MANCHESTER UNIVERSITY PHYSICAL CHEMISTRY I (CHEM 341)



Kathy Davis
Manchester University

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Manchester University Physical Chemistry I (CHEM 341)

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1.1: Prelude to the Foundations of Quantum Mechanics

The concepts of quantum mechanics were invented to explain experimental observations that otherwise were totally inexplicable. This period of invention extended from 1900 when Max Planck introduced the revolutionary concept of quantization to 1925 when Erwin Schrödinger and Werner Heisenberg independently introduced two mathematically different but equivalent formulations of a general quantum mechanical theory. The Heisenberg method uses properties of matrices, while the Schrödinger method involves partial differential equations. We will develop and utilize Schrödinger's approach because students usually are more familiar with elementary calculus than with matrix algebra, and because this approach provides direct insight into charge distributions in molecules, which are of prime interest in chemistry.

Heisenberg and Schrödinger were inspired by four key experimental observations: the spectral distribution of black-body radiation, the characteristics of the photoelectric effect, the Compton effect, and the luminescence spectrum of the hydrogen atom. Explanation of these phenomena required the introduction of two revolutionary concepts:

1. physical quantities previously thought to be continuously variable, such as energy and momentum, are quantized, and
2. momentum, p, and wavelength, λ, are related, $p = \frac{h}{\lambda}$, where h is a fundamental constant.

We will use a quasi-historical approach in this chapter to emphasize that individuals created knowledge by inventing new ideas or concepts. What is not apparent here is that these new ideas initially were greeted with considerable skepticism, and acceptance was slow because of counter proposals that were not so revolutionary. Only after some time did inconsistencies in the counter proposals become apparent. By "quantized," we mean that only certain values are possible or allowed. For example, money is quantized. Money does not come in continuous denominations. In the United States the smallest unit of money is a penny, and everything costs some integer multiple of a penny.

From high school and freshman physics, as well as from everyday experience, we learn that particles have momentum, which is mass times velocity. Although more abstract, the wave properties of light are clearly demonstrated by interference, diffraction and refraction effects. That a relationship between momentum (a particle property) and wavelength (a wave property) applies to both particles and light was, and remains, somewhat amazing and revolutionary. This relationship, called the "wave-particle duality," means that particles have wave-like properties and light waves have particle-like properties.

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1.2: Blackbody Radiation Cannot Be Explained Classically

Learning Objectives

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

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

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

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



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

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

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

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

Any body at any temperature above absolute zero **will** radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter.* So how do we construct a perfect absorber in the laboratory? In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven

with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find (Figure 1.1.2).

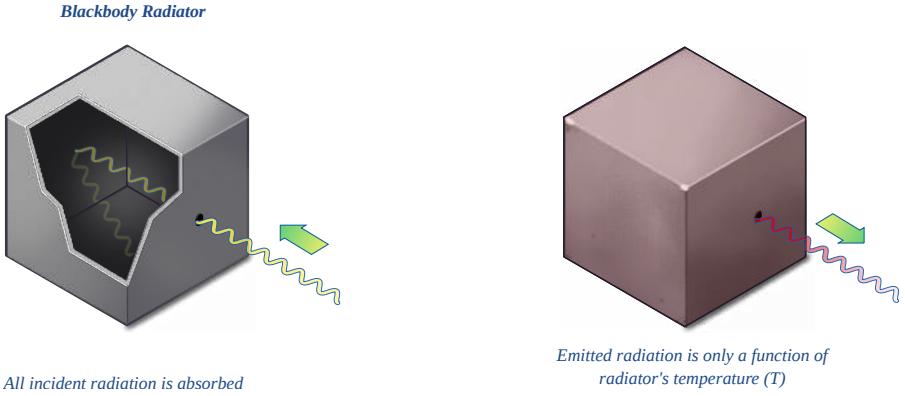


Figure 1.1.2 : Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya via LibreTexts)

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

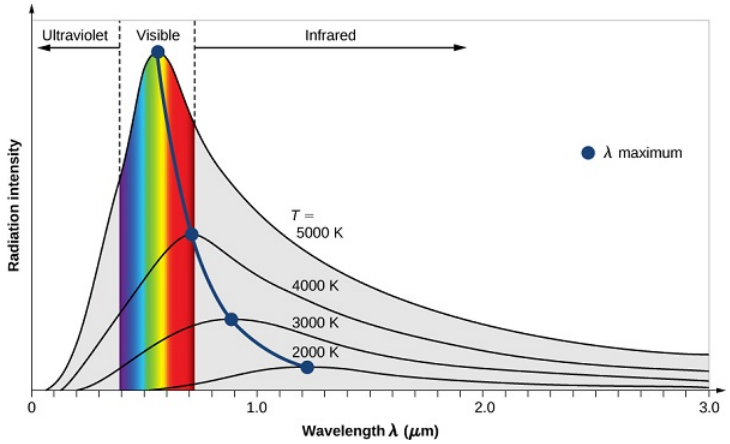
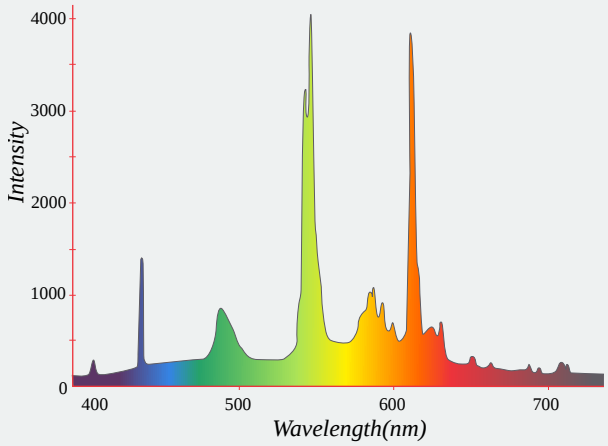


Figure 1.1.3 : Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength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

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

Not all radiators are blackbody radiators

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



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

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

The Stefan-Boltzmann Law

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

$$P = \sigma T^4 \tag{1.2.1}$$

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.

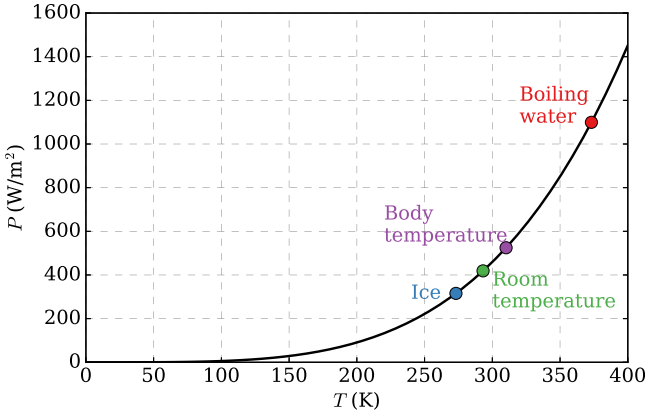


Figure 1.1.4 : Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature T according to the Stefan–Boltzmann law. (CC BY-SA 4.0; Nicoguaro)

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 1.2.1).

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

This value is per square meter.

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

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

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:

$$\nu_{max} \propto T \tag{1.2.2}$$

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 1.2.2) in terms of the peak wavelength of light is

$$\lambda_{max} = \frac{b}{T} \tag{1.2.3}$$

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 1.2.1). 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 1.2.3, 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 1.2.3 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

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

$$d\rho\left(\nu,T\right)=\rho_{\nu}\left(T\right)d\nu \tag{1.2.4}$$

$$=\frac{8\pi k_{B}T}{c^{3}}\nu^{2}d\nu \tag{1.2.5}$$

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 1.2.5). Ehrenfest later dubbed this the "ultraviolet catastrophe". It is important to emphasizing that Equation 1.2.5 is a **classical** result: the only inputs are classical dynamics and Maxwell's electromagnetic theory.

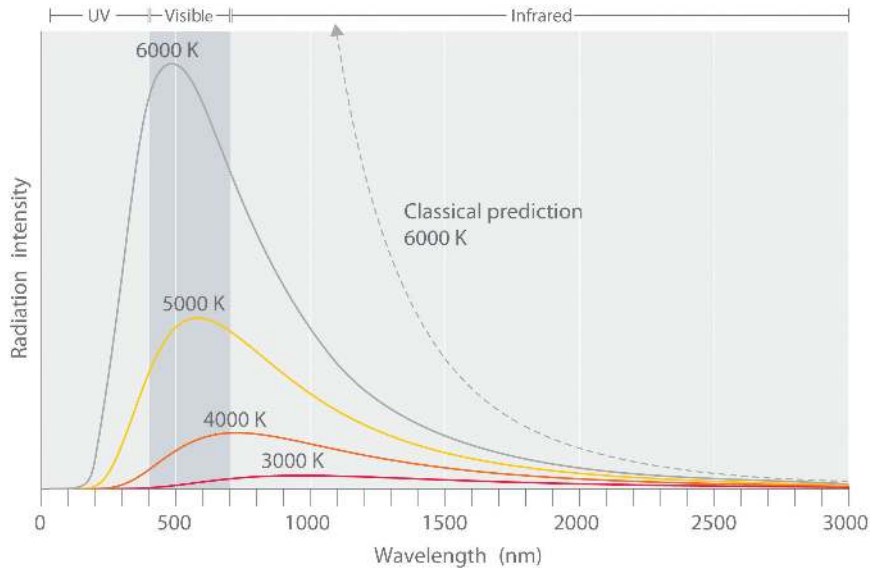


Figure 1.1.5 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 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 1.2.5:

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 1.2.5 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)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

- ACuriousMind (StackExchange)

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1.3: Quantum Hypothesis used for Blackbody Radiation Law

Learning Objectives

- To understand how energy is quantized in blackbody radiation

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

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

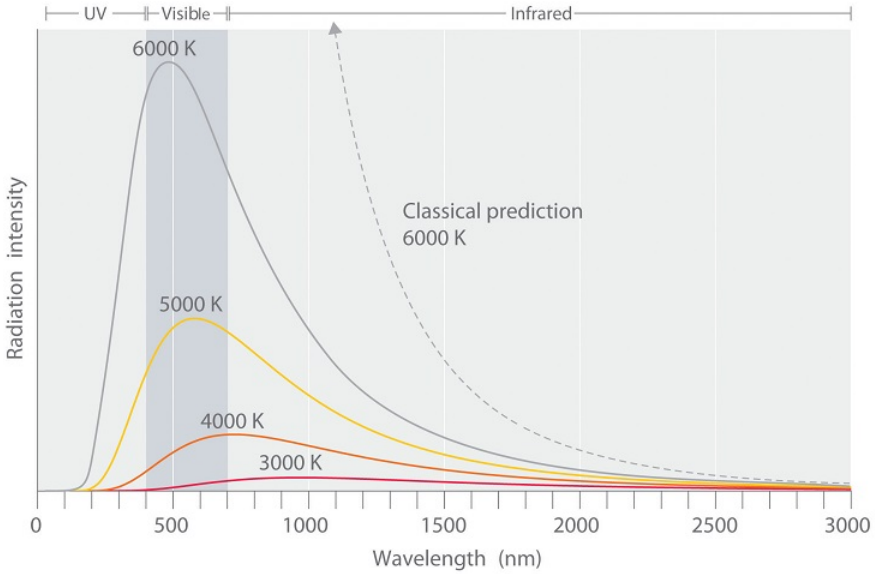


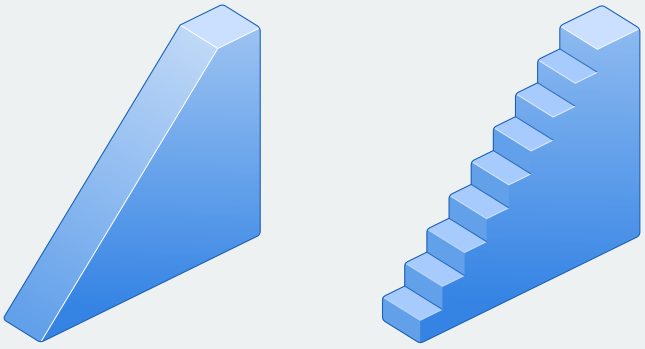
Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases,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

Quantizing Electrons in the Radiator

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

Quantization

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



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

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

$$E = h\nu \tag{1.3.1}$$

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 1.3.1).

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

$$d\rho(\nu, T) = \rho_\nu(T)d\nu \tag{1.3.2}$$

$$= \frac{2h\nu^3}{c^2} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} d\nu \tag{1.3.3}$$

with

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

Planck's radiation energy density (Equation 1.3.3) can also be expressed in terms of wavelength λ.

$$\rho(\lambda, T) = \frac{2hc^2}{\lambda^5} \left(\frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \right) \tag{1.3.4}$$

With a wavelength of maximum energy density at:

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

Planck's equation (Equation 1.3.4) gave an excellent agreement with the experimental observations for all temperatures (Figure 1.2.2).

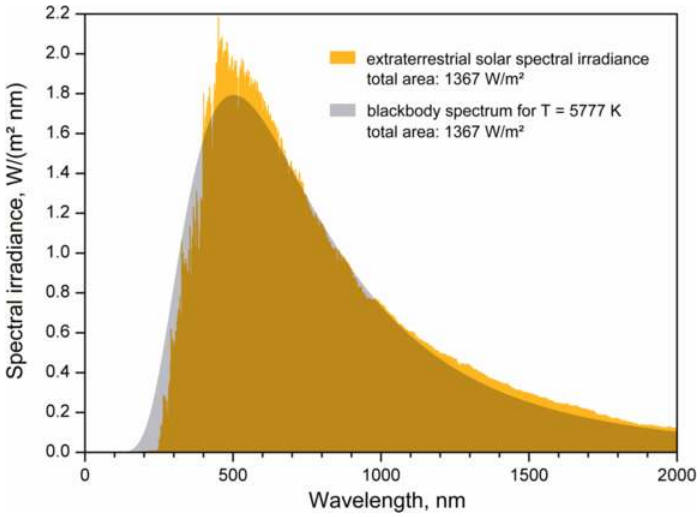
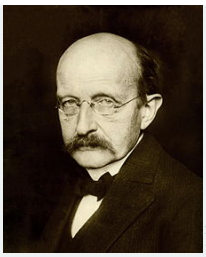


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

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.



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

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

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

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

$$E = nh\nu$$

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

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

Summary

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

Contributors and Attributions

- 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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1.4: Photoelectric Effect Explained with Quantum Hypothesis

Learning Objectives

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

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

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

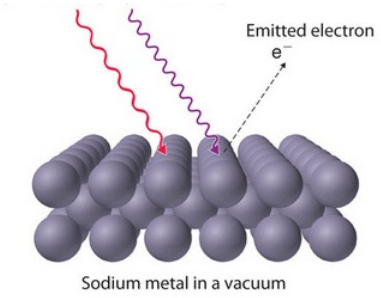


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

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

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

Lenard's Experimental Results (Intensity Dependence)

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

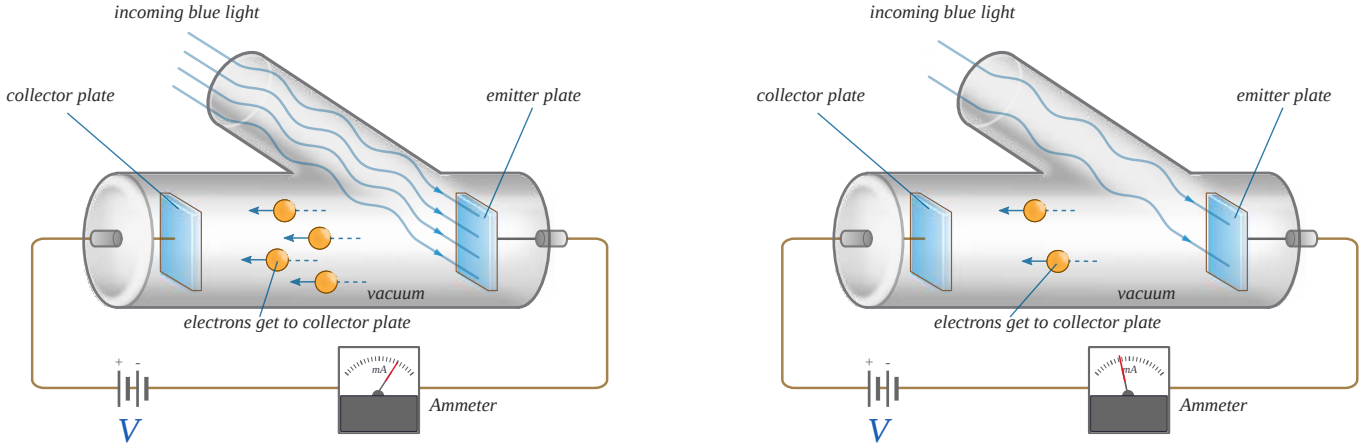


Figure 1.4.2: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

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

Millikan's Experimental Results (Wavelength Dependence)

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

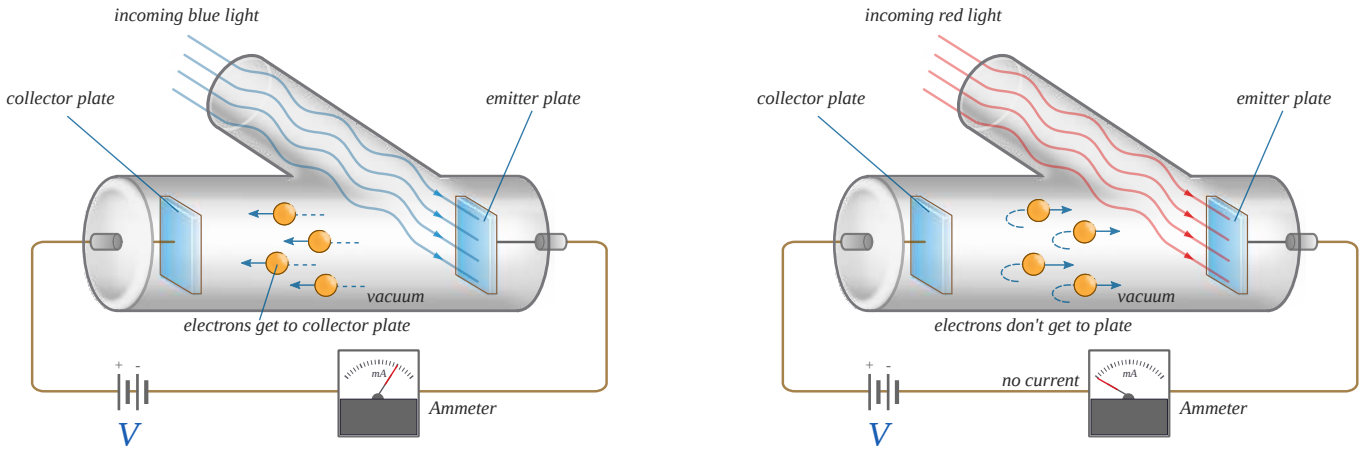


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector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

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

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

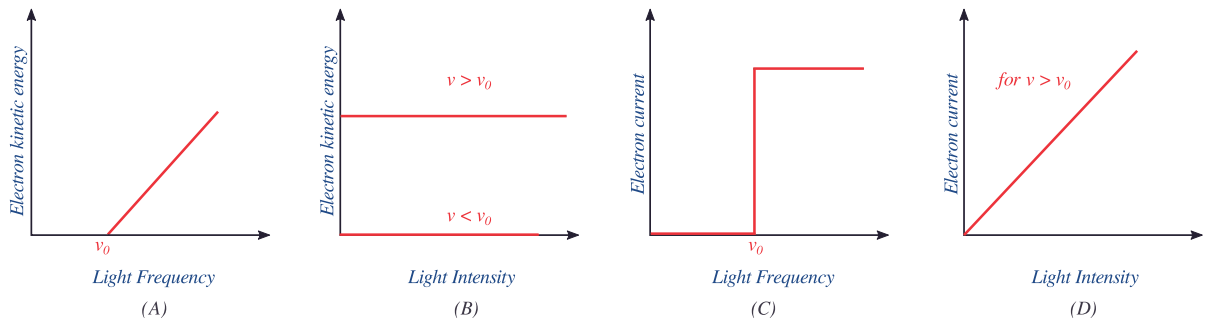


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the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

Classical Theory does not Describe Experiment

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

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex physics and instrumentation, which will be ignored for now.

Einstein's Quantum Picture

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

$$KE = h\nu - \Phi \tag{1.4.1}$$

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,

$$eV_{stop} = h\nu - \Phi \tag{1.4.2}$$

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 1.4.4*A*). 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 1.4.1). 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 1.4.1 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 1.4.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new field of photoelectron spectroscopy. Einstein's theory of the photoelectron presented a completely different way to measure Planck's constant than from black-body radiation.

The Workfunction (Φ)

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

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

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

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

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

Table 1.3.1 : Workfunctions and Ionization Energies of Select Elements

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Lithium (Li)	2.93	5.39
Beryllium (Be)	4.98	9.32
Boron (B)	4.45	8.298
Carbon (C)	5.0	11.26
Sodium (Na)	2.36	5.13
Aluminum (Al)	4.20	5.98
Silicon (Si)	4.85	8.15
Potassium (K)	2.3	4.34
Iron (Fe)	4.67	7.87
Cobalt (Co)	4.89	7.88
Copper (Cu)	4.7	7.7

Element	Workfunction Φ (eV)	Ionization Energy (eV)
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 1.4.1 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

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

Converting to eV, the energy of the photon is

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

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of Equation 1.4.1. 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.

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.

Conceptual Questions

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

Contributors and Attributions

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

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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1.5: 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:

$$\lambda = \frac{h}{p} \tag{1.5.1}$$

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

$$E = \sqrt{p^2c^2 + m^2c^4} \tag{1.5.2}$$

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 1.5.2 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

$$h\nu = \frac{hc}{\lambda} = pc \tag{1.5.3}$$

Solving for the wavelength λ gives Equation 1.5.1:

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

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 1.5.1 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 1.5.1), 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:

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

$$= \frac{p^2}{2m} = 1000\ eV$$

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

$$p = \sqrt{(3.1 \times 10^{-16}\ kg \cdot m^2/s^2)(9.109383 \times 10^{-31}\ kg)}$$

$$= \sqrt{2.9 \times 10^{-40}\ kg^2\ m^2/s^2}$$

$$= 1.7 \times 10^{-23} kg \cdot m/s$$

Now substitute the momentum into the equation for de Broglie's wavelength (Equation 1.5.1) with Planck's constant ($h = 6.626069 \times 10^{-34}\ J \cdot s$). After expanding units in Plank's constant

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

$$= \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{1.7 \times 10^{-23} kg \cdot m/s}$$

$$= 3.87 \times 10^{-11}\ m$$

$$= 38.9\ pm$$

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.

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

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

The de Broglie wavelength of this fast ball is:

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

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 1.5.1 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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1.6: de Broglie Waves can be Experimentally Observed

Learning Objectives

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

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

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

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

Diffraction of Light (Light as a Wave)

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

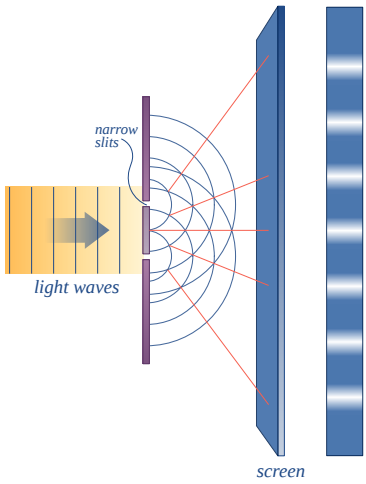


Figure 1.7.1 : Young double slit experiment. Two slits are illuminated by a plane light waves. (CC BY-NC; Ümit Kaya via LibreTexts)

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

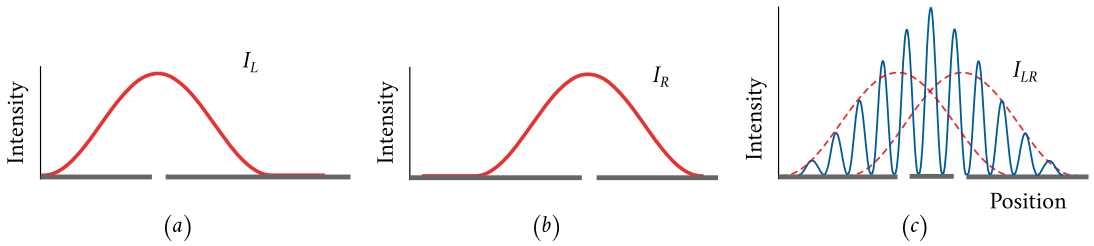


Figure 1.7.2 : Amplitude of particles through (a) left slit, (b) right slit, (c) through both slits. In absence of wavelength interference behavior, the intensity will be the sum of each single slit results (red) and when there is interference, pronounced oscillations in intensity is observed (blue curve).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

The wave nature of light causes the light waves passing through the two slits to interfere, producing bright and dark bands on the screen – a result that would not be expected if light consisted of classical particles (Figure 1.6.0*c*). However, the light is always found to be absorbed at the screen at discrete points, as individual particles (not waves); the interference pattern appears via the varying density of these particle hits on the screen. Furthermore, versions of the experiment that include detectors at the slits find that each detected photon passes through one slit (as would a classical particle), and not through both slits (as would a wave).

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

Diffraction of Electrons (Electrons as Waves)

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

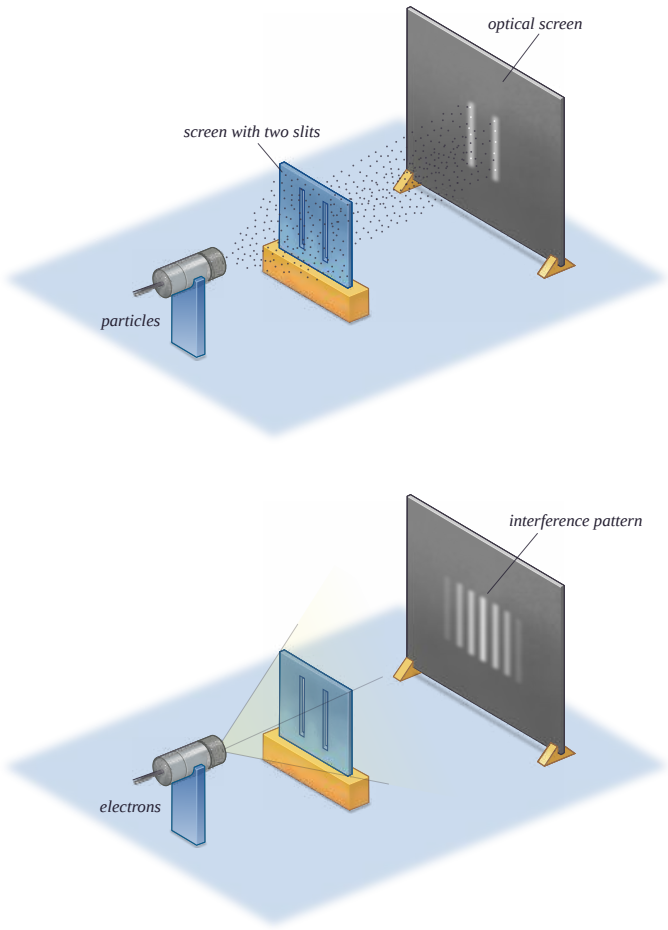


Figure 1.7.3 : (left) classical model of electrons. (right) wave property of electrons. (CC BY-NC; Ümit Kaya via LibreTexts)

However, if the slits are made small enough and close enough together, we actually observe the electrons are *diffracting* through the slits and *interfering* with each other just like waves (Figure 1.7.3 (right) and Figure 1.7.2 a,b). This means that the electrons have **wave-particle duality**, just like photons, in agreement with de Broglie's hypothesis discussed previously. In this case, they must have properties like wavelength and frequency. We can deduce the properties from the behavior of the electrons as they pass through our diffraction grating.

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



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

An electron microscope use a beam of accelerated electrons as a source of illumination. Since the wavelength of electrons can be up to 100,000 times shorter than that of visible light photons, electron microscopes have a higher resolving power than light

microscopes and can reveal the structure of smaller objects. A transmission electron microscope can achieve better than 50 pm resolution and magnifications of up to about 10,000,000x whereas most light microscopes are limited by diffraction to about 200 nm resolution and useful magnifications below 2000x (Figure 1.7.4).

Is Matter a Particle or a Wave?

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

Neutron Diffraction (Neutrons as Waves)

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

Example 1.7.1 : Neutron Diffraction

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

Solution

This is a simple use of de Broglie's equation

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

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

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

The relationship for kinetic energy is

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

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

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

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

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1.7: The Wave Properties of Matter

The fact that light (electromagnetic radiation) exhibited properties of particles became clear from the Compton scattering experiments where a momentum of $p = h/\lambda$ had to be associated with the x-rays to explain the experimental observations. In 1924 Louis de Broglie proposed that if light waves exhibited properties of particles, then matter particles should exhibit properties of waves, and the wavelength of these waves should be given by the same equation,

$$\lambda = \frac{\hbar}{p} \tag{1.7.1}$$

Since the wave vector k is defined as $k = \frac{2\pi}{\lambda}$, we can rewrite this equation as

$$p = \hbar k \tag{1.7.2}$$

Example 1.7.1

Calculate the de Broglie wavelength for an electron with a kinetic energy of 1000 eV. Could such electrons be used to obtain diffraction patterns of molecules?

Example 1.7.2

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 observed.

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 electrons and electromagnetic radiation. Diffraction patterns are obtained if the wavelength is comparable to the spacing between scattering centers. Immediately below in the box are two hyperlinks that show you patterns obtained by electron diffraction and by x-ray diffraction. You can find others on the Internet by searching x-ray diffraction pattern and electron diffraction pattern to see how electron and x-ray diffraction are being used in modern research.

De Broglie's proposal can be applied to Bohr's view of the hydrogen atom to show why angular momentum is quantized in units of $\hbar$. If the electron in the hydrogen atom is orbiting the nucleus in a stable orbit, then it should be described by a stable or stationary wave. Such a wave is called a standing wave. In a standing wave, the maximum and minimum amplitudes (crests and troughs) of the wave and the nodes (points where the amplitude is zero) are always found at the same position. In a traveling wave the crests, troughs, and nodes move from one position to another as a function of time. To place a standing wave in the shape of a round orbit, the circumference $2\pi r$ must be an integer multiple of the wavelength, i.e.

$$2\pi r = n\lambda \tag{1.7.3}$$

Now using the wavelength-momentum relationship $\lambda = \frac{\hbar}{p}$ to replace λ we get

$$rp = \frac{nh}{2\pi} \tag{1.7.4}$$

Since rp equals the angular momentum, we have

$$M = n\hbar \tag{1.7.5}$$

By saying the electron has the property of a standing wave around the orbit, we are led to the conclusion that angular momentum of the electron is quantized in units of ħ. The assumption of quantization thereby is replaced by the postulate that particles have wave properties characterized by a wavelength $\lambda = \frac{\hbar}{p}$, and quantization is a consequence of this new postulate.

This insight regarding the wave properties of particles led Erwin Schrödinger to build on the mathematical description of waves and develop a general theory of Quantum Mechanics, as we will see in the next chapter.

Example 1.7.3

Draw standing waves with 2, 4, and 6 nodes on a Bohr electron orbit.

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1.8: The Hydrogen Atomic Spectrum

Overview

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

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

Atomic Line Spectra

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

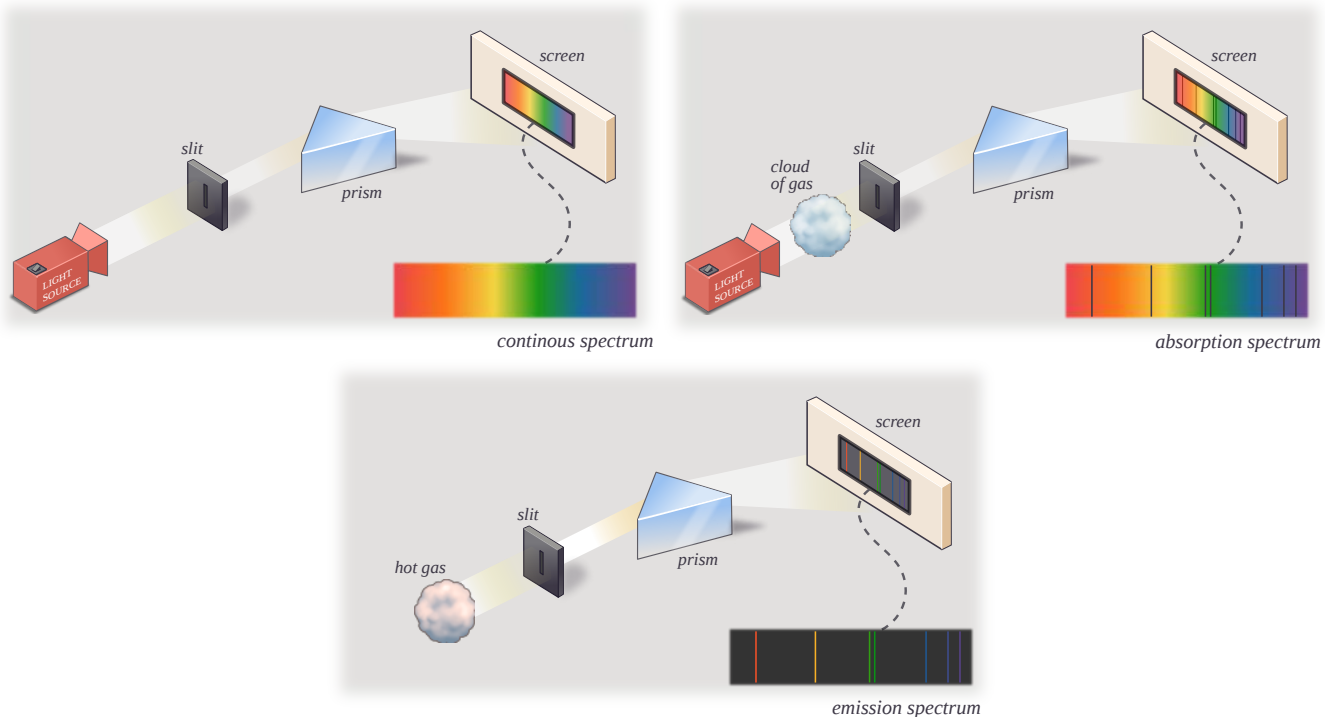


Figure 1.4.1 : Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen without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

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

collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas.

Fraunhofer Lines

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

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

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

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

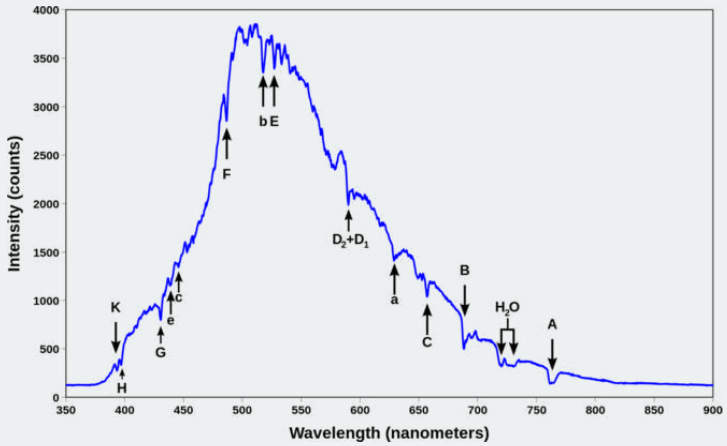


Figure 1.4.2 : Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun,

Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

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

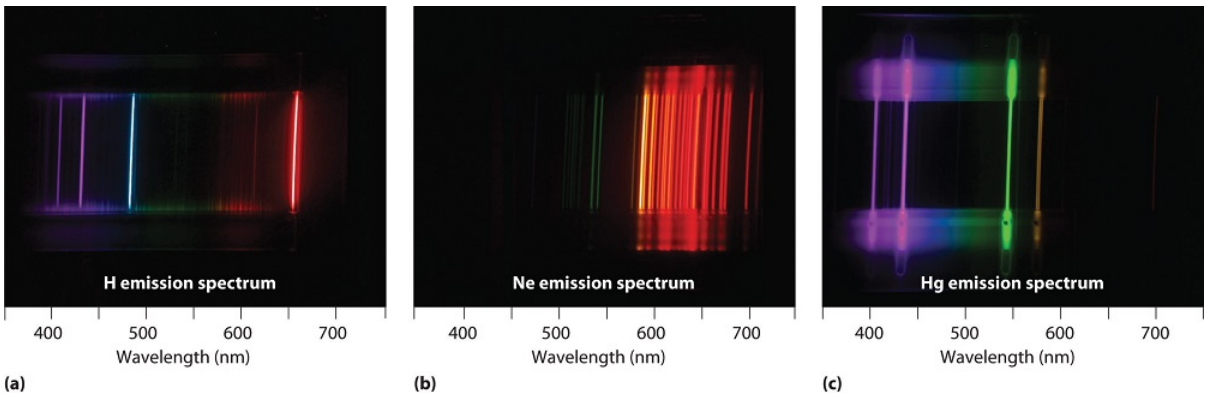


Figure 1.4.3 : The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The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

The Balmer Series of Hydrogen

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

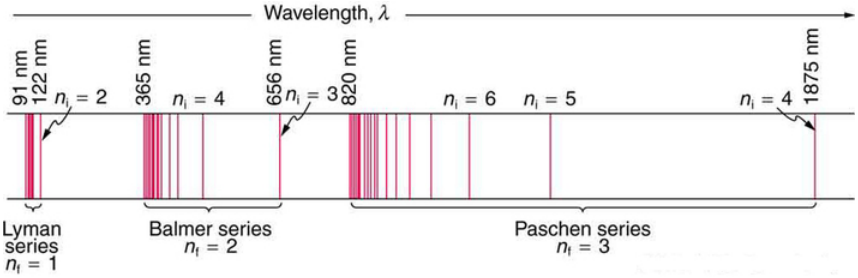


Figure 1.4.4 : A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and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

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Ångström had measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure 1.4.4). Balmer concentrated on just these four numbers, and found they were represented by the phenomenological formula:

$$\lambda = b\left(\frac{n_2^2}{n_2^2-4}\right) \tag{1.8.1}$$

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

The first four wavelengths of Equation 1.8.1 (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 1.8.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.8.2}$$

$$= R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \tag{1.8.3}$$

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

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

The Wavenumber as a Unit of Frequency

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda \nu = c$$

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

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

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

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

$$E = \frac{hc}{\lambda}$$
$$= hc \times \frac{1}{\lambda}$$
$$= hc\tilde{\nu}$$
$$\propto \tilde{\nu}$$

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 1.8.1 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 1.8.3*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 1.8.3) 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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1.9: 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:

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.9.1}$$

$$= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.9.2}$$

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

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

Other Series

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

$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{1.9.3}$$

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

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

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

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

Other Series

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

- Lyman series with $n_1 = 1$

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

Example 1.5.1 : The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy

A. Substitute the appropriate values into Equation 1.9.2 (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 1.9.2) 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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1.10: The Bohr Theory of the Hydrogen Atom

Learning Objectives

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

Rutherford's Failed Planetary Atom

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

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

$$F_{gravity} \propto \frac{m_1 m_2}{r^2} \tag{1.10.1}$$

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

$$F_{Coulomb} \propto \frac{Q_1 Q_2}{r^2} \tag{1.10.2}$$

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.

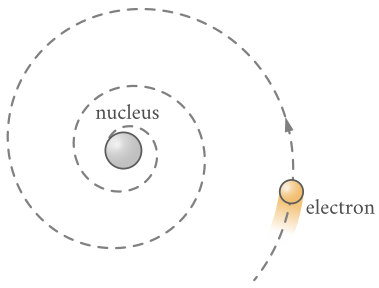


Figure 1.8.1 : The classical death spiral of an electron around a nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

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 1.10.2) comes from the corresponding Coulomb potential (sometimes call electrostatic potential)

$$V(r) = \frac{kQ_1Q_2}{r} \tag{1.10.3}$$

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

$$F(r) = -\frac{dV}{dr} \tag{1.10.4}$$

As r is varied, the energy will change, so that we have an example of a potential energy curve $V(r)$ (Figure $1.10.2; left$). If Q_1 and Q_2 are the same sign, then the curve which is a purely **repulsive potential**, i.e., the energy increases monotonically as the charges are brought together and decreases monotonically as they are separated. From this, it is easy to see that like charges (charges of the same sign) repel each other.

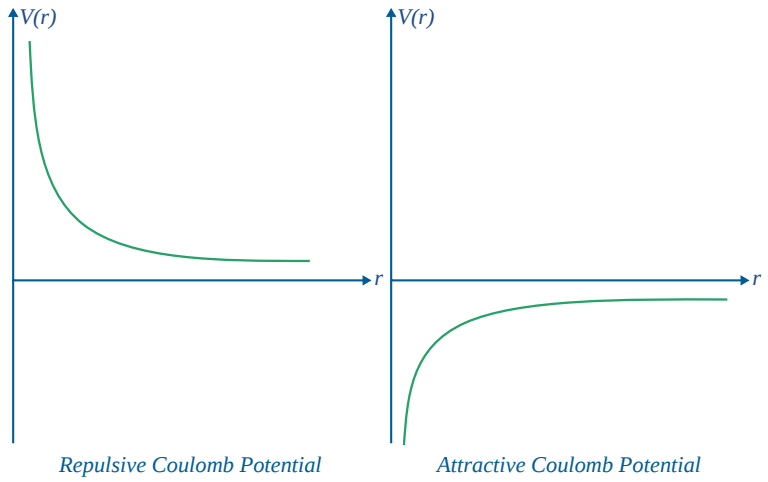


Figure 1.8.2 : Potential energy curve for the Coulomb interactions between two charges of same sign (left) and opposite signs (right). (CC BY-NC; Ümit Kaya via LibreTexts)

If the charges are of opposite sign, then the curve appears roughly Figure 1.10.2; $right$ and this is a purely **attractive potential**. Thus, the energy decreases as the charges are brought together, implying that opposite charges attract

The Bohr Model

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

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

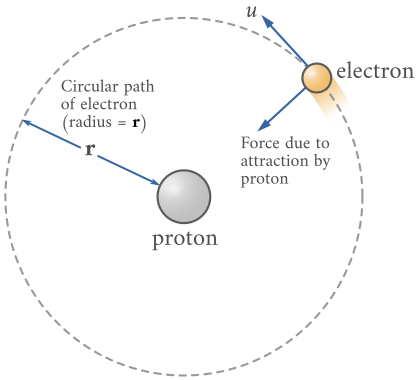


Figure 1.8.3 : Bohr atom with an electron revolving around a fixed nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

Consider a nucleus with charge $+Ze$ and one electron orbiting the nucleus. In this analysis, we will use another representation of the constant k in Coulomb's law (Equation 1.10.3), which is more commonly represented in the form:

$$k = \frac{1}{4\pi\epsilon_0} \tag{1.10.5}$$

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

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

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

The force on the electron is

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

and its magnitude is

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

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

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

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

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

or

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

or

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = (m_e v r)^2 \tag{1.10.6}$$

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

$$m_e vr = n\hbar \tag{1.10.7}$$

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

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

Substituting Equation 1.10.7 into the Equation 1.10.6, we find

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = n^2(\hbar)^2 \tag{1.10.8}$$

Equation 1.10.8 implies that orbits could only have certain allowed radii

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{Ze^2 m_e}n^2 \tag{1.10.9}$$

$$= \frac{a_0}{Z}n^2 \tag{1.10.10}$$

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

$$\begin{aligned} p_n r_n &= n\hbar \\ p_n &= \frac{n\hbar}{r_n} \\ &= \frac{\hbar Z}{a_0 n} \\ &= \frac{Ze^2 m_e}{4\pi\epsilon_0\hbar n} \end{aligned}$$

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

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

Substituting in the expressions for p_n and r_n and simplifying gives

$$E_n = -\frac{Z^2 e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2}\frac{1}{n^2} = -\frac{e^4 m_e}{8\epsilon_0^2 h^2}\frac{Z^2}{n^2} \tag{1.10.11}$$

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 1.10.11) as

$$E_n = -(2.18 \times 10^{-18})\frac{Z^2}{n^2}\ J = -\frac{Z^2}{n^2}\ R_y \tag{1.10.12}$$

Hence, the energy of the electron in an atom also is quantized. Equation 1.10.12 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).

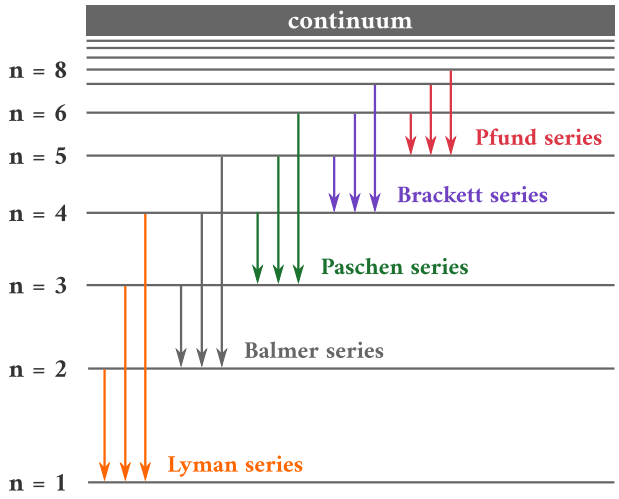


Figure 1.8.4 : Energy levels predicted by the Bohr model of hydrogen ($Z = 1$). (CC BY-NC; Ümit Kaya via LibreTexts)

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 1.10.8 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 1.10.8 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 $n = 1$

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

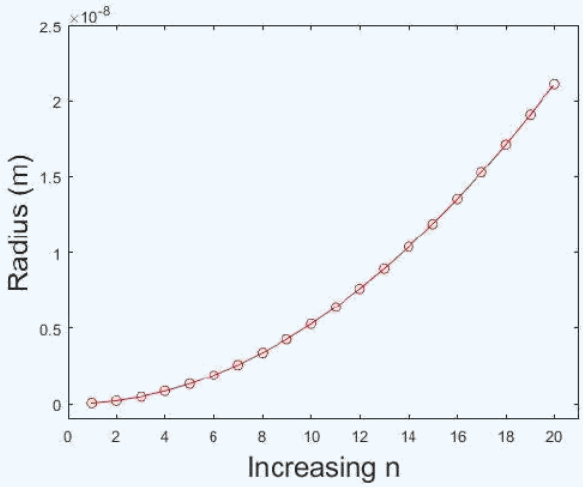
As expected, the Li^{2+} has a smaller radius than the H atoms because of the increased nuclear charge.

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 1.10.10 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

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

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

$$r_n = \frac{\left(5.292 \times 10^{-11}\right)}{(1)}(40000)$$

$$= 2.117 \times 10^{-6} m$$

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

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 1.10.7) 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 1.10.12), 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 $1.10.1A$). If not, then the waves will overlap imperfectly and cancel out (i.e., the electron will cease to exist) as demonstrated in Figure $1.10.1B$.

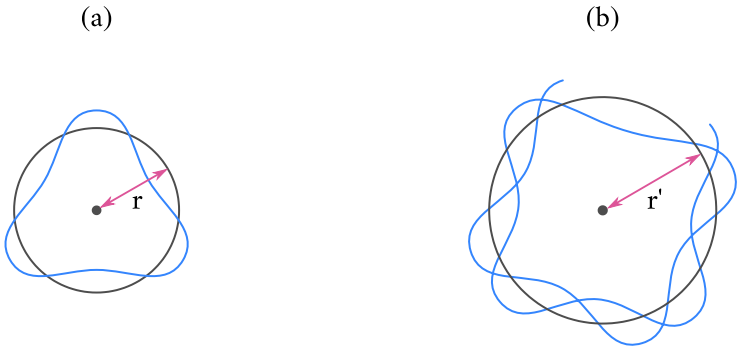


Figure 1.8.5 : Waves on a string have a wavelength related to the length of the string, allowing them to interfere constructively. (A) If we imagine the string bent into a closed circle, we get a rough idea of how electrons in circular orbits can interfere constructively. (B) If the wavelength does not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

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

Derivation of the Rydberg Equation from Bohr Model

Given a prediction of the allowed energies of a system, how could we go about verifying them? The general experimental technique known as *spectroscopy* permits us to probe the various differences between the allowed energies. Thus, if the prediction of the actual energies, themselves, is correct, we should also be able to predict these differences. Let us assume that we are able to place the electron in Bohr's hydrogen atom into an energy state E_n for $n > 1$, i.e. one of its so-called *excited states*. The electron

will rapidly return to its lowest energy state, known as the *ground state* and, in doing so, emit light. The energy carried away by the light is determined by the condition that the total energy is conserved (Figure 1.8.6).

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

Thus, if n_i is the integer that characterizes the initial (excited) state of the electron, and n_f is the final state (here we imagine that $n_f = 1$, but is applicable in cases that $n_f < n_i$, i.e., emission)

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

or

$$\nu = \frac{E_{ni} - E_{nf}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{1.10.13}$$

We can now identify the Rydberg constant R_H with the ratio of constants on the right hand side of Equation 1.10.13

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

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.

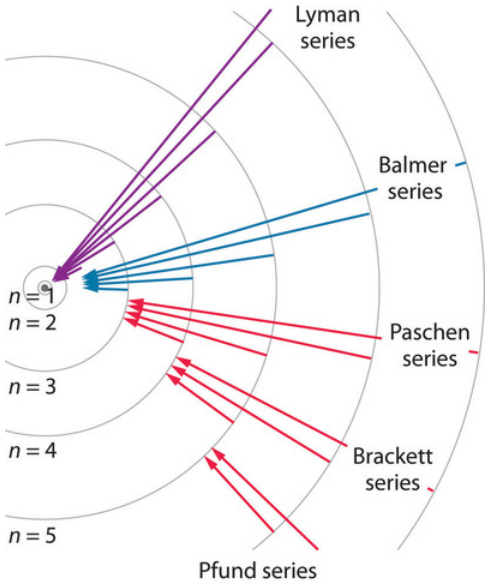


Figure 1.8.7 : Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding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

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

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CHAPTER OVERVIEW

2: New Game, New Rules (Postulates of Quantum Mechanics)

2.1: Introduction to the Schrödinger Equation
2.2: The One-Dimensional Wave Equation
2.3: A Classical Wave Equation
2.4: The Schrödinger Equation
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2.6: The Wavefunction Specifies the State of a System
2.7: Quantum Operators Represent Classical Variables
2.8: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators
2.9: The Eigenfunctions of Operators are Orthogonal
2.10: The Time-Dependent Schrödinger Equation
2.11: Implication of QM Postulates - Uncertainty, Part 1
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2.1: Introduction to the Schrödinger Equation

A scientific postulate is a generally accepted statement, which is accepted because it is consistent with experimental observation and serves to predict or explain a variety of observations. These postulates also are known as physical laws. Postulates cannot be derived by any other fundamental considerations. Newton's second law, $f = ma$, is an example of a postulate that is accepted and used because it explains the motion of objects like baseballs, bicycles, rockets, and cars. One goal of science is to find the smallest and most general set of postulates that can explain all observations. A whole new set of postulates was added with the invention of Quantum Mechanics. The Schrödinger equation is the fundamental postulate of Quantum Mechanics. In the previous chapter we saw that many individual quantum postulates were introduced to explain otherwise inexplicable phenomena. We will see that quantization and the relations $E = h\nu$ and $p = \frac{h}{\lambda}$, discussed in the last chapter, are consequences of the Schrödinger equation. In other words the Schrödinger equation is a more general and fundamental postulate.

A differential equation is a mathematical equation involving one or more derivatives. The analytical solution to a differential equation is the expression or function for the dependent variable that gives an identity when substituted into the differential equation. A mathematical function is a rule that assigns a value to one quantity using the values of other quantities. Any mathematical function can be expressed not only by a mathematical formula, but also in words, as a table of data, or by a graph. Numerical solutions to differential equations also can be obtained. In numerical solutions, the behavior of the dependent variable is expressed as a table of data or by a graph; no explicit function is provided.

Example 2.1.1

The differential equation $\frac{dy(x)}{dx} = 2$ has the solution $y(x) = 2x + b$, where b is a constant. This function $y(x)$ defines the family of straight lines on a graph with a slope of 2. Show that this function is a solution to the differential equation by substituting for $y(x)$ in the differential equation. How many solutions are there to this differential equation? For one of these solutions, construct a table of data showing pairs of x and y values, and use the data to sketch a graph of the function. Describe this function in words.

Some differential equations have the property that the derivative of the function gives the function back multiplied by a constant. The differential equation for a first-order chemical reaction is one example. This differential equation and the solution for the concentration of the reactant are given below.

$$\frac{dC(t)}{dt} = -kC(t) \tag{2.1.1}$$

$$C(t) = C_0 e^{-kt} \tag{2.1.2}$$

Example 2.1.2

Show that C(t) is a solution to the differential equation.

Another kind of differential equation has the property that the second derivative of the function yields the function multiplied by a constant. Both of these types of differential equations are found in Quantum Mechanics.

$$\frac{d^2\psi(x)}{dx^2} = k\psi(x) \tag{2.1.3}$$

Example 3.3

What is the value of the constant in the above differential equation when $\psi(x) = \cos(3x)$?

Example 2.1.4

What other functions, in addition to the cosine, have the property that the second derivative of the function yields the function multiplied by a constant?

Since some mathematical functions, such as the sine and cosine, go through repeating periodic maxima and minima, they produce graphs that look like waves. Such functions can themselves be thought of as waves and can be called wavefunctions. We now make a mathematically intuitive leap. If electrons, atoms, and molecules have wave-like properties, then there must be a mathematical function that is the solution to a differential equation that describes electrons, atoms, and molecules. This differential equation is called the wave equation, and the solution is called the wavefunction. Such thoughts may have motivated Erwin Schrödinger to argue that the wave equation is a key component of Quantum Mechanics.

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2.2: The One-Dimensional Wave Equation

Learning Objectives

- To introduce the wave equation including time and position dependence

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

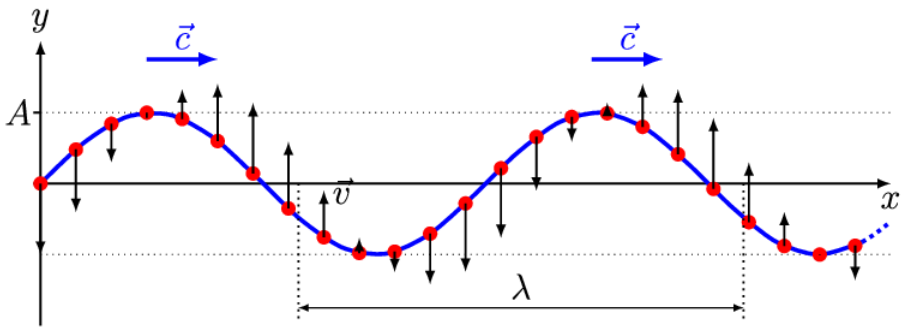


Figure 2.1.1 : A simple translational (transverse) wave. (CC BY-SA 4.0 International; And1mu via Wikimedia Commons)

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

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

where

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

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

Traveling Waves

Traveling waves, such as ocean waves or electromagnetic radiation, are waves that “move,” meaning that they have a frequency and are propagated through time and space. Another way of describing this property of “wave movement” is in terms of energy transmission – a wave travels, or transmits energy, over a set distance. The most important kinds of traveling waves in everyday life are electromagnetic waves, sound waves, and perhaps water waves, depending on where you live. It is difficult to analyze waves spreading out in three dimensions, reflecting off objects, etc., so we begin with the simplest interesting examples of waves, those restricted to move along a line. Let’s start with a rope, like a clothesline, stretched between two hooks. You take one end off the hook, holding the rope, and, keeping it stretched fairly tight, wave your hand up and back once. If you do it fast enough, you’ll see a single bump travel along the rope:

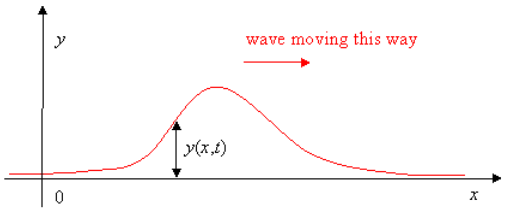


Figure 2.1.2 : A one-dimensional traveling wave at one instance of time t.

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

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

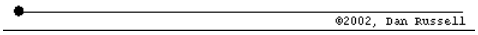


Figure 2.1.3 : A one-dimensional traveling wave at as a function of time. Traveling waves propagate energy from one spot to another with a fixed velocity v. (CC BY-NC-ND; Daniel A. Russell).

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

$$y(x,t) = f(x - vt) \tag{2.2.1}$$

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

Standing Waves

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

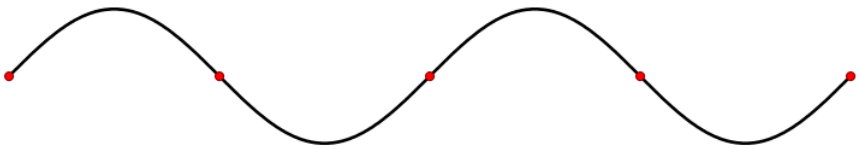


Figure 2.1.4 : Animation of standing wave in the stationary medium with marked wave nodes (red circles). (public domain; LucasVB).

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.

The Wave Equation

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

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{2.2.2}$$

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 2.2.2 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 2.2.2 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

$$u(0,t) = 0 \tag{2.2.3}$$

and

$$u(L,t) = 0 \tag{2.2.4}$$

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 2.2.2 subject to the boundary conditions in Equations 2.2.3 and 2.2.4 (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).

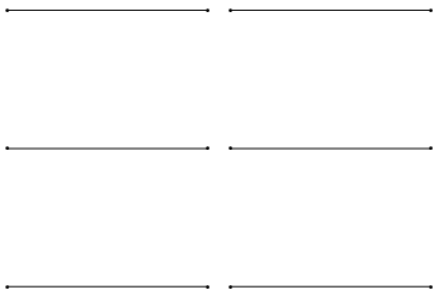


Figure 2.1.5 : Standing waves in a string (both spatially and temporally). The first six solutions ($u(x,t)$. from Wikipedia.

Curvature of Wave Solutions

Since the acceleration of the wave amplitude (right side of Equation 2.2.2) is proportional to $\frac{\partial^2}{\partial x^2}$, the greater curvature in the material produces a greater acceleration, i.e., greater changing velocity of the wave (Figure 2.1.4) and greater frequency of oscillation. As discussed later, the higher frequency waves (i..e, more nodes) are higher energy solutions; this as expected from the experiments discussed in Chapter 1 including Plank's equation $E = h\nu$.

Summary

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

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2.3: A Classical Wave Equation

The easiest way to find a differential equation that will provide wavefunctions as solutions is to start with a wavefunction and work backwards. We will consider a sine wave, take its first and second derivatives, and then examine the results. The amplitude of a sine wave can depend upon position, x, in space,

$$A(x) = A_0 \sin\left(\frac{2\pi x}{\lambda}\right) \tag{2.3.1}$$

or upon time, t,

$$A(t) = A_0 \sin(2\pi\nu t) \tag{2.3.2}$$

or upon both space and time,

$$A(x,t) = A_0 \sin\left(\frac{2\pi x}{\lambda} - 2\pi\nu t\right) \tag{2.3.3}$$

We can simplify the notation by using the definitions of a wave vector, $k = \frac{2\pi}{\lambda}$, and the angular frequency, $\omega = 2\pi\nu$ to get

$$A(x,t) = A_0 \sin(kx - \omega t) \tag{2.3.4}$$

When we take partial derivatives of A(x,t) with respect to both x and t, we find that the second derivatives are remarkably simple and similar.

$$\frac{\partial^2 A(x,t)}{\partial x^2} = -k^2 A_0 \sin(kx - \omega t) = -k^2 A(x,t) \tag{2.3.5}$$

$$\frac{\partial^2 A(x,t)}{\partial t^2} = -\omega^2 A_0 \sin(kx - \omega t) = -\omega^2 A(x,t) \tag{2.3.6}$$

By looking for relationships between the second derivatives, we find that both involve $A(x,t)$; consequently an equality is revealed.

$$k^{-2}\frac{\partial^2 A(x,t)}{\partial x^2} = -A(x,t) = \omega^{-2}\frac{\partial^2 A(x,t)}{\partial t^2} \tag{2.3.7}$$

Recall that ν and λ are related; their product gives the velocity of the wave, $\nu\lambda = v$. Be careful to distinguish between the similar but different symbols for frequency ν and the velocity v. If in ω = 2πν we replace ν with v/λ, then

$$\omega = \frac{2\pi\nu}{\lambda} = \nu k \tag{2.3.8}$$

and Equation 2.3.7 can be rewritten to give what is known as the classical wave equation in one dimension. This equation is very important. It is a differential equation whose solution describes all waves in one dimension that move with a constant velocity (e.g. the vibrations of strings in musical instruments) and it can be generalized to three dimensions. The classical wave equation in one-dimension is

$$\frac{\partial^2 A(x,t)}{\partial x^2} = \nu^{-2}\frac{\partial^2 A(x,t)}{\partial t^2} \tag{2.3.9}$$

Example 2.3.1

Complete the steps leading from Equation 2.3.3 to Equations 2.3.5 and 2.3.6 and then to Equation 2.3.9.

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2.4: The Schrödinger Equation

Learning Objectives

- To be introduced to the general properties of the Schrödinger equation and its solutions.

De Broglie's doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in the fall of 1925 Pieter Debye, Professor of Theoretical Physics at Zurich and Einstein's successor, suggested to Erwin Schrödinger that he give a seminar on de Broglie's work. Schrödinger gave a polished presentation, but at the end Debye remarked that he considered the whole theory rather childish: why should a wave confine itself to a circle in space? It wasn't as if the circle was a waving circular string, real waves in space diffracted and diffused, in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem and constructing his equation. There is no rigorous derivation of Schrödinger's equation from previously established theory, but it can be made very plausible by thinking about the connection between light waves and photons, and construction an analogous structure for de Broglie's waves and electrons (and later, other particles).

The Schrödinger Equation: A Better Approach

While the Bohr model is able to predict the allowed energies of any single-electron atom or cation, it by no means, a general approach. Moreover, it relies heavily on classical ideas, clumsily grafting quantization onto an essentially classical picture, and therefore, provides no real insights into the true quantum nature of the atom. Any rule that might be capable of predicting the allowed energies of a quantum system must also account for the *wave-particle duality* and implicitly include a wave-like description for particles. Nonetheless, we will attempt a heuristic argument to make the result at least plausible. In classical electromagnetic theory, it follows from Maxwell's equations that each component of the electric and magnetic fields in vacuum is a solution of the 3-D wave equation for electromagnetic waves:

$$\nabla^2\Psi(x,y,z,t) - \frac{1}{c^2}\frac{\partial^2\Psi(x,y,z,t)}{\partial t^2} = 0 \tag{2.4.1}$$

The wave equation in Equation 2.4.1 is the three-dimensional analog to the wave equation presented earlier (Equation 2.1.1) with the velocity fixed to the known speed of light: c. Instead of a partial derivative $\dfrac{\partial^2}{\partial x^2}$ in one dimension, the Laplacian (or "del-squared") operator is introduced:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{2.4.2}$$

Corresponding, the solution to this 3D equation wave equation is a function of *four* independent variables: x, y, z, and t and is generally called the **wavefunction** ψ.

We will attempt now to create an analogous equation for de Broglie's matter waves. Accordingly, let us consider a only 1-dimensional wave motion propagating in the *x*-direction. At a given instant of time, the form of a wave might be represented by a function such as

$$\Psi(x) = f\left(\frac{2\pi x}{\lambda}\right) \tag{2.4.3}$$

where $f(\theta)$ represents a sinusoidal function such as $\sin\theta$, $\cos\theta$, $e^{i\theta}$, $e^{-i\theta}$ or some linear combination of these. The most suggestive form will turn out to be the complex exponential, which is related to the sine and cosine by Euler's formula

$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta \tag{2.4.4}$$

Each of the above is a periodic function, its value repeating every time its argument increases by 2π. This happens whenever x increases by one wavelength λ. At a fixed point in space, the time-dependence of the wave has an analogous structure:

$$T(t) = f(2\pi\nu t) \tag{2.4.5}$$

where ν gives the number of cycles of the wave per unit time. Taking into account both x and t dependence, we consider a wavefunction of the form

$$\Psi(x,t) = exp\left[2\pi i\left(\frac{x}{\lambda} - \nu t\right)\right] \tag{2.4.6}$$

representing waves traveling from left to right. Now we make use of the Planck formula ($E = h\nu$) and de Broglie formulas ($p = \frac{h}{\lambda}$) to replace ν and λ by their particle analogs. This gives

$$\Psi(x,t) = \exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{2.4.7}$$

where

$$\hbar \equiv \frac{h}{2\pi} \tag{2.4.8}$$

Since Planck's constant occurs in most formulas with the denominator 2π, the $\hbar$ symbol was introduced by Paul Dirac. Equation 2.4.5 represents in some way the wavelike nature of a particle with energy E and momentum p. The time derivative of Equation 2.4.7 gives

$$\frac{\partial \Psi}{\partial t} = -\left(\frac{iE}{\hbar}\right)\exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{2.4.9}$$

Thus from a simple comparison of Equations 2.4.7 and 2.4.9

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi \tag{2.4.10}$$

or analogously differentiation of Equation 2.4.9 with respect to x

$$-i\hbar\frac{\partial \Psi}{\partial x} = p\Psi \tag{2.4.11}$$

and then the second derivative

$$-\hbar^2\frac{\partial^2 \Psi}{\partial x^2} = p^2\Psi \tag{2.4.12}$$

The energy and momentum for a *nonrelativistic* free particle (i.e., all energy is kinetic with no potential energy involved) are related by

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{2.4.13}$$

Substituting Equations 2.4.12 and 2.4.10 into Equation 2.4.13 shows that $\Psi(x,t)$ satisfies the following partial differential equation

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} \tag{2.4.14}$$

Equation 2.4.14 is the applicable differential equation describing the wavefunction of a *free particle* that is not bound by any external forces or equivalently not in a region where its potential energy $V(x,t)$ varies.

For a particle with a non-zero potential energy $V(x)$, the total energy E is then a sum of kinetics and potential energies

$$E = \frac{p^2}{2m} + V(x) \tag{2.4.15}$$

we postulate that Equation 2.4.3 for matter waves can be generalized to

$$\underbrace{i\hbar\frac{\partial \Psi(x,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t)}_{\text{time-dependent Schrödinger equation in 1D}} \tag{2.4.16}$$

For matter waves in three dimensions, Equation 2.4.6 is then expanded

$$\underbrace{i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\Psi(\vec{r},t)}_{\text{time-dependent Schrödinger equation in 3D}} \tag{2.4.17}$$

Here the potential energy and the wavefunctions Ψ depend on the three space coordinates x, y, z, which we write for brevity as $\vec{r}$. Notice that the potential energy is assumed to depend on position only and not time (i.e., particle motion). This is applicable for conservative forces that a potential energy function $V(\vec{r})$ can be formulated.

The Laplacian Operator

The three second derivatives in parentheses together are called the Laplacian operator, or del-squared,

$$\begin{aligned}\nabla^2 &= \nabla\cdot\nabla \\ &= \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\end{aligned} \tag{2.4.18}$$

with the del operator,

$$\nabla=\left(\vec{x}\frac{\partial}{\partial x}+\vec{y}\frac{\partial}{\partial y}+\vec{z}\frac{\partial}{\partial z}\right) \tag{2.4.19}$$

Remember from basic calculus that when the del operator is direclty operates on a field (e.g, $\nabla f(x,y,x)$), it denotes the gradient (i.e, the locally steepest slope) of the field. The symbols with arrows in Equation 2.4.19 are unit vectors.

Equation 2.4.17 is the *time-dependent Schrödinger* equation describing the wavefunction amplitude $\Psi(\vec{r},t)$ of matter waves associated with the particle within a specified potential $V(\vec{r})$. Its formulation in 1926 represents the start of modern quantum mechanics (Heisenberg in 1925 proposed another version known as matrix mechanics).

For *conservative* systems, the energy is a constant, and the time-dependent factor from Equation 2.4.7 can be separated from the space-only factor (via the *Separation of Variables* technique discussed in Section 2.2)

$$\Psi(\vec{r},t)=\psi(\vec{r})e^{-iEt/\hbar} \tag{2.4.20}$$

where $\psi(\vec{r})$ is a wavefunction dependent (or time-independent) wavefuction that only depends on space coordinates. Putting Equation 2.4.20 into Equation 2.4.17 and cancelling the exponential factors, we obtain the time-independent Schrödinger equation:

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r})=E\psi(\vec{r})}_{\text{time-independent Schrödinger equation}} \tag{2.4.21}$$

The overall form of the Equation 2.4.21 is not unusual or unexpected as it uses the principle of the **conservation of energy**. Most of our applications of quantum mechanics to chemistry will be based on this equation (with the exception of spectroscopy). The terms of the time-independent Schrödinger equation can then be interpreted as total energy of the system, equal to the system kinetic energy plus the system potential energy. In this respect, it is just the same as in classical physics.

Time Dependence to the Wavefunctions

Notice that the wavefunctions used with the time-independent Schrödinger equation (i.e., $\psi(\vec{r})$) do not have explicit t dependences like the wavefunctions of time-dependent analog in Equation 2.4.17 (i.e., $\Psi(\vec{r},t)$). That does **not imply** that there is no time dependence to the wavefunction. Equation 2.4.20 argues that the time-dependent (i.e., full spatial and temporal) wavefunction ($\Psi(\vec{r},t)$) differs from from the time-independent (i.e., spatial only) wavefunction $\psi(\vec{r})$ by a "phase factor" of constant magnitude. Using the Euler relationship in Equation 2.4.4, the total wavefunction above can be expanded

$$\Psi(\vec{r},t)=\psi(\vec{r})\left(\cos\frac{Et}{\hbar}-i\,\sin\frac{Et}{\hbar}\right) \tag{2.4.22}$$

This means the total wavefunction has a **complex behavior** with a real part and an imaginary part. Moreover, using the trigonometry identity $\sin(\theta)=\cos(\theta-\pi/2)$ Equation 2.4.22 can further simplified to

$$\Psi(\vec{r},t) = \psi(\vec{r})\cos\left(\frac{Et}{\hbar}\right) - i\psi(\vec{r})\cos\left(\frac{Et}{\hbar} - \frac{\pi}{2}\right)$$

This shows that both the real and the imaginary components of the total wavefunction oscillate, the imaginary part of the total wavefunction oscillates **out of phase** by $\frac{\pi}{2}$ with respect to the real part.

Note that while all wavefunctions have a time-dependence, that dependence may not impact in simple quantum problems as the next sections discuss and can often be ignored.

Before we embark on this, however, let us pause to comment on the validity of quantum mechanics. Despite its weirdness, its abstractness, and its strange view of the universe as a place of randomness and unpredictability, quantum theory has been subject to intense experimental scrutiny. It has been found to agree with experiments to better than $10^{-10}\%$ for all cases studied so far. When the Schrödinger Equation is combined with a quantum description of the electromagnetic field, a theory known as *quantum electrodynamics*, the result is one of the most accurate theories of matter that has ever been put forth. Keeping this in mind, let us forge ahead in our discussion of the quantum universe and how to apply quantum theory to both model and real situations.

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2.5: Invention of the Schrödinger Equation

From the previous section, the the classical wave equation in one-dimension was discussed:

$$\frac{\partial^2 A(x,t)}{\partial x^2} = \nu^{-2} \frac{\partial^2 A(x,t)}{\partial t^2} \tag{2.5.1}$$

Although we used a sine function to obtain the classical wave equation, functions other than the sine function can be substituted for A in Equation 2.5.1. Our goal as chemists is to seek a method for finding the wavefunctions that are appropriate for describing electrons, atoms, and molecules. In order to reach this objective, we need the appropriate wave equation.

Exercise 2.5.1

Show that the functions $e^{i(kx+\omega t)}$ and $\cos(k\,x - \omega\,t)$ also satisfy the classical wave equation (Equation 2.5.1). Note that i is a constant equal to $\sqrt{-1}$.

A general method for finding solutions to differential equations that depend on more than one variable (x and t in this case) is to separate the variables into different terms. This separation makes it possible to write the solution as a product of two functions, one that depends on x and one that depends on t. This important technique is called the Method of Separation of Variables. This technique is used in most of the applications that we will be considering.

For the classical wave equation, Equation 2.5.1, separating variables is very easy because x and t do not appear together in the same term in the differential equation. In fact, they are on opposite sides of the equation. The variables already have been separated, and we only have to see what happens when we substitute a product function into this equation. It is common in Quantum Mechanics to symbolize the functions that are solutions to Schrödinger's equation as ψ, ψ, or ϕ, so we use $\Phi(x)$ as the x-function, and examine the consequences of using $\cos(\omega t)$ as one possibility for the t-function.

$$\psi(x,t) = \psi(x) cos(\omega t) \tag{2.5.2}$$

After substituting Equation 2.5.2 into the classical wave Equation 2.5.1 and differentiating, we obtain

$$\cos(\omega t)\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{\omega^2}{\nu^2}\psi(x)\cos(\omega t) \tag{2.5.3}$$

which yields, after simplifying and rearranging,

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{\omega^2}{\nu^2}\psi(x) = 0 \tag{2.5.4}$$

We now include the idea that we are trying to find a wave equation for a particle. We introduce the particle momentum by using de Broglie's relation to replace $\frac{\omega^2}{v^2}$ with $\frac{p^2}{\hbar^2}$, where $\hbar = \frac{h}{2\pi}$ (called h-bar).

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{p^2}{\hbar^2}\psi(x) = 0 \tag{2.5.5}$$

Exercise 2.5.2

Show that $\frac{\omega^2}{v^2} = \frac{p^2}{\hbar^2}$.

Next we will use the total energy of a particle as the sum of the kinetic energy and potential energy to replace the momentum in Equation.

$$E = T + V(x) = \frac{p^2}{2m} + V(x) \tag{2.5.6}$$

Note that we have included the idea that the potential energy is a function of position. Each atomic or molecular system we will consider in the following chapters will have different potential energy functions.

Solving Equation 2.5.6 for p^2 and substituting it into Equation 2.5.5 gives us **the Schrödinger Equation**,

$$\frac{\partial^2\psi(x)}{\partial x^2}+\frac{2m}{\hbar^2}(E-V(x))\psi(x)=0 \tag{2.5.7}$$

which usually is written in rearranged form,

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x) \tag{2.5.8}$$

Notice that the left side of Equation 2.5.8 consists of the two terms corresponding to the kinetic energy and the potential energy. When we look at the left side of Equation 2.5.8, we can deduce a method of extracting the total energy from a known wavefunction, or we can use Equation 2.5.8) to find the wavefunction. Finding wavefunctions for models of interesting chemical phenomena will be one of the tasks we will accomplish in this text.

Exercise 2.5.3

Show the steps that lead from Equations 2.5.1 and 2.5.2 to Equation 2.5.8.

More precisely, Equation 2.5.8 is the Schrödinger equation for a particle of mass m moving in one dimension (x) in a potential field specified by $V(x)$. Since this equation does not contain time, it often is called the Time-Independent Schrödinger Equation. As mentioned previously, functions like ψ(x) are called wavefunctions because they are solutions to this wave equation. The term, wave, simply denotes oscillatory behavior or properties. The significance of the wavefunction will become clear as we proceed. For now, ψ(x) is the wavefunction that accounts for or describes the wave-like properties of particles.

The Schrödinger equation for a particle moving in three dimensions (x, y, z) is obtained simply by adding the other second derivative terms and by including the three-dimensional potential energy function. The wavefunction ψ then depends on the three variables x, y, and z.

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z) \tag{2.5.9}$$

Exercise 2.5.4

Write the Schrödinger equation for a particle of mass m moving in a 2-dimensional space with the potential energy given by

$$V(x,y)=-\frac{(x^2+y^2)}{2}. \tag{2.5.10}$$

The three second derivatives in parentheses together are called the Laplacian operator, or del-squared,

$$\nabla^2=\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) \tag{2.5.11}$$

with the del operator,

$$\nabla=\left(\vec{x}\frac{\partial}{\partial x}+\vec{y}\frac{\partial}{\partial y}+\vec{z}\frac{\partial}{\partial z}\right) \tag{2.5.12}$$

also is used in Quantum Mechanics. Remember, symbols with arrows over them are unit vectors.

Exercise 2.5.5

Write the del-operator and the Laplacian operator for two dimensions and rewrite your answer to Exercise 2.5.4 in terms of the Laplacian operator.

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2.6: 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).

$$P(x) = \psi^*(x)\psi(x) \tag{2.6.1}$$

$$= |\psi(x)|^2 \tag{2.6.2}$$

Hence, for valid (e.g., well-behaved) wavefunctions, the normalized probability in Equation 2.6.2 holds true, such that the integral over all space is equal to 1.

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\, dx = 1 \tag{2.6.3}$$

Equation 2.6.3 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 2.6.3 can be satisfied (so that the Born Interpretation to be applicable).

Definition: Square-Integrable Functions

A complex-valued function, $f(x)$, is a *square-integrable* function if the integral of the square of the absolute value is finite.

$$\int_{-\infty}^{\infty} f^*(x)f(x)\, dx < \infty$$

For this to be true, the integrals of the positive and negative portions of the real and imaginary parts of $f(x)$ must both be finite.

Let us examine this set of examples in further detail in Figure 4.1.1 . The first wavefunction ψ_1 is sharply peaked at a particular value of x, and the probability density, being its square, is likewise peaked there as well. This is the wavefunction for a particle well localized at a position given by the center of the peak, as the probability density is high there, and the width of the peak is small, so the uncertainty in the position is very small.

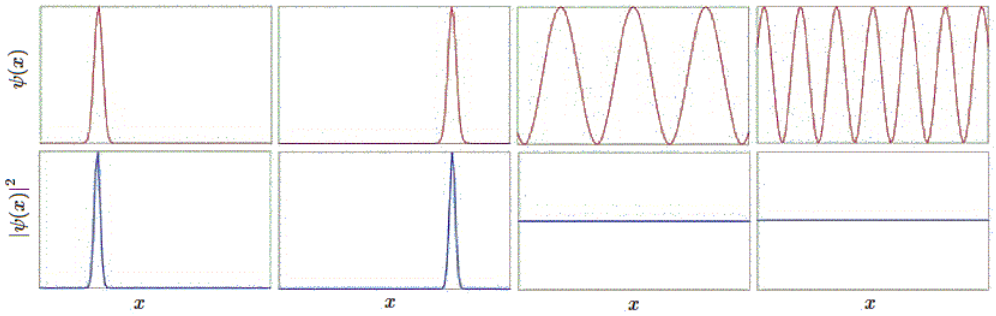


Figure 4.1.1 : Examples of good wavefunctions, $\psi(x)$, (red, top) and corresponding probability densities, $P(x)$, (blue, bottom).

The second wavefunction ψ_2 has the same peak profile, but shifted to a different position center. All of the properties of the first wavefunction hold here too, so this simply describes a particle that is well-localized at that different position. The third and fourth wavefunctions ψ_3 and ψ_4 respectively look like sinusoids of different spatial periods. The wavefunctions are actually complex of the form

$$\psi(x) = Ne^{ikx}$$

so only the real part is being plotted in Figure 4.1.1 . Note that even though the periods, k, of the oscillating wavefunctions are different,

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

for all k, so the corresponding probability densities, $P(x)$, are the same except for the normalization constant (Equation 2.6.2). We saw before that it does not make a whole lot of sense to think of a sinusoidal wave as being localized in some place. Indeed, the positions for these two wavefunctions are ill-defined, so they are not well-localized, and the uncertainty in the position is large in each case. This is Heisenberg Uncertainty Principle in action.

Ill-behaved (invalid) Wavefunctions

The Born interpretation in Equation 2.6.2 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 2.6.3 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.

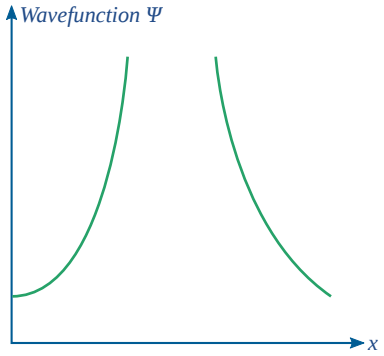


Figure 4.1.2 : This function is an invalid wavefunction since the amplitude is going to infinity over a region (the middle in this case). (CC BY-NC; Ümit Kaya via LibreTexts)

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.

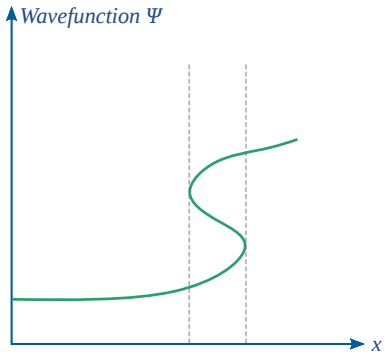


Figure 4.1.3 : This function is an invalid wavefunction since it is not a proper function (i. e., not one-to-one). (CC BY-NC; Ümit Kaya via LibreTexts)

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.

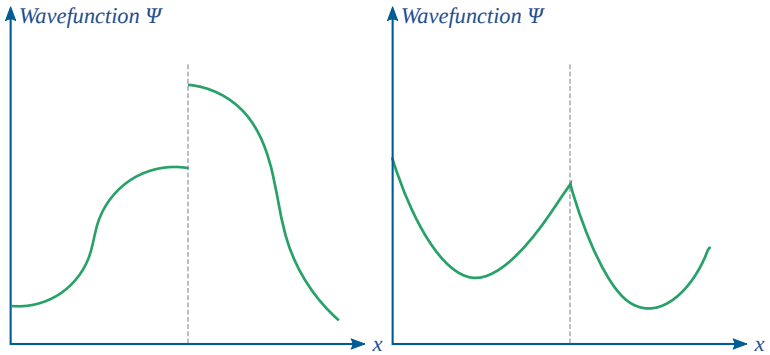


Figure 4.1.4 : These functions are invalid wavefunctions. (left) The first derivative of a function gives its gradient at a given point, and it thus exists as long as the function is continuous - only if there is a break in the function is there a point at which its first derivative does not exist. (right) The second derivative of this wavefunction is discontinuous at the point indicated, where the gradient of the line changes by more than 180º. 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

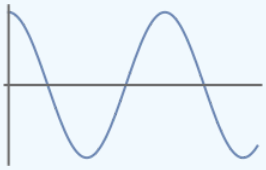
Determine if each of the following functions is acceptable as a wavefunction over the indicated regions:

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

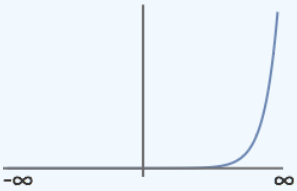
This is not an acceptable wavefunction. It is **single-valued** across the entire range. There is a single value for each value of x. It is **continuous** over the defined limits of integration, as we can see from a plot given below. However, it is not square-integrable.

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



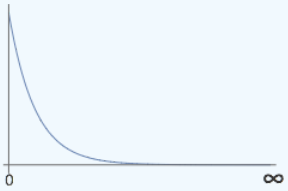
Solution b

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 ∞.



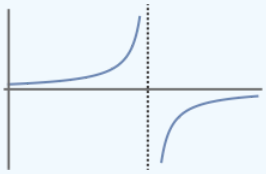
Solution c

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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2.7: 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:

$$\vec{r} = (x,y,z) \tag{2.7.1}$$

$$= x\vec{i} + y\vec{j} + z\vec{k} \tag{2.7.2}$$

The operator for a component of linear momentum is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{2.7.3}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = \left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \tag{2.7.4}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \tag{2.7.5}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2 \tag{2.7.6}$$

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

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{2.7.7}$$

The Hamiltonian Operator

The Hamiltonian operator is named after the Irish mathematician William Hamilton and comes from the his formulation of Classical Mechanics that is based on the total energy:

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

rather than Newton's second law,

$$\vec{F} = m\vec{a}$$

In many cases only the kinetic energy of the particles and the electrostatic or Coulomb potential energy due to their charges are considered, but in general all terms that contribute to the energy appear in the Hamiltonian. These additional terms account for such things as external electric and magnetic fields and magnetic interactions due to magnetic moments of the particles and their motion.

Table 4.2.1 : Some common Operators in Quantum Mechanics

Name	Observable Symbol	Operator Symbol	Operation
Position (in 1D)	x	$\hat{X}$	Multiply by x
Position (in 3D)	$\vec{r}$	$\hat{R}$	Multiply by $\vec{r}$
Momentum (in 1D)	p_x	$\hat{P}_x$	$-\imath\hbar\frac{d}{dx}$
Momentum (in 3D)	$\vec{p}$	$\hat{P}$	$-\imath\hbar\left[\hat{i}\,\frac{d}{dx}+\hat{j}\frac{d}{dy}+\hat{k}\frac{d}{dz}\right]$
Kinetic Energy (in 1D)	T_x	$\hat{T_x}$	$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$
Kinetic Energy (in 3D)	T	$\hat{T}$	$\frac{-\hbar^2}{2m}\left[\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right]$ Which can be simplified to $\frac{-\hbar^2}{2m}\bigtriangledown^2$
Potential Energy (in 1D)	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
Potential Energy (in 3D)	$V(x,y,z)$	$\hat{V}(x,y,z)$	Multiply by $V(x,y,z)$
Total Energy	E	$\hat{E}$	$\frac{-\hbar^2}{2m}\nabla^2+V(x,y,z)$
Angular Momentum (x axis component)	L_x	$\hat{L_x}$	$-\imath\hbar\left[y\frac{d}{dz}-z\frac{d}{dy}\right]$
Angular Momentum (y axis component)	L_y	$\hat{L_y}$	$-\imath\hbar\left[z\frac{d}{dx}-x\frac{d}{dz}\right]$
Angular Momentum (z axis component)	L_z	$\hat{L_z}$	$-\imath\hbar\left[x\frac{d}{dy}-y\frac{d}{dx}\right]$

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2.8: 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.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{2.8.1}$$

Using this notation, we write the Schrödinger Equation as

$$\hat{H}|\psi(x,y,z)\rangle = E|\psi(x,y,z)\rangle \tag{2.8.2}$$

Equation 2.8.2 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 2.8.2 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.

$$\hat{A}|\Psi\rangle = a|\Psi\rangle \tag{2.8.3}$$

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

$$A|\psi_a(x)\rangle = a|\psi_a(x)\rangle \tag{2.8.4}$$

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 2.8.4 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 2.8.4.

Expectation Values

We have seen that $|\psi(x,t)|^2$ is the probability density of a measurement of a particle's displacement yielding the value x at time t. Suppose that we made a large number of independent measurements of the displacement on an equally large number of identical quantum systems. In general, measurements made on different systems will yield different results. However, from the definition of probability, the mean of all these results is simply

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx \tag{2.8.5}$$

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

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi|^2 dx. \tag{2.8.6}$$

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 $\langle a\rangle$:

$$\langle a\rangle = \langle\psi|a|\psi\rangle \tag{2.8.7}$$

$$= \int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx \tag{2.8.8}$$

If an unnormalized wavefunction where used, then Equation 2.8.8 changes to

$$\langle a\rangle = \frac{\langle\psi|a|\psi\rangle}{\langle\psi|\psi\rangle} \tag{2.8.9}$$

$$= \frac{\int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx}{\int_{-\infty}^{\infty} \psi^*\psi dx} \tag{2.8.10}$$

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

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 |\psi|^2 dx \tag{2.8.11}$$

$$\equiv \langle x^2 \rangle - \langle x \rangle^2, \tag{2.8.12}$$

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).

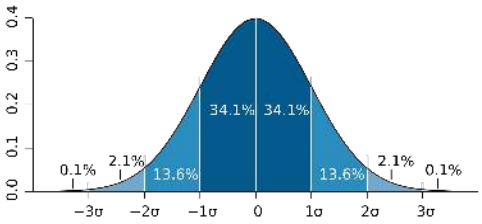


Figure 4.3.1 : A plot of a normal distribution (or bell-shaped curve) where each band has a width of 1 standard deviation. image usd with permission from Wikipedia.

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 2.8.8 is the relevant equation to use.

Solution a

The expectation value of the **position** is:

$$\begin{aligned} \langle x \rangle &= \int \psi^* x \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} x \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{L}{2} \end{aligned}$$

Solution b

The expectation value of the **momentum** is:

$$\begin{aligned}\langle p \rangle &= \int \psi^* \hat{p} \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2i\hbar\pi}{L^2} \int_0^L \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) dx \\ &= 0\end{aligned}$$

Solution c

The expectation value of the **kinetic energy** is:

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

A position "on average" is in the middle of the box ($L/2$). It has equal probability of traveling towards the left or right, so the average momentum and velocity must be zero.

Solution d

The average kinetic energy must be equal to the total energy of the ground state of the particle in the box, as there is no other energy component (i.e, $V = 0$).

Expanding the Wavefunction

It is also possible to demonstrate that the eigenstates of an operator attributed to a observable form a **complete set** (*i.e.*, that any general wavefunction can be written as a linear combination of these eigenstates). However, the proof is quite difficult, and we shall not attempt it here.

In summary, given an operator $\hat{A}$, any general wavefunction, $\psi(x)$, can be written

$$\psi = \sum_i c_i \phi_i$$

where the c_i are complex weights, and the $\phi(x)$ are the properly normalized (and mutually orthogonal) eigenstates of $\hat{A}$: i.e.,

$$A\phi_i = a_i \phi_i$$

where a_i is the eigenvalue corresponding to the eigenstate ϕ_i, and

$$\int_{-\infty}^{\infty} \phi_i^* \phi_j dx = \delta_{ij}. \tag{2.8.13}$$

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 2.8.10 and 2.8.13 that

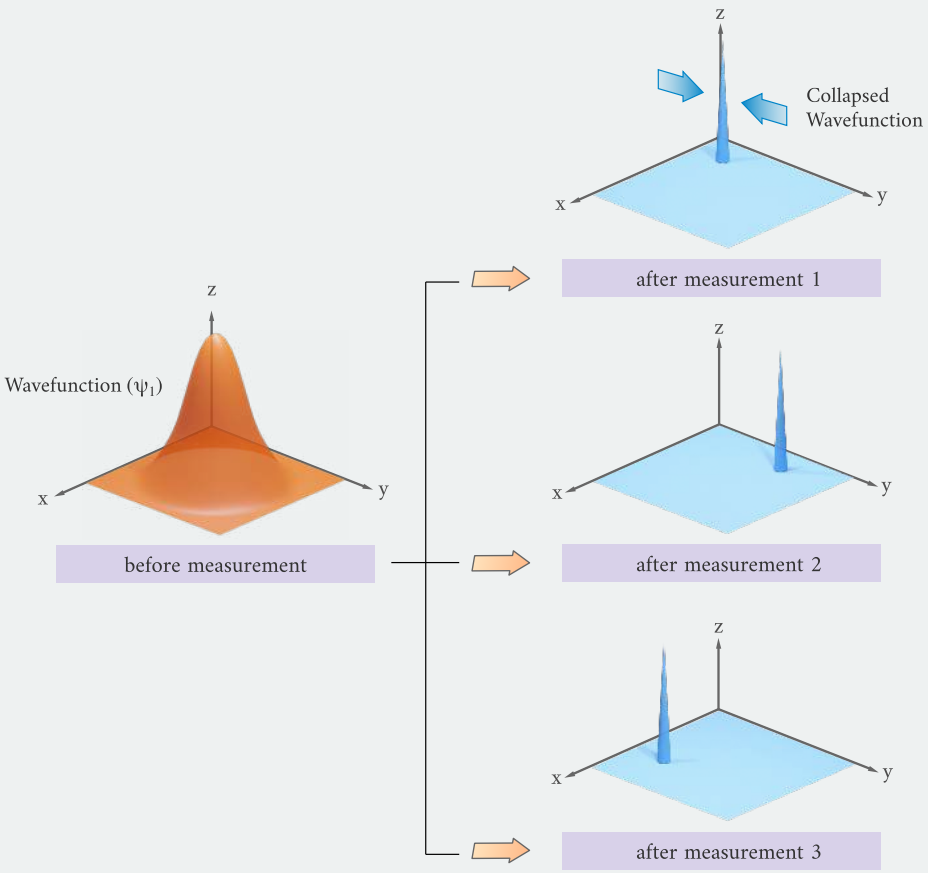
$$c_i = \int_{-\infty}^{\infty} \phi_i^* \psi dx. \tag{2.8.14}$$

Thus, the expansion coefficients in Equation 2.8.14 are easily determined, given the wavefunction ψ and the eigenstates ϕ_i. Moreover, if ψ is a properly normalized wavefunction then Equations 2.8.10 and 2.8.13 yield

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

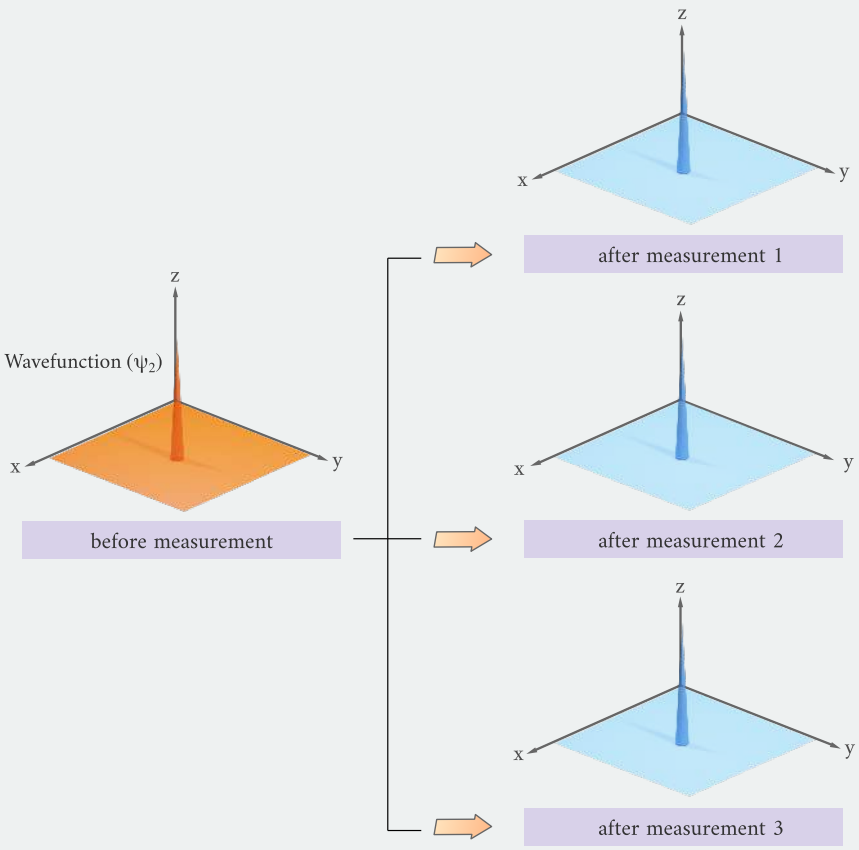
Collapsing the Wavefunction

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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2.9: The Eigenfunctions of Operators are Orthogonal

Learning Objectives

- Understand the properties of a Hermitian operator and their associated eigenstates
- Recognize that all experimental obervables are obtained by Hermitian operators

Consideration of the quantum mechanical description of the particle-in-a-box exposed two important properties of quantum mechanical systems. We saw that the eigenfunctions of the Hamiltonian operator are orthogonal, and we also saw that the position and momentum of the particle could not be determined exactly. We now examine the generality of these insights by stating and proving some fundamental theorems. These theorems use the Hermitian property of quantum mechanical operators that correspond to observables, which is discuss first.

Hermitian Operators

Since the eigenvalues of a quantum mechanical operator correspond to measurable quantities, the eigenvalues must be real, and consequently a quantum mechanical operator must be Hermitian. To prove this, we start with the premises that ψ and φ are functions, $\int d\tau$ represents integration over all coordinates, and the operator $\hat{A}$ is **Hermitian** by definition if

$$\int \psi^* \hat{A} \psi \, d\tau = \int (\hat{A}^* \psi^*) \psi \, d\tau \tag{2.9.1}$$

This equation means that the complex conjugate of $\hat{A}$ can operate on ψ^* to produce the same result after integration as $\hat{A}$ operating on φ, followed by integration. To prove that a quantum mechanical operator $\hat{A}$ is Hermitian, consider the eigenvalue equation and its complex conjugate.

$$\hat{A}\psi = a\psi \tag{2.9.2}$$

$$\hat{A}^* \psi^* = a^* \psi^* = a\psi^* \tag{2.9.3}$$

Note that $a^* = a$ because the eigenvalue is real. Multiply Equation 2.9.2 and 2.9.3 from the left by ψ^* and ψ, respectively, and integrate over the full range of all the coordinates. Note that ψ is normalized. The results are

$$\int \psi^* \hat{A} \psi \, d\tau = a \int \psi^* \psi \, d\tau = a \tag{2.9.4}$$

$$\int \psi \hat{A}^* \psi^* \, d\tau = a \int \psi \psi^* \, d\tau = a \tag{2.9.5}$$

Since both integrals equal a, they must be equivalent.

$$\int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau \tag{2.9.6}$$

The operator acting on the function,

$$\hat{A}^* \int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau_*$$

produces a new function. Since functions commute, Equation 2.9.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{2.9.7}$$

This equality means that $\hat{A}$ is Hermitian.

Orthogonality Theorem

Eigenfunctions of a Hermitian operator are orthogonal if they have different eigenvalues.

Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.

Proof

ψ and φ are two eigenfunctions of the operator $\hat{A}$ with real eigenvalues a_1 and a_2, respectively. Since the eigenvalues are real, $a_1^* = a_1$ and $a_2^* = a_2$.

$$\hat{A}\psi = a_1\psi$$

$$\hat{A}^*\psi^* = a_2\psi^*$$

Multiply the first equation by φ^* and the second by ψ and integrate.

$$\int \psi^* \hat{A}\psi \, d\tau = a_1 \int \psi^* \psi \, d\tau$$

$$\int \psi \hat{A}^* \psi^* \, d\tau = a_2 \int \psi\psi^* \, d\tau \tag{2.9.8}$$

Subtract the two equations in Equation 2.9.8 to obtain

$$\int \psi^* \hat{A}\psi \, d\tau - \int \psi \hat{A}^* \psi^* \, d\tau = (a_1 - a_2) \int \psi^* \psi \, d\tau \tag{2.9.9}$$

The left-hand side of Equation 2.9.9 is zero because $\hat{A}$ is Hermitian yielding

$$0 = (a_1 - a_2) \int \psi^* \psi \, d\tau \tag{2.9.10}$$

If a_1 and a_2 in Equation 2.9.10 are not equal, then the integral **must** be zero. This result proves that **nondegenerate eigenfunctions** of the same operator are orthogonal.

□

Two wavefunctions, $\psi_1(x)$ and $\psi_2(x)$, are said to be *orthogonal* if

$$\int_{-\infty}^{\infty} \psi_1^* \psi_2 \, dx = 0. \tag{2.9.11}$$

Consider two eigenstates of $\hat{A}$, $\psi_a(x)$ and $\psi_{a'}(x)$, which correspond to the two *different* eigenvalues a and a', respectively. Thus,

$$A\psi_a = a\psi_a \tag{2.9.12}$$

$$A\psi_a' = a'\psi_a' \tag{2.9.13}$$

Multiplying the complex conjugate of the first equation by $\psi_{a'}(x)$, and the second equation by $\psi_{a'}^*(x)$, and then integrating over all x, we obtain

$$\int_{-\infty}^{\infty} (A\psi_a)^* \psi_{a'} dx = a \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx, \tag{2.9.14}$$

$$\int_{-\infty}^{\infty} \psi_a^* (A\psi_{a'}) dx = a' \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx. \tag{2.9.15}$$

However, from Equation 2.9.9, the left-hand sides of the above two equations are equal. Hence, we can write

$$(a - a') \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0.$$

By assumption, $a \neq a'$, yielding

$$\int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0.$$

In other words, eigenstates of an Hermitian operator corresponding to *different* eigenvalues are automatically *orthogonal*.

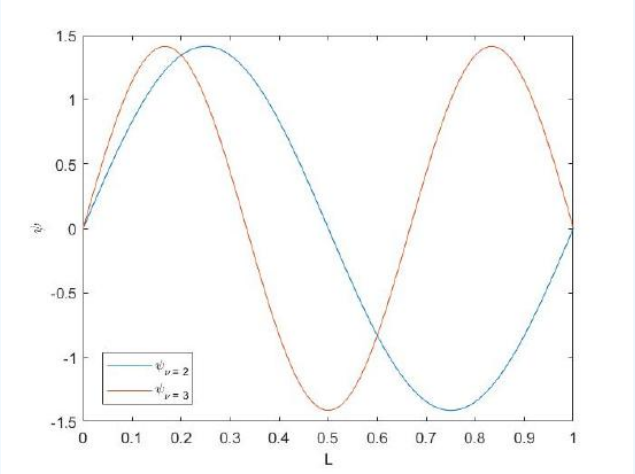
> The eigenvalues of operators associated with experimental measurements are all *real*.

Example4.5.1

Draw graphs and use them to show that the particle-in-a-box wavefunctions for $\psi(n=2)$ and $\psi(n=3)$ are orthogonal to each other.

Solution

The two PIB wavefunctions are qualitatively similar when plotted



These wavefunctions are orthogonal when

$$\int_{-\infty}^{\infty} \psi(n=2)\psi(n=3)dx = 0$$

and when the PIB wavefunctions are substituted this integral becomes

$$\int_0^L \sqrt{\frac{2}{L}}\sin\left(\frac{2n}{L}x\right)\sqrt{\frac{2}{L}}\sin\left(\frac{2n}{L}x\right)dx = ?$$

$$\frac{2}{L}\int_0^L \sin\left(\frac{2}{L}x\right)\sin\left(\frac{3}{L}x\right) = ?$$

We can expand the integrand using trigonometric identities to help solve the integral, but it is easier to take advantage of the symmetry of the integrand, specifically, the $\psi(n=2)$ wavefunction is even (blue curves in above figure) and the $\psi(n=3)$ is odd (purple curve). Their product (even times odd) is an odd function and the integral over an odd function is zero. Therefore $\psi(n=2)$ and $\psi(n=3)$ wavefunctions are orthogonal.

This can be repeated an infinite number of times to confirm the entire set of PIB wavefunctions are mutually orthogonal as the Orthogonality Theorem guarantees.

Orthogonality of Degenerate Eigenstates

Consider two eigenstates of $\hat{A}$, ψ_a and ψ'_a, which correspond to the *same* eigenvalue, a. Such eigenstates are termed **degenerate**. The above proof of the orthogonality of different eigenstates fails for degenerate eigenstates. Note, however, that *any* linear combination of ψ_a and ψ'_a is also an eigenstate of $\hat{A}$ corresponding to the eigenvalue a. Thus, even if ψ_a and ψ'_a are not orthogonal, we can always choose two linear combinations of these eigenstates which are orthogonal. For instance, if ψ_a and ψ'_a are properly normalized, we can define the **overlap integral**

$$S = \int_{-\infty}^{\infty} \psi_a^* \psi_a' dx, \tag{2.9.16}$$

It is easily demonstrated (but not here) that

$$\psi_a'' = \frac{|S|}{\sqrt{1-|S|^2}} \left(\psi_a - S^{-1}\psi_a'\right) \tag{2.9.17}$$

is a properly normalized eigenstate of $\hat{A}$, corresponding to the eigenvalue a, which is orthogonal to ψ_a. It is straightforward to generalize the above argument to three or more degenerate eigenstates. Hence, we conclude that the eigenstates of a Hermitian operator are, or can be chosen to be, **mutually orthogonal.**

Theorem: Gram-Schmidt Orthogonalization

Degenerate eigenfunctions are **not** automatically orthogonal, but can be made so mathematically via the Gram-Schmidt Orthogonalization.

The above theorem argues that if the eigenvalues of two eigenfunctions are the same then the functions are said to be degenerate and linear combinations of the degenerate functions can be formed that will be orthogonal to each other. Since the two eigenfunctions have the same eigenvalues, the linear combination also will be an eigenfunction with the same eigenvalue. The proof of this theorem shows us one way to produce orthogonal degenerate functions.

Proof

If ψ_a and ψ_a' are degenerate, but not orthogonal, we can define a new composite wavefunction $\psi_a'' = \psi_a' - S\psi_a$ where S is the overlap integral:

$$S = \langle \psi_a | \psi_a' \rangle$$

then ψ_a and ψ_a'' will be orthogonal.

$$\begin{aligned} \langle \psi_a | \psi_a'' \rangle &= \langle \psi_a | \psi_a' - S\psi_a \rangle \\ &= \cancel{\langle \psi_a | \psi_a' \rangle}^{S} - S \cancel{\langle \psi_a | \psi_a \rangle}^{1} \\ &= S - S = 0 \end{aligned}$$

$$\int \psi_a^* \psi_a d\tau$$

then ψ_a and Φ will be orthogonal.

$$\begin{aligned} \int \psi_A^* \Phi d\tau &= \int \psi_a^* (\psi_a' - S\psi_a) d\tau \\ &= \int \psi_a^* \psi_a' d\tau - S \int \psi_a^* \psi_a d\tau \\ &= S - S = 0 \end{aligned}$$

□

Exercise 4.5.2

Find N that normalizes ψ if $\psi = N(\varphi_1 - S\varphi_2)$ where φ_1 and φ_2 are normalized wavefunctions and S is their overlap integral.

$$S = \langle \varphi_1 | \varphi_2 \rangle$$

Answer

Remember that to normalize an arbitrary wavefunction, we find a constant N such that $\langle\psi|\psi\rangle = 1$. This equates to the following procedure:

$$\begin{aligned}
\langle\psi|\psi\rangle = \langle N(\varphi_1 - S\varphi_2)\,|\,N(\varphi_1 - S\varphi_2)\rangle &= 1 \\
N^2\,\langle(\varphi_1 - S\varphi_2)\,|\,(\varphi_1 - S\varphi_2)\rangle &= 1 \\
N^2\left[\cancelto{1}{\langle\varphi_1|\varphi_1\rangle} - S\cancelto{S}{\langle\varphi_2|\varphi_1\rangle} - S\cancelto{S}{\langle\varphi_1|\varphi_2\rangle} + S^2\cancelto{1}{\langle\varphi_2|\varphi_2\rangle}\right] &= 1 \\
N^2(1 - S^2 \cancel{- S^2} + \cancel{S^2}) &= 1 \\
N^2(1 - S^2) &= 1
\end{aligned}$$

therefore

$$N = \frac{1}{\sqrt{1 - S^2}}$$

We conclude that the eigenstates of operators are, or can be chosen to be, **mutually orthogonal**.

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2.10: The Time-Dependent Schrödinger Equation

Learning Objectives

- Recognize the differences between the time-dependent and the time-independent Schrödinger equations
- To distinguish between stationary and non-stationary wavefunctions

There are two "flavors" of Schrödinger equations: the time-dependent and the time-independent versions. While the time-dependent Schrödinger equation predicts that wavefunctions can form standing waves (called stationary states), that if classified and understood, then it becomes easier to solve the time-dependent Schrödinger equation for any state. Stationary states can also be described by the time-independent Schrödinger equation (used only when the Hamiltonian is not explicitly time dependent). However, it should be noted that the solutions to the time-independent Schrödinger equation still have time dependencies.

Time-Dependent Wavefunctions

Recall that the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \tag{2.10.1}$$

yields the allowed energies and corresponding wavefunctions. However, it does not tell us how the system evolves in time. It would seem that something is missing, since, after all, classical mechanics tells us how the positions and velocities of a classical system evolve in time. The time dependence is given by solving Newton's second law

$$m\frac{d^2x}{dt^2} = F(x) \tag{2.10.2}$$

But where is t in quantum mechanics? First of all, what is it that must evolve in time? The answer is that the wavefunction (and associated probability density) must evolve. Suppose, therefore, that we prepare a system at $t = 0$ according to a particular probability density $p(x, 0)$ related to an amplitude $\Psi(x, 0)$ by

$$p(x, 0) = |\Psi(x, 0)|^2 \tag{2.10.3}$$

How will this initial amplitude $\Psi(x, 0)$ look at time t later? Note, by the way, that $\Psi(x, 0)$ does *not* necessarily need to be one of the eigenstates $\psi_n(x)$. To address this, we refer to the time-dependent Schrödinger equation that tells us how $\Psi(x, t)$ will evolve starting from the initial condition $\Psi(x, 0)$:

$$\hat{H}\Psi(x, t) = i\hbar\frac{\partial}{\partial t}\Psi(x, t) \tag{2.10.4}$$

It is important to know how it works physically and when it is sufficient to work with the time-independent version of the Schrödinger equation (Equation 2.10.1).

Postulate V

The time dependence of wavefunctions is governed by the Time-Dependent Schrödinger Equation (Equation 2.10.4).

Stationary States

Suppose that we are lucky enough to choose

$$\Psi(x, 0) = \psi_n(x)$$

with corresponding probability density

$$p(x, 0) = |\psi_n(x)|^2 \tag{2.10.5}$$

We will show that

$$\Psi(x, t) = \psi_n(x)e^{-iE_nt/\hbar} \tag{2.10.6}$$

From the time-dependent Schrödinger equation

$$\frac{d\Psi}{dt} = \psi_n(x)\left(\frac{-iE_n}{\hbar}\right)e^{-iE_nt/\hbar}$$

$$i\hbar\frac{d\Psi}{dt} = E_n\psi_n(x)e^{-iE_nt/\hbar}$$

Similarly

$$\begin{aligned}\hat{H}\Psi(x,t) &= e^{-iE_nt/\hbar}\hat{H}\psi_n(x)\\ &= e^{-iE_nt/\hbar}E_n\psi_n(x)\end{aligned}$$

Hence $\psi_n(x)exp(-iE_nt/\hbar)$ satisfies the Time-Dependent Schrödinger Equation (Equation 2.10.4).

Consider the probability density for this wavefunction: $p(x,t) = |\Psi(x,t)|^2$

$$\begin{aligned}p(x,t) &= \left[\psi_n(x)e^{iE_nt/\hbar}\right]\left[\psi_n(x)e^{-iE_nt/\hbar}\right]\\ &= \psi_n^2(x)e^{iE_nt/\hbar}e^{-iE_nt/\hbar}\\ &= |\psi_n(x)|^2 = p(x,0)\end{aligned}$$

the probability does not change in time and for this reason, $\psi_n(x)$ is called a *stationary state*. In such a state, the energy remains **fixed** at the well-defined value E_n.

Nonstationary States

Suppose, however, that we had chosen $\Psi(x,0)$ to be some arbitrary linear combination of the two lowest energy states:

$$\Psi(x,0) = a\psi_1(x) + b\psi_2(x) \tag{2.10.7}$$

for example

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)] \tag{2.10.8}$$

as in the previous example. Then, the probability density at time t

$$p(x,t) = |\Psi(x,t)|^2 \neq p(x,0) \tag{2.10.9}$$

For such a mixture to be possible, there must be sufficient energy in the system that there is some probability of measuring the particle to be in its excited state.

Finally, suppose we start with a state

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)]$$

and we let this state evolve in time. At any point in time, the state $\Psi(x,t)$ will be some mixture of $\psi_1(x)$ and $\psi_2(x)$, and this mixture changes with time. Now, at some specific instance in time t, we measure the energy and obtain a value E_1. What is the state of the system *just after* the measurement is made? Once we make the measurement, then we know with 100% certainty that the energy is E_1. From the above discussion, there is only one possibility for the state of the system, and that has to be the wavefunction $\psi_1(x)$, since in this state we know with 100% certainty that the energy is E_1. Hence, just after the measurement, the state *must be* $\psi_1(x)$, which means that because of the measurement, any further dependence on $\psi_2(x)$ drops out, and for all time thereafter, there is *no* dependence on $\psi_2(x)$. Consequently, any subsequent measurement of the energy would yield the value E_1 with 100% certainty. This discontinuous change in the quantum state of the system as a result of the measurement is known as the **collapse of the wavefunction**. The idea that the evolution of a system can change as a result of a measurement is one of the topics that is currently debated among quantum theorists.

The Quantum Observer Effect

The fact that measuring a quantum system changes its time evolution means that the experimenter is now coupled to the quantum system. This **observer effect** means that the act of observing will influence the phenomenon being observed. In

classical mechanics, this coupling does not exist. A classical system will evolve according to Newton's laws of motion independent of whether or not we observe it. This is not true for quantum systems. The very act of observing the system changes how it evolves in time.

Put another way, by simply observing a system, we change it!

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2.11: Implication of QM Postulates - Uncertainty, Part 1

Learning Objectives

- To connect the Heisenberg Uncertainty principle to the commutation relations.
- Develop proficiency in calculating the commutator of two operators.

If two operators commute then both quantities can be measured at the same time with infinite precision, if not then there is a tradeoff in the accuracy in the measurement for one quantity vs. the other. This is the mathematical representation of the Heisenberg Uncertainty principle.

Commuting Operators

One important property of operators is that the order of operation matters. Thus in general

$$\hat{A}\hat{E}f(x) \neq \hat{E}\hat{A}f(x)$$

unless the two operators **commute**. Two operators commute if the following equation is true:

$$\left[\hat{A},\hat{E}\right] = \hat{A}\hat{E} - \hat{E}\hat{A} = 0$$

To determine whether two operators commute first operate $\hat{A}\hat{E}$ on a function $f(x)$. Then operate$\hat{E}\hat{A}$ the same function $f(x)$. If the same answer is obtained subtracting the two functions will equal zero and the two operators will commute.on

If two operators commute, then they can have the same set of eigenfunctions. By definition, two operators $\hat{A}$ and $\hat{B}$ commute if the effect of applying $\hat{A}$ then $\hat{B}$ is the same as applying $\hat{B}$ then $\hat{A}$, i.e.

$$\hat{A}\hat{B} = \hat{B}\hat{A}.$$

For example, the operations brushing-your-teeth and combing-your-hair commute, while the operations getting-dressed and taking-a-shower do not. This theorem is very important. If two operators commute and consequently have the same set of eigenfunctions, then the corresponding physical quantities can be evaluated or measured exactly simultaneously with no limit on the uncertainty. As mentioned previously, the eigenvalues of the operators correspond to the measured values.

If $\hat{A}$ and $\hat{B}$ commute and ψ is an eigenfunction of $\hat{A}$ with eigenvalue b, then

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \tag{2.11.1}$$

Equation 2.11.1 says that $\hat{A}\psi$ is an eigenfunction of $\hat{B}$ with eigenvalue b, which means that when $\hat{A}$ operates on ψ, it cannot change ψ. At most, $\hat{A}$ operating on ψ can produce a constant times ψ.

$$\hat{A}\psi = a\psi \tag{2.11.2}$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \tag{2.11.3}$$

Equation 2.11.3 shows that Equation 2.11.2 is consistent with Equation 2.11.1. Consequently ψ also is an eigenfunction of $\hat{A}$ with eigenvalue a.

Example 4.6.1

Do the following pairs of operators commute?

a. $\hat{A} = \dfrac{d}{dx}$ and $\hat{E} = x^2$

b. $\hat{B} = \dfrac{h}{x}$ and $\hat{C}\{f(x)\} = f(x) + 3$

c. $\hat{J} = 3x$ and $\hat{O} = x^{-1}$

Solution a

This requires evaluating $\left[\hat{A},\hat{E}\right]$, which requires solving for $\hat{A}\{\hat{E}f(x)\}$ and $\hat{E}\{\hat{A}f(x)\}$ for arbitrary wavefunction $f(x)$ and asking if they are equal.

$$\hat{A}\{\hat{E}f(x)\} = \hat{A}\{x^2 f(x)\} = \frac{d}{dx}\{x^2 f(x)\} = 2xf(x) + x^2 f'(x)$$

From the product rule of differentiation.

$$\hat{E}\{\hat{A}f(x)\} = \hat{E}\{f'(x)\} = x^2 f'(x)$$

Now ask if they are equal

$$\left[\hat{A},\hat{E}\right] = 2xf(x) + x^2 f'(x) - x^2 f'(x) = 2xf(x) \neq 0$$

Therefore the two operators do not commute.

Solution b

This requires evaluating $\left[\hat{B},\hat{C}\right]$ like in Example 4.6.1 .

$$\hat{B}\{\hat{C}f(x)\} = \hat{B}\{f(x)+3\} = \frac{h}{x}(f(x)+3) = \frac{hf(x)}{x} + \frac{3h}{x}$$

$$\hat{C}\{\hat{B}f(x)\} = \hat{C}\{\frac{h}{x}f(x)\} = \frac{hf(x)}{x} + 3$$

Now ask if they are equal

$$\left[\hat{B},\hat{C}\right] = \frac{hf(x)}{x} + \frac{3h}{x} - \frac{hf(x)}{x} - 3 \neq 0$$

The two operators do **not** commute.

Solution c

This requires evaluating $\left[\hat{J},\hat{O}\right]$

$$\hat{J}\{\hat{O}f(x)\} = \hat{J}\{f(x)3x\} = f(x)3x/x = 3f(x)$$

$$\hat{O}\{\hat{J}f(x)\} = \hat{O}\{\frac{f(x)}{x}\} = \frac{f(x)3x}{x} = 3f(x)$$

$$\left[\hat{J},\hat{O}\right] = 3f(x) - 3f(x) = 0$$

Because the difference is zero, the two operators commute.

General Heisenberg Uncertainty Principle

Although it will not be proven here, there is a general statement of the uncertainty principle in terms of the commutation property of operators. If two operators $\hat{A}$ and $\hat{B}$ do not commute, then the uncertainties (standard deviations σ) in the physical quantities associated with these operators must satisfy

$$\sigma_A \sigma_B \geq \left| \int \psi^* [\hat{A}\hat{B} - \hat{B}\hat{A}] \psi \, d\tau \right| \tag{2.11.4}$$

where the integral inside the square brackets is called the **commutator**, and $\left|\ \right|$ signifies the modulus or absolute value. If $\hat{A}$ and $\hat{B}$ commute, then the right-hand-side of Equation 2.11.4 is zero, so either or both σ_A and σ_B could be zero, and there is no restriction on the uncertainties in the measurements of the eigenvalues a and b. If $\hat{A}$ and $\hat{B}$ do not commute, then the right-hand-side of Equation 2.11.4 will not be zero, and neither σ_A nor σ_B can be zero unless the other is infinite. Consequently, both a and b cannot be eigenvalues of the same wavefunctions and cannot be measured simultaneously to arbitrary precision.

Exercise4.6.1

Show that the commutator for position and momentum in one dimension equals $-i\hbar$ and that the right-hand-side of Equation 2.11.4 therefore equals $\hbar/2$ giving $\sigma_x\sigma_{px} \geq \frac{\hbar}{2}$.

Applications

Operators are very common with a variety of purposes. They are used to figure out the energy of a wavefunction using the Schrödinger Equation.

$$\hat{H}\psi = E\psi$$

They also help to explain observations made in the experimentally. An example of this is the relationship between the magnitude of the angular momentum and the components.

$$\left[\hat{L}^2, \hat{L}_x^2\right] = \left[\hat{L}^2, \hat{L}_y^2\right] = \left[\hat{L}^2, \hat{L}_z^2\right] = 0$$

However the components do not commute themselves. An additional property of commuters that commute is that both quantities can be measured simultaneously. Thus, the magnitude of the angular momentum and ONE of the components (usually z) can be known at the same time however, NOTHING is known about the other components.

> *The physical quantities corresponding to operators that commute can be measured simultaneously to any precision.*

Example

Determine whether the following two operators commute:

$$\hat{K} = \alpha \int [1]^{[\infty]} d[x]$$

and

$$\hat{H} = d/dx$$

Solution

Evaluate

$$\left[\hat{K}, \hat{H}\right]$$

Example

Determine whether the following two operators commute:

$$\hat{I} = 5$$

and

$$\hat{L} = \int_{[1]}^{[\infty]} d[x]$$

Solution

The identity operator, $\hat{I}$ is a real number and commutes with everything. Thus, these two operators commute. We can also directly evaluate the commutator:

$$\left[\hat{I}, \hat{L}\right]$$

$$\left[\hat{I}, \hat{L}\right] f(x) = 5\int_1^\infty f(x)d(x) - \int_1^\infty 5f(x)d(x) = 0$$

Exercise

Show that the components of the angular momentum do not commute.

$$\hat{L}_x = -i\hbar\left[-\sin\left(\phi\frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi\frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_y = -i\hbar\left[\cos\left(\phi\frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi\frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_z = -i\hbar\frac{\delta}{\delta\theta}$$

Solution

This requires evaluating the following commucators:

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$$

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$$

References

1. Gohberg, I. Basic Operator Theory; Birkhäuser: Boston, 2001
2. McQuarrie, D.A. Quantum Chemistry, 2nd Edition; University Science Books:Sausalito, 2008
3. Schechter, M. Operator Methods in Quantum Mechanics; Dover Publications, 2003

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2.12: Implication of QM Postulates - Uncertainty, Part 2

Learning Objectives

- Expand on the introduction of Heisenberg's Uncertainty Principle by calculating the Δx or Δp directly from the wavefunction

As will be discussed in Section 4.6, the operators $\hat{x}$ and $\hat{p}$ are not compatible and there is **no** measurement that can precisely determine the coresponding observables (x and p) simultaneously. Hence, there must be an uncertainty relation between them that specifies how uncertain we are about one quantity given a definite precision in the measurement of the other. Presumably, if one can be determined with infinite precision, then there will be an infinite uncertainty in the other. The uncertainty in a general quantity A is

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \tag{2.12.1}$$

where $\langle A^2 \rangle$ and $\langle A \rangle$ are the expectation values of $\hat{A}^2$ and $\hat{A}$ operators for a specific wavefunction. Extending Equation 2.12.1 to x and p results in the following uncertainties

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{2.12.2}$$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{2.12.3}$$

These quantities can be expressed explicitly in terms of the (time-dependent) wavefunction $\Psi(x,t)$ using the fact that

$$\langle x \rangle = \langle \Psi(t) | \hat{x} | \Psi(t) \rangle \tag{2.12.4}$$

$$= \int \Psi^*(x,t) x \Psi(x,t)\, dx \tag{2.12.5}$$

and

$$\langle x^2 \rangle = \langle \Psi(t) | \hat{x}^2 | \Psi(t) \rangle \tag{2.12.6}$$

$$= \int \Psi^*(x,t) x^2 \Psi(x,t)\, dx \tag{2.12.7}$$

The middle terms in both Equations 2.12.4 and 2.12.6 are the integrals expressed in Dirac's Bra-ket notation. Similarly using the definition of the linear momentum operator:

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

So

$$\langle p \rangle = \langle \Psi(t) | \hat{p} | \Psi(t) \rangle \tag{2.12.8}$$

$$= \int \Psi^*(x,t) - i\hbar \frac{\partial}{\partial x} \Psi(x,t)\, dx \tag{2.12.9}$$

and

$$\langle p^2 \rangle = \langle \Psi(t) | \hat{p}^2 | \Psi(t) \rangle \tag{2.12.10}$$

$$= \int \Psi^*(x,t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \Psi(x,t)\, dx \tag{2.12.11}$$

Time-dependent vs. time-independent wavefunction

The expectation values above are formulated with the total time-dependence wavefunction $\psi(x,t)$ that are functions of x and t. However, it is easy to show that the same expectation value would be obtained if the time-independent wavefunction $\psi(x)$ that are functions of only x are used. If $V(x)$ in $\hat{H}$ is time independent, then the wavefunctions are stationary and the

expectation value are time-independent. You can easily confirm that by comparing the expectation values using the general formula for a stationary wavefunction

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

and for $\psi(x)$.

The Heisenberg uncertainty principle can be quantitatively connected to the properties of a wavefunction, i.e., calculated via the expectation values outlined above:

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{2.12.12}$$

This essentially states that the greater certainty that a measurement of x or p can be made, the greater will be the *uncertainty* in the other. Hence, as Δp approaches 0, Δx must approach ∞, which is the case of the free particle (e.g, with $V(x) = 0$) where the momentum of a particles can be determined precisely.

Example 3.8.1 : Uncertainty with a Gaussian wavefunction

A particle is in a state described by the wavefunction

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \tag{2.12.13}$$

where a is a constant and $-\infty \leq x \leq \infty$. Verify that the value of the product $\Delta p\, \Delta\, x$ is consistent with the predictions from the uncertainty principle (Equation 2.12.12).

Solution

Let's calculate the average of x:

$$\begin{aligned}
\langle x \rangle &= \int_{-\infty}^{\infty} \psi^* x \psi \, dx \\
&= \int_{-\infty}^{\infty} (2a/\pi)^{\frac{1}{4}} e^{-ax^2} x (2a/\pi)^{\frac{1}{4}} e^{-ax^2} \, dx \\
&= \int_{-\infty}^{\infty} x (2a/\pi)^{\frac{1}{2}} e^{-2ax^2} \, dx \\
&= 0
\end{aligned}$$

since the integrand is an odd function (an even function times an odd function is an odd function). This makes sense given that the gaussian wavefunction is symmetric around $x = 0$.

Let's calculate the average of x^2:

$$\begin{aligned}
\langle x^2 \rangle &= \int_{-\infty}^{\infty} \psi^* x^2 \psi \, dx \\
&= \int_{-\infty}^{\infty} (2a/\pi)^{\frac{1}{4}} e^{-ax^2} (x^2) (2a/\pi)^{\frac{1}{4}} e^{-ax^2} \, dx \\
&= \int_{-\infty}^{\infty} x^2 (2a/\pi)^{\frac{1}{2}} e^{-2ax^2} \, dx \\
&= \frac{1}{4a}
\end{aligned}$$

Let's calculate the average in p:

$$\begin{aligned}\langle p\rangle &= \int_{-\infty}^{\infty} \psi^* p \psi \, dx \\ &= \int_{-\infty}^{\infty} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} - i\hbar \frac{d}{dx}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \, dx \\ &= \int_{-\infty}^{\infty} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} (-i\hbar) \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} (-2ax) \, dx \\ &= 0\end{aligned}$$

since the integrand is an odd function.

Let's calculate the average of p^2:

$$\begin{aligned}\langle p^2\rangle &= \int_{-\infty}^{\infty} \psi^* p^2 \psi dx \\ &= -\hbar^2 \left(\frac{2a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} 2a(ax^2 - 1) e^{-2ax^2} dx \\ &= -4\hbar^2 a^2 \left(\frac{2a}{\pi}\right)^{1/2} \int_0^{\infty} x^2 e^{-2ax^2} dx + 4\hbar^2 a \left(\frac{2a}{\pi}\right)^{1/2} \int_0^{\infty} e^{-2ax^2} dx \\ &= a\hbar^2\end{aligned}$$

We use Equation 2.12.1 to check on the uncertainty

$$\begin{aligned}\Delta x^2 &= \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{4a} - 0 \\ \Delta x &= \sqrt{\Delta x^2} = \frac{1}{2\sqrt{a}} \\ \Delta p^2 &= \langle p^2\rangle - \langle p\rangle^2 = a\hbar^2 - 0 \\ \Delta p &= \sqrt{\Delta p^2} = \hbar\sqrt{a}\end{aligned}$$

Finally we have

$$\Delta p \Delta x = \left(\frac{1}{2\sqrt{a}}\right)(\hbar\sqrt{a}) = \frac{\hbar}{2}$$

Not only does the Heisenburg uncertainly principle hold (Equation 2.12.12), but the equality is established for this wavefunction. This is because the Gaussian wavefunction (Equation 2.12.13) is special as discussed later.

? Exercise 3.8.1

A particle is in a state described by the ground state wavefunction of a particle in a box

$$\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

where L is the length of the box and $0 \le x \le L$. Verify that the value of the product $\Delta p \, \Delta x$ is consistent with the predictions from the uncertainty principle (Equation 2.12.12).

The uncertainty principle is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space.

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CHAPTER OVERVIEW

3: First QM System (Particle on a Line/Particle in a Box)

3.1: The Quantum Mechanical Free Particle
3.2: The Energy of a Particle in a Box is Quantized
3.3: The Average Momentum of a Particle in a Box is Zero
3.4: A Particle in a Two-Dimensional Box
3.5: A Particle in a Three-Dimensional Box
3.6: Particle in a Finite Box and Tunneling (optional)

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3.1: The Quantum Mechanical Free Particle

Learning Objectives

- To desribe the quantum mechanical free particle
- To recognize the application of the heisenburg uncertainty principle applied to the free particle
- To identify the lack of quantization of the free particle and understand why.

The simplest system in quantum mechanics has the potential energy $V = 0$ everywhere. This is called a **free particle** since it has no forces acting on it. We consider the one-dimensional case, with motion only in the x-direction, giving the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{3.1.1}$$

or more simply

$$\hat{H}\psi(x) = E\psi(x) \tag{3.1.2}$$

with

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{3.1.3}$$

Total derivatives can be used since there is one independent variable. The equation simplifies to

$$\psi''(x) + k^2\psi(x) = 0 \tag{3.1.4}$$

with the definition

$$k^2 \equiv \frac{2mE}{\hbar^2} \tag{3.1.5}$$

Possible solutions of Equation 3.1.4 are

$$\psi(x) = const \left\{ \begin{array}{c} \sin(kx) \\ \cos(kx) \\ e^{\pm ikx} \end{array} \right\} \tag{3.1.6}$$

There is no restriction on the value of k. Thus a free particle, even in quantum mechanics, can have any non-negative value of the energy

$$E = \frac{\hbar^2 k^2}{2m} \geq 0 \tag{3.1.7}$$

The energy levels in this case are *not* quantized and correspond to the same continuum of kinetic energy shown by a classical particle.

Example 3.1.1: Eigenstates of the Hamiltonian of a free particle

Consider for a free particle (i.e., $V(x) = 0$) moving in one dimension.

a. Demonstrate that $\sin(kx)$, $\cos(kx)$, and $e^{\pm ikx}$ are indeed eigenfunctions of $\hat{H}$.
b. What are their corresponding eigenstates?
c. What are the energies not quantized?

Approach

To demonstrate that a function is indeed a specific eigenfunction $f(x)$ of an operator $\hat{O}$, we have to ask if this Eigenvalue equation is correct, i.e.,

$$\hat{O}f(x) = \lambda f(x) \tag{3.1.8}$$

where λ is the eigenvalue associated with that eigenfunction associated with the operator. Change the operator and the eigenfunctions and eigenvalues will change. Change the eigenfunction and the eigenvalue will change. They are all connected like the Mufasa's "Circle of Life."

Solution a

Let's take the $\sin(kx)$ function and the Hamiltonian operator (Equation 3.1.3) and insert it into Equation 3.1.8and is if the equality is ensured. Keep in mind that any value of $lambda$ will work as long as it is a constant.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sin(kx) \stackrel{?}{=} \lambda \sin(kx) \tag{3.1.9}$$

first step in evaluating the 2nd derivative

$$-\frac{\hbar^2}{2m}k\frac{d}{dx}(\cos(kx)) \stackrel{?}{=} \lambda \sin(kx) \tag{3.1.10}$$

and second step

$$+\frac{\hbar^2}{2m}k^2(\sin(kx)) \stackrel{?}{=} \lambda \sin(kx) \tag{3.1.11}$$

This equation is confirmed when

$$\lambda = +\frac{\hbar^2 k^2}{2m} \tag{3.1.12}$$

Which makes sense when compared to Equation 3.1.7since the Hamiltonian gives the total energy E.

Solution b

As shown in the Solution a, the Eigenvalue equation is confirm to be correct for all $\sin(kx)$ functions (so they are eigenfunctions of the Hamiltonian) and the eigenvalues are

$$\lambda = +\frac{\hbar^2 k^2}{2m}. \tag{3.1.13}$$

Eigenvalues can be positive, negative, real, imaginary and complex and all of the above.

Solution c

Since any value of k is allowed in the $\sin(kx)$ eigenfunctions (i.e., the Eigenvalue equation holds for all values of k), then there is no quantization. We need boundary conditions to force the quantization like with the Bohr hydrogen atom.

? Exercise 3.1.1

Consider for a free particle (i.e., $V(x) = 0$) moving in one dimension.

a. Demonstrate that $\cos(kx)$ and $e^{\pm ikx}$ are eigenfunctions of $\hat{H}$.
b. What are their corresponding eigenstates?
c. Is momentum quantized for a free particle?

It is of interest also to consider the x-component of linear momentum for the free-particle solutions (Equation 3.1.6). The eigenvalue equation for momentum is

$$\hat{p}_x\psi(x) = -i\hbar\frac{d\psi(x)}{dx} = p\psi(x) \tag{3.1.14}$$

where we have denoted the momentum eigenvalue as p.

It is easily shown that neither of the functions $\sin kx$ or $\cos kx$ from Equation 3.1.6 is an eigenfunction of $\hat{p}_x$. However, $e^{\pm ikx}$ are both eigenfunctions with eigenvalues $p = \pm\hbar k$, respectively. Evidently the momentum p can take on any real value between -∞ and +∞. The kinetic energy, equal to $E = p^2/2m$, can correspondingly have any value between 0 and +∞.

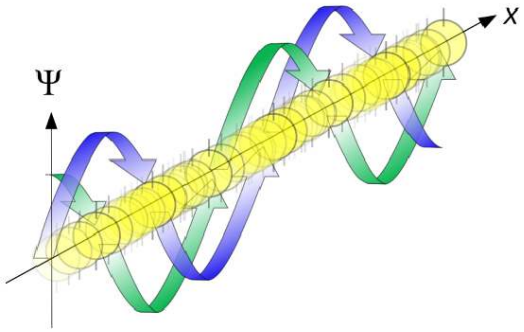


Figure 3.1.1: Propagation of quantum free particle (i.e. de Broglie waves) in 1D space. The real part of the complex amplitude is blue and imaginary part is green. The probability (shown as the yellow opacity) of finding the particle at a given point x is spread out evenly over space, there is no definite position of the particle. (Public Domain; Maschen).

> *A free particle, even in quantum mechanics, can have any non-negative value of the energy*

Example 3.1.2: Eigenstates of Momentum of a Free Particle

Consider for a free particle (i.e., $V(x) = 0$) moving in one dimension.

a. Demonstrate that $e^{\pm ikx}$ are eigenfunctions of $\hat{p}_x$.
b. What are their corresponding eigenstates?

Exercise 3.1.2

Show that neither $\sin kx$ nor $\cos kx$ are eigenstates of $\hat{p}_x$ for a free particle (i.e., $V(x) = 0$) moving in one dimension.

Superpositions

The functions $\sin kx$ and $\cos kx$, while not eigenfunctions of $\hat{p}_x$, are each *superpositions* of the two eigenfunctions $e^{\pm ikx}$, by virtue of the trigonometric identities

$$\cos(kx) = \frac{1}{2}(e^{ikx} + e^{-ikx}) \tag{3.1.15}$$

and

$$\sin(kx) = \frac{1}{2i}(e^{ikx} - e^{-ikx}) \tag{3.1.16}$$

The eigenfunction e^{ikx} for $k > 0$ represents the particle moving from left to right on the *x-axis* (blue curve in Figure 3.1.2) with momentum $p > 0$. Correspondingly, e^{-ikx} represents motion from right to left with $p < 0$ (red curve in Figure 3.1.2).

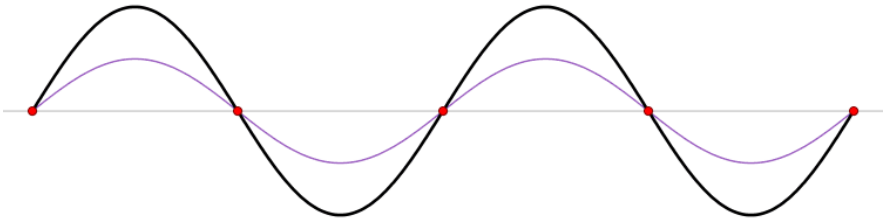


Figure 3.1.2: Two waves traveling in opposite directions across the same medium combine linearly. In this animation, both waves have the same wavelength and the sum of amplitudes results in a standing wave. (Public Domain; LucasVB)

The functions $\sin(kx)$ and $\cos(kx)$ represent *standing waves*, obtained by superposition of opposing complex waves. Although these two trigonometry functions are not eigenfunctions of $\hat{p}_x$, they *are* eigenfunctions of $\hat{p}_x^2$ and hence they are eigenfunctions of the Hamiltonian operator $\hat{H}$.

Not every wavefunction is an eigenstate

It is important to note that while $\sin kx$ nor $\cos kx$ are **not** eigenstates of momentum, these functions can be decomposed into a combination of functions that are eigenstates (Equation 3.1.14 and 3.1.16). The ability to decompose wavefunctions into (linear) combinations of eigenstates is used throughout quantum mechanics and will be discussed in more detail in further Sections.

Wavepackets - The Superposition Principle in Action

Consider the wavefunction corresponding to a free electron traveling through a cathode ray tube. The electron leaves the cathode, shoots through the vacuum, and impinges on the screen. At an intermediate point in this process, it is moving through the vacuum and the wavefunction must be nonzero over some volume, but zero in the places the electron has not possibly reached yet, and zero in the places it has definitely left.

However, if the electron has a precise energy (which is all kinetic energy), it also has a precise *momentum*. De Broglie argued that this necessarily implies that the electron wave has a precise *wavelength*. However, since it is a free particle ($V = 0$, the only wave with a *precise* wavelength λ has the form

$$\psi(x,t) = Ae^{i(kx-\omega t)} \tag{3.1.17}$$

where $k = \frac{2\pi}{\lambda}$ and $\omega = 2\pi\nu$. The wavefunctions of Equation 3.1.17 are the solutions to the full time-independent Schrödinger equation (not just the spatial component discussed above).

The problem with using the wavefunctions of Equation 3.1.17 to represent free particles is that plane sine waves extend to infinity in both spatial directions, so cannot represent a particle whose wavefunction is nonzero in a limited region of space. Physically, that it must have a wavefunction that goes to zero far away in either direction. A localized wavefunction of this type is called a "**wavepacket**". We shall discover that a wavepacket can be constructed by adding plane waves together. To represent a localized particle, we must superpose waves having different wavelengths. Now, the plane waves we add together will individually be solutions of the Schrödinger equation.

The Schrödinger Equation is a Linear Differential Equation

As discussed in previously for a classical wave equation, it quantum equivalent, i.e., Schrödinger equation (both time dependent and independent), are *linear* equations. That is, if $\psi_1(x,y,z,t), \psi_2(x,y,z,t)$ are both solutions of the equation, then so is

$$\psi(x,y,z,t) = c_1\psi_1(x,y,z,t) + c_2\psi_2(x,y,z,t) \tag{3.1.18}$$

where c_1 and c_2 are arbitrary constants, as is easy to check. This previously called this property the **Principle of Superposition**.

The essential point is that in Schrödinger's equation every term contains a factor ψ, but no term contains a factor ψ^2 (or a higher power). That is what is meant by a "linear" equation. If the equation *did* contain a constant term, or a term including ψ^2,

superposition wouldn't work—the sum of two solutions to the equation would not itself be a solution to the equation.

In fact, we have been assuming this linearity all along: when we analyze interference and diffraction of waves, we just add the two wave amplitudes at each spot. For the double slit, we take it that if the wave radiating from one slit satisfies the wave equation, then adding the two waves together will give a new wave which also satisfies the equation.

Building Wavepackets

If we add together two sine waves with frequencies close together, we get "beats." This pattern can be viewed as a string of wavepackets. For example considering adding to sine waves together with spatial and temporal frequencies of $(k \pm \Delta k)$ and ($\omega \pm \Delta\omega$), respectively.

$$\sin[(k-\Delta k)x-(\omega-\Delta\omega)t]+\sin[(k+\Delta k)x-(\omega+\Delta\omega)t]) \tag{3.1.19}$$

If we use the trigonometric addition formula, the sum in Equation 3.1.19 can be simplified to

$$2\sin(kx-\omega t)\cos[(\Delta k)x-(\Delta\omega)t] \tag{3.1.20}$$

Equation 3.1.20 exhibits the phenomenon of beats between waves close in frequency. The first term, $\sin(kx-\omega t)$, oscillates at the average of the two frequencies. It is modulated by the slowly varying second term, often called the "**envelope function**", which oscillates once over a spatial extent of order $\pi/\Delta k$. This is the distance over which waves initially in phase at the origin become completely out of phase. Of course, going a further distance of order $\pi/\Delta k$, the waves will become synchronized again.

That is, beating two close frequencies together breaks up the continuous wave into a series of packets, the beats. To describe a single electron moving through space, we need a single packet. This can be achieved by superposing waves having a continuous distribution of wavelengths, or wave numbers within of order Δk, say, of k. In this case, the waves will be out of phase after a distance of order $\pi/\Delta k$, but since they have many different wavelengths, they will never get back in phase again.

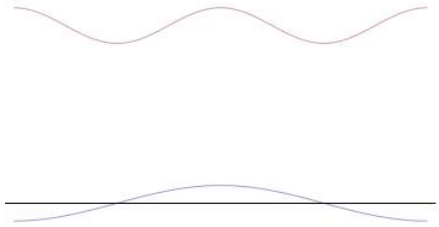


Figure 3.1.3: The superposition of several plane waves to form a wave packet. This wave packet becomes increasingly localized with the addition of many waves. The Fourier transform is a mathematical operation that separates a wave packet into its individual plane waves. Note that the waves shown here are real for illustrative purposes only, whereas in quantum mechanics the wavefunction is generally complex. (Public Domain; Teply).

We have seen how two sine waves of equal amplitude close together in frequency produce beats: if the waves are in phase at the origin, as we go along the *x*-axis they gradually fall out of phase, and cancel each other at a distance $x = \dfrac{\pi}{2\Delta}$, where 2Δ is the difference in k of the two $\sin kx$ waves (Figure 3.1.3). (For the moment, we are ignoring the time development of these waves: we're just looking at *t* = 0.). If we continue along the *x*-axis to $\dfrac{\pi}{\Delta}$, the two waves will be back in phase again, this is the next beat. Now, if instead of adding *two* waves, we add *many* waves, all of different k, but with the k's taken from some small interval of size of order Δk, and all these waves are in phase at the origin, then, again, they will all stay more or less in phase for a distance of order $x = \dfrac{\pi}{2\Delta}$.

However, as we proceed past that point, the chances of them all getting back in phase again get rapidly smaller as we increase the number of different waves. This wavepacket perspective of a free particle is shown in Figure 3.1.4, where the wavefunction amplitude (both real and imaginary) is localized and tapers off on either side (contrast this image with Figure 3.1.1 that exhibits uniform amplitude over all space since it is an oscillatory eigenfunction.

Gaussian Wavepackets

Fortunately, there is a simple explicit mathematical realization of the addition of plane waves to form a localized function: the *Gaussian wavepacket:*

$$\psi(x, t=0) = A \underbrace{e^{ik_0 x}}_{\text{oscillating term}} \overbrace{e^{-x^2/2\Delta^2}}^{\text{Gaussian envelope}} \tag{3.1.21}$$

where k_0 is an average wavenumber. Topically, the equation for Gaussian wavepackets has an oscillating term with a Gaussian envelope function. This wavepacket wavefunction may be used to represent a localized electron with a negligible probability of finding the electron outside in a small section of length dx at x(Figure 3.1.3).

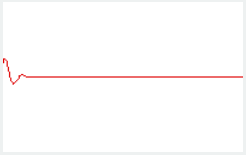


Figure 3.1.4: A time-dependent (moving) gaussian wavepacket (real or imaginary part). (Public Domain; Wikipedia)

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

Learning Objectives

- Solve the particle-in-a-box model used to describing a trapped particle in 1 D well
- Characterize the particle-in-a-box eigenstates (i.e., wavefunctions) and the eigenenergies as a function of the quantum number
- Demonstrate that the eigenstates are orthogonal

The *particle in the box* model system is the simplest non-trivial application of the Schrödinger equation, but one which illustrates many of the fundamental concepts of quantum mechanics. For a particle moving in one dimension (again along the x- axis), the Schrödinger equation can be written

$$-\frac{\hbar^2}{2m}\psi''(x)+V(x)\psi(x)=E\psi(x)$$

Assume that the particle can move freely between two endpoints $x=0$ and $x=L$, but cannot penetrate past either end. This is equivalent to a potential energy dependent on x with

$$V(x)=\begin{cases}0 & 0\le x\le L\\ \infty & x<0\ and\ x>L\end{cases}$$

This potential is represented in Figure 3.5.1 . The infinite potential energy constitutes an impenetrable barrier since the particle would have an infinite potential energy if found there, which is clearly impossible.

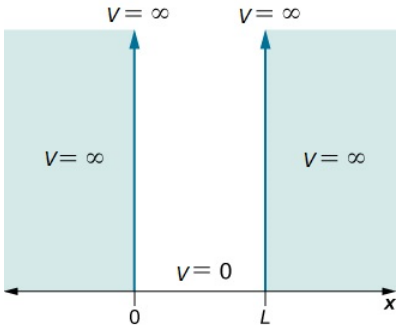


Figure 3.5.1 : The barriers outside a one-dimensional box have infinitely large potential, while the interior of the box has a constant, zero potential. (CC-BY 4.0; OpenStax).

The particle is thus bound to a *"potential well"* since the particle cannot penetrate beyond $x=0$ or $x=L$

$$\psi(x)=0 \quad for\ \ x<0\ \ and\ \ x>L \tag{3.2.1}$$

By the requirement that the wavefunction be continuous, it must be true as well that

$$\psi(0)=0 \quad and \quad \psi(L)=0 \tag{3.2.2}$$

which constitutes a pair of boundary conditions on the wavefunction within the box. Inside the box, $V(x)=0$, so the Schrödinger equation reduces to the free-particle form:

$$-\frac{\hbar^2}{2m}\psi''(x)=E\psi(x) \tag{3.2.3}$$

with $0\le x\le L$.

We again have the differential equation

$$\psi''(x)+k^2\psi(x)=0 \tag{3.2.4}$$

with

$$k^2 = \frac{2mE}{\hbar^2} \tag{3.2.5}$$

The general solution can be written

$$\psi(x) = A\ \sin\ kx\ +\ B\ \cos\ kx \tag{3.2.6}$$

where A and B are constants to be determined by the boundary conditions in Equation 3.2.2. By the first condition, we find

$$\psi(0) = A\ \sin\ 0\ +\ B\ \cos\ 0\ =\ B\ = 0 \tag{3.2.7}$$

The second boundary condition at $x = L$ then implies

$$\psi(a) = A\ \sin\ kL\ =\ 0 \tag{3.2.8}$$

It is assumed that $A \neq 0$, for otherwise $\psi(x)$ would be zero everywhere and the particle would disappear (i.e., the trivial solution). The condition that $\sin kx = 0$ implies that

$$kL\ =\ n\pi \tag{3.2.9}$$

where n is a integer, positive, negative or zero. The case $n = 0$ must be excluded, for then $k = 0$ and again $\psi(x)$ would vanish everywhere. Eliminating k between Equation 3.2.4 and 3.2.9, we obtain

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}\ n^2 = \frac{h^2}{8mL^2}n^2 \tag{3.2.10}$$

with $n = 1, 2, , 3\ldots$

These are the only values of the energy which allows solutions of the Schrödinger Equation 3.2.3 consistent with the boundary conditions in Equation 3.2.2. The integer n, called a **quantum number**, is appended as a subscript on E to label the allowed energy levels. Negative values of n add nothing new because the energies in Equation 3.2.10 depends on n^2.

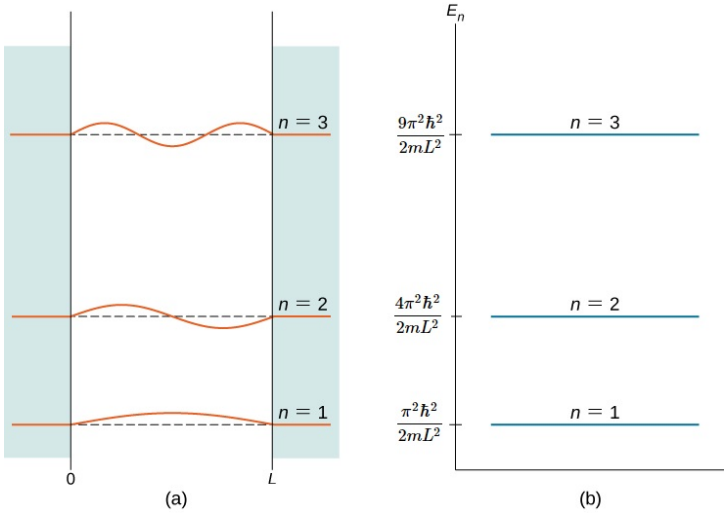


Figure 3.5.2 : A plot of $\psi_n(x)$ for the first four wavefunctions. (CC-BY 4.0; OpenStax).

Figure 3.5.2 shows part of the energy-level diagram for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space. For the free particle, the absence of confinement allowed an energy continuum. Note that, in both cases, the number of energy levels is infinite-denumerably infinite for the particle in a box, but nondenumerably infinite for the free particle.

The particle in a box assumes its lowest possible energy when $n = 1$, namely

$$E_1 = \frac{h^2}{8mL^2} \tag{3.2.11}$$

The state of lowest energy for a quantum system is termed its *ground state*.

Zero Point Energy

An interesting point is that $E_1 > 0$, whereas the corresponding classical system would have a minimum energy of zero. This is a recurrent phenomenon in quantum mechanics. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as **zero point energy**. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero. The minimum value of momentum is found by equating E_1 to $p^2/2m$, giving $p_{min} = \pm h/2L$. This can be expressed as an *uncertainty* in momentum given by $\Delta p \approx h/L$. Coupling this with the uncertainty in position, $\Delta x \approx L$, from the size of the box, we can write

$$\Delta x \Delta p \approx h \tag{3.2.12}$$

This is in accord with the *Heisenberg uncertainty principle*.

The particle-in-a-box eigenfunctions are given by Equation 3.2.13, with $B = 0$ and $k = n\pi/L = a$, in accordance with Equation 3.2.9

$$\psi_n(x) = A \sin \frac{n\pi x}{L} \tag{3.2.13}$$

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

These, like the energies, can be labeled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi_n(x)$ is normalized. The normalization condition is, in this case,

$$\int_0^a \left[\psi_n(x)\right]^2 dx = 1 \tag{3.2.14}$$

the integration running over the domain of the particle $0 \leq x \leq L$. Substituting Equation 3.2.13into Equation 3.2.14,

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = A^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2 \theta \, d\theta \tag{3.2.15}$$

$$= A^2 \frac{L}{2} = 1 \tag{3.2.16}$$

We have made the substitution $\theta = n\pi x/L$ and used the fact that the average value of $\sin^2 \theta$ over an integral number of half wavelengths equals 1/2 (alternatively, one could refer to standard integral tables). From Equation 3.2.16, we can identify the general normalization constant

$$A = \sqrt{\frac{2}{L}}$$

for all values of n. Finally we can write the normalized eigenfunctions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{3.2.17}$$

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

The first few eigenfunctions and the corresponding probability distributions are plotted in Figure 3.5.3 . There is a close analogy between the states of this quantum system and the modes of vibration of a violin string. The patterns of standing waves on the string are, in fact, identical in form with the wavefunctions in Equation 3.2.17.

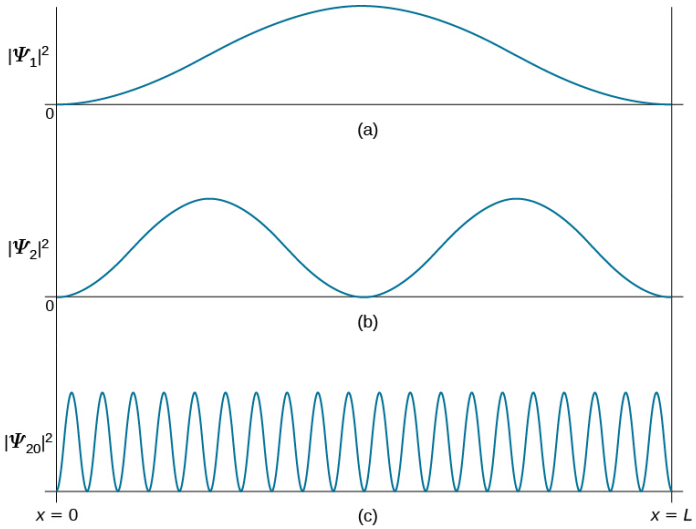


Figure 3.5.3 : The probability density distribution $|\psi_n(x)|^2$ for a quantum particle in a box for: (a) the ground state, $n = 1$; (b) the first excited state, $n = 2$; and, (c) the nineteenth excited state, $n = 20$. (CC-BY 4.0; OpenStax).

Nodes and Curvature

A significant feature of the particle-in-a-box quantum states is the occurrence of *nodes*. These are points, other than the two end points (which are fixed by the boundary conditions), at which the wavefunction vanishes. At a node there is exactly zero probability of finding the particle. The *n*th quantum state has, in fact, $n - 1$ nodes. It is generally true that the number of nodes increases with the energy of the quantum state, which can be rationalized by the following qualitative argument. As the number of nodes increases, so does the number and the steepness of the 'wiggles' in the wavefunction. It's like skiing down a slalom course. Accordingly, the average curvature, given by the second derivative, must increase. But the second derivative is proportional to the kinetic energy operator. Therefore, the more nodes, the higher the energy. This will prove to be an invaluable guide in more complex quantum systems.

Example 3.5.1 : Excited State Probabilities

For a particle in a one-dimensional box of length L, the second excited state wavefunction ($n = 3$) is

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

a. What is the probability that the particle is in the left half of the box?
b. What is the probability that the particle is in the middle third of the box?

Strategy

Probability that the particle will be found between a and b is

$$P(a,b) = \int_a^b \psi^2 \, dx$$

For this problem,

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

therefore,

$$P(a,b) = \frac{2}{L}\int_a^b \sin^2\frac{3\pi x}{L}\,dx$$
$$= \frac{2}{L}\left(\frac{x}{2} - \frac{L\sin\left(\frac{6\pi x}{L}\right)}{12\pi}\right)\Bigg|_a^b$$
$$= \frac{b-a}{L} - \frac{1}{6\pi}\left[\sin\left(\frac{6\pi b}{L}\right) - \sin\left(\frac{6\pi a}{L}\right)\right]$$

Solution a

The probability that the particle is in the left half of the box is

$$P\left(0,\frac{L}{2}\right) = \frac{\frac{L}{2}-0}{L} - \frac{1}{6\pi}\left[\sin\left(\frac{6\pi\left(\frac{L}{2}\right)}{L}\right) - \sin\left(\frac{6\pi(0)}{L}\right)\right]$$
$$= \frac{1}{2}$$

Solution b

The probability that the particle is in the middle third of the box

$$P\left(\frac{L}{3},\frac{2L}{3}\right) = \frac{\frac{2L}{3}-\frac{L}{3}}{L} - \frac{1}{6\pi}\left[\sin\frac{6\pi\left(\frac{2L}{3}\right)}{L} - \sin\frac{6\pi\left(\frac{L}{3}\right)}{L}\right]$$
$$= \frac{1}{3}$$

Exercise 3.5.1 : Ground State Probability

For a particle in a one-dimensional box, the ground state wavefunction is

$$\psi_1 = \sqrt{\frac{2}{L}}\sin\frac{x\pi}{L}$$

What is the probability that the particle is in the left half of the box in the ground state?

Answer

$$P\left(0,\frac{L}{2}\right) = \frac{2}{L}\int_0^{\frac{L}{2}} \sin^2\frac{x\pi}{L}dx$$
$$= \frac{2}{L}\frac{\frac{L\pi}{L} + \sin 0 + \sin\frac{L\pi}{L}}{\frac{4\pi}{L}}$$
$$= \frac{1}{2}$$

This is the same answer as for the ψ_3 state in Example 3.5.1 . This is because the eigenstate squared (.e., probability density) for the particle in a 1D box will always be symmetric around the center of the box. So there will be equal probability to be on either side (i.e., no side is favored).

Time Dependence and Complex Nature of Wavefunctions

Recall that the time-dependence of the wavefunction with time-independent potential was discussed in Section 3.1 and is expressed as

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

so for the particle in a box, these are

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}e^{-iE_nt/\hbar} \tag{3.2.18}$$

with E_n given by Equation 3.2.10.

The phase part of Equation 3.2.18 can be expanded into a real part and a complex components. So the total wavefunction for a particle in a box is

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_nt}{\hbar}\right)}_{\text{real part}} - \underbrace{i\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\sin\frac{E_nt}{\hbar}\right)}_{\text{imaginary part}}$$

which can be simplified (slightly) to

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_nt}{\hbar}\right)}_{\text{real part}} - \underbrace{i\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_nt}{\hbar}-\frac{\pi}{2}\right)}_{\text{imaginary part}}$$

As discussed previously, the imaginary part of the total wavefunction oscillates out of phase by $\pi/2$ with respect to the real part (we call this "out of phase"). This is demonstrated in the time-dependent behavior of the first three eigenfunctions in Figure 3.5.4 .

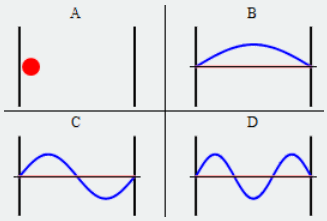


Figure 3.5.4 : Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-D). In (B-D), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B, C, D) are energy eigenstates. (Public Domain; Sbyrnes321 via Wikipedia).

Note that as n increased, the energy of the wavefunction increases (Equation 3.2.10) and both the number of nodes and antinodes increase and the frequency of oscillation of the wavefunction increases.

> *It is generally true in quantum systems (not just for particles in boxes) that the number of nodes in a wavefunction increases with the energy of the quantum state.*

Orthonormality of the Eigenstates

Another important property of the eigenfunctions in Equation 3.2.17 applies to the integral over a product of two *different* eigenfunctions (Equation 3.2.17). It is easy to see from Figure 3.5.5 that the integral

$$\int_0^L \psi_2(x)\psi_1(x)dx = 0 \tag{3.2.19}$$

The integral in Equation 3.2.19 is zero when the two eignestates differ and when integrated over the entire range of the system (from $-\infty$ to ∞ for a 1-D particle in the box, but this can be a narrow region of 0 to L since the eigenstates are zero outside of the box).

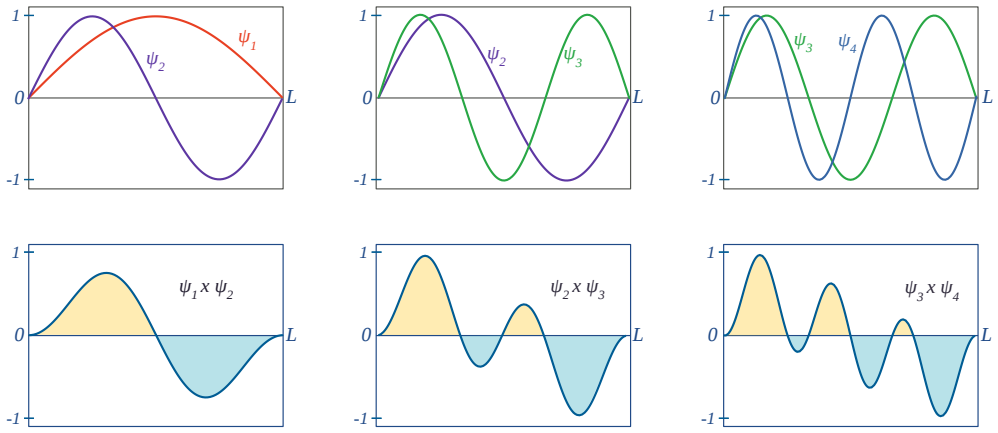


Figure 3.5.5 : (Top Row): Select plots of the $n = 1$ (red curves), $n = 2$ (purple curves), $n = 3$ (green curves), and $n = 4$ (blue curves) eigenfunctions. (Bottom Row): Product of different eigenstates with positive (tan) and negative (cyan) areas emphasized. Note that the negative and positive areas perfectly cancel when added together. Created via fooplot (CC BY-NC; Ümit Kaya via LibreTexts)

To prove Equation 3.2.19 for a particle in a box model, we can use the trigonometric identity

$$\sin\,\alpha\,\sin\,\beta = \frac{1}{2}[\,\cos(\alpha-\beta) - \cos(\alpha+\beta)\,] \tag{3.2.20}$$

to show that

$$\int_0^L \psi_m(x)\psi_n(x)dx = 0 \quad if \quad m \neq n \tag{3.2.21}$$

This property is called **orthogonality**. We will show in the next chapter, that this is a general result from quantum-mechanical eigenfunctions. The normalization (Equation 3.2.19) together with the orthogonality (Equation 3.2.21) can be combined into a single relationship

$$\int_0^L \psi_m(x)\psi_n(x)dx = \delta_{mn} \tag{3.2.22}$$

In terms of the *Kronecker delta*

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \tag{3.2.23}$$

A set of functions $\{\,\psi_n\,\}$ which obeys Equation 3.2.22 is called *orthonormal*.

Example 3.5.2

Evaluate

a. $\langle\psi_3|\psi_3\rangle$
b. $\langle\psi_4|\psi_4\rangle$
c. $\langle\psi_3|\psi_4\rangle$
d. $\langle\psi_4|\psi_3\rangle$

for the normalized wavefunctions:

$$|\psi_3\rangle = \sqrt{\frac{2}{L}}\,\sin\frac{3\pi x}{L}$$

and

$$|\psi_4\rangle = \sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L}$$

Strategy

These are four different integrals and we can solve them directly or use orthonormality (Equation 3.2.23) to evaluate.

Solution a

$$\begin{aligned}\langle \psi_3 | \psi_3 \rangle &= \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) dx \\ &= \frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{3\pi x}{L} \, dx\end{aligned}$$

This is an integration over an even function, so it cannot be tossed out via symmetry. We can use the Trigonometry relationship in Equation 3.2.20 to get

$$\frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{3\pi x}{L} \, dx = \frac{2}{L} \int_{-\infty}^{+\infty} \frac{1}{2} \left(1 - \cos \frac{6\pi x}{L} \right) dx$$

and we can continue the fun. However, there is no need. Since the we can recognize that $\langle \psi_3 | \psi_3 \rangle$ is 1 by the normalization criteria which is folded into the orthonormal criteria (Equation 3.2.23).

Therefore $\langle \psi_3 | \psi_3 \rangle = 1$.

Solution b

$$\begin{aligned}\langle \psi_4 | \psi_4 \rangle &= \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) dx \\ &= \frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{4\pi x}{L} \, dx\end{aligned}$$

We can expand and solve, but again there is no need. The wavefunctions are normalized therefore $\langle \psi_4 | \psi_4 \rangle = 1$.

Solution c

$$\begin{aligned}\langle \psi_3 | \psi_4 \rangle &= \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) dx \\ &= \frac{2}{L} \int_{-\infty}^{+\infty} \sin\left(\frac{3\pi x}{L} \right) \sin\left(\frac{4\pi x}{L} \right) dx\end{aligned}$$

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.2.23).

Solution d

$$\begin{aligned}\langle \psi_4 | \psi_3 \rangle &= \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) dx \\ &= \frac{2}{L} \int_{-\infty}^{+\infty} \sin\left(\frac{4\pi x}{L} \right) \sin\left(\frac{3\pi x}{L} \right) dx\end{aligned}$$

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd function), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.2.23).

However, since the wavefunctions are real, then

$$\langle \psi_4 | \psi_3 \rangle = \langle \psi_3 | \psi_4 \rangle$$

which also means

$$\langle \psi_4 | \psi_3 \rangle = 0$$

from the results of section c.

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

Learning Objectives

- Calculate the expectation value for a measurement
- Apply the expectation value concept to calculate average properties of a participle in a box model
- Understand the origin of a zero-point energy/zero-point motion.
- Extend the concept of orthogonality from vectors to mathematical functions (and wavefunctions).

Now that we have mathematical expressions for the wavefunctions and energies for the particle-in-a-box, we can answer a number of interesting questions. The answers to these questions use quantum mechanics to predict some important and general properties for electrons, atoms, molecules, gases, liquids, and solids. Key to addressing these questions is the formulation and use of expectation values. This is demonstrated below and used in the context of evaluating average properties (momentum of the particle in a box for the case below).

Classical Expectation Values

The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It is not the most probable value of a measurement; indeed the expectation value may even have zero probability of occurring. The expected value (or expectation, mathematical expectation, mean, or first moment) refers to the value of a variable one would "expect" to find if one could repeat the random variable process an infinite number of times and take the average of the values obtained. More formally, the expected value is a weighted average of all possible values.

Example 3.7.1 : Classical Expectation Value of Exam Scores (a discretized example)

A classical example is calculating the expectation value (i.e. average) of the exam grades in the class. For example if the class scores for an exam were

65	67	94	43	67	76	94	67

The discrete way is to sum up all scores and divide by the number of students:

$$\langle s \rangle = \frac{\sum_{i}^{N} s(i)}{N} \tag{3.3.1}$$

which of this example of scores is

$$\begin{aligned} \langle s \rangle &= \frac{65+67+94+43+67+76+94+76}{8} \\ &= 71.625 \end{aligned}$$

Notice that the average is not an allowable score on an individual exam. Equation 3.3.1 can be rewritten with "probability" or "probability weights"

$$\langle s \rangle = \sum_{i}^{N} s(i) P_s(i) \tag{3.3.2}$$

where $P_s(i)$ is the probability of observing a score of s. This is just the number of times it occurs in a dataset divided by the number of elements in that data set. Applying Equation 3.3.2 to the set of scores, we need to calculate these weights:

Score	65	67	94	43	76
$\boldsymbol{P_s}$	1/8	3/8	2/8	1/8	1/8

As with all probabilities, the sum of all probabilities possible must be one. These confirm that for the weights here:

$$\frac{1}{8}+\frac{3}{8}+\frac{2}{8}+\frac{1}{8}+\frac{1}{8}=\frac{8}{8}=1$$

This is the discretized "normalization" criterion (the same as why we normalize wavefunctions).

So, now we can use Equation 3.3.2 properly

$$\begin{aligned}\langle s\rangle &= 65\times\frac{1}{8}+67\times\frac{3}{8}+94\times\frac{2}{8}+43\times\frac{1}{8}+76\times\frac{1}{8}\\ &= 71.625\end{aligned}$$

Hence, Equation 3.3.2 gives the same result, as expected, from Equation 3.3.1.

Quantum Expectation Values

The extension of the classical expectation (average) approach in Example 3.7.1 using Equation 3.3.2 to evaluating quantum mechanical expectation values requires three small changes:

1. Switch from descretized to continuous variables
2. Substitute the wavefunction squared for the probability weights (i.e., the probability distribution)
3. Use an operator instead of the scalar

Hence, the quantum mechanical expectation value $\langle o\rangle$ for an observable, o, associated with an operator, $\hat{O}$, is given by

$$\langle o\rangle = \int_{-\infty}^{+\infty}\psi^*\hat{O}\psi\,dx \tag{3.3.3}$$

where x is the range of space that is integrated over (i.e., an integration over all possible probabilities). The expectation value changes as the wavefunction changes and the operator used (i.e, which observable you are averaging over).

> *In general, changing the wavefunction changes the expectation value for that operator for a state defined by that wavefunction.*

Average Energy of a Particle in a Box

If we generalize this conclusion, such integrals give the average value for any physical quantity by using the operator corresponding to that physical observable in the integral in Equation 3.3.3. In the equation below, the symbol $\langle H\rangle$ is used to denote the average value for the total energy.

$$\langle H\rangle = \int_{-\infty}^{\infty}\psi^*(x)\hat{H}\psi(x)dx \tag{3.3.4}$$

$$= \int_{-\infty}^{\infty}\psi^*(x)\hat{KE}\psi(x)dx + \int_{-\infty}^{\infty}\psi^*(x)\hat{V}\psi(x)dx \tag{3.3.5}$$

$$= \underbrace{\int_{-\infty}^{\infty}\psi^*(x)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x)dx}_{\text{average kinetic energy}} + \underbrace{\int_{-\infty}^{\infty}\psi^*(x)\hat{V}(x)\psi(x)dx}_{\text{average potential energy}} \tag{3.3.6}$$

The Hamiltonian operator consists of a kinetic energy term and a potential energy term. The kinetic energy operator involves differentiation of the wavefunction to the right of it. This step must be completed before multiplying by the complex conjugate of the wavefunction. The potential energy, however, usually depends only on position and not momentum (i.e., it involves conservative forces). The potential energy operator therefore only involves the coordinates of a particle and does not involve differentiation. For this reason we do not need to use a caret over V in Equation 3.3.6.

Equation 3.3.6 can be simplified

$$\langle H\rangle = \langle KE\rangle + \langle V\rangle \tag{3.3.7}$$

The potential energy integral then involves only products of functions, and the order of multiplication does not affect the result, e.g. 6×4 = 4×6 = 24. This property is called the **commutative property**. The average potential energy therefore can be written as

$$\langle V \rangle = \int_{-\infty}^{\infty} V(x)\psi^*(x)\psi(x)dx \tag{3.3.8}$$

This integral is telling us to take the probability that the particle is in the interval dx at x, which is $\psi^*(x)\psi(x)dx$, multiply this probability by the potential energy at x, and sum (i.e., integrate) over all possible values of x. This procedure is just the way to calculate the average potential energy $\langle V \rangle$ of the particle.

Exercise 3.7.2 : Particle in Box

Evaluate the two integrals in Equation 3.3.6 for the PIB wavefunction $\psi(x) = \sqrt{\frac{2}{L}}\sin(kx)$ with the potential function $V(x) = 0$ from 0 to the length of a box L with $k = \frac{\pi}{L}$.

Solution

The *average kinetic energy* is

$$\begin{aligned}
\langle KE \rangle &= \int_0^L \left(\sqrt{\frac{2}{L}}\right)\sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\left(\sqrt{\frac{2}{L}}\right)\sin(kx)dx \\
&= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial}{\partial x}\cos(kx)(k)dx \\
&= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\sin(kx)(k)(-k)dx \\
&= \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx
\end{aligned}$$

We can solve this intergral using the standard half-angle representation from an integral table. Or we can recognize that we already did this integral when we normalized the PIB wavefunction by rewriting this integral:

$$\begin{aligned}
\langle KE \rangle &= \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx \\
&= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \left(\frac{2}{L}\right)\sin^2(kx)dx \\
&= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \psi^*(x)\psi(x)dx \quad (\int_0^L \psi^*(x)\psi(x)dx = 1) \\
&= \frac{k^2\hbar^2}{2m}
\end{aligned}$$

Thus, the average value for the total energy of this particular system is

$$\langle KE \rangle = \frac{k^2\hbar^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2}$$

Hence, the average kinetic energy of the wavefunction is dependent on the n quantum number

The *average potential energy* is

$$\langle V \rangle = \int_{-\infty}^{\infty} \sin(kx) 0 \sin(kx) dx = 0$$

Thus, the average potential energy of the PIB is 0 irrespective of the wavefunction.

Hence via Equation 3.3.7 for this system and set of wavefunctions

$$\langle H \rangle = \frac{\pi^2 \hbar^2}{2mL^2}$$

This is the same result obtained from solving the eigenvalue equation for the PIB. However, if the wavefunctions used were NOT eigenstates of energy, then we cannot use the eigenvalue approach and need to rely on the expectation values to describe the energy of the system.

What is the lowest energy for a particle in a box? The lowest energy level is E_1, and it is important to recognize that this lowest energy of a particle in a box is not zero. This finite energy is called the **zero-point energy**, and the motion associated with this energy is called the zero-point motion. Any system that is restricted to some region of space is said to be bound. The zero-point energy and motion are manifestations of the wave properties and the Heisenberg Uncertainty Principle, and are general properties of bound quantum mechanical systems.

? Exercise 3.7.2 : Progressing to the Classical Limit

What happens to the energy level spacing for a particle-in-a-box when mL^2 becomes much larger than h^2? What does this result imply about the relevance of quantization of energy to baseballs in a box between the pitching mound and home plate? What implications does quantum mechanics have for the game of baseball in a world where h is so large that baseballs exhibit quantum effects?

Answer

As mL^2 becomes much larger than h^2, as everyday objects are, the spacing between energy levels becomes much smaller. This shows how the quantizations of energy levels become irrelevant for an everyday object, as the quantizations of the energy of baseballs in a box between the pitching mound and home plate would appear particularly continuous for such a relatively large mass and box length. If h were so large that a baseball experiences quantum effects then a game of baseball would be far less predictable, in a classical world the position of a baseball can be easily predicted by the everyday understanding of projectile motion, however, in such a quantum world the baseball would not behave with expected projectile motion but instead behave wave-like with a probability of being in a certain position.

The first derivative of a function is the rate of change of the function, and the second derivative is the rate of change in the rate of change, also known as the curvature. A function with a large second derivative is changing very rapidly. Since the second derivative of the wavefunction occurs in the Hamiltonian operator that is used to calculate the energy by using the Schrödinger equation, a wavefunction that has sharper curvatures than another, i.e. larger second derivatives, should correspond to a state having a higher energy. A wavefunction with more nodes than another over the same region of space must have sharper curvatures and larger second derivatives, and therefore should correspond to a higher energy state.

? Exercise 3.7.3 : Nodes and Energies

Identify a relationship between the number of nodes in a wavefunction and its energy by examining the graphs you made above. A node is the point where the amplitude passes through zero. What does the presence of many nodes mean about the shape of the wavefunction?

Average Position of a Particle in a Box

We can calculate the most probable position of the particle from knowledge of probability distribution, $\psi^*\psi$. For the ground-state particle in a box wavefunction with $n = 1$ (Figure $3.3.1a$)

$$\psi_{n=1} = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \tag{3.3.9}$$

This state has the following probability distribution (Figure $3.3.1b$):

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

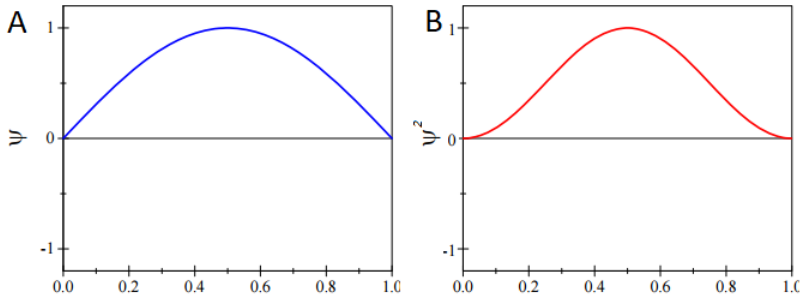


Figure 3.7.1 : (left) The ground-state ($n = 1$) wavefunction for a particle in a box. (right) The ground-state ($n = 1$) probability for a particle in a box.

The expectation value for position with the $\hat{x} = x$ operation for any wavefunction (Equation 3.3.3) is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* x \psi \, dx$$

which for the ground-state wavefunction (Equation 3.3.9) shown in Figure 3.7.1 is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) x \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \tag{3.3.10}$$

$$= \frac{2}{L} \int_{-\infty}^{+\infty} x \sin^2\left(\frac{\pi x}{L}\right) \tag{3.3.11}$$

Solution by Inspection

Without even having to evaluate Equation 3.3.11, we can get the expectation value from simply inspecting $\psi^*_{n=1}\psi_{n=1}$ in (Figure $3.3.1; right$). This is a symmetric distribution around the center of the box ($L/2$) so it is just as likely to be found in the left half than the right half. Moreover, specifically at any point a fixed distance away from the mean, i.e.

$$\psi^*_{n=1}\psi_{n=1}(L/2 + \Delta x) = \psi^*_{n=1}\psi_{n=1}(L/2 - \Delta x)$$

Therefore, the particle is most likely to be found at the center of the box. So

$$\langle x \rangle = \frac{L}{2}$$

Exercise 3.7.4

Use the general form of the particle-in-a-box wavefunction for any n to find the mathematical expression for the position expectation value $\langle x \rangle$ for a box of length L. How does $\langle x \rangle$ depend on n?

Average Momentum of a Particle in a Box

What is the average momentum of a particle in the box? We start with Equation 3.3.3 and use the momentum operator

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.3.12}$$

We note that the particle-in-a-box wavefunctions are **not** eigenfunctions of the momentum operator (Exercise 3.7.4). However, this does not mean that Equation 3.3.3 is inapplicable as Example 3.7.2 demonstrates.

Example 3.7.3 : The Average Momentum of a Particle in a Box is Zero

Even though the wavefunctions are not momentum eigenfunctions, we can calculate the expectation value for the momentum. Show that the expectation or average value for the momentum of an electron in the box is zero in every state (i.e., arbitrary values of n).

Strategy

First write the expectation value integral (Equation 3.3.3) with the momentum operator. Then insert the expression for the wavefunction and evaluate the integral as shown here.

Solution

$$\begin{aligned}
\langle p \rangle &= \int_0^L \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)dx \\
&= \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)\left(-i\hbar\frac{d}{dx}\right)\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)dx \\
&= -i\hbar\left(\frac{2}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(\frac{d}{dx}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\
&= -i\hbar\left(\frac{2}{L}\right)\left(\frac{n\pi}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx \\
&= 0
\end{aligned}$$

Note that this makes sense since the particles spends an equal amount of time traveling in the $+x$ and $-x$ direction.

Interpretation

It may seem that this means the particle in a box does not have any momentum, which is incorrect because we know the energy is never zero. In fact, the energy that we obtained for the particle-in-a-box is entirely kinetic energy because we set the potential energy at 0. Since the kinetic energy is the momentum squared divided by twice the mass, it is easy to understand how the average momentum can be zero and the kinetic energy finite

Exercise 3.7.5

Show that the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator (Equation 3.3.12).

Answer

The easiest way to address this question is asking if the PIB wavefunction also satisfies the eigenvalue equation using the momentum operation instead of the Hamiltonian operator (3rd postulate of QM). That is

$$\hat{p}_x\psi(n) = p\psi(n)$$

with the following PIB wavefunctions

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

and

$$\hat{p} = -i\hbar\frac{d}{dx}$$

and p is a real scalar (since it is a measurable).

$$\begin{aligned}\hat{p}_x\psi_n &= -i\hbar\frac{d}{dx}\left[\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\right] \\ &= -i\hbar\sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right)\left(\frac{n\pi}{L}\right) \\ &\neq p\psi_n\end{aligned}$$

Hence, the PIB wavefunctions are NOT eigenfunctions of the momentum operator.

Alternative Solution

An alternative, albeit more complicated, approach is to recognize that the uncertainty of p must be zero if the wavefunction is an eigenstate of the momentum operator. Hence

$$\sqrt{\langle p^2\rangle - \langle p\rangle^2} = 0$$

This requires calculating the $\langle p^2\rangle$ and $\langle p\rangle$ expectation values:

$$\begin{aligned}\langle p\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]\psi dx \\ &= -i\hbar\int_0^L \frac{2}{L}\sin\left(\frac{n\pi x}{L}\right)\frac{d}{dx}x\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -i\frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx \\ &= 0\end{aligned}$$

This integral is zero via orthonormality of the sine and cosine functions (although you can expand the integrand and confirm this).

$$\begin{aligned}\langle p^2\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]^2\psi dx \\ &= \frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{L}\right)dx \\ &= \frac{-\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -\frac{\mathrm{h}^2}{L}\end{aligned}$$

Now the integral above is 1 using orthonormality (although you can expand the integrand and confirm this). Now we calculate the uncertainty in momentum in the PIB wavefunctions:

$$\begin{aligned}\sqrt{\langle p^2\rangle - \langle p\rangle^2} &= \sqrt{\frac{-\mathrm{h}^2}{L} - 0^2} \\ &= \sqrt{\frac{-\mathrm{h}^2}{L}} \\ &\neq 0 \rightarrow\end{aligned}$$

Since the uncertainty is not 0, different measurements (experiments) will results in different values of momentum being quantified. Hence, the PIB wavefunctions are **not** eigenfunctions of the momentum operator.

It must be equally likely for the particle-in-a-box to have a momentum $-p$ as $+p$. The average of $+p$ and $-p$ is zero, yet p^2 and the average of p^2 are not zero. The information that the particle is equally likely to have a momentum of $+p$ or $-p$ is contained in the wavefunction. In fact, the sine function is a representation of the two momentum eigenfunctions e^{+ikx} and e^{-ikx} (Figure 3.7.2).

? Exercise 3.7.6

Write the particle-in-a-box wavefunction as a normalized linear combination of the momentum eigenfunctions e^{ikx} and e^{-ikx} by using Euler's formula. Show that the momentum eigenvalues for these two functions are $p = +\hbar k$ and $-\hbar k$.

The interpretation of the results of Exercise 3.7.6 is physically interesting. The exponential wavefunctions in the linear combination for the sine function represent the two opposite directions in which the electron can move. One exponential term represents movement to the left and the other term represents movement to the right (Figure 3.7.2).

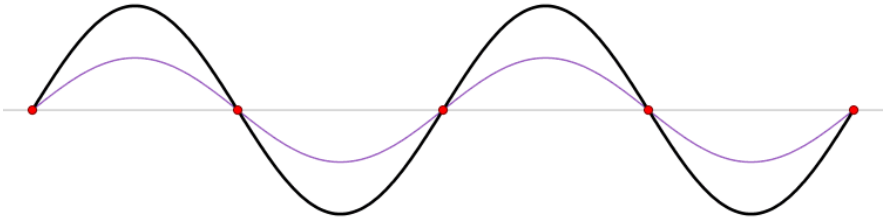


Figure 3.7.2 : Two waves traveling in opposite directions across the same medium combine linearly. In this animation, both waves have the same wavelength and the sum of amplitudes results in a standing wave. (Public Domain; LucasVB).

> *The electrons are moving, they have kinetic energy and momentum, yet the average momentum is zero.*

Did we just Violate the Uncertainty Principle?

Does the fact that the average momentum of an electron is zero and the average position is $L/2$ violate the Heisenberg Uncertainty Principle? No, because the Heisenberg Uncertainty Principle pertains to the uncertainty in the momentum and in the position, not to the average values. Quantitative values for these uncertainties can be obtained to compare with the limit set by the Heisenberg Uncertainty Principle for the product of the uncertainties in the momentum and position. However, to do this we need a quantitative definition of uncertainty, which is discussed in the following Section.

Orthogonality

In vector calculus, *orthogonality* is the relation of two lines at right angles to one another (i.e., perpendicularity), but is generalized into n dimensions via zero amplitude "dot products" or "inner products." Hence, orthogonality is thought of as describing **non-overlapping**, **uncorrelated**, or **independent** objects of some kind. The concept of orthogonality extends to functions (wavefunctions or otherwise) too. Two functions ψ_A and ψ_B are said to be orthogonal if

$$\int_{allspace} \psi_A^* \psi_B d\tau = 0 \tag{3.3.13}$$

In general, eigenfunctions of a quantum mechanical operator with different eigenvalues are orthogonal. Are the eigenfunctions of the particle-in-a-box Hamiltonian orthogonal?

? Exercise 3.7.7

Evaluate the integral $\int \psi_1^* \psi_3 dx$ for all possible pairs of particle-in-a-box eigenfunctions from $n = 1$ to $n = 3$ (use symmetry arguments whenever possible) and explain what the results say about orthogonality of the functions.

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3.4: A Particle in a Two-Dimensional Box

Learning Objectives

- Manipulate probability, energy, and transition problems involving multidimensional wavefunctions
- Apply the Separation of Variables to solve a multi-dimensional Schrödinger equation
- Manipulate problems with multiple quantum numbers
- To be introduced to the concepts of non-singular nodes (e.g., nodal lines)
- To be introduced to the concept of degeneracy

Let us now consider the Schrödinger Equation for an electron confined to a two dimensional box, $0 < x < a$ and $0 < y < b$. That is to say, within this rectangle the electron wavefunction behaves as a free particle ($V(x, y) = 0$), but the walls are impenetrable so the wavefunction $\psi(x, y, t) = 0$ at the walls.

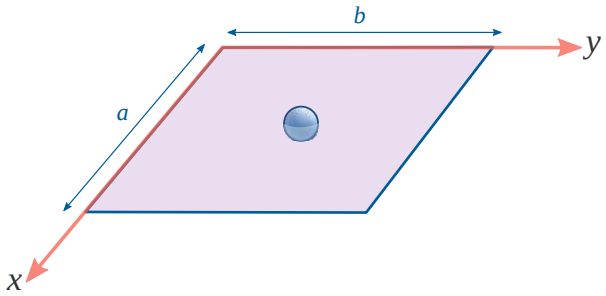


Figure 3.4.1: A particle in a $a \times b$ 2-dimensional box with infinite height can only be found within the box (highlighted). (CC BY-NC; Ümit Kaya)

Extending the (time-independent) Schrödinger equation for a one-dimensional system

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{d\,x^2} + V(x)\psi(x) = E\psi(x) \tag{3.4.1}$$

to a two-dimensional system is not difficult

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y)}{\partial x^2} + \frac{\partial^2\psi(x,y)}{\partial y^2}\right) + V(x,y)\psi(x,y) = E\psi(x,y). \tag{3.4.2}$$

Equation 3.4.2 can be simplified for the particle in a 2D box since we know that $V(x, y) = 0$ within the box and $V(x, y) = \infty$ outside the box, ii.e.

$$V(x,y) = \begin{cases} 0 & 0 \le x \le a \text{ and } 0 \le y \le b \\ \infty & x < 0 \text{ and } x > a \\ \infty & y < 0 \text{ and } y > b \end{cases}$$

So Equation 3.4.2 becomes

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y)}{\partial x^2} + \frac{\partial^2\psi(x,y)}{\partial y^2}\right) = E\psi(x,y). \tag{3.4.3}$$

Since the Hamiltonian (i.e. left side of Equation 3.4.3) is the sum of two terms with independent (separate) variables, we try a product wavefunction like in the Separation of Variables approach used to separate time-dependence from the spatial dependence previously. Within this approach we express the 2-D wavefunction as a product of two independent 1-D components

$$\psi(x,y) = X(x)Y(y). \tag{3.4.4}$$

This ansatz separates Equation 3.4.3 into two independent one-dimensional Schrödinger equations

$$-\frac{\hbar^2}{2m}\left(\frac{d^2X(x)}{dx^2}\right) = \varepsilon_x X(x). \tag{3.4.5}$$

$$-\frac{\hbar^2}{2m}\left(\frac{d^2Y(y)}{dy^2}\right)=\varepsilon_y Y(y). \tag{3.4.6}$$

where the total energy of the particle is the sum of the energies from each one-dimensional Schrödinger equation

$$E=\varepsilon_x+\varepsilon_y \tag{3.4.7}$$

The differential equations in Equations 3.4.5 and 3.4.6 are familiar as they were found for the particle in a 1-D box previously. They have the general solution

$$X(x)=A_x\sin(k_x x)+B_x\cos(k_x x) \tag{3.4.8}$$

$$Y(y)=A_y\sin(k_y y)+B_y\cos(k_y y) \tag{3.4.9}$$

Applying Boundary Conditions

The general solutions in Equations 3.4.8 and 3.4.9 can be simplified to address boundary conditions dictated by the potential, i.e., $\psi(0,y)=0$ and $\psi(x,0)=0$. Therefore, $B_x=0$ and $B_y=0$.

Thus, we can combine Equations 3.4.8, 3.4.9, and 3.4.4 to construct the wavefunction $\psi(x,y)$ for a particle in a 2D box of the form

$$\psi(x,y)=N\sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right)\sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right) \tag{3.4.10}$$

We still need to satisfy the remaining boundary conditions $\psi(L,y)=0$ and $\psi(x,L)=0$

$$N\sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L\right)\sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right)=0 \tag{3.4.11}$$

and

$$N\sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right)\sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L\right)=0 \tag{3.4.12}$$

Equation 3.4.11 can be satisfied if

$$\sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L\right)=0 \tag{3.4.13}$$

independent of the value of y, while Equation 3.4.12 can be satisfied if

$$\sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L\right)=0 \tag{3.4.14}$$

independent of the value of x. These are the same conditions that we encountered for the one-dimensional box, hence we already know the sin function in each case can be zero in many places. In fact, these two conditions are satisfied if

$$\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L=n_x\pi \tag{3.4.15}$$

and

$$\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L=n_y\pi \tag{3.4.16}$$

which yield the allowed values of ε_x and ε_y as

$$\varepsilon_{n_x}=\frac{\hbar^2\pi^2}{2mL^2}n_x^2 \tag{3.4.17}$$

and

$$\varepsilon_{n_y} = \frac{\hbar^2 \pi^2}{2mL^2} n_y^2 \tag{3.4.18}$$

We need two different integers n_x and n_y because the conditions are completely independent and can be satisfied by any two different (or similar) values of these integers. The allowed values of the total energy are now given by

$$E_{n_x,n_y} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2) \tag{3.4.19}$$

Note that the allowed energies now depend on two integers n_x and n_y rather than one. These arise from the *two* independent boundary conditions in the x and y directions. As in the one-dimensional box, the values of n_x and n_y are both restricted to the natural numbers $1, 2, 3, \ldots$Note, therefore, that the ground state energy $E_{1,1}$ is

$$E_{1,1} = \frac{\hbar^2 \pi^2}{mL^2} \tag{3.4.20}$$

is larger than for the one-dimensional box because of the contributions from kinetic energy in the x and y directions.

Once the conditions on ε_{n_x} and ε_{n_y} are substituted into Equation 3.4.10, the wavefunctions become

$$\psi_{n_x,n_y}(x,y) = N \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \tag{3.4.21}$$

The constant N is now determined by the normalization condition

$$\begin{aligned} \int_0^L \int_0^L |\psi_{n_x,n_y}(x,y)|^2 dx\, dy &= 1 \\ N^2 \int_0^L \sin^2\left(\frac{n_x \pi x}{L}\right) dx \int_0^L \sin^2\left(\frac{n_y \pi y}{L}\right) dy &= 1 \\ N^2 \frac{L}{2} \cdot \frac{L}{2} &= 1 \\ N &= \frac{2}{L} \end{aligned}$$

so that the complete normalized 2D wavefunction is

$$\psi_{n_x,n_y}(x,y) = \frac{2}{L} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \tag{3.4.22}$$

The Separability of the Hamiltonian

Because the Halmiltonian in Equation 3.4.3 can be expressed as a simple sum of independent terms, the solutions can be expressed as simple **products** of the one-dimensional solution (Equation 3.4.22) with energies that are expressed as the **sum** of one-dimensional energies (Equation 3.4.19). This observation extends to higher dimensional wavefunctions as demonstrated later.

The wavefunctions in Equation 3.4.22 are somewhat more difficult that 1-D analogs to visualize because they are two dimensional. Nevertheless, we can still visualize them, and Figure 3.4.1 shows the following wavefunctions: $\psi_{1,1}(x,y)$, $\psi_{2,1}(x,y)$ and $\psi_{2,2}(x,y)$.

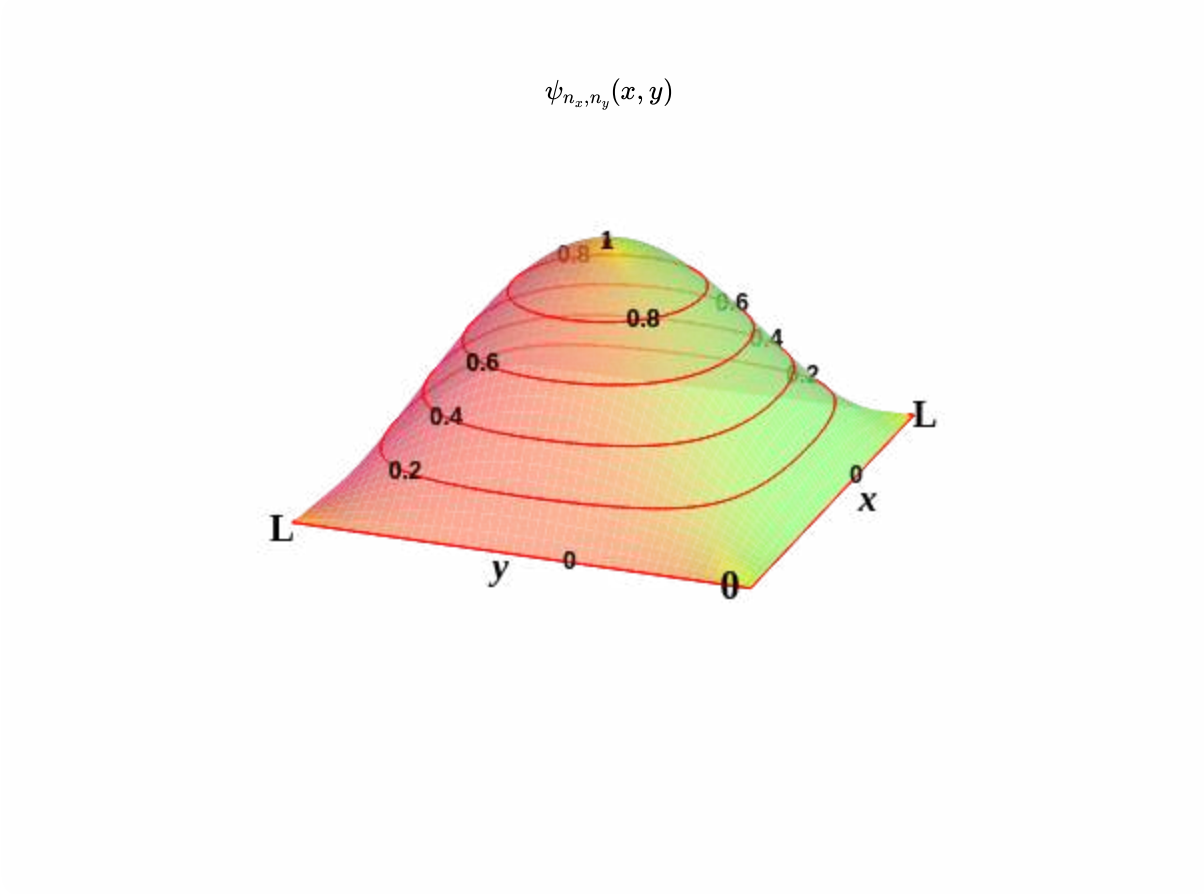


***Figure* 3.4.1**: *Visualizing the first six wavefunctions for a particle in a two-dimensional square box ($L_x = L_y = L$). Use the slide bar to independently change either n_x or n_y quantum number and see the changing wavefunction.*

It is important to note that the wavefunctions can be either positive or negative, even though the associated probability density $p_{n_x,n_y}(x,y) = |\psi_{n_x,n_y}(x,y)|^2$ is strictly positive.

$\psi_{n_x,n_y}(x,y)$ $|\psi_{n_x,n_y}(x,y)|^2$

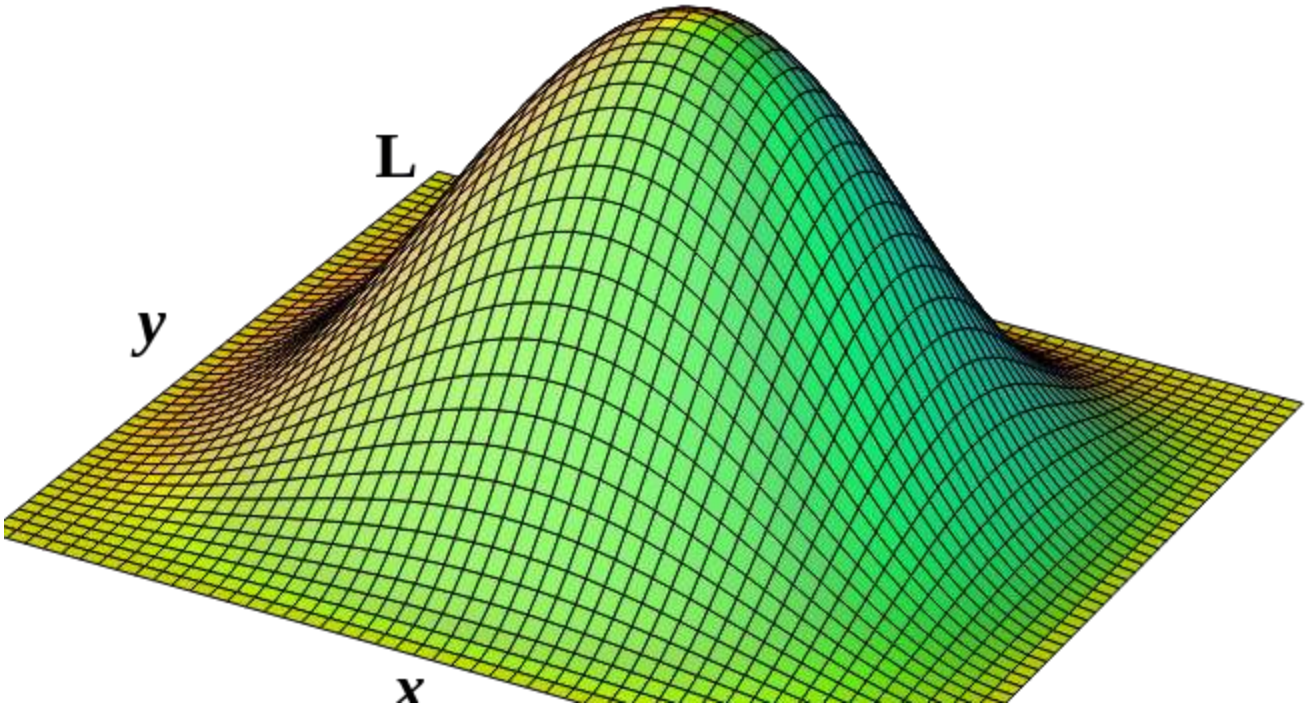


***Figure* 3.4.2**: *Visualizing the first six wavefunctions and associated probability densities for a particle in a two-dimensional square box ($L_x = L_y = L$). Use the slide bar to independently change either n_x or n_y quantum number and see the changing wavefunction.*

Unlike in the one-dimensional analoge, where nodes in the wavefunction are points where $\psi_n(x) = 0$, here entire lines can be nodal (called *nodal lines)*. For example, in the state $\psi_{2,1}(x,y)$, there is a nodal line at $\psi_{2,1}(L/2,y)$. Along the entire line $x = L/2$, the wavefunction is 0 independent of the value of y. The wavefunction $\psi_{2,2}(x,y)$ has two nodal lines when $x = L/2$ and when $y = L/2$. The sign of the wavefunction and its nodal structure will play central roles later when we consider chemical bonding.

The fact that the wavefunction $\psi_{n_x n_y}(x,y)$ is a product of one-dimensional wavefunctions:

$$\psi_{n_x n_y}(x,y) = \psi_{n_x}(x)\psi_{n_y}(y) \tag{3.4.23}$$

makes the calculation of probabilities rather easy. The probability that a measurement the particle's position will yield a value of $x \in [a,b]$ and $y \in [c,d]$ is

$$\begin{aligned} P(x \in [a,b] \; and \; y \in [c,d]) &= \int_a^b dx \int_c^d dy |\psi_{n_x n_y}(x,y)|^2 \\ &= \int_a^b dx \int_c^d dy \psi^2_{n_x}(x)\psi^2_{n_y}(y) \\ &= \left[\int_a^b \psi^2_{n_x}(x)dx\right]\left[\int_c^d \psi^2_{n_y}(y)dy\right] \end{aligned} \tag{3.4.24}$$

Example 3.4.1: Probability

For a particle in a two-dimensional square box of length L, if the particle is in the $\psi_{1,2}(x,y)$ state, what is the probability that a measurement of the particle's position will yield $x \in [0, L/2]$ and $y \in [0, L/2]$?

Solution

Substituting the limits of integration into Equation 3.4.24, we have

$$\begin{aligned} P(x \in [0, L/2] \; and \; y \in [0, L/2] &= \left[\int_0^{L/2} \psi_1^2(x)dx\right]\left[\int_0^{L/2} \psi_2^2(y)dy\right] \\ &= \left[\frac{2}{L}\int_0^{L/2} \sin^2\left(\frac{\pi x}{L}\right)dx\right]\left[\frac{2}{L}\int_0^{L/2} \sin^2\left(\frac{2\pi y}{L}\right)dy\right] \\ &= \left[\frac{2}{L}\frac{L}{4}\right]\left[\frac{2}{L}\frac{L}{4}\right] \\ &= \frac{1}{4} \end{aligned}$$

This can be graphically confirmed by exploring the probability densities in Figure 3.4.2 for the $\psi_{1,2}(x,y)$ state.

Exercise 3.4.1

For a particle in a two-dimensional square box of length L, if the particle is in the state $\psi_{2,3}(x,y)$, what is the probability that a measurement of the particle's position will yield $x \in [0, L/2]$ and $y \in [0, L/3]$?

Answer

$$P = \frac{1}{6}$$

Confirmed this by exploring the probability densities in Figure 3.4.2for the $\psi_{2,3}(x,y)$ state.

Note that if the box were rectangular rather than square, then instead of having a length of L on both sides, there would be two different lengths L_x and L_y. The formulas for the energies and wavefunctions become only slightly more complicated:

$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) \tag{3.4.25}$$

instead of Equation 3.4.19 and

$$\psi_{n_x,n_y}(x,y) = \frac{2}{\sqrt{L_x L_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right) \tag{3.4.26}$$

instead of Equation 3.4.22.

Degeneracy

Two distinct wavefunctions are said to be *degenerate* if they correspond to the same energy. If the sides *a*, *b* of the rectangle are such that *a*/*b* is irrational (the general case), there will be no degeneracies. The *most* degenerate case is the square, $L_x = L_y$, for which clearly $E_{m,n} = E_{n,m}$. Degeneracies in quantum physics are most often associated with symmetries in this way. Figure 3.4.3 shows the wavefunctions (3,2) and (2,3) for a rectangle. These are contour maps for the time-independent solution, with white being the highest point. These two wavefunctions do not correspond to the same energy, although they would, of course, for a square.

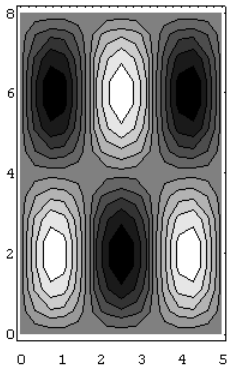


Figure 3.4.2: Contours of the $n_x = 2$ and $n_y = 3$ wavefunction (left) and $n_x = 3$ and $n_y = 2$ wavefunction (right).

The energy of the particle in a 2-D square box (i.e., $L_x = L_y = L$) in the **ground state** is given by Equation 3.4.25 with $n_x = 1$ and $n_y = 1$. This energy (E_{11}) is hence

$$E_{1,1} = \frac{2\hbar^2\pi^2}{2mL^2} \tag{3.4.27}$$

For the ground state of the particle in a 2D box, there is one wavefunction (and no other) with this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 2-D box potential, the energy of a state depends upon the sum of the squares of the two quantum numbers. The particle having a particular value of energy in the excited state *may* has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be **degenerate**.

For the first excited state, three combinations of the quantum numbers $(n_x,\ n_y)$ are $(2,\ 1)$ and $(1, 2)$. The sum of squares of the quantum numbers in each combination is same (equal to 5). Each waveunction has same energy:

$$E_{2,1} = E_{1,2} = \frac{5\hbar^2\pi^2}{2mL^2} \tag{3.4.28}$$

Corresponding to these combinations three different wavefunctions and **two** different states are possible. Hence, the first excited state is said to be doubly degenerate. The number of independent wavefunctions for the stationary states with *a shared energy* is called as the **degree of degeneracy** of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

$$n^2\ = n_x^2 + n_y^2 \tag{3.4.29}$$

as well as the degree of degeneracy are depicted in Table 3.4.1.

Table 3.4.1: Degeneracy properties of the particle in a 2-D box with $L_x = L$ and $L_y = L$.

$n_x^2 + n_y^2$	Combinations of Degeneracy (n_x, n_y)			Total Energy (E_{n_x,n_y})	Degree of Degeneracy
2	(1, 1)			$\frac{2\hbar^2\pi^2}{2mL^2}$	1
5	(2, 1)	(1, 2)		$\frac{5\hbar^2\pi^2}{2mL^2}$	2
8	(2, 2)			$\frac{8\hbar^2\pi^2}{2mL^2}$	1
10	(3, 1)	(1, 3)		$\frac{10\hbar^2\pi^2}{2mL^2}$	2
13	(3, 2)	(2, 3)		$\frac{13\hbar^2\pi^2}{2mL^2}$	2
18	(3,3)			$\frac{18\hbar^2\pi^2}{2mL^2}$	1

Note that all the states above would be non-degenerate if $L_x \neq L_y$. However, a degeneracy will be "accidentally" observed for states that fulfill this requirement:

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}. \tag{3.4.30}$$

Example 3.4.2: Transition Energy

An electron in a 2D infinite potential well needs to absorb electromagnetic wave with wavelength 4040 nm (IR radiation) to be excited from lowest excited state to next higher energy state. What is the length of the box if this potential well is a square ($L_x = L_y = L$)?

Solution

The energy of a particle in a 2-D well is given by Equation 3.4.25:

$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)$$

and for a square well $L_x = L_y = L$ this simplifies to Equation 3.4.19:

$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2\right)$$

When the electron absorbs an electromagnetic wave and it transitions from one state (e.g., $(n_x = 1, n_y = 2)$ or $(n_x = 2, n_y = 1)$ since are degenerate states as Table 3.4.1 demonstrates) to a higher energetic state, e.g., $(n_x = 2, n_y = 2)$.

The energy of the lowest excited state is $\frac{5h^2}{8mL^2}$ and the energy of the next higher excited state is $\frac{8h^2}{8mL^2}$, so we can equate the difference in energies of these state to the energy of the absorbed photon

$$\begin{aligned} h\nu &= E_{2,1} - E_{1,1} \\ &= \frac{5\hbar^2\pi^2}{2mL^2} - \frac{2\hbar^2\pi^2}{2mL^2} \\ &= \frac{3\hbar^2\pi^2}{2mL^2} \end{aligned}$$

Converting frequency (ν) to wavelength (λ):

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

results in an expresstion relating wavelength of absorbed light to box length L:

$$\frac{hc}{\lambda} = \frac{3\hbar^2\pi^2}{2mL^2}$$

and solving for L

$$L = \sqrt{\frac{3\hbar^2\pi^2}{2mhc}\lambda}$$

or

$$\begin{aligned} L &= \sqrt{\frac{3\hbar\pi}{4mc}\lambda} \\ &= 1.91\, nm \end{aligned}$$

Exercise 3.4.2

An electron in a 2D infinite potential well needs to absorb electromagnetic wave with wavelength 4040 nm to be excited from $(n_x = 2, n_y = 2)$ state to the $(n_x = 3, n_y = 3)$ state.

a. What is the length of the box if this potential well is a square ($L_x = L_y = L$)?
b. How many wavefunction exist between these two states (do not count the start or ending states)

Answer a

$L = 3.5\, nm$

Answer b

From the energies in Table $3.4.1$, four wavefunctions exist between $(n_x = 2, n_y = 2)$ state to the $(n_x = 3, n_y = 3)$ state. However, due to degeneracy, only two possible energies exist.

Contributors and Attributions

- Mark Tuckerman (New York University)
- Michael Fowler (Beams Professor, Department of Physics, University of Virginia)

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3.5: A Particle in a Three-Dimensional Box

Learning Objectives

- To demonstrate how the particle in 1-D box problem can extend to a particle in a 3D box
- Introduction to nodal surfaces (e.g., nodal planes)

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimensions as demonstrated elsewhere for a quantum particle in a 2D box. Here we continue the expansion into a particle trapped in a 3D box with three lengths L_x, L_y, and L_z. As with the other systems, there is NO FORCE (i.e., no potential) acting on the particles *inside* the box (Figure 3.9.1).

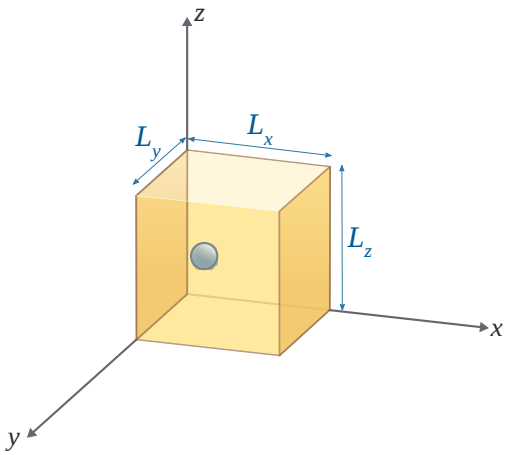


Figure 3.9.1 : A particle in 3D box with three lengths L_x, L_y, and L_z. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The potential for the particle inside the box

$$V(\vec{r}) = 0$$

- $0 \leq x \leq L_x$
- $0 \leq y \leq L_y$
- $0 \leq z \leq L_z$
- $L_x < x < 0$
- $L_y < y < 0$
- $L_z < z < 0$

$\vec{r}$ is the vector with all three components along the three axes of the 3-D box: $\vec{r} = L_x\hat{x} + L_y\hat{y} + L_z\hat{z}$. When the potential energy is infinite, then the wavefunction equals zero. When the potential energy is zero, then the wavefunction obeys the Time-Independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{3.5.1}$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrondinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \tag{3.5.2}$$

The easiest way in solving this partial differential equation is by having the wavefunction equal to a **product** of individual function for each independent variable (e.g., the Separation of Variables technique):

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{3.5.3}$$

Now each function has its own variable:

- $X(x)$ is a function of variable x only

- $Y(y)$ is a function of variable y only
- $Z(z)$ is a function of variable z only

Now substitute Equation 3.5.3 into Equation 3.5.2 and divide it by the xyz product:

$$\frac{d^2\psi}{dx^2} = YZ\frac{d^2X}{dx^2} \Rightarrow \frac{1}{X}\frac{d^2X}{dx^2}$$

$$\frac{d^2\psi}{dy^2} = XZ\frac{d^2Y}{dy^2} \Rightarrow \frac{1}{Y}\frac{d^2Y}{dy^2}$$

$$\frac{d^2\psi}{dz^2} = XY\frac{d^2Z}{dz^2} \Rightarrow \frac{1}{Z}\frac{d^2Z}{dz^2}$$

$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right) = E \tag{3.5.4}$$

E is an energy constant, and is the sum of x, y, and z. For this to work, each term must equal its own constant. For example,

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

Now separate each term in Equation 3.5.4 to equal zero:

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

$$\frac{d^2Y}{dy^2} + \frac{2m}{\hbar^2}\varepsilon_y Y = 0$$

$$\frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2}\varepsilon_z Z = 0$$

Now we can add all the energies together to get the total energy:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \tag{3.5.5}$$

Do these equations look familiar? They should because we have now reduced the 3D box into three particle in a 1D box problems!

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{3.5.6}$$

Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,

$$n = 1, 2, ..\infty$$

Use the normalization wavefunction equation for each variable:

$$\psi(x) = \begin{cases} \sqrt{\frac{2}{L_x}}\sin\frac{n\pi x}{L_x} & \text{if } 0 \le x \le L \\ 0 & \text{if } L < x < 0 \end{cases}$$

Normalization wavefunction equation for each variable (that substitute into Equation 3.5.3):

$$X(x) = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x\pi x}{L_x}\right) \tag{3.5.7}$$

$$Y(y) = \sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y\pi y}{L_y}\right) \tag{3.5.8}$$

$$Z(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n_z\pi z}{L_z}\right) \tag{3.5.9}$$

The limits of the three quantum numbers

- $n_x = 1, 2, 3, \ldots \infty$
- $n_y = 1, 2, 3, \ldots \infty$
- $n_z = 1, 2, 3, \ldots \infty$

For each constant use the de Broglie Energy equation:

$$\varepsilon_x = \frac{n_x^2 h^2}{8mL_x^2} \tag{3.5.10}$$

with $n_x = 1 \ldots \infty$

Do the same for variables n_y and n_z. Combine Equation 3.5.3 with Equations 3.5.7-3.5.9 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.5.11}$$

with

$$V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}}$$

To find the Total Energy, add Equation 3.5.10 and Equation 3.5.5.

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{3.5.12}$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.5.12) and a 1D box.

Degeneracy in a 3D Cube

The energy of the particle in a 3-D cube (i.e., $L_x = L_y = L$) in the *ground state* is given by Equation 3.5.12 with $n_x = 1$, $n_y = 1$, and $n_z = 1$. This energy ($E_{1,1,1}$) is hence

$$E_{1,1,1} = \frac{3h^2}{8mL^2}$$

The ground state has only one wavefunction and no other state has this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 3-D cubical box potential the energy of a state depends upon the sum of the squares of the quantum numbers (Equation 3.5.11). The particle having a particular value of energy in the excited state *MAY* has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be **degenerate**.

For the first excited state, three combinations of the quantum numbers (n_x, n_y, n_z) are $(2, 1, 1)$, $(1, 2, 1)$, $(1, 1, 2)$ The sum of squares of the quantum numbers in each combination is same (equal to 6). Each wavefunction has same energy:

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2}$$

Corresponding to these combinations three different wavefunctions and **three** different states are possible. Hence, the first excited state is said to be three-fold or triply degenerate. The number of independent wavefunctions for the stationary states of an energy level is called as the **degree of degeneracy** of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

as well as the degree of degeneracy are depicted in Table 3.9.1 .

Table 3.9.1 : Degeneracy properties of the particle in a 3-D cube with $L_x = L_y = L$.

$n_x^2 + n_y^2 + n_z^2$	Combinations of Degeneracy (n_x, n_y, n_z)	Total Energy (E_{n_x, n_y, n_z})	Degree of Degeneracy

$n_x^2+n_y^2+n_z^2$	Combinations of Degeneracy (n_x, n_y, n_z)						Total Energy (E_{n_x,n_y,n_z})	Degree of Degeneracy
3	(1,1,1)						$\frac{3h^2}{8mL^2}$	1
6	(2,1,1)	(1,2,1)	(1,1,2)				$\frac{6h^2}{8mL^2}$	3
9	(2,2,1)	(1,2,2)	(2,1,2)				$\frac{9h^2}{8mL^2}$	3
11	(3,1,1)	(1,3,1)	(1,1,3)				$\frac{11h^2}{8mL^2}$	3
12	(2,2,2)						$\frac{12h^2}{8mL^2}$	1
14	(3,2,1)	(3,1,2)	(2,3,1)	(2,1,3)	(1,3,2)	(1,2,3)	$\frac{14h^2}{8mL^2}$	6
17	(2,2,3)	(3,2,2)	(2,3,2)				$\frac{17h^2}{8mL^2}$	3
18	(1,1,4)	(1,4,1)	(4,1,1)				$\frac{18h^2}{8mL^2}$	3
19	(1,3,3)	(3,1,3)	(3,3,1)				$\frac{19h^2}{8mL^2}$	3
21	(1,2,4)	(1,4,2)	(2,1,4)	(2,4,1)	(4,1,2)	(4,2,1)	$\frac{21h^2}{8mL^2}$	6

Example 3.9.1 : Accidental Degeneracies

When is there degeneracy in a 3-D box when none of the sides are of equal length (i.e., $L_x \neq L_y \neq L_z$)?

Solution

From simple inspection of Equation 3.5.12 or Table 3.9.1 , it is clear that degeneracy originates from different combinations of n_x^2/L_x^2, n_y^2/L_y^2 and n_z^2/L_z^2 that give the same value. These will occur at common multiples of at least two of these quantities (the Least Common Multiple is one example). For example

if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}$$

there will be a degeneracy. Also degeneracies will exist if

$$\frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}$$

or if

$$\frac{n_x^2}{L_x^2} = \frac{n_z^2}{L_z^2}$$

and especially if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}.$$

There are two general kinds of degeneracies in quantum mechanics: degeneracies due to a symmetry (i.e., $L_x = L_y$) and accidental degeneracies like those above.

Exercise 3.9.1

The 6th energy level of a particle in a 3D Cube box is 6-fold degenerate.

a. What is the energy of the 7th energy level?
b. What is the degeneracy of the 7th energy level?

Answer a

$$\frac{17h^2}{8mL^2}$$

Answer b

three-fold (i.e., there are three wavefunctions that share the same energy.

References

1. Atkins, Peter. Physical Chemistry 5th Ed. USA. 1994.
2. Fitts, Donald. Principles of Quantum Mechanics. United Kingdom, Cambridge. University Press. 1999
3. McQuarrie. Donald. Physical Chemistry A Molecular Approach. Sausalito, CA. University Science Books. 1997.
4. Riggs. N. V. Quantum Chemistry. Toronto, Ontario. The Macmillan Company. 1969
5. C. A. Hollingsworth, Accidental Degeneracies of the Particle in a Box, J. Chem. Educ., 1990, 67 (12), p 999

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3.6: Particle in a Finite Box and Tunneling (optional)

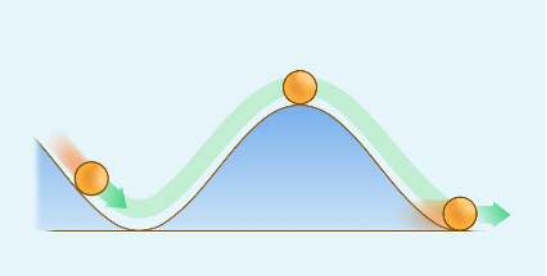
Learning Objectives

- Understand the basics of quantum tunneling and when to expect it be observable phenomenon
- Understand how the wavefunction and energies of the particle in a box changes when the box has finite heights (not infinite potential)
- Introduce the concept of binding energies

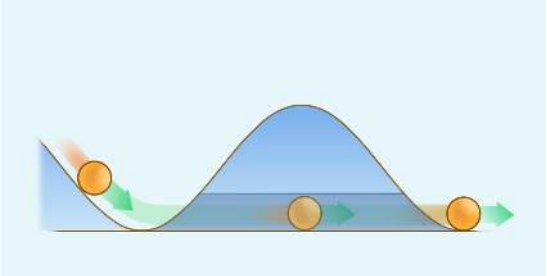
Tunneling Through a Barrier

Tunneling is a quantum mechanical phenomenon when a particle is able to penetrate through a potential energy barrier that is higher in energy than the particle's kinetic energy. This amazing property of microscopic particles play important roles in explaining several physical phenomena including radioactive decay. Additionally, the principle of tunneling leads to the development of Scanning Tunneling Microscope (STM) which had a profound impact on chemical, biological and material science research.

Consider a ball rolling from one valley to another over a hill (Figure 3.6.1). If the ball has enough energy (E) to overcome the potential energy (V) at the top of the barrier between each valley, then it can roll from one valley to the other. This is the classical picture and is controlled by the simple Law of Conservation of Energy approach taught in beginning physics courses. However, If the ball does not have enough kinetic energy ($E < V$), to overcome the barrier it will never roll from one valley to the other. In contrast, when quantum effects are taken into effect, the ball can "tunnel" through the barrier to the other valley, even if its kinetic energy is less than the potential energy of the barrier to the top of one of the hills.



In Classical Mechanics, electrons must climb the potential hill to appear on the other side



Quantum Mechanics allows electron with less energy to tunnel thru the barrier and appear on the other side

Figure 3.6.1: Contrasting classical (over the barrier) motion vs. quantum (through the barrier) motion. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The Heisenberg Uncertainty Principle in Action

The reason for the difference between classical and quantum motion comes from wave-particle nature of matter. One interpretation of this duality involves the Heisenberg uncertainty principle, which defines a limit on how precisely the position and the momentum of a particle can be known at the same time. This implies that there are no solutions with a probability of exactly zero (or one), though a solution may approach infinity if, for example, the calculation for its position was taken as a probability of 1, the other, i.e. its speed, would have to be infinity. Hence, the probability of a given particle's existence on the opposite side of an intervening barrier is non-zero, and such particles will appear on the 'other' (a semantically difficult word in this instance) side with a relative frequency proportional to this probability.

Microscopic particles such as protons, or electrons would behave differently as a consequence of wave-particle duality. Consider a particle with energy E that is confined in a box which has a barrier of height V. Classically, the box will prevent these particles from escaping due to the insufficiency in kinetic energy of these particles to get over the barrier. However, if the thickness of the

barrier is thin, the particles have some probability of penetrating through the barrier **without** sufficient energy and appear on the other side of the box (Figure 3.6.2).

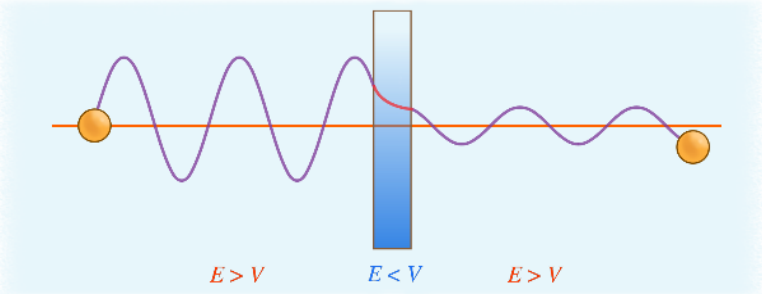


Figure 3.6.2: Quantum tunneling through a barrier. The energy of the tunneled particle is the same but the amplitude is decreased. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Tunneling is found from the Schrödinger equation, so we will start there. To simplify the calculations, the time-independent, one-dimensional Schrödinger equation is used (Equation 3.6.1).

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V(r)\psi=E\psi \tag{3.6.1}$$

To find solutions to a particular system, the potential $V(x)$ must be defined. In this case, we will set the potential to zero for all space, except for the region between 0 and a, which we will set as V_0. This is represented by the piecewise function in Equation 3.6.2.

$$V=\begin{cases}0 & \text{if } -\infty<x\leq 0\\ V_0 & \text{if } 0<x<a\\ 0 & \text{if } a\leq x<\infty\end{cases} \tag{3.6.2}$$

To solve this, the equation must be solved separately for each region. However, the boundary conditions at 0 and a for each region must be consistent such that $\psi(x)$ is continuous for all x, so that $\psi(x)$ is a valid wavefunction. The general solution for each region, before applying the boundary conditions, is then

$$\psi=\begin{cases}A\sin kx+B\cos kx & \text{if } -\infty<x\leq 0\\ Ce^{-\alpha x}+De^{\alpha x} & \text{if } 0<x<a\\ E\sin kx+F\cos kx & \text{if } a\leq x<\infty\end{cases} \tag{3.6.3}$$

where

$$k=\frac{\sqrt{2mE}}{\hbar} \tag{3.6.4}$$

and

$$\alpha=\frac{\sqrt{2m(V_o-E)}}{\hbar}. \tag{3.6.5}$$

To enforce continuity, the boundaries of each region are set equal. This is expressed as $\psi_1(0)=\psi_2(0)$ and $\psi_1(a)=\psi_2(a)$.

$$A\sin 0+B\cos 0=Ce^0+De^0 \tag{3.6.6}$$

which implies that $A=0$, and $B=C+D$. At the opposite boundary,

$$A\sin ka+B\cos ka=Ce^{-\alpha a}+De^{\alpha a} \tag{3.6.7}$$

It may be observed that, as a goes to infinity, the right hand side of this equation goes to infinity, which does not make physical sense. To reconcile this, D is set to zero. For the final region, E and F, present a potentially intractable problem. However, if one realizes that the value at the boundary a is driving the wave in the region a to ∞, it may also be realized that the wavefunction could be rewritten as $Ce^{-\alpha a}\cos(k(x-a))$, phase shifting the wavefunction by the value of a and setting the amplitude to the boundary value. The wavefunction is then

$$\psi = \begin{cases} B\cos kx & \text{if } -\infty < x \leq 0 \\ Be^{-\alpha x} & \text{if } 0 < x < a \\ Be^{-\alpha a}\cos(k(x-a)) & \text{if } a \leq x < \infty \end{cases} \tag{3.6.8}$$

The amplitude of the wavefunction before the barrier is B and after the barrier is $Be^{-\alpha a}$ where a represents the width of the barrier. So barrier attenuates the wavefunction by

$$\exp\left[-a\frac{\sqrt{2m(V_o - E)}}{\hbar}\right]$$

where $(V_o - E)$ is the difference between the potential energy of the barrier and the current energy of the particle (Figure 3.6.2).

Since the square of the wavefunction is the probability distribution, the probability of transmission through a barrier is

$$P_t = \exp\left[-2a\frac{\sqrt{2m(V_o - E)}}{\hbar}\right] \tag{3.6.9}$$

As the barrier width or height approaches zero, the probability of a particle traveling through the barrier becomes 1. Also of note is that k is unchanged on the other side of the barrier. This implies that the energy of the particles are exactly the same as it was before they tunneled through the barrier, as stated earlier, the only thing that changes is the quantity of particles going in that direction. The rest are reflected off the barrier, and go back the way they came.

Example 3.6.1

An electron having total kinetic energy E of 4.50 eV approaches a rectangular energy barrier with $V = 5.00\,eV$ and $L = 950\,pm$. Classically, the electron cannot pass through the barrier because $E < V$. Calculate probability of tunneling of this electron through the barrier.

Solution

This is a straightforward application of Equation 3.6.9. The electronvolt (eV) is a unit of energy that is equal to approximately $1.6 \times 10^{-19}\ J$, which is the conversion used below.

The mass of an electron is $9.10 \times 10^{-31}\ kg$

$$P = \exp\left[\left(\frac{(2)(950 \times 10^{-12}\ m)(\pi)}{1.0546 \times 10^{-34} m^2 kg/s}\right)\sqrt{(2)(9.10 \times 10^{-31}\ kg)(5.00 - 4.50\ \cancel{eV})(1.60 \times 10^{-19} J/\ \cancel{eV})}\right]$$

$$= \exp^{-6.88} = 1.03 \times 10^{-3}$$

There is a ~0.1% probability of the electrons tunneling though the barrier.

While tunneling is always possible for any system with finite height barriers, for a particle to *appreciably* tunnel through a barrier three conditions must be met.

Tunneling "Rules"

1. The height of the barrier must be **finite** and the thickness of the barrier should be **thin**.
2. The potential energy of the barrier exceeds the kinetic energy of the particle ($E < V$).
3. The particle has wave properties because the wavefunction is able to penetrate through the barrier. This suggests that quantum tunneling only apply to microscopic objects such protons or electrons and does not apply to macroscopic objects.

If these conditions are met, there would be some probability of finding the particles on the other side of the barrier. Beginning as a sinusoidal wave, a particle begins tunneling through the barrier and goes into exponential decay until it exits the barrier and gets transmitted out the other side as a final sinusoidal wave with a smaller amplitude. The act of tunneling decreases the wave amplitude due the reflection of the incident wave when it comes into the contact with the barrier but does not affect the wave equation.

Tunneling in a Particle in a Finite Height Box

The finite potential well is an extension of the infinite potential well from the previous section. The main difference between these two systems is that now the particle has a non-zero probability of finding itself outside the well, although its kinetic energy is less than that required, according to classical mechanics, for scaling the potential barrier. This type of problem is more realistic, but more difficult to solve due to the yielding of transcendental equations. The particle is again confined to a box, but one which has finite, not infinite, potential walls. We consider a potential well of height V_0 (Figure 3.6.3).

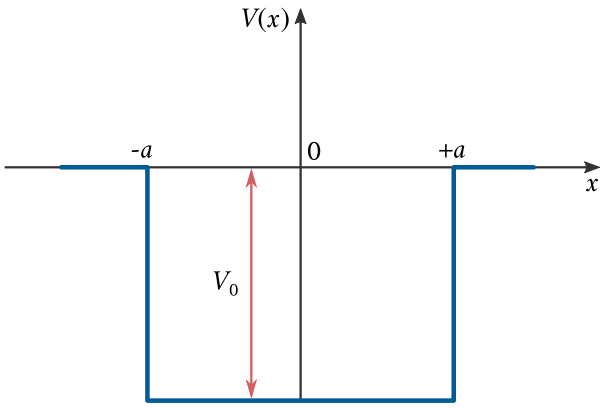


Figure 3.6.3: Square well with finite potential. Here, $a = L/2$. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

We have the following potential, $V(x)$, given by the boundary conditions shown in Figure 3.6.3:

$$V(x) = \begin{cases} -V_0 & |x| < L \\ 0 & |x| > L \end{cases} \tag{3.6.10}$$

In this example, the origin of the x-axis was chosen at the center of the well. By doing so, the potential is symmetric about $x = 0$, giving rise to **parity** (Note: this could also be applied to a symmetric infinite wells). For the finite well, two cases must be distinguished, corresponding to positive or negative values of the energy E. It is possible for the particle to be bound, or unbound. The case $E < 0$ corresponds to a particle which is confined (and whose energy is less than the well depth) and hence is in a bound state [1]. When $E > 0$, the particle is unconfined and corresponds to a scattering problem. The latter case will only briefly be discussed.

Figure 3.6.4 provides a prelude to what the wavefunctions and probability distributions for several states will look like in a finite well. Comparing Figure 3.6.4 with the infinite case, we see that in the finite case, the wavefunctions do not have to be zero at the walls of the well. In the finite case, the wavelengths are slightly longer, implying that the allowed energies will be somewhat smaller.

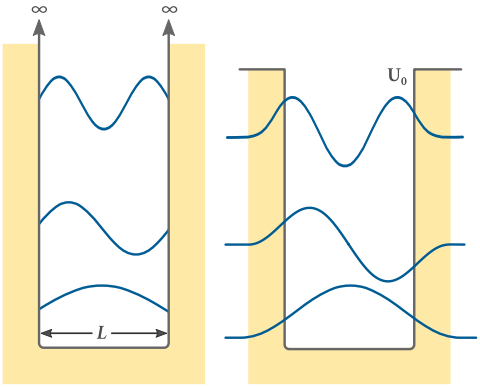


Figure 3.6.4: (left) Wavefunctions for a particle in an infinite height box compared to (right) wavefunctions in a box of finite height. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Bound States

In the bound state we have,$-V_0 <= E < 0$ (since E cannot be lower than the absolute minimum of the potential. The Schrödinger equation for the two regions is given by:

- $|x| < L$ (inside the well):

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) - V_0\psi(x) = -|E|\psi(x) \tag{3.6.11}$$

- $|x| > L$ (outside the well):

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = -|E|\psi(x) \tag{3.6.12}$$

Here, the **binding energy**, $|E|$ of the particle is introduced ($|E| = -E$). To simplify the Schrödinger equations, let,

$$\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - |E|)} \tag{3.6.13}$$

and

$$\beta = \sqrt{\frac{2m}{\hbar^2}|E|} \tag{3.6.14}$$

The solutions of the Schrödinger equation separate into even and odd functions, and we need only consider positive values of x (which could be inferred from the potential). With the application of the boundary conditions, the even solutions are given as

$$\psi^F(x) = \begin{cases} A\cos(\alpha\alpha) & 0 < x < L \\ Ce^{-\beta\hbar} & x > L \end{cases} \tag{3.6.15}$$

and the odd solutions are given as

$$\psi^o(x) = \begin{cases} A\sin(\alpha\alpha) & 0 < x < L \\ Ce^{-\beta_x} & x > L \end{cases} \tag{3.6.16}$$

Despite the discontinuous nature of the potential at $x = L$, the wavefunction and its derivative are still continuous, and these conditions provide the required boundary conditions to determine the quantized energies. The requirements that $\psi_O = \psi E(x)$ and yields two equations:

$$\begin{aligned} A\cos(\alpha L) &= Ce^{-\beta L} \\ -\alpha A\sin(\alpha L) &= -\beta Ce^{-\beta L} \end{aligned} \tag{3.6.17}$$

These can be combined to give the even eigenvalue condition (which depends on the energies but not on the constants A and C) is

$$\alpha \tan(\alpha L) = \beta \tag{3.6.18}$$

The odd eigenvalue condition is found to be

$$\alpha \cot(\alpha L) = -\beta \tag{3.6.19}$$

The energy levels of the bound states are found by solving these transcendental equations, either graphically or numerically. In doing so, it is helpful to change to dimensionless variables. We introduce the dimensionless quantities

$$\begin{aligned} \xi &= \alpha L \\ \eta &= \beta L \end{aligned} \tag{3.6.20}$$

Upon substitution these quantities, the transcendental equations become

- Even States: $\xi \tan \xi = \eta$
- Odd States: $\xi \cot \xi = -\eta$

The graphical determination of the energy levels are obtained by finding the points of intersection of the circle (Figure 3.6.3)

$$\xi^2 + \eta^2 = \gamma^2 \tag{3.6.21}$$

where γ is of known radius (found by simple substitution),

$$\gamma = \sqrt{\frac{2mV_oL^2}{\hbar^2}} \tag{3.6.22}$$

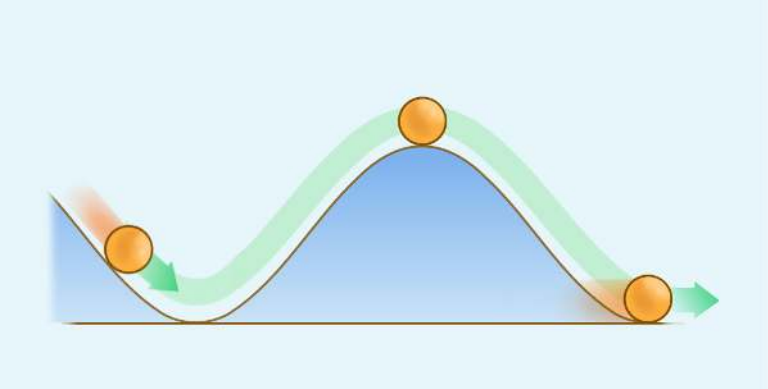


Figure 3.6.5: The left graph shows energy levels for even states, while the right graph represents odd states. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

What can be concluded from Figure 3.6.5?

- The bound-state energy levels are non-degenerate.
- The bound-state energy levels are finite, but increase without bound and depend on the parameter γ. Thus, deeper and wider potentials have a larger number of bound states.
- The bound state spectrum consists of alternating even and odd states, with the ground state always being even.

Unbound States

The finite well problem shows that wavefunctions are not localized in the vicinity of the well. This is the case of unbound states, where eigenvalues of energy are a continuum. In this problem, a particle is incident upon the well from the left, interacts with the well, and gets transmitted or reflected. The solution of the Schrödinger equation is outlined briefly. Note that in one dimension,

there is a lack of symmetry between the external regions to the left and right of the potential, since the particle is assumed to be incident on the potential in a given direction. Therefore, there is no need to exercise parity.

For the external regions, the solution of the Schrödinger equation is given by

$$\psi(x) = \begin{cases} Ae^{|\alpha_\alpha} + Be^{-ib} & x < -L \\ Ce^{|\alpha,} & x > L \end{cases} \tag{3.6.23}$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{3.6.24}$$

In the region of x<−L, the wavefunction is seen to consist of an incident wave of amplitude A and a reflected wave of amplitude B. In the region of x>L, the wavefunction is seen as a pure transmitted wave of amplitude C.

For the internal region, the solution of the Schrödinger equation is given by

$$\psi(x) = Fe^{i\omega} + Ge^{-i\omega} \tag{3.6.25}$$

where

$$\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 + E)} \tag{3.6.26}$$

By applying continuity at $x = L$ and $x = -L$, F and G are eliminated and the ratios of B/A and C/A can be solved to obtain the reflection coefficient, R=|B/A|2, and the transmission coefficient, T=|C/A|2. An important aspect to briefly point out is that the transmission coefficient is generally less than unity, which is in contradiction to the classical prediction that suggests that the particle should always be transmitted

Summary

Quantum tunneling is a phenomenon where particles may "tunnel through" a barrier which they have insufficient kinetic energy to overcome according to classical mechanics. Tunneling is a result of the wavelike nature of quantum particles, and cannot be predicted by any classical system. The major differences between a particle in a finite box and an infinite well are:

- Only a finite number of energy levels exist (bound state)
- Tunneling into the barrier (wall) is possible
- Higher energy states are less tightly bound than lower ones
- A particle provided with enough energy can escape the well (unbound state)

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CHAPTER OVERVIEW

4: QM for Rotational and Vibrational Motion

4.1: A Harmonic Oscillator Obeys Hooke's Law
4.2: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials
4.3: Hermite Polynomials are either Even or Odd Functions
4.4: The Harmonic Oscillator Energy Levels
4.5: The Harmonic Oscillator Approximates Molecular Vibrations
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4.8: The Energy Levels of a Rigid Rotor

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4.1: A Harmonic Oscillator Obeys Hooke's Law

The motion of two atoms in a diatomic molecule can be separated into translational, vibrational, and rotational motions. Both rotation and vibrational motions are internal motions that do not change the center of mass for the molecule (Figure 5.1.1), which is described by translational motion. Quantum translational motions can be modeled with the particle in a box model discussed previously and rotation and vibration can be modeled via the **rigid rotor** and **harmonic oscillator** models, respectively.



Figure 5.1.1 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY, 3.0; www.cleonis.nl).

Before delving into the quantum mechanical harmonic oscillator, we will introduce the classical harmonic oscillator (i.e., involving classical mechanics) to build an intuition that we will extend to the quantum world. A classical description of the vibration of a diatomic molecule is needed because the quantum mechanical description begins with replacing the classical energy with the Hamiltonian operator in the Schrödinger equation. It also is interesting to compare and contrast the classical description with the quantum mechanical picture.

The Classical Harmonic Oscillator

Simple harmonic oscillators about a potential energy minimum can be thought of as a ball rolling frictionlessly in a curved dish or a pendulum swinging frictionlessly back and forth (Figure 5.1.2). The restoring forces are precisely the same in either horizontal direction.

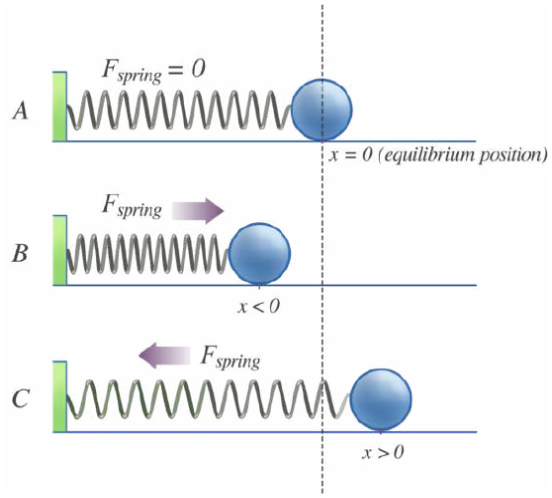


Figure 5.1.2 : A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (CC BY-NC; Ümit Kaya via LibreTexts)

If we consider the bond to behave like a mass on a spring (Figure 5.1.2), then this restoring force (F) is proportional to the displacement (x) from the equilibrium length (x_o) - this is *Hooke's Law*:

$$F = -kx \tag{4.1.1}$$

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.

$$V(x) = \frac{1}{2}kx^2 \tag{4.1.2}$$

Hooke's Law or the harmonic (i.e. quadratic) potential given by Equation 4.1.2 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.

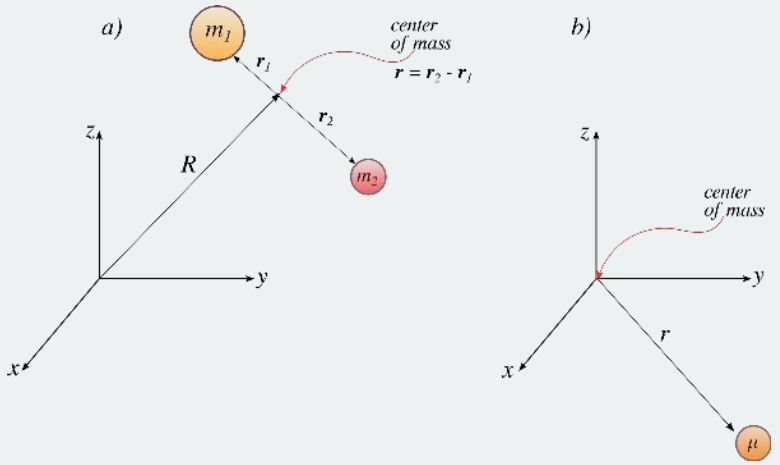


Figure 5.1.3 : Diagrams of the coordinate systems and relevant vectors for the motion of (a) a two-particle diatomic molecule with atoms of mass m_1 and m_2 and (b) the equivalent one-particle pseudo-particle of reduced mass μ. (CC BY-NC; Ümit Kaya via LibreTexts)

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 4.1.2 with respect to x is the Hooke's Law force in Equation 4.1.1.
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 4.1.1). 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

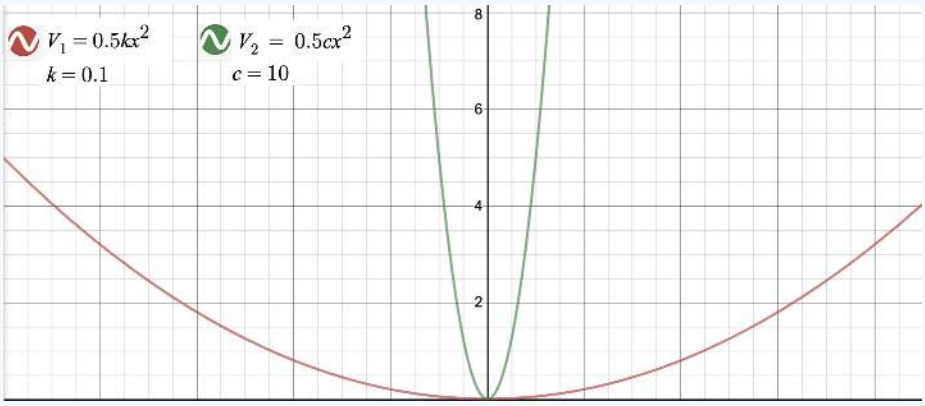
$$V\text{''}(x) = \frac{d}{dx}kx = k$$

Thus, the second derivative of this equation for potential energy is equal to the force constant, k.

Solution c

To find the minimum potential energy, it is easiest to set the first derivative equal to zero and solve for x. When $V'(x) = kx = 0$ then x must be equal to zero. Thus, the minimum potential energy is when x=0. Plugging this into Hooke's Law, $F(0) = -k(0) = 0$ so this is also the value for x when the force is zero.

Solution d



The force constant has a drastic effect on both the potential energy and the force. A system with a large force constant requires minimal change in x to have a drastic change in potential energy or force, whereas a system with a small force constant is the exact opposite phenomenon.

Solving the Harmonic Oscillator Model

The classical equation of motion for a one-dimensional simple harmonic oscillator with a particle of mass m attached to a spring having spring constant k is

$$m\frac{d^2x(t)}{dt^2} = -kx(t) \tag{4.1.3}$$

which can be rewritten in the standardform:

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0 \tag{4.1.4}$$

Equation 4.1.3 is a linear second-order differential equation that can be solved by the standard method of factoring and integrating. The resulting solution to Equation 4.1.3 is

$$x(t) = x_o \sin(\omega t + \phi) \tag{4.1.5}$$

with

$$\omega = \sqrt{\frac{k}{m}} \tag{4.1.6}$$

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**.

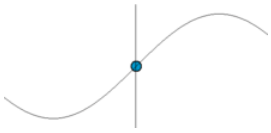


Figure 5.1.4 : Solution to the Harmonic Oscillator. Displacement (y-axis) is plotted as a function of time.

Example 5.1.2

Substitute the following functions into Equation 4.1.4 to demonstrate that they are both possible solutions to the classical equation of motion.

a. $x(t) = x_0 e^{i\omega t}$
b. $x(t) = x_0 e^{-i\omega t}$

where

$$\omega = \sqrt{\frac{k}{m}}$$

Note that the Greek symbol ω for frequency represents the angular frequency $2\pi\nu$.

Solution a

This requires simply placing the given function $x(t) = x_0 e^{i\omega t}$ into Equation 4.1.4.

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

Solution b

This requires simply placing the given function $x(t) = x_0 e^{-i\omega t}$ into Equation 4.1.4.

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

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

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

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

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

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

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

Exercise 5.1.1

Show that sine and cosine functions also are solutions to Equation 4.1.4.

Answer

Using Equation 4.1.4

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

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 4.1.4

$$-\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) + \frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) = 0$$

Hence, the sine equation is a solution to Equation 4.1.4

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 4.1.4

$$-\frac{k}{m} x_o \cos\left(\sqrt{\frac{k}{m}} t + \phi\right) + \frac{k}{m} x_o \cos\left(\sqrt{\frac{k}{m}} t + \phi\right) = 0$$

The cosine equation is also a solution to Equation 4.1.4

? 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 4.1.6 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.

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

$$p = m\frac{dx}{dt} \tag{4.1.7}$$

so combining Equations 4.1.7 and 4.1.2, the total energy can be written as

$$E = T + V \tag{4.1.8}$$

$$= \frac{p^2}{2m} + \frac{k}{2}x^2 \tag{4.1.9}$$

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 4.1.9) is continuously being shifted between potential energy stored in the spring and kinetic energy of the mass.

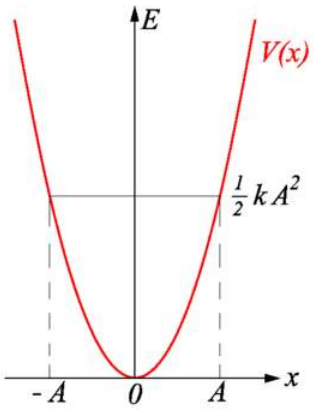


Figure 5.1.5 : The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x. The potential energy $V(x) = ½kx^2$ is shown in red. (Paul Wormer Wikipedia).

The motion of a classical oscillator is confined to the region where its kinetic energy is nonnegative, which is what the energy relation Equation 4.1.9 says. Physically, it means that a classical oscillator can never be found beyond its turning points, and its energy depends only on how far the turning points are from its equilibrium position. The energy of a classical oscillator changes in a continuous way. The lowest energy that a classical oscillator may have is zero, which corresponds to a situation where an object is at rest at its equilibrium position. The zero-energy state of a classical oscillator simply means no oscillations and no motion at all (a classical particle sitting at the bottom of the potential well in Figure 5.1.5). When an object oscillates, no matter how big or small its energy may be, it spends the longest time near the turning points, because this is where it slows down and reverses its direction of motion. Therefore, the probability of finding a classical oscillator between the turning points is highest near the turning points and lowest at the equilibrium position. (Note that this is not a statement of preference of the object to go to lower energy. It is a statement about how quickly the object moves through various regions.)

Example5.1.3

a. What happens to the frequency of the oscillation as the vibration is excited with more and more energy?
b. What happens to the maximum amplitude of the vibration as it is excited with more and more energy?

Solution

a. Frequency

The energy of the harmonic oscillator can be written as

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

and the frequency of oscillation is $\omega = \sqrt{\frac{k}{m}}$. Notice that the frequency depends only on the stiffness (k) and reduced mass (μ) of the oscillator and not on the energy. Hence, increasing the energy of the vibrations does not affects its frequency.

b. Amplitude

The kinetic and potential terms for energy of the harmonic oscillator can be written as

$$\begin{aligned} E &= K + V \\ &= \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t + \frac{1}{2}kA^2 \cos^2 \omega t \end{aligned}$$

with $\omega = \sqrt{\frac{k}{m}}$ so

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

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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4.2: 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, $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \tag{4.2.1}$$

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero. As shown in Equation 4.2.1, 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,

$$\hat{H}(q) = \frac{1}{2\mu}\hat{P}_q^2 + \frac{k}{2}\hat{q}^2 \tag{4.2.2}$$

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

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{k}{2}q^2 \tag{4.2.3}$$

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

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(q)}{dq^2} + \frac{k}{2}q^2\psi_v(q) = E_v\psi_v(q) \tag{4.2.4}$$

or upon rearranging

$$\frac{d^2\psi_v(q)}{dq^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{k}{2}q^2\right)\psi_v(q) = 0 \tag{4.2.5}$$

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

$$\beta^2 = \frac{\hbar}{\sqrt{\mu k}} \tag{4.2.6}$$

and then changing the variable from q to x where

$$x = \frac{q}{\beta} \tag{4.2.7}$$

so that

$$\frac{d^2}{dq^2} = \frac{1}{\beta^2}\frac{d^2}{dx^2} \tag{4.2.8}$$

After substituting Equations 4.2.6 and 4.2.8 into Equation 4.2.5, the differential equation for the harmonic oscillator becomes

$$\frac{d^2\psi_v(x)}{dx^2} + \left(\frac{2\mu\beta^2 E_v}{\hbar^2} - x^2\right)\psi_v(x) = 0 \tag{4.2.9}$$

? Exercise 5.6.1

Make the substitutions given in Equations 4.2.6 and 4.2.8 into Equation 4.2.5 to get Equation 4.2.9.

Solving for the Quantum Wavefunctions

A common strategy for solving differential equations, which is employed here, is to find a solution that is valid for large values of the variable and then develop the complete solution as a product of this asymptotic solution and a power series. Since the potential energy approaches infinity as x and the coordinate q approach infinity, the wavefunctions must approach zero (this is, the wavefunctions must **converge to zero**):

$$\lim_{x\to\infty} \psi_v(x) = 0 \tag{4.2.10}$$

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

$$\lim_{x\to\infty} \phi_v(x)\exp\left(\frac{-x^2}{2}\right) = 0 \tag{4.2.11}$$

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.

$$\sum_{n=0}^{v} c_n x^n \tag{4.2.12}$$

Each of the truncations of the power series in Equation 4.2.12 can be multiplied by the exponential function in Equation 4.2.11 to create a family of valid solutions to the differential equation in Equation 4.2.9.

$$\psi_v(x) = \sum_{n=0}^{v} c_n x^n \exp\left(\frac{-x^2}{2}\right) \tag{4.2.13}$$

? Exercise 5.6.2

Write the first four polynomials, $v = 0$ to $v = 1$, $v = 12$, $v = 13$, $v = 14$ for Equation 4.2.12 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 4.2.13 is a solution to the harmonic oscillator Schrödinger Equation in Equation 4.2.9 for $v = 0$ and $v = 1$.

Hermite Polynomials

While polynomials in general approach ∞ (or $-\infty$) as x approaches ∞, the decreasing exponential term overpowers the polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of x or $-x$. The exact forms

of polynomials that solve Equation 4.2.9 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.

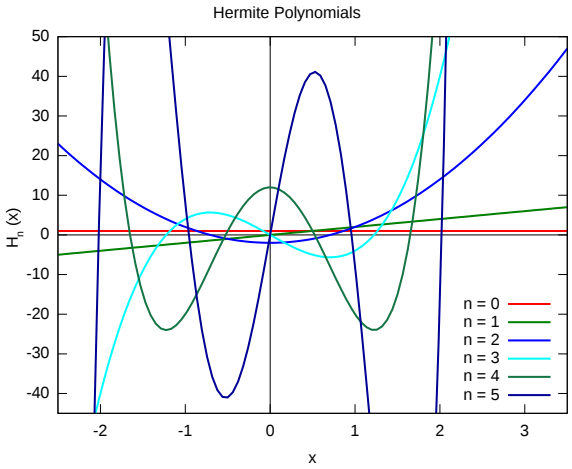


Figure 5.6.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

? 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.

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \tag{4.2.14}$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \tag{4.2.15}$$

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 4.2.7) and a different constant α:

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

so Equation 4.2.15becomes

$$\psi_v(x) = N_v'' H_v(\sqrt{\alpha} Q) e^{-\alpha Q^2/2}$$

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

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \tag{4.2.16}$$

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 4.2.16, 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.

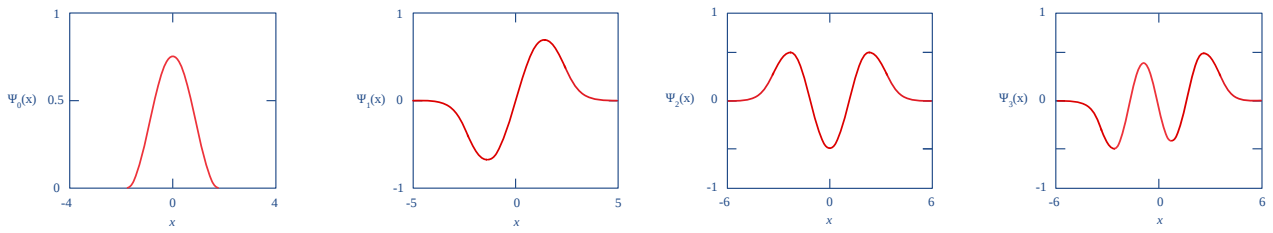


Figure 5.6.2 : The harmonic oscillator wavefunctions describing the four lowest energy states.

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?

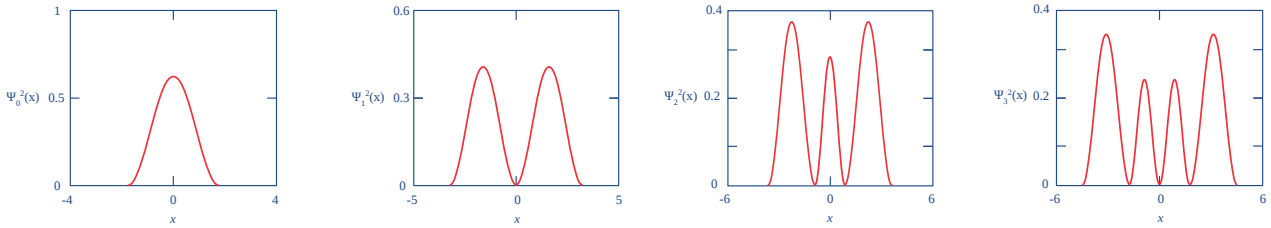


Figure 5.6.3 : The probability densities for the four lowest energy states of the harmonic oscillator.

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.

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

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \tag{4.2.17}$$

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

$$P[\text{allowed}] = 2\int_0^{Q_0} \psi_0^*(Q)\psi_0(Q)dQ \tag{4.2.18}$$

The factor 2 appears in Equation 4.2.18 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 4.2.18, 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 4.2.18 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}}\int_0^1 \exp(-x^2)dx \tag{4.2.19}$$

The integral in Equation 4.2.19 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 4.2.19 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

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4.3: 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 .

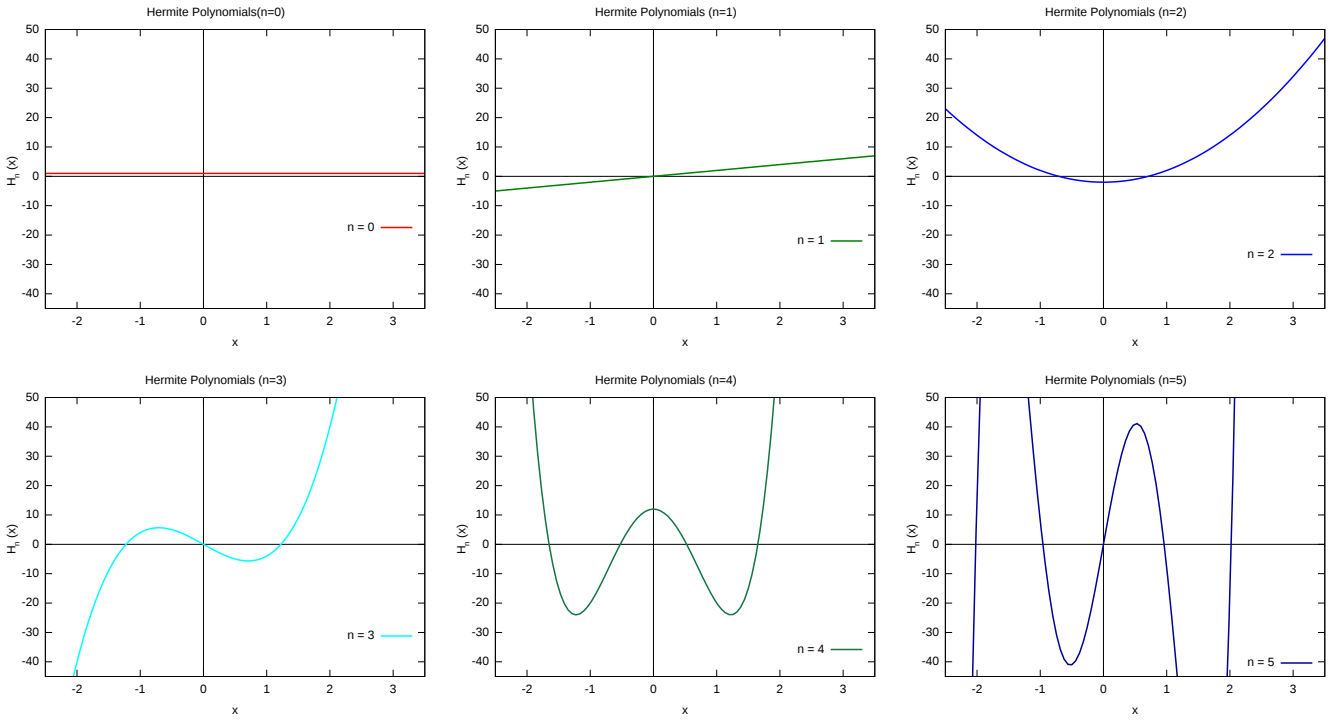


Figure 5.7.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

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

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x). \tag{4.3.1}$$

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

$$H_n(-x) = (-1)^n H_n(x) \tag{4.3.2}$$

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

Integration over Symmetric Functions

You often consider integrals of the form

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

If f is odd or even, then sometimes you can make solving this integral easier. For example, we can rewrite that integral in the following way:

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x = \int_{-a}^{0} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{4.3.3}$$

$$= \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{4.3.4}$$

For an even function, we have $f(-x) = f(x)$ and Equation 4.3.4 can be simplified

$$I = \int_0^a f(-x)\,\mathrm{d}x + \int_0^a f(x)\,\mathrm{d}x$$
$$= 2\int_0^a f(x)\,\mathrm{d}x$$

For an odd function, we have $f(-x) = -f(x)$ and Equation 4.3.4 can be simplified

$$I = -\int_0^a f(x)\,\mathrm{d}x + \int_0^a f(x)\,\mathrm{d}x$$
$$= 0$$

That's what it means to simplify the integration: the integral of an odd or even function over the interval $[-L, L]$ can be put into a nicer form (and sometimes we can see that it vanishes without ever computing an integral).

Example 5.7.1

Technically, evaluating the orthogonality of Hermite polynomials requires integrating over the $\exp(-x^2)$ weight function (Equations 4.3.5 and 4.3.6).

Solution

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

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

While the $H_2(x)H_3(x)$ product is indeed an odd function (Table 5.7.1), while $exp(-x^2)$ is even. Their product is odd, and thus $\langle f, g\rangle$ certainly ought to be zero.

Symmetry is an important aspect of quantum mechanics and mathematics, especially in calculating integrals. Using this symmetry, integrals can be identified to be equal to zero without explicitly solving them. For example, the integral of an odd integrand over all possible values will **always** be zero irrespective of the exact nature of the function:

$$\int_{-\infty}^{\infty} f(x)\,dx = 0$$

This simplifies calculations greatly as demonstrated in the following chapters.

Hermite Polynomials are Orthogonal

Hermite polynomials $H_n(x)$ are *n*th-degree polynomials for *n* = 0, 1, 2, 3 and form an orthogonal set of functions for the weight function $e^{-x^2/2}$. The exact relation is:

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 0 \tag{4.3.5}$$

if $m \neq n$ and

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 2^n n!\sqrt{\pi} \tag{4.3.6}$$

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 4.3.6 is important for normalizing the quantum harmonic oscillator wavefunctions discussed in last Section.

Example 5.7.2 : Hermite Polynomials are Orthogonal

Demonstrate that $H_2(x)$ and $H_3(x)$ are orthogonal.

Solution

We need to confirm

$$\int_{-\infty}^{\infty} H_2(x)H_3(x)dx = 0$$

or when substituted

$$\int_{-\infty}^{\infty} (4x^2-2)(8x^3-12x)dx = 0$$

because it says I need to show it's orthogonal on $[-\infty, \infty]$ or we can just evaluate it on a finite interval $[-L, L]$, where L is a constant.

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

Concluding

Hermite polynomials are a component in the harmonic oscillator wavefunction that dictates the symmetry of the wavefunctions. If your integration interval is symmetric around 0, then the integral over *any* integrable odd function is zero, no exception. Therefore as soon as you've found that your integrand is odd and your integration interval is symmetric, you're done. Also, for general functions, if you can easily split them into even and odd parts, you only have to consider the integral over the even part for symmetric integration intervals.

Another important property is that the product of two even or of two odd functions is even, and the product of an even and an odd function is odd. For example, if ff is even, $x \mapsto f(x)\sin(x)$ is odd, and therefore the integral over it is zero (provided it is well defined).

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4.4: 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.

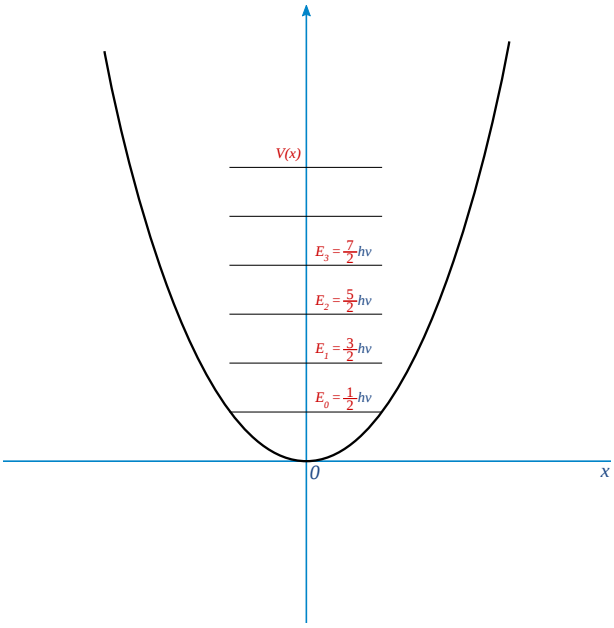


Figure 5.4.1 : Potential energy function and first few energy levels for harmonic oscillator. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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 4.4.1 and Figure 5.4.1 .

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \left(v + \frac{1}{2}\right)h\nu \tag{4.4.1}$$

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

$$P_{Q \to Q+dQ} = \int_{Q}^{Q+dQ} \psi_v^*(Q)\psi_v(Q)dQ \tag{4.4.2}$$

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

$$\int_{-\infty}^{\infty} \psi_v^*(x)\psi_v(x)dx = 1 \tag{4.4.3}$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x)\psi_v(x)dx = 0 \quad \text{for} \quad v' \neq v \tag{4.4.4}$$

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

$$\frac{\hbar\omega}{2} = \frac{kQ_0^2}{2} \tag{4.4.5}$$

> *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 4.4.1 which is

$$\omega = \sqrt{\frac{k}{\mu}} \tag{4.4.6}$$

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4.5: The Harmonic Oscillator Approximates Molecular Vibrations

Learning Objectives

- Understand the utility and limits of using the quantum harmonic oscillator as a model for molecular vibrations

The quantum harmonic oscillator is one of the most important model systems in quantum mechanics. This is due in partially to the fact that an arbitrary potential curve $V(x)$ can usually be *approximated* as a harmonic potential at the vicinity of a stable equilibrium point. Furthermore, it is one of the few quantum-mechanical systems for which an exact, analytical solution exists. Solving other potentials typically require either approximations or numerical approaches to identify the corresponding eigenstates and eigenvalues (i.e., wavefunctions and energies).

A general potential energy ($V(x)$) curve for a molecular vibration can be expanded as a Taylor series

$$V(x) = V(x_0) + \frac{dV(x)}{dx}\bigg|_{x_0}^{x}(x-x_0) + \frac{1}{2!}\frac{d^2V(x)}{dx^2}\bigg|_{x_0}^{x}(x-x_0)^2 + \ldots + \frac{1}{n!}\frac{d^nV(x)}{dx^n}\bigg|_{x_0}^{x}(x-x_0)^n \tag{4.5.1}$$

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

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 \tag{4.5.2}$$

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).

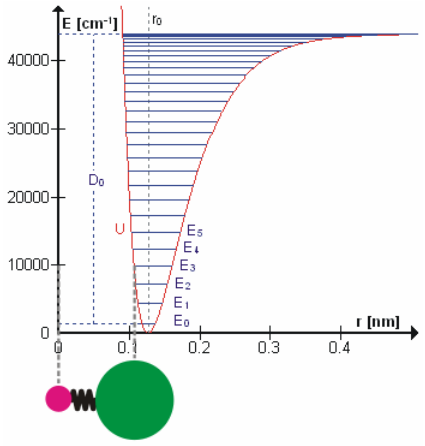


Figure 5.3.1 : The vibration of the HCl molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, HCl is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed 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 4.5.2) 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.

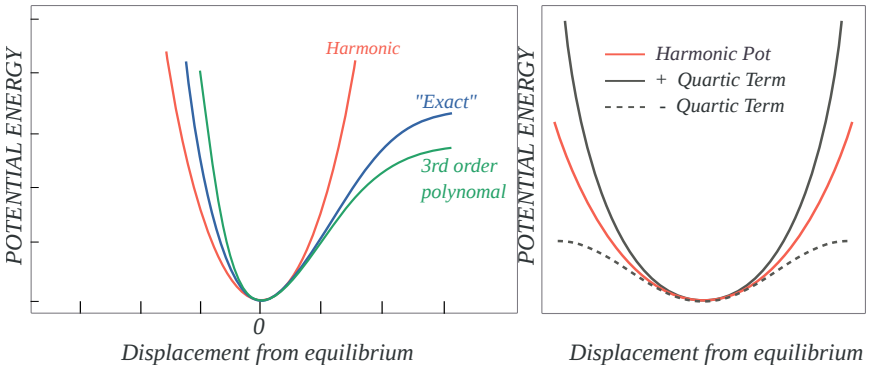


Figure 5.3.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

Naturally, adding higher order anharmonic terms, like quartic terms (Figure $4.5.2; right$) improve the approximation. Almost all diatomics have experimentally determined potentials for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 with terms up to $n < 10$ determined of Equation 4.5.1.

Figure 5.3.1 shows the the general potential with (numerically) calculated energy levels (E_0, E_1 etc.). D_o is the dissociation energy, which is different from the well depth D_e. These vibrational energy levels of this plot can be calculated using the harmonic oscillator model (i.e., Equation 5.3.1 with the Schrödinger equation) and have the general form

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

where v is the vibrational quantum number and x_e and y_e are the first and second anharmonicity constants, respectively.

The $v = 0$ level is the vibrational ground state. Because this potential is less confining than a parabola used in the harmonic oscillator, the energy levels become **less widely** spaced at high excitation (Figure 5.3.1 ; top of potential).

Limitations of the Harmonic Oscillator Model for Molecular Vibrations

The harmonic oscillation is a great approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of energy, all transitions occur at the **same** frequency (i.e. single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

Morse Potentials are better Approximations of Vibrational Motion

A more powerful approach than just "patching up" the harmonic oscillator solution with anharmonic corrections is to adopt a different potential ($V(x)$). One such approach is the Morse potential, named after physicist Philip M. Morse, and a better approximation for the vibrational structure of the molecule than the harmonic oscillator because it explicitly includes the effects of *bond breaking* and accounts for the anharmonicity of real bonds (Figure 5.3.4).

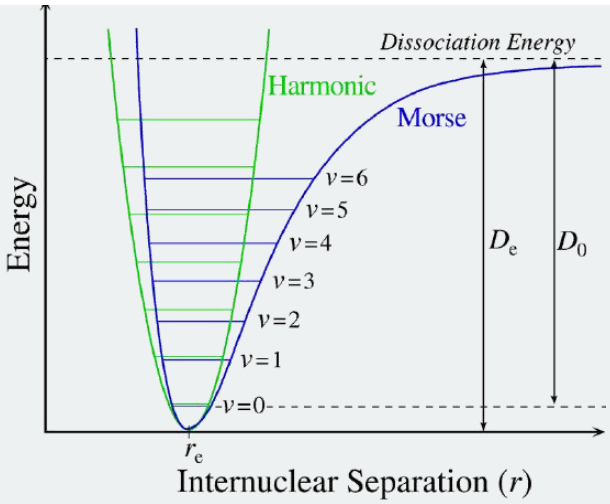


Figure 5.3.4 : The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation D_0 due to the zero point energy of the lowest ($v = 0$) vibrational level. from Wikipedia.

The Morse Potential is a good approximation to $V(x)$ and is best when looking for a general formula for all x from 0 to ∞, not just applicable for the local region around the x_o:

$$V(x) = D(1 - e^{-\beta(x-x_0)})^2 \tag{4.5.3}$$

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 4.5.3) 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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4.6: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

Learning Objectives

- Demonstrate how to use the 3D regid rotor to describe a rotating diatomic molecules
- Demonstate how microwave spectroscopy can get used to characterize rotating diatomic molecules
- Interprete a simple microwave spectrum for a diatomic molecule

To develop a description of the rotational states, we will consider the molecule to be a rigid object, i.e. the bond lengths are fixed and the molecule cannot vibrate. This model for rotation is called the rigid-rotor model. It is a good approximation (even though a molecule vibrates as it rotates, and the bonds are elastic rather than rigid) because the amplitude of the vibration is small compared to the bond length.

The rotation of a rigid object in space is very simple to visualize. Pick up any object and rotate it. There are orthogonal rotations about each of the three Cartesian coordinate axes just as there are orthogonal translations in each of the directions in three-dimensional space (Figures 5.9.1 and 5.9.2). These rotations are said to be *orthogonal* because one can not describe a rotation about one axis in terms of rotations about the other axes just as one can not describe a translation along the x-axis in terms of translations along the y- and z-axes. For a linear molecule, the motion around the interatomic axis (x-axis) is not considered a rotation.

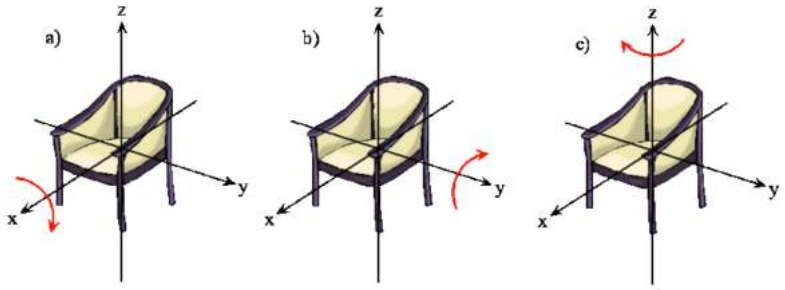


Figure 5.9.1 : Cartesian rotations of a chair. Rotations about the (a) x axis, (b) y axis, and (c) z axis.

In this section we examine the rotational states for a diatomic molecule by comparing the classical interpretation of the angular momentum vector with the probabilistic interpretation of the angular momentum wavefunctions. We want to answer the following types of questions. How do we describe the orientation of a rotating diatomic molecule in space? Is the molecule actually rotating? What properties of the molecule can be physically observed? In what ways does the quantum mechanical description of a rotating molecule differ from the classical image of a rotating molecule?

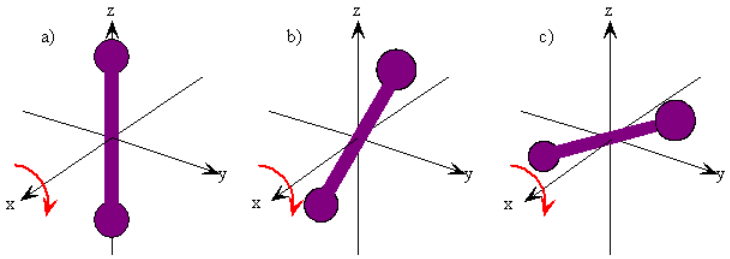


Figure 5.9.2 : Rotation of a diatomic molecule about the x axis.

Introduction to Microwave Spectroscopy

The permanent electric dipole moments of polar molecules can couple to the electric field of electromagnetic radiation. This coupling induces transitions between the rotational states of the molecules. The energies that are associated with these transitions are detected in the far infrared and microwave regions of the spectrum. For example, the microwave spectrum for carbon monoxide spans a frequency range of 100 to 1200 GHz, which corresponds to 3 - 40 cm^{-1}.

The selection rules for the rotational transitions are derived from the transition moment integral by using the spherical harmonic functions and the appropriate dipole moment operator, $\hat{\mu}$.

$$\mu_T = \int Y_{J_f}^{m_f *} \hat{\mu} Y_{J_i}^{m_i} \sin\theta \, d\theta \, d\varphi \tag{4.6.1}$$

or in braket notation

$$\mu_T = \langle Y_{J_f}^{m_f} | \hat{\mu} | Y_{J_i}^{m_i} \rangle \tag{4.6.2}$$

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,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \tag{4.6.3}$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \tag{4.6.4}$$

and

$$\Delta m_J = 0, \pm 1 \tag{4.6.5}$$

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

$$E_J = J(J+1)\frac{\hbar^2}{2I} \tag{4.6.6}$$

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

Microwave Transition Energies

The transition energies for absorption of radiation are given by

$$E_{photon} = \Delta E \tag{4.6.7}$$
$$= E_f - E_i \tag{4.6.8}$$
$$= h\nu \tag{4.6.9}$$
$$= hc\bar{\nu} \tag{4.6.10}$$

Substituting the relationship for energy (Equation 4.6.6) into Equation 4.6.8 results in

$$E_{photon} = E_f - E_i \tag{4.6.11}$$
$$= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \tag{4.6.12}$$

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 4.6.12 can be replaced by $J_i + 1$, since the selection rule requires $J_f - J_i = 1$ for the absorption of a photon (Equation 4.6.4). The equation for absorption transitions (Equation 4.6.12) then can be written in terms of the only the quantum number J_i of the initial state.

$$E_{photon} = h\nu \tag{4.6.13}$$

$$= hc\bar{\nu} \tag{4.6.14}$$

$$= 2(J_i + 1)\frac{\hbar^2}{2I} \tag{4.6.15}$$

Equation 4.6.15 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

$$B = \frac{\hbar^2}{2I} \tag{4.6.16}$$

Often spectroscopists want to express the rotational constant in terms of *frequency* of the absorbed photon and do so by dividing Equation 4.6.16 by h

$$B(\text{in freq}) = \frac{B}{h} \tag{4.6.17}$$

$$= \frac{h}{8\pi^2\mu r_0^2} \tag{4.6.18}$$

More often, spectroscopists want to express the rotational constant in terms of *wavenumbers* ($\bar{\nu}$) of the absorbed photon by dividing Equation 4.6.16 by hc,

$$\tilde{B} = \frac{B}{hc} = \frac{h}{8\pi^2 c\mu r_0^2} \tag{4.6.19}$$

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 4.6.12 to Equation 4.6.16 and identify the units of B at the end.

Answer

$$\begin{aligned}
\Delta E_{photon} &= E_f - Ei \\
E_{r.rotor} &= J(J+1)\frac{\hbar^2}{2I} \\
E_{photon} = h_\nu = hc\tilde{\nu} &= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \\
J_f - J_i &= 1 \\
J_f &= 1 + J_i \\
E_{photon} = h_\nu = hc\tilde{\nu} &= (1+J_i)(2+J_i)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \\
&= \frac{\hbar^2}{2I}[2+3J_i+J_i^2-J_i^2-J_i] \\
&= \frac{\hbar^2}{2I}2(J_i+1) \\
&= 2B(J_i+1)
\end{aligned}$$

Now we do a standard dimensional analysis

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

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

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

? Exercise 5.9.4

Infrared spectroscopists use units of wavenumbers. Rewrite the steps going from Equation 4.6.12 to Equation 4.6.16 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.

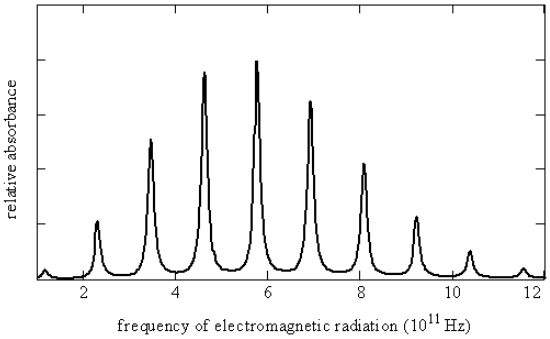


Figure 5.9.3: The rotation spectrum of $^{12}C^{16}O$ at 40 K. The peaks are tabulated in Table 5.9.1.

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

J	ν_J (MHz)	Spacing from previous line (MHz)	γ_{max}
$1 \rightarrow 2$	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 4.6.19 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%.

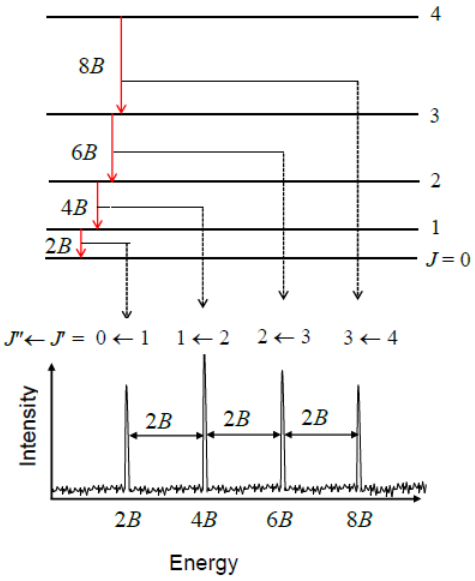


Figure 5.9.4 : Energy levels and line positions calculated in the rigid rotor approximation. (CC BY-SA 3.0; Nrrw via Wikipedia)

Exercise 5.9.5

Use Equation 4.6.19 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 $2.94\times10^{11}\ Hz$. 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 $1\ au=1.66\times10^{-27}\ kg$. Multiplying this by 0.9655gives a reduced mass of $1.603\times10^{-27}\ kg$. Substituting in for R_e gives

$$\begin{aligned}R_e&=\sqrt{\frac{(1.055\times10^{-34}\ J\cdot s)}{2\pi(1.603\times10^{-27}\ kg)(2.94\times10^{11}\ Hz)}}\\&=1.899\times10^{-10}\ m\\&=1.89\ \mathring{A}\end{aligned}$$

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

$$\begin{aligned}\Delta v&=230538.01\text{ MHz}-115271.21\text{ MHz}\\&=115266.8\text{ MHz}\\&=1.153\times10^{11}\text{ Hz}\\&=\frac{\hbar}{2\pi\mu R_e^2}\end{aligned}$$

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 4.6.16) 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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4.7: 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:

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_l^{m_l}(\theta,\phi) \tag{4.7.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and ϕ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the nucleus in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\phi)|^2$, evaluated at r, θ, and ϕ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and ϕ.

? Exercise 6.2.1

What is the value of the integral (in braket notation)

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

or expanded in integral notation (in Cartesian coordinates)

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} |\psi(x,y,z)|^2 \, dx \, dy \, dz$$

or expanded in integral notation (in spherical coordinates)

$$\int_{0}^{+\infty}\int_{0}^{\pi}\int_{0}^{+2\pi} |\psi(r,\theta,\phi)|^2 r^2 \sin\theta \, d\theta \, d\phi \, dr$$

Answer

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 $Y_J^m(\theta,\phi)$.

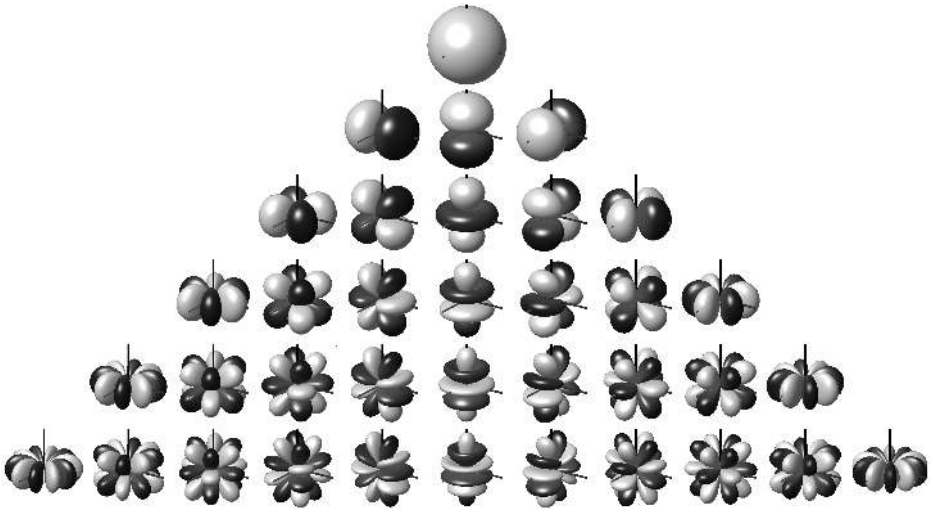


Figure 6.2.1: Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.

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:

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

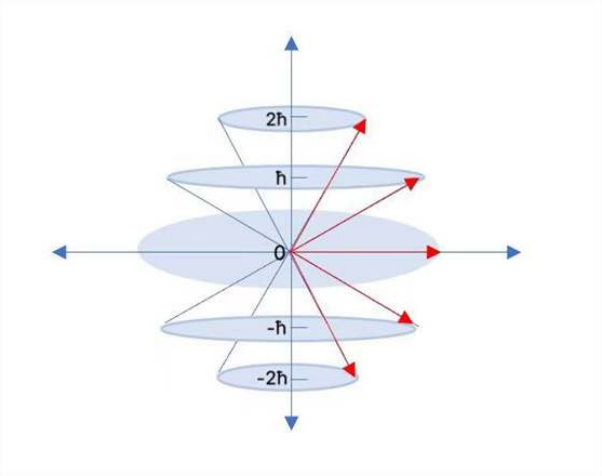
and angular momentum

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

c. Magnetic quantum number:

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

d.



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	$m_l = 0$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(27-18\frac{Zr}{a_0}+2$
ψ_{310}	3	1	$m_l = 0$	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}$

	n	l	m_l	ψ_{n,l,m_l}
$\psi_{31\pm1}$	3	1	$m_l = \pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right)e^{-\frac{Zr}{3a_0}}$
ψ_{320}	3	2	$m_l = 0$	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}}\left(3\cos^2\theta\right.$
$\psi_{32\pm1}$	3	2	$m_l = \pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}}\sin\theta\cos\theta$
$\psi_{32\pm2}$	3	2	$m_l = \pm2$	$\frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}}\sin^2\theta e^{\pm2}$

We can take superposition states of the solutions to obtain real wavefunctions that do not have any imaginary components:

Table 6.2.2 : The real solutions to the Schrödinger equation for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

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

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 .

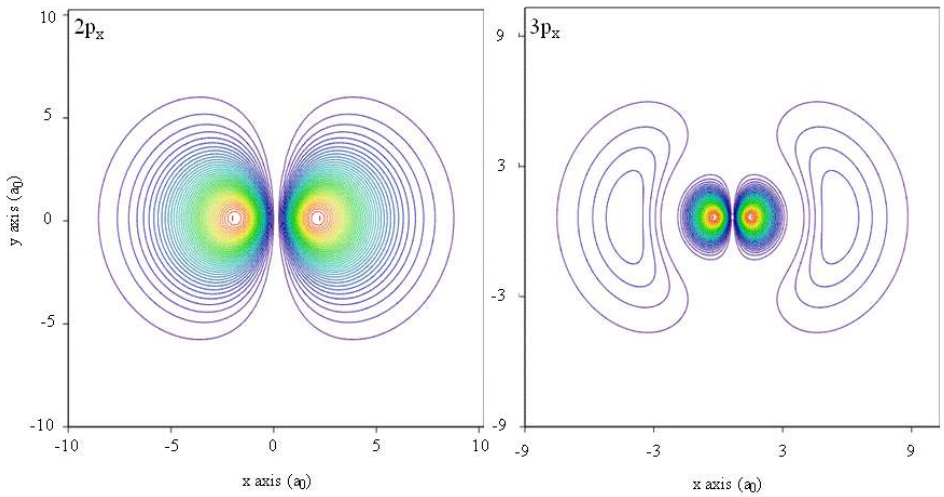


Figure 6.2.2: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical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

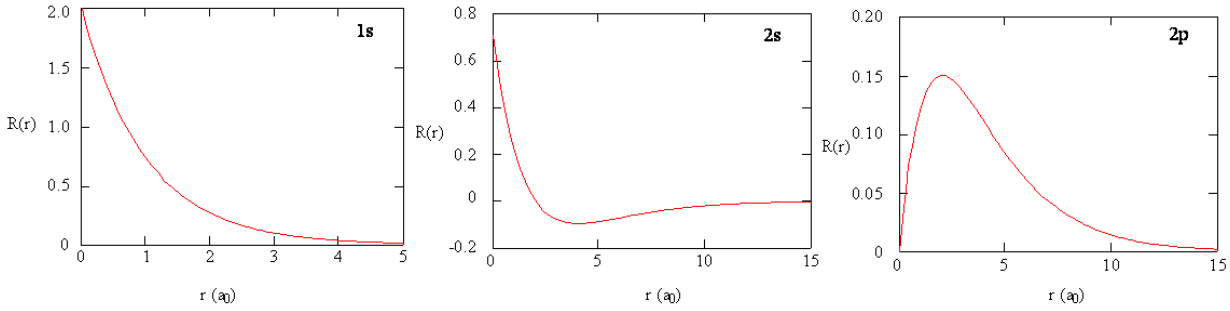


Figure 6.2.3: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

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 .

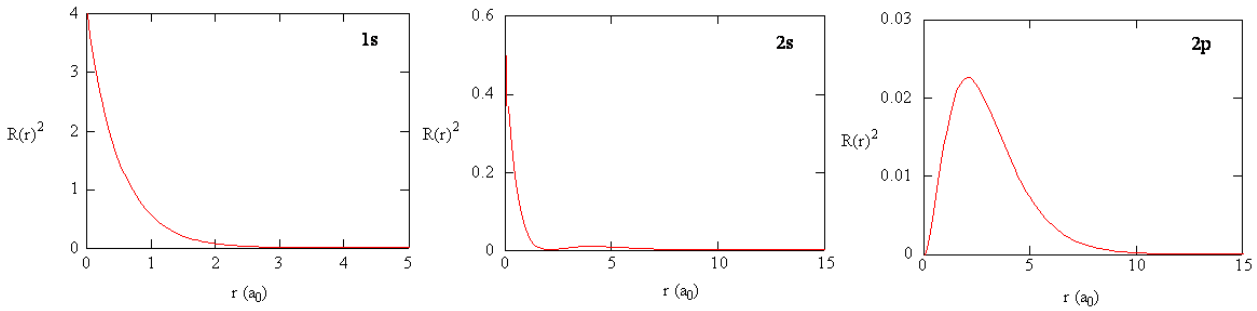


Figure 6.2.4: Radial probability densities for the 1s, 2s, and 2p orbitals.

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.

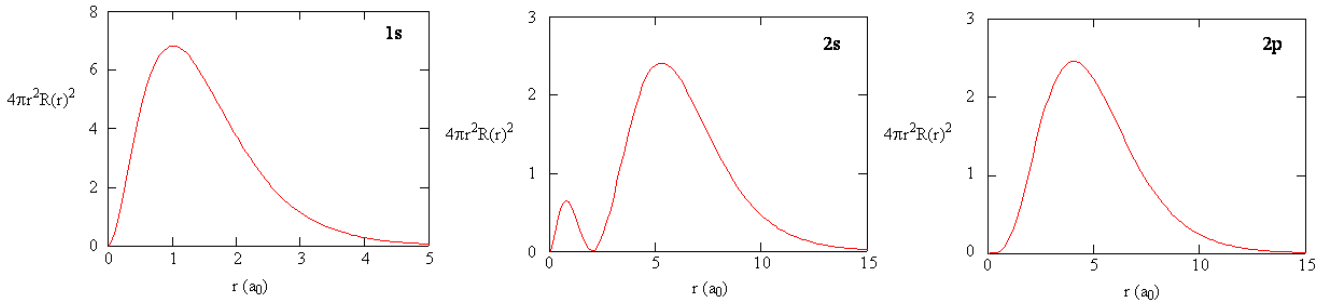


Figure 6.2.5: The radial distribution function for the 1s, 2s, and 2p orbitals.

? 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.

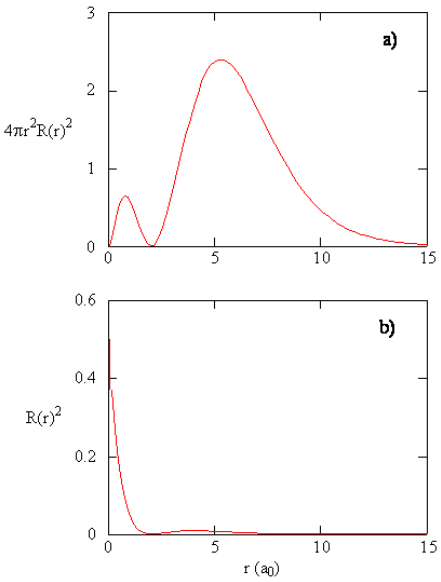


Figure 6.2.6: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

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4.8: The Energy Levels of a Rigid Rotor

Learning Objectives

- Compare the classical and quantum rigid rotor in three dimensions
- Demonstrate how to use the Separation of Variable technique to solve the 3D rigid rotor Schrödinger Equation
- Identify and interpret the two quantum numbers for a 3D quantum rigid rotor including the range of allowed values
- Describe the wavefunctions of the 3D quantum rigid rotor in terms of nodes, average displacements and most probable displacements
- Describe the energies of the 3D quantum rigid rotor in terms of values and degeneracies

Rigid rotor means when the distance between particles do not change as they rotate. A rigid rotor only approximates a rotating diatomic molecular if vibration is ignored.

The Classical Rigid Rotor in 3D

The **rigid rotor** is a mechanical model that is used to explain rotating systems. The linear rigid rotor model consists of two point masses located at fixed distances from their center of mass. The fixed distance between the two masses and the values of the masses are the only characteristics of the rigid model. However, for many actual diatomics this model is too restrictive since distances are usually not completely fixed and corrections on the rigid model can be made to compensate for small variations in the distance. Even in such a case the rigid rotor model is a useful model system to master.

For a rigid rotor, the total energy is the sum of kinetic (T) and potential (V) energies

$$E_{tot} = T + V \tag{4.8.1}$$

The potential energy, V, is set to 0 because the distance between particles does not change within the rigid rotor approximation. However, In reality, $V \neq 0$ because even though the average distance between particles does not change, the particles still vibrate. The rigid rotor approximation greatly simplifys our discussion.

Since $V = 0$ then $E_{tot} = T$ and we can also say that:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{4.8.2}$$

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

$$\omega = \frac{v}{r} \tag{4.8.3}$$

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

$$v_i = \omega X r_i \tag{4.8.4}$$

Thus we can rewrite Equation 4.8.2 as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{4.8.5}$$

Since ω is a scalar constant, we can rewrite Equation 4.8.5 as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{4.8.6}$$

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,

$$L = I\omega \tag{4.8.7}$$

where I is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite Equation 4.8.2 as

$$T = \omega\frac{I\omega}{2} = \frac{1}{2}I\omega^2 \tag{4.8.8}$$

Equation 4.8.8 shows that the energy of the rigid rotor scales with increasing angular frequency (i.e., the faster is rotates) and with increasing moment of inertia (i.e, the inertial resistance to rotation). Also, as expected, the classical rotational energy is not quantized (i.e., all possible rotational frequencies are possible).

The Quantum Rigid Rotor in 3D

It is convenient to discuss rotation with in the spherical coordinate system rather than the Cartesian system (Figure 5.8.1).

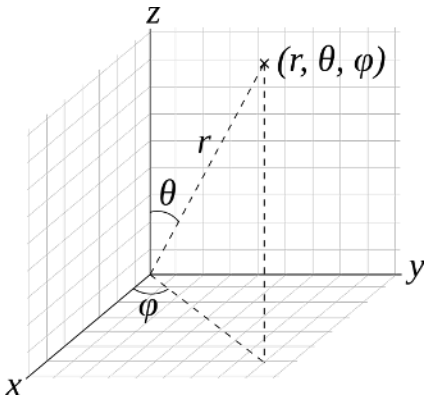


Figure 5.8.1 : The spherical coordinate system in terms of the Cartesian system. (Public Domain; Andeggs via Wikipedia).

To solve the Schrödinger equation for the rigid rotor, we will separate the variables and form single-variable equations that can be solved independently. Only two variables θ and φ are required in the rigid rotor model because the bond length, r, is taken to be the constant r_0. We first write the rigid rotor wavefunctions as the product of a theta-function depending only on θ and a phi-function depending only on φ

$$|\psi(\theta,\varphi)\rangle = |\Theta(\theta)\Phi(\varphi)\rangle \tag{4.8.9}$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 4.8.10

$$\hat{H}|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{4.8.10}$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{\partial}{\partial r_0}r_0^2\frac{\partial}{\partial r_0}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{4.8.11}$$

Since $r = r_0$ is constant for the **rigid rotor** and does not appear as a variable in the functions, the partial derivatives with respect to r are zero; i.e. the functions do not change with respect to r. We also can substitute the symbol I for the moment of inertia, μr_0^2 in the denominator of the left hand side of Equation 4.8.11, to give

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{4.8.12}$$

To begin the process of the Separating of Variables technique, multiply each side of Equation 4.8.12 by $\frac{2I}{\hbar^2}$ and $\frac{-\sin^2\theta}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi) = \frac{-2IE\sin^2\theta}{\hbar^2} \tag{4.8.13}$$

Simplify the appearance of the right-hand side of Equation 4.8.13 by defining a parameter λ:

$$\lambda = \frac{2IE}{\hbar^2}. \tag{4.8.14}$$

Note that this λ has no connection to a wavelength; it is merely being used as an algebraic symbol for the combination of constants shown in Equation 4.8.14.

Inserting λ, evaluating partial derivatives, and rearranging Equation 4.8.13 produces

$$\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta\right)\Theta(\theta)\right]=-\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) \tag{4.8.15}$$

? Exercise 5.8.1

Carry out the steps leading from Equation 4.8.13 to Equation 4.8.15. Keep in mind that, if y is not a function of x,

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

Equation 4.8.15 says that the function on the left, depending only on the variable θ, always equals the function on the right, depending only on the variable φ, for all values of θ and φ. The only way two different functions of independent variables can be equal for all values of the variables is if both functions are equal to a constant (review separation of variables). We call this constant m_J^2 because soon we will need the square root of it. The two differential equations to solve are the θ-equation

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta-m_J^2\right)\Theta(\theta)=0 \tag{4.8.16}$$

and the φ-equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_J^2\Phi(\varphi)=0 \tag{4.8.17}$$

The partial derivatives have been replaced by total derivatives because only a single variable is involved in each equation.

> *Often m_J is referred to as just m for convenience.*

? Exercise 5.8.2

Show how Equations 4.8.16 and 4.8.17 are obtained from Equation 4.8.15.

Solving the φ Equation

The φ-equation is similar to the Schrödinger Equation for the free particle. Since we already solved this previously, we immediately write the solutions:

$$\Phi_m(\varphi)=Ne^{\pm im_J\varphi} \tag{4.8.18}$$

where we introduce the number m to track how many wavelengths of the wavefunction occur around one rotation (similar to the wavelength description of the Bohr atom).

? Exercise 5.8.3

Substitute Equation 4.8.18 into Equation 4.8.17 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

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

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

Thus

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

is a solution to the differential equations.

The normalization condition, Equation 4.8.19 is used to find a value for N that satisfies Equation 4.8.18.

$$\int_0^{2\pi}\Phi^*(\varphi)\Phi(\varphi)d\varphi=1 \tag{4.8.19}$$

The range of the integral is only from 0 to 2π because the angle φ specifies the position of the internuclear axis relative to the x-axis of the coordinate system and angles greater than 2π do not specify additional new positions.

? Exercise 5.8.4

Use the normalization condition in Equation 4.8.19 to demonstrate that $N=1/\sqrt{2\pi}$.

Answer

We need to evaluate Equation 4.8.19 with $\psi(\varphi)=Ne^{\pm imJ\varphi}$

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

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.

$$e^{im_J\varphi}=e^{im_J(\varphi+2\pi)} \tag{4.8.20}$$
$$=e^{im_J\varphi}e^{im_J2\pi} \tag{4.8.21}$$

For the equality in Equation 4.8.21 to hold, $e^{im_J2\pi}$ must equal 1, which is true only when

$$m_J=\cdots,-3,-2,-1,0,1,2,3,\cdots \tag{4.8.22}$$

In other words m_J can equal **any positive or negative integer or zero.**

? Exercise 5.8.5 : Cyclic Boundary Conditions

Use Euler's Formula to show that $e^{im_J2\pi}$ equals 1 for m_J equal to zero or any positive or negative integer.

Thus, the Φ function is

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

with

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

Solving the $\Theta(\theta)$ Equation

Finding the $\Theta(\theta)$ functions that are solutions to the θ-equation (Equation 4.8.16) is a more complicated process. Solutions are found to be a set of power series called *Associated Legendre Functions* (Table M2), which are power series of trigonometric functions, i.e., products and powers of sine and cosine functions. The $\Theta(\theta)$ functions, along with their normalization constants, are shown in the third column of Table 5.8.1 .

Table 5.8.1 : Spherical Harmonic Wavefunctions

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta,\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

The solution to the θ-equation requires that λ in Equation 4.8.15 be given by

$$\lambda = J(J+1) \tag{4.8.23}$$

where

$$J \geq |m_J| \tag{4.8.24}$$

J can be 0 or any positive integer greater than or equal to m_J. Each pair of values for the quantum numbers, J and m_J, identifies a rotational state with a wavefunction (Equation 4.8.9) and energy (below). Equation 4.8.24 means that J controls the allowed values of m_J.

> *Each pair of values for the quantum numbers, J and m_J, identifies a rotational state and hence a specific wavefunction with associated energy.*

The combination of Equations 4.8.14 and 4.8.23 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2\lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{4.8.25}$$

Using Equation 4.8.25, you can construct a rotational energy level diagram (Figure 5.8.2). For simplicity, use energy units of $\frac{\hbar^2}{2I}$.

- $J = 0$: The lowest energy state has $J = 0$ and $m_J = 0$. This state has an energy $E_0 = 0$. There is only **one state** with this energy, i.e. one set of quantum numbers, one wavefunction, and one set of properties for the molecule.
- $J = 1$: The next energy level is $J = 1$ with energy $\frac{2\hbar^2}{2I}$. There are **three states** with this energy because m_J can equal +1, 0, or -1. These different states correspond to different orientations of the rotating molecule in space. States with the same energy are said to be degenerate. The degeneracy of an energy level is the number of states with that energy. The degeneracy of the $J = 1$ energy level is 3 because there are three states with the energy $\frac{2\hbar^2}{2I}$.
- $J = 2$: The next energy level is for $J = 2$. The energy is $\frac{6\hbar^2}{2I}$, and there are **five states** with this energy corresponding to $m_J = +2,\ +1,\ 0,\ -1,\ -2$. The energy level degeneracy is five. Note that the spacing between energy levels increases as J increases. Also note that the degeneracy increases. The degeneracy is always $2J+1$ because m_J ranges from $+J$ to $-J$ in integer steps, including 0.

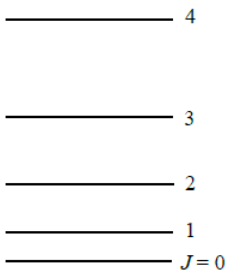


Figure 5.8.2 : Energy spacing for a rigid rotor (in 3D). Notice the energy depends only on J and not depend on m_J. That is, the energy of the rotor is not affected by its orientation.

> *Each allowed energy of rigid rotor is $(2J+1)$-fold degenerate. Hence, there exist $(2J+1)$ different wavefunctions with that energy.*

Exercise 5.8.6

Compute the energy levels for a rotating molecule for $J = 0$ to $J = 5$ using units of $\frac{\hbar^2}{2I}$.

Answer

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 4.8.25):

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

Using this equation, we can plug in the different values of the J quantum number so that

For J=0, $E = (0)(1)(\hbar^2/2I) = 0$ For J=1, $E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$

This shows that as J increases, the energy levels get farther apart (Figure 5.8.2).

- For J=2, $E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For J=3, $E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For J=4, $E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For J=5, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

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 4.8.25), which measures the length of the vector, not its direction given mb m_J.

Example 5.8.7 : Molecular Oxygen

Calculate $J = 0$ to $J = 1$ rotational transition of the O_2 molecule with a bond length of 121 pm.

Solution

$$E = \frac{\hbar^2}{I} = \frac{\hbar^2}{\mu r^2}$$

$$\mu_{O2} = \frac{m_O m_O}{m_O + m_O} = \frac{(15.9994)(15.9994)}{15.9994 + 15.9994} = 7.9997$$

convert from atomic units to kilogram using the conversion: 1 au = 1.66 x 10^{-27} kg. Plug and chug.

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

Spherical Harmonics

A wavefunction that is a solution to the rigid rotor Schrödinger Equation (Equation 4.8.9) can be written as a single function $Y(\theta, \varphi)$, which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{4.8.26}$$

The spherical harmonic wavefunction is labeled with m_J and J because its functional form depends on both of these quantum numbers. These functions are tabulated above for $J = 0$ through $J = 2$ and for $J = 3$ in the Spherical Harmonics Table (M4)

Polar plots of some of the θ-functions are shown in Figure 5.8.3 .

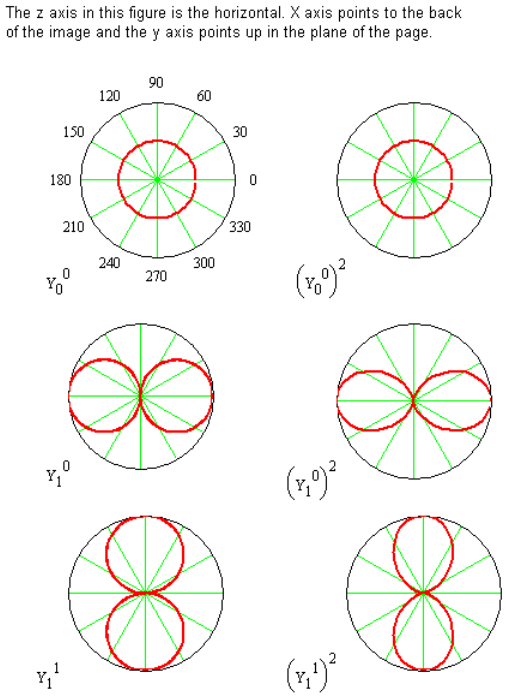


Figure 5.8.3 : Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

The two-dimensional space for a rigid rotor is defined as the surface of a sphere of radius r_0, as shown in Figure 5.8.2 .

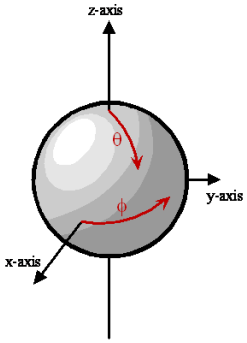


Figure 5.8.4 : Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

The probability of finding the internuclear axis at specific coordinates θ_0 and φ_0 within an infinitesimal area ds on this curved surface is given by

$$Pr\left[\theta_0, \varphi_0\right] = Y_J^{m_{J*}}(\theta_0, \varphi_0) Y_J^{m_J}(\theta_0, \varphi_0) ds \tag{4.8.27}$$

where the area element ds is centered at θ_0 and φ_0.

Within the Copenhagen interpretation of wavefunctions, the absolute square (or modulus squared) of the rigid rotor wavefunction $Y_J^{m_{J*}}(\theta, \varphi) Y_J^{m_J}(\theta, \varphi)$ gives the probability density for finding the internuclear axis oriented at θ to the z-axis and φ to the x-axis. In spherical coordinates the area element used for integrating θ and φ is

$$ds = \sin\theta \, d\theta \, d\varphi \tag{4.8.28}$$

? Exercise 5.8.8

Use calculus to evaluate the probability of finding the internuclear axis of a molecule described by the $J = 1$, $m_J = 0$ wavefunction somewhere in the region defined by a range in θ of 0° to 45°, and a range in of 0° to 90°. Note that a double

integral will be needed. Sketch this region as a shaded area on Figure 5.8.1 .

Consider the significance of the probability density function by examining the $J = 1$, $m_J = 0$ wavefunction. The Spherical Harmonic for this case is

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \tag{4.8.29}$$

The polar plot of $(Y_1^0)^2$ is shown in Figure 5.8.1 . For $J = 1$ and $m_J = 0$, the probability of finding the internuclear axis is independent of the angle φ from the x-axis, and greatest for finding the internuclear axis along the z-axis, but there also is a probability for finding it at other values of θ as well. So, although the internuclear axis is not always aligned with the z-axis, the probability is highest for this alignment. Also, since the probability is independent of the angle φ, the internuclear axis can be found in any plane containing the z-axis with equal probability.

The $J = 1$, $m_J = 0$ function is 0 when θ = 90°. Therefore, the entire xy-plane is a **node**. This fact means the probability of finding the internuclear axis in this particular horizontal plane is 0 in contradiction to our classical picture of a rotating molecule. In the classical picture, a molecule rotating in a plane perpendicular to the xy-plane must have the internuclear axis lie in the xy-plane twice every revolution, but the quantum mechanical description says that the probability of being in the xy-plane is zero. This conclusion means that molecules are not rotating in the classical sense, but they still have some, but not all, of the properties associated with classical rotation. The properties they retain are associated with angular momentum.

? Exercise 5.8.9

For each state with $J = 0$ and $J = 1$, use the function form of the Y spherical harmonics and Figure 5.8.1 to determine the most probable orientation of the internuclear axis in a diatomic molecule, i.e., the most probable values for θ and θ.

? Exercise 5.8.10

Write a paragraph describing the information about a rotating molecule that is provided in the polar plot of $Pr[\theta, \theta]$ for the $J = 1$, $m_J = \pm 1$ state in Figure 5.8.1 . Compare this information to the classical picture of a rotating object.

Summary

There are two quantum numbers that describe the quantum behavior of a rigid rotor in three-deminesions: J is the total angular momentum quantum number and m_J is the z-component of the angular momentum. The spherical harmonics called $Y_J^{m_J}$ are functions whose probability $|Y_J^{m_J}|^2$ has the well known shapes of the s, p and d orbitals etc learned in general chemistry.

References

1. Anderson, J.M. Introduction to Quantum Chemistry, 1969, W.A. Benjamin, Inc, pg.91-100.
2. Atkins, Peter and de Paula, Julio. Physical Chemistry for the Life Sciences. New York: W.H. Freeman and Company. p. 515.

Contributors and Attributions

- Ian Huh
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Mark Tuckerman (New York University)
- MIT OpenCourseWare (Robert Guy Griffin and Troy Van Voorhis)

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CHAPTER OVERVIEW

5: Rotational and Vibrational Spectroscopy

5.1: The Harmonic Oscillator and Infrared Spectra
5.2: The Harmonic Oscillator Selection Rule
5.3: Rotations Accompany Vibrational Transitions
5.4: The Selection Rule for the Rigid Rotor
5.5: Unequal Spacings in Vibration-Rotation Spectra
5.6: Unequal Spacings in Pure Rotational Spectra
5.7: Vibrational Overtones
5.8: Normal Modes in Polyatomic Molecules
5.9: Group Theory Determines Infrared Activity

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5.1: The Harmonic Oscillator and Infrared Spectra

Learning Objectives

- Understand how the quantum harmonic oscillator model can be used to interpret the infrared spectra of diatomic molecules
- Understand the origin of the transition moment integral and selection rules and how they are related

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups. IR spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

IR Spectroscopy

Transitions between vibrational energy levels can be induced about by absorption or emission of radiation. To understand this, knowledge of both the initial and final eigenstates is needed. The energy of the vth eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.1.1}$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞. Equation 5.1.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \tag{5.1.2}$$

where ν_m is the vibrational frequency of the vibration. Equation 5.1.2 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

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v)\, h\nu_m \end{aligned} \tag{5.1.3}$$

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 5.1.3 simplifies to

$$h\nu_{photon} = h\nu_m$$
$$= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.1.4}$$

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:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{5.1.5}$$
$$= \frac{\nu\,(Hz)}{c\,(cm/s)} \tag{5.1.6}$$

Equation 5.1.3 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{5.1.7}$$

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

$$\omega = 2\pi\nu$$
$$= 5.54 \times 10^{14}\,rad/s$$

We can then extra the ground state vibrational energy (aka zero-point energy) from

$$E_o = \frac{1}{2}\hbar\omega$$
$$= \frac{1}{2}\hbar(5.54 \times 10^{14} rad/s)$$
$$= 2.916 \times 10^{-20}\ J$$

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

$$\text{Percent bond length} = \frac{Q_0}{x_{eq}} \times 100\%$$
$$= \frac{0.110\, nm}{0.127\, nm} \times 100\%$$
$$= 86.6\%$$

Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can transition from one vibrational energy state to another. Which transitions between vibrational states are allowed? When discussing the Bohr hydrogen atom in Chapter 1, we identified multiple transitions between different states as being responsible for the line spectra emission of the hydrogen atom. No limitations were identified so that any transition between any starting state and ending state was possible and this resulted in a complex pattern in the spectra. As we will identify later on, when considering mulit-electron atoms, there are **selection rules** that limits which transitions will be observed (i.e., are allowed).

A similar situation exist for the harmonic oscillator and IR transitions and a set of selection rules must be satisfied to ensure a particular transition is allowed. Selection rules result from evaluating a **transition moment integral** that expresses the probability of a transition from the v to the v' eigenstates:

$$\mu_T = \langle \psi_{v'} | \hat{\mu}(x) | \psi_v \rangle \tag{5.1.8}$$
$$= \int_{-\infty}^{\infty} \psi_{v'}^*(x)\hat{\mu}(x)\psi_v(x)dx \tag{5.1.9}$$

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.

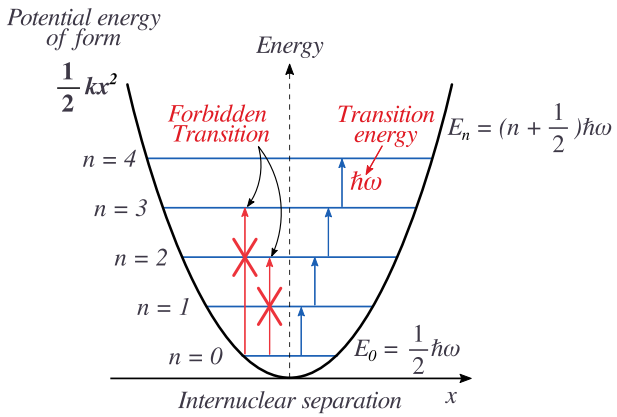


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 5.1.9, 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

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{5.1.10}$$

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 ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left.\frac{d\mu(x)}{dx}\right|_{x=0} x + \left.\frac{d^2\mu(x)}{dx^2}\right|_{x=0} x^2 + \cdots \tag{5.1.11}$$

Retaining only the first two terms and substituting into Equation 5.1.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left.\frac{d\mu(x)}{dx}\right|_{x=0} \int_{-\infty}^{\infty} x\psi^*_{v'}(x)\psi_v(x)dx \tag{5.1.12}$$

where $\mu_{x=0} = 0$ 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 5.1.11. 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 5.1.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 5.1.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1 . Also note that the second term is zero if

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0} = 0 \tag{5.1.13}$$

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 5.1.12 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 5.1.13 **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

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{5.1.14}$$

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 5.1.4. 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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5.2: The Harmonic Oscillator Selection Rule

Selection rules are a very important concept in spectroscopy and physical chemistry, as they directly complement the concept that systems on the atomic level are quantized. Quantization tells us how electrons, neutrons, and protons are set up, and selection rules tell us how, energetically speaking, they may move about. For example, the principal quantum number, n, determines the energy state of particles in the Particle in a Box model. With respect to real systems, the quantum number n describes electronic transitions, such as the excitation of an electron. There are other transitions, such as the rotational transition, which applies to the rigid rotator model and occurs where there are spherical harmonics. Vibrational transitions occur where there is a system that can be visualized as two masses connected by a spring, such as a diatomic molecule.

Selection rules can be very useful in spectroscopy for obtaining information about an unknown substance; any given substance has properties and behaviors that operate within the selection rules and determine the wavelengths of electromagnetic radiation (light) that cause transitions. By tracking these properties, chemists can use techniques like IR spectroscopy to determine the chemical structure of a molecule. For example, a selection rule might govern how a quantum number changes during a transition. That quantum number appears in equations that determine the energy transition based on the mass and other structural properties of a molecule. Thus, if one knows the selection rules and the energy transition, he or she can determine other properties about the molecule, such as its mass or its bond strength.

✔ Example: Evaluating vibrational transitions using a transition moment integral.

Vibrational systems are described by the harmonic oscillator wavefunctions, which look like

$$\Psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

A transition dipole moment can be written to describe a transition along the z-axis.

$$\mu_z = \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}\mu_z(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

μ is the dipole moment, so we pull it out of the integral.

$$\mu_z = \mu_z \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

Using the idea that the transition moment μ_z changes on x, we express it as a derivative.

$$\mu_z = \frac{d\mu}{dx} \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

To evaluate the integral, we take advantage of a special Hermite relationship: $\sqrt{\alpha}x H_v(\sqrt{\alpha}x) = vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)$

$$\mu_z = \frac{N_v N_{v+1}}{\sqrt{\alpha}}\left(\frac{d\mu}{dx}\right) \int_{-\infty}^{\infty} H_{v+1}(\sqrt{\alpha}x)e^{(}-\alpha x^2/2)[vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)]dx$$

By inspection, it is clear that the integral only allows transitions of $\Delta v = \pm 1$, because for any other value, the integral will be zero.

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5.3: Rotations Accompany Vibrational Transitions

Each of the modes of vibration of diatomic molecules in the gas phase also contains closely-spaced (1-10 cm^{-1} difference) energy states attributable to rotational transitions that accompany the vibrational transitions. A molecule's rotation can be affected by its vibrational transition because there is a change in bond length, so these rotational transitions are expected to occur. Since vibrational energy states are on the order of 1000 cm^{-1}, the rotational energy states can be superimposed upon the vibrational energy states.

Selection Rules

Rotational and Vibration transitions (also known as rigid rotor and harmonic oscillator) of molecules help us identify how molecules interact with each other, their bond length as mentioned in previous section. In order to know each transitions, we have to consider other terms like wavenumber, force constant, quantum number, etc. There are rotational energy levels associated with all vibrational levels. From this, vibrational transitions can couple with rotational transitions to give **rovibrational spectra**. Rovibrational spectra can be analyzed to determine average bond length.

We treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete levels and given by

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

Where v is the vibrational quantum number and can have integer values 0, 1, 2..., and ν is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)\frac{1}{2}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{5.3.1}$$

We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_r = \frac{h^2}{8\pi^2 I}J(J+1)$$

In which I is the moment of inertia, given by

$$I = \mu r^2$$

where μ is the reduced mass (Equation 5.3.1) and r is the equilibrium bond length.

Experimentally, frequencies or wavenumbers are measured rather than energies, and dividing by h or hc gives more commonly seen term symbols, $F(J)$ using the rotational quantum number J and the rotational constant B in either frequency

$$F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I}J(J+1) = BJ(J+1)$$

or wavenumbers

$$\tilde{F}(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = \tilde{B}J(J+1)$$

> It is important to note in which units one is working since the rotational constant is always represented as B, whether in frequency or wavenumbers.

- **Vibrational Transition Selection Rules**: At room temperature, typically only the lowest energy vibrational state v= 0 is populated, so typically v_0 = 0 and Δv = +1. The full selection rule is technically that Δv = ±1, however here we assume energy

can only go upwards because of the lack of population in the upper vibrational states.

- **Rotational Transition Selection Rules**: At room temperature, states with J≠0 can be populated since they represent the fine structure of vibrational states and have smaller energy differences than successive vibrational levels. Additionally, ΔJ = ±1 since a photon contains one quantum **of angular momentum** and we abide by the principle of **conservation of energy**. This is also the selection rule for rotational transitions.

These two selection rules mean that the transition ΔJ = 0 (i.e. J" = 0 and J' = 0, but $\nu_0 \neq 0$ is forbidden and the pure vibrational transition is not observed in most cases. The rotational selection rule gives rise to an R-branch (when ΔJ = +1) and a P-branch (when ΔJ = -1). Each line of the branch is labeled R(J) or P(J), where J represents the value of the lower state Figure 13.2.1).

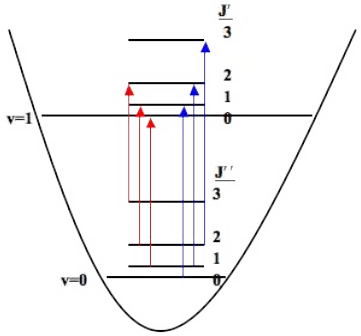


Figure 13.2.1 : Rotation-Vibration Transitions. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.

R-branch

When ΔJ = +1, i.e. the rotational quantum number in the ground state is one more than the rotational quantum number in the excited state – R branch (in French, *riche* or rich). To find the energy of a line of the R-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{5.3.2}$$

$$= h\nu_0 + hB[(J+1)(J+2) - J(J+1)] \tag{5.3.3}$$

$$= h\nu_0 + 2hB(J+1) \tag{5.3.4}$$

P-branch

When ΔJ = -1, i.e. the rotational quantum number in the ground state is one less than the rotational quantum number in the excited state – P branch (in French, *pauvre* or poor). To find the energy of a line of the P-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{5.3.5}$$

$$= h\nu_0 + hB[J(J-1) - J(J+1)] \tag{5.3.6}$$

$$= h\nu_0 - 2hBJ \tag{5.3.7}$$

Q-branch

When ΔJ = 0, i.e. the rotational quantum number in the ground state is the same as the rotational quantum number in the excited state – Q branch (simple, the letter between P and R). To find the energy of a line of the Q-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{5.3.8}$$

$$= h\nu_0 \tag{5.3.9}$$

The Q-branch can be observed in polyatomic molecules and diatomic molecules with electronic angular momentum in the ground electronic state, e.g. nitric oxide, NO. Most diatomics, such as O_2, have a small moment of inertia and thus very small angular momentum and yield no Q-branch.

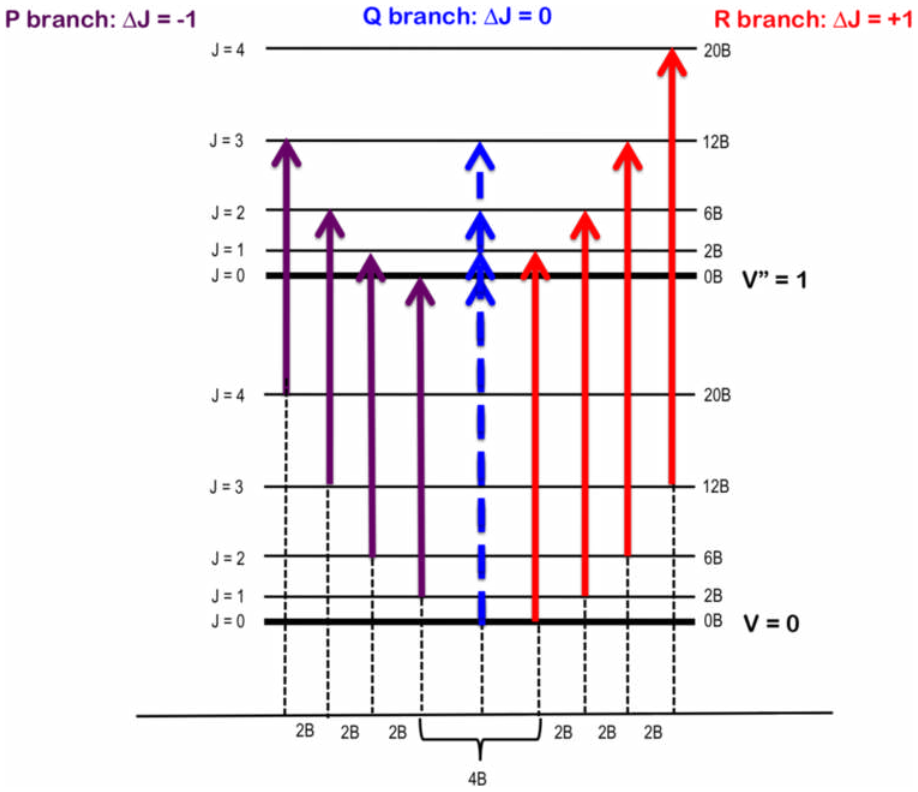


Figure 13.2.3 : Cartoon depiction of rotational energy levels, J, imposed on vibrational energy levels, v. The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.

As seen in Figure 13.2.2 , the lines of the P-branch (represented by purple arrows) and R-branch (represented by red arrows) are separated by specific multiples of B (i.e, $2B$), thus the bond length can be deduced without the need for pure rotational spectroscopy.

The total nuclear energy of the combined rotation-vibration terms, $S(v, J)$, can be written as the sum of the vibrational energy and the rotational energy

$$S(v, J) = G(v) + F(J)$$

where $G(v)$ represents the energy of the harmonic oscillator, ignoring anharmonic components and $S(J)$ represents the energy of a rigid rotor, ignoring centrifugal distortion.

From this, we can derive

$$S(v, J) = \nu_0 \left(v + \frac{1}{2} \right) + BJ(J+1)$$

The spectrum we expect, based on the conditions described above, consists of lines equidistant in energy from one another, separated by a value of $2B$. The *relative* intensity of the lines is a function of the rotational populations of the ground states, i.e. the intensity is proportional to the number of molecules that have made the transition. The *overall* intensity of the lines depends on the vibrational transition dipole moment.

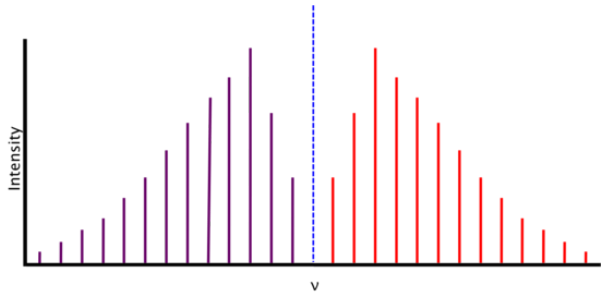


Figure 13.2.3 : A cartoon depiction of an ideal rovibrational spectrum.

In Figure 13.2.2 , between $P(1)$ and $R(0)$ lies the zero gap, where the the first lines of both the P- and R-branch are separated by $4B$, assuming that the rotational constant B is equal for both energy levels. The zero gap is also where we would expect the Q-branch, depicted as the dotted line, if it is allowed.

Advanced Concept: Occupations (Peak Intensities)

The relative intensity of the P- and R-branch lines depends on the thermal distribution of electrons; more specifically, they depend on the population of the lower J state. If we represent the population of the Jth upper level as N_J and the population of the lower state as N_0, we can find the population of the upper state relative to the lower state using the Boltzmann distribution:

$$\frac{N_J}{N_0} = (2J+1)e^{\left(-\frac{E_r}{kT}\right)}$$

(2J+1) gives the degeneracy of the Jth upper level arising from the allowed values of M_J (+J to –J). As J increases, the degeneracy factor increases and the exponential factor decreases until at high J, the exponential factor wins out and N_J/N_0 approaches zero at a certain level, J_{max}. Thus, when

$$\frac{d}{dJ}\left(\frac{N_J}{N_0}\right) = 0$$

by differentiation, we obtain

$$J_{max} = \left(\frac{kT}{2hB}\right)^{\frac{1}{2}} - \frac{1}{2}$$

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 13.2.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

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5.4: The Selection Rule for the Rigid Rotor

A **selection rule** describes how the probability of transitioning from one level to another cannot be **zero**. It has two sub-pieces: a **gross selection rule** and a **specific selection rule**. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. Incident electromagnetic radiation presents an oscillating electric field $E_0 \cos(\omega t)$ that interacts with a transition dipole. The dipole operator is $\mu = e \cdot r$ where r is a vector pointing in a direction of space.

A dipole moment of a given state is

$$\mu_z = \int \Psi_1{}^* \mu_z \Psi_1 \, d\tau$$

A transition dipole moment is a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule

$$(\mu_z)_{12} = \int \Psi_1{}^* \mu_z \Psi_2 \, d\tau$$

In an experiment we present an electric field along the z axis (in the laboratory frame) and we may consider specifically the interaction between the transition dipole along the x, y, or z axis of the molecule with this radiation. If μ_z is zero then a transition is forbidden. The selection rule is a statement of when μ_z is non-zero.

> *The selection rule is a statement of when μ_z is non-zero.*

Rotational transitions

We can use the definition of the transition moment and the spherical harmonics to derive selection rules for a rigid rotator. Once again we assume that radiation is along the z axis.

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta,\phi) \mu_z Y_J^M(\theta,\phi) \sin\theta \, d\phi, d\theta$$

Notice that m must be non-zero in order for the transition moment to be non-zero. This proves that a molecule must have a permanent dipole moment in order to have a rotational spectrum. The spherical harmonics can be written as

$$Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi}$$

where N_{JM} is a normalization constant. Using the standard substitution of $x = \cos q$ we can express the rotational transition moment as

$$(\mu_z)_{J,M,J',M'} = \mu \, N_{JM} N_{J'M'} \int_0^{2\pi} e^{I(M-M')\phi} \, d\phi \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

The integral over f is zero unless M = M' so $\Delta M = 0$ is part of the rigid rotator selection rule. Integration over ϕ for $M = M'$ gives 2π so we have

$$(\mu_z)_{J,M,J',M'} = 2\pi\mu \, N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

We can evaluate this integral using the identity

$$(2J+1)x \, P_J^{|M|}(x) = (J-|M|+1) P_{J+1}^{|M|}(x) + (J-|M|) P_{J-1}^{|M|}(x)$$

Substituting into the integral one obtains an integral which will vanish unless $J' = J+1$ or $J' = J-1$.

$$\int_{-1}^{1} P_{J'}^{|M'|}(x) \left(\frac{(J-|M|+1)}{(2J+1)} P_{J+1}^{|M|}(x) + \frac{(J-|M|)}{(2J+1)} P_{J-1}^{|M|}(x) \right) dx$$

This leads to the selection rule $\Delta J = \pm 1$ for absorptive rotational transitions. Keep in mind the physical interpretation of the quantum numbers J and M as the total angular momentum and z-component of angular momentum, respectively. As stated above in the section on electronic transitions, these selection rules also apply to the orbital angular momentum ($\Delta l = \pm 1$, $\Delta m = 0$).

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5.5: Unequal Spacings in Vibration-Rotation Spectra

We find that real rovibrational spectra do not exhibit the equal spacing expectations from the treatment in the previous section and look more like the idealized spectrum in Figure 13.3.1 . As energy increases, the R-branch lines become increasingly similar in energy (i.e., the lines move closer together) and as energy decreases, the P-branch lines become increasingly dissimilar in energy (i.e. the lines move farther apart). This is attributable to two phenomena: *rotational-vibrational coupling* and *centrifugal distortion*.

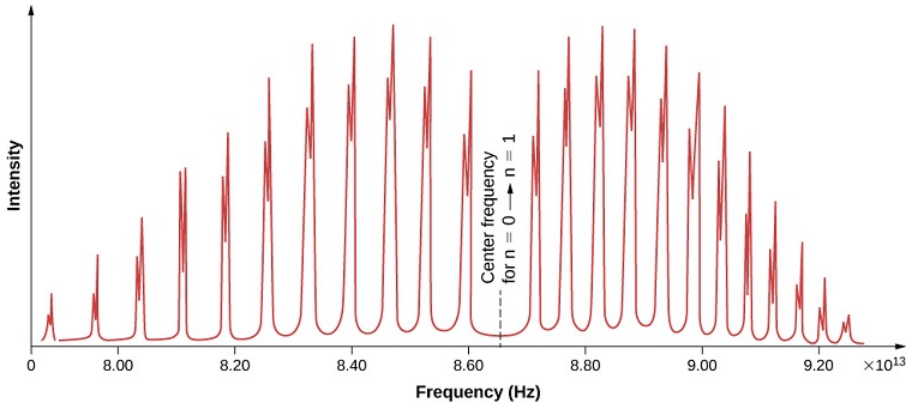


Figure 13.3.1 : Absorption spectrum of hydrogen chloride (HCl) from the $n = 0$ to $n = 1$ vibrational levels. The discrete peaks indicate a quantization of the angular momentum of the molecule. The bands to the left indicate a decrease in angular momentum, whereas those to the right indicate an increase in angular momentum. (CC-SA; OpenStax).

Experimental data shows that the P branch has closer spaces between the lines as the frequencies decrease while R branch has further spaces between the lines as the frequencies increase. On the spectrum, R region is on the left and P region is on the right separated by a large gap in between. There are other graphs show differently, but the regions can be labeled using their spacing characteristic discussed below.

Vibration-Rotation Interaction

Consider the rotational constant for a rigid rotator $\tilde{B} = h/8\pi^2 c\mu R_e^2$ where $\tilde{B}$ is the rotational constant, and R_e^2 is the bond length. It is clear from the equation that $\tilde{B}$ depends on R_e^2 in a inverse manner, so $\tilde{B}$ will decrease as R_e^2 increase, and vice versa.

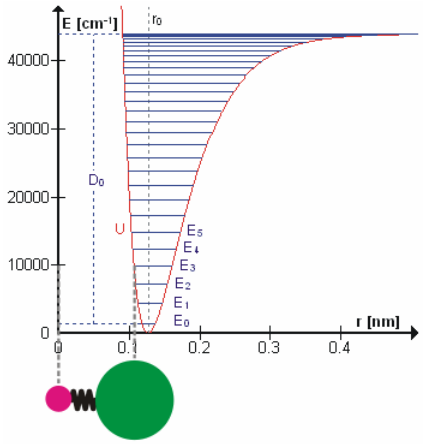


Figure 13.3.2 : Anharmonic Oscillator and Bond Length. Figure used with permission from Wikipedia.

Vibrational state and the bond length also possess a relationship, and that is bond length, R_e^2, will increase as the vibrational state, v increases. High vibrational states have large vibrational amplitudes (the amplitude can be visualized as the distance from one side to the other on the harmonic-oscillator parabola, and higher states has greater distance). On a potential graph, imagine a diatomic molecule with one of the atom fixed at the origin, the bond is along the x-axis, and the molecule vibrate toward and away from the origin along x-axis. The range at how much the bond can stretch or squeeze depend on the vibrational amplitude. So, at high vibrational state (thus high amplitude), the bond can squeeze in and stretch out more (just a little more) on the regular harmonic-oscillator potential, but it can stretch out greatly on an anharmonic oscillator. That's why bond length increase with vibrational state.

Note

The two relationship established above

- $\tilde{B} \propto R_e^2$ (inversely proportional)

and

- $R_e^2 \propto v$ (directly proportional)

Therefore,

- $\tilde{B} \propto v$ (inversely proportional)

The rotational constant dependent on the vibrational state is denoted as $\tilde{B}_v$, and the dependence of $\tilde{B}$ on v is the vibrational-rotational interaction.

Let's calculate the frequencies of R and P Branches with vibrational dependent rotational constants. The energies of the rigid rotator-harmonic oscillator is

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}J(J+1)$$

or in term of $\tilde{B}_v$

$$\tilde{E}_{v,J} = \tilde{\nu}\left(v + \frac{1}{2}\right) + \tilde{B}_v J(J+1)$$

According to the vibration-rotation interaction, $\tilde{B}_1 < \tilde{B}_0$ because $R_e^2(v=1) > R_e^2(v=0)$. Hence, the frequencies of rovibrational transitions from $v = 0 \rightarrow 1$ can be calculated as the following:

For R branch, allowed $J = 0, 1, 2, \ldots$

$$\tilde{\nu}_R(\Delta J = +1) = \tilde{E}_{1,J+1} - \tilde{E}_{0,J}$$

$$= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

For P branch, allowed $J = 1, 2, 3, \ldots$

$$\tilde{\nu}_P(\Delta J = -1) = \tilde{E}_{1,J-1} - \tilde{E}_{0,J}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

Decrease in Spacing of Lines in the R Branch with Increasing J

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu} +$(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu} -$(smaller and smaller

value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

References

1. McQuarrie, Donald A. Quantum Chemistry. New York: University Science Books, 2007.
2. Hollas, M. J. *Modern spectroscopy*. (3rd ed.). Chichester: John Wiley & Sons, 1996.
3. Hollas, M. J. *Basic atomic and molecular spectroscopy*. Cambridge: The Royal Society of Chemistry, 2002.
4. Herzberg, G. *Molecular spectra and molecular structure*. (2nd ed.). New York: Prentice-Hall, 1950.
5. Fetterolf, Monty L. Enhanced Intensity Distribution Analysis of the Rotational–Vibrational Spectrum of HCl. J. Chem. Ed. **2007**, *84*, 1064. DOI: 10.1021/ed084p1062

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5.6: Unequal Spacings in Pure Rotational Spectra

Vibrational energy which is a consequence of the oscillations/ vibrations of the nuclei along inter nuclear axis, is possible only when the distance between the nuclei is not fixed/ rigid; that means the separation between the two nuclei is flexible/ elastic (non-rigid rotator). Consequently, centrifugal force, when the molecule is rotating, tends to fly the reduced mass μ away from the axis of rotation. To keep the mass rotating about the axis, there must be some restoring force to counter balance the centrifugal force. The work done to supply this force is stored as potential energy. Therefore, unlike the case of rigid rotator, total energy of rotation in a molecule comprises of kinetic and the potential energy corresponding to centrifugal force of rotation.

Let r_e is the distance between the nuclei when the separation is taken to be rigid and r_c under the action of the centrifugal force. According to Hook's law, restoring force is proportional to change in internuclear distance $(r_c - r_e)$, or $= k(r_c - r_e)$ which in turn, will be equal to the centrifugal force.

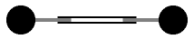


Figure 5.6.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{5.6.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{5.6.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{5.6.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 5.6.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{5.6.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\left(r_c - r_e\right)^2 \tag{5.6.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 5.6.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1 + \Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{5.6.6}$$

$$= \frac{L^2(1 - 2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{5.6.7}$$

using

$$(1 + \Delta r/r_e)^{-2} \approx (1 - 2\Delta r/r_e) \tag{5.6.8}$$

$$E_r = \frac{L^2}{2\mu {r_e}^2} - \frac{L^4}{k\mu^2 {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{5.6.9}$$

$$= \frac{L^2}{2\mu {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2 {r_e}^6} \tag{5.6.10}$$

$$= \frac{\hbar^2\ J(J+1)}{2\mu {r_e}^2} - \frac{\hbar^4\ J^2(J+1)^2}{2k\mu^2 {r_e}^6} \tag{5.6.11}$$

Use of Equation 5.6.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\sqrt{J(J+1)} \tag{5.6.12}$$

has been made to obtain relation in Equation 5.6.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{5.6.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\ \mu {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{5.6.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\ \mu^2 {r_e}^6\ c}\ (\text{in cm}^{-1}) \tag{5.6.15}$$

First term in the Equation 5.6.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 5.6.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 5.6.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 5.6.2.

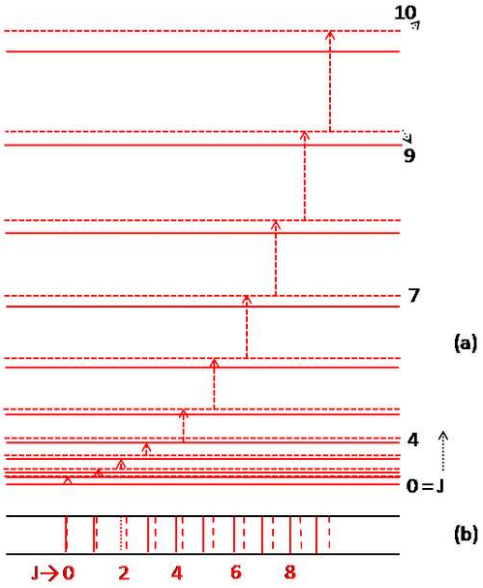


Figure 5.6.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational

lines decreases with increase in J , as shown in the Figure $5.6.2$. It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4\ \ cm^{-1}$ and $D \sim 0.0004\, cm^{-1}$. Usually, D is ignored in the calculations. Figure $5.6.2$ exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

Contributors and Attributions

- 202.141.40.218/wiki/index.php...r_Spectroscopy

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5.7: Vibrational Overtones

Although the harmonic oscillator proves useful at lower energy levels, like $v = 1$, it fails at higher numbers of v, failing not only to properly model atomic bonds and dissociations, but also unable to match spectra showing additional lines than is accounted for in the harmonic oscillator model.

Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to transition from $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure 13.5.1). For exaple, unlike the parabola given in the Harmonic Oscillator approximation, atoms that are too far apart will dissociate.

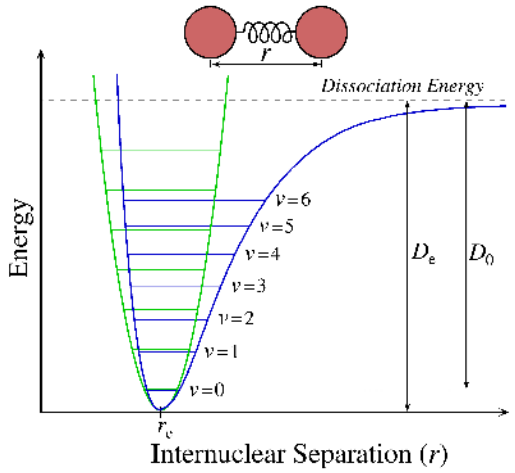


Figure 13.5.1 : Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure 13.5.1 , the harmonic oscillator potential (in green) well only roughly fits over the more accurate anharmonic oscillator well (in blue). The solid line accounts for dissociation at large R values, which the dotted lines does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \quad (5.7.1)$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant (and ignore the absolute energy term) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 5.7.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \quad (5.7.2)$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and
- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

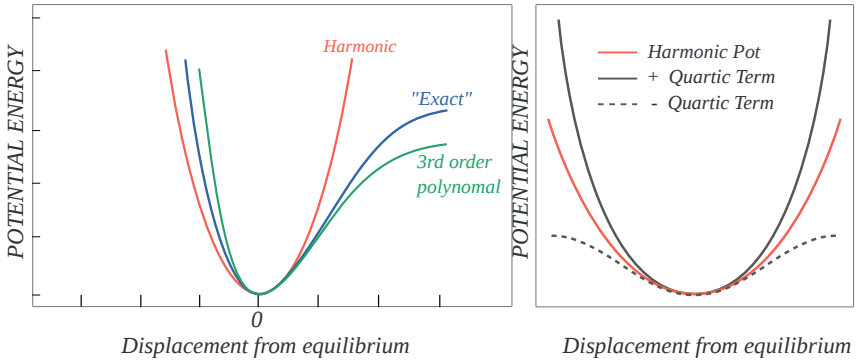


Figure 13.5.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation and gives by the following energies:

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

When cubic terms in the expansion (Equation 5.7.2) is included, then Schrödinger equation solved, using perturbation theory, gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although $G(n)$ technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 5.7.1.

Overtones

The Harmonic Oscillator approximation predicts that there will be only one line the spectrum of a diatomic molecule, and while experimental data shows there is in fact one dominant line--**the fundamental**--there are also other, weaker lines. How can we account for these extra lines?

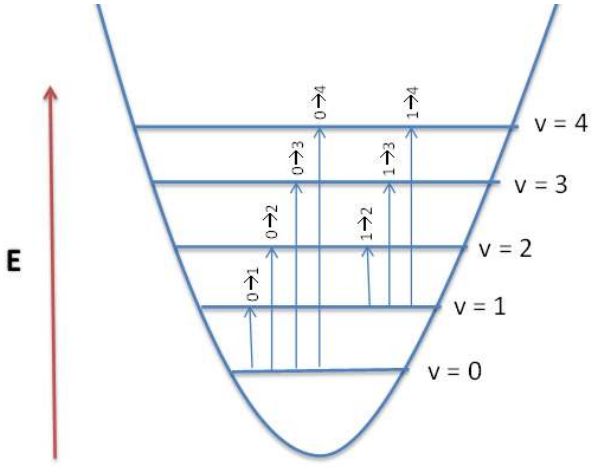


Figure 13.5.3 : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n<1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 1 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

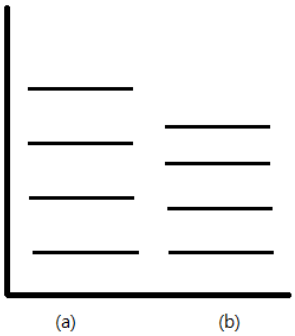


Figure 13.5.4 : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, is implied by Figure 13.5.4 . Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V =$ any number . That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapid decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

Table 13.5.1 : HCl vibrational spectrum.

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table 13.5.1 that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi_e}$.

Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

References

1. Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry; Part B: Application in Coordination, Organometallic, and Bioinorganic Chemistry, 5th Edition (Nakamoto, Kazuo)
2. Lyle McAfee Journal of Chemical Education 2000 77 (9), 1122
3. Stuart, Barbara. *Infrared Spectroscopy: Fundamentals and Applications.* Wiley, 2004. Print.

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5.8: Normal Modes in Polyatomic Molecules

Normal modes are used to describe the different vibrational motions in molecules. Each mode can be characterized by a different type of motion and each mode has a certain symmetry associated with it. Group theory is a useful tool in order to determine what symmetries the normal modes contain and predict if these modes are IR and/or Raman active. Consequently, IR and Raman spectroscopy is often used for vibrational spectra.

Degrees of Freedom

In general, a normal mode is an independent motion of atoms in a molecule that occurs without causing movement to any of the other modes. Normal modes, as implied by their name, are orthogonal to each other. In order to discuss the quantum-mechanical equations that govern molecular vibrations it is convenient to convert Cartesian coordinates into so called normal coordinates. Vibrations in polyatomic molecules are represented by these normal coordinates.

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into three categories.

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Table 13.9.1 : Overview of degrees of freedom

	Total Degrees of Freedom	Translational degrees of freedom	Rotational degrees of freedom	Vibrational degrees of freedom
Nonlinear Molecules	3N	3	3	3N -**6**
Linear Molecules	3N	3	2	3N - 5

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Example 13.9.1 : Ethane vs. Carbon Dioxide

Ethane, C_2H_6 has eight atoms ($N = 8$) and is a nonlinear molecule so of the $3N = 24$ degrees of freedom, three are translational and three are rotational. The remaining 18 degrees of freedom are internal (vibrational). This is consistent with:

$$3N - 6 = 3(8) - 6 = 18$$

Carbon Dioxide, CO_2 has three atoms ($N = 3$ and is a linear molecule so of the $3N = 9$ degrees of freedom, three are translational and two are rotational. The remaining 4 degrees of freedom are vibrational. This is consistent with:

$$3N - 5 = 3(3) - 5 = 4$$

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

Symmetricical Stretching	**Asymmetrical Stretching**	**Wagging**

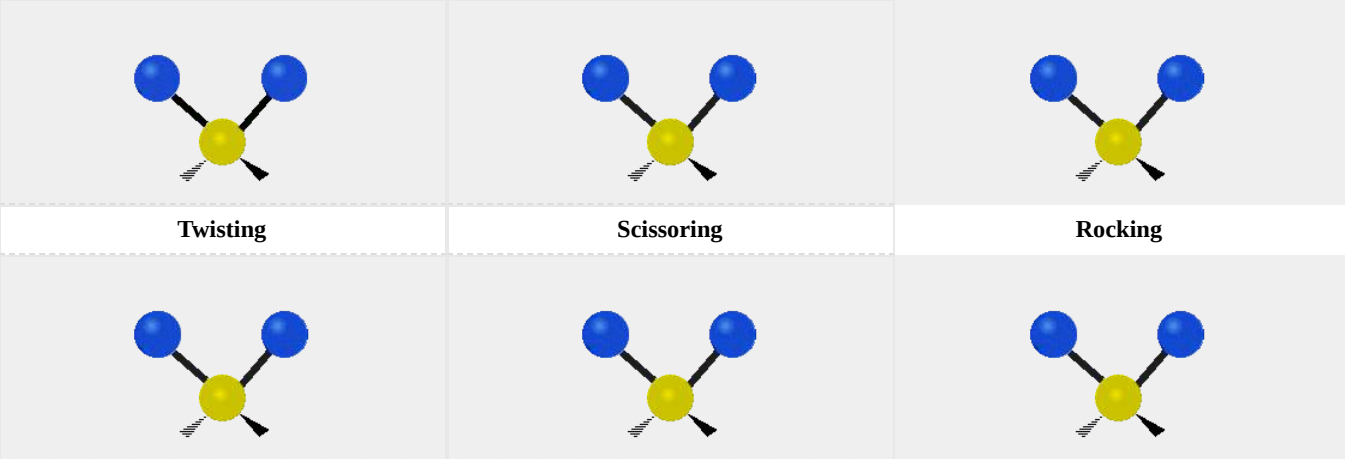


Figure 13.9.1 : *Six types of Vibrational Modes. Taken from publisher en.Wikipedia.org/wiki/Infrared_spectroscopy with permission from copyright holder.*

Normal Modes

If there is no external field present, the energy of a molecule does not depend on its orientation in space (its translational degrees of freedom) nor its center of mass (its rotational degrees of freedom). The potential energy of the molecule is therefore made up of its vibrational degrees of freedom only of $3N-6$ (or $3N-5$ for linear molecules). The difference in potential energy is given by:

$$\Delta V = V(q_1, q_2, q_3, \ldots, q_n) - V(0, 0, 0, \ldots, 0) \tag{5.8.1}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{vib}} \sum_{j=1}^{N_{vib}} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j \tag{5.8.2}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{vib}} \sum_{j=1}^{N_{vib}} f_{ij} q_i q_j \tag{5.8.3}$$

where q represents the equilibrium displacement and N_{vib} the number of vibrational degrees of freedom.

For simplicity, the *anharmonic* terms are neglected in this equation (i.e., higher order terms are ignore). A theorem of classical mechanics states that the cross terms can be eliminated from the above equation (the details of the theorem are very complex and will not be discussed in detail). By using matrix algebra a new set of coordinates $\{Q_j\}$ can be found such that

$$\Delta V = \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{5.8.4}$$

Note that there are no cross terms in this new expression. These new coordinates are called **normal coordinates** or **normal modes**. With these new normal coordinates in hand, the Hamiltonian operator for vibrations can be written as follows:

$$\hat{H}_{vib} = -\sum_{j=1}^{N_{vib}} \frac{\hbar^2}{2\mu_i} \frac{d^2}{dQ_j^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{5.8.5}$$

The total wavefunction is a product of the individual wavefunctions and the energy is the sum of independent energies. This leads to:

$$\hat{H}_{vib} = \sum_{j=1}^{N_{vib}} \hat{H}_{vib,j} = \sum_{j=1}^{N_{vib}} \left(\frac{-\hbar^2}{2\mu_j} \frac{d^2}{dQ_i^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \right) \tag{5.8.6}$$

and the wavefunction is then

$$\begin{aligned} \psi_{vib} &= Q_1, Q_2, Q_3 \ldots, Q_{vib} \\ &= \psi_{vib,1}(Q_1) \psi_{vib,2}(Q_2) \psi_{vib,3}(Q_3), \ldots, \psi_{vib,N_{vib}}(Q_{N_{vib}}) \end{aligned}$$

and the total vibrational energy of the molecule is

$$E_{vib} = \sum_{j=1}^{N_{vib}} h\nu_j \left(v_j + \frac{1}{2} \right) \tag{5.8.7}$$

where $v_j = 0, 1, 2, 3 \ldots$

The consequence of the result stated in the above equations is that each vibrational mode can be treated as a harmonic oscillator approximation. There are N_{vib} harmonic oscillators corresponding to the total number of vibrational modes present in the molecule.

Pictorial description of normal coordinates using CO

The normal coordinate q is used to follow the path of a normal mode of vibration. As shown in Figure 13.9.2 the displacement of the C atom, denoted by $\Delta r_o(\mathrm{C})$, and the displacement of the O atom, denoted by $\Delta r_o(\mathrm{O})$, occur at the same frequency. The displacement of atoms is measured from the equilibrium distance in ground vibrational state, r_o.

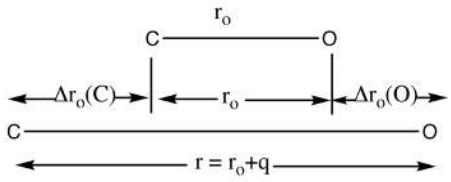


Figure 13.9.2 : The Normal coordinate for CO is equation to $\Delta r(C) + \Delta r(O)$

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5.9: Group Theory Determines Infrared Activity

Determining if a Normal Modes is IR or Raman Active

A transition from $v \rightarrow v'$ is IR active if the **transition moment integral** contains the totally symmetric irreducible representation of the point group the molecule belongs to. The transition moment integral is derived from the one-dimensional harmonic oscillator. Using the definition of electric dipole moment μ, the integral is:

$$M(v \rightarrow v') = \langle \text{final wavefunction} | \vec{\mu} | \text{initial wavefunction} \rangle$$

or in terms of vibrational wavefunctions for a specific normal mode $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \vec{\mu} | \phi(v = 0) \rangle \tag{5.9.1}$$

assuming the transition from the $v = 0$ wavefunction to the $v' \neq 0$ wavefunction.

Now, consider the case that $\vec{\mu}$, is a constant and therefore independent of the vibration (i.e., the electric dipole moment does not change during the vibration). This it could be taken outside the integral in Equation 5.9.1 becomes

$$M(v \rightarrow v') = \vec{\mu} \langle \phi(v' \neq 0) | \phi(v = 0) \rangle \tag{5.9.2}$$

Since $|\phi(v = 0)\rangle$ and $|\phi(v = \neq 0)\rangle$ are mutually orthogonal to each other, the integral in Equation 5.9.1 will equal zero and the transition will **not** be allowed (i.e., it is forbidden). For the M to be nonzero, $\vec{\mu}$ must change during a vibration. This selection rule explains why homonuclear diatomic molecules do not produce an IR spectrum. There is no change in dipole moment resulting in a transition moment integral of zero and a transition that is forbidden.

For a transition to be Raman active, the same rules apply. The transition moment integral must contain the totally symmetric irreducible representation of the point group. The integral contains the polarizability tensor α (usually represented by a square matrix):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \alpha | \phi(v = 0) \rangle \tag{5.9.3}$$

Following a similar argument as above, α must be nonzero for the transition to be allowed and exhibits Raman scattering.

Character Table

For a molecule to be IR active the dipole moment has to change during the vibration. For a molecule to be Raman active the polarizability of the molecule has to change during the vibration. The reducible representation $\mathbf{\Gamma_{vib}}$ can also be found by determining the reducible representation of the 3N degrees of freedom of H_2O, $\mathbf{\Gamma}_{tot}$. By applying Group Theory it is straightforward to find $\mathbf{\Gamma_{x,y,z}}$ as well as UMA (number of unmoved atoms). Again, using water as an example with C_{2v} symmetry where 3N = 9, $\mathbf{\Gamma_{tot}}$ can be determined:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\mathbf{T_{x,y,z}}$	3	-1	1	1	
UMA	3	1	1	3	
$\mathbf{\Gamma_{tot}}$	**9**	**-1**	**1**	**3**	**=3a_1 + a_2 + 2b_1 + 3b_2**
Note that $\mathbf{\Gamma}_{tot}$ contains nine degrees of freedom consistent with 3N = 9.					

$\mathbf{\Gamma}_{tot}$ contains $\mathbf{\Gamma}_{translational}$, $\mathbf{\Gamma}_{rotational}$ as well as $\mathbf{\Gamma}_{vibrational}$. $\mathbf{\Gamma}_{trans}$ can be obtained by finding the irreducible representations corresponding to x,y and z in the right side of the character table, $\mathbf{\Gamma}_{rot}$ by finding the ones corresponding to R_x, R_y and R_z. $\mathbf{\Gamma}_{vib}$ can be obtained by $\mathbf{\Gamma}_{tot}$ - $\mathbf{\Gamma}_{trans}$ - $\mathbf{\Gamma}_{rot}$.

$$\Gamma_{vib}(H_2O) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2$$

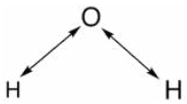
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation $\mathbf{\Gamma}_{vib}$ is necessary. If they contain the same irreducible representation, the mode is IR active.

For H_2O, z transforms as a_1, x as b_1 and y as b_2. The modes a1 and b2 are IR active since Γvib contains $2a_1 + b_2$.

In order to determine which modes are Raman active, the irreducible representation that corresponds to z^2, x^2-y^2, xy, xz and yz is used and again cross checked with Γvib. For H_2O, z^2 and x^2-y^2 transform as a_1, xy as a_2, xz as b_1 and yz as b_2.The modes a_1 and b_2 are also Raman active since Γ_{vib} contains both these modes.

The IR spectrum of H2O does indeed have three bands as predicted by Group Theory. The two symmetric stretches v1 and v2 occur at 3756 and 3657 cm-1 whereas the bending v3 motion occurs at 1595 cm-1.

In order to determine which normal modes are stretching vibrations and which one are bending vibrations, a stretching analysis can be performed. Then the stretching vibrations can be deducted from the total vibrations in order to obtain the bending vibrations. A double-headed arrow is drawn between the atom as depicted below:



Then a determination of how the arrows transform under each symmetry operation in C2v symmetry will yield the following results:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\mathbf{\Gamma_{stretch}}$	2	0	0	2	**= $a_1 + b_2$**

$$\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} = 2a_1 + b_2 - a_1 - b_2 = a_1$$

H_2O has two stretching vibrations as well as one bending vibration. This concept can be expanded to complex molecules such as $PtCl4^-$. Four double headed arrows can be drawn between the atoms of the molecule and determine how these transform in D_{4h} symmetry. Once the irreducible representation for $\mathbf{\Gamma}_{stretch}$ has been worked out, $\mathbf{\Gamma}_{bend}$ can be determined by $\mathbf{\Gamma}_{bend} = \mathbf{\Gamma}_{vib} - \mathbf{\Gamma}_{stretch}$.

Most molecules are in their zero point energy at room temperature. Therefore, most transitions do originate from the v=0 state. Some molecules do have a significant population of the v=1 state at room temperature and transitions from this thermally excited state are called **hot** bands.

References

1. Merlin, J.C., Cornard, J.P., *J. Chem. Educ*., **2006**, 83 (9), p 1383. **DOI:** 10.1021/ed083p1393
2. McGuinn, C.J., *J. Chem. Educ*., **1982**, 59 (10), p 813. **DOI:** 10.1021/ed059p813
3. Harris, D.C., Bertolucci, M.D., *Symmetry and Spectroscopy: An introduction to Vibrational and Electronic Spectroscopy*. Dover Publocations, Inc., New York, **1989**.
4. McQuarrie, D. A., Simon, J.D., *Physical Chemistry: A Molecular Approach*, University Science Books, Sausalito, California, **1997**; 518-521.
5. Housecroft, C.E., Sharpe, A.G., **Inorganic Chemistry.** Pearson Education Limited, England, **2008**, 107.
6. Atkins, P., dePaula, J., *Physical Chemistry*, W.H. Freeman and Company, New York, **2002**, 520-523.
7. Bishop, D.M., *Group Theory and Chemistry*, Dover Publications, Inc, New York, **1973**, 166.

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CHAPTER OVERVIEW

6: One-Electron Atoms and Ions

6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly
6.2: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers
6.3: s-orbitals are Spherically Symmetric
6.4: Orbital Angular Momentum and the p-Orbitals
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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: 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**.

$$\psi_{n,l,m_l}(r,\theta,\varphi) = \underbrace{R_{n,l}(r)}_{radial}\underbrace{Y_l^{m_l}(\theta,\varphi)}_{angular} \tag{6.2.1}$$

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 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?

Radial Part of the Wavefunction

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

$$R_{\text{asymptotic}}(r) \sim \exp\left(-\frac{r}{n}a_0\right) \tag{6.2.2}$$

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.

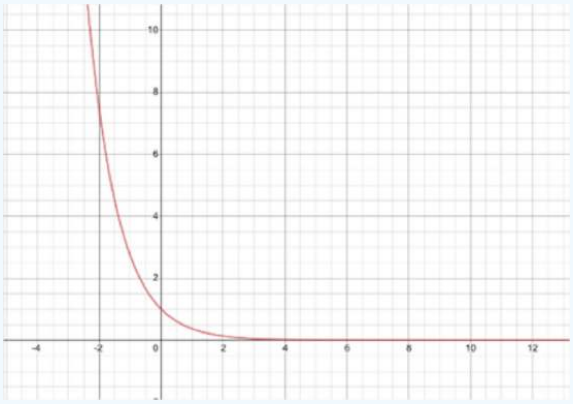
? Exercise 6.4.2

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.

$$L_{n,l}(r) = \sum_{r=0}^{n-l-1} c_i r^i \tag{6.2.3}$$

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 6.2.1).

The $R(r)$ functions that solve the radial differential Equation 6.2.1, are products of the associated Laguerre polynomials and the exponential factor, multiplied by a normalization factor $(N_{n,l})$ and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,l}\left(\frac{r}{a_0}\right)^l L_{n,l}(r) e^{-\frac{r}{na_0}} \tag{6.2.4}$$

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	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\rho+2\rho^2)e^{-}$
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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6.3: s-orbitals are Spherically Symmetric

The hydrogen atom wavefunctions, $\psi(r, \theta, \varphi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1$, l = 0 is called the 1s orbital, and an electron that is described by this function is said to be “in” the ls orbital, i.e. have a 1s orbital state. The constraints on n, l, and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

Visualizing the variation of an electronic wavefunction with r, θ, and φ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

We can obtain an energy and one or more wavefunctions for every value of n, the principal quantum number, by solving Schrödinger's equation for the hydrogen atom. A knowledge of the wavefunctions, or probability amplitudes ψ_n, allows us to calculate the probability distributions for the electron in any given quantum level. When n = 1, the wavefunction and the derived probability function are independent of direction and depend only on the distance r between the electron and the nucleus. In Figure 6.5.1 , we plot both ψ_1 and P_1 versus r, showing the variation in these functions as the electron is moved further and further from the nucleus in any one direction. (These and all succeeding graphs are plotted in terms of the atomic unit of length, $a_0 = 0.529 \times 10^{-8}\ cm$.)

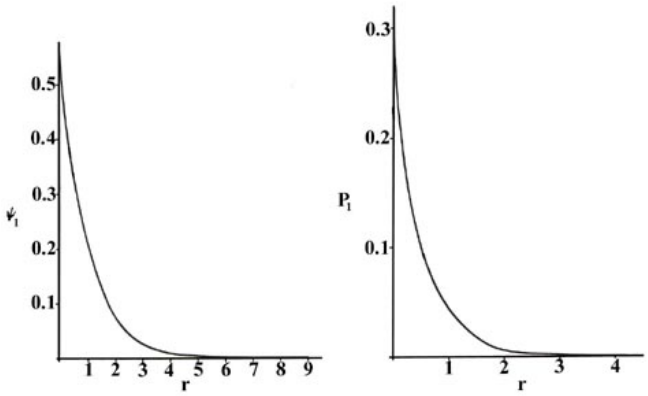


Figure 6.5.1 : The wavefunction and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

Two interpretations can again be given to the P_1 curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Figure 6.5.1 for P_1. That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing r. The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than 10^{-8} cm will be greater than K, the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret P_1 as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of P_n for every small volume element over all space adds up to unity, i.e., one electron and one electronic charge.)

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately does not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane (Figure 6.5.2), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line (Figure 6.5.2). Since the electron density depends only on *r*, the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.

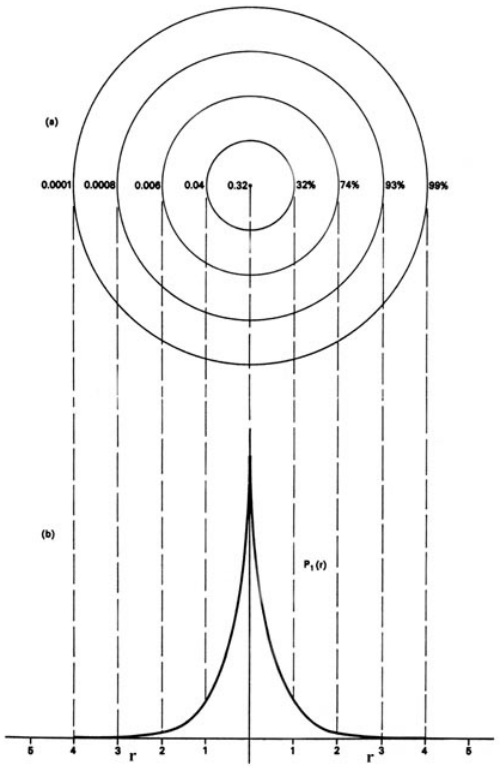


Figure 6.5.2 : (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter = $4.2 \times 10^{-8}\ cm$). (b) This is a profile of the contour map along a line through the nucleus. It is, of course, the same as that given previously in Figure 6.5.1 for P_1, but now plotted from the nucleus in both directions.

When the electron is in a definite energy level we shall refer to the P_n distributions as ***electron density distributions***, since they describe the manner in which the total electronic charge is distributed in space. The electron density is expressed in terms of the number of electronic charges per unit volume of space, e^-/V. The volume V is usually expressed in atomic units of length cubed, and one atomic unit of electron density is then e^-/a_0^3. To give an idea of the order of magnitude of an atomic density unit, 1 au of charge density e^-/a_0^3 = 6.7 electronic charges per cubic Ångstrom. That is, a cube with a length of $0.52917 \times 10^{-8}\ cm$, if uniformly filled with an electronic charge density of 1 au, would contain 6.7 electronic charges.

For every value of the energy E_n, for the hydrogen atom, there is a degeneracy equal to n^2. Therefore, for n = 1, there is but one atomic orbital and one electron density distribution. However, for n = 2, there are four different atomic orbitals and four different electron density distributions, all of which possess the same value for the energy, E_2. Thus for all values of the principal quantum number n there are n^2 different ways in which the electronic charge may be distributed in three-dimensional space and still possess the same value for the energy. For every value of the principal quantum number, ***one*** of the possible atomic orbitals is independent of direction and gives a spherical electron density distribution which can be represented by circular contours as has been exemplified above for the case of n = 1. The other atomic orbitals for a given value of n exhibit a directional dependence and predict density distributions which are not spherical but are concentrated in planes or along certain axes. The angular dependence of the atomic orbitals for the hydrogen atom and the shapes of the contours of the corresponding electron density distributions are intimately connected with the angular momentum possessed by the electron.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s and 2s orbitals plotted in Figure 6.5.3 . The 1s function in Figure $6.3.3; left$ starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

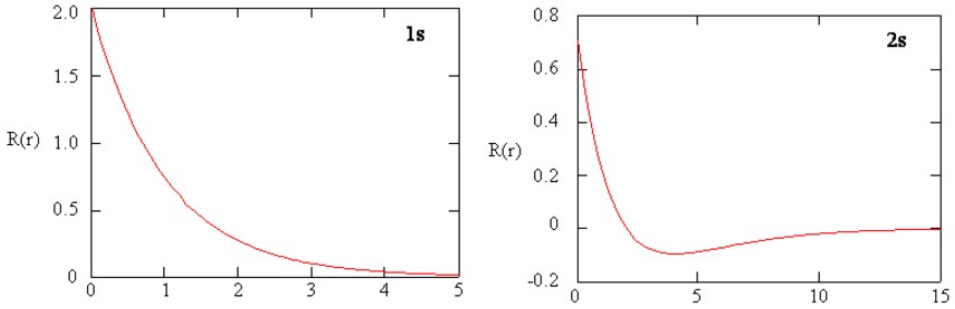


Figure 6.5.3 : Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click here.

Next notice how the radial function for the 2s orbital, Figure $6.3.3; right$, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$.

? Exercise 6.5.1

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

? Exercise 6.5.2

What mathematical feature of each of the radial functions controls the number of radial nodes?

? Exercise 6.5.3 : Radial Nodes

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

? Exercise 6.5.4

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Answer

	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

	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 = 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 .

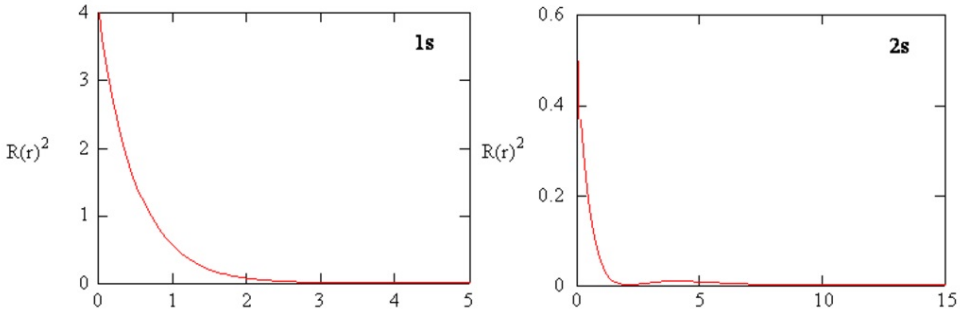


Figure 6.5.4 : Radial densities ($R(r)^* R(r)$) for the 1s and 2s orbitals.

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:

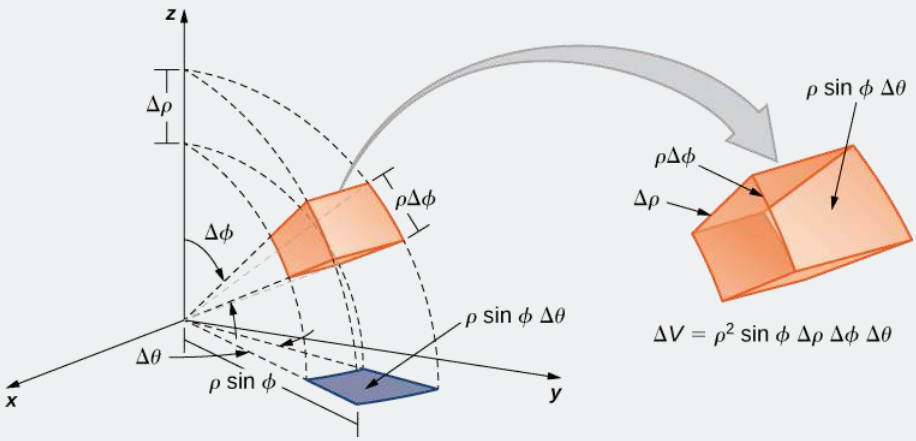
$$\frac{4}{3}\pi\left[(r+\Delta r)^3 - r^3\right]$$

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.

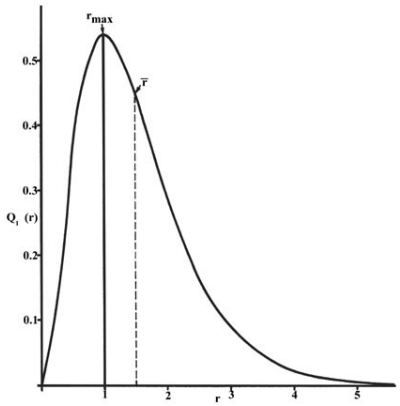


Figure 6.5.5 : The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r+\delta r$.

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.

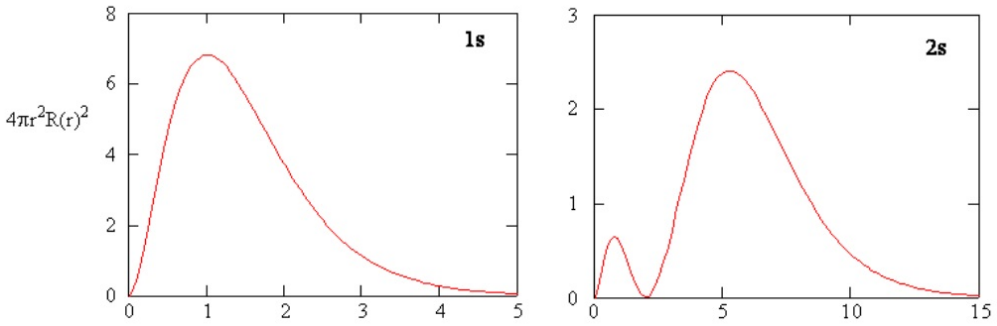


Figure 6.5.6 : The radial distribution function ($4\pi r^2 R(r)^* R(r)$) for the 1s and 2s orbitals. Compare to the radial functions in Figure 6.5.3 or the radial densities in Figure 6.5.4 . For an interactive graph click here.

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 $\rho = \dfrac{r}{a_0}$.

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

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

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

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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6.4: Orbital Angular Momentum and the p-Orbitals

Learning Objectives

- To relate the classical orbital angular momentum for an particle to the quantum equivalent
- Characterize the mangnitude and orientation of orbital angular momentum for an electron in terms of quantum numbers

Classical Orbital Angular Momentum

The physical quantity known as angular momentum plays a dominant role in the understanding of the electronic structure of atoms. To gain a physical picture and feeling for the angular momentum it is necessary to consider a model system from the classical point of view. The simplest classical model of the hydrogen atom is one in which the electron moves in a circular orbit with a constant speed or angular velocity (Figure 6.6.1). Just as the linear momentum $m\vec{v}$ plays a dominant role in the analysis of linear motion, so angular momentum (L) plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.

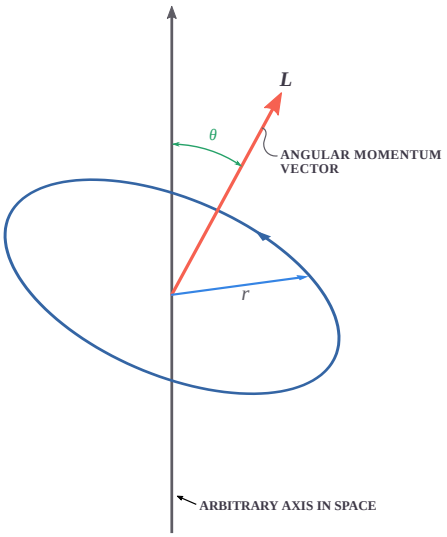


Figure 6.6.1 : The angular momentum vector for a classical model of the atom. (CC BY-NC; Ümit Kaya via LibreTexts)

In Figure 6.6.1 , m is the mass of the electron, $\vec{v}$ is the linear velocity (the velocity the electron would possess if it continued moving at a tangent to the orbit) and r is the radius of the orbit. The linear velocity $\vec{v}$ is a vector since it possesses at any instant both a magnitude and a direction in space. Obviously, as the electron rotates in the orbit the direction of $\vec{v}$ is constantly changing, and thus the linear momentum $m\vec{v}$ is ***not*** constant for the circular motion. This is so even though the speed of the electron (i.e, the magnitude of $\vec{v}$ which is denoted by $|\vec{v}|$) remains unchanged. According to Newton's second law, a force must be acting on the electron if its momentum changes with time. This is the force which prevents the electron from flying on tangent to its orbit. In an atom the attractive force which contains the electron is the electrostatic force of attraction between the nucleus and the electron, directed along the radius *r* at right angles to the direction of the electron's motion.

The angular momentum, like the linear momentum, is a vector and is defined as follows:

$$|\vec{L}| = m\nu r$$

The angular momentum vector $\vec{L}$ is directed along the axis of rotation. From the definition it is evident that the angular momentum vector will remain constant as long as the speed of the electron in the orbit is constant ($|\vec{v}|$ remains unchanged) and the plane and radius of the orbit remain unchanged. Thus for a given orbit, the angular momentum is constant as long as the angular velocity of the particle in the orbit is constant. In an atom the only force on the electron in the orbit is directed along r; it has no component in the direction of the motion. The force acts in such a way as to change only the linear momentum. Therefore, while the linear momentum is not constant during the circular motion, the angular momentum is. A force exerted on the particle in the direction of the vector $\vec{v}$ would change the angular velocity and the angular momentum. When a force is applied which does change $\vec{L}$, a ***torque***

is said to be acting on the system. Thus angular momentum and torque are related in the same way as are linear momentum and force.

Quantum Angular Momentum

The important point of the above discussion is that both the angular momentum and the energy of an atom remain constant if the atom is left undisturbed. Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system. Thus both the energy and the angular momentum are quantized for an atom.

> *Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system.*

There is a quantum number, denoted by *l*, which governs the magnitude of the angular momentum, just as the quantum number n determines the energy. The ***magnitude*** of the angular momentum may assume only those values given by:

$$|L| = \sqrt{l(l+1)}\hbar \tag{6.4.1}$$

with $l = 0, 1, 2, 3, \ldots n-1$.

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 6.4.1 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 .

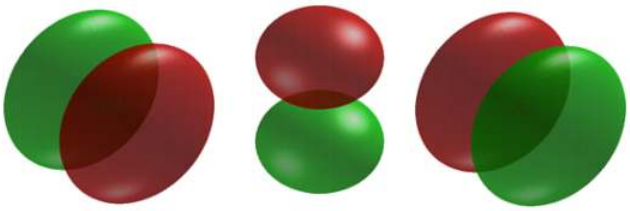


Figure 6.6.2 : The appearance of the three 2p orbitals in three-dimensional space. (CC BY-SA 3.0; I, Sarxos).

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.*

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.

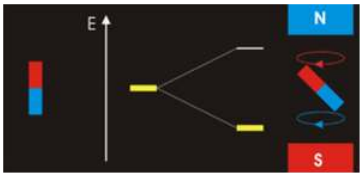


Figure 6.6.3 : The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left). However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative orientations of the magnet to the external field. (CC SA-BY 3.0; Darekk2).

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.

$$|\psi_{2,1,0}\rangle = r\cos\theta R(r) \tag{6.4.2}$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2}\sin\theta e^{i\phi} R(r) \tag{6.4.3}$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2}\sin\theta e^{-i\phi} R(r) \tag{6.4.4}$$

The notation is $|\psi_{n,l,m_l}\rangle$ with $R(r)$ is the radial component of this wavefuction, θ is the angle with respect to the z-axis and ϕ is the angle with respect to the xz-plane.

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

in which Z is the atomic number (or probably better nuclear charge) and a_0 is the Bohr radius.

In switching from spherical to Cartesian coordinates, we make the substitution $z = r\cos\theta$, so:

$$|\psi_{2,1,0}\rangle = zR(r)$$

This is ψ_{2p_z} since the value of ψ is dependent on z: when $z = 0$; $\psi = 0$, which is expected since $z = 0$ describes the xy-plane.

The other two wavefunctions are degenerate in the xy-plane. An equivalent statement is that these two orbitals do not lie on the x- and y-axes, but rather bisect them. Thus it is typical to take linear combinations of them to make the equation look prettier. If any set of wavefunctions is a solution to the Schrödinger equation, then any set of linear combinations of these wavefunctions must also be a solution (Section 2.4). We can do this because of the linearity of the Schrödinger equation.

In the equations below, we're going to make use of some trigonometry, notably Euler's formula:

$$e^{i\phi} = \cos\phi + i\sin\phi \tag{6.4.5}$$

$$\sin\phi = \frac{e^{i\phi} - e^{-i\phi}}{2i} \tag{6.4.6}$$

$$\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2} \tag{6.4.7}$$

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

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

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

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 $l = 4, 5, 6 \rightarrow g, h, i, \ldots$..

We have not as yet accounted for the full degeneracy of the hydrogen atom orbitals which we stated earlier to be n^2 for every value of n. For example, when $n = 2$, there are four distinct atomic orbitals. The remaining degeneracy is again determined by the angular momentum of the system. Since angular momentum like linear momentum is a vector quantity, we may refer to the component of the angular momentum vector which lies along some chosen axis. For reasons we shall investigate, the number of values a particular component can assume for a given value of l is $(2l + 1)$. Thus when $l = 0$, there is no angular momentum and there is but a single orbital, an s orbital. When $l = 1$, there are three possible values for the component $(2 \times 1 + 1)$ of the total angular momentum which are physically distinguishable from one another. There are, therefore, three p orbitals. Similarly there are five d orbitals, $(2 \times 2 + 1)$, seven f orbitals, $(2 \times 3 + 1)$, etc. All of the orbitals with the same value of n and l, the three 2p orbitals for example, are similar but differ in their spatial orientations.

To gain a better understanding of this final element of degeneracy, we must consider in more detail what quantum mechanics predicts concerning the angular momentum of an electron in an atom.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)
- Stack Exchange (Ben Norris and Loong)

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6.5: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

Learning Objectives

- Understand how to measure the orbital angular momentum of an electron around a nucleus.
- Understand how the Heisenburgh Uncertainty Principle extends to orbital angular momenta.
- Manipulate the angular momenta cyclic permutations that allow two of the three projects to be simultaneous measured

Consider a particle described by the Cartesian coordinates $(x, y, z) \equiv \vec{r}$ and their conjugate momenta $(p_x, p_y, p_z) \equiv \vec{p}$. The classical definition of the *orbital angular momentum* of such a particle about the origin is (i.e., via the vector cross product):

$$\vec{L} = \vec{r} \times \vec{p}$$

which can be separated into projections into each of the primary axes :

$$\begin{aligned} L_x &= y\, p_z - z\, p_y, \\ L_y &= z\, p_x - x\, p_z \\ L_z &= x\, p_y - y\, p_x \end{aligned}$$

Extending this discussion to the quantum mechanics, we can assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \vec{L}$ - that represent the components of orbital angular momentum in quantum mechanics - can be defined in an analogous manner to the corresponding components of classical angular momentum. In other words, we are going to assume that the above equations specify the angular momentum operators in terms of the position and linear momentum operators.

In Cartesian coordinates, the three operators for the orbital angular momentum components can be written as

$$\hat{L}_x = -\mathrm{i}\,\hbar \left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y} \right) \tag{6.5.1}$$

$$\hat{L}_y = -\mathrm{i}\,\hbar \left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z} \right) \tag{6.5.2}$$

$$\hat{L}_z = -\mathrm{i}\,\hbar \left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x} \right) \tag{6.5.3}$$

These can be transforming to operators in standard spherical polar coordinates,

$$\begin{aligned} x &= r\,\sin\theta\,\cos\varphi \\ y &= r\,\sin\theta\,\sin\varphi \\ z &= r\cos\theta \end{aligned}$$

we obtain

$$\begin{aligned} \hat{L}_x &= \mathrm{i}\,\hbar \left(\sin\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\,\frac{\partial}{\partial\varphi} \right) \\ \hat{L}_y &= -\mathrm{i}\,\hbar \left(\cos\varphi\,\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\,\frac{\partial}{\partial\varphi} \right) \\ \hat{L}_z &= -\mathrm{i}\,\hbar\,\frac{\partial}{\partial\varphi} \end{aligned}$$

We can introduce a new operator $\hat{L^2}$:

$$\hat{L^2} = \hat{L}_x^{\,2} + \hat{L}_y^{\,2} + \hat{L}_z^{\,2} \tag{6.5.4}$$

$$= -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right) \tag{6.5.5}$$

The eigenvalue problem for $\hat{L^2}$ takes the form

$$\hat{L^2}|\psi\rangle = \lambda\,\hbar^2|\psi\rangle \tag{6.5.6}$$

where $\psi(r,\theta,\varphi)$ is the wavefunction, and λ is a number. Let us write

$$\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi) \tag{6.5.7}$$

By definition,

$$\boxed{L^2\,Y_l^{m_l} = l\,(l+1)\,\hbar^2\,Y_l^{m_l}} \tag{6.5.8}$$

where l is an integer. This is an important conclusion that argues the angular momentum is quantized with the square of the magnitude of the angular momentum only capable of assume one of the discrete set of values (Equation 6.5.8). From this, the **amplitude** of angular momentum can be expressed

$$\boxed{|\vec{L}| = \sqrt{L^2} = \sqrt{l(l+1)}\,\hbar} \tag{6.5.9}$$

Warning

We often refer to a particle in a state with angular momentum quantum number l as having angular momentum l, rather than saying that it has angular momentum of $\sqrt{l(l+1)}\,\hbar$ magnitude, primarily since it is awkward to say quickly.

The properties of spherical harmonics that the z-component of the angular momentum (L_z) is also quantized and can only assume a one of a discrete set of values

$$L_z\,Y_l^{m_l} = m\,\hbar\,Y_l^{m_l} \tag{6.5.10}$$

where m_l is an integer lying in the range $-l \le m_l \le l$.

- l is sometimes called "azimuthal quantum number" or "orbital quantum number"
- m_l is sometimes called "magnetic quantum number"

Simultaneous Measurements

Note that observables associated with $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ can, in principle, be measured. However, to determine if they can be measured *simultaneously* with infinite precision, the corresponding operators must **commute**. Remember that the fundamental commutation relations satisfied by the position and linear momentum operators are:

$$[\hat{x}_i, \hat{x}_j] = 0$$

$$[\hat{p}_i, \hat{p}_j] = 0$$

$$[\hat{x}_i, \hat{p}_j] = \mathrm{i}\,\hbar\,\delta_{ij}$$

where i and j stand for either x, y, or z. Consider the commutator of the operators $\hat{L}_x$ and $\hat{L}_z$:

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= [(y\,p_z - z\,p_y), (z\,p_x - x\,p_z)] \\ &= y\,[p_z, z]\,p_x + x\,p_y\,[z, p_z] \\ &= \mathrm{i}\,\hbar\,(-y\,p_x + x\,p_y) \\ &= \mathrm{i}\,\hbar\,\hat{L}_z\end{aligned}$$

The **cyclic permutations** of the above result yield the fundamental commutation relations satisfied by the components of an orbital angular momentum:

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\,\hbar\,\hat{L}_z \tag{6.5.11}$$

$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\,\hbar\,\hat{L}_x \tag{6.5.12}$$

$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\,\hbar\,\hat{L}_y \tag{6.5.13}$$

The three commutation relations (Equations 6.5.11 - 6.5.13) are the foundation for the whole theory of angular momentum in quantum mechanics. Whenever we encounter three operators having these commutation relations, we know that the dynamical variables that they represent have identical properties to those of the components of an angular momentum (which we are about to derive). In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 6.5.11 - 6.5.13) represent the components of some sort of angular momentum.

> *Any three operators that satisfy the cyclic commutation relations represent the components of some sort of angular momentum.*

Example 6.3.1 : Commutators

Show that the $\hat{L^2}$ and $\hat{L}_x$ operators commute.

Solution

We want to confirm that $[\hat{L^2}, \hat{L}_x] = 0$ that from Equation 6.5.4 this can be expanded

$$[\hat{L^2}, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x]$$

from the properties of commutators, this can be expanded

$$[\hat{L^2}, \hat{L}_x] = [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]$$

However,

$$[\hat{L}_x^2, \hat{L}_x] = \hat{L}_x^2\hat{L}_x - \hat{L}_x\hat{L}_x^2 = \hat{L}_x\hat{L}_x\hat{L}_x - \hat{L}_x\hat{L}_x\hat{L}_x = 0$$

So

$$\begin{aligned}[\hat{L^2}, \hat{L}_x] &= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\ &= \hat{L}_y^2\hat{L}_x - \hat{L}_x\hat{L}_y^2 + \hat{L}_z^2\hat{L}_x - \hat{L}_x\hat{L}_z^2 \\ &= \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z\end{aligned}$$

Lets look at some related forms which can be used to simplify the above expression. The first two terms can and final two terms can be rewritten as different commutators

$$\begin{aligned}[\hat{L}_y, \hat{L}_x] &= \hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] \\ &= (\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y)\hat{L}_y + \hat{L}_y(\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y) \\ &= \cancel{\hat{L}_y\hat{L}_x\hat{L}_y} - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_y\hat{L}_y\hat{L}_x - \cancel{\hat{L}_y\hat{L}_x\hat{L}_y}\end{aligned}$$

The first & fourth terms cancel, giving

$$[\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] = \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y$$

Similarly,

$$[Lz, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] = \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z$$

So,

$$\begin{aligned}[\hat{L^2}, \hat{L}_x] &= [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\ &= -i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + ih\hat{L}_z\hat{L}_y \\ &= 0\end{aligned}$$

One can also show similarly that

$$[\hat{L^2}, \hat{L}_y] = [\hat{L^2}, \hat{L}_z] = 0$$

Example 6.3.1 shows that while L_z can be known with certainty, L_x and L_y would **unknown**. This means that every vector with the appropriate length and *z*-component can drawn to represent $\vec{L}$, which forms a cone (Figure 6.3.1). The expected value of the angular momentum for a given ensemble of systems in the quantum state characterized by l and m_l could be somewhere on this cone while it cannot be defined for a single system (since the components of L do not commute with each other).

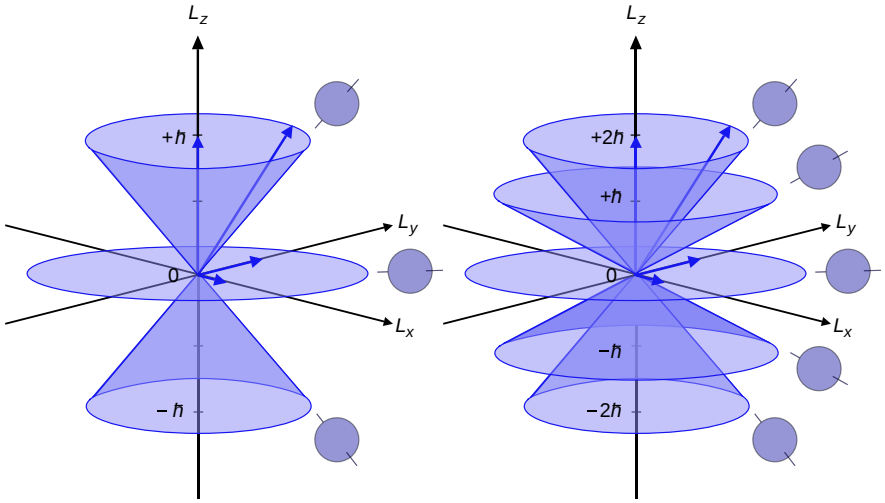


Figure 6.3.1 : Illustration of the vector model of orbital angular momentum. (left) A set of states with quantum numbers $l = 1$, and $m_l = -1, 0, +1,$. (right) A set of states with quantum numbers $l = 2$, and $m_l = -2, -1, 0, +1, +2$. (Public Domain; Maschen via Wikipedia)

The Meaning of Commutation of Two Operators

The mathematics of commutation relations is relatively straightforward, but what does it physically mean for an observable (Hermitian operator) to commute with another observable (Hermitian operator) in quantum mechanics?

If two operators $\hat{A}$ and $\hat{B}$ commute with each other then

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0,$$

which can be rearranged to

$$\hat{A}\hat{B} = \hat{B}\hat{A}.$$

This is not a trivial statement and many operations do not commute and hence the end-result depends on how you have ordered the operations.

If you recall that operators act on quantum mechanical states and give you a new state in return, then this means that with $\hat{A}$ and $\hat{B}$ commuting, the state you obtain from letting first $\hat{A}$ act and then $\hat{B}$ act on some initial state is the same as if you let first $\hat{B}$ and then $\hat{A}$ act on that state, i.e.,

$$\hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle.$$

Recall that when you perform a quantum mechanical measurement, you will always measure an eigenvalue of your operator, and after the measurement your state is left in the corresponding eigenstate. The eigenstates to the operator are precisely those

states for which there is **no uncertainty** in the measurement: You will **always** measure the eigenvalue.

Therefore, $\hat{B}|a\rangle$ must be an eigenfunction of $\hat{A}$ with eigenvalue a just like $|a\rangle$ itself is. That is essentially saying that $|a\rangle$ is an eigenfunction of $\hat{B}$.

A key example of this is since $\hat{L^2}$ and $\hat{L}_x$ commute (Example 6.3.1) then both operators share the same eigenstates. Hence, we do no need to solve two eignevalue problems:

$$\hat{L^2}|\psi\rangle = \lambda|\psi\rangle$$

and

$$\hat{L}_x|\psi\rangle = \beta|\psi\rangle$$

If we solve one, we then know the eigenvalues ($|\psi\rangle$) for the other!

What does it mean when some observable $\hat{A}$ commutes with the Hamiltonian $\hat{H}$? First, we get all the result from above: There is a simultaneous eigenbasis of the energy-eigenstates and the eigenstates of $\hat{A}$. This can yield a tremendous simplification of the task of solving Schrödinger equations. For example, the Hamiltonian of the hydrogen atom commutes with $\hat{L}$, the angular momentum operator, and with $\hat{L}_z$, its z-component. This tells you that you can classify the eigenstates by an angular- and magnetic quantum number l and m.

Summary

In the quantum world, angular momentum is quantized. The square of the magnitude of the angular momentum (determined by the eigenvalues of the $\hat{L^2}$ operator) can only assume one of the discrete set of values

$$L^2 = l(l+1)\hbar^2$$

or the magnitude of the angular momentum

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

with $l = 0, 1, 2, \ldots$

The z-component of the angular momentum (i.e., projection of L onto the z-axis) is also quantized with

$$L_z = m_l\hbar$$

with $m_l = -l, 0-1, \ldots, 0, \ldots + l + 1, l$ for a given value of l. Hence, l and m_l are the *angular momentum quantum number* and the *magnetic quantum number*, respectively.

Contributors and Attributions

- Richard Fitzpatrick (Professor of Physics, The University of Texas at Austin)

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CHAPTER OVERVIEW

7: So You Can't Solve the Schrodinger Equation Exactly...What Next? (Approximation Methods)

7.1: The Helium Atom Cannot Be Solved Exactly
7.2: The Variational Method Approximation
7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems
7.5: Perturbation Theory and the Variational Method for Helium
7.6: Atomic and Molecular Calculations are Expressed in Atomic Units
7.7: Hartree-Fock Equations are Solved by the Self-Consistent Field Method
7.8: An Electron has an Intrinsic Spin Angular Momentum
7.9: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

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7.1: The Helium Atom Cannot Be Solved Exactly

Learning Objectives

- Adding electrons to the quantum hydrogen atom results in analytically unsolvable Schrödinger Equations (they exist, we just do not have analytical forms for them)
- A basic aspect of the corresponding multi-electron Hamiltonians is that they are NOT separable with respect to the spatial coordinate of each electron
- The solutions to multi-electron Schrödinger Equations are called multi-electron wavefunctions and they are often approximated as a product of single-electron wavefunctions (called the orbital approximation).

Multi-electron Hamiltonians

The second element in the periodic table provides our first example of a quantum-mechanical problem which *cannot* be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

Figure 6.7.1 shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors r_1 and r_2. The electrons are separated by a distance $r_{12} = |r_1 - r_2|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

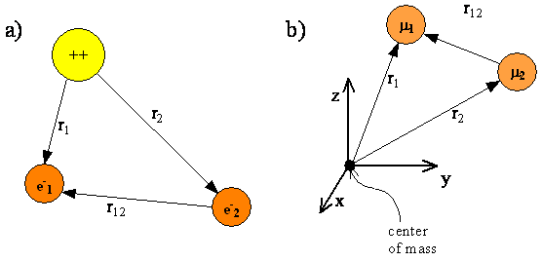


Figure 6.7.1 : (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Hamiltonian operator for the hydrogen atom serves as a reference point for writing the Hamiltonian operator for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} \tag{7.1.1}$$

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

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \tag{7.1.2}$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{7.1.3}$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{7.1.4}$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{7.1.5}$$

The two-electron Hamiltonian in Equation 7.1.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{7.1.6}$$

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

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i\neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \tag{7.1.7}$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 7.1.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 7.1.3 and 7.1.4). 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 7.1.7):

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}B atom.
b. Would it be any different for a $^{11}B^+$ ion?
c. Would it be any different for a ^{10}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, $^{11}B^+$ has one less electron than ^{11}B. Its Hamiltonian is

$$\hat{H}_{\mathrm{B}^+}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = -\frac{\hbar^2}{2m_e}\sum_i^4 \nabla_i^2 + \sum_i^4 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{4,4} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

or expanded to 14 terms

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

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

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 7.1.7 would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their Coulomb repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends *simultaneously* upon the coordinates of all the electrons; i.e., **a multi-electron wavefunction**,

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \cdots \vec{r}_n)$$

The modulus squared of such a wavefunction would describe the probability of finding the electrons (though not specific ones) at a designated volume (V) in the atom.

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

All of the electrons are described simultaneously by a multi-electron wavefunction, so the total amount of electron density represented by the wavefunction equals the number of electrons in the atom.

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

Unfortunately, the Coulomb repulsion terms (Equation 7.1.5) 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 7.1.7) involve writing a multi-electron wavefunction ($\psi(r_1, r_2, \cdots, r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1, r_2, \cdots, r_n) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_n(r_n) \tag{7.1.8}$$

or in Dirac notation

$$|\psi(r_1, r_2, \cdots, r_n)\rangle \approx |\varphi_1(r_1)\rangle|\varphi_2(r_2)\rangle\cdots|\varphi_n(r_n)\rangle \tag{7.1.9}$$

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 7.1.8, 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 7.1.8 or 7.1.9), 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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7.2: The Variational Method Approximation

Learning Objectives

- Appreciate the complexity of solving muliti-electron atoms
- Characterize multi-electron interactions within shielding and penetration concepts
- Use the variational method as an approximation to study insolvable problems
- User variational method to evaluate the effective nuclear charge for a specific atom

In this section we introduce the powerful and versatile variational method and use it to improve the approximate solutions we found for the helium atom using the independent electron approximation.

The True (Experimentally Determined) Energy of the Helium Atom

The helium atom has two electrons bound to a nucleus with charge $Z = 2$. The *successive* removal of the two electrons can be considered stepwise:

$$\mathrm{He} \xrightarrow{I_1} \mathrm{He}^+ + e^- \xrightarrow{I_2} \mathrm{He}^{++} + 2e^- \tag{7.2.1}$$

The *first ionization energy* I_1 is the minimum energy required to remove the first electron from helium gas and is experimentally determined:

$$I_1 = -E_{1s}(\mathrm{He}) = 24.59\ eV$$

While the second ionization energy, I_2 can be experimentally determined, it can also be calculated exactly from the hydrogen atom solutions since He^+ is a hydrogen-like ion with $Z = 2$. Hence, we have

$$\begin{aligned} I_2 &= -E_{1s}(\mathrm{He}^+) \\ &= \frac{Z^2}{2n^2} \\ &= 54.42\ \mathrm{eV} \end{aligned}$$

The energy of the three separated particles on the right side of Equation 7.2.1 is zero (by definition). Therefore the ground-state energy of helium atom is given by

$$\begin{aligned} E_{true} &= -(I_1 + I_2) \\ &= -79.02\ \mathrm{eV}. \end{aligned}$$

which can be expressed in terms of the ***Rydberg*** constant ($R_H = 13.6\ eV$) that also describes the lowest energy of the hydrogen atom

$$E_{true} = -5.8066\, R_H$$

We will attempt to reproduce this **true value**, as close as possible, by different theoretical approaches (all approximations).

The "Ignorance is Bliss" Approximation

The Hamiltonian for the Helium atom is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \cancel{\frac{e^2}{4\pi\epsilon_0 r_{12}}} \tag{7.2.2}$$

If we simply *ignore* the electron-electron repulsion term, then Equation 7.2.2 can be simplified to

$$\hat{H} \approx -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{7.2.3}$$

$$\approx h_1(r_1) + h_2(r_2) \tag{7.2.4}$$

where h_1 and h_2 are one electron Hamiltonians for electron 1 and 2, respectively, and are just the hydrogen-like Hamiltonians. The approximation in Equation 7.2.4 is convenient since electron 1 is *separable* from electron 2, so that the two-electron wavefunction is approximated as a product to two one-electron wavefunctions:

$$\Psi_{total} = \psi_{el_1}\psi_{el_2} \tag{7.2.5}$$

or in braket notation

$$|\Psi_{total}\rangle = \hat{H}|\psi_{el_1}\psi_{el_2}\rangle \tag{7.2.6}$$

With some operator algebra, something important arises - the one electron energies are **additive**:

$$\hat{H}\Psi_{total} = (\hat{H}_{el_1} + \hat{H}_{el_2})\psi_{n\,el_1}\psi_{n\,el_2} = (E_{n_1} + E_{n_2})\psi_{n\,el_1}\psi_{n\,el_2}$$

or in bra-ket notation

$$\begin{aligned}\hat{H}|\Psi_{total}\rangle &= \hat{H}|\psi_{el_1}\psi_{el_2}\rangle \\ &= (E_{n_1} + E_{n_2})|\psi_1\psi_2\rangle\end{aligned}$$

The energy for a ground state Helium atom (both electrons in lowest state) is then

$$\begin{aligned}E_{He_{1s}} &= \underbrace{E_{n_1}}_{\text{energy of single electron in helium}} + \underbrace{E_{n_2}}_{\text{energy of single electron in helium}} \\ &= -R_H\left(\frac{Z^2}{1}\right) - R_H\left(\frac{Z^2}{1}\right) \\ &= -8R_H\end{aligned}$$

This approximation significantly overestimates the true energy of the helium atom $E_{He_{1s}} = -5.8066\,R$. This is a poor approximation and we need to address electron-electron repulsion properly (or better at least).

Shielding and Penetration

One way to take electron-electron repulsion into account is to modify the form of the wavefunction. A logical modification is to change the nuclear charge, Z, in the wavefunctions to an effective nuclear charge (Z_{eff}), from +2 to a smaller value. The rationale for making this modification is that one electron partially shields the nuclear charge from the other electron, as shown in Figure 7.1.1 .

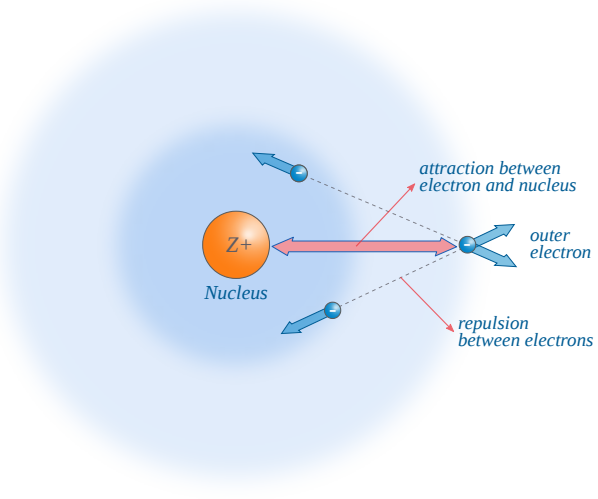


Figure 7.1.1 : Electron-electron shielding leading to a reduced effective nuclear charge. The attractive force of the nucleus on the outer electron is partially countered by the repulsive force between inner electrons and the outer electron. (CC BY-SA; Ümit Kaya via LibreTexts)

A region of negative charge density between one of the electrons and the +2 nucleus makes the potential energy between them more positive (decreases the attraction between them). We can effect this change mathematically by using $\zeta < 2$ in the

wavefunction expression. If the shielding were complete, then Z_{eff} would equal 1. If there is no shielding, then $Z_{eff} = 2$. So a way to take into account the electron-electron interaction is by saying it produces a shielding effect. The shielding is not zero, and it is not complete, so the effective nuclear charge varies between one and two.

In general, a theory should be able to make predictions in advance of knowledge of the experimental result. Consequently, a principle and method for choosing the best value for Z_{eff} or any other adjustable parameter that is to be optimized in a calculation is needed. The Variational Principle provides the required criterion and method and says that the best value for any variable parameter in an approximate wavefunction is the value that gives the **lowest energy for the ground state**; i.e., the value that minimizes the energy. The variational method is the procedure that is used to find the lowest energy and the best values for the variable parameters.

A Better Approximation: The Variational Method

The variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions and is the variational principle. The method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an **upper bound** to the ground state energy.

The variational principle means that the expectation value for the binding energy obtained using an approximate wavefunction and the exact Hamiltonian operator will be higher than or equal to the true energy for the system. This idea is really powerful. When implemented, it permits us to find the best approximate wavefunction from a given wavefunction that contains one or more adjustable parameters, called a **trial wavefunction**. A mathematical statement of the variational principle is

$$E_{trial} \geq E_{true} \tag{7.2.7}$$

where

$$E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{7.2.8}$$

$$= \frac{\int \psi^*_{trial} \hat{H} \psi_{trial} \, d\tau}{\int \psi^*_{trial} \psi_{trial} \, d\tau} \tag{7.2.9}$$

Equation 7.2.7 is called the variational theorem and states that for a time-independent Hamiltonian operator, any trial wavefunction will have an variational energy (i.e., expectation value) that is **greater than or equal** to the true ground state wavefunction corresponding to the given Hamiltonian (Equation 7.2.7). Because of this, the variational energy is an upper bound to the true ground state energy of a given molecule. The general approach of this method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible (Figure 7.1.2).

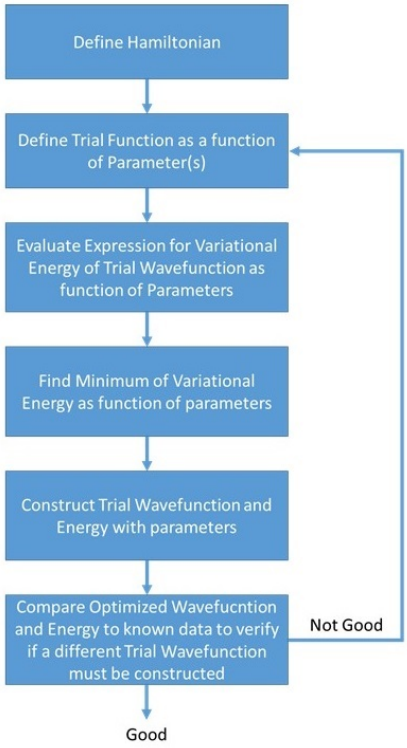


Figure 7.1.2 : Simplified algorithmic flowchart of the Variational Method approximation

> *The variational energy E_{trial} is only equal to the true energy E_{true} when the the corresponding trial wavefunction ψ_{trial} is equal to the true wavefunction ψ_{true}.*

Application to the Helium atom Ground State

Often the expectation values (numerator) and normalization integrals (denominator) in Equation 7.2.9 can be evaluated analytically. For the case of the He atom, let's consider the trial wavefunction as the product wavefunction given by Equation 7.2.10(this is called the **orbital approximation**),

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{7.2.10}$$

The adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ, and the Hamiltonian is the complete form given below (Note: quantum calculations typically refer to effective nuclear charge as ζ rather than Z_{eff} as we used previously).

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{7.2.11}$$

the adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ (would be equal to $\zeta = 2$ if fully unshielded), and the Hamiltonian is the complete form. When the expectation value for the trial energy (Equation 7.2.9) is evaluated for helium, the result is a variational energy that depends on the adjustable parameter, ζ.

$$E_{trial}(\zeta) = \frac{\mu e^4}{4\epsilon_0^2 h}\left(\zeta^2 - \frac{27}{8}\zeta\right) \tag{7.2.12}$$

This function is plotted in Figure 7.1.3 as a function of ζ. According to the variational principle (Equation 7.2.7), the minimum value of the energy on this graph is the best approximation of the true energy of the system, and the associated value of ζ is the best value for the adjustable parameter.

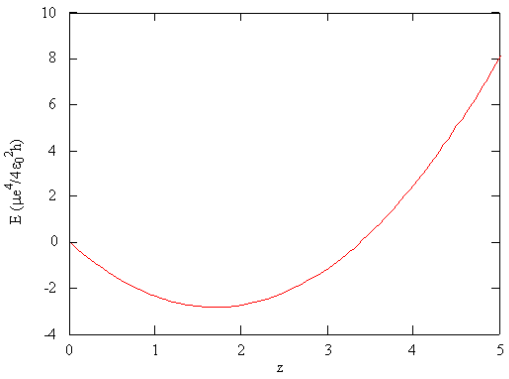


Figure 7.1.3 : Graph of trial energies for helium atom as a function of the adjustable parameter ζ in Equation 7.2.12 that represents the effective nuclear charge felt by the electrons.

Using the mathematical function for the energy of a system, the minimum energy with respect to the adjustable parameter can be found by taking the derivative of the energy with respect to that parameter, setting the resulting expression equal to zero, and solving for the parameter, in this case ζ. This is a standard method in calculus for finding maxima and minima.

? Exercise 7.1.1

Find the value for ζ that minimizes the helium binding energy for the product trial wavefunction in Equation 7.2.10 with the Hamiltonian in Equation 7.2.11. and compare the binding energy to the experimental value. What is the percent error in the calculated value?

Solution

The variational method requires following the workflow in Figure 7.1.2 .

- Step 1: Define the Hamiltonian - This is given by Equation 7.2.11.
- Step 2: Define the trial wavefunction as a function of at least one parameter - This is given by Equation 7.2.10.
- Step 3: Evaluate variational energy (E_{trial} integral (Equation 7.2.9) - This procedure was already above in Equation 7.2.12.
- Step 4: Minimize the variational energy as a function of the parameter(s) - Following the standard approach to find extrema in calculus, evaluate the derivative of E_{trial} with respect to ζ and set to zero:

$$\frac{dE_{trial}}{d\zeta} = \frac{\mu e^4}{4\epsilon_0^2 h}\left(2\zeta - \frac{27}{8}\right) = 0$$

then find solve for the roots of this polynomial

$$2\zeta - \frac{27}{8} = 0$$

or

$$\zeta = \frac{27}{16} \approx 1.6875$$

- Step 5-6: The question does not ask for the optimized wavefunction (Step 5) or to compare the result with the true value to evaluate the quality of the approximation (Step 6). We can skip these steps.

From Exercise 7.1.1 , the $\zeta = 1.6875$ and the approximate energy we calculate using this approximation method, E_{approx} = -77.483 eV. Table 7.1.1 show that a substantial improvement in the accuracy of the computed binding energy is obtained by using shielding to account for the electron-electron interaction. Including the effect of electron shielding in the wavefunction reduces the error in the binding energy to about 2%. This idea is very simple, elegant, and significant.

Table 7.1.1 : Comparison of the results of three approximation methods to experiment.

Method	He binding energy (eV)

Method	He binding energy (eV)
"Ignorance is Bliss" Approximation (neglect repulsion between electrons)	-108.8
Variational method with variable effective charge	-77.483
Experimental	-79.0

The improvement we have seen in the total energy calculations using a variable parameter ζ indicates that an important contribution of electron-electron interaction or repulsion to the total binding energy arises from the fact that each electron shields the nuclear charge from the other electron. It is reasonable to assume the electrons are independent; i.e., that they move independently, but the shielding must be taken into account in order to fine-tune the wavefunctions. The inclusion of optimizable parameters in the wavefunction allows us to develop a clear physical image of the consequences of our variation calculation. Calculating energies correctly is important, and it is also important to be able to visualize electron densities for multi-electron systems. In the next two sections, we take a temporary break from our consideration of approximation methods in order to examine multi-electron wavefunctions more closely.

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7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

Learning Objectives

- Demonstrate that variational problems can include changing parameters within the elements (normal variational method) and changing coefficients of a basis set (linear variational method)

An alternative approach to the general problem of introducing variational parameters into wavefunctions is the construction of a wavefunction as a linear combination of other functions each with one or multiple parameters that can be varied

For hydrogen, the radial function decays, or decreases in amplitude, exponentially as the distance from the nucleus increases. For helium and other multi-electron atoms, the radial dependence of the total probability density does not fall off as a simple exponential with increasing distance from the nucleus as it does for hydrogen. More complex single-electron functions therefore are needed in order to model the effects of electron-electron interactions on the total radial distribution function. One way to obtain more appropriate single-electron functions is to use a sum of exponential functions in place of the hydrogenic spin-orbitals.

An example of such a wavefunction created from a sum or linear combination of exponential functions is written as

$$\varphi_{1s}(r_1) = \sum_j c_j e^{-\zeta_j r_j / a_o} \tag{7.3.1}$$

The linear combination permits weighing of the different exponentials through the adjustable coefficients (c_j) for each term in the sum. Each exponential term has a different rate of decay through the zeta-parameter ζ_j. The exponential functions in Equation 7.3.1 are called **basis functions**. Basis functions are the functions used in linear combinations to produce the single-electron orbitals that in turn combine to create the product multi-electron wavefunctions. Originally the most popular basis functions used were the STO's, but today STO's are not used in most quantum chemistry calculations. However, they are often the functions to which more computationally efficient basis functions are fitted.

Physically, the ζ_j parameters account for the effective nuclear charge (often denoted with Z_{eff}). The use of several zeta values in the linear combination essentially allows the effective nuclear charge to vary with the distance of an electron from the nucleus. This variation makes sense physically. When an electron is close to the nucleus, the effective nuclear charge should be close to the actual nuclear charge. When the electron is far from the nucleus, the effective nuclear charge should be much smaller. See Slater's rules for a rule-of-thumb approach to evaluate Z_{eff} values.

A term in Equation 7.3.1 with a small ζ will decay slowly with distance from the nucleus. A term with a large ζ will decay rapidly with distance and not contribute at large distances. The need for such a linear combination of exponentials is a consequence of the electron-electron repulsion and its effect of screening the nucleus for each electron due to the presence of the other electrons.

Exercise 7.3.1

Make plots of φ in Equation 7.3.1 using three equally weighted terms with ζ = 1.0, 2.0, and 5.0. Also plot each term separately.

Computational procedures in which an exponential parameter like ζ is varied are more precisely called the Nonlinear Variational Method because the variational parameter is part of the wavefunction and the change in the function and energy caused by a change in the parameter is not linear. The optimum values for the zeta parameters in any particular calculation are determined by doing a variational calculation for each orbital to minimize the ground-state energy. When this calculation involves a nonlinear variational calculation for the zetas, it requires a large amount of computer time. The use of the variational method to find values for the coefficients, $\{c_j\}$, in the linear combination given by Equation 7.3.1 above is called the Linear Variational Method because the single-electron function whose energy is to be minimized (in this case φ_{1s}) depends linearly on the coefficients. Although the idea is the same, it usually is much easier to implement the linear variational method in practice.

Nonlinear variational calculations are extremely costly in terms of computer time because each time a zeta parameter is changed, all of the integrals need to be recalculated. In the linear variation, where only the coefficients in a linear combination are varied, the basis functions and the integrals do not change. Consequently, an optimum set of zeta parameters were chosen from variational

calculations on many small multi-electron systems, and these values, which are given in Table 7.3.1 , generally can be used in the STOs for other and larger systems.

Table 7.3.1 : Orbital Exponents for Slater Orbitals

Atom	ζ_{1s}	$\zeta_{2s,2p}$
H	1.24	-
He	1.69	-
Li	2.69	0.80
Be	3.68	1.15
B	4.68	1.50
C	5.67	1.72
N	6.67	1.95
O	7.66	2.25
F	8.56	2.55
Ne	9.64	2.88

Exercise 7.3.2

Compare the value ζ_{1s} = 1.24 in Table 7.3.1 for hydrogen with the value you obtained in Exercise 7.3.1 . and comment on possible reasons for any difference. Why are the zeta values larger for 1s than for 2s and 2p orbitals? Why do the ζ_{1s} values increase by essentially one unit for each element from He to Ne while the increase for the $\zeta_{2s,2p}$ values is much smaller?

Answer

ζ values represent the rate of decay in the radial function of an orbital. ζ values are larger for 1s than 2s and 2p orbitals because 1s orbitals have a smaller radial function. As a result, 1s orbitals decrease faster in radial function as you move further from the nucleus, and have a larger ζ value to represent this faster decay. The ζ values for 1s increase essentially by one unit for each element from He to Ne because the 1s orbital is closest to the nucleus, and experiences the greatest effects from change in electronegativity as nuclear density increases from He to Ne. This increase in electronegativity causes the radial function to decay more and more rapidly as atomic number/nucleus density increase. The 2s and 2p orbitals don't experience as great a change in radial function decay rate because they are shielded by the 1s orbital.

The discussion above gives us some new ideas about how to write flexible, useful single-electron wavefunctions that can be used to construct multi-electron wavefunctions for variational calculations. Single-electron functions built from the basis function approach are flexible because they have several adjustable parameters, and useful because the adjustable parameters still have clear physical interpretations. Such functions will be needed in the Hartree-Fock method discussed elsewhere.

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7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

Learning Objectives

- Use perturbation theory to approximate the energies of systems as a series of perturbation of a solved system.
- Use perturbation theory to approximate the wavefunctions of systems as a series of perturbation of a solved system.

It is easier to compute the changes in the energy levels and wavefunctions with a scheme of successive corrections to the zero-field values. This method, termed **perturbation theory**, is the single most important method of solving problems in quantum mechanics and is widely used in atomic physics, condensed matter and particle physics. Perturbation theory is another approach to finding approximate solutions to a problem, by starting from the exact solution of a related, simpler problem. A critical feature of the technique is a middle step that breaks the problem into "solvable" and "perturbation" parts. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a "small" term to the mathematical description of the exactly solvable problem.

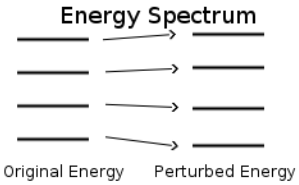


Figure 7.4.1 : Perturbed Energy Spectrum. (CC BY-SA 2.0, Frontier via Wikipedia)

We begin with a Hamiltonian $\hat{H}^0$ having known eigenstates and eigenenergies:

$$\hat{H}^o|n^o\rangle = E_n^o|n^o\rangle \tag{7.4.1}$$

The task is to find how these eigenstates and eigenenergies change if a small term H^1 (an external field, for example) is added to the Hamiltonian, so:

$$(\hat{H}^0 + \hat{H}^1)|n\rangle = E_n|n\rangle \tag{7.4.2}$$

That is to say, on switching on $\hat{H}^1$ changes the wavefunctions:

$$\underbrace{|n^o\rangle}_{\text{unperturbed}} \Rightarrow \underbrace{|n\rangle}_{\text{Perturbed}} \tag{7.4.3}$$

and energies (Figure 7.4.1):

$$\underbrace{E_n^o}_{\text{unperturbed}} \Rightarrow \underbrace{E_n}_{\text{Perturbed}} \tag{7.4.4}$$

> *The basic assumption in perturbation theory is that H^1 is sufficiently small that the leading corrections are the same order of magnitude as H^1 itself, and the true energies can be better and better approximated by a successive series of corrections, each of order H^1/H^o compared with the previous one.*

The strategy is to **expand** the true wavefunction and corresponding eigenenergy as series in $\hat{H}^1/\hat{H}^o$. These series are then fed into Equation 7.4.2, and terms of the same order of magnitude in $\hat{H}^1/\hat{H}^o$ on the two sides are set equal. The equations thus generated are solved one by one to give progressively more accurate results.

To make it easier to identify terms of the same order in $\hat{H}^1/\hat{H}^o$ on the two sides of the equation, it is convenient to introduce a dimensionless parameter λ which always goes with $\hat{H}^1$, and then expand both eigenstates and eigenenergies as power series in λ,

$$|n\rangle = \sum_{i}^{m} \lambda^i |n^i\rangle \tag{7.4.5}$$

$$E_n = \sum_{i=0}^{m} \lambda^i E_n^i \tag{7.4.6}$$

where m is how many terms in the expansion we are considering. The ket $|n^i\rangle$ is multiplied by λ^i and is therefore of order $(H^1/H^o)^i$.

> *λ is purely a bookkeeping device: we will set it equal to 1 when we are through! It's just there to keep track of the orders of magnitudes of the various terms.*

For example, in first order perturbation theory, Equations 7.4.5 are truncated at $m = 1$ (and setting $\lambda = 1$):

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.7}$$

$$E_n \approx E_n^o + E_n^1 \tag{7.4.8}$$

However, let's consider the general case for now. Adding the full expansions for the eigenstate (Equation 7.4.5) and energies (Equation 7.4.6) into the Schrödinger equation for the perturbation Equation 7.4.2 in

$$(\hat{H}^o + \lambda \hat{H}^1)|n\rangle = E_n|n\rangle \tag{7.4.9}$$

we have

$$(\hat{H}^o + \lambda \hat{H}^1)\left(\sum_{i=0}^{m} \lambda^i |n^i\rangle\right) = \left(\sum_{i=0}^{m} \lambda^i E_n^i\right)\left(\sum_{i=0}^{m} \lambda^i |n^i\rangle\right) \tag{7.4.10}$$

We're now ready to match the two sides term by term in powers of λ. Note that the zeroth-order term, of course, just gives back the unperturbed Schrödinger Equation (Equation 7.4.1).

Let's look at Equation 7.4.10 with the first few terms of the expansion:

$$(\hat{H}^o + \lambda \hat{H}^1)\left(|n^o\rangle + \lambda|n^1\rangle\right) = \left(E_n^0 + \lambda E_n^1\right)\left(|n^o\rangle + \lambda|n^1\rangle\right) \tag{7.4.11}$$

$$\hat{H}^o|n^o\rangle + \lambda\hat{H}^1|n^o\rangle + \lambda H^o|n^1\rangle + \lambda^2\hat{H}^1|n^1\rangle = E_n^0|n^o\rangle + \lambda E_n^1|n^o\rangle + \lambda E_n^0|n^1\rangle + \lambda^2 E_n^1|n^1\rangle \tag{7.4.12}$$

Collecting terms in order of λ and coloring to indicate different orders

$$\underset{\text{zero order}}{\hat{H}^o|n^o\rangle} + \underset{\text{1st order}}{\lambda(\hat{H}^1|n^o\rangle + \hat{H}^o|n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2\hat{H}^1|n^1\rangle} = \underset{\text{zero order}}{E_n^0|n^o\rangle} + \underset{\text{1st order}}{\lambda(E_n^1|n^o\rangle + E_n^0|n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 E_n^1|n^1\rangle} \tag{7.4.13}$$

If we expanded Equation 7.4.10 further we could express the energies and wavefunctions in higher order components.

Zero-Order Terms ($\lambda = 0$)

Collecting the zero order terms in the expansion (black terms in Equation 7.4.13) results in just the Schrödinger Equation for the unperturbed system

$$\hat{H}^o|n^o\rangle = E_n^o|n^o\rangle \tag{7.4.14}$$

First-Order Expression of Energy ($\lambda = 1$)

The summations in Equations 7.4.5, 7.4.6, and 7.4.10 can be truncated at any order of λ. For example, the first order perturbation theory has the truncation at $\lambda = 1$. Matching the terms that linear in λ (red terms in Equation 7.4.13) and setting $\lambda = 1$ on both sides of Equation 7.4.13:

$$\hat{H}^o|n^1\rangle + \hat{H}^1|n^o\rangle = E_n^o|n^1\rangle + E_n^1|n^o\rangle \tag{7.4.15}$$

Equation 7.4.15 is the key to finding the first-order change in energy E_n^1. Taking the **inner product** of both sides with $\langle n^o|$:

$$\langle n^o|\hat{H}^o|n^1\rangle + \langle n^o|\hat{H}^1|n^o\rangle = \langle n^o|E_n^o|n^1\rangle + \langle n^o|E_n^1|n^o\rangle \tag{7.4.16}$$

since operating the zero-order Hamiltonian on the bra wavefunction (this is just the Schrödinger equation; Equation 7.4.14) is

$$\langle n^o|\hat{H}^o = \langle n^o|E_n^o \tag{7.4.17}$$

and via the orthonormality of the unperturbed $|n^o\rangle$ wavefunctions both

$$\langle n^o|n^o\rangle = 1 \tag{7.4.18}$$

and Equation 7.4.8 can be simplified

$$\cancel{E_n^o\langle n^o|n^1\rangle} + \langle n^o|H^1|n^o\rangle = \cancel{E_n^o\langle n^o|n^1\rangle} + E_n^1\,\langle n^o|n^o\rangle^1 \tag{7.4.19}$$

since the unperturbed set of eigenstates are orthogonal (Equation 7.4.18) and we can cancel the other term on each side of the equation, we find that

$$E_n^1 = \langle n^o|\hat{H}^1|n^o\rangle \tag{7.4.20}$$

> *The first-order change in the energy of a state resulting from adding a perturbing term $\hat{H}^1$ to the Hamiltonian is just the **expectation value** of $\hat{H}^1$ in the **unperturbed** wavefunctions.*

That is, the first order energies (Equation 7.4.15) are given by

$$E_n \approx E_n^o + E_n^1 \tag{7.4.21}$$

$$\approx \underbrace{E_n^o + \langle n^o|H^1|n^o\rangle}_{\text{First Order Perturbation}} \tag{7.4.22}$$

Example : A Perturbed Particle in a Box

Estimate the energy of the ground-state and first excited-state wavefunction within first-order perturbation theory of a system with the following potential energy

$$V(x) = \begin{cases} V_o & 0 \le x \le L \\ \infty & x < 0 \text{ and } x > L \end{cases}$$

Solution

The first step in any perturbation problem is to write the Hamiltonian in terms of a unperturbed component that the solutions (both eigenstates and energy) are known and a perturbation component (Equation 7.4.2). For this system, the unperturbed Hamilonian and solutions is the particle in an infiinitely high box and the perturbation is a shift of the potential within the box by V_o.

$$\hat{H}^1 = V_o$$

Using Equation 7.4.20 for the first-order term in the energy of the ground-state

$$E_n^1 = \langle n^o|H^1|n^o\rangle$$

with the wavefunctions known from the particle in the box problem

$$|n^o\rangle = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

At this stage we can do two problems independently (i.e., the ground-state with $|1\rangle$ and the first excited-state $|2\rangle$). However, in this case, the first-order perturbation to any particle-in-the-box state can be easily derived.

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

or better yet, instead of evaluating this integrals we can simplify the expression

$$E_n^1 = \langle n^o|H^1|n^o\rangle = \langle n^o|V_o|n^o\rangle = V_o\langle n^o|n^o\rangle = V_o$$

so via Equation 7.4.22, the energy of each perturbed eigenstate is

$$\begin{aligned} E_n &\approx E_n^o + E_n^1 \\ &\approx \frac{h^2}{8mL^2}n^2 + V_o \end{aligned}$$

While this is the first order perturbation to the energy, it is also the exact value.

Example : An Even More Perturbed Particle in a Box

Estimate the energy of the ground-state wavefunction within first-order perturbation theory of a system with the following potential energy

$$V(x) = \begin{cases} V_o & 0 \le x \le L/2 \\ \infty & x < 0 \; and \; x > L \end{cases}$$

Solution

As with Example 7.4.1 , we recognize that unperturbed component of the problem (Equation 7.4.2) is the particle in an infinitely high well. For this system, the unperturbed Hamiltonian and solution is the particle in an infinitely high box and the perturbation is a shift of the potential within half a box by V_o. This is essentially a step function.

Using Equation 7.4.20 for the first-order term in the energy of the any state

$$\begin{aligned} E_n^1 &= \langle n^o|H^1|n^o\rangle \\ &= \int_0^{L/2} \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) V_o \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)dx + \int_{L/2}^{L} \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) 0 \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)dx \end{aligned}$$

The second integral is zero and the first integral is simplified to

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

this is evaluated to

$$\begin{aligned} E_n^1 &= \frac{2V_o}{L}\left[\frac{-1}{2\frac{\pi n}{a}}\cos\left(\frac{n\pi}{L}x\right)\sin\left(\frac{n\pi}{L}x\right) + \frac{x}{2}\right]_0^{L/2} \\ &= \frac{2V_o}{\not{L}}\frac{\not{L}}{4} = \frac{V_o}{2} \end{aligned}$$

The energy of each perturbed eigenstate, via Equation 7.4.22, is

$$\begin{aligned} E_n &\approx E_n^o + \frac{V_o}{2} \\ &\approx \frac{h^2}{8mL^2}n^2 + \frac{V_o}{2} \end{aligned}$$

First-Order Expression of Wavefunction ($\lambda = 1$)

The general expression for the first-order change in the *wavefunction* is found by taking the inner product of the first-order expansion (Equation 7.4.15) with the bra $\langle m^o|$ with $m \neq n$,

$$\langle m^o|H^o|n^1\rangle + \langle m^o|H^1|n^o\rangle = \langle m^o|E_n^o|n^1\rangle + \langle m^o|E_n^1|n^o\rangle \tag{7.4.23}$$

Last term on right side of Equation 7.4.23

The last integral on the right hand side of Equation 7.4.23 is zero, since $m \neq n$ so

$$\langle m^o|E_n^1|n^o\rangle = E_n^1\langle m^o|n^o\rangle \tag{7.4.24}$$

and

$$\langle m^o|n^0\rangle = 0 \tag{7.4.25}$$

First term on right side of Equation 7.4.23

The first integral is more complicated and can be expanded back into the H^o

$$E_m^o\langle m^o|n^1\rangle = \langle m^o|E_m^o|n^1\rangle = \langle m^o|H^o|n^1\rangle \tag{7.4.26}$$

since

$$\langle m^o|H^o = \langle m^o|E_m^o \tag{7.4.27}$$

so

$$\langle m^o|n^1\rangle = \frac{\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o} \tag{7.4.28}$$

and therefore the wavefunction corrected to first order is:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.29}$$

$$\approx \underbrace{|n^o\rangle + \sum_{m\neq n}\frac{|m^o\rangle\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o}}_{\text{First Order Perturbation Theory}} \tag{7.4.30}$$

Equation 7.4.30 is essentially is an expansion of the unknown wavefunction correction as a **linear combination** of known unperturbed wavefunctions 7.4.32:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.31}$$

$$\approx |n^o\rangle + \sum_{m\neq n} c_{m,n}|m^o\rangle \tag{7.4.32}$$

with the expansion coefficients determined by

$$c_{m,n} = \frac{\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o} \tag{7.4.33}$$

This is justified since the set of original zero-order wavefunctions forms a **complete basis set** that can describe any function.

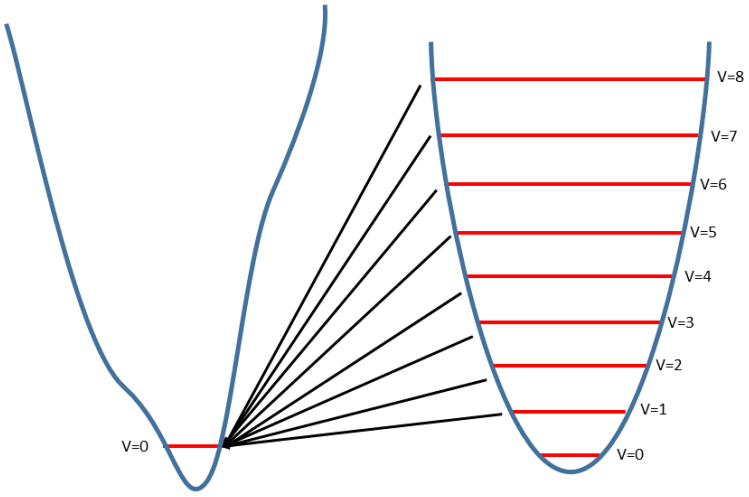


Figure 7.4.2 : The first order perturbation of the ground-state wavefunction for a perturbed (left potential) can be expressed as a linear combination of all excited-state wavefunctions of the unperturbed potential (Equation 7.4.32), shown as a harmonic oscillator in this example (right potential). Note that the ground-state harmonic oscillator wavefunction is not part of this expression and all wavefunctions need to be included in the expression, not just the first eight wavefunctions shown here. (CC BY 4.0; Delmar Larsen)

Calculating the first order perturbation to the wavefunctions is in general an infinite sum of off diagonal matrix elements of H^1 (Figure 7.4.2).

- However, the denominator argues that terms in this sum will be weighted by states that are of **comparable energy**. That means in principle, these sum can be truncated easily based off of some criterion.
- Another point to consider is that many of these matrix elements will equal zero depending on the symmetry of the $\{|n^o\rangle\}$ basis and H^1 (e.g., some $\langle m^o|H^1|n^o\rangle$ integrals in Equation 7.4.30 could be zero due to the integrand having an odd symmetry; see Example 7.4.3).

> *The denominators in Equation 7.4.30 argues that terms in this sum will be preferentially dictated by states that are of **comparable energy**. That is, eigenstates that have energies significantly greater or lower than the unperturbed eigenstate will weakly contribute to the perturbed wavefunction.*

Example 7.4.2 : A Harmonic Oscillator with a Cubic Perturbation

Estimate the energy of the ground-state wavefunction associated with the Hamiltonian using perturbation theory

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \epsilon x^3$$

Solution

The first step in a perturbation theory problem is to identify the reference system with the known eigenstates and energies. For this example, this is clearly the harmonic oscillator model.

Energy

The first steps in flowchart for applying perturbation theory (Figure 7.4.1) is to separate the Hamiltonian of the difficult (or unsolvable) problem into a solvable one with a perturbation. For this case, we can rewrite the Hamiltonian as

$$\hat{H}^o + \hat{H}^1$$

where

- $\hat{H}^o$ is the Hamitonian for the standard Harmonic Oscillator with **known** eigenstates and eigenenergies

$$\hat{H}^{(0)} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

- $\hat{H}^1$ is the pertubtiation

$$\hat{H}^1 = \epsilon x^3$$

The first order perturbation is given by Equation 7.4.20, which for this problem is

$$E_n^1 = \langle n^o | \epsilon x^3 | n^o \rangle$$

Notice that the integrand has an odd symmetry (i.e., $f(x) = -f(-x)$) with the perturbation Hamiltonian being odd and the ground state harmonic oscillator wavefunctions being even. So

$$E_n^1 = 0$$

This means to first order pertubation theory, this cubic terms does not alter the ground state energy (via Equation 7.4.22). However, this is not the case if second-order perturbation theory were used, which is more accurate (not shown).

Wavefunction

Calculating the first order perturbation to the wavefunctions (Equation 7.4.30) is more difficult than energy since multiple integrals must be evaluated (an infinite number if symmetry arguments are not applicable). The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate:

$$|\Psi_v(x)\rangle = N_v'' H_v(\sqrt{\alpha}Q) e^{-\alpha Q^2/2}$$

with α

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

and

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Let's consider only the first six wavefunctions that use these Hermite polynomials $H_v(x)$:

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$

The first order perturbation to the ground-state wavefunction (Equation 7.4.30)

$$|0^1\rangle = \sum_{m \neq 0}^{5} \frac{|m^o\rangle\langle m^o|H^1|0^o\rangle}{E_0^o - E_m^o} \tag{7.4.34}$$

given these truncated wavefunctions (we should technically use the infinite sum) and that we are considering only the ground state with $n = 0$:

$$|0^1\rangle = \frac{\langle 1^o|H^1|0^o\rangle}{E_0^o - E_1^o}|1^o\rangle + \frac{\langle 2^o|H^1|0^o\rangle}{E_0^o - E_2^o}|2^o\rangle + \frac{\langle 3^o|H^1|0^o\rangle}{E_0^o - E_3^o}|3^o\rangle + \frac{\langle 4^o|H^1|0^o\rangle}{E_0^o - E_4^o}|4^o\rangle + \frac{\langle 5^o|H^1|0^o\rangle}{E_0^o - E_5^o}|5^o\rangle$$

We can use symmetry of the perturbation and unperturbed wavefunctions to solve the integrals above. We know that the unperturbed harmonic oscillator wavefunctions $\{|n^0\}\rangle$ alternate between even (when v is even) and odd (when v is odd) as shown previously. Since the perturbation is an odd function, only when $m = 2k+1$ with $k = 1, 2, 3$ would these integrals be non-zero (i.e., for $m = 1, 3, 5, \ldots$).

So of the original five unperturbed wavefunctions, only $|m=1\rangle$, $|m=3\rangle$, and $|m=5\rangle$ mix to make the first-order perturbed ground-state wavefunction so

$$|0^1\rangle = \frac{\langle 1^o|H^1|0^o\rangle}{E_0^o - E_1^o}|1^o\rangle + \frac{\langle 3^o|H^1|0^o\rangle}{E_0^o - E_3^o}|3^o\rangle + \frac{\langle 5^o|H^1|0^o\rangle}{E_0^o - E_5^o}|5^o\rangle$$

At this stage, the integrals have to be manually calculated using the defined wavefuctions above, which is left as an exercise. Notice that each unperturbed wavefunction that can "mix" to generate the perturbed wavefunction will have a reciprocally decreasing contribution (w.r.t. energy) due to the growing denominator in Equation 7.4.34.

Exercise 7.4.3 : Harmonic Oscillator with a Quartic Perturbation

Use perturbation theory to estimate the energy of the ground-state wavefunction associated with this Hamiltonian

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \gamma x^4.$$

Answer

The model that we are using is the harmonic oscillator model which has a Hamiltonian

$$H^0 = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

Making the perturbed Hamiltonian

$$H^1 = \gamma x^4$$

To find the perturbed energy we approximate it using Equation 7.4.22

$$E^1 = \langle n^0 \left| H^1 \right| n^0 \rangle$$

where is the wavefunction of the ground state harmonic oscillator

$$n^0 = \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}}$$

When we substitute in the Hamiltonian and the wavefunction we get

$$E^1 = \left\langle \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}} \middle| \gamma x^4 \middle| \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}} \right\rangle$$

Changing this into integral form, and combining the wavefunctions,

$$E^1 = \int_{-\infty}^{\infty} \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} e^{\frac{-ax^2}{2}} \gamma x^4 dx$$

$$= \gamma \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx$$

Now we use the integral table value

$$\int_0^{\infty} x^{2\pi} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{m+1} a^n} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

Where we plug in $\mathrm{n} = 2$ and $\mathrm{a} = \alpha$ for our integral

$$E^1 = 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \int_0^{\infty} x^4 e^{-ax^2} dx$$

$$= 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \frac{1 \cdot 3}{2^3 a^2} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

This is our perturbed energy.

Now we have to find our ground state energy using the formula for the energy of a harmonic oscillator that we already know,

$$E_r^0 = \left(v + \frac{1}{2}\right) h\nu$$

Where in the ground state $v = 0$ so the energy for the ground state of the quantum harmonic oscillator is

$$E_{\mathrm{r}}^0 = \frac{1}{2} h\nu$$

Putting both of our energy terms together gives us the ground state energy of the wavefunction of the given Hamiltonian,

$$\begin{aligned} E &= E^0 + E^1 \\ &= \frac{1}{2} h\nu + \gamma \frac{3}{4a^2} \end{aligned}$$

Second-Order Terms ($\lambda = 2$)

There are higher energy terms in the expansion of Equation 7.4.5 (e.g., the blue terms in Equation 7.4.13), but are not discussed further here other than noting the whole perturbation process is an infinite series of corrections that ideally converge to the correct answer. It is truncating this series as a finite number of steps that is the approximation. The general approach to perturbation theory applications is giving in the flowchart in Figure 7.4.1 .

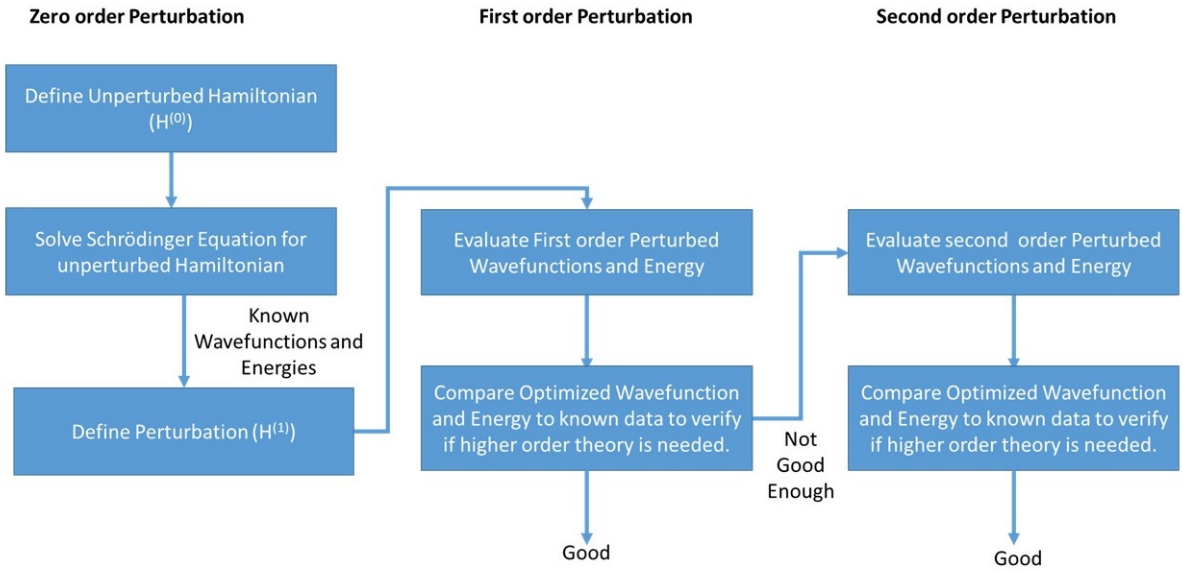


Figure 7.4.1 : Simplified algorithmic flowchart of the Perturbation Theory approximation showing the first two perturbation orders. The process can be continued to third and higher orders. (CC BY 4.0; Delmar Larsen)

Perturbation Theory Does not always Work

It should be noted that there *are* problems that cannot be solved using perturbation theory, even when the perturbation is very weak, although such problems are the exception rather than the rule. One such case is the one-dimensional problem of free particles perturbed by a localized potential of strength λ. Switching on an arbitrarily weak attractive potential causes the $k = 0$ free particle wavefunction to drop below the continuum of plane wave energies and become a localized bound state with binding energy of order λ^2. However, changing the sign of λ to give a repulsive potential there is no bound state, the lowest energy plane wave state stays at energy zero. Therefore the energy shift on switching on the perturbation **cannot** be represented as a power series in λ, the strength of the perturbation.

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7.5: Perturbation Theory and the Variational Method for Helium

Learning Objectives

- Demonstrate that both perturbation theory and variational methods can be used to solve the electron structure of the helium atom.

Both perturbation theory and variation method (especially the linear variational method) provide good results in approximating the energy and wavefunctions of multi-electron atoms. Below we address both approximations with respect to the helium atom.

Perturbation Theory of the Helium Atom

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a **zero-order Hamiltonian**. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. For example, we call the simplified or starting Hamiltonian, $\hat{H}^0$, the zero order term, and the correction term $\hat{H}^1$.

$$\hat{H} = \hat{H}^0 + \hat{H}^1 \tag{7.5.1}$$

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

$$\hat{H}^0 = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}}_{\text{H atom Hamiltonian}} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}}_{\text{H atom Hamiltonian}} \tag{7.5.2}$$

$$\hat{H}^1 = \frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \tag{7.5.3}$$

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

$$\begin{aligned} E^1 &= \langle \psi^0 | \hat{H}^1 | \psi^0 \rangle \\ &= \int \psi^{0*} \hat{H}^1 \psi^0 \, d\tau \end{aligned} \tag{7.5.4}$$

Equation 7.5.4 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 7.5.2) 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 7.5.4 is

$$E^1 = \iint \varphi_{1s}(r_1)\varphi_{1s}(r_2)\frac{1}{r_{12}}\varphi_{1s}(r_1)\varphi_{1s}(r_2)\, d\tau_1 d\tau_2 \tag{7.5.5}$$

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

$$E_{approx2} = E^0 + E^1 = -74.8eV \tag{7.5.6}$$

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy:

$$E^0 = \frac{2}{n^2} + \frac{2}{n^2} = 4 \underbrace{E_h}_{hartrees} = 108.8\, eV$$

so the interaction of the two electrons is an important part of the total energy of the helium atom. We can continue with perturbation theory and find the additional corrections, E^2, E^3, etc. For example,

$$E^0 + E^1 + E^2 = -79.2\, eV.$$

So with two corrections to the energy, the calculated result is within 0.3% of the experimental value of -79.01 eV. It takes thirteenth-order perturbation theory (adding E^1 through E^{13} to E^0) to compute an energy for helium that agrees with experiment to within the experimental uncertainty. Interestingly, while we have improved the calculated energy so that it is much closer to the experimental value, we learn nothing new about the helium atom wavefunction by applying the first-order perturbation theory to the energy above. He need to expand the wavefunctions to first order perturbation theory, which requires more effort. Below, we will employ the variational method approximation to modify zero-order wavefunctions to address one of the ways that electrons are expected to interact with each other.

The Hartree Unit of Energy

The hartree is the atomic unit of energy (named after the British physicist Douglas Hartree) and is defined as

$$E_h = 2R_H hc$$

where R_H is the Rydberg constant, h is the Planck constant and c is the speed of light.

$$\begin{aligned} E_h &= 4.359 \times 10^{-18}\, J \\ &= 27.21\, eV. \end{aligned}$$

The hartree is usually used as a unit of energy in atomic physics and computational chemistry. As discussed before for hydrogen emission, IR, and microwave spectroscopies, experimental measurements prefer the electronvolt (eV) or the wavenumber (cm^{-1}).

Variational Method Applied to the Helium Method

As discussed in Section 6.7, because of the electron-electron interactions, the Schrödinger's Equation cannot be solved exactly for the helium atom or more complicated atomic or ionic species. However, the ground-state energy of the helium atom can be estimated using approximate methods. One of these is the variational method which requires the minimizing of the following variational integral.

$$E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{7.5.7}$$

$$= \frac{\int_0^\infty \psi^*_{trial} \hat{H} \psi_{trial}\, d\tau}{\int_0^\infty \psi^2_{trial}\, d\tau} \tag{7.5.8}$$

The five trial wavefunctions discussions below are equally "valid" trial wavefunctions that describe the probability of finding each electron (technically the wavefunction squared). What separates the "poor" approximations from the "good" approximation is whether the trial wavefunction predicts experimental results. Consequently, for all the approximations used for the rest of this TextMap, it is important to compare the theoretical results to the "true" (i.e., experimental) results. No matter how complicated an approximation is, it is only as good as the accuracy of its predicted values to experimental values.

Trial Wavefunction #1: Simple Orbital Approximation with One Parameter

As is clear from Equation 7.5.7, 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.

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{7.5.9}$$

$$= \exp[-\alpha(r_1 + r_2)] \tag{7.5.10}$$

The variational energy obtained after minimizing Equation 7.5.8 after substituting the trial wavefunction (Equation 7.5.10) 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

$$E_{\text{exp}} = I_1 + I_2 = -2.90372\ E_h \tag{7.5.11}$$

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

$$\left|\frac{E_{trial}(\alpha)-E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.84766\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.5.12}$$

$$= 1.93\% \tag{7.5.13}$$

The value of -2.8477 hartrees is within 2% of the known ground-state energy of the helium atom. The error in the calculation is attributed to the fact that the wavefunction is based on the orbital approximation and, therefore, does not adequately take electron-electron interactions into account. In other words, this wavefunction gives the electrons too much independence, given that they have like charges and tend to avoid one another.

Trial Wavefunction #2: Orbital Approximation with Two Parameters

Some electron-electron interactions can be built into the multi-electron wavefunction by assuming that each electron is in an orbital which is a linear combination of two different and scaled hydrogen 1s orbitals.

$$\phi(r_1) = \exp(-\alpha r_1) + \exp(-\beta r_1) \tag{7.5.14}$$

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

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{7.5.15}$$

$$= \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2) \tag{7.5.16}$$

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 7.5.8). 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 7.5.8 after substituting the trial wavefunction (Equation 7.5.16) 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 7.5.11) is

$$\left|\frac{E_{trial}(\alpha,\beta)-E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.86035\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.5.17}$$

$$= 1.49\% \tag{7.5.18}$$

Clearly introducing some electron-electron interactions into the trial wavefunction has improved the agreement between theory and experiment (Equation 7.5.13 vs. 7.5.18).

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 7.5.16). This yields a multi-electron wavefunction of the form,

$$|\psi(1,2)\rangle_{trial} = \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) \tag{7.5.19}$$

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 7.5.8 after substituting the trial wavefunction (Equation 7.5.19) 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 7.5.11) is

$$\left|\frac{E_{trial}(\alpha,\beta)-E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.87566\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.5.20}$$

$$= 0.97\% \tag{7.5.21}$$

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

Trial Wavefunction #4: Approximation with Two Parameters

The third trial wavefunction, however, still rests on the orbital approximation and, therefore, does not treat electron-electron interactions adequately. Hylleraas took the calculation a step further by introducing electron-electron interactions directly into the first trial wavefunction

by adding a term, r_{12}, involving the inter-electron separation.

$$|\psi_{trial}(1,2)\rangle = (\exp[-\alpha(r_1+r_2)])\,(1+\beta r_{12}) \tag{7.5.22}$$

In the trial multi-electron wavefunction of Equation 7.5.22, 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 7.5.8 after substituting the trial wavefunction (Equation 7.5.22) 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 7.5.11) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.89112\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.5.23}$$

$$= 0.43\% \tag{7.5.24}$$

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

Fifth Trial Wavefunction #5: Approximation with Three Parameters

Chandrasakar brought about further improvement by adding Hylleraas's r_{12} term to the third trial wavefunction (Equation 7.5.19) as shown here.

$$|\psi(1,2)\rangle_{trial} = [\exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)]\,[1+\gamma r_{12}] \tag{7.5.25}$$

Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground-state energy. The variational energy obtained after minimizing Equation 7.5.8 after substituting the trial wavefunction (Equation 7.5.25) 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 7.5.11) is

$$\left|\frac{E_{trial}(\alpha,\beta,\gamma) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.90143 + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{7.5.26}$$

$$= 0.0789\% \tag{7.5.27}$$

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

Summary

The purpose of this section is to examine five trial wavefunctions for the helium atom used within the Perturbation Theory and Variational method approximation. For the Variational method approximation, the calculations begin with an uncorrelated wavefunction in which both electrons are placed in a hydrogenic orbital with scale factor α. The next four trial functions use several methods to increase the amount of electron-electron interactions in the wavefunction. As the summary of results that is appended shows this gives increasingly more favorable agreement with the experimentally determined value for the ground-state energy of the species under study. The detailed calculations show that the reason for this improved agreement with experiment is due to a reduction in electron-electron repulsion.

Five variational method calculations that have been outlined above for the helium atom ($Z = 2$) can be repeated for two-electron atoms (e.g., H^-, Li^+, Be^{2+}, etc). The hydride anion is a particularly interesting case because the first two trial wavefunctions do not predict a stable ion (i.e., they are poor approximations). This indicates that electron-electron interactions is an especially important issue for atoms and ions with small nuclear charge.

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7.6: Atomic and Molecular Calculations are Expressed in Atomic Units

Learning Objectives

- Demonstrate how solving electron structure problems are less cluttered by switching to atomic units instead of SI units.

Atomic units (au or a.u.) form a system of natural units which is especially convenient for atomic physics calculations. Atomic units, like SI units, have a unit of mass, a unit of length, and so on. However, the use and notation is somewhat different from SI. Suppose a particle with a mass of m has 3.4 times the mass of electron. The value of mass m can be written in three ways:

- $m = 3.4\ m_e$: This is the clearest notation (but least common), where the atomic unit is included explicitly as a symbol.
- $m = 3.4\ a.u.$: This notation is ambiguous, but is common. Here, it means that the mass m is 3.4 times the atomic unit of mass. If considering a length L of 3.4 times the atomic unit of length, the equation would look the same, $L = 3.4\ a.u.$ The dimension needs to be inferred from context, which is sloppy.
- $m = 3.4$: This notation is similar to the previous one, and has the same dimensional ambiguity. It comes from formally setting the atomic units to 1 (Table 8.1.1).

This article deals with "Hartree type" of atomic units, where the numerical values of the following four fundamental physical constants are all unity by definition:

Table 8.1.1 : Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units	Value in Atomic Units
mass	electron rest mass	m_e	9.109×10^{-31} kg	1
charge	elementary charge	e	1.602×10^{-19} C	1
action	reduced Planck's constant	$\hbar = \frac{h}{2\pi}$	1.054×10^{-34} J·s	1
electric constant^{-1}	Coulomb force constant	$k_e = \frac{1}{4\pi\epsilon_o}$	8.987 x 10^9 kg·m^3·s^{-2}·C^{-2}	1

Example 8.1.1 : Simplifying the Hamiltonian

Use the atomic units definitions in Table 8.1.1 to contrast the Hamiltonian for a Helium atom in Si units and in atomic units.

Solution

In SI units, the Hamiltonian for a Helium atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

In atomic units, the same Hamiltonian

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

All the units that make the SI version of the Hamiltonian disappear to emphasize the key aspects of the operator.

Atomic units are derived from certain fundamental properties of the physical world, and are free of anthropocentric considerations. It should be kept in mind that atomic units were designed for atomic-scale calculations in the present-day universe, with units normalize the reduced Planck constant and also mass and charge of the electron are set to 1, and, as a result, the speed of light in atomic units is a large value, $1/\alpha \approx 137$. For example, the orbital velocity of an electron around a small atom is of the order of 1 in atomic units. Table 8.1.2 give a few derived units. Some of them have proper names and symbols assigned, as indicated in the table.

Table 8.1.2 : Derived atomic units

Dimension	Name	Symbol	Expression	Value in SI units	Value in more common units
length	bohr	a_o	$4\pi\epsilon_0\hbar^2/(m_e e^2) = \hbar/(m_e c\alpha)$	5.291×10^{-11} m	0.052 nm = 0.529 Å
energy	hartree	E_h	$m_e e^4/(4\pi\epsilon_0\hbar)^2 = \alpha^2 m_e c^2$	4.359×10^{-18} J	27.2 eV = 627.5 kcal·mol^{-1}
time			$\hbar/E_\mathrm{h}$	2.418×10^{-17} s	
velocity			$a_0 E_\mathrm{h}/\hbar = \alpha c$	2.187×10^{6} m·s^{-1}	

Bohr model in atomic units

Atomic units are chosen to reflect the properties of electrons in atoms. This is particularly clear from the classical Bohr model of the hydrogen atom in its ground state. The ground state electron orbiting the hydrogen nucleus has (in the classical Bohr model):

- Orbital velocity = 1
- Orbital radius = 1
- Angular momentum = 1
- Orbital period = 2π
- Ionization energy = ½
- Electric field (due to nucleus) = 1
- Electrical attractive force (due to nucleus) = 1

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

Learning Objectives

- Show how the Hartree approximation can be used to solve for the wavefunctions and energies of multi-electron atoms.
- Understand the orbital approach of independent orbitals is an approximation to a mutlti-electron system with the motions of all electrons coupled together.
- Demonstate how the Self-Consistant Field (SCF) calculation is needed to support the Hartree approximation

The Hartree method is used to approximate the wavefunction and the energy of a quantum multi-electron system in a stationary state. This approximation assumes that the exact N-body wavefunction of the system can be approximated by a product of single-electron wavefunctions. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree wavefunction and energy of the system. It is one step better than the "Ignorance is Bliss" approach, discussed previously, but still far from modern state-off-the-art methods.

Unsolvable Systems

The Hamiltonian for a generic multielectron atom includes nucleus-electron attraction terms for the additional electrons with a general charge Z; e.g.

$$V_{\text{nuclear-electron}}(r_1) = -\frac{Z}{|\mathbf{r}-\mathbf{R}|} \tag{7.7.1}$$

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

$$\hat{H}(r_1, r_2, \ldots r_n) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V_{\text{nuclear-electron}}(r_i) + \sum_{i\neq j} V_{\text{electron-electron}}(r_{ij}) \tag{7.7.2}$$

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 7.7.2) 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:

$$|\psi(r_1, r_2, \cdots r_i)\rangle \tag{7.7.3}$$

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

The Hartree Approximation

The method for finding best possible one-electron wavefunctions that was published by Douglas Hartree in 1948 and improved two years later by Vladimir Fock. For the Schrödinger equation to be analytically solvable, the variables must be separable - the variables are the coordinates of the electrons. To separate the variables in a way that retains information about electron-electron interactions, the electron-electron term (Equation 7.7.1) 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 7.7.3 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:

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

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

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

3. **Electron-Electron Coulombic Repulsion Energy:** Coulomb repulsion energies with all of the $N-1$ other electrons, which are assumed to occupy other atomic orbitals denoted ϕ_K, with this energy computed as

   $$\sum_{j\neq k}\langle\phi_j(r)\phi_k(r')|\frac{e^2}{|r-r'|}|\phi_j(r)\phi_k(r')\rangle. \tag{7.7.4}$$

   The Dirac notation $\langle\phi_j(r)\phi_k(r')|\frac{e^2}{|r-r'|}|\phi_j(r)\phi_k(r')\rangle$ is used to represent the two-electron (six-dimensional) Coulomb integral

$$J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r - r'} dr dr'$$

that describes the Coulomb repulsion between the charge density $|\phi_j(r)|^2$ for the electron in ϕ_j and the charge density $|\phi_k(r')|^2$ for the electron in ϕ_k. Of course, the sum over k must be limited to exclude $k = j$ to avoid counting a "self-interaction" of the electron in orbital ϕ_j with itself.

Adding these all together to get the total energy ϵ_j of the orbital ϕ_j:

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

This treatment of the electrons and their orbitals is referred to as the **Hartree-level of theory**.

When screened hydrogenic atomic orbitals are used to approximate the ϕ_j and ϕ_K orbitals, the resultant ϵ_J values do **not** produce accurate predictions. For example, the negative of ϵ_J should approximate the ionization energy for removal of an electron from the orbitals ϕ_j. Such ionization potentials (IP s) can be measured, and the measured values do not agree well with the theoretical values when a crude screening approximation is made for the atomic orbitals.

The Self-Consistant Field (SCF) Approach to the Variational Method

The Hartree Equations are nonlinear and must be solved iteratively. This is because if particles interact, that interaction must be in the Hamiltonian. So until we know where the particles are, we cannot write down the Hamiltonian, but until we know the Hamiltonian, we cannot tell where the particles are.

The idea is to solve the Schrödinger equation for an electron moving in the potential of the nucleus and all the other electrons. We start with a guess for the trial electron charge density, solve N/2 one-particle Schrödinger equations (initially identical) to obtain N electron wavefunctions. Then we construct the potential for each wavefunction from that of the nucleus and that of all the other electrons, symmetrize it, and solve the N/2 Schrödinger equations again. This method is ideal for a computer, because it is easily written as an algorithm (Figure 8.3.1).

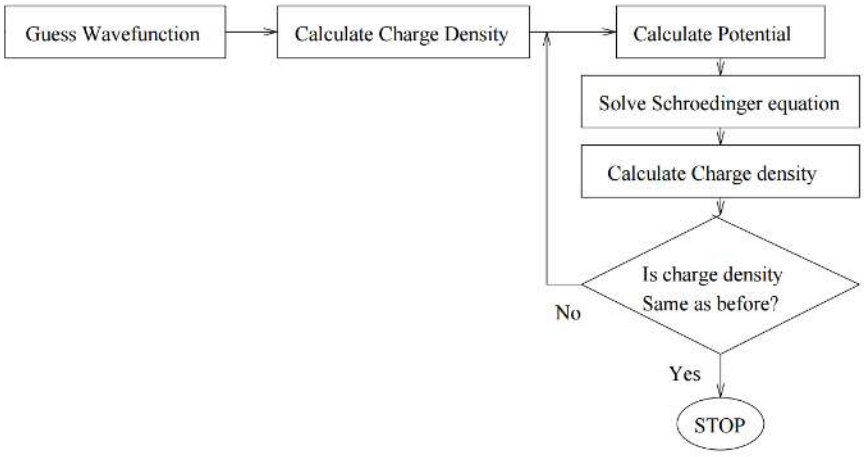


Figure 8.3.1 : Algorithm for Self-consistent field theory.

Although we are concerned here with atoms, the same methodology is used for molecules or even solids (with appropriate potential symmetries and boundary conditions). This is a variational method, so wherever we refer to wavefunctions, we assume that they are expanded in some appropriate basis set.

> *Fock improved on Hartree's method by using proper "antisymmetrized wavefunctions" (called the Hartree-Fock method) instead of simple one-electron wavefunctions.*

Shielding and Effective Charges Concepts are Useful

The hydrogen-like orbitals provide qualitative descriptions of orbitals of atoms with more than a single electron. By introducing the concept of screening as a way to represent the repulsive interactions among the electrons of an atom, an effective nuclear charge Z_{eff} can be used in place of Z in the hydrogenic $\psi_{n,l,m}$ and $E_{n,l}$ formulas to generate approximate atomic orbitals to be filled by electrons in a many-electron atom. For example, in the crudest approximation of a carbon atom, the two $1s$ electrons experience the full nuclear attraction so $Z_{\text{eff}} = 6$ for them, whereas the $2s$ and $2p$ electrons are screened by the two $1s$ electrons, so $Z_{\text{eff}} = 4$ for them. Within this approximation, one then occupies two $1s$ orbitals with $Z = 6$, two $2s$ orbitals with $Z = 4$ and two $2p$ orbitals with $Z = 4$ in forming the full six-electron product wavefunction of the lowest-energy state of carbon

$$|\psi(1,2,\ldots,6)\rangle = |\psi_{1s}(1)\psi_{1s}(2)\psi_{2s}(3)\ldots\psi_{1p}(6)\rangle. \tag{7.7.5}$$

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).

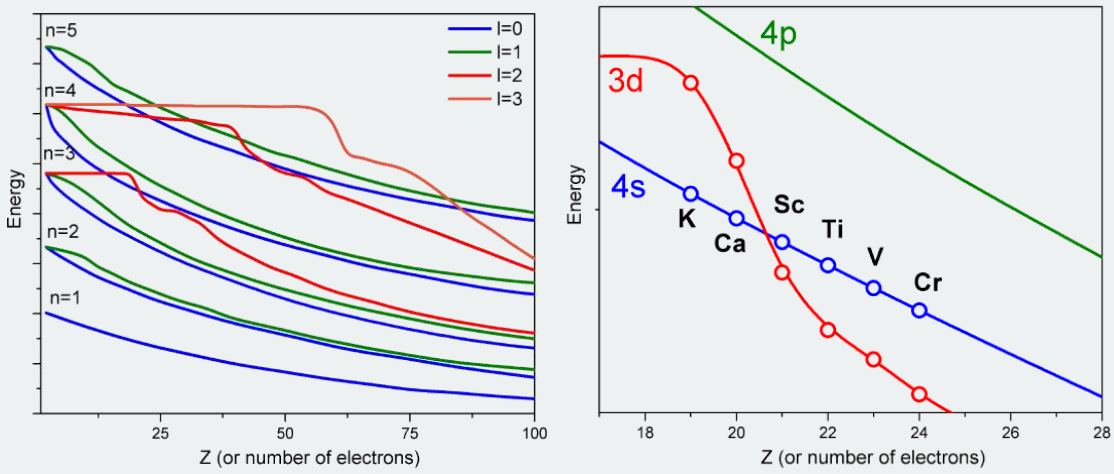


Figure 8.3.2 : Energies of Atomic Orbitals as Functions of the number of electrons in Neutral Atoms. (CC BY 4.0; Delmar Larsen).

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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7.8: An Electron has an Intrinsic Spin Angular Momentum

Learning Objectives

- Understand the forth quantum number for electrons - spin.
- Understand how spin is connected to magnetic properties of the electrons and atoms.
- Understand how to break degeneracy via externally applied magnetic fields in electrons and atoms.

Imagine doing a hypothetical experiment that would lead to the discovery of electron spin. Your laboratory has just purchased a microwave spectrometer with variable magnetic field capacity. We try the new instrument with hydrogen atoms using a magnetic field of 10^4 Gauss and look for the absorption of microwave radiation as we scan the frequency of our microwave generator (Figure 8.4.1).

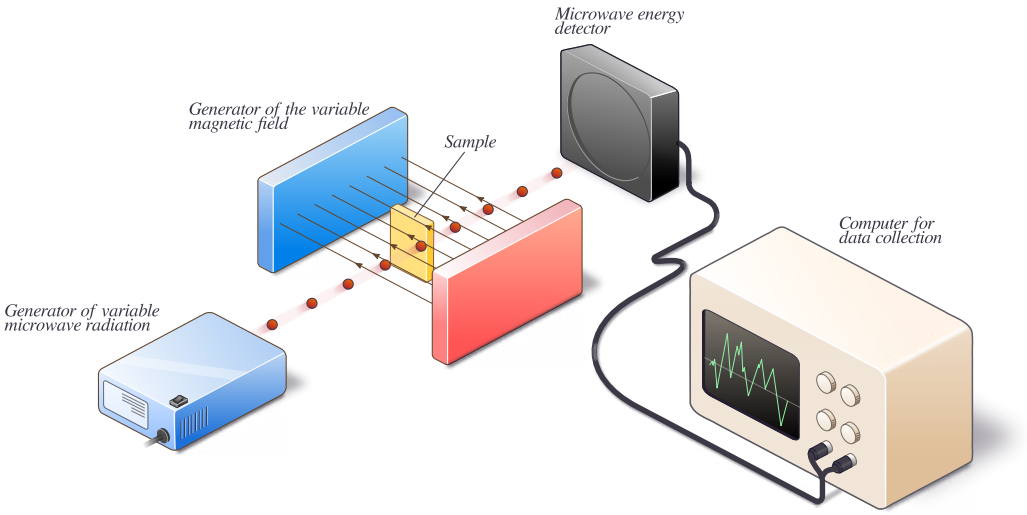


Figure 8.4.1 : Schematic diagram of a microwave spectrometer with the sample in a variable magnetic field. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Finally we see absorption at a microwave photon frequency of $28 \times 10^9\ Hz$ (28 gigahertz). This result is really surprising from several perspectives. Each hydrogen atom is in its ground state, with the electron in a 1s orbital. The lowest energy electronic transition that we predict based on existing theory (the electronic transition from the ground state (ψ_{100} to ψ_{21m}) requires an energy that lies in the vacuum ultraviolet (the lower Lyman line at 121 nm), not the microwave, region of the spectrum. Furthermore, when we vary the magnetic field we note that the frequency at which the absorption occurs varies in proportion to the magnetic field.

The Zeeman Effect: Breaking Degeneracies with Magnetic Fields

Magnetism results from the circular motion of charged particles. This property is demonstrated on a macroscopic scale by making an electromagnet from a coil of wire and a battery. Electrons moving through the coil produce a magnetic field, which can be thought of as originating from a magnetic dipole or a bar magnet. Electrons in atoms also are moving charges with angular momentum so they too produce a magnetic dipole, which is why some materials are magnetic. A **magnetic dipole** interacts with a magnetic field, and the energy of this interaction is given by the scalar product of the magnetic dipole moment, and the magnetic field, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{7.8.1}$$

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:

$$\langle E \rangle = E_n + \frac{e\hbar B_z m_l}{2m_e} \tag{7.8.2}$$

$$= E_n + \mu_B B_z m_l \tag{7.8.3}$$

The factor

$$\frac{e\hbar}{2m_e} = -\gamma_e \hbar = \mu_B \tag{7.8.4}$$

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 7.8.3 demonstrates that that m_l quantum number degeneracy of the hydrogen atom is removed by the externally applied magnetic field. For example, the three hydrogen atom eigenstates $|\psi_{211}\rangle$, $|\psi_{21-1}\rangle$, and $|\psi_{210}\rangle$ are degenerate in zero magnetic field, but have different energies in an externally applied magnetic field (Figure 8.4.2).

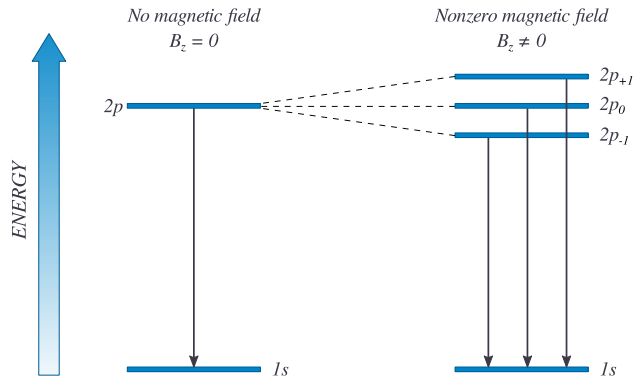


Figure 8.4.2 : The Zeeman effect for the $2s \rightarrow 1s$ transition. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field. (CC BY-NC; Ümit Kaya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

The $m_l = 0$ state, for which the component of angular momentum and hence also the magnetic moment in the external field direction is zero, experiences no interaction with the magnetic field. The $m_l = +1$ state, for which the angular momentum in the z-direction is +ħ and the magnetic moment is in the opposite direction, against the field, experiences a raising of energy in the presence of a field. Maintaining the magnetic dipole against the external field direction is like holding a small bar magnet with its poles aligned exactly opposite to the poles of a large magnet. It is a higher energy situation than when the magnetic moments are aligned with each other.

Electron Spin and the Stern-Gerlach Experiment

To discover new things, experimentalists sometimes must explore new areas in spite of contrary theoretical predictions. Our theory of the hydrogen atom at this point gives no reason to look for absorption in the microwave region of the spectrum. By doing the crazy experiment outlines above, we discovered that when an electron is in the $|1s\rangle$ orbital of the hydrogen atom, there are two different states that have the same energy. When a magnetic field is applied, this degeneracy is removed, and microwave radiation can cause transitions between the two states. In the rest of this section, we see what can be deduced from this experimental observation. This experiment actually could be done with electron spin resonance spectrometers available today (Figure 8.4.1). To explain our observations, a new model for the hydrogen atom. Our original model for the hydrogen atom accounted for the motion of the electron and proton in our three-dimensional world; the new model needs something else that can give rise to an additional Zeeman-like effect. We need a charged particle with angular momentum to produce a magnetic moment, just like that obtained by the orbital motion of the electron. We can postulate that our observation results from a motion of the electron that was not considered in the last section - electron spin. We have a charged particle spinning on its axis. We then have charge moving in a circle, angular momentum, and a magnetic moment, which interacts with the magnetic field and gives us the Zeeman-like effect that we observed (Figure 8.4.2).

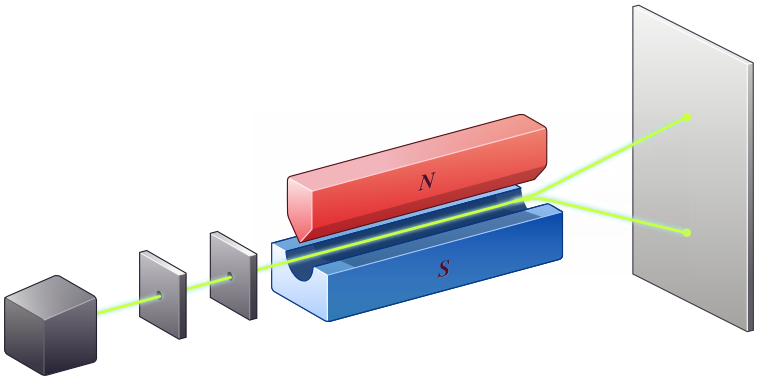


Figure 8.4.2 : Stern–Gerlach experiment: silver atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the **Electron Spin Quantum Number** and denoted by m_s. In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might by explained by assuming electrons act as if it has a spin, which can be denoted by an arrow pointing up, which is +1/2, or an arrow pointing down, which is -1/2. The Stern and Gerlach experiment which demonstrated this was done with a beam of vaporized silver atoms that split into two beams after passing through a magnetic field (Figure 8.4.2). An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the *one unpaired electron* in the atom will determine the spin.

Spin Eigenstates and Eigenvalues

To describe electron spin from a quantum mechanical perspective, we must have spin wavefunctions and spin operators. The properties of the spin states are deduced from experimental observations and by analogy with our treatment of the states arising from the orbital angular momentum of the electron. The important feature of the spinning electron is the spin angular momentum vector, which we label S by analogy with the orbital angular momentum L. We define spin angular momentum operators with the same properties that we found for the rotational and orbital angular momentum operators. After all, angular momentum is angular momentum, no matter if it is *orbital* or *spin* in nature.

We found that

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

so by analogy for the spin states, we must have

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

where σ is a spin wavefunction with quantum numbers s and m_s that obey the same rules as the quantum numbers l and m_l associated with the spherical harmonic wavefunction Y. We also found the project of the orbital angular momentum on the z-axis is

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

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

$$\hat{S}_z|\sigma_s^{m_s}\rangle = m_s\hbar|\sigma_s^{m_s}\rangle \tag{7.8.5}$$

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

$$
\begin{aligned}
m_{s,f} - m_{s,i} &= 1 \\
(+s) - (-s) &= 1 \\
2s &= 1 \\
s &= \frac{1}{2}
\end{aligned} \tag{7.8.6}
$$

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 $|\beta\rangle$.

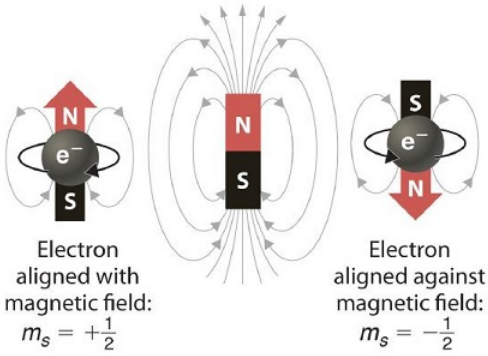


Figure 8.4.3 : Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden. (CC BY-SA-NC 3.0; Anonymous).

From Equation 7.8.5, the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s \hbar \tag{7.8.7}$$

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.

$$\int \alpha^* \alpha \, d\tau_s = \int \beta^* \beta \, d\tau_s = 1 \tag{7.8.8}$$

or in braket notation

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \tag{7.8.9}$$

and

$$\int \alpha^* \beta \, d\tau_s = \int \beta^* \alpha \, d\tau_s = 0 \tag{7.8.10}$$

or in braket notation

$$\langle \alpha | \beta \rangle = \langle \alpha | \beta \rangle = 0 \tag{7.8.11}$$

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

$$\Delta E = h\nu \tag{7.8.12}$$

$$= E_\alpha - E_\beta \tag{7.8.13}$$

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.

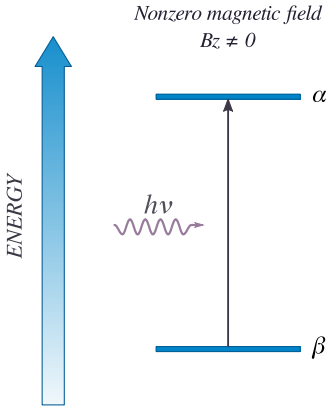


Figure 8.4.4 : Absorption of a photon to cause a transition from the β to the α state. (CC BY-NC; Ümit Kaya via LibreTexts)

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 7.8.1.

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

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

Substituting the two equations above into the expression for the photon (Equation 7.8.13) energy gives

$$h\nu = E_\alpha - E_\beta \tag{7.8.14}$$

$$= (E_{1s} - \mu_{s,\alpha} \cdot B) - (E_{1s} - \mu_{s,\beta} \cdot B) \tag{7.8.15}$$

$$= (\mu_{s,\beta} - \mu_{s,\alpha}) \cdot B \tag{7.8.16}$$

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 7.8.16 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 7.8.7 and rearranging Equation 7.8.16 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 7.8.4 i.e. $\gamma_s \hbar = 2.0023, \gamma_e \hbar$, or

$$\gamma_s = 2.0023 \gamma_e \tag{7.8.17}$$

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

Learning Objectives

- Interprete the consequence of exchanging two electrons in a multi-electron atom on the wavelengths
- Connect the Pauli's Exclusion Principle to the permutation symmetry of multi-electron atoms

Quantum mechanics allows us to predict the results of experiments. If we conduct an experiment with indistinguishable particles a correct quantum description cannot allow anything which distinguishes between them. For example, if the wavefunctions of two particles overlap, and we detect a particle, which one is it? The answer to this is not only that we do not know, but that we cannot know. Quantum mechanics can only tell us the probability of finding a particle in a given region. The wavefunction must therefore describe both particles.

The Schrödinger equation for the helium atom is then:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_1^2)-V(\mathbf{r}_1)-V(\mathbf{r}_2)+V_{12}(\mathbf{r}_1,\mathbf{r}_2)\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2)$$

where the subscripts label each particle, and there are six coordinates, three for each particle. While $|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ is a six dimensional wavefunction (three for each electron) and contains all the information we can measure (a Postulate of Quantum Mechanics), it only provide the probability of finding the electron at a specific volume element, and does **not** tell us which particle is which (e.g., is it electon 1 or electron 2?).

What basis states would be appropriate for $|\psi\rangle$? If we consider the orbital approximation that uses a product wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle=|\varphi_a(\mathbf{r}_1)\rangle|\varphi_b(\mathbf{r}_2)\rangle$$

where $|\varphi_a(\mathbf{r}_1)\rangle$ and $|\varphi_b(\mathbf{r}_2)\rangle$ are one-particle spin-orbitals (with both spin and spatial components) of atoms 1 and 2. This approximation allows us to separate the two particle equation into two one-electron equations:

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2+V(\mathbf{r}_1)\right]|\varphi_a(\mathbf{r}_1)\rangle=E|\varphi_a(\mathbf{r}_1)\rangle$$

$$\left[-\frac{\hbar^2}{2m}\nabla_2^2+V(\mathbf{r}_2)\right]|\varphi_b(\mathbf{r}_2)\rangle=E|\varphi_a(\mathbf{r}_2)\rangle$$

provided that the particles do not interact (e.g., ∇_1^2 does not act on $|\varphi_b(\mathbf{r}_2)\rangle$ and $V_{12}=0$).

Unfortunately, by doing this we have introduced unphysical *labels* to the indistinguishable particles. And this is wrong: the effect of it is that the particles do not interfere with each other because they are in different dimensions (six dimensional space - remember?). When we construct a two particle wavefunction out of two one-particle wavefunctions we must be ensure that the probability density (the measurable quantity $|\psi|^2$) is independent of the **artificial** labels.

The Exchange Operator

We can deepen our understanding of the quantum mechanical description of multi-electron atoms by examining the concepts of electron indistinguishability and the Pauli Exclusion Principle in detail. We will use the following statement as a guide to keep our explorations focused on the development of a clear picture of the multi-electron atom: "When a multi-electron wavefunction is built as a product of single-electron wavefunctions, the corresponding concept is that exactly one electron's worth of charge density is described by each atomic spin-orbital."

A subtle, but important part of the conceptual picture, is that the electrons in a multi-electron system are not distinguishable from one another by any experimental means. Since the electrons are indistinguishable, the probability density we calculate by squaring the modulus of our multi-electron wavefunction also cannot change when the electrons are interchanged (permuted) between different orbitals. In general, if we interchange two identical particles, the world does not change. As we will see below, this requirement leads to the idea that the world can be divided into two types of particles based on their behavior with respect to permutation or interchange.

In order for the probability density to remain unchanged when two particles are permuted, the wavefunction itself can change only by a factor of $e^{i\varphi}$, which represents a complex number, when the particles described by that wavefunction are permuted. As we will show below, the $e^{i\varphi}$ factor is possible because the probability density depends on the absolute square of the function and all expectation values involve $\psi\psi^*$. Consequently $e^{i\varphi}$ disappears in any calculation that relates to the real world because $e^{i\varphi}e^{-i\varphi} = 1$.

We could symbolically write an approximate two-particle wavefunction as $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 ($\mathbf{r}_1$) for the coordinates of particle 2 ($\mathbf{r}_2$) and vice versa, to get the new wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This new wavefunction must have the property that

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = \psi(\mathbf{r}_2, \mathbf{r}_1)^*\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{7.9.1}$$

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

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{7.9.2}$$

so that

$$\left(e^{-i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right)\left(e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{7.9.3}$$

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.,

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \tag{7.9.4}$$

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:

$$\hat{P}_{12}|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \pm|\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{7.9.5}$$

Bosons and femions

Physical solutions must be eigenfunctions of $\hat{P}_{12}$ (i.e., $\hat{H}$ and $\hat{P}_{12}$ commute). Moveover, Equation 7.9.5 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

$$|\psi(\mathbf{r}_1,\mathbf{r}_2,\cdots r_i)\rangle \approx \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\cdots\varphi_i(r_i) \tag{7.9.6}$$

? 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.

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 7.9.6 does **not** satisfy this (unless $\varphi_a = \varphi_b$). A **linear combination of all permutations** is required to satisfy indistinguishability constraints.

For a two particle system (e.g., Helium) there is the asymmetric combination

$$|\psi^-\rangle = \frac{1}{\sqrt{2}}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{7.9.7}$$

and symmetric combination

$$|\psi^+\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle + C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle + C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{7.9.8}$$

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

> *Note that the antisymmetric combination (Equation 7.9.7) **cannot** include terms where both particles are in the same state (spin-orbital), but there are three possibilities for the symmetric state (Equation 7.9.8).*

Although any linear combinations of C_{ab}, C_{bb}, and C_{aa} in Equation 7.9.8 is possible, there are three limiting expressions for possible symmetric combinations:

$$|\psi_1^{+i}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{7.9.9}$$

$$|\psi_2^{+i}\rangle = C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle \tag{7.9.10}$$

$$|\psi_3^{+i}\rangle = C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{7.9.11}$$

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

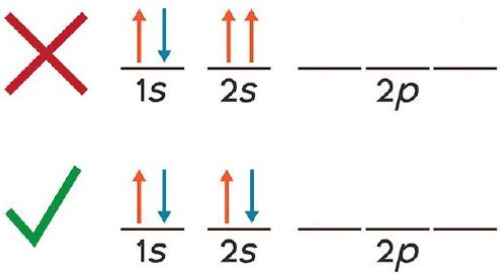


Figure 8.5.1 : The 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, since each electrons is described by a specific spin-orbital and each orbital (spatial) can hold either an α or a β electron (i.e., they must have opposite spins). Otherwise they will have the same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

The Pauli Exclusion Principle argues that two electrons **could not** be described by the same spin-orbital. To see the relationship between this statement and the requirement that the wavefunction be antisymmetric for electrons, try to construct an anti-symmetric wavefunction for two electrons that are described by the same spin-orbital

$$|\varphi_b(\mathbf{r}_1)\rangle = \varphi_a(\mathbf{r}_2)\rangle$$

For example, if this were the case for the anti-symmetric combination for helium (Equation 7.9.7), 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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CHAPTER OVERVIEW

8: Electronic Spectroscopy

8.1: Most Molecules Have Excited Electronic States
8.2: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
8.3: The Franck-Condon Principle
8.4: Term Symbols Gives a Detailed Description of an Electron Configuration
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8.1: Most Molecules Have Excited Electronic States

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8.2: 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.

Electron Transitions are not Purely Electronic

We have thus far studied *rovibrational transitions*--that is, transitions involving both the vibrational and rotational states. Similarly, electronic transitions tend to accompany both rotational and vibrational transitions. These are often portrayed as an electronic potential energy cure with the vibrational level drawn on each curve. Additionally, each vibrational level has a set of rotational levels associated with it.

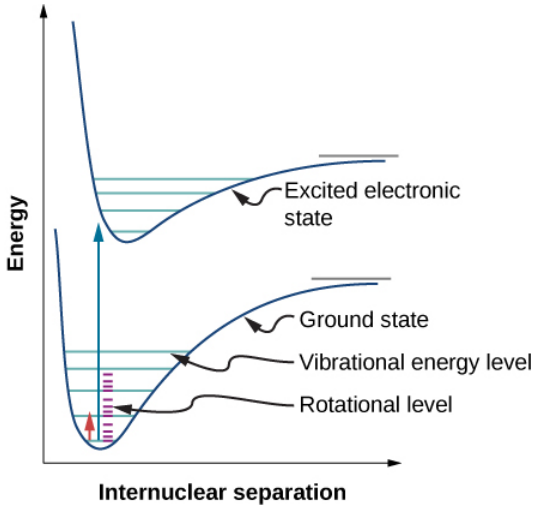


Figure 13.6.1 : Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

Recall that in the Born-Oppenheimer approximation, nuclear kinetic energies can be ignored (e.g., fixed) to solve for electronic wavefunctions and energies, which are much faster than rotation or vibration. As such, it is important to note that unlike rovibrational transitions, electronic transitions aren't dependent on rotational or transitional terms and are assumed to be separate. Therefore, when using an anharmonic oscillator-nonrigid rotator approximation (and excluding translation energy), the total energy of a diatomic is:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{8.2.1}$$

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 8.2.1 can be expanded accordingly:

$$\tilde{E}_{total} = \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{8.2.2}$$

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.

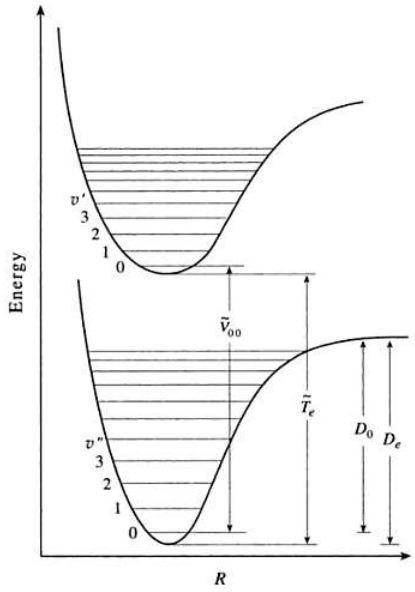


Figure 13.6.2 : As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded.

The eigenstate-to-eigenstate transitions (e.g., $1 \rightarrow 2$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{8.2.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 8.2.3 is

$$\tilde{\nu}_{obs} = \tilde{E''(v'')} - \tilde{E'(v')}$$

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 8.2.2 can be used with Equation 8.2.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{8.2.4}$$

A common transition of importance is the $\tilde{\nu}_{00}$, which is the $0 \rightarrow 0$ transition and include no vibrational change. For this case, equation 8.2.4 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.

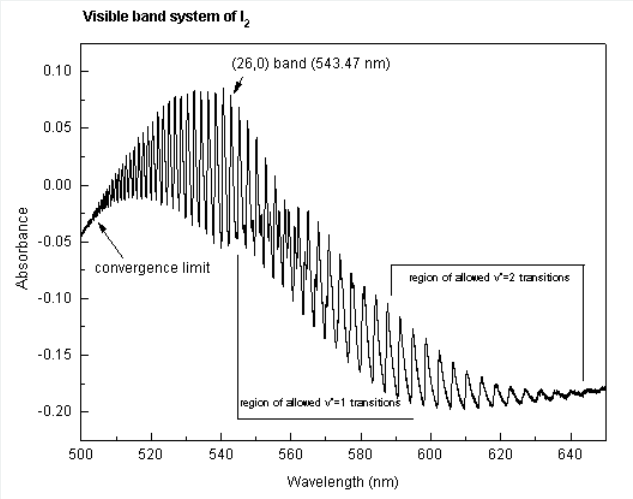
Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 8.2.4 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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8.3: 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.

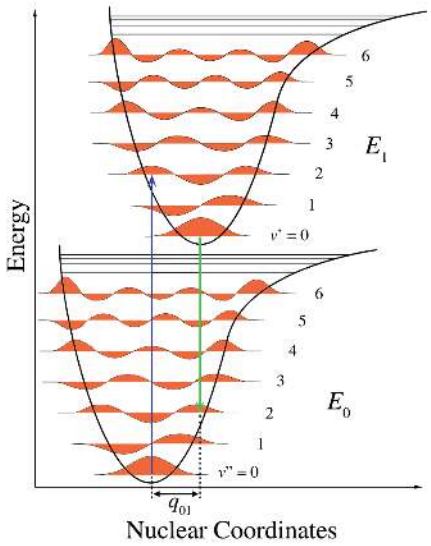


Figure 13.7.1 : Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure 13.7.1 , the nuclear axis shows a consequence of the internuclear separation and the vibronic transition is indicated by the blue and green vertical arrows. This figure demonstrates three things:

1. An absorption leads to a higher energy state,
2. fluorescence leads to a lower energy state, and
3. the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential. The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

The Classical Condon approximation

Condon approximation is the assumption that the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

This change in vibration is maintained during a state termed the **rapid electronic excitation**. The resulting Coulombic forces produce an equilibrium as shown in the figure for the nuclei termed a turning point. The turning point can be mapped by drawing a

vertical line from the minimum of the lower curve to the intersection of the higher electronic state. This procedure is termed a **vertical transition** and was discussed before in the context of photoelectron spectroscopy (another electronic spectroscoy).

The Franck-Condon Principle explains the relative intensities of vibronic transitions by relating the probability of a vibrational transition to the overlap of the vibrational wavefunctions. It states that the probability of a vibrational transition occurring is weighted by the Franck-Condon overlap integral:

$$\begin{aligned} {}_{i\rightarrow f} &= |\langle \psi^*_{final}|\boldsymbol{\mu}|\psi_{initial}\rangle|^2 \\ &= \left|\int \psi^*_{final}\boldsymbol{\mu}\psi_{initial}\,d\tau\right|^2 \end{aligned}$$

Within the Franck-Condon approximation, the nuclei are considered "fixed" during electronic transitions. Thus, electronic transitions can be considered vertical transitions on electronic potential energy curves (vierical transitions in Figure 13.7.1).

The Quantum Franck-Condon Principle

The Franck-Condon Principle has both a Classical and Quantum application. Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic q and nuclear Q wavefunctions given the total wavefunction.

$$|\psi_{total}(Q,q) = |\psi_{nuc}(Q)\rangle\psi_{el}(Q;q)\rangle$$

Since the transition operator, $\hat{\mu}(q)$, is dependent only on the electronic component, the nuclear components can be separated from the transition moment integral that dictates the probability of the transition occurring:

$$\langle\psi^*_{total,f}|\hat{\mu}|\psi_{total,i}\rangle = \langle\psi^*_{nuc,f}|\langle\psi^*_{el,f}|\boldsymbol{\mu}|\psi_{el,i}\rangle|\psi_{nuc,i}\rangle \tag{8.3.1}$$

$$= \underbrace{\langle\psi^*_{nuc,f}|\psi_{nuc,i}\rangle}_{\text{nuclear overlap}}\langle\psi^*_{el,f}|\boldsymbol{\mu}|\psi_{el,i}\rangle \tag{8.3.2}$$

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.

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

- $\alpha = \dfrac{\sqrt{mk}}{\hbar}$
- R_e is the equilibrium bond length in the ground electronic state
- Q_e is the equilibrium bond length in the excited electronic state

The nuclear overlap integral is

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{8.3.3}$$

The exponent in Equation 8.3.3 can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{8.3.4}$$

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 8.3.4 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

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{8.3.5}$$

this integral has been solved already, from a table of integrals, Equation 8.3.5 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}.

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 $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{8.3.6}$$

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 8.3.6) 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.

Franck-Condon Progressions

To understand the significance of the above formula for the FC factor, let us examine a ground and excited state potential energy surface at $T = 0$ Kelvin. Shown below are two states separated by 8,000 cm^{-1} in energy. This is energy separation between the bottoms of their potential wells, but also between the respective zero-point energy levels. Let us assume that the wavenumber of the vibrational mode is 1,000 cm^{-1} and that the bond length is increased due to the fact that an electron is removed from a bonding orbital and placed in an anti-bonding orbital upon electronic excitation.

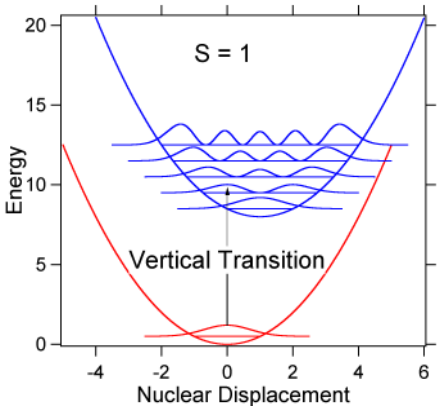


Figure 13.7.2 : Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure 13.7.3) where each vibrational transition is infinitely narrow and transition can only occur when $E = h\nu$ exactly. For example, the potential energy surfaces were given for S = 1 and the transition probability at each level is given by the sticks (black) in the figure below.

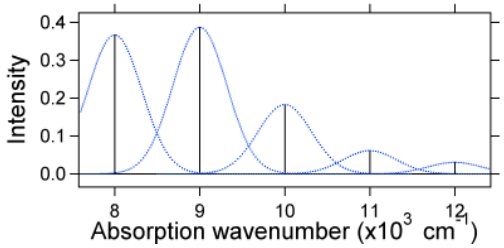


Figure 13.7.3 : Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure 13.7.2 .

The dotted Gaussians that surround each stick give a more realistic picture of what the absorption spectrum should look like. In this first place each energy level (stick) will be given some width by the fact that the state has a finite lifetime. Such broadening is called homogeneous broadening since it affects all of the molecules in the ensemble in a similar fashion. There is also broadening due to small differences in the environment of each molecule. This type of broadening is called inhomogeneous broadening. Regardless of origin the model above was created using a Gaussian broadening

The nuclear displacement between the ground and excited state determines the shape of the absorption spectrum. Let us examine both a smaller and a large excited state displacement. If $S = ½$ and the potential energy surfaces in this case are:

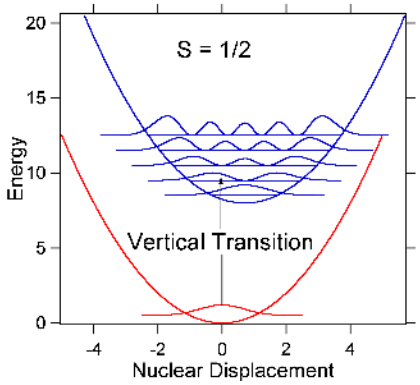


Figure 13.7.4 : Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure 13.7.5

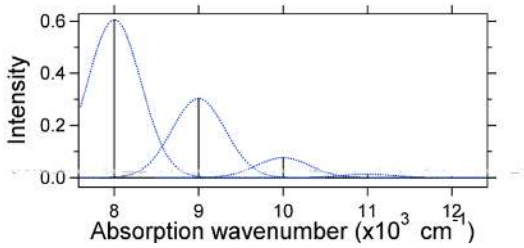


Figure 13.7.5 : Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure 13.7.4 .

Note that the zero-zero or $S_{0,0}$ vibrational transition is much large in the case where the displacement is small.

> As a general rule of thumb the S constant gives the ratio of the intensity of the $v = 2$ transition to the $v = 1$ transition. In this case since $S = 0.5$, the $v = 2$ transition is 0.5 the intensity of $v = 1$ transition.

As an example of a larger displacement the disposition of the potential energy surfaces for S = 2 is shown below.

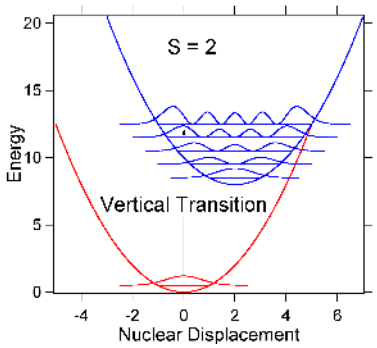


Figure 13.7.6 : Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

The larger displacement results in decreased overlap of the ground state level with the v = 0 level of the excited state. The maximum intensity will be achieved in higher vibrational levels as shown in the stick spectrum.

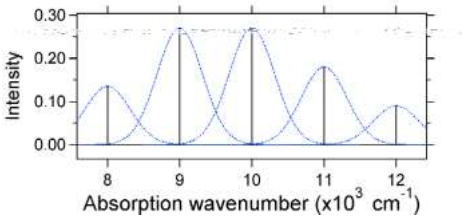


Figure 13.7.7 : Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure 13.7.6 .

The absorption spectra plotted below all have the same integrated intensity, however their shapes are altered because of the differing extent of displacement of the excited state potential energy surface.

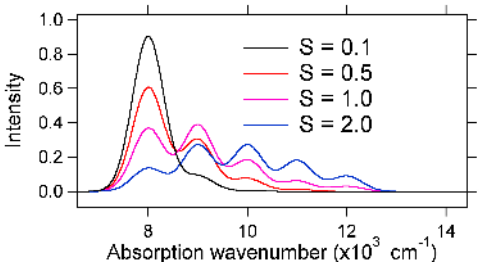


Figure 13.7.8 : Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

So the nature of the relative vibronic band intensities can tell us whether there is a displacement of the equilibrium nuclear coordinate that accompanied a transition. When will there be an increase in bond length (i.e., $Q_e > R_e$)? This occurs when an electron is promoted from a bonding molecular orbital to a non-bonding or anti-bonding molecular orbitals (i.e., when the bond order is less in the excited state than the ground state).

- Non-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ non-bonding molecular orbital

In short, when the bond order is lower in the excited state than in the ground state, then $Q_e > R_e$; an increase in bond length will occur when this happens.

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

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8.4: Term Symbols Gives a Detailed Description of an Electron Configuration

Learning Objectives

- Understand how electron configurations results in different manifestations of angular momenta (both oribital and spin)
- Describe the manifestations in atoms via atomic term symbols

Atoms have quantum numbers that are directly analogous to the electronic quantum numbers.

The Total Orbital Angular Momentum Quantum Number: L

One might naively think that you could get the total angular momentum of an atom (L) by simply adding up the l values of the individual electrons. The problem with this idea is that the angular momenta of the various electrons are not necessarily pointing in the same direction. Let's consider the case of adding two 2p-orbitals together (i.e., with $l = 1$ quantum numbers).

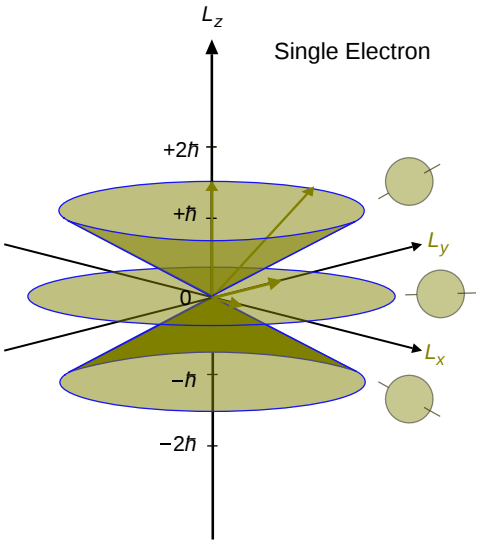


Figure 8.8.1 : The three possible angular momenta vectors for a p-orbital.

As discussed in Section 6.3, each of these electrons has $\sqrt{2}\hbar$ of angular momentum, but oriented in three different directions given by three different m_l values of 1, 0, and -1 (Figure 8.8.1).

$$L = \sum_{i}^{n} l_i \tag{8.4.1}$$

However, we must recognize that while the magnitude of angular momentum is a scalar (represented by l), angular momenta are really vector quantities and to add them together will require vector addition (vs. scalar addition) to do properly and must address all possible orientations of l for each electron.

For example, if two electrons are revolving in the same direction as each other (i.e., same m_l values), one would add just their l values together

$$L(\text{same direction}) = \sqrt{2}\hbar + \sqrt{2}\hbar = 2\hbar$$

If the two elections were revolving in opposites direction (e.., opposite m_l values, you subtract their values.

$$L(\text{same direction}) = \sqrt{2}\hbar - \sqrt{2}\hbar = 0$$

If they are revolving at some off-angle relative to each other (one revolving in a plane and one off plane), you would partially subtract them.

$$L(\text{same direction}) = \sqrt{2}\hbar + 0 = \sqrt{2}\hbar$$

To figure out all of the possible combinations of l for a pair of electrons, simply add them together to get the co-aligned case, subtract them to get the opposing case, and then fill in all the numbers in between to get the off-angle cases. For the two p-orbital case, there are no other possibilities (remember that l and hence L must be non-negative since they represent the magnitude of angular momenta (addressing the m_l values is a different story as we discuss below).

If you prefer to have a formula for the possibilities of L, you can use this:

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, \ldots, |l_1 - l_2| \tag{8.4.2}$$

Technically, Equation 8.4.2 should include all electrons in a system, not just two, to account for all possible combinations of orbital angular momenta, however, there are some tricks that aid in applying this equations to address larger multi-electron atoms. First, electrons in s-orbitals have no orbital angular momentum, so they can be ignored. Second, if block of orbitals are completely filled (e.g., all six p-block spin-orbitals or all 10 d-block spin-orbitals), then the orbital angular momentum vector of each electron will be countered by another electron in the system; these are called **closed-shell** systems. Systems with partially unfilled blocks are called **open-shell** systems.

Hence, conveniently for chemists, an atom's electronic state depends entirely on its unfilled sub shells. Because electrons distribute themselves in a symmetric manner, the inner shell electrons end up canceling out each other's momenta. For an atom in the configuration $1s^2 2s^2 p^2$, only the two p-electrons matter. For an atom in the configuration $1s^2 2s^1 2p^1$, we have to examine only the 2s and 2p electrons (and can ignore the s electrons too).

Example 8.8.1 : Total Orbital Angular Momentum of Carbon

What are the possible L values for the electrons in the $1s^2 2s^2 2p^2$ configuration of carbon?

Solution

Both open-shell electrons (i.e., the 2p electrons) are $l = 1$. The possible combinations are 2, 1, 0.

Example 8.8.2 : Total Orbital Angular Momentum of Unknown Species

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We can ignore the electrons in the $[Xe]$ core and the electrons in the $6s$ block. So all we have to consider is the f electron $l = 3$ and d electron $l = 2$.

The two extremes possible (Equation 8.4.2) are

$$3 + 2 = 5$$

and

$$3 - 2 = 1$$

The possible combinations are thus 5, 4, 3, 2, and 1.

The Total Magnetic Quantum Number: M_l

The Total Magnetic Quantum Number M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much total angular momentum there is in the system, M_l tells you which direction it is pointing. Like L, a given configuration can have several possible values of M_l, depending on the electrons' relative orientation. Unlike L, M_l is allowed to have negative values. To list the possible M_l values for a two electron system, take the case where both m_l are positive, then take the case where they are both negative, and then fill in the numbers in between (Figure 8.8.1).

$$M_l = m_{l1} + m_{l2}, m_{l1} + m_{l2} - 1, \ldots, -m_{l1} - m_{l2} \tag{8.4.3}$$

Note that there is no absolute value function in Equation 8.4.3 like in Equation 8.4.2.

Example 8.8.3 : Total Magnetic Quantum Number of the Zirconium Ground State

What are the possible values M_l of a zirconium atom with the $[Kr]5s^24d^2$ electron configuration?

Solution

Both open-shell electrons (i.e., the 4d electrons) are $l = 2$, so the values are 4, 3, 2, 1, 0, -1, -2, -3, -4.

The Total Spin Magnetic Quantum Number: M_s

M_s is the sum total of the z-components of the electrons' inherent spin. Do not confuse it with M_l, which is the sum total of the z-component of the **orbital angular momentum**. It is easily computed by finding all of the possible combinations of m_s. Since m_s for each individual electron can only be +1/2 or - 1/2, this isn't too complicated.

$$M_s = m_{s1} + m_{s2}, m_{s1} + m_{s2}\text{-}1, \ldots, m_{s1}\text{-}m_{s2} \tag{8.4.4}$$

Example 8.8.4 : Total Spin Magnetic Quantum Number of the Carbon Ground State

What are the M s values for $1s^22s^22p^2$?

Solution

$M_s = 1, 0, \text{-}1$

The Total Intrinsic Spin Quantum Number: S

The sum total of the spin vectors of all of the electrons is called S. The difference between S and M_s is subtle, but vital for understanding multiplicity. M_s measures the total z-component of the electrons' spins, while S measures the entire resultant vector. The values of S are computing in a manner very similar to M_s. Because S measures the magnitude of a vector, it cannot ever be negative.

$$S = |s_1 + s_2|, |s_1 + s_2\text{-}1|, \ldots, |s_1\text{-}s_2| \tag{8.4.5}$$

Example 8.8.5 : The Hydrogen Ground State

Find S for $1s^1$.

Solution

S clearly has to be ½ since that's the spin of a single electron and there's only one electron to worry about.

Example 8.8.6 : The Beryllium Excited State

Find S for $1s^22s^12p^1$.

Solution

$S = 1, 0$

Example 8.8.7 : The Carbon Ground State

Find S for carbon atoms with the $1s^22s^22p^2$ electron configuration.

Solution

$S = 1, 0$ This is the same as the previous problem. Notice that S is not affected by which orbitals the electrons are in. S only cares about how many **open-shell electrons** (i.e., unpaired electrons) there are, not about where they are. This is because S measures an inherent property of the electrons themselves

Example 8.8.8

Find S for nitrogen atoms with the $1s^22s^22p^3$ electron configuration.

Solution

We have not done a three electron case yet, but they are not hard. Find all the combinations for a single pair first, and then factor in the third electron. For two electrons, we already know that the two possible S values are S=1,0. A third electron can either add or subtract ½ from these values, so the final S can be $S = 3/2, 1, 1/2$.

The Total Angular Momentum Quantum Number J

The total orbital angular momentum of an atom (measured in terms of l), and the total spin angular momentum of an atom (measure in S) combine to form total angular momentum, a number that is quantized by the number J. L and S do not necessarily have to be pointing in the same direction (Figure 8.8.1), so J can range from $L + S$ to $|L– S|$.

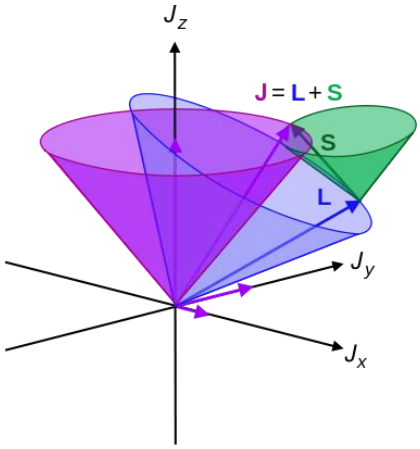


Figure 8.8.1 : Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

Table 8.8.1 : Quantum Numbers and associated ranges

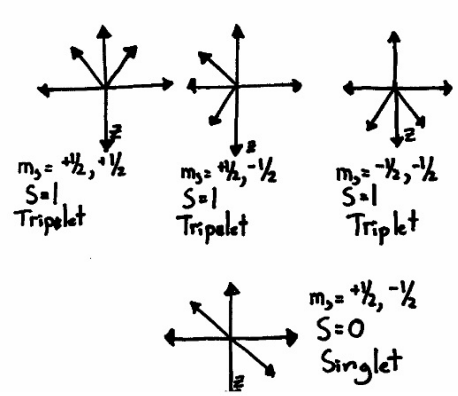
Symbol	Name	Allowed Range
l	Total orbital angular momentum	$\|l_1 + l_2\|, \ldots, \|l_1 - l_2\|$
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, \ldots, - m_{l1} - m_{l2}]$
M_s	Spin Magnetic Quantum Number	$\|m_{s1} + m_{s2}\|, \ldots, \|m_{s1} - m_{s2}\|$
S	Inherent Spin Number	$\|s_1 + s_2\|, \ldots, \|s_1 - s_2\|$
M	Multiplicity	2S+1
J	Total Angular Momentum	$L + S, \ldots, \|L - S\|$

Multiplicity

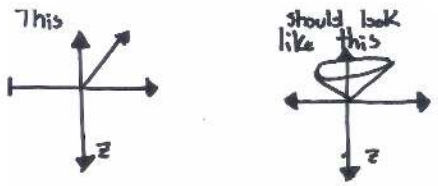
Multiplicity is a simple - sounding concept that defies simple explanations. You know from your first - year education that a singlet is when the net spin (S) is equal to zero (e.g. all the electrons are spin paired), and a triplet happens when the net spin is equal to 1 (e.g. two electrons are pointing in the same direction). They are called “singlet” and “triplet” because there are 3 ways to combine a pair of electron spins to get S=1, but only one way to get $S = 0$. If you draw a picture of the possible ways that two electrons can arrange their spins, you get something like this:



Figure 8.8.1 : When we call an electron spin “up,” what we really mean is that it has a positive z-component (e.g. $m_s = +½$).



While this picture is an improvement over the simple up-down model, it is still misleading. The three spin axes of an electron share a Heisenberg Uncertainty Principle. The more you know about S_x, the less you can know about either S_y or S_z. The same is true for all other combinations of x, y and z. Since we have defined S_z as a known and fixed value, the values of S_x and S_y must be **completely unknown**. This causes the x and y orientations of the electrons to become smeared out across all possible values:



Constructing Term Symbols

Atomic term symbols contain two pieces of information. They tell you the total orbital angular momentum of the atom (l), and they tell you the multiplicity (M). l is denoted by a simple code, similar to the code used to delineate the types of atomic orbitals:

- $L = 0 \rightarrow S$
- $L = 1 \rightarrow P$
- $L = 2 \rightarrow D$
- $L = 3 \rightarrow F$

Note that while the notation is similar, L does NOT say anything about what types of orbitals the electrons are in. A state that has the term symbol P does NOT necessarily have an open p-shell. The multiplicity is indicated by appending a number to the upper left of the symbol. A $L = 2$, $M = 3$ state would be represented by ${}^3D$. The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration. An atom that only has closed shells will always be $1S$.

Each term symbol represents a discrete energy level. We can place these levels in the correct order by using these simple rules:

- 1: High multiplicity values mean low energy
- 2: If there is a tie, high l values mean low energy
- 3a: If there is still a tie and the shell is less than half full, then low J means low energy
- 3b: If the shell is more than half full, then high J means low energy

These rules reliably predict the ground state. They have only erratic agreement with experiment when ordering the other levels.

Example 8.8.9 : Hydrogen Ground State

What are the term symbols for the microstates possible for $1s^1$ electronic configuration of hydrogen?

Solution

Since there is only one electron, this is a simple problem. $L = 0$ and $M = 1$, so the only possible term symbol is ${}^2S$. With only one electron, $S = ½$, so $J = 0 + ½ = ½$. Only one microstate exists for this configuration and it has a term symbol of ${}^2S_{½}$.

Example 8.8.10 : Boron

What are the term symbols for the microstates possible for $1s^2 2s^2 2p^1$ electronic configuration of boron?

Solution

There still only one open shell electron, so $L = 1$, $M = 1$ and $S = ½$. We get a term symbol of the type ^2P, which gets split into separate symbols because $J = 3/2$ and $1/2$. Two possible microstates exist for this system with term symbols of $^2P_{3/2}$ and $^2P_{1/2}$.

Example 8.8.11 : Beryllium Excited State

What are the term symbols for the microstates possible for the $1s^2 2s^1 2p^1$ excited-state electronic configuration of Beryllium?

Solution

Now we have two electrons to worry about. Since $l_1 = 0$ and $l_2 = 1$, the only possible combination is $L = 1$. The possible combinations of S are: $S = 1, 0$. This means that $M = 3$ or $M = 1$. The term symbols will be of the form ^1P and ^3P. For the ^1P state, $L = 1$ and $S = 0$, so $J = 1$. For the second state, $L = 1$ and $S = 1$, so $J = 2, 1, 0$. There are four microstates for this configuration with term symbols of $^1P_1$ and $^3P_2$, $^3P_1$, and $^3P_0$.

Example 8.8.12 : Zirconium

What are the term symbols for the microstates possible for the $[Kr]5s^2 4d^2$ ground-state electronic configuration of zirconium?

Solution

This is a much harder problem. We will need to use a special technique to disentangle all of the possible combinations of l and M. Let's start be listing the relevant quantum numbers for the two open-shell electrons:

$l_1 = 2$	$l_2 = 2$
$m_{l1} = 2, 1, 0, -1, -2$	$m_{l2} = 2, 1, 0, -1, -2$
$m_{s1} = ½, -½$	$m_{s1} = ½, -½$

Let's combine these numbers to generate the atomic quantum numbers:

$$L = 4, 3, 2, 1, 0$$

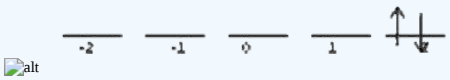
$$M_l = 4, 3, 2, 1, 0, -1, -2, -3, -4$$

$$M_s = 1, 0$$

We know that there will at least one each of S, P, D, F and G. It isn't immediately clear which of these will be singlets and which will be triplets. To figure this out, we need to systematically examine the possible microstates. It turns out that there are **45** possible ways to put distribute two electrons between 5 d orbitals. That's a lot! The easiest way to list the states is to organize them into a chart:

$M_s = -1$	$M_s = 0$	$M_s = +1$

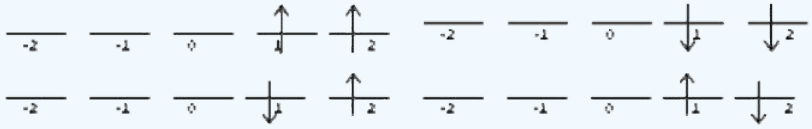
Attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_l = 4$? It turns out there is only one possible combination that does this:



This state is has $M_s = 0$. This means that there is only 1 microstate that corresponds to $M_l = 4$ and $M_s = 0$, and none that correspond to $M_l = 4$ and $M_s = \pm$-1. We add this microstate to the chart like this:

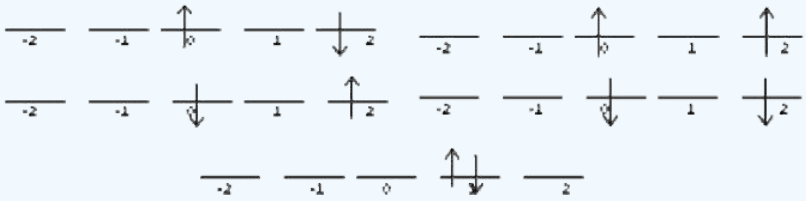
M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0

Now, how many ways are there to get $M_l = 3$?



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1

For $M_l = 2$, we find the following states:



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1

You should be able to draw the microstates on your own by now. You should find 8 states, four of which are singlet and four of which are triplets.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	2	4	2

There are only nine possible ways to arrange the electrons to get $M_l = 0$

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2

The rest of the chart will be symmetric to the first half, so we do not need to do any more work:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	0	1	0

Now that we have a listing of all of the microstates, we need to figure out how to divide them up between the term symbols. It turns out that each term symbol can have, at most, one microstate from each box on the chart. The term symbols always end up claiming a “box” of microstates, centered on the middle of the chart. This is easier shown than said.

Attacking the chart from the top, we can see that the $M_l = 4$ $M_s = 0$ state clearly belongs to a ^1G symbol. The M_l =-4 $M_s = 0$ box also clearly belongs to this symbol. If I connect these states with a “box,” I get this:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
~~4~~	~~0~~	~~1~~	~~0~~
3	1	2	1

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
~~-4~~	~~0~~	~~1~~	~~0~~

The strickthough configurations all belong to the ^1G state. Let's subtract them from the chart to indicate that they are not available for other term symbols.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1

The next row indicates a $L = 3$ state. Because there are three M_s values available, this is a **triplet**. The term symbol will be ^3F, which reduces the chart down to

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	2	4	2
0	2	5	2
-1	2	4	2

The next state will be ^1D. Leaving us with

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	1	1	1
0	1	2	1
-1	1	1	1

Next is a ^3P state. The chart is getting pretty small now wtih

M_l	$M_s = 0$
	0

The last remaining microstate comprises the ^1S term symbol.

The total listing is

$$^1G, ^3F, ^1D, ^3P, ^1S.$$

Assigning J values, we get

$$^1G_4, ^3F_4, ^3F_3, ^3F_2, ^1D_2, ^3P_2, ^3P_1, ^3P_0, ^1S_0$$

If you can do this problem, you can do almost any atomic term symbol.

Note

The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration.

Shortcuts

There is a deep symmetry that connects different electronic configurations. It turns out that a p^1 configuration has the same term symbols as a p^5. Similarly, $p^2 = p^4$. A similar relationship can be used to figure out high electron number term symbols for the d and f orbitals.

8.4: Term Symbols Gives a Detailed Description of an Electron Configuration is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Mattanjah de Vries.

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8.5: The Allowed Values of J - the Total Angular Momentum Quantum Number

Learning Objectives

- Compate two spin-orbit coupling schemes that couple the total spin angular momenta and total orbital angular momenta of a multi-electron spectra

We need to be able to identify the electronic states that result from a given electron configuration and determine their relative energies. An electronic state of an atom is characterized by a specific energy, wavefunction (including spin), electron configuration, total angular momentum, and the way the orbital and spin angular momenta of the different electrons are coupled together. There are two descriptions for the coupling of angular momentum. One is called **j-j coupling**, and the other is called **L-S coupling**. The j-j coupling scheme is used for heavy elements (z > 40) and the L-S coupling scheme is used for the lighter elements. Only L-S coupling is discussed below.

L-S Coupling of Angular Momenta

L-S coupling also is called R-S or Russell-Saunders coupling. In L-S coupling, the orbital and spin angular momenta of all the electrons are combined separately

$$L = \sum_i l_i \tag{8.5.1}$$

$$S = \sum_i s_i \tag{8.5.2}$$

The total angular momentum vector then is the sum of the total orbital angular momentum vector and the total spin angular momentum vector.

$$J = L + S \tag{8.5.3}$$

The total angular momentum quantum number parameterizes the total angular momentum of a given particle, by combining its orbital angular momentum and its intrinsic angular momentum (i.e., its spin). Due to the spin-orbit interaction in the atom, the orbital angular momentum no longer commutes with the Hamiltonian, nor does the spin.

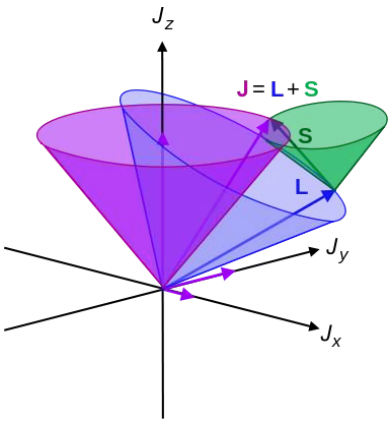


Figure 8.9.1 : "Vector cones" of total angular momentum J (purple), orbital L (blue), and spin S (green). The cones arise due to quantum uncertainty between measuring angular momentum components (see vector model of the atom). (Public Domain; Maschen).

However the total angular momentum J does commute with the Hamiltonian and so is a constant of motion (does not change in time). The relevant definitions of the angular momenta are:

Orbital Angular Momentum

$$|\vec{L}| = \hbar\sqrt{\ell(\ell+1)}$$

with its projection on the z-axis

$$L_z = m_\ell \hbar$$

Spin Angular Momentum

$$|\vec{S}| = \hbar\sqrt{s(s+1)}$$

with its projection on the z-axis

$$S_z = m_s \hbar$$

Total Angular Momentum

$$|\vec{J}| = \hbar\sqrt{j(j+1)}$$

with its projection on the z-axis

$$J_z = m_j \hbar$$

where

- l is the azimuthal quantum number of a single electron,
- s is the spin quantum number intrinsic to the electron,
- j is the total angular momentum quantum number of the electron,

The quantum numbers take the values:

$$m_\ell \in \{-\ell, -(\ell-1) \cdots \ell-1, \ell\}, \quad \ell \in \{0, 1 \cdots n-1\} \tag{8.5.4}$$
$$m_s \in \{-s, -(s-1) \cdots s-1, s\}, \tag{8.5.5}$$
$$m_j \in \{-j, -(j-1) \cdots j-1, j\}, \tag{8.5.6}$$
$$m_j = m_\ell + m_s, \quad j = |\ell + s| \tag{8.5.7}$$

and the magnitudes are:

$$|\mathbf{J}| = \hbar\sqrt{j(j+1)} \tag{8.5.8}$$
$$|\mathbf{J}_1| = \hbar\sqrt{j_1(j_1+1)} \tag{8.5.9}$$
$$|\mathbf{J}_2| = \hbar\sqrt{j_2(j_2+1)} \tag{8.5.10}$$

in which

$$j \in \{|j_1 - j_2|, |j_1 - j_2| - 1 \cdots j_1 + j_2 - 1, j_1 + j_2\}$$

This process may be repeated for a third electron, then the fourth etc. until the total angular momentum has been found.

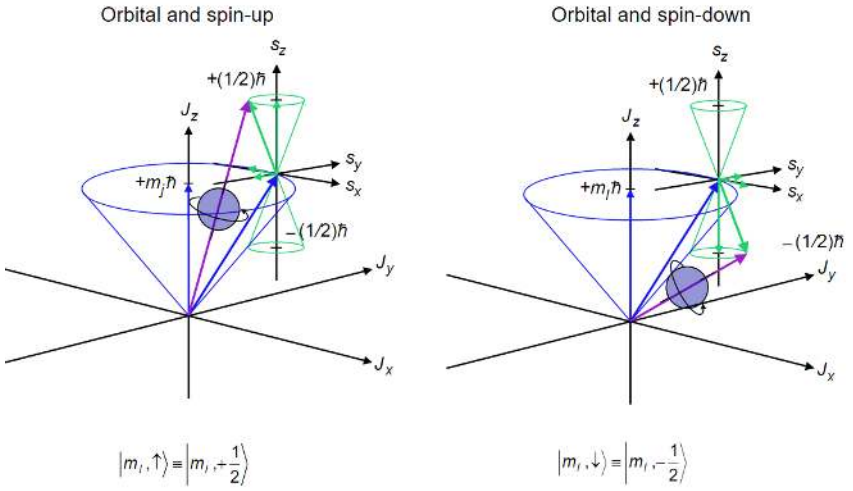


Figure 8.9.2 : Vector model of total angular momentum: spin and orbital coupling (spin-1/2 particles). (Public Domain; Maschen).

The result of these vector sums is specified in a code that is called a Russell-Saunders term symbol, and each term symbol identifies an energy level of the atom. Consequently, the energy levels also are called terms. A term symbol has the form ${}^{2s+1}L_J$ where the code letter that is used for the total orbital angular momentum quantum number L = 0, 1, 2, 3, 4, 5 is S, P, D, F, G, H, respectively. Note how this code matches that used for the atomic orbitals. The superscript $2S+1$ gives the spin multiplicity of the state, where S is the total spin angular momentum quantum number. The spin multiplicity is the number of spin states associated with a given electronic state. In order not to confuse the code letter S for the orbital angular momentum with the spin quantum number S, you must examine the context in which it is used carefully. In the term symbol, the subscript J gives the total angular momentum quantum number. Because of spin-orbit coupling, only J and M_j are valid quantum numbers, but because the spin-orbit coupling is weak L, M_l, S, and m_s still serve to identify and characterize the states for the lighter elements.

For example, the ground state, i.e. the lowest energy state, of the hydrogen atom corresponds to the electron configuration in which the electron occupies the 1s spatial orbital and can have either spin α or spin β. The term symbol for the ground state is ${}^2S_{1/2}$, which is read as “doublet S 1/2”. The spin quantum number is 1/2 so the superscript 2S+1 = 2, which gives the spin multiplicity of the state, i.e. the number of spin states equals 2 corresponding to α and β. The S in the term symbol indicates that the total orbital angular momentum quantum number is 0 (For the ground state of hydrogen, there is only one electron and it is in an s-orbital with $l = 0$). The subscript ½ refers to the total angular momentum quantum number. The total angular momentum is the sum of the spin and orbital angular momenta for the electrons in an atom. In this case, the total angular momentum quantum number is just the spin angular momentum quantum number, ½, since the orbital angular momentum is zero. The ground state has a degeneracy of two because the total angular momentum can have a z-axis projection of $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, corresponding to m_J = +1/2 or -1/2 resulting from the two electron spin states α and β. We also can say, equivalently, that the ground state term or energy level is two-fold degenerate.

? Exercise 8.9.1

Write the term symbol for a state that has 0 for both the spin and orbital angular momentum quantum numbers.

? Exercise 8.9.2

Write the term symbol for a state that has 0 for the spin and 1 for the orbital angular momentum quantum numbers

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8.6: Hund's Rules Determine the Term Symbols of the Ground Electronic States

Learning Objectives

- Define Hund three rules
- Use Hunds three rules to predict the lowest energy configuration and term symbols for multi-electron systems

The Aufbau section discussed how that electrons fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there a problem with this rule. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. What about the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule, which make a lot more sense in the context of generated term symbols that are used to combine the various L and S values represent vector additions of possible microstates.

Hund's Rules

1. State with the largest value of S is most stable and stability decreases with decreasing S.
2. For states with same values of S, the state with the largest value of L is the most stable.
3. If states have same values of L and S then, for a subshell that is less than half filled, state with smallest J is most stable; for subshells that are more than half filled, state with largest value of J is most stable.

Example 8.10.1

Rank these terms associated with an electronic configuration of an atom based on energy (via Hund's rules):

$$^3D, ^3P, ^3S, ^1D, ^1P, ^1S$$

Hund's First Rule (Maximize Spin Multiplicity)

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus.

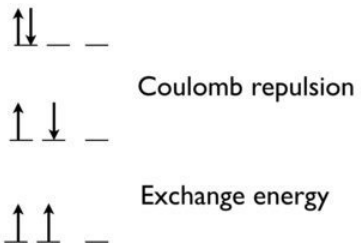


Figure 8.10.1 : Origin of Hund's First Rule. Hund's first rule is that for a given electron configuration, a state in which the spins are unpaired has lower total energy than one in which the spins are paired.

There's a Coulomb repulsion between two electrons to put them in the same orbital (a spin pairing energy often discussed in Crystal Field Theory). However, there's also a quantum mechanical effect. The *exchange energy* (which is favorable) increases with the number of possible exchanges between electrons with the same spin and energy. In transitioning from the top state to the middle state of Figure 8.10.1 , we remove the Coulomb repulsion between electrons in the same orbital. Moreover, In transitioning from the middle state to the bottom state (most stable state predicted by Hund's first rule), we *gain* the *exchange energy*, because these two electrons are indistinguishable.

Hund's Second Rule (Maximize Orbital Angular Multiplicity)

What matters is the total (scalar) angular momentum, not the direction. The negative and positive signs refer only to the direction of the angular momentum, not the magnitude. The direction is furthermore arbitrary (except in, say, a magnetic or electric field). So is the spin direction, incidentally. By convention we usually draw the first electron in each orbital as "up" (positive spin). However we could just as easily draw it "down". It makes no difference - in the absence of an external EM field, the energy is the same, if

only because molecules/atoms are rotating with respect to the lab frame anyway. "Up" and "down", in other words, is artificial. What matters is the *relative* momentum vectors of the various electrons in the system, and hence their sum total.

Hund's Third Rule (Minimize less than half filled or maximize greater than half filled shells)

A long time ago someone offering a reasonably simple explanation related to the fact that when the shell is more than half full, it's easier to visualize the system as an interaction between the spin and orbital momenta of holes rather than electrons, in which case the energetic stabilization term is reversed in sign. This would be because the spin angular momentum of a single hole would be opposite in sign compared to the spin angular momentum of a single electron. Taking as an example - the three p-orbitals. A situation with 1 electron and 5 electrons are functionally similar, except that one has a single electron and one has a single hole. All things being equal, the total spin angular momentum of the 1 electron system would be opposite in sign to whatever the total spin angular momentum of the 5 electron system is. So the expectations for Hund's rules would be switched. You can kind of see this if you draw out all the microstates of the 1-electron and 5-electron configurations: the everything is pretty much changed in sign in the latter case.

Example 8.10.2

What terms and levels can arise from an atom with the ground-state configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^1 3d^{\text{?}}$? Which is the most stable (lowest in energy) state?

Solution

Possible states include:

$$^1F_3, ^1D_2, ^1P_1, ^3F_4, ^3F_3, ^3F_2, ^3D_3, ^3D_2, ^3D_1, ^3P_2, ^3P_1, ^3P_0.$$

There are two unpaired electrons in this system from the electron configuration.

- Rule 1 predicts that the ground state will be a triplet with $S = 1$ so $2S + 1 = 3$. So the ground state is from this more narrowed list: $^3F_4, ^3F_3, ^3F_2, ^3D_3, ^3D_2, ^3D_1, ^3P_2, ^3P_1, ^3P_0$.
- Rule 2 predicts a F state since that is the highest multiplicity with $L = 3$: So the ground state is from this more narrowed list: $^3F_4, ^3F_3, ^3F_2$
- Rule 3 predicts the lowest J term since the d shell is less than half full. That is the $J = 2$ state.

Therefore for this system, the atom will have a ground-state structure of

$$^3F_2$$

Example 8.10.3 : Titanium cation

The ground configuration of a Ti^{2+} ion is $[Ar]3d^2$. What is the term of lowest energy state?

Solution

- Rule 1: two unpaired electrons ⇒ highest S = 1 ⇒ 2S + 1 = 3
- Rule 2: two in d in parallel spin ⇒ highest L = 1 + 2 = 3 ⇒ 3F
- Rule 3:.L = 3, S = 1 ⇒ J = 4, 3, 2; less than half-filled ⇒ $^3F_2$

Exercise 8.10.3

What is the term of lowest energy state for the following atoms and ions.

- C: $[He]2s^2 2p^2$
- N: $[He]2s^2 2p^3$
- O: $[He]2s^2 2p^4$
- Cr^{3+}: $[Ar]3d^3$
- Mn^{3+}: $[Ar]3d^4$
- Fe^{3+}: $[Ar]3d^5$

Answer

$^3P_0$, $^4S_{3/2}$, $^3P_2$, $^4F_{3/2}$, $^5D_0$, and $^6S_{5/2}$, respectively.

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8.7: Using Atomic Term Symbols to Interpret Atomic Spectra

Learning Objectives

- Demonstrate how spin-orbit coupling is experimentally observed in atomic spectra
- Use atomic terms symbols to ascribe transitions to specific angular momenta states described by atomic term symbols

Around 1930, several spectroscopists using high resolution instruments found that lines in the hydrogen atom spectrum actually are not single lines but they are multiplets as shown for an isotopic mixture of hydrogen,(H_α^1) and deuterium, (H_α^2), in Figure 8.11.1 . A multiplet consists of two or more closely spaced lines. Two lines together form a doublet, three a triplet, etc. Multiplets also are called fine structure. The term fine structure means the lines are spaced close together, i.e. finely spaced. Such fine structure also was found in spectra of one-electron ions such as He^+.

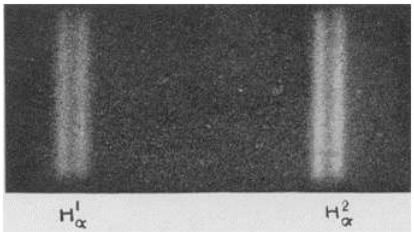


Figure 8.11.1 : Photograph of the first line in the Balmer series for atomic hydrogen and deuterium. These lines are identified as H_α^1 (hydrogen) and H_α^2 (deuterium), respectively. From H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) p. 132 and G.N. Lewis and F.H. Spedding, Phys. Rev. 43, 964 (1933). The doublet splitting for H_α^1 at 656.279 nm was measured to be 0.326 cm^{-1}.

You should recall that the H_α^1 line in the Balmer series at 656.279 nm was understood as resulting from a single transition of an electron from the n = 3 energy level to the n = 2 level. The observation of fine structure revealed that an orbital energy level diagram does not completely describe the energy levels of atoms. This fine structure also provided key evidence at the time for the existence of electron spin, which was used not only to give a qualitative explanation for the multiplets but also to furnish highly accurate calculations of the multiplet splittings.

Spin-Orbit Coupling

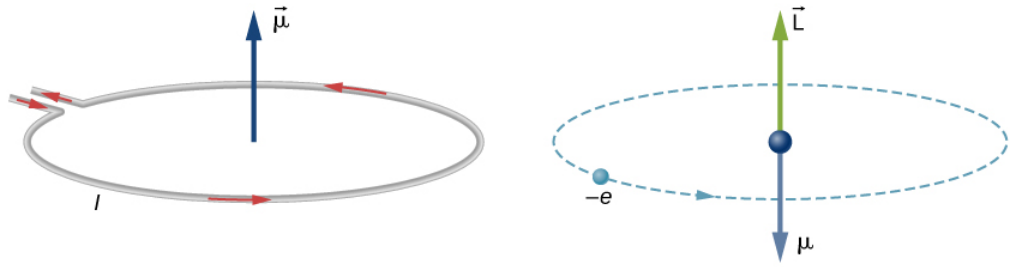
Specifying the orbital configuration of an atom does not uniquely identify the electronic state of the atom because the orbital angular momentum, the spin angular momentum, and the total angular momentum are not precisely specified. For example in the hydrogen $2p^1$ configuration, the electron can be in any of the three p-orbitals, m_l = +1, 0, and –1, and have spins with m_s = +1/2 or –1/2. Thus, there are 3 times 2 different possibilities or states. Also, the orbital and spin angular momentum of the electrons combine in multiple ways to produce angular momentum vectors that are characteristic of the entire atom not just individual electrons, and these different combinations can have different energies. This coupling of orbital and spin angular momentum occurs because both the electron spin and orbital motion produce magnetic dipole moments. As we have seen previously, the relationship between the angular momentum and the magnetic moment is given by the gyromagnetic ratio. These magnetic dipoles interact just like two tiny bar magnets attracting and repelling each other. This interaction is called **spin-orbit interaction**. The interaction energy is proportional to the scalar product of the magnetic dipole moments, which are proportional to the angular momentum vectors.

$$E_{s-o} \propto S \cdot L$$

with the following terms added to the Hamiltonian

$$\hat{H}_{s-o} \propto \hat{S} \cdot \hat{L}$$

where the constant of proportionality is called the spin-orbit coupling constant. The spin-orbit interaction couples the spin motion and orbital motion of all the electrons together. This coupling means that exact wavefunctions are not eigenfunctions of the spin and orbital angular momentum operators separately. Rather the total angular momentum $J = L + S$, the vector sum of the spin and orbital angular momentum, is required to be coupled for a completely accurate description of the system. Trying to describe the coupled system in terms of spin and orbital angular momentum separately is analogous to trying to describe the positions of two coupled bar magnets independently. It cannot be done; their interaction must be taken into account (Figure 8.11.1).



(a) Current-carrying loop (b) Hydrogen atom

Figure 8.11.1 : An electron that orbits the nucleus induces a "current" and a magnetic field. Similarly, the rotating electron (really intrinsic spin) of the electron induces a different magnet. Both a magnetic (dipole) moments will interact with each other via spin-orbit coupling to generate fine structure atomic spectra.(CC-SA OpenStax).

Atomic Spectroscopy

Higher energy or excited orbital configurations also exist. The hydrogen atom can absorb energy, and the electron can be promoted to a higher energy orbital. The electronic states that result from these excited orbital configurations also are characterized or labeled by term symbols. The details of how to determine the term symbols for multi-electron atoms and for cases where both the orbital and spin angular momentum differ from zero are given elsewhere, along with rules for determining the relative energies of the terms.

We have found that the selection rules for promoting a single electron moving from one atomic orbital to another via the absorption or emission of light are

$$\Delta l = \pm 1$$

$$\Delta m_l = 0, \pm 1$$

These selection rules arise from the conservation fo angular momentum during a spectroscopic transition and the fact that a photon has a spin 1. Within the limits of L-S coupling, these rules can be expressed in terms of atomic term symbols resulting in the resulting Russell-Saunders selection rules:

$$\Delta S = 0 \tag{8.7.1}$$

$$\Delta L = 0, \pm 1 \tag{8.7.2}$$

$$\Delta J = 0, \pm 1, \tag{8.7.3}$$

but the $J = 0$ to $J = 0$ transition is forbidden

$$\Delta m_J = 0, \pm 1 \tag{8.7.4}$$

but the $m_J = 0$ to $m_J = 0$ transition is forbidden if $\Delta J = 0$.

These selection rules result from the general properties of angular momentum such as the conservation of angular momentum and commutation relations. The $\Delta L = 0$ option in Equation 8.7.2 does not violate the conservation of angular momentum discussed previously, since $\Delta l = \pm 1$ is still required. The orbital angular momentum of an electron must change upon absorption, but this does not necessarily affect the overall momentum of the state given by Equation 8.7.2.

The selection rules apply only to atoms that can be described with Russell-Saunders (LS) coupling. These rules fail as the atomic number increases because the S and L quantum numbers become "bad" quantum numbers; this occurs when the jj-coupling coupling approach is more applicable. For example, the transition between single ($S = 1/2$ and triplet $S = 1$ states (violation of selection rule in Equation 8.7.1) are allowed and experimentally observed, in heavy atoms.

Example 8.11.1 : Sodium Atoms

An example of this fine structure is the emission of sodium atoms.

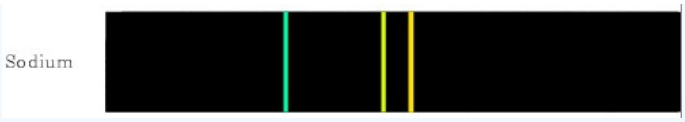


Figure above does not show this splitting).

616.07 nm	615.42 nm	589.00 nm	589.59 nm	568.82 nm	568.26 nm

How can these transitions be described in terms of transitions between microstates

Solution

We need to discussed states in terms of not only electron configurations, but in terms of microstates (i.e., term symbols) and the principal quantum number of the valence electron, n:

- The ground state has a $(Ne]ns^1$ configuration, which has only one microstate $^2S_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]np^1$, which has two microstates: $^2P_{3/2}$ and $^2P_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]nd^1$, which has two microstates of $^2D_{5/2}$ and $^2D_{3/2}$

Observed lines can be explained:

- $5S \rightarrow 3P$ gives two lines since the initial configuration has two microstates: 616.07, 615.42 nm
- $3P \rightarrow 3S$ gives two lines since the terminal configuration has two microstates: 589.00, 589.59 nm
- $4D \rightarrow 3P$ gives two lines since the terminal configuration has two microstates: 568.82, 568.26 nm

Splitting of the Sodium D Line

One notable atomic spectral line of sodium vapor is the so-called D-line, which may be observed directly as the sodium flame-test line and also the major light output of low -pressure sodium lamps (these produce pressure sodium lamps (these produce an unnatural yellow). The D-line is one of the classified Fraunhofer lines in Sodium vapor in the upper layers of lines. Sodium vapor in the upper layers of the sun creates a dark line in the emitted spectrum of electromagnetic radiation by absorbing visible light in a band of wavelengths around 589.5 nm. This wavelength corresponds to transitions in atomic sodium in which the valence-electron transitions from a 3s to 3p electronic state.

Closer examination of the visible spectrum of atomic sodium reveals that the D-line actually consists of two lines called the D_1 and D_2 lines at 589 6 nm and 589.0 nm, respectively. The splitting between these lines arises because of spin-orbit coupling. Na has one unpaired electron ($S = ½$). If we consider the $S \rightarrow P$ transition, then for the excited state, P, we have $L = 1$. Thus, $J = 3/2$ or $J = 1/2$.

Now we want to apply these ideas to understand why multiplet structure is found in the luminescence spectrum of hydrogen and single electron ions. As we have said, the H_α line in the Balmer series at 656.279 nm can be understood via a transition of an electron in a n = 3 atomic orbital to a n = 2 atomic orbital. When this spectral line was examined using high-resolution instruments, it was found actually to be a doublet, i.e. two lines separated by 0.326 cm^{-1}.

There are 9 degenerate orbitals associated with the n = 3 level, and 4 associated with the n = 2 level. Since an electron can be in any orbital with any one of two spins, we expect the total number of states to be twice the number of orbitals. The number of orbitals is given by n^2 so there should be 8 states associated with n = 2 and 18 states associated with n = 3. Using the ideas of vector addition of angular momentum, the terms that result from having an electron in any one of these orbitals are given in Table 8.11.1 .

Table 8.11.1 : H Atom Terms Originating from n = 1, 2, and 3

Orbital Configuration	Term Symbols	Degeneracy
$1s^1$	$^2S_{1/2}$	2
$2s^1$	$^2S_{1/2}$	2
$2p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4

Orbital Configuration	Term Symbols	Degeneracy
$3s^1$	$^2S_{1/2}$	2
$3p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3d^1$	$^2D_{3/2}$, $^2D_{5/2}$	4, 6

Table 8.11.1 shows that there are three terms associated with n = 2, and 5 terms associated with n = 3. In principle, each term can have a different energy. The degeneracy of each term is determined by the number of projections that the total angular momentum vector has on the z-axis. These projections depend on the m_J quantum number, which ranges from $+J$ to $-J$ in integer steps. J is the total angular momentum quantum number, which is given by the subscript in the term symbol. This relationship between m_J and J (m_J varies from $+J$ to $-J$ in integer steps) is true for any angular momentum vector.

? Exercise 8.11.3

Confirm that the nine term symbols in Table 8.11.1 are correct.

? Exercise 8.11.4

Confirm that the values for the degeneracy in Table 8.11.1 are correct and that the total number of states add up to 8 for n = 2 and 18 for n = 3.

The energies of the terms depend upon spin-orbit coupling and relativistic corrections that need to be included in the Hamiltonian operator in order to provide a more complete description of the hydrogen atom. As a consequence of these effects, all terms with the same n and (J\) quantum numbers have the **same energy,** while terms with different values for n or J have different energies. The theoretical term splittings as given by H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) pp. 132-137 and are shown in Figure 8.11.2 .

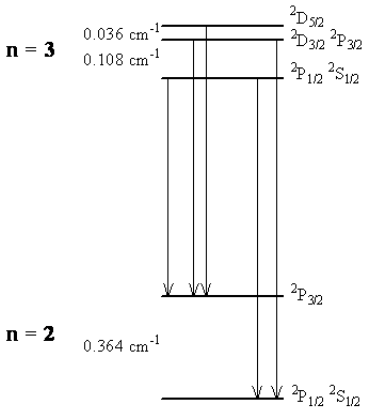


Figure 8.11.2 : Energy level diagram for the electronic states of hydrogen corresponding to an electron with the principal quantum number n = 3 and n = 2. While the relative energies of the terms are drawn to scale, the energy of n = 3 relative to n = 2 is not. Transitions to the $2P_{3/2}$ and ($2P_{1/2}$ and $2S_{1/2}$) levels correspond to the two lines in the H_α^1 band, which have a measured separation of 0.326 cm^{-1}.

Figure 8.11.2 shows 5 allowed transitions for the electron in the states associated with n = 3 to the states associated with n = 2. Of these five, two are most intense and are responsible for the doublet structure. These two transitions are indicated by the wide black lines at the bottom of the figure to correspond to the lines observed in the photographic spectrum shown in Figure 8.11.2 . The other transitions contribute to the width of these lines or are not observed. The theoretical value for the doublet splitting is 0.328 cm^{-1}, which is in excellent agreement with the measured value of 0.326 cm^{-1}. The value of 0.328 cm^{-1} is obtained by taking the difference, 0.364 – 0.036 cm^{-1},in the term splittings.

As we have just seen, the electronic states, as identified by the term symbols, are essential in understanding the spectra and energy level structure of atoms, but it also is important to associate the term symbols and states with the orbital electron configurations.

The orbital configurations help us understand many of the general or coarse features of spectra and are necessary to produce a physical picture of how the electron density changes because of a spectroscopic transition.

? Exercise 8.11.5

Use the Russell-Saunders selection rules to determine which transitions contribute to the H_α line in the hydrogen spectrum.

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CHAPTER OVERVIEW

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9.1: 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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9.2: The H_2^+ Prototypical Species

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion H_2^+.

The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely 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 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.

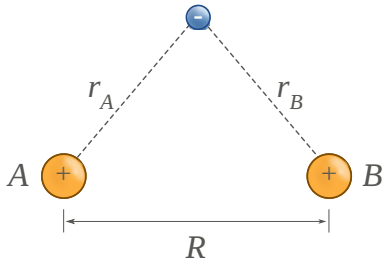


Figure 9.2.1 : Hydrogen molecular ion H_2^+ with fixed nuclei A and B, internuclear distance R. (CC BY-NC; Ümit Kaya via LibreTexts)

The electronic Hamiltonian for H_2^+ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{9.2.1}$$

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

Although the Schrödinger equation for H_2^+ can be solved exactly (albeit within the Born-Oppenheimer approximation where the nuclei are fixed) because there is only one electron, we will develop approximate solutions in a manner applicable to other diatomic molecules that have more than one electron.

Linear Combination of Atomic Orbitals

For the case where the protons in H_2^+ are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other. The electronic wavefunction would just be $1s_A(r)$ or $1s_B(r)$ depending upon which proton, labeled A or B, the electron is near. Here $1s_A$ denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position r of the electron is specified. Similarly $1s_B$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

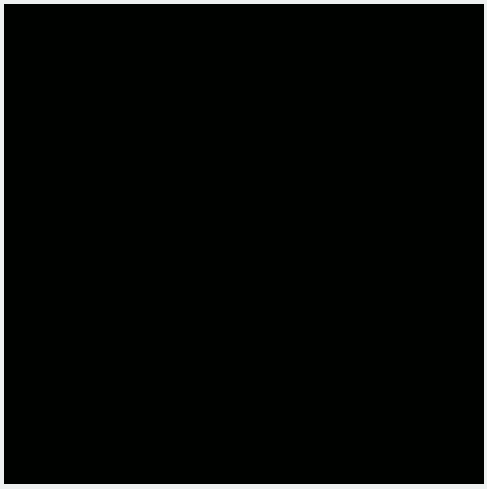
$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{9.2.2}$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals $1s_A$ and $1s_B$.

The Linear Combination of Atomic Orbitals (LCAO) Approximation and Interference

The LCAO approximation is an example of the linear variational method discussed previously with the true molecular orbital wavefunction approximated as an expansion of a basis set of atomic orbitals on each atom of the molecule with variable coefficients that can be optimized (e.g., via the secular equations). As discussed previously, the number of wavefunctions (solutions) extracted from solving the secular determinant is equal the number of elements in the expansion. So for the expansion in Equation 9.2.2 with two atomic orbitals contributing result in two molecule orbitals.

This method yields a approximate picture of the molecular orbitals in a molecules. The figure below shows two atoms approaching along the axis of one of their $2p$ states. In the top row, the two lobes facing one another have the same sign; in the bottom row they have opposite sign. These are two different linear combinations of the same two atomic states, on different atoms and with difference phases (i.e., signs of C_A vs. C_B in the expansion). In the first example, the electron density increases between the nuclei and in the second example, a very steep-sided node between the two nuclei causes all the probability density to face away from the atom opposite.



For H_2^+, the simplest molecule, the starting function is given by Equation 9.2.2. We must determine the values for the coefficients, C_A and C_B. We could use the variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition $|C_A|^2 = |C_B|^2$; namely, $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{9.2.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{9.2.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced (Figure 9.2.2 (bottom) between the two protons, whereas it is diminished for ψ_- as shown in Figures 9.2.2 (top). ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons.

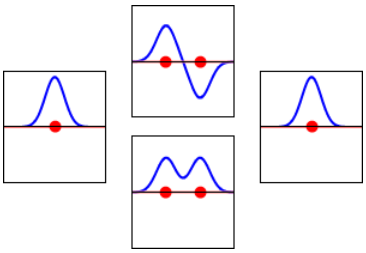


Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional .)

So ψ_+ is called a **bonding molecular orbital**. If the electron were described by ψ_-, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an **antibonding molecular orbital**.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Rudolf Winter (Aberystwyth University)

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9.3: The Overlap Integral

For H_2^+, the simplest molecule, we must determine the values for the coefficients, C_A and C_B for the LCAO approximation for the molecular orbital as a linear combination of the two atomic orbitals

$$|\psi(r)\rangle = C_A 1s_A(r) + C_B 1s_B(r)$$

We could use the linear variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition

$$|C_A|^2 = |C_B|^2$$

so $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\underbrace{|\psi_+\rangle = C_+(1s_A + 1s_B)}_{\text{bonding molecular orbital}} \tag{9.3.1}$$

and

$$\underbrace{|\psi_-\rangle = C_-(1s_A - 1s_B)}_{\text{antibonding molecular orbital}} \tag{9.3.2}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for $|\psi_+\rangle$ is enhanced between the two protons, whereas it is diminished for $|\psi_-\rangle$ as shown in Figures 9.3.1 . ψ_- has a node in the middle while $|\psi_+\rangle$ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So $|\psi_+\rangle$ is called a *bonding molecular orbital*. If the electron were described by $|\psi_-\rangle$, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so $|\psi_-\rangle$ is called an *antibonding molecular orbital*.

Now we want to evaluate C_+ and C_- and then calculate the energy. The bonding and antibonding character of ψ_+ and ψ_- also should be reflected in the energy. If $|\psi_+\rangle$ indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts H_2^+ to be stable or not and also how much energy is required to dissociate this molecule.

The constants C_+ and C_- are evaluated from the standard normalization condition:

$$\int \psi_\pm^* \psi_\pm d\tau = \langle \psi_\pm | \psi_\pm \rangle = 1 \tag{9.3.3}$$

$$\langle C_\pm(1s_A \pm 1s_B) | C_\pm(1s_A \pm 1s_B) \rangle = 1 \tag{9.3.4}$$

$$|C_\pm|^2 [\underbrace{\langle 1s_A | 1s_A \rangle}_{1} + \underbrace{\langle 1s_B | 1s_B \rangle}_{1} \pm \underbrace{\langle 1s_B | 1s_A \rangle}_{S} \pm \underbrace{\langle 1s_A | 1s_B \rangle}_{S^*}] = 1 \tag{9.3.5}$$

Since the atomic orbitals are normalized, the first two integrals are just 1. The last two integrals are called *overlap integrals* and are symbolized by S and S^*, respectively, since one is the complex conjugate of the other.

The overlap integrals are telling us to take the value of $1s_B$ at a point multiply by the value of $1s_A$ at that point and sum (integrate) such a product over all of space (Figure 9.3.1). If the functions do not overlap, i.e. if one is zero when the other one is not and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancelation of positive and negative contributions.

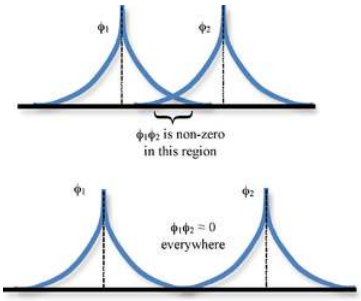


Figure 9.3.1 : The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close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

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from $R = \infty$ to $R = 0$. Clearly when the protons are infinite distance apart, there is no overlap, and when $R = 0$ both functions are centered on one nucleus and $\langle 1s_A | 1s_B \rangle$ becomes identical to $\langle 1s_B | 1s_A \rangle$, which is normalized to 1, because $1s_A = 1s_B$.

With these considerations and using the fact that $1s$ wavefunctions are real so

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle = S \tag{9.3.6}$$

Equation 9.3.5 becomes

$$|C_{\pm}|^2 (2 \pm 2S) = 1 \tag{9.3.7}$$

The solution to Equation 9.3.7 is given by

$$C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} \tag{9.3.8}$$

Hence, the normalized molecular orbitals in Equations 9.3.1 and 9.3.1 are

$$|\psi_+\rangle = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \tag{9.3.9}$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \tag{9.3.10}$$

The energies associated with these wavefunctions requires a bit more effort to calculate though as demonstrated in the following section.

For the overlap integral of two 1s orbitals from the hydrogen dimer discussed above is difficult to evaluate analytically and is explained here. The final answer is:

$$S(R) = \langle 1s_A | 1s_B \rangle \tag{9.3.11}$$

$$= e^{-R/a_o} \left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2} \right) \tag{9.3.12}$$

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

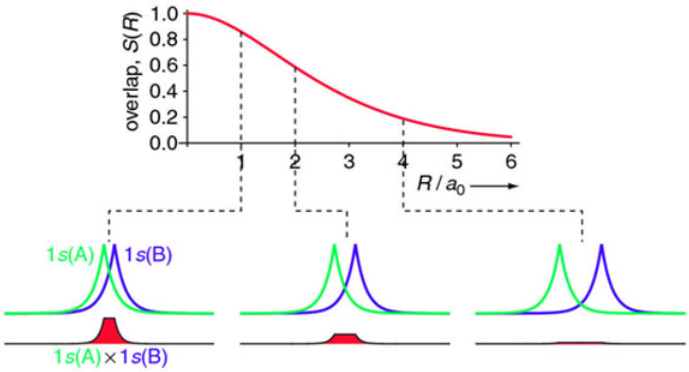


Figure 9.3.2 : The overlap integral at different proton separations.

Example 9.3.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for H_2^+ for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

Solution

The electronic charge density is calculated with the formula $|e\psi^2|$ where $e = 1.602 \times 10^{-19} C$

a: Bonding Molecular Orbital

First, squaring the bonding molecular orbital (Equation 9.3.9) gives us:

$$\begin{aligned}\psi_+^2 &= \frac{1}{2(1+S)}(1s_A + 1s_B)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3}\left(e^{-r_A/a_0} + e^{-r_B/a_0}\right)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3} \\ &= (0.561)^2 \times \left(\frac{1}{\pi \times (52.9 \text{ pm})^3}\right) = 6.7672 \times 10^{-7} \text{ pm}^{-3}\end{aligned}$$

(Note: The value of C^2 is obtained from equation 9.3.12 and the value of S is from Equation 9.3.12)

To find the density at halfway between A and B for the bonding orbital evalulate at 1/2 R,

$$r_A = \frac{1}{2}R \text{ and } r_B = \frac{1}{2}R$$

$$\psi_+^2 = 3.7 \times 10^{-7} \text{ pm}^{-3}$$

Now multiply this answer by e to generate the electronic charge density,

$$P = \left(3.7 \times 10^{-7} \text{ pm}^{-3}\right) \times \left(1.602 \times 10^{-19}\right) \text{ C} = 5.93 \times 10^{-26} C/pm^3$$

b: Antibonding Molecular Orbital

To find the halfway between A and B for the anti-bonding orbital at $r_A = \frac{1}{2}R$ and $r_B = \frac{1}{2}R$. However, simple inspection of Equation 9.3.10 or Figure 9.3.1 shows this will be zero.

$$\text{e}\psi_-^2 = 0$$

Obviously, when multiplied by e, the answer is still zero. This makes logical sense as there would be no charge density between the two atoms as there lies a node with no probability of finding an electron.

? Exercise 9.3.1

Show that for two arbitrary functions $\langle \varphi_B | \varphi_A \rangle$ is the complex conjugate of $\langle \varphi_A | \varphi_B \rangle$ and that these two integrals are equal if the functions are real.

Contributors and Attributions

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

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9.4: Chemical Bond Stability

Learning Objectives

- Identify the nature of the energy of molecular orbitals of a diatomic as a function of intermolecular distance
- Identify the three integrals involved in calculation the total Molecular Orbital Energy: coulomb Integral, exchange integral, and overlap integral

As shown previously, we can construct two molecular orbitals for the H_2^+ system using the LCAO approximation with a basis set of two 1s atomic orbitals (i.e., the $1s$ orbitals on hydrogen A ($1s_A$) and hydrogen B ($1s_B$):

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}}(1s_A \pm 1s_B) \tag{9.4.1}$$

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

$$E_{\pm} = \left\langle \psi_{\pm} | \hat{H}_{elec} | \psi_{\pm} \right\rangle \tag{9.4.2}$$

which can be expanded using the expanded molecular orbital wavefunctions in Equations 9.4.1 to give

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[\underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{BA}} \right] \tag{9.4.3}$$

where S is the overlap integral between the two atomic orbitals of the basis. The four integrals in Equation 9.4.3 can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively.

$$E_{\pm} = \frac{1}{2(1 \pm S)} [H_{AA} + H_{BB} \pm H_{AB} \pm H_{BA}] \tag{9.4.4}$$

Exercise 9.4.1

Show that Equation 9.4.2 expands to give Equation 9.4.3 within the LCAO approximation that uses a basis set of only two 1s atomic orbitals.

Answer

Here we have the wavefunction within the LCAO approximation that uses a basis set of only two 1s atomic orbitals (Equation 9.4.1).

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

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

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

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):

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

Now we can see this is now equivalent to Equation 9.4.3 if the equation above is inserted (and adding a subscript to emphasize this only applies to the electronic wavefunction):

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

Notice that A and B appear equivalently in the Hamiltonian operator for H_2^+. This equivalence means that integrals involving $1s_A$ must be the same as corresponding integrals involving $1s_B$, i.e.

$$H_{AA} = H_{BB} \tag{9.4.5}$$

and since the wavefunctions are real

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

so

$$H_{AB} = H_{BA} \tag{9.4.6}$$

These two equalities simplify Equation 9.4.4:

$$E_{\pm} = \frac{1}{1 \pm S}(H_{AA} \pm H_{AB}) \tag{9.4.7}$$

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

$$H_{AA} = \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_A \right\rangle}_{E_H} + \frac{e^2}{4\pi\epsilon_0 R} \underbrace{\langle 1s_A | 1s_A \rangle}^{1} \underbrace{- \left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle}_{J_{AB}} \tag{9.4.8}$$

- The first term is just the integral for the energy of the hydrogen atom of the 1s orbital, E_H.
- The second integral is equal to 1 by normalization; the prefactor is just the Coulomb repulsion of the two protons.
- The last integral, *including the minus sign*, is represented by J and is called the **Coulomb integral**.

Physically J_{AB} is the potential energy of interaction of the electron located around proton A with proton B. It is negative because it is an attractive interaction. It is the average interaction energy of an electron described by the $1s_A$ function with proton B.

The Coulomb Integral ()

The **Coulomb Integral** is the potential energy of electrostatic repulsion between the electron with the electron density in $1S_A$ and the the electron with the electron density function $1S_B$

Now consider H_{AB}.

$$H_{AB} = \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_B \right\rangle}_{E_H S} + \frac{e^2}{4\pi\epsilon_0 R} \underbrace{\langle 1s_A | 1s_B \rangle}^{S} \underbrace{- \left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle}_{K_{AB}} \tag{9.4.9}$$

- In the first integral we have the hydrogen atom Hamiltonian and the H atom function $1s_B$. The function $1s_B$ is an eigenfunction of the operator with eigenvalue E_H. Since E_H is a constant it factors out of the integral, which then becomes the overlap integral, S. The first integral therefore reduces to $E_H S$.
- The second term is just the Coulombic energy of the two protons times the overlap integral.
- The third term, *including the minus sign*, is given the symbol K and is called the *exchange integral* because the electron is described by the $1s_A$ orbital on one side and by the $1s_B$ orbital on the other side of the operator. The electron changes or exchanges position in the molecule.

The Exchange Integral ()

In a **coulomb integral**, the electron always is in the same orbital; whereas, in an *Exchange Integral*, the electron is in one orbital on one side of the operator and in a different orbital on the other side.

Using the expressions for H_{AA} (Equation 9.4.8) and H_{AB} (Equation 9.4.9) and substituting into Equation 9.4.7 produces:

$$E_{\pm} = \frac{1}{1 \pm S}\left[\left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right)(1 \pm S) + J \pm K\right] \tag{9.4.10}$$

$$= E_H + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.4.11}$$

Equation 9.4.11 tells us that the energy of the H_2^+ molecule is the energy of a hydrogen atom plus the repulsive energy of two protons plus some additional electrostatic interactions of the electron with the protons. These additional interactions are given by the last term

$$\frac{J \pm K}{1 \pm S}.$$

If the protons are infinitely far apart then only E_H is nonzero, which we can set to zero by subtracting off:

$$\Delta E_{\pm} = E_{\pm} - E_H \tag{9.4.12}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.4.13}$$

To get a chemical bond and a stable H_2^+ molecule $\Delta E_{\pm}$ must be less than zero and have a minimum, i.e. $\frac{J \pm K}{1 \pm S}$ must be sufficiently negative to overcome the positive repulsive energy of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ for some value of R. For large R, these terms are zero, and for small R, the **Coulomb repulsion of the protons rises to infinity.**

? Exercise 9.4.2

Show that Equation 9.2.1 follows from Equation 9.4.7

The Coulomb and Exchange Integrals

We will examine more closely how the Coulomb repulsion term and the integrals J, K, and S depend on the separation of the protons, but first we want to discuss the physical significance of J, the Coulomb integral, and K, the exchange integral. J and K have been defined as

$$J_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_A}(r)\frac{e^2}{4\pi\epsilon_0 r_B}d\tau \tag{9.4.14}$$

$$K_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_B}(r)\frac{e^2}{4\pi\epsilon_0 r_A}d\tau \tag{9.4.15}$$

Figure 9.4.2 shows graphs of the four terms contributing to the energy of H_2^+ (Equation 9.4.13). In Figure 9.4.2 , you can see that as the internuclear distance R approaches zero,

- the Coulomb repulsion of the two protons goes from near zero to a large positive number,
- the overlap integral goes for zero to one, and
- J and K become increasingly negative.

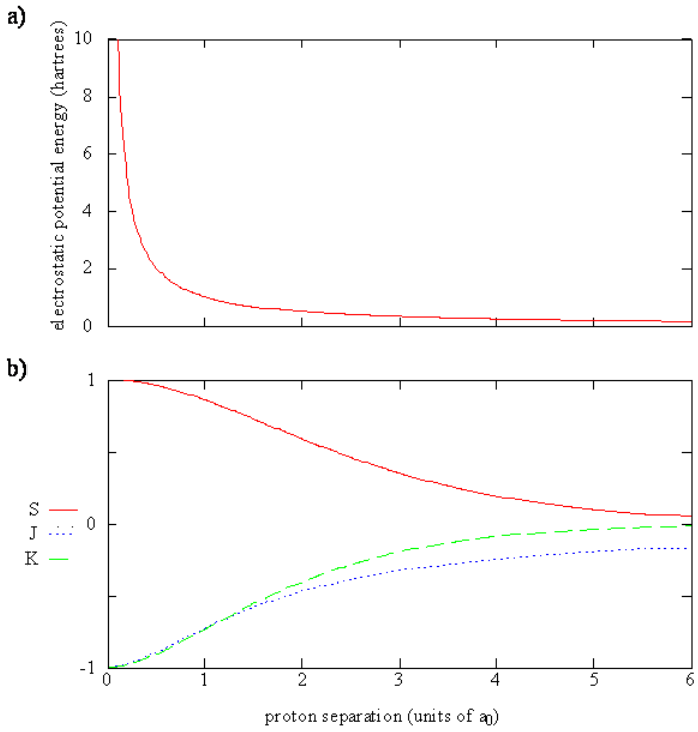


Figure 9.4.2 : (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). (b) The overlap (S), Coulomb (J), and exchange (K) integrals at different proton separations. The units for J and K are hartrees; S has no units. (CC BY-SA-NC; 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 9.4.14 and 9.4.15 are positive. In the Coulomb integral, $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the charge density of the electron around proton A, since **r** represents the coordinates of the electron relative to proton A. Since r_B is the distance of this electron to proton B, the Coulomb integral gives the potential energy of the charge density around proton A interacting with proton B. J can be interpreted as an average potential energy of this interaction because $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the probability density for the electron at point r, and $\frac{e^2}{4\pi\epsilon_0 r_B}$ is the potential energy of the electron at that point due to the interaction with proton B. Essentially, J accounts for the attraction of proton B to the electron density of hydrogen atom A. As the two protons get further apart, this integral goes to zero because all values for r_B become very large and all values for $1/r_B$ become very small.

In the **exchange integral**, K, the product of the two functions is nonzero **only** in the regions of space where the two functions overlap. If one function is zero or very small at some point then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the $1/r$ values become zero. The product $e\varphi^*_{1s_A}(r)\varphi_{1a_B}(r)$ is called the *overlap charge density*. Since the overlap charge density is significant in the region of space between the two nuclei, it makes an important contribution to the chemical bond. The exchange integral, K, is the potential energy due to the interaction of the overlap charge density with one of the protons. While J accounts for the attraction of proton B to the electron density of hydrogen atom A, K accounts for the added attraction of the proton due the build-up of electron charge density between the two protons.

? Exercise 9.4.3

Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for H_2^+.

Figure 9.4.3 shows the energy of H_2^+ relative to the energy of a separated hydrogen atom and a proton as given by Equation 9.4.11. For the electron in the ψ_- orbital, the energy of the molecule, $E_{el}(R)$, **always** is greater than the energy of the separated atom and proton.

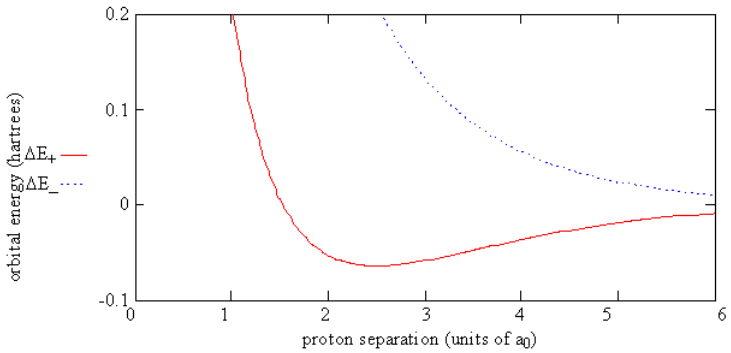


Figure 9.4.3 : Energy of the H_2^+ bonding molecular orbital ΔE_+ and the molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

For the electron in the ψ_+ orbital, you can see that the big effect for the energy of the bonding orbital, $E_+(R)$, is the balance between the repulsion of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ and J and K, which are both negative. J and K manage to compensate for the repulsion of the two protons until their separation is less than 100 pm (i.e the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. This minimum represents the formation of a chemical bond. The effect of S is small. It only causes the denominator in Equation 9.4.11 to increase from 1 to 2 as R approaches 0.

For the antibonding orbital, $-K$ is a positive quantity and essentially cancels J so there is not sufficient compensation for the Coulomb repulsion of the protons. The effect of the -K in the expression, Equation 9.4.11, for E_- is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for ψ_- is even lower than that given by the atomic orbitals.

Contributors and Attributions

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

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9.5: Bonding and Antibonding Orbitals

Learning Objectives

- Characterize the bonding and anti-bonding molecular orbitals in H^+

The two molecular orbitals of the H^+ ion were created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the jth molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$|\psi_J\rangle = \sum_i^N c_{J,i}|\phi_i\rangle \tag{9.5.1}$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 9.5.1). Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 9.5.1).

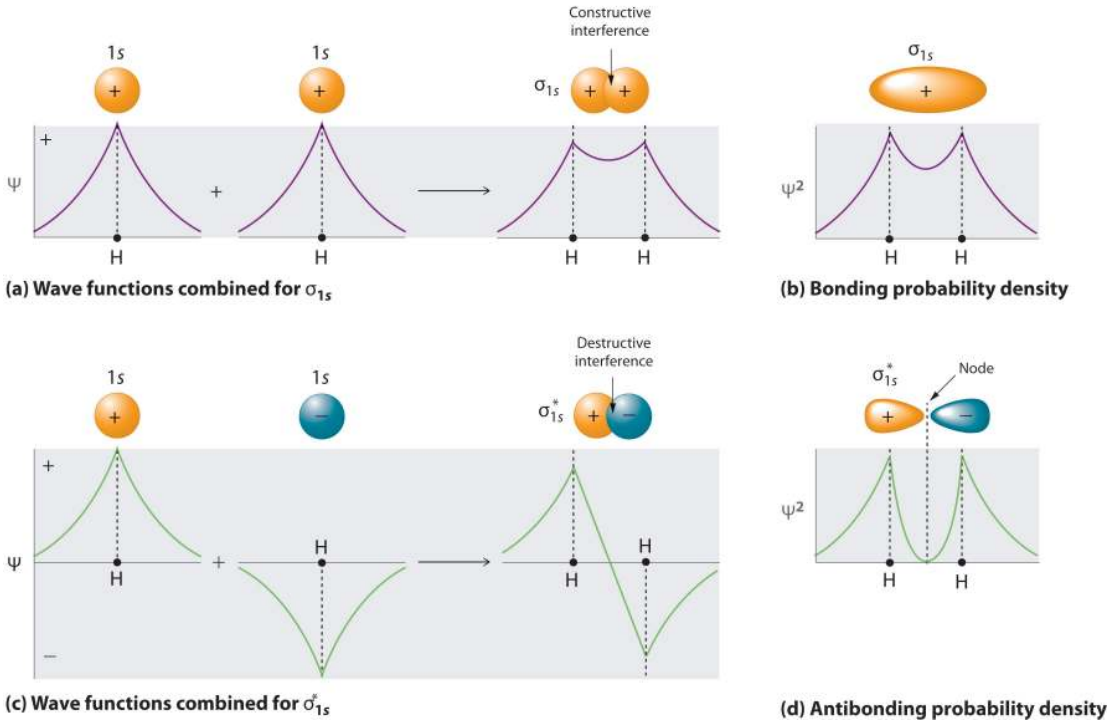


Figure 9.5.1 : Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wavefunctions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wavefunction (Ψ^2) for the bonding σ1s molecular orbital illustrates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

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}}(|1s_A\rangle + |1s_B\rangle) \tag{9.5.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 9.5.1). The

resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} and has a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$|\sigma^*_{1s}\rangle = \frac{1}{\sqrt{2(1-S)}}(|1s_A\rangle - |1s_B\rangle) \tag{9.5.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wavefunctions. In contrast, electrons in the $\sigma^\star_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^\star_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wavefunctions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^\star_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the $\sigma^\star_{1s}$ 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 $\sigma^\star_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 9.5.2

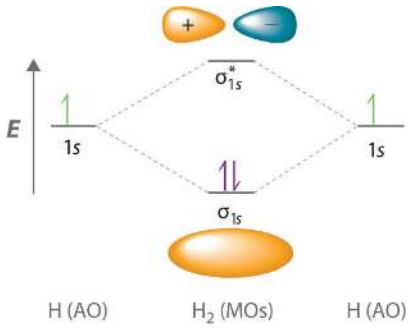


Figure 9.5.2 : Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (at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

> *A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).*

Expanding Beyond the 1s Orbital Basis Set

This picture of bonding in H_2^+ in the previous section is very simple, but gives reasonable results when compared to an exact calculation. The equilibrium bond distance is 134 pm compared to 106 pm (exact), and a dissociation energy is 1.8 eV compared to 2.8 eV (exact). To better describe chemical bonding we need to account for the increase in electron density between the two nuclei. The 1s orbitals alone are not particularly good for this purpose because they are spherically symmetric and show no preference for the space between the atomic nuclei. The use of additional atomic orbitals can correct this situation and provide additional parameters, which can be optimized by the linear variational method, to give a better function with a lower energy and more accurate description of the charge density.

The energy of the non-normalized molecular orbital can be calculated from the expectation value integral of the Hamiltonian,

$$E_J = \frac{\left\langle \psi_J | \hat{H}_{elec} | \psi_J \right\rangle}{\langle \psi_J | \psi_J \rangle} \tag{9.5.4}$$

This is the variational energy using $|\psi_J\rangle$ as the trail wavefunction. After substituting the LCAO expansion for $|\psi_J\rangle$ (Equation 9.5.1) into the energy expression of Equation 9.5.4 results in:

$$E_J = \frac{\left\langle \sum_i c^*_{J,i}\phi_i \middle| \hat{H}_{elec} \middle| \sum_j c_{J,i}\phi_j \right\rangle}{\left\langle \sum_i c^*_{J,i}\phi_j \middle| \sum_j c_{J,j}\phi_j \right\rangle} \tag{9.5.5}$$

$$= \frac{\sum_{i,j} c^*_{J,i} c_{J,j} \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle}{\sum_{i,j} c^*_{J,i} c_{J,j} \langle \phi_i | \phi_j \rangle} \tag{9.5.6}$$

$$= \frac{\sum_{i,j} c^*_{J,i} c_{J,j} H_{ij}}{\sum_{i,j} c^*_{J,i} c_{J,j} S_{ij}} \tag{9.5.7}$$

where H_{ij} is the Hamiltonian matrix element.

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

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

$$\frac{\partial E_J}{\partial c_k} = 0 \tag{9.5.8}$$

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

$$\sum_{i=1}^{N} c_i (H_{ki} - E S_{ki}) = 0 \tag{9.5.9}$$

These equations are the **secular equations** and were discussed previously in the context of the linear variational method approximation. For the two basis set expansion (N) in Figure 9.5.1 , these are

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{9.5.10}$$

where c_1 and c_2 are the coefficients in the linear combination of the atomic orbitals used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{9.5.11}$$

Solving these secular equations with N different atomic orbitals in the expansion (Equation 9.5.1) requires finding the N roots of an N order polynomial.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0 \tag{9.5.12}$$

Each molecular orbital ($|\psi_J\rangle$) from this treatment has an energy E_J that is given by a different set of coefficients, $\{c_{ij}\}$ where i runs over all N functions in the basis (i.e., number of the atomic orbitals in the LCAO approximation of Equation 9.5.1), and J runs over molecular orbitals. Solve the set of linear equations using that specific E_J to determine c_{ij} values.

Steps in a Solving the Secular Equations

1. Select a set of N basis functions
2. Determine all N(N –1)/2 values of both H_{ij} and S_{ij}
3. Form the secular determinant; determine N roots E_j of secular equation
4. For each E_J solve the set of linear equations to determine the basis set coefficients \(c_{ij\}) for the j-th molecular orbital

For more information on solving the Secular equations check here.

The greater the number of atomic orbitals N that combine to genera the molecular orbitals (Equation 9.5.1), the more accurate the LCAO approximation is. This is expected based on our discussions of the variational method examples. Hence, the ψ_+ and ψ_- molecular orbitals for H_2^+ are better expressed with higher energy hydrogenic wavefunctions

$$|\psi_J\rangle = c_{J,1}1s_A + c_{J,2}1s_B + c_{J,3}2s_A + c_{J,4}2s_B + c_{J,5}2p_{z,A} + c_{J,6}2p_{z,B} \tag{9.5.13}$$

The reasons that only the p_z atomic orbitals are included in this expansion are discussed later.

Contributors and Attributions

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

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

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$|\psi_i\rangle = \sum_j c_{ij}\varphi_j \tag{9.6.1}$$

where

- j is the index for the 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,

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1) \\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2) \end{vmatrix} \tag{9.6.2}$$

Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, ϵ. Following the Aufbau Principle, two electrons with different spins (α and β, consistent with the Pauli Exclusion Principle discussed for muliti-electron atoms) are assigned to each spatial molecular orbital in order of increasing energy. For the ground state of the 2n electron molecule, the n lowest energy spatial orbitals will be occupied, and the electron configuration will be given as $\psi_1^2\psi_2^2\psi_3^2 \ldots \psi_n^2$. The electron configuration also can be specified by an orbital energy level diagram as shown in Figure 9.6.1 . Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure 9.6.1 .

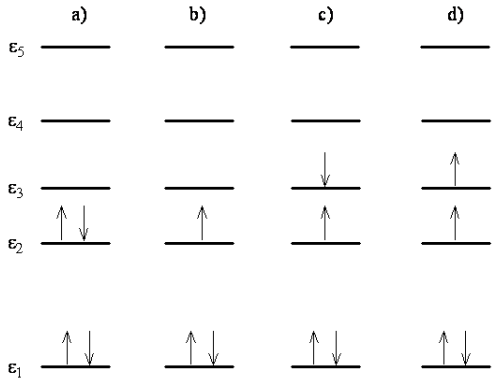


Figure 9.6.1 : a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

Symmetry

Molecular orbitals usually are identified by their symmetry or angular momentum properties. For example, a typical symbol used to represent an orbital in an electronic configuration of a diatomic molecule is $2\sigma_g^2$. The superscript in symbol means that this orbital is occupied by two electrons; the prefix means that it is the second sigma orbital with *gerade* symmetry.

Diatomic molecules retain a component of angular momentum along the internuclear axis. The molecular orbitals of diatomic molecule therefore can be identified in terms of this angular momentum. A Greek letter, e.g. σ or π, encodes this information, as well as information about the symmetry of the orbital. A σ means the component of angular momentum is 0, and there is no node in any plane containing the internuclear axis, so the orbital must be symmetric with respect to reflection in such a plane. A π means there is a node and the wavefunction is antisymmetric with respect to reflection in a plane containing the internuclear axis. For homonuclear diatomic molecules, a *g* or a *u* is added as a subscript to designate whether the orbital is symmetric or antisymmetric with respect to the center of inversion of the molecule.

A homonuclear diatomic molecule has a center of inversion in the middle of the bond. This center of inversion means that $\psi(x,y,z) = \pm\psi(-x,-y,-z)$ with the origin at the inversion center. Inversion takes you from (x,y,z) to $(-x,-y,-z)$. For a heteronuclear diatomic molecule, there is no center of inversion so the symbols g and u are not used. A prefix 1, 2, 3, etc. simply means the first, second, third, etc. orbital of that type. We can specify an electronic configuration of a diatomic molecule by these symbols by using a superscript to denote the number of electrons in that orbital, e.g. the lowest energy configuration of N_2 is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \tag{9.6.3}$$

Contrasting LCAO with other Quantum Chemistry Methods

As we have already seen, the LCAO approach is very approximate, yielding only qualitative results. It should be noted that the Hartree-Fock method discussed earlier for atoms can also be used for molecules. For example, the molecule He_2^+ has three electrons, and the Li atom also has three electrons. As usual with Hartree-Fock, the idea is to optimize the shapes of the single-electron orbitals $\psi_1(r)$, $\psi_2(r)$ and $\psi_3(r)$ by minimizing the guess to the ground state energy E_g. Of course, we will not get the same answer as for Li because there is a different V_{en} energy for He_2^+ due to the presence of two positively charge nuclei $(charge = +2e)$ separated by a distance R in contrast to the single $+3e$ charged nucleus for Li. When the shapes of the orbitals are optimized, we also obtain three energy ε_1, ε_2 and ε_3. Not unexpectedly, we find that two of the HF orbitals resemble $1\sigma_g$ while the third resembles $1\sigma_u^*$ and the first two energies ε_1 and ε_2 will be nearly equal, while the third ε_3 will be noticeably higher. To contrast with the LCAO approach, in LCAO, we do not optimize the shapes of the orbitals (these are assumed *a priori* to be $1s$ shaped). All we do is choose the mixing coefficients so as to minimize the guess to the ground-state energy E_g.

We note, finally, that the density functional theory alluded to earlier can also be used for molecules. It is often the case that density functional theory yields a more accurate description than Hartree-Fock, but this depends on the molecule. In any case, both are more accurate than LCAO. There is also a hierarchy of methods called *post Hartree-Fock* methods, all of which are based on the wavefunction rather than the electron density, that can be used to improve upon the HF approximation systematically. The greater the accuracy that is desired for the calculation, the more costly computationally the post HF methods become, so quantum chemistry is often a trade-off between accuracy and efficiency, an issue that becomes more critical to take into account when calculations on large molecules must be carried out!

Contributors and Attributions

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

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9.7: Molecular Orbitals Can Be Ordered According to Their Energies

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they are often ignored in constructing molecular orbitals. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

Molecular Orbitals Formed from *ns* Orbitals

The molecular orbitals diagrams formatted for the dihydrogen species are similar to the diagrams to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 9.7.1 , where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

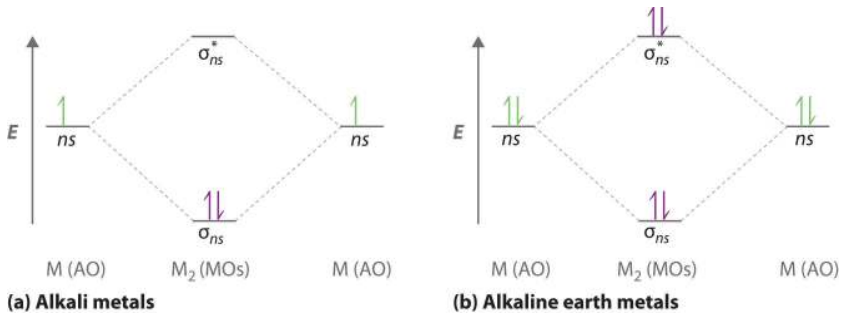


Figure 9.7.1 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ^*_{ns} (nonbonding) levels, leading to a predicted bond order of 0. (CC BY-SA-NC; anonymous).

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule. As shown in Figure 9.7.1*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

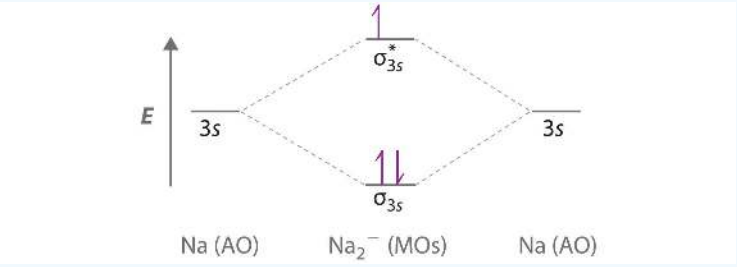
Strategy

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 $(\sigma_{3s})^2(\sigma^\star_{3s})^1$ 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 $(\sigma_{4s})^2(\sigma^\star_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from n*p* Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{9.7.1}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 9.7.2 , it is the mathematical *difference* of their wavefunctions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{9.7.2}$$

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

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{9.7.3}$$

In this combination, shown in part (b) in Figure 9.7.2 , the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

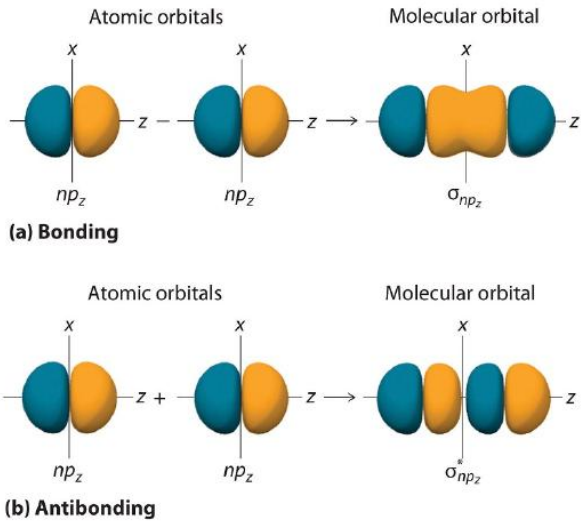


Figure 9.7.2 : Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 9.7.3 , we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{9.7.4}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{9.7.5}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

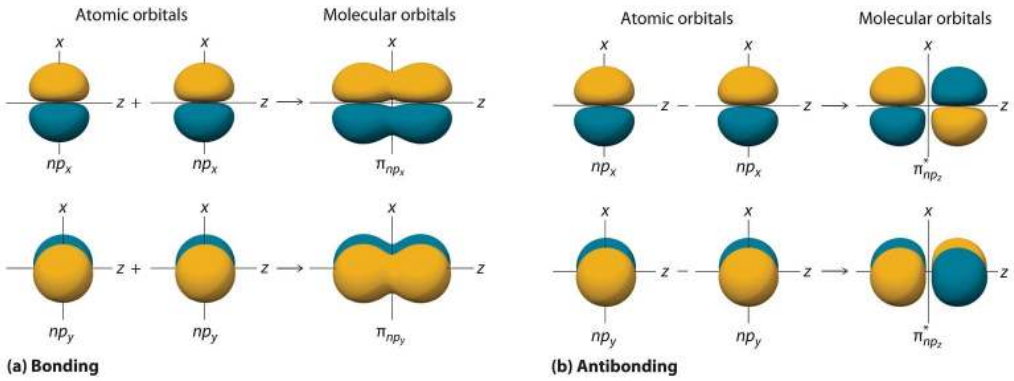


Figure 9.7.3 : Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

Energies for Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Figure 9.7.4 is an energy-level diagram that can be applied to two *identical* interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

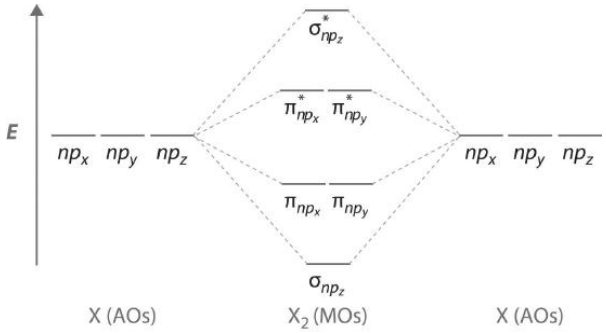


Figure 9.7.4 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals. (CC BY-SA-NC; anonymous).

> *The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.*

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in Figure 9.7.5*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 $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rules. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons.

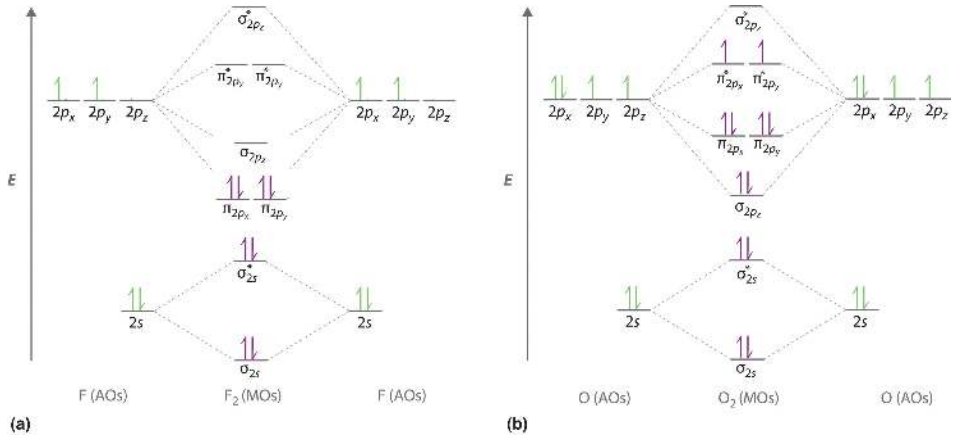


Figure 9.7.5 : Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^{\star}_{np_x},\ \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; anonymous).

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the $2p_z$ orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 9.7.6 . Experimentally, the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 9.7.6). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

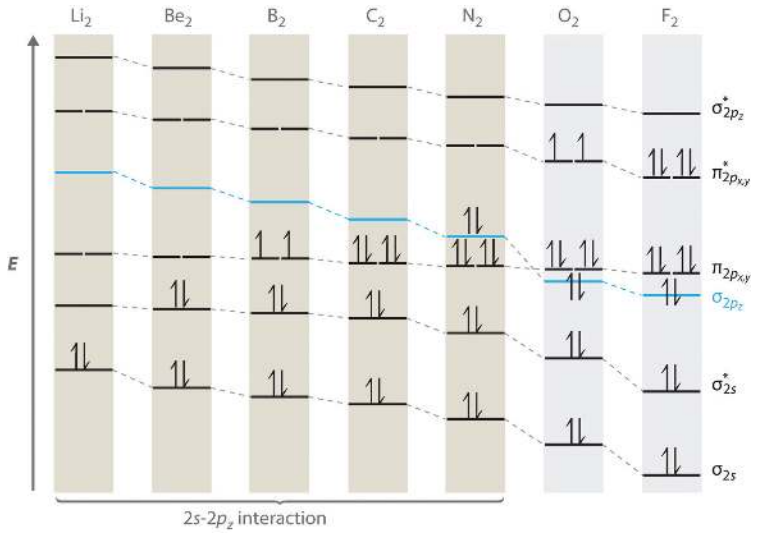


Figure 9.7.6 : Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2s and 2*p* atomic orbitals as the nuclear charge increases across the row. (CC BY-SA-NC; anonymous).

Example 9.7.2 : Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

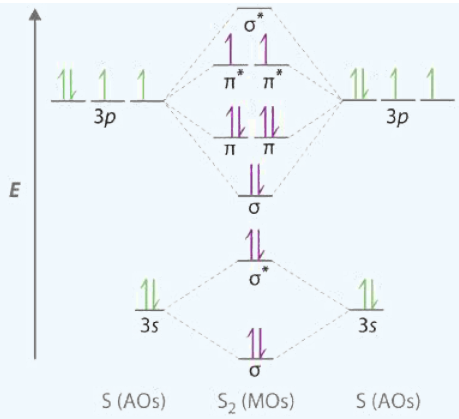
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ 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 $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases, the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



(CC BY-SA-NC; anonymous).

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ and $\pi^{\star}_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^{\star}_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 9.7.2

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^{\star}_{2s})^2(\sigma_{2p_z})^2\left(\pi_{2p_{x,y}}\right)^4(\pi_{2p^{\star}_{x,y}})^4$ bond order of 1; no unpaired electrons

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.

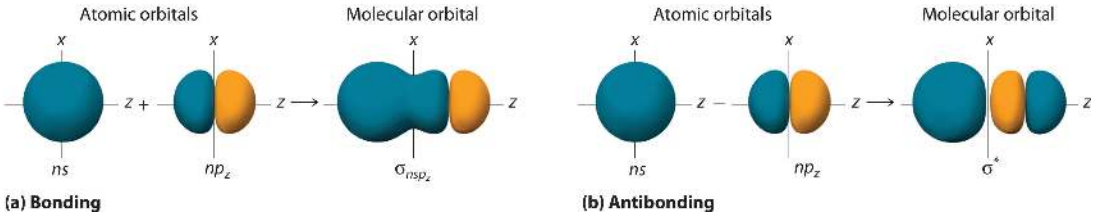


Figure 9.7.7 : Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a 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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9.8: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 9.8.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

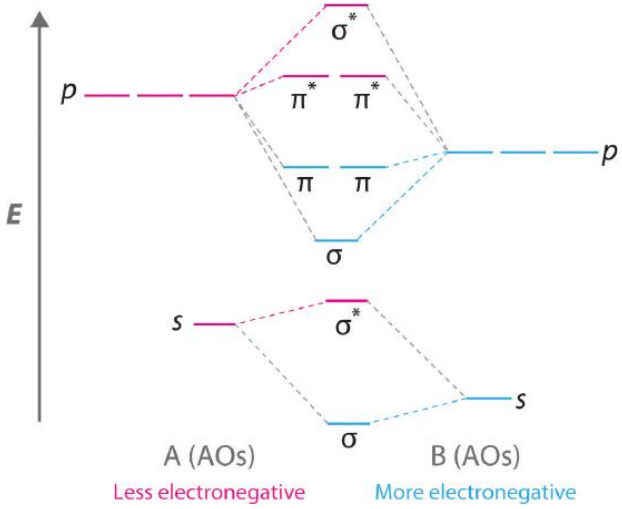


Figure 9.8.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 9.8.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 9.8.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

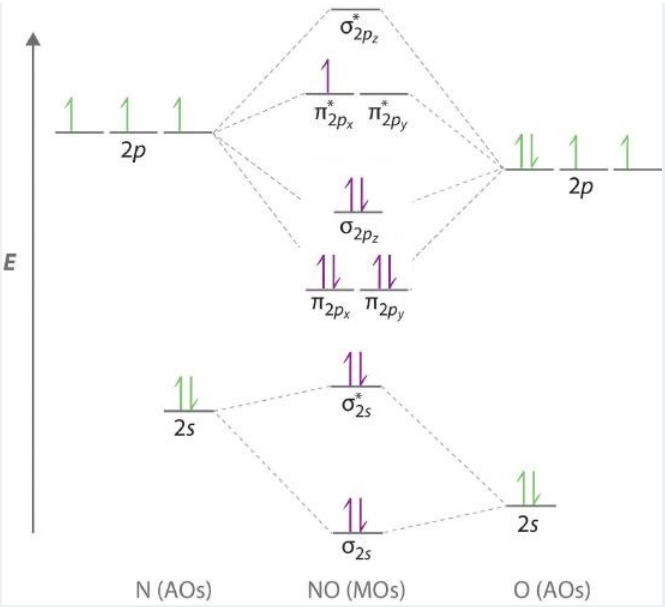


Figure 9.8.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_x},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\left(\sigma^{\star}_{2s}\right)^2\left(\pi_{2p_{x,y}}\right)^4\left(\sigma_{2p_z}\right)^2\left(\pi_{2p^{\star}_{x,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 9.8.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 9.8.13, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^{+} cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 9.8.6 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}--Cl^{\delta-}$.

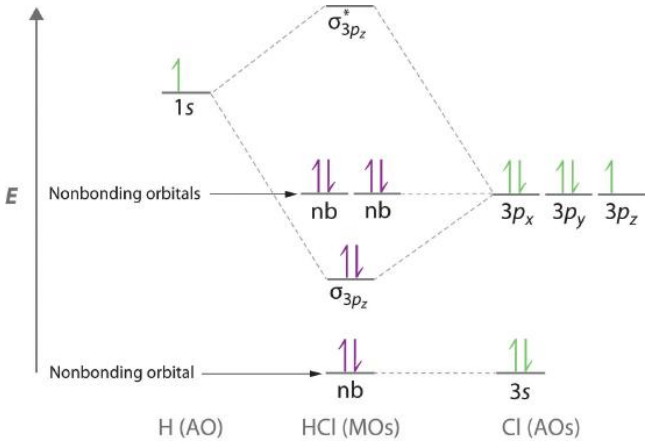


Figure 9.8.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the 3p_z orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have no effect on bond order.*

Example 9.8.4: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 9.8.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

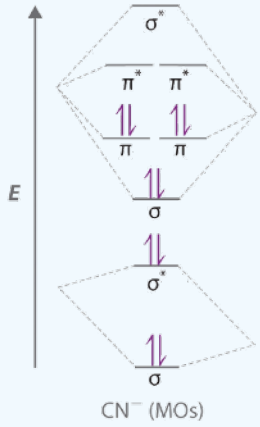
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 9.8.4 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 9.8.4 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise 9.8.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.



Summary

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

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9.9: Molecular Term Symbols Describe Electronic States of Molecules

Molecular term symbols specify molecular electronic energy levels. Term symbols for diatomic molecules are based on irreducible representations in linear symmetry groups, derived from spectroscopic notations. They usually consist of four parts: spin multiplicity, azimuthal angular momentum, total angular momentum and symmetry. All molecular term symbols discussed here are based on Russel-Saunders coupling.

Introduction

Molecular term symbols mark different electronic energy levels of a diatomic molecule. These symbols are similar to atomic term symbols, since both follow the Russell-Saunders coupling scheme. Molecular term symbols employ symmetry labels from group theory. The possibility of an electronic transition can be deducted from molecular term symbols following selection rules. For multi-atomic molecules, symmetry labels play most of term symbols' roles.

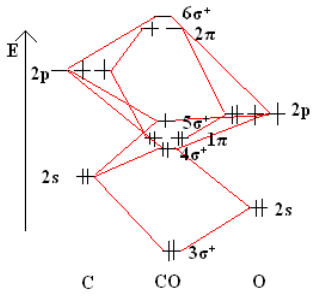
For homonuclear diatomics, the term symbol has the following form:

$$^{2S+1}\Lambda_{\Omega,(g/u)}^{(+/-)} \tag{9.9.1}$$

whereas Λ is the projection of the orbital angular momentum along the internuclear axis: Ω is the projection of the total angular momentum along the internuclear axis; *g*/*u* is the parity; and +/− is the reflection symmetry along an arbitrary plane containing the internuclear axis. Λ may be one of the greek letters in the sequence: Σ Π Δ Φ... when Λ = 0, 1, 2, 3..., respectively. For heteronuclear diatomics, the term symbol does not include the *g*/*u* part, for there is not inversion center in the molecule.

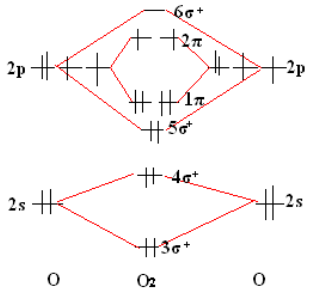
Determining term symbols of diatomics

Let's start with CO again. As we have seen before, the molecule has a close-shell configuration. Its ground state is a totally symmetric singlet, $^1\Sigma^+$, since the only possible values of (*S*, Λ) are (0, 0). If one of the HOMO electrons on the $5\sigma^+$ orbital has jumped to the LUMO, this molecule will be in an excited state as follows.



Suppose a CO molecule is in the excited state shown above. In order to know the term symbol of this state, a direct product of the labels is required for the two MO's with unpaired electrons. The multiplication is such as $\Pi \times \Sigma^+ = \Pi$. According to Pauli's exclusion rule, these two unpaired electrons can never share the same set of quantum numbers, therefore the spin degeneracy *S* can reach its maximum 3. The resulting term symbols are $^1\Pi$ and $^3\Pi$.

Now if we look at O_2, it does not have a close-shell configuration at its ground state. There are two unpaired electrons each occupying one of the two degenerate 2π orbitals, which can be seen in the diagram below.



The term symbol for oxygen molecule at its ground state is therefore derived such as Π x Π = Σ^+ + Σ^- + [Δ], as the symbol in brackets does not allow the oxygen atoms to commute.

Transition between electronic states of diatomics

We'll focus on selection rules. Like atomic electronic states, different selection rules apply when differently incurred transitions occur. Usually for electric dipole field induced transitions, the selection rules are the same as for atoms.

1. $\Delta\Lambda = 0, \pm1$ except $\Lambda = 0 \ddagger \Lambda' = 0$
2. $\Delta S = 0$
3. $\Delta\Omega = 0; \pm1$ except $\Omega = 0 \ddagger \Omega' = 0$

References

1. Harris, Daniel C. (republished in 1989). *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy.* Dover Publications. pp. 421-478. ISBN 0-486-66144-X
2. D. J. Willock (2009). *Molecular Symmetry*. John Wiley & Sons Ltd. ISBN 0-470-85348-4

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9.10: Molecular Term Symbols Designate Symmetry

The quantum numbers for diatomic molecules are similar from the atomic quantum numbers. Be cautious, because the rules for finding the possible combinations are different. The total orbital angular momentum quantum number For the molecular case, this number is called Λ instead of L. It follows the same naming convention as L, except that instead of using capital English letters, it uses capital Greek letters:

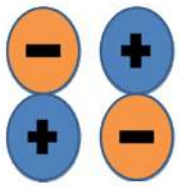
- $\Lambda = 0 \rightarrow \Sigma$
- $\Lambda = 1 \rightarrow \Pi$
- $\Lambda = 2 \rightarrow \Delta$
- $\Lambda = 3 \rightarrow \Phi$

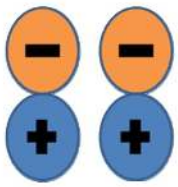
Unlike L, there is not a general formula for finding the possible combinations of Λ. You have to examine the individual microstates. This is easier than it sounds.

- **The total magnetic quantum number** M_L: M_L works like M_l with atoms, except that there is no formula for finding the combinations.
- **The total spin magnetic quantum number** M_S: M_S works exactly like M_s. Electrons can either point with or against the z - axis, and being in a molecular orbital versus an atomic orbital doesn't change this. M_S can range from $m_{s1} + m_{s2}$ to $m_{s1} - m_{s2}$.

Two New Symmetries: Parity and Reflection

Molecular orbitals are more complex than atomic ones and require more modifiers to completely define. **Parity** (sometimes called "inversion") tells you if the orbital is *symmetric* or *anti-symmetric* when an inversion operation is performed. The symmetry notation **u** and **g** are sometimes used when describing molecular orbitals. This refers to the operation of inversion, which requires starting at an arbitrary point in the orbital, traveling straight through the center, and then continuing outwards an equal distance from the center. The orbital is designated **g** (for gerade, even) if the phase is the same, and **u** (for ungerade, uneven) if the phase changes sign.


This pi orbital is gerade


This pi orbital is ungerade

To determine whether or not a given state is g or u, find the parity of each individual open-shell electron and uses these simple (Laporte rules):

- $g + g \rightarrow g$
- $g + u \rightarrow u$
- $u + u \rightarrow g$

Example 9.15.1: Closed Shell Configuration

What is the parity of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

Since both open shell electrons are ungerade, the overall parity is g. Helpful hint: bonding sigma orbitals and anti - bonding pi orbitals are always gerade. Anti - bonding sigmas and bonding pis are always ungerade. Draw them and see for yourself.

Reflection determines if a given orbital is symmetric or anti-symmetric upon reflection through a plane that contains both nuclei. The choice of symmetry planes is arbitrary. As long as you pick a plane and stick with it, you will always get the right answer. When an orbital is symmetric, it is labeled +. When an orbital is anti - symmetric, it is labeled - . To find the overall reflection of a state, use these rules:

- (+)(+) \rightarrow +

- (+)(-) \rightarrow -
- (-)(-) \rightarrow +

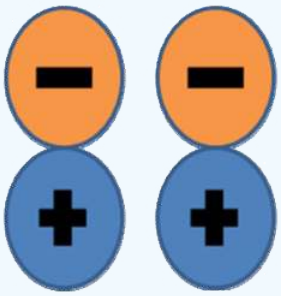
Reflection only applies to Σ states! For $\Lambda > 0$, there are no reflection labels! If you experiment with the rules, you will quickly realize why this is the case.

Example 9.15.2

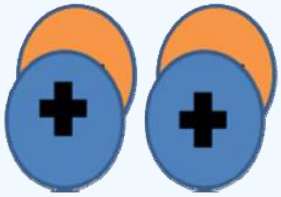
What is the reflection of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

You need to know what the orbitals look like. Draw a picture and then pick a plane. For this example, the plane of the page is selcted, but the orthogonal plane would have worked just as well.



The “vertical” orbital is +



The “horizontal” orbital is -

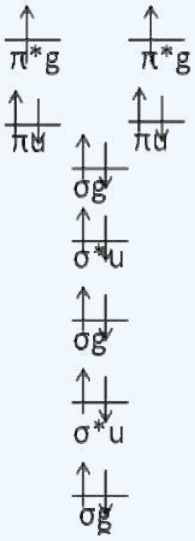
The “vertical” orbital is + The “horizontal” orbital is - Since one is + and one is - , the overall reflection is - . Try using the orthogonal plane and convince yourself that you still get the same answer.

Example 9.15.3: Oxygen

What are the term symbols for O_2 ?

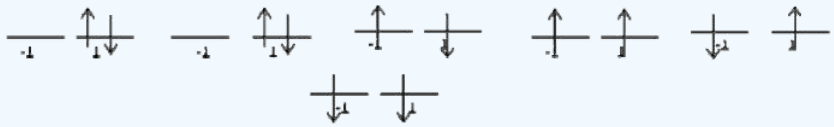
Solution

The molecular orbital diagram for O_2 is



Where I chose arbitrary configurations for the last two electrons.

There are two open - shell electrons occupying the anti-bonding π_g orbitals. These are the only electrons that matter. It is easiest to simply draw all of the permutations and figure out the bounds on Λ and M_L by inspection. If we do this, it is easy to see that $\Lambda = 2, 0$ and that $M_L = 2, 0, -2$



$M_s = -1$	$M_s = 0$	$M_s = 2$
0	**1**	0
1	2	1
0	1	0

The top row is a $\Lambda = 2$ $M_S = 0$ state, so it is $^1\Delta$. Both electrons are in the rightmost orbital. This orbital is gerade, and (g)(g) = g, so the parity label is g. We do not assign reflection labels to non Σ states, so the term symbol is $^1\Delta_g$. After removing the used up microstates, the chart becomes

$M_s = -1$	$M_s = 0$	$M_s = 2$
1	**1**	0

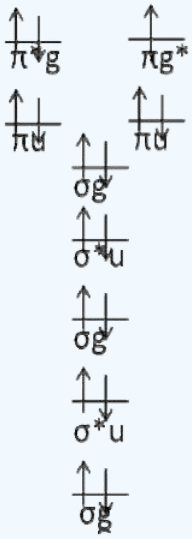
This is a Λ =0 state with three possible spin configurations, so it is $^3\Sigma$. We know that the electrons are in different sub-orbitals (if you cannot see this, try drawing all of the possible combinations that give $\Lambda = 0$). Both of the orbitals are gerade, so the overall parity is gerade. One of the orbitals will be +, the other will be - . The final answer is $^1\Delta_g \backslash (^3\Sigma_g^+$

Exercise 9.15.1

Write the term symbols for O_2^-

Solution

First draw the electron configuration diagram.



There are only two possible configurations. It should be easy to see that the term symbol is $^2\Pi_g$.

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CHAPTER OVERVIEW

10: Polyatomic Molecules

10.1: Hybrid Orbitals Account for Molecular Shape
10.2: Hybrid Orbitals in Water
10.3: BeH_2 is Linear and H_2O is Bent
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10.1: Hybrid Orbitals Account for Molecular Shape

Learning Objectives

- Introduce hybrid orbital to explain non-linear molecular structure

Valence bond (VB) theory is one of two basic theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

Review of Diatomics

Let us consider H_2. Recall that the Lewis structure for a single H atom is $H\cdot$ and for H_2, it is $H:H$. Thus, each hydrogen brings one unpaired electron to the bond. Let the two protons be denoted A and B and the two electrons 1 and 2. Now, consider the potential energy

$$V = V_{ee} + V_{en} + V_{nn} \tag{10.1.1}$$

$$= \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}}\right] \tag{10.1.2}$$

But as $R_{AB} \to \infty$, the $1/r_{12}$, $1/r_{1B}$, $1/r_{2A}$, and $1/R_{AB}$ terms vanish and the potential energy becomes simply that of two noninteracting hydrogen atoms

$$V \to -\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{1A}} + \frac{1}{r_{2B}}\right]$$

Since the potential energy becomes a simple sum of separate energies for electrons 1 and 2, the wavefunction should simply be a product $\psi_{1s}(r_1 - r_A)\psi_{1s}(r_2 - r_B)$. But as we let $R_{AB} \to R_e$, where R_e is the equilibrium bond length, the electrons mix, and we can no longer tell if electron 1 belongs to atom A or atom B and the same for electron 2. Thus, we need to construct a combination of products that is consistent with the Pauli exclusion principle. If we just consider the coordinates r_1 and r_2 of the electrons, then the only wavefunction we can construct from a product of 1s orbitals is

$$\psi_u(r_1, r_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

where the u designator indicates that this is an odd function. The constant C_u is the overall noramlization constant. Unfortunately, like in the LCAO method, such a wavefunction is antibonding and is not a good representation of the ground state. If, however, we construct the wavefunction

$$\psi_g(r_1, r_2) = C_g[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

(where g designates that this is an even function), we violate the Pauli exclusion principle, even though such a wavefunction leads to a stable chemical bond.

What is missing here is the fact that we have not considered the spins of the electrons. Since the electrons are identical, if we exchange coordinates *and* spins, then the wavefunction should change sign. Thus, we can make both wavefunctions above consistent with the Pauli exclusion principle by multiplying by an appropriate spin wavefunction. We obtain

$$\psi_u(r_1, r_2, s_1, s_2) = \psi_u(x_1, x_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.3}$$

$$\psi_g(r_1, r_2, s_1, s_2) = \psi_g(x_1, x_2) = C_g[\psi^A_{1s}(r_1)\psi_{1s}B(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.4}$$

where s_1 and s_2 are the z-components of spin for electrons 1 and 2, respectively. We can now use ψ_g as an approximate 2-electron wavefunction that leads to a stable chemical bond in H_2.

The fact that ψ_u is antibonding can be easily determined by looking for a nodal plane between the two atoms, in this case, in the plane that exactly bisects the line joining the two atoms, midway between them. That this is, indeed, a nodal plane can be seen by considering two points r_1 and r_2 for the two electrons that are taken to lie in this plane. By symmetry, the functions $\psi^A_{1s}(r_1)$ and $\psi^B_{1s}(r_1)$ have the same value for r_1 in this plane, and the same for $\psi^B_{1s}(r_2)$ and $\psi^A_{1s}(r_2)$. Let us assign the following values:

$$\psi_{1s}^{A}(r_1) = \psi_{1s}^{B}(r_1) = A \tag{10.1.5}$$

$$\psi_{1s}^{B}(r_2) = \psi_{1s}^{A}(r_2) = A' \tag{10.1.6}$$

Substituting these into $\psi_u(x_1, x_2)$, we obtain

$$\psi_u(x_1, x_2) = C_u[AA' - A'A][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] = 0$$

Since the wavefunction has a node midway between the two atoms, it is clearly antibonding and should have a *higher energy* than the corresponding bonding wavefunction ψ_g.

A similar argument can be used for the molecule F_2. Each F has an electronic configuration

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

and the Lewis structure of F_2 is



Figure 10.1.1 : Lewis structure of F_2.

Most of the electrons are in lone pairs, but the $2p_z$ electrons, which are unpaired in each F come together to form the bond. Thus, the bonding wavefunction should be a 2-electron wavefunction constructed from $2p_z$ orbitals. The bonding wavefunction takes the "gerade" form as in H_2:

$$\psi_g(r_1, r_2, s_1, s_2) = C_g[\psi_{2p_z}^{A}(r_1)\psi_{2p_z}^{B}(r_2) + \psi_{2p_z}^{A}(r_2)\psi_{2p_z}^{B}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]$$

For HF, the $2p_z$ orbital on F and $1s$ orbital on H come together to form the bonding wavefunction. To be consistent with the Pauli principle, we need a wavefunction of the form

$$\psi(r_1, r_2, s_1, s_2) = [\psi_{1s}^{H}(1)\psi_{2p_z}^{F}(2) + \psi_{1s}^{H}(2)\psi_{2p_z}^{F}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]) \tag{10.1.7}$$

Looking at the HF example, it becomes clear how much valence bond theory attempts to appear as a "quantum version" of the Lewis dot structure model. Valence bond theory attempts to construct very approximate wavefunctions for the bonding electrons in a Lewis structure, leaving the orbitals unused in the construction of the valence bond wavefunctions for the lone pair electrons. In the case of HF, we use the $2p_z$ orbitals of F, which leaves the $2s$, $2p_x$ and $2p_y$ orbitals unused. Since there are three lone pairs, these three orbitals are sufficient to hold each of the lone pairs as spin-up/spin-down couples.

Hybridization

For polyatomic molecules, the valence bond theory becomes a very poor approximation because the directionalities of the $2s$ and $2p$ orbitals is too restrictive to describe molecules with steric numbers ranging between 2 and 4. The example considered above of H_2O illustrates this rather dramatically! Let us consider an even simpler molecule, BeH_2, which has a steric number of 2 and is linear. Let the atoms lie entirely along the z-axis in the arrangement $H - Be - H$.

Although Be has a ground-state electronic configuration of $1s^2 2s^2$, but if we "promote" one of the $2s$ electrons to a state with higher energy and allow its electronic structure to be $1s^2 2s 2p_z$, then the unpaired electrons in the $2s$ and $2p_z$ orbitals can combine with the unpaired electrons in each of the hydrogen atoms to form bonds. The energy needed to excite the electron in Be would be ``repaid" by the energy gained in the formation of stable bonds. The two valence-bond wavefunctions we would construct would be

$$\psi_1(1,2) = C_1\left[\psi_{1s}^{H_1}(1)\psi_{2s}^{Be}(2) + \psi_{1s}^{H_1}(2)\psi_{2s}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.8}$$

$$\psi_2(1,2) = C_2\left[\psi_{1s}^{H_2}(1)\psi_{2p_z}^{Be}(2) + \psi_{1s}^{H_2}(2)\psi_{2p_z}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.9}$$

Unfortunately, even this simple scheme does not work entirely because the two $Be - H$ bonds would be different due to their construction from different combinations of orbitals. By symmetry, however, we can see that the two BeH bonds should be equivalent. A solution to this problem was proposed by Linus Pauling in the 30s in the form of *orbital hybridization*, a scheme that we still use today.

Pauling used the fact that in the first and second periods, the $2s$ and $2p$ orbitals have similar energies. Indeed, for H, the energies are exactly the same. Given that these energies are not that different, we can combine s and p orbitals and still have a valid solution

of the Schrödinger equation. That is, a general orbital

$$\chi(r) = C_1\psi_{2s}(r) + C_2\psi_{2p_x}(r) + C_3\psi_{2p_y}(r) + C_4\psi_{2p_z}(r)$$

is also a solution of the Schrödinger equation with the same energy as a $2s$ or $2p$ orbitals individually (this is exactly true for H). In the case of BeH_2, the external potential on the electrons in Be by the two hydrogens changes the energy levels and creates a near degeneracy between the $2s$ and $2p_z$ orbitals, hence, we are now free to combine the into linear combinations that are more suitable to the construction both of valence bond wavefunctions *and* MOs via the LCAO procedure.

sp Hybrid Orbitals

For Be, we now allow the s and p orbitals to mix and create two *hybrid* orbitals known as *sp* orbitals. The two new hybrid wavefunctions as linear combination of the functions for 2s and $2p_z$ (using Dirac Notation):

$$|\chi_i\rangle = a_1|2s\rangle + b_1|2p_z\rangle \tag{10.1.10}$$

$$|\chi_j\rangle = a_2|2s\rangle + b_2|2p_z\rangle \tag{10.1.11}$$

These two wavefunctions must be orthogonal.

$$\langle\chi_i|\chi_j\rangle = \delta_{ij}$$

Which can be separated into the following relationships:

$$\langle\chi_i|\chi_i\rangle = 1 \tag{10.1.12}$$

and

$$\langle\chi_j|\chi_j\rangle = 1 \tag{10.1.13}$$

and

$$\langle\chi_i|\chi_j\rangle = \langle\chi_j|\chi_i\rangle = 0 \tag{10.1.14}$$

Equations 10.1.12 and 10.1.13 are the normality requirement and Equation 10.1.14 is the orthogonality requirement for the new hybrid wavefunctions. Substituting 10.1.10 into 10.1.12 results in

$$\langle\chi_i|\chi_i\rangle = a_1^2\ \cancel{\langle 2s|2s\rangle}^{\,1} + a_1b_1\ \cancel{\langle 2s|2p_z\rangle}^{\,0} + a_1b_1\ \cancel{\langle 2p_z|2s\rangle}^{\,0} + b_1^2\ \cancel{\langle 2p_z|2p_z\rangle}^{\,1} = 1$$

and similarly for $\langle\chi_j|\chi_j\rangle$

$$\langle\chi_j|\chi_j\rangle = a_2^2\ \cancel{\langle 2s|2s\rangle}^{\,1} + a_2b_2\ \cancel{\langle 2s|2p_z\rangle}^{\,0} + a_2b_2\ \cancel{\langle 2p_z|2s\rangle}^{\,0} + b_2^2\ \cancel{\langle 2p_z|2p_z\rangle}^{\,1} = 1$$

results in the following relationships

$$\langle\chi_i|\chi_i\rangle = a_1^2 + b_1^2 = 1 \tag{10.1.15}$$

$$\langle\chi_j|\chi_j\rangle = a_2^2 + b_2^2 = 1 \tag{10.1.16}$$

and

$$\langle\chi_i|\chi_j\rangle = a_1a_2 + b_1b_2 = 0 \tag{10.1.17}$$

These are four unknowns and three equations. The fourth "constraint" is that we assume contribution of $|s\rangle$ is the same for both hybrid orbitals.

$$a_1 = a_2$$

Equations 10.1.15 to 10.1.17 revert to

$$a_1^2 + b_1^2 = 1 \tag{10.1.18}$$

$$a_1^2 + b_2^2 = 1 \tag{10.1.19}$$

$$b_1^2 = b_2^2 \tag{10.1.20}$$

Therefore

$$b_1 = -b_2$$

and

$$a_1 = b_1 \tag{10.1.21}$$

Insert Equation 10.1.21into 10.1.20to get

$$a_1 = \frac{1}{\sqrt{2}}$$

and the two hybrid orbitals are

$$\chi_1(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \tag{10.1.22}$$

$$\chi_2(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)] \tag{10.1.23}$$

Note that these orbitals are both normalized and orthogonal:

$$\int |\chi_1(r)|^2 dV = 1\ ;\ \int |\chi_2(r)|^2 dV = 1\ ;\ \int \chi_1^*(r)\chi_2(r) dV = 0$$

These orbitals appear as shown in Figure 10.1.3

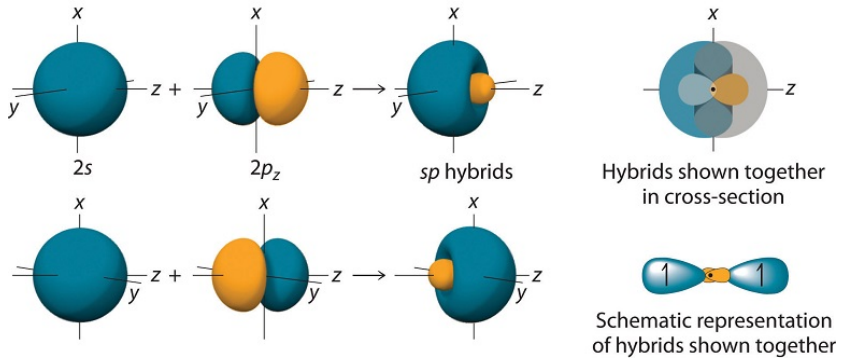


Figure 10.1.3 : The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

Given that the two *sp* hybrid orbitals are mirror images of each other, they can overlap with the $1s$ orbital of H (shown in the figure) and create two equal bonds, as needed for BeH_2. Using the valence bond formulation, now, one of the BeH bonds will be described by a wavefunction of the form:

$$\psi_1(1,2) = C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.24}$$

$$\psi_2(1,2) = C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.25}$$

In the above wavefunctions, it is clear that H_1 is on the right and H_2 is on the left, based on the directionalities of χ_1 and χ_2.

sp^2 Hybrid Orbitals

For trigonal planar molecules such as BH_3, we start with the electronic configuration of B, which is $1s^2 2s^2 2p_x$, and we promote one of the $2s$ electrons to a $2p_y$ orbital, so that we have $1s^2 2s 2p_x 2p_y$. Suppose the geometry of BH_3 is such that one of the hydrogens lies along the positive x axis. The remaining hydrogens would be in the 3rd and 4th quadrants, respectively, as shown in Figure 10.1.4 .

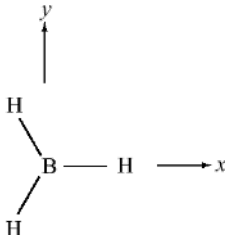


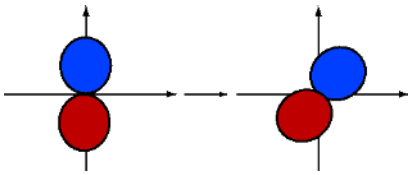
Figure 10.1.4 : Geometry of BH_3.

If we simply combine the $2s$ with the $2p_x$ and $2p_y$ orbitals of boron, the resulting hybrid orbitals will not point in the correct direction. For this reason, we will create rotated versions of the p_x and p_y orbitals, which, as we will see are tantamount to taking new combinations of $2p_x$ and $2p_y$ orbitals to combine with the $2s$. Since the rotation occurs in the xy plane, the coordinate that controls this is the azimuthal angle ϕ. For the p_x and p_y orbitals, the ϕ dependence is

$$\psi_{2p_x} \sim \cos\phi \; ; \; \psi_{2p_y} \sim \sin\phi$$

If we rotate $2p_y$ by -30 degrees (Figure 10.1.5 ; blue is positive and red is negative), the ϕ dependence becomes

$$\psi_{2p_y}^{(rot)} \sim \sin(\phi + 30)$$


Figure 10.1.5 : Rotation of a $2p_y$ orbital by -30 degrees.

Using the fact that

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm cos\alpha sin\beta$$

this rotation gives

$$\psi_{2p_y}^{(rot,1)} \sim \sin\phi\cos 30 + \cos\phi\sin 30 \tag{10.1.26}$$

$$\sim \left[\frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi\right] \tag{10.1.27}$$

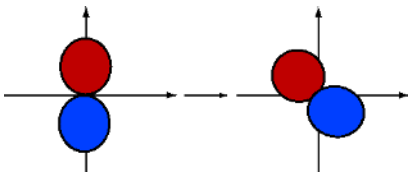
$$\sim \left[\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x}\right] \tag{10.1.28}$$

Similarly, consider rotating $-\psi_{2p_y}$ by $+30$ degrees (Figure 10.1.6). This gives

$$-\psi_{2p_y}^{(rot,2)} \sim -\sin(\phi - 30) \tag{10.1.29}$$

$$\sim -\left[\frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi\right] \tag{10.1.30}$$

$$\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x} \tag{10.1.31}$$


Figure 10.1.6 : Rotation of a $-2p_y$ orbital by 30 degrees.

So, we now take the hybrid orbitals to be of the form

$$\chi_1(r) = a\psi_{2s}(r) - b\psi_{2p_x} \tag{10.1.32}$$

$$\chi_2(r) = c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \tag{10.1.33}$$

$$\chi_3(r) = c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r) \tag{10.1.34}$$

The coefficients a, b, and c are determined by requiring that the orbitals are normalized and mutually orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_2(r)dV = 0 \tag{10.1.35}$$

$$\int |\chi_2(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_3(r)dV = 0 \tag{10.1.36}$$

$$\int |\chi_3(r)|^2 dV = 1 \; ; \; \int \chi_2^*(r)\chi_3(r)dV = 0 \tag{10.1.37}$$

Carrying out the algebra, we obtain the following sp^2 hybrid orbitals:

$$\chi_1(r) = \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \tag{10.1.38}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.39}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.40}$$

The sp^2 hybrids allow bonding at 120° degrees, and these orbitals appear as shown in Figure 10.1.7 :

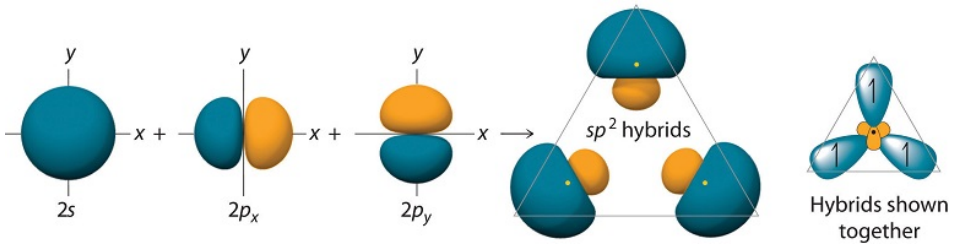


Figure 10.1.7 : Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

The figure also shows the overlaps of these orbitals with the $1s$ orbitals of H.

sp^3 Hybrid Orbitals

Finally, we consider the case of methane CH_4. The electronic configuration of C is $1s^2 2s^2 2p_x 2p_y$. We now promote one of the $2s$ orbitals to the $2p_z$ orbital and write C as $1s^2 2s 2p_x 2p_y 2p_z$. We can now hybridize the $2s$ orbital with each of the $2p$ orbitals to create four hybrids:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.41}$$

$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.42}$$

$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.43}$$

$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.44}$$

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 10.1.8). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

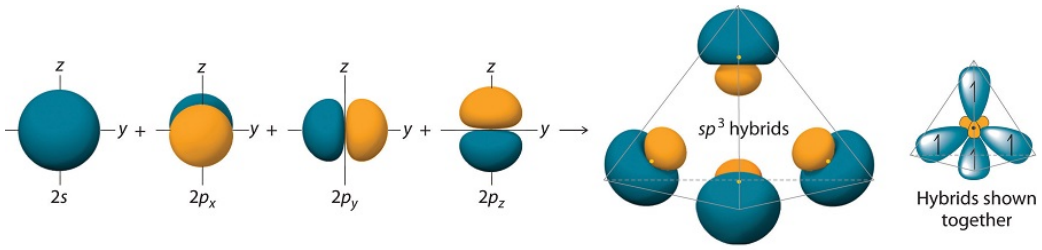


Figure 10.1.8 : Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Are hybrid orbitals Real?

Hybridization is an often misconceived concept. It only is a mathematical interpretation, which explains a certain bonding situation (in an intuitive fashion). In a molecule the equilibrium geometry will result from various factors, such as steric and electronic interactions, and further more interactions with the surroundings like a solvent or external field. The geometric arrangement will not be formed because a molecule is hybridized in a certain way, it is the other way around, i.e. a result of the geometry or more precise and interpretation of the wavefunction for the given molecular arrangement.

The justification we gave for invoking hybridization in molecules such as BeH_2, BF_3 and CH_4 was that the bonds in each are geometrically and chemically equivalent, whereas the atomic *s*- and *p*-orbitals on the central atoms are not. By combining these into new orbitals of *sp*, sp^2 and sp^3 types we obtain the required number of completely equivalent orbitals. This seemed easy enough to do on paper; we just drew little boxes and wrote "sp^2" or whatever below them. But what is really going on here?

The full answer is beyond the scope of this course, so we can only offer the following very general explanation. First, recall what we mean by "orbital": a mathematical function ψ having the character of a standing wave whose square ψ^2 is proportional to the probability of finding the electron at any particular location in space. The latter, the *electron density distribution*, can be observed (by X-ray scattering, for example), and in this sense is the only thing that is "real".

A given standing wave (ψ-function) can be synthesized by combining all kinds of fundamental wave patterns (that is, atomic orbitals) in much the same way that a color we observe can be reproduced by combining different sets of primary colors in various proportions. In neither case does it follow that these original orbitals (or colors) are actually present in the final product. So one could well argue that hybrid orbitals are not "real"; they simply turn out to be convenient for understanding the bonding of simple molecules at the elementary level, and this is why we use them.

Summary

The shape and bonding valecies of polyatomic molecules can be accounted for by hybrid orbitals. Molecular orbitals are formed from linear combinations of atomic orbitals which are similar in energy. These atomic orbitals could come from different atoms, or from the same atom. For example, the 2 sand 2patomic orbitals are very close energetically. When a linear combo of more than one atomic orbital from the **same atom** is formed, we have a hybrid orbital.

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10.2: Hybrid Orbitals in Water

The goal of applying Valence Bond Theory to water is to describe the bonding in H_2O and account for its structure (i.e., appropriate bond angle and two lone pairs predicted from VSEPR theory).

The ground state electronic configuration of atomic oxygen atom is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ and of course the ground state electronic configuration of atomic hydrogen atom is $1s^1$, i.e., a spherical atomic orbital with no preferential orientation. If only the unfilled $2p_y$ and $2p_z$ atomic orbitals of the oxygen were used as bonding orbitals, then two bonds would be predicted. These bonding wavefunctions would be mixture of only $|2p_y\rangle$ and $|2p_z\rangle$ orbitals on oxygen and the $|1s\rangle$ orbitals on the hydrogens (H_1 and H_2):

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + b_1|2p_y\rangle_O \tag{10.2.1}$$

$$|\chi_2\rangle = a_2|1s\rangle_{H_2} + b_2|2p_z\rangle_O \tag{10.2.2}$$

However, with a H-O-H bond angle for these bonds would be expected to be 90° since $2p_y$ and $2p_z$ are oriented 90° with respect to each other. Note that $|\chi_1\rangle$ and $|\chi_2\rangle$ are two-center bonding orbitals common to Valence Bond theory.

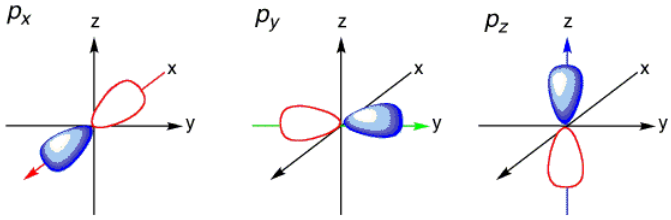


Figure 10.2.1 : The three p-orbitals are aligned along perpendicular axis (CC-SA-BY-NC; Nick Greeves ChemTube3D);

Using the oxygen atomic orbitals directly is obviously not a good model for describing bonding in water, since we know from experiment that the bond angle for water is 104.45° (Figure 10.2.2), which is also in agreement with VSEPR theory. Since the $2s$ orbital is spherical, mixing some $2s$ character into the $2p_z$ orbitals can adjust the bond angle as discussed previously by creating new hybrid orbitals.

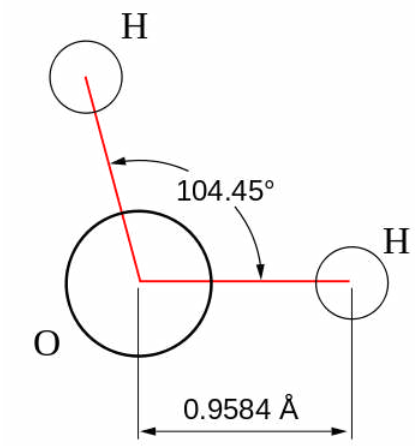


Figure 10.2.2 : Experimentally determined geometry of the water molecule (CC BY-SA 3.0 Booyabazooka).

Historically, Valence Bond theory was used to explain bend angles in small molecules. Of course, it was only qualitatively correct in doing this, as the following example shows. Let us construct the Valence Bond wavefunctions for the two bonding pairs in H_2O by mixing the $|2s\rangle$, $|2p_x\rangle$, $|2p_y\rangle$, and $|2p_z\rangle$ into four new sp^3 hybrid orbitals:

$$\begin{aligned}
\chi_1(r) &= \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \\
\chi_2(r) &= \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \\
\chi_3(r) &= \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \\
\chi_4(r) &= \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right]
\end{aligned}$$

Hence, the three $2p$ orbitals of the oxygen atom combined with the $2s$ orbitals of the oxygen to form four sp^3 hybrid orbitals (Figure 10.2.3).



Figure 10.2.4: This would leave the $2s$ and $2p_z$ orbitals of oxygen left over for the two lone pairs on the oxygen.

The bond angle for four groups of electrons around a central atom is 109.5 degrees. However, for water the experimental bond angle is 104.45°. The VSPER picture (general chemistry) for this is that the smaller angle can be explained by the presence of the two lone-pairs of electrons on the oxygen atom. Since they take up more volume of space compared to a bonding pair of electrons the repulsions between lone pairs and bonding pairs is expected to be greater causing the H-O-H bond angle to be smaller than the ideal 109.5°.

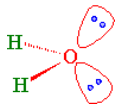


Figure 10.2.4 : Among the four hybrid orbitals, two are half filled and the remaining two are completely filled.

We can rationalize this by thinking about the s and p characters of the hybrids. In a perfectly sp^3 hybridized set of hybrid orbitals, each sp^3 orbital should have: 25% s character and and 75% p character. Since the bond angle is not 109.5° in water, the hybrid orbitals cannot have exactly this ratio of s and p character. So there there is uneven distribution of s and p character between the 4 hybrid orbitals. First we will write down the wavefunction and see what this means and then we will rationalize it.

Note: A few cautionary words about hybridization.

Hybridization is an often misconceived concept. It only is a mathematical interpretation, which explains a certain bonding situation (in an intuitive fashion). In a molecule the equilibrium geometry will result from various factors, such as steric and electronic interactions, and further more interactions with the surroundings like a solvent or external field. The geometric arrangement will **not** be formed because a molecule is hybridized in a certain way, it is the other way around, i.e., a result of the geometry or more precise and interpretation of the wavefunction for the given molecular arrangement.

Estimating Character of Hybrid Orbitals

The terminology we use for hybridization actually is just an abbreviation:

$$\mathrm{sp}^x = \mathrm{s}^{\frac{1}{x+1}}\,\mathrm{p}^{\frac{x}{x+1}}$$

In theory x can have any value, hence any of the following combinations constitute valid hybridization schemes for 1 s orbital and 3 p orbitals:

$$\begin{aligned} 1\times\mathrm{s}, 3\times\mathrm{p} &\rightsquigarrow 4\times\mathrm{sp}^3 \\ &\rightsquigarrow 3\times\mathrm{sp}^2, 1\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}, 2\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}^3, 1\times\mathrm{sp}, 1\times\mathrm{p} \\ &\rightsquigarrow \text{etc. pp.} \\ &\rightsquigarrow 2\times\mathrm{sp}^4, 1\times\mathrm{p}, 1\times\mathrm{sp}^{(2/3)} \end{aligned}$$

There are virtually infinite possibilities of combinations. Which one is "valid" is only determined by experiment (e.g., structure or spectroscopy). The generic sp^x hybrid orbitals wavefunction can be roughly written in terms of atomic orbital character:

$$|\chi_i\rangle = N(p+\gamma s) \tag{10.2.3}$$

where N is a normalization constant and γ is the relative contribution of s character to the hybrid orbital. For a pure sp^3 hybrid, γ would be 0.25 and for a pure sp hybrid, γ would be 1. The question is how to determine γ to get a better picture of the hybridization of water. Starting with the normalization criteria for wavefunctions:

$$\langle \chi_i | \chi_i \rangle = 1$$

and substituting Equation 10.2.3 into to get

$$\langle N(p+\gamma s) | N(p+\gamma s) \rangle = 1$$

which in integral notation is

$$\int N^2 (p+\gamma s)^2 d\tau = 1$$

where $d\tau$ represents all space. This is then expanded to

$$N^2 \int p^2 \, d\tau + N^2 2\gamma \int sp \, d\tau + N^2 \gamma^2 \int s^2 \, d\tau = 1 \tag{10.2.4}$$

These terms simplify either due to orthogonality or normality of the constitute atomic orbitals. Equation 10.2.4 simplifies to

$$N^2 + N^2 \gamma^2 = 1$$

and thus the normalization factor can be expressed in terms of γ

$$N = \frac{1}{\sqrt{1+\gamma^2}}$$

and the generic normalized sp^x hybrid orbital (Equation 10.2.3) is

$$|\chi_i\rangle = \frac{1}{\sqrt{1+\gamma^2}} (p+\gamma s) \tag{10.2.5}$$

The s and p characters to a hybrid orbital are now easy to obtain by squaring $|\chi_i\rangle$

- The magnitude of p-character is

$$\left(\frac{1}{\sqrt{1+\gamma^2}} \right)^2 = \frac{1}{1+\gamma^2} \tag{10.2.6}$$

  as $\gamma \rightarrow 0$, then the p character of the hybrid goes to 100%
- The magnitude of s-character is

$$\left(\frac{1}{\sqrt{1+\gamma^2}} \gamma^2 \right)^2 = \frac{\gamma^2}{1+\gamma^2} \tag{10.2.7}$$

  as $\gamma \rightarrow 1$, then the s character of the hybrid goes to 50%

As mentioned above, the geometric arrangement will **not** be formed because a molecule is hybridized in a certain way, it is the other way around. How do we choose the correct value of γ for the hybrid orbitals? The mixing coefficient γ is clearly related to the bond angle θ. Using some simple trigonometric relationships, it can be proven that:

$$\cos\theta = -\gamma^2 \tag{10.2.8}$$

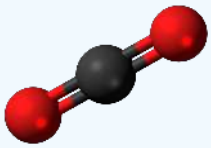
Equation 10.2.8 is an important equation as it related experimentally determined structure to the nature of the bonding and specifically, the composition of the atomic orbitals that create the hybrid orbitals used in the bonding.

Example 10.2.1 : Carbon Dioxide

What is the s-character in the hybrid orbitals for CO_2.

Solution

We know from simple VSEPR theory that the geometry of CO_2 is a linear triatomic molecule.



Thus $\theta = 180^\circ$ and via Equation 10.2.8, $\gamma = 1$ since $\cos 180^\circ = -1$. Hence, Equation 10.2.7 argues that the hybrid orbitals used in the bonding of CO_2 have 50% character; i.e., they are sp hybrid orbitals

$$|\chi_1\rangle = \frac{1}{\sqrt{2}}(s+p)$$

and

$$|\chi_2\rangle = \frac{1}{\sqrt{2}}(s-p)$$

Now, let's apply Equation 10.2.7 to water to find the character of the hybrid orbitals in water. The bond angle in water is 104.45° (Figure 10.2.2) hence

$$\cos 104.5^\circ = -0.25$$

and

$$\gamma = \sqrt{0.25} = 0.5$$

From Equation 10.2.6, then the amount of p character in the hybrid orbitals are

$$\frac{1}{1+\gamma^2} = \frac{1}{1+0.5^2} = 0.80\%$$

which leave 20% for s character (Equation 10.2.7).

$$\frac{\gamma^2}{1+\gamma^2} = \frac{0.5^2}{1+0.5^2} = 0.20$$

The two hybridized atomic orbitals of oxygen involved in bonding are each 80% p and 20% s character. This are not perfect sp^3 hybrid orbitals, as expected. Actually, the orbitals involved in the bonds would be better described as sp^4 hybridized. It does not mean that there are 4 p-orbitals in the hybrid orbital, but that each hybrid consists of 20% of s and 80% of p atomic orbitals.

Lone Pairs

Water has two sets of non-bonding electron pairs (Figure 10.2.4). Without a bond angle to start from, we cannot derive γ that describes the nonbonding hybrid orbitals that they occupy. However, we do know that the O atom has three p orbitals. So the TOTAL absolute p-character in all hybrid orbitals must be 3.

Let x be the p-character in the lone pairs hybrid orbitals:

$$0.8 + 0.8 + x + x = 3$$

This is assuming the lone pairs are **identical**. Solving for this, x = 0.7 (i.e. 70% p and 30% s). From this we can estimate the angle between the lone pair using Equations 10.2.6 and 10.2.8

- p-character:

$$\frac{1}{1+\gamma^2} = 0.7$$

so

$$-\gamma^2 = \frac{1}{0.7-1} = -0.42$$

and $\theta = 115^\circ$.

The angle between the lone pairs is greater (115°) than the bond angle (104.5°). The sp^3 hybrid atomic orbitals of the lone pairs have > 25% s-character. These hybrid orbitals are less directional and held more tightly to the O atom. The sp^3 hybrid atomic orbitals of the bonding pairs have < 25% s-character. They are more directional (i.e., more p-character) and electron density found in the bonding region between O and H.

Warning

It should be noted that the valence bond theory application described above predicts that the two lone electron pairs are in the same hybrid orbitals and hence have the same energies. As discussed in the next sections, that is not experimentally observed in photoelectron spectroscopy, which is a shortcoming of valence bond theory's application to water.

Contributors and Attributions

- Andrew Wolff (Adjunct Professor of Chemistry)
- Martin (Stackexchange)

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10.3: BeH_2 is Linear and H_2O is Bent

In this section, we will construct approximate molecular orbitals for a water molecule by considering a simple linear triatomic of the general form HXH, where X is a second row element. We will take a multi-centered molecular orbital approach instead of the two-centered valence bond/hybrid approach discussed previously. As with previous discussions of Molecular Orbitals, we approximate them as a linear combinations of atomic orbitals (LCAO). In molecular orbital theory linear combinations of **all** available (atomic) orbitals will form molecular orbitals. These are spread over the whole molecule, or delocalized, and in a quantum chemical interpretation they are called canonical orbitals. Since it is absolutely wrong to assume that there are only three types of sp^x hybrid orbitals, it is possible, that there are multiple different types of orbitals involved in bonding for a certain atom.

AH_2 Molecules

We want to construct a reasonable argument for the energetic ordering and structure of the molecular orbitals. We first note that each H will donate a $1s$ orbital in the LCAO scheme, and A will likely donate at least $2s$ and possible $2p$ orbitals, depending on its chemical identity. In general, if we consider only the first row A elements, the molecule orbitals (via the LCAO) can be expressed as combination of $1s$ orbitals on the two Hydrogens (H_1 and H_2) and the four n=2 orbitals ($2s$ $2p_x$ $2p_y$; $2p_z$) on the A atom:

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_2|1s\rangle_{H_2} + a_3|2s\rangle_A + a_4|2p_x\rangle_A + a_5|2p_y\rangle_A + a_6|2p_z\rangle_A \tag{10.3.1}$$

These molecular orbitals were created with six atomic orbitals and hence six different $|\chi\rangle$ molecular orbitals can be created. As with previous molecular orbitals problems, the coefficients of this expansion ($\{a_i\}$) are determined by solving the secular determinant.

If we consider only linear AH_2 molecules, then Equation 10.3.1 can be simplified by ignoring $2p_x$ and $2p_y$ atomic orbitals since they are perpendicular to the bonds and are hence non-bonding (only for linear AH_2 molecules). Moreover, the molecule is symmetric about the center (the position of A), hence the orbitals have to have the same symmetry.

Only the $2p$ orbital of A that will overlap with $1s$ of H is the $2p_z$. Hence, Equation 10.3.1 can be simplified to consider the combination

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A + a_6|2p_z\rangle_A \tag{10.3.2}$$

Note that the two coefficients in front of the $1s$ orbitals of hydrogen are the same by symmetry. This since no hydrogen is "special" and they must have the same contribution to the molecular orbital.

Mixing Amplitudes

How big should the $2s$ orbital contributors of A be compared to the $1s$ orbital of H?

This depends on several things. First, is the nuclear charge on A and the second is the **electronegativity** difference between H and A. The first determines how quickly the $2s$ orbitals, remembering that the exponential part is $exp(-Zr/a_0)$, and the electronegativity difference determines the relative magnitude of H_1 compared to H_2.

The six $|\chi\rangle$ molecular orbitals from Equation 10.3.1 are shown in Figure 10.3.1 .

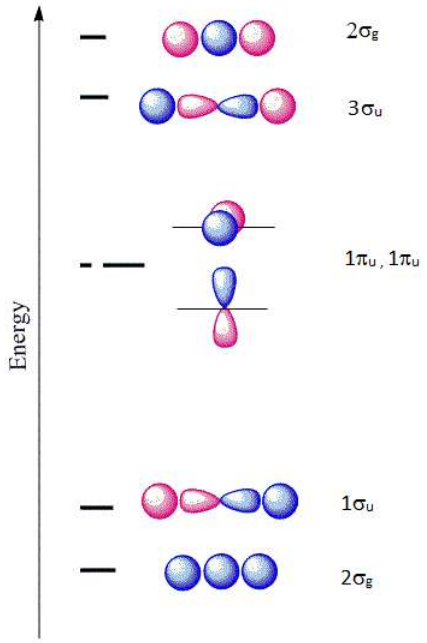


Figure 10.3.1 : The six molecular orbitals for the AH_2 molecule constrained to a linear geometry. The symmetry labels for each molecular orbital are indicated.

The first molecular orbital $|\chi_1\rangle$ constructed from Equation 10.3.1 is purely bonding because the $2s$ orbital is positive near the A nucleus, but becomes negative as we go away from the nucleus. This orbital is also even (*garade symmetry*), so we can denote it as a $2\sigma_g$ orbital signifying that it is constructed from a $2s$ orbital of A combined with the two $1s$ orbitals of H. The only other MO that can be constructed that has the right symmetry is $|\chi_6\rangle$ which is denoted as $2\sigma_u$. This is an antibonding molecular orbital and is also even (*garade symmetry*). The corresponding wavefunctions are:

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A$$

$$|\chi_6\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} - a_3|2s\rangle_A$$

Next, if we combine a $2p_z$ orbital of A with the $1s$ of H, there are two possibilities that have the right symmetry. The first is

$$|\chi_2\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

which is a bonding orbital and denoted as $1\sigma_u$. This is purely antibonding and has an odd symmetry (*ungarede*). The other combination is

$$|\chi_5\rangle = a_1|1s\rangle_{H_1} - a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

Hence, we denote this as $2\sigma_g$. The orbitals $2p_x$ and $2p_y$ from X are nonbonding and become π_{2p_x} and π_{2p_y} nonbonding orbitals and designated as $1\pi_u$ orbitals:

$$|\chi_3\rangle = |2p_x\rangle_A$$

$$|\chi_4\rangle = |2p_y\rangle_A$$

Beryllium Hydride (BeH_2) is Linear

Consider the BeF_2 molecule: Be has a $1s^2\ 2s^2$ electron configuration with is no unpaired electrons available for bonding. From a perspective of using only atomic orbitals to generate the bonding orbitals, we would conclude that the molecule could not exist since no free orientals exist on Be to bond. Clearly, atomic orbitals are not adequate to describe orbitals in molecules, but this can be solved by allowing the 2s and one 2p orbital on Be to mix to form *sp* hybrid orbitals. The experimental H-Be-H bond angle is 180°. Presumably, one electron from Be is shared with each unpaired electrons from H. We could promote and electron from the 2s orbital on Be to the 2p orbital to get two unpaired electrons for bonding (predicting 90° bond angles, not 180°). Thus the geometry is still not explained with atomic orbitals alone.

Be has 2s and 2p orbitals, and it is in the middle. H has 1s orbitals; there are 2 H atoms on the outside. We initially make combinations of the H atomic orbitals that we previously used to make diatomic hydrogen, except there is no overlap (i.e., $S = 0$). These combinations will mix with the 2s and $2p_z$ on Be, as shown in Figure 10.3.2 .

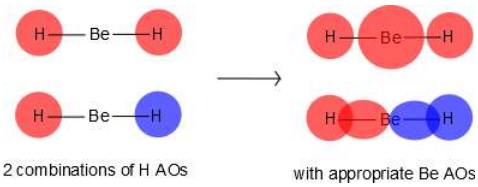


Figure 10.3.2 : Forming molecular orbitals for BeH_2.

Then we can put the Molecular Orbital diagram together, starting with the outside, drawing in bonding, non-bonding and anti-bonding MOs, and filling the electrons (Figure 10.3.3). The bond order is 2.

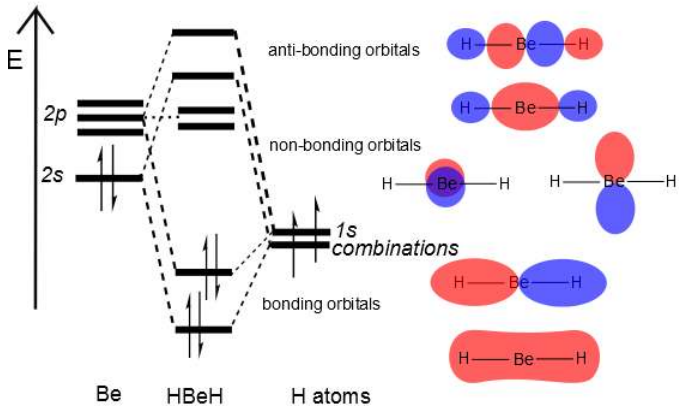


Figure 10.3.3 : Molecular orbitals diagram for BeH_2.

Walsh Correlation Diagrams

Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital energies of a molecule versus a distortion coordinate, used for making quick predictions about the geometries of small molecules. By plotting the change in molecular orbital levels of a molecule as a function of geometrical change, Walsh diagrams explain why molecules are more stable in certain spatial configurations (i.e. why water adopts a bent conformation).

A major application of Walsh diagrams is to explain the regularity in structure observed for related molecules having identical numbers of valence electrons (i.e. why H_2O and H_2S look similar), and to account for how molecules alter their geometries as their number of electrons or spin state changes. Additionally, Walsh diagrams can be used to predict distortions of molecular geometry from knowledge of how the LUMO (Lowest Unoccupied Molecular Orbital) affects the HOMO (Highest Occupied Molecular Orbital) when the molecule experiences geometrical perturbation. Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.

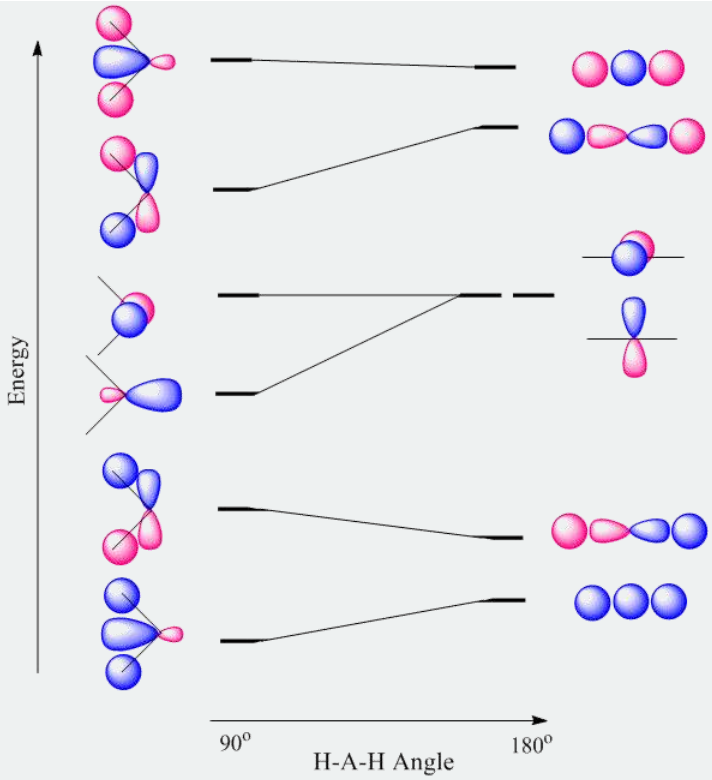


Figure 10.3.4 : A Walsh diagram for an AH_2 molecule. (public domain).

For the AH_2 molecular system, Walsh produced the first angular correlation diagram by plotting the orbital energy curves for the canonical molecular orbitals while changing the bond angle from 90° to 180° (Figure 10.3.4). As the bond angle is distorted, the energy for each of the orbitals can be followed along the lines, allowing a quick approximation of molecular energy as a function of conformation.

A typical prediction result for water is an bond angle of 90°, which is not even close to the experimental value of 104°. At best, the method is able to differentiate between a bent and linear molecule.

> *Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.*

Figure 10.3.4 illustrates the difference between the actual linear case we just analyzed and the truly bent molecule, e.g. H_2O. The geometry changes the ordering somewhat, but the qualitative picture we obtain from the linear case makes it a useful construction. The oxygen atomic orbitals are labeled according to their symmetry (Figure 10.3.5) as a_1 for the 2s orbital and b_1 $(2p_x)$, b_2 $(2p_y)$ and a_1 $(2p_z)$ for the three 2p orbitals. The two hydrogen 1s orbitals are premixed to form a_1 and b_2 molecular orbitals.

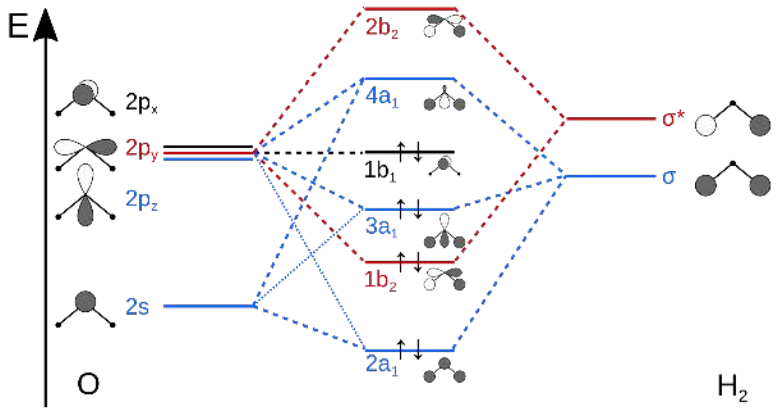


Figure 10.3.5 : MO diagram for water. (CC-SA-BY-3.0; Officer781).

Mixing takes place between same-symmetry orbitals of comparable energy resulting a new set of MO's for water:

- $2a_1$ MO from mixing of the oxygen 2s atomic orbital and the hydrogen σ MO. Small oxygen $2p_z$ atomic orbital admixture strengthens bonding and lowers the orbital energy.
- $1b_2$ MO from mixing of the oxygen $2p_y$ atomic orbital and the hydrogen σ* MO.
- $3a_1$ MO from mixing of the oxygen $2p_z$ atomic orbital and the hydrogen σ MO. Small oxygen 2s atomic orbital admixture weakens bonding and raises the orbital energy.
- $1b_1$ nonbonding MO from the oxygen $2p_x$ atomic orbital (the p-orbital perpendicular to the molecular plane).

In the water molecule the highest occupied orbital, $(1b_1)$ is non-bonding and highly localized on the oxygen atom, similar to the non-bonding orbitals of hydrogen fluoride. The next lowest orbital $(2a_1)$ can be thought of as a non-bonding orbital, as it has a lobe pointing away from the two hydrogens. From the lower energy bonding orbitals, it is possible to see that oxygen also takes more than its "fair share" of the total electron density. The electronic configuration of water in the ground state (Figure 10.3.5) is therefore

$$(a_1)^2(b_2)^2(a_1)^2(b_1)^2$$

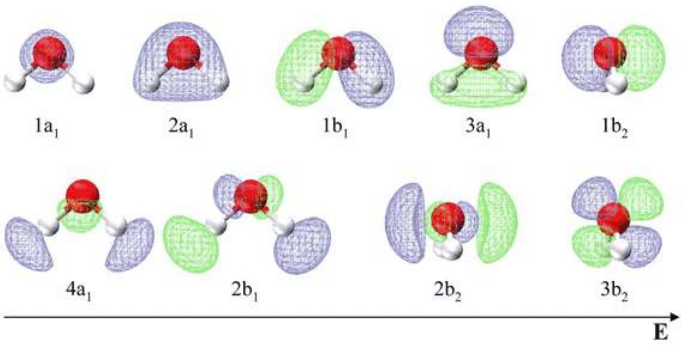


Figure 10.3.5 . Image from Anna Krylov (USC)

Table 10.3.1 list the respective LCAO coefficients for the six atomic orbitals. Table 10.3.1 combines the energy values with the description derived from the character table for molecules of point group C_{2v}

Table 10.3.1 : LCAO Coefficients of first six molecular orbitals of water

Energy	Symbol	s(H)	s(O)	p_x(O)	p_y(O)	p_z(O)	s(H)
6.728	$2b_2$	0.525	0	0	-0.669	0	-0.525
5.440	$3a_1$	-0.553	0.306	0	0	-0.544	0.553
-12.191	$1b_1$	0	0	-1.000	0	0	0
-14.467	$2a_1$	-0.309	0.354	0	0	0.827	-0.309
-19.113	$1b_2$	-0.473	0	0	-0.743	0	0.473

Energy	Symbol	s(H)	s(O)	p_x(O)	p_y(O)	p_z(O)	s(H)
-40.032	$1a_1$	0.315	0.884	0	0	-0.143	0.315

Note in contrast to the valence bond theory discussed previous for water, the two lone electron pairs are **not in identical orbitals**. The $1b_1$ MO is a lone pair, while the $3a_1$, $1b_2$ and $2a_1$ MO's can be localized to give two O−H bonds and an in-plane lone pair. This is in agreement with the experimentally measured photoelectron spectrum discussed in the next section.

Summary

Walsh correlation diagram is a plot of molecular orbital energy as a function of some systematic change in molecular geometry. For example, the correlation between orbital energies and bond angle for an AH_2 molecule. The geometry of a molecule is determined by which possible structure is lowest in energy. We can use the Walsh diagram to determine the energy trends based on which orbitals are occupied.

Contributors and Attributions

- Mark Tuckerman (New York University)
- Emily V Eames (City College of San Francisco)

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10.4: Photoelectron Spectroscopy

Learning Objectives

- Demonstrate how photoelectron spectroscopy can be used to resolve the absolute energies of molecular orbitals.

Photoelectron spectroscopy (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

- **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels.
- **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.

Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:

$$E = h\nu \tag{10.4.1}$$

where h is Planck constant and ν is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the topic of this page.

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy). In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

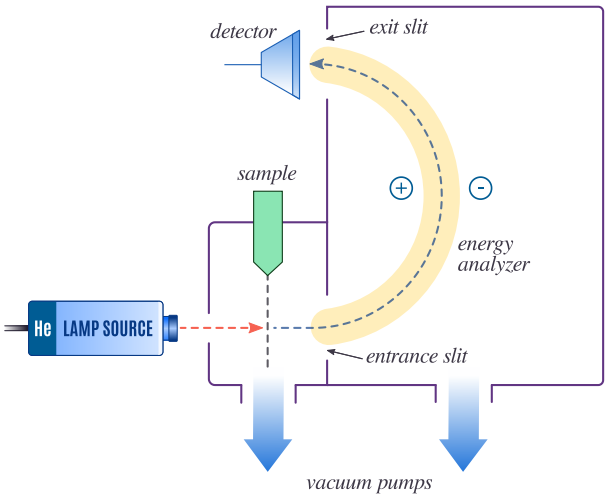


Figure 10.4.1 : Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit. (CC BY-NC; Ümit Kaya via LibreTexts)

The process of photoionization can be considered in several ways. One way is to look at the overall process for a species A:

$$A + \text{photon} \rightarrow A^+ + e^- \tag{10.4.2}$$

Conservation of energy then requires that (after using Equation 10.4.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{10.4.3}$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^-) = KE$$

Equation 10.4.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - \left[E(A^+) - E(A)\right] \tag{10.4.4}$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the **vertical ionization energy** (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE \tag{10.4.5}$$

or

$$IE = h\nu - KE \tag{10.4.6}$$

The vertical ionization energy is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (i.e., a free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

Note

Equation 10.4.5 may look familiar to you as it the same equation Einstein used to describe the photoelectric effect except the vertical ionization energy (IE) is substituted for workfunction Φ. Both vertical ionization energy and workfunctions are metrics for the binding energy of an electron in the sample.

At a fundamental level, ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the molecular orbitals detailed and specific quantitative information regarding the electronic structure and bonding in molecules.

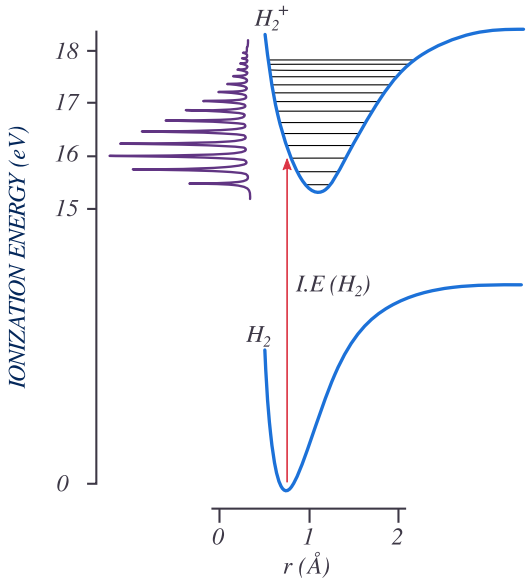


Figure 10.4.2 : Vertical ionization process for molecular hydrogen. (CC BY-NC; Ümit Kaya via LibreTexts)

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 10.4.6 and as illustrated in the Figure 10.4.2 . Nonetheless, the information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals by Koopmans' theorem, which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the *vertical ionization energy* to the ion state formed by removal of an electron from that orbital (Figure 10.4.3), provided the distributions of the remaining electrons do not change (i.e., frozen).

$$I_j = -\epsilon_j \tag{10.4.7}$$

There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.

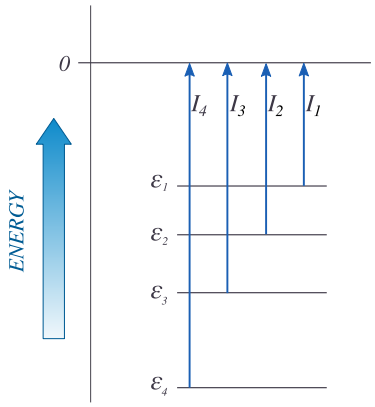


Figure 10.4.3 : Within Koopmans' Theorem, the energies of the orbitals (\epsilon\) have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization potential (I). (CC BY-NC; Ümit Kaya via LibreTexts)

Koopmans' Theorem

Koopmans' theorem argues that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital.

Several different ionization energies can be defined, depending on the degree of vibrational excitation of the cations. In general, the following two types of ionization energies are considered (Figure 10.4.4):

- Adiabatic ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v" = 0) + h\nu \rightarrow M^+(x, v' = 0) + e^-$$

  Adiabatic ionization energy that is, the minimum energy required to eject an electron from a molecule in its ground vibrational state and transform it into a cation in the lowest vibrational level of an electronic state x of the cation.
- Vertical ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v" = 0) + h\nu \rightarrow M^+(x, v' = n) + e^-$$

  where, the value n of the vibrational quantum number v' corresponds to the vibrational level whose wavefunction gives the largest overlap with the v" = 0 wavefunction. This is the most probable transition and usually corresponds to the vertical transition where the internuclear separations of the ionic state are similar to those of the ground state.

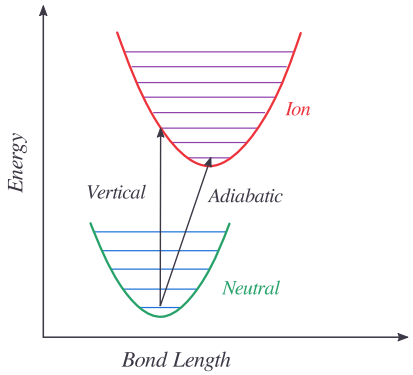


Figure 10.4.4 : Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system. (CC BY-NC; Ümit Kaya via LibreTexts)

The geometry of an ion may be different from the neutral molecule. The measured ionzation energy in a PES experiment can refer to the vertical ionization energy, in which case the ion is in the same geometry as the neutral, or to the adiabatic ionzaiton energy, in which case the ion is in its lowest energy, relaxed geometry (mostly the former though). This is illustrated in the Figure 10.4.4 . For a diatomic the only geometry change possible is the bond length. The figure shows an ion with a slightly longer bond length than the neutral. The harmonic potential energy surfaces are shown in green (neutral) and red (ion) with vibrational energy levels. The vertical ionzation energy is **always greater** than the adiabatic ionzation energy.

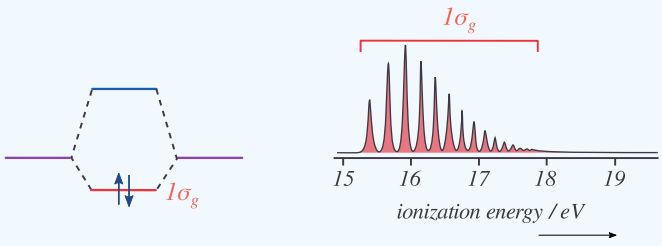
Differing Ionization Energies

You have been exposed to three metrics of ionization energies already, which are similar, but with distinct differences:

- The *ionization energy* (also called *adiabatic ionization energy*) is the lowest energy required to effect the removal of an electron from a molecule or atom, and corresponds to the transition from the lowest electronic, vibrational and rotational level of the isolated molecule to the lowest electronic, vibrational and rotational level of the isolated ion.
- The *binding energy* (also called *vertical ionization energy*) is the energy change corresponding to an ionization reaction leading to formation of the ion in a configuration which is the same as that of the equilibrium geometry of the ground state neutral molecule.
- The *workfunction* is the minimum energy needed to remove an electron from a (bulk) solid to a point in the vacuum.

Example 10.4.1 : Molecular Hydrogen

As you remember, the molecular orbital description of hydrogen involves two $|1s\rangle$ atomic orbitals generating a bonding $1\sigma_g$ and antibonding $2\sigma_u^*$ molecular orbitals. The two electrons that are responsible for the H_2 bond are occupied in the $1\sigma_g$.

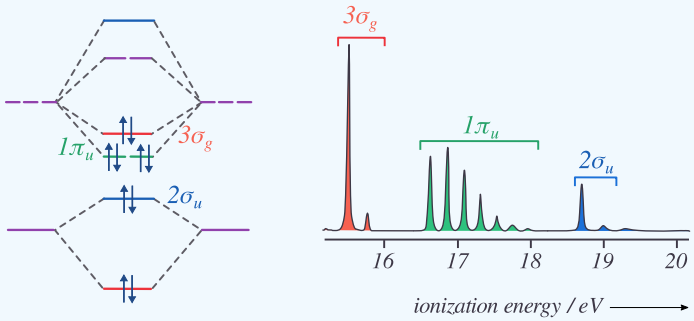


MO diagram and PES spectrum of H_2. (CC BY-NC; Ümit Kaya via LibreTexts)

The PES spectrum has a single band that corresponds to the ionization of a $1\sigma_g$ electron. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length since the bond order has been reduced).

Example 10.4.2 : Molecular Nitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Four molecular orbitals are occupied (the two $1\pi_u$ orbitals are both occupied). The UV photoelectron spectrum of N_2, has three bands corresponding to $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ occupied molecular orbitals. Both $3\sigma_g$ and $2\sigma_u$ are weakly bonding and antibonding. The $1\sigma_g$ orbital is not resolved in this spectrum since the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital.



MO diagram and PES spectrum of N_2. (CC BY-NC; Ümit Kaya via LibreTexts)

Note that extensive vibrational structure for the $1\pi_u$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

Hydrogen Chloride

The molecular energy level diagram for HCl is reproduced in Figure 10.4.5

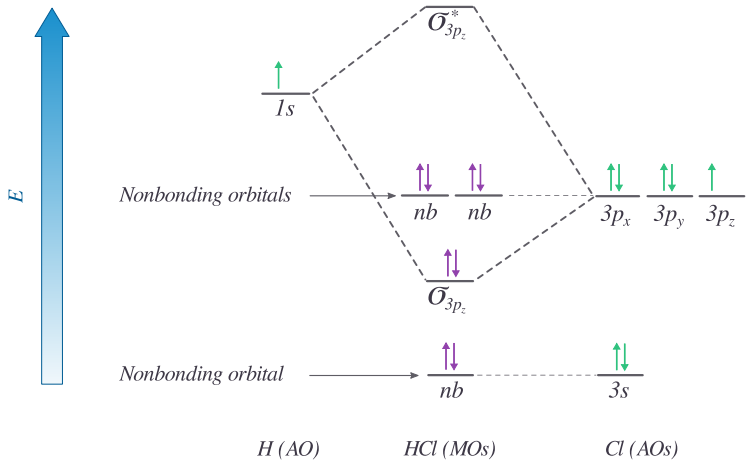


Figure 10.4.5 : Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1. (CC BY-NC; Ümit Kaya via LibreTexts)

Important aspects of molecular orbital diagram in Figure 10.4.5 :

- The H 1*s* energy lies well above the Cl 2*s* and 2*p* atomic orbitals;
- The valence electron configuration can be written $3\sigma^2 1\pi^4$;
- The H 1*s* orbital contributes only to the σ molecular orbitals, as does one of the Cl 2*p* orbitals (hence the lines in Figure 10.4.5 connecting these atomic orbitals and the 3σ and 4σ molecular orbitals);

- The remaining Cl 2*p* orbitals (ie those perpendicular to the bond axis) are unaffected by bonding, and these form the 1π molecular orbitals;
- The 1π orbitals are nonbonding - they are not affected energetically by the interaction between the atoms, and are hence neither bonding nor antibonding;
- The 3σ orbital is weakly bonding, and largely Cl 2*p*;
- The 3σ* orbital is antibonding, and primarily of H 1*s* character;

Figure 10.4.6 shows the analogous MO diagram and photoelectron spectrum for HCl. The spectrum has two bands corresponding to non-bonding 1*p* (or 1π) molecular orbitals (with negligible vibrational structure) and the 3*s* bonding molecular orbital (vibrational structure).

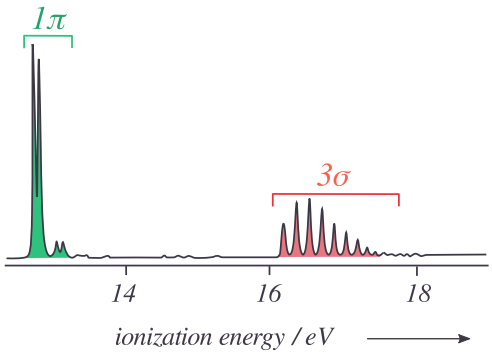


Figure 10.4.6 : Photoelectron spectrum HCl. (CC BY-NC; Ümit Kaya via LibreTexts)

The higher energy (more stabilized) core molecular orbitals are not observed since the incident photon energy $h\nu$ is below their ionization energies.

Water

In the simplified valence bond theory perspective of the water molecule, the oxygen atom form four sp^3 hybrid orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. Within the molecular orbital picture, the electronic configuration of the H_2O^+ molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ where the symbols a_1, b_2 and b_1 are orbital labels based on molecular symmetry that will be discussed later (Figure 10.4.7). Within Koopmans' theorem:

- The energy of the $1b_1$ HOMO corresponds to the ionization energy to form the H_2O^+ ion in its ground state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$.
- The energy of the second-highest molecular orbitals $3a_1$ refers to the ion in the excited state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

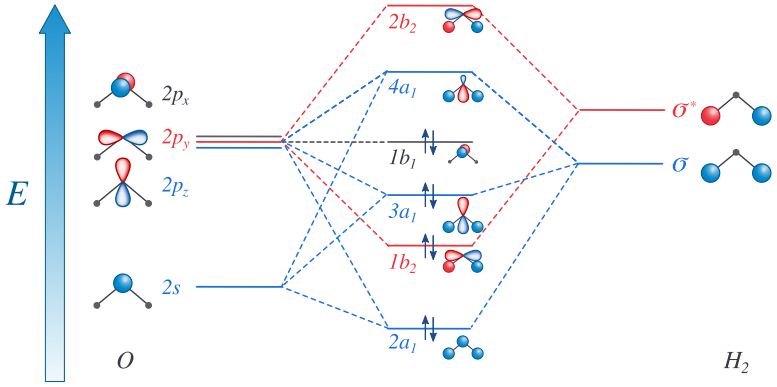


Figure 10.4.7 : MO diagram for water. (CC BY-NC; Ümit Kaya via LibreTexts)

The Hartree–Fock orbital energies (with sign changed) of these orbitals are tabulated below and compared to the experimental ionization energies.

Molecular orbital	Hartree–Fock orbital Energies (eV)	Experimental Ionization Energies (eV)
$2a_1$	36.7	32.2
$1b_2$	19.5	18.5
$3a_1$	15.9	14.7
$1b_1$	13.8	12.6

As explained above, the deviations between orbital energy and ionization energy is small and due to the effects of orbital relaxation as well as differences in electron correlation energy between the molecular and the various ionized states.

The molecular orbital perspective has the lone pair in different orbitals (one in a non-bonding orbital ($1b_1$ and one in the bonding orbitals). We tern to the photoelectron spectroscopy to help identify which theory is more accurate (i.e., describes reality better). The photoelectron spectrum of water in Figure 10.4.6 can be interpreted as having three major peaks with some fine structure arises from vibrational energy changes. The light source used in this experiment is not sufficiently energetic to ionize electrons from the lowest lying molecular orbitals.

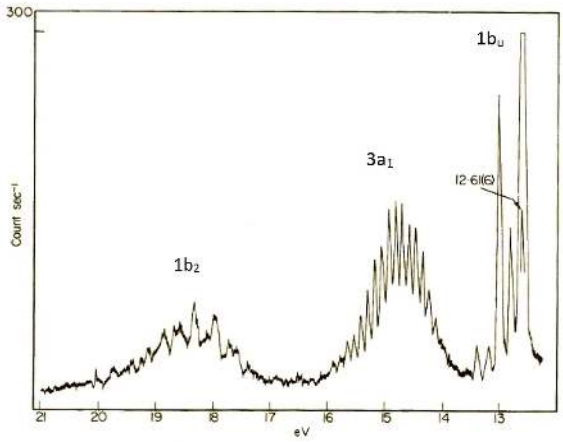


Figure 10.4.8 : Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page.his spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

If water was formed two identical O-H bonds and two lone pairs on the oxygen atom line valence bond theory predicts, then the PES in Figure 10.4.8 would have two (degenerate) peaks, one for the two bonds and one for the two lone pairs. The photoelectron spectrum clearly shows three peaks in the positions expected for the molecular orbitals in Figure 10.4.8 .

If the molecular orbitals in Figure 10.4.7 represent the real electronic structure, how do we view the bonding? These molecular orbitals are delocalized and bare little relationship to the familiar 2-center bonds used in valence bond theory. For example, the $2a_1$ $1b_1$ and $3a_1$ molecular orbitals all have contributions from all three atoms, they are really 3-centered molecular orbitals. The bonds however can be thought of as representing a build up of the total electron density which loosely put is a total of all the orbital contributions. Despite this, we keep the ideas of hybridization and 2-center bonds because they are useful NOT because they represent reality

Summary

A photoelecton spectrum can show the relative energies of occupied molecular orbitals by ionization. (i.e. ejection of an electron). A photoelectron spectrum can also be used to determine energy spacing between vibrational levels of a given electronic state. Each orbital energy band has a structure showing ionization to different vibrational levels.

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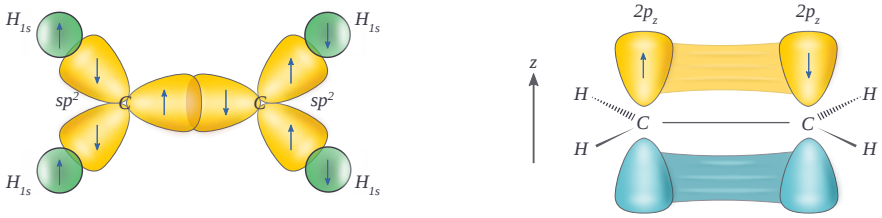
10.5: The pi-Electron Approximation of Conjugation

Learning Objectives

- Demonstrate how Hückel's theory approximates the full molecular orbital picture of molecules by treating the σ-bonding and π-bonding networks independently.

Molecular orbital theory has been very successfully applied to large conjugated systems, especially those containing chains of carbon atoms with alternating single and double bonds. An approximation introduced by Hückel in 1931 considers only the delocalized *p* electrons moving in a framework of π-bonds. This is, in fact, a more sophisticated version of a free-electron model.

The simplest hydrocarbon to consider that exhibits π bonding is ethylene (ethene), which is made up of four hydrogen atoms and two carbon atoms. Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + *s*) and one C–C (sp^2 + sp^2) (part (a) of Figure 10.5.1).



(a) C_2H_4 σ - bonded framework *(b) C_2H_4 π bonding*

Figure 10.5.1 : (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.) (CC BY-NC; Ümit Kaya via LibreTexts)

The Hückel approximation is used to determine the energies and shapes of the π molecular orbitals in conjugated systems. Within the Hückel approximation, the covalent bonding in these hydrocarbones can be separated into two independent "frameworks": the σ-bonding framework and the the σ-bonding framework. The wavefunctions used to describe the bonding orbitals in each framework results from different combinations of atomic orbitals. The method limits itself to addressing conjugated hydrocarbons and specifically only π electron molecular orbitals are included because these determine the general properties of these molecules; the sigma electrons are ignored. This is referred to as *sigma-pi separability* and is justified by the orthogonality of σ and π orbitals in planar molecules. For this reason, the Hückel method is limited to planar systems. Hückel approximation assumes that the electrons in the π bonds “feel” an electrostatic potential due to the entire σ-bonding framework in the molecule (i.e. it focuses only on the formation of π bonds, given that the σ bonding framework has already been formed).

Conjugated Systems

A conjugated system has a region of overlapping p-orbitals, bridging the interjacent single bonds, that allow a *delocalization* of π electrons across all the adjacent aligned p-orbitals. These π electrons do not belong to a single bond or atom, but rather to a group of atoms.

Ethylene

Before considering the Hückel treatment for ethylene, it is beneficial to review the general bonding picture of the molecule. Bonding in ethylene involves the sp^2 hybridization of the $2s$, $2p_x$, and $2p_y$ atomic orbitals on each carbon atom; leaving the $2p_z$ orbitals untouched (Figure 10.5.2).

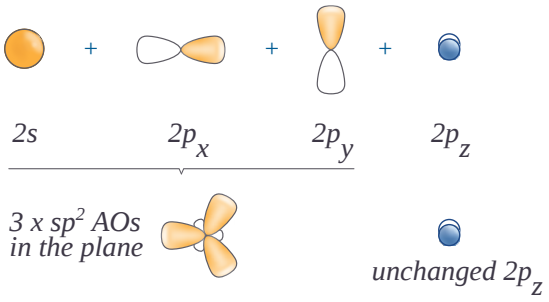


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

The use of hybrid orbitals in the molecular orbital approach describe here is merely a convenience and not invoking valence bond theory (directly). An identical description can be extracted using exclusively atomic orbitals on carbon, but the interpretation of the resulting wavefunctions is less intuitive. For example, the i[th] molecular orbital can be described via hybrid orbitals

$$|\psi_1\rangle = c_1|sp_1^2\rangle + c_2|1s_a\rangle$$

or via atomic orbitals.

$$|\psi_1\rangle = a_1|2s\rangle + a_1|2p_x\rangle + a_1|2p_y\rangle + a_4|1s_a\rangle$$

where $\{a_i\}$ and $\{c_i\}$ are coefficients of the expansion. Either describe will work and both are identical approaches since

$$|sp_1^2\rangle = b_1|2s\rangle + b_1|2p_x\rangle + b_1|2p_y\rangle$$

where $\{c_i\}$ are coefficients describing the hybridized orbital.

The bonding occurs via the mixing of the electrons in the sp^2 hybrid orbitals on carbon and the electrons in the $1s$ atomic orbitals of the four hydrogen atoms (Figure 10.5.1 ; left) resulting in the σ-bonding framework. The π-bonding framework results from the unhybridized $2p_z$ orbitals (Figure 10.5.2 ; right). The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram in Figure 10.5.3 ; Hückel theory is concerned only with describing the molecular orbitals and energies of the π bonding framework.

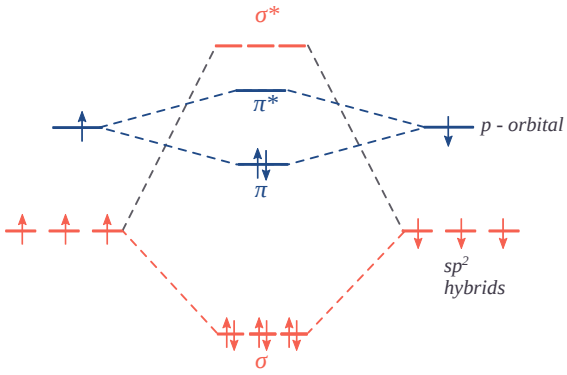


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the π-bonding framework (blue) and the σ-bonding frameworks (red) of ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

> *Hückel treatment is concerned only with describing the molecular orbitals and energies of the π bonding framework.*

Since Hückel theory is a special consideration of molecular orbital theory, the molecular orbitals $|\psi_i\rangle$ can be described as a linear combination of the $2p_z$ atomic orbitals ϕ at carbon with their corresponding $\{c_i\}$ coefficients:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{10.5.1}$$

This equation is substituted in the Schrödinger equation:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

with $\hat{H}$ the Hamiltonian and E_i the energy corresponding to the molecular orbital to give:

$$\hat{H}c_1|\phi_1\rangle + \hat{H}c_2|\phi_2\rangle = Ec_1|\phi_1\rangle + Ec_2|\phi_2\rangle \tag{10.5.2}$$

If Equation 10.5.2 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{10.5.3}$$

where H_{ij} are the Hamiltonian matrix elements (see note below)

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i \phi_j \mathrm{d}v$$

If Equation 10.5.2 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{10.5.4}$$

Both Equations 10.5.3 and 10.5.4 can better represented in matrix notation,

$$\begin{bmatrix} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) \\ c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) \end{bmatrix} = 0$$

or more simply as a product of matrices.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.5}$$

All diagonal Hamiltonian integrals H_{ii} are called **Coulomb integrals** and those of type H_{ij} are called **resonance integrals**. Both integrals are negative and the resonance integrals determines the strength of the bonding interactions. The equations described by Equation 10.5.5 are called the ***secular equations*** and will also have the trivial solution of

$$c_1 = c_2 = 0$$

Within linear algebra, the secular equations in Equation 10.5.5 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{10.5.6}$$

or in shorthand notation

$$\det(H - ES) = 0$$

Everything in Equation 10.5.6 is a known number except E. Since the secular determinant for ethylene is a 2×2 matrix, finding E, requires solving a quadratic equation (after expanding the determinant)

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{21})(H_{12} - ES_{12}) = 0$$

There will be two values of E which satisfy this equation and they are the molecular orbital energies. For ethylene, one will be the bonding energy and the other the antibonding energy for the π-orbitals formed by the combination of the two carbon $2p_z$ orbitals (Equation 10.5.1). However, if more than two $|\phi\rangle$ atomic orbitals were used, e.g., in a bigger molecule, then more energies would be estimated by solving the secular determinant.

Solving the secular determinant is simplified within Hückel method via the following four assumptions:

1. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the $\pi-$ orbitals are directed perpendicular to the direction of their bonds (Figure 10.5.1). This assumption is often call neglect of differential overlap (NDO).
2. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.

3. All resonance integrals H_{ij} between neighboring atoms are equal and set to β.
4. All coulomb integrals H_{ii} are set equal to α.

These assumptions are mathematically expressed as

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

Assumptions 1 means that the overlap integral between the two atomic orbitals is 0

$$S_{11} = S_{22} = 1$$

$$S_{12} = S_{21} = 0$$

Matrix Representation of the Hamiltonian

The Coulomb integrals

$$H_{ii} = \langle \phi_i | H | \phi_i \rangle$$

and resonance integrals.

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \;\; (i \neq i)$$

are often described within the matrix representation of the Hamiltonian (specifically within the $|\phi\rangle$ basis):

$$\hat{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

or within the Hückel assumptions

$$\hat{H} = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix}$$

The Hückel assumptions reduces Equation 10.5.5 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.7}$$

if Equation 10.5.7 is divided by β:

$$\begin{bmatrix} \dfrac{\alpha - E}{\beta} & 1 \\ 1 & \dfrac{\alpha - E}{\beta} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

and then a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.5.8}$$

then Equation 10.5.7 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.9}$$

The trivial solution gives both wavefunction coefficients equal to zero and the other (non-trivial) solution is determined by solving the secular determinant

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

which when expanded is $x^2 - 1 = 0$ so $x = \pm 1$.

Knowing that $E = \alpha - x\beta$ from Equation 10.5.8, the energy levels can be found to be

$$E = \alpha - \pm 1 \times \beta$$

or

$$E = \alpha \mp \beta$$

Since β is negative, the two energies are ordered (Figure 10.5.4)

- For π_1: $E_1 = \alpha + \beta$
- For π_2: $E_2 = \alpha - \beta$

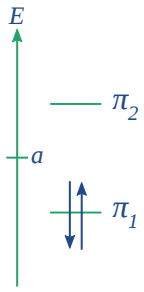


Figure 10.5.4 : π energies of ethylene with occupation. (CC BY-NC; Ümit Kaya via LibreTexts)

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 10.5.9). For the lower energy state ($x = -1$)

$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 10.5.1):

$$|\psi_1\rangle = N_1(|\phi_1\rangle + |\phi_2\rangle) \tag{10.5.10}$$

where N_1 is the normalization constant for this molecular orbital; this is the **bonding** molecular orbital.

For the higher energy molecular orbital ($x = -1$) and then

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = -c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 10.5.1):

$$\psi_2\rangle = N_2(|\phi_1\rangle - |\phi_2\rangle) \tag{10.5.11}$$

where N_2 is the normalization constant for this molecular orbital; this is the **anti-bonding** molecular orbital.

The normalization constants for both molecular orbitals can obtained via the standard normalization approach (i.e., $\langle\psi_i|\psi_i\rangle = 1$) to obtain

$$N_1 = N_2 = \frac{1}{\sqrt{2}}$$

These molecular orbitals form the π-bonding framework and since each carbon contributes one electron to this framework, only the lowest molecular orbital ($|\psi_1\rangle$) is occupied (Figure 10.5.5) in the ground state. The corresponding electron configuration is then π_1^2.

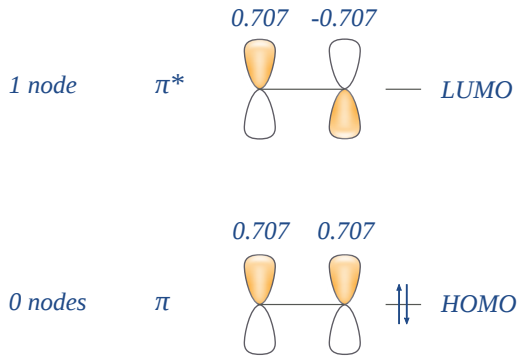


Figure 10.5.5 : Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy. (CC BY-NC; Ümit Kaya via LibreTexts)

> *HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively and are often referred to as frontier orbitals. The energy difference between the HOMO and LUMO is termed the HOMO–LUMO gap.*

The 3-D calculated π molecular orbitals are shown in Figure 10.5.6 .

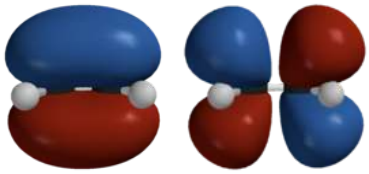


Figure 10.5.6 : Calculated π molecular orbitals for ethylene . (left) the bonding orbital (|\psi_1 \rangle\) and (right) the antibonding $(|\psi_2\rangle$ orbital.

Limitations of Hückel Theory

Hückel theory was developed in the 1930's when computers were unavailable and a simple mathematical approaches were very important for understanding experiment. Although the assumptions in Hückel theory are drastic they enabled the early calculations of molecular orbitals to be performed with mechanical calculators or by hand. Hückel Theory can be extended to address other types of atoms in conjugated molecules (e.g., nitrogen and oxygen). Moreover, it can be extended to also treat σ orbitals and this "Extended Hückel Theory" is still used today. Despite the utility of Hückel Theory, it is highly qualitative and we should remember the limitations of Hückel Theory:

- Hückel Theory is very approximate
- Hückel Theory cannot calculate energies accurately (electron-electron repulsion is not calculated)
- Hückel Theory typically overestimates predicted dipole moments

Hückel Theory is best used to provide simplified models for understanding chemistry and for a detailed understanding modern *ab initio* molecular methods discussed in Chapter 11 are needed.

Contributors

- Seymour Blinder (Professor Emeritus of Chemistry and Physics at the University of Michigan, Ann Arbor)
- Wikipedia
- StackExchange (Philipp)

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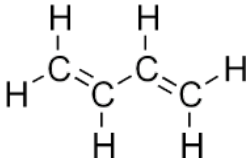
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10.6: Butadiene is Stabilized by a Delocalization Energy

Learning Objectives

- Apply Hückel theory to an extended π-bonding network
- Identify the origin of delocalization energy from Hückel theory and relate it to resonances structures in valence bond theory

1,3-Butadiene is a simple conjugated diene with the formula C_4H_6 and can be viewed structurally as two vinyl groups ($CH_2{=}CH_2$) joined together with a single bond. Butadiene can occupy either a cis or trans conformers and at room temperature, 96% of butadiene exists as the trans conformer, which is 2.3 kcal/mole more stable than the cis structure.



trans-1,3-Butadiene

For the simple application of applying Hückel theory for understanding the electronic structure of butadiene, we will ignore the energetic differences between the two conformers. As discussed previously, the molecular orbitals are linear combination of the four $|p\rangle$ atomic orbitals on the carbon atoms that are not participating in the σ bonding network:

$$|\psi_i\rangle = \sum_j^4 c_{ij}|p_i\rangle$$

or explicitly

$$|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}|p_2\rangle + c_{i3}|p_3\rangle + c_{i4}|p_4\rangle \tag{10.6.1}$$

for the i[th] molecular orbital $|\psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.2}$$

If the standard Hückel theory approximations were used

$$H_{ii} - ES_{ii} = \alpha$$

and

$$H_{ij} - ES_{ij} = \beta$$

when $i = j \pm 1$, otherwise

$$H_{ij} - ES_{ij} = 0$$

then the secular equations for butadiene in Equation 10.6.2 become

$$\begin{bmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.3}$$

Solving Equation 10.6.3 for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{10.6.4}$$

If both sides of Equation 10.6.4 were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.6.5}$$

then Equation 10.6.4 simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.6.6}$$

This is essentially the connection matrix for the butadiene molecule. Each pair of connected atoms is represented by 1, each non-connected pair by 0 and each diagonal element by x. Expansion of the determinant in Equation 10.6.6 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{10.6.7}$$

While solving 4th order equations typically require numerical estimation, Equation 10.6.7 can be further simplified by recognizing that it is a quadratic equation in terms of x^2. Therefore, the roots are

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

or $x = \pm\, 0.618$ and $x = \pm\, 1.618$. Since α and β are negative, these molecular orbital energies can ordered in terms of energy (from lowest to highest):

$$E_1 = \alpha + 1.618\beta \tag{10.6.8}$$

$$E_2 = \alpha + 0.618\beta \tag{10.6.9}$$

$$E_3 = \alpha - 0.618\beta \tag{10.6.10}$$

$$E_4 = \alpha - 1.618\beta \tag{10.6.11}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1 .

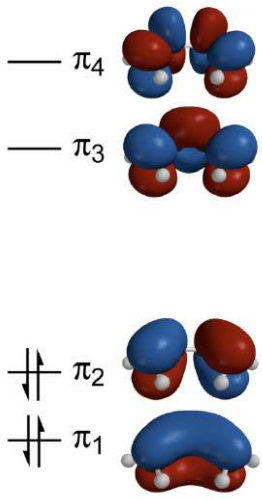


Figure 10.6.1 : The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

Each p atomic orbital of carbon contributes a single electron to the π manifold, so the ground-state occupation of the resulting four π electrons have a $\pi_1^2\pi_2^2$ configuration (Figure 10.6.1). The the total π-electron energy is then determined by adding up the energies in Equations 10.6.8-10.6.11 and scaling by their occupations to get

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_1 + 2\times E_2 + 0\times E_3 + 0\times E_4 \\ &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{10.6.12}$$

If the bonding of butadiene were described only as two localized double bond as in its dominant valence-bond structure (Figure 10.6.1), then its π-electron energy would be given by twice the E_π predicted for the ethlyene molecule:

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_\pi(\text{ethylene}) \\ &= 2\times 2(\alpha+\beta) \\ &= 4\alpha + 4\beta \end{aligned} \tag{10.6.13}$$

Comparing Equation 10.6.12 with Equation 10.6.12, the total π energy of butadiene lies lower than the total π energy of two double bonds by 0.48β(the σ bond does not contribute). This difference is known as the **delocalization energy**; a typical estimate of β is around -75 kJ/mol, which results in a *delocalization energy* for butadiene of -35 kJ/mol.

> *The delocalization energy is the extra stabilization resulting from the electrons extending over the whole molecule.*

Delocalization Energy in Valence Bond Theory

Delocalization energy is intrinsic to molecular orbital theory, since it results from breaking the two-center bond concept with the molecular orbitals that spread over more that just one pair of atoms. However, within the two-center theory of valence bond theory, the delocalization energy results from a stabilization energy attributed to resonance. Several conventional valence bond resonance structures that can be written for 1,3-butadiene, four of which are shown in Figure 10.6.2 . However, while structure $2a$ dominates, the other resonance structures also contribute to describing the total molecule and hence predict a corresponding stabilization energy akin to the delocalization energy in molecular orbital theory.

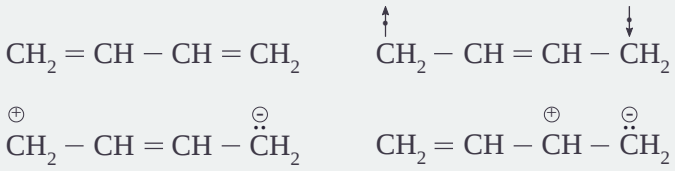


Figure 10.6.2 : Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (CC BY-NC; Ümit Kaya via LibreTexts)

In general, the true description of the bonding within the valence bond theory is a superposition of resonance structures with amplitudes that are determined via a variational optimization to find the lowest possible energy for the valence bond wavefunctions.

The solving the secular equations (Equation 10.6.2) gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 10.6.1 (not demonstrated):

$$|\psi_1\rangle = 0.37|p_1\rangle + 0.60|p_2\rangle + 0.60|p_3\rangle + 0.37|p_4\rangle \tag{10.6.14}$$

$$|\psi_3\rangle = 0.60|p_1\rangle + 0.37|p_2\rangle - 0.37|p_3\rangle - 0.60|p_4\rangle \tag{10.6.15}$$

$$|\psi_3\rangle = 0.60|p_1\rangle - 0.37|p_2\rangle - 0.37|p_3\rangle + 0.60|p_4\rangle \tag{10.6.16}$$

$$|\psi_4\rangle = 0.37|p_1\rangle - 0.60|p_2\rangle + 0.60|p_3\rangle - 0.37|p_4\rangle \tag{10.6.17}$$

These are depicted in Figure 10.6.3 .

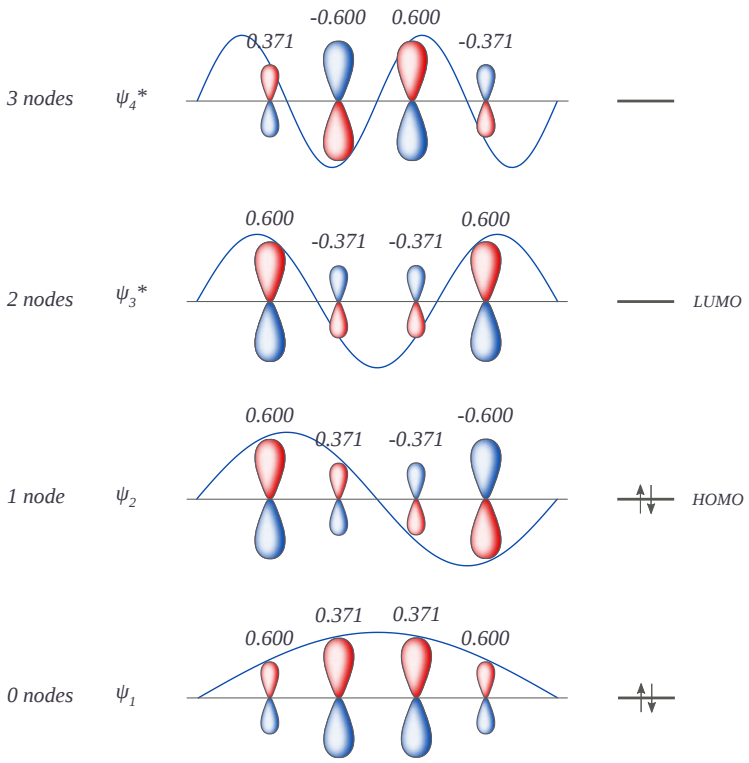


Figure 10.6.3 : Energy level diagram and decomposition of the π molecular orbitals of butadiene. This is view three-dimensionally in Figure 10.6.1 . (CC BY-NC; Ümit Kaya via LibreTexts)

Note the correlation of the energy of the π molecular orbitals of butadiene to the number of nodes in the wavefunction; this is the general trend observed in previous systems like the particle in the box and atomic orbitals. The four 3-D calculated molecular orbitals are contrasted in Figure 10.6.1 .

Exercise 10.6.1

What would Hückel theory predict for the energy levels and π molecular orbitals of cis-butadiene? Do you believe this approach adequately describes the energy levels of the cis-trans isomerization reaction of butadiene?

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10.7: Benzene and Aromaticity

Learning Objectives

- Apply Hückel theory to describing the pi bonding in cyclical conjugated system
- Identify the origin of aromaticity within Hückel theory to describe extra stabilization in certain cyclical conjugated systems

The previous sections addressed the π orbitals of linear conjugated system. Here we address conjugated systems of **cyclic conjugated hydrocarbons** with the general formula of CnHn where n is the number of carbon atoms in the ring. The molecule from this important class of organic molecule that you are most familiar with is benzene ($\mathrm{C_6H_6}$) with $n = 6$, although many other molecules exist like cyclobutadiene ($\mathrm{C_4H_4}$) with $n = 4$ (Figure 10.7.1).

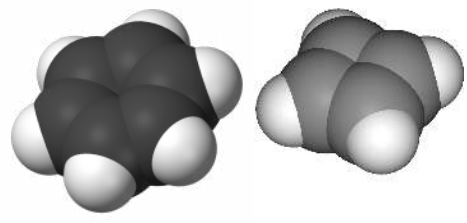


Figure 10.7.1 : Space-filling model of benzene (left) and cyclobutadiene (right). Carbon atoms are indicated in black, while hydrogen atoms are indicated in white. (Public domain; Benjah-bmm27 and Edgar181, respectively).

Structure of Benzene

The structure of benzene is an interesting historical topic. In 1865, the German chemist Friedrich August Kekulé published a paper suggesting that the structure of benzene contained a ring of six carbon atoms with alternating single and double bonds. Within this argument, two resonance structures can be formulated.

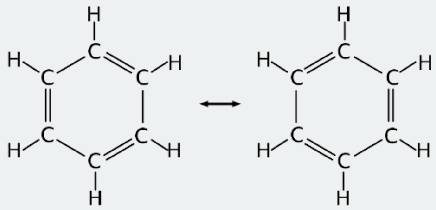


Figure 10.7.2 : Resonance structures of benzene.

However, X-ray diffraction shows that all six carbon-carbon bonds in benzene are of the same length, at 140 pm. The C–C bond lengths are greater than a double bond (135 pm), but shorter than a typical single bond (147 pm). This means that neither of the structures in Figure 10.7.2 are correct and the true 'structure' of benzene is a mixture of the two. As discussed previously, that such a valence bond perspective results in a **delocalization energy** within a molecular orbital approach.

Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular determinant

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.7.1}$$

with the six roots $x = \pm 2, \pm 1, \pm 1$. This corresponds to the following energies (ordered from most stable to least since $\beta < 0$):

- $E_1 = \alpha + 2\beta$
- $E_2 = \alpha + \beta$
- $E_3 = \alpha + \beta$

- $E_4 = \alpha - \beta$
- $E_5 = \alpha - \beta$
- $E_6 = \alpha - 2\beta$

The two pairs of $E = \alpha \pm \beta$ energy levels are two-fold degenerate (Figure 10.7.3).

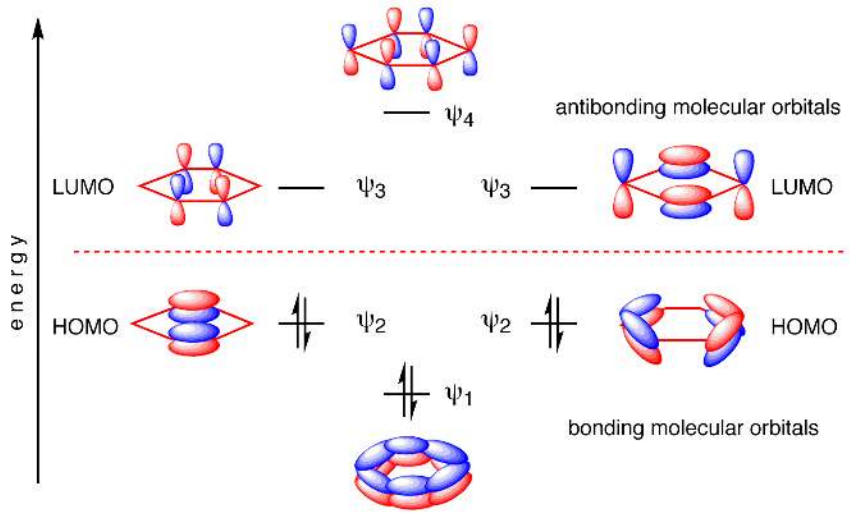


Figure 10.7.3 : The π molecular orbitals for benzene. The dashed lines represent the energy of an isolated p orbitals and all orbitals below this line are bonding. All orbitals above it are antibonding. (CC BY-NC-SA 4.0; Nick Greeves via ChemTube3D)

The resulting wavefunctions are below (expanded in terms of carbon $|2p\rangle$ atomic orbitals).

$$
\begin{aligned}
|\psi_1\rangle &= \frac{1}{\sqrt{6}}[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle] \\
|\psi_2\rangle &= \frac{1}{\sqrt{4}}[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle] \\
|\psi_3\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle\right] \\
|\psi_4\rangle &= \frac{1}{\sqrt{4}}[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle] \\
|\psi_5\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle\right] \\
|\psi_6\rangle &= \frac{1}{\sqrt{6}}[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle]
\end{aligned}
$$

Each of the carbons in benzene contributes one electron to the π-bonding framework (Figure 10.7.3). This means that all bonding molecular orbitals are fully occupied and benzene then has an electron configuration of $\pi_1^2\pi_2^2\pi_3^2$. With the three lowest molecular orbitals occupied, the total π-bonding energy is

$$
\begin{aligned}
E_{tot}(\text{benzene}) &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\
&= 6\alpha + 8\beta
\end{aligned} \tag{10.7.2}
$$

Since the energy of a localized double bond is $2(\alpha + \beta)$, as determined from the analysis of ethylene, the delocalization energy of benzene is

$$
\begin{aligned}
\Delta E &= E_{tot}(\text{benzene}) - 3E_{tot}(\text{ethylene}) \\
&= (6\alpha + 8\beta) - 3 \times 2(\alpha + \beta) \\
&= 2\beta
\end{aligned}
$$

The experimental thermochemical value is -152 kJ mol^{-1}.

Aromaticity

In general, cyclic polyenes are only closed shell (i.e., each electron paired up) and extra stable for with $(4n+2)\pi$ electrons (n=0,1,2…). These special molecules have the highest delocalization energies and are said to be “aromatic”. For benzene this is 2β (Equation 10.7.2), which is the energy by which the delocalized π electrons in benzene are more stable than those in three isolated double bonds.

Hückel's Rule

A stable, closed-shell conjugated cyclic structure is obtained for molecules with $(4n+2)\pi$ electrons with n=2, 6, 10, ... electrons.

Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product.

$$\mathrm{C_6H_6 + 3\,H_2 \longrightarrow C_6H_{12}}$$

In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 11.9 kJ mol^{-1}. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 23.9 kJ mol^{-1} on complete hydrogenation, and 1,3,5-cyclohexatriene to release 35.9 kJ mol^{-1}. These heats of hydrogenation ΔH_{hyd} reflect the relative thermodynamic stability of the compounds (Figure 10.7.4).

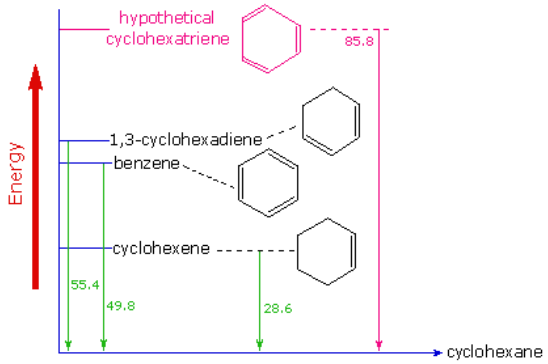


Figure 10.7.4 : Experimental evidence for aromatic stabilization energy in benzene from the heat of hydrogenation. Energies are in kcal/mol. (CC BY-NC-SA 4.0; William Resuch);

In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 8.1 kJ mol^{-1}, presumably due to conjugation of the double bonds. Benzene, however, is an extraordinary 15 kJ mol-1 more stable than expected. This additional stability is a characteristic of all aromatic compounds.

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CHAPTER OVERVIEW

11: Computational Quantum Chemistry

Computational chemistry is the field of chemistry that uses mathematical approximations and computer programs to solve problems of chemical interest. Quantum chemistry is a subfield that addresses the equations and approximations derived from the postulates of quantum mechanics; specifically involving solving the Schrödinger equation for molecular systems. Quantum chemistry is typically separated into a*b initio*, which uses methods that do not include any empirical parameters or experimental data and semi-empirical which do.

11.1: Overview of Quantum Calculations

11.2: Gaussian Basis Sets

11.3: Extended Basis Sets

11.4: Orbital Polarization Terms in Basis Sets

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11.1: Overview of Quantum Calculations

Multielectron Electronic Wavefunctions

We could symbolically write an approximate two-particle wavefunction as $\psi(r_1, r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_l) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_1, r_2)$. This new wavefunction must have the property that

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^* \psi(r_2, r_1) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.1.1}$$

Equation 11.1.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1, r_2) = e^{i\varphi} \psi(r_1, r_2)$$

so that

$$\left(e^{-i\varphi} \psi(r_1, r_2)^*\right) \left(e^{i\varphi} \psi(r_1, r_2)^*\right) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.1.2}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi} e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

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

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature, but the behavior of elections is that the wavefunction be antisymmetric with respect to permutation $(e^{i\varphi} = -1)$. A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\psi(r_2, r_1) = e^{i\varphi} \psi(r_1, r_2) = -\psi(r_1, r_2)$$

Blindly following the first statement of the Pauli Exclusion Principle, that each electron in a multi-electron atom **must** be described by a different spin-orbital, we try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) \tag{11.1.3}$$

After permutation of the electrons, this becomes

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1) \tag{11.1.4}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. However, an antisymmetric function must produce the same function multiplied by (–1) after permutation, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make a linear combination of functions. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 11.1.4 from the right-hand side of Equation 11.1.3 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1)]$$

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a Slater determinant.

The Slater determinant for the two-electron wavefunction for the ground state H_2 system (with the two electrons occupying the σ_{1s} molecular orbital)

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_{1s}(1)\alpha(1) & \sigma_{1s}(1)\beta(1) \\ \sigma_{1s}(2)\alpha(2) & \sigma_{1s}(2)\beta(2) \end{vmatrix}$$

We can introduce a shorthand notation for the arbitrary **spin-orbital**

$$\chi_{i\alpha}(\mathbf{r}) = \varphi_i\alpha$$

or

$$\chi_{i\beta}(\mathbf{r}) = \varphi_i\beta$$

as determined by the m_s quantum number. A shorthand notation for the determinant in Equation 8.6.4 is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = 2^{-\frac{1}{2}}\, Det|\chi_{1s\alpha}(\mathbf{r}_1)\alpha\chi_{1s\beta}(\mathbf{r}_2)\beta|$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is

$$(N!)^{-\frac{1}{2}}$$

for a system of N electrons.

The generalized Slater determinant for a multe-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{r}_1)\alpha & \chi_1(\mathbf{r}_1)\beta & \cdots & \chi_{N/2}(\mathbf{r}_1)\beta \\ \chi_1(\mathbf{r}_2)\alpha & \chi_2(\mathbf{r}_2)\beta & \cdots & \chi_{N/2}(\mathbf{r}_2)\beta \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_N)\alpha & \chi_2(\mathbf{r}_N)\beta & \cdots & \chi_{N/2}(\mathbf{r}_N)\beta \end{vmatrix} \tag{11.1.5}$$

In a modern *ab initio* electronic structure calculation on a closed shell molecule, the electronic Hamiltonian is used with a single determinant wavefunction. This wavefunction, Ψ, is constructed from molecular orbitals, ψ that are written as linear combinations of contracted Gaussian basis functions, φ

$$\varphi_j = \sum_k c_{jk}\psi_k \tag{11.1.6}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals. The exponential parameters in the STOs are optimized by calculations on small molecules using the nonlinear variational method and then those values are used with other molecules. The problem is to calculate the electronic energy from

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \tag{11.1.7}$$

or in bra-ket notation

$$E = \frac{\left\langle \Psi | \hat{H} | \Psi \right\rangle}{\langle \psi | \psi \rangle}$$

The the optimum coefficients c_{jk} for each molecular orbital in Equation 11.1.6 by using the Self Consistent Field Method and the Linear Variational Method to minimize the energy as was described previously for atoms.

The variational principle says an approximate energy is an upper bound to the exact energy, so the lowest energy that we calculate is the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single determinant wavefunction (e.g., Equation 11.1.5). This limit is called the *Hartree-Fock limit*, the energy

is the *Hartree-Fock energy*, the molecular orbitals producing this limit are called *Hartree-Fock orbitals*, and the determinant is the *Hartree-Fock wavefunction*.

Hartree-Fock Calculations

You may encounter the terms *restricted* and *unrestricted* Hartree-Fock. The above discussion pertains to a restricted HF calculation. In a restricted HF calculation, electrons with α spin are restricted or constrained to occupy the same spatial orbitals as electrons with β spin. This constraint is removed in an unrestricted calculation. For example, the spin orbital for electron 1 could be $\psi_A(r_1)\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(r_2)\beta(2)$, where both the spatial molecular orbital and the spin function differ for the two electrons. Such spin orbitals are called *unrestricted*. If both electrons are constrained to have the same spatial orbital, e.g. $\psi_A(r_1)\alpha(1)$ and $\psi_A(r_2)\beta(2)$, then the spin orbital is said to be *restricted*. While unrestricted spin orbitals can provide a better description of the electrons, twice as many spatial orbitals are needed, so the demands of the calculation are much higher. Using unrestricted orbitals is particular beneficial when a molecule contains an odd number of electrons because there are more electrons in one spin state than in the other.

Example 11.1.1 : Carbon Monoxide

It is well known that carbon monoxide is a poison that acts by binding to the iron in hemoglobin and preventing oxygen from binding. As a result, oxygen is not transported by the blood to cells. Which end of carbon monoxide, carbon or oxygen, do you think binds to iron by donating electrons? We all know that oxygen is more electron-rich than carbon (8 vs 6 electrons) and more electronegative. A reasonable answer to this question therefore is *oxygen*, but experimentally it is carbon that binds to iron.

A quantum mechanical calculation done by Winifred M. Huo, published in J. Chem. Phys. 43, 624 (1965), provides an explanation for this counter-intuitive result. The basis set used in the calculation consisted of 10 functions: the ls, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of C and O. Ten molecular orbitals (mo's) were defined as linear combinations of the ten atomic orbitals (Equation 11.1.6. The ground state wavefunction Ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 11.1.7 gives the energy of the ground state, where the denominator accounts for the normalization requirement. The coefficients C_{kj} in the linear combination are determined by the variational method to minimize the energy. The solution of this problem gives the following equations for the molecular orbitals. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

- $1s \approx 0.941 s_o$. The 1 says this is the first σ orbital. The σ says it is symmetric with respect to reflection in the plane of the molecule. The large coefficient, 0.94, means this is essentially the 1s atomic orbital of oxygen. The oxygen 1s orbital should have a lower energy than that of carbon because the positive charge on the oxygen nucleus is greater.
- $2s \approx 0.921 s_c$. This orbital is essentially the 1s atomic orbital of carbon. Both the 1σ and 2σ are "nonbonding" orbitals since they are localized on a particular atom and do not directly determine the charge density between atoms.
- $3s \approx (0.722 s_o + 0.182 p_{zo}) + (0.282 s_c + 0.162 p_{zc})$. This orbital is a "bonding" molecular orbital because the electrons are delocalized over C and O in a way that enhances the charge density between the atoms. The 3 means this is the third σ orbital. This orbital also illustrates the concept of hybridization. One can say the 2s and 2p orbitals on each atom are hybridized and the molecular orbital is formed from these hybrids although the calculation just obtains the linear combination of the four orbitals directly without the *à priori* introduction of hybridization. In other words, hybridization just falls out of the calculation. The hybridization in this bonding LCAO increases the amplitude of the function in the region of space between the two atoms and decreases it in the region of space outside of the bonding region of the atoms.
- $4s \approx (0.372 s_c + 0.12 p_{zc}) + (0.542 p_{zo} - 0.432 s_0)$. This molecular orbital also can be thought of as being a hybrid formed from atomic orbitals. The hybridization of oxygen atomic orbitals, because of the negative coefficient with $2s_O$, decreases the electron density between the nuclei and enhances electron density on the side of oxygen facing away from the carbon atom. If we follow how this function varies along the internuclear axis, we see that near carbon the function is positive whereas near oxygen it is negative or possibly small and positive. This change means there must be a node between the two nuclei or at the oxygen nucleus. Because of the node, the electron density between the two nuclei is low so the electrons in this orbital do not serve to shield the two positive nuclei from each other. This orbital therefore is called an "antibonding" molecular orbital and the electrons assigned to it are called antibonding electrons. This orbital is the antibonding partner to the 3σ orbital.

- $1\pi \approx 0.322p_{xc} + 0.442p_{xo} \text{and} 2\pi \approx 0.322p_{yc} + 0.442p_{yo}$ These two orbitals are degenerate and correspond to bonding orbitals made up from the p_x and p_y atomic orbitals from each atom. These orbitals are degenerate because the x and y directions are equivalent in this molecule. π tells us that these orbitals are antisymmetric with respect to reflection in a plane containing the nuclei.
- $5\sigma \approx 0.382_{sC} - 0.382_{pC} - 0.292p_{zO}$. This orbital is the sp hybrid of the carbon atomic orbitals. The negative coefficient for $2p_C$ puts the largest amplitude on the side of carbon away from oxygen. There is no node between the atoms. We conclude this is a nonbonding orbital with the nonbonding electrons on carbon. This is not a "bonding" orbital because the electron density between the nuclei is lowered by hybridization. It also is not an antibonding orbital because there is no node between the nuclei. When carbon monoxide binds to Fe in hemoglobin, the bond is made between the C and the Fe. This bond involves the donation of the 5σ nonbonding electrons on C to empty d orbitals on Fe. Thus molecular orbital theory allows us to understand why the C end of the molecule is involved in this electron donation when we might naively expect O to be more electron-rich and capable of donating electrons to iron.

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11.2: Gaussian Basis Sets

A basis set in theoretical and computational chemistry is a set of functions (called **basis functions**) which are combined in linear combinations (generally as part of a quantum chemical calculation) to create molecular orbitals. For convenience these functions are typically atomic orbitals centered on atoms, but can theoretically be any function; plane waves are frequently used in materials calculations.

The Variational Method and Basis Sets

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$\psi_i = \sum_j c_{ij}\varphi_j \tag{11.2.1}$$

The linear variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in chemical structure.

> *Selecting the ab initio model for a chemical system is almost always involves a trade-off between accuracy and computational cost. More accurate methods and larger basis sets make jobs run longer.*

In modern computational chemistry, quantum chemical calculations are typically performed using a finite set of basis functions. In these cases, the wavefunctions of the system in question are represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions in the basis set used.

The molecular spin-orbitals that are used in the Slater determinant usually are expressed as a linear combination of some chosen functions, which are called *basis functions*. This set of functions is called the *basis set*. The fact that one function can be represented by a linear combination of other functions is a general property. All that is necessary is that the basis functions *span-the-space*, which means that the functions must form a complete set and must be describing the same thing. For example, spherical harmonics cannot be used to describe a hydrogen atom radial function because they do not involve the distance r, but they can be used to describe the angular properties of anything in three-dimensional space.

This span-the-space property of functions is just like the corresponding property of vectors. The unit vectors ($\vec{x}$, $\vec{y}$, $\vec{z}$) describe points in space and form a complete set since any position in space can be specified by a linear combination of these three unit vectors. These unit vectors also could be called basis vectors.

? Exercise 11.2.1 : "Spanning the Space"

Explain why the unit vectors ($\vec{x}$, $\vec{y}$) do not form a complete set to describe your (three-dimensional) classroom.

Just as we discussed for atoms, parameters in the basis functions and the coefficients in the linear combination can be optimized in accord with the Variational Principle to produce a self-consistent field (SCF) for the electrons. This optimization means that the ground state energy calculated with the wavefunction is minimized with respect to variation of the parameters and coefficients

defining the function. As a result, that ground state energy is larger than the exact energy, but is the best value that can be obtained with that wavefunction.

Slater Type Orbitals (STOs)

Intuitively one might select hydrogenic atomic orbitals as the basis set for molecular orbitals. After all, molecules are composed of atoms, and hydrogenic orbitals describe atoms exactly if the electron-electron interactions are neglected. At a better level of approximation, the nuclear charge that appears in these functions can be used as a variational parameter to account for the shielding effects due to the electron-electron interactions. Also, the use of atomic orbitals allows us to interpret molecular properties and charge distributions in terms of atomic properties and charges, which is very appealing since we picture molecules as composed of atoms. As described in the previous chapter, calculations with hydrogenic functions were not very efficient so other basis functions, **Slater-type atomic orbitals (STOs)**, were invented.

A minimal basis set of STOs for a molecule includes only those STOs that would be occupied by electrons in the atoms forming the molecule. As with most variational method calculations, a larger basis set improves the accuracy of the calculations by providing more variable parameters to produce a better approximate wavefunction. However, this is at the expense of increased computational time (i.e., calculation "cost" or "expense"). STOs have the following radial part (the spherical harmonic functions are used to describe the angular part)

$$R(r) = Nr^{n-1}e^{-\zeta r}$$

where

- n is a natural number that plays the role of principal quantum number, $n = 1,\ 2,\ \ldots,$
- N is a normalizing constant,
- r is the distance of the electron from the atomic nucleus, and ζ is a constant related to the effective charge of the nucleus, the nuclear charge being partly shielded by electrons. Historically, the effective nuclear charge was estimated by Slater's rules.

Double-zeta basis Sets

One can use more than one STO to represent one atomic orbital, as shown in Equation 11.2.2, and rather than doing a nonlinear variational calculation to optimize each ζ value, use two STOs with different ζ variables. The linear variation calculation then will produce the coefficients (C_1 and C_2) for these two functions in the linear combination that **best** describes the charge distribution in the molecule (for the ground state). The function with the large zeta accounts for charge near the nucleus, while the function with the smaller zeta accounts for the charge distribution at larger values of the distance from the nucleus. This expanded basis set is called a **double-zeta basis set**.

$$R_{2s}(r) = C_1 re^{-\zeta_1 r} + C_2 re^{-\zeta_2 r} \tag{11.2.2}$$

The use of double zeta functions in basis sets is especially important because without them orbitals of the same type are constrained to be identical even though in the molecule they may be chemically inequivalent. For example, in acetylene the p_z orbital along the internuclear axis is in a quite different chemical environment and is being used to account for quite different bonding than the p_x and p_y orbitals. With a double zeta basis set the p_z orbital is not constrained to be the same size as the p_x and p_y orbitals.

Example 11.2.1

Explain why the p_x, p_y, and p_z orbitals in a molecule might be constrained to be the same in a single-zeta basis set calculation, and how the use of a double-zeta basis set would allow the p_x, p_y, and p_z orbitals to differ.

Gaussian Orbitals

Although any basis set that sufficiently spans the space of electron distribution could be used, the concept of Molecular Orbitals as **Linear Combinations of Atomic Orbitals** **(LCAO)** suggests a very natural set of basis functions: AO-type functions centered on each nuclei. One obvious choice are the exact hydrogen AO's, known as **Slater-type orbitals (STO)** -describing the radial component of the functions. However, the computation of the integrals is greatly simplified by using **Gaussian-type orbitals (GTO)** for basis functions.

While the STO basis set was an improvement over hydrogenic orbitals in terms of computational efficiency, representing the STOs with Gaussian functions produced further improvements that were needed to accurately describe molecules. A Gaussian basis

function has the form shown in Equation 11.2.3. Note that in all the basis sets, only the radial part of the orbital changes, and the spherical harmonic functions are used in all of them to describe the angular part of the orbital.

$$G_{nlm}(r,\theta,\psi) = N_n \underbrace{r^{n-1}e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta,\psi)}_{\text{angular part}} \tag{11.2.3}$$

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at $r = 0$, and they fall off more rapidly at large values of r (Figure 11.2.1).

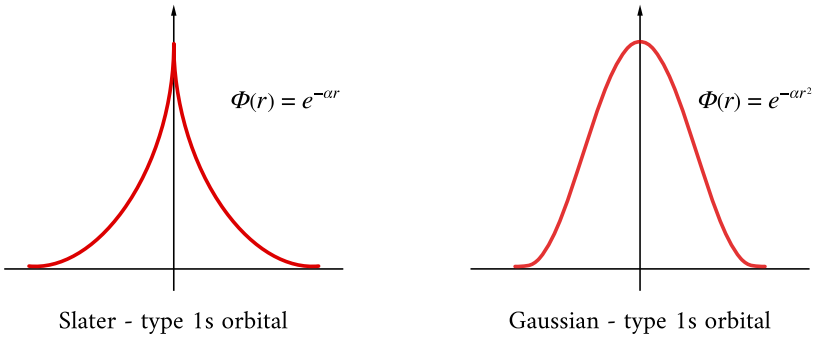


Figure 11.2.1 : Radial Dependence of Slater and Gaussian Basis Functions. (CC BY 4.0; Ümit Kaya via LibreTexts)

To compensate for this problem, each STO is replaced with a number of Gaussian functions with different values for the exponential parameter. These Gaussian functions form a *primitive Gaussian basis set*. Linear combinations of the primitive Gaussians are formed to approximate the radial part of an STO. This linear combination is not optimized further in the energy variational calculation, but rather is frozen and treated as a single function. The linear combination of **primitive Gaussian functions** is called a **contracted Gaussian function**. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials, so there is a net gain in the efficiency of the calculation.

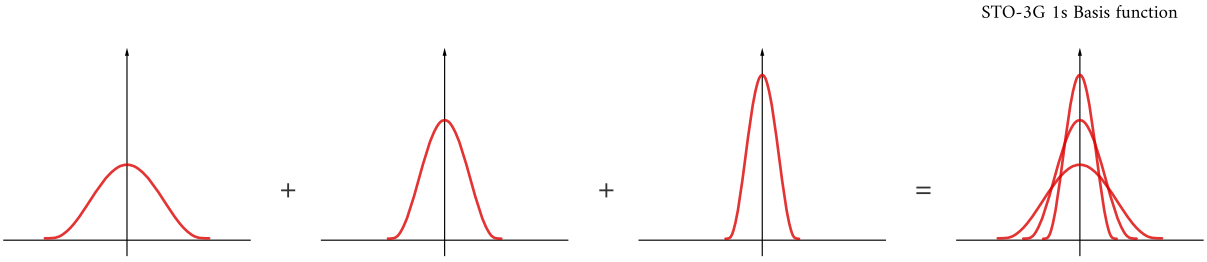


Figure 11.2.2 : To better represent the cusp in the electron density at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTOs (CGTO). The earliest CGTO basis sets, where constructed from N GTOs that best fit the desired STO. These are called STO-NG basis sets. (CC BY 4.0; Ümit Kaya via LibreTexts)

Gaussian basis sets are identified by abbreviations such as N-MPG*. N is the number of Gaussian primitives used for each inner-shell orbital. The hyphen indicates a split-basis set where the valence orbitals are double zeta. The M indicates the number of primitives that form the large zeta function (for the inner valence region), and P indicates the number that form the small zeta function (for the outer valence region). G identifies the set a being Gaussian. The addition of an asterisk to this notation means that a single set of Gaussian 3d polarization functions (discussed elsewhere) is included. A double asterisk means that a single set of Gaussian 2p functions is included for each hydrogen atom.

For example, 3G means each STO is represented by a linear combination of three primitive Gaussian functions. 6-31G means each inner shell (1s orbital) STO is a linear combination of 6 primitives and each valence shell STO is split into an inner and outer part (double zeta) using 3 and 1 primitive Gaussians, respectively (see Table 11.2.1 for other examples).

Table 11.2.1 : Different Gaussian Basis sets

Basis set	# functions	Basis set	# functions	Basis set	# functions

Basis set	# functions		Basis set	# functions		Basis set	# functions
STO-3G	5		6-31G	9		6-311G	13
3-21G	9		6-31G*	15		6-311G*	18*
4-31G	9		6-31+G*	19		6-311+G*	22*

Example 11.2.2

The 1s Slater-type orbital $S_1(r) = \sqrt{4\zeta_1 e^{-\zeta_1 r}}$ with $\zeta_1 = 1.24$ is represented as a sum of three primitive Gaussian functions,

$$S_G(r) = \sum_{j=1}^{3} C_j e^{-\alpha_j r^2}$$

This sum is the contracted Gaussian function for the STO.

a. Make plots of the STO and the contracted Gaussian function on the same graph so they can be compared easily. All distances should be in units of the Bohr radius. Use the following values for the coefficients, C, and the exponential parameters, α.

index j	α_j	C_j
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

b. Change the values of the coefficients and exponential parameters to see if a better fit can be obtained.
c. Comment on the ability of a linear combination of Gaussian functions to accurately describe a STO.

Summary

When molecular calculations are performed, it is common to use a basis composed of a finite number of atomic orbitals (Equation 11.2.1), centered at each atomic nucleus within the molecule (linear combination of atomic orbitals ansatz). These atomic orbitals are well described with Slater-type orbitals (STOs), as STOs decay exponentially with distance from the nuclei, accurately describing the long-range overlap between atoms, and reach a maximum at zero, well describing the charge and spin at the nucleus. STOs are computationally difficult and it was later realized by Frank Boys that these Slater-type orbitals could in turn be approximated as linear combinations of Gaussian orbitals instead. Because it is easier to calculate overlap and other integrals with Gaussian basis functions, this led to huge computational savings

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11.3: Extended Basis Sets

Today, there are hundreds of basis sets composed of Gaussian Type Orbitals (GTOs). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain literally dozens to hundreds of basis functions on each atom.

Minimum Basis sets

A minimum basis set is one in which a **single** basis function is used for each orbital in a Hartree-Fock calculation on the atom. However, for atoms such as lithium, basis functions of p type are added to the basis functions corresponding to the 1s and 2s orbitals of each atom. For example, each atom in the first row of the periodic system (Li - Ne) would have a basis set of five functions (two s functions and three p functions).

> *In a minimum basis set, a single basis function is used for each atomic orbital on each constituent atom in the system.*

The most common minimal basis set is STO-nG, where n is an integer. This n value represents the number GTOs used to approximate the Slater Type orbital (STO) for both core and valence orbitals. Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper (less calculations requires) than the larger basis sets discussed below. Commonly used minimal basis sets of this type are: STO-3G, STO-4G, and STO-6G.

Two is Often Better than One

Minimal basis sets are not flexible enough for accurate representation of, which requires the use multiple functions to represent each atomic orbital. The distribution of the electron density of valence electrons is better represented by the sum of two orbitals with different "effective charges". This is a double-ζ basis sets and includes split-valence set (inner and valence) and linear combination of two orbitals of same type, but with different effective charges (i.e., ζ). This flexibility can be used to generate atomic orbital of adjustable sizes.

For example, the double-zeta basis set allows us to treat each orbital separately when we conduct the Hartree-Fock calculation.

$$\phi_i = a_1 \phi_{2s}^{STO}(r, \zeta_1) + a_2 \phi_{2s}^{STO}(r, \zeta_2) \tag{11.3.1}$$

The 2s atomic orbital approximated as a sum of two STOs. The two equations are the same except for the value of ζ which accounts for how large the orbital is. The constants a_1 and a_2 determines how much each STO contributes to the final atomic orbital, which will vary depending on the type of atom that the atomic orbit (i.e., hydrogen and lithium orbitals will have different a_1, a_2, ζ_1, and ζ_2 values).

Extended Basis Sets

The triple and quadruple-zeta basis sets work the same way, except use three and four STOs instead of two like in 11.3.1. The typical trade-off applies here as well, better accuracy, however with more expensive calculations. There are several different types of **extended basis sets** including: n split-valence, n polarized sets, n diffuse sets, and n correlation consistent sets. The notation of this sort of basis set (with a Gaussian basis) is

$$N - MPG$$

for describing split-valence basis set. N is the number of Gaussian functions describing inner-shell orbitals, while the hyphen denotes a split-valence set. M and P designate the number of Gaussian functions used to fit the two orbitals of the valence shell:

- M corresponds to number of Gaussian functions used to describe the smaller orbital
- P corresponds to number of Gaussian functions used to describe the larger orbital (e.g., 6-31G and 3-21G).

A minimal basis set is when one basis function for each atomic orbital in the atom, while a double-ζ, has two two basis functions for each atomic orbital. Correspondingly, a triple and quadruple-ζ set had three and four basis functions for each atomic orbital, respectively. Higher order basis set have been constructed too, e.g., 5Z, 6Z,)..

There are hundreds of basis sets composed of Gaussian-type orbitals (Figure Figure 11.3.1). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain dozens to hundreds of basis functions on each atom.

Figure 11.3.1 : Commonly used split-valence basis sets

3-21G	3-21G	3-21G	3-21G* - Polarized	3-21+G - Diffuse functions	3-21+G* - With polarization and diffuse functions
4-21G	4-31G	4-31G	4-31G	4-31G	
6-21G	6-31G	6-31G*	6-31+G*	6-31G(3df, 3pd)	6-311G
6-311G	6-311G*	6-311+G*			

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11.4: Orbital Polarization Terms in Basis Sets

Polarization functions denoted in Pople's sets by an asterisk. Two asterisks, indicate that polarization functions are also added to light atoms (hydrogen and helium). n Polarization functions have one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1 s atomic orbital. When polarization is added to this basis set, a p -function is also added to the basis set. The 6-31G** is synonymous to 6-31 G(d,p).

The use of a minimal basis set with fixed zeta parameters severely limits how much the electronic charge can be changed from the atomic charge distribution to describe molecules and chemical bonds. This limitation is removed if STOs with larger n values and different spherical harmonic functions, the $Y_l^m(\theta, \varphi)$ in the definition of STO's are included. Adding such functions is another way to expand the basis set and obtain more accurate results. Such functions are called polarization functions because they allow for charge polarization away form the atomic distribution to occur.

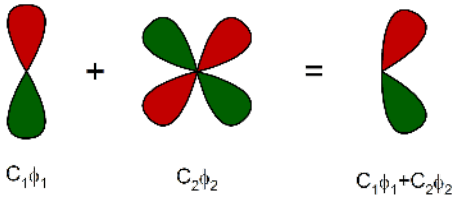


Figure 11.4.1 : A d-polarization function added to a p orbital. (CC-BY-SA-3.0; Rifleman 82)

The most common addition to minimal basis sets is probably the addition of polarization functions, denoted (in the names of basis sets developed by Pople) by an asterisk, *. Two asterisks, **, indicate that polarization functions are also added to light atoms (hydrogen and helium). These are auxiliary functions with one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1s atomic orbital. When polarization is added to this basis set, a p-function is also added to the basis set. This adds some additional needed flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen nucleus.

This is an important result when considering accurate representations of bonding between atoms, because the very presence of the bonded atom makes the energetic environment of the electrons spherically asymmetric. Similarly, d-type functions can be added to a basis set with valence p orbitals, and f-functions to a basis set with d-type orbitals, and so on. Another, more precise notation indicates exactly which and how many functions are added to the basis set, such as (d, p).

Diffuse Functions

Another common addition to basis sets is the addition of **diffuse functions**, denoted in Pople-type sets by a plus sign, +, and in Dunning-type sets by "aug" (from "augmented"). Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). These are very shallow Gaussian basis functions, which more accurately represent the "tail" portion of the atomic orbitals, which are distant from the atomic nuclei. These additional basis functions can be important when considering anions and other large, "soft" molecular systems.

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12.1: Quantum Mechanics for Nuclear Motion (Harmonic Oscillator and Rigid Rotor)

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