PHYSICAL CHEMISTRY FOR BIOLOGICAL SCIENCES



Carey Southern
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Physical Chemistry for Biological Sciences

Carey Southern

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CHAPTER OVERVIEW

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).**

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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).

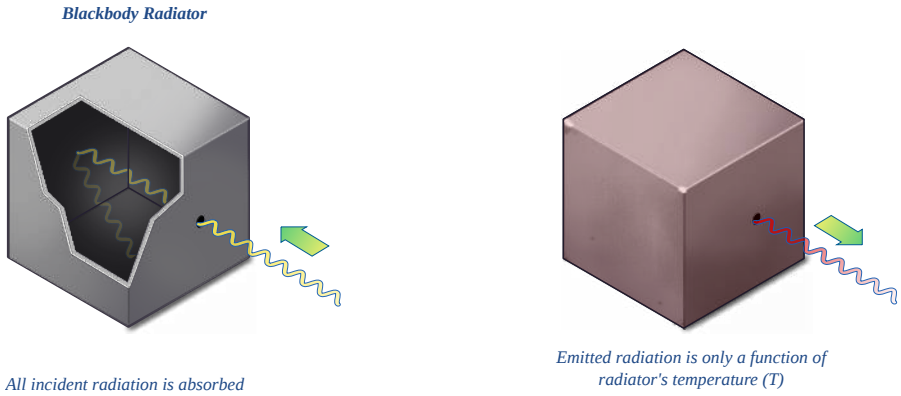


Figure 1.1.2 : Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya via LibreTexts)

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 .

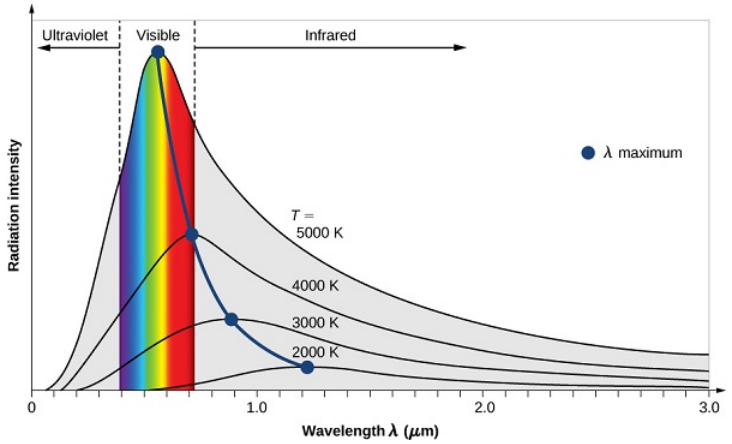
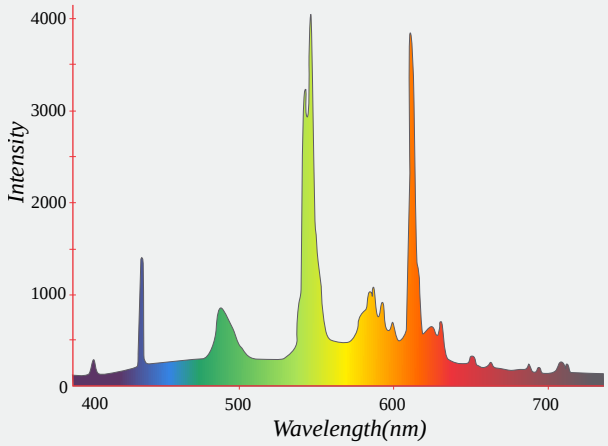


Figure 1.1.3 : Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength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

1.1.1: 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.

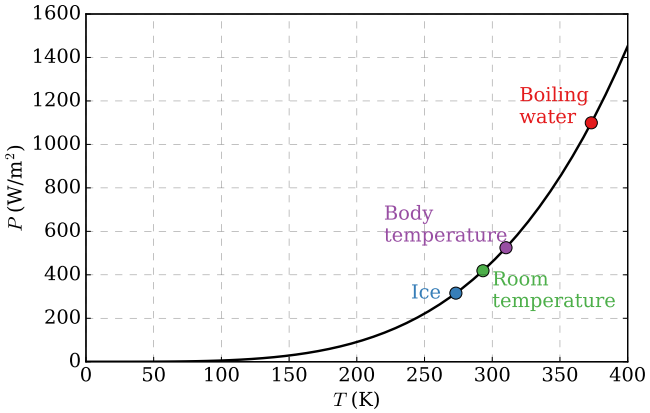


Figure 1.1.4 : Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature T according to the Stefan–Boltzmann law. (CC BY-SA 4.0; Nicoguaro)

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 $A = 4\pi R^2$.

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

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

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

This value is per square meter.

(b) To calculate the total power radiated by the sun is thus:

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

1.1.2: 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 $P = \sigma T^4$.

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

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

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

The total radiant energy density in Watts is :

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

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

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

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

500 nm

Answer b

10.0 microns

1.1.3: 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.

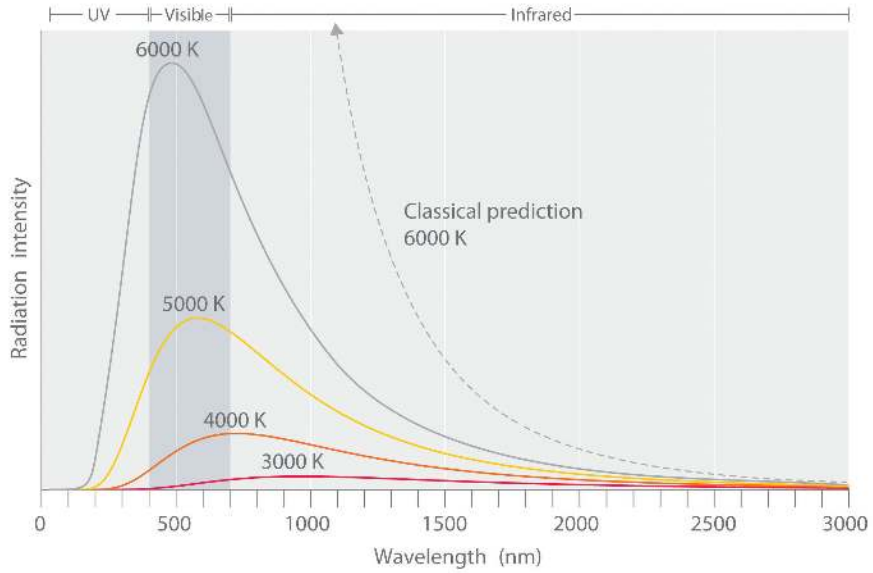


Figure 1.1.5 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 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; 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

- Michael Fowler (Beams Professor, Department of Physics, University of Virginia)
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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.

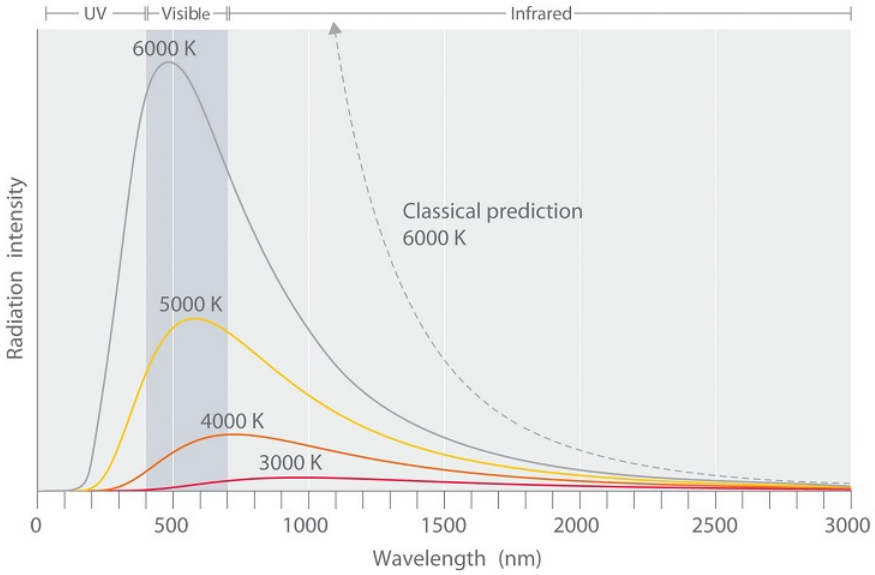


Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, 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).

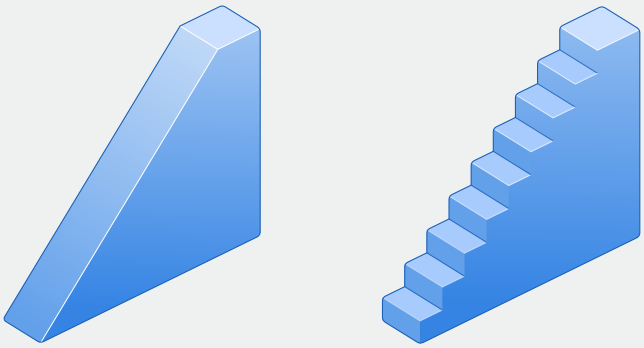
1.2.1: Quantizing Electrons in the Radiator

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:

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

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

with

- $\pi = 3.14159$
- $h = 6.626 \times 10^{-34} J \cdot s$
- $c = 3.00 \times 10^8 m/s$
- $\nu = 1/s$
- $k_B = 1.38 \times 10^{-23} J/K$
- T is absolute temperature (in Kelvin)

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

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

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

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

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

or

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

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

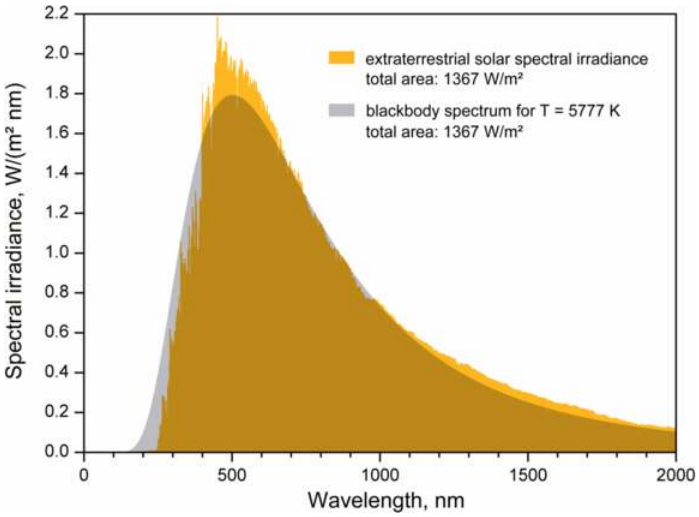
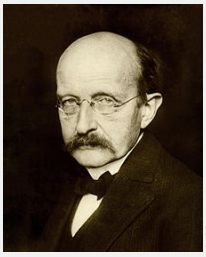


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

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.*

1.2.2: 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

- Michael Fowler (Beams Professor, Department of Physics, University of Virginia)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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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).

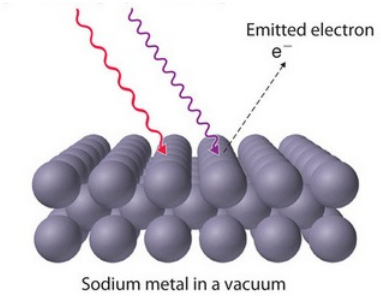


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

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.

1.3.1: 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.

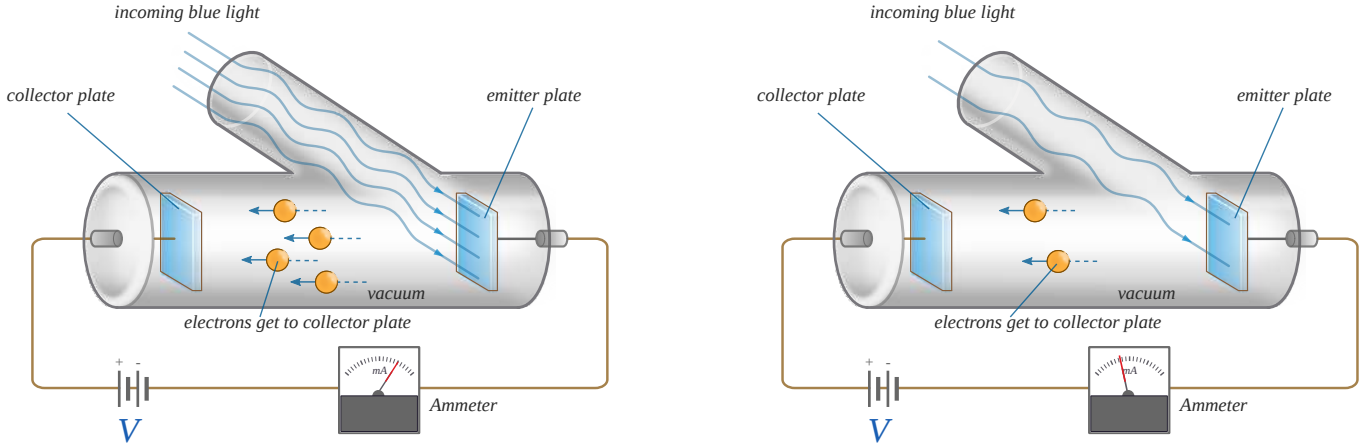


Figure **1.3.2**: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; 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).

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).

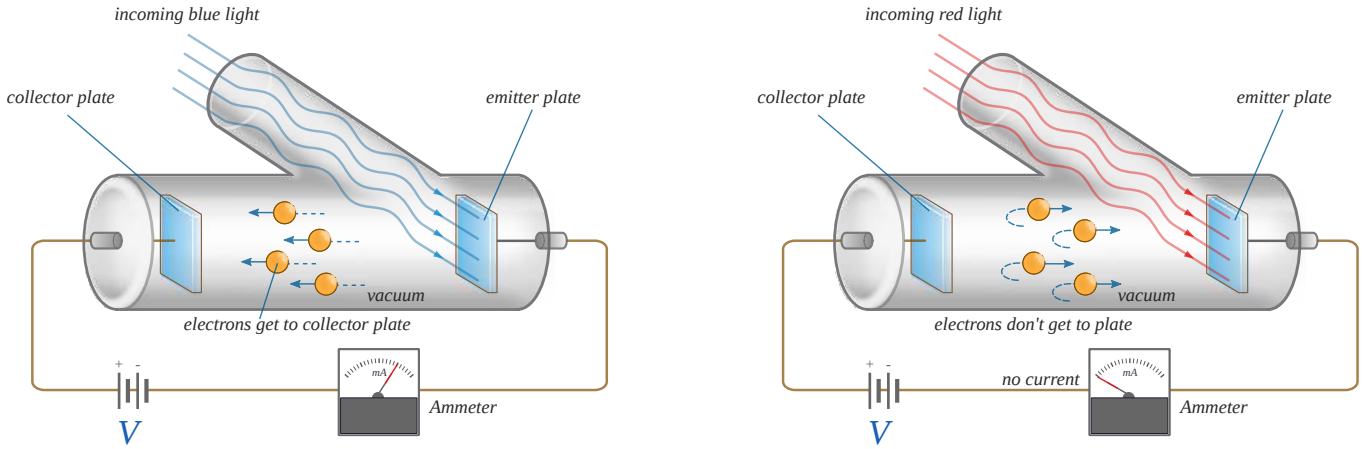


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector 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).

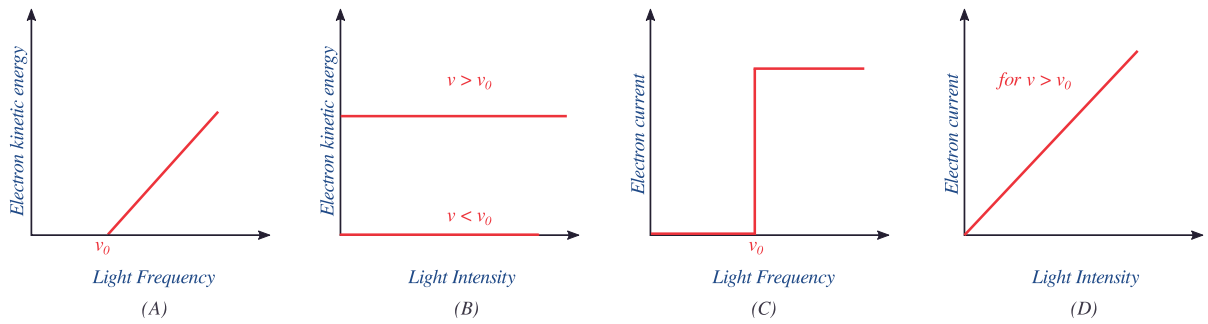


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the 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.

1.3.3: 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.

1.3.4: 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**).

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

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.

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

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

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.

? Exercise 1.3.2

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

Answer

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.

1.3.5: 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 $KE_e = h\nu - \Phi$, where $h\nu$ is the photon energy and Φ is the workfunction (or binding energy) of the electron to the particular material.

1.3.6: 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.

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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.

1.4.1: 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).

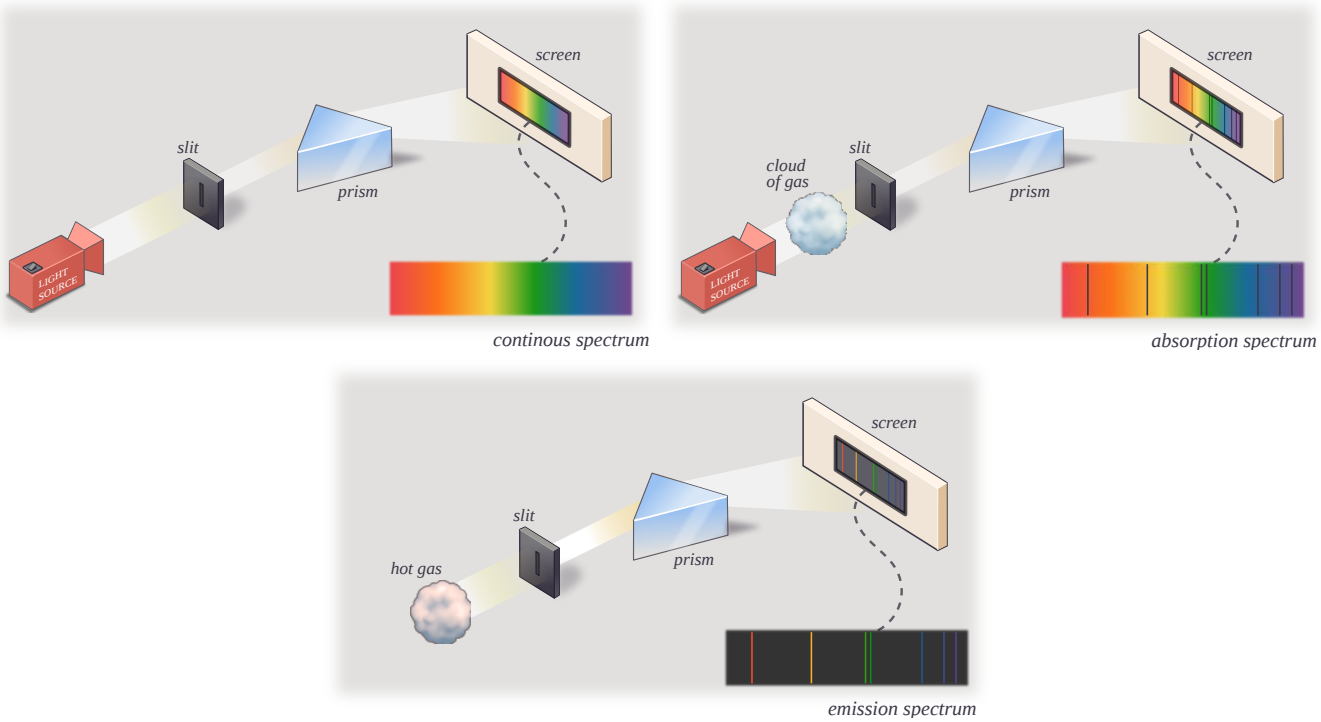


Figure 1.4.1 : Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen without 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.

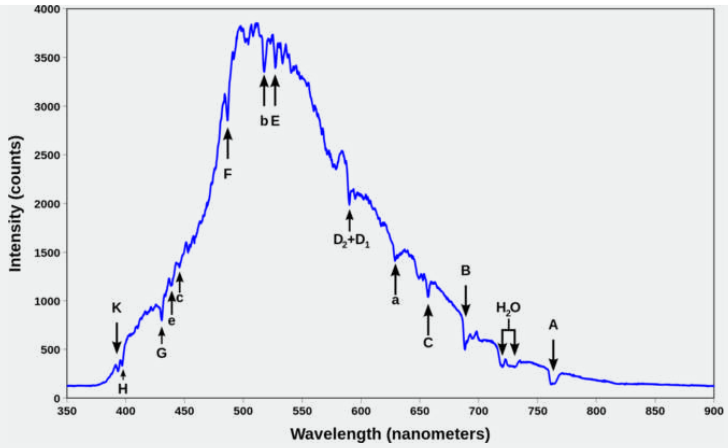


Figure 1.4.2 : Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

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 .

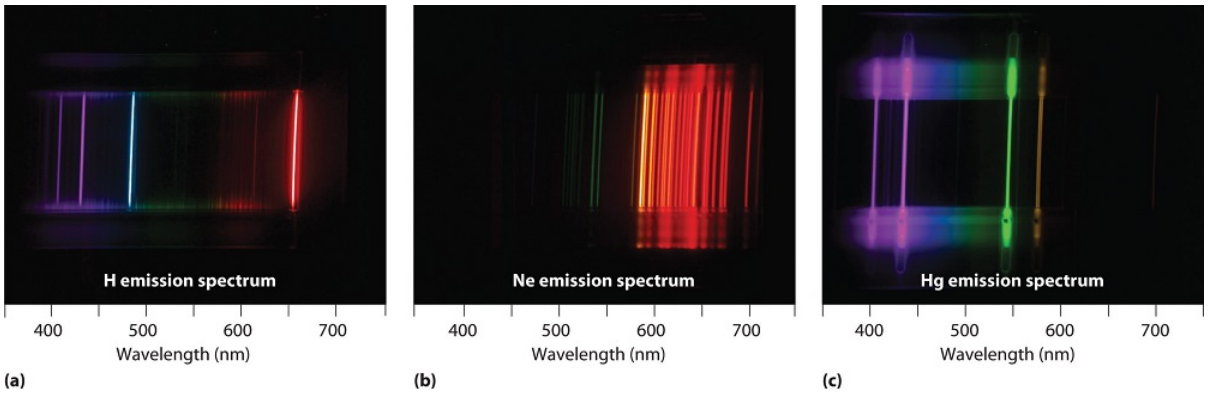


Figure 1.4.3 : The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The 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).

1.4.2: 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.

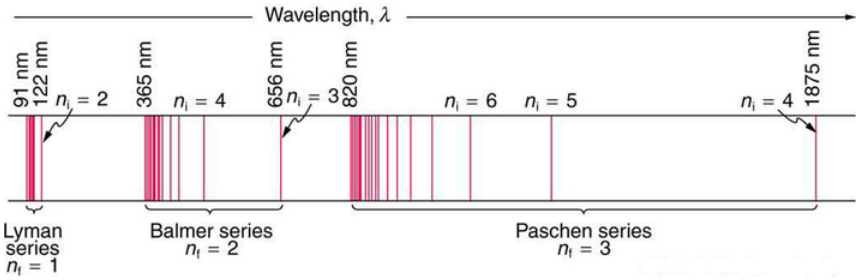


Figure 1.4.4 : A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and 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

$$\begin{aligned}\tilde{\nu} &= \frac{1}{\lambda} \\ &= \frac{\nu}{c}\end{aligned}$$

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 1.4.3*a*).

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.

1.5.1: 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., $n_1 = 1$)?

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

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 $n_2 = 4, 5, 6, 7, ...$ 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 $n_1 = 1$

- 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

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

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.

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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

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.

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

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

The de Broglie wavelength of this fast ball is:

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

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

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.

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.

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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.

1.7.1: 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.

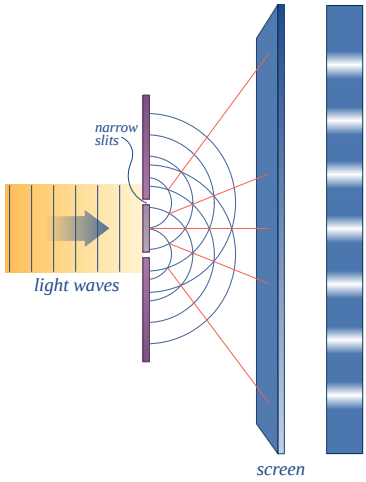


Figure 1.7.1 : Young double slit experiment. Two slits are illuminated by a plane light waves. (CC BY-NC; Ümit Kaya via LibreTexts)

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).

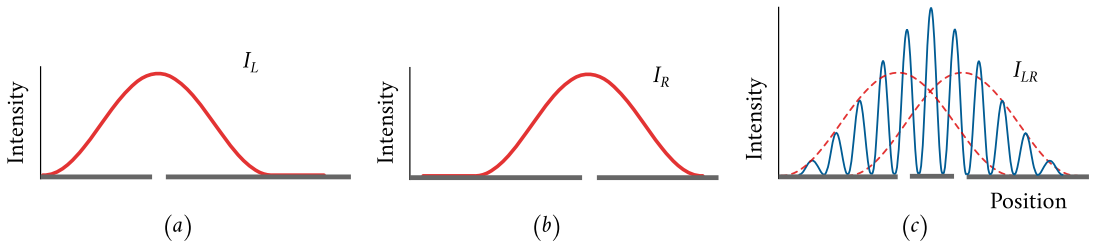


Figure 1.7.2 : Amplitude of particles through (a) left slit, (b) right slit, (c) through both slits. In absence of wavelength interference behavior, the intensity will be the sum of each single slit results (red) and when there is interference, pronounced oscillations in intensity is observed (blue curve).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

1.7.2: 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).

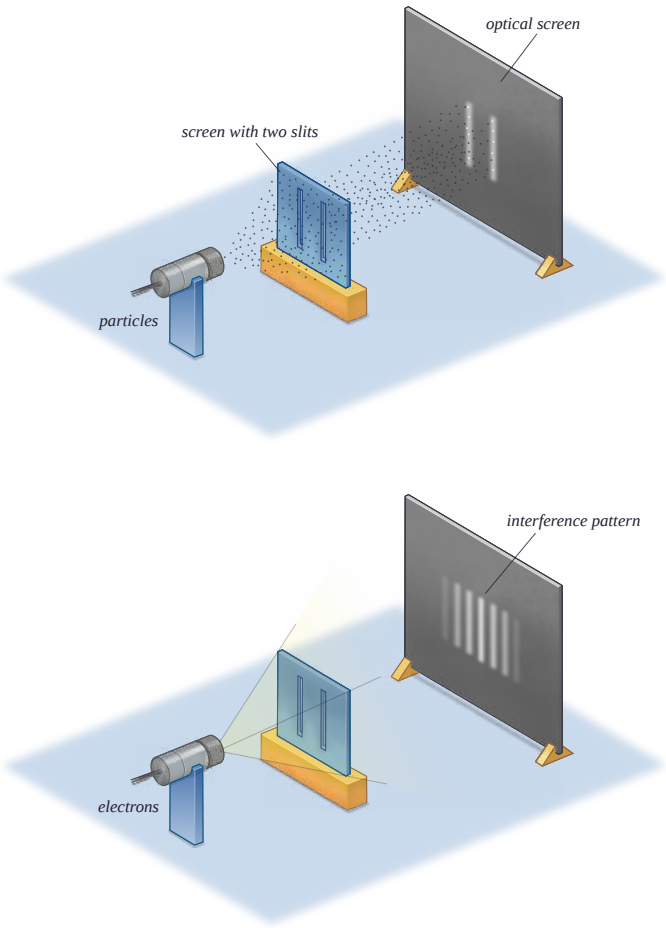


Figure 1.7.3 : (left) classical model of electrons. (right) wave property of electrons. (CC BY-NC; Ümit Kaya via LibreTexts)

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.

1.7.3: 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

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

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

1.8.1: 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.

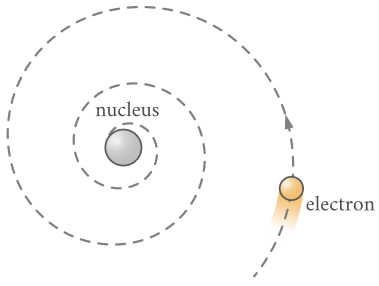


Figure 1.8.1 : The classical death spiral of an electron around a nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

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;). 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.

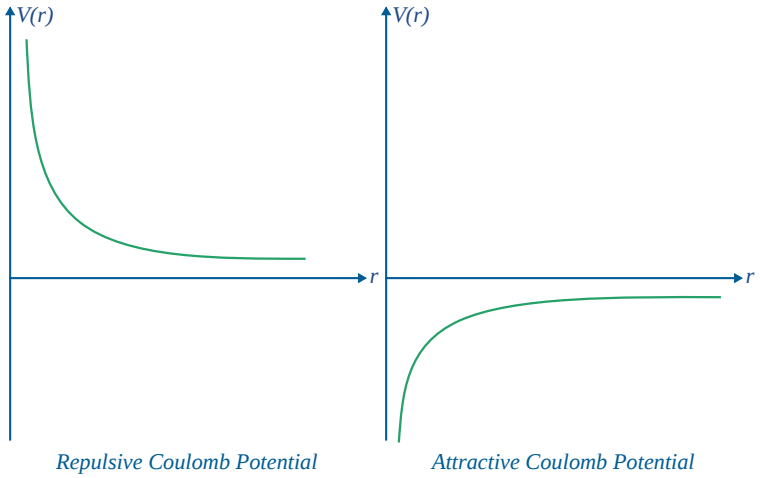


Figure 1.8.2 : Potential energy curve for the Coulomb interactions between two charges of same sign (left) and opposite signs (right). (CC BY-NC; Ümit Kaya via LibreTexts)

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

1.8.2: 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**, $\mathbf{He^{+}}$, $\mathbf{Li^{2+}}$, $\mathbf{Be^{3+}}$, 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.

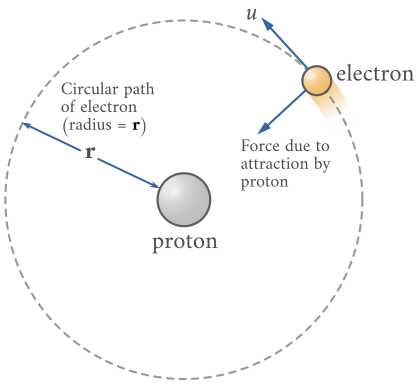


Figure 1.8.3 : Bohr atom with an electron revolving around a fixed nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

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

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

since $\vec{F} = m_e\vec{a}$, the magnitude, it follows that $\left|\vec{F}\right| = m_e|\vec{a}|$. 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

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = (m_e v r)^2 \tag{1.8.6}$$

The reason for writing the equation this way is that the quantity $m_e vr$ 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 $m_e vr$ of the electron could only take on specific values

$$m_e vr = n\hbar \tag{1.8.7}$$

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

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

Equation 1.8.8 implies that orbits could only have certain allowed radii

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

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

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

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

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

We can also calculate the allowed momenta since $m_e vr = n\hbar$, and $p = m_e v$. Thus,

$$p_n r_n = n\hbar$$

$$p_n = \frac{n\hbar}{r_n}$$

$$= \frac{\hbar Z}{a_0 n}$$

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

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

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r_n}$$

Substituting in the expressions for p_n and r_n and simplifying gives

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

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

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

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).

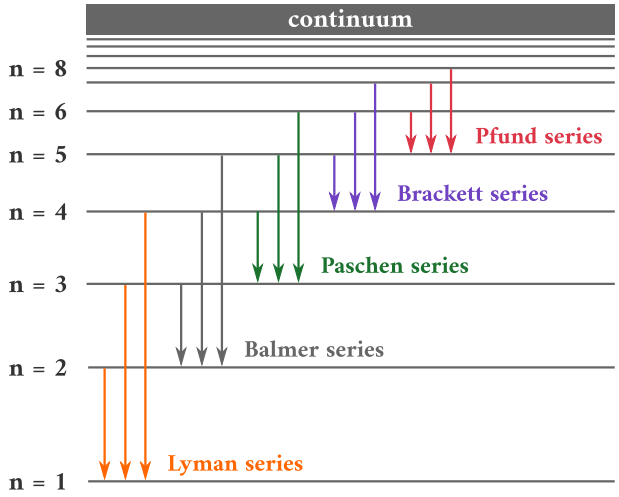


Figure 1.8.4 : Energy levels predicted by the Bohr model of hydrogen ($Z = 1$). (CC BY-NC; Ümit Kaya via LibreTexts)

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

Starting from Equation 1.8.8 and solving for r:

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

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

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: $\epsilon_o = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$
- $\hbar$ is the reduced planks constant: $\hbar = 1.0546 \times 10^{-34} m^2 kg/s$

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

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

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

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

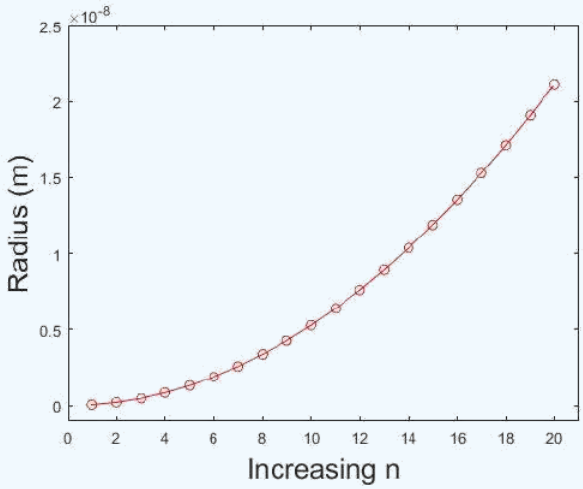
As expected, the $\mathbf{Li^{2+}}$ has a smaller radius than the $\mathbf{H}$ atoms because of the increased nuclear charge.

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

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)

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

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

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 $a_0 = 5.292 \times 10^{-11}\text{m}$ 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 $\text{n} = 200$ state. The diameter is then $4.234 \times 10^{-6}\text{m}$.

1.8.3: 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 1.8.1*A*). If not, then the waves will overlap imperfectly and cancel out (i.e., the electron will cease to exist) as demonstrated in Figure 1.8.1*B*.

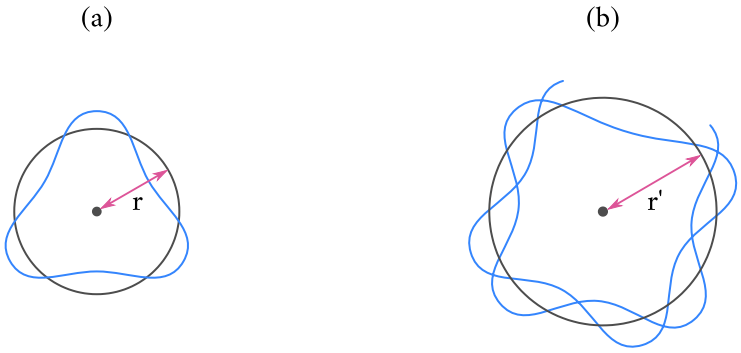


Figure 1.8.5 : Waves on a string have a wavelength related to the length of the string, allowing them to interfere constructively. (A) If we imagine the string bent into a closed circle, we get a rough idea of how electrons in circular orbits can interfere constructively. (B) If the wavelength does not 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.

1.8.4: 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).

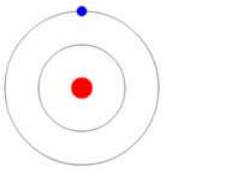


Figure 1.8.6 : A simple illustration of Bohr's model of the atom, with an electron making quantum leaps. (CC BY-SA 3.0 unported; Kurzon via Wikipedia)

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.

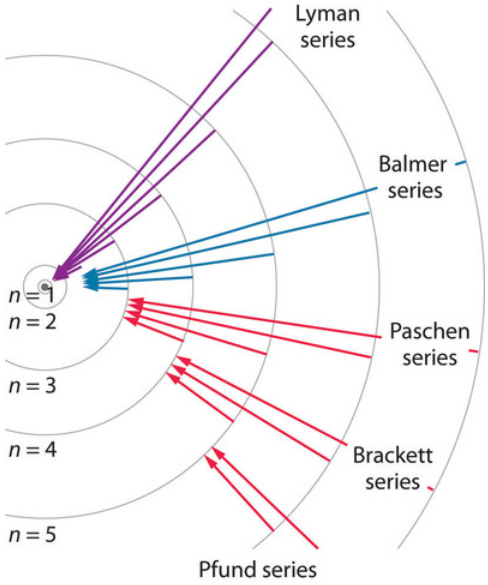


Figure 1.8.7 : Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding 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

a:

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

b:

As $n_i \to \infty$

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

$$\frac{1}{n_i^2} \to 0$$

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

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

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- Template:Contriboundless

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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.

1.9.1: 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).

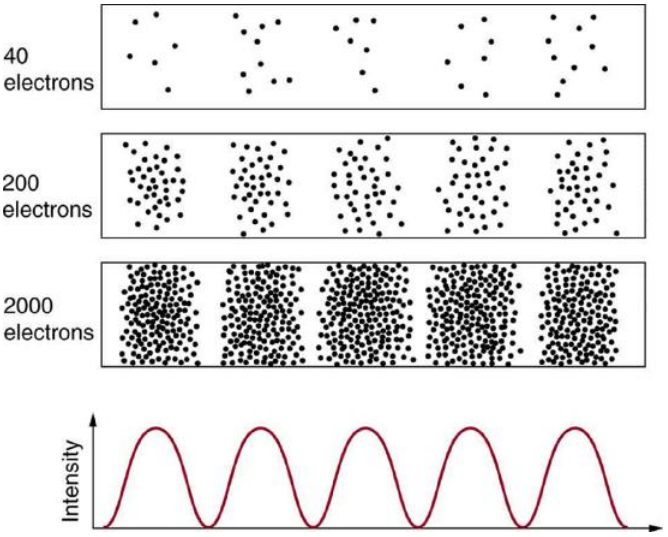


Figure 1.9.1 : The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength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

1.9.2: 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).

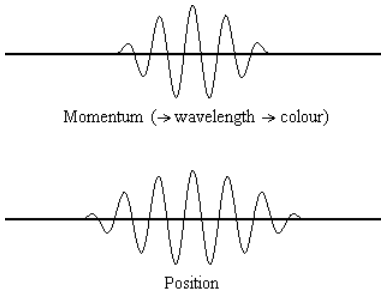


Figure 1.9.2 : The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength 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: $\Delta x = 150 \times 10^{-12} m$

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

$$= 3.9 \times 10^5\ m/s$$

Exercise 1.9.1

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

Answer

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

1.9.3: 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.



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

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.

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!"

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

(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 $\mathbf{1.30\ kW/m^2}$ (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 $\boldsymbol{KE_e = h\nu - \Phi}$ 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?

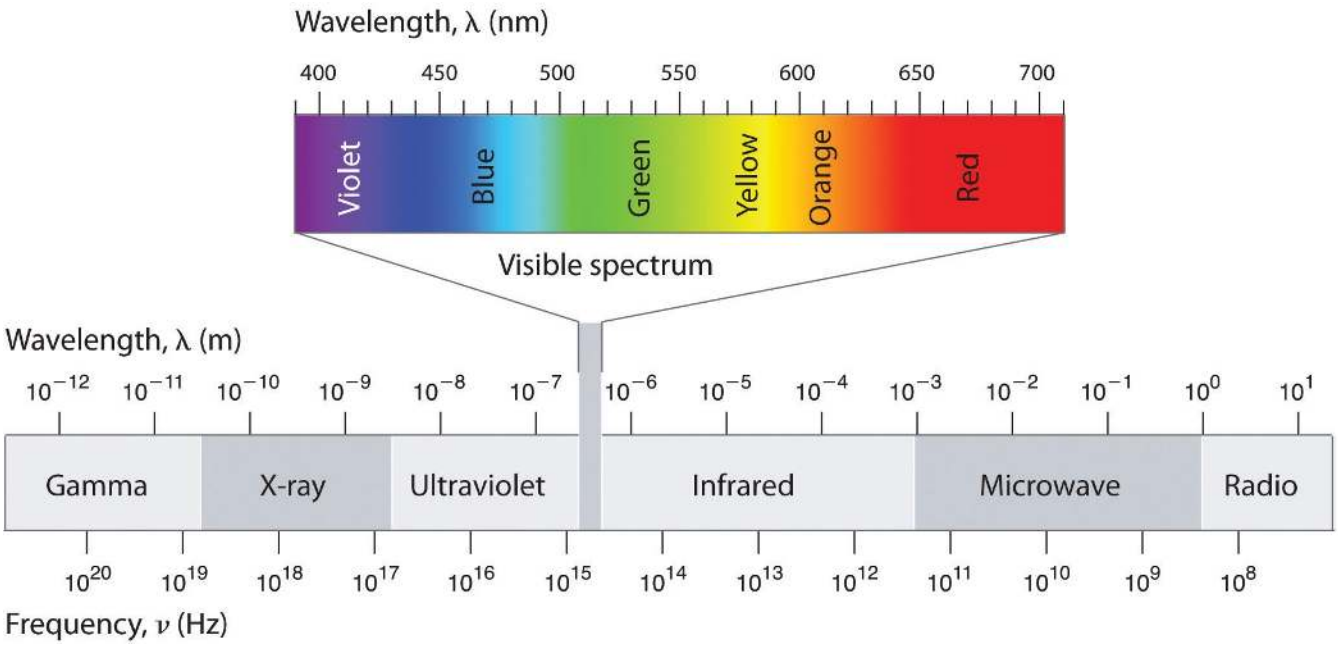
1.2B

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 2.0×10^4 **MHz**, calculate v, λ, and energy per photon for this radiation and then compare the results with figure below.



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

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

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:

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

Given: T = 7500K

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

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

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

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

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

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

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.

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

$$50eV\left(\frac{1.602 \times 10^{-19} J}{1eV}\right) = \frac{(v^2)(9.109 \times 10^{-31} kg)}{2}$$

$$v = 4.19 \times 10^6\, m \cdot s^{-1}$$

So

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

b. Replace m_e with m_p in (a) to find $\lambda = 2.86 \times 10^{-3} nm$.

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

$$v = \frac{(1.602 \times 10^{-19} C)^2}{2(2)(6.626 \times 10^{-34} J \cdot s)(8.854 \times 10^{-12} C^2 J^{-1} m^{-1})}$$
$$= 1.09 \times 10^6 m \cdot s^{-1}$$

So

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

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 $9.1 \times 10^{-31}\text{kg}$.

Solution

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

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

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

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

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

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

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

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

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

$$T = 293.5K$$
$$= 20.35°C$$

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 $\mathbf{He^{+}}$ or $\mathbf{Li^{2+}}$.

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.

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

Simplifying this expression we find that

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

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

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

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 $\frac{Ze^2}{4r^2\pi\epsilon_o} = \frac{m_e\nu^2}{r}$ We find that

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

Now solving for the total energy of the system

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

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

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

Substituting r from above we quantize the energy such that

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

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

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

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

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

1.32

The series in the $\mathbf{He^+}$ 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 $n_2 = 4$

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

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

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

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 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 nth 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 $\Delta t \leq h/(mc^2)$. 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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CHAPTER OVERVIEW

2: Waves and the Schrödinger 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 Schrödinger Equation

2.3: Linear Operators in Quantum Mechanics

2.4: The Schrödinger Equation is an Eigenvalue Problem

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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).

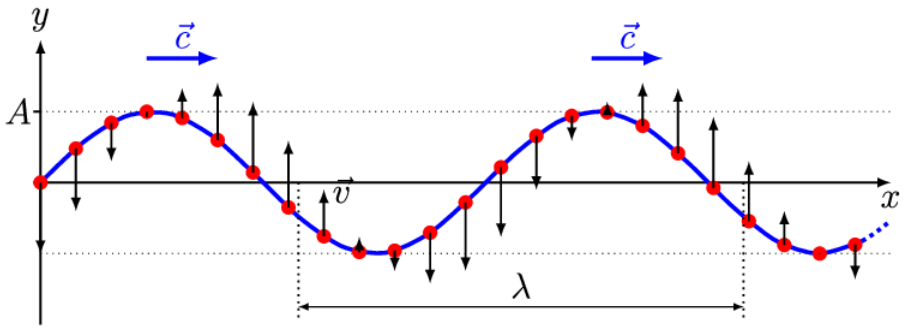


Figure 2.1.1 : A simple translational (transverse) wave. (CC BY-SA 4.0 International; And1mu via Wikimedia Commons)

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*.

2.1.1: 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:

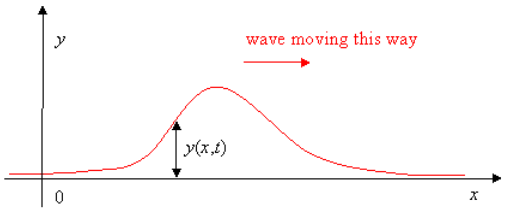


Figure 2.1.2 : A one-dimensional traveling wave at one instance of time t.

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.

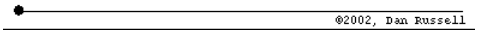


Figure 2.1.3 : A one-dimensional traveling wave at as a function of time. Traveling waves propagate energy from one spot to another with a fixed velocity v. (CC BY-NC-ND; Daniel A. Russell).

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.

2.1.2: 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 *nodes*. The places of maximum oscillation are *antinodes*.

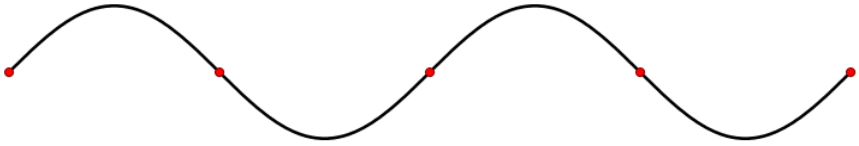


Figure 2.1.4 : Animation of standing wave in the stationary medium with marked wave nodes (red circles). (public domain; LucasVB).

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.

2.1.3: 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).

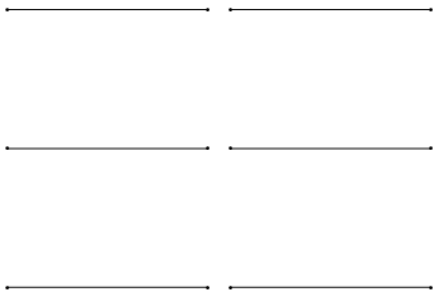


Figure 2.1.5 : Standing waves in a string (both spatially and temporally). The first six solutions ($u(x,t)$. from Wikipedia.

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 $E = h\nu$.

2.1.4: 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 Schrödinger Equation

3.01: The Schrödinger Equation

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2.3: Linear Operators in Quantum Mechanics

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2.4: The Schrödinger Equation is an Eigenvalue Problem

3.03: The Schrödinger Equation is an Eigenvalue Problem

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CHAPTER OVERVIEW

3: Postulates and Principles of Quantum Mechanics

3.1: The Wavefunction Specifies the State of a System

3.2: Wavefunctions Have a Probabilistic Interpretation

3.3: Wavefunctions Must Be Normalized

3.4: Quantum Operators Represent Classical Variables

3.5: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

3.6: The Time-Dependent Schrödinger Equation

3.E: Postulates and Principles of Quantum Mechanics (Exercises)

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3.1: 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 $r=(x_1,y_1,z_1,x_2,y_2,z_2,\ldots x_n,y_n,z_n)$. 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).

$$P(x)=\psi^*(x)\psi(x) \tag{3.1.1}$$

$$=|\psi(x)|^2 \tag{3.1.2}$$

Hence, for valid (e.g., well-behaved) wavefunctions, the normalized probability in Equation 3.1.2 holds true, such that the integral over all space is equal to 1.

$$\int_{-\infty}^{\infty}\psi^*(x)\psi(x)\,dx=1 \tag{3.1.3}$$

Equation 3.1.3 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 3.1.3 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.

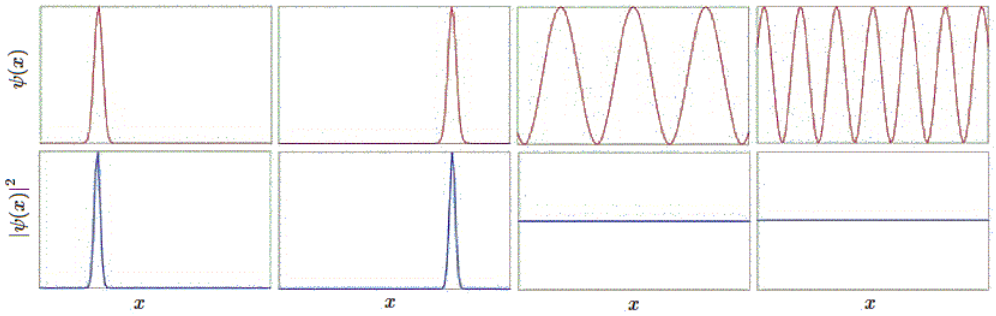


Figure 4.1.1 : Examples of good wavefunctions, $\psi(x)$, (red, top) and corresponding probability densities, $P(x)$, (blue, bottom).

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,

$$\begin{aligned} P(x) &= \psi^*(x)\psi(x) \\ &= \left|e^{ikx}\right|^2 \\ &= N^2\left(e^{-ikx}\right)\left(e^{ikx}\right) \\ &= N^2 \end{aligned}$$

for all k, so the corresponding probability densities, $P(x)$, are the same except for the normalization constant (Equation 3.1.2). 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.

3.1.1: Ill-behaved (invalid) Wavefunctions

The Born interpretation in Equation 3.1.2 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 3.1.3 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.

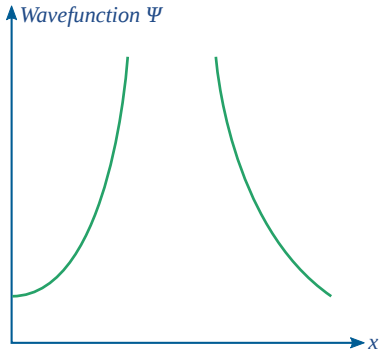


Figure 4.1.2 : This function is an invalid wavefunction since the amplitude is going to infinity over a region (the middle in this case). (CC BY-NC; Ümit Kaya via LibreTexts)

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.

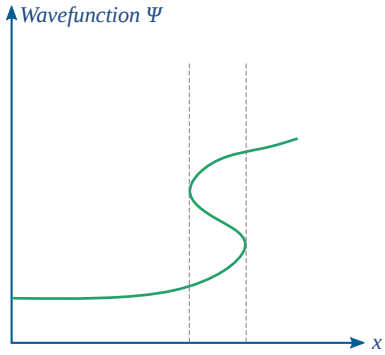


Figure 4.1.3 : This function is an invalid wavefunction since it is not a proper function (i. e., not one-to-one). (CC BY-NC; Ümit Kaya via LibreTexts)

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.

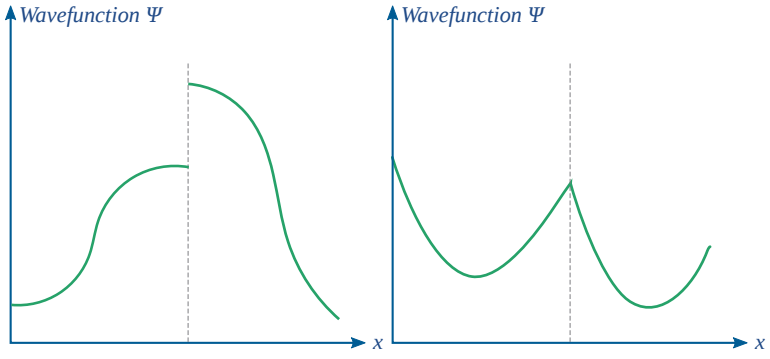


Figure 4.1.4 : These functions are invalid wavefunctions. (left) The first derivative of a function gives its gradient at a given point, and it thus exists as long as the function is continuous - only if there is a break in the function is there a point at which its first derivative does not exist. (right) 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

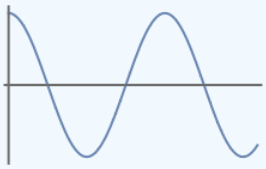
Determine if each of the following functions is acceptable as a wavefunction over the indicated regions:

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

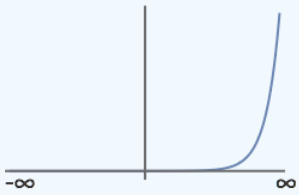
This is not an acceptable wavefunction. It is **single-valued** across the entire range. There is a single value for each value of x. It is **continuous** over the defined limits of integration, as we can see from a plot given below. However, it is not square-integrable.

$$\int_0^{\infty} |\cos(x)|^2 dx \not< \infty$$



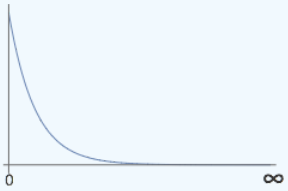
Solution b

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 ∞.



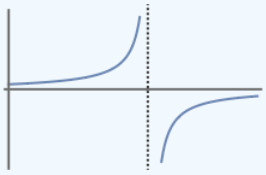
Solution c

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 $\int_0^{\infty} |\Psi(x)|^2 dx = \frac{1}{2}$.



Solution d

This is not an acceptable wavefunction. It is discontinuous over the limits of integration.



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3.4: 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:

$$\vec{r} = (x,y,z) \tag{3.4.1}$$

$$= x\vec{i} + y\vec{j} + z\vec{k} \tag{3.4.2}$$

The operator for a component of linear momentum is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.4.3}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = \left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \tag{3.4.4}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \tag{3.4.5}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2 \tag{3.4.6}$$

The total energy operator is called the Hamiltonian operator, $\hat{H}$ and consists of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{3.4.7}$$

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	$\hat{P}_x$	$-i\hbar\frac{d}{dx}$
Momentum (in 3D)	$\vec{p}$	$\hat{P}$	$-i\hbar\left[\hat{i}\,\frac{d}{dx} + \hat{j}\frac{d}{dy} + \hat{k}\frac{d}{dz}\right]$
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 $\frac{-\hbar^2}{2m}\nabla^2$
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	$\hat{L_x}$	$-i\hbar\left[y\frac{d}{dz} - z\frac{d}{dy}\right]$
Angular Momentum (y axis component)	L_y	$\hat{L_y}$	$-i\hbar\left[z\frac{d}{dx} - x\frac{d}{dz}\right]$
Angular Momentum (z axis component)	L_z	$\hat{L_z}$	$-i\hbar\left[x\frac{d}{dy} - y\frac{d}{dx}\right]$

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3.5: 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.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{3.5.1}$$

Using this notation, we write the Schrödinger Equation as

$$\hat{H}\,|\psi(x,y,z)\rangle = E|\,\psi(x,y,z)\rangle \tag{3.5.2}$$

Equation 3.5.2 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 3.5.2 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.

$$\hat{A}\,|\Psi\rangle = a|\,\Psi\rangle \tag{3.5.3}$$

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

$$A\,|\psi_a(x)\rangle = a|\,\psi_a(x)\rangle \tag{3.5.4}$$

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 3.5.4 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 3.5.4.

3.5.1: 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

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx \tag{3.5.5}$$

Here, $\langle x\rangle$ is called the *expectation value* of x. Similarly the expectation value of any function of x is

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi|^2 dx. \tag{3.5.6}$$

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 $\langle a\rangle$:

$$\langle a\rangle = \langle \psi\,|a|\,\psi\rangle \tag{3.5.7}$$

$$= \int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx \tag{3.5.8}$$

If an unnormalized wavefunction where used, then Equation 3.5.8 changes to

$$\langle a\rangle = \frac{\langle \psi\,|a|\,\psi\rangle}{\langle\psi|\psi\rangle} \tag{3.5.9}$$

$$= \frac{\int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx}{\int_{-\infty}^{\infty} \psi^*\psi dx} \tag{3.5.10}$$

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

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x\rangle)^2 |\psi|^2 dx \tag{3.5.11}$$

$$\equiv \langle x^2\rangle - \langle x\rangle^2, \tag{3.5.12}$$

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).

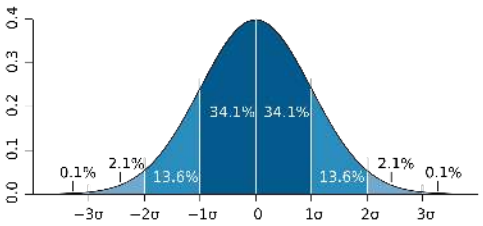


Figure 4.3.1 : A plot of a normal distribution (or bell-shaped curve) where each band has a width of 1 standard deviation. image usd with permission from Wikipedia.

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 3.5.8 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:

$$\langle T \rangle = \int \psi^* \hat{K} \psi \, d\tau = \frac{2}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\right) \sin\left(\frac{\pi x}{L}\right) dx$$
$$= \frac{\hbar^2 \pi^2}{2mL^2} \frac{2}{L} \int_0^L \sin^2\left(\frac{\pi x}{L}\right) dx$$
$$= \frac{\hbar^2 \pi^2}{2mL^2}$$

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, $V = 0$).

3.5.2: 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

$$\int_{-\infty}^{\infty} \phi_i^* \phi_j dx = \delta_{ij}. \tag{3.5.13}$$

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 3.5.10 and 3.5.13 that

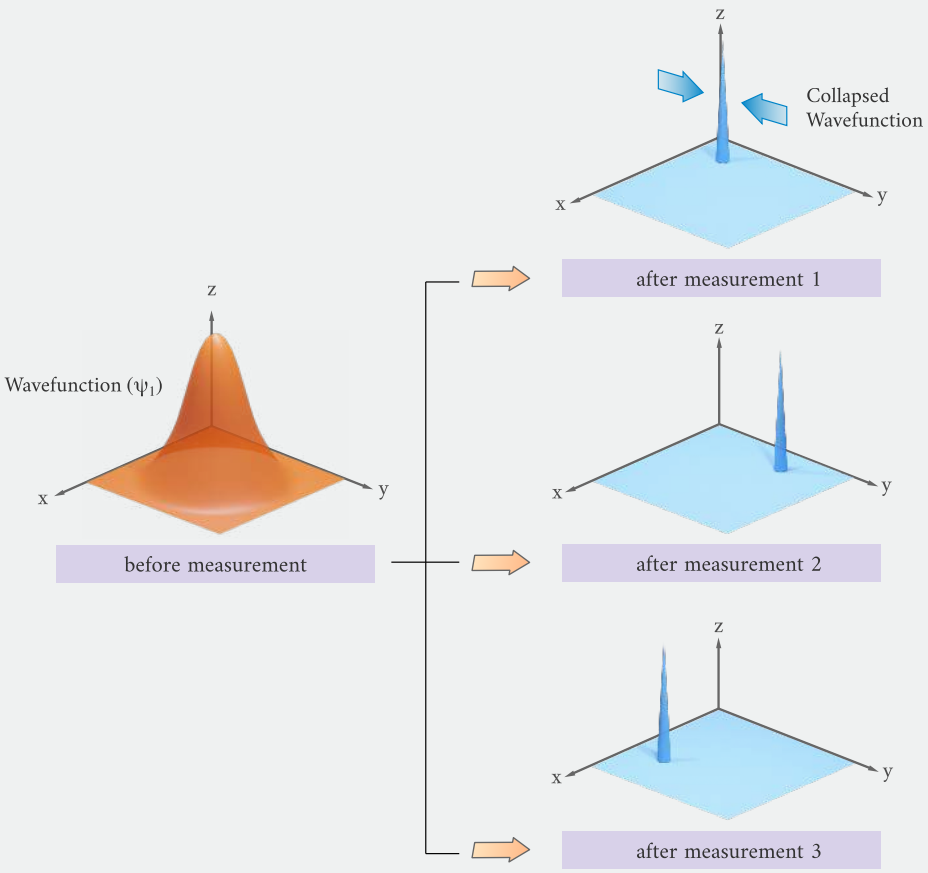
$$c_i = \int_{-\infty}^{\infty} \phi_i^* \psi dx. \tag{3.5.14}$$

Thus, the expansion coefficients in Equation 3.5.14 are easily determined, given the wavefunction ψ and the eigenstates ϕ_i. Moreover, if ψ is a properly normalized wavefunction then Equations 3.5.10 and 3.5.13 yield

$$\sum_i |c_i|^2 = 1.$$

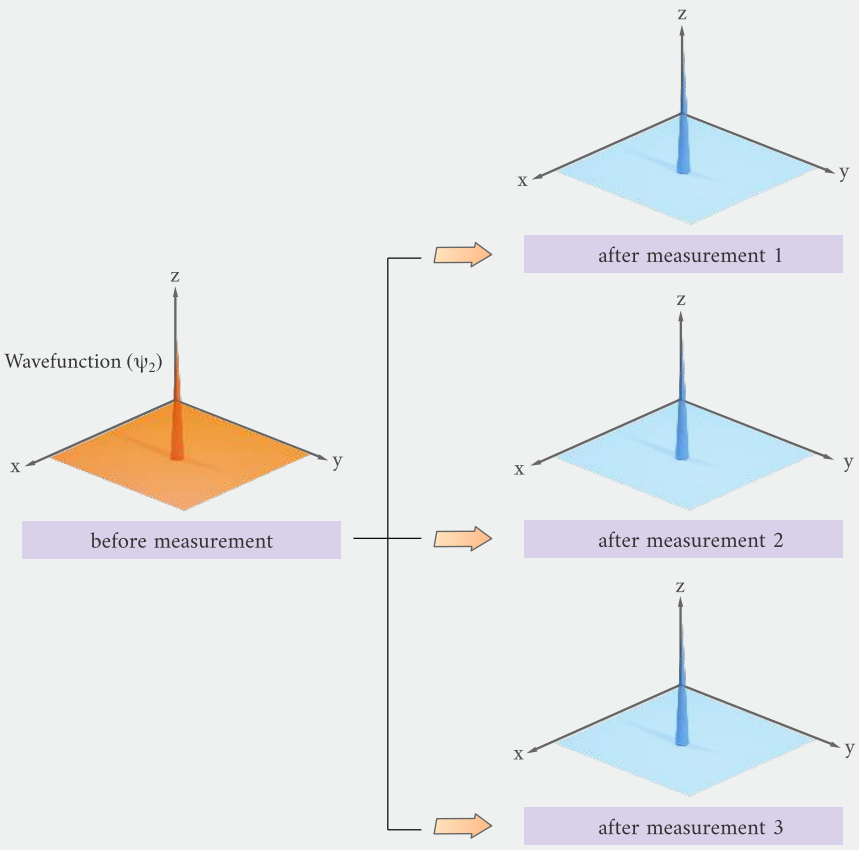
Collapsing the Wavefunction

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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3.6: The Time-Dependent Schrödinger Equation

4.04: The Time-Dependent Schrödinger Equation

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3.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. $\psi = N\cos\frac{n\pi x}{L}$

b. $\psi = \frac{N}{\sin\frac{n\pi x}{a}}$

c. $\psi = N\tan\frac{a_{\pi x}}{a}$

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 $x = \frac{a}{2}$

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 $n = m$

$$\int_0^L \psi^*\psi dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$
$$= \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx$$
$$\frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = 1$$

Letting $n \neq m$

$$\int_0^L \psi^*\psi dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right)dx$$
$$= \frac{2}{L}\frac{1}{2}\int_0^L \left[\cos\left(\frac{(n-m)\pi x}{L}\right) - \cos\left(\frac{(n+m)\pi x}{L}\right)\right]dx$$
$$= \frac{1}{L}\left[\frac{L}{(n-m)\pi}\left[\sin\left(\frac{(n-m)\pi L}{L}\right) - \sin\left(\frac{(n-m)\pi 0}{L}\right)\right] - \frac{L}{(n+m)\pi}\left[\sin\left(\frac{(n+m)\pi L}{L}\right) - \sin\left(\frac{(n+m)\pi 0}{L}\right)\right]\right] = 0$$

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.

$$[\mathbf{L}_z, \mathbf{L}_x] = (xp_y - yp_x)(yp_z - zp_y)\Psi - (yp_z - zp_y)(xp_y - yp_x)\Psi$$

$$= (yp_zxp_y - y^2p_zp_x - zxp_yp_y - zyp_zp_y)\Psi - (xp_yyp_z - xzp_yp_y + y^2p_xp_z + yzp_yp_x)\Psi$$

$$[\mathbf{L}_z, \mathbf{L}_x] = i\hbar\mathbf{L}_y,$$

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

$$[\hat{K}_x, \hat{L}_x] = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, -i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\right]$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left(-i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\right) - -i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\frac{i\hbar^3}{2m}\left(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\right) - \frac{i\hbar^3}{2m}\left(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\right) = 0$$

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

\[\hat{H}\Psi(x,t) =iħ ∂Ψ(x,y)/∂t\nonumber \]

Plug Ψ(x,t) into the time-dependent equation.

\[\hat{H}c$_n$Ψ$_n$(x)e$^{-iE_nt/ ħ}$ + c$_m$Ψ$_m$(x)e$^{-iE_mt/ ħ}$ = iħ ∂/∂tc$_n$Ψ$_n$(x)e$^{-iE_nt/ ħ}$ + c$_m$Ψ$_m$(x)e$^{-iE_mt/ ħ}$ \nonumber \]

\[\hat{H}c$_n$Ψ$_n$(x)e$^{-iE_nt/ ħ}$ + c$_m$Ψ$_m$(x)e$^{-iE_mt/ ħ}$ = E$_n$c$_n$Ψ$_n$(x)e$^{-iE_nt/ ħ}$ + E$_m$c$_m$Ψ$_m$(x)e$^{-iE_mt/ ħ}$\nonumber \]

\[∂/∂tc$_n$Ψ$_n$(x)e$^{-iE_nt/ ħ}$ + c$_m$Ψ$_m$(x)e$^{-iE_mt/ ħ}$ = -[(iE$_m$c$_m$e$^{-iE_mt/ ħ}$Ψ$_m$(x))/ħ]-[(iE$_n$c$_n$e$^{-iE_nt/ ħ}$Ψ$_n$(x))/ħ]\nonumber \]

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

$$\int vdu = uv + \int udv$$

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

$$\psi_1(x) = A\sin(k_1x) + B\cos(k_1x) \tag{3.E.1}$$

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

$$R = \frac{B^2}{A^2} \tag{3.E.2}$$

Derive the simplest expression of R based on the terms from the boundary conditions provided above.

Solution

Since

$$A + B = C, k_1(A - B) = k_2C \tag{3.E.3}$$

,

$$k_1(A - B) = k_2(A + B) \tag{3.E.4}$$

$$k_1A - k_1B = k_2A + k_2B \tag{3.E.5}$$

$$(k_1 - k_2)A = (k_1 + k_2)B \tag{3.E.6}$$

Thus,

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2} \tag{3.E.7}$$

$$R = \frac{B^2}{A^2} = \left(\frac{B}{A}\right)^2 = \left(\frac{k_1 - k2}{k_1 + k_2}\right)^2 \tag{3.E.8}$$

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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CHAPTER OVERVIEW

4: The 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.

4.1: The Energy of a Particle in a Box is Quantized

4.2: The Average Momentum of a Particle in a Box is Zero

4.3: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

4.4: A Particle in a Three-Dimensional Box

4.E: The Schrödinger Equation and a Particle in a Box (Exercises)

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4.1: The Energy of a Particle in a Box is Quantized

3.05: The Energy of a Particle in a Box is Quantized

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4.2: The Average Momentum of a Particle in a Box is Zero

3.07: The Average Momentum of a Particle in a Box is Zero

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4.3: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

3.08: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

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4.4: A Particle in a Three-Dimensional Box

3.09: A Particle in a Three-Dimensional Box

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4.E: The Schrödinger Equation and a Particle in a Box (Exercises)

3.E: The Schrödinger Equation and a Particle in a Box (Exercises)

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CHAPTER OVERVIEW

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 Wavefunctions involve Hermite Polynomials

5.6: Hermite Polynomials are either Even or Odd Functions

5.7: The Harmonic Oscillator and Infrared Spectra

5.8: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

5.9: The Energy Levels of a Rigid Rotor

5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

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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.

5.1.1: 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.

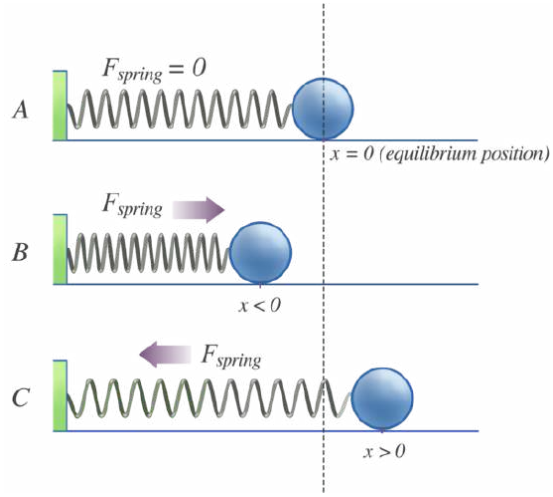


Figure 5.1.2 : A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (CC BY-NC; Ümit Kaya via LibreTexts)

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.

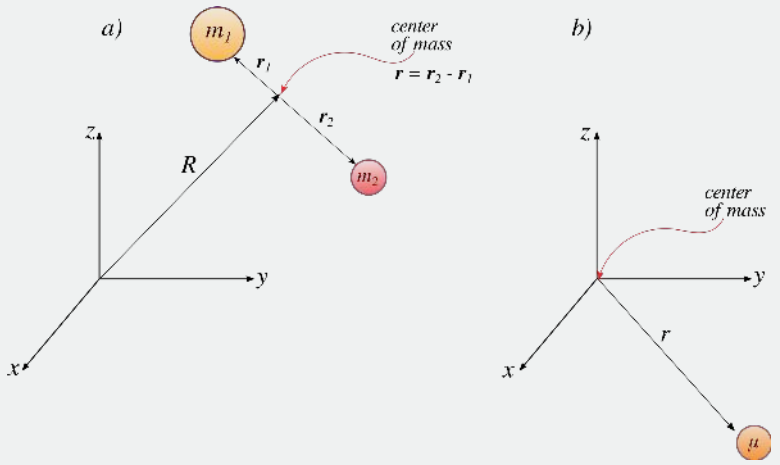


Figure 5.1.3 : Diagrams of the coordinate systems and relevant vectors for the motion of (a) a two-particle diatomic molecule with atoms of mass m_1 and m_2 and (b) the equivalent one-particle pseudo-particle of reduced mass μ. (CC BY-NC; Ümit Kaya via LibreTexts)

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

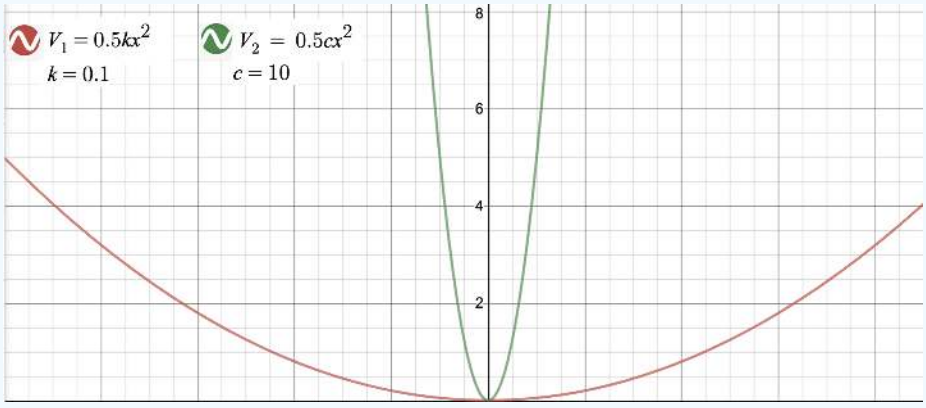
$$V''(x) = \frac{d}{dx}kx = k$$

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.

5.1.2: 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**.

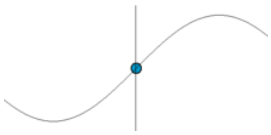


Figure 5.1.4 : Solution to the Harmonic Oscillator. Displacement (y-axis) is plotted as a function of time.

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. $x(t) = x_0e^{i\omega t}$
b. $x(t) = x_0e^{-i\omega t}$

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 $x(t) = x_0e^{i\omega t}$ into Equation 5.1.4.

$$\begin{aligned} \frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) &= 0 \\ \frac{d^2}{dt^2}\left(x_oe^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_o\frac{d^2}{dt^2}\left(e^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2\left(e^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2e^{i\omega t} + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2 + \frac{k}{m}x_o &= 0 \\ -x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \quad &\text{with} \quad \omega = \sqrt{\frac{k}{m}} \end{aligned}$$

Solution b

This requires simply placing the given function $x(t) = x_0e^{-i\omega t}$ into Equation 5.1.4.

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

$$\frac{d^2}{dt^2}\left(x_o e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o\frac{d^2}{dt^2}\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 e^{-i\omega t} + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$

$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \text{ with } \omega = \sqrt{\frac{k}{m}}$$

? Exercise 5.1.1

Show that sine and cosine functions also are solutions to Equation 5.1.4.

Answer

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 $x(t)$

$$\begin{aligned}\frac{d^2x(t)}{dt} &= -\omega^2 x_o\sin(\omega t + \phi)\\ &= \omega^2 x_o\sin(\omega t + \phi)\\ &= -\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right)\end{aligned}$$

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 $x(t)$

$$\begin{aligned}\frac{d^2x(t)}{dt} &= -\omega^2 x_o\cos(\omega t + \phi)\\ &= -\omega^2 x_o\cos(\omega t + \phi)\\ &= -\frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t + \phi\right)\end{aligned}$$

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.

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

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.

5.1.3: 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.

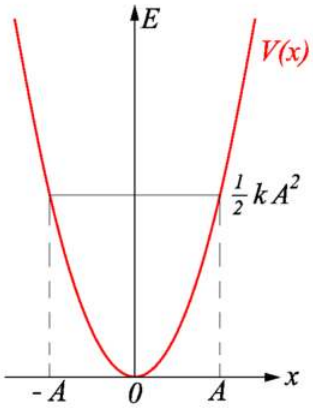


Figure 5.1.5 : The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x. The potential energy $V(x)=½kx^2$ is shown in red. (Paul Wormer Wikipedia).

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

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

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

$$\begin{aligned} E &= \frac{1}{2}kA^2\left(\sin^2 \omega t + \cos^2 \omega t\right) \\ &= \frac{1}{2}kA^2 \end{aligned}$$

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

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.

5.2.1: 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.

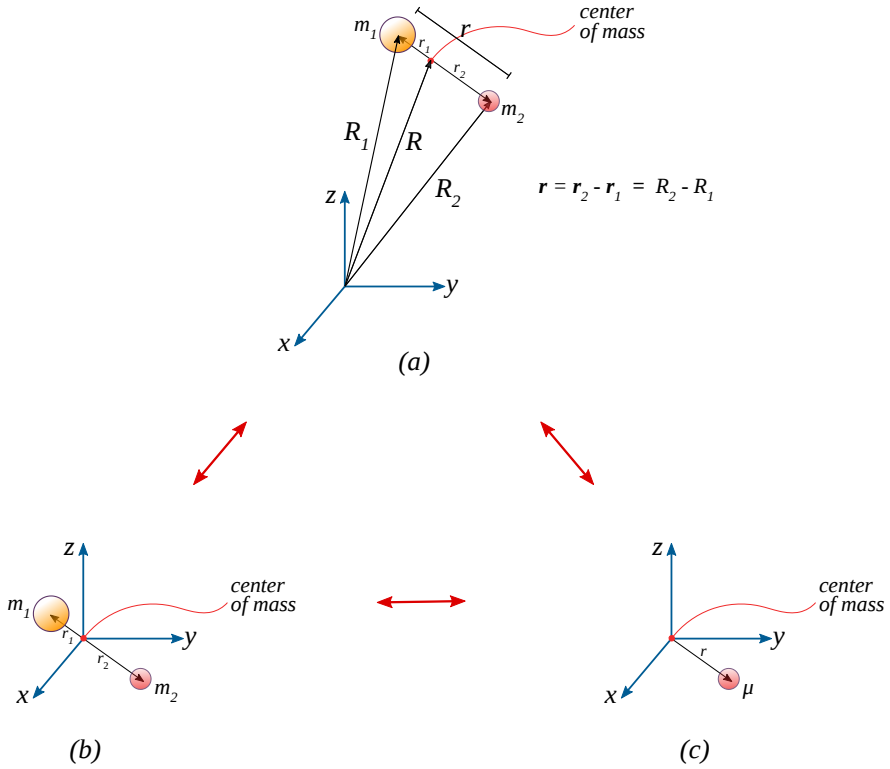


Figure 5.2.1 : a) the individual vectors to the particles m_1 and m_2 in the coordinate space and the resultant vector. b) center of mass. c) reduced mass. (CC BY-NC; Ümit Kaya via LibreTexts)

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

$$\mu_{pe} = \frac{(1.6727 \times 10^{-27})(9.110 \times 10^{-31})}{1.6727 \times 10^{-27} + 9.110 \times 10^{-31}}$$
$$= 9.105 \times 10^{-31} kg$$

5.2.2: 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.

$$\hat{H}\left|\psi\right\rangle = \left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]\left|\psi\right\rangle = E|\psi\rangle$$

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
^{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 $^{1}H^{37}Cl$:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{478\,N/m}{1.629 \times 10^{-27}\,kg}}$$

$$= 8.621 \times 10^{13} s^{-1}$$

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 $H^{35}Cl$ and $H^{37}Cl$. What are the vibration frequencies in these two diatomic molecules.

Answer

$H^{35}Cl$: 2886 cm^{-1}

$D^{35}Cl$: 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

$$V(x) = V(x_0) + \left.\frac{dV(x)}{dx}\right|_{x_0}^{x} (x - x_0) + \frac{1}{2!}\left.\frac{d^2V(x)}{dx^2}\right|_{x_0}^{x} (x - x_0)^2 + \ldots + \frac{1}{n!}\left.\frac{d^nV(x)}{dx^n}\right|_{x_0}^{x} (x - x_0)^n \tag{5.3.1}$$

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).

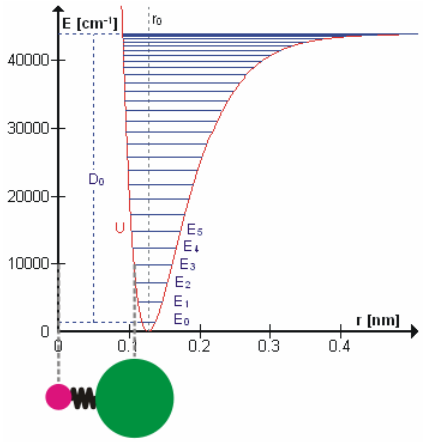


Figure 5.3.1 : The vibration of the **HCl** molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, **HCl** is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed 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.

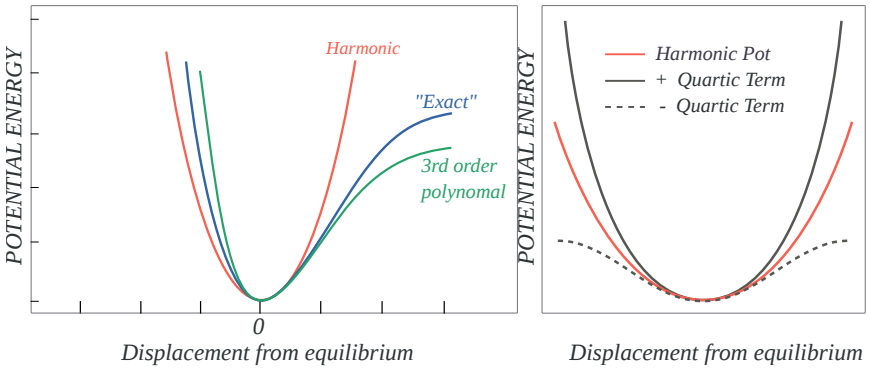


Figure 5.3.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

Naturally, adding higher order anharmonic terms, like quartic terms (Figure **5.3.2;**) improve the approximation. Almost all diatomics have experimentally determined potentials for their lowest energy states. $\mathbf{H_2}$, $\mathbf{Li_2}$, $\mathbf{O_2}$, $\mathbf{N_2}$, and $\mathbf{F_2}$ 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

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v+\frac{1}{2}\right)^2 v_e x_e + \left(v+\frac{1}{2}\right)^3 v_e y_e + \textbf{higher terms}$$

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).

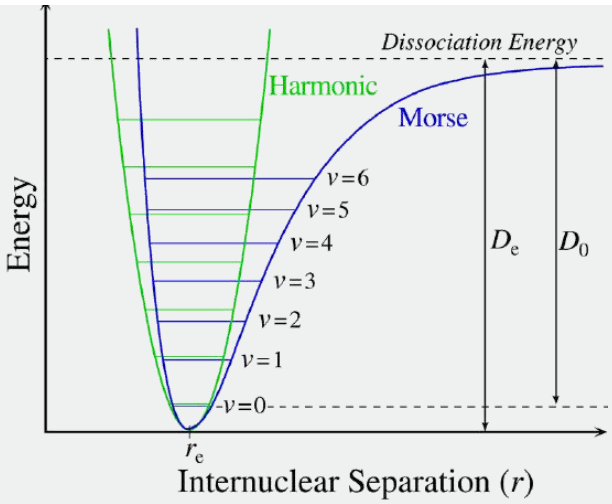


Figure 5.3.4 : The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e 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.

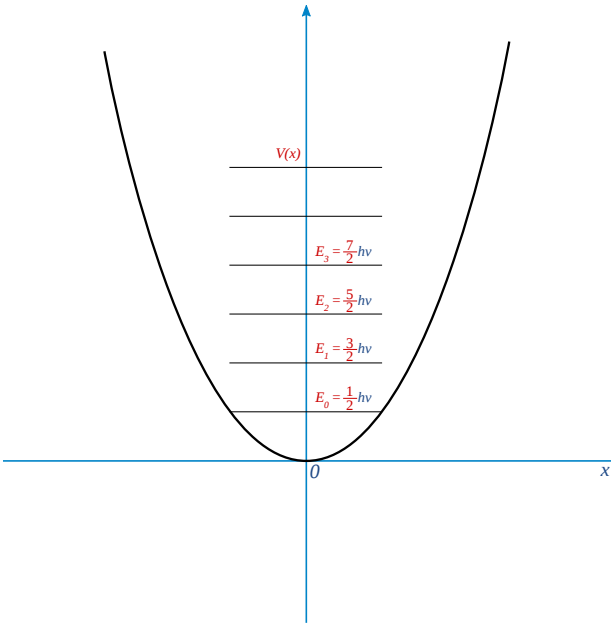


Figure 5.4.1 : Potential energy function and first few energy levels for harmonic oscillator. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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

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.

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

$$\omega = \sqrt{\frac{k}{\mu}} \tag{5.4.6}$$

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5.5: 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, $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \tag{5.5.1}$$

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero. As shown in Equation 5.5.1, 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,

$$\hat{H}(q) = \frac{1}{2\mu}\hat{P}_q^2 + \frac{k}{2}\hat{q}^2 \tag{5.5.2}$$

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

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{k}{2}q^2 \tag{5.5.3}$$

since the operator for position or displacement is just the position or displacement. The time-independent Schrödinger Equation then becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(q)}{dq^2} + \frac{k}{2}q^2\psi_v(q) = E_v\psi_v(q) \tag{5.5.4}$$

or upon rearranging

$$\frac{d^2\psi_v(q)}{dq^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{k}{2}q^2\right)\psi_v(q) = 0 \tag{5.5.5}$$

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 5.5.5 are to simplify the equation by collecting constants in the parameter β

$$\beta^2 = \frac{\hbar}{\sqrt{\mu k}} \tag{5.5.6}$$

and then changing the variable from q to x where

$$x = \frac{q}{\beta} \tag{5.5.7}$$

so that

$$\frac{d^2}{dq^2} = \frac{1}{\beta^2}\frac{d^2}{dx^2} \tag{5.5.8}$$

After substituting Equations 5.5.6 and 5.5.8 into Equation 5.5.5, the differential equation for the harmonic oscillator becomes

$$\frac{d^2\psi_v(x)}{dx^2} + \left(\frac{2\mu\beta^2 E_v}{\hbar^2} - x^2\right)\psi_v(x) = 0 \tag{5.5.9}$$

? Exercise 5.6.1

Make the substitutions given in Equations 5.5.6 and 5.5.8 into Equation 5.5.5 to get Equation 5.5.9.

5.5.1: 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**):

$$\lim_{x\to\infty} \psi_v(x) = 0 \tag{5.5.10}$$

The function that has this property and satisfies the differential equation for large values of x is the exponential function, i.e.,

$$\lim_{x\to\infty} \phi_v(x)\exp\left(\frac{-x^2}{2}\right) = 0 \tag{5.5.11}$$

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.

$$\sum_{n=0}^{v} c_n x^n \tag{5.5.12}$$

Each of the truncations of the power series in Equation 5.5.12 can be multiplied by the exponential function in Equation 5.5.11 to create a family of valid solutions to the differential equation in Equation 5.5.9.

$$\psi_v(x) = \sum_{n=0}^{v} c_n x^n \exp\left(\frac{-x^2}{2}\right) \tag{5.5.13}$$

? Exercise 5.6.2

Write the first four polynomials, $v = 0$ to $v = 1$, $v = 12$, $v = 13$, $v = 14$ for Equation 5.5.12 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 5.5.13 is a solution to the harmonic oscillator Schrödinger Equation in Equation 5.5.9 for $v = 0$ and $v = 1$.

5.5.1.1: 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 5.5.9 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.

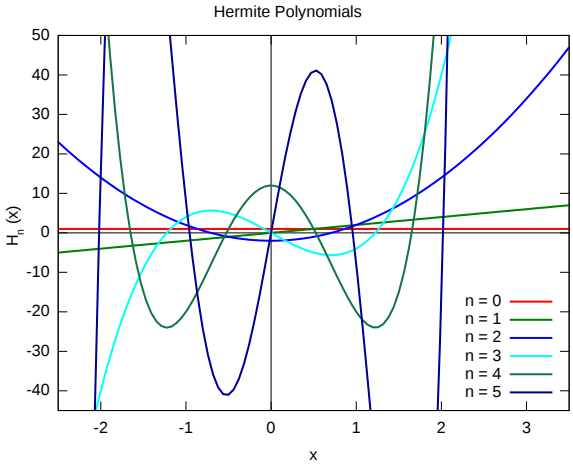


Figure 5.6.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

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.

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \tag{5.5.14}$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \tag{5.5.15}$$

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 5.5.7) and a different constant α:

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

so Equation 5.5.15 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

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \tag{5.5.16}$$

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 5.5.16, 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.

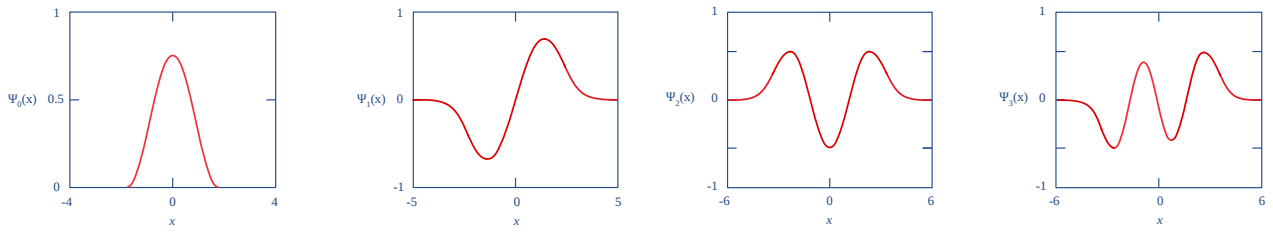


Figure 5.6.2 : The harmonic oscillator wavefunctions describing the four lowest energy states.

? 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?

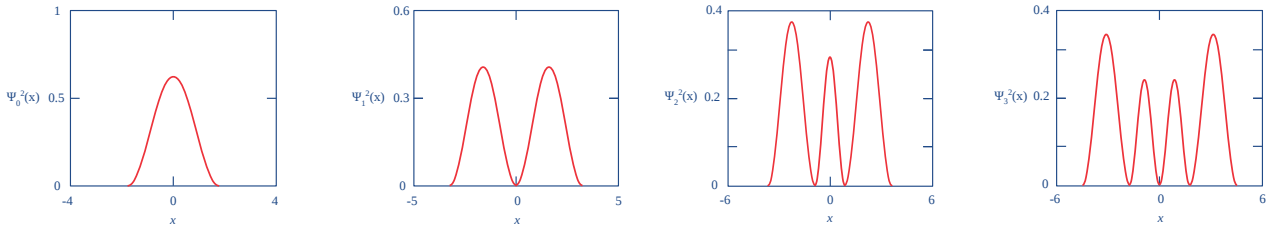


Figure 5.6.3 : The probability densities for the four lowest energy states of the harmonic oscillator.

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

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).

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.

5.5.2: 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

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \tag{5.5.17}$$

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

$$P[\text{allowed}] = 2\int_0^{Q_0} \psi_0^*(Q)\psi_0(Q)dQ \tag{5.5.18}$$

The factor 2 appears in Equation 5.5.18 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 5.5.18, 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 5.5.18 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}}\int_0^1 \exp(-x^2)dx \tag{5.5.19}$$

The integral in Equation 5.5.19 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 5.5.19 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

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5.6: 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 .

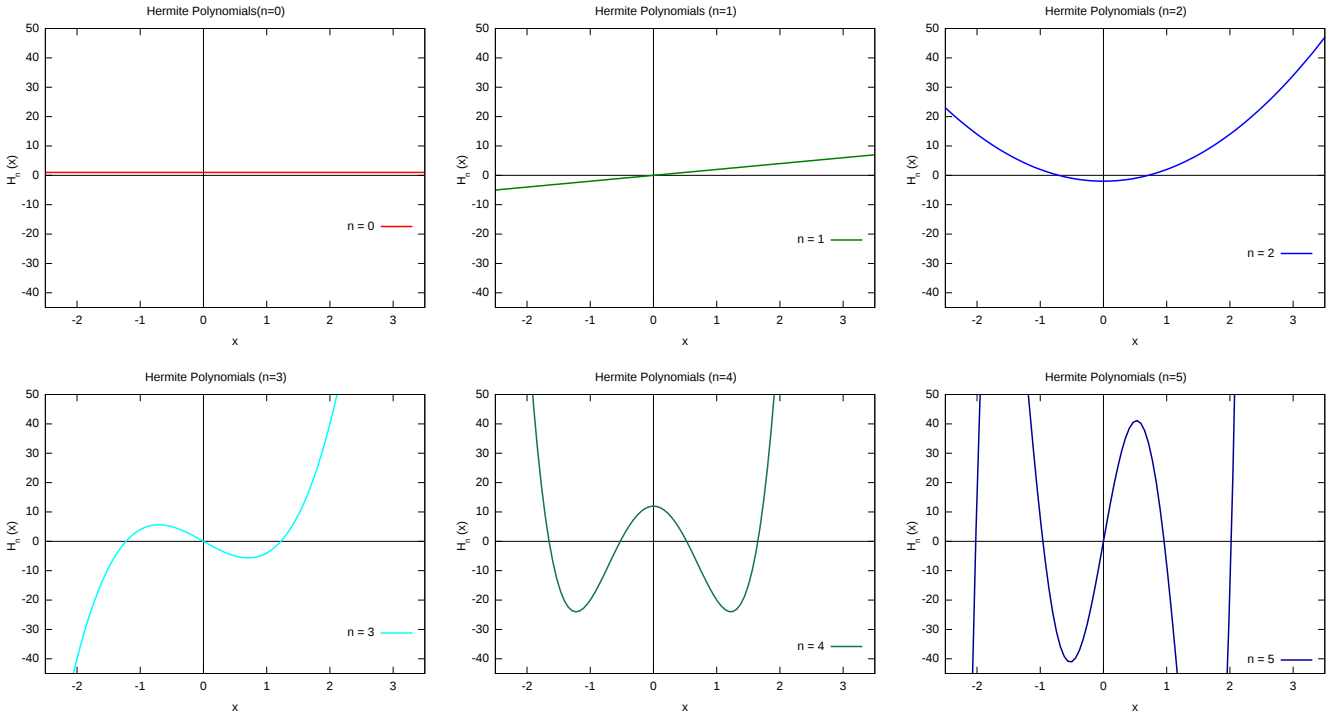


Figure 5.7.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

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

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x). \tag{5.6.1}$$

5.6.1: 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

$$H_n(-x) = (-1)^n H_n(x) \tag{5.6.2}$$

- $H_n(x)$ is an even function, when n is even.
- $H_n(x)$ is an odd function, when n is odd.

5.6.2: 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:

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x = \int_{-a}^{0} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{5.6.3}$$

$$= \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{5.6.4}$$

For an even function, we have $f(-x) = f(x)$ and Equation 5.6.4 can be simplified

$$\begin{aligned} I &= \int_0^a f(-x)\,dx + \int_0^a f(x)\,dx \\ &= 2\int_0^a f(x)\,dx \end{aligned}$$

For an odd function, we have $f(-x) = -f(x)$ and Equation 5.6.4 can be simplified

$$\begin{aligned} I &= -\int_0^a f(x)\,dx + \int_0^a f(x)\,dx \\ &= 0 \end{aligned}$$

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 5.6.5 and 5.6.6).

Solution

For the Hermite polynomials $H_n(x)$, the relevant inner product (using Dirac Notation)

$$\langle f, g\rangle = \int_{-\infty}^{\infty} f(x)g(x)\exp(-x^2)\,dx$$

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.

5.6.3: 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:

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 0 \tag{5.6.5}$$

if $m \neq n$ and

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 2^n n!\sqrt{\pi} \tag{5.6.6}$$

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 5.6.6 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.

$$\begin{aligned}\int_{-L}^{L}(4x^2-2)(8x^3-12x)dx &= 8\left(\frac{2x^6}{3}-2x^4+\frac{3x^2}{2}\right)\Bigg|_{-L}^{L}\\ &= 8\left(\frac{2L^6}{3}-2L^4+\frac{3L^2}{2}\right)-8\left(\frac{2(-L)^6}{3}-2(-L)^4+\frac{3(-L)^2}{2}\right)\\ &= 0.\end{aligned}$$

5.6.4: 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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5.7: 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.

5.7.1: 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 vth eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.7.1}$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞. Equation 5.7.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \tag{5.7.2}$$

where ν_m is the vibrational frequency of the vibration. Equation 5.7.2 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

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v)\, h\nu_m \end{aligned} \tag{5.7.3}$$

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 5.7.3 simplifies to

$$h\nu_{photon} = h\nu_m$$
$$= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.7.4}$$

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:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{5.7.5}$$
$$= \frac{\nu\,(Hz)}{c\,(cm/s)} \tag{5.7.6}$$

Equation 5.7.3 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{5.7.7}$$

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 ($rad \cdot s^{-1}$)
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

$$\omega = 5.45 \times 10^{14} rad \cdot s^{-1}$$

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 vth 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,

$$2.916 \times 10^{-20} J = \frac{1}{2}481Q_0^2$$

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

$$\begin{aligned} \textbf{Percent bond length} &= \frac{Q_0}{x_{eq}} \times 100\% \\ &= \frac{0.0110\, nm}{0.127\, nm} \times 100\% \\ &= 8.66\% \end{aligned}$$

5.7.2: 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:

$$\mu_T = \langle \psi_{v'} \left| \hat{\mu}(x) \right| \psi_v \rangle \tag{5.7.8}$$

$$= \int_{-\infty}^{\infty} \psi_{v'}^*(x) \hat{\mu}(x) \psi_v(x) dx \tag{5.7.9}$$

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.

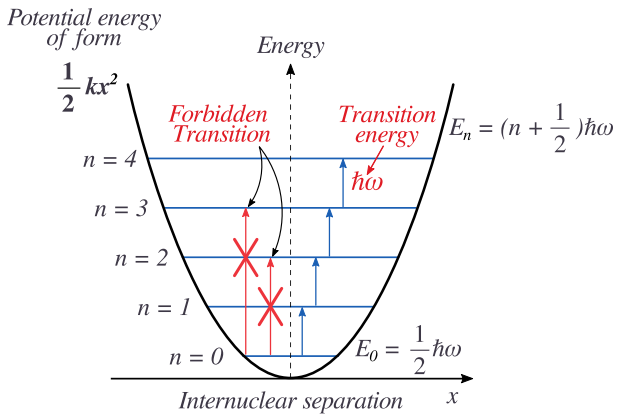


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 5.7.9, 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

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{5.7.10}$$

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 ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left.\frac{d\mu(x)}{dx}\right|_{x=0} x + \left.\frac{d^2\mu(x)}{dx^2}\right|_{x=0} x^2 + \cdots \tag{5.7.11}$$

Retaining only the first two terms and substituting into Equation 5.7.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left.\frac{d\mu(x)}{dx}\right|_{x=0} \int_{-\infty}^{\infty} x\psi_{v'}^*(x)\psi_v(x)dx \tag{5.7.12}$$

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 5.7.11. 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 5.7.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 5.7.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1 . Also note that the second term is zero if

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0} = 0 \tag{5.7.13}$$

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 5.7.12 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 5.7.13 **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

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{5.7.14}$$

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

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

$$\mu_T = \langle \psi_{v'} \,|\, \hat{\mu}(x) \,|\, \psi_v \rangle$$

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.

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 5.7.4. 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.

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= h\nu_{photon} \\ &= \hbar\omega_{oscillator}\end{aligned}$$

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 $v = 0$ to $v = 1$ and from $v = 1$ to $v = 2$, 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, $\Delta v = 2$, generally appears at a frequency slightly less than twice that of the fundamental, i.e. the frequency due to the $\Delta v = 1$ 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}.

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5.8: 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.

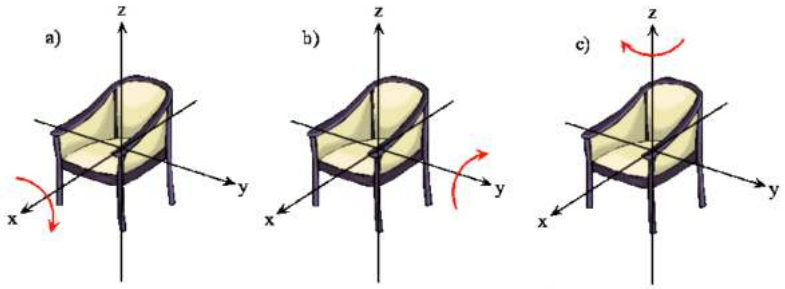


Figure 5.9.1 : Cartesian rotations of a chair. Rotations about the (a) x axis, (b) y axis, and (c) z axis.

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?

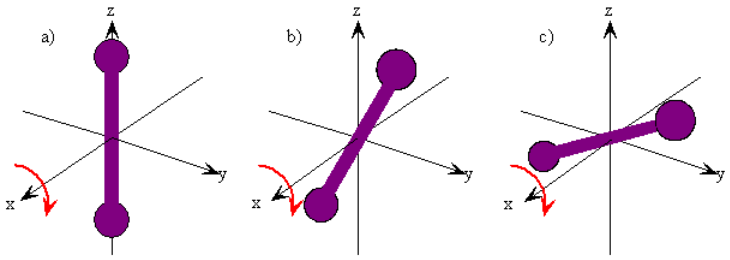


Figure 5.9.2 : Rotation of a diatomic molecule about the x axis.

5.8.1: 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, $\hat{\mu}$.

$$\mu_T = \int Y_{J_f}^{m_f *} \hat{\mu} Y_{J_i}^{m_i} \sin\theta \, d\theta \, d\varphi \tag{5.8.1}$$

or in braket notation

$$\mu_T = \langle Y_{J_f}^{m_f} \left| \hat{\mu} \right| Y_{J_i}^{m_i} \rangle \tag{5.8.2}$$

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,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \tag{5.8.3}$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \tag{5.8.4}$$

and

$$\Delta m_J = 0, \pm 1 \tag{5.8.5}$$

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 Jth rotational levels are given by

$$E_J = J(J+1)\frac{\hbar^2}{2I} \tag{5.8.6}$$

with each Jth energy level having a degeneracy of $2J+1$ due to the different possible m_J values.

5.8.2: Microwave Transition Energies

The transition energies for absorption of radiation are given by

$$E_{photon} = \Delta E \tag{5.8.7}$$
$$= E_f - E_i \tag{5.8.8}$$
$$= h\nu \tag{5.8.9}$$
$$= hc\bar{\nu} \tag{5.8.10}$$

Substituting the relationship for energy (Equation 5.8.6) into Equation 5.8.8 results in

$$E_{photon} = E_f - E_i \tag{5.8.11}$$
$$= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \tag{5.8.12}$$

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 5.8.12 can be replaced by $J_i + 1$, since the selection rule requires $J_f - J_i = 1$ for the

absorption of a photon (Equation 5.8.4). The equation for absorption transitions (Equation 5.8.12) then can be written in terms of the only the quantum number J_i of the initial state.

$$E_{photon} = h\nu \tag{5.8.13}$$

$$= hc\bar{\nu} \tag{5.8.14}$$

$$= 2(J_i + 1)\frac{\hbar^2}{2I} \tag{5.8.15}$$

Equation 5.8.15 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

$$B = \frac{\hbar^2}{2I} \tag{5.8.16}$$

Often spectroscopists want to express the rotational constant in terms of *frequency* of the absorbed photon and do so by dividing Equation 5.8.16 by h

$$B(\text{in freq}) = \frac{B}{h} \tag{5.8.17}$$

$$= \frac{h}{8\pi^2\mu r_0^2} \tag{5.8.18}$$

More often, spectroscopists want to express the rotational constant in terms of *wavenumbers* ($\bar{\nu}$) of the absorbed photon by dividing Equation 5.8.16 by hc,

$$\tilde{B} = \frac{B}{hc} = \frac{h}{8\pi^2 c\mu r_0^2} \tag{5.8.19}$$

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 5.8.12 to Equation 5.8.16 and identify the units of B at the end.

Answer

$$\Delta E_{photon} = E_f - Ei$$

$$E_{r.rotor} = J(J+1)\frac{\hbar^2}{2I}$$

$$E_{photon} = h_\nu = hc\tilde{\nu} = J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I}$$

$$J_f - J_i = 1$$

$$J_f = 1 + J_i$$

$$E_{photon} = h_\nu = hc\tilde{\nu} = (1+J_i)(2+J_i)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I}$$

$$= \frac{\hbar^2}{2I}[2 + 3J_i + J_i^2 - J_i^2 - J_i]$$

$$= \frac{\hbar^2}{2I}2(J_i+1)$$

$$= 2B(J_i+1)$$

Now we do a standard dimensional analysis

$$B = \frac{\hbar^2}{2I} \equiv \left[\frac{kgm^2}{s^2}\right] = [J]$$

$$\frac{B}{h} = B(infreq.) = \frac{h}{8\pi^2\mu r_o^2} \equiv \left[\frac{1}{s}\right]$$

$$\frac{B}{hc} = \widetilde{B} = \frac{h}{8\pi^2\mu c r_o^2} \equiv \left[\frac{s}{m}\right]$$

? Exercise 5.9.4

Infrared spectroscopists use units of wavenumbers. Rewrite the steps going from Equation 5.8.12 to Equation 5.8.16 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.

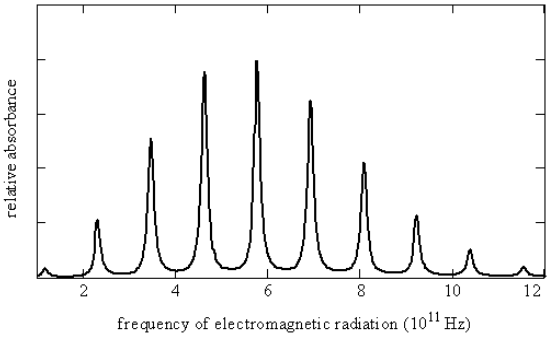


Figure 5.9.3: The rotation spectrum of $^{12}C^{16}O$ at 40 K. The peaks are tabulated in Table 5.9.1.

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
$4 \rightarrow 5$	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 5.8.19 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%.

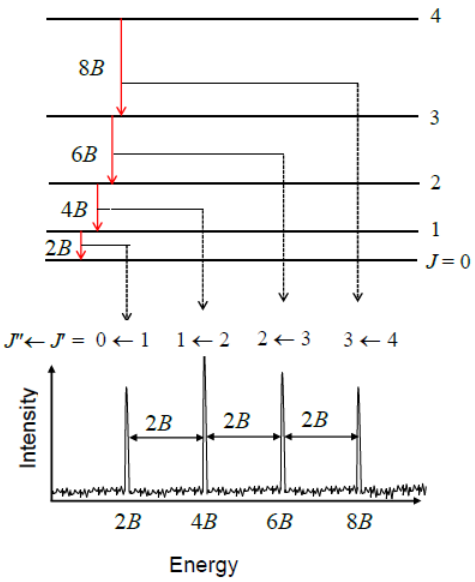


Figure 5.9.4 : Energy levels and line positions calculated in the rigid rotor approximation. (CC BY-SA 3.0; Nrrw via Wikipedia)

Exercise 5.9.5

Use Equation 5.8.19 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

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 $2B$.

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: $v_0 = 115271.21$ MHz
- J=1: $v_1 = 230538.01$ 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

$$6.86 amu \left(\frac{1.661 \times 10^{-27}\ \text{kg}}{12\ \text{amu}}\right) = 1.139 \times 10^{-26}\ \text{kg}$$

$$\begin{aligned}R_e &= \sqrt{\frac{\hbar}{2\pi\mu\Delta v}} \\ &= \sqrt{\frac{1.055 \times 10^{-34}\ J \cdot s}{2\pi \cdot 1.139 \times 10^{-26}\ \text{kg} \cdot 1.153 \times 10^{11}\ \text{Hz}}} \\ &= 1.131 \times 10^{-10}\text{m} \\ &= 1.131\ \mathring{A}\end{aligned}$$

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 5.8.16) 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

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5.8: The Rigid Rotator is a Model for a Rotating Diatomic Molecule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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5.9: 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.

5.9.1: 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

$$E_{tot} = T + V \tag{5.9.1}$$

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:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{5.9.2}$$

However, we have to determine v_i in terms of rotation since we are dealing with rotation motion. Since,

$$\omega = \frac{v}{r} \tag{5.9.3}$$

where ω is the **angular velocity**, we can say that:

$$v_i = \omega X r_i \tag{5.9.4}$$

Thus we can rewrite Equation 5.9.2 as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{5.9.5}$$

Since ω is a scalar constant, we can rewrite Equation 5.9.5 as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{5.9.6}$$

where l_i is the **angular momentum** of the ith particle, and L is the angular momentum of the *entire system*. Also, we know from physics that,

$$L = I\omega \tag{5.9.7}$$

where I is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite Equation 5.9.2 as

$$T = \omega \frac{I\omega}{2} = \frac{1}{2} I\omega^2 \tag{5.9.8}$$

Equation 5.9.8 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).

5.9.2: 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).

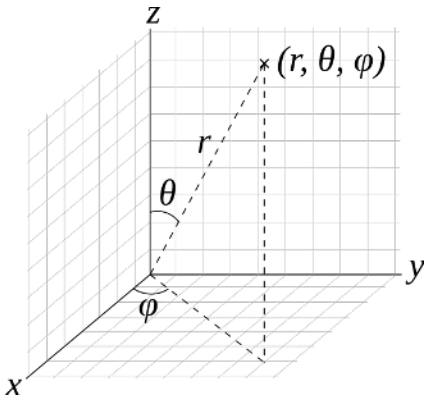


Figure 5.8.1 : The spherical coordinate system in terms of the Cartesian system. (Public Domain; Andeggs via Wikipedia).

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

$$|\psi(\theta,\varphi)\rangle = |\Theta(\theta)\Phi(\varphi)\rangle \tag{5.9.9}$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 5.9.10

$$\hat{H}\,|\Theta(\theta)\Phi(\varphi)\rangle = E|\,\Theta(\theta)\Phi(\varphi)\rangle \tag{5.9.10}$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{\partial}{\partial r_0} r_0^2 \frac{\partial}{\partial r_0} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\,\Theta(\theta)\Phi(\varphi)\rangle \tag{5.9.11}$$

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 5.9.11, to give

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\,\Theta(\theta)\Phi(\varphi)\rangle \tag{5.9.12}$$

To begin the process of the Separating of Variables technique, multiply each side of Equation 5.9.12 by $\frac{2I}{\hbar^2}$ and $\frac{-\sin^2\theta}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi) = \frac{-2IE\sin^2\theta}{\hbar^2} \tag{5.9.13}$$

Simplify the appearance of the right-hand side of Equation 5.9.13 by defining a parameter λ:

$$\lambda = \frac{2IE}{\hbar^2}. \tag{5.9.14}$$

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 5.9.14.

Inserting λ, evaluating partial derivatives, and rearranging Equation 5.9.13 produces

$$\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta\right)\Theta(\theta)\right]=-\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) \tag{5.9.15}$$

? Exercise 5.8.1

Carry out the steps leading from Equation 5.9.13 to Equation 5.9.15. Keep in mind that, if y is not a function of x,

$$\frac{dy}{dx}=y\frac{d}{dx}$$

Equation 5.9.15 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

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta-m_J^2\right)\Theta(\theta)=0 \tag{5.9.16}$$

and the φ-equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_J^2\Phi(\varphi)=0 \tag{5.9.17}$$

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 5.9.16 and 5.9.17 are obtained from Equation 5.9.15.

5.9.2.1: 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:

$$\Phi_m(\varphi)=Ne^{\pm im_J\varphi} \tag{5.9.18}$$

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 5.9.18 into Equation 5.9.17 to show that it is a solution to that differential equation.

Answer

Substitute

$$\Phi_m(\varphi)=\mathrm{N}e^{\pm\mathrm{i}m_J\varphi}$$

into

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_J^2\Phi(\varphi)=0$$

$$\frac{d^2}{d\varphi^2}\Phi_{\mathrm{m}}(\varphi) + m_J^2\Phi_{\mathrm{m}}(\varphi) = \frac{d}{d\varphi}\left(\mathrm{N}\left(\pm i m_J\right) e^{\pm i m_J \varphi}\right) + m_J^2\Phi_{\mathrm{m}}(\varphi)$$
$$= \mathrm{N}\left(\pm i m_J\right)^2 e^{\pm i m_J \varphi}\Big) + m_J^2\left(\mathrm{N}e^{\pm i m_J \varphi}\right)$$
$$= -\mathrm{N}m_J^2 e^{\pm i m_J \varphi} + \mathrm{N}m_J^2 e^{\pm i m_J \varphi} = 0$$

Thus

$$\Phi_m(\varphi) = Ne^{\pm i m_J \varphi}$$

is a solution to the differential equations.

The normalization condition, Equation 5.9.19 is used to find a value for N that satisfies Equation 5.9.18.

$$\int_0^{2\pi} \Phi^*(\varphi)\Phi(\varphi)d\varphi = 1 \tag{5.9.19}$$

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 5.9.19 to demonstrate that $N = 1/\sqrt{2\pi}$.

Answer

We need to evaluate Equation 5.9.19 with $\psi(\varphi) = Ne^{\pm imJ\varphi}$

$$\psi^*(\varphi)\psi(\varphi) = Ne^{+imJ\varphi}Ne^{-imJ\varphi}$$
$$= N^2$$
$$1 = \int_0^{2\pi} N^*Nd\varphi = 1$$
$$N^2(2\pi) = 1$$
$$N = \sqrt{1/2\pi}$$

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.

$$e^{im_J\varphi} = e^{im_J(\varphi+2\pi)} \tag{5.9.20}$$
$$= e^{im_J\varphi}e^{im_J2\pi} \tag{5.9.21}$$

For the equality in Equation 5.9.21 to hold, $e^{im_J2\pi}$ must equal 1, which is true only when

$$m_J = \cdots, -3, -2, -1, 0, 1, 2, 3, \cdots \tag{5.9.22}$$

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

$$\Phi_{m_J}(\varphi) = \sqrt{\frac{1}{2\pi}}e^{\pm i m_J \varphi}$$

with

$$m_J = 0, \pm 1, \pm 2, \cdots$$

5.9.2.2: Solving the $\Theta(\theta)$ Equation

Finding the $\Theta(\theta)$ functions that are solutions to the θ-equation (Equation 5.9.16) 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 5.9.15 be given by

$$\lambda = J(J+1) \tag{5.9.23}$$

where

$$J \geq |m_J| \tag{5.9.24}$$

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 5.9.9) and energy (below). Equation 5.9.24 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 5.9.14 and 5.9.23 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2\lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{5.9.25}$$

Using Equation 5.9.25, 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.

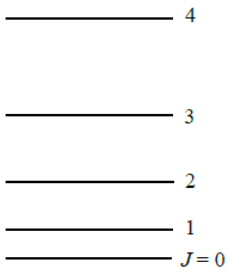


Figure 5.8.2 : Energy spacing for a rigid rotor (in 3D). Notice the energy depends only on J and not depend on m_J. That is, the energy of the rotor is not affected by its orientation.

> *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

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 5.9.25):

$$E = J(J + 1)(\hbar^2/2I)$$

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, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

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

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.

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 5.9.25), 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.

$$E = 5.71 \times 10^{-27}\ Joules$$

5.9.3: Spherical Harmonics

A wavefunction that is a solution to the rigid rotor Schrödinger Equation (Equation 5.9.9) can be written as a single function $Y(\theta, \varphi)$, which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{5.9.26}$$

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 .

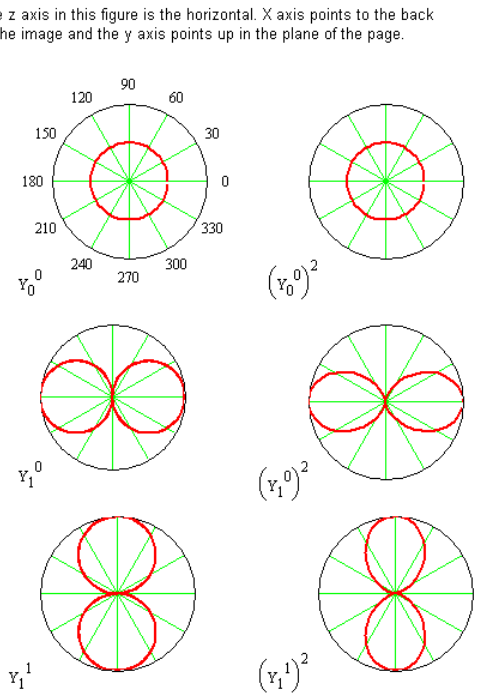


Figure 5.8.3 : Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

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 .

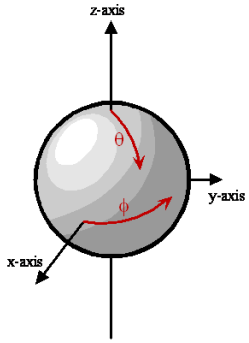


Figure 5.8.4 : Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

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

$$Pr\left[\theta_0, \varphi_0\right] = Y_J^{m_{J*}}(\theta_0, \varphi_0) Y_J^{m_J}(\theta_0, \varphi_0) ds \tag{5.9.27}$$

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

$$ds = \sin\theta \, d\theta \, d\varphi \tag{5.9.28}$$

? 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

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \tag{5.9.29}$$

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.

5.9.4: 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.

5.9.5: 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)

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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

$$\mu = \frac{(79\ amu)^2}{79\ amu + 79\ amu} = 39.5 amu$$

and convert to Kg:

$1.66e^{-27}$ kg•amu^{-1}

substitute the given values

$$\nu = \frac{1}{2\pi}\sqrt{\frac{240 kg\ m\ s^{-2}\ s}{39.5 amu \times 1.66 \times 10^{-27} kg\ amu^{-1}}} = 9.63 \times 10^{12} s^{-1}$$

It can also be convert to wavenumber (inverse centimeter cm^{-1}):

$$\nu_{cm^{-1}} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{9.63 \times 10^{12} s^{-1}}{3.0 \times 10^{10} cm\ s^{-1}} = 321 cm^{-1}$$

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 $\psi_{\circ}(x)$ given that $\hat{a}_{-} = 2^{-1/2}(\hat{x} + i\hat{p})$ and that $\hat{a_{-}}\psi_{\circ} = 0$ Then find the unnormalized wave function for $\psi_1(x)$ using $\hat{a}_{+}$.

Solution

It was given that $\hat{a}_{-}\psi_{\circ} = 0$, so substituting in $\hat{a}_{-}$ so we know

$$\hat{a_{-}} = 2^{-1/2}(\hat{x} + i\hat{p})\psi_{\circ} = 0$$

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 $\psi_{\circ}(x)$ 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

$$\mu_{deuterium} = \frac{(9.109390 \times 10^{-31}kg)(3.343586 \times 10^{-27}kg)}{(9.109390 \times 10^{-31}kg + 3.343586 \times 10^{-27}kg)}$$

$$\mu_{deuterium} = 9.106909 \times 10^{-31}kg = 0.9997277m_e$$

R_H = Rydberg constant

$$R_H = (109,737.2cm^{-1})(0.9997277m_e) = 109,707.3cm^{-1}$$

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 $\mathbf{9.106909 \times 10^{-31} kg}$ and the reduced mass of hydrogen is $\mathbf{9.104431 \times 10^{-31} kg}$. Compare both of these answers with the experimental result ($\mathbf{109677.6 cm^{-1}}$). 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 $\mathbf{2.7 \times 10^{-2}\%}$.

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 $\mathbf{9.1 \times 10^{-5}\%}$.

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

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

$$\mu = \frac{(1.00)(35.00)}{36.00} 1.603 \times 10^{-27} kg = 1.558 \times 10^{-27} kg$$

5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

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: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

6.4: s-orbitals are Spherically Symmetric

6.5: Orbital Angular Momentum and the p-Orbitals

6.6: The Helium Atom Cannot Be Solved Exactly

6.E: The Hydrogen Atom (Exercises)

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6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly

6.01: The Schrödinger Equation for the Hydrogen Atom Can Be Solved Exactly

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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)

$$\langle\psi(r,\theta,\phi)|\psi(r,\theta,\phi)\rangle \text{ ?}$$

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

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.

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 $m = 0, \pm1, \pm2 \ldots \pm\infty$. 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 $Y_J^m(\theta,\phi)$.

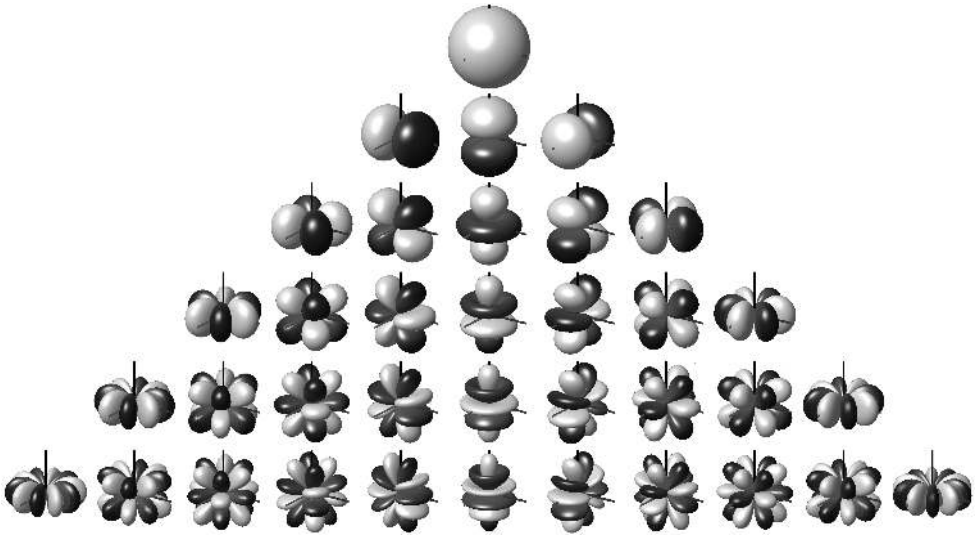


Figure 6.2.1: Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.

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

a. $n = 3$ and $l = 2$

b. Energy:

$$E_n = \frac{E_1}{n^2} = \frac{-13.6\text{eV}}{9} = -1.51\text{eV}$$

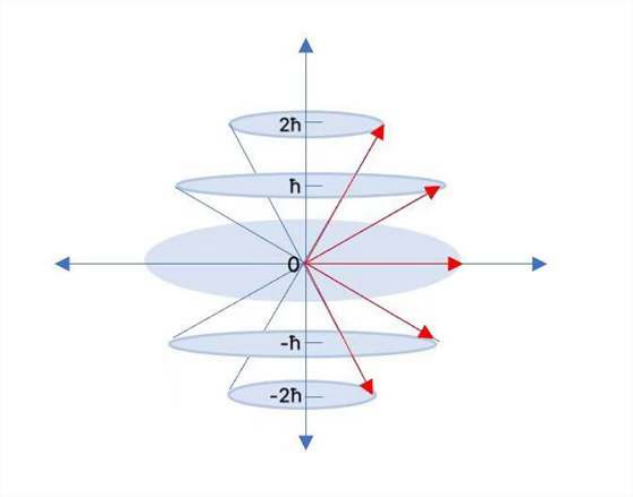
and angular momentum

$$\sqrt{l(l+1)}\hbar = \sqrt{2 \times 3}\hbar = 2.584 \times 10^{-34} J \cdot S$$

c. Magnetic quantum number:

$$m_l = -2, -1, 0, 1, 2$$

d.



6.2.1: 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	$m_l = 0$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right.$
ψ_{310}	3	1	$m_l = 0$	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\cos$
$\psi_{31\pm1}$	3	1	$m_l = \pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\sin$
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	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\cos\theta$
ψ_{2p_x}	2	1	±1	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\sin\theta\cos\phi$
ψ_{2p_y}	2	1	±1	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\sin\theta\sin\phi$
ψ_{3s}	3	0	0	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right.$
ψ_{3p_z}	3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\cos$
ψ_{3p_x}	3	1	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\sin$
ψ_{3p_y}	3	1	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\sin$
$\psi_{3d_{z^2}}$	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	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}}\sin\theta\cos\theta\cos$
$\psi_{3d_{yz}}$	3	2	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}}\sin\theta\cos\theta\sin$
$\psi_{3d_{x^2-y^2}}$	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 .

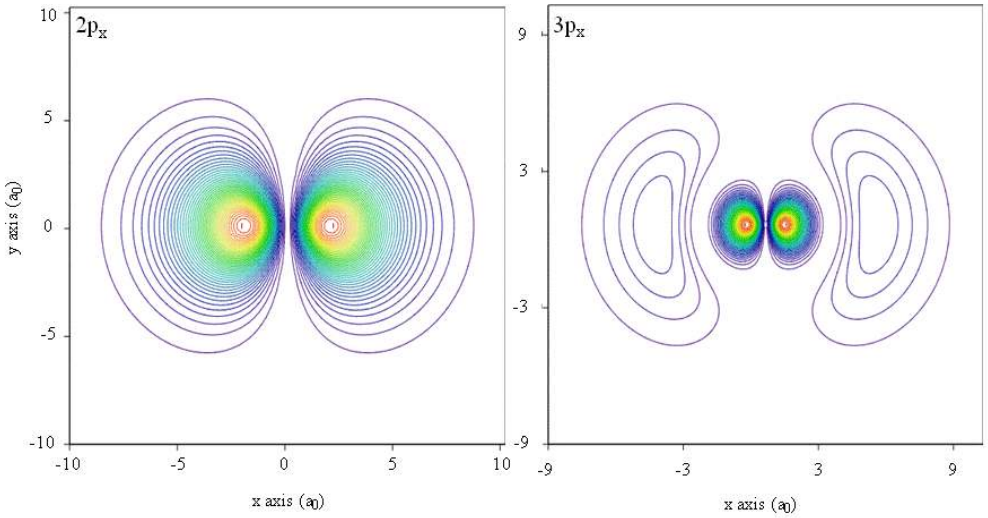


Figure 6.2.2: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical 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 .

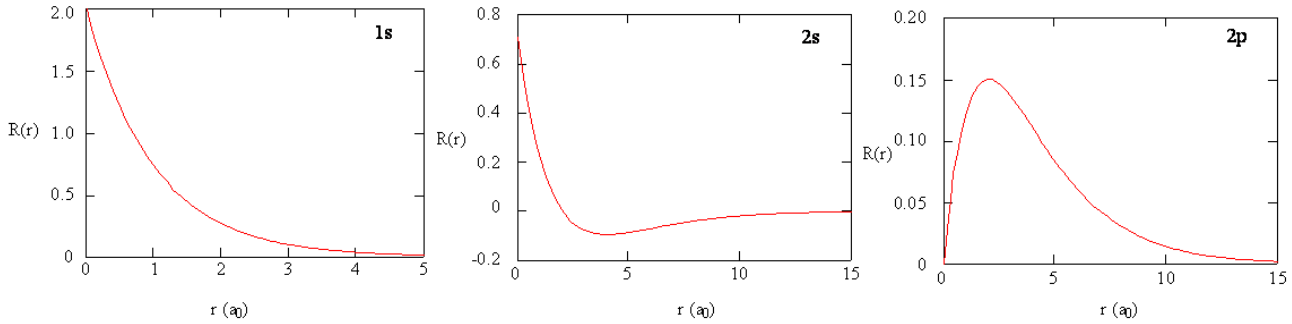


Figure 6.2.3: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

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

The Laguerre polynomial controls the radial nodes with the number of roots for the Laguerre polynomial is the number of radial nodes.

Exercise 6.2.7 : Radial Node

At what value of r does the 2s radial node occur?

Answer

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

$$r = 2\alpha_0$$

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

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.

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 .

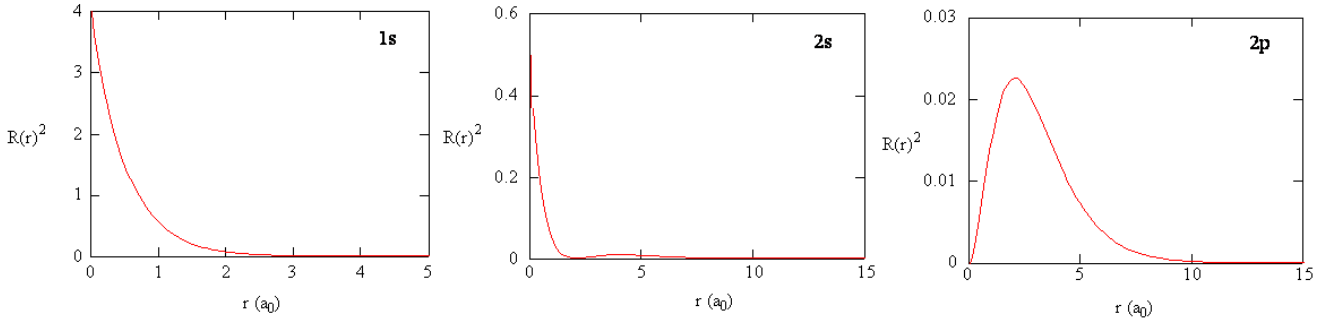


Figure 6.2.4: Radial probability densities for the 1s, 2s, and 2p orbitals.

6.2.2: 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.

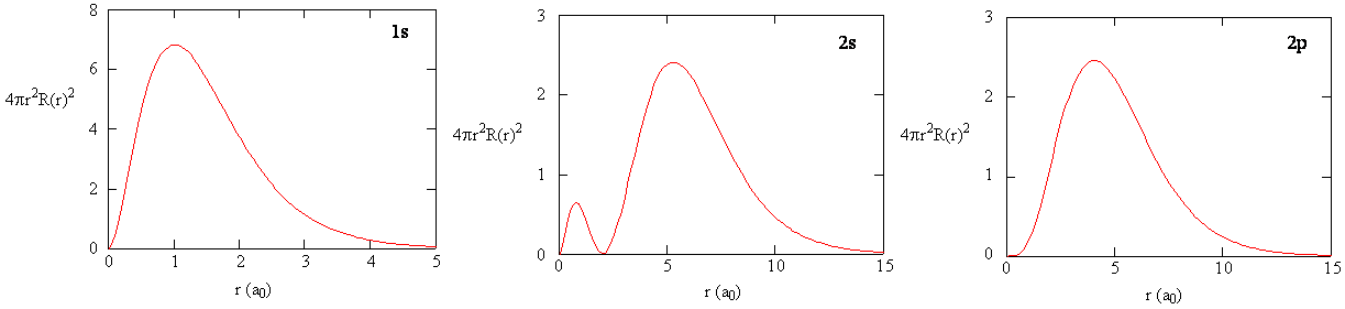


Figure 6.2.5: The radial distribution function for the 1s, 2s, and 2p orbitals.

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

$R(r)$ 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.

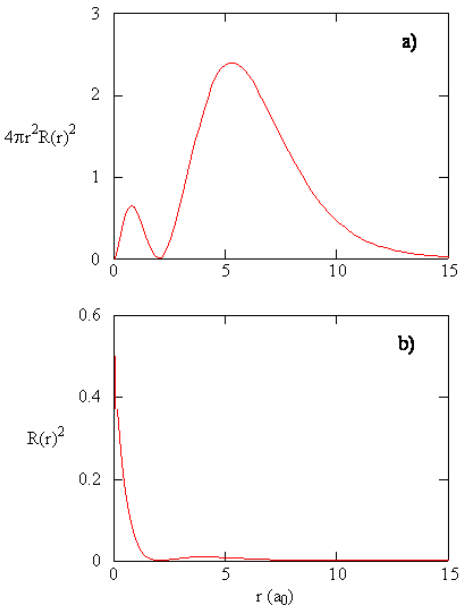


Figure 6.2.6: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

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6.3: 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**.

$$\psi_{n,l,m_l}(r,\theta,\varphi) = \underbrace{R_{n,l}(r)}_{radial}\underbrace{Y_l^{m_l}(\theta,\varphi)}_{angular} \tag{6.3.1}$$

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

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

$$\begin{aligned}
\langle\psi(r,\theta,\varphi)|\psi(r',\theta',\varphi')\rangle &= \int_{allspace}\psi^*(r,\theta,\varphi)\psi(r',\theta',\varphi')d\tau \\
&= \int_0^\infty dr\int_0^\pi d\theta\int_0^{2\pi} d\varphi(r^2\sin(\theta))\,\overbrace{\psi*(r,\theta,\varphi)}^{R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)}\overbrace{\psi(r,\theta,\varphi)}^{R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)} \\
&= \int_0^\infty dr\int_0^\pi d\theta\int_0^{2\pi} d\varphi(r^2\sin(\theta))[R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)][R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)] \\
&= \left[\int_0^\infty r^2[R_{n,l}(r)R_{n',l'}(r)]dr\right]\left[\int_0^{2\pi}\int_0^\pi \sin(\theta)[Y_l^{m_l}(\theta,\varphi)Y_{l'}^{m_l'}(\theta,\varphi)]d\theta d\varphi\right] \\
&= \langle R_{n,l}(r)|R_{n',l'}(r)\rangle\langle Y_l^{m_l}(\theta,\varphi)|Y_{l'}^{m_l'}(\theta,\varphi)\rangle \\
&= (\delta_{nn'}\delta_{ll'})(\delta_{ll'}\delta_{mm'}) = \delta_{nn'}\delta_{ll'}\delta_{mm'}
\end{aligned}$$

While part a demonstrates normality of the eigenstates, part b demonstrates the orthogonality of the eigenstate (and normality too).

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?

6.3.1: Radial Part of the Wavefunction

The asymptotic behavior (i.e., far away from the nucleus) to the radial part of the wavefunction is

$$R_{\text{asymptotic}}(r) \sim \exp\left(-\frac{r}{n}a_0\right) \tag{6.3.2}$$

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.

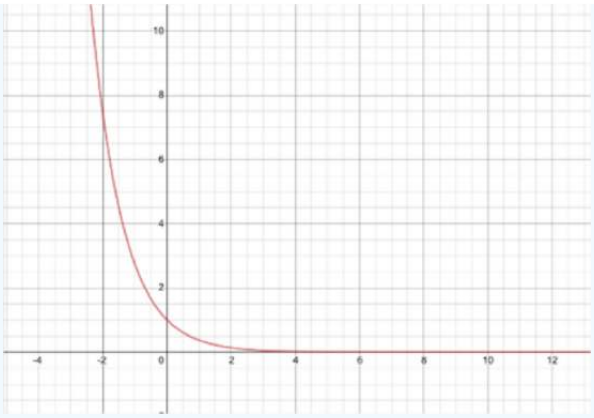
? Exercise 6.4.2

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

$$R(r) = e^{-\frac{c}{n}a_0}$$

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.



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.

$$L_{n,l}(r) = \sum_{r=0}^{n-l-1} c_i r^i \tag{6.3.3}$$

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 6.3.1).

The $R(r)$ functions that solve the radial differential Equation 6.3.1, are products of the associated Laguerre polynomials and the exponential factor, multiplied by a normalization factor ($N_{n,l}$) and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,l}\left(\frac{r}{a_0}\right)^l L_{n,l}(r) e^{-\frac{r}{na_0}} \tag{6.3.4}$$

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")

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6.4: 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, $a_0 = 0.529 \times 10^{-8}\,cm$.)

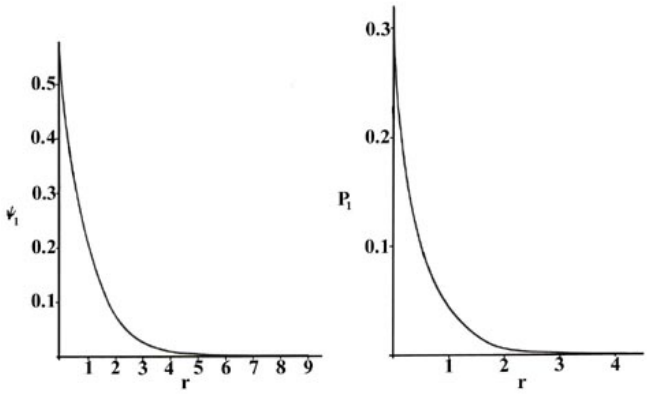


Figure 6.5.1 : The wavefunction and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

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.

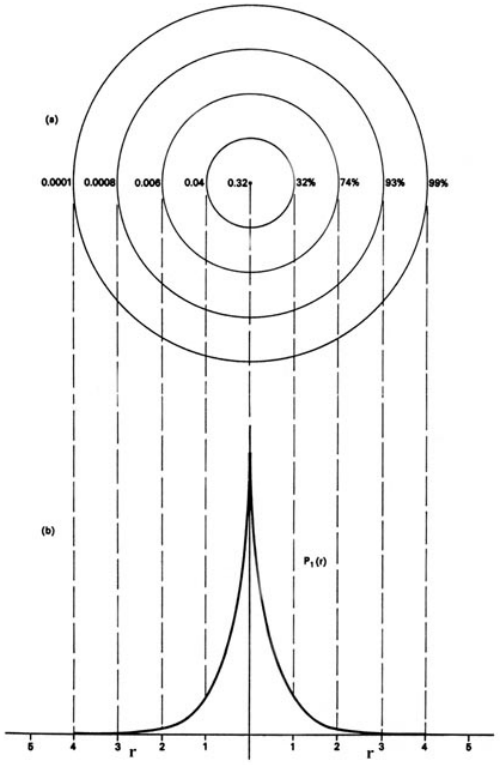


Figure 6.5.2 : (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand 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 = 4.2×10^{-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 0.52917×10^{-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 **6.4.3;** 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.

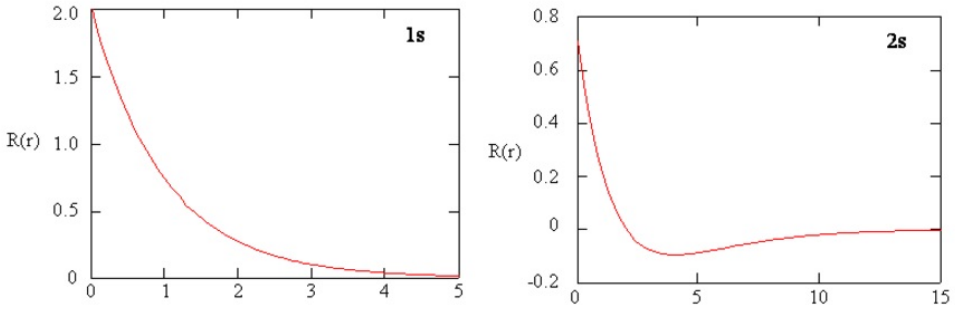


Figure 6.5.3 : Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click here.

Next notice how the radial function for the 2s orbital, Figure **6.4.3;**, 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 $r = 0$.

? 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

	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.

Radial probability densities for the 1s and 2s atomic orbitals are plotted in Figure 6.5.4 .

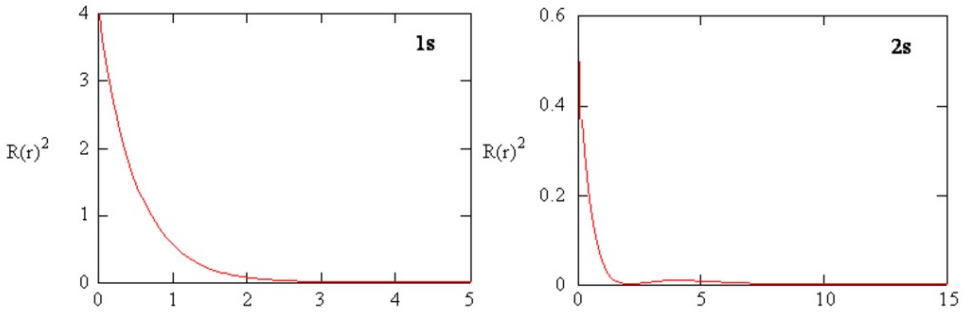


Figure 6.5.4 : Radial densities ($R(r)^*R(r)$) for the 1s and 2s orbitals.

6.4.1: 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

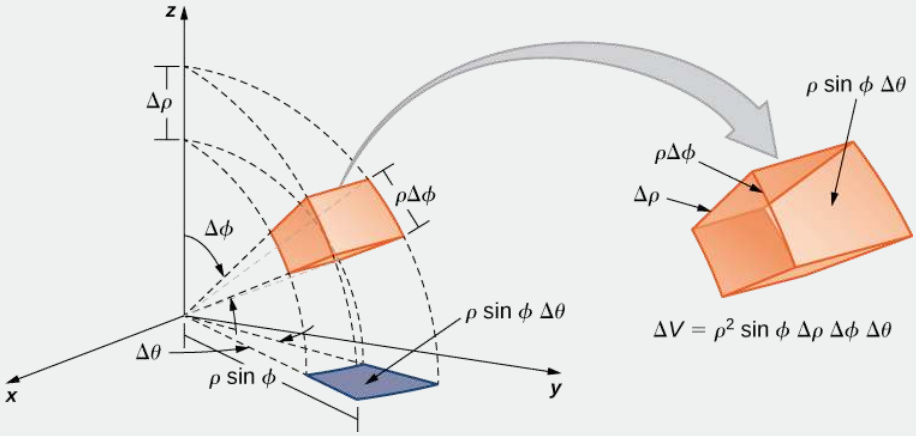
The reader may wonder why the volume of the shell is not taken as:

$$\frac{4}{3}\pi\left[(r+\Delta r)^3 - r^3\right]$$

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.

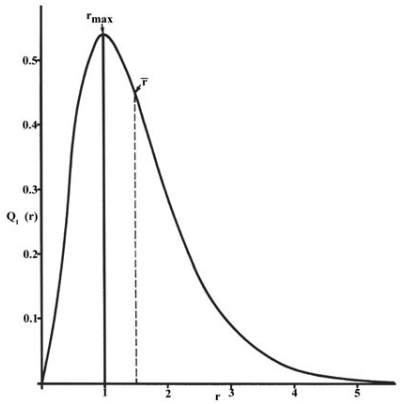


Figure 6.5.5 : The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r + \delta r$.

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.

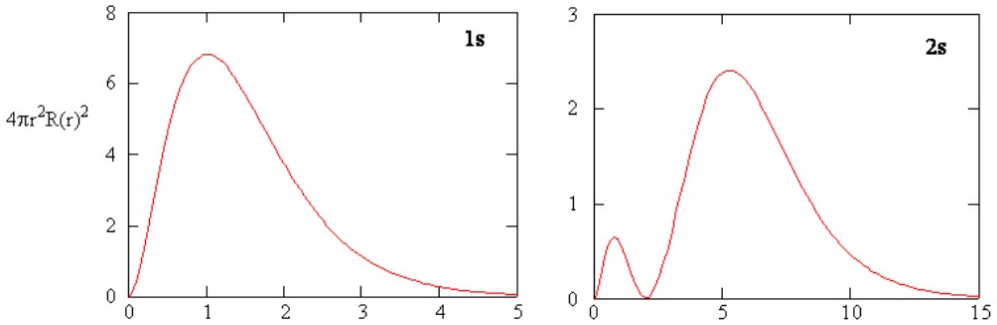


Figure 6.5.6 : The radial distribution function ($4\pi r^2 R(r)^* R(r)$) for the 1s and 2s orbitals. Compare to the radial functions in Figure 6.5.3 or the radial densities in Figure 6.5.4 . For an interactive graph click here.

Example 6.5.1 :

Calculate the probability of finding a 1s hydrogen electron being found within distance $2a_o$ from the nucleus.

Solution

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

$$\begin{aligned} prob &= 2 \times 2\pi \times \frac{1}{\pi a_0^3} \int_0^2 a_0(-a_0/2) r^2 de^{-2r/a_0} \\ &= \frac{4}{a_0^3}\left(-\frac{a_0}{2}\right)\left(r^2 e^{-2r/a_0}\Big|_0^{2a_0} - \int_0^{2a_0} 2re^{-2r/a_0} dr\right) \\ &= -\frac{2}{a_0^2}\left[(2a_0)^2 e^{-4} - 0 - 2\int_0^{2a_0} r\left(-\frac{a_0}{2}\right) de^{-2r/a_0}\right] \\ &= -\frac{2}{a_0^2} 4a_0^2 e^{-4} + \frac{4}{a_0^2}\left(-\frac{a_0}{2}\right)\left(re^{-2r/a_0}\Big|_0^{2a_0} - \int_0^{2a_0} e^{-2r/a_0} dr\right) \\ &= -8e^{-4} - \frac{2}{a_0}\left[2a_0 e^{-4} - 0 - \left(-\frac{a_0}{2}\right) e^{-2r/a_0}\Big|_0^{2a_0}\right] \\ &= -8e^{-4} - 4e^{-4} - e^{2r/a_0}\Big|_0^{2a_0} \\ &= -12e^{-4} - (e^{-4} - 1) = 1 - 13e^{-4} = 0.762 \end{aligned}$$

There is a 76.2% probability that the electrons will be within $2a_o$ of the nucleus in the 1s eigenstate.

6.4.2: 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")

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6.5: 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

6.5.1: 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.

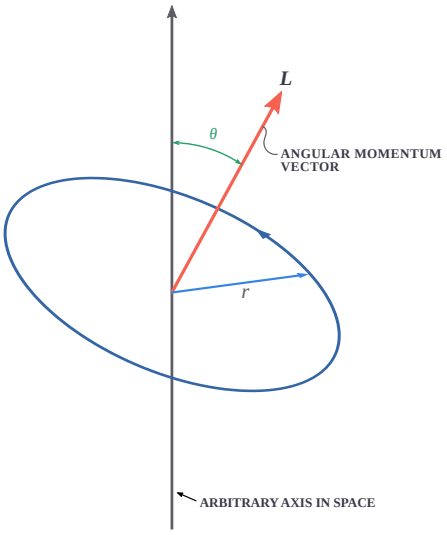


Figure 6.6.1 : The angular momentum vector for a classical model of the atom. (CC BY-NC; Ümit Kaya via LibreTexts)

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:

$$|\vec{L}| = mvr$$

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.

6.5.2: 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:

$$|L| = \sqrt{l(l+1)}\hbar \tag{6.5.1}$$

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 6.5.1 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 1*s*, 2*s*, 3*s*, 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 2*s* orbital the hydrogen atom is in a state for which $n = 2$ and $l = 0$.

Comparing these results with those for the 1*s* 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 .

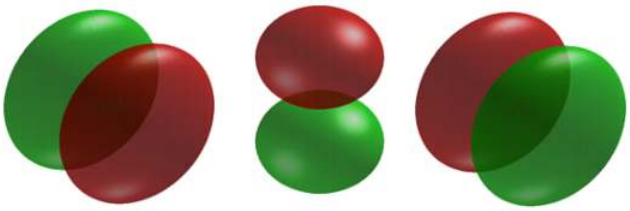


Figure 6.6.2 : The appearance of the three 2p orbitals in three-dimensional space. (CC BY-SA 3.0; I, Sarxos).

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 1*s* 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.*

6.5.3: 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.

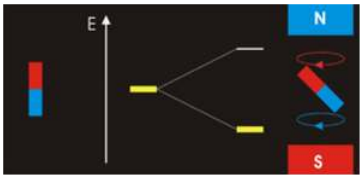


Figure 6.6.3 : The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left). However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative 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.

$$|\psi_{2,1,0}\rangle = r\cos\theta R(r) \tag{6.5.2}$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2}\sin\theta e^{i\phi} R(r) \tag{6.5.3}$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2}\sin\theta e^{-i\phi} R(r) \tag{6.5.4}$$

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.

$$R(r) = \sqrt{\frac{Z^5}{32\pi a_0^5}} e^{-Zr/2a_0}$$

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:

$$e^{i\phi} = \cos\phi + i\sin\phi \tag{6.5.5}$$

$$\sin\phi = \frac{e^{i\phi} - e^{-i\phi}}{2i} \tag{6.5.6}$$

$$\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2} \tag{6.5.7}$$

We're also going to use $x = \sin\theta\cos\phi$ and $y = \sin\theta\sin\phi$.

$$\begin{aligned}
\psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} - \psi_{2,1,-1}\right) \\
&= \frac{1}{2}\left(e^{i\phi} + e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\cos\phi f(r) = x f(r) \\
\psi_{2p_y} &= \frac{i}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right) \\
&= \frac{1}{2i}\left(e^{i\phi} - e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\sin\phi f(r) = y f(r)
\end{aligned}$$

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 $(|p_x\rangle - |p_y\rangle)$.

6.5.4: 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")
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6.6: 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).

6.6.1: 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 $\boldsymbol{r_1}$ and $\boldsymbol{r_2}$. The electrons are separated by a distance $\boldsymbol{r_{12} = |r_1 - r_2|}$. 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.

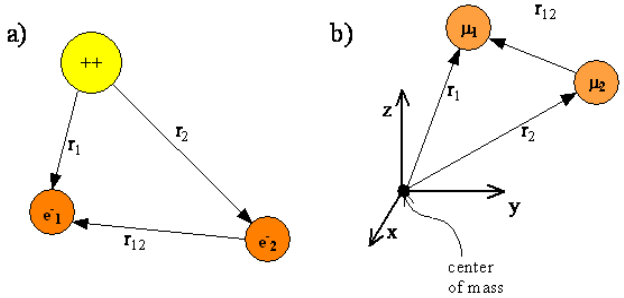


Figure 6.7.1 : (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that $\boldsymbol{\mu_1}$ and $\boldsymbol{\mu_2 \approx m_e}$.

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

$$\hat{H} = \hat{T} + \hat{V} \tag{6.6.1}$$

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

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \tag{6.6.2}$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{6.6.3}$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{6.6.4}$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{6.6.5}$$

The two-electron Hamiltonian in Equation 6.6.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{6.6.6}$$

and including terms for the additional electrons. The subsequent multi-electron atom with n electron is

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i\neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \tag{6.6.7}$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 6.6.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 6.6.3 and 6.6.4). 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 6.6.7):

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 $^{11}\mathbf{B}$ atom.
b. Would it be any different for a $^{11}\mathbf{B}^+$ ion?
c. Would it be any different for a $^{10}\mathbf{B}$ atom?

Answer

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, $^{11}\mathbf{B}^+$ has one less electron than $^{11}\mathbf{B}$. 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

$$\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{\hbar^2}{2m_e}\nabla_4^2 - \frac{-5e^2}{4\pi\epsilon_0 r_1} - \frac{-5e^2}{4\pi\epsilon_0 r_2} - \frac{-5e^2}{4\pi\epsilon_0 r_3} - \frac{-5e^2}{4\pi\epsilon_0 r_4} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{34}}$$

c. No effect. Changing the number of neutrons in the nucleus does not affect kinetic nor potential energies of the electrons. The Hamilitonian for $^{10}\mathbf{B}$ is identical to $^{11}\mathbf{B}$. 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.

6.6.2: 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 6.6.7 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.

$$p(V) = \int_V \left|\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_n)\right|^2 d\tau$$

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.

$$\int_{\text{all space}} \left|\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_i)\right|^2 d\tau = n$$

Unfortunately, the Coulomb repulsion terms (Equation 6.6.5) 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 6.6.7) involve writing a multi-electron wavefunction ($\psi(r_1,r_2,\cdots,r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1,r_2,\cdots,r_n) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_n(r_n) \tag{6.6.8}$$

or in Dirac notation

$$|\psi(r_1,r_2,\cdots,r_n)\rangle \approx |\varphi_1(r_1)\rangle\,|\varphi_2(r_2)\rangle\cdots|\,\varphi_n(r_n)\rangle \tag{6.6.9}$$

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 6.6.8, 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 6.6.8 or 6.6.9), 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.

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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

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2}{6561\pi}\right)\left(\frac{z^3}{a_o^3}\right)\sigma^3(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}\left(\cos^2\theta + \sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2z^3\sigma^2(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}}{6561\pi a_o^3}\right)\left(\cos^2\theta + \sin^2\theta\left(\cos^2\phi + \sin^2\phi\right)\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2z^3\sigma^2(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}}{6561\pi a_o^3}\right)$$

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

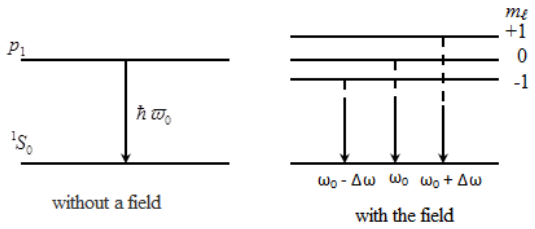
$$I = \frac{q_e m_e v r}{2\pi m_e r^2}$$
$$I = \frac{q_e L}{2\pi m_e r^2}$$

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.



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

$$\hat{L_+}\hat{L_-} - hat{L_-}\hat{L_+} = \hat{L^2} - \hat{L_z^2} + \hbar\hat{L_z} - \hat{L^2} + \hat{L_z^2} - \hbar\hat{L_z}$$

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

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:

$$E_\phi = \frac{\langle \phi \left| \hat{H} \right| \phi \rangle}{\langle \phi | \phi \rangle}$$

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

$$\langle \phi \left| \hat{H} \right| \phi \rangle$$

$$= \frac{n^2 h^2}{8mL^2} \cdot \sqrt{\frac{2}{L}}$$

so

$$E_\phi = \frac{\frac{n^2 h^2}{8mL^2} \cdot \sqrt{\frac{2}{L}}}{\sqrt{\frac{2}{L}}}$$

so

$$E_\phi = \frac{n^2 h^2}{8mL^2}$$

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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CHAPTER OVERVIEW

7: 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.

7.1: Perturbation Theory and the Variational Method for Helium

7.2: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

7.3: An Electron has an Intrinsic Spin Angular Momentum

7.4: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

7.5: Hartree-Fock Calculations Give Good Agreement with Experimental Data

7.E: Multielectron Atoms (Exercises)

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7.1: 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.

7.1.1: 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 $\hat{H}^1$.

$$\hat{H} = \hat{H}^0 + \hat{H}^1 \tag{7.1.1}$$

The Hamilonian for the helium atom (in atomic units) is:

$$\hat{H}^0 = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}}_{\text{H atom Hamiltonian}} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}}_{\text{H atom Hamiltonian}} \tag{7.1.2}$$

$$\hat{H}^1 = \frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \tag{7.1.3}$$

The expression for the first-order correction to the energy is

$$\begin{aligned} E^1 &= \langle \psi^0 \left| \hat{H}^1 \right| \psi^0 \rangle \\ &= \int \psi^{0*} \hat{H}^1 \psi^0 \, d\tau \end{aligned}$$

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 7.1.2) 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

$$E^1 = \iint \varphi_{1s}(r_1)\varphi_{1s}(r_2)\frac{1}{r_{12}}\varphi_{1s}(r_1)\varphi_{1s}(r_2)\, d\tau_1 d\tau_2 \tag{7.1.4}$$

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

$$E_{approx2} = E^0 + E^1 = -74.8eV \tag{7.1.5}$$

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}).

7.1.2: 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.

$$E_{trial} = \frac{\langle \psi_{trial} \left| \hat{H} \right| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{7.1.6}$$

$$= \frac{\int_0^\infty \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int_0^\infty \psi^2_{trial}\, d\tau} \tag{7.1.7}$$

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.

7.1.2.1: Trial Wavefunction #1: Simple Orbital Approximation with One Parameter

As is clear from Equation 7.1.6, 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.

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{7.1.8}$$

$$= \exp\left[-\alpha(r_1 + r_2)\right] \tag{7.1.9}$$

The variational energy obtained after minimizing Equation 7.1.7 after substituting the trial wavefunction (Equation 7.1.9) 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

$$E_{\text{exp}} = I_1 + I_2 = -2.90372\ E_h \tag{7.1.10}$$

The deviation of energy for the optimized trial wavefunction from the experimental value is

$$\left|\frac{E_{trial}(\alpha) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.84766\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.1.11}$$

$$= 1.93\% \tag{7.1.12}$$

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.

7.1.2.2: 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.

$$\phi(r_1) = \exp(-\alpha r_1) + \exp(-\beta r_1) \tag{7.1.13}$$

Under the orbital approximation this assumption gives a trial wavefunction of the form

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{7.1.14}$$

$$= \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2) \tag{7.1.15}$$

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 7.1.7). 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 7.1.7 after substituting the trial wavefunction (Equation 7.1.15) 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 7.1.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.86035\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.1.16}$$

$$= 1.49\% \tag{7.1.17}$$

Clearly introducing some electron-electron interactions into the trial wavefunction has improved the agreement between theory and experiment (Equation 7.1.12 vs. 7.1.17).

7.1.2.3: 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 7.1.15). This yields a multi-electron wavefunction of the form,

$$|\psi(1,2)\rangle_{trial} = \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) \tag{7.1.18}$$

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 7.1.7 after substituting the trial wavefunction (Equation 7.1.18) 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 7.1.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.87566\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.1.19}$$

$$= 0.97\% \tag{7.1.20}$$

This result is within 1% of the actual ground-state energy of the helium atom.

7.1.2.4: 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.

$$|\psi_{trial}(1,2)\rangle = (\exp[-\alpha(r_1 + r_2)])\,(1 + \beta r_{12}) \tag{7.1.21}$$

In the trial multi-electron wavefunction of Equation 7.1.21, 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 7.1.7 after substituting the trial wavefunction (Equation 7.1.21) 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 7.1.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.89112\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.1.22}$$

$$= 0.43\% \tag{7.1.23}$$

This modification of the trial wavefunction has further improved the agreement between theory and experiment to within 0.5%.

7.1.2.5: 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 7.1.18) as shown here.

$$|\psi(1,2)\rangle_{trial} = [\exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)]\,[1 + \gamma r_{12}] \tag{7.1.24}$$

Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground-state energy. The variational energy obtained after minimizing Equation 7.1.7 after substituting the trial wavefunction (Equation 7.1.24) 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 7.1.10) is

$$\left|\frac{E_{trial}(\alpha,\beta,\gamma) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.90143 + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.1.25}$$

$$= 0.0789\% \tag{7.1.26}$$

Chandrasakar's wavefunction gives a result for helium that is within 0.07% of the experimental value for the ground-state energy.

7.1.3: 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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7.2: 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.

7.2.1: 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.

$$V_{\text{nuclear-electron}}(r_1) = -\frac{Z}{|\mathbf{r}-\mathbf{R}|} \tag{7.2.1}$$

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

$$\hat{H}(r_1, r_2, ...r_n) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V_{\text{nuclear-electron}}(r_i) + \sum_{i\neq j} V_{\text{electron-electron}}(r_{ij}) \tag{7.2.2}$$

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 7.2.2) 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:

$$|\psi(r_1, r_2, \cdots r_i)\rangle \tag{7.2.3}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms.

7.2.2: 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 7.2.1) 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 7.2.3 can be expanded as a product of single-electron wavefunctions (i.e., orbitals)

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\rangle \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ldots\psi_N(\mathbf{r}_N)$$

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:

   $$KE = \langle\phi_j\left|\frac{-\hbar^2}{2m}\nabla^2\right|\phi_j\rangle$$

2. **Nuclear-Electron Coulombic Attraction Energy:** Coulombic attraction energy with the nucleus of charge Z:

   $$\langle\phi_j\left|\frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|}\right|\phi_j\rangle$$

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

   $$\sum_{j\neq k}\langle\phi_j(r)\phi_k(r')\left|\frac{e^2}{|r-r'|}\right|\phi_j(r)\phi_k(r')\rangle. \tag{7.2.4}$$

The Dirac notation $\langle\phi_j(r)\phi_k(r')\left|\frac{e^2}{|r-r'|}\right|\phi_j(r)\phi_k(r')\rangle$ 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:

$$\epsilon_J = \langle\phi_j\left|\frac{-\hbar^2}{2m}\nabla^2\right|\phi_j\rangle + \langle\phi_j\left|\frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|}\right|\phi_j\rangle + \sum_{j\neq k}\langle\phi_j(r)\phi_k(r')\left|\frac{e^2}{|r-r'|}\right|\phi_j(r)\phi_k(r')\rangle.$$

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.

7.2.3: 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).

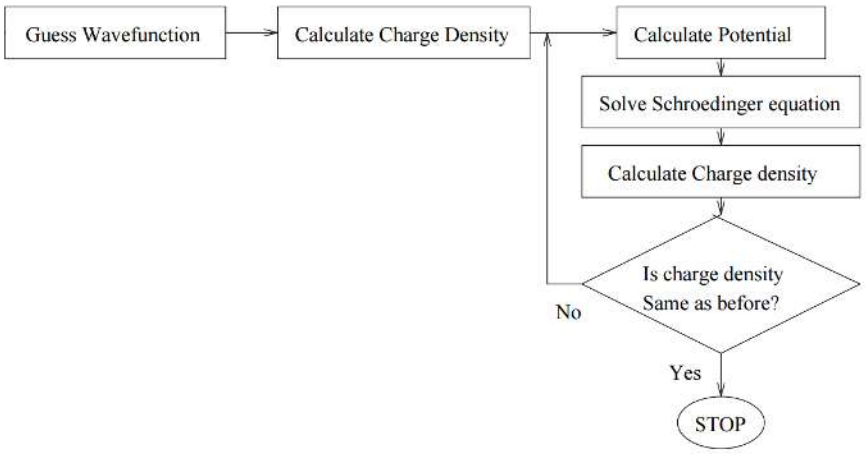


Figure 8.3.1 : Algorithm for Self-consistent field theory.

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

$$|\psi(1,2,\ldots,6)\rangle = |\psi_{1s}(1)\psi_{1s}(2)\psi_{2s}(3)\ldots\psi_{1p}(6)\rangle. \tag{7.2.5}$$

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).

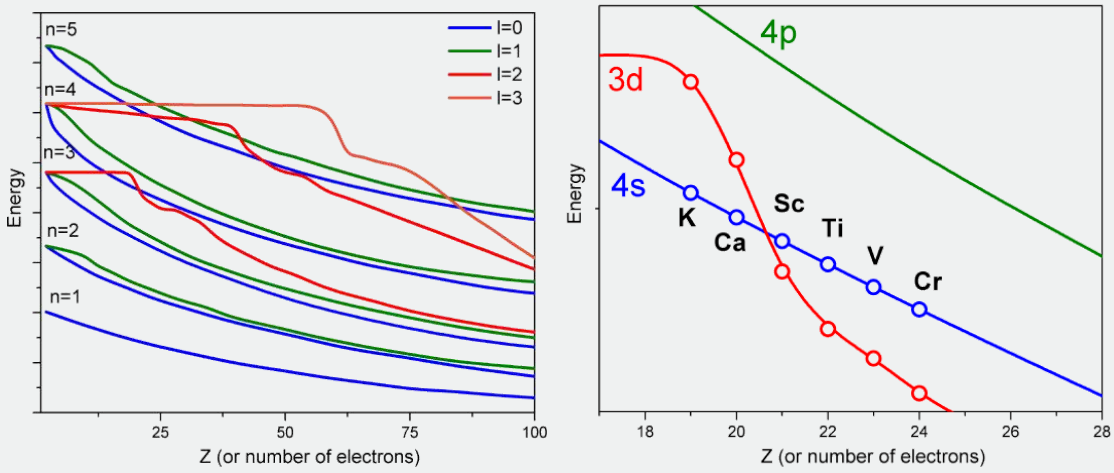


Figure 8.3.2 : Energies of Atomic Orbitals as Functions of the number of electrons in Neutral Atoms. (CC BY 4.0; Delmar Larsen).

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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7.3: 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).

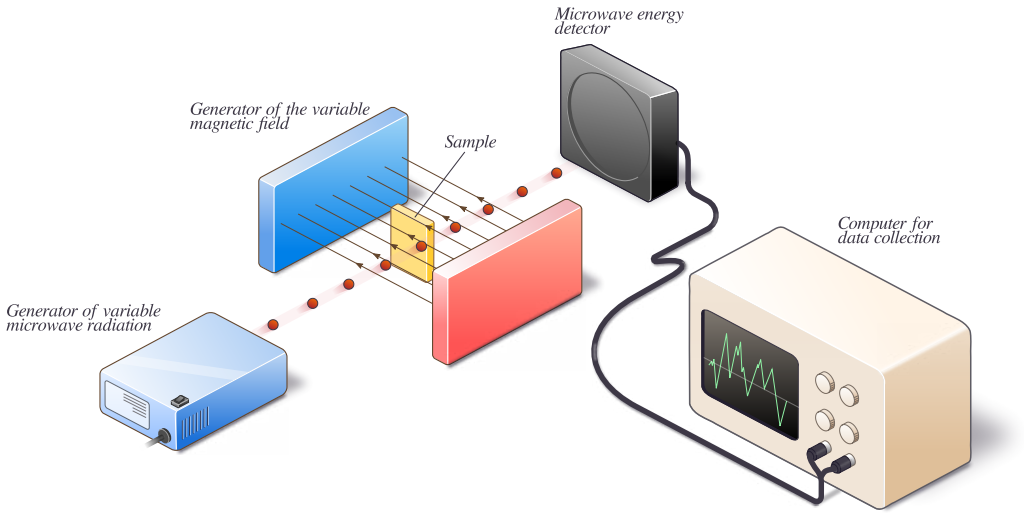


Figure 8.4.1 : Schematic diagram of a microwave spectrometer with the sample in a variable magnetic field. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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.

7.3.1: 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, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{7.3.1}$$

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:

$$\langle E \rangle = E_n + \frac{e\hbar B_z m_l}{2m_e} \tag{7.3.2}$$

$$= E_n + \mu_B B_z m_l \tag{7.3.3}$$

The factor

$$\frac{e\hbar}{2m_e} = -\gamma_e \hbar = \mu_B \tag{7.3.4}$$

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 7.3.3 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).

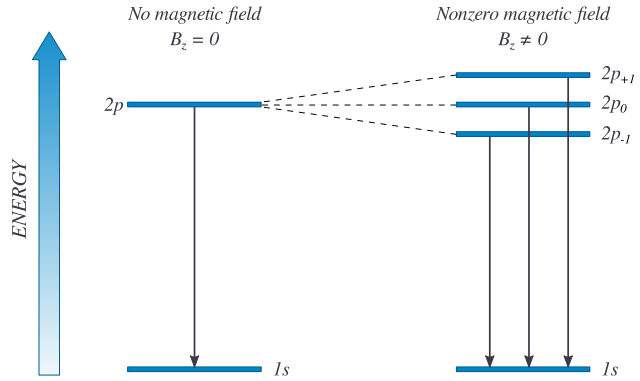


Figure 8.4.2 : The Zeeman effect for the $2s \rightarrow 1s$ transition. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field. (CC BY-NC; Ümit Kaya 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.

7.3.2: 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).

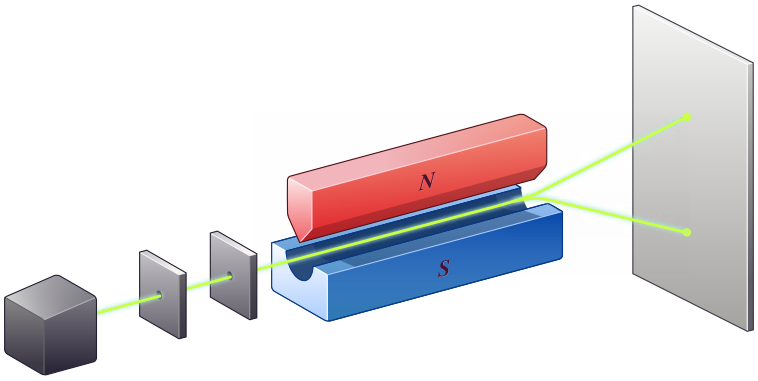


Figure 8.4.2 : Stern–Gerlach experiment: silver atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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.

7.3.3: 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 $\boldsymbol{S}$ by analogy with the orbital angular momentum $\boldsymbol{L}$. 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

$$\hat{L}^2 \left| Y_l^{m_l} \right\rangle = l(l+1)\hbar^2 \left| Y_l^{m_l} \right\rangle$$

so by analogy for the spin states, we must have

$$\hat{S}^2 \left| \sigma_s^{m_s} \right\rangle = s(s+1)\hbar^2 \left| \sigma_s^{m_s} \right\rangle$$

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

$$\hat{L}_z \left| Y_l^{m_l} \right\rangle = m_l\hbar \left| Y_l^{m_l} \right\rangle$$

so by analogy, we must have a similar projection for the spin angular momentum:

$$\hat{S}_z \left| \sigma_s^{m_s} \right\rangle = m_s\hbar \left| \sigma_s^{m_s} \right\rangle \tag{7.3.5}$$

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

$$\begin{aligned} m_{s,f} - m_{s,i} &= 1 \\ (+s) - (-s) &= 1 \\ 2s &= 1 \\ s &= \frac{1}{2} \end{aligned} \tag{7.3.6}$$

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 $|\beta\rangle$.

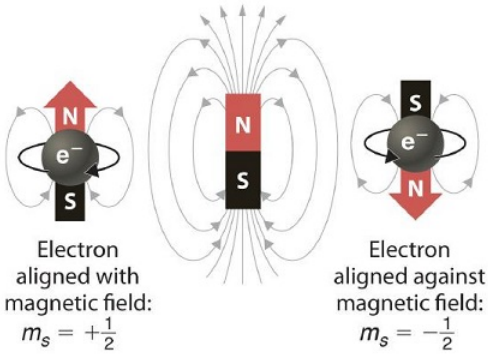


Figure 8.4.3 : Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden. (CC BY-SA-NC 3.0; Anonymous).

From Equation 7.3.5, the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s \hbar \tag{7.3.7}$$

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.

$$\int \alpha^* \alpha \, d\tau_s = \int \beta^* \beta \, d\tau_s = 1 \tag{7.3.8}$$

or in braket notation

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \tag{7.3.9}$$

and

$$\int \alpha^* \beta \, d\tau_s = \int \beta^* \alpha \, d\tau_s = 0 \tag{7.3.10}$$

or in braket notation

$$\langle\alpha|\beta\rangle = \langle\alpha|\beta\rangle = 0 \tag{7.3.11}$$

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

$$\Delta E = h\nu \tag{7.3.12}$$

$$= E_\alpha - E_\beta \tag{7.3.13}$$

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.

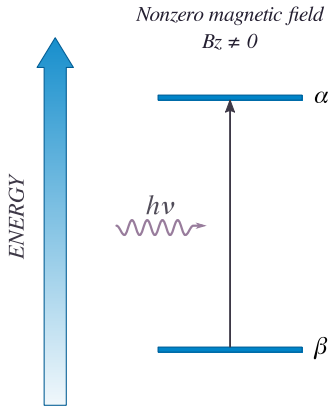


Figure 8.4.4 : Absorption of a photon to cause a transition from the β to the α state. (CC BY-NC; Ümit Kaya via LibreTexts)

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 7.3.1.

$$E_\alpha = E_{1s} - \mu_{s,\alpha} \cdot B$$

$$E_\beta = E_{1s} - \mu_{s,\beta} \cdot B$$

Substituting the two equations above into the expression for the photon (Equation 7.3.13) energy gives

$$h\nu = E_\alpha - E_\beta \tag{7.3.14}$$

$$= (E_{1s} - \mu_{s,\alpha} \cdot B) - (E_{1s} - \mu_{s,\beta} \cdot B) \tag{7.3.15}$$

$$= (\mu_{s,\beta} - \mu_{s,\alpha}) \cdot B \tag{7.3.16}$$

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 7.3.16 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 7.3.7 and rearranging Equation 7.3.16 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 7.3.4 i.e. $\gamma_s\hbar = 2.0023, \gamma_e\hbar$, or

$$\gamma_s = 2.0023\gamma_e \tag{7.3.17}$$

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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7.4: 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.

7.4.1: 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

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = \psi(\mathbf{r}_2, \mathbf{r}_1)^*\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{7.4.1}$$

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 7.4.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{7.4.2}$$

so that

$$\left(e^{-i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right)\left(e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{7.4.3}$$

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.,

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \tag{7.4.4}$$

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:

$$\hat{P}_{12}\,|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \pm|\,\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{7.4.5}$$

Bosons and femions

Physical solutions must be eigenfunctions of $\hat{P}_{12}$ (i.e., $\hat{H}$ and $\hat{P}_{12}$ commute). Moveover, Equation 7.4.5 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

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \cdots r_i)\rangle \approx \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\cdots\varphi_i(r_i) \tag{7.4.6}$$

? 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

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.

7.4.2: 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 7.4.6 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

$$|\psi^-\rangle = \frac{1}{\sqrt{2}}\Big|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{7.4.7}$$

and symmetric combination

$$|\psi^+\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle + C_{aa}\,|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle + C_{bb}|\,\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{7.4.8}$$

where the C_{ab} terms are expansion and normalization parameters.

> *Note that the antisymmetric combination (Equation 7.4.7) **cannot** include terms where both particles are in the same state (spin-orbital), but there are three possibilities for the symmetric state (Equation 7.4.8).*

Although any linear combinations of C_{ab}, C_{bb}, and C_{aa} in Equation 7.4.8 is possible, there are three limiting expressions for possible symmetric combinations:

$$|\psi_1^{+i}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{7.4.9}$$

$$|\psi_2^{+i}\rangle = C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle \tag{7.4.10}$$

$$|\psi_3^{+i}\rangle = C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{7.4.11}$$

If $\varphi_a(\mathbf{r}_1) = \varphi_a(\mathbf{r}_2)$, then $|\varphi^{-i}\rangle = \mathbf{0}$. Thus there is no possible antisymmetric combination involving electrons in the same state (spin-orbit). This is the **Pauli exclusion principle**.

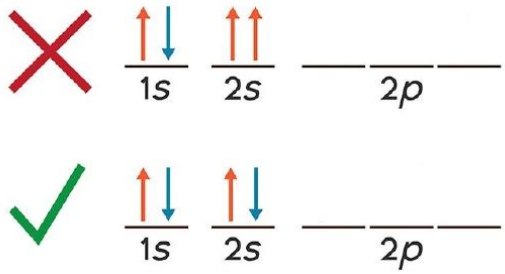


Figure 8.5.1 : The 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, since each electrons is described by a specific spin-orbital and each orbital (spatial) can hold either an α or a β electron (i.e., they must have opposite spins). Otherwise they will have the same 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 7.4.7), 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.*

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7.5: 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.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) \tag{7.5.1}$$

which clearly cannot be satisfied by the multi-electron wavefunctions of the form used in the Hartree Approximation, i.e., the orbital approximation (Equation 7.5.2).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_N(\mathbf{r}_N) \tag{7.5.2}$$

This indistinguishability condition can be satisfied by forming a Slater determinant of single-particle orbitals

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N}} |\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\dots\psi(\mathbf{r}_N)| \tag{7.5.3}$$

This decouples the electrons resulting in N single-particle **Hartree-Fock** equations:

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})}_{\text{kinetic energy}} + \underbrace{V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{electron-nucleus potential}} + \underbrace{V_{electron}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{Hartree Term}} - \sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}). \tag{7.5.4}$$

As with the *Hartree equations*, the first term is the kinetic energy of the ith electron

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})$$

and the second term is the electron-nucleus potential between the ith 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 ith electron and the **average** charge distribution of the other $N-1$ electrons.

$$V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) = J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr' \tag{7.5.5}$$

These three terms are identical to Hartree Equations with the product wavefunction ansatz (i.e., orbital approximation). The fourth term of Equation 7.5.4 is not in the Hartree Equations:

$$\sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

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 7.5.3). 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 7.5.4 can be recast as series of Schrödinger-like equations:

$$\hat{F}\left|\varphi_i\right\rangle = \epsilon_i\left|\varphi_i\right\rangle \tag{7.5.6}$$

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 7.5.6. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving Equation 7.5.6 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

$$\begin{aligned}\hat{F} &= \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \\ &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)\end{aligned} \tag{7.5.7}$$

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 7.5.7) 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.

7.5.1: 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

7.5.2: 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)

$$E_{N-1} - E_N = -\epsilon_k \tag{7.5.8}$$

- and for electron attachment (electron affinities)

$$E_N - E_{N+1} = -\epsilon_k. \tag{7.5.9}$$

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.

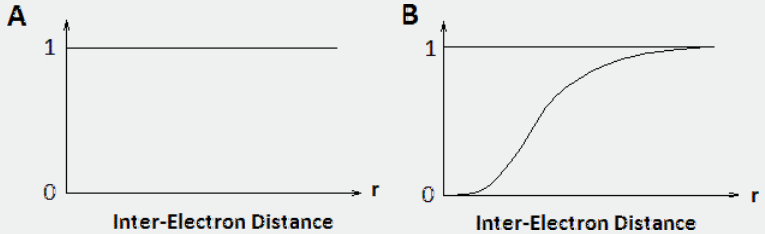


Figure 8.7.2 : Normalized Conditional Probability for from electron-electron interactions (excluding coulomb effects) in (A) the Hartree approximation and (B) the Hartree-Fock approximation.

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).

7.5.3: 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 7.5.8) and Electron Affinities (Equation 7.5.9) 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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7.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:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1dr_2d\sigma_1d\sigma_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1dr_2d\sigma_1d\sigma_2}$$

can be rewritten as:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1dr_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1dr_2}$$

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:

$$\psi_{ColumnSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

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 $^3P_0$ 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 $^3P_2$

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 configuration np^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 and M_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

$$J = (L + S), (L + S - 1), (L + S - 2), \ldots\ldots\ldots, (|L + S|),$$

The final results given the term symbols below:

$^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

($\boldsymbol{L}$ + $\boldsymbol{S}$) ($\boldsymbol{L}$ + $\boldsymbol{S}$ - 1) (|$\boldsymbol{L}$ - $\boldsymbol{S}$|) (|$\boldsymbol{L}$ + $\boldsymbol{S}$|)

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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CHAPTER OVERVIEW

8: 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.

8.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

8.2: The H_2^+ Prototypical Species

8.3: The Overlap Integral

8.4: Chemical Bond Stability

8.5: Bonding and Antibonding Orbitals

8.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital

8.7: Molecular Orbitals Can Be Ordered According to Their Energies

8.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

8.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle

8.10: SCF-LCAO-MO Wavefunctions are Molecular Orbitals formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently

8.11: Most Molecules Have Excited Electronic States

8.E: Chemical Bond in Diatomic Molecules (Exercises)

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8.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

9.01: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

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8.2: 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 $\mathbf{H_2^+}$.

8.2.1: The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely $\mathbf{H_2^+}$. 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 $\mathbf{H_2^+}$ 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.

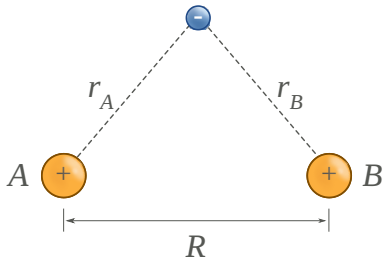


Figure 9.2.1 : Hydrogen molecular ion $\mathbf{H_2^+}$ with fixed nuclei $\boldsymbol{A}$ and $\boldsymbol{B}$, internuclear distance $\boldsymbol{R}$. (CC BY-NC; Ümit Kaya via LibreTexts)

The electronic Hamiltonian for $\mathbf{H_2^+}$ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{8.2.1}$$

where r_A and r_B are the distances electron from the $\boldsymbol{A}$ and $\boldsymbol{B}$ hydrogen nuclei, respectively and $\boldsymbol{R}$ is the distance between the two protons.

Although the Schrödinger equation for $\mathbf{H_2^+}$ 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.

8.2.2: 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 $\boldsymbol{A}$ or $\boldsymbol{B}$, 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

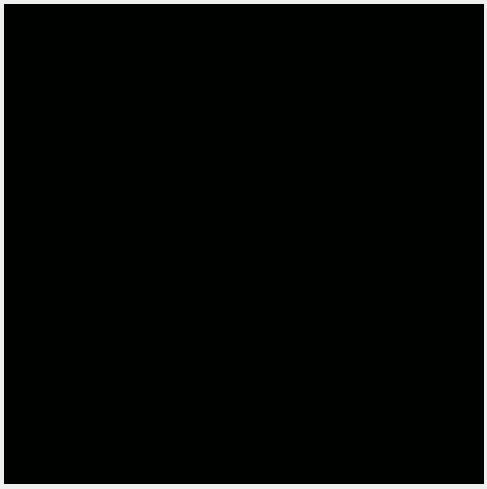
$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{8.2.2}$$

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 8.2.2 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 8.2.2. 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:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{8.2.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{8.2.4}$$

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.

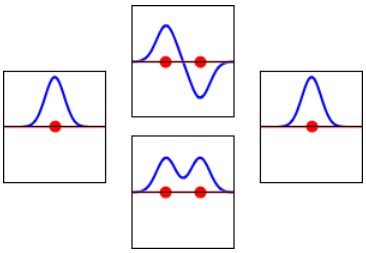


Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots 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")
- Rudolf Winter (Aberystwyth University)

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8.3: 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:

$$\underbrace{|\psi_+\rangle = C_+(1s_A + 1s_B)}_{\text{bonding molecular orbital}} \tag{8.3.1}$$

and

$$\underbrace{|\psi_-\rangle = C_-(1s_A - 1s_B)}_{\text{antibonding molecular orbital}} \tag{8.3.2}$$

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:

$$\int \psi_\pm^* \psi_\pm d\tau = \langle \psi_\pm | \psi_\pm \rangle = 1 \tag{8.3.3}$$

$$\langle C_\pm(1s_A \pm 1s_B) | C_\pm(1s_A \pm 1s_B) \rangle = 1 \tag{8.3.4}$$

$$|C_\pm|^2[\underbrace{\langle 1s_A|1s_A\rangle}_{1} + \underbrace{\langle 1s_B|1s_B\rangle}_{1} \pm \underbrace{\langle 1s_B|1s_A\rangle}_{S} \pm \underbrace{\langle 1s_A|1s_B\rangle}_{S^*}] = 1 \tag{8.3.5}$$

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.

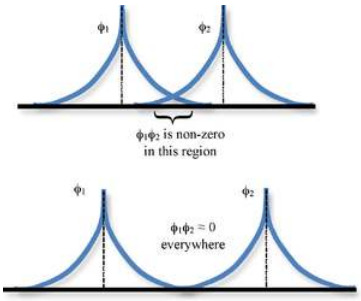


Figure 9.3.1 : The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close 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

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle = S \tag{8.3.6}$$

Equation 8.3.5 becomes

$$|C_{\pm}|^2 (2 \pm 2S) = 1 \tag{8.3.7}$$

The solution to Equation 8.3.7 is given by

$$C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} \tag{8.3.8}$$

Hence, the normalized molecular orbitals in Equations 8.3.1 and 8.3.1 are

$$|\psi_+\rangle = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \tag{8.3.9}$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \tag{8.3.10}$$

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:

$$S(R) = \langle 1s_A | 1s_B \rangle \tag{8.3.11}$$

$$= e^{-R/a_o} \left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2} \right) \tag{8.3.12}$$

The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

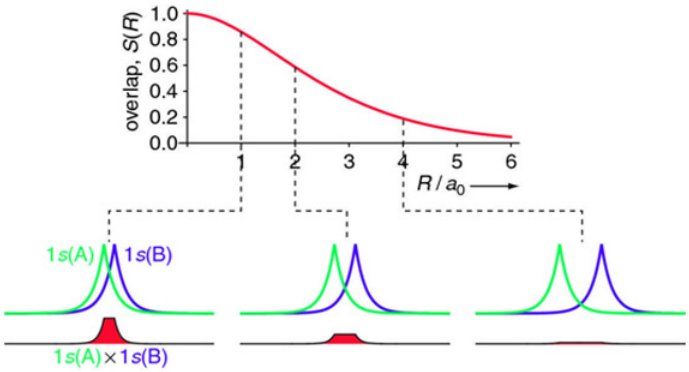


Figure 9.3.2 : The overlap integral at different proton separations.

Example 9.3.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for $\mathbf{H_2^+}$ 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 8.3.9) 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 8.3.12)

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 8.3.10 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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8.4: 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 ($1s_B$):

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}}(1s_A \pm 1s_B) \tag{8.4.1}$$

The energy of these two molecular orbitals can be calculated from the expectation value integral of the Hamiltonian,

$$E_{\pm} = \left\langle \psi_{\pm} \middle| \hat{H}_{elec} \middle| \psi_{\pm} \right\rangle \tag{8.4.2}$$

which can be expanded using the expanded molecular orbital wavefunctions in Equations 8.4.1 to give

$$E_{\pm} = \frac{1}{2(1 \pm S)} \tag{8.4.3}$$

$$\left[\underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{BA}} \right]$$

where S is the overlap integral between the two atomic orbitals of the basis. The four integrals in Equation 8.4.3 can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively.

$$E_{\pm} = \frac{1}{2(1 \pm S)} [H_{AA} + H_{BB} \pm H_{AB} \pm H_{BA}] \tag{8.4.4}$$

Exercise 9.4.1

Show that Equation 8.4.2 expands to give Equation 8.4.3 within the LCAO approximation that uses a basis set of only two 1s atomic orbitals.

Answer

Here we have the wavefunction within the LCAO approximation that uses a basis set of only two 1s atomic orbitals (Equation 8.4.1).

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}} (1_{Sa} \pm 1_{Sb})$$

And our LCAO approximation is equivalent to this if we plug in the wavefunction directly.

$$E_{\pm} = \langle \psi_{\pm} \left| \hat{H} \right| \psi_{\pm} \rangle = N^2 \langle (1_{Sa} \pm 1_{Sb}) \left| \hat{H} \right| (1_{Sa} - 1_{Sb}) \rangle$$

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):

$$\langle 1_{Sa} \left| \hat{H} \right| 1_{Sa} \rangle + \langle 1_{Sb} \left| \hat{H} \right| 1_{Sb} \rangle \pm \langle 1_{Sa} \left| \hat{H} \right| 1_{Sb} \rangle \pm \langle 1_{Sb} \left| \hat{H} \right| 1_{Sa} \rangle$$

Now we can see this is now equivalent to Equation 8.4.3 if the equation above is inserted (and adding a subscript to emphasize this only applies to the electronic wavefunction):

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[\underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{BA}} \right]$$

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.

$$H_{AA} = H_{BB} \tag{8.4.5}$$

and since the wavefunctions are real

$$|A\rangle = \langle A|$$

so

$$H_{AB} = H_{BA} \tag{8.4.6}$$

These two equalities simplify Equation 8.4.4:

$$E_{\pm} = \frac{1}{1 \pm S}(H_{AA} \pm H_{AB}) \tag{8.4.7}$$

Now examine the details of H_{AA} after inserting the Hamiltonian operator for H_2^+ (Equation 9.2.1):

$$H_{AA} = \underbrace{\left\langle 1s_A \middle| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \middle| 1s_A \right\rangle}_{E_H} + \frac{e^2}{4\pi\epsilon_0 R} \cancelto{1}{\langle 1s_A | 1s_A \rangle} \underbrace{- \left\langle 1s_A \middle| \frac{e^2}{4\pi\epsilon_0 r_B} \middle| 1s_A \right\rangle}_{J_{AB}} \tag{8.4.8}$$

- 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.

J The Coulomb Integral ()

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}.

$$H_{AB} = \underbrace{\left\langle 1s_A \middle| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_B} \middle| 1s_B \right\rangle}_{E_H S} + \frac{e^2}{4\pi\epsilon_0 R} \cancelto{S}{\langle 1s_A | 1s_B \rangle} - \underbrace{\left\langle 1s_A \middle| \frac{e^2}{4\pi\epsilon_0 r_A} \middle| 1s_B \right\rangle}_{K_{AB}} \tag{8.4.9}$$

- 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.

K The Exchange Integral ()

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 8.4.8) and H_{AB} (Equation 8.4.9) and substituting into Equation 8.4.7 produces:

$$E_{\pm} = \frac{1}{1 \pm S}\left[\left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right)(1 \pm S) + J \pm K\right] \tag{8.4.10}$$

$$= E_H + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{8.4.11}$$

Equation 8.4.11 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:

$$\Delta E_{\pm} = E_{\pm} - E_H \tag{8.4.12}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{8.4.13}$$

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 8.4.7

8.4.1: 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

$$J_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_A}(r)\frac{e^2}{4\pi\epsilon_0 r_B}d\tau \tag{8.4.14}$$

$$K_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_B}(r)\frac{e^2}{4\pi\epsilon_0 r_A}d\tau \tag{8.4.15}$$

Figure 9.4.2 shows graphs of the four terms contributing to the energy of H_2^+ (Equation 8.4.13). 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.

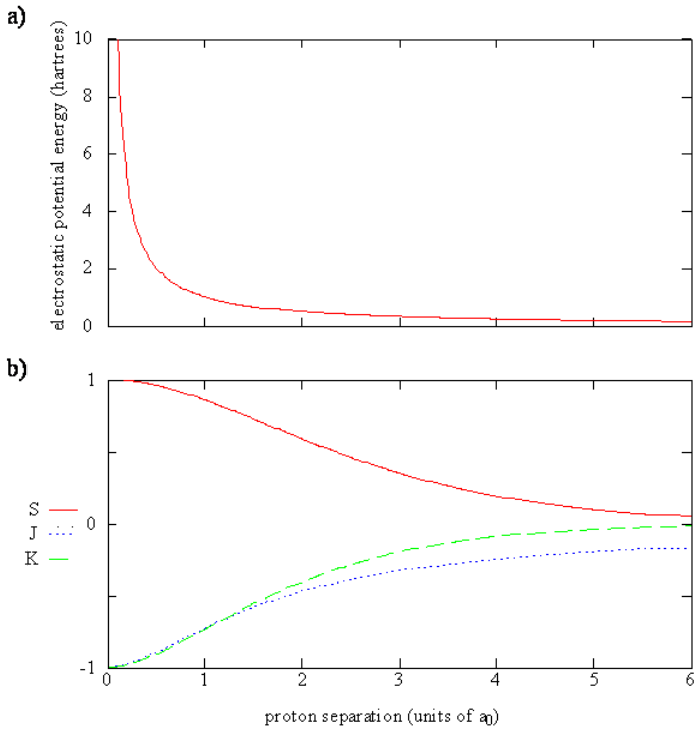


Figure 9.4.2 : (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). (b) The overlap (S), Coulomb (J), and exchange (K) integrals at different proton separations. The units for J and K are hartrees; S has no units. (CC BY-SA-NC; David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski via ChemEdDL)

Note that both J and K integrals are **negative** since all quantities in the integrands of Equation 8.4.14 and 8.4.15 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 8.4.11. 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.

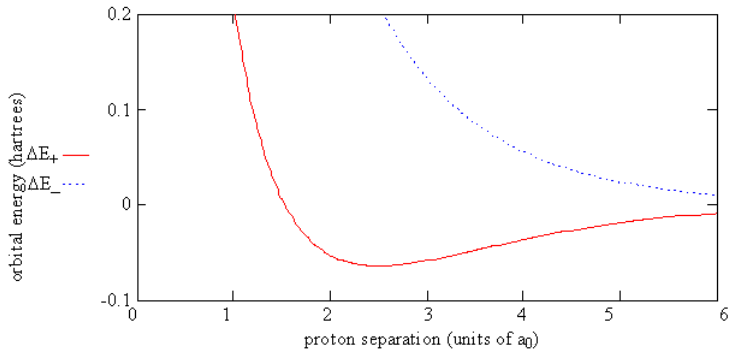


Figure 9.4.3 : Energy of the H_2^+ bonding molecular orbital ΔE_+ and the molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

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 8.4.11 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 8.4.11, 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")

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8.5: Bonding and Antibonding Orbitals

Learning Objectives

- Characterize the bonding and anti-bonding molecular orbitals in $\mathbf{H^+}$

The two molecular orbitals of the $\mathbf{H^+}$ 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 jth molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$|\psi_J\rangle = \sum_i^N c_{J,i} \Big| \phi_i \rangle \tag{8.5.1}$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 8.5.1). 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 1*s* orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 9.5.1).

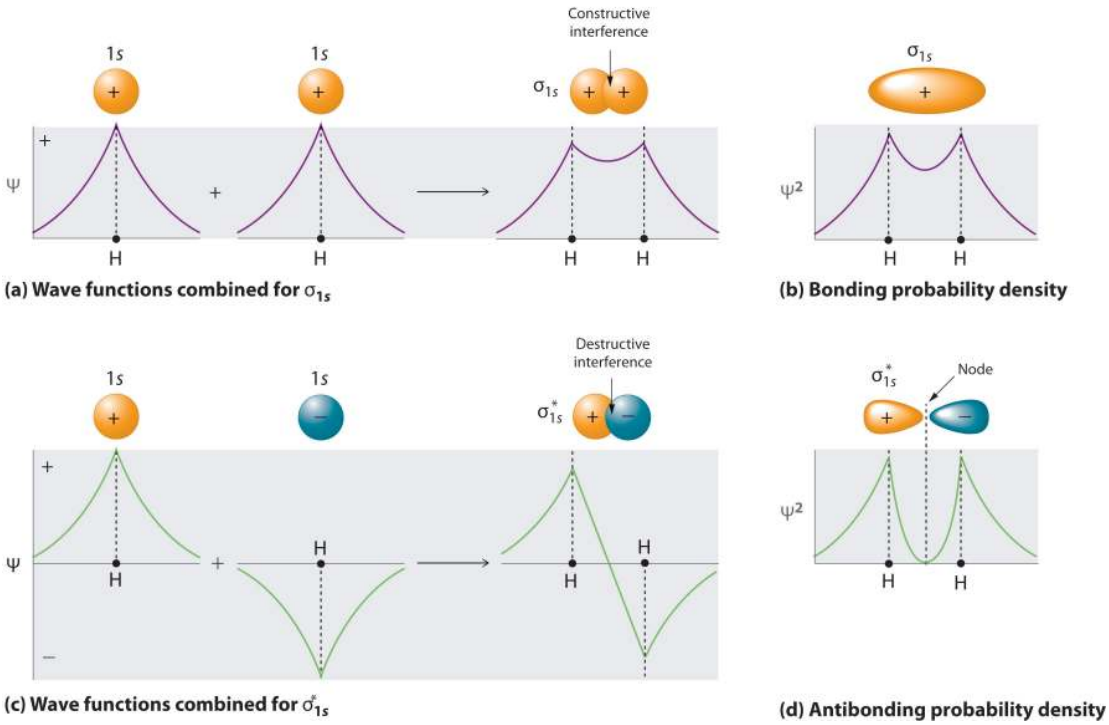


Figure 9.5.1 : Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wavefunctions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wavefunction (Ψ^2) for the bonding σ1s molecular orbital illustrates 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 1*s* denotes the atomic orbitals from which the molecular orbital was derived.

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}} \left(|1s_A\rangle + |1s_B\rangle\right) \tag{8.5.2}$$

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:

$$|\sigma^*_{1s}\rangle = \frac{1}{\sqrt{2(1-S)}}\left(|1s_A\rangle - |1s_B\rangle\right) \tag{8.5.3}$$

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 σ^*_{1s} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ^*_{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 1*s* atomic orbitals. Conversely, electrons in the σ^*_{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 1*s* atomic orbitals. Consequently, the σ^*_{1s} molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the σ^*_{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

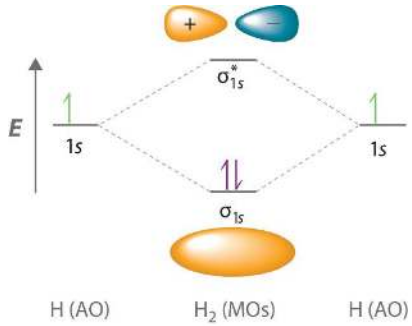


Figure 9.5.2 : Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (at 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).*

8.5.1: 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,

$$E_J = \frac{\left\langle \psi_J \middle| \hat{H}_{elec} \middle| \psi_J \right\rangle}{\langle \psi_J | \psi_J \rangle} \tag{8.5.4}$$

This is the variational energy using $|\psi_J\rangle$ as the trail wavefunction. After substituting the LCAO expansion for $|\psi_J\rangle$ (Equation 8.5.1) into the energy expression of Equation 8.5.4 results in:

$$E_J = \frac{\left\langle \sum_i c_{J,i}^* \phi_i \middle| \hat{H}_{elec} \middle| \sum_j c_{J,i} \phi_j \right\rangle}{\left\langle \sum_i c_{J,i}^* \phi_j \middle| \sum_j c_{J,j} \phi_j \right\rangle} \tag{8.5.5}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle}{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \phi_j \rangle} \tag{8.5.6}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} H_{ij}}{\sum_{i,j} c_{J,i}^* c_{J,j} S_{ij}} \tag{8.5.7}$$

where H_{ij} is the Hamiltonian matrix element.

$$H_{ij} = \langle \phi_i \left| \hat{H}_{elec} \right| \phi_j \rangle$$

Following the variational theorem, to determine the coefficients of the LCAO expansion c_i, we need to minimize E_J

$$\frac{\partial E_J}{\partial c_k} = 0 \tag{8.5.8}$$

for all k. This requires solving N linear equations to hold true (where N is the number of atomic orbitals in the basis)

$$\sum_{i=1}^{N} c_i (H_{ki} - E S_{ki}) = 0 \tag{8.5.9}$$

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

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{8.5.10}$$

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

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{8.5.11}$$

Solving these secular equations with N different atomic orbitals in the expansion (Equation 8.5.1) requires finding the N roots of an N order polynomial.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \ldots \\ \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{8.5.12}$$

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 8.5.1), 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 8.5.1), 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

$$|\psi_J\rangle = c_{J,1}1s_A + c_{J,2}1s_B + c_{J,3}2s_A + c_{J,4}2s_B + c_{J,5}2p_{z,A} + c_{J,6}2p_{z,B} \tag{8.5.13}$$

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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8.6: 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.

$$|\psi_i\rangle = \sum_j c_{ij}\varphi_j \tag{8.6.1}$$

where

- j is the index for the jth basis function (e.g., atomic orbital)
- i is the ith molecular orbitals and
- c_{ij} is the expansion coefficient of the jth basis function for the ith 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,

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1)\\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2)\end{vmatrix} \tag{8.6.2}$$

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 .

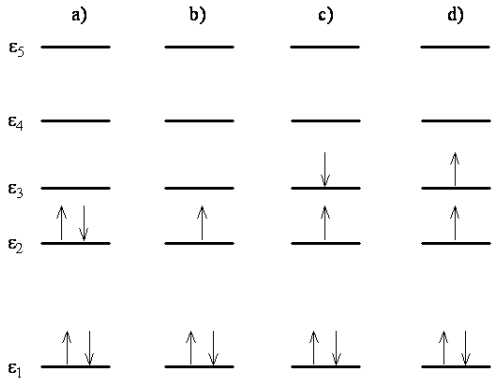


Figure 9.6.1 : a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

8.6.1: 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

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \tag{8.6.3}$$

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

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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8.7: 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.

8.7.1: 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.

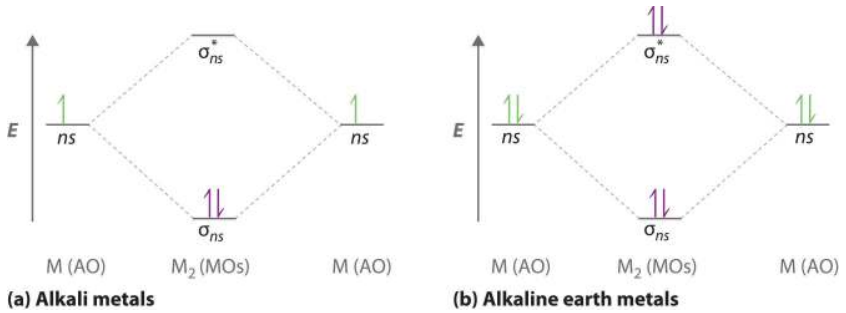


Figure 9.7.1 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, 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 **8.7.1*b***, 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.

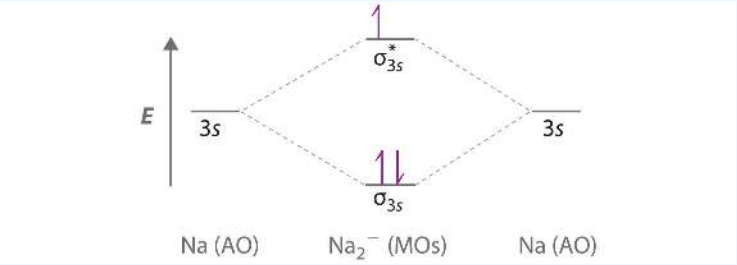
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

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 1*s* 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 $(\sigma_{3s})^2 (\sigma^*_{3s})^1$ 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

Ca_2^+ has a $(\sigma_{4s})^2 (\sigma^*_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

8.7.2: 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.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{8.7.1}$$

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):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{8.7.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{8.7.3}$$

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).

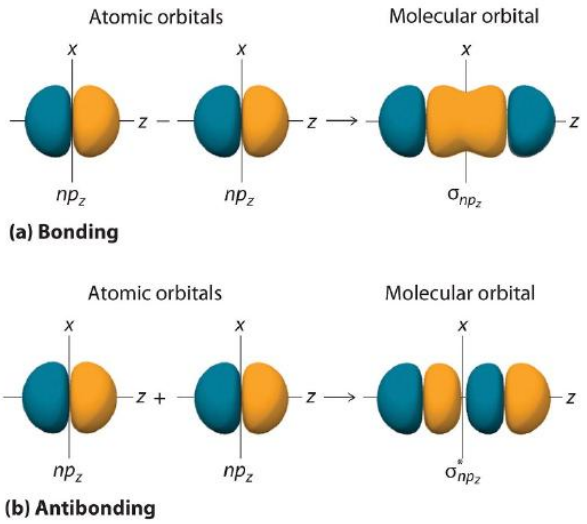


Figure 9.7.2 : Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +z to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, 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..

$$\pi_{np_z} = np_x\,(A) + np_x\,(B) \tag{8.7.4}$$

$$\pi^*_{np_z} = np_x\,(A) - np_x\,(B) \tag{8.7.5}$$

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 $\pi^*_{np_y}$ 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_z} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^*_{np_z}$ and $\pi^*_{np_y}$ molecular orbitals.

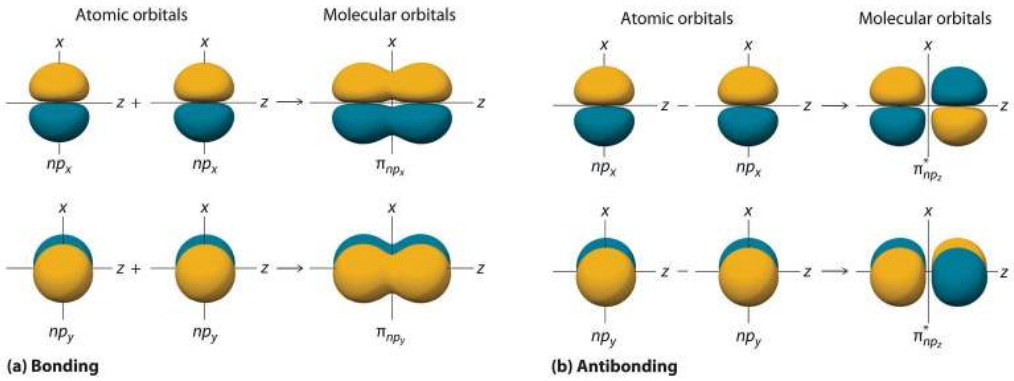


Figure 9.7.3 : Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In 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).

8.7.3: 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.

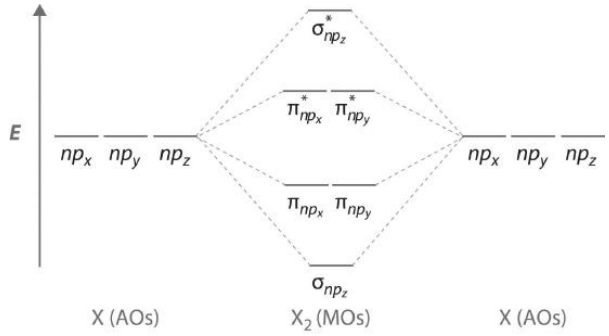


Figure 9.7.4 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals 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 **8.7.5***a*; 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 $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ 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.

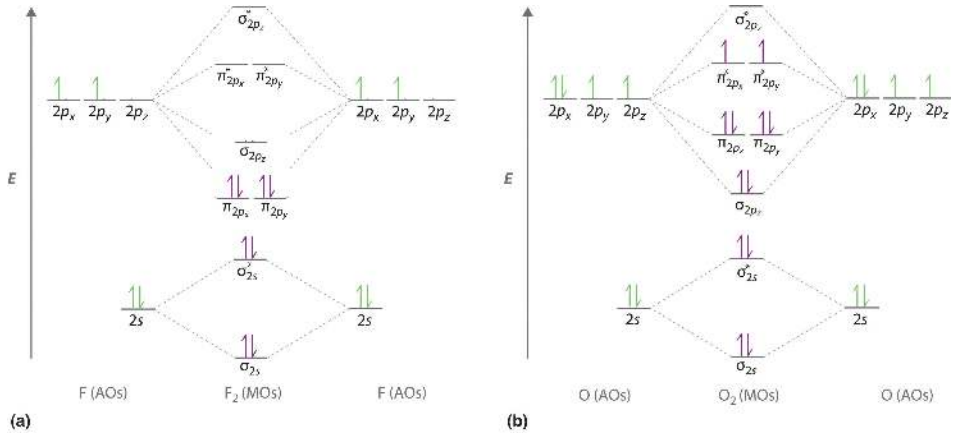


Figure 9.7.5 : Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_x}, \pi^*_{np_y}\right)$ 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 $\pi^*_{np_x}$ and $\pi^*_{np_y}$ 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.

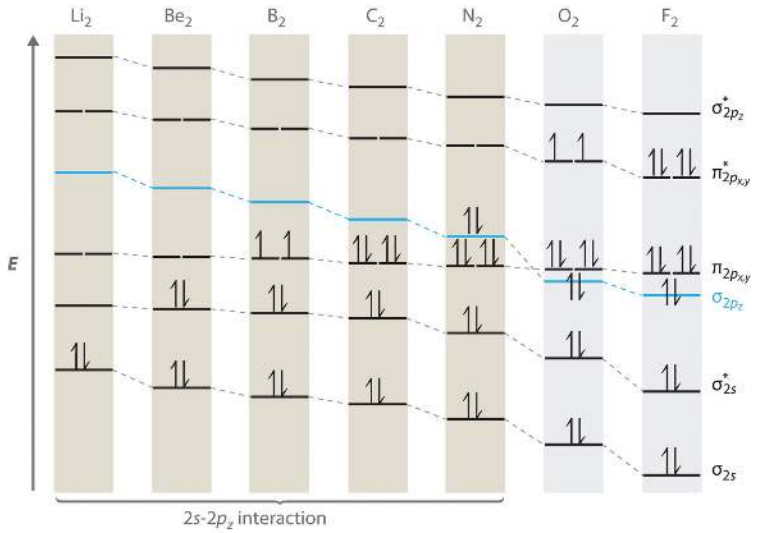


Figure 9.7.6 : Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For 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

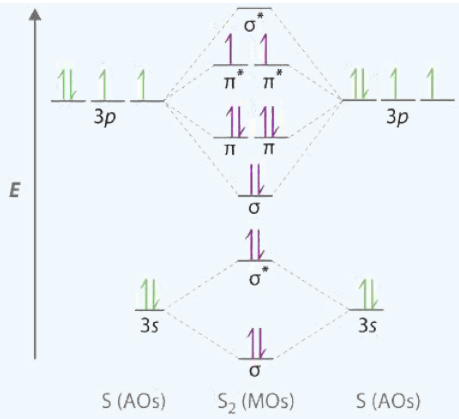
Strategy:

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 $[Ne]3s^23p^4$ 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 $\pi_{3p_{z,y}}$ 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 $\pi_{3p_{z,y}}$ 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_z} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_z}$ and $\pi^*_{3p_y}$ 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 $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi^*_{3p_{x,y}})^2$ 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

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi^*_{2p_{x,y}})^4$ bond order of 1; no unpaired electrons

8.7.4: 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.

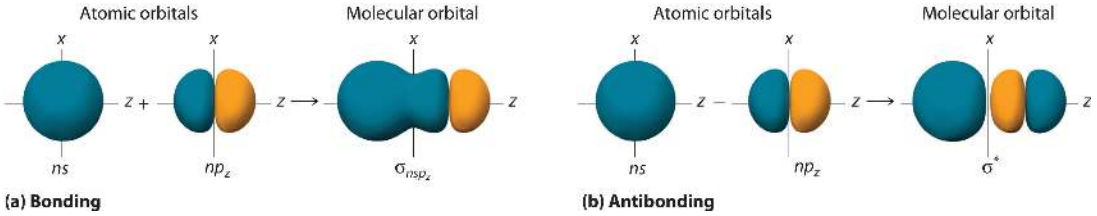


Figure 9.7.7 : Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

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8.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

Learning Objectives

- Using bond order as a metric for the existance of molecules

8.8.1: 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:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{8.8.1}$$

To calculate the bond order of H_2, we know that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\text{bond order} = \frac{2-0}{2} = 1 \tag{8.8.2}$$

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.

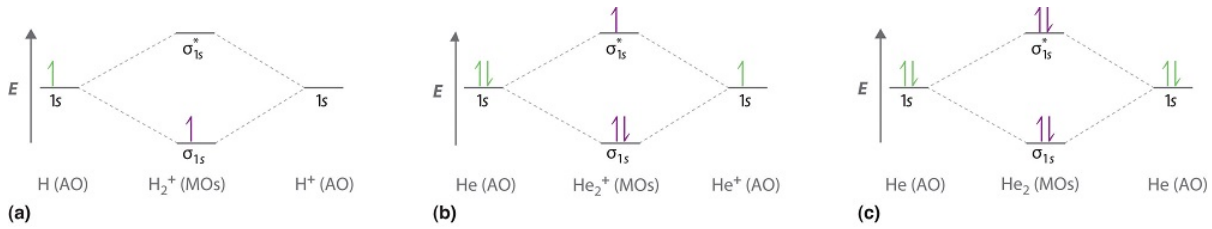


Figure 9.8.1 : Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. (CC BY-SA-NC; anonymous)

Figure 8.8.1*a* 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 8.8.1)

$$\text{bond order} = \frac{1-0}{2} = 1/2$$

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^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0	5,500	4.6×10^{-5}

Figure 8.8.1*b* is the molecular orbital energy-level diagram for $\mathbf{He_2^{2+}}$. 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 σ^*_{1s} antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration. This electron configuration gives a bond order (via Equation 8.8.1) 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).

He_2^{2+} ✔ Example 9.8.1 : The ion

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the $\mathbf{He_2^{2+}}$ ion.

Given: chemical species

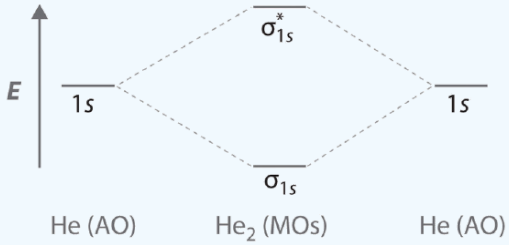
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

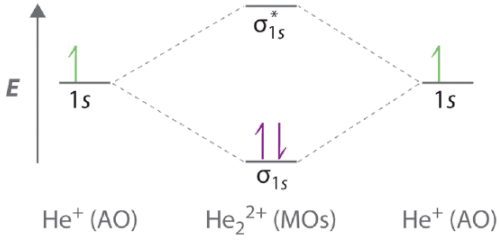
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning 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 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ^*_{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 1*s* 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 8.8.1)

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

H_2^{2-}? Exercise 9.8.1 : The Ion

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

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.

8.8.2: The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure 8.8.1*c* is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ_{1s}^* antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration, with a predicted bond order (via Equation 8.8.1) of

$$\text{bond order}=\frac{2-2}{2}=0 \tag{8.8.3}$$

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 σ_{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 σ_{1s}^* molecular orbital:

$$\Delta E_\pm = E_\pm - E_H \tag{8.8.4}$$

$$= \frac{e^2}{4\pi\epsilon_0 R}+\frac{J\pm K}{1\pm S} \tag{8.8.5}$$

Hence, the anti-bonding σ_{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 σ_{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 σ_{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 8.8.3). 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, $\mathbf{He_2}$ 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).

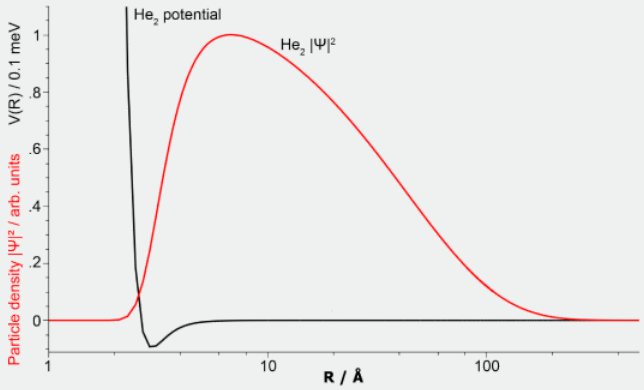


Figure 9.8.2 : The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i..e, tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses ($\mathbf{He_2}$ 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)

8.8.3: 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.

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8.9: 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:

$$|\psi\rangle = |1\sigma^1\alpha^1\rangle|1\sigma^2\beta^2\rangle \tag{8.9.1}$$

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!

$$\hat{p}_{12}|\psi\rangle = |1\sigma^2\alpha^2\rangle|1\sigma^1\beta^1\rangle \neq -|\psi\rangle. \tag{8.9.2}$$

Instead, we can take a linear combination of spin functions to make a new wavefunction:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle - |1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle\right) \tag{8.9.3}$$

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:

$$\begin{aligned}\hat{p}_{12}|\psi\rangle &= \frac{1}{\sqrt{2}}\left(|1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle - |1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle\right)\\ &= -\frac{1}{\sqrt{2}}\left(|1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle - |1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle\right)\\ &= -|\psi\rangle.\end{aligned} \tag{8.9.4}$$

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

$$|\psi\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} |1\sigma^1\alpha^1\rangle & |1\sigma^1\beta^1\rangle \\ |1\sigma^2\alpha^2\rangle & |1\sigma^2\beta^2\rangle \end{vmatrix}, \tag{8.9.5}$$

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):

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\phi_1^1\alpha^1\rangle & |\phi_1^1\beta^1\rangle & |\phi_2^1\alpha^1\rangle & |\phi_2^1\beta^1\rangle & \cdots & |\phi_{N/2}^1\alpha^1\rangle & |\phi_{N/2}^1\beta^1\rangle \\ |\phi_1^2\alpha^2\rangle & |\phi_1^2\beta^2\rangle & |\phi_2^2\alpha^2\rangle & |\phi_2^2\beta^2\rangle & \cdots & |\phi_{N/2}^2\alpha^2\rangle & |\phi_{N/2}^2\beta^2\rangle \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ |\phi_1^N\alpha^N\rangle & |\phi_1^N\beta^N\rangle & |\phi_2^N\alpha^N\rangle & |\phi_2^N\beta^N\rangle & \cdots & |\phi_{N/2}^N\alpha^N\rangle & |\phi_{N/2}^N\beta^N\rangle \end{vmatrix} \tag{8.9.6}$$

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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8.10: 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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8.11: Most Molecules Have Excited Electronic States

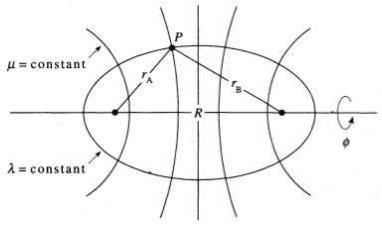
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8.E: Chemical Bond in Diatomic Molecules (Exercises)

Solutions to select questions can be found online.

8.E.1: 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.



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 → 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:

$$\begin{aligned}
S &= \frac{Z^3}{\pi} \int dr e^{-Zr_A} e^{-Zr)B} \\
&= \frac{Z^3}{\pi} \int_0^{2\pi} d\phi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu R^3/8(\lambda^2 - \mu^2) e^{-Z(r_A + r_B)} \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) e^{-ZR\lambda} \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda e^{-ZR\lambda} \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda e^{-ZR\lambda} (2\lambda^2 - 2/3) \\
&= \frac{R^3 Z^3}{2} \left[(1/ZR + 2/Z^2R^2 + 2/Z^3R^3) e^{-ZR} - 1/3ZRe^{-ZR} \right] \\
&= e^{-ZR}(1 + ZR + Z^2R^2/3)
\end{aligned}$$

8.E.2: 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

$$E_- = \frac{2E_{1s}(1 + S) + 2J - 2K}{2(1 - S)}$$

8.E.3: 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.

8.E.4: 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.

8.E.5: 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

8.E.6: 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.

8.E.7: 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.

8.E.8: 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^+

8.E.9: 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 $2\frac{1}{2}$

8.E.10: 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

8.E.11: 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?

8.E.12: 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 ν, we can find φ, which is the energy of the molecular orbital occupied by the electron being ionized.

8.E.13: 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.

8.E.14: 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

8.E.15: 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.

8.E.16: 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.

8.E.17: 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

$$^2\Sigma_g^+ \tag{8.E.1}$$

$(1\sigma_g)^2$ 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

$$^1\Sigma_g^+ \tag{8.E.2}$$

8.E.18: 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: $^3\Sigma_g^-$

8.E.19: 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) $(1\pi_g 2p_x)^1(1\pi_g 2py)^1$, 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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CHAPTER OVERVIEW

9: 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.

9.1: The Electromagnetic Spectrum
9.2: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
9.3: The Franck-Condon Principle
9.4: What Causes Molecules to Absorb UV and Visible Light
9.5: Fluorescence and Phosphorescence
9.6: Jablonski diagram
9.E: Molecular Spectroscopy (Exercises)

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9.1: 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.

9.1.1: 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.

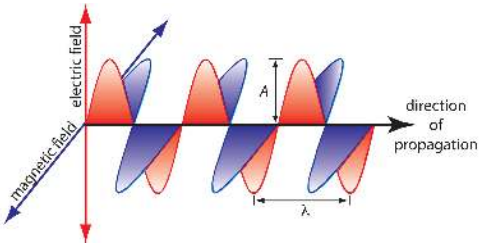


Figure 13.1.1 : Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic 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

$$A_t = A_m \sin(2\pi\nu t + \phi)$$

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.

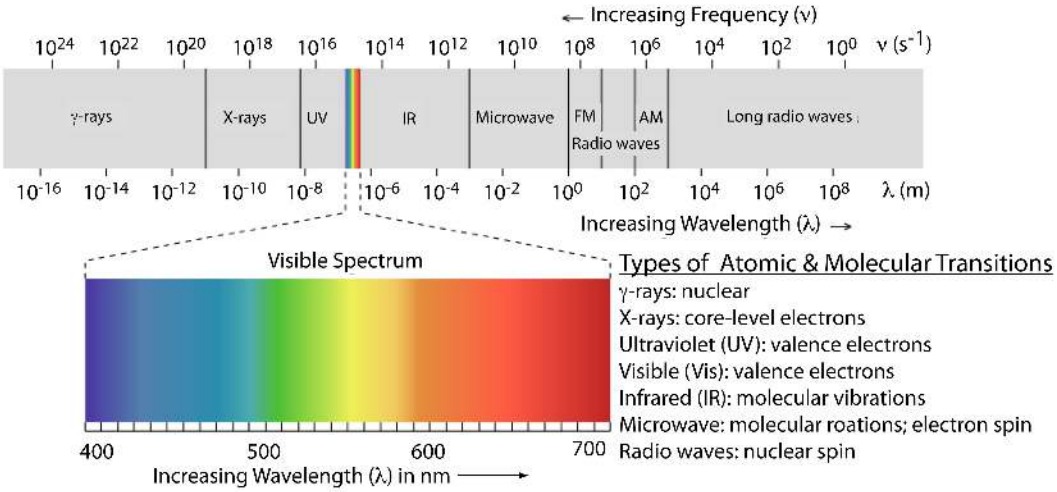


Figure 13.1.2 : The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

9.1.2: 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
	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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9.2: 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.

9.2.1: 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.

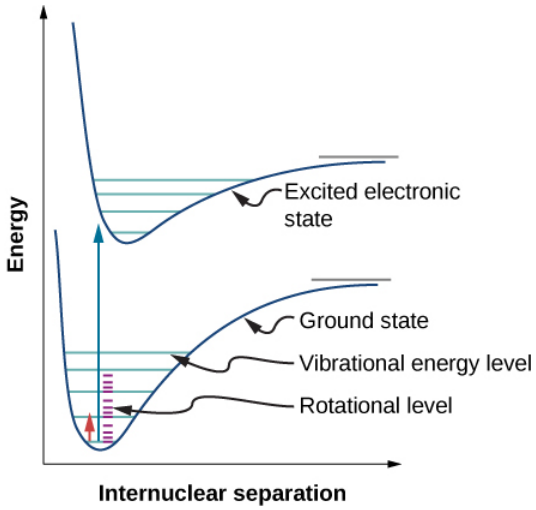


Figure **9.2.1** : Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

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:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{9.2.1}$$

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 9.2.1 can be expanded accordingly:

$$\tilde{E}_{total} = \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{9.2.2}$$

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.

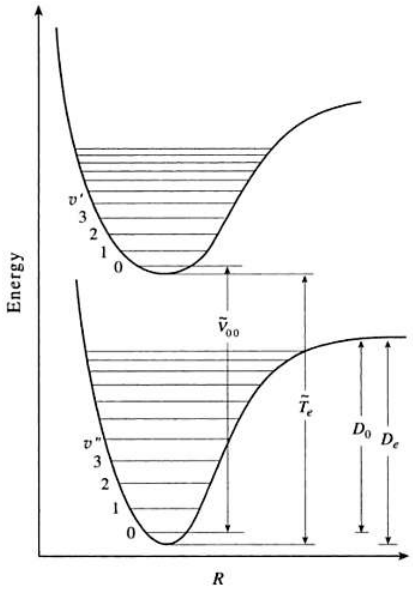


Figure **9.2.2** : As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded.

The eigenstate-to-eigenstate transitions (e.g., $\mathbf{1 \rightarrow 2}$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{9.2.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 9.2.3 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 9.2.2 can be used with Equation 9.2.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{9.2.4}$$

A common transition of importance is the $\tilde{\nu}_{00}$, which is the $\mathbf{0 \rightarrow 0}$ transition and include no vibrational change. For this case, equation 9.2.4 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.

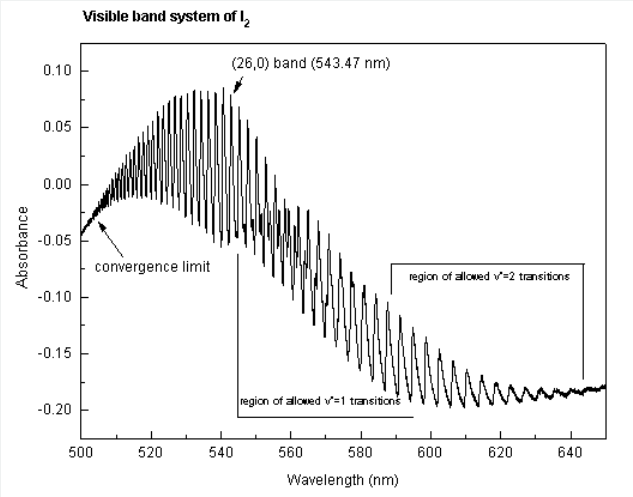
Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 9.2.4 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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9.3: 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.

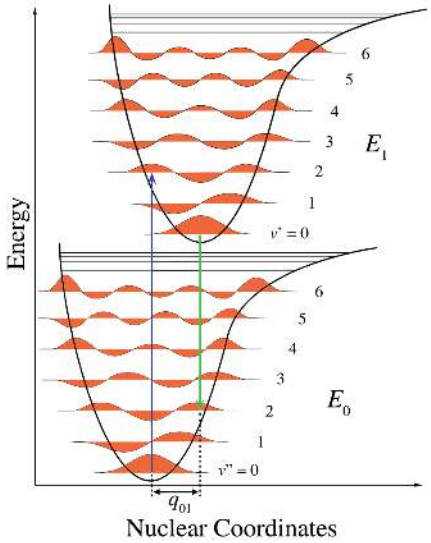


Figure **9.3.1** : Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure **9.3.1** , 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:

$$\begin{aligned} _{i\rightarrow f} &= \left|\langle \psi^*_{final} \left|\mu\right| \psi_{initial}\rangle\right|^2 \\ &= \left|\int \psi^*_{final} \mu \psi_{initial} d\tau\right|^2 \end{aligned}$$

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 **9.3.1**).

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:

$$\langle \psi^*_{total,f} \left|\hat{\mu}\right| \psi_{total,i}\rangle = \langle \psi^*_{nuc,f} \left|\langle \psi^*_{el,f} \left|\mu\right| \psi_{el,i}\rangle\right| \psi_{nuc,i}\rangle \tag{9.3.1}$$

$$= \underbrace{\langle \psi^*_{nuc,f} | \psi_{nuc,i}\rangle}_{\text{nuclear overlap}} \langle \psi^*_{el,f} \left|\mu\right| \psi_{el,i}\rangle \tag{9.3.2}$$

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.

9.3.1: 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

$$|\psi(R)\rangle = \left|\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2}\right\rangle$$

The zero-point wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \left|\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-Q_e)^2/2}\right\rangle$$

where

- $\alpha = \frac{\sqrt{mk}}{\hbar}$
- 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

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{9.3.3}$$

The exponent in Equation 9.3.3 can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{9.3.4}$$

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 9.3.4 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

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{9.3.5}$$

this integral has been solved already, from a table of integrals, Equation 9.3.5 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}.

9.3.2: 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 $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{9.3.6}$$

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 9.3.6) 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.

9.3.3: 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.

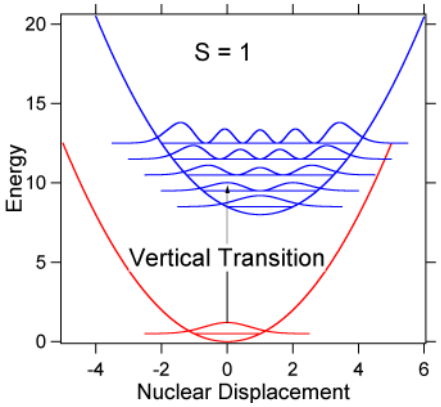


Figure **9.3.2** : Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure **9.3.3**) 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.

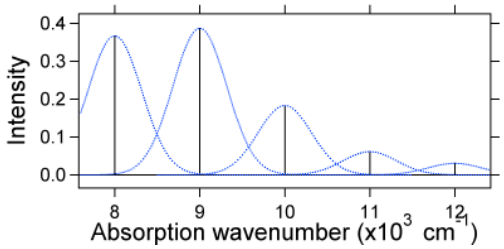


Figure **9.3.3** : Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure **9.3.2** .

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:

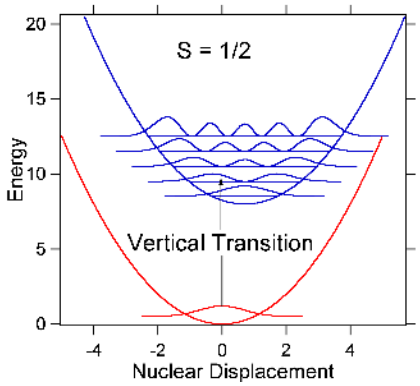


Figure **9.3.4** : Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure **9.3.5**

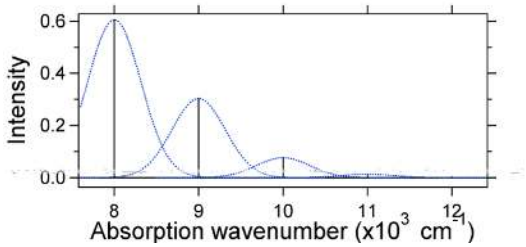


Figure **9.3.5** : Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure **9.3.4**.

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.

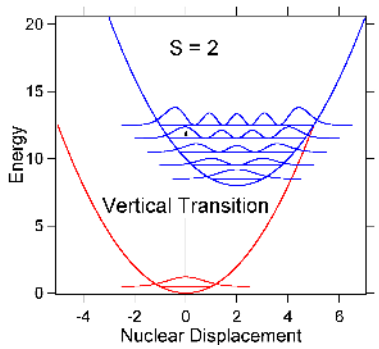


Figure **9.3.6** : Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

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.

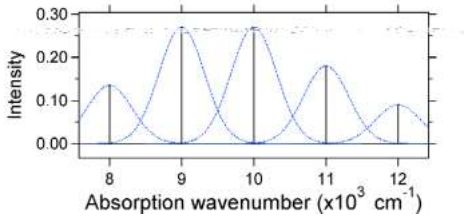


Figure **9.3.7** : Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure **9.3.6**.

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.

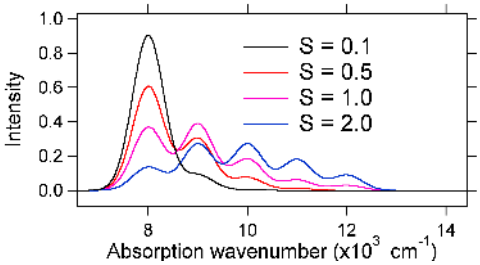


Figure **9.3.8** : Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

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.

9.3.4: References

1. J.M. Luis, D.M. Bishop, B. Kirtman. *A different approach for calculating Franck–Condon factors including anharmonicity.* J. Chem. Phys., 120 (2004), pp. 813–822.
2. Atkins, Peter and Julio de Paula. Physical Chemistry for the Life Sciences. 2006. New York, NY: W.H. Freeman and Company. p. 563-564
3. Franck-Condon Principle. 1996, 68, 2243. IUPAC Compendium of Chemical Terminology 2nd Edition (1997). www.iupac.org/goldbook/F02510.pdf
4. E.Rabinowitch and Govindjee. Light Absorption and Fate of Excitation of Energy. 1969. Franck-Condon Principle. http://www.life.uiuc.edu/govindjee/b...em494/Abs.html

9.3: The Franck-Condon Principle is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Stefan Franzen & Matthew Ziering.

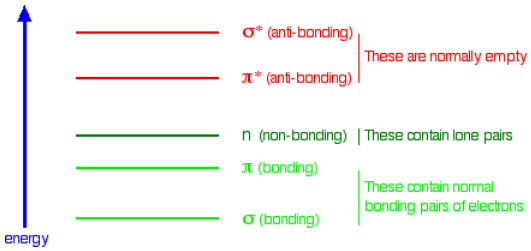
- **13.7: The Franck-Condon Principle** by Matthew Ziering, Stefan Franzen is licensed CC BY-NC-SA 4.0.

9.4: What Causes Molecules to Absorb UV and Visible Light

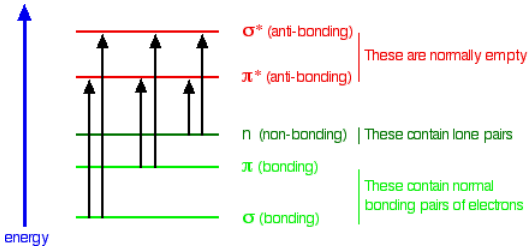
This page explains what happens when organic compounds absorb UV or visible light, and why the wavelength of light absorbed varies from compound to compound.

What happens when light is absorbed by molecules?

When we were talking about the various sorts of orbitals present in organic compounds on the introductory page (see above), you will have come across this diagram showing their relative energies:

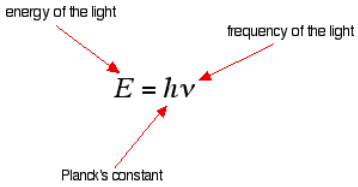


Remember that the diagram isn't intended to be to scale - it just shows the relative placing of the different orbitals. When light passes through the compound, energy from the light is used to promote an electron from a bonding or non-bonding orbital into one of the empty anti-bonding orbitals. The possible electron jumps that light might cause are:

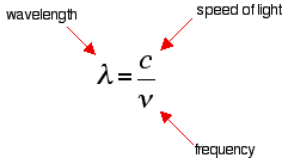


In each possible case, an electron is excited from a full orbital into an empty anti-bonding orbital. Each jump takes energy from the light, and a big jump obviously needs more energy than a small one. Each wavelength of light has a particular energy associated with it. If that particular amount of energy is just right for making one of these energy jumps, then that wavelength will be absorbed - its energy will have been used in promoting an electron.

We need to work out what the relationship is between the energy gap and the wavelength absorbed. Does, for example, a bigger energy gap mean that light of a lower wavelength will be absorbed - or what? It is easier to start with the relationship between the frequency of light absorbed and its energy:



You can see that if you want a high energy jump, you will have to absorb light of a higher frequency. The greater the frequency, the greater the energy. That's easy - but unfortunately UV-visible absorption spectra are always given using wavelengths of light rather than frequency. That means that you need to know the relationship between wavelength and frequency.

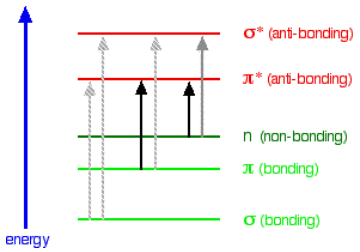


You can see from this that the higher the frequency is, the lower the wavelength is. So, if you have a bigger energy jump, you will absorb light with a higher frequency - which is the same as saying that you will absorb light with a lower wavelength.

> *Important summary: The larger the energy jump, the lower the wavelength of the light absorbed.*

Some jumps are more important than others for absorption spectrometry

An absorption spectrometer works in a range from about 200 nm (in the near ultra-violet) to about 800 nm (in the very near infra-red). Only a limited number of the possible electron jumps absorb light in that region. Look again at the possible jumps. This time, the important jumps are shown in black, and a less important one in grey. The grey dotted arrows show jumps which absorb light outside the region of the spectrum we are working in.



Remember that bigger jumps need more energy and so absorb light with a shorter wavelength. The jumps shown with grey dotted arrows absorb UV light of wavelength less that 200 nm. The important jumps are:

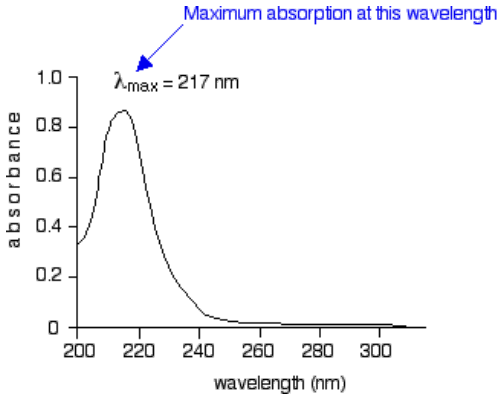
- from pi bonding orbitals to pi anti-bonding orbitals;
- from non-bonding orbitals to pi anti-bonding orbitals;
- from non-bonding orbitals to sigma anti-bonding orbitals.

That means that in order to absorb light in the region from 200 - 800 nm (which is where the spectra are measured), the molecule must contain either pi bonds or atoms with non-bonding orbitals. Remember that a non-bonding orbital is a lone pair on, say, oxygen, nitrogen or a halogen.

> *Groups in a molecule which absorb light are known as chromophores.*

What does an absorption spectrum look like

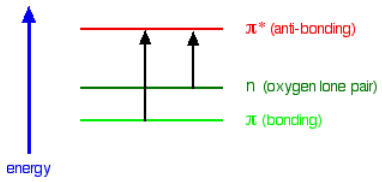
The diagram below shows a simple UV-visible absorption spectrum for buta-1,3-diene - a molecule we will talk more about later. Absorbance (on the vertical axis) is just a measure of the amount of light absorbed. The higher the value, the more of a particular wavelength is being absorbed.



You will see that absorption peaks at a value of 217 nm. This is in the ultra-violet and so there would be no visible sign of any light being absorbed - buta-1,3-diene is colorless. You read the symbol on the graph as "lambda-max". In buta-1,3-diene, CH_2=CH-CH=CH_2, there are no non-bonding electrons. That means that the only electron jumps taking place (within the range that the spectrometer can measure) are from pi bonding to pi anti-bonding orbitals.

A chromophore producing two peaks

A chromophore such as the carbon-oxygen double bond in ethanal, for example, obviously has pi electrons as a part of the double bond, but also has lone pairs on the oxygen atom. That means that both of the important absorptions from the last energy diagram are possible. You can get an electron excited from a pi bonding to a pi anti-bonding orbital, or you can get one excited from an oxygen lone pair (a non-bonding orbital) into a pi anti-bonding orbital.



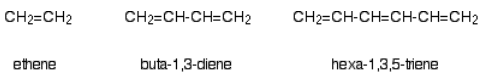
The non-bonding orbital has a higher energy than a pi bonding orbital. That means that the jump from an oxygen lone pair into a pi anti-bonding orbital needs less energy. That means it absorbs light of a lower frequency and therefore a higher wavelength. Ethanal can therefore absorb light of two different wavelengths:

- the pi bonding to pi anti-bonding absorption peaks at 180 nm;
- the non-bonding to pi anti-bonding absorption peaks at 290 nm.

Both of these absorptions are in the ultra-violet, but most spectrometers won't pick up the one at 180 nm because they work in the range from 200 - 800 nm.

The importance of conjugation and delocalisation

Consider these three molecules:



Ethene contains a simple isolated carbon-carbon double bond, but the other two have conjugated double bonds. In these cases, there is delocalization of the pi bonding orbitals over the whole molecule. Now look at the wavelengths of the light which each of these molecules absorbs.

molecule	wavelength of maximum absorption (nm)
ethene	171
buta-1,3-diene	217
hexa-1,3,5-triene	258

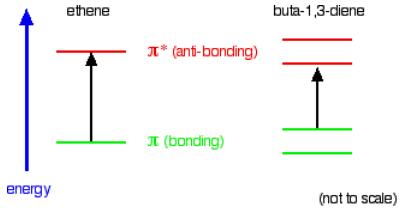
All of the molecules give similar UV-visible absorption spectra - the only difference being that the absorptions move to longer and longer wavelengths as the amount of delocalization in the molecule increases.

Why is this? You can actually work out what must be happening.

- The maximum absorption is moving to longer wavelengths as the amount of delocalization increases.
- Therefore maximum absorption is moving to shorter frequencies as the amount of delocalization increases.
- Therefore absorption needs less energy as the amount of delocalization increases.
- Therefore there must be less energy gap between the bonding and anti-bonding orbitals as the amount of delocalization increases.

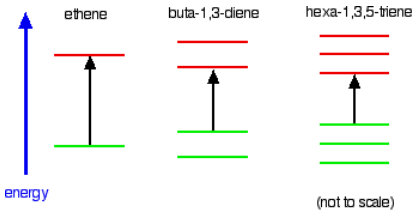
. . . and that's what is happening.

Compare ethene with buta-1,3-diene. In ethene, there is one pi bonding orbital and one pi anti-bonding orbital. In buta-1,3-diene, there are two pi bonding orbitals and two pi anti-bonding orbitals. This is all discussed in detail on the introductory page that you should have read.



The highest occupied molecular orbital is often referred to as the HOMO - in these cases, it is a pi bonding orbital. The lowest unoccupied molecular orbital (the LUMO) is a pi anti-bonding orbital. Notice that the gap between these has fallen. It takes less energy to excite an electron in the buta-1,3-diene case than with ethene.

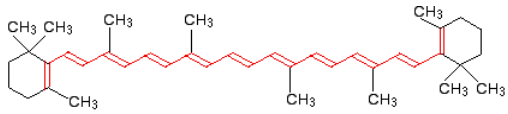
In the hexa-1,3,5-triene case, it is less still.



If you extend this to compounds with really massive delocalisation, the wavelength absorbed will eventually be high enough to be in the visible region of the spectrum, and the compound will then be seen as colored. A good example of this is the orange plant pigment, beta-carotene - present in carrots, for example.

Why is beta-carotene orange?

Beta-carotene has the sort of delocalization that we've just been looking at, but on a much greater scale with 11 carbon-carbon double bonds conjugated together. The diagram shows the structure of beta-carotene with the alternating double and single bonds shown in red.



The more delocalization there is, the smaller the gap between the highest energy pi bonding orbital and the lowest energy pi anti-bonding orbital. To promote an electron therefore takes less energy in beta-carotene than in the cases we've looked at so far - because the gap between the levels is less.

Remember that less energy means a lower frequency of light gets absorbed - and that's equivalent to a longer wavelength. Beta-carotene absorbs throughout the ultra-violet region into the violet - but particularly strongly in the visible region between about 400 and 500 nm with a peak about 470 nm. If you have read the page in this section about electromagnetic radiation, you might remember that the wavelengths associated with the various colors are approximately:

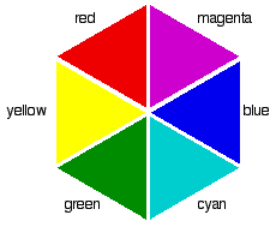
color region	wavelength (nm)
violet	380 - 435
blue	435 - 500
cyan	500 - 520
green	520 - 565
yellow	565 - 590
orange	590 - 625
red	625 - 740

So if the absorption is strongest in the violet to cyan region, what color will you actually see? It is tempting to think that you can work it out from the colors that are left - and in this particular case, you wouldn't be far wrong. Unfortunately, it isn't as simple as that!

Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

Complementary colors

If you arrange some colors in a circle, you get a "color wheel". The diagram shows one possible version of this. An internet search will throw up many different versions!



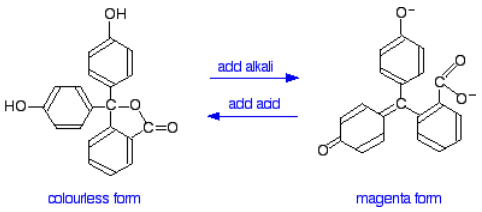
colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light.

What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. In the beta-carotene case, the situation is more confused because you are absorbing such a range of wavelengths. However, if you think of the peak absorption running from the blue into the cyan, it would be reasonable to think of the color you would see as being opposite that where yellow runs into red - in other words, orange.

Applying this to the color changes of two indicators

Phenolphthalein

You have probably used phenolphthalein as an acid-base indicator, and will know that it is colorless in acidic conditions and magenta (bright pink) in an alkaline solution. How is this color change related to changes in the molecule? The structures of the two differently colored forms are:

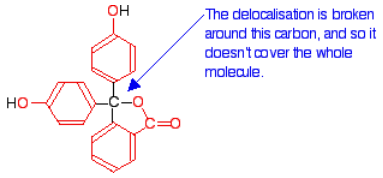


Both of these absorb light in the ultra-violet, but the one on the right also absorbs in the visible with a peak at 553 nm. The molecule in acid solution is colorless because our eyes can't detect the fact that some light is being absorbed in the ultra-violet. However, our eyes do detect the absorption at 553 nm produced by the form in alkaline solution.

553 nm is in the green region of the spectrum. If you look back at the color wheel, you will find that the complementary color of green is magenta - and that's the color you see.

So why does the color change as the structure changes? What we have is a shift to absorption at a higher wavelength in alkaline solution. As we've already seen, a shift to higher wavelength is associated with a greater degree of delocalisation.

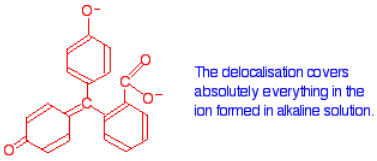
Here is a modified diagram of the structure of the form in acidic solution - the colorless form. The extent of the delocalization is shown in red.



Notice that there is delocalization over each of the three rings - extending out over the carbon-oxygen double bond, and to the various oxygen atoms because of their lone pairs.

But the delocalization doesn't extend over the whole molecule. The carbon atom in the centre with its four single bonds prevents the three delocalized regions interacting with each other.

Now compare that with the magenta form:

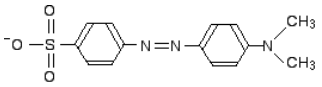


The rearrangement now lets the delocalization extend over the entire ion. This greater delocalization lowers the energy gap between the highest occupied molecular orbital and the lowest unoccupied pi anti-bonding orbital. It needs less energy to make the jump and so a longer wavelength of light is absorbed.

> *Increasing the amount of delocalization shifts the absorption peak to a higher wavelength.*

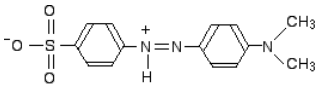
Methyl orange

You will know that methyl orange is yellow in alkaline solutions and red in acidic ones. The structure in alkaline solution is:

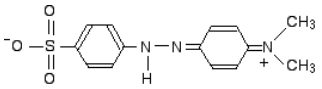


yellow form of methyl orange

In acid solution, a hydrogen ion is (perhaps unexpectedly) picked up on one of the nitrogens in the nitrogen-nitrogen double bond.



This now gets a lot more complicated! The positive charge on the nitrogen is delocalized (spread around over the structure) - especially out towards the right-hand end of the molecule as we've written it. The normally drawn structure for the red form of methyl orange is . . .



red form of methyl orange

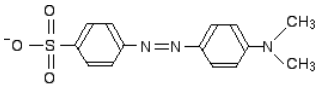
But this can be seriously misleading as regards the amount of delocalization in the structure for reasons discussed below (after the red warning box) if you are interested.

Which is the more delocalized structure?

Let's work backwards from the absorption spectra to see if that helps. The yellow form has an absorption peak at about 440 nm. That's in the blue region of the spectrum, and the complementary color of blue is yellow. That's exactly what you would expect. The red form has an absorption peak at about 520 nm. That's at the edge of the cyan region of the spectrum, and the complementary color of cyan is red. Again, there's nothing unexpected here.

Notice that the change from the yellow form to the red form has produced an increase in the wavelength absorbed. An increase in wavelength suggests an increase in delocalisation. That means that there must be more delocalization in the red form than in the

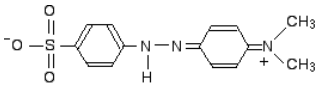
yellow one. Here again is the structure of the yellow form:



yellow form of methyl orange

delocalization will extend over most of the structure - out as far as the lone pair on the right-hand nitrogen atom.

If you use the normally written structure for the red form, the delocalization seems to be broken in the middle - the pattern of alternating single and double bonds seems to be lost.

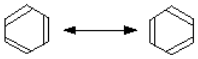


red form of methyl orange

But that is to misunderstand what this last structure represents.

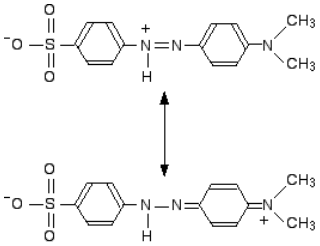
Canonical forms

If you draw the two possible Kekulé structures for benzene, you will know that the real structure of benzene isn't like either of them. The real structure is somewhere between the two - all the bonds are identical and somewhere between single and double in character. That's because of the delocalization in benzene.

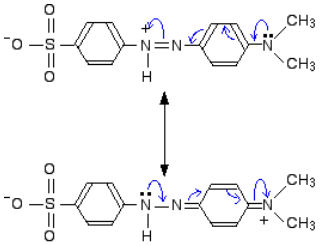


The two structures are known as canonical forms, and they can each be thought of as adding some knowledge to the real structure. For example, the bond drawn at the top right of the molecule is neither truly single or double, but somewhere in between. Similarly with all the other bonds.

The two structures we've previously drawn for the red form of methyl orange are also canonical forms - two out of lots of forms that could be drawn for this structure. We could represent the delocalized structure by:



These two forms can be thought of as the result of electron movements in the structure, and curly arrows are often used to show how one structure can lead to the other.



In reality, the electrons haven't shifted fully either one way or the other. Just as in the benzene case, the actual structure lies somewhere in between these.

You must also realize that drawing canonical forms has no effect on the underlying geometry of the structure. Bond types or lengths or angles don't change in the real structure.

For example, the lone pairs on the nitrogen atoms shown in the last diagram are both involved with the delocalisation. For this to happen all the bonds around these nitrogens must be in the same plane, with the lone pair sticking up so that it can overlap sideways with orbitals on the next-door atoms. The fact that in each of the two canonical forms one of these nitrogens is shown as if it had an ammonia-like arrangement of the bonds is potentially misleading - and makes it look as if the delocalization is broken.

The problem is that there is no easy way of representing a complex delocalized structure in simple structural diagrams. It is bad enough with benzene - with something as complicated as methyl orange any method just leads to possible confusion if you aren't used to working with canonical forms.

It gets even more complicated! If you were doing this properly there would be a host of other canonical forms with different arrangements of double and single bonds and with the positive charge located at various places around the rings and on the other nitrogen atom.

The real structure can't be represented properly by any one of this multitude of canonical forms, but each gives a hint of how the delocalization works.

If we take the two forms we have written as perhaps the two most important ones, it suggests that there is delocalization of the electrons over the whole structure, but that electron density is a bit low around the two nitrogens carrying the positive charge on one canonical form or the other.

Why is the red form more delocalized

Finally, we get around to an attempt at an explanation as to why the delocalization is greater in the red form of methyl orange in acid solution than in the yellow one in alkaline solution. The answer may lie in the fact that the lone pair on the nitrogen at the right-hand end of the structure as we've drawn it is more fully involved in the delocalization in the red form. The canonical form with the positive charge on that nitrogen suggests a significant movement of that lone pair towards the rest of the molecule.

Doesn't the same thing happen to the lone pair on the same nitrogen in the yellow form of methyl orange? Not to the same extent.

Any canonical form that you draw in which that happens produces another negatively charged atom somewhere in the rest of the structure. Separating negative and positive charges like this is energetically unfavourable. In the red form, we aren't producing a new separation of charge - just shifting a positive charge around the structure.

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9.5: Fluorescence and Phosphorescence

Fluorescence and phosphorescence are types of molecular luminescence methods. A molecule of analyte absorbs a photon and excites a species. The emission spectrum can provide qualitative and quantitative analysis. The term fluorescence and phosphorescence are usually referred as photoluminescence because both are alike in excitation brought by absorption of a photon. Fluorescence differs from phosphorescence in that the electronic energy transition that is responsible for fluorescence does not change in electron spin, which results in short-live electrons ($<10^{-5}$ s) in the excited state of fluorescence. In phosphorescence, there is a change in electron spin, which results in a longer lifetime of the excited state (second to minutes). Fluorescence and phosphorescence occurs at longer wavelength than the excitation radiation.

Introduction

Fluorescence can occur in gaseous, liquid, and solid chemical systems. The simple kind of fluorescence is by dilute atomic vapors. A fluorescence example would be if a 3s electron of a vaporized sodium atom is excited to the 3p state by absorption of a radiation at wavelength 589.6 and 589.0 nm. After 10^{-8} s, the electron returns to ground state and on its return it emits radiation of the two wavelengths in all directions. This type of fluorescence in which the absorbed radiation is remitted without a change in frequency is known as resonance fluorescence. Resonance fluorescence can also occur in molecular species. Molecular fluorescence band centers at wavelengths longer than resonance lines. The shift toward longer wavelength is referred to as the Stokes Shift.

Singlet and Triplet Excited State

Understanding the difference between fluorescence and phosphorescence requires the knowledge of electron spin and the differences between singlet and triplet 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) and only two electrons can occupy each orbital where they must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules do not exhibit a magnetic field and are diamagnetic. In diamagnetic molecules, electrons are not attracted or repelled by the static electric field. Free radicals are paramagnetic because they contain unpaired electrons have magnetic moments that are attracted to the magnetic field.

Singlet state is defined 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 into a magnetic field. A doublet state occurs when there is an unpaired electron that gives two possible orientations when exposed in a magnetic field and imparts different energy to the system. A singlet or a triplet can form when one electron is excited to a higher energy level. In an excited singlet state, the electron is promoted in the same spin orientation as it was in the ground state (paired). In a triplet excited stated, the electron that is promoted has the same spin orientation (parallel) to the other unpaired electron. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure **9.5.1**. Singlet, doublet and triplet is 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 calculated the S for the excited singlet state, the equation would be 2(+1/2 + -1/2)+1 = 2(0)+1 = 1, therefore making the center orbital in the figure a singlet state. If the spin multiplicity for the excited triplet state was calculated, we obtain 2(+1/2 + +1/2)+1 = 2(1)+1 =3, which gives a triplet state as expected.

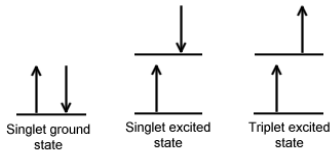


Figure **9.5.1**: Spin in the ground and excited states.

The difference between a molecule in the ground and excited state is that the electrons is diamagnetic in the ground state and paramagnetic in the triplet state.This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) more improbable than the singlet-to-singlet transitions. This singlet to triplet (or reverse) transition involves a change in *electronic* state. For this reason, the lifetime of the triplet state is longer the singlet state by approximately 10^4 seconds fold difference.The radiation that induced the transition from ground to excited triplet state has a low probability of occurring, thus their absorption bands are less intense than singlet-singlet state absorption. The excited triplet state can be populated from the excited singlet state of certain

molecules which results in phosphorescence. These spin multiplicities in ground and excited states can be used to explain transition in photoluminescence molecules by the Jablonski diagram.

Jablonski Diagrams

The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of 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, majority of the molecules in a solution are in this state.

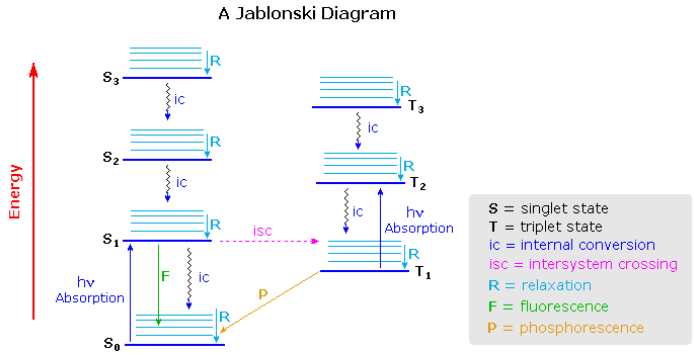


Figure 9.5.2: Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. from Bill Reusch.

The upper lines represent the energy state of the three excited electronic states: $S_1$and S_2 represent the electronic singlet state (left) and T_1 represents the first electronic triplet state (right). The upper darkest line represents the ground vibrational state of the three excited electronic state.The energy of the triplet state is lower than the energy of the corresponding singlet state.

There are numerous vibrational levels that can be associated with each electronic state as denoted by the thinner lines. Absorption transitions (blues lines in Figure 9.5.2) can occur from the ground singlet electronic state (S_o) to various vibrational levels in the singlet excited vibrational states. It is unlikely that a transition from the ground singlet electronic state to the triplet electronic state because the electron spin is parallel to the spin in its ground state (Figure 9.5.1). This transition leads to a change in multiplicity and thus has a low probability of occurring which is a **forbidden transition.** Molecules also go through vibration relaxation to lose any excess vibrational energy that remains when excited to the electronic states (S_1 and S_2) as demonstrated in wavy lines in Figure 9.5.2. The knowledge of forbidden transition is used to explain and compare the peaks of absorption and emission.

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 9.5.1: Rates of Absorption and Emission comparison.

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

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 **9.5.2**.The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrow in Figure **9.5.2**. The wiggly arrows in Figure **9.5.2** are deactivation processes without the use of radiation. The favored deactivation process is the route that is most rapid and spends less time in the excited state.If the rate constant for fluorescence is more favorable in the radiationless path, the fluorescence will be less intense or absent.

- **Vibrational Relaxation:** A molecule maybe to promoted to several vibrational levels during the electronic excitation process.Collision of molecules with the excited species and solvent leads to rapid energy transfer and a slight increase in temperature of the solvent. Vibrational relaxation is so rapid that the lifetime of a vibrational excited molecule ($<10^{-12}$) is less than the lifetime of the electronically excited state. For this reason, fluorescence from a solution always involves the transition of the lowest vibrational level of the excited state. Since the space of the emission lines are so close together, the transition of the vibrational relaxation can terminate in any vibrational level of the ground state.
- **Internal Conversion:** Internal conversion is an intermolecular process of molecule that passes to a lower electronic state without the emission of radiation.It is a crossover of two states with the same multiplicity meaning singlet-to-singlet or triplet-to-triplet states.The internal conversion is more efficient when two electronic energy levels are close enough that two vibrational energy levels can overlap as shown in between S_1 and S_2. Internal conversion can also occur between S_0 and S_1 from a loss of energy by fluorescence from a higher excited state, but it is less probable. The mechanism of internal conversion from S_1 to S_0 is poorly understood. For some molecules, the vibrational levels of the ground state overlaps with the first excited electronic state, which leads to fast deactivation.These usually occur with aliphatic compounds (compound that do not contain ring structure), which would account for the compound is seldom fluorescing. Deactivation by energy transfer of these molecules occurs so rapidly that the molecule does not have time to fluoresce.
- **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 leads to enhanced fluorescence because they reduce the number of collision between molecules, thus slowing down the deactivation process.
- **Intersystem Crossing:** Intersystem crossing is a process where there is a crossover between electronic states of different multiplicity as demonstrated in the singlet state to a triplet state (S_1 to T_1) on Figure **9.5.1**. The probability of intersystem crossing is enhanced if the vibration levels of the two states overlap. Intersystem crossing is most commonly observed with molecules that contain heavy atom such as iodine or bromine. The spin and orbital interaction increase and the spin become more favorable.Paramagnetic species also enhances intersystem crossing, which consequently decreases fluorescence.
- **Phosphorescence**: Deactivation of the electronic excited state is also involved in phosphorescence. After the molecule transitions through intersystem crossing to the triplet state, further deactivation occurs through internal or external fluorescence or phosphorescence. A triplet-to-singlet transition is more probable than a singlet-to-singlet internal crossing. In phosphorescence, the excited state lifetime is inversely proportional to the probability that the molecule will transition back to the ground state. Since the lifetime of the molecule in the triplet state is large (10^{-4} to 10 second or more), transition is less probable which suggest that it will persist for some time even after irradiation has stopped. Since the external and internal conversion compete so effectively with phosphorescence, the molecule has to be observed at lower temperature in highly viscous media to protect the triplet state.

Variables that affect Fluorescence

After discussing all the possible deactivation processes, variable that affect the emissions to occur. Molecular structure and its chemical environment influence whether a substance will fluoresce and the intensities of these emissions. The **quantum yield** or **quantum efficiency** is used to measure the probability that a molecule will fluoresce or phosphoresce. For fluorescence and phosphorescence is the ratio of the number of molecules that luminescent to the total number of excited molecules. For highly fluoresce molecules, the quantum efficiency approaches to one.Molecules that do not fluoresce have quantum efficiencies that approach to zero.

Fluorescence quantum yield (ϕ) for a compound is determined by the relative rate constants (k) of various deactivation processes by which the lowest excited singlet state is deactivated to the ground state. The deactivation processes including fluorescence (kf), intersystem crossing (k_i), internal conversion (kic), predissociation (kpd), dissociation (kd), and external conversion (kec) allows

one to qualitatively interpret the structural and environmental factors that influence the intensity of the fluorescence. They are related by the quantum yield equation given below:

$$\frac{k_f}{k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d} \tag{9.5.1}$$

Using this equation as an example to explain fluorescence, a high fluorescence rate (k_f) value and low values of the all the other relative rate constant terms ($k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d$) will give a large ϕ, which suggest that fluorescence is enhanced. The magnitudes of kf , kd, and kpd depend on the chemical structure, while the rest of the constants ki, kec, and kic are strongly influenced by the environment.

Fluorescence rarely results from absorption of ultraviolet radiation of wavelength shorter than 250 nm because radiation at this wavelength has sufficient energy to deactivate the electron in the excited state by predissociation or dissociation. The bond of some organic molecules would rupture at 140 kcal/mol, which corresponds to 200-nm of radiation. For this reason, $\sigma \rightarrow \sigma^*$ transition in fluorescence are rarely observed. Instead, emissions from the less energetic transition will occur which are either $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transition.

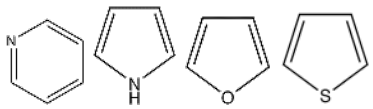
Molecules that are excited electronically will return to the lowest excited state by rapid vibrational relaxation and internal conversion, which produces no radiation emission. Fluorescence arises from a transition from the lowest vibrational level of the first excited electronic state to one of the vibrational levels in the electronic ground state. In most fluorescent compounds, radiation is produced by a $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transition depending on which requires the least energy for the transition to occur.

Fluorescence is most commonly found in compounds in which the lowest energy transition is $\pi \rightarrow \pi^*$ (excited singlet state) than $n \rightarrow \pi^*$ which suggest that the quantum efficiency is greater for $\pi \rightarrow \pi^*$ transitions. The reason for this is that the molar absorptivity, which measures the probability that a transition will occur, of the $\pi \rightarrow \pi^*$ transition is 100 to 1000 fold greater than $n \rightarrow \pi^*$ process. The lifetime of $\pi \rightarrow \pi^*$ (10^{-7} to 10^{-9} s) is shorter than the lifetime of $n \rightarrow \pi^*$ (10^{-5} to 10^{-7}).

Phosphorescent quantum efficiency is the opposite of fluorescence in that it occurs in the $n \rightarrow \pi^*$ excited state which tends to be short lived and less suceptable to deactivation than the $\pi \rightarrow \pi^*$ triplet state. Intersystem crossing is also more probable for $\pi \rightarrow \pi^*$ excited state than for the $n \rightarrow \pi^*$state because the energy difference between the singlet and triplet state is large and spin-orbit coupling is less likely to occur.

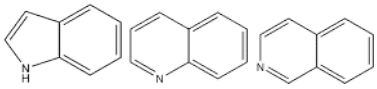
Fluorescence and Structure

The most intense fluorescence is found in compounds containing aromatic group with low-energy $\pi \rightarrow \pi^*$ transitions. A few aliphatic, alicyclic carbonyl, and highly conjugated double-bond structures also exhibit fluorescence as well. Most unsubstituted aromatic hydrocarbons fluoresce in solution too. The quantum efficiency increases as the number of rings and the degree of condensation increases. Simple heterocycles such as the structures listed below do not exhibit fluorescence.



Pyridine Pyrrole Furan Thiophene

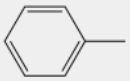
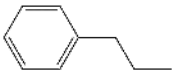
With nitrogen heterocyclics, the lowest energy transitions is involved in $n \rightarrow \pi^*$ system that rapidly converts to the triplet state and prevents fluorescence. Although simple heterocyclics do not fluoresce, fused-ring structures do. For instance, a fusion of a benzene ring to a hetercyclic structure results in an increase in molar absorptivity of the absorption band. The lifetime of the excited state in fused structure and fluorescence is observed. Examples of fluorescent compounds is shown below.



quinoline

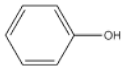
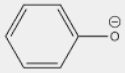
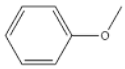
Benzene ring substitution causes a shift in the absorption maxima of the wavelength and changes in fluorescence emission. The table below is used to demonstrate and visually show that as benzene is substituted with increasing methyl addition, the relative intensity of fluorescence increases.

Table 2. Relative intensity of fluorescence comparison with alkane substituted benzenes.

Compound	Structure	Wavelength of Fluorescence (nm)	Relative intensity of Fluorescence
Benzene		270-310	10
Toluene		270-320	17
Propyl Benzene		270-320	17

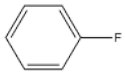
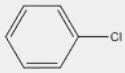
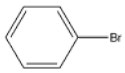
The relative intensity of fluorescence increases as oxygenated species increases in substitution. The values for such increase is demonstrated in the table below.

Table **9.5.3**: Relative intensity of fluorescence comparison with benzene with oxygenated substituted benzene

Compound	Structure	Wavelength of Fluorescence (nm)	Relative intensity of Fluorescence
Phenol		285-365	18
Phenolate ion		310-400	10
Anisole		285-345	20

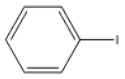
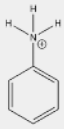
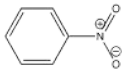
Influence of a halogen substitution decreases fluorescence as the molar mass of the halogen increases. This is an example of the "heavy atom effect" which suggest that the probability of intersystem crossing increases as the size of the molecule increases. As demonstrated in the table below, as the molar mass of the substituted compound increases, the relative intensity of the fluorescence decreases.

Table **9.5.4**: Relative intensity fluorescence comparison with halogen substituted compounds

Compound	Structure	Wavelength of Fluorescence (nm)	Relative intensity of Fluorescence
Fluorobenzene		270-320	10
Chlorobenzene		275-345	7
Bromobenzene		290-380	5

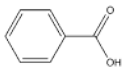
In heavy atom substitution such as nitro derivatives or heavy halogen substitution such as iodobenzene, the compounds are subject to predissociation. These compounds have bonds that easily rupture that can then absorb excitation energy and go through internal conversion. Therefore, the relative intensity of fluorescence and fluorescent wavelength is not observed and this is demonstrated in the table below.

Table **9.5.5**: Relative fluorescent intensities of iodobenzene and nitro derivative compounds

Compound	Structure	Wavelength of Fluorescence (nm)	Relative intensity of Fluorescence
Iodobenzene		None	0
Anilinium ion		None	0
Nitrobenzene		None	0

Carboxylic acid or carbonyl group on aromatic ring generally inhibits fluorescence since the energy of the $n \rightarrow \pi^*$ transition is less than $\pi \rightarrow \pi^*$ transition. Therefore, the fluorescence yield from $n \rightarrow \pi^*$ transition is low.

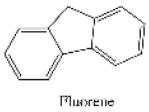
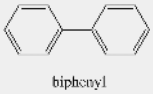
Table 9.5.6: Relative fluorescent intensity of benzoic acid

Compound	Structure	Wavelength of Fluorescence (nm)	Relative intensity of Fluorescence
Benzoic Acid		310-390	3

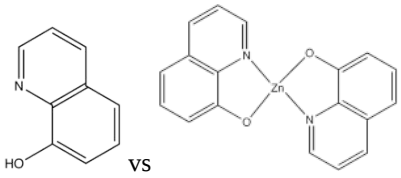
Effect of Structural Rigidity on Fluorescence

Fluorescence is particularly favored in molecules with rigid structures. The table below compares the quantum efficiencies of fluorine and biphenyl which are both similar in structure that there is a bond between the two benzene group. The difference is that fluorene is more rigid from the addition methylene bridging group. By looking at the table below, rigid fluorene has a higher quantum efficiency than unrigid biphenyl which indicates that fluorescence is favored in rigid molecules.

Table 9.5.7: Quantum Efficiencies in Rigid vs. Nonrigid structures

Compound	Structure	Quantum Efficiency
Fluorene		1.0
Biphenyl		0.2

This concept of rigidity was used to explain the increase in fluorescence of organic chelating agent when the compound is complexed with a metal ion. The fluorescence intensity of 8-hydroxyquinoline is much less than its zinc complex.



8-hydroxyquinoline 8-hydroxyquinoline with Zinc complexed

The explanation for lower quantum efficiency or lack of rigidity in caused by the enhanced internal conversion rate (k_{ic}) which increases the probability that there will be radiationless deactivation. Nonrigid molecules can also undergo low-frequency vibration which accounts for small energy loss.

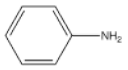
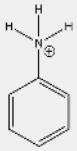
Temperature and Solvent Effects

Quantum efficiency of Fluorescence decreases with increasing temperature. As the temperature increases, the frequency of the collision increases which increases the probability of deactivation by external conversion. Solvents with lower viscosity have higher possibility of deactivation by external conversion. Fluorescence of a molecule decreases when its solvent contains heavy atoms such as carbon tetrabromide and ethyl iodide, or when heavy atoms are substituted into the fluorescing compound. Orbital spin interaction result from an increase in the rate of triplet formation, which decreases the possibility of fluorescence. Heavy atoms are usually incorporated into solvent to enhance phosphorescence.

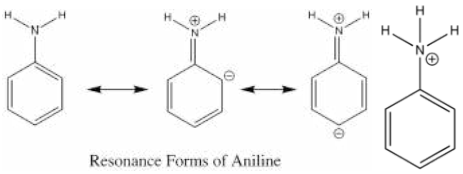
Effect of pH on Fluorescence

The fluorescence of aromatic compound with basic or acid substituent rings are usually pH dependent. The wavelength and emission intensity is different for protonated and unprotonated forms of the compound as illustrated in the table below:

Table 9.5.8: Quantum efficiency comparison due to protonation

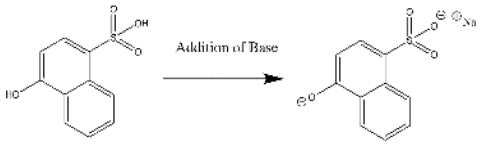
Compound	Structure	Wavelength of Fluorescence (nm)	Relative intensity of Fluorescence
aniline		310-405	20
Anilinium ion		None	0

The emission changes of this compound arises from different number of resonance structures associated with the acidic and basic forms of the molecule.The additional resonance forms provides a more stable first excited state, thus leading to fluorescence in the ultraviolet region.The resonance structures of basic aniline and acidic anilinium ion is shown below:



Resonance Forms of Aniline

basic Aniline Fluorescence of certain compounds have been used a detection of end points in acid-base titrations.An example of this type of fluorescence seen in compound as a function of pH is the phenolic form of 1-naphthol-4-sulfonic acid.This compound is not detectable with the eye because it occurs in the ultraviolet region, but with an addition of a base, it becomes converted to a phenolate ion, the emission band shifts to the visible wavelength where it can be visually seen. Acid dissociation constant for excited molecules differs for the same species in the ground state.These changes in acid or base dissociation constant differ in four or five orders of magnitude.



1-naphthol-4-sulfonic acid (Phenolic Form) 1-naphthol-4-sulfonic acid (Phenolate ion)

Dissolved oxygen reduces the intensity of fluorescence in solution, which results from a photochemically induced oxidation of fluorescing species.Quenching takes place from the paramagnetic properties of molecular oxygen that promotes intersystem crossing and conversion of excited molecules to triplet state.Paramagnetic properties tend to quench fluorescence.

Effects of Concentration on Fluorescence Intensity

The power of fluorescence emission F is proportional to the radiant power is proportional to the radiant power of the excitation beam that is absorbed by the system. The equation below best describes this relationship.

$$F=\phi_f K"(P_0-P)=K'(P_0-P) \quad (1)$$

Since $\phi_f K''$ is constant in the system, it is represented at K'. The table below defines the variables in this equation.

Table 9: Definitions of all the variables defined in the Fluorescence Emission (F) in Equation 1.

Variable	Definition
F	Power of fluorescence emission
P0	Power of incident beam on solution
P	Power after transversing length b in medium
K"	Constant dependent on geometry and other factors
ϕ_f	Quantum efficiency

Fluorescence emission (F) can be related to concentration (c) using Beer's Law stating:

$$F = \epsilon bc \quad (9.5.2)$$

where ϵ is the molar absorptivity of the molecule that is fluorescing. Rewriting Equation 2 gives:

$$P = P_o 10^{-\epsilon bc} \quad (9.5.3)$$

Plugging this Equation 9.5.3 into Equation ??? and factoring out \(P__0\) gives us this equation:

$$F = K' P_0 \left(1 - 10^{-\epsilon bc}\right) \quad (9.5.4)$$

The MacLaurin series could be used to solved the exponential term.

$$F = K' P_0 \left[2.303\varepsilon bc - \frac{(2.303\varepsilon bc)^2}{2!} + \frac{(2.303\varepsilon bc)^3}{3!} + \frac{(2.303\varepsilon bc)^4}{4!} + \ldots \frac{(2.303\varepsilon bc)^n}{n!}\right]_1 \quad (9.5.5)$$

Given that $(2.303\epsilon bc = \text{Absorbance} < 0.05$, all the subsequent terms after the first can be dropped since the maximum error is 0.13%. Using only the first term, Equation ??? can be rewritten as:

$$F = K' P_0 2.303\varepsilon bc \quad (9.5.6)$$

Equation ??? can be expanded to the equation below and simplified to compare the fluorescence emission F with concentration. If the equation below were to be plotted with F versus c, a linear relation would be observed.

$$F = \phi_f K'' P_0 2.303\varepsilon bc \quad (9.5.7)$$

If c becomes so great that the absorbance > 0.05, the higher terms start to become taken into account and the linearity is lost. F then lies below the extrapolation of the straight-line plot. This excessive absorption is the **primary absorption.** Another cause of this negative downfall of linearity is the **secondary absorption** when the wavelength of emission overlaps the absorption band. This occurs when the emission transverse the solution and gets reabsorbed by other molecules by analyte or other species in the solution, which leads to a decrease in fluorescence.

Quenching Methods

Dynamic Quenching is a nonradiative energy transfer between the excited and the quenching agent species (Q).The requirements for a successful dynamic quenching are that the two collision species the concentration must be high so that there is a higher possibility of collision between the two species.Temperature and quenching agent viscosity play a role on the rate of dynamic quenching.Dynamic quenching reduces fluorescence quantum yield and the fluorescence lifetime.

Dissolved oxygen in a solution increases the intensity of the fluorescence by photochemically inducing oxidation of the fluorescing species.Quenching results from the paramagnetic properties of molecular oxygen that promotes intersystem crossing and converts the excited molecules to triplet state.Paramagnetic species and dissolved oxygen tend to quench fluorescence and quench the triplet state.

Static quenching occurs when the quencher and ground state fluorophore forms a dark complex.Fluorescence is usually observed from unbound fluorophore.Static quenching can be differentiated from dynamic quenching in that the lifetime is not affected in static quenching.In long range (Förster) quenching, energy transfer occurs without collision between molecules, but dipole-dipole coupling occurs between excited fluorophore and quencher.

Emission and Excitation Spectra

One of the ways to visually distinguish the difference between each photoluminescence is to compare the relative intensities of emission/excitation at each wavelength. An example of the three types of photoluminescence (absorption, fluorescence and phosphorescence) is shown for phenanthrene in the spectrum below.In the spectrum, the luminescent intensity is measure in a wavelength is fixed while the excitation wavelength is varied. The spectrum in red represents the excitation spectrum, which is identical to the absorption spectrum because in order for fluorescence emission to occur, radiation needs to be absorbed to create an excited state.The spectrum in blue represent fluorescence and green spectrum represents the phosphorescence.

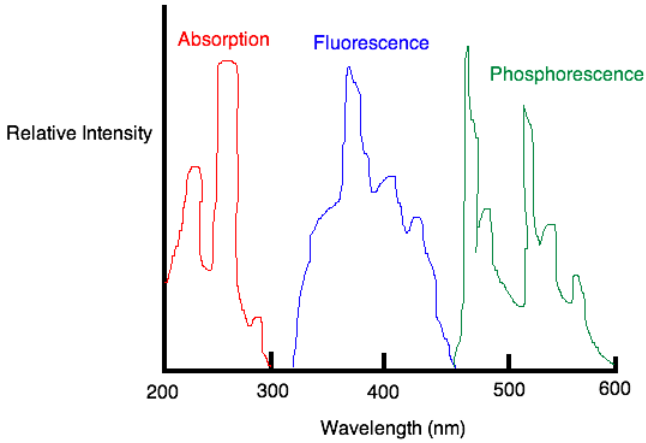


Figure 3: Wavelength Intensities of Absorption, Fluorescence, and Phosphorescence

Fluorescence and Phosphorescence occur at wavelengths that are longer than their absorption wavelengths.Phosphorescence bands are found at a longer wavelength than fluorescence band because the excited triplet state is lower in energy than the singlet state.The difference in wavelength could also be used to measure the energy difference between the singlet and triplet state of the molecule. The wavelength (λ) of a molecule is inversely related to the energy (E) by the equation below:

$$E = \frac{hc}{\lambda} \tag{9.5.8}$$

As the wavelength increases, the energy of the molecule decrease and vice versa.

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.

Problems

1. Draw and label the Jablonski Diagram.
2. How do spin states differ in ground singlet state versus excite singlet state and triplet excited state?
3. Describe the rates of deactivation process.
4. What is quantum yield and how is it used to compare the fluorescence of different types of molecule?
5. What roles do solvent play in fluorescence?

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9.6: Jablonski diagram

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. He developed a written representation that generally shows a portion of the possible consequences of applying photons from the visible spectrum of light to a particular molecule. These schematics are referred to as Jablonski diagrams.

Introduction

A Jablonski diagram is basically 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 vibronic 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. As electronic energy states increase, the difference in energy becomes continually less, eventually becoming a continuum that can be approach with classical mechanics. Additionally, as the electronic energy levels get closer together, the overlap of vibronic energy levels increases.

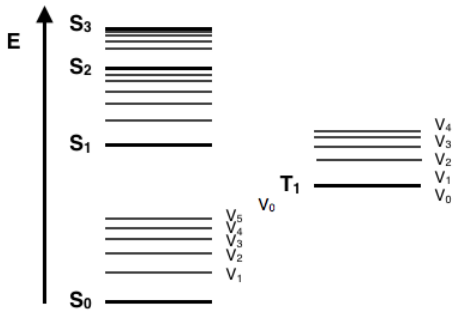


Figure 9.6.1: The Foundation of a typical Jablonski Diagram

Through the use of straight and curved 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. Curved lines show transitions of electrons without any interaction with light. Within a Jablonski diagram several different pathways show how an electron may accept and then dissipate the energy from a photon of a particular wavelength. Thus, most diagrams start with arrows going from the ground electronic state and finish with arrows going to the ground electronic state.

Absorbance

The first transition in most Jablonski diagrams is the absorbance of a photon of a particular energy by the molecule of interest. This is indicated by a straight arrow pointing up. Absorbance is the method by which an electron is excited from a lower energy level to a higher energy level. The energy of the photon is transferred to the particular electron. That electron then transitions to a different eigenstate corresponding to the amount of energy transferred. Only certain wavelengths of light are possible for absorbance, that is, wavelengths that have energies that correspond to the energy difference between two different eigenstates of the particular molecule. Absorbance is a very fast transition, on the order of 10^{-15} seconds. Most Jablonski diagrams, however, do not indicate a time scale for the phenomenon being indicated. This transition will usually occur from the lowest (ground) electronic state due to the statistical mechanical issue of most electrons occupying a low lying state at reasonable temperatures. There is a Boltzmann distribution of electrons within this low lying levels, based on the the energy available to the molecules. This energy available is a function of the Boltzmann's constant and the temperature of the system. These low lying electrons will transition to an excited electronic state as well as some excited vibrational state.

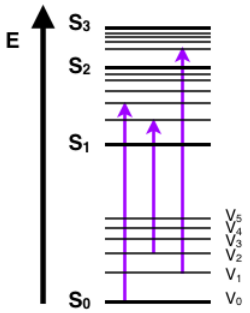


Figure **9.6.2**: Three possible absorption transitions represented.

Vibrational Relaxation and Internal Conversion

Once an electron is excited, there are a multitude of ways that energy may be dissipated. The first is through vibrational relaxation, a non-radiative process. This is indicated on the Jablonski diagram as a curved arrow between vibrational levels. Vibrational relaxation is where the energy deposited by the photon into the electron is given away to other vibrational modes as kinetic energy. This kinetic energy may stay within the same molecule, or it may be transferred to other molecules around the excited molecule, largely depending on the phase of the probed sample. This process is also very fast, between 10^{-14} and 10^{-11} seconds. Since this is a very fast transition, it is extremely likely to occur immediately following absorbance. This relaxation occurs between vibrational levels, so generally electrons will not change from one electronic level to another through this method.

However, if vibrational energy levels strongly overlap electronic energy levels, a possibility exists that the excited electron can transition from a vibration level in one electronic state to another vibration level in a lower electronic state. This process is called internal conversion and mechanistically is identical to vibrational relaxation. It is also indicated as a curved line on a Jablonski diagram, between two vibrational levels in different electronic states. Internal Conversion occurs because of the overlap of vibrational and electronic energy states. As energies increase, the manifold of vibrational and electronic eigenstates becomes ever closer distributed. At energy levels greater than the first excited state, the manifold of vibrational energy levels strongly overlap with the electronic levels. This overlap gives a higher degree of probability that the electron can transition between vibrational levels that will lower the electronic state. Internal conversion occurs in the same time frame as vibrational relaxation, therefore, is a very likely way for molecules to dissipate energy from light perturbation. However, due to a lack of vibrational and electronic energy state overlap and a large energy difference between the ground state and first excited state, internal conversion is very slow for an electron to return to the ground state. This slow return to the ground state lets other transitive processes compete with internal conversion at the first electronically excited state. Both vibrational relaxation and internal conversion occur in most perturbations, yet are seldom the final transition.

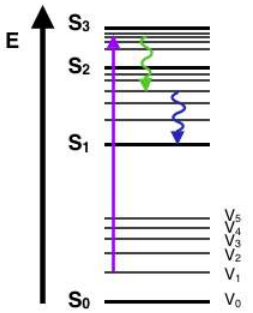


Figure **9.6.3**: Possible scenario with absorption, internal conversion, and vibrational relaxation *processes shown.*

Fluorescence

Another pathway for molecules to deal with energy received from photons is to emit a photon. This is termed fluorescence. It is indicated on a Jablonski diagram as a straight line going down on the energy axis between electronic states. Fluorescence is a slow process on the order of 10^{-9} to 10^{-7} seconds; therefore, it is not a very likely path for an electron to dissipate energy especially at electronic energy states higher than the first excited state. While this transition is slow, it is an allowed transition with the electron

staying in the same multiplicity manifold. Fluorescence is most often observed between the first excited electron state and the ground state for any particular molecule because at higher energies it is more likely that energy will be dissipated through internal conversion and vibrational relaxation. At the first excited state, fluorescence can compete in regard to timescales with other non-radiative processes. The energy of the photon emitted in fluorescence is the same energy as the difference between the eigenstates of the transition; however, the energy of fluorescent photons is always less than that of the exciting photons. This difference is because energy is lost in internal conversion and vibrational relaxation, where it is transferred away from the electron. Due to the large number of vibrational levels that can be coupled into the transition between electronic states, measured emission is usually distributed over a range of wavelengths.

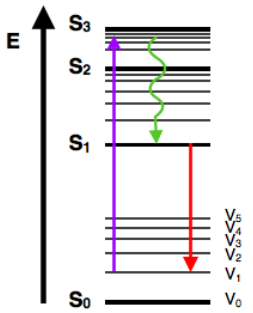


Figure 9.6.4: *Possible scenario with absorption, internal conversion and vibrational relaxation, and fluorescence processes shown.*

Intersystem Crossing

Yet another path a molecule may take in the dissipation of energy is called intersystem crossing. This where the electron changes spin multiplicity from an excited singlet state to an excited triplet state. It is indicated by a horizontal, curved arrow from one column to another. This is the slowest process in the Jablonski diagram, several orders of magnitude slower than fluorescence. This slow transition is a forbidden transition, that is, a transition that based strictly on electronic selection rules should not happen. However, by coupling vibrational factors into the selection rules, the transition become weakly allowed and able to compete with the time scale of fluorescence. Intersystem crossing leads to several interesting routes back to the ground electronic state. One direct transition is phosphorescence, where a radiative transition from an excited triplet state to a singlet ground state occurs.This is also a very slow, forbidden transition. Another possibility is delayed fluorescence, the transition back to the first excited singlet level, leading to the emitting transition to the ground electronic state.

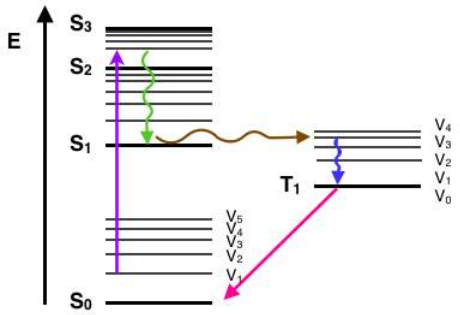


Figure 9.6.5: *Possible scenario with absorption, internal conversion, vibrational relaxation, intersystem crossing, and phosphorescence processes shown.*

Other non-emitting transitions from excited state to ground state exist and account for the majority of molecules not exhibiting fluorescence or phosphorescent behavior. One process is the energy transfer between molecules through molecular collisions (e.g., external conversion). Another path is through quenching, energy transfer between molecules through overlap in absorption and fluorescence spectra. These are non-emitting processes that will compete with fluorescence as the molecule relaxes back down to the ground electronic state. In a Jablonski diagram, each of these processes are indicated with a curved line going down to on the energy scale.

Time Scales

It is important to note that a Jablonski diagram shows what sorts of transitions that can possibly happen in a particular molecule. Each of these possibilities is dependent on the time scales of each transition. The faster the transition, the more likely it is to happen as determined by selection rules. Therefore, understanding the time scales each process can happen is imperative to understanding if the process may happen. Below is a table of average time scales for basic radiative and non-radiative processes.

Table 1: Average timescales for radiative and non-radiative processes

Transition	Time Scale	Radiative Process?
Internal Conversion	10^{-14} - 10^{-11} s	no
Vibrational Relaxation	10^{-14} - 10^{-11} s	no
Absorption	10^{-15} s	yes
Phosphorescence	10^{-4} - 10^{-1} s	yes
Intersystem Crossing	10^{-8} - 10^{-3} s	no
Fluorescence	10^{-9} - 10^{-7} s	yes

Each process outlined above can be combined into a single Jablonski diagram for a particular molecule to give a overall picture of possible results of perturbation of a molecule by light energy. Jablonski diagrams are used to easily visualize the complex inner workings of how electrons change eigenstates in different conditions. Through this simple model, specific quantum mechanical phenomena are easily communicated.

References

1. H. H. Jaffe and Albert L. Miller "The fates of electronic excitation energy" *J. Chem. Educ.*, 1966, 43 (9), p 469 **DOI:**10.1021/ed043p469
2. E. B. Priestley and A. Haug "Phosphorescence Spectrum of Pure Crystalline Naphthalene" J. Chem. Phys. 49, 622 (1968), DOI:10.1063/1.1670118

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9.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

$$G(v) = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2 \chi_e \nu_e \tag{9.E.1}$$

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

$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{9.E.2}$$

Use this result to show that the dissociation energy of the diatomic molecule can be written as

$$D_e = \frac{\nu_e - \nu_e \chi_e^2}{4\chi_e} \approx \frac{\nu_e}{4\chi_e} \tag{9.E.3}$$

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
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 $38269.48 cm^{-1}$.

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

$$0 = \nu_e - 2\chi_e\nu_e(v_{max}+1) \tag{9.E.4}$$

$$2\chi_e(v_{max}+1) = 1 \tag{9.E.5}$$

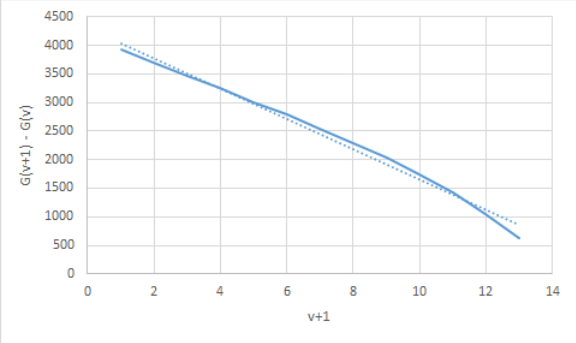
$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{9.E.6}$$

The molecule dissociates in the limit $\Delta G \to 0$, so the dissociation energy is given by

$$D_e = G(v_{max}) = (\frac{1}{2\chi_e} - \frac{1}{2})\nu_e - (\frac{1}{2\chi_e} - \frac{1}{2})^2\chi_e\nu_e = \frac{\nu_e}{2\chi_e}(1-\chi_e) - \frac{\nu_e}{4\chi_e}(1-\chi_e)^2 \tag{9.E.7}$$
$$= \frac{\nu_e}{4\chi_e}(2-2\chi_e-1+2\chi_e-\chi_e^2) = \frac{\nu_e}{4\chi_e}(1-\chi_e^2) \approx \frac{\nu_e}{4\chi_e}$$

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 $\nu_e = 4164.4 cm^{-1}$ and the slope is $-2\chi_e\nu_e = -232.01 cm^{-1}$. Thus, $\chi_e = 0.0279$. Then, the dissociation energy is

$$D_e = \frac{\nu_e}{4\chi_e} = 37400 cm^{-1} \tag{9.E.8}$$

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 $\nu_{max} = \frac{1}{2\tilde{x}_e} - 1$ to determine the number of bound vibrational levels for ground state of Na_2.

S13.21

First solve for $\tilde{x}$:

$$\tilde{x} = \frac{0.7255\ cm^{-1}}{159.125\ cm^{-1}} = 4.5593 \times 10^{-3}\ cm^{-1} \tag{9.E.9}$$

Then plug it in to the equation:

$$\nu_{max} = \frac{1}{2 \times 4.5593 \times 10^{-3}\ cm^{-1}} - 1 = 109.67\ cm^{-1} \tag{9.E.10}$$

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

$$U(q) = D_e(1 - e^{-/betaq})^2 \tag{9.E.11}$$

where $q = R - R_e$. Prove the force constant for the Morse Potential is evaluated

$$k = 2D_e\beta^2 \tag{9.E.12}$$

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

$$U(q) = D_e(1 - e^{-\beta q})^2 = D_e(1 - (1 - \beta q + \frac{\beta^2 q^2}{2}O(q)^3))^2 = D_e(\beta^2 q^2 + O(q)^3) \tag{9.E.13}$$

We know that

$$U(q) = \frac{kq^2}{2} \tag{9.E.14}$$

assuming that $O(q)^3$ approaches zero, we get

$$\frac{kq^2}{2} = D_e(\beta^2 q^2 + O(q)^3) \implies k = 2D_e\beta^2 \tag{9.E.15}$$

Plugging in our given values, we get

$$l = 2(6.23 \times 10^{-19} J \cdot Molecule^{-1})(1.37 \times 10^{10})^2 = 234 N \cdot m^{-1} \tag{9.E.16}$$

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:

$$\tilde{v}_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{9.E.17}$$

We can find k from the parameters given in the problem. Solving for k gives

$$k = (2\pi c \tilde{v}_e)^2 \mu \tag{9.E.18}$$

$$= [2\pi(3 \times 10^{10} cm \cdot s^{-1})(1580.0 cm^{-1})]^2 (7.9975 amu)(1.661 x 10^{-27} kg \cdot amu^{-1}) \tag{9.E.19}$$

$$= 1176.3 N \cdot m^{-1} \tag{9.E.20}$$

Using the equation:

$$\beta = \left(\frac{k}{2D_e}\right)^{1/2} \tag{9.E.21}$$

We can solve for β using the information above

$$\beta = \left[\frac{1176.3 N \cdot m^{-1}}{2(7.33 \times 10^{-19} J)}\right]^{1/2} \tag{9.E.22}$$

$$= 2.84 \times 10^{10} m^{-1} \tag{9.E.23}$$

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

$$\tilde{v} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e \tag{9.E.24}$$

and

$$\tilde{v} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e, \tag{9.E.25}$$

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.

$$\tilde{v}_e = [3(2143.0) - 4260.0] cm^{-1} = 2169.0 cm^{-1} \tag{9.E.26}$$

Then multiply the fundamental frequency by 2 and subtract from the overtone.

$$\tilde{x}_e\tilde{v}_e = 13.0cm^{-1} \tag{9.E.27}$$

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

$$H^{35}Cl \tag{9.E.28}$$

given

$$\tilde{v}_e = 2990.946cm^{-1} \tag{9.E.29}$$

$$\tilde{x}_e\tilde{v}_e = 52.819cm^{-1} \tag{9.E.30}$$

S13-25

Use equation,

$$\tilde{v_{obs}} = \tilde{v}_e\nu - \tilde{x}_e\tilde{v}_e\nu(\nu+1) \tag{9.E.31}$$

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:

$$\tilde{v_{obs}} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e = 2990.946cm^{-1} - 2(52.819cm^{-1}) = 2885.308cm^{-1} \tag{9.E.32}$$

First overtone:

$$\tilde{v_{obs}} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e = 2990.946cm^{-1} - 6(52.819cm^{-1}) = 5664.978cm^{-1} \tag{9.E.33}$$

Second overtone:

$$\tilde{v_{obs}} = 3\tilde{v}_e - 12\tilde{x}_e\tilde{v}_e = 3(2990.946cm^{-1}) - 12(52.819cm^{-1}) = 8339.01cm^{-1} \tag{9.E.34}$$

Q13.26

Plot the

$$\frac{\nu_{obs}}{\nu} \tag{9.E.35}$$

versus

$$(\nu+1) \tag{9.E.36}$$

for the anharmonic oscillator approximation and use it to determine the values of

$$\nu_e \tag{9.E.37}$$

and

$$x_e\nu_e \tag{9.E.38}$$

for

$$H^35Cl \tag{9.E.39}$$

. Use the information in Table13.4.

S13.26

$$\nu_{obs} = \nu_{obs}\nu - x_e\nu_e\nu(\nu+1) \tag{9.E.40}$$

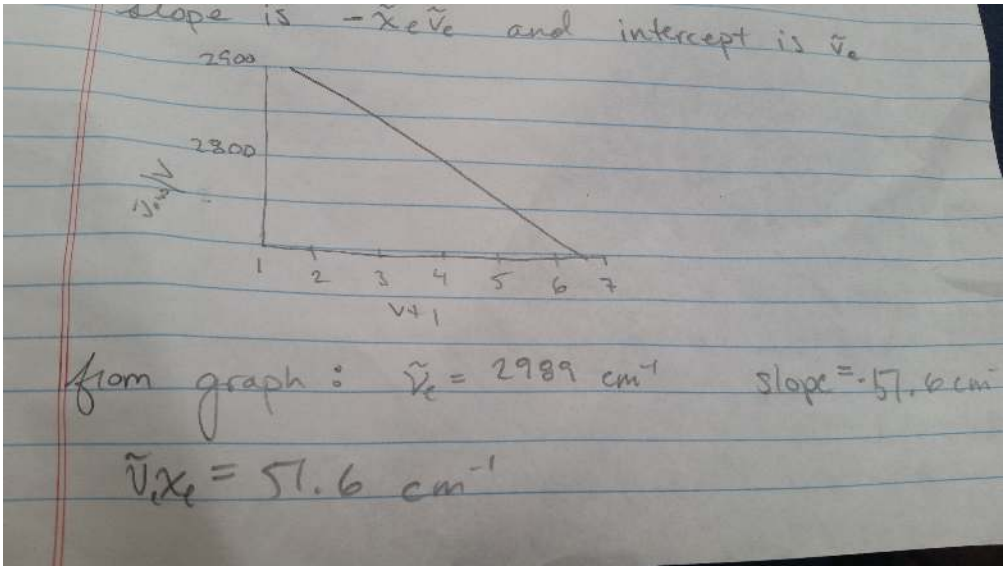
$$\frac{\nu_{obs}}{\nu} = \nu_e - x_e\nu_e(\nu+1) \tag{9.E.41}$$

The slope is

$$-x_e\nu_e \tag{9.E.42}$$

and the intercept is

$$\nu_e \tag{9.E.43}$$



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	$\tilde{\nu_{abs}}\ [cm^{-1}]$
$0 \rightarrow 0$	39,699.10
$0 \rightarrow 1$	40,786.80
$0 \rightarrow 2$	41,858.90

S13.31

We will use the following equation:

$$\tilde{\nu_{abs}} = \tilde{\nu_{0,0}}' + \tilde{\nu_e}'\tilde{\nu}' - \tilde{\chi_e}'\tilde{\nu_e}'\tilde{\nu}'(\nu'+1) \tag{9.E.44}$$

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.

- $\nu' = 0$:

$$\tilde{\nu_{0,0}}' = 29,699.10\ cm^{-1} \quad (1)$$

- $\nu' = 1$:

$$\tilde{\nu_{0,0}}' + \tilde{\nu_e}' - 2\tilde{\chi_e}'\tilde{\nu_e}' = 40,786.80\ cm^{-1} \quad (2)$$

- $\nu' = 2$:

$$\tilde{\nu_{0,0}}' + 2\tilde{\nu_e}' - 6\tilde{\chi_e}'\tilde{\nu_e}' = 41,858.90\ cm^{-1} \quad (3)$$

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:

$$\tilde{\chi_e}'\tilde{\nu_e}' = 1103.3\ cm^{-1} \quad (9.E.45)$$

and

$$\tilde{\nu_e}' = 7.80\ cm^{-1} \quad (9.E.46)$$

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	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$
$\tilde{\nu}_{obs}/cm^{-1}$	12376	89706	15219

*not accurate values for NaCl

Use these data to calculate the values of $\tilde{\nu}_e$ and $\tilde{\nu}_e\tilde{x}_e$ for the excited state of NaCl

S13.32

$A = \tilde{v}'_e, B = \tilde{v}'_e\tilde{x}'_e$

$12376 = \tilde{\nu}_0, 0$

$89706 = \tilde{\nu}_0, 0 + \tilde{v}'_e - 2\tilde{v}'_e\tilde{x}'_e - 12376 = \tilde{\nu}_0, 0 = 77330 = +\tilde{v}'_e - 2\tilde{v}'_e\tilde{x}'_e$ (1)

$15219 = \tilde{\nu}_0, 0 + 2\tilde{v}'_e - 6\tilde{v}'_e\tilde{x}'_e - 12376 = \tilde{\nu}_0, 0 = 2843 = 2\tilde{v}'_e - 6\tilde{v}'_e\tilde{x}'_e$ (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

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(sin^2 30°) = \frac{3}{2}m \tag{9.E.47}$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(cos^2 30°) = \frac{3}{2}m \tag{9.E.48}$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m \tag{9.E.49}$$

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

$$I_{xx} = 2\cos^2\theta + 8\sin^2\theta \tag{9.E.50}$$

$$I_{yy} = 8\cos^2\theta + 2\sin^2\theta \tag{9.E.51}$$

$$I_{xy} = -6\cos\theta\sin\theta \tag{9.E.52}$$

Solve the secular determinant equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0 \tag{9.E.53}$$

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 $\theta = 180°$. 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

$$I_{xx} = \sum m_i y_i^2 = 2(1)(2\sin\theta)^2 + 2(1)\left[\sin\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\sin^2\theta + 2\cos^2\theta \tag{9.E.54}$$

$$I_{yy} = \sum m_i x_i^2 = 2(1)(2\cos\theta)^2 + 2(1)\left[\cos\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\cos^2\theta + 2\sin^2\theta \tag{9.E.55}$$

$$\begin{aligned} I_{xy} = -\sum m_i x_i y_i &= -(2\cos\theta)(2\sin\theta) - 2\left[\cos(\pi) + \theta\right]\left[\sin(\pi) + \theta\right] \\ &\quad - \left[\sin\left(\frac{\pi}{2}\right) - \theta\right]\left[\cos\left(\frac{\pi}{2}\right) - \theta\right] - \left[\cos\left(\frac{\pi}{2}\right) + \theta\right]\left[\sin\left(\frac{\pi}{2}\right) + \theta\right] \\ &= -6\cos\theta\sin\theta \end{aligned} \tag{9.E.56}$$

The secular determinantal equation becomes

$$\begin{vmatrix} 8\sin^2\theta + 2\cos^2\theta - \lambda & -6\cos\theta\sin\theta \\ -6\cos\theta\sin\theta & 8\cos^2\theta + 2\sin^2\theta - \lambda \end{vmatrix} = 0 \tag{9.E.57}$$

Expanding the determinant gives

$$0 = \lambda^2 - \lambda(10)(\sin\theta^2 + \cos\theta^2) + 16(\sin\theta^2 + \cos\theta^2)^2 \tag{9.E.58}$$

$$0 = \lambda^2 - 10\lambda + 16 \tag{9.E.59}$$

$$\lambda = 5 \pm 3 \tag{9.E.60}$$

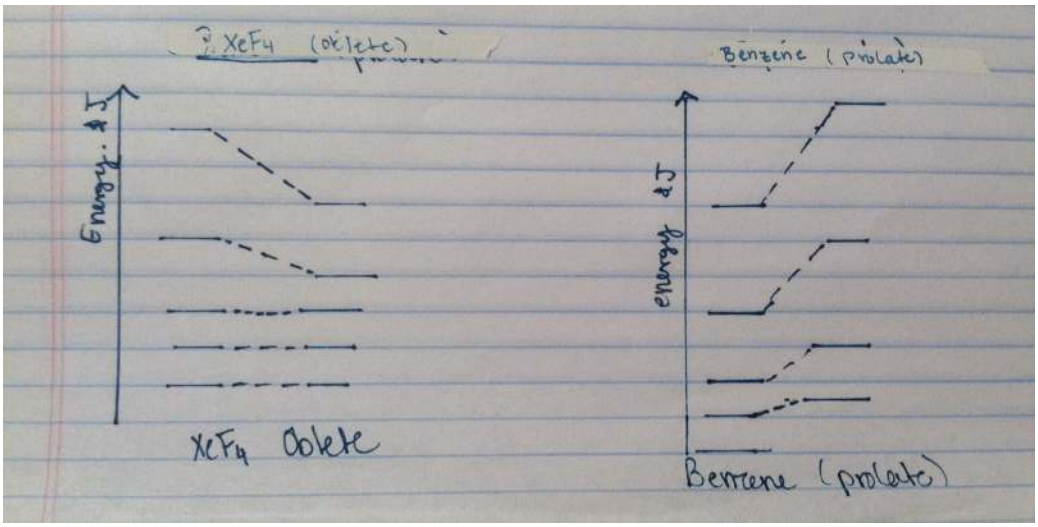
If $\theta = 180°$ then $I_{xx} = 2, I_{yy} = 8, and I_{xy} = 0$. If $\theta = 90°$ then $I_{xx} = 8, I_{yy} = 2, and I_{xy} = 0$. This tells us that the coordinate system does not affect the values of the principal momentum of inertia.

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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CHAPTER OVERVIEW

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10.1: Overview of Classical Thermodynamics

One of the pioneers in the field of modern thermodynamics was James P. Joule (1818 - 1889). Among the experiments Joule carried out, was an attempt to measure the effect on the temperature of a sample of water that was caused by doing work on the water. Using a clever apparatus to perform work on water by using a falling weight to turn paddles within an insulated canister filled with water, Joule was able to measure a temperature increase in the water.

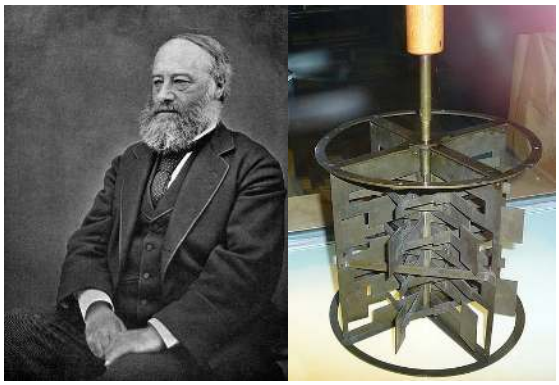


Figure **10.1.1**: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

Thus, Joule was able to show that work and heat can have the same effect on matter – a change in temperature! It would then be reasonable to conclude that heating, as well as doing work on a system will increase its energy content, and thus it's ability to perform work in the surroundings. This leads to an important construct of the **First Law of Thermodynamics**:

> *The capacity of a system to do work is increased by heating the system or doing work on it.*

The **internal energy** (U) of a system is a measure of its capacity to supply energy that can do work within the surroundings, making U the ideal variable to keep track of the flow of heat and work energy into and out of a system. Changes in the internal energy of a system (ΔU) can be calculated by

$$\Delta U = U_f - U_i \tag{10.1.1}$$

where the subscripts i and f indicate initial and final states of the system. U as it turns out, is a state variable. In other words, the amount of energy available in a system to be supplied to the surroundings is independent on how that energy came to be available. That's important because the manner in which energy is transferred is path dependent.

There are two main methods energy can be transferred to or from a system. These are suggested in the previous statement of the first law of thermodynamics. Mathematically, we can restate the first law as

$$\Delta U = q + w$$

or

$$dU = dq + dw$$

where q is defined as the amount of energy that flows into a system in the form of **heat** and w is the amount of energy lost due to the system doing **work** on the surroundings.

10.1.1: Heat

Heat is the kind of energy that in the absence of other changes would have the effect of changing the temperature of the system. A process in which heat flows into a system is **endothermic** from the standpoint of the system ($q_{system} > 0$, $q_{surroundings} < 0$). Likewise, a process in which heat flows out of the system (into the surroundings) is called **exothermic** ($q_{system} < 0$, $q_{surroundings} > 0$). In the absence of any energy flow in the form or work, the flow of heat into or out of a system can be measured by a change in temperature. In cases where it is difficult to measure temperature changes of the system directly, the amount of heat energy

transferred in a process can be measured using a change in temperature of the soundings. (This concept will be used later in the discussion of calorimetry).

An infinitesimal amount of heat flow into or out of a system can be related to a change in temperature by

$$dq = C\,dT$$

where C is the **heat capacity** and has the definition

$$C = \frac{dq}{\partial T}$$

Heat capacities generally have units of (J mol^{-1} K^{-1}) and magnitudes equal to the number of J needed to raise the temperature of 1 mol of substance by 1 K. Similar to a heat capacity is a **specific heat** which is defined per unit mass rather than per mol. The specific heat of water, for example, has a value of 4.184 J g^{-1} K^{-1} (at constant pressure – a pathway distinction that will be discussed later.)

Example 10.1.1: Heat required to Raise Temperature

How much energy is needed to raise the temperature of 5.0 g of water from 21.0 °C to 25.0 °C?

Solution

$$\begin{aligned} q &= mC\Delta T \\ &= (5.0\ \cancel{g})(4.184\frac{J}{\cancel{g}\ \cancel{^\circ C}})(25.0\cancel{^\circ C} - 21.0\cancel{^\circ C}) \\ &= 84\,J \end{aligned}$$

What is a partial derivative?

A partial derivative, like a total derivative, is a slope. It gives a magnitude as to how quickly a function changes value when one of the dependent variables changes. Mathematically, a partial derivative is defined for a function $f(x_1, x_2, \ldots x_n)$ by

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i} = \lim_{\Delta_i \to 0}\left(\frac{f(x_1 + \Delta x_1, x_2 + \Delta x_2, \ldots, x_i + \Delta x_i, \ldots x_n + \Delta x_n) - f(x_1, x_2, \ldots x_i, \ldots x_n)}{\Delta x_i}\right)$$

Because it measures how much a function changes for a change in a given dependent variable, infinitesimal changes in the in the function can be described by

$$df = \sum_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i}$$

So that each contribution to the total change in the function f can be considered separately.

For simplicity, consider an ideal gas. The pressure can be calculated for the gas using the ideal gas law. In this expression, pressure is a function of temperature and molar volume.

$$p(V,T) = \frac{RT}{V}$$

The partial derivatives of p can be expressed in terms of T and V as well.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{10.1.2}$$

and

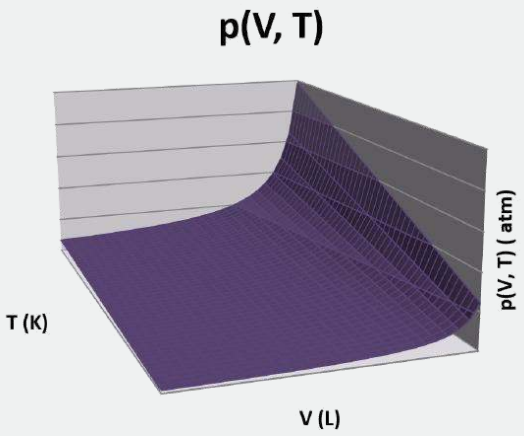
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{10.1.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{10.1.4}$$

or by substituting Equations 10.1.2 and 10.1.3

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT$$



Macroscopic changes can be expressed by integrating the individual pieces of Equation 10.1.4 over appropriate intervals.

$$\Delta p = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial p}{\partial T}\right)_V dT$$

This can be thought of as two consecutive changes. The first is an **isothermal** (constant temperature) expansion from V_1 to V_2 at T_1 and the second is an **isochoric** (constant volume) temperature change from T_1 to T_2 at V_2. For example, suppose one needs to calculate the change in pressure for an ideal gas expanding from 1.0 L/mol at 200 K to 3.0 L/mol at 400 K. The set up might look as follows.

$$\Delta p = \underbrace{\int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV}_{\text{isothermal expansion}} + \underbrace{\int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT}_{\text{isochoric heating}}$$

or

$$\begin{aligned}
\Delta p &= \int_{1.0\ L/mol}^{3.0\ L/mol} \left(-\frac{R(400\ K)}{V^2}\right) dV + \int_{200\ K}^{400,\ K} \left(\frac{R}{1.0\ L/mol}\right) dT \\
&= \left[\frac{R(200\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol} + \left[\frac{RT}{3.0\ L/mol}\right]_{200\ K}^{400\ K} \\
&= R\left[\left(\frac{200\ K}{3.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{200\ K}{3.0\ L/mol}\right)\right] \\
&= -5.47\ atm
\end{aligned}$$

Alternatively, one could calculate the change as an isochoric temperature change from T_1 to T_2 at V_1 followed by an isothermal expansion from V_1 to V_2 at T_2:

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT + \int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV$$

or

$$\begin{aligned}\Delta p &= \int_{200\ K}^{400,\ K}\left(\frac{R}{1.0\ L/mol}\right)dT + \int_{1.0\ L/mol}^{3.0\ L/mol}\left(-\frac{R(400\ K)}{V^2}\right)dV \\ &= \left[\frac{RT}{1.0\ L/mol}\right]_{200\ K}^{400\ K} + \left[\frac{R(400\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol} \\ &= R\left[\left(\frac{400\ K}{1.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{400\ K}{1.0\ L/mol}\right)\right] \\ &= -5.47\ atm\end{aligned}$$

This results demonstrates an important property of pressure in that pressure is a state variable, and so the calculation of changes in pressure do not depend on the pathway!

10.1.2: Work

Work can take several forms, such as expansion against a resisting pressure, extending length against a resisting tension (like stretching a rubber band), stretching a surface against a surface tension (like stretching a balloon as it inflates) or pushing electrons through a circuit against a resistance. The key to defining the work that flows in a process is to start with an infinitesimal amount of work defined by what is changing in the system.

Table 3.1.1: Changes to the System

Type of work	Displacement	Resistance	dw
Expansion	dV (volume)	-p_{ext} (pressure)	-p_{ext}dV
Electrical	dQ (charge)	W (resistence)	-W dQ
Extension	dL (length)	-t (tension)	t dL
Stretching	dA	-s (surf. tens.)	sdA

The pattern followed is always an infinitesimal displacement multiplied by a resisting force. The total work can then be determined by integrating along the pathway the change follows.

✔ Example 10.1.2: Work from a Gas Expansion

What is the work done by 1.00 mol an ideal gas expanding from a volume of 22.4 L to a volume of 44.8 L against a constant external pressure of 0.500 atm?

Solution

$$dw = -p_{ext}dV$$

since the pressure is constant, we can integrate easily to get total work

$$\begin{aligned}w &= -p_{exp}\int_{V_1}^{V_2} dV \\ &= -p_{exp}(V_2 - V_1) \\ &= -(0.500\ atm)(44.8\ L - 22.4\ L)\left(\frac{8.314\ J}{0.08206\ atm\ L}\right) \\ &= -1130\ J = -1.14\ kJ\end{aligned}$$

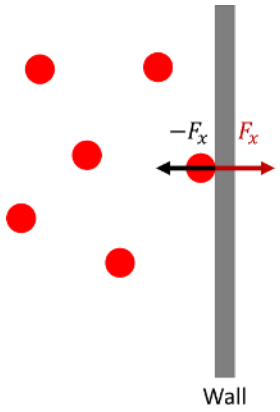
Note: The ratio of gas law constants can be used to convert between atm·L and J quite conveniently!

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10.2: 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

$$-F_x = ma_x = m\frac{\Delta v_x}{\Delta t} \tag{10.2.1}$$

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

$$-F_x = -2m\frac{v_x}{\Delta t} \tag{10.2.2}$$

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 $\Delta t = \frac{2a}{v_x}$. Consequently, the force is:

$$-F_x = -\frac{mv_x^2}{a} \tag{10.2.3}$$

Thus, the force that the particle exerts on the wall is:

$$F_x = \frac{mv_x^2}{a} \tag{10.2.4}$$

The mechanical definition of pressure is the average force over area:

$$P = \frac{\langle F \rangle}{A} \tag{10.2.5}$$

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

$$P = \frac{N\langle F_x \rangle}{a^2} \tag{10.2.6}$$

because we have N particles hitting the wall. Hence:

$$P = \frac{Nm\langle v_x^2 \rangle}{a^3} \tag{10.2.7}$$

from our study of the Maxwell-Boltzmann distribution, we found that:

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \tag{10.2.8}$$

Hence, since $a^3 = V$:

$$\begin{aligned} P &= \frac{Nk_B T}{V} \\ &= \frac{nRT}{V} \end{aligned} \tag{10.2.9}$$

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.

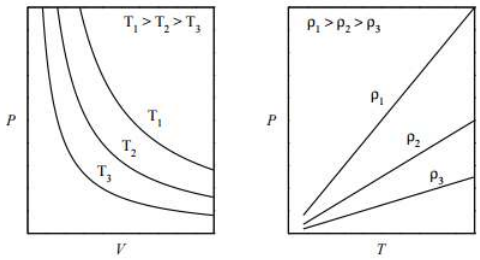


Figure 16.1.1 : (Left) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (Right) Pressure vs. temperature for different densities $\rho = N/V$.

We can rearrange the ideal gas equation of state to put all the constants and variables on one side:

$$\frac{PV}{nRT} = 1 = Z \tag{10.2.10}$$

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.

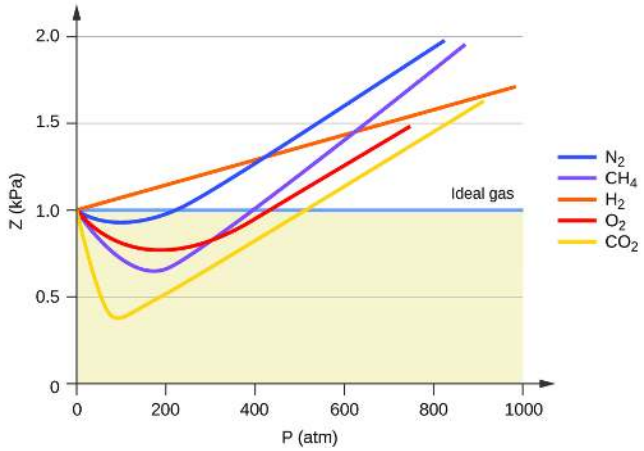


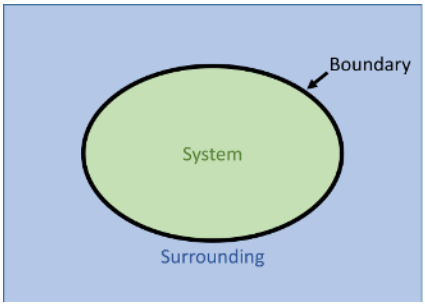
Figure 16.1.2 : A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law. from Openstax (CC-BY)

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.

10.2.1: 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:

$$\begin{aligned} PV &= nRT \\ P\bar{V} &= RT \\ P &= \rho RT \end{aligned} \tag{10.2.11}$$

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)

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10.3: 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.

10.3.1: 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:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{10.3.1}$$

Equation 10.3.1 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.

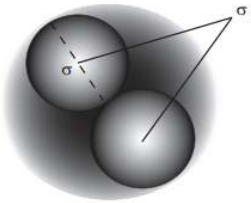


Figure 16.2.1 : Two hard spheres of diameter σ at closest contact. The distance between their centers is also σ. A sphere of radius σ just containing the two particles is shown in cross-section.

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:

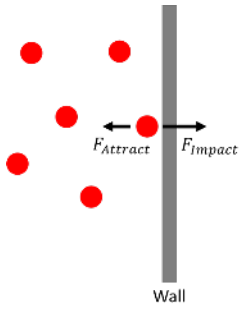
$$b = \frac{2}{3}\pi\sigma^3 N_0$$

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 $\left(\frac{L^2 \cdot bar}{mol^2}\right)$	b $\left(\frac{L}{mole}\right)$
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.*

10.3.2: 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 10.3.1) and proposed the following expressions:

$$\left(P+\frac{a}{\sqrt{T}\bar{V}(\bar{V}+b)}\right)(\bar{V}-b)=RT \tag{10.3.2}$$

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 10.3.2, 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:

$$a=0.42780\frac{R^2T_c^{2.5}}{P_c} \tag{10.3.3}$$

$$b=0.086640\frac{RT_c}{P_c} \tag{10.3.4}$$

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 10.3.2 into:

$$\bar{v}^3-\left(\frac{RT}{P}\right)\bar{v}^2+\frac{1}{P}\left(\frac{1}{T^{0.5}}-bRT-Pb^2\right)\bar{v}-\frac{ab}{PT^{0.5}}=0 \tag{10.3.5}$$

and, by defining the following parameters:

$$A=\frac{aP}{R^2T^{2.5}} \tag{10.3.6}$$

$$B=\frac{bP}{RT} \tag{10.3.7}$$

and introducing the compressibility factor definition:

$$Z=\frac{P\bar{v}}{RT}$$

we get:

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \tag{10.3.8}$$

We may also verify the two-parameter corresponding state theory by introducing Equations 10.3.3, 10.3.4, and 10.3.5 into Equation 10.3.8:

$$Z^3-Z^2+\frac{P_r}{T_r}\left(\frac{0.42748}{T_r^{1.5}}-0.08664-0.007506\frac{P_r}{T_r}\right)Z-0.03704\frac{P_r^2}{T_r^{3.5}}=0 \tag{10.3.9}$$

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 10.3.9, 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 10.3.9 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 10.3.2 through 10.3.9, 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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10.4: 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.

10.4.1: 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:

$$P = \frac{F}{A}$$

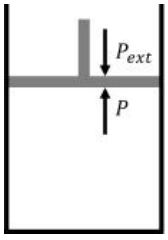


Figure 19.2.1 : A piston with internal pressure P and external pressure P_{ext}.

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:

$$w_{volume} = \int \left(\frac{F}{A}\right)(A\,ds) = \int P\,dV \tag{10.4.1}$$

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 10.4.1) 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.

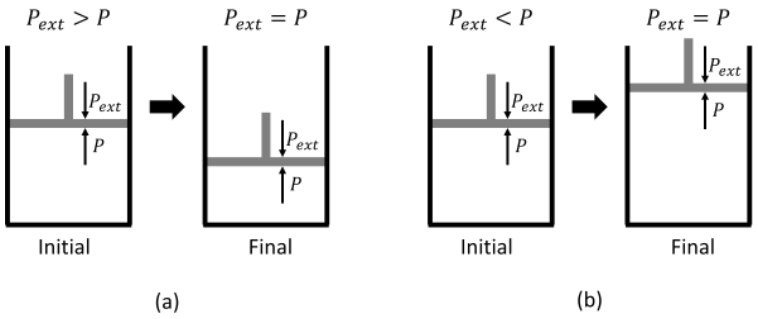


Figure 19.2.2 : Pistons showing a compression (left) and an expansion (right).

If the pressure, P_{ext}, being exerted on the system is constant, then the integral becomes:

$$w = -P_{ext} \int_{V_{initial}}^{V_{final}} dV = -P_{ext} \Delta V \tag{10.4.2}$$

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.

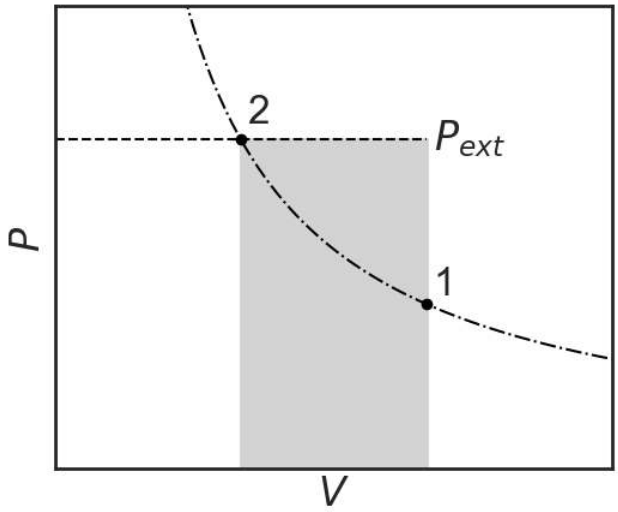


Figure 19.2.3 : A system is compressed under constant external pressure, P_{ext}, from state 1 to state 2. The shaded area shows the amount of work being done for the compression. The dash-dot line is an isotherm, a path of constant temperature, showing that the initial and final temperature of the irreversible 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:

$$w = -\int_{V_{initial}}^{V_{final}} P_{ext}(V)\, dV$$

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10.5: Work and Heat are not State Functions

10.5.1: 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**.

10.5.2: 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.

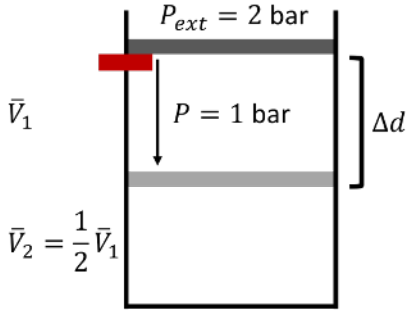


Figure 19.3.1 : A piston is being irreversibly and isothermally compressed under constant external pressure from state 1 to state 2.

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.

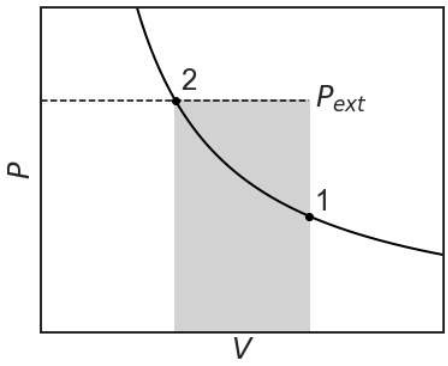


Figure 19.3.1 : The system is being irreversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area.

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 $P_{ext} = P_{system}$:

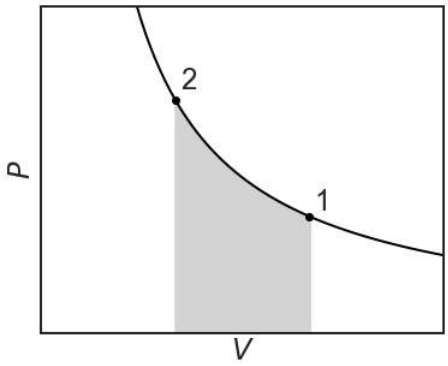


Figure 19.3.1 : The system is being reversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area. Note that for a compression, a reversible process does less work than an irreversible process.

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.

10.5.2.1: 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.

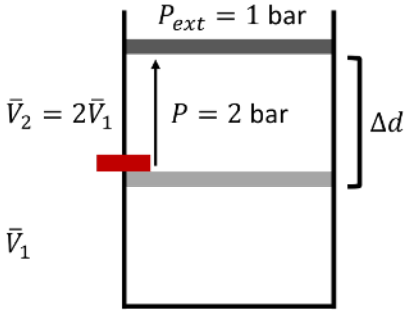


Figure 19.3.1 : A piston is being irreversibly and isothermally expanded under constant external pressure from state 1 to state 2.

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.

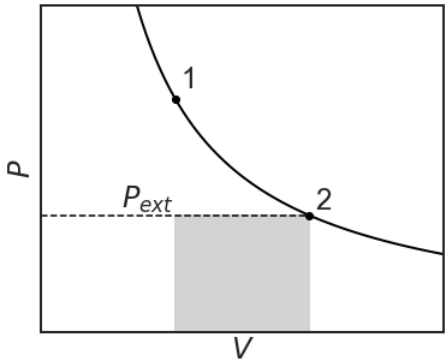


Figure 19.3.1 : The system is being irreversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area.

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 $P_{ext} = P_{system}$:

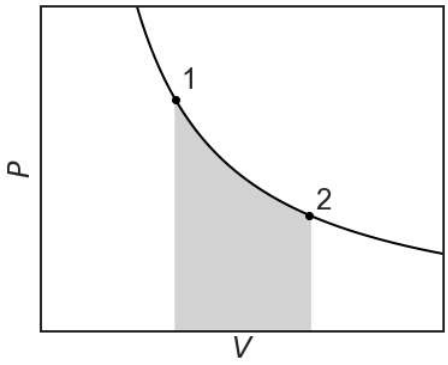


Figure 19.3.1 : The system is being reversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area. Note that for an expansion, a reversible process does more work than an irreversible process.

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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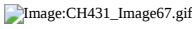
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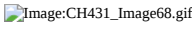
10.6: Work and Heat Have a Simple Molecular Interpretation

10.6.1: Statistical interpretation

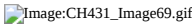
We can use what we know about the statistical side of thermodynamics to give a simple interpretation to a change dU:

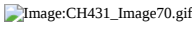
we see that because $\delta w_{rev} = -PdV$





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:





Once again we can find an important quantity of our system by manipulating the partition function Q.

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10.7: Energy is a State Function

10.7.1: 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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10.8: Heat Capacity is a Path Function

10.8.1: 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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10.9: An Adiabatic Process is a Process in which No Energy as Heat is Transferred

10.9.1: 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.

10.9.2: 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: $\delta q = 0$).

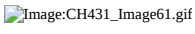
$$dU = \delta w_{rev}$$

This implies that the temperature must drop, because if U changes, then T must change.

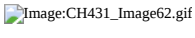
The change of energy with temperature at constant volume is known as the heat capacity (at constant volume) C_v

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

For an ideal gas U only changes with temperature, so that



or:



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

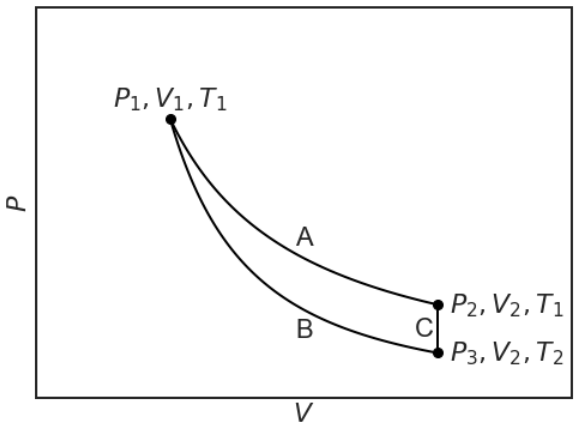


Figure __:

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:

Image:CH431_Image63.gif

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):

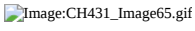
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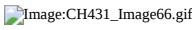
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10.10: The Temperature of a Gas Decreases in a Reversible Adiabatic Expansion

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:



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.:



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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10.11: 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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10.12: 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 .

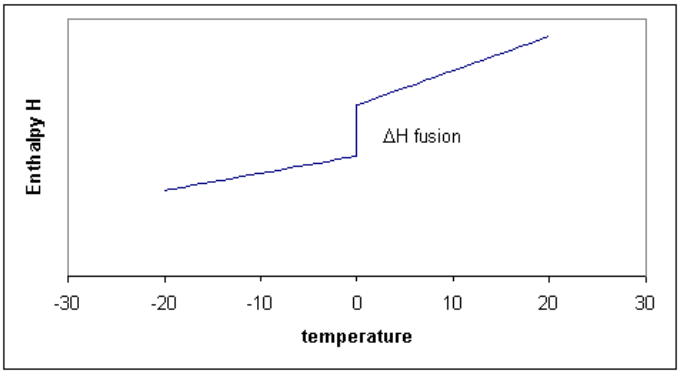


Figure 19.10.1 *: Schematic enthalpy function showing the jump at the melting point*

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:

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

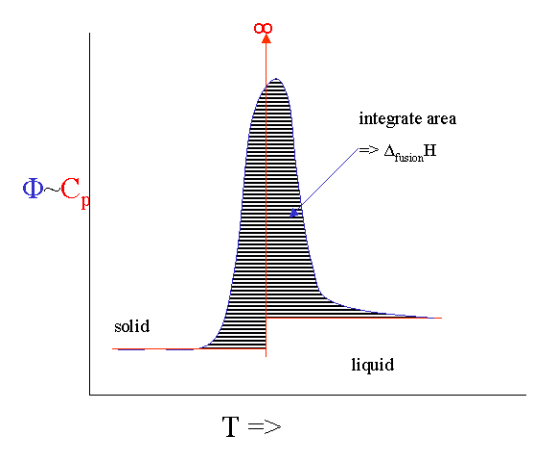
This derivative, the heat capacity must undergo a singularity: the slope is infinitely large (i.e, the H curve goes straight up). When there are more phase transitions, more discontinuities in H and singularities in C_p result (Figure 19.10.1). Note that $H(T) - H(0)$, not $H(T)$ is plotted to avoid 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 $\Delta_{fusion}H$ 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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10.13: Enthalpy Changes for Chemical Equations are Additive

10.13.1: 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.

10.13.1.1: 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)

10.13.1.2: 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

10.13.1.3: 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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10.14: 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 10.14.1:

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

$$2\times\Delta H_1 = -787.02\,kJ$$

$$2\times\Delta H_2 = 221.06\,kJ$$

$$2\times\Delta H_1 + 2\times\Delta H_2 = -565.96\,kJ$$

10.14.1: 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°). Some examples are

- $NaCl(s)$:

- $NaCl(s)$:

$$Na(s) + ½Cl_2(g) \rightarrow NaCl(s)$$

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

$$\begin{aligned} \Delta_{rxn} &= (1\, mol)\left(\Delta H_f^o(CO_2)\right) + (2\, mol)\left(\Delta H_f^o(H_2O)\right) - (1\, mol)\left(\Delta H_f^o(CH_4)\right) && (10.14.1)\\ &= (1\, mol)(-393.5\, kJ/mol) + (2\, mol)\,(-285.8\, kJ/mol) && (10.14.2)\\ &\quad - (1\, mol)\,(-74.6\, kJ/mol) \\ &= -890.5\, kJ/mol && (10.14.3) \end{aligned}$$

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.

10.14.2: 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 $-\Delta H(0K) \equiv 3^{rd} EA$.

10.14.3: 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

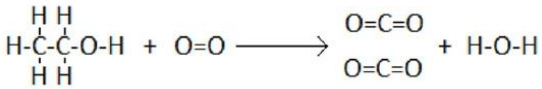
$$XY(g) \rightarrow X(g) + Y(g)$$

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

$$\begin{aligned}\Delta H_c &= 5(413\,kJ/mol) + 1(348\,kJ/mol) + 1(358\,kJ/mol) \\ &\quad + 1(495\,kJ/mol) - 4(799\,kJ/mol) - 2(463\,kJ/mol) \\ &= -856\,kJ/mol\end{aligned} \tag{10.14.4}$$

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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10.15: 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

$$\Delta H = \int_{T_2}^{T_2} C_p\,dT \tag{10.15.1}$$

Equation 10.15.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p\,\Delta T \tag{10.15.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 10.15.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{10.15.3}$$

After combining Equations 10.15.3 and 10.15.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) dT \tag{10.15.4}$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2}T^2 - \frac{c}{T}\right]_{T_1}^{T_2} \tag{10.15.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{10.15.6}$$

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 **10.15.1**: *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 10.15.1: 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 10.15.1 with a temperature dependence C_p given by Equation 10.15.1 using the parameters in Table **10.15.1**. This results in the integral form (Equation 10.15.6):

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

when substituted with the relevant parameters of Pb(s) from Table **10.15.1**.

$$\begin{aligned}\Delta H =& (22.14\,\frac{J}{mol\,K}(353\,K - 273\,K) \\ &+ \frac{1.172 \times 10^{-2}\frac{J}{mol\,K^2}}{2}\left((353\,K)^2 - (273\,K)^2\right) \\ &- 9.6 \times 10^4 \frac{J\,K}{mol}\left(\frac{1}{(353\,K)} - \frac{1}{(273\,K)}\right) \\ \Delta H =& 1770.4\,\frac{J}{mol} + 295.5\,\frac{J}{mol} + 470.5\,\frac{J}{mol} \\ =& 2534.4\,\frac{J}{mol}\end{aligned}$$

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 10.15.2: Enthalpy of Formation

The enthalpy of formation of NH_3(g) is -46.11 kJ/mol at 25 ^oC. Calculate the enthalpy of formation at 100 ^oC.

Solution

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

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

$$\begin{aligned}\Delta H(373\,K) &= \Delta H(298\,K) + \Delta C_p \Delta T \\ &= -46110 + \frac{J}{mol} \\ &\quad \left[2\left(35.06\frac{J}{mol\,K}\right) - \left(29.12\,\frac{J}{mol\,K}\right) - 3\left(28.82\,\frac{J}{mol\,K}\right)\right](373\,K - 298\,K) \\ &= -49.5\,\frac{kJ}{mol}\end{aligned}$$

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10.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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{10.E.1}$$

You can see from Equation 10.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 10.*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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CHAPTER OVERVIEW

11: Entropy and The Second Law of Thermodynamics

11.1: Energy Does not Determine Spontaneity

11.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Energy Dispersal

11.3: Unlike heat, Entropy is a State Function

11.4: The Second Law of Thermodynamics

11.5: The Famous Equation of Statistical Thermodynamics is S=k ln W

11.6: We Must Always Devise a Reversible Process to Calculate Entropy Changes

11.7: Thermodynamics Provides Insight into the Conversion of Heat into Work

11.E: Entropy and The Second Law of Thermodynamics (Exercises)

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11.1: 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 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.

11.1.1: 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?

11.1.2: 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.

11.1.2.1: 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?



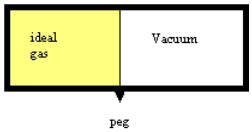
An adult White Stork. from Wikipedia (credit: Frank Vassen).

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.

11.1.3: Changing the size of the box with the particles in it

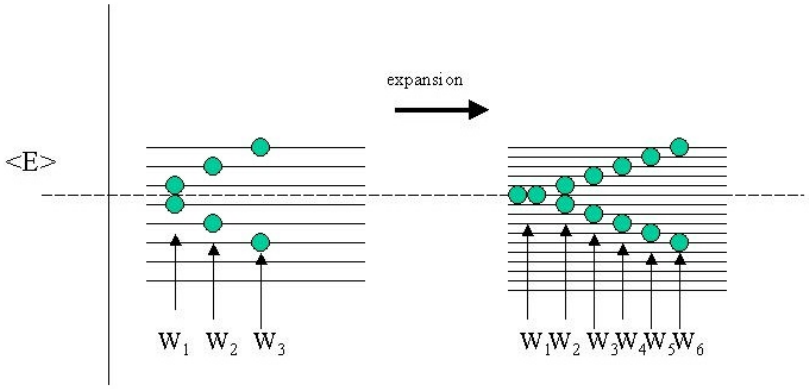
The expansion of an ideal gas against vacuum is really a wonderful *model experiment*, because *nothing else happens* but a spontaneous expansion and a change in entropy. No energy change, no heat, no work, no change in mass, no interactions, nothing. In fact, it does not even matter whether we consider 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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11.2: 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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11.3: Unlike heat, Entropy is a State Function

11.3.1: 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).

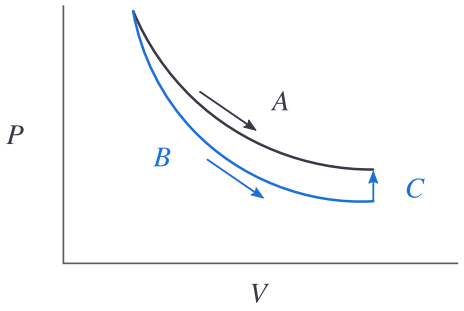


Figure 20.3.1 : A: isothermal expansion, B:adiabat, C:isochore (CC BY-NC; Ümit Kaya via LibreTexts)

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:

$$\Delta S_{B+C} = nR \ln \frac{V_2}{V_1} \tag{11.3.1}$$

(Notice sign in Equation 11.3.1 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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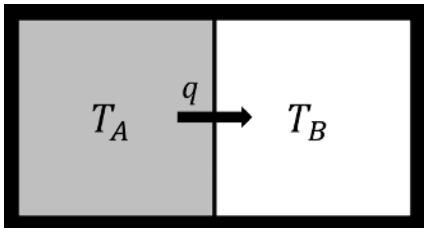
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11.4: The Second Law of Thermodynamics

11.4.1: 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:

$$dS = \frac{\delta q_{rev}}{T}$$

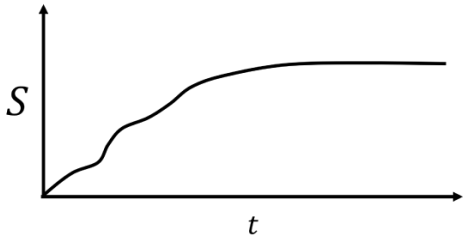
In this particular case:

$$TdS = \delta q_{rev} = dU$$

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***.

11.4.2: 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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11.5: 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:

$$S = k_b \ln(W) \tag{11.5.1}$$

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 11.5.1).



Figure 11.5.1: Ludwig Boltzmann (1844 - 1906)

Example 11.5.1:

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 11.5.1):

$$S = nK \ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$\begin{aligned} S &= \left(1.00\, mol \cot \frac{6.022 \times 10^{23}}{1\, mol}\right)(1.38 \times 10^{-23} J/K) \ln 2 \\ &= 5.76\, J/K \end{aligned}$$

11.5.1: Contributors and Attributions

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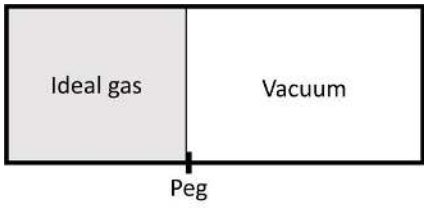
11.6: We Must Always Devise a Reversible Process to Calculate Entropy Changes

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.

11.6.1: 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:

$$q_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right) \tag{11.6.1}$$

The Claussius definition of entropy change can be used to find ΔS (under constant temperature).

$$\Delta S = \frac{q_{rev}}{T} \tag{11.6.2}$$

Substituting Equation 11.6.1 into Equation 11.6.2 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:

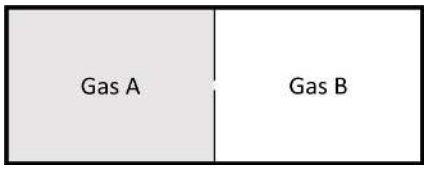
$$dS = \frac{\delta q}{T}$$

Therefore, the total entropy change for the reversible process is zero:

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) - nR\ln\left(\frac{V_2}{V_1}\right) \\ &= 0\end{aligned}$$

11.6.2: 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:

$$\frac{\Delta S}{n_{tot}} = R\frac{\left[n_B\ln\frac{n_{tot}}{n_B} + n_A\ln\frac{n_{tot}}{n_A}\right]}{n_{tot}} \tag{11.6.3}$$

Equation 11.6.3 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:

$$\Delta\bar{S} = -R[\chi_A \ln \chi_A + \chi_B \ln \chi_B] \tag{11.6.4}$$

In the case of mixing of more than two gases, Equation 11.6.4 can be expressed as:

$$\Delta\bar{S} = -R\sum \chi_i \ln \chi_i \tag{11.6.5}$$

This entropy expressed in Equations 11.6.4 and 11.6.5 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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11.7: 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.

11.7.1: The Carnot Cycle

Let's consider a circular, reversible path of an ideal gas on a PV diagram in Figure **11.7.1**:

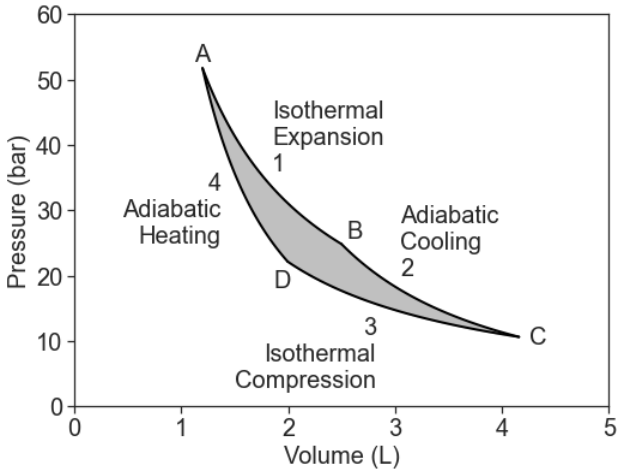


Figure 11.7.1: A circular, reversible path of a Carnot cycle as an ideal gas on a PV diagram. (CC BY 4.0; Jerry LaRue via LibreTexts)

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

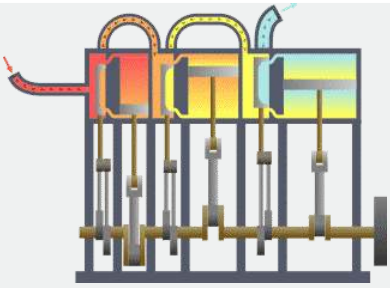


Figure **11.7.2**: Animation of a typical vertical triple-expansion engine. (CC SA-BY 2.5; Emoscopes)

11.7.2: 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 $q_h \rightarrow q_c$ 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. $dU = \delta w = \bar{C}_V dT \rightarrow w_2 = \bar{C}_V (T_c - T_h)$
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}:

$$\begin{aligned} w_{\text{cycle}} &= -RT_h \ln\left(\frac{V_B}{V_A}\right) + \bar{C}_V (T_c - T_h) - RT_c \ln\left(\frac{V_D}{V_C}\right) + \bar{C}_V (T_h - T_c) \\ &= -RT_h \ln\left(\frac{V_B}{V_A}\right) - RT_c \ln\left(\frac{V_D}{V_C}\right) = -R(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right) \end{aligned}$$

We have an expression for work, so we can evaluate the efficiency, η. The efficiency of the Carnot engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{R(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)}{RT_h \ln\left(\frac{V_B}{V_A}\right)} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$

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:

$$\eta = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \tag{11.7.1}$$

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 11.7.1 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 11.7.3 should then be three times as fat as the one that says w.

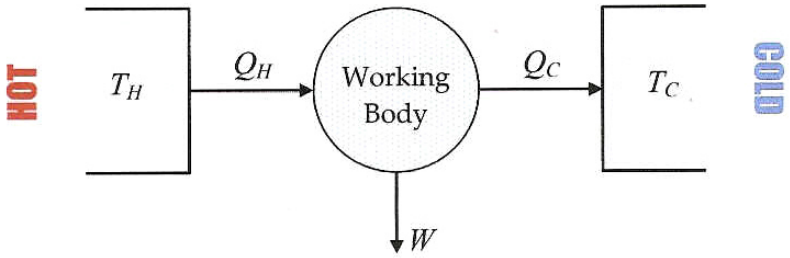


Figure 11.7.3: Carnot engine diagram (modern) - where an amount of heat Q_H flows from a high temperature T_H furnace through the fluid of the "working body" (working substance) and the remaining heat Q_C flows into the cold sink T_C, thus forcing the working substance to do mechanical work W on the surroundings, via cycles of contractions and expansions. (Public Domain; Eric Gaba)

11.7.3: 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.

11.7.4: 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 11.7.4:

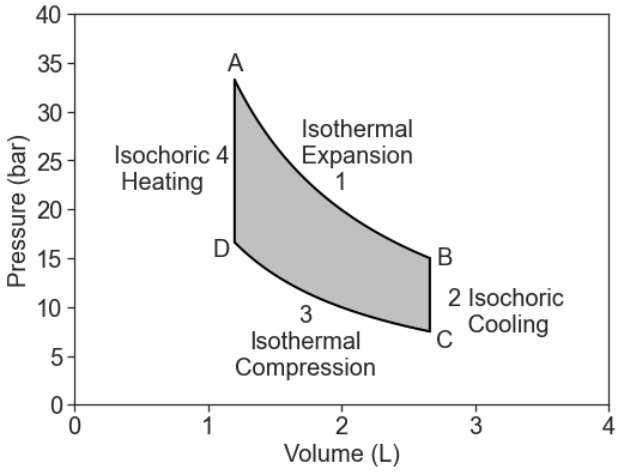


Figure **11.7.4**: an ideal PV diagram of the Stirling engine. (CC BY 4.0; Jerry LaRue via LibreTexts)

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):

   $$q_2 = \frac{C_V}{\Delta T} \tag{11.7.2}$$

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):

   $$q_4 = -\frac{C_V}{\Delta T} \tag{11.7.3}$$

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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11.E: Entropy and The Second Law of Thermodynamics (Exercises)

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CHAPTER OVERVIEW

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12.1: 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**:

$$A \equiv U - TS$$

$$dA = dU - TdS - SdT \tag{12.1.1}$$

If we also set T constant, we see that Equation 12.1.1 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.

12.1.1: 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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12.2: 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***.

12.2.1: 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°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.

12.2.2: 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.

12.2.3: 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!

12.2.4: 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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12.3: 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 $dU = dq + dw$):

$$dU = TdS - pdV \tag{12.3.1}$$

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!

12.3.1: 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 12.3.1 can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{12.3.2}$$

Also, by inspection (comparing the two expressions for dU in Equations 12.3.1 and 12.3.2) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{12.3.3}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{12.3.4}$$

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 12.3.3 and 12.3.4, 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.

$$dH = TdS + Vdp \tag{12.3.5}$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{12.3.6}$$

Comparing Equations 12.3.5 and 12.3.6 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{12.3.7}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{12.3.8}$$

It is worth noting at this point that both Equation 12.3.3

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and Equation 12.3.7

$$\left(\frac{\partial H}{\partial S}\right)_p$$

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 12.3.1.

Table 12.3.1: 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 12.3.1

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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12.4: 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:

$$G = H - TS \tag{12.4.1}$$

Consider an isothermal change in pressure, so taking the partial derivative of each side of Equation 12.4.1, we get:

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{12.4.2}$$

For an ideal gas

$$\frac{\partial V}{\partial T} = \frac{nR}{P}$$

so Equation 12.4.2 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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12.5: 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.

12.5.1: 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.

12.5.2: 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,

$$dU = TdS - pdV \tag{12.5.1}$$

The above equation is the fundamental equation for U with natural variables of entropy S and volume$V$.

12.5.2.1: 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.

12.5.3: Enthalpy

Mathematically, enthalpy is defined as

$$H = U + pV \tag{12.5.2}$$

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 12.5.2) and the fundamental equation for internal energy (Equation 12.5.1) :

$$\begin{aligned} dH &= dU + d(pV) \\ &= dU + pdV + VdP \\ dU &= TdS - pdV \\ dH &= TdS - pdV + pdV + Vdp \\ dH &= TdS + Vdp \end{aligned}$$

The above equation is the fundamental equation for H. The natural variables of enthalpy are S and p, entropy and pressure.

12.5.4: Gibbs Energy

The mathematical description of Gibbs energy is as follows

$$\begin{aligned} G &= U + pV - TS \\ &= H - TS \end{aligned} \tag{12.5.3}$$

where G is the Gibbs energy of the system. The fundamental thermodynamic equation for Gibbs Energy follows directly from its definition 12.5.3 and the fundamental equation for enthalpy 12.5.2:

$$\begin{aligned} dG &= dH - d(TS) \\ & dH - TdS - SdT \end{aligned}$$

Since

$$\begin{aligned} dH &= TdS + VdP \\ dG &= TdS + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned} \tag{12.5.4}$$

The above equation is the fundamental equation for G. The natural variables of Gibbs energy are P and T.

12.5.5: Helmholtz Energy

Mathematically, Helmholtz energy is defined as

$$A = U - TS \tag{12.5.5}$$

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 12.5.5) and the fundamental equation for internal energy (Equation 12.5.1):

$$\begin{aligned} dA &= dU - d(TS) \\ &= dU - TdS - SdT \end{aligned}$$

Since

$$\begin{aligned} dU &= TdS - pdV \\ dA &= TdS - pdV - TdS - SdT \\ &= -pdV - SdT \end{aligned} \tag{12.5.6}$$

Equation 12.5.6 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.

12.5.6: 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.

12.5.7: 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

12.5.8: 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 12.5.6) 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 12.5.4 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 12.5.1

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

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 12.5.2

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

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 12.5.3

Derive the Maxwell Relations.

Answer

See the Maxwell Relations section.

? Exercise 12.5.4

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

$(\frac{\partial H}{\partial P})_{T,n} = 0$ 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 12.5.5

Using the definition of Gibbs energy and the conditions observed at phase equilibria, derive the Clapeyron equation.

Answer

See the third outside link.

12.5.9: 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.

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12.6: 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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12.7: The Gibbs-Helmholtz Equation

12.7.0.1: 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 $G^{\ominus}_{molar}$

12.7.0.1: 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:

$$G(P_{final}) = G(P_{initial}) + \int V dP(\text{from init to final})$$
$$\approx G(P_{initial}) + V \int dP(\text{from init to final}) = G(P_{initial}) + V\Delta P$$

12.7.1: 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

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{\cancel{C_P}}{\cancel{T}} - \frac{\cancel{C_P}}{\cancel{T}} \tag{12.7.1}$$
$$= -\frac{H}{T^2} \tag{12.7.2}$$

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.

12.7.2: 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.

$$H(T) = H(0) + \int_0^{T_{fus}} C_p(T)_{solid} dT + \Delta H_{fus} + \int_{T_{fus}}^{T_{boil}} C_p(T)_{liquid} dT + \Delta H_{vap} + etc. \tag{12.7.3}$$

$$S(T) = S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \Delta S_{fus} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \Delta S_{vap} + etc. \tag{12.7.4}$$

$$= S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + etc. \tag{12.7.5}$$

with $H(T = 0) = \textbf{undefined}$ 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 12.7.3 and 12.7.5):

$$G(T) = H(T) - TS(T)$$

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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12.E: Helmholtz and Gibbs Energies (Exercises)

22.E: Helmholtz and Gibbs Energies (Exercises)

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CHAPTER OVERVIEW

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13.1: 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.

13.1.1: 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}.

13.1.2: 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

13.1.3: 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.

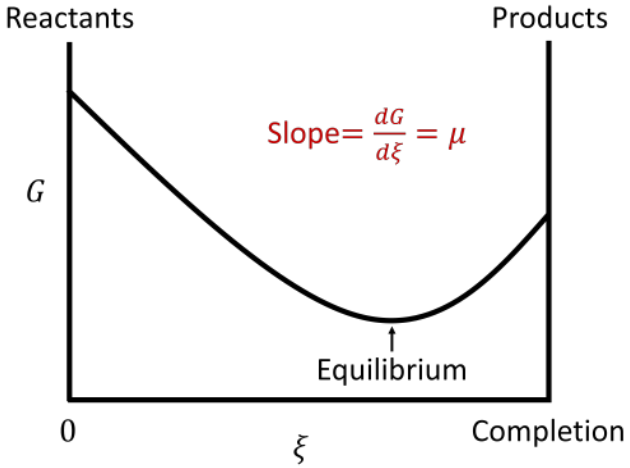


Figure 1. Gibbs energy plotted as a function of the extent of reaction. Equilibrium results when the Gibbs energy is minimized.

13.1.4: 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 $\Delta_r G$ 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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13.2: 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:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

13.2.1: 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.

13.2.2: Concentration

The gas law contains a hidden definition of concentration:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = cRT$$

$$c = \frac{P}{RT} \tag{13.2.1}$$

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

$$K = \frac{c_{eq,Y}^{v_Y} c_{eq,Z}^{v_Z}}{c_{eq,A}^{v_A} c_{eq,B}^{v_B}} \tag{13.2.2}$$

However, c (Equation 13.2.1) is substituted into K (Equation 13.2.2), then not all the factors of RT cancel. The missing term g. ln[RT] depends on the stoichiometric coefficients:

$$g = v_Y + v_Z - v_A - v_B$$

The term is generally *incorporated* in $\Delta_r G^\circ$ 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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13.3: Standard Gibbs Energies of Formation Can Be Used to Calculate Equilibrium Constants

13.3.1:

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_+:

$$z_+\mathrm{H^+(aq)} + \text{elements} \rightarrow (z_+/2)\mathrm{H_2(g)} + \mathrm{M^{z+}(aq)}$$

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:

$$\Delta_r H^\circ = \Delta_f H^\circ(\mathrm{M^{z+}}) \tag{11.8.25}$$

$$\Delta_r S^\circ = (z_+/2)S^\circ_m(\mathrm{H_2}) + S^\circ_m(\mathrm{M^{z+}}) - \sum_{\text{elements}} S^\circ_i \tag{11.8.26}$$

$$\Delta_r G^\circ = \Delta_f G^\circ(\mathrm{M^{z+}}) \tag{11.8.27}$$

Then, from $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, we find

$$\Delta_f G^\circ(\mathrm{M^{z+}}) = \Delta_f H^\circ(\mathrm{M^{z+}}) \quad - T\left[S^\circ_m(\mathrm{M^{z+}}) - \sum_{\text{elements}} S^\circ_i + (z_+/2)S^\circ_m(\mathrm{H_2})\right] \tag{11.8.28}$$

For example, the standard molar Gibbs energy of the aqueous mercury(I) ion is found from

$$\Delta_f G^\circ(\mathrm{Hg_2{}^{2+}}) = \Delta_f H^\circ(\mathrm{Hg_2{}^{2+}}) - TS^\circ_m(\mathrm{Hg_2{}^{2+}}) + 2TS^\circ_m(\mathrm{Hg}) - \tfrac{2}{2}TS^\circ_m(\mathrm{H_2}) \tag{11.8.29}$$

For an anion $\mathrm{X^{z-}}$ with negative charge number z_-, using the hypothetical reaction

$$|z_-/2|\mathrm{H_2(g)} + \text{elements} \rightarrow |z_-|\,\mathrm{H^+(aq)} + \mathrm{X^{z-}(aq)}$$

we find by the same method

$$\Delta_f G^\circ(\mathrm{X^{z-}}) = \Delta_f H^\circ(\mathrm{X^{z-}}) - T\left[S^\circ_m(\mathrm{X^{z-}}) - \sum_{\text{elements}} S^\circ_i - |z_-/2|\,S^\circ_m(\mathrm{H_2})\right] \tag{11.8.30}$$

For example, the calculation for the nitrate ion is

$$\begin{aligned}&\Delta_f G^\circ(\mathrm{NO_3{}^-}) \\ &= \Delta_f H^\circ(\mathrm{NO_3{}^-}) - TS^\circ_m(\mathrm{NO_3{}^-}) + \tfrac{1}{2}TS^\circ_m(\mathrm{N_2}) + \tfrac{3}{2}TS^\circ_m(\mathrm{O_2}) + \tfrac{1}{2}TS^\circ_m(\mathrm{H_2})\end{aligned} \tag{11.8.31}$$

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13.4: 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 $\mathbf{A} \rightleftharpoons \mathbf{B}$, 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 **13.4.1**). 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?

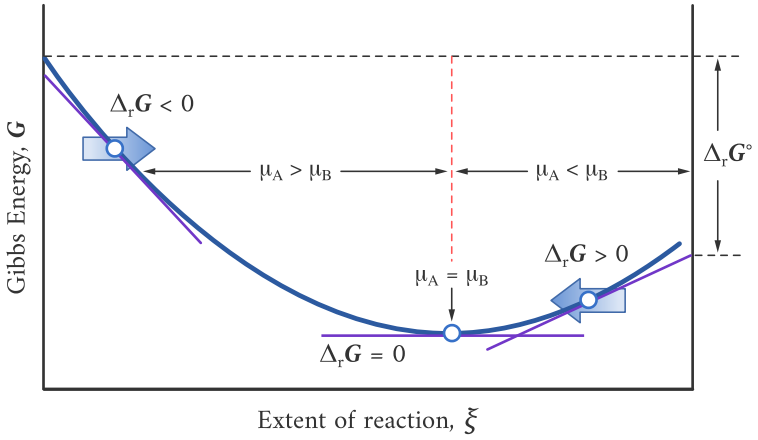


Figure **13.4.1**: Reactive Gibbs Energy and Equilibria. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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.

13.4.1: 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.

$$\mathbf{A} \rightleftharpoons \mathbf{B}$$

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.

$$\Delta G_{\text{mix}} = nRT\left(\chi_A \ln \chi_A + \chi_B \ln \chi_B\right) \tag{13.4.1}$$

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 13.4.1 is at a minimum when the amounts of **A** equal **B**.

Thus, if we have a reaction $\mathbf{A} \rightleftharpoons \mathbf{B}$ 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**.

$$\begin{aligned}\Delta_r G^o &= \mu_B^o - \mu_A^o \\ \Delta_r G &= \Delta_r G^o + RT\ln\frac{P_B}{P_A}\end{aligned} \tag{13.4.2}$$

There are two parts to Equation 13.4.2. 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 13.4.2). 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.

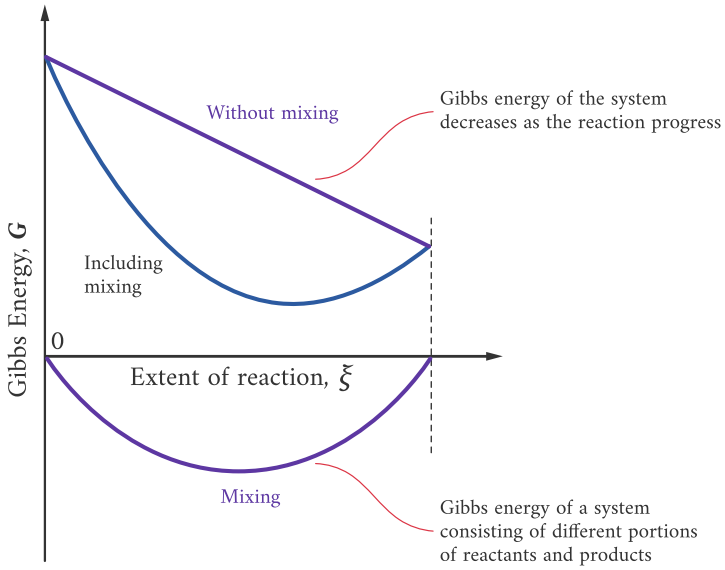


Figure **13.4.2**: Molecular interpretation of the minimum in the reaction Gibbs energy Gibbs energy of the system decreases as the reaction progress Gibbs energy of a system consisting of different portions of reactants and products. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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 **13.4.1**) 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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13.5: 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:

$$aA + bB \rightleftharpoons cC + dD \tag{13.5.1}$$

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:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{13.5.2}$$

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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13.6: 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, $\Delta_r G°$. The ° 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:

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g)$$

$$\Delta_r G° = -32.9\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

If the reaction was run under standard state conditions (1 bar partial pressure of each gas), the reaction would shift towards the products since $\Delta_r G° < 0$. 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:

$$\Delta_r G = \Delta_r G° + RT \ln Q = \Delta_r G° + RT \ln \left(\frac{P_{\mathrm{NH_3}}^2}{P_{\mathrm{N_2}} P_{\mathrm{H_2}}^3} \right)$$

At equilibrium, the minimum Gibbs energy of reaction will be reached:

$$\Delta_r G = 0\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

And the reaction quotient will equal the equilibrium constant:

$$Q = K$$

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13.7: 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

$$K = e^{-\Delta_r G^o/RT} \tag{13.7.1}$$

However, since under constant pressure and temperature

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Equation 13.7.1 becomes

$$K = e^{-\Delta H^o/RT} e^{\Delta S^o/R} \tag{13.7.2}$$

Taking the natural log of both sides, we obtain a linear relation between $\ln K$and the standard enthalpies and entropies:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \tag{13.7.3}$$

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 $\Delta_r S^o/R$.

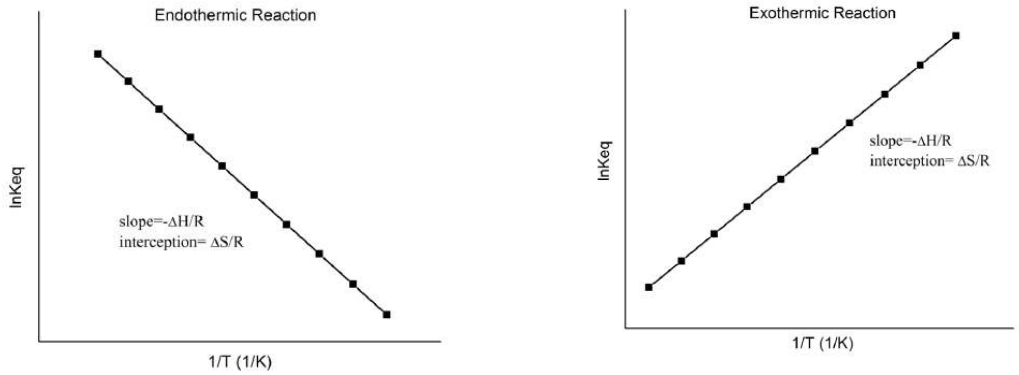


Figure 26.7.1 : Endothermic Reaction (left) and Exothermic Reaction van 't Hoff Plots (right). Figures used with permission of Wikipedia

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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13.8: 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:

$$K = K_\gamma K_c / K_{c^{\ominus}}$$

$$K_\gamma = [\gamma_{eq,Y}{}^{\nu_Y} \gamma_{eq,Z}{}^{\nu_Z} / \gamma_{eq,A}{}^{\nu_A} \gamma_{eq,B}{}^{\nu_B}]$$

$$K_c = [c_{eq,Y}{}^{\nu_Y} c_{eq,Z}{}^{\nu_Z} / c_{eq,A}{}^{\nu_A} c_{eq,B}{}^{\nu_B}]$$

$$K_{c^{\ominus}} = [c_{c^{\ominus}}{}^{\nu_Y} c_{c^{\ominus}}{}^{\nu_Z} / c_{c^{\ominus}}{}^{\nu_A} c_{c^{\ominus}}{}^{\nu_B}]$$

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.

13.8.1: 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

$$d\mu = RTd\ln a$$

We can study the pressure dependence by considering:

$$\partial \mu / \partial P |_T = V_{\text{partial molar}} \; (V_{bar})$$

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
1083

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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13.9: Activities are Important for Ionic Species

13.9.0.1: 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?

13.9.1: 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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13.10: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{13.10.1}$$

You can see from Equation 13.10.1 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 13.10.1

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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CHAPTER OVERVIEW

14: Solutions I - Volatile Solutes

14.1: A Mixture is a Combination of Two or More Substances
14.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium
14.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears
14.4: Ideal Solutions obey Raoult's Law
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14.6: Vapor Pressures of Volatile Binary Solutions
14.7: Activities of Nonideal Solutions
14.8: Activities are Calculated with Respect to Standard States
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14.E: Solutions I- Liquid-Liquid Solutions (Exercises)

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14.1: 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.

14.1.1: 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.

14.1.2: 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):

$$P_{total} = P_1 + P_2 \tag{14.1.1}$$

14.1.3: 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

14.1.4: 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.

14.1.5: 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:

$$y_i = \frac{P_i}{P_{total}} \tag{14.1.2}$$

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:

$$P_i = \chi_i P_i^\circ \tag{14.1.3}$$

- 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 ith 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.

14.1.6: 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:

$$\begin{aligned} P_{total} &= P_1 + P_2 \\ &= \chi_1 P_1^\circ + \chi_2 P_2^\circ \\ &= \chi_1 P_1^\circ + (1-\chi_1) P_2^\circ \\ &= P_2^\circ - \chi_1 (P_2^\circ - P_1^\circ) \end{aligned} \tag{14.1.4}$$

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 14.1.2) and substitute Raoult's Law (Equation 14.1.3) in the numerator and the straight line in the denominator we get:

$$y_1 = \frac{\chi_1 P_1^\circ}{P_2^\circ - \chi_1 (P_2^\circ - P_1^\circ)} \tag{14.1.5}$$

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 14.1.4 and 14.1.5 to plot the total pressure as function of y_1:

$$P_{total} = \frac{P_1^\circ P_2^\circ}{P_1^\circ + (P_2^\circ - P_1^\circ) y_1} \tag{14.1.6}$$

This is *not* a straight line.

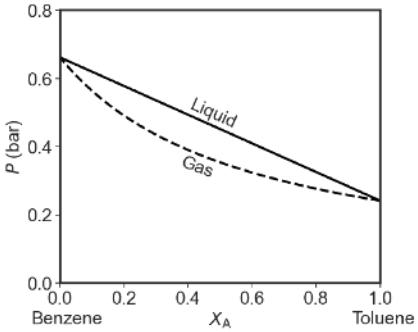


Figure 24.1.1: an ideal-ideal phase diagram for the binary system of toluene (A) and benzene (B). The curves are calculated from Equations 14.1.4 and 14.1.6.

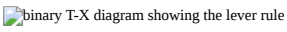
As you can see when we plot both lines we get a diagram with three regions. At high pressures we just have a liquid. At low pressures we just have a gas. In between we have a ***phase gap*** or ***two phase region***. Points inside this region represent states that the system cannot achieve homogeneously. 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.

14.1.7: 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

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.

14.1.7.1: 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:

$$\frac{n_{1+2}^{liq}}{n_{1+2}^{gas}} = \frac{y_2 - x_{all}}{x_{all} - x_2}$$

14.1.7.2: 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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14.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium

At **equilibrium**, there is no change in chemical potential for the system:

$$\sum_i n_i d\mu_i = 0 \tag{14.2.1}$$

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:

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{14.2.2}$$

For a system at constant temperature and pressure:

$$V\ dp - s\ dT = 0 \tag{14.2.3}$$

Substituting Equation 14.2.3 into 14.2.2 results in the **Gibbs-Duhem equation** (Equation 14.2.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium.

14.2.1: **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 ($d\mu_B$).*

14.2.2: 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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14.3: 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:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} \tag{14.3.1}$$

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 **14.3.1**: 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 14.3.1). 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:

$$\int_{\mu^o}^{\mu} d\mu = \int_{P^o}^{P} V\, dP \tag{14.3.2}$$

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 14.3.2 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 14.3.2 then becomes:

$$\int_{\mu^o}^{\mu} d\mu = RTint_{P^o}^{P} \frac{dP}{P} \tag{14.3.3}$$

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.

14.3.1: 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:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{14.3.4}$$

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:

$$\mu_1^{*liq} = \mu_1^o + RT \ln \frac{P_1^*}{P^o} \tag{14.3.5}$$

Combining Equations 14.3.5 and 14.3.4 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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14.4: 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.

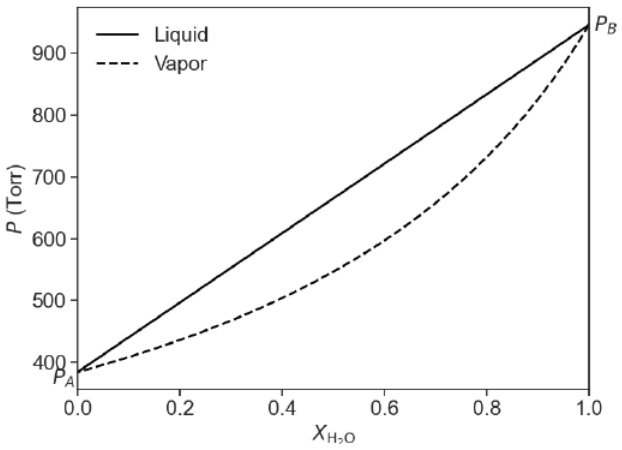


Figure 24.4.1: The composition of the liquid phase (solid line) and the vapor phase (dashed lined) as a function of mole fraction according to Raoult's law. The solution is a mixture of water and ethanol. P_A is the vapor pressure of pure water and P_B is the vapor pressure of pure ethanol at 75 °C

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.

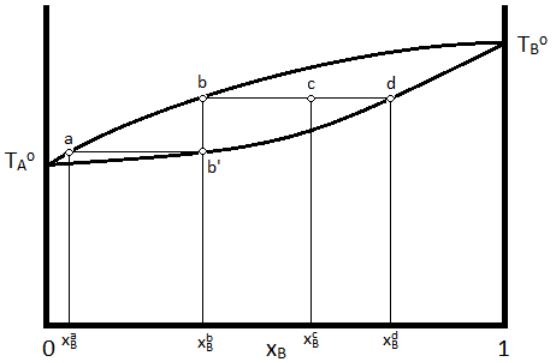


Figure 24.4.2: A typical temperature vs. composition diagram.

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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.

14.4.1: 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.

14.4.2: 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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14.5: 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).

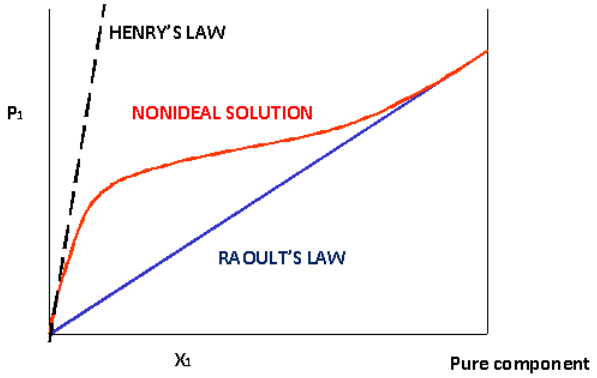


Figure 24.5.1 : Vapor pressure above an ideal and a non-ideal solution

> 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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14.6: 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 **14.6.1**.

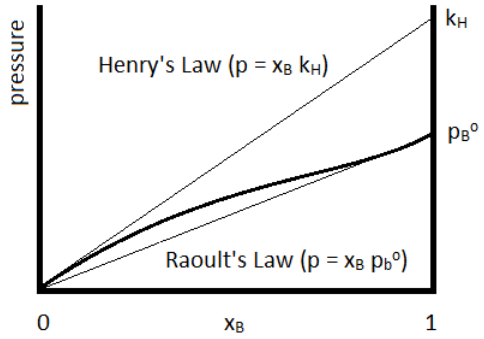


Figure **14.6.1**: The relationship between Raoult's Law and Henry's Law for a binary mixture.

Henry's Law is depicted by the upper straight line and Raoult's Law by the lower.

Example 14.6.1: 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

$$10^5\,Pa = 5.98\times10^{-4}k_H$$

or

$$k_H = 1.67\times10^9\,Pa$$

14.6.1: Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

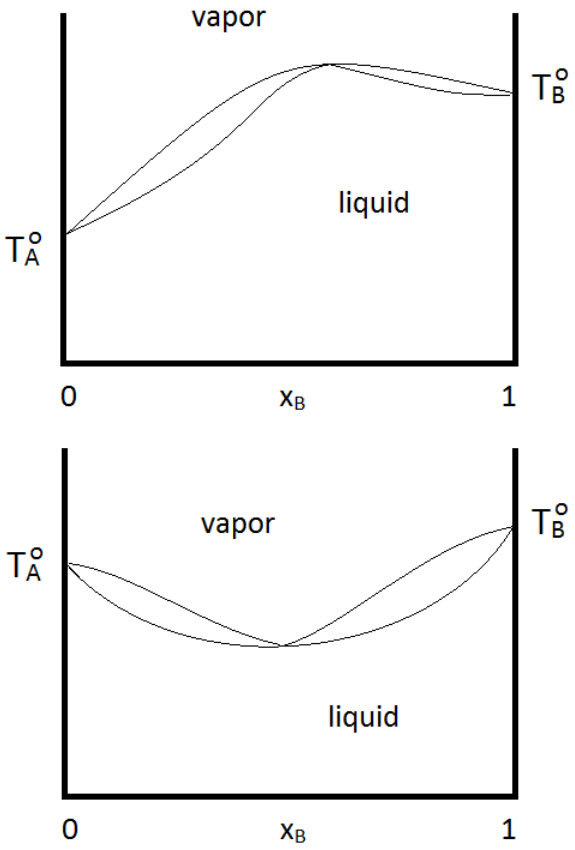


Figure **14.6.2**: Phase diagrams for (left) a maximum boiling point azeotrope and (right) Ta maximum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as show in Figure **14.6.2**;. 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 **14.6.2**;:

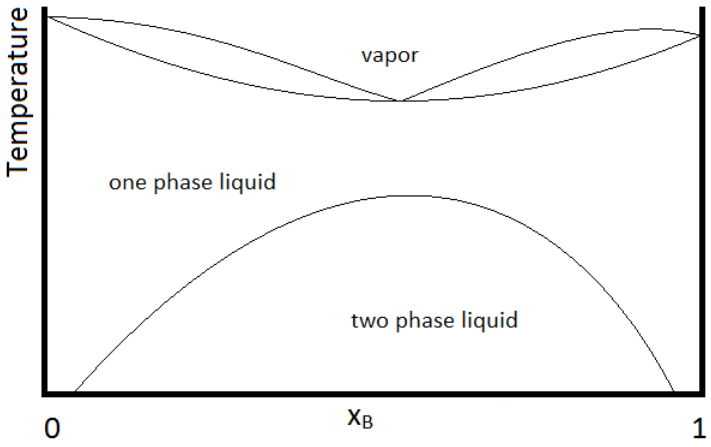
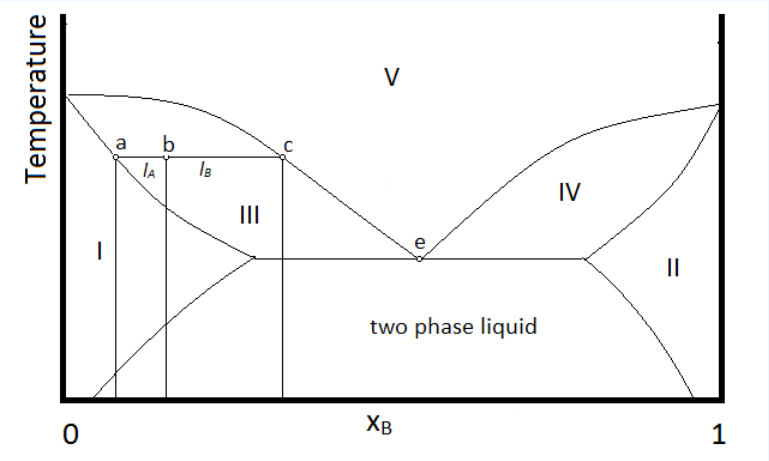


Figure **14.6.3**: *Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher that when components are miscible (single phase).*

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 **14.6.3**.

Example 14.6.1:

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.

14.6.1.1: Gibbs-Duhem and Henry's law

What happens when Raoult does *not* hold over the whole range? Recall that in a gas:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{14.6.1}$$

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

$$\frac{x_1}{x_1} = x_2\frac{\partial \ln P_2}{\partial x_2}$$

$$1 = x_2\frac{\partial \ln P_2}{\partial x_2}$$

$$\frac{1}{x_2} = \frac{\partial \ln P_2}{\partial x_2} \tag{14.6.2}$$

We can integrate Equation 14.6.2 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 *some* 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.)

14.6.2: 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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14.7: 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.

14.7.1: 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

$$M_x X_y(s) \rightarrow xM^{y+}(aq) + yX^{x-}(aq)$$

the expression for the mean activity coefficient is given by

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{1/x+y}$$

14.7.1.1: 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 ^oC,

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:

$$a_i = \gamma_i x_i$$

14.7.2: 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.

14.7.3: 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.

14.7.4: 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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14.8: 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:

$$a_i = \gamma i \frac{[A]}{1\ \underline{M}}$$

General chemistry and organic chemistry use ideal reactants where $\gamma_i = 1$:

$$a_i = \frac{[A]}{1\ \underline{M}}$$

The activity for a solid or liquid:

$$a_i = 1$$

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14.9: Gibbs Energy of Mixing of Binary Solutions in Terms of the Activity Coefficient

14.9.0.1: 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.

14.9.0.1: 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.

14.9.0.0.1: 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.

14.9.1: 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.

14.9.2: Boiling non-ideal solutions

14.9.2.1: 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.

14.9.2.2: 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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14.E: Solutions I- Liquid-Liquid Solutions (Exercises)

TBA

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CHAPTER OVERVIEW

15: Solutions II - Nonvolatile Solutes

15.1: Standard State of Nonvolatile Solutions
15.2: The Activities of Nonvolatile Solutes
15.3: Colligative Properties Depend only on Number Density
15.4: Osmotic Pressure can Determine Molecular Masses
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15.8: Homework Problems

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15.1: 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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15.2: 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:

$$\mu_{\text{non-ideal}} = \mu^{-\ominus} + RT \ln a, \tag{15.2.1}$$

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 $P^{-\ominus} = 1$ 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:

$$\mu_i^{\text{vapor}} = \mu_i^{-\ominus} + RT \ln \frac{P_i}{P^{-\ominus}}. \tag{15.2.2}$$

If the gas phase is in equilibrium with the liquid solution, then:

$$\mu_i^{\text{solution}} = \mu_i^{\text{vapor}} = \mu_i^*, \tag{15.2.3}$$

where μ_i^* is the chemical potential of the pure element. Subtracting Equation 15.2.3 from Equation 15.2.2, we obtain:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \frac{P_i}{P_i^*}. \tag{15.2.4}$$

For an ideal solution, we can use Raoult's law, Equation 13.1.1, to rewrite Equation 15.2.4 as:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln x_i, \tag{15.2.5}$$

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 15.2.4 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:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln (\gamma_i x_i), \tag{15.2.6}$$

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:

$$a_i = \gamma_i x_i, \tag{15.2.7}$$

where γ_i is defined as the **activity coefficient**. The partial pressure of the component can then be related to its vapor pressure, using:

$$P_i = a_i P_i^*. \tag{15.2.8}$$

Comparing Equation 15.2.8 with Raoult's law, we can calculate the activity coefficient as:

$$\gamma_i = \frac{P_i}{x_i P_i^*} = \frac{P_i}{P_i^{\text{R}}}, \tag{15.2.9}$$

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 15.2.9 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 15.2.1.

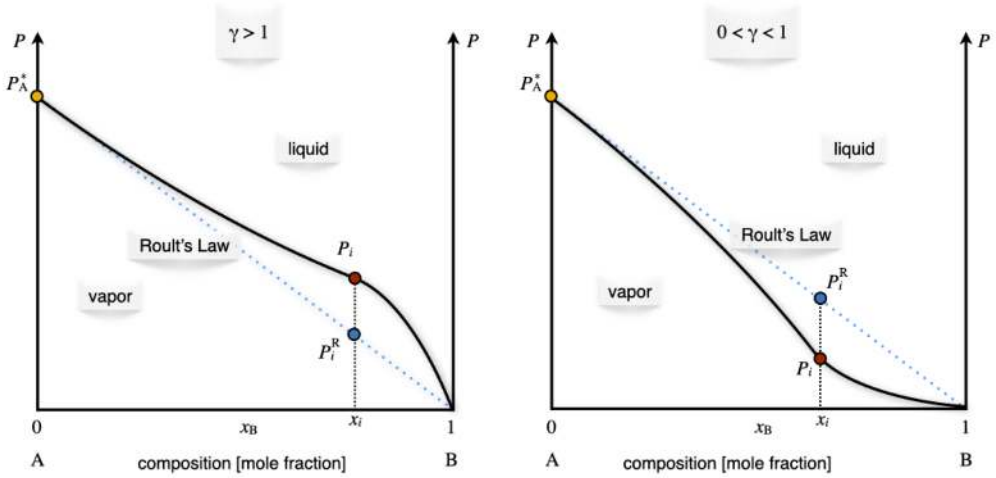


Figure **15.2.1**: Positive and Negative Deviation from Raoult's Law in the Pressure–Composition Phase Diagram of Non-Ideal Solutions at Constant Temperature.

- 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]

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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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15.3: Colligative Properties Depend only on Number Density

Colligative properties are important properties of **solutions** as they describe how the properties of the **solvent** will change as **solute** (or solutes) is (are) added. Before discussing these important properties, let us first review some definitions.

- **Solution** – a homogeneous mixture.
- **Solvent** – The component of a solution with the largest mole fraction
- **Solute** – Any component of a solution that is not the solvent.

Solutions can exist in solid (alloys of metals are an example of solid-phase solutions), liquid, or gaseous forms. For the most part, this discussion will focus on liquid-phase solutions.

15.3.1: Freezing Point Depression

In general (and as will be discussed in Chapter 8 in more detail) a liquid will freeze when

$$\mu_{solid} \leq \mu_{liquid}$$

As such, the freezing point of the solvent in a solution will be affected by anything that changes the chemical potential of the solvent. As it turns out, the chemical potential of the solvent is reduced by the presence of a solute.

In a mixture, the chemical potential of component A can be calculated by

$$\mu_A = \mu_A^o + RT \ln \chi_A \tag{15.3.1}$$

And because χ_A is always less than (or equal to) 1, the chemical potential is always reduced by the addition of another component.

The condition under which the solvent will freeze is

$$\mu_{A,solid} = \mu_{A,liquid}$$

where the chemical potential of the liquid is given by Equation 15.3.1, which rearrangement to

$$\frac{\mu_A - \mu_A^o}{RT} = \ln \chi_A$$

To evaluate the temperature dependence of the chemical potential, it is useful to consider the temperature derivative at constant pressure.

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_A - \mu_A^o}{RT}\right)\right]_p = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

$$-\frac{\mu_A - \mu_A^o}{RT^2} + \frac{1}{RT}\left[\left(\frac{\partial \mu_A}{\partial T}\right)_p - \left(\frac{\partial \mu_A^o}{\partial T}\right)_p\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{15.3.2}$$

Recalling that

$$\mu = H = TS$$

and

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$$

Equation 15.3.2 becomes

$$-\frac{(H_A - TS_A - H_A^o + TS_A^o)}{RT^2} + \frac{1}{RT}\left[-S_A + S_A^o\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{15.3.3}$$

And noting that in the case of the solvent freezing, H_A^o is the enthalpy of the pure solvent in solid form, and H_A is the enthalpy of the solvent in the liquid solution. So

$$H_A^o - H_a = \Delta H_{fus}$$

Equation 15.3.3 then becomes

$$\frac{\Delta H_{fus}}{RT^2} - \frac{-S_A + S_A^o}{RT} + \frac{-S_A + S_A^o}{RT} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

or

$$\frac{\Delta H_{fus}}{RT^2} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

Separating the variables puts the equation into an integrable form.

$$\int_{T^o}^{T} \frac{\Delta H_{fus}}{RT^2} dT = \int d \ln \chi_A \tag{15.3.4}$$

where T^o is the freezing point of the pure solvent and T is the temperature at which the solvent will begin to solidify in the solution. After integration of Equation 15.3.4:

$$-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^o}\right) = \ln \chi_A \tag{15.3.5}$$

This can be simplified further by noting that

$$\frac{1}{T} - \frac{1}{T^o} = \frac{T^o - T}{TT^o} = \frac{\Delta T}{TT^o}$$

where ΔT is the difference between the freezing temperature of the pure solvent and that of the solvent in the solution. Also, for small deviations from the pure freezing point, TT^o can be replaced by the approximate value $(T^o)^2$. So the Equation 15.3.5 becomes

$$-\frac{\Delta H_{fus}}{R(T^o)^2}\Delta T = \ln \chi_A \tag{15.3.6}$$

Further, for dilute solutions, for which χ_A, the mole fraction of the solvent is very nearly 1, then

$$\ln \chi_A \approx -(1 - \chi_A) = -\chi_B$$

where χ_B is the mole fraction of the solute. After a small bit of rearrangement, this results in an expression for freezing point depression of

$$\Delta T = \left(\frac{R(T^o)^2}{\Delta H_{fus}}\right)\chi_B$$

The first factor can be replaced by K_f:

$$\frac{R(T^o)^2}{\Delta H_{fus}} = K_f$$

which is the **cryoscopic constant** for the solvent.

ΔT gives the magnitude of the reduction of freezing point for the solution. Since ΔH_{fus} and T^o are properties of the solvent, the freezing point depression property is independent of the solute and is a property based solely on the nature of the solvent. Further, since χ_B was introduced as $(1 - \chi_A)$, it represents the sum of the mole fractions of all solutes present in the solution.

It is important to keep in mind that for a real solution, freezing of the solvent changes the composition of the solution by decreasing the mole fraction of the solvent and increasing that of the solute. As such, the magnitude of ΔT will change as the freezing process continually removes solvent from the liquid phase of the solution.

15.3.2: Boiling Point Elevation

The derivation of an expression describing boiling point elevation is similar to that for freezing point depression. In short, the introduction of a solute into a liquid solvent lowers the chemical potential of the solvent, cause it to favor the liquid phase over the vapor phase. As sch, the temperature must be increased to increase the chemical potential of the solvent in the liquid solution until it is equal to that of the vapor-phase solvent. The increase in the boiling point can be expressed as

$$\Delta T = K_b \chi_B$$

where

$$\frac{R(T^o)^2}{\Delta H_{vap}} = K_b$$

is called the **ebullioscopic constant** and, like the cryoscopic constant, is a property of the solvent that is independent of the solute or solutes. A very elegant derivation of the form of the models for freezing point depression and boiling point elevation has been shared by F. E. Schubert (Schubert, 1983).

Cryoscopic and ebullioscopic constants are generally tabulated using molality as the unit of solute concentration rather than mole fraction. In this form, the equation for calculating the magnitude of the freezing point decrease or the boiling point increase is

$$\Delta T = K_f m$$

or

$$\Delta T = K_b m$$

where m is the concentration of the solute in moles per kg of solvent. Some values of K_f and K_b are shown in the table below.

Substance	K_f (°C kg mol-1)	T_f^o (°C)	K_b (°C kg mol-1)	T_b^o (°C)
Water	1.86	0.0	0.51	100.0
Benzene	5.12	5.5	2.53	80.1
Ethanol	1.99	-114.6	1.22	78.4
CCl_4	29.8	-22.3	5.02	76.8

Example 15.3.1:

The boiling point of a solution of 3.00 g of an unknown compound in 25.0 g of CCl_4 raises the boiling point to 81.5 °C. What is the molar mass of the compound?

Solution

The approach here is to find the number of moles of solute in the solution. First, find the concentration of the solution:

$$(85.5\,°C - 76.8\,°C) = (5.02\,°C\,Kg/mol)\,m$$

$$m = 0.936\,mol/kg$$

Using the number of kg of solvent, one finds the number for moles of solute:

$$\left(0.936\,mol/\cancel{kg}\right)(0.02\,\cancel{kg}) = 0.0234\,mol$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00\,g}{0.0234} = 128 g/mol$$

15.3.3: Vapor Pressure Lowering

For much the same reason as the lowering of freezing points and the elevation of boiling points for solvents into which a solute has been introduced, the vapor pressure of a volatile solvent will be decreased due to the introduction of a solute. The magnitude of this decrease can be quantified by examining the effect the solute has on the chemical potential of the solvent.

In order to establish equilibrium between the solvent in the solution and the solvent in the vapor phase above the solution, the chemical potentials of the two phases must be equal.

$$\mu_{vapor} = \mu_{solvent}$$

If the solute is not volatile, the vapor will be pure, so (assuming ideal behavior)

$$\mu^o_{vap} + RT \ln \frac{p'}{p^o} = \mu^o_A + RT \ln \chi_A \tag{15.3.7}$$

Where p' is the vapor pressure of the solvent over the solution. Similarly, for the pure solvent in equilibrium with its vapor

$$\mu^o_A = \mu^o_{vap} + RT \ln \frac{p_A}{p^o} \tag{15.3.8}$$

where p^o is the standard pressure of 1 atm, and p_A is the vapor pressure of the pure solvent. Substituting Equation 15.3.8 into Equation 15.3.7 yields

$$\cancel{\mu^o_{vap}} + RT \ln \frac{p'}{p^o} = \left(\cancel{\mu^o_{vap}} + RT \ln \frac{p_A}{p^o} \right) + RT \ln \chi_A$$

The terms for μ^o_{vap} cancel, leaving

$$RT \ln \frac{p'}{p^o} = RT \ln \frac{p_A}{p^o} + RT \ln \chi_A$$

Subtracting $RT \ln(P_A/P^o)$ from both side produces

$$RT \ln \frac{p'}{p^o} - RT \ln \frac{p_A}{p^o} = RT \ln \chi_A$$

which rearranges to

$$RT \ln \frac{p'}{p_A} = RT \ln \chi_A$$

Dividing both sides by RT and then exponentiating yields

$$\frac{p'}{p_A} = \chi_A$$

or

$$p' = \chi_A p_A \tag{15.3.9}$$

This last result is Raoult's Law. A more formal derivation would use the fugacities of the vapor phases, but would look essentially the same. Also, as in the case of freezing point depression and boiling point elevations, this derivation did not rely on the nature of the solute! However, unlike freezing point depression and boiling point elevation, this derivation did not rely on the solute being dilute, so the result should apply the entire range of concentrations of the solution.

Example 15.3.2:

Consider a mixture of two volatile liquids A and B. The vapor pressure of pure A is 150 Torr at some temperature, and that of pure B is 300 Torr at the same temperature. What is the total vapor pressure above a mixture of these compounds with the mole fraction of B of 0.600. What is the mole fraction of B in the vapor that is in equilibrium with the liquid mixture?

Solution

Using Raoult's Law (Equation 15.3.9)

$$p_A = (0.400)(150\,Toor) = 60.0\,Torr$$

$$p_B = (0.600)(300\,Toor) = 180.0\,Torr$$

$$p_{tot} = p_A + p_B = 240\,Torr$$

To get the mole fractions in the gas phase, one can use Dalton's Law of partial pressures.

$$\chi_A = \frac{p_A}{p_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250$$

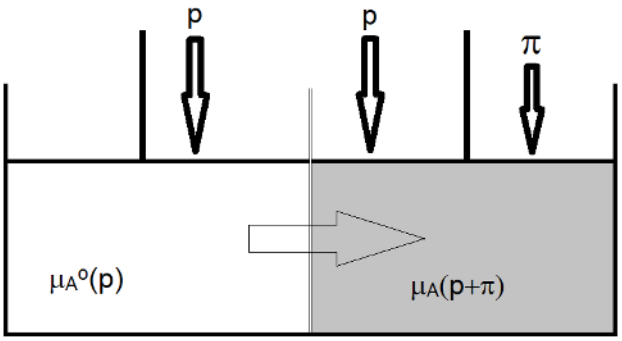
$$\chi_B = \frac{p_B}{p_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

$$\chi_A + \chi_B = 1$$

15.3.4: Osmotic Pressure

Osmosis is a process by which solvent can pass through a semi-permeable membrane (a membrane through which solvent can pass, but not solute) from an area of low solute concentration to a region of high solute concentration. The **osmotic pressure** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.



The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln \chi_A$$

And since $x_A < 1$, the chemical potential is of the solvent in a solution is always lower than that of the pure solvent. So, to prevent osmosis from occurring, something needs to be done to raise the chemical potential of the solvent in the solution. This can be accomplished by applying pressure to the solution. Specifically, the process of osmosis will stop when the chemical potential solvent in the solution is increased to the point of being equal to that of the pure solvent. The criterion, therefore, for osmosis to cease is

$$\mu_A^o(p) = \mu_A(\chi_b, +\pi)$$

To solve the problem to determine the magnitude of p, the pressure dependence of the chemical potential is needed in addition to understanding the effect the solute has on lowering the chemical potential of the solvent in the solution. The magnitude, therefore, of the increase in chemical potential due to the application of excess pressure p must be equal to the magnitude of the reduction of chemical potential by the reduced mole fraction of the solvent in the solution. We already know that the chemical potential of the solvent in the solution is reduced by an amount given by

$$\mu_A^o - \mu_A = RT \ln \chi_A$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(p+\pi) = \mu(p) + \int_p^\pi \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

The integrals on the right can be evaluated by recognizing

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

where V is the molar volume of the substance. Combining these expressions results in

$$-RT\ln\chi_A = \int_p^{p+\pi} V\,dp$$

If the molar volume of the solvent is independent of pressure (has a very small value of κ_T – which is the case for most liquids) the term on the right becomes.

$$\int_p^{\pi} V\,dP = Vp\Big|_p^{p+\pi} = V\pi$$

Also, for values of χ_A very close to 1

$$\ln\chi_A \approx -(1-\chi_A) = -\chi_B$$

So, for dilute solutions

$$\chi_B RT = V\pi$$

Or after rearrangement

$$\pi\frac{\chi_B RT}{V}$$

again, where V is the molar volume of the solvent. And finally, since χ_B/V is the concentration of the solute B for cases where $n_B \ll n_A$. This allows one to write a simplified version of the expression which can be used in the case of very dilute solutions

$$\pi = [B]RT$$

When a pressure exceeding the osmotic pressure π is applied to the solution, the chemical potential of the solvent in the solution can be made to exceed that of the pure solvent on the other side of the membrane, causing reverse osmosis to occur. This is a very effective method, for example, for recovering pure water from a mixture such as a salt/water solution.

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

15.3.5: 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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15.4: 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.

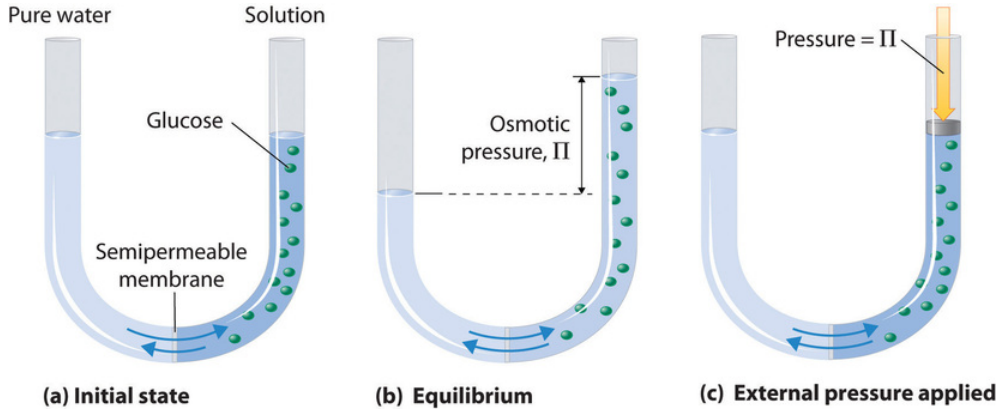


Figure 25.4.1 : Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (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.

15.4.1: 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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15.5: 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 $\sim r^{-6}$ 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:

$$C_{\nu_+}A_{\nu_-} \rightarrow \nu_+ C^{z+} + \nu_- A^{z-} \tag{15.5.1}$$

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:

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{15.5.2}$$

15.5.1: Thermodynamic potentials versus the dissociation

For the salt, we can write:

$$\mu_2 = \mu_2^o + RT \ln a_2 \tag{15.5.3}$$

However, we need to take into account the dissociation of the salt. To do so, we write:

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_- \tag{15.5.4}$$

This implies:

$$\mu_2^o = \nu_+ \mu_+^o + \nu_- \mu_-^o \tag{15.5.5}$$

where

$$\mu_+ = \mu_-^o + RT \ln a_+ \tag{15.5.6}$$

$$\mu_- = \mu_-^o + RT \ln a_- \tag{15.5.7}$$

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:

$$\nu_+ \ln a_+ + \nu_- \ln a_- = \ln a_2 \tag{15.5.8}$$

Taking the exponent of either side of Equation 15.5.8, we get:

$$a_2 = a_+^{\nu_+} a_-^{\nu_-} \tag{15.5.9}$$

Notice that the stoichiometric coefficients (Equation 15.5.1) are *exponents* in Equation 15.5.9. We now introduce the sum of the stoichiometric coefficients:

$$\nu_+ + \nu_- = \nu \tag{15.5.10}$$

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: $\nu = 1+1 = \mathbf{2}$: $a_\pm{}^{\mathbf{2}} = a_{NaCl}$

- For $Al_2(SO_4)_3$: ν= 2+3 = **5**: $a_{\pm}{}^{5} = a_{Al_2(SO_4)_3}$

15.5.2: 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:

$$a_+ = \gamma_+ m_+ \tag{15.5.11}$$

$$a_- = \gamma_- m_- \tag{15.5.12}$$

Stoichiometry dictates the molalities of the individual ions must be related to the ***molality of the salt*** m by:

$$m_- = \nu_- m \tag{15.5.13}$$

$$m_+ = \nu_+ m \tag{15.5.14}$$

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:

$$m_{\pm}^{\nu} \equiv m_+^{\nu+} m_-^{\nu-} \tag{15.5.15}$$

We can do the same for the **mean ionic activity coefficient**:

$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu+} \gamma_-^{\nu-} \tag{15.5.16}$$

Using this definitions we can rewrite:

$$a_2 = a_{\pm}^{\nu} = a_+^{\nu+} a_-^{\nu-} \tag{15.5.17}$$

as:

$$a_2 = a_{\pm}^{\nu} = \gamma_{\pm}^{\nu} m_{\pm}^{\nu} \tag{15.5.18}$$

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:

- ν= 2+3 = **5**
- $a_{\pm}{}^{5} = a_{Al_2(SO_4)_3}$
- m_-=3m
- m_+=2m

So:

$m_{\pm}{}^{\nu} = m_{+}{}^{\nu_+} m_{-}{}^{\nu_-} = (2m)^2 (3m)^3 = \mathbf{108} m^5$

$a_{Al_2(SO_4)_3} = a_{\pm}{}^{\mathbf{5}} = \mathbf{108} m^5 \gamma_{\pm}{}^5$

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).

15.5.3: 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.

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15.6: 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 **15.6.1**). 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.

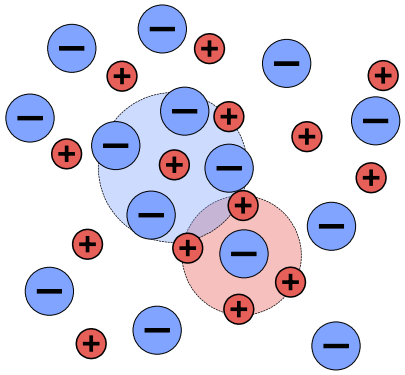


Figure **15.6.1**: An idealized representation of a solution of a 1:1 electrolyte. (CC BY-SA 3.0 unported; Roland1952 via Wikipedia)

15.6.1: 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:

$$\log_{10} \gamma_{\pm} = -Az_j^2 \frac{\sqrt{I}}{1 + Ba_0\sqrt{I}} \tag{15.6.1}$$

with:

$$A = \frac{e^2 B}{2.303 \times 8\pi\epsilon_0\epsilon_r k_B T}$$

$$B = \left(\frac{2e^2 N}{\epsilon_0\epsilon_r k_B T}\right)^{1/2}$$

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 15.6.2). 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.

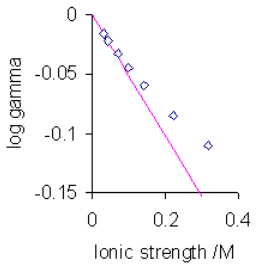


Figure 15.6.2: Experimental $\log \gamma_{\pm}$ values for KBr at 25°C (points) and Debye–Hückel limiting law (coloured line) (Public Domain; Petergans via Wikipedia)

The most significant aspect of Equation 15.6.1 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.

$$2n\,AuCl_4(aq)^- + n\ citrate^{3-}(aq) + 2n\ H_2O(l) \rightarrow$$
$$2n\ Au(colloid) + 3n\ CH_2O(aq) + 3n\ CO_2(g) + 8n\ Cl^-(aq) + 3n\ H^+(aq)$$

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 **15.6.3**). This charged cloud prevents the particle form coalescing with other particles by electrostatic repulsion.

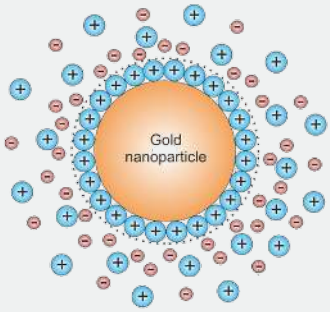


Figure **15.6.3**: Potential difference as a function of distance from gold nanoparticle surface. (CC-SA-BY-3.0; Larryisgood)

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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15.7: Extending Debye-Hückel Theory to Higher Concentrations

The equation for $\log \gamma_{\pm}$ predicted from Debye–Hückel limiting law is:

$$\log_{10} \gamma_{\pm} = -Az_j^2 \frac{\sqrt{I}}{1 + Ba_0\sqrt{I}} \tag{15.7.1}$$

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.

15.7.1: 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.

15.7.2: 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 $Mg^{2+}SO_4^{2-}$.

Plot of activity coefficients calculated using the Davies equation.

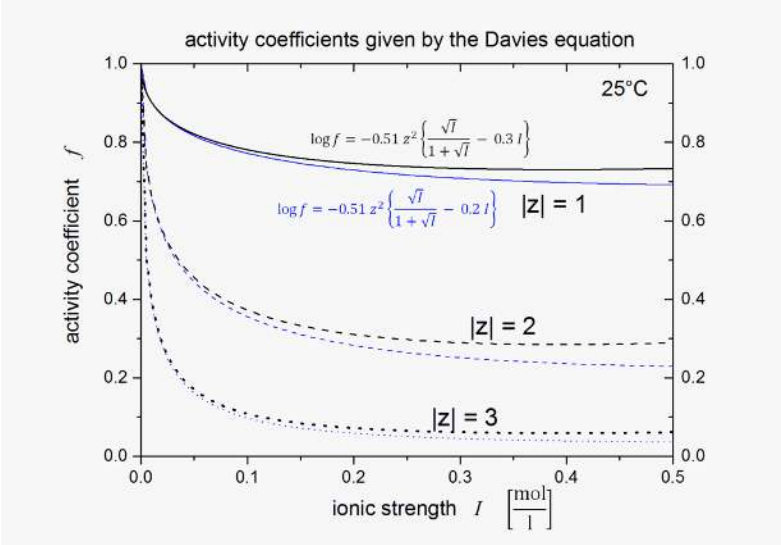


Figure 15.7.1: Semi-log plot of activity coefficients calculated using the Davies equation. (CC BY-SA 4.0; PChemiker via Wikipedia)

15.7.3: 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.

15.7.4: 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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15.8: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.8.1}$$

You can see from Equation 15.8.1 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 15.8.1

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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CHAPTER OVERVIEW

16: Chemical Kinetics I - Rate Laws

16.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

16.2: Rate Laws Must Be Determined Experimentally

16.3: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

16.4: Different Rate Laws Predict Different Kinetics

16.5: Reactions can also be Reversible

16.E: Chemical Kinetics I - Rate Laws (Exercises)

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16.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

16.1.1: 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 16.1.1:

Under a certain set of conditions, the rate of the reaction

$$\mathrm{N_2 + 3\,H_2 \rightarrow 2\,NH_3}$$

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.

16.1.2: 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

$$\text{rate} = k[Cl_2]^{3/2}[CO]$$

In this equation, k is the rate constant, and $[Cl_2]$ and $[CO]$ 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.

16.1.3: Contributors and Attributions

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- Tom Neils (Grand Rapids Community College)

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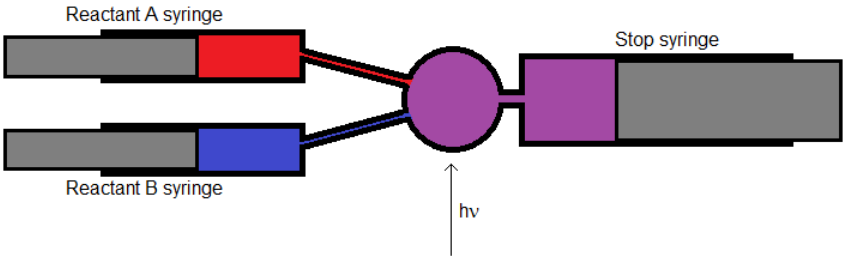
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16.2: Rate Laws Must Be Determined Experimentally

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.

16.2.1: 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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16.3: 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

$$\ln[A] = \ln[A]_o - kt \tag{16.3.1}$$

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 $\ln[A]_0$.

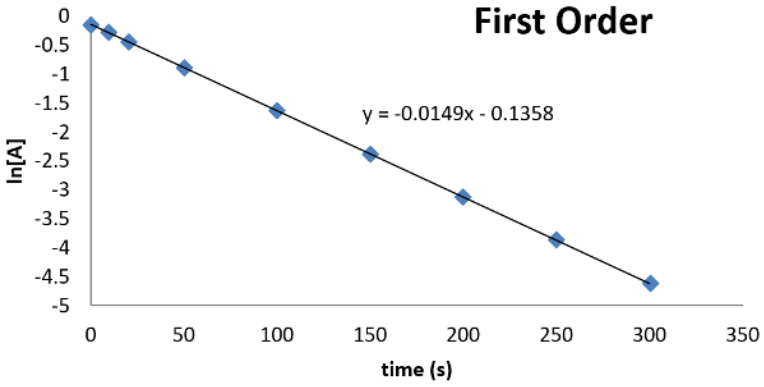
Example 16.3.1:

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 **16.3.1**) 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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16.4: Different Rate Laws Predict Different Kinetics

Difference rate laws predict different kinetics

16.4.1: 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 0th order kinetics. If they are not, other possibilities must be considered.

16.4.2: Second Order Kinetics

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2 \tag{16.4.1}$$

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

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} k\,dt \tag{16.4.2}$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result of integration Equation 16.4.2 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].

$$[A] = [A]_o - [P] \tag{16.4.3}$$

and

$$[B] = [B]_o - [P] \tag{16.4.4}$$

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.

$$\frac{d[P]}{dt} = k[A][B] \tag{16.4.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 16.4.3 and 16.4.4) into the rate law expression (Equation 16.4.5) yields

$$\frac{d[P]}{dt} = k([A]_o - [P])([B] = [B]_o - [P]) \tag{16.4.6}$$

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

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right)\Bigg|_0^{[A]} = k\,t\Big|_0^t$$

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right) - \frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0}{[A]_0}\right) = k\,t \tag{16.4.7}$$

Substituting Equations 16.4.3 and 16.4.4 into Equation 16.4.7 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 16.4.1 and the integrated rate law is (as before)

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

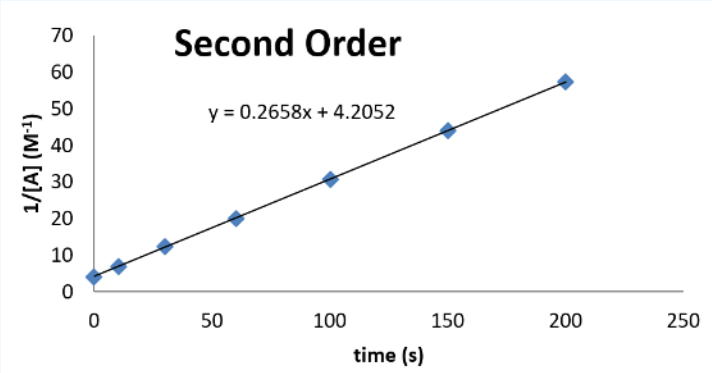
Example 16.4.2: Confirming Second Order Kinetics

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 16.4.3

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

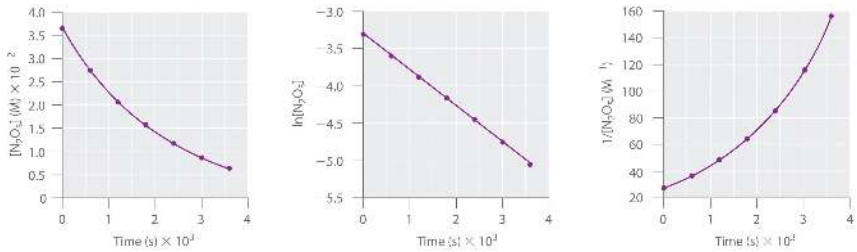
Strategy:

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 $k = 4.820 \times 10^{-4}\ s^{-1}$.

16.4.3: Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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16.5: Reactions can also be Reversible

Reversible and irreversible reactions are prevalent in nature and are responsible for reactions such as the breakdown of ammonia.

16.5.1: 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

16.5.2: 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:

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O \tag{16.5.1}$$

16.5.3: 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:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \tag{16.5.2}$$

This reversible reaction can be broken into two reactions.

Reaction 1:

$$A + B \xrightarrow{k_1} C + D \tag{16.5.3}$$

Reaction 2:

$$C + D \xrightarrow{k_{-1}} A + B \tag{16.5.4}$$

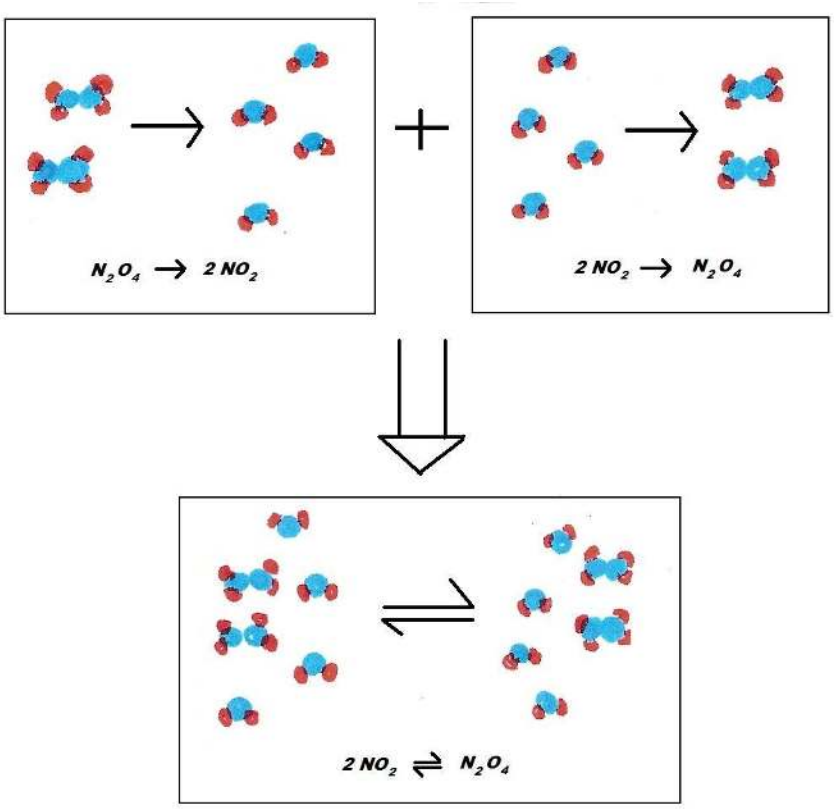
These two reactions are occurring ***simultaneously***, which means that the reactants are reacting to yield the products, as the products are reacting to produce the reactants. Collisions of the reacting molecules cause chemical reactions in a closed system. After products are formed, the bonds between 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.

16.5.4: 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.

16.5.5: Contributors and Attributions

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16.E: Chemical Kinetics I - Rate Laws (Exercises)

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CHAPTER OVERVIEW

17: Chemical Kinetics II- Reaction Mechanisms

17.1: A Mechanism is a Sequence of Elementary Reactions
17.2: The Principle of Detailed Balance
17.3: Multiple Mechanisms are often Indistinguishable
17.4: The Steady-State Approximation
17.5: Rate Laws Do Not Imply Unique Mechanism
17.6: The Lindemann Mechanism
17.7: Some Reaction Mechanisms Involve Chain Reactions
17.8: A Catalyst Affects the Mechanism and Activation Energy
17.9: The Michaelis-Menten Mechanism for Enzyme Catalysis
17.E: Chemical Kinetics II- Reaction Mechanisms (Exercises)

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17.1: 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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17.2: 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* $\boldsymbol{A}$ *and creating situation* $\boldsymbol{B}$ *will be equal to the number of processes producing* $\boldsymbol{A}$ *and destroying* $\boldsymbol{B}$

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

$$A \to B \to C ... Y \to Z \tag{17.2.1}$$

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:

$$A \rightleftharpoons B \rightleftharpoons C ... Y \rightleftharpoons Z \tag{17.2.2}$$

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17.3: 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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17.4: 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

$$A + B \rightarrow C \tag{17.4.1}$$

is proposed to follow the mechanism

$$A + A \xrightarrow{k_1} A_2 \tag{17.4.2}$$

$$A_2 + B \xrightarrow{k_2} C + A \tag{17.4.3}$$

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 17.4.1 is proposed to be

$$A \xrightarrow{k_1} A^* \tag{17.4.4}$$

$$A^* + B \xrightarrow{k_2} C \tag{17.4.5}$$

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

$$\frac{d[C]}{dt} = k_2[A^*][B] \tag{17.4.6}$$

$$= \cancel{k_2}\left(\frac{k_1[A]}{\cancel{k_2}\,\cancel{[B]}}\right)\cancel{[B]} \tag{17.4.7}$$

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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17.5: 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

$$\mathrm{A} + \mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

whose kinetics are described by the following simultaneous differential equations:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_1[A][B] + k_2[C]$$

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C]$$

$$\frac{d[D]}{dt} = k_3[C]$$

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.

17.5.1: 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

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \rightleftharpoons \mathrm{C}$$

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.

17.5.2: 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 $K_{eq}[B]_0 \ll 1$.

17.5.3: 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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17.6: 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.

17.6.1: General Mechanism

The schematic reaction $A + M \rightarrow P$ is assumed to consist of two elementary steps:

STEP 1: Bimolecular activation of A

$$A + M \rightleftharpoons A^* + M \tag{17.6.1}$$

with

- forward activation reaction rate: k_1
- reverse deactivation reaction rate: k_{-1}

STEP 2: Unimolecular reaction of $A*$

$$A^* \xrightarrow{k_2} P \tag{17.6.2}$$

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 17.6.1) and A^* is consumed both in the reverse first step and in the forward second step. The respective rates of consumption of A^* are:

$$\frac{d[A^*]}{dt} = \underbrace{k_1[A][M]}_{\text{(forward first step)}} - \underbrace{k_{-1}[A^*][M]}_{\text{(reverse first step)}} - \underbrace{k_2[A^*]}_{\text{(forward second step)}} \tag{17.6.3}$$

According to the steady-state approximation,

$$\frac{d[A^*]}{dt} \approx 0 \tag{17.6.4}$$

Therefore the rate of production of A^* (first term in Equation 17.6.3) equals the rate of consumption (second and third terms in Equation 17.6.3):

$$k_1[A][M] = k_{-1}[A^*][M] + k_2[A^*] \tag{17.6.5}$$

Solving for $[A^*]$, it is found that

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2} \tag{17.6.6}$$

The overall reaction rate is (Equation 17.6.2)

$$\frac{d[P]}{dt} = k_2[A^*] \tag{17.6.7}$$

Now, by substituting the calculated value for $[A^*]$ (Equation 17.6.6 into Equation 17.6.7), the overall reaction rate can be expressed in terms of the original reactants A and M as follows:

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} \tag{17.6.8}$$

The rate law for the Lindemann mechanism is not a simple first or second order reaction. However, under certain conditions (discussed below), Equation 17.6.8 can be simplified.

Three Principles of the Lindemann Mechanism

1. Energy is transferred by collision (forward reaction of Equation 17.6.1)
2. There is a time delay Δt between collision and reaction (Equation 17.6.2)
3. Molecules may be de-activated by another collision during Δt (reverse reaction of Equation 17.6.1)

N_2O_5 Example 29.6.1 : Dissociation of

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.

17.6.2: 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 1st order rate kinetics. Experimentally, however, 1st order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2nd order rate law:

$$\frac{d[CH_3NC]}{dt} = -k[CH_3NC]^2 \tag{17.6.9}$$

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

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{17.6.10}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{B} \tag{17.6.11}$$

where $\mathbf{M}$ can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of $\mathbf{A^*}$ 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 $\mathbf{B}$ with time:

$$\frac{d[\mathrm{A}^*]}{dt} = k_1[\mathrm{A}][\mathrm{M}] - k_{-1}[\mathrm{A}^*]_{ss}[\mathrm{M}] - k_2[\mathrm{A}^*]_{ss} \approx 0 \tag{17.6.12}$$

Solving for $[\mathbf{A^*}]$,

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{17.6.13}$$

The reaction rates of species $\mathbf{A}$ and $\mathbf{B}$ can be written as

$$-\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = k_2[\mathrm{A}^*] = \frac{k_1 k_2[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} = k_{\mathrm{obs}}[\mathrm{A}] \tag{17.6.14}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2[\mathrm{M}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{17.6.15}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}[\mathrm{M}] \gg k_2$. Equation 17.6.14 then becomes

$$-\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \tag{17.6.16}$$

which follows 1st order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}[\mathrm{M}] \ll k_2$. In this scenario, Equation 17.6.14 becomes

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{M}] \tag{17.6.17}$$

which follows second order rate kinetics, consistent with experimental observations.

17.6.3: References

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17.7: 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

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \tag{17.7.1}$$

A proposed mechanism is

$$Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br^{\cdot} \tag{17.7.2}$$

$$2Br^{\cdot} + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H^{\cdot} \tag{17.7.3}$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot} \tag{17.7.4}$$

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 17.7.1)! In this case,

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$

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17.8: 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.

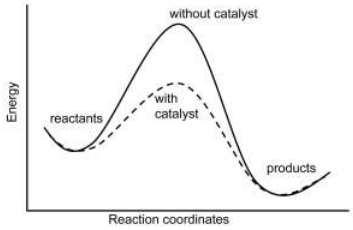


Figure 29.8.1 : Comparison of energy profiles with and without catalyst present.

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

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_{cat}} \mathrm{P} + \mathrm{C}$$

and the reaction rate as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] - k_{cat}[\mathrm{A}][\mathrm{C}]$$

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. $k_{cat} \gg k$), the first term can often be ignored.

17.8.1: 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

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{S}]$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S} + \mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^+ + \mathrm{A}^- \tag{17.8.1}$$

$$\mathrm{S}H^+ + H_2O \xrightarrow{k_2} \mathrm{P} + H_3O^+ \tag{17.8.2}$$

$$H_3O^+ + \mathrm{A}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H + H_2O \tag{17.8.3}$$

The full set of kinetic equations is

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] \tag{17.8.4}$$

$$\frac{d[\mathrm{A}H]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_{-3}[\mathrm{A}H] + k_3[H_3O^+][\mathrm{A}^-] \tag{17.8.5}$$

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{S}H^+] \tag{17.8.6}$$

$$\frac{d[\mathrm{A}^-]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{A}^-][H_3O^+] + k_{-3}[\mathrm{A}H] \tag{17.8.7}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] \tag{17.8.8}$$

$$\frac{d[H_3O^+]}{dt} = -k_2[\mathrm{S}H^+] - k_3[H_3O^+][\mathrm{A}^-] + k_{-3}[\mathrm{A}H] \tag{17.8.9}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}[\mathrm{A}^-]$ and $k_2 \ll k_{-1}[\mathrm{A}^-]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{A}^-][\mathrm{S}H^+] - k_2[\mathrm{S}H^+] = 0$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$[\mathrm{S}H^+] = \frac{k_1[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2}$$

and the rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2}$$

In the case where $k_2 \gg k_{-1}[\mathrm{A}^-]$, Equation 29.8.17 can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{S}][\mathrm{A}H]$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}[\mathrm{A}^-]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-]} = \frac{k_1k_2}{k_{-1}K}[\mathrm{S}][H^+]$$

where K is the acid dissociation constant:

$$K = \frac{[\mathrm{A}^-][H^+]}{[\mathrm{A}H]}$$

In this case, the reaction is hydrogen ion-catalyzed.

17.8.2: 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

$$\mathrm{A}(g) + \mathrm{S}(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}(s)$$

$$\mathrm{AS}(s) \xrightarrow{k_2} \mathrm{P}(g) + \mathrm{S}(g)$$

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.

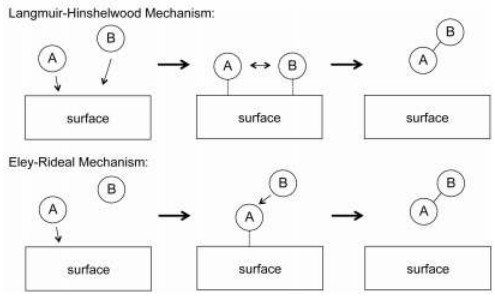


Figure 29.8.2 : Illustrations of the Langmuir-Hinshelwood and Eley-Rideal mechanisms for heterogeneous catalysis of bimolecular gas-phase reactions.

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

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{B}\,(g) + \mathrm{S}\,(s) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{BS}\,(s)$$

$$\mathrm{AS}\,(s) + \mathrm{BS}\,(s) \xrightarrow{k_3} \mathrm{P}$$

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

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{AS}\,(s) + \mathrm{B}\,(g) \xrightarrow{k_2} \mathrm{P}\,(g) + \mathrm{S}\,(s)$$

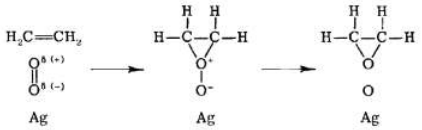


Figure 29.8.3 : Illustrations of the reaction mechanism for the partial oxidation of ethylene to ethylene oxide. [Reproduced from Kilty, PA and WMH Sacthler. Catal. Rev., 10, 1]

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, $\mathbf{S_0}$ 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

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{AS}]_{ss}[\mathrm{B}] = k_2\theta[\mathrm{S}]_0[\mathrm{B}] = \frac{k_1k_2[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1}}[\mathrm{S}]_0[\mathrm{B}]$$

We can also write the above expression in terms of the equilibrium constant, K, which is equal to k_1/k_{-1}

$$\frac{d[\mathrm{P}]}{dt} = Kk_2[\mathrm{B}]\frac{K[\mathrm{A}]}{K[\mathrm{A}] + 1}$$

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17.9: 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.

17.9.1: 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:

$$\mathbf{E} + \mathbf{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{ES} \xrightarrow{k_2} \mathbf{E} + \mathbf{P}$$

where $\mathbf{E}$ is the enzyme, $\mathbf{ES}$ is the enzyme-substrate complex, and $\mathbf{P}$ 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, $\mathbf{ES}$, is small and employ a steady-state approximation:

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} - k_2[\mathrm{ES}]_{ss} \approx 0 \tag{17.9.1}$$

Furthermore, because the enzyme is unchanged throughout the reaction, we express the total enzyme concentration as a sum of enzyme and enzyme-substrate complex:

$$[\mathrm{E}]_0 = [\mathrm{ES}] + [\mathrm{E}] \tag{17.9.2}$$

Plugging Equation 17.9.2 into Equation 17.9.1, we obtain

$$0 = k_1([\mathrm{E}]_0 - [\mathrm{ES}]_{ss})[\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} + k_2[\mathrm{ES}]_{ss} \tag{17.9.3}$$

Solving for $[\mathrm{ES}]_{ss}$

$$[\mathrm{ES}]_{ss} = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_1[\mathrm{S}] + k_{-1} + k_2} = \frac{[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \frac{k_{-1} + k_2}{k_1}} \tag{17.9.4}$$

We can then write the reaction rate of the product as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}]_{ss} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \frac{k_{-1} + k_2}{k_1}} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_M} \tag{17.9.5}$$

where K_M is the Michaelis constant. Equation 17.9.5 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 ($[\mathrm{S}] \gg K_M$) Equation 17.9.5 reduces to

$$\frac{d[\mathrm{P}]}{dt} = r_{\max} = k_2[\mathrm{E}]_0 \tag{17.9.6}$$

which is a 0th order reaction, since $[E]_0$ is a constant. The value $k_2 [E]_0$ 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, $[S]$. This plot is known as the Michaelis-Menten plot. Examining the figure, we can see that the reaction rate reaches a maximum value of $k_2 [E]_0$ at large values of $[S]$.

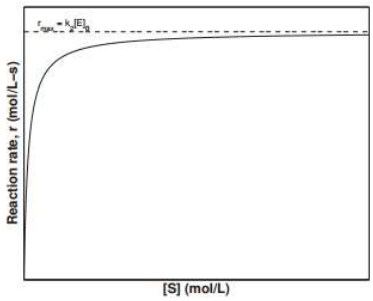


Figure 29.9.4 : Rate dependence on substrate concentration for an enzymatic reaction.

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 $1/[S]$. Rearranging Equation 17.9.5,

$$\frac{1}{r} = \frac{K_M + [S]}{k_2 [E]_0 [S]} = \frac{K_M}{k_2 [E]_0} \frac{1}{[S]} + \frac{1}{k_2 [E]_0} \tag{17.9.7}$$

The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M / k_2 [E]_0$ and y-intercept equal to $1/k_2 [E]_0$.

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CHAPTER OVERVIEW

18: Kinetics- Temperature Dependence and Relaxation Methods

18.1: Rate Constants Are Usually Strongly Temperature Dependent

18.2: The Rate Constants of a Reversible Reaction Can Be Determined Using Relaxation Techniques

18.3: Transition-State Theory Can Be Used to Estimate Reaction Rate Constants

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18.1: Rate Constants Are Usually Strongly Temperature Dependent

In general, increases in temperature increase the rates of chemical reactions. It is easy to see why, since most chemical reactions depend on molecular collisions. And as we discussed in Chapter 2, the frequency with which molecules collide increases with increased temperature. But also, the kinetic energy of the molecules increases, which should increase the probability that a collision event will lead to a reaction. An empirical model was proposed by Arrhenius to account for this phenomenon. The **Arrhenius model** (Arrhenius, 1889) can be expressed as

$$k = Ae^{-E_a/RT}$$

Although the model is empirical, some of the parameters can be interpreted in terms of the energy profile of the reaction. E_a, for example, is the **activation energy**, which represents the energy barrier that must be overcome in a collision to lead to a reaction.

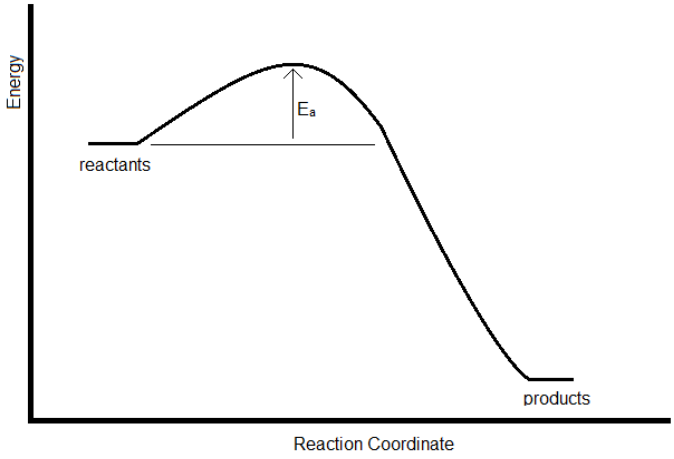


Figure 11.9.1: Reaction profile for an elementary sttep over an activated barrier of height E_a.

If the rate constant for a reaction is measure at two temperatures, the activation energy can be determined by taking the ratio. This leads to the following expression for the Arrhenius model:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{18.1.1}$$

Example 18.1.1:

For a given reaction, the rate constant doubles when the temperature is increased form 25 °C to 35 °C. What is the Arrhenius activation energy for this reaction?

Solution

The energy of activation can be calculated from the Arrhenius Equation (Equation 18.1.1).

$$\ln\left(\frac{2k_1}{k_1}\right) = -\frac{E_a}{8.314\,\frac{J}{mol\,K}}\left(\frac{1}{308\,K} - \frac{1}{298\,K}\right)$$

From this reaction:

$$E_a = 52.9\,kJ/mol$$

Preferably, however, the rate constant is measured at several temperatures, and then the activation energy can be determined using all of the measurements, by fitting them to the expression

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

This can be done graphically by plotting the natural logarithm of the rate constant as a function of $1/T$ (with the temperature measured in K). The result should be a straight line (for a well-behaved reaction!) with a slope of $-E_a/R$.

There are some theoretical models (such as collision theory and transition state theory) which suggest the form of the Arrhenius model, but the model itself is purely empirical. A general feature, however, of the theoretical approaches is to interpret the activation energy as an energy barrier which a reaction must overcome in order to lead to a chemical reaction.

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18.2: 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?

18.2.1: 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.

18.2.1.1: 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.

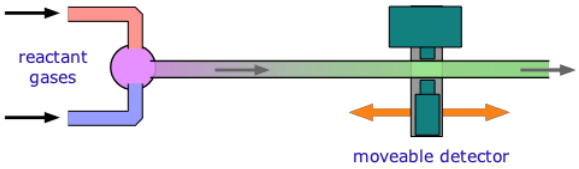


Figure **18.2.1**: A continuous flow fast kinetic system.

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.

18.2.1.2: 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.

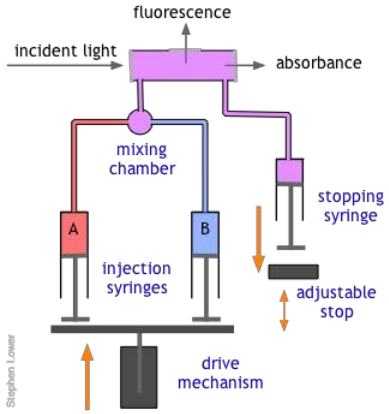


Figure **18.2.2**: A stop flow fast kinetic system.

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.

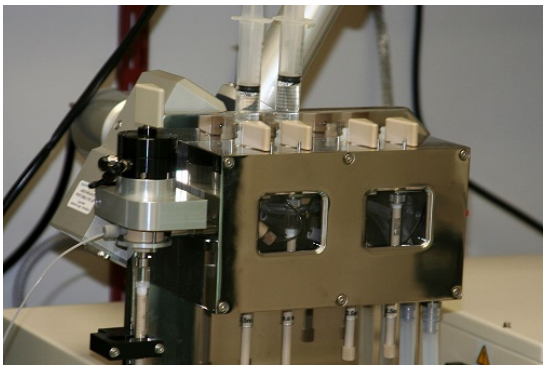


Figure **18.2.3**: Stop-flow equipment at a biochemistry research laboratory for measuring rapid reactions and properties such as enzyme kinetics. from Wladimir Labeikovsky.

18.2.1.3: 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.

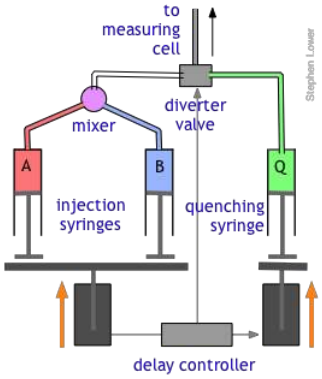


Figure **18.2.4**: A quench flow fast kinetic system.

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.

18.2.2: 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.

18.2.2.1: 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.

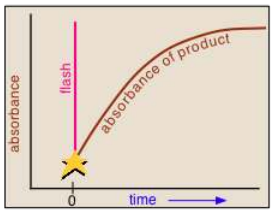


Figure **18.2.5**: Basic principle of a flash-photolysis relaxation experiment where an excitation pulse purturbed a system at equilibrium and the subsequent dynamics are resolved in time.

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.

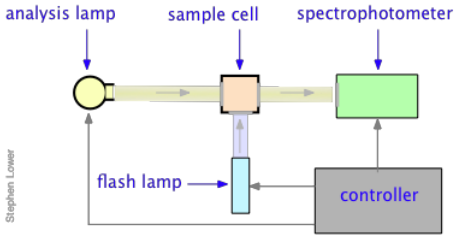


Figure **18.2.6**: A flash-photolysis relaxation experiment

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

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{18.2.1}$$

and the formation of the triiodide ion in aqueous solution

$$I^- + I_2 \rightarrow I_3^- \tag{18.2.2}$$

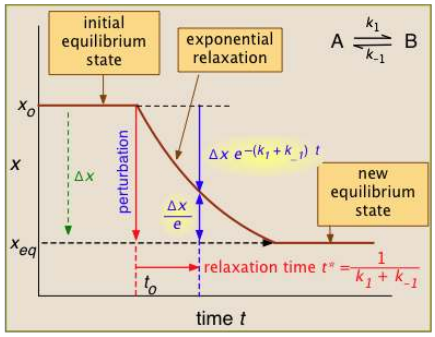
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

18.2.2.2: 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

$$\mathbf{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{B} \tag{18.2.3}$$

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

$$x_t = x_o e^{-kt} \tag{18.2.4}$$

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 \($\Delta x/e = \Delta x/2.718$\). 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 18.2.3 can be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\,[\mathrm{A}] - k_{-1}\,[\mathrm{B}] \tag{18.2.5}$$

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

$$[\mathrm{A}] = [\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}] \tag{18.2.6}$$

The rate of change of species **B** can then be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\left([\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}]\right) - k_{-1}\,[\mathrm{B}] = k_1\,[\mathrm{B}]_{\mathrm{eq},1} - (k_1 + k_{-1})\,[\mathrm{B}] \tag{18.2.7}$$

At equilibrium, $d\,[\mathrm{B}]\,/dt = 0$ and $[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq},2}$, allowing us to write

$$k_1\,[\mathrm{B}]_{\mathrm{eq},1} = (k_1 + k_{-1})\,[\mathrm{B}]_{\mathrm{eq},2} \tag{18.2.8}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathrm{B}}{\left([\mathrm{B}]_{\mathrm{eq},2} - [\mathrm{B}]\right)} = (k_1 + k_{-1})\,dt \tag{18.2.9}$$

Integrating yields

$$-\ln\left([\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}\right)=-\left(k_1+k_{-1}\right)t+C \tag{18.2.10}$$

We can rearrange the above equation in terms of $\mathbf{B}$

$$[\mathrm{B}]=Ce^{-(k_1+k_{-1})t}+[\mathrm{B}]_{\mathrm{eq},2} \tag{18.2.11}$$

At $t=0$, $[\mathrm{B}]=[\mathrm{B}]_{\mathrm{eq},1}$, so $C=[\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}$. Plugging the the value of C, we arrive at

$$[\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}=\left([\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}\right)e^{-(k_1+k_{-1})t} \tag{18.2.12}$$

which can also be expressed as

$$\Delta[\mathrm{B}]=\Delta[\mathrm{B}]_0\,e^{-(k_1+k_{-1})t}=\Delta[\mathrm{B}]_0\,e^{-t/\tau} \tag{18.2.13}$$

where $\Delta[\mathrm{B}]$ is the difference in the concentration of $\mathbf{B}$ from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln\left(\Delta[\mathrm{B}]/\Delta[\mathrm{B}]_0\right)$ versus t will be linear with a slope of $-(k_1+k_{-1})$, where k_1 and k_{-1} are the rate constants at temperature, T_2.

18.2.3: Contributors and Attributions

- Mark Tuckerman (New York University)
- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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18.3: Transition-State Theory Can Be Used to Estimate Reaction Rate Constants

18.3.1: 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 $\mathbf{A}+\mathbf{B}$, and we do not have $\mathbf{C}$. 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 $\mathbf{x}$ for the complete set of coordinates and momenta of all of the atoms in the system. Generally, the reaction coordinate q is a function $q(\mathbf{x})$ of all of the coordinates and momenta, although typically, $q(\mathbf{x})$ is a function of a subset of the coordinates and, possibly, the momenta.

As an example, let us consider two atoms $\mathbf{A}$ and $\mathbf{B}$ undergoing a collision. An appropriate reaction coordinate could simply be the distance r between $\mathbf{A}$ and $\mathbf{B}$. This distance is a function of the positions $\mathbf{r}_{\mathbf{A}}$ and $\mathbf{r}_{\mathbf{B}}$ of the two atoms, in that

$$q = r = |\mathbf{r}_{\mathbf{A}} - \mathbf{r}_{\mathbf{B}}| \tag{18.3.1}$$

When $\mathbf{A}$ and $\mathbf{B}$ are molecules, such as proteins, $q(\mathbf{x})$ is a much more complicated function of $\mathbf{x}$.

Now, recall that the mechanical energy $\mathcal{E}(\mathbf{x})$ is given by

$$\mathcal{E}(\mathbf{x}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_1} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{18.3.2}$$

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

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \tag{18.3.3}$$

2. We start a trajectory obeying this equation of motion with an initial condition $\mathbf{x}$ that makes $q(\mathbf{x}) = q^{\ddagger}$ and such that $\dot{q}(\mathbf{x}) > 0$ so that the reaction coordinate proceeds initial to the right, i.e., toward products.
3. We follow the motion $\mathbf{x}_t$ of the coordinates and momenta in time starting from this initial condition $\mathbf{x}$, which gives us a unique function $\mathbf{x}_t(\mathbf{x})$.
4. If $q(\mathbf{x}_t(\mathbf{x})) > q^{\ddagger}$ 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

$$k(t) = \frac{1}{hQ_r} \int_{q(\mathbf{x})=q^{\ddagger}} d\mathbf{x}\, e^{-\beta\mathcal{E}(\mathbf{x})} |\dot{q}(\mathbf{x})| \, \theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right) \tag{18.3.4}$$

where h is Planck's constant. Here Q_r is the partition function of the reactants

$$Q_r = \int d\mathbf{x}\, e^{-\beta\mathcal{E}(\mathbf{x})} \theta\left(q^{\ddagger} - q(\mathbf{x})\right) \tag{18.3.5}$$

The meaning of Equation 18.3.4 is an ensemble average over a canonical ensemble of the product $|\dot{q}(\mathbf{x})|$ and $\theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right)$. The first factor in this product $|\dot{q}(\mathbf{x})|$ forces the initial velocity of the reaction coordinate to be positive, i.e., toward products, and the step function $\theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right)$ requires that the trajectory of $q(\mathbf{x}_t(\mathbf{x}))$ be reactive, otherwise, the step function will give no contribution to the flux. The function $k(t)$ in Equation 18.3.4 is known as the *reactive flux*. In the definition of Q_r the step function $\theta\left(q^{\ddagger} - q(\mathbf{x})\right)$ 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,

$$k = \lim_{t\to\infty} k(t) \tag{18.3.6}$$

gives the true rate constant. On the other hand, a common approximation is to take the value $k(0)$ as an estimate of the rate constant, and this is known as the transition *state theory approximation* to k, i.e.,

$$k^{(\mathrm{TST})} = k(0) \tag{18.3.7}$$

$$= \frac{1}{Q_r} \int_{q(\mathbf{x})=q^\ddagger} d\mathbf{x}\, e^{-\beta \mathcal{E}(\mathbf{x})} \left|\dot{q}(\mathbf{x})\right| \theta\left(q(\mathbf{x}) - q^\ddagger\right) \tag{18.3.8}$$

However, note that since we require $\dot{q}(\mathbf{x})$ to initially be toward products, then by definition, at $t = 0$, $q(\mathbf{x}) \geq q^\ddagger$, and the step function in the above expression is redundant. In addition, if $\dot{q}(\mathbf{x})$ only depends on momenta (or velocities) and not actually on coordinates, which will be true if $q(\mathbf{x})$ is not curvilinear (and is true for some curvilinear coordinates $q(\mathbf{x})$), and if $q(\mathbf{x})$ only depends on coordinates, then Equation ??? reduces to

$$k^{(\mathrm{TST})} = \frac{1}{hQ_r} \int d\mathbf{x}_\mathbf{p} e^{-\beta \sum_{i=1}^N \mathbf{p}_i^2/2m_i} \left|\dot{q}(\mathbf{p}_1, \ldots, \mathbf{p}_N)\right| \int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^\ddagger} d\mathbf{x}_\mathbf{r} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{18.3.9}$$

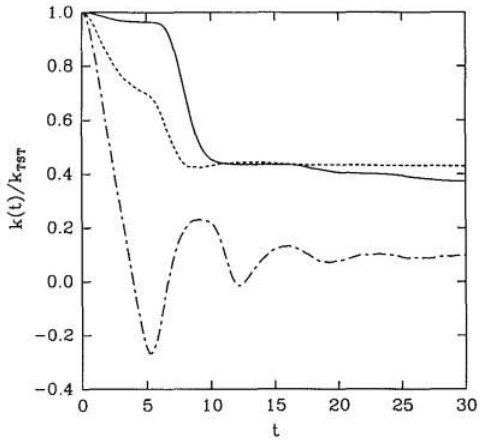


Figure 28.8.2 : Examples of the reactive flux $k(t)$.

The integral

$$Z^\ddagger = \int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^\ddagger} d\mathbf{x}_\mathbf{r} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

counts the number of microscopic states consistent with the condition $q(\mathbf{r}_1, \ldots, \mathbf{r}_N) = q^\ddagger$ 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

$$F^\ddagger \propto -k_B T \ln Z^\ddagger \tag{18.3.10}$$

Similarly, if we divide Q_r into its ideal-gas and configurational contributions

$$Q_r = Q_r^{(\mathrm{ideal})} Z_r \tag{18.3.11}$$

then we can take

$$Z_r = e^{-\beta F_r} \tag{18.3.12}$$

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 $Q_r^{(\mathrm{ideal})}$, the momentum integral we need is

$$\int_0^\infty e^{-\beta p^2/2\mu} \frac{p}{\mu} = k_B T \tag{18.3.13}$$

which gives the final expression for the transition state theory rate constant

$$k^{(\mathrm{TST})} = \frac{k_B T}{h} e^{-\beta(F^\ddagger - F_r)} = \frac{k_B T}{h} e^{-\beta \Delta F^\ddagger} \tag{18.3.14}$$

Figure 28.8.2 actually shows $k(t)/k^{(TST)}$, which must start at 1. As the figure shows, in addition, for $t > 0$, $k(t) < k^{(TST)}$. Hence, $k^{(TST)}$ 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.

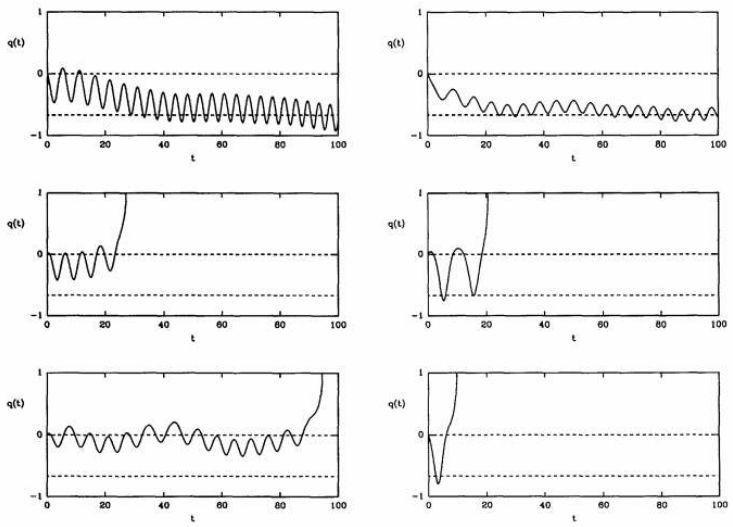


Figure 28.8.3 : Examples of the trajectories in a typical system, some of which are reactive but some of which return to reactants.

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 $k^{(TST)}$, and we can write

$$k = \kappa k^{(TST)} \tag{18.3.15}$$

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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