic energy of the moving reactants consists of two parts, one due to the relative motion of the two reactant particles, and one due to the motion of the center of mass. The energy due to the motion of the center of mass will not contribute to the reaction, as will soon be shown. Only the energy due to the relative motion of the reacting molecules $\frac{1}{2}\mu v_r^2$ will contribute to overcoming the energy barrier of the energy of the reaction. And only a fraction of that energy will contribute because the molecules are not colliding head-on. Figure 30.5.1 gives a view of the progress of the reaction at several times.

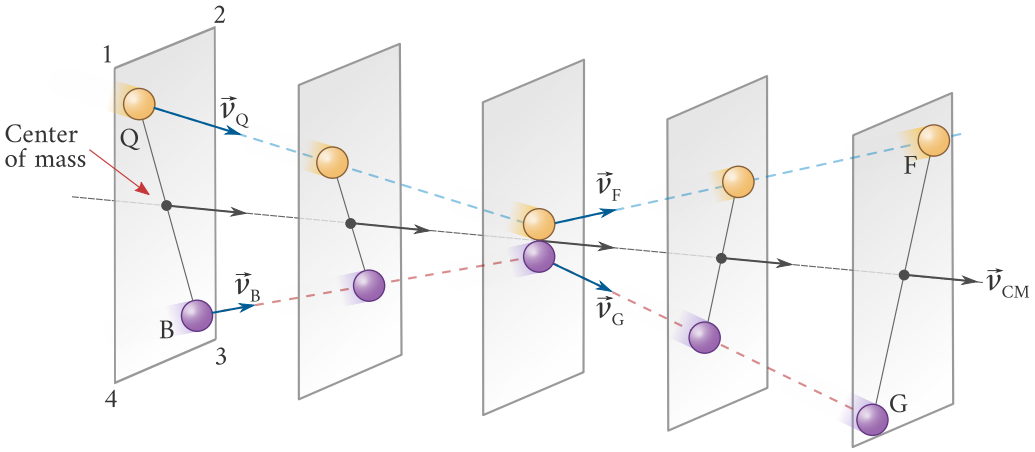


Figure 30.5.1: A diagram showing the progress of a reaction collision occurring along the path of the center of mass as time passes. The velocity of the center of mass remains constant at all times. The energy that can be contributed towards the reaction by each reactant particles is the component of its own velocity that is co-linear with the collision direction. As shown by Equation 30.5.1, this energy contribution of the reacting particles is combined in the term $\frac{1}{2}\mu v_r^2$. (CC BY-NC; Ümit Kaya via LibreTexts)

Removing the Center of Mass Term

Once F and G have formed, the post-reaction center of mass, $\mathbf{R}$ is defined as

$$\mathbf{R} = \frac{m_F\vec{r}_F + m_G\vec{r}_G}{M}$$

where m_F and m_G are the masses of the individual reactants, and M is the total mass, $m_F + m_G$. That means that the velocity of the center of mass, $\vec{v}_{cm}$ is

$$\vec{v}_{cm} = \frac{m_F\vec{v}_F + m_G\vec{v}_G}{M}$$

The kinetic energy of the reacting system is

$$\mathrm{KE}_{react} = \frac{1}{2}m_F v_F^2 + \frac{1}{2}m_G v_G^2$$

This equation can be rewritten as

$$\mathrm{KE}_{react} = \frac{1}{2}M v_{cm}^2 + \frac{1}{2}\mu_P v_{P_r}^2$$

Because the products have different individual masses than the reactants, the reduced mass μ_P and the relative speed v_{P_r} of the products must be denoted as having different values from those of the reactants. The total mass is conserved, however, as is $\vec{v}_{cm}$, the velocity of the center of mass. Because linear momentum must be conserved,

$$m_B\vec{v}_B + m_Q\vec{v}_Q = m_F\vec{v}_F + m_G\vec{v}_G = M\vec{v}_{cm}$$

Because mass is conserved and velocity of the center of mass is constant, the energy contribution of the motion of the center of mass is also constant, and thus does not contribute to the kinetic energy used to attain a successful reaction collision.

Estimating the Total Internal Energy

Using the center of mass model for a reaction, we have found the kinetic energy terms for the reactants, $\frac{1}{2}\mu v_r^2$, and products, $\frac{1}{2}\mu_P v_{P_r}^2$. Thus the law of conservation of energy tells us

$$E_{Reactant_{(internal)}} + \frac{1}{2}\mu v_r^2 = E_{Product_{(internal)}} + \frac{1}{2}\mu_P v_{P_r}^2$$

This relationship can be rewritten as

$$E_{Reactant_{(internal)}} + E_{Reactant_{(translational)}} = E_{Product_{(internal)}} + E_{Product_{(translational)}}$$

or

$$E_{R_{(int)}} + E_{R_{(trans)}} = E_{P_{(int)}} + E_{P_{(trans)}}$$

The velocity of the products can be defined based on the laws of conservation of energy and momentum. Unfortunately, the angle between the velocity vector of the reactants $\vec{v}_r$ and the velocity vector of the products $\vec{v}_{P_r}$cannot be determined because products molecules can theoretically disperse from the collision in any direction.

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30.6: Reactive Collisions Can be Studied Using Crossed Molecular Beam Machines

Crossed molecular beam experiments are chemical experiments where two beams of atoms or molecules are collided together to study the dynamics of the chemical reaction. These experiments can detect individual reactive collisions as well as determine the distribution of velocities and the scattering angle of the reaction products.[1]

Technique

In a crossed molecular beam apparatus, two collimated beams of gas-phase atoms or molecules, each dilute enough to ignore collisions within each beam, intersect in a vacuum chamber, as shown in Figure $30.6.1a$. The direction and velocity of the resulting product molecules are then measured. These data are frequently coupled with mass spectrometric data to yield information about the partitioning of energy among translational, rotational, and vibrational modes of the product molecules.[2]

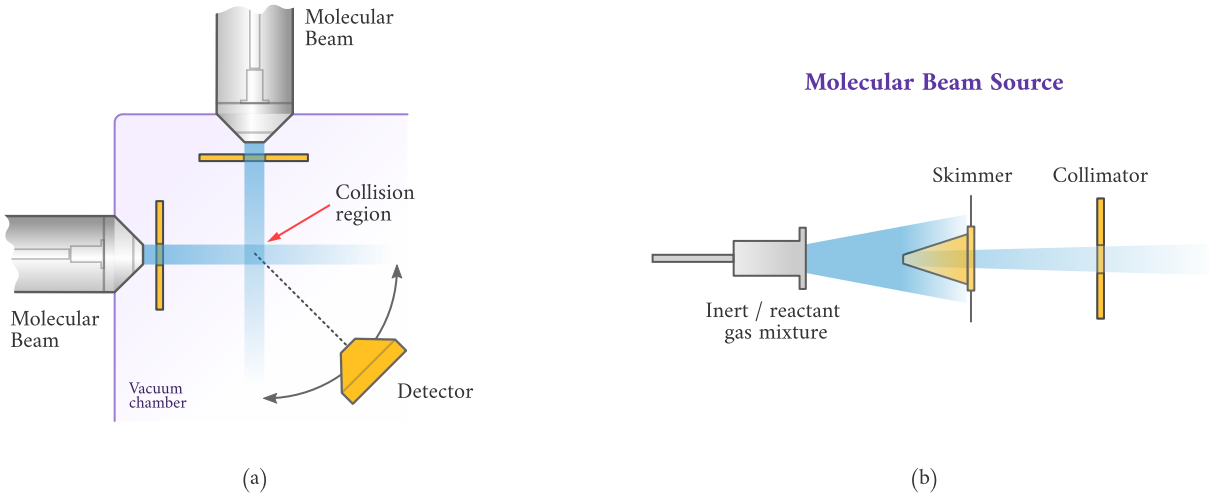


Figure $30.6.1$ a) A schematic diagram of a crossed molecular beam apparatus. The two molecular beams, each containing particles of a single reactant species, intersect at the collision region. The product particles travel away from the collision region. A mass spectrometer with a moveable inlet is used to detect the product particles. b) A schematic diagram of a supersonic molecular beam source. (CC BY-NC; Ümit Kaya via LibreTexts)

History

The crossed molecular beam technique was developed by Dudley Herschbach and Yuan T. Lee, for which they were awarded the 1986 Nobel Prize in Chemistry.[3] While the technique was demonstrated in 1953 by Taylor and Datz of Oak Ridge National Laboratory,[4] Herschbach and Lee refined the apparatus and began probing gas-phase reactions in unprecedented detail.

Early crossed beam experiments investigated alkali metals such as potassium, rubidium, and cesium. When the scattered alkali metal atoms collided with a hot metal filament, they ionized, creating a small electric current. Because this detection method is nearly perfectly efficient, the technique was quite sensitive.[2] Unfortunately, this simple detection system only detects alkali metals. New techniques for detection were needed to analyze main group elements.

Detecting scattered particles through a metal filament gave a good indication of angular distribution but has no sensitivity to kinetic energy. In order to gain insight into the kinetic energy distribution, early crossed molecular beam apparatuses used a pair of slotted disks placed between the collision center and the detector. By controlling the rotation speed of the disks, only particles

with a certain known velocity could pass through and be detected.[2] With information about the velocity, angular distribution, and identity of the scattered species, useful information about the dynamics of the system can be derived.

Later improvements included the use of quadrupole mass filters to select only the products of interest,[5] as well as time-of-flight mass spectrometers to allow easy measurement of kinetic energy. These improvements also allowed the detection of a vast array of compounds, marking the advent of the "universal" crossed molecular beam apparatus.

The inclusion of supersonic nozzles (figure $30.6.1b$) to collimate the gases expanded the variety and scope of experiments, and the use of lasers to excite the beams (either before impact or at the point of reaction) further broadened the applicability of this technique.[2]

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30.7: Reactions Can Produce Vibrationally Excited Molecules

As shown at the end of section 30.5, using the center of mass reaction model allows us to state that

$$E_{R_{(int)}} + E_{R_{(trans)}} = E_{P_{(int)}} + E_{P_{(trans)}} \tag{30.7.1}$$

where $E_{R_{(int)}}$ and $E_{P_{(int)}}$ represent the rotational, vibrational, and electronic energies collectively described as the internal energy of the reactants and the products, respectively. If we apply equation 30.7.1 to the well-studied gas-phase reaction

$$\mathrm{F\,(g) + D_2\,(g) \longrightarrow DF\,(g) + D\,(g)}$$

we can discuss the distribution of a fixed total collision energy between $E_{P_{(int)}}$ and $E_{P_{(trans)}}$. Specifically, if we assume that $\mathrm{F\,(g)}$ and $\mathrm{D\,(g)}$ are in their ground electronic states, that $\mathrm{D_2\,(g)}$ is in its ground rotational, vibrational, and electronic states, and that $\mathrm{DF\,(g)}$ is in its ground rotational and electronic states, we can focus on the possible vibrational states of the $\mathrm{DF\,(g)}$ that can be populated. Figure 30.7.1 shows the potential energy curve of the process that is described below.

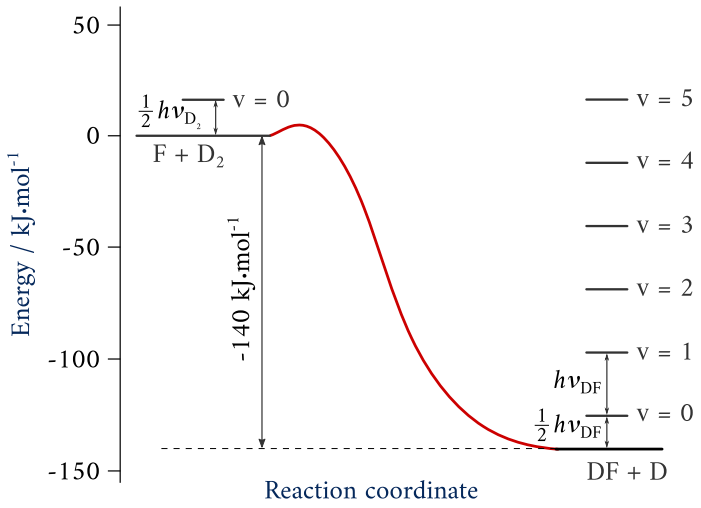


Figure 30.7.1: The potential energy diagram for the reaction $\mathrm{F\,(g) + D_2\,(g) \longrightarrow DF\,(g) + D\,(g)}$. *(CC BY-NC; Ümit Kaya via LibreTexts)*

Expanding Equation 30.7.1 to describe this assumed process, we get

$$E_{R_{(rot)}} + E_{R_{(vib)}} + E_{R_{(elec)}} + E_{R_{(trans)}} = E_{P_{(rot)}} + E_{P_{(vib)}} + E_{P_{(elec)}} + E_{P_{(trans)}} \tag{30.7.2}$$

Let's assume that $\mathrm{D_2}$ and DF are harmonic oscillators with $\tilde{\nu}_{D_2}$ = 2990 cm^{-1} and $\tilde{\nu}_{DF}$ = 2907 cm^{-1}.

If D_2 and DF are in their ground electronic states, then $E_{R_{(elec)}} = -D_e(D_2)$ and $E_{P_{(elec)}} = -D_e(DF)$. From experiments, we know that

$$-D_e(DF) - (-D_e(D_2)) = -140 kJ/mol$$

We also know from experiments, that the activation energy for this reaction is about 6 kJ/mol[1], so if we assume that the relative translational energy of the reactants is 7.1 kJ/mol, they will have sufficient energy to overcome the activation energy barrier.

With these data, we can write Equation 30.7.2 as

$$0 + E_{R_{(vib)}} - D_e(D_2) + 7.1\frac{kJ}{mol} = 0 + E_{P_{(vib)}} - D_e(DF) + E_{P_{(trans)}}$$

then

$$E_{R_{(vib)}} + 7.1\frac{kJ}{mol} = E_{P_{(vib)}} + (-D_e(DF) - (-D_e(D_2)) + E_{P_{(trans)}}$$

then

$$E_{R_{(vib)}} + 7.1\frac{kJ}{mol} = E_{P_{(vib)}} - 140\frac{kJ}{mol} + E_{P_{(trans)}}$$

Because $\mathrm{D_2}$ is in its ground vibrational state, $E_{R_{(vib)}} = \frac{1}{2}h\nu_{D_2} = 17.9\frac{kJ}{mol}$

Putting this altogether,

$$17.9\frac{kJ}{mol} + 140\frac{kJ}{mol} + 7.1\frac{kJ}{mol} - E_{P_{(vib)}} = E_{P_{(trans)}}$$

$$165\frac{kJ}{mol} - E_{P_{(vib)}} = E_{P_{(trans)}} \tag{30.7.3}$$

Equation 30.7.3 tells us that the reaction will occur only if $E_{P_{(vib)}}$ is less than 165 kJ/mol because $E_{P_{(trans)}}$ must be a positive value.

If $\mathrm{DF\,(g)}$ is a harmonic oscillator, then

$$\begin{aligned} E_{P_{(vib)}} &= \left(v + \frac{1}{2}\right) h\nu_{DF} \\ &= \left(v + \frac{1}{2}\right) (34.8\,kJ/mol) < 165\,kJ/mol \end{aligned}$$

Vibrational states, v = 0, 1, 2, 3, and 4 will result in $E_{P_{(vib)}} \leq$ 165 kJ/mol. Thus $\mathrm{DF\,(g)}$ molecules in these five vibrational states will be produced by the reaction. Note that under these set of assumptions, the DF molecules produced in different vibrational states will have correspondingly different $E_{P_{(trans)}}$.

[1]Average of experimental E_a values listed at https://kinetics.nist.gov/kinetics/ accessed 9/22/2021

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30.8: The Velocity and Angular Distribution of the Products of a Reactive Collision

Calculation of the speed distribution for DF molecules based upon the vibrational state of the molecule

This section describes how data from crossed molecular beam experiments allow us to describe the velocity and angular distribution of particles produced by the simple bi-molecular collision

$$\mathrm{F\,(g) + D_2\,(g) \longrightarrow DF\,(g) + D\,(g)} \tag{30.8.1}$$

As noted in the previous section, the internal vibrational energy of the products will affect the velocity and distribution because if $\mathrm{DF\,(g)}$ is a harmonic oscillator, then

$$E_{P_{(trans)}} + E_{P_{(vib)}} = 165\frac{kJ}{mol}$$

and

$$E_{P_{(vib)}} = \left(v + \frac{1}{2}\right)(34.8\frac{kJ}{mol})$$

Thus

$$\begin{aligned} E_{P_{(trans)}} + E_{P_{(vib)}} &= \frac{1}{2}\mu_P v_{P_r} + \left(v + \frac{1}{2}\right)\left(34.8\frac{kJ}{mol}\right) \\ &= 165\frac{kJ}{mol} \end{aligned} \tag{30.8.2}$$

The reduced mass of the products μ_P is

$$\frac{(21.01\,g/mol)(2.014\,g/mol)}{21.01\,g/mol + 2.014\,g/mol} = 1.84\,g/mol = 0.00184\,kg/mol$$

so that solving for the product velocity in Equation 30.8.2 for v_{P_r} gives

$$v_{P_r} = \sqrt{\left(\frac{2}{0.00184\,kg/mol}\right)\left(1.65\times10^5\,\frac{J}{mol} - \left(v+\frac{1}{2}\right)(3.48\times10^4)\frac{J}{mol}\right)}$$

It can be shown that the corresponding relative velocity of the DF molecule and the center of mass,$|\vec{v}_{DF} - \vec{v}_{cm}|$, is equal to $\frac{m_D}{M}v_{P_r}$ for this reaction, with $M = m_{D_2} + m_F$. Table 30.8.1 shows the values of v_{P_r} and $|\vec{v}_{DF} - \vec{v}_{cm}|$ for vibrational states $v = 0 - 4$.

Table 30.8.1

Vibrational state, v	relative velocity of the products, v_{P_r} in m/s	$\lvert\vec{v}_{DF} - \vec{v}_{cm}\rvert$, in m/s
0	12,700	1111
1	11,100	971
2	9270	811
3	6930	606
4	3200	280

Analysis of Crossed Molecular Beam Data

This link takes you to the 1986 Nobel Prize acceptance lecture of Yuan Tseh Lee, in which he describes the crossed molecular beam studies that his group carried out on the reaction 30.8.1. On page 3 of the lecture, you will see a center-of-mass velocity flux contour map for the reaction. This map measures the speed distribution and the angular dispersion distribution as a result of collisions between one D_2 molecule approaching from the left and one F atom approaching from the right. Moving away from the center of the graph in any direction represents an increase in speed. The dashed line circles represent the maximum speed that a molecule in that given vibrational state can obtain. Notice that the highest vibrational state is closest to the nucleus. Thus, the map is consistent with theory, which claims that as the vibrational energy increases, the translational energy decreases.

The contour areas on the map represent a constant number of DF(g) molecules. The more closely spaced the contour lines, the greater the number of $\mathrm{DF(g)}$ molecules with that velocity in that vibrational state. An estimate of the population distribution is that roughly half the molecules are in the $v = 3$ state, roughly 25% of the molecules occupy the $v = 2$ state, and roughly 25% of the molecules occupy the $v = 4$ state. Very few molecules occupy the $v = 0$ or $v = 1$ states. The fact that there are molecules with velocities between the dashed lines shows that these DF molecules are in various rotational states within each vibrational state. If E_{rot} = 0 and $J = 0$, the molecular velocity distribution would be centered on each dashed line. But because these molecules do exist in various rotational states, their E_{rot} is greater than 0, and their translational energy is in between the energies of those molecules in rotational ground states. The distribution of vibrational states among the DF product molecules more closely resembles a normal distribution (i.e., Gaussian-like) than a Boltzmann distribution.

Example 30.8.1

Determine the populations of the five lowest vibrational states of $\mathrm{DF}(v)$ relative to $\mathrm{DF}(v = 3)$, assuming that the distribution is in thermal equilibrium at 298 K. You can assume that the DF molecules act as harmonic oscillators with $\tilde{\nu}_{DF}$ = 2907 cm^{-1}.

Solution

If the $\mathrm{DF(g)}$ molecules are in thermal equilibrium, the population of vibrational states will follow a Boltzmann distribution. Therefore,

$$N(v) = e^{-\frac{(v+1/2)h\nu_{DF}}{k_BT}}$$

and

$$N(v=3) = e^{-\frac{(3+1/2)h\nu_{DF}}{k_BT}}$$

so

$$\frac{N(v)}{N(v=3)} = e^{-\frac{(v-3)h\nu_{DF}}{k_BT}}$$

v	$\frac{N(v)}{N(v=3)}$
0	2.03 x 10^{18}
1	1.60 x 10^{12}
2	1.26 x 10^{6}
3	1
4	7.90 x 10^{-7}

It is clear that when the molecules are at thermal equilibrium, the population of the vibrational states decreases with an increasing v, which is not the population pattern found from the experiment.

The map also shows that a majority of $\mathrm{DF}\,(\mathrm{g})$ molecules generally head back towards the direction from which the F atom originally approached the collision. Some even head directly back from whence they came. This type of collision is called a rebound reaction. We will see in the next section that not all reactions are rebound reactions.

A different style of contour map is shown in figure $30.8.1$. In this view, the density of the dots and the intensity of their color represent the number of particles being scattered at specific angles. This map does not show the vibrational state of the DF molecules.

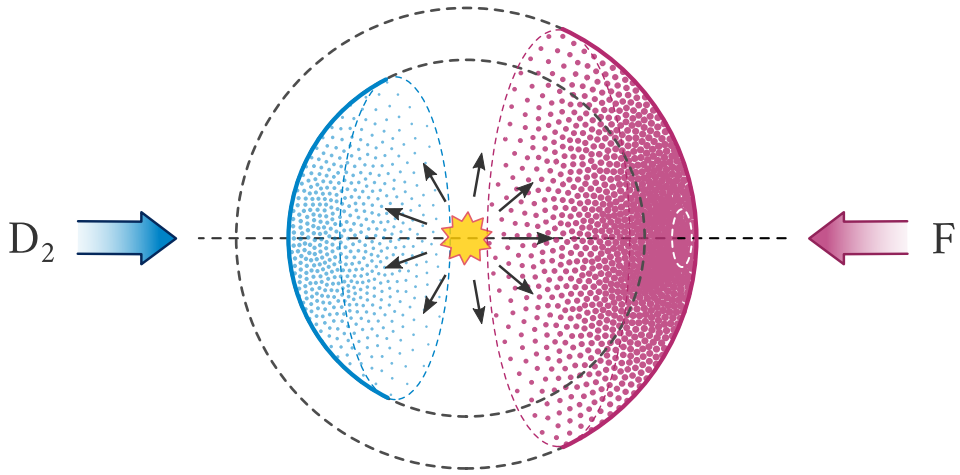


Figure $30.8.1$: A center-of-mass velocity flux contour map for the reaction $\mathrm{D_2 + F \longrightarrow DF + D}$. This map shows the angular dispersion distribution as a result of collisions between one D_2 molecule approaching from the left and one F atom approaching from the right. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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30.9: Not All Gas-Phase Chemical Reactions are Rebound Reactions

Stripping Reactions

In the previous section we showed that the reaction

$$\mathrm{D_2\,(g) + F\,(g) \longrightarrow DF\,(g) + D\,(g)}$$

is a rebound reaction because the vast majority of DF molecules bounce off from the collision with $\mathrm{D_2}$ back toward the general direction from which they came. In this section we will look at **stripping reactions**, reactions in which a majority of the product molecules continue moving on after the collision in the same direction that the precursor reactant molecules were going.

In stripping reactions, the experimental hard-sphere collision cross section is generally found to be larger than the theoretical estimate. The experimental cross-section is so large that it would be possible for two particles to remain inside the collision area and yet pass by each other without colliding. It has been determined experimentally that an electron transfer between the two particles occurs before they collide. The resulting ions are then drawn toward each other because of the Coulomb potential created by the opposite charges. One such reaction involves $\mathrm{K\,(g)}$ and $\mathrm{I_2\,(g)}$. The mechanism is:

$$\mathrm{K\,(g) + I_2\,(g) \longrightarrow K^+\,(g) + {I_2}^-\,(g)} \qquad \text{(step 1)}$$

$$\mathrm{K^+\,(g) + {I_2}^-\,(g) \longrightarrow KI\,(g) + I\,(g)} \qquad \text{(step 2)}$$

After the collision, the KI molecule moves off in the same general direction as the incoming K atom.

Meta-stable Intermediates

There are other bimolecular gas-phase collision reactions in which the product molecules disperse in both forward and reverse directions after the reaction. There is no explanation for these types of post-collision scattering patterns if we insist on using a simple hard-sphere collision model. However, if the colliding particles form a single atom-molecule structure that lasts long enough for the structure to undergo many rotations before splitting apart into products, it is reasonable for the newly formed products to scatter in the forward and reverse direction.

The discovery of these various reaction types was made possible by the development and use of the crossed molecular beam instruments described in Section 30.6.

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30.10: The Potential-Energy Surface Can Be Calculated Using Quantum Mechanics

A potential energy surface (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms. The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a potential energy curve or energy profile. It is helpful to use the analogy of a landscape: for a system with two degrees of freedom (e.g. two bond lengths), the value of the energy (analogy: the height of the land) is a function of two bond lengths (analogy: the coordinates of the position on the ground). The Potential Energy Surface represents the concept that each geometry (both external and internal) of the atoms of the molecules in a chemical reaction has associated with it a unique potential energy. This creates a smooth energy “landscape” and chemistry can be viewed from a topology perspective of particles evolving as they pass through potential energy "valleys" and "passes".

The PES concept finds application in fields such as chemistry and physics, especially in the theoretical sub-branches of these subjects. It can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction.

Potential Energy Curves (2-D Potential Energy Surfaces)

The energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning “no interaction”. At distances of several atomic diameters, attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. Plots that illustrate this relationship are quite useful in defining certain properties of a chemical bond (Figure 30.10.1).

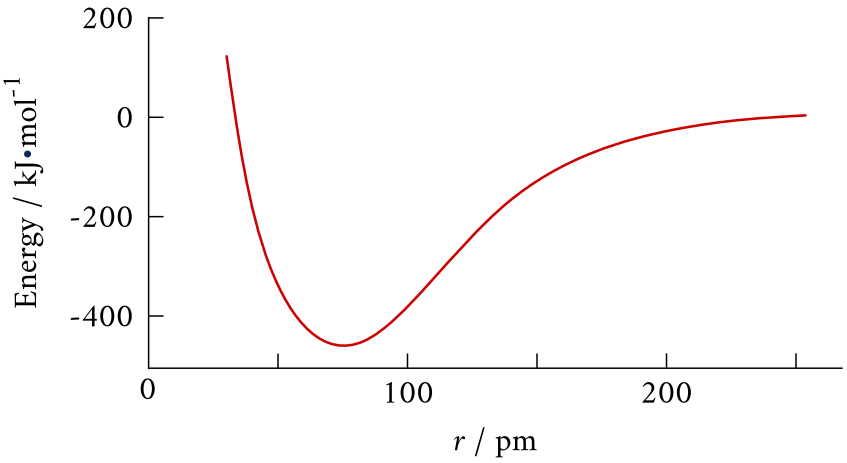


Figure 30.10.1: A potential energy curve for the covalent bond in a H_2 molecule. The distance r is the distance between the nuclei of the two H atoms. (CC BY-NC; Ümit Kaya via LibreTexts)

The internuclear distance at which the potential energy minimum occurs defines the **bond length**. This is more correctly known as the *equilibrium* bond length because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller the bond length.

Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of *RT*, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H_2. The weak attraction between argon atoms does not allow Ar_2 to exist as a molecule, but it does give rise to the *van der Waals force* that holds argon atoms together in their liquid and solid forms.

Potential, Kinetic, and Total Energy for a System

Potential energy and kinetic energy quantum theory tell us that an electron in an atom possesses kinetic energy K as well as potential energy V, so the total energy E is always the sum of the two: $E = V + K$. The relation between them is surprisingly simple: $K = -0.5V$. This means that when a chemical bond forms (an exothermic process with $\Delta E < 0$), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy $-\Delta E$ has half the magnitude of the decrease in potential energy.

Mathematical Definition and Computation of a Potential Energy Surface

The geometry of a set of atoms can be described by a vector, r, whose elements represent the atom positions. The vector r could be the set of the Cartesian coordinates of the atoms, or could also be a set of inter-atomic distances and angles. Given r, the energy as a function of the positions, $V(r)$, is the value of $V(r)$ for all values of r of interest. Using the landscape analogy from the introduction, $V(r)$ gives the height on the "energy landscape" so that the concept of a potential energy surface arises. An example is the PES for water molecule (Figure $30.10.2$) that shows the energy minimum corresponding to optimized molecular structure for water- O-H bond lengths of 0.0958 nm and H-O-H bond angle of 104.5°

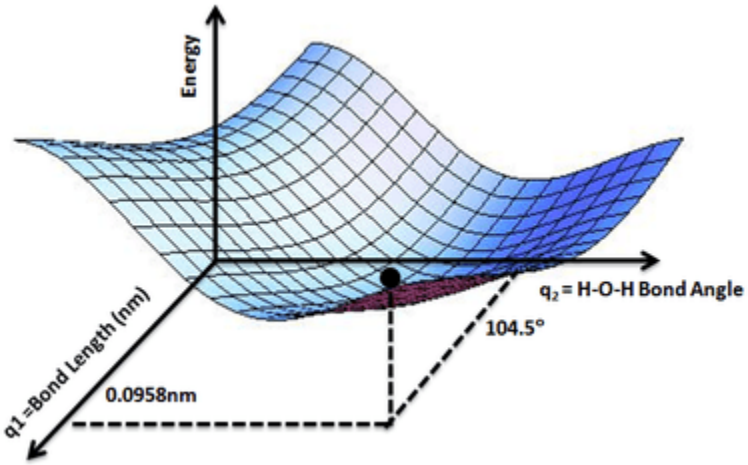


Figure $30.10.2$: PES for water molecule showing the energy minimum corresponding to optimized molecular structure for water- O-H bond lengths of 0.0958nm and H-O-H bond angle of 104.5°. of Wikipedia (Credit: Aimnature).

The Dimensionality of a Potential Energy Surface

To define an atom's location in 3-dimensional space requires three coordinates (e.g., x, y,and z or r, θ and phi in Cartesian and Spherical coordinates) or *degrees of freedom*. However, a reaction and hence the corresponding PESs do not depend on the absolute position of the reaction, only the relative positions (internal degrees). Hence both translation and rotation of the entire system can be removed (each with 3 degrees of freedom, assuming non-linear geometries). So the dimensionality of a PES is

$$3N - 6$$

where N is the number of atoms involves in the reaction, i.e., the number of atoms in each reactant). The PES is a hypersurface with many degrees of freedom and typically only a few are plotted at any one time for understanding. See Calculate Number of Vibrational Modes to get a more detailed picture of how this applies to calculating the number of vibrations in a molecule

To study a chemical reaction using the PES as a function of atomic positions, it is necessary to calculate the energy for **every atomic** arrangement of interest. Methods of calculating the energy of a particular atomic arrangement of atoms are well known.

For very simple chemical systems or when simplifying approximations are made about inter-atomic interactions, it is sometimes possible to use an analytically derived expression for the energy as a function of the atomic positions. An example is

$$\mathrm{H} + \mathrm{H_2} \longrightarrow \mathrm{H_2} + \mathrm{H} \tag{30.10.1}$$

a system that is described by a function of the **three** $\mathrm{H}-\mathrm{H}$ distances. For more complicated systems, calculation of the energy of a particular arrangement of atoms is often too computationally expensive for large-scale representations of the surface to be feasible.

Applications of Potential Energy Surfaces

A PES is a conceptual tool for aiding the analysis of molecular geometry and chemical reaction dynamics. Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy with respect to position, which respectively are the gradient and the curvature. Stationary points (or points with a zero gradient) have physical meaning: energy minima correspond to physically stable chemical species and **saddle points** correspond to transition states, the highest energy point on the reaction coordinate (which is the lowest energy pathway connecting a chemical reactant to a chemical product).

A Hypothetical Endothermic Reaction PES

Figure $30.10.3$ shows an example of a PES for a hypothetical reaction system, with the corresponding 2-D energy contour map projected on the plane below. The contour map shows isolines of potential energy, using color to differentiate between high and low energies. In this figure, the highest potential energy is indicated with red, and as the color changes along the ROYGBIV scale, the potential energy decreases until violet is reached, indicating the lowest potential energy. In the PES, the z axis represents the potential energy, with the energy of the plane in the PES defined as 0 kJ. The color scheme of the PES has the same meaning as that of the 2-D contour map - red is high potential energy and violet is low potential energy.

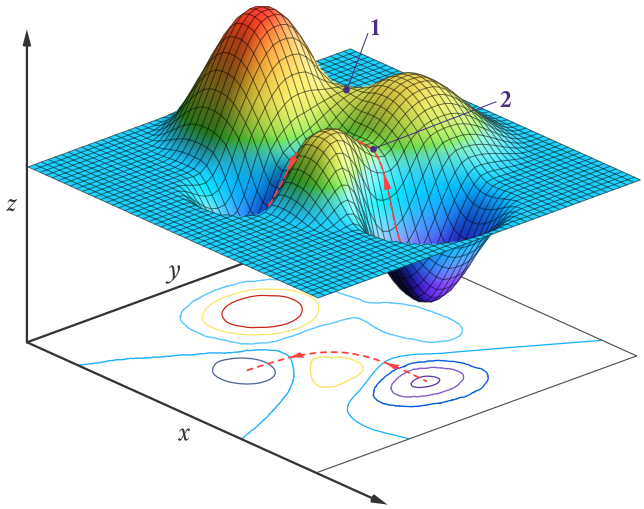


Figure $30.10.3$: A 2-D contour map and corresponding Potential Energy Surface for a hypothetical endothermic reaction. See the text for a detailed explanation. (CC BY-NC; Ümit Kaya via LibreTexts)

Before the reaction, the reactants are found at (or near) the energy minimum on the right. (The deep well in the PES and the smallest, violet oval in the contour map.) As the reaction proceeds, the reactants are shown following the minimum energy pathway toward the products, as designated by the dashed red line. The point "2" designates the transition state at the saddle point, the highest energy point of the reaction process. The reaction then moves on to form the products, which sit in the potential energy well on the left. (Designated by the shallower well on the PES and by the dark blue oval on the left in the contour map.) Because the potential energy of the reactants is less than the potential energy of the products, this reaction is an endothermic reaction. The point "1" represents a second, higher energy saddle point which is the transition state for an alternative reaction that is possible for this set of chemicals.

The Exchange Reaction $H_A + H_BH_C \Rightarrow H_AH_B + H_C$

A specific application of a PES is the mapping of the reaction shown in equation 30.10.1, the exchange of hydrogen atoms in an H_2 molecule. In this map, the individual H atoms are labeled as

$$H_A + H_BH_C \rightarrow H_AH_B + H_C$$

We must take into account the collision angle between the H_A atom and the H_BH_C molecule. If we fix this collision angle at 180°, we are able to plot a PES that is dependent on the two parameters of R_{BC} and R_{AB}. The resulting PES (figure 30.10.4*a*) and energy contour map (figure 30.10.4*b*) show us that if the particles are far enough apart, the potential energy of the reaction system starts out being described by the potential energy curve for the H_BH_C molecule, and ends up being described by the potential energy curve of the H_AH_B molecule. Individually, these curves both have appearances similar to the curve shown in Figure 30.10.1 . The PES and the energy contour map show the symmetrical nature of the potential energy changes that occur in this exchange process that involves products that are equivalent to the reactants.

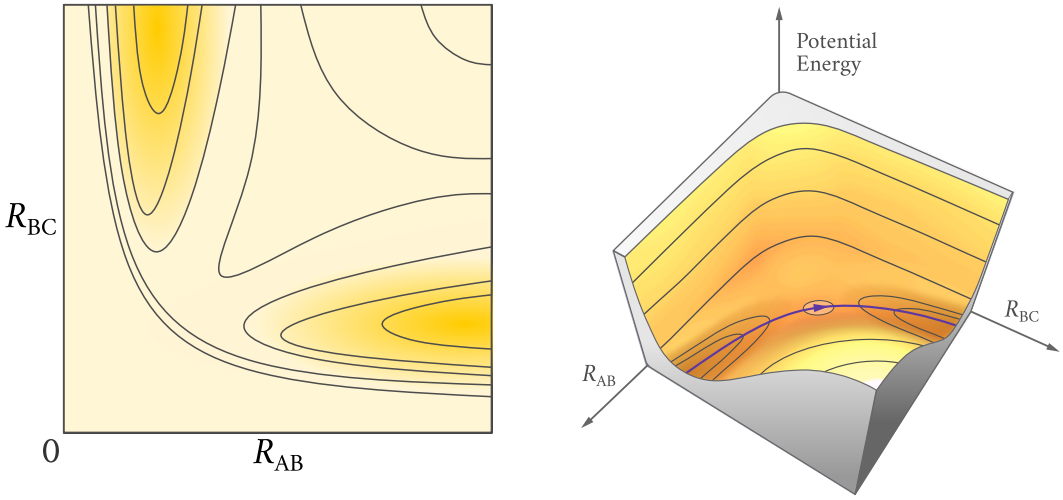


Figure 30.10.4*a*: (left) The potential energy contour map for the exchange reaction $H_A + H_BH_C \rightarrow H_AH_B + H_C$. The x-axis is R_{AB}, the interatomic distance between H_A and H_B. These two atoms begin very far apart, but end up being bonded together. The y-axis is R_{BC}, the interatomic distance between H_B and H_C. These two atoms start out bonded together but end up separated and far apart. The darker the color, the lower the potential energy. (right) The 3-D potential energy surface for the exchange reaction $H_A + H_BH_C \rightarrow H_AH_B + H_C$. The darker the color, the lower the potential energy. (CC BY-NC; Ümit Kaya via LibreTexts)

As the H_A atom more closely approaches the H_BH_C molecule, the interactions between these particles begin to affect the potential energy of the system. There are many possible potential energy pathways that the reaction could follow. Figure 30.10.5 shows the energy contour map for three possible reaction pathways:

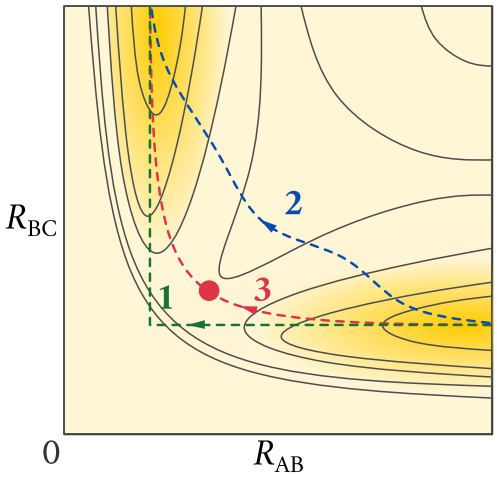


Figure 30.10.5: An energy contour map showing three possible reaction pathways for the reaction

$$H_A + H_BH_C \rightarrow H_AH_B + H_C$$

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In pathway 1, the H_BH_C bond length R_{BC} is held constant as the distance R_{AB} decreases. This type of interaction would lead to a continually increasing potential energy for the system as the H_A atom moves closer and closer to the H_BH_C molecule. Eventually, the new H_AH_B molecule would form, and the H_C atom would break off and would move farther and farther away.

Pathway 2 shows a second possible reaction pathway in which the H_BH_C bond length R_{BC} increases even though the H_A atom is still relatively far away. This pathway is unlikely because it requires a great deal of potential energy to stretch the H_BH_C bond before the attractive force from the H_A atom influences this bond lengthening.

As the particles travel along Pathway 3, the reactants still must pass through a potential energy maximum at the saddle point, but this local maximum is the lowest energy barrier separating reactants from products. As noted above, this saddle point is called the transition state structure (designated by the red dot in pathway 3). This is the structure that is equally poised to return to the reactants or move forward to form products. Pathway 3 is the minimum energy pathway, and thus the one most likely to be followed during a successful reaction.

It is sometimes useful to create energy contour maps that include information about the vibrational state of reactants and products, as shown in figure 30.10.6.

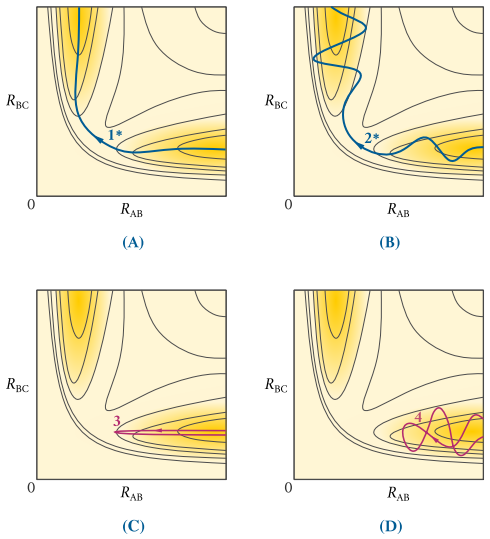


Figure 30.10.6: Four possible collision outcomes for the exchange reaction $H_A + H_BH_C \rightarrow H_AH_B + H_C$. 6A) The minimum energy pathway which leads to a successful exchange. 6B) The successful collision of a vibrating H_BH_C molecule with an H_A atom, resulting in the formation of a vibrating H_AH_B molecule. 6C) The approach of an H_A atom to a non-vibrating, slow-moving H_BH_C molecule that has insufficient kinetic energy to escape the potential energy well, leading to an unsuccessful exchange reaction. 6D) The approach of an H_A atom to a vibrating, slow-moving H_BH_C molecule that has insufficient kinetic energy to escape the potential energy well, leading to an unsuccessful exchange reaction. (CC BY-NC; Ümit Kaya via LibreTexts)

The Exchange Reaction F + D_2 ⇒ DF + D

When modeling the potential energy for the reaction

$$\mathrm{F\,(g) + D_2\,(g) \longrightarrow DF\,(g) + D\,(g)}$$

it is useful to differentiate between the two deuterium atoms, so we can designate them as D_A and D_B. Doing so allows us to determine how the potential energy of the pre-reaction system is affected by the F to D_A distance $R_{\mathrm{D}_A\mathrm{F}}$ and the D_A to D_B distance $R_{\mathrm{D}_A\mathrm{D}_B}$ (figure 30.10.7).

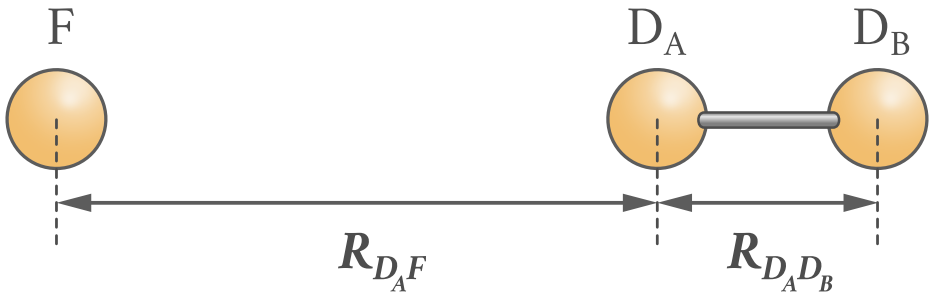


Figure 30.10.7: Defining the distances $R_{\mathrm{D}_A\mathrm{F}}$ and $R_{\mathrm{D}_A\mathrm{D}_B}$ (CC BY-NC; Ümit Kaya via LibreTexts)

As the F atom more closely approaches the D_2 molecule, the interactions between these particles begin to affect the potential energy of the system. There are many possible potential energy pathways that the reaction could follow. Figure 30.10.8 shows the energy contour map for three possible reaction pathways:

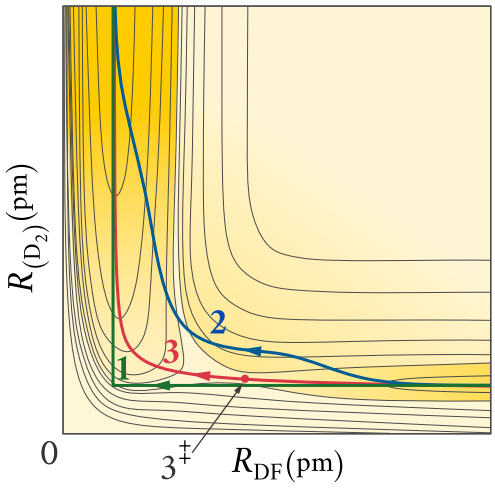


Figure 30.10.8: Three possible reaction pathways for the $\mathrm{F\,(g) + D_2\,(g) \longrightarrow DF\,(g) + D}$ reaction. (CC BY-NC; Ümit Kaya via LibreTexts)

In pathway 1, the $\mathrm{D_2}$ bond length $R_{\mathrm{D}_A\mathrm{D}_B}$ is held constant as the distance $R_{\mathrm{D}_A\mathrm{F}}$ decreases. This type of interaction would lead to a continually increasing potential energy for the system as the F atom moves closer and closer to the $\mathrm{D_2}$ molecule. Eventually, the new $\mathrm{D}_A\mathrm{F}$ molecule would form, and the D_B atom would break off and would move farther and farther away.

Pathway 2 shows a second possible reaction pathway in which the $\mathrm{D_2}$ bond length $R_{\mathrm{D}_A\mathrm{D}_B}$ increases even though the F atom is still relatively far away. This pathway is unlikely because it requires a great deal of potential energy to stretch the $\mathrm{D_2}$ bond before the attractive force from the F atom influences this bond lengthening.

As the particles travel along Pathway 3, the reactants still must pass through a potential energy maximum at the saddle point, but this local maximum is the lowest energy barrier separating reactants from products. As noted above, this saddle point is called the transition state structure (designated by the red dot in pathway 3, labeled as $3^{\ddagger}$). This is the structure that is equally poised to return to the reactants or move forward to form products. Pathway 3 is the minimum energy pathway, and thus the one most likely to be followed during a successful reaction.

If we were to plot the potential energy curve for the reaction pathway along the minimum energy pathway, we would get the familiar potential energy curve of a reaction similar to that shown in Figure 30.10.9.

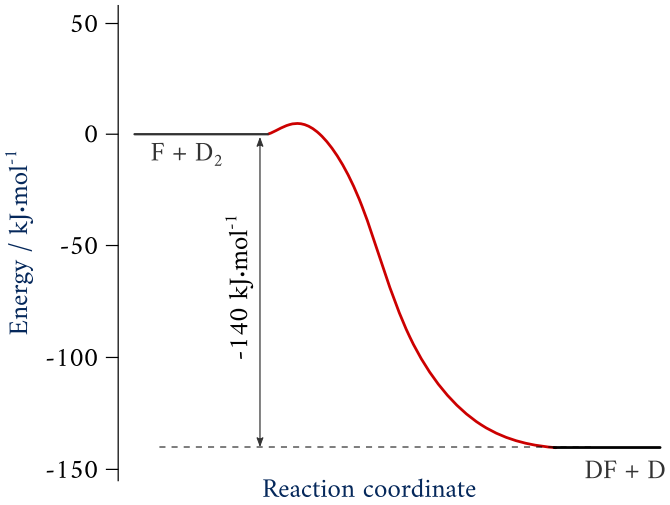


Figure 30.10.9: This graph shows the potential energy relationships for the reaction $\mathrm{F + D_2 \longrightarrow DF + D}$. The activation energy for the forward reaction is about 6 kJ/mol. The difference in potential energy between the reactants and the products is $D_e(\mathrm{D_2}) - D_e(\mathrm{DF})$. The curve's peak represents the transition state. (CC BY-NC; Ümit Kaya via LibreTexts)

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30.E: Gas-Phase Reaction Dynamics (Exercises)

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31: SOLIDS AND SURFACE CHEMISTRY

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31.1: The Unit Cell is the Fundamental Building Block of a Crystal

The regular three-dimensional arrangement of atoms or ions in a crystal is usually described in terms of a space lattice and a unit cell. To see what these two terms mean, let us first consider the two-dimensional patterns shown in Figure 31.1.1. We can think of each of these three structures as a large number of repetitions in two directions. Each light purple parallelogram represents one unit cell. Three valid unit cells and one invalid unit cell for the pattern of light and dark dots are shown.

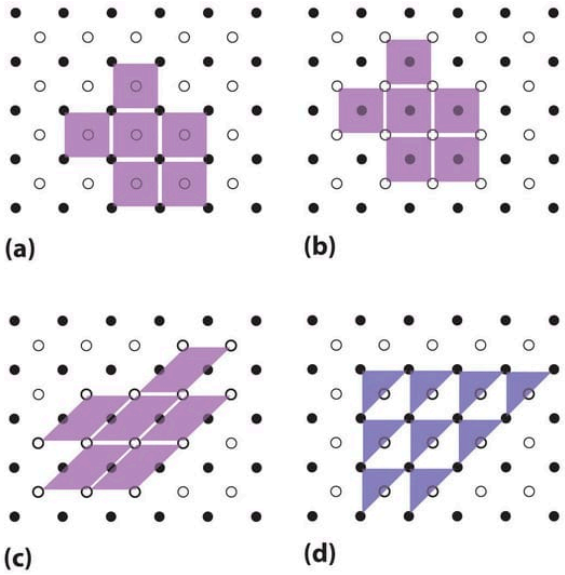


Figure 31.1.1: Unit Cells in Two Dimensions. (a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern. (CC BY-NC-SA; anonymous)

Finding the unit cell in a three-dimensional crystal structure can be a challenge. Figure 31.1.2 shows three representations of one class of three-dimensional structures: the three types of cubic unit cells. The black lines and gray spheres in the top right corner of the bottom pictures show one unit cell within a larger collection of unit cells.

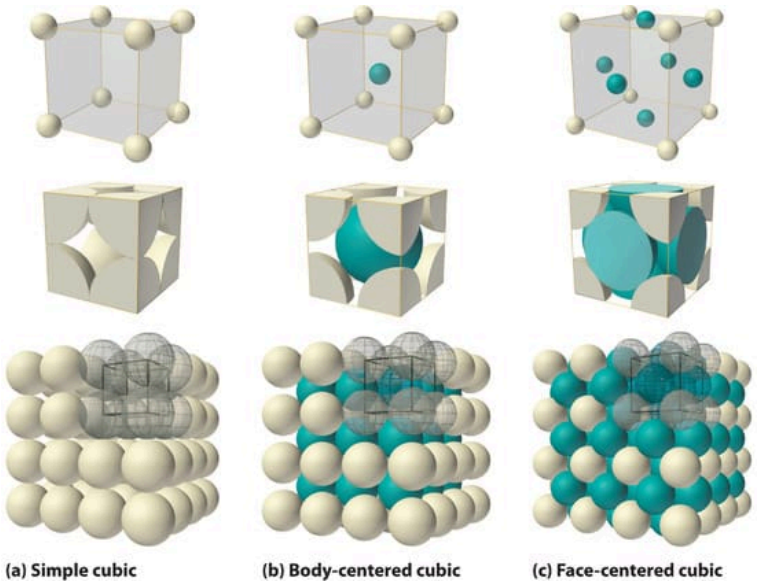


Figure 31.1.2: The Three Kinds of Cubic Unit Cell. For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells. (CC BY-NC-SA; anonymous)

Figure 31.1.3 illustrates the space lattice and the unit cell for a real three-dimensional crystal structure—that of sodium chloride.

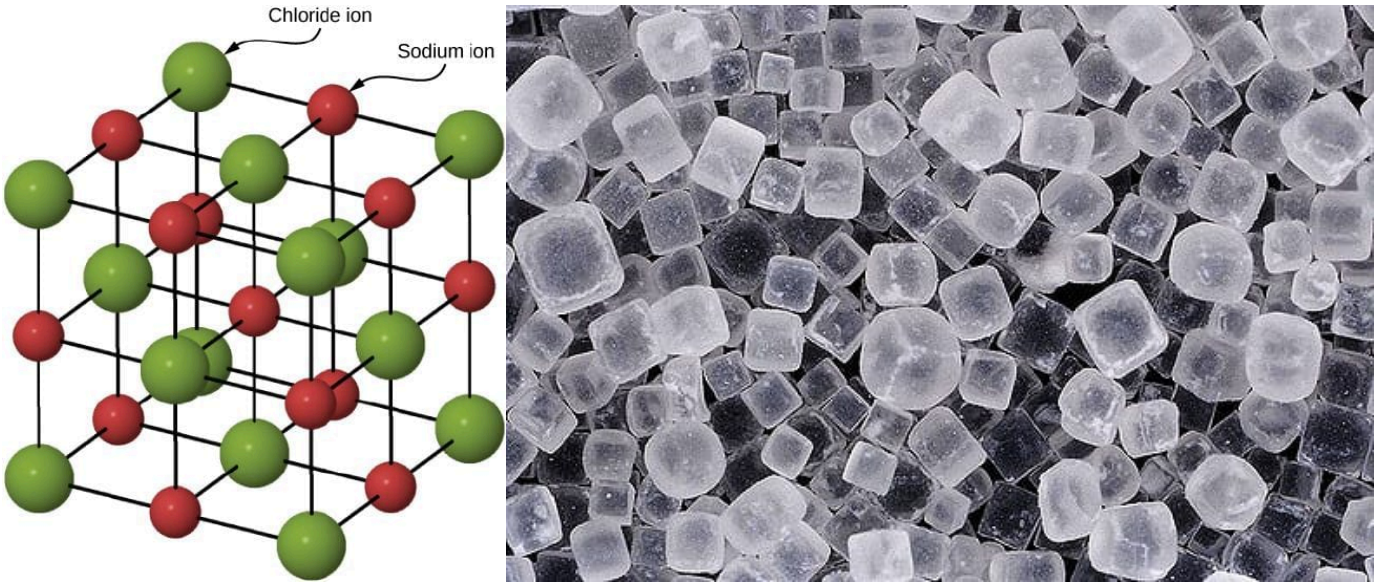


Figure 31.1.3: (left) The crystal lattice and unit cell of a crystal of sodium chloride. Structure of the sodium chloride crystal. The sodium and chloride ions are around in a face-centered cubic (FCC) structure. Sodium ions, Na^+, are shown in red. Chloride ions, Cl^-, are shown in green. (right) The macroscopic image on the right shows salt cubes, which demonstrate the cubic unit cell of NaCl (It doesn't always turn out this way. Because crystal growth is a complex process it is not guaranteed that the macroscopic crystal structure matches the unit cell). (CC BY; OpenStax)

A unit cell for this structure is a cube whose comers are all occupied by sodium ions. Alternatively, the unit cell could be chosen with chloride ions at the corners. The unit cell of sodium chloride contains *four* sodium ions and *four* chloride ions. In arriving at such an answer we must bear in mind that many of the ions are shared by several adjacent cells (part *c* of Figure 31.1.2 shows this well). Specifically, the sodium ions at the centers of the square faces of the cell are shared by two cells, so that only half of each lies within the unit cell. Since there are six faces to a cube, this makes a total of three sodium ions. In the middle of each edge of the unit cell is a chloride ion which is shared by four adjacent cells and so counts one-quarter. Since there are twelve edges, this makes three chloride ions. At each comer of the cube, a sodium ion is shared by eight other cells. Since there are eight comers, this totals to one more sodium ion. Finally, there is a chloride ion in the body of the cube unshared by any other cell. The grand

total is thus four sodium and four chloride ions.

A general formula can be derived from the arguments just presented for counting *N*, the number of atoms or ions in a unit cell. It is

$$N = N_{\text{body}} + \frac{N_{\text{face}}}{2} + \frac{N_{\text{edge}}}{4} + \frac{N_{\text{corner}}}{8}$$

Crystal Systems

Unit cells need not be cubes, but they *must* be parallel-sided, three-dimensional figures. A general example is shown in Figure 31.1.4. Such a cell can be described in terms of the lengths of three adjacent edges, *a, b*, and *c*, and the angles between them, α, β, and γ.

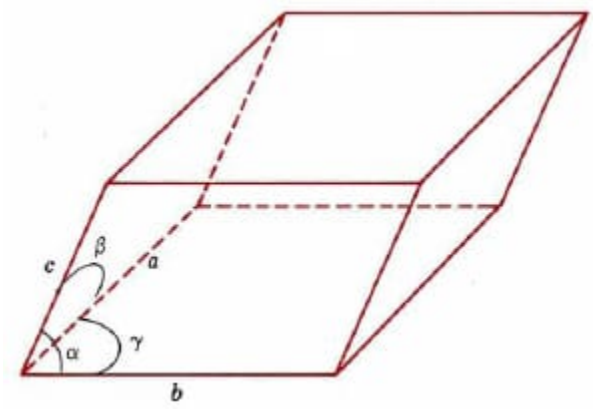


Figure 31.1.4 A generalized unit cell with sides a, b, and c, and angles α, β, and γ.

Crystals are usually classified as belonging to one of fourteen Bravais lattices, depending on the shape of the unit cell and the number of atoms in the unit cell. These fourteen systems are shown in Figure 31.1.5 below. Figure 31.1.6 lists the details about each of the lattice systems.

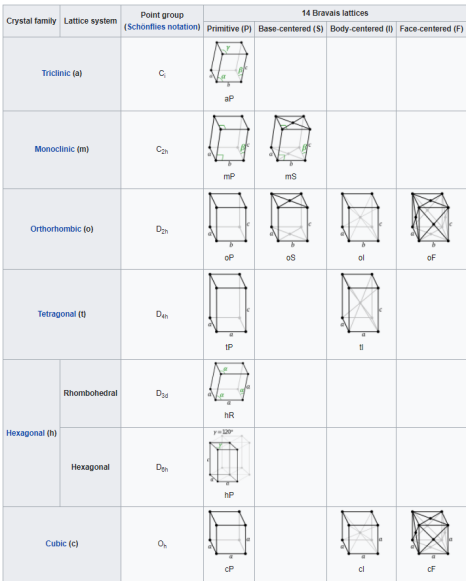


Figure 31.1.5: The seven lattice systems and fourteen Bravais lattices. (Wikipedia contributors. (2021, September 2). Bravais lattice. In Wikipedia, The Free Encyclopedia. Retrieved 01:22, October 3, 2021, from https://en.Wikipedia.org/w/index.php?title=Bravais_lattice&oldid=1042012012)

Crystal family	Lattice system	Volume	Axial distances (edge lengths)[7]	Axial angles[7]	Corresponding examples
Triclinic		$abc\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma}$	(All remaining cases)		$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, H_3BO_3
Monoclinic		$abc\sin\beta$	$a \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	Monoclinic sulphur, $Na_2SO_4 \cdot 10H_2O$, $PbCrO_3$
Orthorhombic		abc	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Tetragonal		a^2c	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
Hexagonal	Rhombohedral	$a^3\sqrt{1-3\cos^2\alpha+2\cos^3\alpha}$	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), cinnabar (HgS)
	Hexagonal	$\frac{\sqrt{3}}{2}a^2c$	$a = b$	$\alpha = \beta = 90°, \gamma = 120°$	Graphite, ZnO, CdS
Cubic		a^3	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, zinc blende, copper metal, KCl, Diamond, Silver

Figure 31.1.6: The six lattice parameters are the three axial distances ($a, b, \text{and } c$) and the three axial angles ($\alpha, , \beta, \text{and } \gamma$). (Wikipedia contributors. (2021, September 2). Bravais lattice. In Wikipedia, The Free Encyclopedia. Retrieved 01:22, October 3, 2021, from https://en.Wikipedia.org/w/index.php?title=Bravais_lattice&oldid=1042012012)

The simplest lattice system is the cubic system, in which all edges of the unit cell are equal and all angles are 90°. The tetragonal and orthorhombic systems also feature rectangular cells, but the edges are not all equal. In the remaining systems, some or all of the angles are not 90°. The least symmetrical is the triclinic, in which no edges are equal and no angles are equal to each other or to 90°.

Close-Packed Systems

An important class of crystal structures is found in many metals and also in the solidified noble gases where the atoms (which are all the same) are packed together as closely as possible. Most of us are familiar with the process of packing spheres together, either from playing with marbles or BB's as children or from trying to stack oranges or other round fruit into a pyramid. On a level surface we can easily arrange a collection of spheres of the same size into a very compact hexagonal layer in which each sphere is touching six of its fellows, as seen Figure 31.1.7.

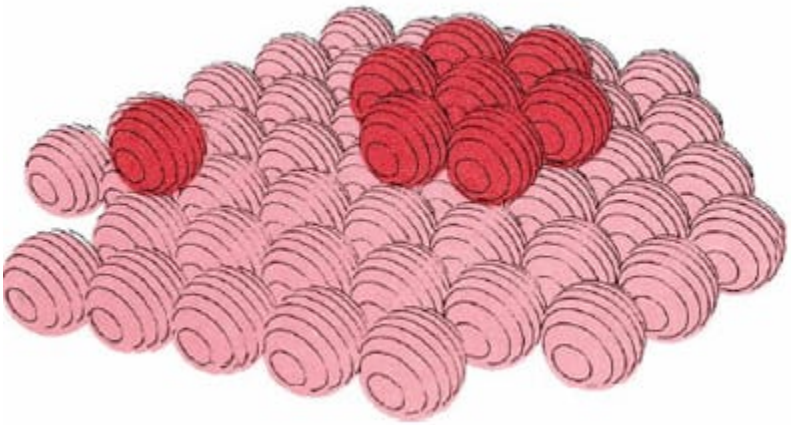


Figure 31.1.7: Spheres can be packed closely together in a hexagonal form, so each sphere is being touched by 6 other spheres on the same level. This is a closest-packed structure.

Then we can add a second layer so that each added sphere snuggles into a depression between three spheres in the layer below. Within this second layer each sphere also contacts six neighbors, and the layer is identical to the first one. It appears that we can add layer after layer indefinitely, or until we run out of spheres. Each sphere will be touching *twelve* of its fellows since it is surrounded by six in the same plane and nestles among three in the plane above and three in the plane below. We say that each sphere has a **coordination number** of 12. It is impossible to make any other structure with a larger coordination number, that is, to pack more spheres within a given volume. Accordingly the structure just described is often referred to as a **close-packed structure**.

It turns out that there are two ways to create a close-packed structure. These two ways are shown in Figure 31.1.8.

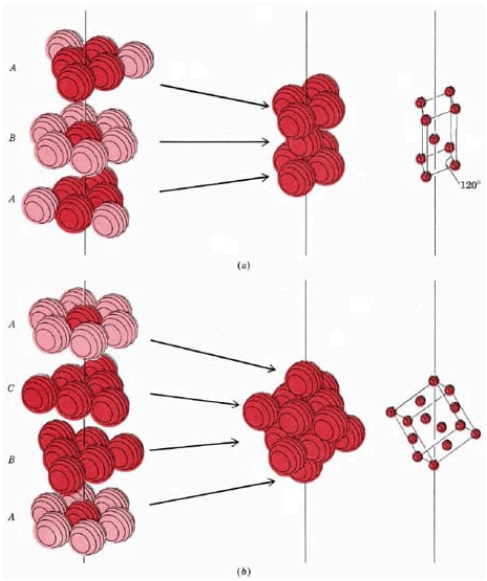


Figure 31.1.8. A closest-packed structure can be formed in two ways. Part a shows packing where two different layer types are used. Part b shows packing with 3 distinct layers.

In part ***a*** of Figure 31.1.8 the first layer of spheres has been labeled *A* and the second labeled *B* to indicate that spheres in the second layer are not directly above those in the first. The third layer is directly above the first, and so it is labeled *A*. If we continue in the fashion shown, adding alternately *A*, then *B*, then *A* layers, we obtain a structure whose unit cell (shown in part *a*) has two equal sides with an angle of 120° between them. Other angles are 90°, and so the cell belongs to the hexagonal crystal system. Hence this structure is called **hexagonal close packed** (hcp).

In part ***b*** of Figure 31.1.8 the first layer of spheres has been labeled *A* and the second labeled *B* to indicate that spheres in the second layer are not directly above those in the first. In this packing system, the third layer is labeled C because it is **not** directly above the first or the second layer; it has its own unique orientation. If we continue in the fashion shown, adding alternately *A*, then *B*, then *C* layers, we obtain a structure whose unit cell (shown in part ***b***) that has three equal sides with all angles at 90°, and so the cell belongs to the cubic crystal system. Hence this structure is called **cubic close packed** (ccp). To repeat, in both the hexagonal close-packed and the cubic close-packed structures each sphere has 12 nearest neighbors.

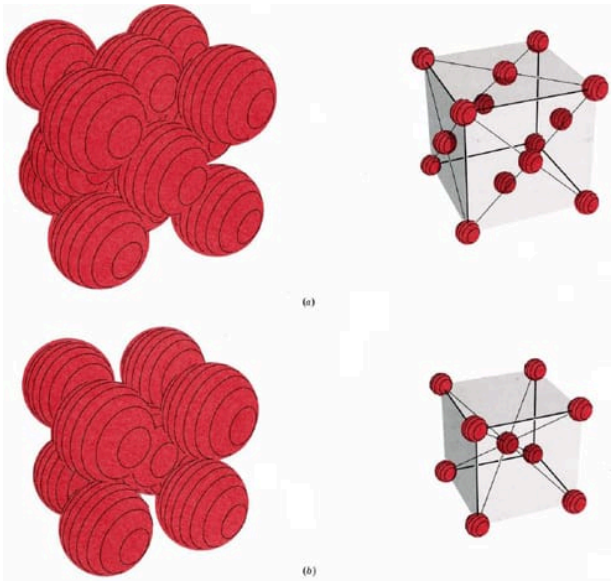


Figure 31.1.9 **.** Part a shows the unit cell for the cubic close-packed or face-centered cubic lattice. Part b shows the unit cell for the body-centered cubic lattice.

Figure 31.1.9 shows two types of cubic lattices, the face-centered cubic and the body-centered cubic. The unit cell of a **body-centered cubic** (bcc) crystal is similar to the fcc structure except that, instead of spheres in the faces, there is a single sphere in

the center of the cube. This central sphere is surrounded by eight neighbors at the corners of the unit cell, giving a coordination number of 8. Hence the bcc structure is not as compactly packed as the close-packed structures which had a coordination number 12.

Example 31.1.1: Unit Cells

Count the number of spheres in the unit cell of (a) a face-centered cubic structure, and (b) a body-centered cubic structure.

Solution

Referring to Figure 31.1.9 and using the equation:

$$N = N_{\text{body}} + \frac{N_{\text{face}}}{2} + \frac{N_{\text{edge}}}{4} + \frac{N_{\text{corner}}}{8}$$

we find

a)

$$N = N_{\text{body}} + \frac{N_{\text{face}}}{2} + \frac{N_{\text{edge}}}{4} + \frac{N_{\text{corner}}}{8} = 0 + \frac{6}{2} + 0 + \frac{8}{8} = 4$$

b)

$$N = 1 + 0 + 0 + \frac{8}{8} = 2$$

Example 31.1.2: Crystal Forms

Silicon has the same crystal structure as diamond. Techniques are now available for growing crystals of this element which are virtually flawless. Analysis of some of these perfect crystals found the side of the unit cell to be 543.102064 pm long. The unit cell is a cube containing eight Si atoms, but is only one of the simple cubic cells discussed already. From the isotope make up, molar mass and density of the crystals, it was determined that one mole of Si in this crystal form has a volume of 12.0588349×10^{-6} m^3. Determine N_A from this data.

Solution This problem uses knowledge of silicon crystal structure to determine N_A. From the edge length, we can obtain the volume of the cubic unit cell. We know that the unit contains eight atoms, and since we know the volume of one mole, we can calculate N_A, with the Avogadro constant defined as the number of particles per unit amount of substance.

$$N_A = \frac{N * V_{\text{m}}}{V_{\text{unit cell}}} = \frac{8 \times 12.0588349 \times 10^{-6}\text{m}^3}{(543.102064 \times 10^{-12}\text{m})^3} = 6.02214179 \times 10^{23}$$

The values used to determine this value were taken from crystals using X Ray Crystal Density(XRCD), to determine side length. These values were used in the most recent analysis published by the Committee on Data for Science and Technology(CODATA)[1], which standardizes definitions of important scientific constants and units. The value you just calculated is therefore the most accurate determination of Avogadro's constant as of 2007.

It is important to note that the spheres in these models can represent atoms, monatomic ions, polyatomic ions, molecules, or a collection of molecules.

1. ↑ Mohr, P.J., Taylor, B.N., and D. B. Newell. "CODATA Recommended Values of the Fundamental Physical Constants:fckLR2006." National Institute of Standards and Technology. December 28, 2007. http://physics.nist.gov/cuu/

Example 31.1.1

Copper has a density of 8.930 $\frac{grams}{cm^3}$ at 20°C. The molar mass of copper is 63.55 $\frac{grams}{mole}$. Copper crystallizes as a face-centered cubic lattice. Calculate the crystallographic radius of a copper atom.

Solution

By looking at figure 31.1.2 c, you can determine that there are 4 atoms per unit cell. Thus, the mass of a unit cell is

$$\frac{(63.55\,grams/mole)(4\,atoms/cell)}{6.022x10^{23}\,atoms/mole} = 4.221x10^{-22}\,grams/cell$$

The volume of the unit cell is

$$V_{cell} = \frac{4.221x10^{-22}\,grams/cell}{8.930\,grams/cm^3} = 4.727x10^{-23}\,cm^3$$

The unit cell is cubic, therefore all sides are the same length, and $V_{cell} = a^3$

$$a = V_{cell}^{1/3} = 3.616x10^{-8}cm = 361.6\,pm$$

As shown in figure 31.1.2 c, the diagonal across the face of the unit cell has a length of 4 times the radius of a copper atom. Thus, the lengtyh of the face diagonal is $\sqrt{2}a$, which equals $\sqrt{2}(361.6\ \mathrm{pm})$ = 511.4 pm. One fourth of 511.4 pm is 127.8 pm.

Contributors and Attributions

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- Tom Neils (Grand Rapids Community College)

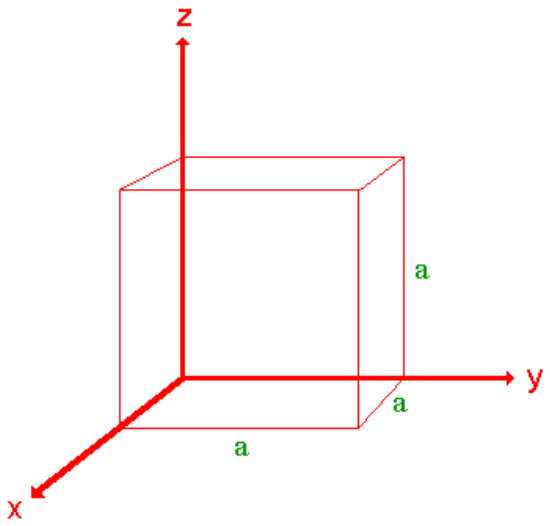
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31.2: The Orientation of a Lattice Plane is Described by its Miller Indices

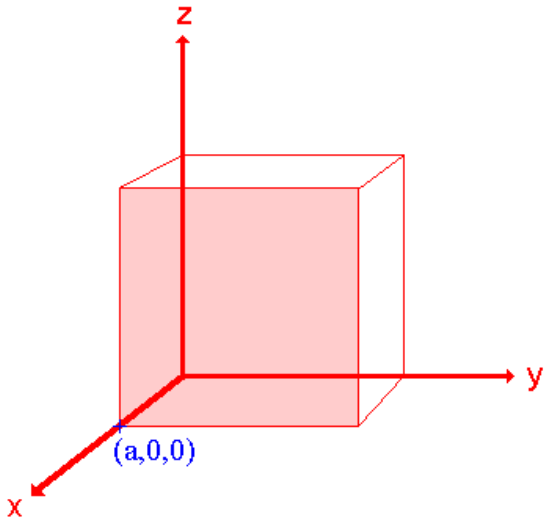
The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid. The application of a set of rules leads to the assignment of the Miller Indices (*hkl*), which are a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

Assigning Miller Indices for a cubic crystal system

The following treatment of the procedure used to assign the Miller Indices is a simplified one (it may be best if you simply regard it as a "recipe") and only a **cubic** crystal system (one having a cubic unit cell with dimensions *a* x *a* x *a*) will be considered.



The procedure is most easily illustrated using an example so we will first consider the following surface/plane:



Step 1: *Identify the intercepts on the x- , y- and z- axes.*

In this case the intercept on the x-axis is at $x = a$ (at the point $(a,0,0)$), but the surface is parallel to the *y*- and *z*-axes - strictly therefore there is no intercept on these two axes but we shall consider the intercept to be at infinity (∞) for the special case where the plane is parallel to an axis. The intercepts on the *x*- , *y*- and *z*-axes are thus

Intercepts: ***a*** **, ∞ , ∞**

Step 2: Specify the intercepts in fractional co-ordinates

Co-ordinates are converted to fractional co-ordinates by dividing by the respective cell-dimension - for example, a point (x,y,z) in a unit cell of dimensions *a* x *b* x *c* has fractional co-ordinates of (x/a , y/b , z/c). In the case of a cubic unit cell each co-ordinate will simply be divided by the cubic cell constant , *a* . This gives

Fractional Intercepts: ***a/a*** **, ∞*/a*, ∞*/a*** i.e. **1 , ∞ , ∞**

Step 3: Take the reciprocals of the fractional intercepts

This final manipulation generates the Miller Indices which (by convention) should then be specified without being separated by any commas or other symbols. The Miller Indices are also enclosed within standard brackets (....) when one is specifying a unique surface such as that being considered here.

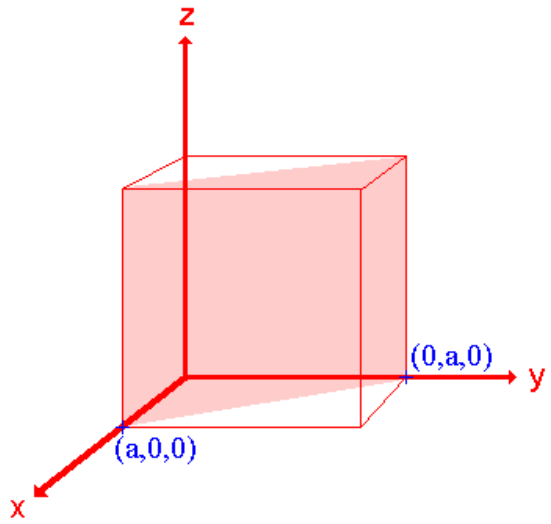
The reciprocals of 1 and ∞ are 1 and 0 respectively, thus yielding

Miller Indices: **(100)**

So the surface/plane illustrated is the (100) plane of the cubic crystal.

Other Examples

1. The (110) surface



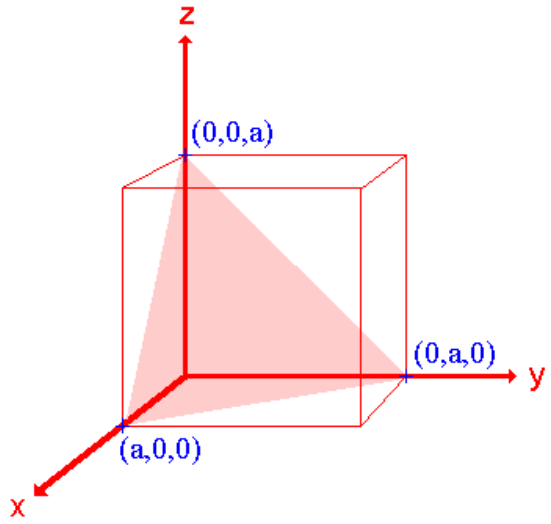
Assignment

Intercepts: *a* , *a* , ∞

Fractional intercepts: 1 , 1 , ∞

Miller Indices: **(110)**

2. The (111) surface



Assignment

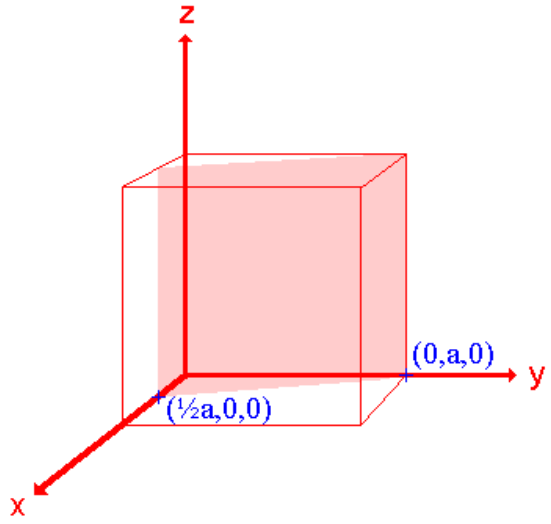
Intercepts: *a* , *a* , *a*

Fractional intercepts: 1 , 1 , 1

Miller Indices: **(111)**

The (100), (110) and (111) surfaces considered above are the so-called low index surfaces of a cubic crystal system (the "low" refers to the Miller indices being small numbers - 0 or 1 in this case). These surfaces have a particular importance but there an infinite number of other planes that may be defined using Miller index notation. We shall just look at one more ...

3. The (210) surface



Assignment

Intercepts: ½ *a* , *a* , ∞

Fractional intercepts: ½ , 1 , ∞

Miller Indices: **(210)**

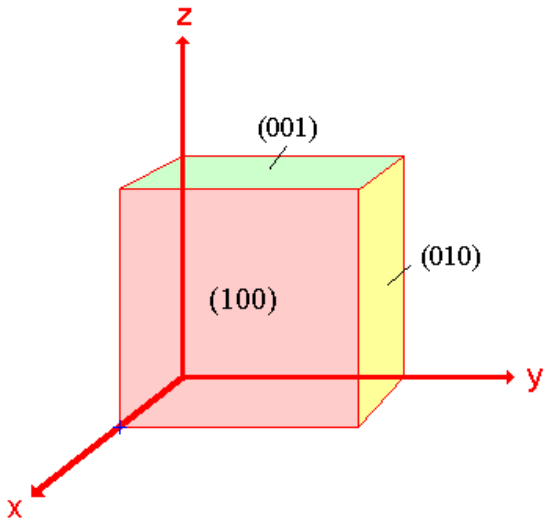
Further notes:

i. in some instances the Miller indices are best multiplied or divided through by a common number in order to simplify them by, for example, removing a common factor. This operation of multiplication simply generates a parallel plane which is at a different distance from the origin of the particular unit cell being considered. e.g. (200) is transformed to (100) by dividing through by 2 .
ii. if any of the intercepts are at negative values on the axes then the negative sign will carry through into the Miller indices; in such cases the negative sign is actually denoted by overstriking the relevant number. e.g. (00 -1) is instead denoted by $(00\bar{1})$.
iii. in the *hcp* crystal system there are four principal axes; this leads to four Miller Indices e.g. you may see articles referring to an *hcp* (0001) surface. It is worth noting, however, that the intercepts on the first three axes are necessarily related and not completely independent; consequently the values of the first three Miller indices are also linked by a simple mathematical

relationship.

What are symmetry-equivalent surfaces?

In the following diagram the three highlighted surfaces are related by the symmetry elements of the cubic crystal - they are entirely equivalent.



In fact, there are a total of 6 faces related by the symmetry elements and equivalent to the (100) surface - any surface belonging to this set of symmetry-related surfaces may be denoted by the more general notation {100} where the Miller indices of one of the surfaces is instead enclosed in curly-brackets.

Final important note: in the cubic system the (*hkl*) plane and the vector [*hkl*], defined in the normal fashion with respect to the origin, are normal to one another **but** this characteristic is unique to the cubic crystal system and does **not** apply to crystal systems of lower symmetry.

The perpendicular distance between planes

The symbol d is used to designate the perpendicular spacing between adjacent planes. Table $31.2.1$ shows the equations for calculating the value of d for four of the seven crystal systems.

Table $31.2.1$*: Equations for calculating the spacing between adjacent planes,* d

System	Equation for d
cubic	$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$
tetragonal	$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$
hexagonal	$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$
orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

Example 31.2.1

If a tetragonal unit cell has dimensions $a = b = 501$ pm and $c = 451$ pm, calculate the perpendicular distance between the 111 planes.

Solution

For a tetragonal unit cell

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}.$$

Thus,

$$\begin{aligned}\frac{1}{d^2} &= \frac{1+1}{(501\,\text{pm})^2} + \frac{1}{(451\,\text{pm})^2} \\ &= 1.29 \times 10^{-5}\,\text{pm}^{-2}.\end{aligned}$$

Then $d = 279\ \text{pm}$

Contributors and Attributions

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31.3: The Spacing Between Lattice Planes Can Be Determined from X-Ray Diffraction Measurements

X-ray crystallography is an instrumental technique used to determine the arrangement of atoms of a crystalline solid in three-dimensional space. This technique takes advantage of the interatomic spacing of most crystalline solids by employing them as a diffraction grating for x-ray light, which has wavelengths on the order of 1 angstrom (10^{-8} cm).

Introduction

In 1895, Wilhelm Rontgen discovered x- rays. The nature of x- rays, whether they were particles or electromagnetic radiation, was a topic of debate until 1912. If the wave idea was correct, researchers knew that the wavelength of this light would need to be on the order of 1 Angstrom (Å) (10^{-8} cm). Diffraction and measurement of such small wavelengths would require a grating with spacing on the same order of magnitude as the light.

In 1912, Max von Laue, at the University of Munich in Germany, postulated that atoms in a crystal lattice had a regular, periodic structure with interatomic distances on the order of 1 Å. Without having any evidence to support his claim on the periodic arrangements of atoms in a lattice, he further postulated that the crystalline structure could be used to diffract x-rays, much like a grating in an infrared spectrometer can diffract infrared light. His postulate was based on the following assumptions: the atomic lattice of a crystal is periodic, x- rays are electromagnetic radiation, and the interatomic distance of a crystal is on the same order of magnitude as x-ray light. Laue's predictions were confirmed when two researchers: Friedrich and Knipping, successfully photographed the diffraction pattern associated with the x-ray radiation of crystalline $CuSO_4 \cdot 5H_2O$. The science of x-ray crystallography was born.

The arrangement of the atoms needs to be in an ordered, periodic structure for them to diffract the x-ray beams. A set of mathematical calculations is then used to produce a diffraction pattern that is characteristic of the particular arrangement of atoms in that crystal. X-ray crystallography remains to this day the primary tool used by researchers in characterizing the structure and bonding of many compounds.

Diffraction

Diffraction is a phenomenon that occurs when light encounters an obstacle. The waves of light can either bend around the obstacle or, in the case of a slit, can travel through the slits. The resulting diffraction pattern will show areas of constructive interference, where two waves interact in phase, and destructive interference, where two waves interact out of phase. Calculation of the phase difference can be explained by examining Figure $31.3.1$ below.

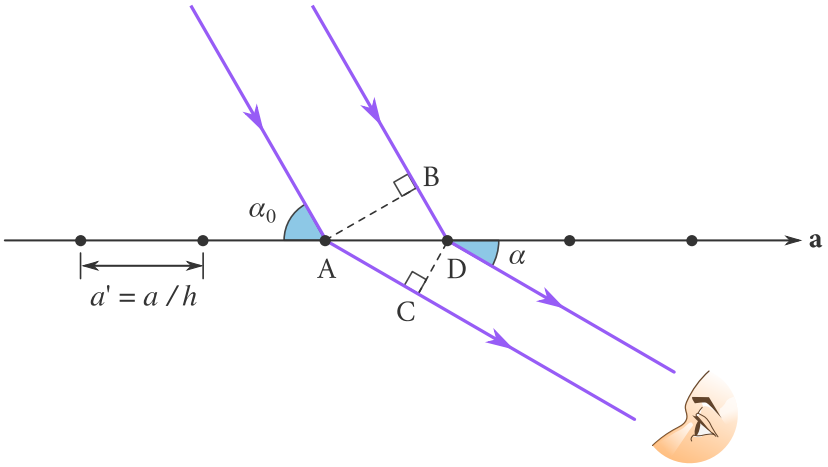


Figure 31.3.1: This figure shows the angular relationship of x-rays scattered by particles lying along the **a** axis in a crystalline solid. The incoming rays enter the crystal at an angle of α_0, the angle of incidence, and scatter from the lattice points at an angle of α. (CC BY-NC; Ümit Kaya via LibreTexts)

In the figure above, two parallel waves are striking a grating at an angle α_o. The incident wave on the right travels farther than the one on the left by a distance of BD before reaching the grating. The scattered wave depicted below the gradient on the left, travels farther than the scattered wave on the right by a distance of AC. So the total path difference between the left wave and the right wave is AC - BD. To observe a wave of high intensity (one created through constructive interference), the difference AC - BD must equal an integer number of wavelengths to be observed at the angle α, AC - BD = $n\lambda$, where λ is the wavelength of the light. Applying some basic trigonometric properties, the following two equations can be shown about the lines:

$$BD = x\cos(\alpha_o)$$

and

$$AC = x\cos(\alpha)$$

where x is the distance between the points where the diffraction repeats. Combining the two equations,

$$x(\cos\alpha - \cos\alpha_o) = n\lambda$$

Rotating Crystal Method

To describe the periodic, three dimensional nature of crystals, the Laue equations are employed:

$$a(\cos\alpha - \cos\alpha_o) = nh\lambda \tag{31.3.1}$$

$$b(\cos\beta - \cos\beta_o) = nk\lambda \tag{31.3.2}$$

$$c(\cos\gamma - \cos\gamma_o) = nl\lambda \tag{31.3.3}$$

where a, b, and c are the three axes of the unit cell, α_o, β_o, γ_o are the angles of incident radiation, and α, β, and γ are the angles of the diffracted radiation. The n term refers to the order of the reflections. If n = 1, then the reflections are first-order reflections. If n = 2, then the reflections are second-order reflections.

A diffraction signal (constructive interference) will arise when h, k, and l are integer values. The rotating crystal method employs these equations. X-ray radiation is shown onto a crystal, surrounded by a cylindrical film, as it rotates around one of its unit cell axis. The beam strikes the crystal at a 90-degree angle. Using equation 1 above, we see that if α_o is 90 degrees, then $\cos\alpha_o = 0$. For the equation to hold true, we can set h=0, given that α= 90. The above three equations will be satisfied at various points as the crystal rotates. This gives rise to a diffraction pattern (shown in figure 31.3.2 as multiple h values). The cylindrical film is then unwrapped and developed.

The following equation can be used to determine the length of the axis around which the crystal was rotated:

$$a = \frac{nh\lambda}{\cos(\tan^{-1}(y/r))}$$

where a is the length of the axis, y is the distance from $h = 0$ to the h of interest, r is the radius of the film (or the distance from the center of the crystal to the detector), and λ is the wavelength of the x-ray radiation used.

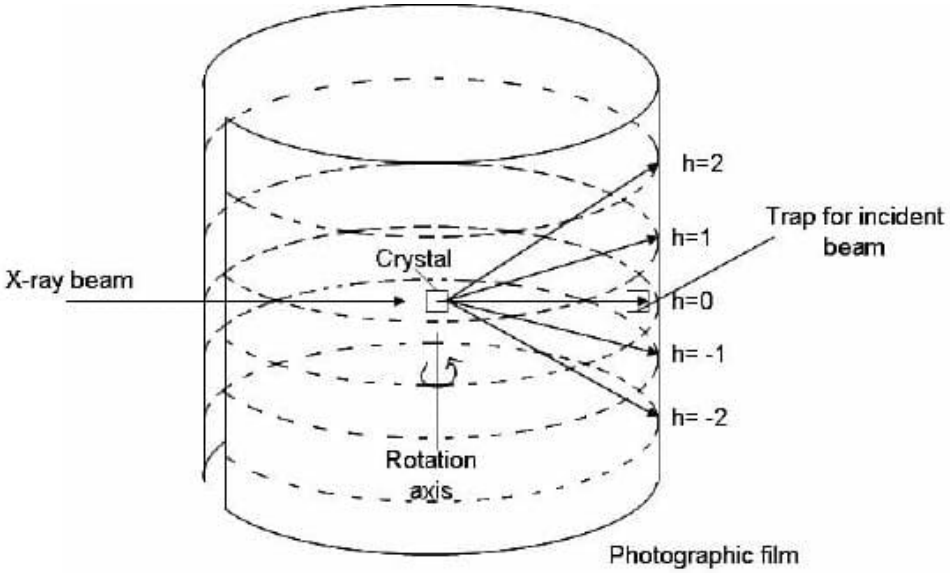


Figure 31.3.2: The x-ray diffraction pattern from the h00 planes of a crystal mounted such that the incoming x-rays are perpendicular to the **a** axis of the crystal.

Modern diffractometers use electronic scintillation detectors or area detectors that act as a sort of electronic "film." With these detectors, the diffraction data can be sent directly to a computer and analyzed much more rapidly than photographic film. Figure 31.3.3 shows a mounted crystal and its x-ray diffraction pattern.Example 31.3.1

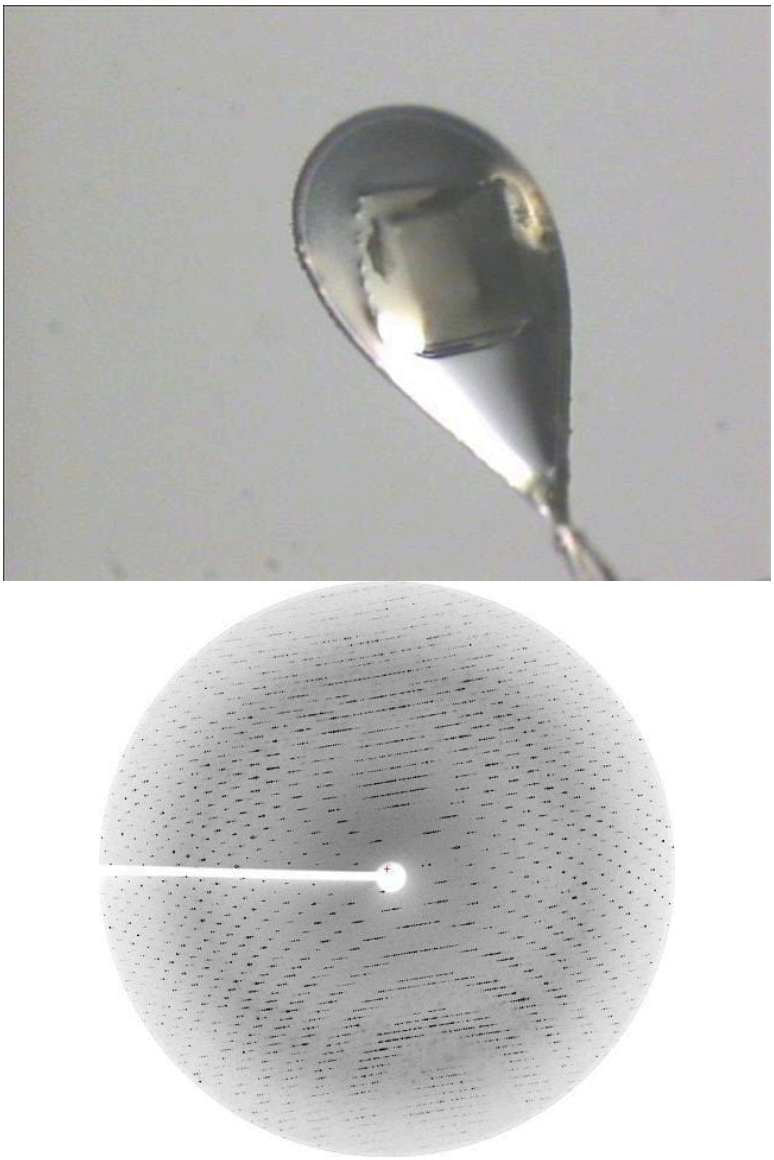


Figure 31.3.3: Top) This is a picture of a protein crystal mounted on a loop (UC Davis Structural Biology Lab);

Bottom) This is a diffraction pattern created from the APS Kinase D63N Mutant of the above crystal (UC Davis Structural Biology Lab)

For a detector with a flat surface, the reflections from a primitive cubic crystal would hit the surface in a pattern similar to that shown in figure $PageIndex4$

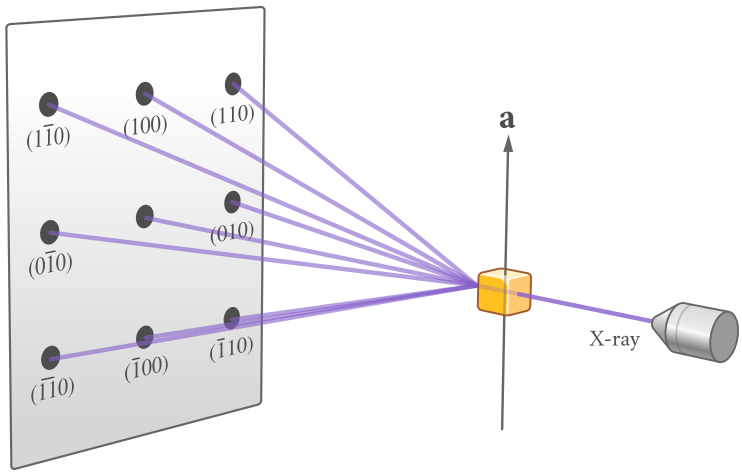


Figure 31.3.1: A portion of the reflection pattern from some hkl planes of a primitive cubic crystal. The crystal is aligned so that the incoming X-ray beam is perpendicular to the **a** axis. This same arrangement is used for the crystal in Example 31.3.1 below. (CC BY-NC; Ümil Kaya via LibreTexts)

Example 31.3.1

Suppose that you wish to measure the length of a unit cell a of a crystal that has primitive cubic unit cell. A close up of the experimental set up is shown in Figure 31.3.4. The crystal is aligned so that the incoming x-rays are perpendicular to the **a**-axis.The distance between the center of the crystal and the detector surface is 5.50 cm. The distance between the detected spots scattered by the 000 planes and the 100 planes is 2.50 cm, and it is scattered at an angle of α. The wavelength of light from the copper x-ray source is 154.4 pm. Determine the length of the unit cell along the **a**-axis.

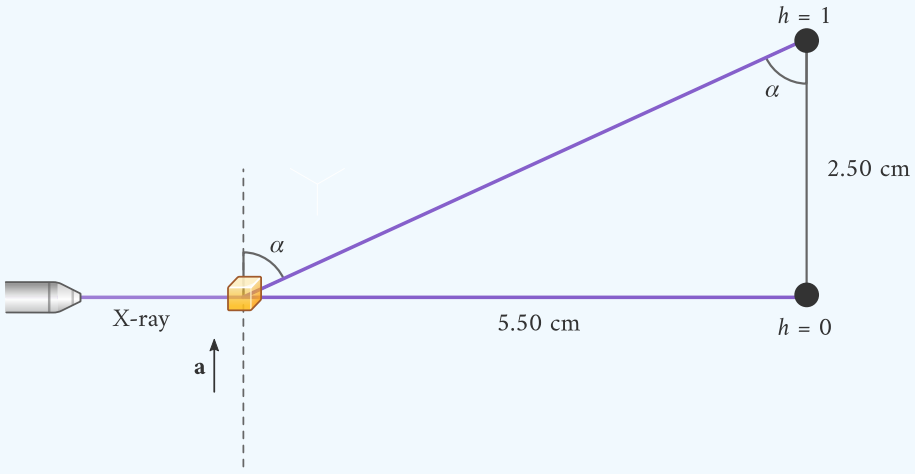


Figure 31.3.4: An expanded view of x-rays undergoing scattering from the 100 planes at an angle of α. (CC BY-NC; Ümit Kaya via LibreTexts)

Solution

The angle α can be determined by the fact that $\tan\alpha = \dfrac{5.50}{2.50}$. Thus $\tan^{-1}(2.2)$, gives α = 65.56. We can then find the length of **a** from equation 30.3.10

$$a = \frac{(1)(154.4\,pm)}{\cos(65.56)} = 373.2\ pm$$

Bragg's Law Applied to Crystals

A second way to analyze the x-ray diffraction is to use Bragg's law. Diffraction of an x-ray beam by crystalline solids occurs when the light interacts with the electron cloud surrounding the atoms of the solid. Because of the periodic crystalline structure of a solid, it is possible to describe it as a series of planes with an equal interplanar distance. As an x-ray beam hits the surface of the crystal at an angle θ, some of the light will be diffracted at that same angle away from the solid (Figure $31.3.5$). The remainder of the light will travel into the crystal and some of that light will interact with the second plane of atoms. Some of the light will be diffracted at an angle $theta$, and the remainder will travel deeper into the solid. This process will repeat for the many planes in the crystal. The x-ray beams travel different path lengths before hitting the various planes of the crystal, so after diffraction, the beams will interact constructively only if the path length difference is equal to an integer number of wavelengths (just like in the normal diffraction case above). In the figure below, the difference in path lengths of the beam striking the first plane and the beam striking the second plane is equal to BG + GF. So, the two diffracted beams will constructively interfere (be in phase) only if $BG + GF = n\lambda$. Basic trigonometry will tell us that the two segments are equal to one another with the interplanar distance times the sine of the angle θ. So we get:

$$BG = BC = d\sin\theta \tag{31.3.4}$$

Thus,

$$2d\sin\theta = n\lambda \tag{31.3.5}$$

This equation is known as Bragg's Law, named after W. H. Bragg and his son, W. L. Bragg; who discovered this geometric relationship in 1912. Bragg's Law relates the distance between two planes in a crystal and the angle of reflection to the x-ray wavelength. The x-rays that are diffracted off the crystal have to be in-phase in order to be observed. Only certain angles that satisfy the following condition will register:

$$\sin\theta = \frac{n\lambda}{2d} \tag{31.3.6}$$

For historical reasons, the resulting diffraction spectrum is represented as intensity vs. 2θ.

Example 31.3.1

Cesium metal has a body-centered cubic crystal structure with a unit cell length of 605.0 pm. Use the Bragg equation to determine the first two observed diffraction angles from the 110 planes when the wavelength of the x-rays is 154.4 pm.

Solution

From section 31.2.3, we found that the interplanar distance for cubic cells can be calculated using the equation

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

If we square equation 31.3.10 we get

$$\sin^2\theta = \frac{n^2\lambda^2}{4d^2}$$

Combining these two equations, we get

$$\sin^2\theta = \frac{n^2\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

The smallest diffraction angle occurs when $n = 1$

$$\sin^2\theta = \frac{(1^2)(154.4\ ,pm)^2}{4(605.0)^2}(1^2+1^2+0^2) = 0.03257$$

Thus, θ = 10.40°

The next largest diffraction angle occurs when $n = 2$

$$\sin^2\theta = \frac{(2^2)(154.4\ ,pm)^2}{4(605.0)^2}(1^2+1^2+0^2) = 0.1303$$

Thus, θ = 21.16°

In the next section, we will discuss the factors that determine the phase and the amplitude of the multiple scattered x-rays produced during diffraction.

References

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5. Actual experimentation done of APS Kinase D63N *Penicillium Chrysogenum*.

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31.4: The Total Scattering Intensity is Related to the Periodic Structure of the Electron Density in the Crystal

Systematic Absences

Diffraction data from a face-centered cubic crystal will be missing reflections (spots) from all *hkl* planes in which *h* + *k*, *h* + *l*, and *k* + *l* are odd numbers. The reason for these absent reflections is that the arrangement of the lattice points leads to total destructive interference of the diffracted X-rays. Although the lack of data may seem like a hindrance to determining a crystal structure, the systematic absence of reflections from specific families of planes actually reveals the presence of symmetry features in the crystal lattice that help identify the lattice type. Crystals with centering features (body-centered cels, face-centered cells, etc.), glide planes, and screw axes will produce diffraction patterns with systematic absences.

The Structure Factor

Systematic reflection absences, as well as variations in reflection intensity, are described mathematically by the structure factor, a mathematical function that incorporates all of the variables that affect how X-rays are scattered by the electrons of the atoms in the crystal lattice. (We do not concern ourselves with the effect of the nucleus on scattering because the mass of the nucleus is so large relative to the mass of an electron.)

The Atomic/Ionic Scattering Factor

The construction of a structure factor begins with the fundamental assumption that the total scattering intensity is related to the electron density of the atoms in the crystal. But the scattering also depends on the scattering angle and the wavelength of the radiation. To account for all of these parameters, an **atomic scattering factor**, f, has been developed:

$$f = 4\pi \int_0^\infty \rho(r) \frac{\sin\ kr}{kr} r^2\, dr$$

In this equation, r is the radius of an idealized spherical atom, $\rho(r)$ is the electron density of this idealized atom. Because the X-ray wavelength used in diffraction experiments is of similar size as the size of the atoms it scatters from, there will be interference among the waves scattered by the electrons on a single atom. The more electrons in an atom and the more diffuse the electron cloud around the atom, the greater the destructive interference among the scattered waves. To account for this intra-atomic interference, the $\frac{\sin\ kr}{kr}$ term is included in the scattering factor. Here, k is equal to $\frac{4\pi \sin\theta}{\lambda}$, where θ is the scattering angle and λ is the wavelength of the X-ray. A plot of f versus $\frac{\sin\theta}{\lambda}$ is shown in figure $31.4.1$. Notice that at θ = 0, f is equal to the number of electrons in the particle. Also notice that, although the isoelectronic ions Ca^{2+} and Cl^- have an identical f value at θ = 0, their f values differ at larger angles because the ions have different electron densities. Finally, notice that H atoms do not scatter a great deal, thus making them difficult to "locate" among the scattering from all of the larger atoms.

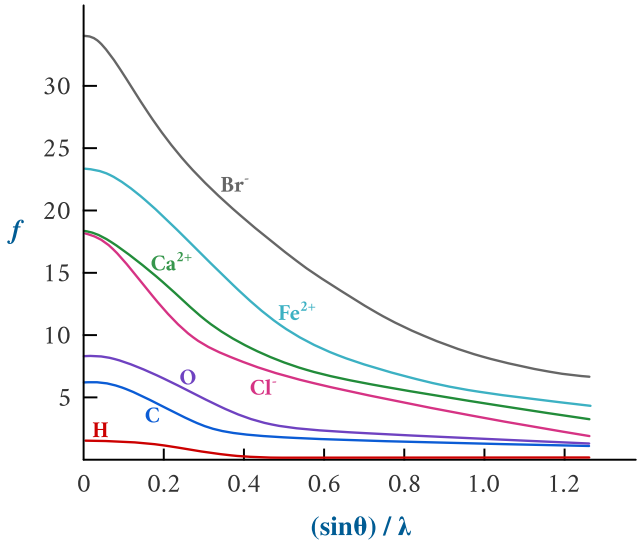


Figure 31.4.1: A graph showing the influence of the number of electrons per particle and the angle of diffraction on the scattering factor of various atoms and monatomic ions irradiated by a fixed wavelength X-ray beam. (CC BY-NC; Ümit Kaya via LibreTexts)

Scattering by Neighboring Atoms and Neighboring Planes

Along with the scattering factor for individual atoms, we must also take into consideration the interferences caused by neighboring atoms in the lattice. As our example, we will analyze a crystal that contains atoms of two elements, here designated **P** and **Q**. We will assume that the respective atoms have scattering factors f_P and f_Q. We will also assume that the distance between successive P atoms is the same as the distance between successive Q atoms. This distance is $\frac{a}{h}$, where a is the length of the unit cell along the **a** axis. Finally, we will assume that the distance between **P** and **Q** atoms is x. In this arrangement, the **P** atoms lie in neighboring *hkl* planes, and the **Q** atoms lie in neighboring *hkl* planes that are interleaved between the *hkl* planes of the **P** atoms. Figure 31.4.2 shows the arrangement of the atoms lying along the **a** axis.

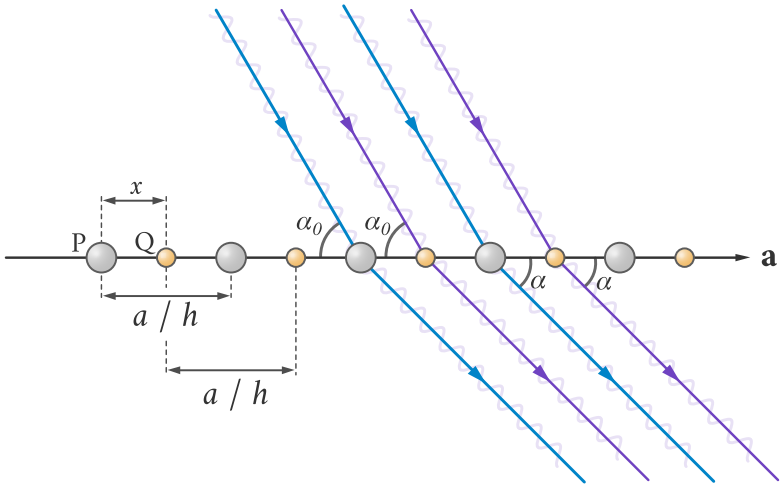


Figure 31.4.2: The scattering from a lattice comprised of atoms of two different elements. The P atoms lie in neighboring hkl planes, and the Q atoms lie in neighboring hkl planes that are interleaved between the hkl planes of the P atoms. (CC BY-NC; Ümit Kaya via LibreTexts)

In this arrangement, the difference in path length of X-rays scattered by successive P atoms, Δ_{PP}, (and the difference in path length of X-rays scattered by successive Q atoms, (Δ_{QQ}) is described by the van Laue equation

$$\Delta PP = \Delta QQ = \frac{a}{h}(cos\alpha - cos\alpha_0) = n\lambda$$

The difference in path length for X-rays diffracted by neighboring **P** and **Q** atoms is thus

$$\Delta PQ = x(\cos\alpha - \cos\alpha_0) = \frac{nh\lambda x}{a}$$

Because of this difference in path length, there is a resulting a phase difference between the scattered beams from neighboring **P** and **Q** atoms due to the difference in the time required to travel the different distances:

$$\phi = 2\pi\frac{\Delta_{PQ}}{\lambda} = 2\pi\frac{h\lambda x}{\lambda a} = \frac{2\pi hx}{a}$$

The light scattered from neighboring **P** and **Q** atoms will have an amplitude dependent on the scattering factors of each atom and the angular frequency of the X-ray radiation, ω

$$A = f_P\, cos\omega t + f_Q\, cos(\omega t + \phi)$$

Replacing the cosine functions with exponential functions will simplify the following mathematical calculation, thus

$$A = f_P\, e^{i\omega t} + f_Q\, e^{i(\omega t+\phi)} \tag{31.4.1}$$

Because intensity is proportional to amplitude squared,

$$I \propto |A|^2 = (f_P\ e^{i\omega t} + f_Q\ e^{i(\omega t+\phi)})(f_P\ e^{-i\omega t} + f_Q\ e^{-i(\omega t+\phi)}$$

which can be simplified to

$$f_P^2 + f_P f_Q e^{i\phi} + f_P f_Q e^{-i\phi} + f_Q^2$$

Switching back to cosine functions, we get

$$f_P^2 + f_Q^2 + 2f_P f_Q cos\phi$$

The f_P^2 term represents the constructive interference of the x-rays scattered from the parallel planes through the **P** atoms. The f_Q^2 term represents the constructive interference of the x-rays scattered from the parallel planes through the **Q** atoms. The $2f_P f_Q cos\phi$ term represents the interference from the scattering from the two sets of interleaved **P** and **Q** planes. From this equation, we can see that the intensity of the scattered light is independent of the angular frequency of the X-ray radiation because there is no term involving ω. Thus, in equation 31.4.1 the frequency-dependent $e^{i\omega t}$ must have a value of 1, and the equation can be rewritten and redefined as the structure factor along the **a** axis of the crystal, $F(h)$

$$F(h) = f_P + f_Q\, e^{i\phi)} = f_P + f_Q\, e^{\frac{2\pi hx}{a}} \tag{31.4.2}$$

For a unit cell with sides of length $a,\ b$, and c that contains atoms of type j positioned at points x_j, y_j and z_j, equation 31.4.2 becomes

$$F(hkl) = \sum_j f_j e^{2\pi(hx_j/a + ky_j/b + lz_j/c)} \tag{31.4.3}$$

Here f_j is the scattering factor for type j atoms, and *hkl* are the Miller indicies of the diffracting planes. By convention, x_j, y_j, and z_j are expressed in units of a, b, and c, so that $x_j^{'} = \frac{x_j}{a}$, $y_j^{'} = \frac{y_j}{b}$, and $z_j^{'} = \frac{z_j}{c}$, to give

$$F(hkl) = \sum_j f_j e^{2\pi(hx_j^{'} + ky_j^{'} + lz_j^{'})} \tag{31.4.4}$$

Combining the Influences

$F(hkl)$ is the structure factor of a crystal, and the intensity of reflections from this crystal are proportional to $|F(hkl)|^2$. The strcuture factor can thus be used to explain the systematic absences described in the introduction to this section. Whenever

$F(hkl)$ = 0 for a set of Miller planes, the reflection will be absent.

Example 31.4.1

Derive an expression for the structure factor of a face-centered cubic unit cell of identical atoms. Determine which *hkl* planes will not produce reflections.

Solution

The coordinates of the lattice points in a face-centered cubic unit cell are (0,0,0), (1,0,0), (0,1,0), (0,0,1), (1,0,1), (1,1,0), (1,1,1), (0,1,1), (0,1/2,1/2), (1/2,1/2,0), (1/2,0,1/2), (1,1/2,1/2), (1/2,1,1/2), (1/2,1/2,1). The length of the sides of the cell is a. Each corner lattice point is shared by 8 cells, so only 1/8 of each of these atoms is considered to be contributing to the scattering. Each face lattice point is shared by 2 cells, so only 1/2 of each of these atoms is considered to be contributing to the scattering. We will use equation 31.4.4 to solve the problem, remembering that $a = b = c$ for a cubic cell:

$$F(hkl) = \frac{1}{8}f(e^{2\pi i(0+0+0)} + e^{2\pi i(h+0+0)} + e^{2\pi i(0+k+0)} + e^{2\pi i(0+0+l)} + e^{2\pi i(h+0+l)} + e^{2\pi i(h+k+0)} + e^{2\pi i(h+k+l)} + e^{2\pi i(0+k+l)}) + \frac{1}{2}f(e^{2\pi i}$$

Because $e^{2\pi i}$ = 1 and $e^{\pi i}$ = -1, equation 31.4.5 becomes

$$F(hkl) = \frac{1}{8}f(1^0 + 1^h + 1^k + 1^l + 1^{h+l} + 1^{h+k} + 1^{h+k+l} + 1^{k+l}) + \frac{1}{2}f((-1)^{k+l} + (-1)^{h+k} + (-1)^{h+l} + (-1)^{2h+k+l} + (-1)^{h+2k+l} + (-1$$

Because $1^n = 1$ for all n,

$$F(hkl) = \frac{1}{8}f(8) + \frac{1}{2}f((-1)^{k+l} + (-1)^{h+k} + (-1)^{h+l} + (-1)^{2h+k+l} + (-1)^{h+2k+l} + (-1)^{h+k+2l})$$

Upon testing a few *hkl* planes, you will see that if h, k, l are a mixture of odd and even numbers, then $F(hkl) = 0$, but if h, k, l are all odd or all even, the value of $F(hkl) = 4f$. Three examples:

All odd $F(111) = f(1 + \frac{1}{2}((-1)^2 + (-1)^2 + (-1)^2 + (-1)^4 + (-1)^4 + (-1)^4 = f(1 + 3) = 4f$

All even $F(222) = f(1 + \frac{1}{2}((-1)^4 + (-1)^4 + (-1)^4 + (-1)^8 + (-1)^8 + (-1)^8 = f(1 + 3) = 4f$

Mix $F(110) = f(1 + \frac{1}{2}((-1)^1 + (-1)^2 + (-1)^1 + (-1)^3 + (-1)^3 + (-1)^2 = f(1 + \frac{1}{2}((-1) + 1 + (-1) + (-1) + (-1) + 1)) = 1 + (-1) = 0$

For crystals comprised of atoms of more than one element, there are often reflections that are weaker than other reflections. These lower intensities are sometimes created when the scattering factors of different elements are not identical, leading to incomplete destructive interference, a smaller $F(hkl)$, and thus a reflection of lower intensity. The lower intensity reflections are also a direct result of the structure factor. For example, for an ionically-bonded compound with the formula MX, which crystallizes in a face-centered cubic lattice, the structure factor can be shown to be

$$f(hkl) = f_+[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}] + f_-[(-1)^{h+k+l} + (-1)^h + (-1)^k + (-1)^l]$$

Inspection of this equation reveals that $F(hkl) = 4(f_+ + f_-)$ if h, k, l are all even, and $F(hkl) = 4(f_+ - f_-)$if h, k, l are all odd. Thus, reflections from the all-even hkl planes are more intense than reflections from the all-odd hkl planes.

See also

The structure factor. P. Coppens. *International Tables for Crystallography* (2006). Vol. B, ch. 1.2, pp. 10-24

Contributors

- ◦ Online Dictionary of Crystallography

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31.5: The Structure Factor and the Electron Density Are Related by a Fourier Transform

Fourier Transform

In mathematics, a Fourier transform is an operation that converts one real function into another. In the case of FTIR, a Fourier transform is applied to a function in the time domain to convert it into the frequency domain. One way of thinking about this is to draw the example of music by writing it down on a sheet of paper. Each note is in a so-called "sheet" domain. These same notes can also be expressed by playing them. The process of playing the notes can be thought of as converting the notes from the "sheet" domain into the "sound" domain. Each note played represents exactly what is on the paper just in a different way. This is precisely what the Fourier transform process is doing to the collected data of x-ray diffraction. This is done in order to determine the electron density around the crystalline atoms in real space. In the previous section, we treated the lattice points as individual, localized electron densities. In reality, the electron density of a unit cell is distributed over a much larger space. The following equations can be used to determine the electrons' positions:

$$p(x,y,z) = \sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty} F(hkl)e^{-2\pi i(hx/a+ky/b+lz/c)} \tag{31.5.1}$$

Employing a Fourier transform

$$F(hkl) \propto \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p(x,y,z)e^{2\pi i(hx/a+ky/b+lz/c)}dx\ dy\ dz \tag{31.5.2}$$

$$F(q) = |F(q)|e^{i\phi(q)} \tag{31.5.3}$$

where $p(xyz)$ is the electron density function, and $F(hkl)$ is the electron density function in real space. Equation 31.5.2 represents the Fourier expansion of the electron density function. To solve for $F(hkl)$, equation 31.5.1 needs to be evaluated over all values of h, k, and l, resulting in equation 31.5.2. The resulting function $F(hkl)$ is generally expressed as a complex number (as seen in equation 31.5.3 above) with $|F(q)|$ representing the magnitude of the function and ϕ representing the phase.

The structure factor may also be expressed as

$$\mathbf{F}_{hkl} = F_{hkl}e^{i\alpha_{hkl}} = \sum_j f_j e^{2\pi i(hx_j+ky_j+lz_j)} = \sum_j f_j\cos[2\pi(hx_j+ky_j+lz_j)] + i\sum_j f_j\sin[2\pi(hx_j+ky_j+lz_j)] \tag{31.5.4}$$

$$= A_{hkl} + iB_{hkl} \tag{31.5.5}$$

where the sum is over all atoms in the unit cell, x_j,y_j,z_j are the positional coordinates of the j th atom, f_j is the scattering factor of the j th atom, and α_{hkl} is the phase of the diffracted beam.The intensity of a diffracted beam is directly related to the amplitude of the structure factor, but the phase must normally be deduced by indirect means. In structure determination, phases are estimated and an initial description of the positions and anisotropic displacements of the scattering atoms is deduced. From this initial model, structure factors are calculated and compared with those experimentally observed. Iterative refinement procedures attempt to minimize the difference between calculation and experiment until a satisfactory fit has been obtained.

Figure 31.5.1 shows an electron density map of a quinoline derivative (and one water molecule) that was determined from X-ray diffraction data.

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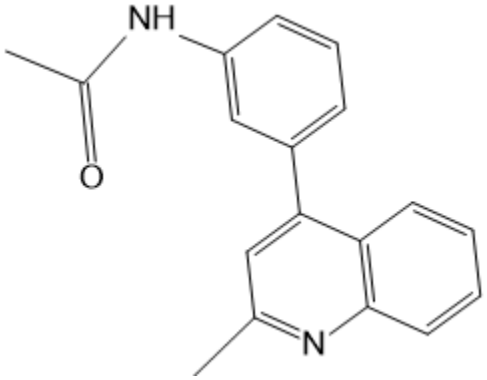


Figure 31.5.1: Electron density map of a quinoline derivative, along with the line structure of the compound. The red sphere at the bottom of the density map is the oxygen of a water molecule that is closely associated with the N atom of the quinoline. (electron density map courtesy of J Med Chem. 2013 Oct 24; 56(20): 8073–8088. © 2013 American Chemical Society, CC-BY)

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31.6: Atoms and Molecules can Physisorb or Chemisorb to a Surface

In this section, we will consider both the energetics of adsorption and factors which influence the kinetics of adsorption by looking at the "potential energy diagram/curve" for the adsorption process. The potential energy curve for the adsorption process is a representation of the variation of the energy (PE or E) of the system as a function of the distance (d) of an adsorbate from a surface.

Within this simple one-dimensional (1D) model, the only variable is the distance (d) of the adsorbing molecule from the substrate surface (Figure $31.6.1$).

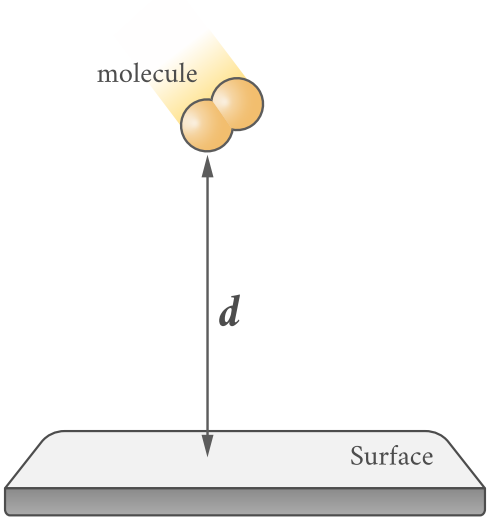


Figure $31.6.1$: A particle approaching a solid surface. (CC BY-NC; Ümit Kaya via LibreTexts)

Thus, the energy of the system is a function only of this variable i.e.

$$E = E(d)$$

It should be remembered that this is a very simplistic model which neglects many other parameters which influence the energy of the system (a single molecule approaching a clean surface), including for example

- *the angular orientation of the molecule*
- *changes in the internal bond angles and bond lengths of the molecule*
- *the position of the molecule parallel to the surface plane*

The interaction of a molecule with a given surface will also clearly be dependent upon the presence of any existing adsorbed species, whether these be surface impurities or simply pre-adsorbed molecules of the same type (in the latter case we are starting to consider the effect of surface coverage on the adsorption characteristics). Nevertheless, it is useful to first consider the interaction of an isolated molecule with a clean surface using the simple 1D model. For the purposes of this section, we will also not be overly concerned whether the "energy" being referred to should strictly be the internal energy, the enthalpy or free energy of the system. We will also make a distinction between physisorption and chemisorption. These two types of interaction with a surface are differentiated by the strength of interaction bewteen the adsorbed particle and the surface. A physisorbed particle will always be farther away from the surface than an identical particle that is chemisorbed (Figures $31.6.2$ and $31.6.3$).

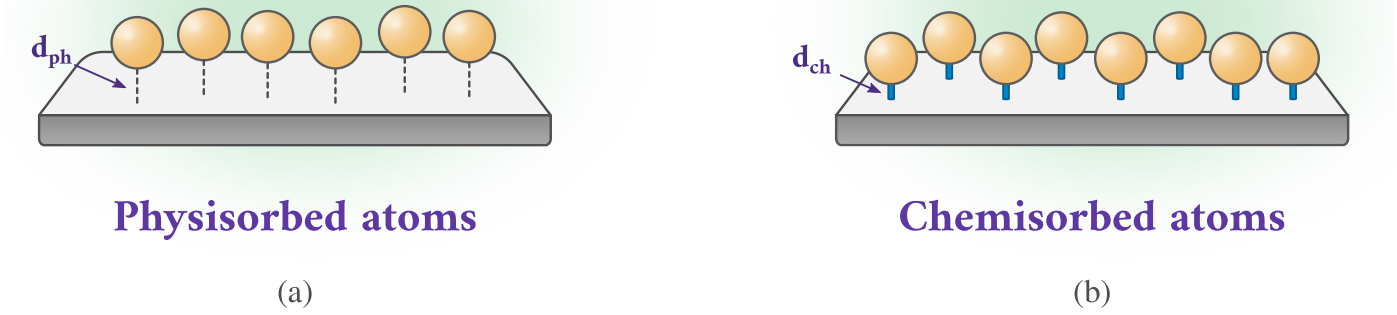


Figure 31.6.2: a) A picture of physisorbed atoms. The atoms are, on average, a distance of d_{ph} from the surface. b) A picture of chemisorbed atoms. The atoms are, on average, a distance of d_{ch} from the surface. Note that d_{ph} is always greater than d_{ch}. (CC BY-NC; Ümit Kaya via LibreTexts)

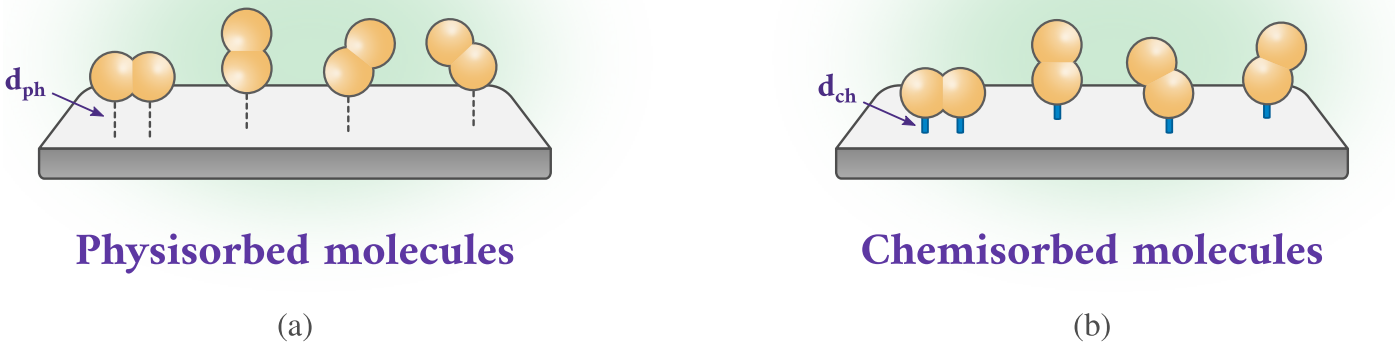


Figure 31.6.3: a) A picture of physisorbed molecules. The molecules are, on average, a distance of d_{ph} from the surface. Note that the molecules can adsorb to the surface at various orientations. b) A picture of chemisorbed molecules. The molecules are, on average, a distance of d_{ch} from the surface. Note that the molecules can adsorb to the surface at various orientations. Also note that d_{ph} is always greater than d_{ch}. (CC BY-NC; Ümit Kaya via LibreTexts)

CASE I - Physisorption

In the case of pure physisorption, e.g., Ar/metals, the only attraction between the adsorbing species and the surface arises from weak, van der Waals forces. As illustrated in Figure 31.6.4 below, these forces give rise to a shallow minimum in the PE curve at a relatively large distance from the surface (typically $d > 0.3\ nm$) before the strong repulsive forces arising from electron density overlap cause a rapid increase in the total energy.

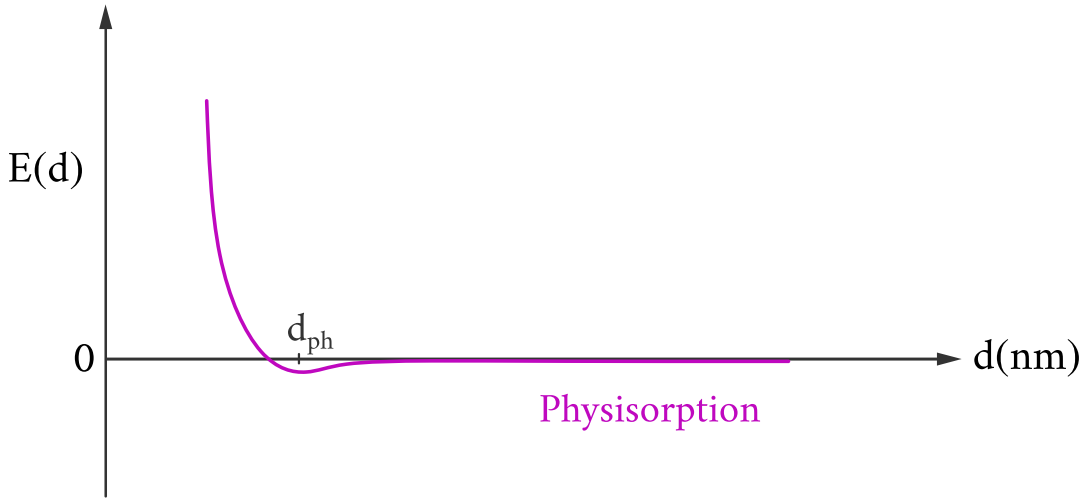


Figure 31.6.4: A graph showing the potential energy change as a particle moves closer and closer to a surface and eventually physisorbs onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

There is no barrier to prevent the atom or molecule which is approaching the surface from entering this physisorption well, i.e. the process is not activated and the kinetics of physisorption are invariably fast.

CASE II - Physisorption + Molecular Chemisorption

The weak physical adsorption forces and the associated long-range attraction will be present to varying degrees in all adsorbate/substrate systems. However, in cases where chemical bond formation between the adsorbate and substrate can also occur, the PE curve is dominated by a much deeper chemisorption minimum at shorter values of *d*, as shown in Figure 31.6.5.

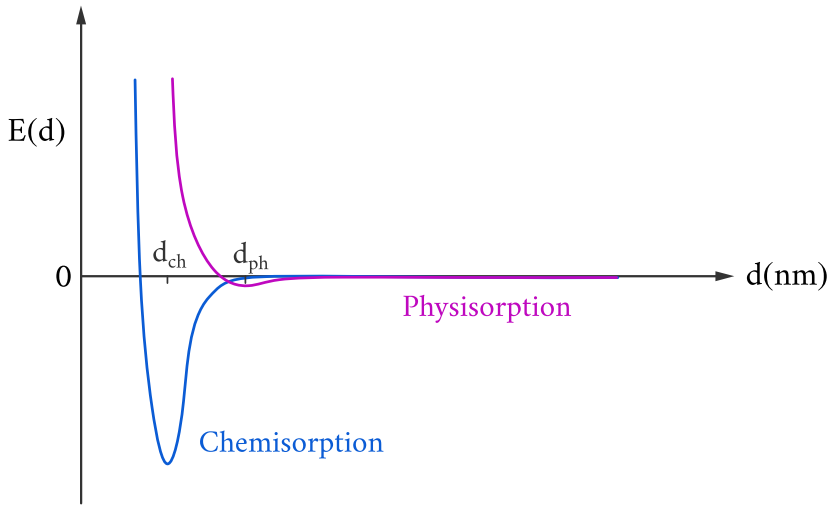


Figure 31.6.5: A graph showing the potential energy change as a particle moves closer and closer to a surface to eventually either physisorb or chemisorb onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

The graph above shows the PE curves due to physisorption and chemisorption separately. In practice, the PE curve for any real molecule capable of undergoing chemisorption is best described by a combination of the two curves, with a curve crossing at the

point at which chemisorption forces begin to dominate over those arising from physisorption alone (Figure 31.6.6).

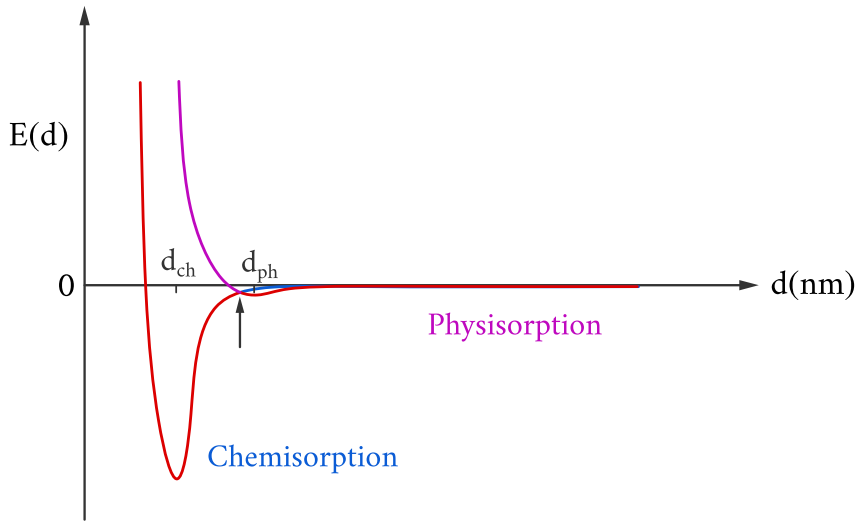


Figure 31.6.6: The red curve is a graph showing the potential energy change as a particle moves closer and closer to a surface, eventually physisorping onto the surface, and then undergoing chemisorption onto that same surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. The vertical arrow points to the crossover point at which the particle approaches close enough to the surface for the forces of chemisorption to dominate. (CC BY-NC; Ümit Kaya via LibreTexts)

The minimum energy pathway obtained by combining the two PE curves is now highlighted in red. Any perturbation of the combined PE curve from the original, separate curves is most likely to be evident close to the highlighted crossing point.

For clarity, we will now consider only the overall PE curve as shown in Figure 31.6.7:

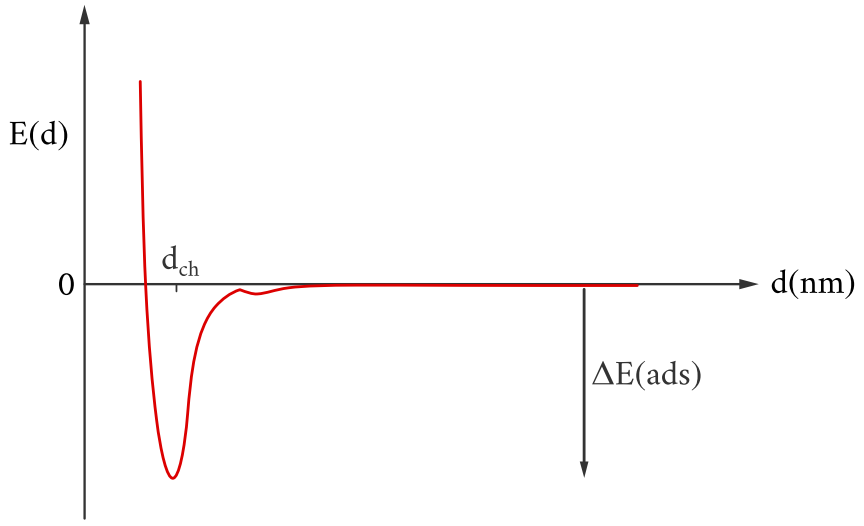


Figure 31.6.7: A graph showing the potential energy change as a particle moves closer and closer to a surface, eventually physisorbing onto the surface, and then undergoing chemisorption onto that same surface. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. The energy of adsorption is represented by $\Delta E(ads)$. (CC BY-NC; Ümit Kaya via LibreTexts)

The depth of the chemisorption well is a measure of the strength of binding to the surface. In fact, it is a direct representation of the energy of adsorption, whilst the location of the global minimum on the horizontal axis corresponds to the equilibrium bond distance (d_{ch}) for the adsorbed molecule on this surface.

The energy of adsorption is *negative*, and because it corresponds to the energy *change* upon adsorption, it is better represented as ΔE (ads) or ΔE_{ads} . However, you will also often find the depth of this well associated with the enthalpy of adsorption, ΔH (ads).

> The "*heat of adsorption*", Q, is taken to be a positive quantity equal in magnitude to the enthalpy of adsorption ; i.e. Q = -ΔH(ads))

In this particular case, there is clearly no barrier to be overcome in the adsorption process and there is no activation energy of adsorption (i.e. $E_a^{ads} = 0$, but do remember the previously mentioned limitations of this simple 1D model). There is of course a significant barrier to the reverse, desorption process; the red arrow in Figure 31.6.8 below represents the activation energy for desorption.

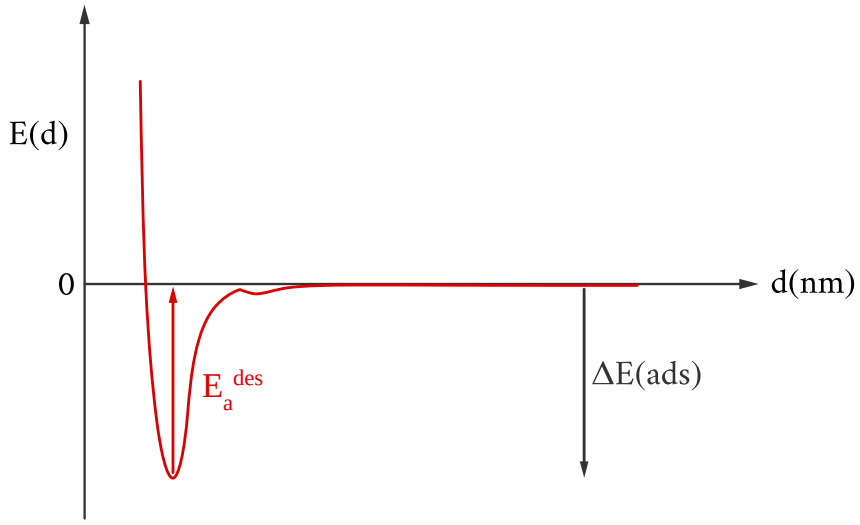


Figure 31.6.8: A graph showing both the energy of adsorption, $\Delta E(ads)$, and the activation energy of desorption, E_a^{des}. (CC BY-NC; Ümit Kaya via LibreTexts)

Clearly, in this particular case, the magnitudes of the energy of adsorption and the activation energy for desorption can also be equated i.e.

$$E_a^{des} = \Delta E(ads)$$

or

$$E_a^{des} \approx -\Delta H(ads)$$

CASE III - Physisorption + Dissociative Chemisorption

In this case, the main differences arise from the substantial changes in the PE curve for the chemisorption process. Again, we start off with the basic PE curve (Figure 31.6.9) for the physisorption process which represents how the molecule can weakly interact with the surface :

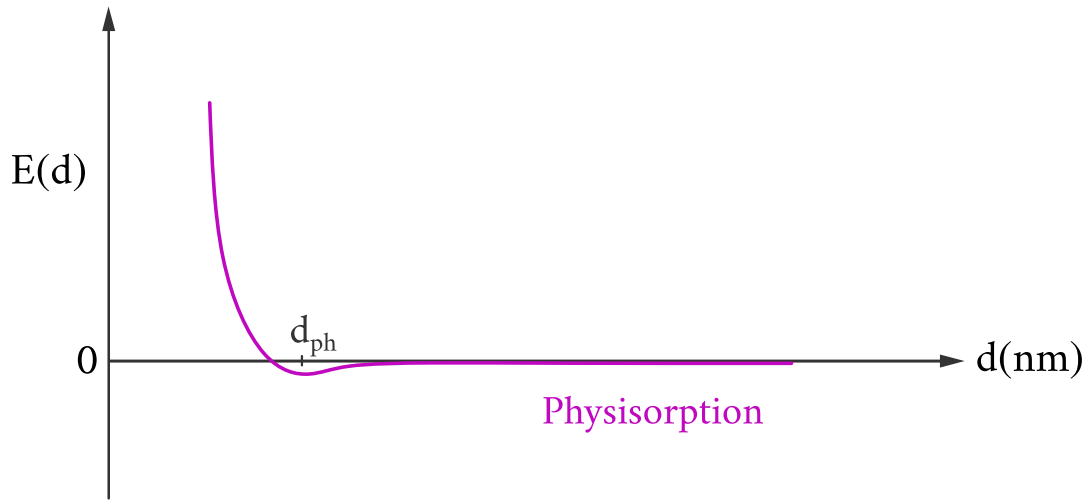


Figure 31.6.9: A graph showing the potential energy change as a particle moves closer and closer to a surface and eventually physisorbs onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

If we now consider a specific molecule such as H_2 and initially treat it as being completely **isolated** from the surface (i.e. when the distance, *d*, is very large), then a substantial amount of energy would need to be put into the system in order to cause dissociation of the molecule.

$$H_2 \longrightarrow H + H$$

This amount of required energy is the bond dissociation energy $D_{(H-H)}$, which is some 435 kJ mol^{-1} or 4.5 eV.

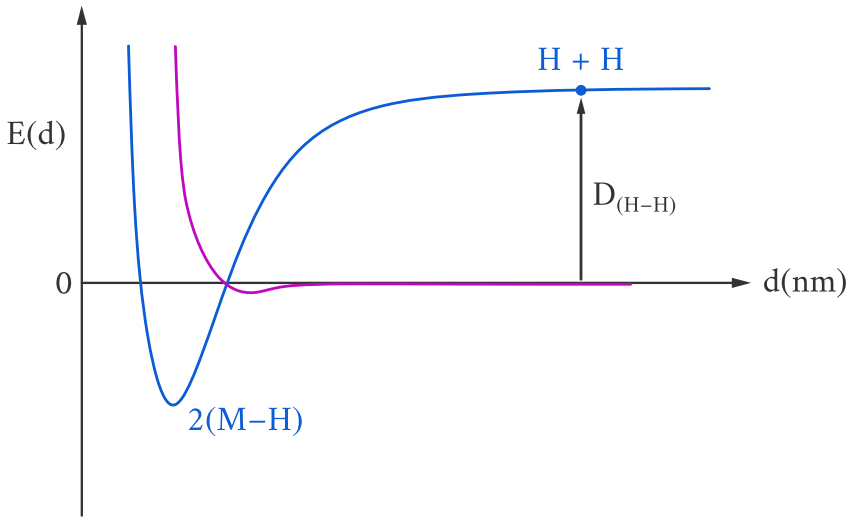


Figure 31.6.10: A graph showing the potential energy changes involved in the dissociation of an H_2 molecule. An H_2 molecule very far away from the surface has two paths by which it can end up as two separate H atoms chemisorbed onto the surface. (a) An input of 435 kJ per mole will break of the H-H bond. The separate H atoms can then eventually approach the surface and bond to it. (The red pathway) (b) The H_2 molecule can approach the surface, physisorb onto the surface, and then undergo dissociative chemisorption. (Starting on the right on the purple pathway, then switching to the red pathway at the crossover point.) (CC BY-NC; Ümit Kaya via LibreTexts)

The red dot in Figure 31.6.10 above thus represents two hydrogen atoms, equidistant (and a long distance) from the surface, and also now well separated from each other. If these atoms are then allowed to approach the surface they may ultimately both form strong chemical bonds to the substrate. This possible bonding of two H atoms to the surface (shown as 2(M-H) in the Figure)

corresponds to the minimum in the red curve which represents the chemisorption PE curve for the two H atoms.

In reality, of course, such a mechanism for dissociative hydrogen chemisorption is not practical; the energy down payment associated with breaking the H-H bond is far too severe. Instead, a hydrogen molecule will initially approach the surface along the physisorption curve. If it has sufficient energy it may pass straight into the chemisorption well ("direct chemisorption") as shown below in Figure 31.6.11.

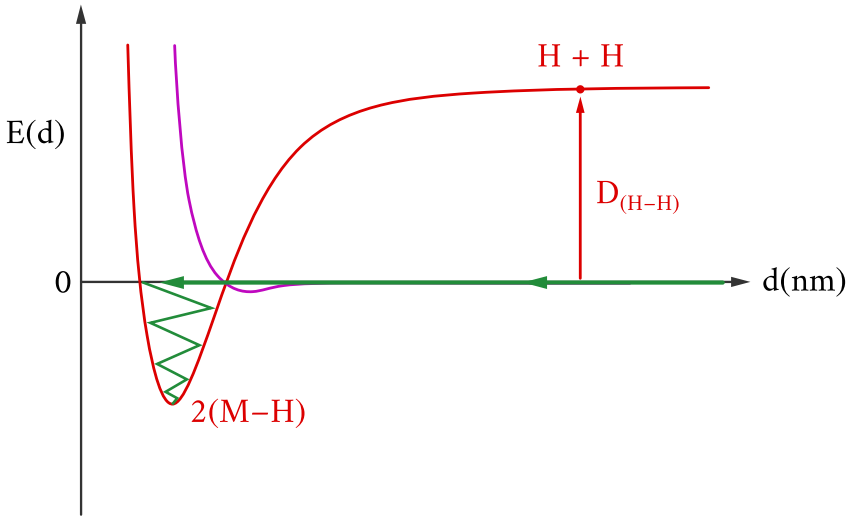


Figure 31.6.11: A graph showing the potential energy changes involved in the direct chemisorption of an H_2 molecule. The H_2 molecule approaches the surface following the green pathway, bypasses physisorption, and instead undergoes direct dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

Alternatively, the hydrogen molecule may first undergo transient physisorption, a state from which it can then either desorb back as a molecule into the gas phase or cross over the barrier into the dissociated, chemisorptive state (as illustrated *schematically* in Figure 31.6.12).

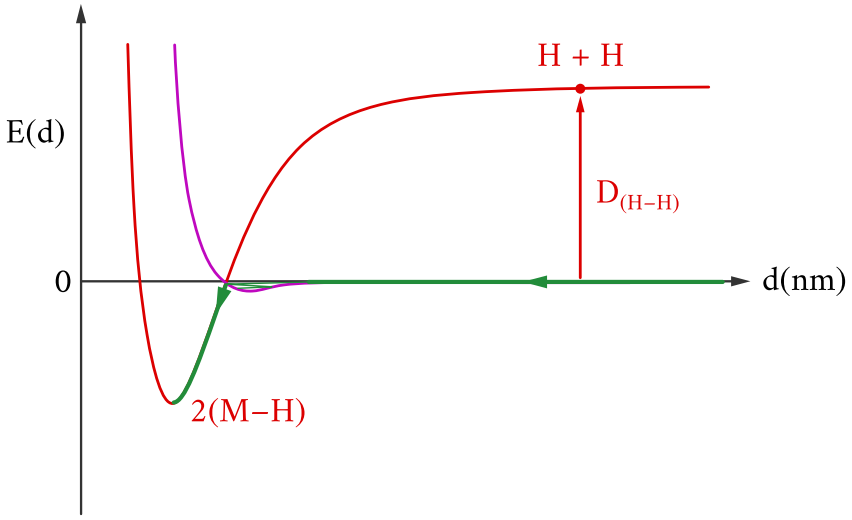


Figure 31.6.12: A graph showing the potential energy changes involved in the precursor-mediated chemisorption of an H_2 molecule. The H_2 molecule approaches the surface following the green pathway, first undergoes physisorption, and then undergoes dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

In this latter case, the molecule can be said to have undergone "precursor-mediated" chemisorption. A picture of the process of the approach, physisorption, and dissociative chemisorption of a molecule is shown in Figure 31.6.13. The molecule in this picture

is following the general potential energy pathway described in either Figure 31.6.11 or Figure 31.6.12.

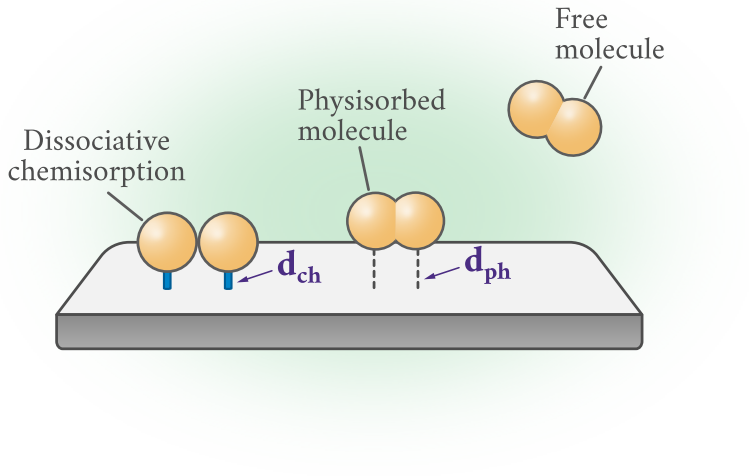


Figure 31.6.13: The sequential process of a free molecule approaching a surface, becoming physisrobed onto the surface, and eventually undergoing dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

The characteristics of this type of dissociative adsorption process are clearly going to be strongly influenced by the position of the crossing point of the two curves (molecular physisorption versus dissociative chemisorption) - relatively small shifts in the position of either of the two curves can significantly alter the size of any barrier to chemisorption.

In the example shown in Figure 31.6.14 below there is no direct activation barrier to dissociative adsorption - the curve crossing is below the initial "zero energy" of the system.

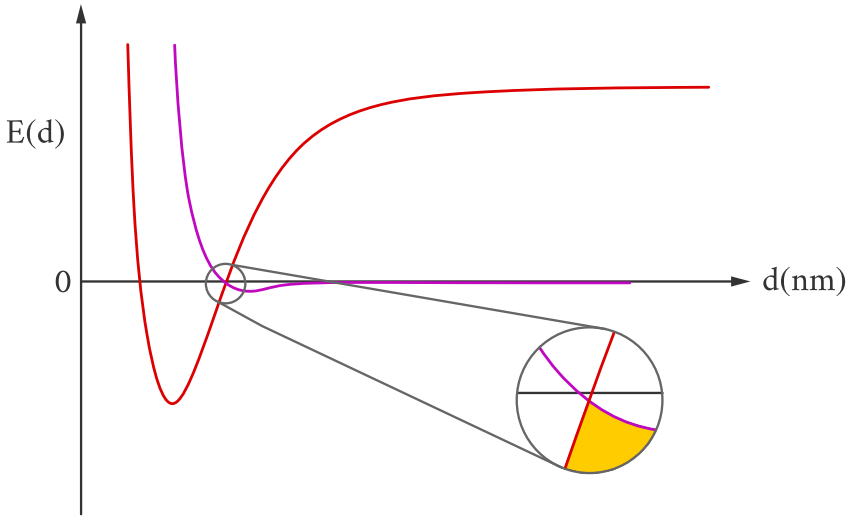


Figure 31.6.14: The potential energy pathway for physisorption followed by dissociative adsorption in which there is no direct activation barrier. (CC BY-NC; Ümit Kaya via LibreTexts)

In the case shown in Figure 31.6.15, there is a substantial barrier to chemisorption. Such a barrier has a major influence on the **kinetics** of adsorption.

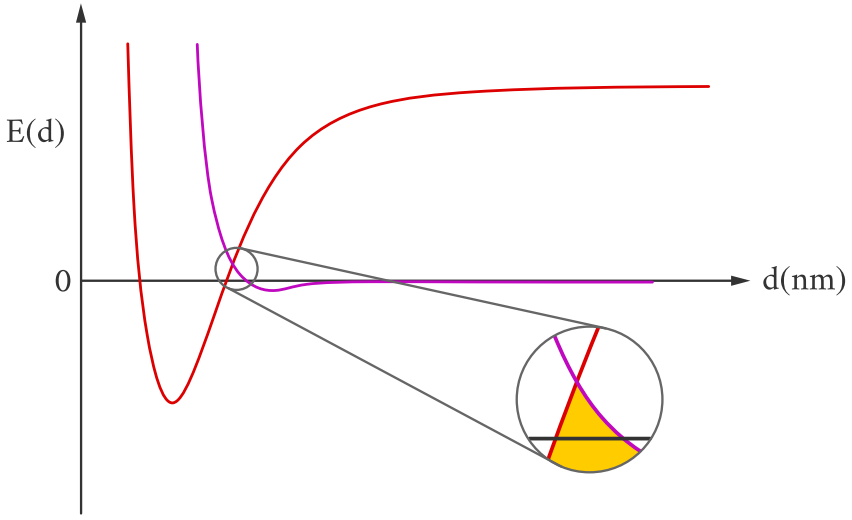


Figure 31.6.15: The potential energy pathway for physisorption followed by dissociative adsorption in which there is an activation barrier. ((CC BY-NC; Ümit Kaya via LibreTexts)

> *The depth of the physisorption well for the hydrogen molecule is actually very small (in some cases negligible), but this is not the case for other molecules and does not alter the basic conclusions regarding dissociative adsorption that result from this model; namely that the process may be either activated or non-activated depending on the exact location of the curve crossing.*

At this point, it is useful to return to consider the effect of such a barrier on the relationship between the activation energies for adsorption and desorption, and the energy (or enthalpy) of adsorption.

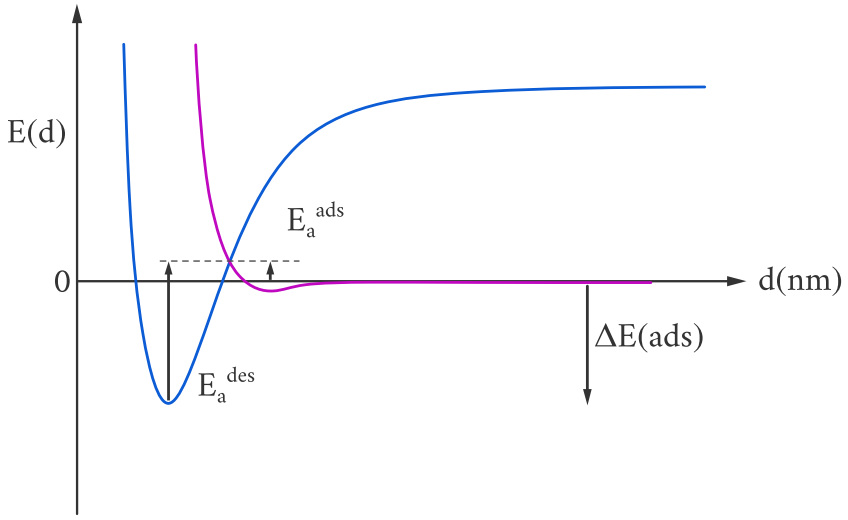


Figure 31.6.16: A comparison of the activation energy of adsorption E_a^{ads}, the activation energy of desorption E_a^{des}, and the energy of adsorption for a molecule that undergoes physisorption, directly followed by dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 31.6.16,

$$E_a^{des} - E_a^{ads} = -\Delta E_{ads}$$

but, because the activation energy for adsorption is nearly always very much smaller than that for desorption, and the difference

between the energy and the enthalpy of adsorption is also very small, it is still quite common to see the relationship

$$E_a^{des} \approx -\Delta H_{ads}$$

For a slightly more detailed treatment of the adsorption process, you are referred to the following examples of More Complex PE Curves & Multi-Dimensional PE Surfaces.

Contributors and Attributions

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31.7: Isotherms are Plots of Surface Coverage as a Function of Gas Pressure at Constant Temperature

Introduction

Whenever a gas is in contact with a solid there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules or atoms) which are bound to the surface of the solid. As with all chemical equilibria, the position of equilibrium will depend upon a number of factors:

1. The relative stabilities of the adsorbed and gas phase species involved
2. The temperature of the system (both the gas and surface, although these are normally the same)
3. The pressure of the gas above the surface

In general, factors (2) and (3) exert opposite effects on the concentration of adsorbed species - that is to say that the surface coverage may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

The Langmuir isotherm was developed by Irving Langmuir in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. There are many other types of isotherm (Temkin, Freundlich ...) which differ in one or more of the assumptions made in deriving the expression for the surface coverage; in particular, on how they treat the surface coverage dependence of the enthalpy of adsorption. Whilst the Langmuir isotherm is one of the simplest, it still provides a useful insight into the pressure dependence of the extent of surface adsorption.

Note: Surface Coverage & the Langmuir Isotherm

When considering adsorption isotherms it is conventional to adopt a definition of **surface coverage** (θ) which defines the maximum (saturation) surface coverage of a particular adsorbate on a given surface always to be unity, i.e. $\theta_{max} = 1$. This way of defining the surface coverage differs from that usually adopted in surface science where the more common practice is to equate θ with the ratio of adsorbate species to surface substrate atoms (which leads to saturation coverages which are almost invariably less than unity).

The Langmuir Isotherm - Derivation from Equilibrium Considerations

We may derive the Langmuir isotherm by treating the adsorption process as we would any other equilibrium process - except in this case the equilibrium is between the gas phase molecules (M), together with vacant surface sites, and the species adsorbed on the surface. Thus, for a non-dissociative (molecular) adsorption process, we consider the adsorption to be represented by the following chemical equation :

$$S-* + M_{(g)} \rightleftharpoons S-M \tag{31.7.1}$$

where :

- $S-*$ represents a vacant surface site

Assumption 1

In writing Equation ref{Eq1} we are making an inherent assumption that there are a fixed number of localized surface sites present on the surface. This is the first major assumption of the Langmuir isotherm.

We may now define an equilibrium constant (K) in terms of the concentrations of "reactants" and "products"

$$K = \frac{[S-M]}{[S-*][M]} \tag{31.7.2}$$

We may also note that :The [S - M] is proportional to the surface coverage of adsorbed molecules, i.e. proportional to θ

- [S - *] is proportional to the number of vacant sites, i.e. proportional to $1-\theta$
- [M] is proportional to the pressure of gas, \(*P*\)

Hence, it is also possible to define another equilibrium constant, *b* , as given below :

$$b = \frac{\theta}{(1-\theta)P} \tag{31.7.3}$$

Rearrangement then gives the following expression for the surface coverage

$$\theta = \frac{bP}{1+bP} \tag{31.7.4}$$

which is the usual form of expressing the Langmuir Isotherm. As with all chemical reactions, the equilibrium constant, b, is both temperature-dependent and related to the Gibbs free energy and hence to the enthalpy change for the process.

Assumption 2

b is only a constant (independent of θ) if the enthalpy of adsorption is independent of coverage. This is the second major assumption of the Langmuir Isotherm.

A plot of θ vs. bP shows that as the pressure increases, θ approaches 1, meaning that nearly the entire surface is coated with a monolayer of adsorbed gas (Figure 31.7.1).

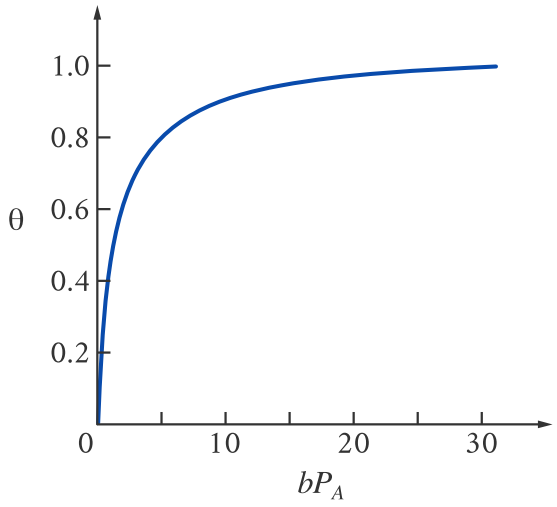


Figure 31.7.1: A plot of equation 31.7.4 which shows the nonlinear relationship between the fraction of surface coverage and the gas pressure. .(CC BY-NC; Ümit Kaya via LibreTexts)

Equation 31.7.4 can be rearranged to the form

$$\frac{1}{\theta} = 1 + \frac{1}{bP} \tag{31.7.5}$$

showing that the inverse of the fraction of occupied surface sites is a linear function of the inverse of the pressure. If we plot experimental data for the adsorption of diatomic oxygen and carbon monoxide onto a silica surface, we can see that the Langmuir adsorption isotherm describes the data well (figure 31.7.2).

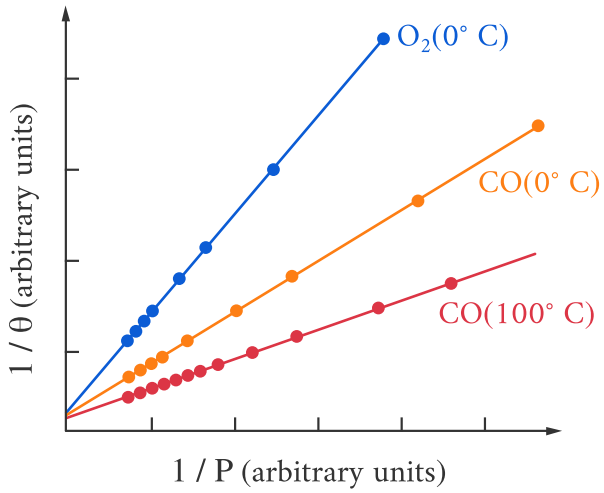


Figure 31.7.2: A plot showing the relationship of the inverse of the fraction of occupied surface sites to the inverse of the gas pressure for O_2 and CO molecules adsorbed onto a silica surface. (CC BY-NC; Ümit Kaya via LibreTexts)

The Langmuir Isotherm from a Kinetics Consideration

The equilibrium that may exist between gas adsorbed on a surface and molecules in the gas phase is a dynamic state, i.e. **the equilibrium represents a state in which the rate of adsorption of molecules onto the surface is exactly counterbalanced by the rate of desorption of molecules back into the gas phase**. It should therefore be possible to derive an isotherm for the adsorption process simply by considering and equating the rates for these two processes.

Expressions for the rate of adsorption and rate of desorption have been derived in Sections 2.3 & 2.6 respectively: specifically ,

$$R_{ads} = \frac{f(\theta)P}{\sqrt{2\pi mkT}}\exp(-E_a^{ads}/RT)$$

$$R_{des} = v\, f'(\theta)\exp(-E_a^{ads}/RT)$$

Equating these two rates yields an equation of the form :

$$\frac{P\, f(\theta)}{f'(\theta)} = C(T) \tag{31.7.6}$$

where θ is the fraction of sites occupied at equilibrium and the terms $f(\theta)$ and $f'(\theta)$ contain the pre-exponential surface coverage dependence of the rates of adsorption and desorption respectively and all other factors have been taken over to the right hand side to give a temperature-dependent "constant" characteristic of this particular adsorption process, $C(T)$. We now need to make certain simplifying assumptions. The first is one of the key assumptions of the Langmuir isotherm.

Assumption 1

Adsorption takes place only at specific localized sites on the surface and the saturation coverage corresponds to complete occupancy of these sites.

Let us initially further restrict our consideration to a simple case of **reversible molecular adsorption**, i.e.

$$S-* + \blacksquare \rightleftharpoons \mathrm{S{-}M} \tag{31.7.7}$$

where

- $S-*$ represents a vacant surface site and
- $\mathrm{S{-}M}$ the adsorption complex.

Under these circumstances it is reasonable to assume coverage dependencies for rates of the two processes of the form :

- **Adsorption** (forward reaction in Equation 31.7.7):

$$f(\theta) = c(1-\theta) \tag{31.7.8}$$

  i.e. proportional to the fraction of sites that are unoccupied.
- **Desorption** (reverse reaction in Equation 31.7.7):

$$f'(\theta) = c'\theta \tag{31.7.9}$$

  i.e. proportional to the fraction of sites which are occupied by adsorbed molecules.

Note

These coverage dependencies in Equations 31.7.8 and 31.7.9 are exactly what would be predicted by noting that the forward and reverse processes are elementary reaction steps, in which case it follows from standard chemical kinetic theory that

- The forward adsorption process will exhibit kinetics having a first order dependence on the concentration of vacant surface sites and first order dependence on the concentration of gas particles (proportional to pressure).
- The reverse desorption process will exhibit kinetics having a first order dependence on the concentration of adsorbed molecules.

Substitution of Equations 31.7.8 and 31.7.9 into Equation 31.7.6 yields:

$$\frac{P(1-\theta)}{\theta} = B(T)$$

where

$$B(T) = \left(\frac{c'}{c}\right) C(T).$$

After rearrangement this gives the *Langmuir Isotherm* expression for the surface coverage

$$\theta = \frac{bP}{1+bP}$$

where $b = 1/B(T)$ is a function of temperature and contains an exponential term of the form

$$b \propto \exp[(E_a^{des} - E_a^{ads})/RT] = \exp[-\Delta H_{ads}/RT]$$

with

$$\Delta H_{ads} = E_a^{des} - E_a^{ads}.$$

Assumption 2

b can be regarded as a **constant** with respect to coverage only if the enthalpy of adsorption is itself **independent** of coverage; this is the second major assumption of the Langmuir Isotherm.

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31.8: Using Langmuir Isotherms to Derive Rate Laws for Surface-Catalyzed Gas-Phase Reactions

It is possible to predict how the kinetics of certain heterogeneously-catalyzed reactions might vary with the partial pressures of the reactant gases above the catalyst surface by using the Langmuir isotherm expression for equilibrium surface coverages.

Unimolecular Decomposition

Consider the surface decomposition of a molecule A, i.e. the process

$$A_{(g)} \rightleftharpoons A_{(ads)} \rightarrow \text{Products}$$

Let us assume that :

1. The decomposition reaction occurs uniformly across the surface sites at which molecule A may be adsorbed and is not restricted to a limited number of special sites.
2. The products are very weakly bound to the surface and, once formed, are rapidly desorbed.
3. The rate determining step (rds) is the surface decomposition step.

Under these circumstances, the molecules of A adsorbed on the surface are in equilibrium with those in the gas phase and we may predict the surface concentration of A from the Langmuir isotherm, i.e.

$$\theta = \frac{bP}{1+bP}$$

The rate of the surface decomposition (and hence of the reaction) is given by an expression of the form

$$\text{rate} = k\theta$$

This is assuming that the decomposition of $A(ads)$ occurs in a simple unimolecular elementary reaction step and that the kinetics are first order with respect to the surface concentration of this adsorbed intermediate). Substituting for the coverage, θ, gives us the required expression for the rate in terms of the pressure of gas above the surface

$$\text{rate} = \frac{kbP}{1+bP} \tag{31.8.1}$$

It is useful to consider two extremes:

Low Pressure/Binding Limit

This is the low pressure (or weak binding. i.e., small b) limit : under these conditions the steady state surface coverage, θ, of the reactant molecule is very small.

$$bP \ll 1$$

then

$$1+bP \approx 1$$

and Equation 31.8.1 can be simplified to

$$\text{rate} \approx kbP$$

Under this limiting case, the kinetics follow a first order reaction (with respect to the partial pressure of A) with an apparent first order rate constant $k' = kb$.

High Pressure/Binding Limit

This is the high pressure (or strong binding, i.e., large b) limit: under these conditions the steady state surface coverage, θ, of the reactant molecule is almost unity and

$$bP \gg 1$$

then

$$1 + bP \approx bP$$

and Equation 31.8.1 can be simplified to

$$rate \approx k$$

Under this limiting case, the kinetics follow a zero-order reaction (with respect to the partial pressure of A). The rate shows the same pressure variation as does the surface coverage, but this is hardly surprising since it is directly proportional to θ.

These two limiting cases can be identified in the general kinetics from Equation 31.8.1 in Figure 31.8.1.

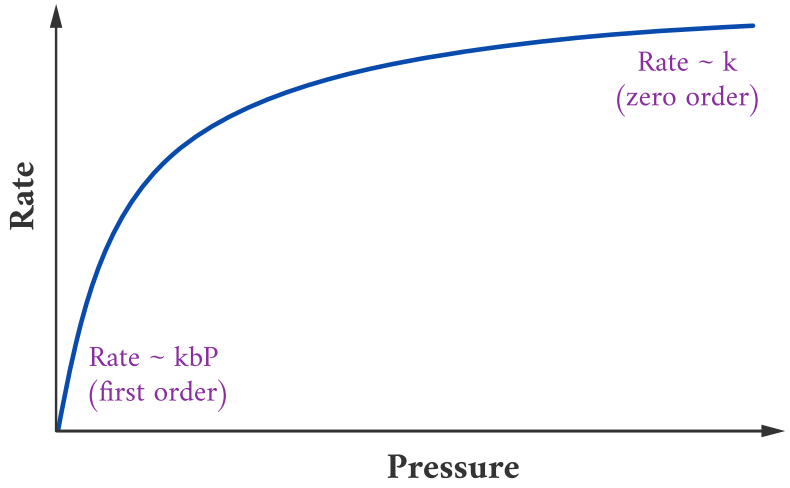


Figure 31.8.1: Plot of reaction rate versus the pressure of the reactant gas. The graph shows that at low pressures, the rate is first order with respect to the pressure of the reacting gas. At high pressures, however, the reaction approaches zero order with respect to the reacting gas.

Bimolecular Reaction (between molecular adsorbates)

Consider a Langmuir-Hinshelwood reaction of the following type:

$$A_{(g)} \rightleftharpoons A_{(ads)} \tag{31.8.2}$$

$$B_{(g)} \rightleftharpoons B_{(ads)} \tag{31.8.3}$$

$$A_{(ads)} + B_{(ads)} \overset{slow}{\longrightarrow} AB_{(ads)} \overset{fast}{\longrightarrow} AB_{(g)} \tag{31.8.4}$$

We will further assume, as noted in the above scheme, that the surface reaction between the two adsorbed species (left side of Equation 31.8.4 is the rate determining step.

If the two adsorbed molecules are mobile on the surface and freely intermix then the rate of the reaction will be given by the following rate expression for the **bimolecular** surface combination step

$$Rate = k\theta_A\theta_B$$

For a single molecular adsorbate the surface coverage (as given by the standard Langmuir isotherm) is

$$\theta = \frac{bP}{1+bP}$$

Where two molecules (A & B) are competing for the same adsorption sites then the relevant expressions are (see derivation):

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B}$$

and

$$\theta_B = \frac{b_B P_B}{1 + b_A P_A + b_B P_B}$$

Substituting these into the rate expression gives :

$$Rate = k\theta_A\theta_B = \frac{k b_A P_A b_B P_B}{(1 + b_A P_A + b_B P_B)^2}$$

Once again, it is interesting to look at several extreme limits

Low Pressure/Binding Limit

$$b_A P_A \ll 1$$

and

$$b_B P_B \ll 1$$

In this limit that θ_A & θ_B are both very low , and

$$rate \rightarrow k b_A P_A b_B P_B = k' P_A P_B$$

i.e. *first order* in both reactants

Mixed Pressure/Binding Limit

$$b_A P_A \ll 1 \ll b_B P_B$$

In this limit $\theta_A \rightarrow 0$, $\theta_B \rightarrow 1$, and

$$Rate \rightarrow \frac{k b_A P_A}{b_B P_B} = \frac{k' P_A}{P_B}$$

i.e. *first order* in A, but *negative first order* in B

Clearly, depending upon the partial pressure and binding strength of the reactants, a given model for the reaction scheme can give rise to a variety of apparent kinetics: this highlights the dangers inherent in the reverse process - namely trying to use kinetic data to obtain information about the reaction mechanism.

Example 31.8.1: CO Oxidation Reaction

On precious metal surfaces (e.g. Pt), the CO oxidation reaction is generally believed to by a *Langmuir-Hinshelwood mechanism* of the following type :

$$CO_{(g)} \rightleftharpoons CO_{(ads)}$$

$$O_{2(g)} \rightleftharpoons 2O_{(ads)}$$

$$CO_{(ads)} + O_{(ads)} \xrightarrow{slow} CO_{2(ads)} \xrightarrow{fast} CO_{2(g)}$$

As CO_2 is comparatively weakly-bound to the surface, the desorption of this product molecule is relatively fast and in many circumstances it is the surface reaction between the two adsorbed species that is the rate determining step.

If the two adsorbed molecules are assumed to be mobile on the surface and freely intermix then the rate of the reaction will be given by the following rate expression for the bimolecular surface combination step

$$Rate = k\,\theta_{CO}\,\theta_O$$

Where two such species (one of which is molecularly adsorbed, and the other dissociatively adsorbed) are competing for the same adsorption sites then the relevant expressions are (see derivation):

$$\theta_{CO} = \frac{b_{CO}P_{CO}}{1 + \sqrt{b_O P_{O_2}} + b_{CO}P_{CO}}$$

and

$$\theta_O = \frac{\sqrt{b_O P_{O_2}}}{1 + \sqrt{b_O P_{O_2}} + b_{CO}P_{CO}}$$

Substituting these into the rate expression gives:

$$rate = k\theta_{CO}\theta_O = \frac{k b_{CO}P_{CO}\sqrt{b_O P_{O_2}}}{(1 + \sqrt{b_O P_{O_2}} + b_{CO}P_{CO})^2} \tag{31.8.5}$$

Once again, it is interesting to look at certain limits. If the CO is much more strongly bound to the surface such that

$$b_{CO}P_{CO} \gg 1 + \sqrt{b_O P_{O_2}}$$

then

$$1 + \sqrt{b_O P_{O_2}} + b_{CO}P_{CO} \approx b_{CO}P_{CO}$$

and the Equation 31.8.5 simplifies to give

$$rate \approx \frac{k\sqrt{b_O P_{O_2}}}{b_{CO}P_{CO}} = k' \frac{P_{O_2}^{1/2}}{P_{CO}}$$

In this limit the kinetics are half-order with respect to the gas phase pressure of molecular oxygen, but negative order with respect to the CO partial pressure, i.e. CO acts as a poison (despite being a reactant) and increasing its pressure slows down the reaction. This is because the CO is so strongly bound to the surface that it blocks oxygen adsorbing, and without sufficient oxygen atoms on the surface the rate of reaction is reduced.

Contributors and Attributions

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31.9: The Structure of a Surface is Different from that of a Bulk Solid

The kinetics and thermodynamics of the chemical and physical processes that occur on the surface of a solid are greatly dependent on the structure of the surface. Few, if any surfaces are perfectly flat, and thus the cavities, protrusions, ridges, and edges of the surface must be treated differently when studying chemisorption and physisorption. Several types of spectroscopies and microscopies are available to study the atomic-scale structure of surfaces.

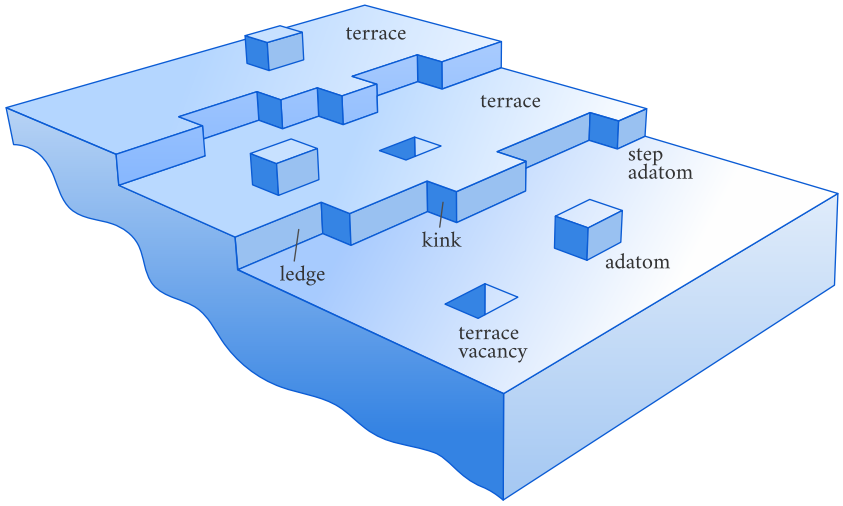


Figure 31.9.1: A schematic of a solid surface showing possible defects. The surface is composed of terraces, ledges, kinks, and steps. Terraces can contain adatoms (lone single atoms) and vacancies (missing atoms that leave cavities). (CC BY-NC; Ümit Kaya via LibreTexts)

Electron Microscopy

The two forms of electron microscopy which are commonly used to provide surface information are

- **Secondary Electron Microscopy** (SEM): which provides a direct image of the topographical nature of the surface from all the emitted secondary electrons
- **Scanning Auger Microscopy** (SAM): which provides compositional maps of a surface by forming an image from the Auger electrons emitted by a particular element.

Both techniques employ the focusing of the probe beam (a beam of high-energy electrons, typically 10 - 50 keV in energy) to obtain spatial localization.

Secondary Electron Microscopy (SEM)

As the primary electron beam is scanned across the surface, electrons of a wide range of energies will be emitted from the surface in the region where the beam is incident. These electrons will include backscattered primary electrons and Auger electrons, but the vast majority will be *secondary electrons* formed in multiple inelastic scattering processes (these are the electrons that contribute to the background and are completely ignored in Auger spectroscopy). The secondary electron current reaching the detector is recorded and the microscope image consists of a "plot" of this current, I, against probe position on the surface. The contrast in the micrograph arises from several mechanisms, but first and foremost from variations in the surface topography. Consequently, the secondary electron micrograph is virtually a direct image of the real surface structure (Figure 31.9.1).

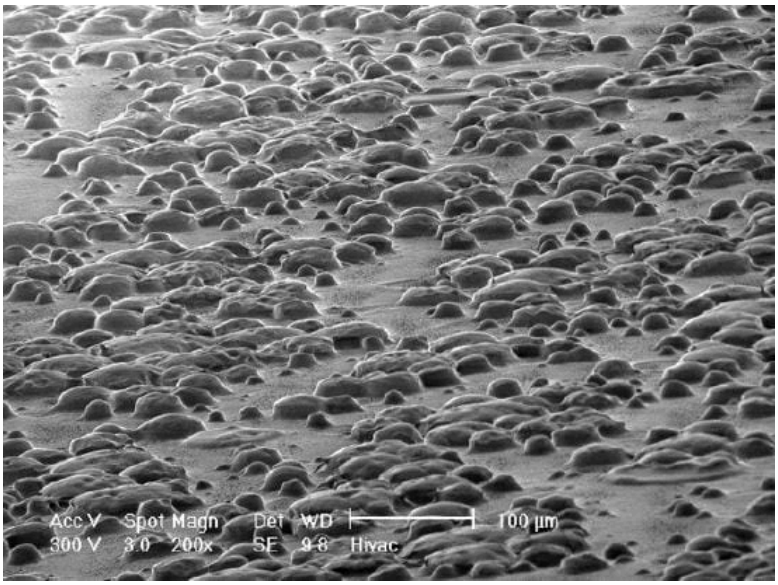


Figure 31.9.2: Low-voltage SEM micrograph (300 V) of distribution of adhesive droplets on a Post-it note. (CC BY-SA 3.0, Chivesud via Wikipedia)

The attainable resolution of the technique is limited by the minimum spot size that can be obtained with the incident electron beam, and ultimately by the scattering of this beam as it interacts with the substrate. With modern instruments, a resolution of better than 5 nm is achievable. This is more than adequate for imaging semiconductor device structures, for example, but insufficient to enable many supported metal catalysts to be studied in any detail.

Scanning Auger Microscopy (SAM)

The incident primary electrons cause the ionization of atoms within the region illuminated by the focused beam. Subsequent relaxation of the ionized atoms leads to the emission of Auger electrons characteristic of the elements present in this part of the sample surface. As with SEM , the attainable resolution is again ultimately limited by the incident beam characteristics. More significantly, however, the resolution is also limited by the need to acquire sufficient Auger signal to form a respectable image within a reasonable time period, and for this reason, the instrumental resolution achievable is rarely better than about 15-20 nm.

Low-Energy Electron Diffraction (LEED) Spectroscopy

LEED is the principal technique for the determination of surface structures. It may be used in one of two ways:

1. **Qualitatively**: where the diffraction pattern is recorded and analysis of the *spot positions* yields information on the size, symmetry, and rotational alignment of the adsorbate unit cell with respect to the substrate unit cell.
2. **Quantitatively**: where the *intensities* of the various diffracted beams are recorded as a function of the incident electron beam energy to generate so-called I-V curves which, by comparison with theoretical curves, may provide accurate information on atomic positions.

The LEED experiment uses a beam of electrons of a well-defined low energy (typically in the range 20 - 200 eV) incident normally on the sample. The sample itself must be a single crystal with a well-ordered surface structure in order to generate a back-scattered electron diffraction pattern. A typical experimental setup is shown in figure 31.9.3 below.

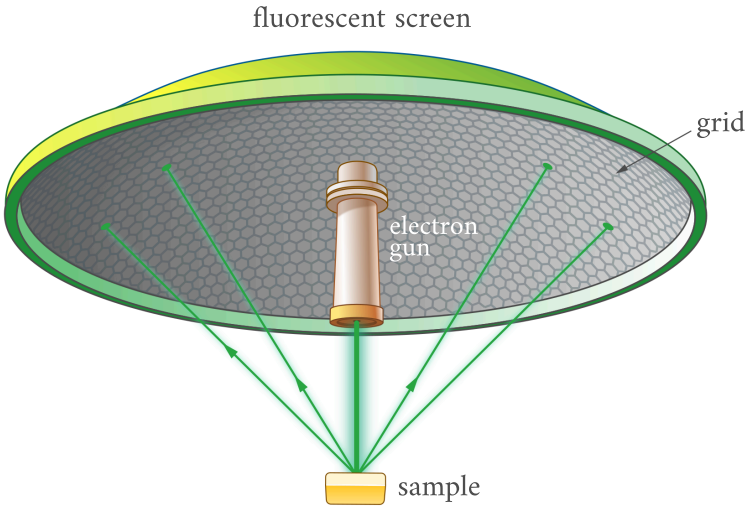


Figure 31.9.3: Schematic of a LEED experimental setup. (CC BY-NC; Ümit Kaya via LibreTexts)

Only the elastically-scattered electrons contribute to the diffraction pattern; the lower energy (secondary) electrons are removed by energy-filtering grids placed in front of the fluorescent screen that is employed to display the pattern.

Example 31.9.1

As shown by the Bragg equation, for the electrons to be diffracted, the de Broglie wavelength of the electrons has to be less than $2d$, which is twice the distance between the atomic planes. The equation used to calculate the wavelength (in nm) of backscattered electrons that are accelarated by a potential, ϕ is

$$\lambda = \left(\frac{1.504\,Vnm^2}{\phi}\right)^{1/2}$$

Calculate the minimum acceleration voltage needed to observe electron diffraction from the surface of a crystal with an interplanar spacing of 0.1250 nm.

Solution

To observe diffraction, the wavelength must be less than $2d$, so λ must be less than 0.2500 nm. Therefore,

$$0.2500\,nm = \left(\frac{1.504\,Vnm^2}{\phi}\right)^{1/2}$$

$$\phi = \frac{1.504\,Vnm^2}{(0.2500\,nm)^2}$$

$$\phi = 24.06V$$

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31.10: The Haber-Bosch Reaction Can Be Surface Catalyzed

The Haber-Bosch Process for Synthesis of Ammonia

An example of an industrial catalytic process is the Haber-Bosch process. Karl Bosch (1874–1940) was a German chemical engineer who was responsible for designing the process that took advantage of Fritz Haber's discoveries regarding the N_2 + H_2/NH_3 equilibrium to make ammonia synthesis via this route cost-effective. He received the Nobel Prize in Chemistry in 1931 for his work. The industrial process is called either the Haber process or the Haber-Bosch process. used to synthesize ammonia via the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

with

$$\Delta H_{rxn} = -91.8\ kJ/mol$$

Because the reaction converts 4 mol of gaseous reactants to only 2 mol of gaseous product, Le Chatelier's principle predicts that the formation of NH_3 will be favored when the pressure is increased. The reaction is exothermic, however (ΔH_{rxn} = –91.8 kJ/mol), so the equilibrium constant decreases with increasing temperature, which causes an equilibrium mixture to contain only relatively small amounts of ammonia at high temperatures (31.10.1). Taken together, these considerations suggest that the maximum yield of NH_3 will be obtained if the reaction is carried out at as low a temperature and as high a pressure as possible. Unfortunately, at temperatures less than approximately 300°C, where the equilibrium yield of ammonia would be relatively high, the reaction is too *slow* to be of any commercial use. The industrial process, therefore, uses a mixed oxide (Fe_2O_3/K_2O) catalyst that enables the reaction to proceed at a significant rate at temperatures of 400°C–530°C, where the formation of ammonia is less unfavorable than at higher temperatures.

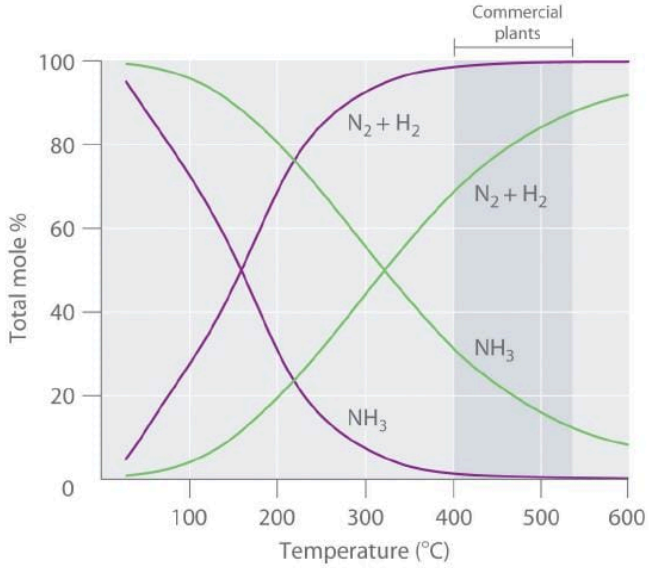


Figure 31.10.1 Effect of Temperature and Pressure on the Equilibrium Composition of Two Systems that Originally Contained a 3:1 Mixture of Hydrogen and Nitrogen: At all temperatures, the total pressure in the systems was initially either 4 atm (purple curves) or 200 atm (green curves). Note the dramatic decrease in the proportion of NH_3 at equilibrium at higher temperatures in both cases, as well as the large increase in the proportion of NH_3 at equilibrium at any temperature for the system at higher pressure (green) versus lower pressure (purple). Commercial plants that use the Haber-Bosch process to synthesize ammonia on an industrial scale operate at temperatures of 400°C–530°C (indicated by the darker gray band) and total pressures of 130–330 atm.

Because of the low value of the equilibrium constant at high temperatures (e.g., K = 0.039 at 800 K), there is no way to produce an equilibrium mixture that contains large proportions of ammonia at high temperatures. We can, however, control the temperature and the pressure while using a catalyst to convert a fraction of the N_2 and H_2 in the reaction mixture to NH_3, as is done in the Haber-Bosch process. This process also makes use of the fact that the product—ammonia—is less volatile than the reactants. Because NH_3 is a liquid at room temperature at pressures greater than 10 atm, cooling the reaction mixture causes NH_3 to condense from the vapor as liquid ammonia, which is easily separated from unreacted N_2 and H_2. The unreacted gases are recycled until the complete conversion of hydrogen and nitrogen to ammonia is eventually achieved. Figure 31.10.2 is a simplified layout of a Haber-Bosch process plant.

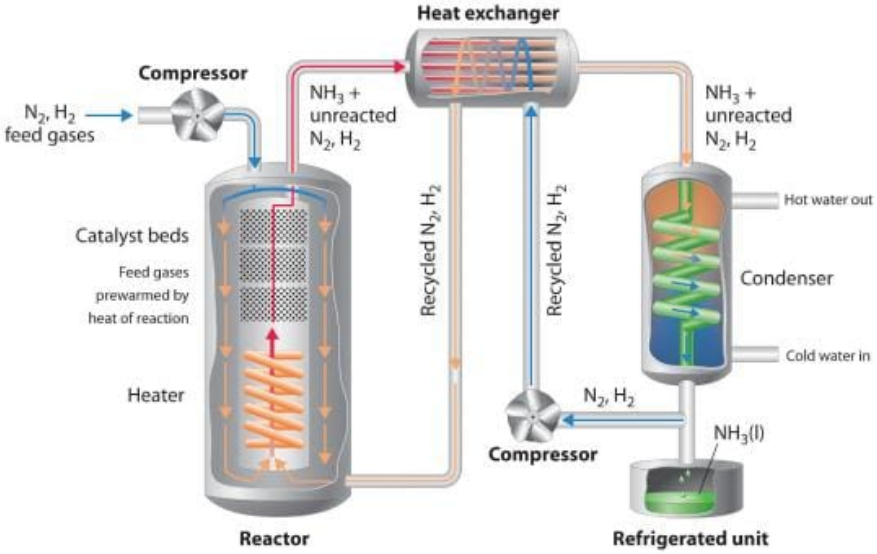


Figure 31.10.2 A Schematic Diagram of an Industrial Plant for the Production of Ammonia via the Haber-Bosch Process: A 3:1 mixture of gaseous H_2 and N_2 is compressed to 130–330 atm, heated to 400°C–530°C, and passed over an Fe_2O_3/K_2O catalyst, which results in partial conversion to gaseous NH_3. The resulting mixture of gaseous NH_3, H_2, and N_2 is passed through a heat exchanger, which uses the hot gases to prewarm recycled N_2 and H_2, and a condenser to cool the NH_3, giving a liquid that is readily separated from unreacted N_2 and H_2. (Although the normal boiling point of NH_3 is –33°C, the boiling point increases rapidly with increasing pressure, to 20°C at 8.5 atm and 126°C at 100 atm.) The unreacted N_2 and H_2 are recycled to form more NH_3.

We can write the seven reactions that are involved in the process where ad indicates that the molecule or atom is adsorbed on the catalyst

$$H_2(g) + 2S(s) \rightleftharpoons 2H(ad) \tag{31.10.1}$$

$$N_2(g) \rightleftharpoons N_2(ad) \tag{31.10.2}$$

$$N_2(ad) + 2S(s) \rightleftharpoons 2N(ad) \tag{31.10.3}$$

$$H(ad) + N(ad) \rightleftharpoons NH(ad) \tag{31.10.4}$$

$$NH(ad) + H(ad) \rightleftharpoons NH_2(ad) \tag{31.10.5}$$

$$NH_2(ad) + H(ad) \rightleftharpoons NH_3(ad) \tag{31.10.6}$$

$$NH_3(ad) \rightleftharpoons NH_3(g) \tag{31.10.7}$$

Reaction 31.10.3 is much the slowest, and therefore the rate determining step. Figure 31.10.3 summarizes the reaction scheme.

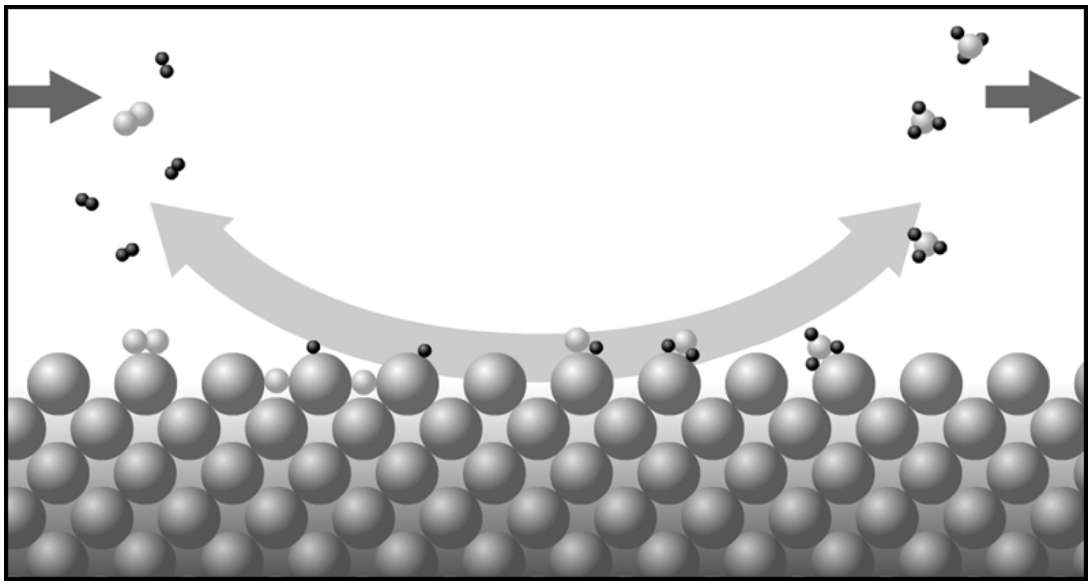


Figure 31.10.3: A representation of the reactions Eqs. 31.10.1 to 31.10.7 with H_2 and N_2 coming in from the left and being adsorbed on the catalyst. The H_2 and N_2 then atomize on the surface of the catalyst, followed by a set of sequential reactions forming NH, NH_2 and finally NH_3 which desorbs from the catalyst as shown on the right

Gerhard Ertl worked out the energetics of the reaction shown in Figure 31.10.4 below shows the amount of energy per mole needed on the catalyst and that which would be needed in the gas phase. Ertl's Nobel Prize speech about his work on the catalytic reactions forming ammonia and other catalytic reactions can be viewed on line.

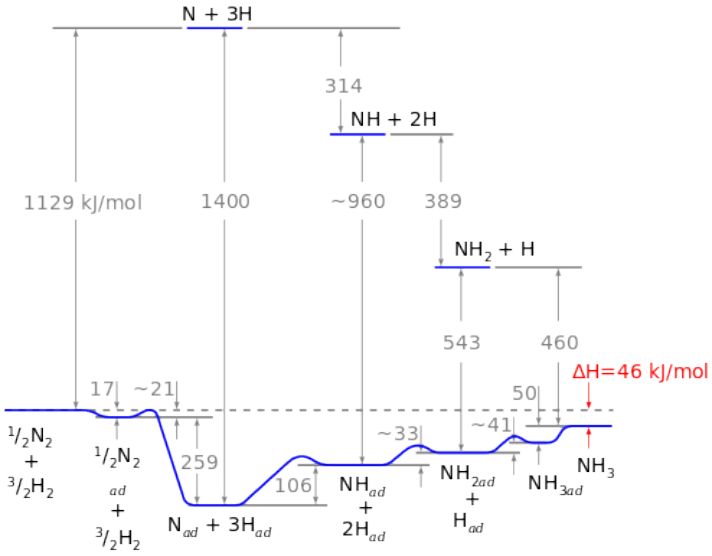


Figure 31.10.4: Ertl's group was able to measure the energy needed for each step of the Bosch-Haber process as opposed to the energy that would be needed in the gas phase.

Further studies of the Fe_2O_3/K_2O catalyst have shown that the rate of the reaction depends on the particular surface on which the reaction is occurring. Figure 31.10.5 shows the reaction rates for the synthesis of ammonia on five different surfaces of the iron.

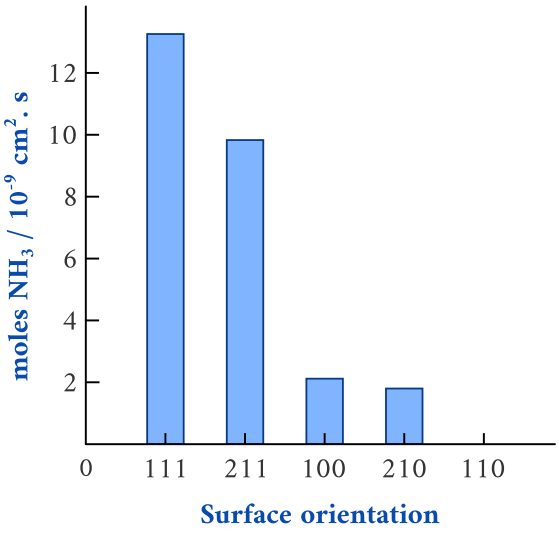


Figure 31.10.5: The rates of ammonia production for various iron catalyst surfaces. (CC BY-NC; Ümit Kaya via LibreTexts)

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Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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31.E: Homework Problems

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32: MATH CHAPTERS

32.1: Complex Numbers

32.2: Probability and Statistics

32.3: Partial Differentiation

32.4: Numerical Methods

32.5: Vectors

32.6: Spherical Coordinates

32.7: Determinants

32.8: Matrices

32.9: Series and Limits

32.10: Fourier Analysis

32.10.1: Fourier Analysis in Matlab

32.10.2: Fourier Synthesis of Periodic Waveforms

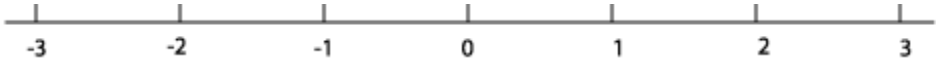
32.11: The Binomial Distribution and Stirling's Appromixation

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32.1: Complex Numbers

Real Numbers

Let us think of the ordinary numbers as set out on a line which goes to infinity in both positive and negative directions. We could start by taking a stretch of the line near the origin (that is, the point representing the number zero) and putting in the integers as follows:



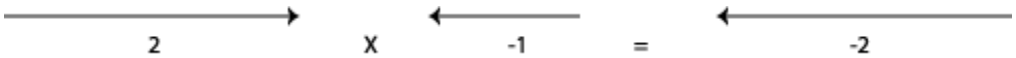
Next, we could add in rational numbers, such as ½, 23/11, etc., then the irrationals like $\sqrt{2}$, then numbers like π, and so on, so any number you can think of has its place on this line. Now let's take a slightly different point of view, and think of the numbers as represented by a *vector* from the origin to that number, so 1 is



and, for example, –2 is represented by:



Note that if a number is multiplied by –1, the corresponding vector is turned through 180 degrees. In pictures,



The "vector" 2 is turned through π, or 180 degrees, when you multiply it by –1.

Example A.1

What are the square roots of 4?

Solution

Well, 2, obviously, but also –2, because multiplying the backwards pointing vector –2 by –2 not only doubles its length, but also turns it through 180 degrees, so it is now pointing in the positive direction. We seem to have invented a hard way of stating that multiplying two negatives gives a positive, but thinking in terms of turning vectors through 180 degrees will pay off soon.

Solving Quadratic Equations

In solving the standard quadratic equation

$$ax^2 + bx + c = 0 \tag{32.1.1}$$

we find the solution to be:

$$x = \frac{-b \pm \sqrt{b^2 - ac}}{2a} \tag{32.1.2}$$

The problem with this is that sometimes the expression inside the square root is negative. What does that signify? For some

problems in physics, it means there is no solution. For example, if I throw a ball directly upwards at 10 meters per sec, and ask when will it reach a height of 20 meters, taking g = 10 m per sec^2, the solution of the quadratic equation for the time t has a negative number inside the square root, and that means that the ball doesn't get to 20 meters, so the question didn't really make sense.

We shall find, however, that there are other problems, in wide areas of physics, where negative numbers inside square roots have an important physical significance. For that reason, we need to come up with a scheme for interpreting them.

The simplest quadratic equation that gives trouble is:

$$x^2 + 1 = 0 \tag{32.1.3}$$

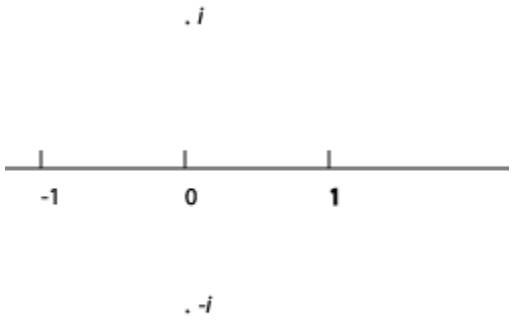
the solutions being

$$x = \pm\sqrt{-1} \tag{32.1.4}$$

What does that mean? We've just seen that the square of a positive number is positive, and the square of a negative number is also positive, since multiplying one negative number, which points backwards, by another, which turns any vector through 180 degrees, gives a positive vector. Another way of saying the same thing is to regard the minus sign itself, -, as an operator which turns the number it is applied to through 180 degrees. Now $(-2) \times (-2)$ has two such rotations in it, giving the full 360 degrees back to the positive axis.

To make sense of the square root of a negative number, we need to find something which when multiplied by itself gives a negative number. Let's concentrate for the moment on the square root of –1, from the quadratic equation above. Think of –1 as the operator – acting on the vector 1, so the – turns the vector through 180 degrees. We need to find the square root of this operator, the operator which applied *twice* gives the rotation through 180 degrees. Put like that, it is pretty obvious that the operator we want rotates the vector 1 through 90 degrees.

But if we take a positive number, such as 1, and rotate its vector through 90 degrees only, it isn't a number at all, at least in our original sense, since we put all known numbers on one line, and we've now rotated 1 away from that line. The new number created in this way is called a pure imaginary number, and is denoted by i.



Once we've found the square root of –1, we can use it to write the square root of any other negative number—for example, $2i$ is the square root of -4. Putting together a real number from the original line with an imaginary number (a multiple of *i*) gives a *complex number*. Evidently, complex numbers fill the entire two-dimensional plane. Taking ordinary Cartesian coordinates, any point P in the plane can be written as (x, y) where the point is reached from the origin by going x units in the direction of the positive real axis, then y units in the direction defined by i, in other words, the y axis.

Thus the point *P* with coordinates (*x*, *y*) can be identified with the complex number *z*, where

$$z = x + iy. \tag{32.1.5}$$

The plane is often called the *complex plane*, and representing complex numbers in this way is sometimes referred to as an Argand Diagram.

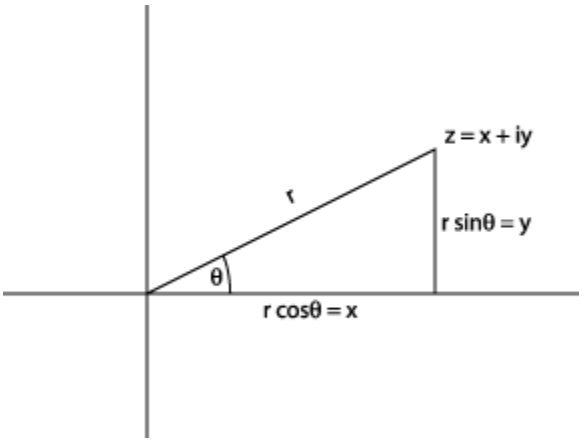
Visualizing the complex numbers as two-dimensional vectors, it is clear how to *add* two of them together. If $z_1 = x_1 + iy_1$, and $z_2 = x_2 + iy_2$, then $z_1 + z_2 = (x_1 + x_2) + i(y_1 + y_2)$. The real parts and imaginary parts are added separately, just like vector components.

Multiplying two complex numbers together does not have quite such a simple interpretation. It is, however, quite straightforward—ordinary algebraic rules apply, with i^2 replaced where it appears by -1. So for example, to multiply $z_1 = x_1 + iy_1$ by $z_2 = x_2 + iy_2$,

$$z_1 z_2 = (x_1 + iy_1)(x_2 + iy_2) = (x_1 x_2 - y_1 y_2) + i(x_1 y_2 + x_2 y_1). \tag{32.1.6}$$

Polar Coordinates

Some properties of complex numbers are most easily understood if they are represented by using the polar coordinates r, θ instead of (x, y) to locate z in the complex plane.



Note that $z = x + iy$ can be written $r(\cos\theta + i\sin\theta)$ from the diagram above. In fact, this representation leads to a clearer picture of multiplication of two complex numbers:

$$z_1 z_2 = r_2(\cos(\theta_1 + i\sin\theta_1) r_2(\cos(\theta_2 + i\sin\theta_2) \tag{32.1.7}$$

$$= r_1 r_2 \left[(\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2) + i(\sin\theta_1 \cos\theta_2 + \cos\theta_1 \sin\theta_2)\right] \tag{32.1.8}$$

$$= r_1 r_2 \left[\cos(\theta_1 + \theta_2) + i\sin(\theta_1 + \theta_2)\right] \tag{32.1.9}$$

So, if

$$z = r(cos\theta + i\sin\theta) = z_1 z_2 \tag{32.1.10}$$

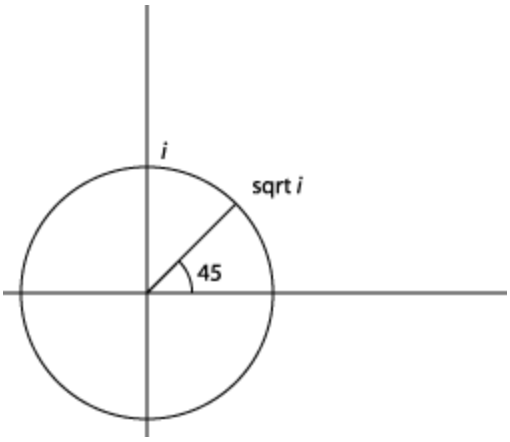
then

$$r = r_1 r_2 \tag{32.1.11}$$

and

$$\theta = \theta_1 \theta_2 \tag{32.1.12}$$

That is to say, to multiply together two complex numbers, we *multiply* the *r*'s – called the *moduli* – and *add* the phases, the θ 's. The modulus r is often denoted by \(|z|\), and called **mod *z***, the phase θ is sometimes referred to as **arg *z***. For example, $|i| = 1$, $\arg\ i = \pi/2$.

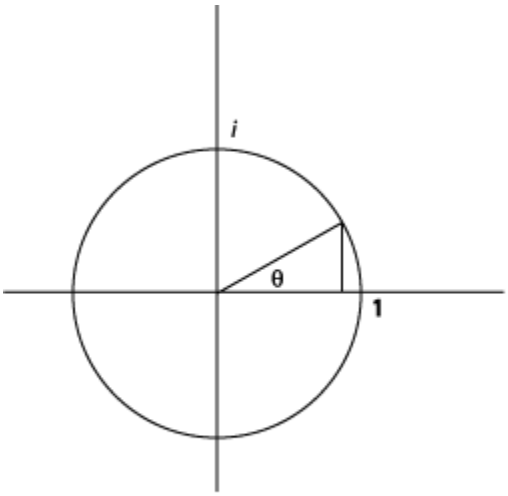


We can now see that, although we had to introduce these complex numbers to have a $\sqrt{-1}$, we do not need to bring in new types of numbers to get $\sqrt{-1}$, or $\sqrt{i}$. Clearly, $|\sqrt{i}| = 1$, $arg\sqrt{i} = 45\ °$. It is on the circle of unit radius centered at the origin, at 45°, and squaring it just doubles the angle.

The Unit Circle

In fact this circle—called the *unit circle*—plays an important part in the theory of complex numbers and every point on the circle has the form

$$z = \cos\theta + i\sin\theta = Cis(\theta) \tag{32.1.13}$$



Since all points on the unit circle have $|z| = 1$, by definition, multiplying any two of them together just amounts to adding the angles, so our new function $Cis(\theta)$ satisfies

$$Cis(\theta_1)Cis(\theta_2) = Cis(\theta_1 + \theta_2). \tag{32.1.14}$$

But that is just how multiplication works for exponents! That is,

$$a^{\theta_1}a^{\theta_2} = a^{\theta_1+\theta_2} \tag{32.1.15}$$

for a any constant, which strongly suggests that maybe our function $Cis(\theta$ is nothing but some constant a raised to the power θ, that is,

$$Cis(\theta) = a^{\theta} \tag{32.1.16}$$

It turns out to be convenient to write $a^{\theta} = e^{(\ln a)\theta} = e^{A\theta}$, where $A = \ln a$. This line of reasoning leads us to write

$$\cos\theta + i\sin\theta = e^{A\theta} \tag{32.1.17}$$

Now, for the above "addition formula" to work for multiplication, A must be a constant, *independent* of θ. Therefore, we can find the value of *A* by choosing θ for which things are simple. We take θ to be very small—in this limit:

$$\cos\theta = 1$$

$$\sin\theta = \theta$$

$$e^{A\theta} = 1 + A\theta$$

with we drop terms of order θ^2 and higher.

Substituting these values into Equation 32.1.17 gives θ

So we find:

$$(\cos\theta + i\sin\theta)e^{i\theta} \tag{32.1.18}$$

To test this result, we expand $e^{i\theta}$:

$$e^{i\theta} = 1 + i\theta + \frac{(i\theta)^2}{2!} + \frac{(i\theta)^3}{3!} + \frac{(i\theta)^4}{4!} + \frac{(i\theta)^5}{5!}\ldots \tag{32.1.19}$$

$$= 1 + i\theta - \frac{\theta^2}{2!} - \frac{i\theta^3}{3!} + \frac{\theta^4}{4!} + \frac{i\theta^5}{5!}\ldots \tag{32.1.20}$$

$$= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!}\right) + i\left(\theta - \frac{i\theta^3}{3!} + \frac{i\theta^5}{5!}\right) \tag{32.1.21}$$

$$= \cos\theta + i\sin\theta \tag{32.1.22}$$

We write $= \cos\theta + i\sin\theta$ in Equation 32.1.22 because the series in the brackets are precisely the Taylor series for $\cos\theta$ and $\sin\theta$ confirming our equation for $e^{i\theta}$. Changing the sign of θ it is easy to see that

$$e^{-i\theta} = \cos\theta - i\sin\theta \tag{32.1.23}$$

so the two trigonometric functions can be expressed in terms of exponentials of complex numbers:

$$\cos(\theta) = \frac{1}{2}\left(e^{i\theta} + e^{-i\theta}\right)$$

$$\sin(\theta) = \frac{1}{2i}\left(e^{i\theta} - e^{-i\theta}\right)$$

Euler Formula

The Euler formula states that any complex number can be written:

$$e^{i\theta} = \cos\theta + i\sin\theta$$

Contributors and Attributions

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32.2: Probability and Statistics

A random variable X can have more than one value x as an outcome. Which value the variable has in a particular case is a matter of *chance* and cannot be predicted other than that we associate a probability to the outcome. **Probability** p is a number between 0 and 1 that indicates the likelihood that the variable X has a particular outcome x. The set of outcomes and their probabilities form a ***probability distribution***. There are two kinds of distributions:

1. discrete ones
2. continuous ones

Total probability should always add up to unity.

Discrete Distributions

A good example of a discrete distribution is a *true coin*. The random variable X can have two values:

1. heads (0)
2. tails (1)

Both have equal probability and as the sum must equal unity, the probability must be ½ for each. 'The probability that X=heads' is written formally as:

$$Pr(X = heads) = Pr(X = 0) = 0.5$$

The random function is written as a combination of three statements.

- Pr(X=0) = ½
- Pr(X=1) = ½
- elsewhere Pr = 0

Continuous Distributions

Now consider a spherical die. One could say it has an infinite number of facets that it can land on. Thus the number of outcomes $n = \infty$, this make each probability

$$p = 1/\infty = 0.$$

This creates a bit of a mathematical problem, because how can we get a total probability of unity by adding up zeros? Also, if we divide the sphere in a northern and a southern hemisphere clearly the probability that it lands on a point in say, the north should be ½. Still, p = 0 for all points. We introduce a new concept: **probability density** over which we *integrate* rather than *sum*. We assign an equal density to each point of the sphere and make sure that if we integrate over a hemisphere we get ½. (This involves two angles θ and φ and an integration over them and I won't go into that).

A bit simpler example of a continuous distribution than the spherical die is the 1D ***uniform*** distribution. It is the one that the Excel function =RAND() produces to good approximation. Its probability density is defined as

- f(x) = 1 for 0<1>
- f(x) = 0 elsewhere

The figure shows a (bivariate) uniform distribution.

The probability that the outcome is smaller than 0.5 is written as Pr(X<0.5) and is found by integrating from 0 to 0.5 over f(x).

$$\Pr(X<0.5) = \int \mathbf{f(x)}.dx \text{ from } 0 \text{ to } 0.5 = \int \mathbf{1}.dx \text{ from } 0 \text{ to } 0.5 = [x]^{0.5}\text{-}[x]_0 = 0.5$$

Notice that in each individual outcome b the probability is indeed zero because an integral from b to b is always zero, even if the probability density f(b) is not zero. Clearly the probability and the probability density are not the same. Unfortunately the distinction between probability and probability density is often not properly made in the physical sciences. Moments can also be computed for continuous distributions by integrating over the probability densityalt

Another well-known continuous distribution is the ***normal*** (or ***Gaussian***) distribution, defined as:

\[f(x) = 1/[√(2π)σ] * exp(-½[(x-μ)/σ]^2) \nonumber \]

(Notice the normalization factor 1/[√(2π)σ])

We can also compute moments of continuous distribution. Instead of using a summation we now have to evaluate an integral:

$$\langle X \rangle = \int [f(x)^* x] dx$$

$$\langle X^2 \rangle = \int [f(x)^* x^2] dx$$

For the normal distribution $\langle X \rangle = \mu$

Exercise

Compute ^{2}> and ^{3}> for the uniform distribution. answer>

Indistinguishable Outcomes

When flipping two coins we could get four outcomes: two heads (0), heads plus tails (1), tails plus heads (1), two tails (2)

Each outcome is equally likely, this implies a probability of ¼ for each:

X_{tot} = X1 + X2 = 0 + 0 = 0 p=¼

X_{tot} = X1 + X2 = 0 + 1 = 1 p=¼

X_{tot} = X1 + X2 = 1 + 0 = 1 p=¼

X_{tot} = X1 + X2 = 1 + 1 = 2 p=¼

The probability of a particular outcome is often abbreviated simply to p. The two middle outcomes collapse into one with p=¼+¼= ½ if the coins are **indistinguishable**. We will see that this concept has very important consequences in statistical thermodynamics.

If we cannot distinguish the two outcomes leading to X_{tot}=1 we get the following random function:

- Pr(X_{tot}=0) = ¼
- Pr(X_{tot}=1) = ½
- Pr(X_{tot}=2) = ¼
- elsewhere Pr = 0

Notice that it is quite possible to have a distribution where the probabilities differ from outcome to outcome. Often the p values are given as f(x), a function of x. An example:

X3 defined as:

- f(x) = (x+1)/6 for x=0,1,2;
- f(x) =0 elsewhere;

The factor 1/6 makes sure the probabilities add up to unity. Such a factor is known as a **normalization factor**. Again this concept is of prime importance in statistical thermodynamics.

Another example of a discrete distribution is a die. If it has 6 sides (the most common die) there are six outcomes, each with p= 1/6. There are also dice with n=4, 12 or 20 sides. Each outcome will then have p= 1/n.

Moments of Distributions

In important aspect of probability distributions are the **moments** of the distribution. They are values computed by summing over the whole distribution.

The **zero** order moment is simply the sum of all p and that is unity:

$$^0> = \Sigma X^0 * p = \Sigma 1 * p = 1$$

The **first** moment multiplies each outcome with its probability and sums over all outcomes:

$$= \Sigma X * p$$

This moment is known as the ***average*** or ***mean***. (It is what we have done to your grades for years...)

For one coin is ½, for two coins is 1. (Exercise: verify this)

The **second** moment is computed by summing the product of the square of X and p:

$$^2> = \Sigma X^2 * p$$

For one coin we have $^2>$ = ½,

For two coins $^2>$= [0*¼ + 1*½ + 4*¼] = 1.5

What is $^2>$ for X3? answer

The notation is used a lot in quantum mechanics, often in the form <ψ*ψ> or <ψ*|h|ψ>. The <.. part is known as the ***bra***, the ..> part as the ***ket***. (Together ***bra***(c)***ket***)

Intermezzo: The strange employer

You have a summer job but your employer likes games of chance. At the end of every day he rolls a die and pays you the square of the outcome in dollars per hour. So on a lucky day you'd make $36.- per hour, but on a bad day $1.-. Is this a bad deal? What would you make on the average over a longer period?

To answer this we must compute the second moment $^2>$ of the distribution:

Answer available at the end of this section.

(I have taken p=1/6 out of brackets because the value is the same for all six outcomes)

As you see in the intermezzo, the value of the second moment is in this case what you ***expect*** to be making on the long term. Moments are examples of what is know as **expectation values**. Another term you may run into that of a **functional**. A functional is a *number* computed by some operation (such as summation or integration) over a whole function. Moments are clearly an example of that too.

Answers

^{2}> = 1/6 *[1+4+9+16+25+36] = 91/6 = $15.17 per hour.

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32.3: Partial Differentiation

The development of thermodynamics would have been unthinkable without calculus in more than one dimension (multivariate calculus) and partial differentiation is essential to the theory.

'Active' Variables

When applying partial differentiation it is very important to keep in mind, which symbol is the variable and which ones are the constants. Mathematicians usually write the variable as x or y and the constants as a, b or c but in Physical Chemistry the symbols are different. It sometimes helps to replace the symbols in your mind.

For example the van der Waals equation can be written as:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \tag{32.3.1}$$

Suppose we must compute the partial differential

$$\left(\frac{\partial P}{\partial \overline{V}}\right)_T$$

In this case molar volume is the variable 'x' and the pressure is the function $f(x)$, the rest is just constants, so Equation 32.3.1 can be rewritten in the form

$$f(x) = \frac{c}{x - b} - \frac{a}{x^2} \tag{32.3.2}$$

When calculating

$$\left(\frac{\partial P}{\partial T}\right)_{\overline{V}}$$

should look at Equation 32.3.1 as:

$$f(x) = cx - d$$

The active variable 'x' is now the temperature T and all the rest is just constants. It is useful to train your eye to pick out the one active one from all the inactive ones. Use highlighters, underline, rewrite, do whatever helps you best.

Cross Derivatives

As shown in Equations H.5 and H.6 there are also higher order partial derivatives versus T and versus V. A very interesting derivative of second order and one that is used extensively in thermodynamics is the mixed second order derivative.

$$\left(\frac{\partial^2 P}{\partial T\, \partial \overline{V}}\right) = \left(\frac{\partial^P}{\partial \overline{V}\, \partial T}\right) \tag{32.3.3}$$

Of course here the 'active' variable is first T, then V. The interesting thing about it is that it does not matter whether you first take T and then V or the other way around.

Example H-2 shows an example of how mixed derivatives can be used to translate one quantity into the other. This trick is used over and over again in thermodynamics because it allows you to replace a quantity that is really hard to measure by one (or more) that are much easier to get good experimental values for.

For example:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

This expression is not obvious at all. It tells you that if you study the pressure P when heating up while keeping the volume the same (which is doable) you're measuring how the entropy changes with volume under isothermal conditions. Entropy will be discussed later, suffice it to say that nobody has ever constructed a working 'entropometer'! So that is an impossible quantity to measure directly.

The Decomposition of Changes

A very important result of multivariate calculus is that if a quantity Q is a function of more than one variable, say A and B that we can decompose any infinitesimal change dQ into infinitesimal changes in A and B in a very simple linear way:

$$dQ = \alpha\, dA + \beta dB \tag{32.3.4}$$

dq is sometimes referred to as the total differential. The coefficients α and β are the partial derivatives of first order versus A and B. This mathematical fact is something we will be using over and over.

Exact and Inexact differentials: State and path functions

The car trip

Suppose you drive your car up and down a mountain. You perform two measurements: you have a barometer that measures the air pressure and you keep an eye on your gas gage. Even though the barometer will show lower values on top of the mountain, its value will return to its initial value when you return home (barring weather changes). You might wish the same would hold for your gas gage particularly at current gas prices!

Pressure is a good example of a **state function** (it returns to its old value if you go back to a previous state). The other (the gas gage) is a path function. (Make a detour and your bank account will tell you difference!).

The difference between state and path functions has its roots deep in mathematics and it comes in as soon as a function has two of more variables.

The gas law is a good example. The pressure depends on both temperature T and (molar) volume V. When changing the pressure a little bit, say by dP we can show that we can write that out in the two possible components dT and dV as:

$$dP = pdT + qdV \tag{32.3.5}$$

$$= \left(\frac{\partial S}{\partial V}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \tag{32.3.6}$$

At first, I wrote arbitrary coefficients p and q in Equation 32.3.5, but as you can see they are really partial derivatives (Equation 32.3.6). This is another way that thermodynamics exploits multivariate calculus: it shows how total changes can be built up of various contributions.

The interesting thing is that ***if*** the function P is a ***state*** function (and your barometer will testify to that) then Equation 32.3.3 **must** hold. However, if the function is a ***path*** function, then this equality does ***not*** hold.

Thermodynamics is largely based upon exploiting the above facts:

- It tries to define state functions to describe energy changes
- It tries to decompose changes into well-defined contributions
- It uses partial differentials to link known quantities to unknown ones

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32.4: Numerical Methods

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32.5: Vectors

In this chapter we will review a few concepts you probably know from your physics courses. This chapter does not intend to cover the topic in a comprehensive manner, but instead touch on a few concepts that you will use in your physical chemistry classes.

A vector is a quantity that has both a magnitude and a direction, and as such they are used to specify the position, velocity and momentum of a particle, or to specify a force. Vectors are usually denoted by boldface symbols (e.g. $\mathbf{u}$) or with an arrow above the symbol (e.g. $\vec{u}$). A tilde placed above or below the name of the vector is also commonly used in shorthand ($\tilde{u}$,$\underset{\sim}{u}$).

If we multiply a number a by a vector $\mathbf{v}$, we obtain a new vector that is parallel to the original but with a length that is a times the length of $\mathbf{v}$. If a is negative $a\mathbf{v}$ points in the opposite direction than $\mathbf{v}$. We can express any vector in terms of the so-called unit vectors. These vectors, which are designated $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$, have unit length and point along the positive x, y and z axis of the cartesian coordinate system (Figure $32.5.1$). The symbol $\hat{\mathbf{i}}$ is read "i-hat". Hats are used to denote that a vector has unit length.

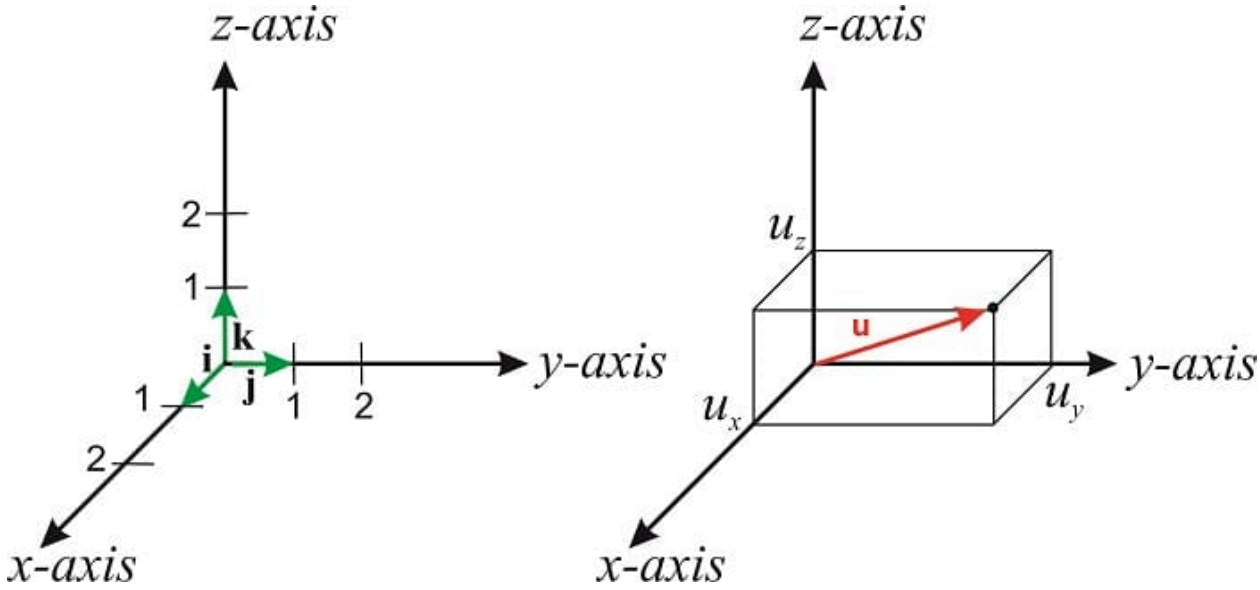


Figure $32.5.1$: Left: The unit vectors. Right: A vector $\mathbf{u}$ can be expressed in terms of the unit vectors as $\mathbf{u} = u_x\hat{\mathbf{i}} + u_y\hat{j} + u_z\hat{\mathbf{k}}$ (CC BY-NC-SA; Marcia Levitus)

The length of $\mathbf{u}$ is its magnitude (or modulus), and is usually denoted by u:

$$u = |u| = (u_x^2 + u_y^2 + u_z^2)^{1/2} \tag{32.5.1}$$

If we have two vectors $\mathbf{u} = u_x\hat{\mathbf{i}} + u_y\hat{\mathbf{j}} + u_z\hat{\mathbf{k}}$ and $\mathbf{v} = v_x\hat{\mathbf{i}} + v_y\hat{\mathbf{j}} + v_z\hat{\mathbf{k}}$, we can add them to obtain

$$\mathbf{u} + \mathbf{v} = (u_x + v_x)\hat{\mathbf{i}} + (u_y + v_y)\hat{\mathbf{j}} + (u_z + v_z)\hat{\mathbf{k}}$$

or subtract them to obtain:

$$\mathbf{u} - \mathbf{v} = (u_x - v_x)\hat{\mathbf{i}} + (u_y - v_y)\hat{\mathbf{j}} + (u_z - v_z)\hat{\mathbf{k}}$$

When it comes to multiplication, we can perform the product of two vectors in two different ways. The first, which gives a scalar (a number) as the result, is called scalar product or dot product. The second, which gives a vector as a result, is called the vector (or cross) product. Both are important operations in physical chemistry.

The Scalar Product

The scalar product of vectors $\mathbf{u}$ and $\mathbf{v}$, also known as the dot product or inner product, is defined as (notice the dot between the

symbols representing the vectors)

$$\mathbf{u}\cdot\mathbf{v}=|\mathbf{u}||\mathbf{v}|\cos\theta$$

where θ is the angle between the vectors. Notice that the dot product is zero if the two vectors are perpendicular to each other, and equals the product of their absolute values if they are parallel. It is easy to prove that

$$\mathbf{u}\cdot\mathbf{v}=u_xv_x+u_yv_y+u_zv_z$$

Example 32.5.1

Show that the vectors

$$\mathbf{u}_1=\frac{1}{\sqrt{3}}\hat{\mathbf{i}}+\frac{1}{\sqrt{3}}\hat{\mathbf{j}}+\frac{1}{\sqrt{3}}\hat{\mathbf{k}}$$
$$\mathbf{u}_2=\frac{1}{\sqrt{6}}\hat{\mathbf{i}}-\frac{2}{\sqrt{6}}\hat{\mathbf{j}}+\frac{1}{\sqrt{6}}\hat{\mathbf{k}}$$
$$\mathbf{u}_3=-\frac{1}{\sqrt{2}}\hat{\mathbf{i}}+\frac{1}{\sqrt{2}}\hat{\mathbf{k}}$$

are of unit length and are mutually perpendicular.

Solution

The length of the vectors are:

$$|\mathbf{u}_1|=\left[\left(\frac{1}{\sqrt{3}}\right)^2+\left(\frac{1}{\sqrt{3}}\right)^2+\left(\frac{1}{\sqrt{3}}\right)^2\right]^{1/2}=\left[\frac{1}{3}+\frac{1}{3}+\frac{1}{3}\right]^{1/2}=1$$
$$|\mathbf{u}_2|=\left[\left(\frac{1}{\sqrt{6}}\right)^2+\left(-\frac{2}{\sqrt{6}}\right)^2+\left(\frac{1}{\sqrt{6}}\right)^2\right]^{1/2}=\left[\frac{1}{6}+\frac{4}{6}+\frac{1}{6}\right]^{1/2}=1$$
$$|\mathbf{u}_3|=\left[\left(-\frac{1}{\sqrt{2}}\right)^2+\left(\frac{1}{\sqrt{2}}\right)^2\right]^{1/2}=\left[\frac{1}{2}+\frac{1}{2}\right]^{1/2}=1$$

To test if two vectors are perpendicular, we perform the dot product:

$$\mathbf{u}_1\cdot\mathbf{u}_2=\left(\frac{1}{\sqrt{3}}\frac{1}{\sqrt{6}}-\frac{1}{\sqrt{3}}\frac{2}{\sqrt{6}}+\frac{1}{\sqrt{3}}\frac{1}{\sqrt{6}}\right)=0$$
$$\mathbf{u}_1\cdot\mathbf{u}_3=\left(-\frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}}\right)=0$$
$$\mathbf{u}_2\cdot\mathbf{u}_3=\left(-\frac{1}{\sqrt{6}}\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{6}}\frac{1}{\sqrt{2}}\right)=0$$

Therefore, we just proved that the three pairs are mutually perpendicular, and the three vectors have unit length. In other words, these vectors are the vectors $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$ rotated in space.

If the dot product of two vectors (of any dimension) is zero, we say that the two vectors are orthogonal. If the vectors have unit length, we say they are normalized. If two vectors are both normalized and they are orthogonal, we say they are orthonormal. The set of vectors shown in the previous example form an orthonormal set.[vectors:orthonormal] These concepts also apply to vectors that contain complex entries, but how do we perform the dot product in this case?

In general, the square of the modulus of a vector is

$$|\mathbf{u}|^2=\mathbf{u}\cdot\mathbf{u}=u_x^2+u_y^2+u_z^2.$$

However, this does not work correctly for complex vectors. The square of i is -1, meaning that we risk having non-positive absolute values. To address this issue, we introduce a more general version of the dot product:

$$\mathbf{u} \cdot \mathbf{v} = u_x^* v_x + u_y^* v_y + u_z^* v_z,$$

where the "$*$" refers to the complex conjugate. Therefore, to calculate the modulus of a vector $\mathbf{u}$ that has complex entries, we use its complex conjugate:

$$|\mathbf{u}|^2 = \mathbf{u}^* \cdot \mathbf{u}$$

Example 32.5.2: Calculating the Modulus of a vector

Calculate the modulus of the following vector:

$$\mathbf{u} = \hat{\mathbf{i}} + i\hat{\mathbf{j}}$$

Solution

$$|\mathbf{u}|^2 = \mathbf{u}^* \cdot \mathbf{u} = (\hat{\mathbf{i}} - i\hat{\mathbf{j}})(\hat{\mathbf{i}} + i\hat{\mathbf{j}}) = (1)(1) + (-i)(i) = 2 \rightarrow |\mathbf{u}| = \sqrt{2}$$

Analogously, if vectors contain complex entries, we can test whether they are orthogonal or not by checking the dot product $\mathbf{u}^* \cdot \mathbf{v}$.

Example 32.5.3: Confirming orthogonality

Determine if the following pair of vectors are orthogonal (do not confuse the irrational number i with the unit vector $\hat{\mathbf{i}}$!)

$$\mathbf{u} = \hat{\mathbf{i}} + (1 - i)\hat{\mathbf{j}}$$

and

$$\mathbf{v} = (1 + i)\hat{\mathbf{i}} + \hat{\mathbf{j}}$$

Solution

$$\mathbf{u}^* \cdot \mathbf{v} = (\hat{\mathbf{i}} + (1 + i)\hat{\mathbf{j}})((1 + i)\hat{\mathbf{i}} + \hat{\mathbf{j}}) = (1)(1 + i) + (1 + i)(1) = 2 + 2i \neq 0$$

Therefore, the vectors are not orthogonal.

The Vector Product

The vector product of two vectors is a vector defined as

$$\mathbf{u} \times \mathbf{v} = |\mathbf{u}||\mathbf{v}|\mathbf{n} \sin\theta$$

where θ is again the angle between the two vectors, and $\mathbf{n}$ is the unit vector perpendicular to the plane formed by $\mathbf{u}$ and $\mathbf{v}$. The direction of the vector $\mathbf{n}$ is given by the right-hand rule. Extend your right hand and point your index finger in the direction of $\mathbf{u}$ (the vector on the left side of the $\times$ symbol) and your forefinger in the direction of $\mathbf{v}$. The direction of $\mathbf{n}$, which determines the direction of $\mathbf{u} \times \mathbf{v}$, is the direction of your thumb. If you want to revert the multiplication, and perform $\mathbf{v} \times \mathbf{u}$, you need to point your index finger in the direction of $\mathbf{v}$ and your forefinger in the direction of $\mathbf{u}$ (still using the right hand!). The resulting vector will point in the opposite direction (Figure 32.5.1).

The magnitude of $\mathbf{u} \times \mathbf{v}$ is the product of the magnitudes of the individual vectors times $\sin\theta$. This magnitude has an interesting geometrical interpretation: it is the area of the parallelogram formed by the two vectors (Figure 32.5.1).

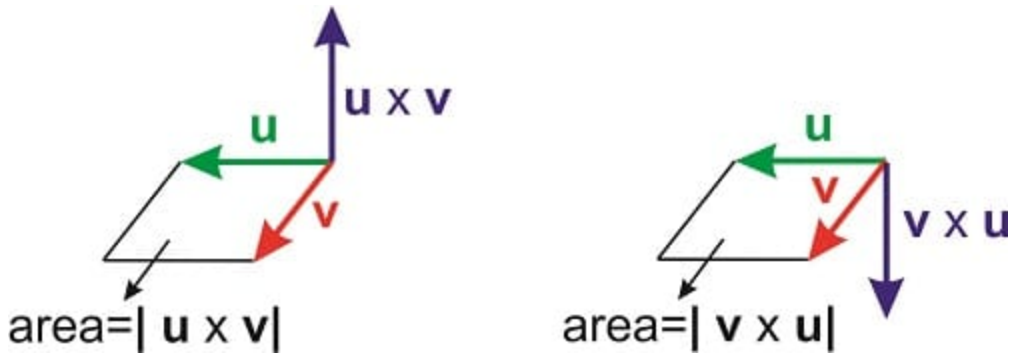


Figure 32.5.1: The vector product (CC BY-NC-SA; Marcia Levitus)

The cross product can also be expressed as a determinant:

$$\mathbf{u}\times\mathbf{v}=\begin{vmatrix}\hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}}\\ u_x & u_y & u_z\\ v_x & v_y & v_z\end{vmatrix}$$

Example 32.5.1:

Given $\mathbf{u}=-2\hat{\mathbf{i}}+\hat{\mathbf{j}}+\hat{\mathbf{k}}$ and $\mathbf{v}=3\hat{\mathbf{i}}-\hat{\mathbf{j}}+\hat{\mathbf{k}}$, calculate $\mathbf{w}=\mathbf{u}\times\mathbf{v}$ and verify that the result is perpendicular to both $\mathbf{u}$ and $\mathbf{v}$.

Solution

$$\begin{aligned}\mathbf{u}\times\mathbf{v}&=\begin{vmatrix}\hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}}\\ u_x & u_y & u_z\\ v_x & v_y & v_z\end{vmatrix}=\begin{vmatrix}\hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}}\\ -2 & 1 & 1\\ 3 & -1 & 1\end{vmatrix}\\ &=\hat{\mathbf{i}}(1+1)-\hat{\mathbf{j}}(-2-3)+\hat{\mathbf{k}}(2-3)\\ &=2\hat{\mathbf{i}}+5\hat{\mathbf{j}}-\hat{\mathbf{k}}\end{aligned}$$

To verify that two vectors are perpendicular we perform the dot product:

$$\mathbf{u}\cdot\mathbf{w}=(-2)(2)+(1)(5)+(1)(-1)=0$$

$$\mathbf{v}\cdot\mathbf{w}=(3)(2)+(-1)(5)+(1)(-1)=0$$

An important application of the cross product involves the definition of the angular momentum. If a particle with mass m moves a velocity $\mathbf{v}$ (a vector), its (linear) momentum is $\mathbf{p}=m\mathbf{v}$. Let $\mathbf{r}$ be the position of the particle (another vector), then the angular momentum of the particle is defined as

$$\mathbf{l}=\mathbf{r}\times\mathbf{p}$$

The angular momentum is therefore a vector perpendicular to both $\mathbf{r}$ and $\mathbf{p}$. Because the position of the particle needs to be defined with respect to a particular origin, this origin needs to be specified when defining the angular momentum.

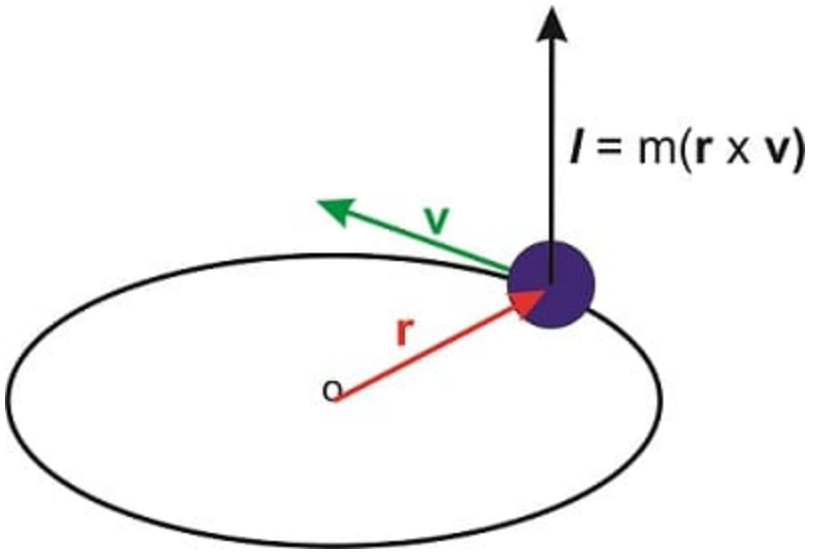


Figure 32.5.2: The angular momentum of a particle of position $\mathbf{r}$ from the origin and momentum $\mathbf{p} = m\mathbf{v}$ (CC BY-NC-SA; Marcia Levitus)

Vector Normalization

A vector of any given length can be divided by its modulus to create a unit vector (i.e. a vector of unit length). We will see applications of unit (or normalized) vectors in the next chapter.

For example, the vector

$$\mathbf{u} = \hat{\mathbf{i}} + \hat{\mathbf{j}} + i\hat{\mathbf{k}}$$

has a magnitude:

$$|\mathbf{u}|^2 = 1^2 + 1^2 + (-i)(i) = 3 \rightarrow |\mathbf{u}| = \sqrt{3}$$

Therefore, to normalize this vector we divide all the components by its length:

$$\hat{\mathbf{u}} = \frac{1}{\sqrt{3}}\hat{\mathbf{i}} + \frac{1}{\sqrt{3}}\hat{\mathbf{j}} + \frac{i}{\sqrt{3}}\hat{\mathbf{k}}$$

Notice that we use the “hat” to indicate that the vector has unit length.

Need help? The links below contain solved examples.

Operations with vectors: http://tinyurl.com/mw4qmz8

External links:

- The dot product: http://patrickjmt.com/vectors-the-dot-product/
- The cross product: http://patrickjmt.com/the-cross-product/
- The dot and cross product: http://www.youtube.com/watch?v=enr7JqvehJs

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32.6: Spherical Coordinates

Objectives

- Understand the concept of area and volume elements in cartesian, polar and spherical coordinates.
- Be able to integrate functions expressed in polar or spherical coordinates.
- Understand how to normalize orbitals expressed in spherical coordinates, and perform calculations involving triple integrals.

Coordinate Systems

The simplest coordinate system consists of coordinate axes oriented perpendicularly to each other. These coordinates are known as cartesian coordinates or rectangular coordinates, and you are already familiar with their two-dimensional and three-dimensional representation. In the plane, any point P can be represented by two signed numbers, usually written as (x, y), where the coordinate x is the distance perpendicular to the x axis, and the coordinate y is the distance perpendicular to the y axis (Figure $32.6.1$, left). In space, a point is represented by three signed numbers, usually written as (x, y, z) (Figure $32.6.1$, right).

Often, positions are represented by a vector, $\vec{r}$, shown in red in Figure $32.6.1$. In three dimensions, this vector can be expressed in terms of the coordinate values as $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$, where $\hat{i} = (1, 0, 0)$, $\hat{j} = (0, 1, 0)$ and $\hat{z} = (0, 0, 1)$ are the so-called unit vectors.

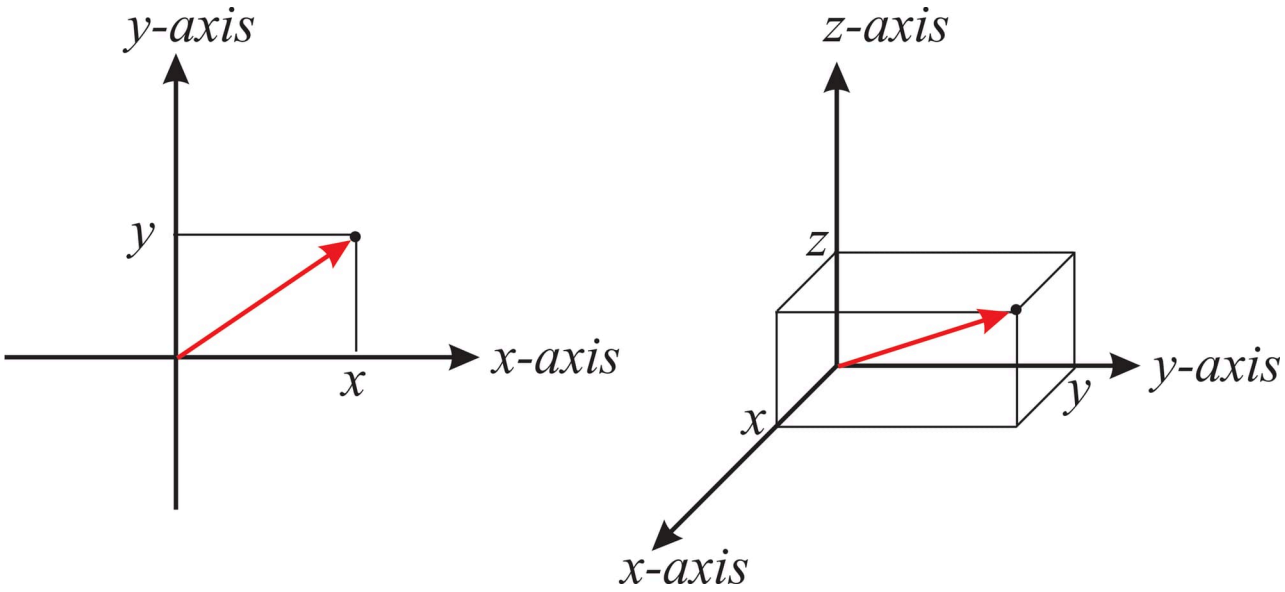


Figure $32.6.1$: Cartesian coordinates (CC BY-NC-SA; Marcia Levitus)

We already know that often the symmetry of a problem makes it natural (and easier!) to use other coordinate systems. In two dimensions, the polar coordinate system defines a point in the plane by two numbers: the distance r to the origin, and the angle θ that the position vector forms with the x-axis. Notice the difference between $\vec{r}$, a vector, and r, the distance to the origin (and therefore the modulus of the vector). Vectors are often denoted in bold face (e.g. **r**) without the arrow on top, so be careful not to confuse it with r, which is a scalar.

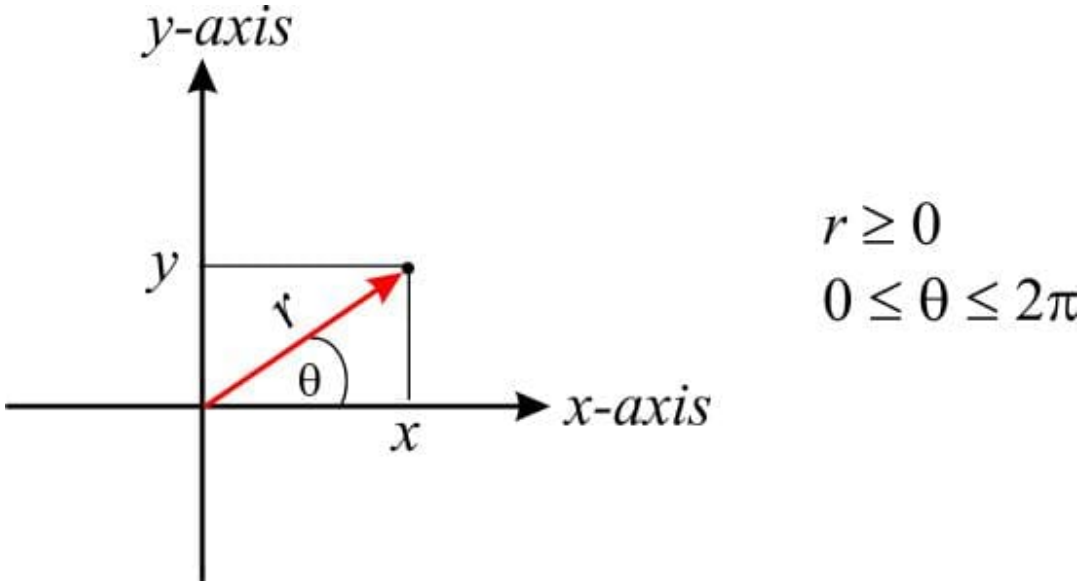


Figure 32.6.2: Plane polar coordinates (CC BY-NC-SA; Marcia Levitus)

While in cartesian coordinates x, y (and z in three-dimensions) can take values from $-\infty$ to ∞, in polar coordinates r is a positive value (consistent with a distance), and θ can take values in the range $[0, 2\pi]$.

The relationship between the cartesian and polar coordinates in two dimensions can be summarized as:

$$x = r\cos\theta \tag{32.6.1}$$

$$y = r\sin\theta \tag{32.6.2}$$

$$r^2 = x^2 + y^2 \tag{32.6.3}$$

$$\tan\theta = y/x \tag{32.6.4}$$

In three dimensions, the spherical coordinate system defines a point in space by three numbers: the distance r to the origin, a polar angle ϕ that measures the angle between the positive x-axis and the line from the origin to the point P projected onto the xy-plane, and the angle θ defined as the is the angle between the z-axis and the line from the origin to the point P:

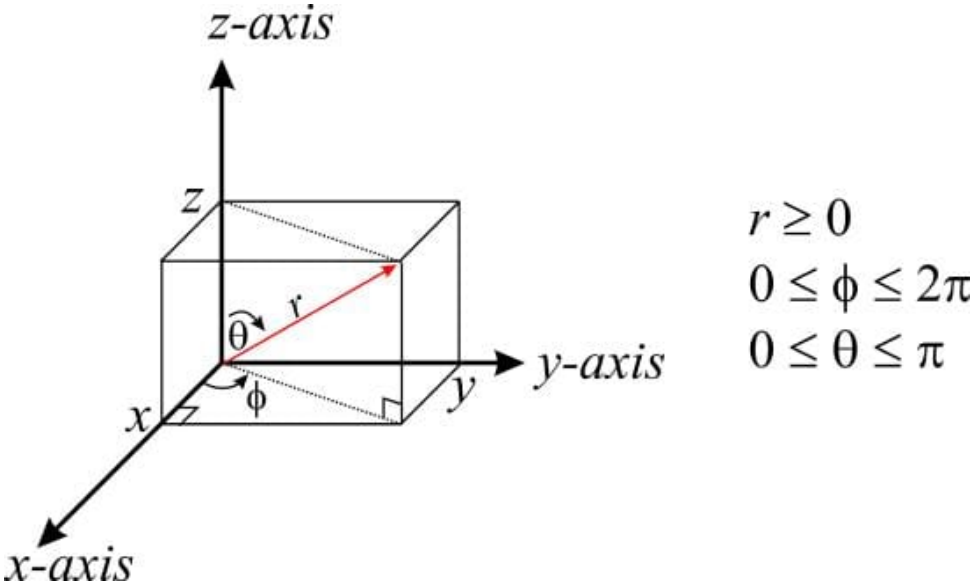


Figure 32.6.3: Spherical coordinates (CC BY-NC-SA; Marcia Levitus)

Before we move on, it is important to mention that depending on the field, you may see the Greek letter θ (instead of ϕ) used for

the angle between the positive x-axis and the line from the origin to the point P projected onto the xy-plane. That is, θ and ϕ may appear interchanged. This can be very confusing, so you will have to be careful. When using spherical coordinates, it is important that you see how these two angles are defined so you can identify which is which.

Spherical coordinates are useful in analyzing systems that are symmetrical about a point. For example a sphere that has the cartesian equation $x^2 + y^2 + z^2 = R^2$ has the very simple equation $r = R$ in spherical coordinates. Spherical coordinates are the natural coordinates for physical situations where there is spherical symmetry (e.g. atoms). The relationship between the cartesian coordinates and the spherical coordinates can be summarized as:

$$x = r \sin\theta \cos\phi \tag{32.6.5}$$

$$y = r \sin\theta \sin\phi \tag{32.6.6}$$

$$z = r \cos\theta \tag{32.6.7}$$

These relationships are not hard to derive if one considers the triangles shown in Figure $32.6.4$:

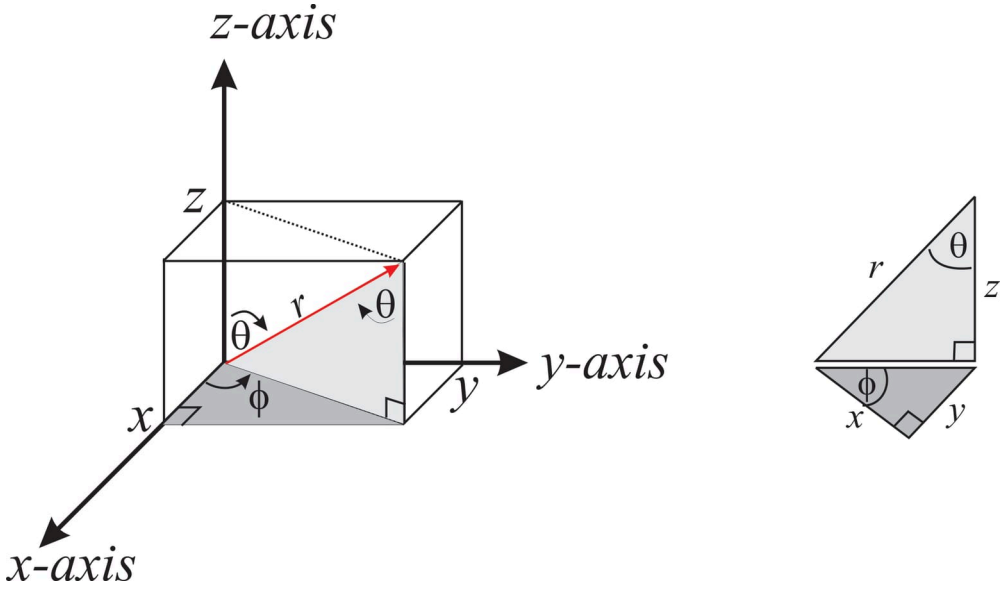


Figure $32.6.4$: Spherical coordinates (CC BY-NC-SA; Marcia Levitus)

Area and Volume Elements

In any coordinate system it is useful to define a differential area and a differential volume element. In cartesian coordinates the differential area element is simply $dA = dx\ \ dy$ (Figure $32.6.1$), and the volume element is simply $dV = dx\ \ dy\ \ dz$.

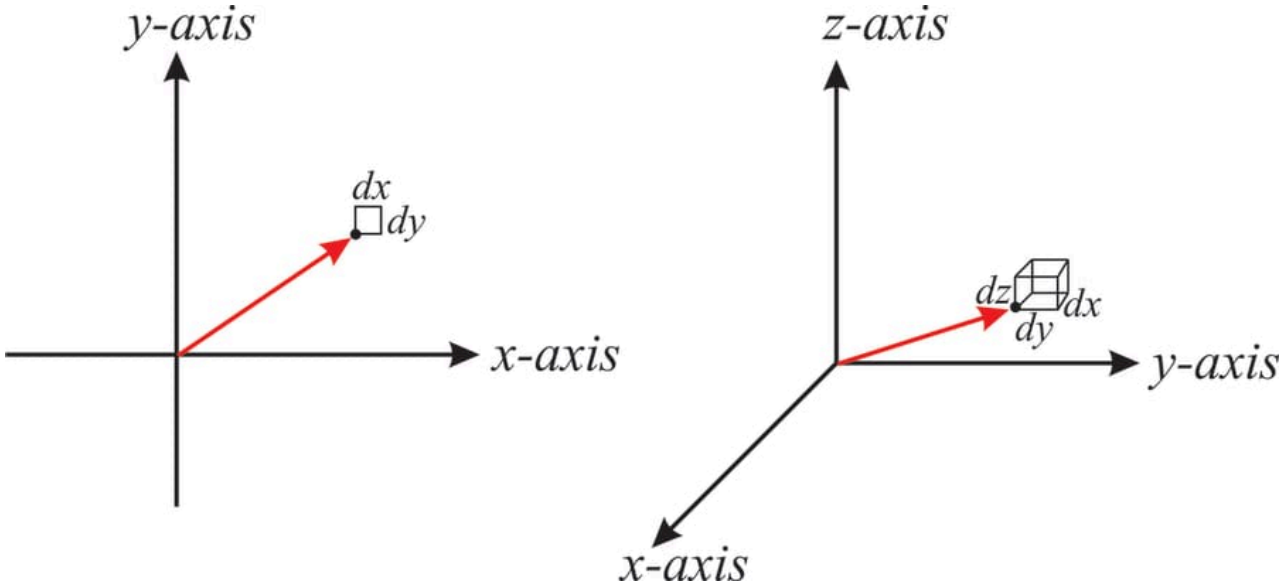


Figure 32.6.1: Area and volume elements in cartesian coordinates (CC BY-NC-SA; Marcia Levitus)

We already performed double and triple integrals in cartesian coordinates, and used the area and volume elements without paying any special attention. For example, in example [c2v:c2vex1], we were required to integrate the function $|\psi(x,y,z)|^2$ over all space, and without thinking too much we used the volume element $dx\ \ dy\ \ dz$ (see page). We also knew that "all space" meant $-\infty \leq x \leq \infty$, $-\infty \leq y \leq \infty$ and $-\infty \leq z \leq \infty$, and therefore we wrote:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z)|^2\, dx\, dy\, dz = 1$$

But what if we had to integrate a function that is expressed in spherical coordinates? Would we just replace $dx\ \ dy\ \ dz$ by $dr\ \ d\theta\ \ d\phi$? The answer is no, because the volume element in spherical coordinates depends also on the actual position of the point. This will make more sense in a minute. Coming back to coordinates in two dimensions, it is intuitive to understand why the area element in cartesian coordinates is $dA = dx\ \ dy$ independently of the values of x and y. This is shown in the left side of Figure 32.6.2. However, in polar coordinates, we see that the areas of the gray sections, which are both constructed by increasing r by dr, and by increasing θ by $d\theta$, depend on the actual value of r. Notice that the area highlighted in gray increases as we move away from the origin.

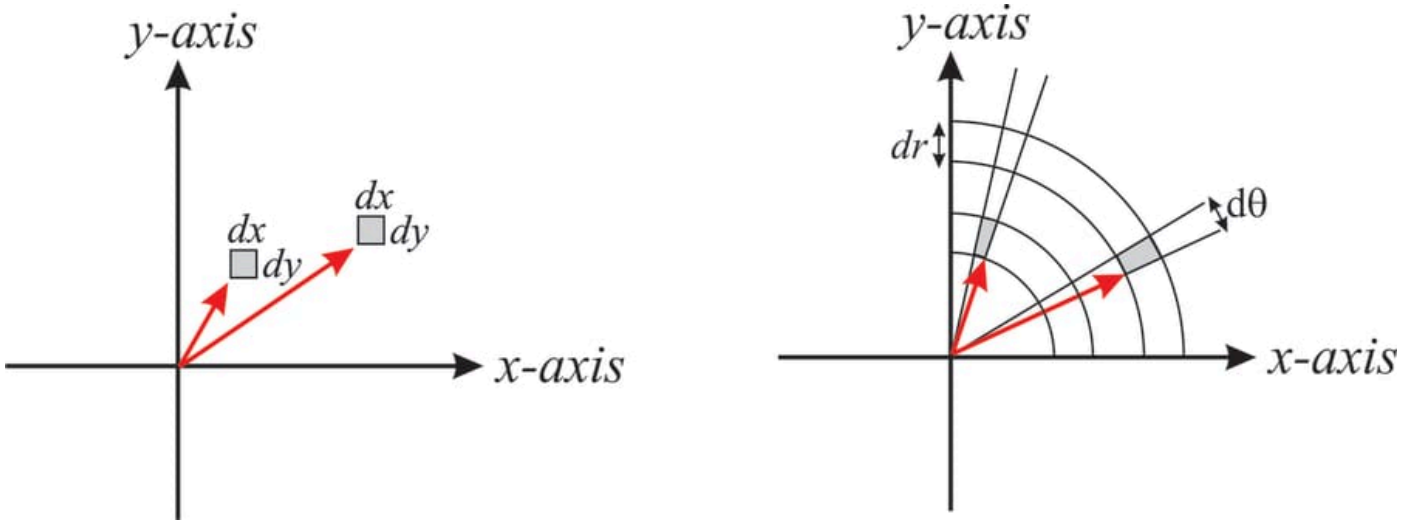


Figure 32.6.2: Differential of area in cartesian and polar coordinates (CC BY-NC-SA; Marcia Levitus)

The area shown in gray can be calculated from geometrical arguments as

$$dA = \left[\pi(r+dr)^2 - \pi r^2\right]\frac{d\theta}{2\pi}.$$

Because $dr << 0$, we can neglect the term $(dr)^2$, and $dA = r\ dr\ d\theta$ (see Figure 10.2.3).

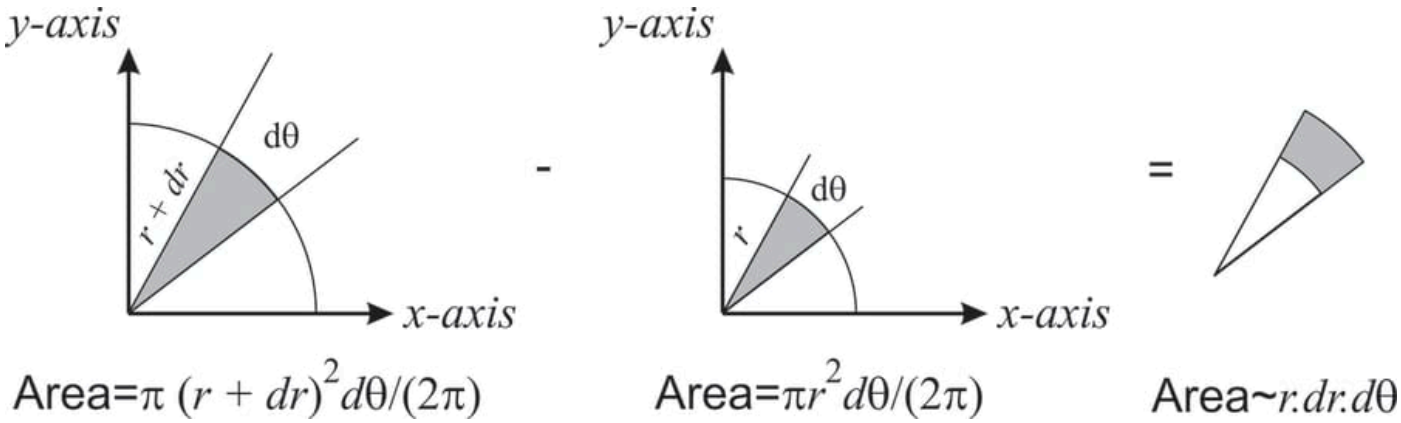


Figure 32.6.3: Differential of area in polar coordinates (CC BY-NC-SA; Marcia Levitus)

Let's see how this affects a double integral with an example from quantum mechanics. The wave function of the ground state of a two dimensional harmonic oscillator is: $\psi(x,y) = Ae^{-a(x^2+y^2)}$. We know that the quantity $|\psi|^2$ represents a probability density, and as such, needs to be normalized:

$$\int\limits_{all\ space} |\psi|^2\ dA = 1$$

This statement is true regardless of whether the function is expressed in polar or cartesian coordinates. However, the limits of integration, and the expression used for dA, will depend on the coordinate system used in the integration.

In cartesian coordinates, "all space" means $-\infty < x < \infty$ and $-\infty < y < \infty$. The differential of area is $dA = dxdy$:

$$\int\limits_{all\ space} |\psi|^2\ dA = \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} A^2 e^{-2a(x^2+y^2)}\ dxdy = 1$$

In polar coordinates, "all space" means $0 < r < \infty$ and $0 < \theta < 2\pi$. The differential of area is $dA = r\ \ drd\theta$. The function $\psi(x,y) = Ae^{-a(x^2+y^2)}$ can be expressed in polar coordinates as: $\psi(r,\theta) = Ae^{-ar^2}$

$$\int\limits_{all\ space} |\psi|^2\ dA = \int\limits_{0}^{\infty}\int\limits_{0}^{2\pi} A^2 e^{-2ar^2} r\ d\theta dr = 1$$

Both versions of the double integral are equivalent, and both can be solved to find the value of the normalization constant (A) that makes the double integral equal to 1. In polar coordinates:

$$\int\limits_{0}^{\infty}\int\limits_{0}^{2\pi} A^2 e^{-2ar^2} r\ d\theta dr = A^2 \int\limits_{0}^{\infty} e^{-2ar^2} r\ dr \int\limits_{0}^{2\pi} d\theta = A^2 \times \frac{1}{4a} \times 2\pi = 1$$

Therefore[1], $A = \sqrt{2a/\pi}$. The same value is of course obtained by integrating in cartesian coordinates.

It is now time to turn our attention to triple integrals in spherical coordinates. In cartesian coordinates, the differential volume element is simply $dV = dx\ dy\ dz$, regardless of the values of x, y and z. Using the same arguments we used for polar coordinates in the plane, we will see that the differential of volume in spherical coordinates is not $dV = dr\ d\theta\ d\phi$. The geometrical derivation of the volume is a little bit more complicated, but from Figure 32.6.4 you should be able to see that dV depends on r and θ, but not on ϕ. The volume of the shaded region is

$$dV = r^2 \sin\theta\, d\theta\, d\phi\, dr \tag{32.6.8}$$

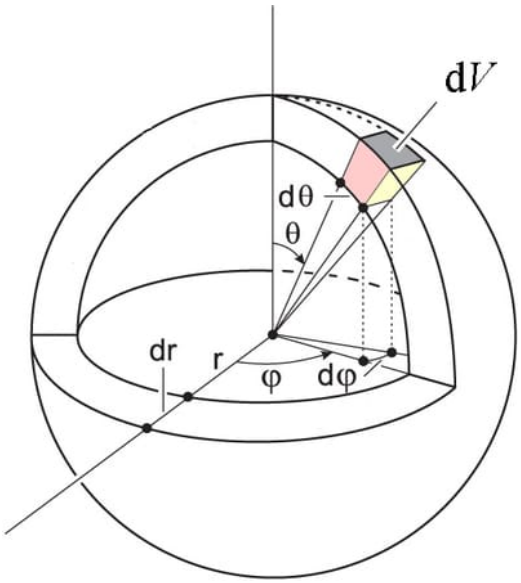


Figure 32.6.4: Differential of volume in spherical coordinates (CC BY-NC-SA; Marcia Levitus)

We will exemplify the use of triple integrals in spherical coordinates with some problems from quantum mechanics. We already introduced the Schrödinger equation, and even solved it for a simple system in Section 5.4. We also mentioned that spherical coordinates are the obvious choice when writing this and other equations for systems such as atoms, which are symmetric around a point.

As we saw in the case of the particle in the box (Section 5.4), the solution of the Schrödinger equation has an arbitrary multiplicative constant. Because of the probabilistic interpretation of wave functions, we determine this constant by normalization. The same situation arises in three dimensions when we solve the Schrödinger equation to obtain the expressions that describe the possible states of the electron in the hydrogen atom (i.e. the orbitals of the atom). The Schrödinger equation is a partial differential equation in three dimensions, and the solutions will be wave functions that are functions of r, θ and ϕ. The lowest energy state, which in chemistry we call the 1s orbital, turns out to be:

$$\psi_{1s} = Ae^{-r/a_0}$$

This particular orbital depends on r only, which should not surprise a chemist given that the electron density in all s-orbitals is spherically symmetric. We will see that p and d orbitals depend on the angles as well. Regardless of the orbital, and the coordinate system, the normalization condition states that:

$$\int\limits_{all\ space} |\psi|^2\, dV = 1$$

For a wave function expressed in cartesian coordinates,

$$\int\limits_{all\ space} |\psi|^2\, dV = \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} \psi^*(x,y,z)\psi(x,y,z)\, dxdydz$$

where we used the fact that $|\psi|^2 = \psi^*\psi$.

In spherical coordinates, "all space" means $0 \le r \le \infty$, $0 \le \phi \le 2\pi$ and $0 \le \theta \le \pi$. The differential dV is $dV = r^2 \sin\theta\ d\theta\ d\phi\ dr$, so

$$\int\limits_{all\ space} |\psi|^2\, dV = \int\limits_{0}^{2\pi}\int\limits_{0}^{\pi}\int\limits_{0}^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, drd\theta d\phi = 1$$

Let's see how we can normalize orbitals using triple integrals in spherical coordinates.

Example 32.6.1

When solving the Schrödinger equation for the hydrogen atom, we obtain $\psi_{1s} = Ae^{-r/a_0}$, where A is an arbitrary constant that needs to be determined by normalization. Find A.

Solution

In spherical coordinates,

$$\int\limits_{all\ space} |\psi|^2\, dV = \int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, dr d\theta d\phi = 1$$

because this orbital is a real function, $\psi^*(r,\theta,\phi)\psi(r,\theta,\phi) = \psi^2(r,\theta,\phi)$. In this case, $\psi^2(r,\theta,\phi) = A^2e^{-2r/a_0}$.

Therefore,

$$\int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, dr d\theta d\phi = \int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty} A^2e^{-2r/a_0}\, r^2 \sin\theta\, dr d\theta d\phi = 1$$

$$\int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty} A^2e^{-2r/a_0}\, r^2 \sin\theta\, dr d\theta d\phi = A^2 \int\limits_0^{2\pi} d\phi \int\limits_0^{\pi} \sin\theta\, d\theta \int\limits_0^{\infty} e^{-2r/a_0}\, r^2\, dr$$

The result is a product of three integrals in one variable:

$$\int\limits_0^{2\pi} d\phi = 2\pi$$

$$\int\limits_0^{\pi} \sin\theta\, d\theta = -\cos\theta|_0^{\pi} = 2$$

$$\int\limits_0^{\infty} e^{-2r/a_0}\, r^2\, dr = ?$$

From the formula sheet:

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}},$$

where $a > 0$ and n is a positive integer.

In this case, $n = 2$ and $a = 2/a_0$, so:

$$\int\limits_0^{\infty} e^{-2r/a_0}\, r^2\, dr = \frac{2!}{(2/a_0)^3} = \frac{2}{8/a_0^3} = \frac{a_0^3}{4}$$

Putting the three pieces together:

$$A^2 \int\limits_0^{2\pi} d\phi \int\limits_0^{\pi} \sin\theta\, d\theta \int\limits_0^{\infty} e^{-2r/a_0}\, r^2\, dr = A^2 \times 2\pi \times 2 \times \frac{a_0^3}{4} = 1$$

$$A^2 \times \pi \times a_0^3 = 1 \rightarrow A = \frac{1}{\sqrt{\pi a_0^3}}$$

The normalized 1s orbital is, therefore:

$$\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

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32.7: Determinants

The determinant is a useful value that can be computed from the elements of a square matrix

Consider row reducing the standard 2x2 matrix. Suppose that a is nonzero.

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

$$\frac{1}{a}R_1 \to R_1, \quad R_2 - cR_1 \to R_2$$

$$\begin{pmatrix} 1 & \frac{b}{a} \\ c & d \end{pmatrix}$$

$$\begin{pmatrix} 1 & \frac{b}{a} \\ 0 & d - \frac{cb}{a} \end{pmatrix}$$

Now notice that we cannot make the lower right corner a 1 if

$$d - \frac{cb}{a} = 0$$

or

$$ad - bc = 0.$$

Definition: The Determinant

We call $ad - bc$ the determinant of the 2 by 2 matrix

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

it tells us when it is possible to row reduce the matrix and find a solution to the linear system.

Example 32.7.1 :

The determinant of the matrix

$$\begin{pmatrix} 3 & 1 \\ 5 & 2 \end{pmatrix}$$

is

$$3(2) - 1(5) = 6 - 5 = 1.$$

Determinants of 3 x 3 Matrices

We define the determinant of a triangular matrix

$$\begin{pmatrix} a & d & e \\ 0 & b & f \\ 0 & 0 & c \end{pmatrix}$$

by

$$\det = abc.$$

Notice that if we multiply a row by a constant k then the new determinant is k times the old one. We list the effect of all three row operations below.

Theorem

The effect of the the three basic row operations on the determinant are as follows

1. Multiplication of a row by a constant multiplies the determinant by that constant.
2. Switching two rows changes the sign of the determinant.
3. Replacing one row by that row + a multiply of another row has no effect on the determinant.

To find the determinant of a matrix we use the operations to make the matrix triangular and then work backwards.

Example 32.7.2 :

Find the determinant of

$$\begin{pmatrix} 2 & 6 & 10 \\ 2 & 4 & -3 \\ 0 & 4 & 2 \end{pmatrix}$$

We use row operations until the matrix is triangular.

$$\frac{1}{2}R_1 \to R_1 (\text{Multiplies the determinant by } \frac{1}{2})$$

$$\begin{pmatrix} 1 & 3 & 5 \\ 2 & 4 & -3 \\ 0 & 4 & 2 \end{pmatrix}$$

$$R_2 - 2R_1 \to R_2 \text{ (No effect on the determinant)}$$

$$\begin{pmatrix} 1 & 3 & 5 \\ 0 & -2 & -13 \\ 0 & 4 & 2 \end{pmatrix}$$

Note that we do not need to zero out the upper middle number. We only need to zero out the bottom left numbers.

$$R_3 + 2R_2 \to R_3 \text{ (No effect on the determinant).}$$

$$\begin{pmatrix} 1 & 3 & 5 \\ 0 & -2 & -13 \\ 0 & 0 & -24 \end{pmatrix}$$

Note that we do not need to make the middle number a 1.

The determinant of this matrix is 48. Since this matrix has $\frac{1}{2}$ the determinant of the original matrix, the determinant of the original matrix has

$$\text{determinant} = 48(2) = 96.$$

Inverses

We call the square matrix I with all 1's down the diagonal and zeros everywhere else the *identity* matrix. It has the unique property that if A is a square matrix with the same dimensions then

$$AI = IA = A.$$

Definition

If A is a square matrix then the inverse A^{-1} of A is the unique matrix such that

$$AA^{-1} = A^{-1}A = I.$$

Example 32.7.3 :

Let

$$A = \begin{pmatrix} 2 & 5 \\ 1 & 3 \end{pmatrix}$$

then

$$A^{-1} = \begin{pmatrix} 3 & -5 \\ -1 & 2 \end{pmatrix}$$

Verify this!

Theorem: ExistEnce

The inverse of a matrix exists if and only if the determinant is nonzero.

To find the inverse of a matrix, we write a new extended matrix with the identity on the right. Then we completely row reduce, the resulting matrix on the right will be the inverse matrix.

Example 32.7.4 :

$$\begin{pmatrix} 2 & -1 \\ 1 & -1 \end{pmatrix}$$

First note that the determinant of this matrix is

$$-2 + 1 = -1$$

hence the inverse exists. Now we set the augmented matrix as

$$\left(\begin{array}{cccc} 2 & -1 & 1 & 0 \\ 1 & -1 & 0 & 1 \end{array} \right)$$

$$R_1 \leftrightarrow R_2$$

$$\left(\begin{array}{cccc} 1 & -1 & 0 & 1 \\ 2 & -1 & 1 & 0 \end{array} \right)$$

$$R_2 - 2R_1 \to R_2$$

$$\begin{pmatrix} 1 & -1 & 0 & 1 \\ 0 & 1 & 1 & -2 \end{pmatrix}$$

$$R_1 + R_2 \to R_1$$

$$\begin{pmatrix} 1 & 0 & 1 & -1 \\ 0 & 1 & 1 & -2 \end{pmatrix}$$

Notice that the left hand part is now the identity. The right hand side is the inverse. Hence

$$A^{-1} = \begin{pmatrix} 1 & -1 \\ 1 & -2 \end{pmatrix}$$

Solving Equations Using Matrices

Example 32.7.5 :

Suppose we have the system

$$2x - y = 3$$

$$x - y = 4$$

Then we can write this in matrix form

$$Ax = b$$

where

$$A = \begin{pmatrix} 2 & -1 \\ 1 & -1 \end{pmatrix}, \quad x = \begin{pmatrix} x \\ y \end{pmatrix}, \quad \text{and } b = \begin{pmatrix} 3 \\ 4 \end{pmatrix}$$

We can multiply both sides by A^{-1}:

$$A^{-1}Ax = A^{-1}b$$

or

$$x = A^{-1}b$$

From before,

$$A^{-1} = \begin{pmatrix} 1 & -1 \\ 1 & -2 \end{pmatrix}$$

Hence our solution is

$$(-1 \quad -5)$$

or

$$x = -1 \text{ and } y = 5$$

Contributors and Attributions

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32.8: Matrices

Chapter Objectives

- Learn the nomenclature used in linear algebra to describe matrices (rows, columns, triangular matrices, diagonal matrices, trace, transpose, singularity, etc).
- Learn how to add, subtract and multiply matrices.
- Learn the concept of inverse.
- Understand the use of matrices as symmetry operators.
- Understand the concept of orthogonality.
- Understand how to calculate the eigenvalues and normalized eigenvectors of a 2 × 2 matrix.
- Understand the concept of Hermitian matrix

Definitions

An $n \times m$ matrix is a two dimensional array of numbers with n rows and m columns. The integers n and m are called the *dimensions* of the matrix. If $n = m$ then the matrix is s*quare*. The numbers in the matrix are known as *matrix element*s (or just elements) and are usually given subscripts to signify their position in the matrix e.g. an element a_{ij} would occupy the i^{th} row and j^{th} column of the matrix. For example:

$$M = \begin{pmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{pmatrix} \tag{32.8.1}$$

is a 3×3 matrix with $a_{11} = 1$, $a_{12} = 2$, $a_{13} = 3$, $a_{21} = 4$ etc

In a square matrix, *diagonal* elements are those for which i=j (the numbers 1, 5, and 9 in the above example). *Off-diagonal* elements are those for which $i \neq j$ (2, 3, 4, 6, 7, and 8 in the above example). If all the off-diagonal elements are equal to zero then we have a *diagonal* matrix. We will see later that diagonal matrices are of considerable importance in group theory.

A *unit matrix* or *identity matrix* (usually given the symbol I) is a diagonal matrix in which all the diagonal elements are equal to 1. A unit matrix acting on another matrix has no effect – it is the same as the identity operation in group theory and is analogous to multiplying a number by 1 in everyday arithmetic.

The *transpose* A^T of a matrix A is the matrix that results from interchanging all the rows and columns. A *symmetric* matrix is the same as its transpose ($A^T = A$ i.e. $a_{ij} = a_{ji}$ for all values of i and j). The transpose of matrix M above (which is not symmetric) is

$$M^T = \begin{pmatrix} 1 & 4 & 7 \\ 2 & 5 & 8 \\ 3 & 6 & 9 \end{pmatrix} \tag{32.8.2}$$

The sum of the diagonal elements in a square matrix is called the *trace* (or *character*) of the matrix (for the above matrix, the trace is $\chi = 1 + 5 + 9 = 15$). The traces of matrices representing symmetry operations will turn out to be of great importance in group theory.

A *vector* is just a special case of a matrix in which one of the dimensions is equal to 1. An $n \times 1$ matrix is a *column vector*; a $1 \times m$ matrix is a *row vector*. The components of a vector are usually only labeled with one index. A *unit vector* has one element equal to 1 and the others equal to zero (it is the same as one row or column of an identity matrix). We can extend the idea further to say that a single number is a matrix (or vector) of dimension 1×1.

Matrix Algebra

i. Two matrices with the same dimensions may be added or subtracted by adding or subtracting the elements occupying the same position in each matrix. e.g.

$$A = \begin{pmatrix} 1 & 0 & 2 \\ 2 & 2 & 1 \\ 3 & 2 & 0 \end{pmatrix} \tag{32.8.3}$$

$$B = \begin{pmatrix} 2 & 0 & -2 \\ 1 & 0 & 1 \\ 1 & -1 & 0 \end{pmatrix} \tag{32.8.4}$$

$$A + B = \begin{pmatrix} 3 & 0 & 0 \\ 3 & 2 & 2 \\ 4 & 1 & 0 \end{pmatrix} \tag{32.8.5}$$

$$A - B = \begin{pmatrix} -1 & 0 & 4 \\ 1 & 2 & 0 \\ 2 & 3 & 0 \end{pmatrix} \tag{32.8.6}$$

ii. A matrix may be multiplied by a constant by multiplying each element by the constant.

$$4B = \begin{pmatrix} 8 & 0 & -8 \\ 4 & 0 & 4 \\ 4 & -4 & 0 \end{pmatrix} \tag{32.8.7}$$

$$3A = \begin{pmatrix} 3 & 0 & 6 \\ 6 & 6 & 3 \\ 9 & 6 & 0 \end{pmatrix} \tag{32.8.8}$$

iii. Two matrices may be multiplied together provided that the number of columns of the first matrix is the same as the number of rows of the second matrix i.e. an $n \times m$ matrix may be multiplied by an $m \times l$ matrix. The resulting matrix will have dimensions $n \times l$. To find the element a_{ij} in the product matrix, we take the dot product of row i of the first matrix and column j of the second matrix (i.e. we multiply consecutive elements together from row i of the first matrix and column j of the second matrix and add them together i.e. $c_{ij} = \Sigma_k \, a_{ik} b_{jk}$ e.g. in the 3×3 matrices A and B used in the above examples, the first element in the product matrix $C = AB$ is $c_{11} = a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31}$

$$AB = \begin{pmatrix} 1 & 0 & 2 \\ 2 & 2 & 1 \\ 3 & 2 & 0 \end{pmatrix} \begin{pmatrix} 2 & 0 & -2 \\ 1 & 0 & 1 \\ 1 & -1 & 0 \end{pmatrix} = \begin{pmatrix} 4 & -2 & -2 \\ 7 & -1 & -2 \\ 8 & 0 & -4 \end{pmatrix} \tag{32.8.9}$$

An example of a matrix multiplying a vector is

$$A\mathbf{v} = \begin{pmatrix} 1 & 0 & 2 \\ 2 & 2 & 1 \\ 3 & 2 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} = \begin{pmatrix} 7 \\ 9 \\ 7 \end{pmatrix} \tag{32.8.10}$$

Matrix multiplication is not generally commutative, a property that mirrors the behavior found earlier for symmetry operations within a point group.

Direct Products

The direct product of two matrices (given the symbol $\otimes$) is a special type of matrix product that generates a matrix of higher dimensionality if both matrices have dimension greater than one. The easiest way to demonstrate how to construct a direct product of two matrices A and B is by an example:

$$A \otimes B = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \otimes \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \tag{32.8.11}$$

$$= \begin{pmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{pmatrix} \tag{32.8.12}$$

$$= \begin{pmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{21} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{pmatrix} \tag{32.8.13}$$

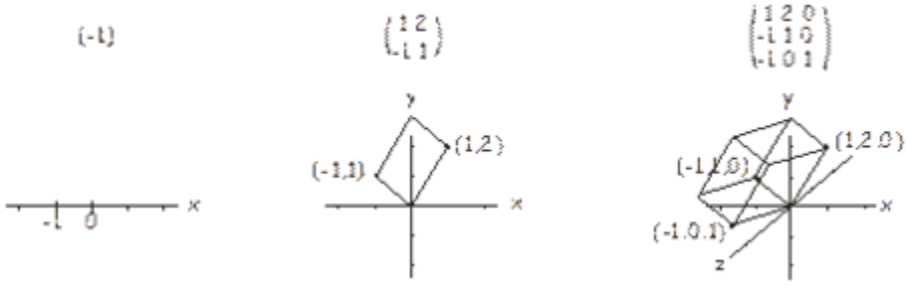
Though this may seem like a somewhat strange operation to carry out, direct products crop up a great deal in group theory.

Inverse Matrices and Determinants

If two square matrices A and B multiply together to give the identity matrix I (i.e. $AB = I$) then B is said to be the *inverse* of A (written A^{-1}). If B is the inverse of A then A is also the inverse of B. Recall that one of the conditions imposed upon the symmetry operations in a group is that each operation must have an inverse. It follows by analogy that any matrices we use to represent symmetry elements must also have inverses. It turns out that a square matrix only has an inverse if its determinant is non-zero. For this reason (and others which will become apparent later on when we need to solve equations involving matrices) we need to learn a little about matrix determinants and their properties.

For every square matrix, there is a unique function of all the elements that yields a single number called the determinant. Initially it probably won't be particularly obvious why this number should be useful, but matrix determinants are of great importance both in pure mathematics and in a number of areas of science. Historically, determinants were actually around before matrices. They arose originally as a property of a system of linear equations that 'determined' whether the system had a unique solution. As we shall see later, when such a system of equations is recast as a matrix equation this property carries over into the matrix determinant.

There are two different definitions of a determinant, one geometric and one algebraic. In the geometric interpretation, we consider the numbers across each row of an $n \times n$ matrix as coordinates in n-dimensional space. In a one-dimensional matrix (i.e. a number), there is only one coordinate, and the determinant can be interpreted as the (signed) length of a vector from the origin to this point. For a 2×2 matrix we have two coordinates in a plane, and the determinant is the (signed) area of the parallelogram that includes these two points and the origin. For a 3×3 matrix the determinant is the (signed) volume of the parallelepiped that includes the three points (in three-dimensional space) defined by the matrix and the origin. This is illustrated below. The idea extends up to higher dimensions in a similar way. In some sense then, the determinant is therefore related to the size of a matrix.



The algebraic definition of the determinant of an nxn matrix is a sum over all the possible products (permutations) of n elements taken from different rows and columns. The number of terms in the sum is $n!$, the number of possible permutations of n values (i.e. 2 for a 2×2 matrix, 6 for a 3×3 matrix etc). Each term in the sum is given a positive or a negative sign depending on whether the number of *permutation inversions* in the product is even or odd. A permutation inversion is just a pair of elements that are out of order when described by their indices. For example, for a set of four elements (a_1, a_2, a_3, a_4), the permutation $a_1a_2a_3a_4$ has all the elements in their correct order (i.e. in order of increasing index). However, the permutation $a_2a_4a_1a_3$ contains the permutation inversions a_2a_1, a_4a_1, a_4a_3.

For example, for a two-dimensional matrix

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \tag{32.8.14}$$

where the subscripts label the row and column positions of the elements, there are 2 possible products/permutations involving elements from different rows and column, $a_{11}a_{22}$ and $a_{12}a_{21}$. In the second term, there is a permutation inversion involving the column indices 2 and 1 (permutation inversions involving the row and column indices should be looked for separately) so this term takes a negative sign, and the determinant is $a_{11}a_{22}$ - $a_{12}a_{21}$.

For a 3×3 matrix

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{32.8.15}$$

the possible combinations of elements from different rows and columns, together with the sign from the number of permutations required to put their indices in numerical order are:

$$\begin{aligned} a_{11}a_{22}a_{33} &\quad (0 \text{ inversions}) \\ -a_{11}a_{23}a_{32} &\quad (1 \text{ inversion - } 3 > 2 \text{ in the column indices}) \\ -a_{12}a_{21}a_{33} &\quad (1 \text{ inversion - } 2 > 1 \text{ in the column indices}) \\ a_{12}a_{23}a_{31} &\quad (2 \text{ inversions - } 2 > 1 \text{ and } 3 > 1 \text{ in the column indices}) \\ a_{13}a_{21}a_{32} &\quad (2 \text{ inversions - } 3 > 1 \text{ and } 3 > 2 \text{ in the column indices}) \\ -a_{13}a_{22}a_{31} &\quad (3 \text{ inversions - } 3 > 2, 3 > 1, \text{ and } 2 > 1 \text{ in the column indices}) \end{aligned} \tag{32.8.16}$$

and the determinant is simply the sum of these terms.

This may all seem a little complicated, but in practice there is a fairly systematic procedure for calculating determinants. The determinant of a matrix A is usually written det(A) or |a|.

For a 2×2 matrix

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix}; det(A) = |A| = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc \tag{32.8.17}$$

For a 3×3 matrix

$$B = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix}; det(B) = a\begin{vmatrix} e & f \\ h & i \end{vmatrix} - b\begin{vmatrix} d & f \\ g & i \end{vmatrix} + c\begin{vmatrix} d & e \\ g & h \end{vmatrix} \tag{32.8.18}$$

For a $4x4$ matrix

$$C = \begin{pmatrix} a & b & c & d \\ e & f & g & h \\ i & j & k & l \\ m & n & o & p \end{pmatrix}; det(C) = a\begin{vmatrix} f & g & h \\ j & k & l \\ n & o & p \end{vmatrix} - b\begin{vmatrix} e & g & h \\ i & k & l \\ m & o & p \end{vmatrix} + c\begin{vmatrix} e & f & h \\ i & j & l \\ m & n & p \end{vmatrix} - d\begin{vmatrix} e & f & g \\ i & j & k \\ m & n & o \end{vmatrix} \tag{32.8.19}$$

and so on in higher dimensions. Note that the submatrices in the 3×3 example above are just the matrices formed from the original matrix B that don't include any elements from the same row or column as the premultiplying factors from the first row.

Matrix determinants have a number of important properties:

i. The determinant of the identity matrix is 1.

$$e.g. \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = 1 \tag{32.8.20}$$

ii. The determinant of a matrix is the same as the determinant of its transpose i.e. det(a) = det(A^T)

$$e.g. \begin{vmatrix} a & b \\ c & d \end{vmatrix} = \begin{vmatrix} a & c \\ b & d \end{vmatrix} \tag{32.8.21}$$

iii. The determinant changes sign when any two rows or any two columns are interchanged

$$e.g. \begin{vmatrix} a & b \\ c & d \end{vmatrix} = - \begin{vmatrix} b & a \\ d & c \end{vmatrix} = - \begin{vmatrix} c & d \\ a & b \end{vmatrix} = \begin{vmatrix} d & c \\ b & a \end{vmatrix} \tag{32.8.22}$$

iv. The determinant is zero if any row or column is entirely zero, or if any two rows or columns are equal or a multiple of one another.

$$e.g. \begin{vmatrix} 1 & 2 \\ 0 & 0 \end{vmatrix} = 0, \begin{vmatrix} 1 & 2 \\ 2 & 4 \end{vmatrix} = 0 \tag{32.8.23}$$

v. The determinant is unchanged by adding any linear combination of rows (or columns) to another row (or column).
vi. The determinant of the product of two matrices is the same as the product of the determinants of the two matrices i.e. det(AB) = det(A)det(B).

The requirement that in order for a matrix to have an inverse it must have a non-zero determinant follows from property vi). As mentioned previously, the product of a matrix and its inverse yields the identity matrix I. We therefore have:

$$\begin{aligned} det(A^{-1}A) = det(A^{-1})det(A) &= det(I) \\ det(A^{-1}) &= det(I)/det(A) = 1/det(A) \end{aligned} \tag{32.8.24}$$

It follows that a matrix A can only have an inverse if its determinant is non-zero, otherwise the determinant of its inverse would be undefined.

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32.9: Series and Limits

Maclaurin Series

A function $f(x)$ can be expressed as a series in powers of x as long as $f(x)$ and all its derivatives are finite at $x = 0$. For example, we will prove shortly that the function $f(x) = \frac{1}{1-x}$ can be expressed as the following infinite sum:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ... \tag{32.9.1}$$

We can write this statement in this more elegant way:

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n \tag{32.9.2}$$

If you are not familiar with this notation, the right side of the equation reads "sum from $n = 0$ to $n = \infty$ of x^n." When $n = 0$, $x^n = 1$, when $n = 1$, $x^n = x$, when $n = 2$, $x^n = x^2$, etc (compare with Equation 32.9.1). The term "series in powers of x" means a sum in which each summand is a power of the variable x. Note that the number 1 is a power of x as well ($x^0 = 1$). Also, note that both Equations 32.9.1 and 32.9.2 are exact, they are not approximations.

Similarly, we will see shortly that the function e^x can be expressed as another infinite sum in powers of x (i.e. a Maclaurin series) as:

$$e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \frac{1}{24}x^4 + ... \tag{32.9.3}$$

Or, more elegantly:

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!}x^n \tag{32.9.4}$$

where $n!$ is read "n factorial" and represents the product $1 \times 2 \times 3... \times n$. If you are not familiar with factorials, be sure you understand why $4! = 24$. Also, remember that by definition $0! = 1$, not zero.

At this point you should have two questions: 1) how do I construct the Maclaurin series of a given function, and 2) why on earth would I want to do this if $\frac{1}{1-x}$ and e^x are fine-looking functions as they are. The answer to the first question is easy, and although you should know this from your calculus classes we will review it again in a moment. The answer to the second question is trickier, and it is what most students find confusing about this topic. We will discuss different examples that aim to show a variety of situations in which expressing functions in this way is helpful.

How to obtain the Maclaurin Series of a Function

In general, a well-behaved function ($f(x)$ and all its derivatives are finite at $x = 0$) will be expressed as an infinite sum of powers of x like this:

$$f(x) = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + ... + a_n x^n \tag{32.9.5}$$

Be sure you understand why the two expressions in Equation 32.9.5 are identical ways of expressing an infinite sum. The terms a_n are called the **coefficients**, and are constants (that is, they are NOT functions of x). If you end up with the variable x in one of your coefficients go back and check what you did wrong! For example, in the case of e^x (Equation 32.9.3), $a_0 = 1, a_1 = 1, a_2 = 1/2, a_3 = 1/6, etc$. In the example of Equation 32.9.1, all the coefficients equal 1. We just saw that two very different functions can be expressed using the same set of functions (the powers of x). What makes $\frac{1}{1-x}$ different from e^x are the coefficients a_n.

As we will see shortly, the coefficients can be negative, positive, or zero.

How do we calculate the coefficients? Each coefficient is calculated as:

$$a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_0 \tag{32.9.6}$$

That is, the n-th coefficient equals one over the factorial of n multiplied by the n-th derivative of the function $f(x)$ evaluated at zero. For example, if we want to calculate a_2 for the function $f(x) = \frac{1}{1-x}$, we need to get the second derivative of $f(x)$, evaluate it at $x = 0$, and divide the result by $2!$. Do it yourself and verify that $a_2 = 1$. In the case of a_0 we need the zeroth-order derivative, which equals the function itself (that is, $a_0 = f(0)$, because $\frac{1}{0!} = 1$). It is important to stress that although the derivatives are usually functions of x, the coefficients are constants because they are expressed in terms of the derivatives evaluated at $x = 0$.

Note that in order to obtain a Maclaurin series we evaluate the function and its derivatives at $x = 0$. This procedure is also called the expansion of the function around (or about) zero. We can expand functions around other numbers, and these series are called Taylor series (see Section 3).

Example 32.9.1

Obtain the Maclaurin series of $sin(x)$.

Solution

We need to obtain all the coefficients ($a_0, a_1 ... etc$). Because there are infinitely many coefficients, we will calculate a few and we will find a general pattern to express the rest. We will need several derivatives of $sin(x)$, so let's make a table:

n	$\frac{d^n f(x)}{dx^n}$	$\left(\frac{d^n f(x)}{dx^n}\right)_0$
0	$\sin(x)$	0
1	$\cos(x)$	1
2	$-\sin(x)$	0
3	$-\cos(x)$	-1
4	$\sin(x)$	0
5	$\cos(x)$	1

Remember that each coefficient equals $\left(\frac{d^n f(x)}{dx^n}\right)_0$ divided by $n!$, therefore:

n	$n!$	a_n
0	1	0
1	1	1
2	2	0
3	6	$-\frac{1}{6}$
4	24	0
5	120	$\frac{1}{120}$

This is enough information to see the pattern (you can go to higher values of n if you don't see it yet):

1. the coefficients for even values of n equal zero.
2. the coefficients for $n = 1, 5, 9, 13, ...$ equal $1/n!$
3. the coefficients for $n = 3, 7, 11, 15, ...$ equal $-1/n!$.

Recall that the general expression for a Maclaurin series is $a_0 + a_1x + a_2x^2...a_nx^n$, and replace $a_0...a_n$ by the coefficients we just found:

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7...$$

This is a correct way of writing the series, but in the next example we will see how to write it more elegantly as a sum.

Example 32.9.2

Express the Maclaurin series of $\sin(x)$ as a sum.

Solution

In the previous example we found that:

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7... \tag{32.9.7}$$

We want to express this as a sum:

$$\sum_{n=0}^{\infty} a_n x^n$$

The key here is to express the coefficients a_n in terms of n. We just concluded that 1) the coefficients for even values of n equal zero, 2) the coefficients for $n = 1, 5, 9, 13, ...$ equal $1/n!$ and 3) the coefficients for $n = 3, 7, 11, ...$ equal $-1/n!$. How do we put all this information together in a unique expression? Here are three possible (and equally good) answers:

- $\sin(x) = \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n+1)!} x^{2n+1}$
- $\sin(x) = \sum_{n=1}^{\infty} (-1)^{(n+1)} \frac{1}{(2n-1)!} x^{2n-1}$
- $\sin(x) = \sum_{n=0}^{\infty} cos(n\pi) \frac{1}{(2n+1)!} x^{2n+1}$

This may look impossibly hard to figure out, but let me share a few tricks with you. First, we notice that the sign in Equation 32.9.7 alternates, starting with a "+". A mathematical way of doing this is with a term $(-1)^n$ if your sum starts with $n = 0$, or $(-1)^{(n+1)}$ if you sum starts with $n = 1$. Note that $\cos(n\pi)$ does the same trick.

n	$(-1)^n$	$(-1)^{n+1}$	$\cos(n\pi)$
0	1	-1	1
1	-1	1	-1
2	1	-1	1
3	-1	1	-1

We have the correct sign for each term, but we need to generate the numbers $1, \frac{1}{3!}, \frac{1}{5!}, \frac{1}{7!}, \ldots$ Notice that the number "1" can be expressed as $\frac{1}{1!}$. To do this, we introduce the second trick of the day: we will use the expression $2n+1$ to generate odd numbers (if you start your sum with $n=0$) or $2n-1$ (if you start at $n=1$). Therefore, the expression $\frac{1}{(2n+1)!}$ gives $1, \frac{1}{3!}, \frac{1}{5!}, \frac{1}{7!}, \ldots$, which is what we need in the first and third examples (when the sum starts at zero).

Lastly, we need to use only odd powers of x. The expression $x^{(2n+1)}$ generates the terms $x, x^3, x^5 \ldots$ when you start at $n=0$, and $x^{(2n-1)}$ achieves the same when you start your series at $n=1$.

Confused about writing sums using the sum operator $(\sum)$? This video will help: http://tinyurl.com/lvwd36q

Need help? The links below contain solved examples.

External links:

Finding the maclaurin series of a function I: http://patrickjmt.com/taylor-and-maclaurin-series-example-1/

Finding the maclaurin series of a function II: http://www.youtube.com/watch?v= dp2ovDuWhro

Finding the maclaurin series of a function III: http://www.youtube.com/watch?v= WWe7pZjc4s8

Graphical Representation

From Equation 32.9.5 and the examples we discussed above, it should be clear at this point that any function whose derivatives are finite at $x=0$ can be expressed by using the same set of functions: the powers of x. We will call these functions the **basis set**. A basis set is a collection of linearly independent functions that can represent other functions when used in a linear combination.

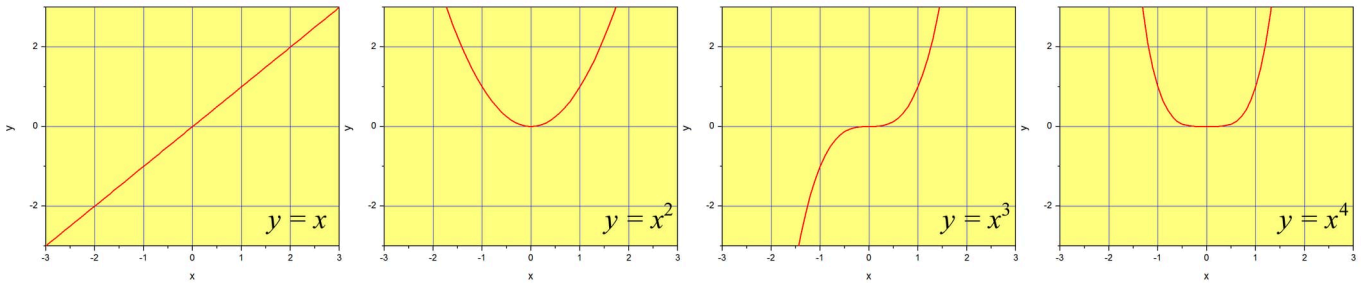


Figure 32.9.1: Some of the functions of the basis set for a Maclaurin expansion (CC BY-NC-SA; Marcia Levitus)

Figure 32.9.1 is a graphic representation of the first four functions of this basis set. To be fair, the first function of the set is $x^0 = 1$, so these would be the second, third, fourth and fifth. The full basis set is of course infinite in length. If we mix all the functions of the set with equal weights (we put the same amount of x^2 than we put x^{245} or x^0), we obtain $(1-x)^{-1}$ (Equation 32.9.1. If we use only the odd terms, alternate the sign starting with a '+', and weigh each term less and less using the expression $1/(2n-1)!$ for the $n-th$ term, we obtain $\sin x$ (Equation 32.9.7). This is illustrated in Figure 32.9.2, where we multiply the even powers of x by zero, and use different weights for the rest. Note that the 'etcetera' is crucial, as we would need to include an infinite number of functions to obtain the function $\sin x$ exactly.

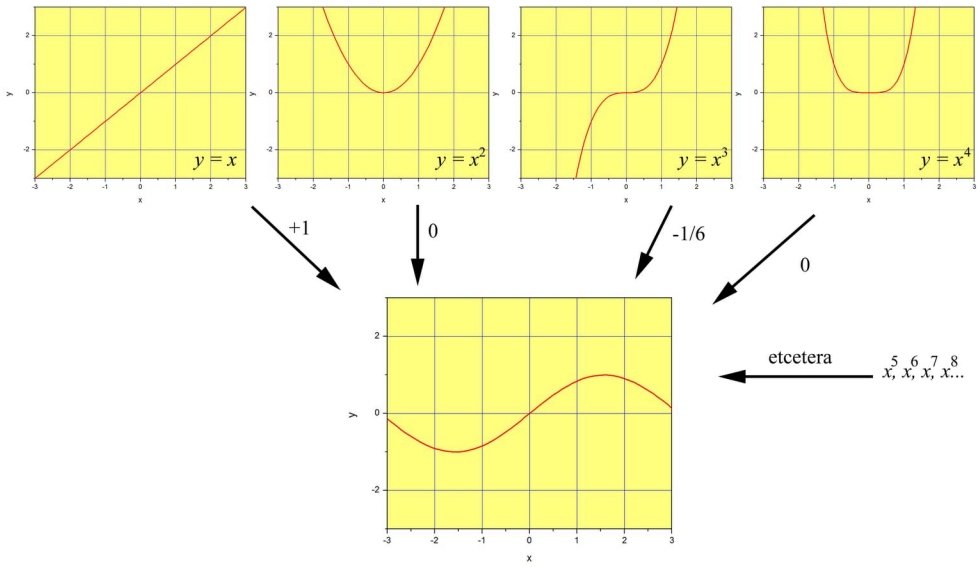


Figure 32.9.2: Construction of $\sin x$ using the powers of x as the basis set. (CC BY-NC-SA; Marcia Levitus)

Although we need an infinite number of terms to express a function exactly (unless the function is a polynomial, of course), in many cases we will observe that the weight (the coefficient) of each power of x gets smaller and smaller as we increase the power. For example, in the case of $\sin x$, the contribution of x^3 is $1/6th$ of the contribution of x (in absolute terms), and the contribution of x^5 is $1/120th$. This tells you that the first terms are much more important than the rest, although all are needed if we want the sum to represent $\sin x$ exactly. What if we are happy with a 'pretty good' approximation of $\sin x$? Let's see what happens if we use up to x^3 and drop the higher terms. The result is plotted in blue in Figure 32.9.3 together with $\sin x$ in red. We can see that the function $x - 1/6x^3$ is a very good approximation of $\sin x$ as long as we stay close to $x = 0$. As we move further away from the origin the approximation gets worse and worse, and we would need to include higher powers of x to get it better. This should be clear from eq. [series:sin], since the terms x^n get smaller and smaller with increasing n if x is a small number. Therefore, if x is small, we could write $\sin(x) \approx x - \frac{1}{3!}x^3$, where the symbol $\approx$ means approximately equal.

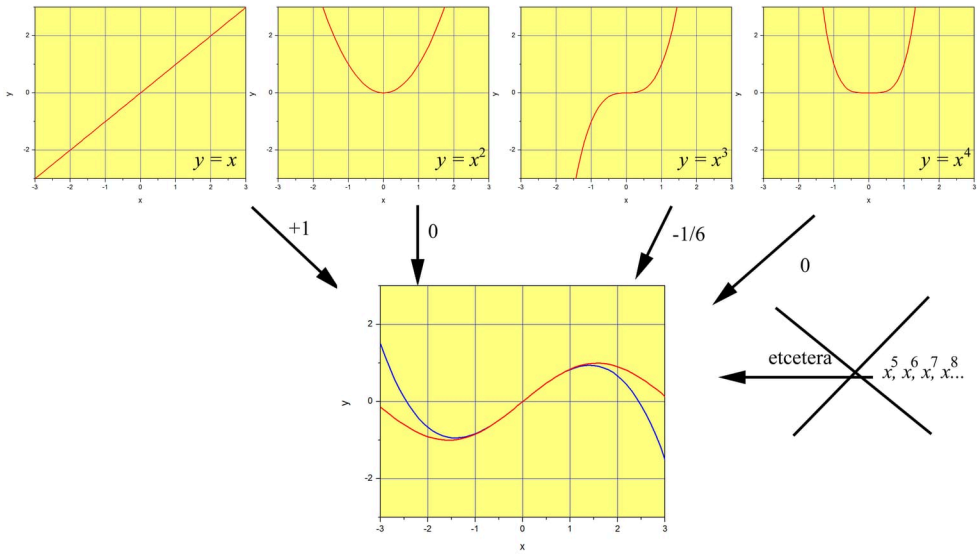


Figure 32.9.3: Approximation of $\sin x$ up to the third power of x. The curve in blue is the function $x - 1/6x^3$, and the curve in red is $\sin x$ (CC BY-NC-SA; Marcia Levitus)

But why stopping at $n = 3$ and not $n = 1$ or 5? The above argument suggests that the function x might be a good approximation of $\sin x$ around $x = 0$, when the term x^3 is much smaller than the term x. This is in fact this is the case, as shown in Figure 32.9.4.

We have seen that we can get good approximations of a function by **truncating** the series (i.e. not using the infinite terms).

Students usually get frustrated and want to know how many terms are 'correct'. It takes a little bit of practice to realize there is no universal answer to this question. We would need some context to analyze how good of an approximation we are happy with. For example, are we satisfied with the small error we see at $x = 0.5$ in Figure $32.9.4$? It all depends on the context. Maybe we are performing experiments where we have other sources of error that are much worse than this, so using an extra term will not improve the overall situation anyway. Maybe we are performing very precise experiments where this difference is significant. As you see, discussing how many terms are needed in an approximation out of context is not very useful. We will discuss this particular approximation when we learn about second order differential equations and analyze the problem of the pendulum, so hopefully things will make more sense then.

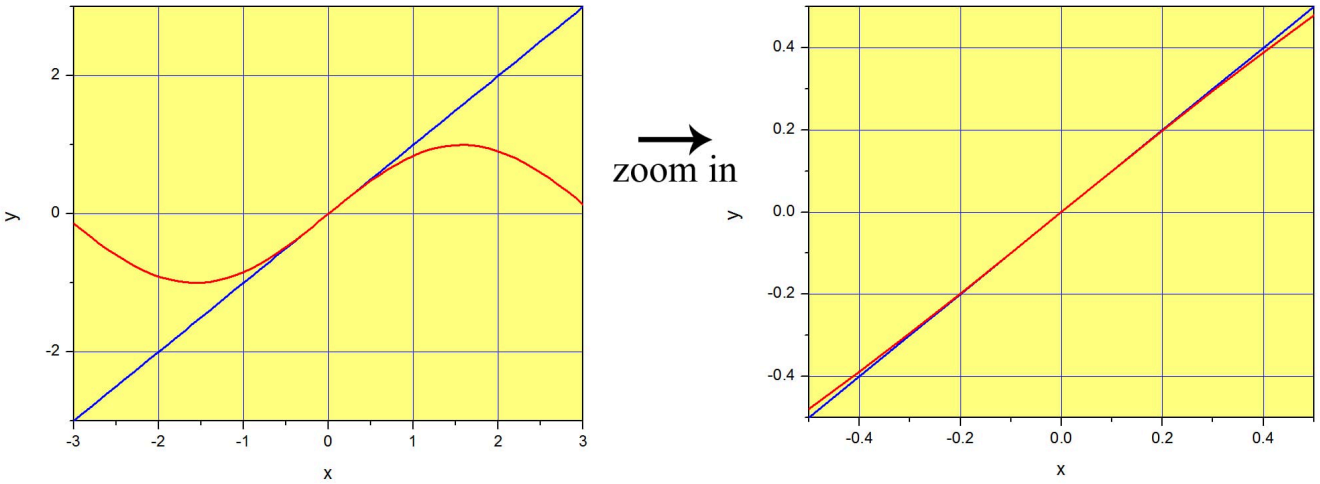


Figure $32.9.4$: Approximation of $\sin x$ up to the first power of x. The curve in blue is the function x, and the curve in red is $\sin x$ (CC BY-NC-SA; Marcia Levitus)

Linear Approximations

If you take a look at Equation $3.1.5$ you will see that we can always approximate a function as $a_0 + a_1 x$ as long as x is small. When we say 'any function' we of course imply that the function and all its derivatives need to be finite at $x = 0$. Looking at the definitions of the coefficients, we can write:

Label 'eq1' multiply defined

We call this a linear approximation because Equation $32.9.1$ is the equation of a straight line. The slope of this line is $f'(0)$ and the y-intercept is $f(0)$.

A fair question at this point is 'why are we even talking about approximations?' What is so complicated about the functions $\sin x$, e^x or $\ln(x+1)$ that we need to look for an approximation? Are we getting too lazy? To illustrate this issue, let's consider the problem of the pendulum, which we will solve in detail in the chapter devoted to differential equations. The problem is illustrated in Figure $32.9.1$, and those of you who took a physics course will recognize the equation below, which represents the law of motion of a simple pendulum. The second derivative refers to the acceleration, and the $\sin\theta$ term is due to the component of the net force along the direction of motion. We will discuss this in more detail later in this semester, so for now just accept the fact that, for this system, Newton's law can be written as:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\sin\theta(t) = 0$$

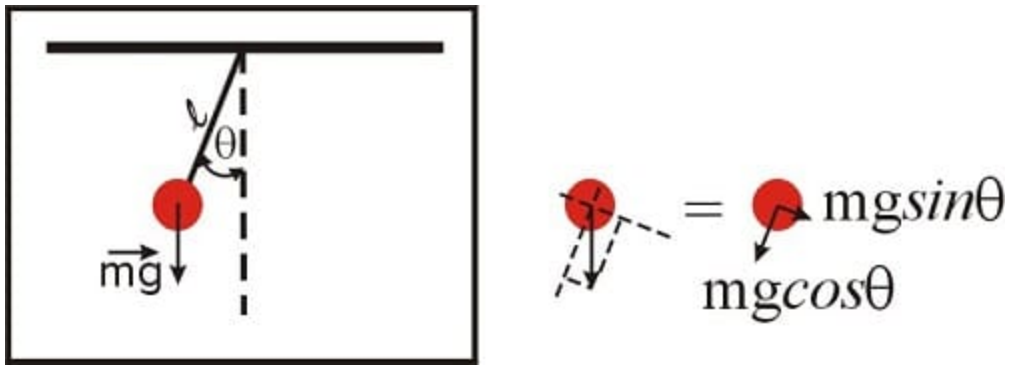


Figure 32.9.1: A rigid pendulum with massless and inextensible cord of length l. The motion is assumed to occur in two dimensions, and the friction is assumed to be negligible. The mass of the object is m, and g is the acceleration due to gravity. (CC BY-NC-SA; Marcia Levitus)

This equation should be easy to solve, right? It has only a few terms, nothing too fancy other than an innocent sine function...How difficult can it be to obtain $\theta(t)$? Unfortunately, this differential equation does not have an analytical solution! An analytical solution means that the solution can be expressed in terms of a finite number of elementary functions (such as sine, cosine, exponentials, etc). Differential equations are sometimes deceiving in this way: they look simple, but they might be incredibly hard to solve, or even impossible! The fact that we cannot write down an analytical solution does not mean there is no solution to the problem. You can swing a pendulum and measure $\theta(t)$ and create a table of numbers, and in principle you can be as precise as you want to be. Yet, you will not be able to create a function that reflects your numeric results. We will see that we can solve equations like this numerically, but not analytically. Disappointing, isn't it? Well... don't be. A lot of what we know about molecules and chemical reactions came from the work of physical chemists, who know how to solve problems using numerical methods. The fact that we cannot obtain an analytical expression that describes a particular physical or chemical system does not mean we cannot solve the problem numerically and learn a lot anyway!

But what if we are interested in small displacements only (that is, the pendulum swings close to the vertical axis at all times)? In this case, $\theta << 1$, and as we saw $\sin\theta \approx \theta$ (see Figure 3.1.4). If this is the case, we have now:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\theta(t) = 0$$

As it turns out, and as we will see in Chapter 2, in this case it is very easy to obtain the solution we are looking for:

$$\theta(t) = \theta(t=0)\cos\left((\frac{g}{l})^{1/2}t\right)$$

This solution is the familiar 'back and forth' oscillatory motion of the pendulum you are familiar with. What you might have not known until today is that this solution assumes $\sin\theta \approx \theta$ and is therefore valid only if $\theta << 1$!

There are lots of 'hidden' linear approximations in the equations you have learned in your physics and chemistry courses. You may recall your teachers telling you that a give equation is valid only at low concentrations, or low pressures, or low... you hopefully get the point. A pendulum is of course not particularly interesting when it comes to chemistry, but as we will see through many examples during the semester, oscillations, generally speaking, are. The example below illustrates the use of series to a problem involving diatomic molecules, but before discussing it we need to provide some background.

The vibrations of a diatomic molecule are often modeled in terms of the so-called *Morse potential*. This equation does not provide an exact description of the vibrations of the molecule under any condition, but it does a pretty good job for many purposes.

$$V(R) = D_e\left(1 - e^{-k(R-R_e)}\right)^2 \tag{32.9.8}$$

Here, R is the distance between the nuclei of the two atoms, R_e is the distance at equilibrium (i.e. the equilibrium bond length), D_e is the dissociation energy of the molecule, k is a constant that measures the strength of the bond, and V is the potential energy. Note that R_e is the distance at which the potential energy is a minimum, and that is why we call this the equilibrium distance. We would need to apply energy to separate the atoms even more, or to push them closer (Figure 32.9.2).

At room temperature, there is enough thermal energy to induce small vibrations that displace the atoms from their equilibrium positions, but for stable molecules, the displacement is very small: $R - R_e \to 0$. In the next example we will prove that under these conditions, the potential looks like a parabola, or in mathematical terms, $V(R)$ is proportional to the square of the displacement.

This type of potential is called a 'harmonic potential'. A vibration is said to be simple harmonic if the potential is proportional to the square of the displacement (as in the simple spring problems you may have studied in physics).

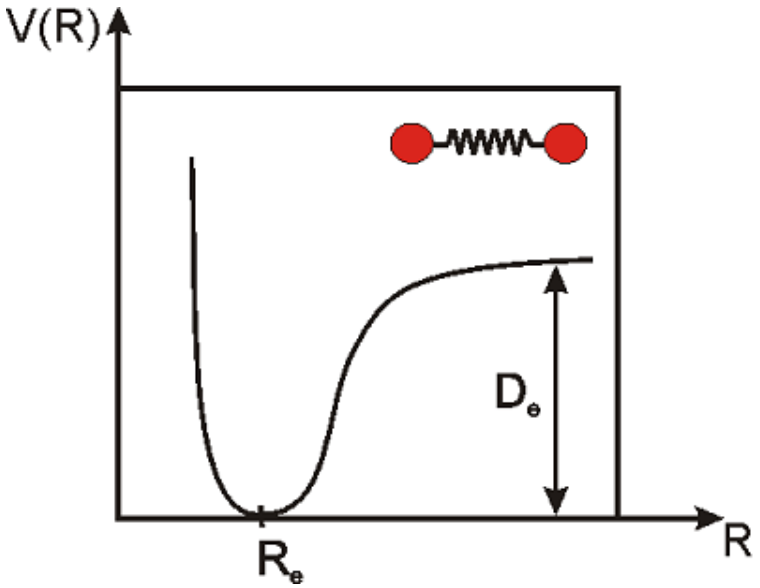


Figure 32.9.2: The Morse potential (CC BY-NC-SA; Marcia Levitus)

Example 32.9.1

Expand the Morse potential as a power series and prove that the vibrations of the molecule are approximately simple harmonic if the displacement $R - R_e$ is small.

Solution

The relevant variable in this problem is the displacement $R - R_e$, not the actual distance R. Let's call the displacement $R - R_e = x$, and let's rewrite Equation 32.9.8 as

$$V(R) = D_e \left(1 - e^{-kx}\right)^2 \tag{32.9.9}$$

The goal is to prove that $V(R) = cx^2$ (i.e. the potential is proportional to the square of the displacement) when $x \to 0$. The constant c is the proportionality constant. We can approach this in two different ways. One option is to expand the function shown in Equation 32.9.9 around zero. This would be correct, but it but involve some unnecessary work. The variable x appears only in the exponential term, so a simpler option is to expand the exponential function, and plug the result of this expansion back in Equation 32.9.9. Let's see how this works:

We want to expand e^{-kx} as $a_0 + a_1x + a_2x^2 ... a_nx^n$, and we know that the coefficients are $a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_0$.
The coefficient a_0 is $f(0) = 1$. The first three derivatives of $f(x) = e^{-kx}$ are

- $f'(x) = -ke^{-kx}$
- $f''(x) = k^2e^{-kx}$
- $f'''(x) = -k^3e^{-kx}$

When evaluated at $x = 0$ we obtain, $-k, k^2, -k^3 ...$

and therefore $a_n = \frac{(-1)^n k^n}{n!}$ for $n = 0, 1, 2....$

Therefore,

$$e^{-kx} = 1 - kx + k^2x^2/2! - k^3x^3/3! + k^4x^4/4! ...$$

and

$$1-e^{-kx}=+kx-k^2x^2/2!+k^3x^3/3!-k^4x^4/4!...$$

From the last result, when $x<<1$, we know that the terms in $x^2, x^3...$ will be increasingly smaller, so $1-e^{-kx}\approx kx$ and $(1-e^{-kx})^2\approx k^2x^2$.

Plugging this result in Equation 32.9.9 we obtain $V(R)\approx D_ek^2x^2$, so we demonstrated that the potential is proportional to the square of the displacement when the displacement is small (the proportionality constant is D_ek^2). Therefore, stable diatomic molecules at room temperatures behave pretty much like a spring! (Don't take this too literally. As we will discuss later, microscopic springs do not behave like macroscopic springs at all).

Taylor Series

Before discussing more applications of Maclaurin series, let's expand our discussion to the more general case where we expand a function around values different from zero. Let's say that we want to expand a function around the number h. If $h=0$, we call the series a Maclaurin series, and if $h\neq 0$ we call the series a Taylor series. Because Maclaurin series are a special case of the more general case, we can call all the series Taylor series and omit the distinction. The following is true for a function $f(x)$ as long as the function and all its derivatives are finite at h:

$$f(x)=a_0+a_1(x-h)+a_2(x-h)^2+...+a_n(x-h)^n=\sum_{n=0}^{\infty}a_n(x-h)^n \tag{32.9.10}$$

The coefficients are calculated as

$$a_n=\frac{1}{n!}\left(\frac{d^nf}{dx^n}\right)_h \tag{32.9.11}$$

Notice that instead of evaluating the function and its derivatives at $x=0$ we now evaluate them at $x=h$, and that the basis set is now $1,(x-h),(x-h)^2,...,(x-h)^n$ instead of $1,x,x^2,...,x^n$. A Taylor series will be a good approximation of the function at values of x close to h, in the same way Maclaurin series provide good approximations close to zero.

To see how this works let's go back to the exponential function. Recall that the Maclaurin expansion of e^x is shown in Equation 3.1.3. We know what happens if we expand around zero, so to practice, let's expand around $h=1$. The coefficient a_0 is $f(1)=e^1=e$. All the derivatives are e^x, so $f'(1)=f''(1)=f'''(1)...=e$. Therefore, $a_n=\frac{e}{n!}$ and the series is therefore

$$e\left[1+(x-1)+\frac{1}{2}(x-1)^2+\frac{1}{6}(x-1)^3+...\right]=\sum_{n=0}^{\infty}\frac{e}{n!}(x-1)^n \tag{32.9.12}$$

We can use the same arguments we used before to conclude that $e^x\approx ex$ if $x\approx 1$. If $x\approx 1$, $(x-1)\approx 0$, and the terms $(x-1)^2,(x-1)^3$ will be smaller and smaller and will contribute less and less to the sum. Therefore,

$$e^x\approx e\left[1+(x-1)\right]=ex.$$

This is the equation of a straight line with slope e and y-intercept 0. In fact, from Equation 3.1.7 we can see that all functions will look linear at values close to h. This is illustrated in Figure 32.9.1, which shows the exponential function (red) together with the functions $1+x$ (magenta) and ex (blue). Not surprisingly, the function $1+x$ provides a good approximation of e^x at values close to zero (see Equation 3.1.3) and the function ex provides a good approximation around $x=1$ (Equation 32.9.12).

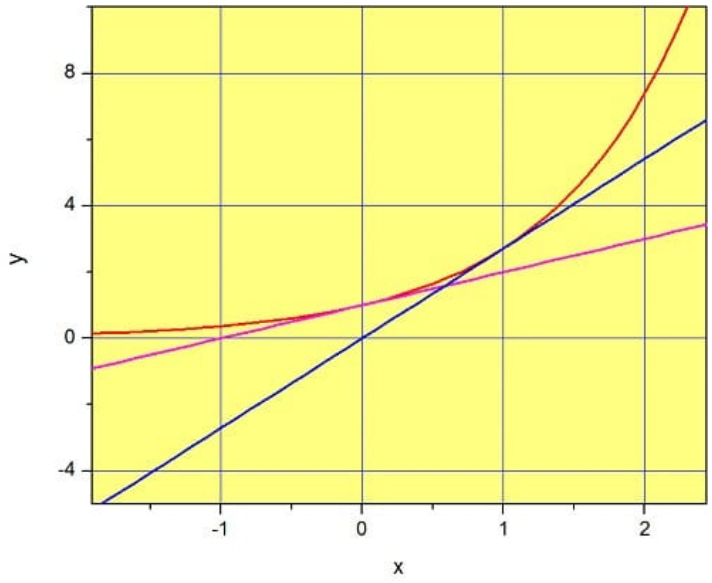


Figure 32.9.1: Two linear approximations of the exponential function. The function e^x is plotted in red together with the function $y = 1 + x$ (magenta) and $y = ex$ (blue). (CC BY-NC-SA; Marcia Levitus)

Example 32.9.1:

Expand $f(x) = \ln x$ about $x = 1$

Solution

$$f(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + \ldots + a_n(x-h)^n, a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_h$$

$$a_0 = f(1) = \ln(1) = 0$$

The derivatives of $\ln x$ are:

$$f'(x) = 1/x, f''(x) = -1/x^2, f'''(x) = 2/x^3, f^{(4)}(x) = -6/x^4, f^{(5)}(x) = 24/x^5 \ldots$$

and therefore,

$$f'(1) = 1, f''(1) = -1, f'''(1) = 2, f^{(4)}(1) = -6, f^{(5)}(1) = 24 \ldots.$$

To calculate the coefficients, we need to divide by $n!$:

- $a_1 = f'(1)/1! = 1$
- $a_2 = f''(1)/2! = -1/2$
- $a_3 = f'''(1)/3! = 2/3! = 1/3$
- $a_4 = f^{(4)}(1)/4! = -6/4! = -1/4$
- $a_n = (-1)^{n+1}/n$

The series is therefore:

$$f(x) = 0 + 1(x-1) - 1/2(x-1)^2 + 1/3(x-1)^3 \ldots = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n}(x-1)^n$$

Note that we start the sum at $n = 1$ because $a_0 = 0$, so the term for $n = 0$ does not have any contribution.

Need help? The links below contain solved examples.

External links:

Finding the Taylor series of a function I: http://patrickjmt.com/taylor-and-maclaurin-series-example-2/

Other Applications of Mclaurin and Taylor series

So far we have discussed how we can use power series to approximate more complex functions around a particular value. This is very common in physical chemistry, and you will apply it frequently in future courses. There are other useful applications of Taylor series in the physical sciences. Sometimes, we may use relationships to derive equations or prove relationships. Example $32.9.1$ illustrates this last point.

Example $32.9.1$

Calculate the following sum (λ is a positive constant)

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!}$$

Solution

Let's 'spell out' the sum:

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = e^{-\lambda}\left[1 + \frac{\lambda^1}{1!} + \frac{\lambda^2}{2!} + \frac{\lambda^3}{3!}...\right]$$

The sum within the brackets is exactly e^{λ}. This is exact, and not an approximation, because we have all infinite terms.

Therefore,

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = e^{-\lambda}e^{\lambda} = 1$$

This would require that you recognize the term within brackets as the Maclaurin series of the exponential function. One simpler version of the problem would be to ask you to prove that the sum equals 1.

There are more ways we can use Taylor series in the physical sciences. We will see another type of application when we study differential equations. In fact, power series are extremely important in finding the solutions of a large number of equations that arise in quantum mechanics. The description of atomic orbitals, for example, require that we solve differential equations that involve expressing functions as power series.

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32.10: FOURIER ANALYSIS

The Fourier transform converts a function vs. continuous (or descrete) time and maps it into a function vs. continuous (or descrete) frequencies. Hence, the transform converts *time-domain* data into *frequency-domain* data (and vice versa). This decomposion of a function into sinusoids of different frequencies is a powerful approach to many experimental and theoretical problems. **Fourier transform spectroscopy** is an approach whereby spectra are collected based on measurements using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation. It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy (FT IR, FT-NIRS), Fourier transform nuclear magnetic resonance (NMR), mass spectrometry and electron spin resonance spectroscopy.

Introduction

Fourier analysis is a subject area which grew out of the study of Fourier series. The subject began with trying to understand when it was possible to represent general functions by sums of simpler trigonometric functions. The attempt to understand functions (or other objects) by breaking them into basic pieces that are easier to understand is one of the central themes in Fourier analysis. Fourier analysis is named after Joseph Fourier who showed that representing a function by a trigonometric series greatly simplified the study of heat propagation. Today the subject of Fourier analysis encompasses a vast spectrum of mathematics with parts that, at first glance, may appear quite different. In the sciences and engineering the process of decomposing a function into simpler pieces is often called an **analysis**. In Fourier analysis, the term Fourier transform often refers to the process that decomposes a given function into the basic pieces. This process results in another function that describes how much of each basic piece are in the original function. However, the transform is often given a more specific name depending upon the domain and other properties of the function being transformed, as elaborated below. Moreover, the original concept of Fourier analysis has been extended over time to apply to more and more abstract and general situations, and the general field is often known as harmonic analysis.

Fourier Series

When the function f is a function of time and represents a physical signal, the transform has a standard interpretation as the frequency spectrum of the signal. The magnitude of the resulting complex-valued function F at frequency ω represents the amplitude of a frequency component whose initial phase is given by the phase of F. However, it is important to realize that Fourier transforms are not limited to functions of time, and temporal frequencies. They can equally be applied to analyze *spatial* frequencies, and indeed for nearly any function domain.

Properties

http://www.math.ubc.ca/~feldman/demos/demo3.html

Continuous Fourier Trasnform (CFT)

Most often, the unqualified term **Fourier transform** refers to the transform of functions of a continuous real argument, such as time (t). In this case the Fourier transform describes a function $f(t)$ in terms of basic complex exponentials of various frequencies. In terms of ordinary frequency ν, the Fourier transform is given by the complex number**:**

$$F(\nu) = \int_{-\infty}^{\infty} f(t) \cdot e^{-2\pi \cdot i \cdot \nu \cdot t} dt.$$

Evaluating this quantity for all values of ν produces the *frequency-domain* function.

Discrete Fourier Transform (DFT)

Experimentally, we collect data that is not continuous, but samples a measurements at specific point. Hence we have to deal with

the discrete version of the Fourier Transform.

Fast Fourier Transfer (FFT)

The discrete version of the Fourier transform (see below) can be evaluated quickly on computers using fast Fourier transform (FFT) algorithms. This algortihm sympically requires a 2^n number of measurements to operate. Hence you will notice data sets often with such dimensions. (Conte & de Boor 1980)

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Contributors and Attributions

- Wikipedia entry (to begin with)
- mmrc.caltech.edu/FTIR/FTIRintro.pdf

32.10.1: Fourier Analysis in Matlab

32.10.2: Fourier Synthesis of Periodic Waveforms

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32.10.1: Fourier Analysis in Matlab

Fourier analysis encompasses a vast spectrum of mathematics with parts that, at first glance, may appear quite different. In the sciences and engineering the process of decomposing a function into simpler pieces is often called an analysis. The corresponding operation of rebuilding the function from these pieces is known as synthesis. In this context the term Fourier synthesis describes the act of rebuilding and the term Fourier analysis describes the process of breaking the function into a sum of simpler pieces. In mathematics, the term Fourier analysis often refers to the study of both operations.

Introduction

In Fourier analysis, the term Fourier transform often refers to the process that decomposes a given function into the basic pieces. This process results in another function that describes how much of each basic piece are in the original function. It is common practice to also use the term Fourier transform to refer to this function. However, the transform is often given a more specific name depending upon the domain and other properties of the function being transformed, as elaborated below. Moreover, the original concept of Fourier analysis has been extended over time to apply to more and more abstract and general situations and the general field is often known as harmonic analysis.

(Continuous) Fourier transform

Most often, the unqualified term Fourier transform refers to the transform of functions of a continuous real argument, such as time (t). In this case the Fourier transform describes a function ƒ(t) in terms of basic complex exponentials of various frequencies. In terms of ordinary frequency ν, the Fourier transform is given by the complex number.

Evaluating this quantity for all values of ν produces the frequency-domain function.

Matlab and the FFT

Matlab's FFT function is an effective tool for computing the discrete Fourier transform of a signal.The following code examples will help you to understand the details of using the FFT function.

Example 1

The typical syntax for computing the FFT of a signal is FFT(x,N) where x is the signal, x[n], you wish to transform, and N is the number of points in the FFT. N must be at least

as large as the number of samples in x[n]. To demonstrate the effect of changing the value of N,

synthesize a cosine with 30 samples at 10 samples per period.

- n = [0:29];
- x = cos(2*pi*n/10);

Define 3 different values for N. Then take the transform of x[n] for each of the 3 values that were

defined. The abs function find the magnitude of the transform, as we are not concerned with distinguishing between real and imaginary components.

- N1 = 64;
- N2 = 128;
- N3 = 256;
- X1 = abs(fft(x,N1));
- X2 = abs(fft(x,N2));
- X3 = abs(fft(x,N3));

The frequency scale begins at 0 and extends to N - 1 for an N-point FFT. We then normalize the scale so that it extends from 0 to 1 - 1/N

- F1 = [0 : N1 - 1]/N1;
- F2 = [0 : N2 - 1]/N2;
- F3 = [0 : N3 - 1]/N3;

Plot each of the transforms one above the other

- subplot(3,1,1)
- plot(F1,X1,'-x'),title('N = 64'),axis([0 1 0 20])
- subplot(3,1,2)
- plot(F2,X2,'-x'),title('N = 128'),axis([0 1 0 20])
- subplot(3,1,3)
- plot(F3,X3,'-x'),title('N = 256'),axis([0 1 0 20])

Upon examining the plot one can see that each of the transforms adheres to the same shape, differing only in the number of samples used to approximate that shape. What happens if N is the same as the number of samples in x[n]? To find out, set N1 = 30. What does the resulting plot look like? Why does it look like this?

Example 2

In the last example the length of x[n] was limited to 3 periods in length. Now, let's choose a large value for N (for a transform with many points), and vary the number of repetitions of the fundamental period.

- n = [0:29];
- x1 = cos(2*pi*n/10); % 3 periods
- x2 = [x1 x1]; % 6 periods
- x3 = [x1 x1 x1]; % 9 periods

- N = 2048;
- X1 = abs(fft(x1,N));
- X2 = abs(fft(x2,N));
- X3 = abs(fft(x3,N));
- F = [0:N-1]/N;

- subplot(3,1,1)
- plot(F,X1),title('3 periods'),axis([0 1 0 50])
- subplot(3,1,2)
- plot(F,X2),title('6 periods'),axis([0 1 0 50])
- subplot(3,1,3)
- plot(F,X3),title('9 periods'),axis([0 1 0 50])

The previous code will produce three plots. The first plot, the transform of 3 periods of a cosine, looks like the magnitude of 2 sincs with the center of the first sinc at 0.1fs and the second at 0.9fs.

The second plot also has a sinc-like appearance, but its frequency is higher and it has a larger magnitude at 0:1fs and 0:9fs. Similarly, the third plot has a larger sinc frequency and magnitude.

As x[n] is extended to a large number of periods, the sincs will begin to look more and more like impulses.

But I thought a sinusoid transformed to an impulse, why do we have sincs in the frequency domain? When the FFT is computed with an N larger than the number of samples in x[n], it fills in the samples after x[n] with zeros. Example 2 had an x[n] that was 30 samples long, but the FFT had an N = 2048. When Matlab computes the FFT, it automatically fills the spaces from n = 30 to n = 2047 with zeros. This is like taking a sinusoid and multiplying it with a rectangular box of length 30. A multiplication of a box and a sinusoid in the time domain should result in the convolution of a sinc with impulses in the frequency domain. Furthermore, increasing the width of the box in the time domain should increase the frequency of the sinc in the frequency domain. The previous Matlab experiment supports this conclusion.

Identifying Signals in noise with FFT

A common use of Fourier transforms is to find the frequency components of a signal buried in a noisy time domain signal. Consider data sampled at 1000 Hz. Form a signal containing a 50 Hz sinusoid of amplitude 0.7 and 120 Hz sinusoid of amplitude 1 and corrupt it with some zero-mean random noise:

- Fs = 1000; % Sampling frequency
- T = 1/Fs; % Sample time
- L = 1000; % Length of signal
- t = (0:L-1)*T; % Time vector
- x = 0.7*sin(2*pi*50*t) + sin(2*pi*120*t);
  % Sum of a 50 Hz sinusoid and a 120 Hz sinusoid
- y = x + 2*randn(size(t)); % Sinusoids plus noise
- plot(Fs*t(1:50),y(1:50))
- title('Signal Corrupted with Zero-Mean Random Noise')
- xlabel('time (milliseconds)')

It is difficult to identify the frequency components by looking at the original signal. Converting to the frequency domain, the discrete Fourier transform of the noisy signal y is found by taking the fast Fourier transform (FFT):

- NFFT = 2^nextpow2(L); % Next power of 2 from length of y
- Y = fft(y,NFFT)/L;
- f = Fs/2*linspace(0,1,NFFT/2+1); % Plot single-sided amplitude spectrum.
- plot(f,2*abs(Y(1:NFFT/2+1)))
- title('Single-Sided Amplitude Spectrum of y(t)')
- xlabel('Frequency (Hz)')
- ylabel('|Y(f)|')

The main reason the amplitudes are not exactly at 0.7 and 1 is because of the noise. Several executions of this code (including recomputation of y) will produce different approximations to 0.7 and 1. The other reason is that you have a finite length signal. Increasing L from 1000 to 10000 in the example above will produce much better approximations on average.

Outside Links

- http://www.chem.uoa.gr/applets/Apple...FourAnal2.html

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32.10.2: Fourier Synthesis of Periodic Waveforms

Java Developed by Dr. Constantinos E. Efstathiou, Laboratory of Analytical Chemistry, National and Kapodistrian University of Athens

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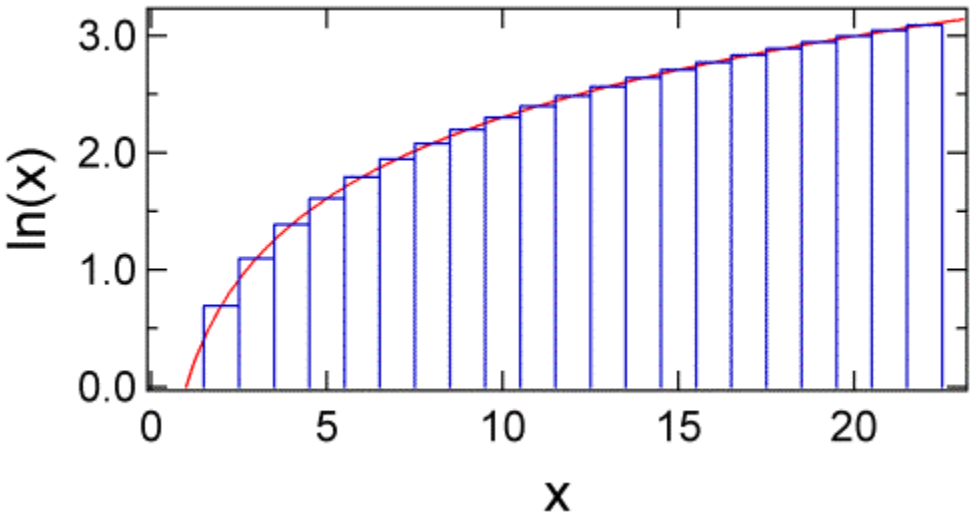
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32.11: The Binomial Distribution and Stirling's Appromixation

Stirling's approximation is named after the Scottish mathematician James Stirling (1692-1770). In confronting statistical problems we often encounter factorials of very large numbers. The factorial $N!$ is a product $N(N-1)(N-2)...(2)(1)$. Therefore, $\ln\ N!$ is a sum

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + ... + \ln N = \sum_{k=1}^{N} \ln k. \tag{32.11.1}$$

where we have used the property of logarithms that $\log(abc) = \log(a) + \log(b) + \log(c)$. The sum is shown in figure below.



Using **Euler-MacLaurin** formula one has

$$\sum_{k=1}^{N} \ln k = \int_{1}^{N} \ln x\, dx + \sum_{k=1}^{p} \frac{B_{2k}}{2k(2k-1)} \left(\frac{1}{n^{2k-1}} - 1 \right) + R, \tag{32.11.2}$$

where B_1 = –1/2, B_2 = 1/6, B_3 = 0, B_4 = –1/30, B_5 = 0, B_6 = 1/42, B_7 = 0, B_8 = –1/30, ... are the **Bernoulli numbers**, and \(R\) is an error term which is normally small for suitable values of \(p\).

Then, for large N,

$$\ln N! \sim \int_{1}^{N} \ln x\, dx \approx N \ln N - N. \tag{32.11.3}$$

after some further manipulation one arrives at (apparently Stirling's contribution was the prefactor of $\sqrt{2\pi}$)

$$N! = \sqrt{2\pi N}\ N^N e^{-N} e^{\lambda_N} \tag{32.11.4}$$

where

$$\frac{1}{12N+1} < \lambda_N < \frac{1}{12N}. \tag{32.11.5}$$

The sum of the area under the blue rectangles shown below up to N is $\ln N!$. As you can see the rectangles begin to closely approximate the red curve as m gets larger. The area under the curve is given the integral of $\ln x$.

$$\ln N! = \sum_{m=1}^{N} \ln m \approx \int_{1}^{N} \ln x \, dx \tag{32.11.6}$$

To solve the integral use integration by parts

$$\int u \, dv = uv - \int v \, dy \tag{32.11.7}$$

Here we let $u = \ln x$ and $dv = dx$. Then $v = x$ and $du = \frac{dx}{x}$.

$$\int_{0}^{N} \ln x \, dx = x \ln x|_{0}^{N} - \int_{0}^{N} x \frac{dx}{x} \tag{32.11.8}$$

Notice that $x/x = 1$ in the last integral and $x \ln x$ is 0 when evaluated at zero, so we have

$$\int_{0}^{N} \ln x \, dx = N \ln N - \int_{0}^{N} dx \tag{32.11.9}$$

Which gives us Stirling's approximation: $\ln N! = N \ln N – N$. As is clear from the figure above Stirling's approximation gets better as the number N gets larger (Table 32.11.1).

Table 32.11.1: Evaluation of Approximation with absolute values

N	N!	ln N!	N ln N – N	Error
10	3.63×10^{6}	15.1	13.02	13.8%
50	3.04×10^{64}	148.4	145.6	1.88%
100	9.33×10^{157}	363.7	360.5	0.88%
150	5.71×10^{262}	605.0	601.6	0.56%

Calculators often overheat at 200!, which is all right since clearly result are converging. In thermodynamics, we are often dealing very large N (i.e., of the order of Avagadro's number) and for these values Stirling's approximation is excellent.

References

1. J. Stirling "Methodus differentialis, sive tractatus de summation et interpolation serierum infinitarium", London (1730). English translation by J. Holliday "The Differential Method: A Treatise of the Summation and Interpolation of Infinite Series" (1749)

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- Stirling's Approximation by SklogWiki, Stefan Franzen is licensed CC BY-NC-SA 4.0. Original source: http://www.sklogwiki.org/SklogWiki/index.php/Stirling%27s_approximation.

33: APPENDICES

33.1: Deriving Planck's Distribution Law
33.2: Bra-Ket Notation

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33.1: Deriving Planck's Distribution Law

Albert Einstein developed a simple but effective analysis of induced emission and absorption of radiation along with spontaneous emission that can be used to derive the Planck formula for thermal radiation.

Consider two energy levels for the molecules in a material. The lower of the two is denoted as E_1 and the higher as E_2. The probability of a transition from level 1 up to level 2 through induced absorption is assumed to be proportional to the energy density per unit frequency interval, $(du/d\nu)$. Likewise the probability of an induced transition from level 2 down to level 1 is assumed also to be proportional to $(du/d\nu)$. These two probabilities are taken to be $B_{12}(du/d\nu)$ and $B_{21}(du/d\nu)$, respectively, where B_{12} and B_{21} are constants. The probability of a spontaneous emission is assumed to be a constant A_{21}.

Let N_1 and N_2 be the number of molecules in energy states 1 and 2, respectively. For **equilibrium** the number of transitions from 1 to 2 has to be equal to the number from 2 to 1; i.e.,

$$\underbrace{N_1\left[B_{12}\left(\frac{du}{d\nu}\right)\right]}_{\text{flow up}} = \underbrace{N_2\left[B_{21}\left(\frac{du}{d\nu}\right)+A_{21}\right]}_{\text{flow down}}$$

This means that the ratio of the occupancies of the energy levels must be

$$\frac{N_2}{N_1} = \frac{B_{12}\left(\frac{du}{d\nu}\right)}{B_{21}\left(\frac{du}{d\nu}\right)+A_{21}} \tag{33.1.1}$$

But the occupancies are given by the Boltzmann distribution as

$$N_1 = N_0 \exp\left(-\frac{E_1}{kT}\right)$$

and

$$N_2 = N_0 \exp\left(-\frac{E_2}{kT}\right)$$

where k is Boltzmann's constant and T is absolute temperature. N_0 is just a constant that is irrelevant for the rest of the analysis.

Thus according to the Boltzmann distribution

$$\frac{N_2}{N_1} = \exp\left(-\frac{E_2-E_1}{kT}\right) \tag{33.1.2}$$

Therefore for radiative equilibrium, Equations 33.1.2 and 33.1.1 can be set to each other and

$$\exp\left(-\frac{E_2-E_1}{kT}\right) = \frac{B_{12}\left(\frac{du}{d\nu}\right)}{B_{21}\left(\frac{du}{d\nu}\right)+A_{21}}$$

This condition can be solved for $(du/d\nu)$; i.e.,

$$\frac{du}{d\nu} = \frac{A_{21}}{B_{12}\exp\left(\frac{E_2-E_1}{kT}\right)-B_{21}}$$

Consider what happens to the above expression for as $T \to \infty$. It goes to

$$\lim_{T\to\infty}\frac{du}{d\nu} = \frac{A_{21}}{B_{12}-B_{21}}$$

Einstein maintained that $(du/d\nu)$ must go to infinity as T goes to infinity. This requires that B_{12} be equal to B_{21}.

Thus

$$\frac{du}{d\nu} = \frac{A_{21}/B_{21}}{\exp\left(\frac{E_2 - E_1}{kT}\right) - 1} \tag{33.1.3}$$

Now Planck's assumption is introduced:

$$E_2 - E_1 = h\nu$$

Thus Equation 33.1.3 becomes

$$\frac{du}{d\nu} = \frac{A_{21}/B_{21}}{\exp\left(\frac{h\nu}{kT}\right) - 1} \tag{33.1.4}$$

The Rayleigh-Jeans Radiation Law says

$$\frac{du}{d\nu} = \frac{8\pi kT\nu^2}{c^3} \tag{33.1.5}$$

The Planck formula must coincide with the Rayleigh-Jeans Law for sufficiently small ν. Note that the exponent in the denominator of Equation 33.1.4 can be expanded (via a Taylor expansion):

$$\exp\left(\frac{h\nu}{kT}\right) \approx 1 + \frac{h\nu}{kT}$$

for sufficiently small ν.

This means that Equation 33.1.4 simplifies to

$$\frac{du}{d\nu} = \frac{A_{21}/B_{21}}{1 + (h\nu/kT) - 1} = \frac{A_{21}/B_{21}}{h\nu/kT}$$

and hence

$$\frac{du}{d\nu} = \left(\frac{A_{21}}{B_{21}}\right)\left(\frac{kT}{h\nu}\right) \tag{33.1.6}$$

Equating Equations 33.1.5 and 33.1.6 for $(du/d\nu)$ gives

$$\left(\frac{A_{21}}{B_{21}}\right)\left(\frac{kT}{h\nu}\right) = \frac{8\pi kT\nu^2}{c^3}$$

which reduces to

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$$

Thus

$$\frac{du}{d\nu} = \frac{8\pi h\nu^3}{c^3}\frac{1}{\exp(h\nu/kT) - 1}$$

This is Planck's formula in terms of frequency.

Reference

1. K.D. Möller, *Optics*, University Science Books, Mill Valley, California, 1988.

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33.2: Bra-Ket Notation

Wavefunctions

$$\psi \rightarrow |\psi\rangle,\ \psi^* \rightarrow \langle\psi|,\ \text{and}\ \int |\psi|^2\,\mathrm{d}\tau = \int \psi^*\psi\,\mathrm{d}\tau \rightarrow \langle\psi|\psi\rangle.$$

Projection operators

$$\psi(x) = \langle x|\psi\rangle,\ \psi^*(x) = \langle\psi|x\rangle$$

and

$$\int \psi^*(x)\psi(x)\,\mathrm{d}x = \int \langle\psi|x\rangle\langle x|\psi\,\mathrm{d}x = \langle\psi|\left(\int |x\rangle\langle x|\,\mathrm{d}x\right)|\psi\rangle.$$

$$\int |x\rangle\langle x|\,\mathrm{d}x = \hat{I}, \text{and} \sum_n |\phi_n\rangle\langle\phi_n| = \hat{I},$$

where $\hat{I}$ is the identity operator, $|\phi_n\rangle$ is one of a complete set of orthonormal basis functions (example: set of particle-in-a-box wavefunctions), and the summation goes over all members of the set. Application of this form of the identity operator is called a "projection" onto a basis.

Expectation values

$$\backslash\text{expect}\hat{A} = \int \psi^*(\vec{r})\hat{A}\psi(\vec{r})d\vec{r} \rightarrow \langle\psi|\hat{A}|\psi\rangle \quad (\text{using} \int |\vec{r}\rangle\langle\vec{r}|\,\mathrm{d}\vec{r} = \hat{I}).$$

The Schrödinger Equation in Dirac notation

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

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34: REFERENCE TABLES

34.1: Table 1 Regions of the Electromagnetic Spectrum

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34.1: Table 1 Regions of the Electromagnetic Spectrum

Frequency(s^{-1})	Energy	Energy(J)	Wavelength
Gamma Rays			
$>1.0x10^{19}$	>41,000 eV	$>6.6x10^{-15}$	<0.03 nm
Hard X-rays			
$1.2x10^{18}$	5,000 eV	$8.0x10^{-16}$	0.25 nm
Soft X-rays			
$1.2x10^{16}$	50 eV	$8.0x10^{-18}$	25 nm
Vacuum UV			
$1.5x10^{15}$	6.2 eV	$9.9x10^{-19}$	200 nm
Ultraviolet			
$7.5x10^{14}$	25,000 cm^{-1}	$5.0x10^{-19}$	400 nm
Visible			
$4.3x10^{14}$	14,000 cm^{-1}	$2.8x10^{-19}$	700 nm
Near IR			
$1.5x10^{14}$	5,000 cm^{-1}	$9.9x10^{-20}$	2.0 μm
Infrared			
$1.0x10^{13}$	330 cm^{-1}	$6.6x10^{-21}$	30 μm
Far Infrared			
$1.0x10^{12}$	33 cm^{-1}	$6.6x10^{-22}$	300 μm
Microwave			
$5.0x10^{9}$	0.17 cm^{-1}	$3.3x10^{-24}$	6.0 cm
Radio Wave			

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34.2: Table 2. Characteristics of Electromagnetic Radiation

ν	frequency of oscillation of the sinusoidal wave
\tau =\frac{1}{\nu }	period of oscillation
ω = 2πν	angular frequency of oscillation
c	speed at which a wave front propagates or moves in vacuum
\lambda =\frac{c}{\nu }	wavelength
{\vec{e}}	polarization (a unit vector specifying the direction of the electric field)
E_0	peak amplitude of the electric field
B_0	peak amplitude of the magnetic field, **B** also is called the magnetic induction
S=E\times H	Poynting's vector, the cross product of the electric and magnetic fields. The units are J/m^2s, which gives the amount where ⍰ is the permeability.

I	The intensity or flux of the radiation gives the amount of energy falling on a square meter area per second. It equals ParseError: invalid DekiScript (click for details)
	`Callstack:`
	`at (Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemist`
	is the permittivity and μ_0 is the permeability of a vacuum.).

k	The wave vector has a magnitude of 2⍰/⍰ and points in the direction of propagation of the wave.
E = *h*ν	Photon energy, where h = Planck's constant.
\bar{\nu }=1/\lambda	wavenumber value, the number of waves or complete cycles per centimeter.

Additional explanation of these quantities will be provided as we encounter them in contexts dealing with atoms and molecules. If you wish to learn more now, see G.R. Fowles, *Introduction to Modern Optics* (Holt, Rinehart, and Winston, New York, 1968) pp. 1-56 or any book on electromagnetism.

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34.3: Table 5. Some Units Commonly Used in Quantum Chemistry

Physical Quantity	Name of Unit	Symbol	SI Equivalent
length	Angstrom	Å	10^{-10} m = 10^{-1} nm
length	micron	?	10^{-6} m
length	Bohr radius	a_0	5.29117 x 10^{-11} m
energy	electron volt	eV	1.60218 x 10^{-19} J
energy* Image:	wavenumber Image:	cm^{-1}	1.98645 x 10^{-23} J
energy* E = h?	hertz ?	s^{-1}	6.62608 x 10^{-34} J
energy	hartree	H	4.35981 x 10^{-18} J
dipole moment	Debye	D	3.33564 x 10^{-30} C m
magnetic field	Gauss	G	10^{-4} T

*Because they are proportional to energy, wavenumbers and frequency (hertz) commonly are used as units of energy by spectroscopists for convenience.

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34.4: Table 8

Physical Constant	Symbol	Value
Avogadro constant	N_A	6.02214×10^{23} mol^{-1}
Boltzmann constant	k_B	1.38066×10^{-23} J/K
electron rest mass	m_e	9.10939×10^{-31} kg
unit of charge*	e	1.60218×10^{-19} C
Planck constant	h	6.62606×10^{-34} Js
proton rest mass	m_p	1.67262×10^{-27} kg
vacuum speed of light	c	2.99792×10^{8} m/s

*The fundamental unit of charge has a positive value, is represented by the letter e, and is the magnitude of the charge on a proton (+e) or an electron (-e).

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34.5: Table 9. The Greek Alphabet

Table 9. The Greek Alphabet

alphaA	betaB	gamma
delta	epsilonE	zetaZ
etaH	theta	iotaI
kappa	lambda	mu
nu	xi	omicron
pi	rho	sigma
tau	upsilon	phi
chi	psi	omega

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34.6: Table 10 - Spherical Harmonic Wavefunctions

Spherical Harmonic Wavefunctions need to add atomic wave function notation to table.

m	J	$\Theta_J^m(\theta)$	$\Phi(\varphi)$	$Y_J^m(\theta, \varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}\left(3\cos^2\theta-1\right)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{-2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$
0	3	$\frac{9\sqrt{14}}{4}\left(5\cos^3\theta-3\cos\theta\right)$	$\frac{1}{\sqrt{2\pi}}$	$\frac{9}{4}\sqrt{\frac{7}{\pi}}\left(5\cos^3\theta-3\cos\theta\right)$
1	3	$\frac{\sqrt{42}}{8}\sin\theta\left(5\cos^2\theta-1\right)$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta\left(5\cos^2\theta-1\right)e^{i\varphi}$

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34.7: Table 11 Radial functions for one-electron atoms and ions.

n	\ell \,	\({R_{n,\ell } \left(\rho \right)\,\)
1	0	\(2{\left(\frac{Z} ParseError: colon expected (click for details) Callstack: at (Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(I ParseError: EOF expected (click for details) Callstack: at (Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(I \,\)
2	0	\(\frac{1}{2\sqrt{2}}{\left(\frac{Z} ParseError: colon expected (click for details) Callstack: at (Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(I (2-\rho)\ ParseError: EOF expected (click for details) Callstack: at (Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(I \)
2	1	\frac{1}{2\sqrt{6}}{{\left(\frac{Z}{{{a}_{0}}} \right)}^{3/2}}\rho \,{{e}^{-{\rho }/{2}\;}}
3	0	\frac{2}{81\sqrt{3}}{{\left(\frac{Z}{{{a}_{0}}} \right)}^{3/2}}\left(27-18\rho +2{{\rho }^{2}} \right){{e}^{-{\rho }/{3}\;}}
3	1	\frac{4}{81\sqrt{6}}{{\left(\frac{Z}{{{a}_{0}}} \right)}^{3/2}}(6\rho -{{\rho }^{2}}){{e}^{-\ {\rho }/{3}\;}}
3	2	\frac{4}{81\sqrt{30}}{{\left(\frac{Z}{{{a}_{0}}} \right)}^{3/2}}{{\rho }^{2}}\ {{e}^{-{\rho }/{3}\;}}
4	0	\frac{1}{768}{{\left(\frac{Z}{{{a}_{0}}} \right)}^{3/2}}(192-144\rho +24{{\rho }^{2}}-{{\rho }^{3}}){{e}^{-{\rho }/{4}\;}}
4	1	\frac{1}{256\sqrt{15}}{{\left(\frac{Z}{{{a}_{0}}} \right)}^{3/2}}(80\rho -20{{\rho }^{2}}+{{\rho }^{3}}){{e}^{-\ {\rho }/{4}\;}}
4	2	\frac{1}{768\sqrt{5}}{{\left(\frac{Z}{{{a}_{0}}} \right)}^{3/2}}(12\rho -{{\rho }^{3}}){{e}^{-{\rho }/{4}\;}}
4	3	\frac{1}{768\sqrt{35}}{{\left(\frac{Z}{{{a}_{0}}} \right)}^{3/2}}{{\rho }^{3}}{{e}^{-\ {\rho }/{4}\;}}

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34.8: Table 14. The ground-state electron configurations of the elements.

Table 14. The ground-state electron configurations of the elements.

Atomic Symbol	Atomic Number	Configuration
H	1	$1s^1$
He	2	$1s^2$
Li	3	$1s^2\ 2s^1$
Be	4	$1s^2\ 2s^2$
B	5	$1s^2\ 2s^2\ 2p^1$
C	6	$1s^2\ 2s^2\ 2p^2$
N	7	$1s^2\ 2s^2\ 2p^3$
O	8	$1s^2\ 2s^2\ 2p^4$
F	9	$1s^2\ 2s^2\ 2p^5$
Ne	10	$1s^2\ 2s^2\ 2p^6$
Na	11	[Ne] $3s^1$
Mg	12	[Ne] $3s^2$
Al	13	[Ne] $3s^2\ 3p^1$
Si	14	[Ne] $3s^2\ 3p^2$
P	15	[Ne] $3s^2\ 3p^3$
S	16	[Ne] $3s^2\ 3p^4$
Cl	17	[Ne] $3s^2\ 3p^5$
Ar	18	[Ne] $3s^2\ 3p^6$
K	19	[Ar] $4s^1$
Ca	20	[Ar] $4s^2$
Sc	21	[Ar] $3d^1\ 4s^2$
Ti	22	[Ar] $3d^2\ 4s^2$
V	23	[Ar] $3d^3\ 4s^2$
Cr	24	[Ar] $3d^5\ 4s^1$
Mn	25	[Ar] $3d^5\ 4s^2$
Fe	26	[Ar] $3d^6\ 4s^2$
Co	27	[Ar] $3d^7\ 4s^2$

Ni	28	[Ar] $3d^8\ 4s^2$
Cu	29	[Ar] $3d^{10}\ 4s^1$
Zn	30	[Ar] $3d^{10}\ 4s^2$
Ga	31	[Ar] $3d^{10}\ 4s^2\ 4p^1$
Ge	32	[Ar] $3d^{10}\ 4s^2\ 4p^2$
As	33	[Ar] $3d^{10}\ 4s^2\ 4p^3$
Se	34	[Ar] $3d^{10}\ 4s^2\ 4p^4$
Br	35	[Ar] $3d^{10}\ 4s^2\ 4p^5$
Kr	36	[Ar] $3d^{10}\ 4s^2\ 4p^1$

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34.9: Solubility Products

The following table provides pK_{sp} and K_{sp} values for selected compounds, organized by the anion. All values are from Martell, A. E.; Smith, R. M. *Critical Stability Constants*, Vol. 4. Plenum Press: New York, 1976. Unless otherwise stated, values are for 25 ^{o}C and zero ionic strength.

Bromide (Br^-)	**pK_{sp}**	**K_{sp}**
CuBr	8.3	$5.\times10^{-9}$ 5.?
AgBr	12.30	5.0×10^{-13}
Hg_2Br_2	22.25	5.6×10–13
$HgBr_2$ (μ = 0.5 M)	18.9	1.3×10^{-19}
$PbBr_2$ (μ = 4.0 M)	5.68	2.1×10^{-6}
Carbonate (CO_3^{2-})	**pK_{sp}**	**K_{sp}**
$MgCO_3$	7.46	3.5×10^{-8}
$CaCO_3$ (calcite)	8.35	4.5×10^{-9}
$CaCO_3$ (aragonite)	8.22	6.0×10^{-9}
$SrCO_3$	9.03	9.3×10^{-10}
$BaCO_3$	8.30	5.0×10^{-9}
$MnCO_3$	9.30	5.0×10^{-10}
$FeCO_3$	10.68	2.1×10^{-11}
$CoCO_3$	9.98	1.0×10^{-10}
$NiCO_3$	6.87	1.3×10^{-7}
Ag_2CO_3	11.09	8.1×10^{-12}
Hg_2CO_3	16.05	8.9×10^{-17}
$ZnCO_3$	10.00	1.0×10^{-10}
$CdCO_3$	13.74	1.8×10^{-14}
$PbCO_3$	13.13	7.4×10^{-14}
Chloride (Cl^-)	**pK_{sp}**	**K_{sp}**
CuCl	6.73	1.9×10^{-7}
AgCl	9.74	1.8×10^{-10}
Hg_2Cl_2	17.91	1.2×10^{-18}

Bromide (Br^-)	**pK_{sp}**	**K_{sp}**
$PbCl_2$	4.78	2.0×10^{-19}
Chromate (CrO_4^{2-})	**pK_{sp}**	**K_{sp}**
$BaCrO_4$	9.67	2.1×10^{-10}
$CuCrO_4$	5.44	3.6×10^{-6}
Ag_2CrO_4	11.92	1.2×10^{-12}
Hg_2CrO_4	8.70	2.0×10^{-9}
Cyanide (CN^-)	**pK_{sp}**	**K_{sp}**
AgCN	15.66	2.2×10^{-16}
$Zn(CN)_2$ (μ = 3.0 M)	15.5	$3.\times10^{-16}$
$Hg_2(CN)_2$	39.3	$5.\times10^{-40}$
Ferrocyanide ($[Fe(CN)_6^{4-}]$)	**pK_{sp}**	**K_{sp}**
$Zn_2[Fe(CN)_6]$	15.68	2.1×10^{-16}
$Cd_2[Fe(CN)_6]$	17.38	4.2×10^{-18}
$Pb_2[Fe(CN)_6]$	18.02	9.5×10^{-19}
Fluoride (F^-)	**pK_{sp}**	**K_{sp}**
MgF_2	8.18	6.6×10^{-9}
CaF_2	10.41	3.9×10^{-11}
SrF_2	8.54	2.9×10^{-9}
BaF_2	5.76	1.7×10^{-6}
PbF_2	7.44	3.6×10^{-8}
Hydroxide (OH^-)	**pK_{sp}**	**K_{sp}**
$Mg(OH)_2$	11.15	7.1×10^{-12}
$Ca(OH)_2$	5.19	6.5×10^{-6}
$Ba(OH)_2\cdot8H_2O$	3.6	$3.\times10^{-4}$
$La(OH)_3$	20.7	$2.\times10^{-21}$
$Mn(OH)_2$	12.8	1.6×10^{-13}
$Fe(OH)_2$	15.1	$8.\times10^{-16}$
$Co(OH)_2$	14.9	1.3×10^{-15}
$Ni(OH)_2$	15.2	$6.\times10^{-16}$

Bromide (Br^-)	pK_{sp}	K_{sp}
$Cu(OH)_2$	19.32	4.8×10^{-20}
$Fe(OH)_3$	38.8	1.6×10^{-39}
$Co(OH)_3$ (T = 19°C)	44.5	$3.\times10^{-45}$
Ag_2O (+ H_2O ⇌ $2Ag^+ + 2OH^-$)	15.42	3.8×10^{-16}
Cu_2O (+ H_2O ⇌ $2Cu^+ + 2OH^-$)	29.4	$4.\times10^{-30}$
$Zn(OH)_2$ (amorphous)	15.52	3.0×10^{-16}
$Cd(OH)_2$ (β)	14.35	4.5×10^{-15}
HgO (red) (+ H_2O ⇌ $Hg^{2+} + 2OH^-$)	25.44	3.6×10^{-26}
SnO (+ H_2O ⇌ $Sn^{2+} + 2OH^-$)	26.2	$6.\times10^{-27}$
PbO (yellow) (+ H_2O ⇌ $Pb^{2+} + 2OH^-$)	15.1	$8.\times10^{-16}$
$Al(OH)_3$ (α)	33.5	$3.\times10^{-34}$
Iodate (IO_3^-)	**pK_{sp}**	**K_{sp}**
$Ca(IO_3)_2$	6.15	7.1×10^{-7}
$Ba(IO_3)_2$	8.81	1.5×10^{-9}
$AgIO_3$	7.51	3.1×10^{-8}
$Hg_2(IO_3)_2$	17.89	1.3×10^{-18}
$Zn(IO_3)_2$	5.41	3.9×10^{-6}
$Cd(IO_3)_2$	7.64	2.3×10^{-8}
$Pb(IO_3)_2$	12.61	2.5×10^{-13}
Iodide (I^-)	**pK_{sp}**	**K_{sp}**
AgI	16.08	8.3×10^{-17}
Hg_2I_2	28.33	4.7×10^{-29}
HgI_2 (μ = 0.5 M)	27.95	1.1×10^{-28}
PbI_2	8.10	7.9×10^{-9}
Oxalate ($C_2O_4^{2-}$)	**pK_{sp}**	**K_{sp}**
CaC_2O_4 (μ = 0.1 M, T = 20 °C)	7.9	1.3×10^{-8}
BaC_2O_4 (μ = 0.1 M, T = 20 °C)	6.0	$1.\times10^{-6}$

Bromide (Br^-)	pK_{sp}	K_{sp}
SrC_2O_4 (μ = 0.1 M, T = 20 °C)	6.4	$4.\times10^{-7}$
Phosphate (PO_4^{3-})	**pK_{sp}**	**K_{sp}**
$Fe_3(PO_4)_2•8H_2O$	36.0	$1.\times10^{-36}$
$Zn_3(PO_4)_2•4H_2O$	35.3	$5.\times10^{-36}$
Ag_3PO_4	17.55	2.8×10^{-18}
$Pb_3(PO_4)_2$ (T = 38 °C)	43.55	3.0×10^{-44}
Sulfate (SO_4^{2-})	**pK_{sp}**	**K_{sp}**
$CaSO_4$	4.62	2.4×10^{-5}
$SrSO_4$	6.50	3.2×10^{-7}
$BaSO_4$	9.96	1.1×10^{-10}
Ag_2SO_4	4.83	1.5×10^{-5}
Hg_2SO_4	6.13	7.4×10^{-7}
$PbSO_4$	7.79	1.6×10^{-8}
Sulfide (S^{2-})	**pKsp**	**Ksp**
MnS (green)	13.5	$3.\times10^{-14}$
FeS	18.1	$8.\times10^{-19}$
CoS (β)	25.6	$3.\times10^{-26}$
NiS (γ)	26.6	$3.\times10^{-27}$
CuS	36.1	$8.\times10^{-37}$
Cu_2S	48.5	$3.\times10^{-49}$
Ag_2S	50.1	$8.\times10^{-51}$
ZnS (α)	24.7	$2.\times10^{-25}$
CdS	27.0	$1.\times10^{-27}$
Hg_2S (red)	53.3	$5.\times10^{-54}$
PbS	27.5	$3.\times10^{-28}$
Thiocyanate (SCN^-)	**pK_{sp}**	**K_{sp}**
CuSCN (μ = 5.0 M)	13.40	4.0×10^{-14}
AgSCN	11.97	1.1×10^{-12}
$Hg_2(SCN)_2$	19.52	3.0×10^{-20}
$Hg(SCN)_2$ (μ = 1.0 M)	19.56	2.8×10^{-20}

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GLOSSARY

A

angular node | An angular node will occur where the angular part of the electronic wavefunction equals zero.

ansatz | An educated guess or an additional assumption made to help solve a problem, and which is later verified to be part of the solution by its results.

Antibonding Orbital | A molecular orbital whose energy is higher than that of constituent atomic orbitals; it destabilizes the system (i.e., opposes binding).

Atomic Orbital, AO | A wavefunction for an electron in a single atom (e.g. hydrogen 1s orbital).

atomic orbitals | Atomic orbital is a mathematical function describing the location and wave-like behavior of a single electron in an atom. This function can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus.

B

Beer's Law | The Beer-Lambert law relates the optical attenuation of a physical material containing a single attenuating species of uniform concentration to the optical path length through the sample and absorptivity of the species.

Bohr magneton | A physical constant and the natural unit for expressing the magnetic moment of an electron caused by either its orbital or spin angular momentum. ($\mu B = e\hbar/2me$)

Bonding Orbital | A molecular orbital whose energy is lower than the constituent atomic orbitals, which leads to a favorable (stabilizing) interaction and thus tends to hold nuclei together.

Born–Oppenheimer Approximation | The approximation that nuclear motion is much slower than electronic motion, so nuclei can be treated as fixed when solving the electronic Schrödinger equation.

Bosons | Bosons are particles with integer spin (s = 0, 1, 2, ...).

Bound state | A state is called bound state if its position probability density at infinite tends to zero for all the time. Roughly speaking, we can expect to find the particle(s) in a finite size region with certain probability.

Bra–ket notation | The bra–ket notation is a way to represent the states and operators of a system by angle brackets and vertical bars, for example, $|\alpha\rangle$ and $|\alpha\rangle\langle\beta|$.

C

Collapse | "Collapse" means the sudden process which the state of the system will "suddenly" change to an eigenstate of the observable during measurement.

commutator | The commutator of two operators elements a and b is defined by [a,b]=ab-ba. The commutator is zero if and only if a and b commute.

commute | The commutator of two operators elements a and b is defined by [a,b]=ab-ba. The commutator is zero if and only if a and b commute.

Correspondence principle | For every observable property of a system there is a corresponding quantum mechanical operator.

Coulomb Integral | The integral representing the classical-type (electrostatic) interaction of an electron in one atomic orbital interacting with the nucleus of that same atom or another atom.

cyclic boundary condition | A boundary condition associated with regularly repeating intervals. For quantum rigid rotors, this implied the wavefunction must equal itself upon a full rotation, i.e., $\psi(0°)=\psi(360°)$.

D

Degeneracy | If the energy of different states (wavefunctions that are not scalar multiple of each other) are the same, the states are called degenerate.

Degenerate energy level | If the energy of different state (wave functions which are not scalar multiple of each other) is the same, the energy level is called degenerate. There is no degeneracy in 1D system.

Density matrix | Physically, the density matrix is a way to represent pure states and mixed states. The density matrix of pure state whose ket is $|\alpha\rangle$ is $|\alpha\rangle\langle\alpha|$.

Density operator | Physically, the density matrix is a way to represent pure states and mixed states. The density matrix of pure state whose ket is $|\alpha\rangle$ is $|\alpha\rangle\langle\alpha|$.

Determinantal Equation | The condition for nontrivial solutions in the generalized eigenvalue problem: (\det

dipole moment | The electric dipole moment is a measure of the separation of positive and negative electrical charges within a system and is a measure of the system's overall polarity.

Dirac notation | The bra–ket notation is a way to represent the states and operators of a system by angle brackets and vertical bars, for example, |α> and |α><β|.

E

Eigenstates | An eigenstate of an operator A is a vector satisfied the eigenvalue equation: A | a > = λ | a >, where λ is a scalar (the eigenvalue).

eigenvalue | Any value of λ that is is a solution to the eigenvalue problem (A·v=λ·v) is known as an eigenvalue of the matrix A.

eigenvalue equation | An eigenvalue problem is A·v=λ·v, where A is an n-by-n matrix, v is a non-zero n-by-1 vector and λ is a scalar (that can be real or complex).

eigenvector | Any value of v that is is a solution to the eigenvalue problem (A·v=λ·v) is known as an eigenvevctor of the matrix A.

Energy spectrum | The energy spectrum refers to the possible energy of a system. For bound system (bound states), the energy spectrum is discrete; for unbound system (scattering states), the energy spectrum is continuous.

even function | A function is even if f(x)=f(-x)

Exchange Integral | A purely quantum-mechanical term that arises from the possibility of “exchange” of electron character between orbitals; it has no classical analog.

Expectation value | The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It can be thought of as an average of all the possible outcomes of a measurement as weighted by their likelihood, and as such it is not the most probable value of a measurement; indeed the expectation value may have zero probability of occurring

F

Fermions | Fermions are particles with half-integer spin (s = 1/2, 3/2, 5/2, ...).

Fine Structure Constant | 1/137 . The fine structure constant is a mathematical constant that is given as the ratio of the classical and quantum electromagnetic constants. It is also known as Sommerfeld's constant.

forbidden transition | A eigentstate to eigenstate transition with zero probability of being observed. This is determined by the relevant transition moment integral

G

g-factor | A dimensionless quantity that characterizes the magnetic moment and angular momentum of an atom, a particle or the nucleus. It is essentially a proportionality constant that relates the observed magnetic moment μ of a particle to its angular momentum quantum number and a unit of magnetic moment. (also known as spin gyromagnetic ratio)

Generalized Eigenvalue Problem | The matrix equation Hc=λSc (rather than a standard eigenvalue problem) that arises when the overlap matrixS is not the identity.

gyromagnetic ratio | The ratio of its magnetic moment to its angular momentum, and it is often denoted by the symbol γ, gamma (also known as magnetogyric ratio)

H

Hamiltonian | The operator represents the total energy of the system.

Hamiltonian Matrix | In the LCAO formalism, the Hamiltonian operator is represented as a matrix in the basis of chosen atomic orbitals (or basis functions). The elements are (\langle \phi_i

Hermite polynomials | A family of orthogonal polynomials. In quantum mechanics, they results from solving the harmonic oscillator model.

Hermitian | A Hermitian matrix is a complex square matrix that is equal to its own conjugate transpose—that is, the element in the i-th row and j-th column is equal to the complex conjugate of the element in the j-th row and i-th column, for all indices i and j. aij=aji* . Hermitian matrices always have real eigenvalues. Operators connected to physical observable are Hermitian since observables must be real.

Hermitian operator | An operator satisfying A = A†.

Hilbert space | Given a system, the possible pure state can be represented as a vector in a Hilbert space. Each ray (vectors differ by phase and magnitude only) in the corresponding Hilbert space represent a state.

I

Identity operator | Operator that does not change the elements it operates on.

Indistinguishable particles | If a system shows measurable differences when one of its particles is replaced by another particle, these two particles are called distinguishable.

K

Ket | A wave function expressed in the form is called a ket.

L

Lambshift | Relativistic correction of the difference in energy levels of the 2S1/2 and 2P1/2 hydrogen atom not predicted by the Dirac equation

Laplacian | The Laplacian is a differential operator that is given by the divergence of the gradient.

LCAO | This is is a simple method of quantum chemistry that yields a qualitative picture of the molecular orbitals in a molecule.

Legendre polynomials | A family of complete and orthogonal polynomials with numerous applications. In quantum mechanics, they results from solving the rigid rotor model.

Linear Combination of Atomic Orbitals, LCAO | A method of constructing molecular orbitals as weighted sums (linear combinations) of atomic orbitals.

M

Maclaurin series | The Maclaurin series is an expansion of a function in an infinite sum of polynomial terms that are expressed in terms of the function's derivatives at zero.

magnetogyric ratio | The ratio of its magnetic moment to its angular momentum, and it is often denoted by the symbol γ, gamma (also known as magnetogyric ratio

Mixed state | A mixed state is a statistical ensemble of pure state.

molecular orbitals | A molecular orbital is a mathematical function describing the location and wave-like behavior of a single electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region. The LCAO approximation is often used to approximate molecular orbitals as a series of atomic orbitals

N

node | Location where the quantum mechanical wavefunction is zero and therefore, with no probability amplitude.

Normalization | The process of scaling a wavefunction such that its inner product with itself is unity.

Normalized wavefunction | A wave function |a > is said to be normalized if < a | a> = 1.

O

Observable | Mathematically, it is represented by a Hermitian operator.

observer effect | When an observed system is disturbed by the act of observation. This is often the result of instruments that, by necessity, alter the state of what they measure in some manner.

odd function | A function is odd if -f(x)=f(-x)

operator | A mathematical entity that transforms one function into another

orbital angular momentum | The classical definition of angular momentum is L = r ⃟ p. The quantum-mechanical counterparts of these objects share the same relationship where r is the quantum position operator, p is the quantum momentum operator, × is cross product, and L is the orbital angular momentum operator. L (just like p and r) is a vector operator whose components operators are Lx, Ly, Lz, which are the projection of L on the x, y, and z axis, respectively

Overlap Integral | The integral $\langle \phi_A | \phi_B \rangle$

Overlap Matrix | A matrixS whose elements are the overlaps

overtone | A band that occurs in a vibrational spectrum of molecule that is associated with the transition from the ground state (v=0) to the second excited state (v=2).

P

Pauli exclusion principle | The principle that two or more identical fermions (e.g., electrons) cannot occupy the same quantum state within the same quantum system simultaneously. An alternative formulation is that no two fermions can have the same set of quantum numbers in a system

Potential Energy Surface, PES | A multidimensional surface (or hypersurface) giving the electronic energy as a function of nuclear coordinates. Its minima correspond to stable molecular structures (equilibrium geometries).

Pure state | A state which can be represented as a wave function / ket in Hilbert space / solution of Schrödinger equation is called pure state. See "mixed state".

Q

Quantum numbers | A way of representing a state by several numbers

R

Radial distribution function | The square of the radial distribution function describes the probability of finding an a electron a given distance from the nucleus. This is related to the radial probability density by adding a factor of 4πr2 (the volumen element of a sphere). The radial distribution functions depend on both n and l.

radial node | A radial node will occur where the radial part of the electronic wavefunction equals zero.

radial probability density | The probability density for the electron to be at a point located the distance r from the nucleus. The radial radial probability density depend on both n and l.

reduced mass | The "effective" inertial mass appearing in the two-body problems. It is a quantity which allows two-body problems to be solved as if they were one-body problems.

rotational constant | A constant commonly used to describe molecular free rotation that depends on the distribution of mass within the molecule (i.e, moment of inertia, I) and other constants: B=h/(8π2cI)

S

selection rule | Selection rules describes when the probability of transitioning from one level to another cannot be zero. They explicitly come from evaluating the relevant transition moment integral

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spherical harmonics | Spherical harmonics are functions of the spherical polar angles θ and φ and appear as eigenfunctions of (squared) orbital angular momentum. They form an orthogonal and complete set. Any harmonic is a function that satisfies Laplace's differential equation.

spin | Spin is a quantized property of all particles, both matter and force, in the Universe. Matter particles have half-integer spin (1/2, 3/2,...) and force particles integer spin (0, 1, 2,...). Spin is intrinsic angular momentum possessed by the particles. The spin of a particle is sort of analogous to that of a spinning top, except that the particle can only spin at one speed, can't stop or even slow down, and is infinitesimally small. It is important to note that in no way are the particles actually spinning.

spin gyromagnetic ratio | A dimensionless quantity that characterizes the magnetic moment and angular momentum of an atom, a particle or the nucleus. It is essentially a proportionality constant that relates the observed magnetic moment μ of a particle to its angular momentum quantum number and a unit of magnetic moment. (also known as g-factor)

square-integrable | A square-integrable function is a real- or complex-valued measurable function for which the integral of the square of the absolute value is finite.

State vector | synonymous to "wave function".

Stationary state | A stationary state of a bound system is an eigenstate of Hamiltonian operator. Classically, it corresponds to standing wave.

stationary states | This is a quantum state with all observables independent of time. It is an eigenvector of the Hamiltonian.

T

Taylor series | The Taylor series is an expansion of a function in an infinite sum of polynomial terms that are expressed in terms of the function's derivatives at a single point.

Time-Independent Schrödinger Equation | A modification of the Time-Dependent Schrödinger equation as an eigenvalue problem. The solutions are energy eigenstate of the system.

transition moment integral | The integral representing the probability for a transition between an initial eigenstate and a final eignestate by the absorption or emission of photon(s)

Trial Function | In variational methods, a guessed approximate wavefunction (with adjustable coefficients) used to approximate the true wavefunction.

U

uncertainty principle | The uncertainty principle (put forward by Werner Heisenberg) states that there will always be an intrinsic uncertainty in determining both a particle's position and momentum (i.e., you cannot know both exactly at the same time). This has nothing to do with science's

ability to detect the properties of momentum and position.

V

Variational Principle | A technique in quantum mechanics stating that the expectation value of the energy for any trial wavefunction is an upper bound to the true ground state energy. You adjust parameters to minimize that expectation value.

W

wavenumber | The wavenumber is a unit of frequency that is equal to the frequency (in Hertz) divided by the speed of light. This is typically in unit of cm-1. Since wavenumbers are proportional to frequency, and to photon energy (by E=hν), it is also a unit of energy.

Z

zero point motion | Fluctuation in the position of an object necessitated by having zero point energy. This is a consequence of the Heisenberg uncertainty principle.

Zero-point energy | Zero-point energy (ZPE) is the lowest possible energy that a quantum mechanical system may have.

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