

CH 231: PHYSICAL CHEMISTRY I, QUANTUM MECHANICS



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PChem, Quantum Mechanics

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CHAPTER OVERVIEW

1: Quantum Mechanics and Atomic Structure

Quantum mechanics is a fundamental branch of physics concerned with processes involving small particles (e.g, atoms and photons). Such processes are said to be quantized with properties that are observed only in integer multiples of the Planck constant. This is utterly inexplicable in classical physics which is a continuum approach.

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1.1: The Wave Theory of Light

Learning Objectives

- to learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.



Figure 1.1.1 A Wave in Water When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 1.1.1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

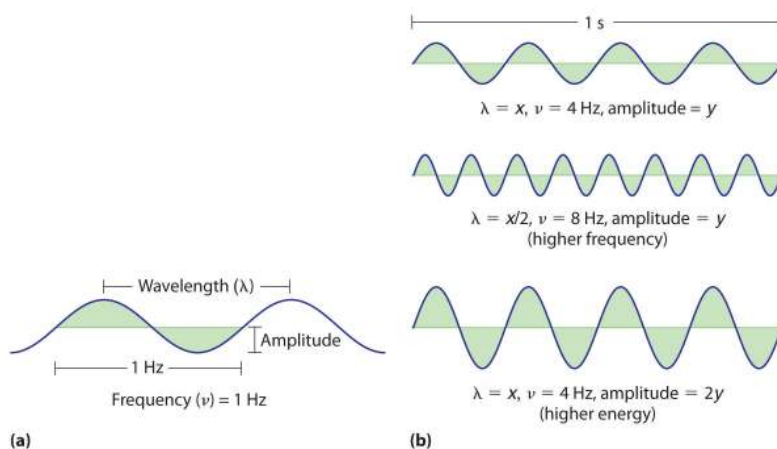


Figure 1.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν , in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 1.1.2). As you may have noticed in Figure 1.1.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the wavelength (λ), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. λ is the lowercase Greek lambda, and ν is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν), the number of oscillations (i.e., of a wave) that pass a particular point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The

usual units are oscillations per second ($1/s = s^{-1}$), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation. The amplitude (the vertical height of a wave, which is defined as half the peak-to-trough height), or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 1.1.2, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), the distance traveled by a wave per unit time, which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(\text{wavelength})(\text{frequency}) = \text{speed}$$

$$\lambda \nu = v \quad (1.1.1a)$$

$$\left(\frac{\text{meters}}{\text{wave}} \right) \left(\frac{\text{wave}}{\text{second}} \right) = \frac{\text{meters}}{\text{second}} \quad (1.1.1b)$$

Be careful not to confuse the symbols for the speed, v , with the frequency, ν . Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as electromagnetic radiation, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 1.1.3). Some forms of electromagnetic radiation are shown in Figure 1.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is the speed with which all forms of electromagnetic radiation travel in a vacuum, a fundamental physical constant with a value of 2.99792458×10^8 m/s (which is about 3.00×10^8 m/s or 1.86×10^5 mi/s). This is about a million times faster than the speed of sound.

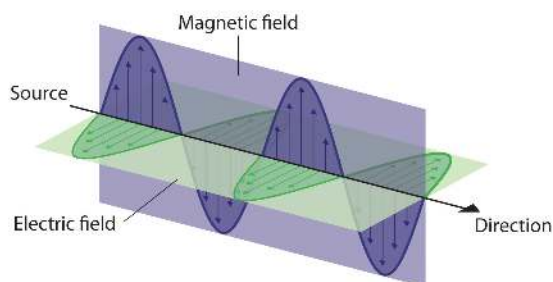


Figure 1.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 1.1.4 and Table 1.1.1, the wavelengths of familiar electromagnetic radiation range from 10^1 m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with c in Equation 6.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda \nu$$

$$\nu = \frac{c}{\lambda} \quad (1.1.2)$$

For example, the frequency of radio waves is about 10^8 Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7×10^{-7} m (700 nm, or 4.3×10^{14} Hz) and 4×10^{-7} m (400 nm, or 7.5×10^{14} Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly when frequency decreases, the wavelength increases.

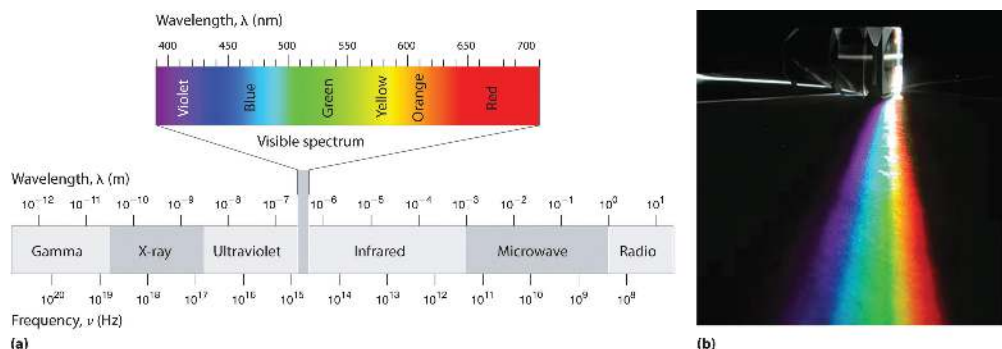


Figure 1.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within this visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 1.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 1.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10 ⁻¹²	gamma ray
angstrom	Å	10 ⁻¹⁰	x-ray
nanometer	nm	10 ⁻⁹	x-ray
micrometer	μm	10 ⁻⁶	infrared
millimeter	mm	10 ⁻³	infrared
centimeter	cm	10 ⁻²	microwave
meter	m	10 ⁰	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu \quad (1.1.3)$$

$$E \propto \frac{1}{\lambda} \quad (1.1.4)$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

The energy of electromagnetic radiation **increases** with **increasing** frequency and **decreasing** wavelength.

✓ Example 1.1.1

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 1.1.2 to calculate the wavelength in meters.

Solution:

From Equation 1.1.2, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is $2.998 \times 10^8 \text{ m/s}$:

$$\lambda\nu = c = 2.998 \times 10^8 \text{ m/s}$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{\nu} = \left(\frac{2.988 \times 10^8 \text{ m/s}}{101.1 \text{ MHz}} \right) \left(\frac{1}{10^6 \text{ s}^{-1}} \right) = 2.965 \text{ m}$$

? Exercise 1.1.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Click to Check Answer

8.45 mm

External Videos & Examples

- [Light Speed, Wavelength and Frequency](#) by Doc Schuster - Explains wavelength and frequency
- [Waves in General](#) by JaHu Productions - a bit faster. Also discusses sound waves
- [Calculating Frequency Given Wavelength](#) - Johnny Cantrell
- [Wavelength Frequency Problems](#) - Cayer Chem
- [Quantum Chemistry](#) - Ohio State
- [Quantum Chemistry Quizzes](#) - mhe education
- [AP Chemistry Chapter 7 Review](#) - Science Geek
- [Quantum Theory of the Atom Practice Quiz](#) - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 6.

Summary

- Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation.

A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A wave is a periodic oscillation by which energy is transmitted through space. All waves are periodic, repeating regularly in both space and time. Waves are characterized by several interrelated properties: wavelength (λ), the distance between successive waves; frequency (ν), the number of waves that pass a fixed point per unit time; speed (v), the rate at which the wave propagates through space; and amplitude, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. Electromagnetic radiation consists of two perpendicular waves, one electric and one magnetic, propagating at the speed of light (c). Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

Contributors

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1.2: Planck's Quantum Theory

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.

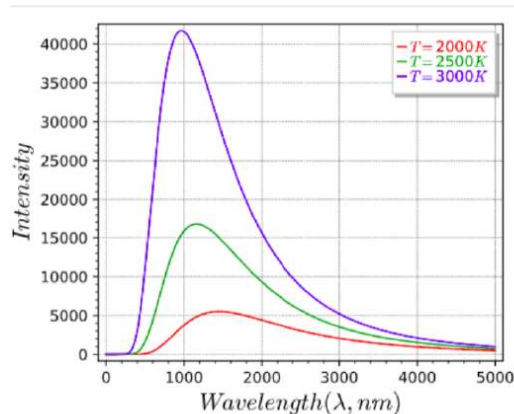


Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases,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

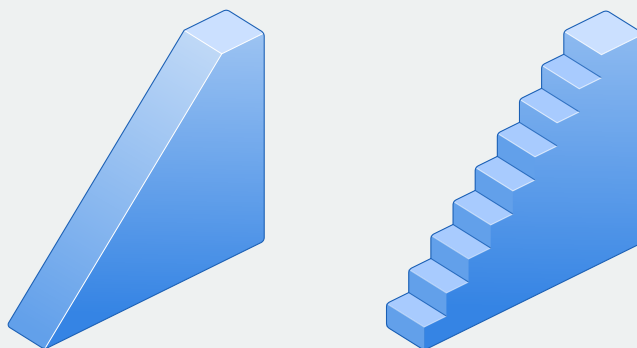
Quantizing Electrons in the Radiator

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 (gravitational) 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 his famous equation:

$$E = h\nu \quad (1.2.1)$$

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

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

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

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

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

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

$$d\rho(\nu, T) = \rho_\nu(T) d\nu \quad (1.2.2)$$

$$= \frac{2h\nu^3}{c^2} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} d\nu \quad (1.2.3)$$

with

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

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

$$\rho(\lambda, T) = \frac{2hc^2}{\lambda^5} \left(\frac{1}{\frac{hc}{\lambda k_B T} - 1} \right) \quad (1.2.4)$$

With a wavelength of maximum energy density at:

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

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

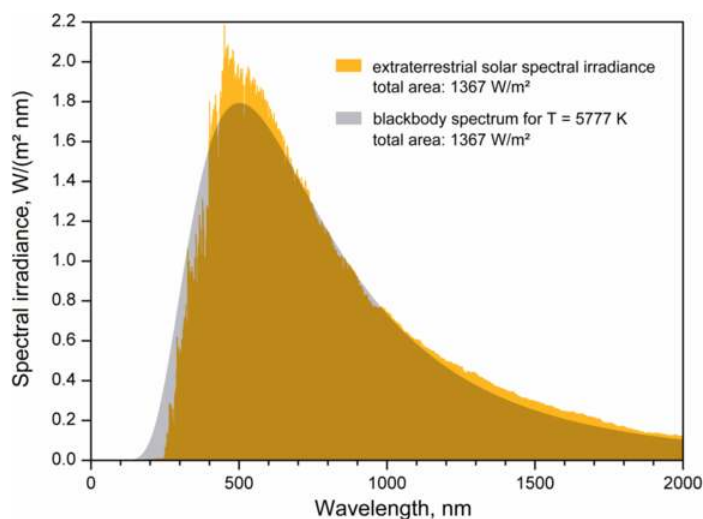


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; [Sch](#)).

📌 Max Planck (1858–1947)

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



MAX-PLANCK-GESELLSCHAFT

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

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

? Exercise 1.2.1

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

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

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

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

$$E = nh\nu$$

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

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

Summary

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

Contributors and Attributions

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1.3: The Photoelectric Effect

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).

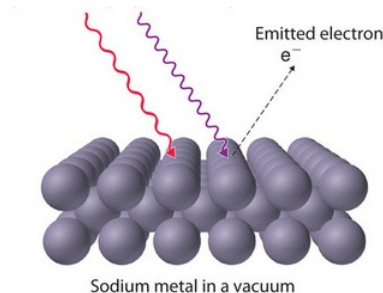


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

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.

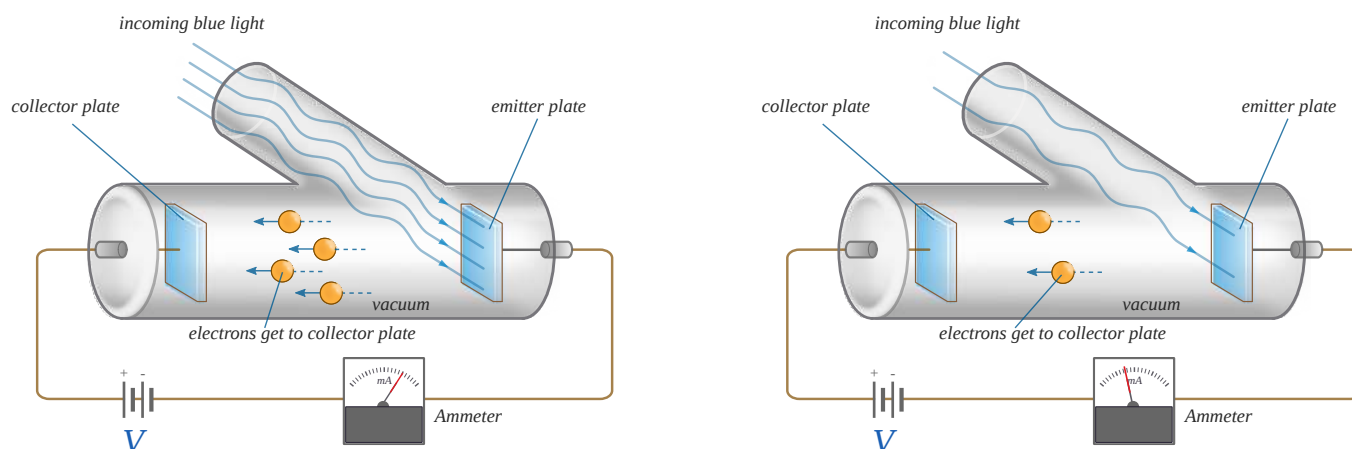


Figure 1.3.2: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit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

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

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).

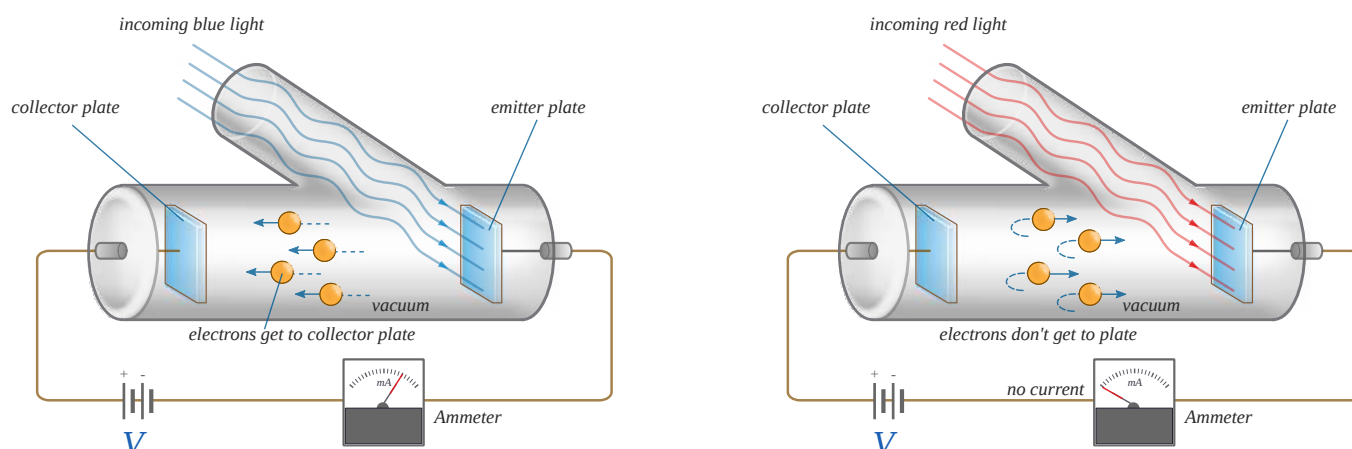


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector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

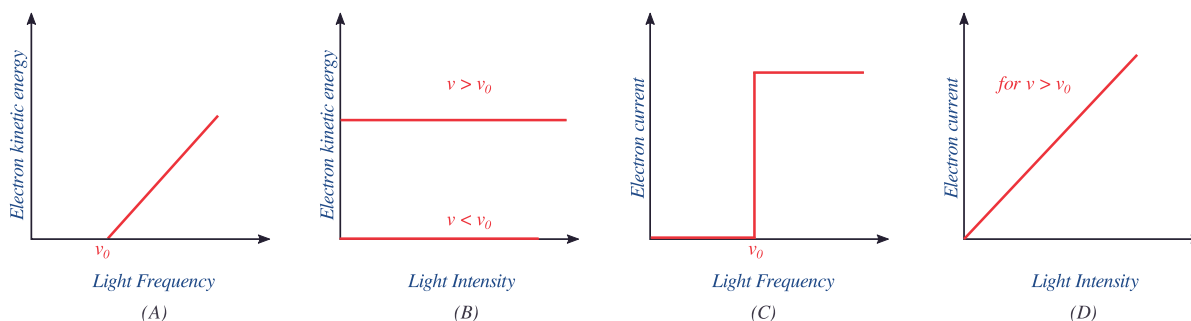


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the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

$$KE = h\nu - \Phi \quad (1.3.1)$$

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

$$eV_{stop} = h\nu - \Phi \quad (1.3.2)$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and V_{stop} plotted as a function of frequency, the slope of the line should be $\frac{h}{e}$ (Figure 1.3.4A). It is also clear that there is a minimum light frequency for a given metal ν_0 , that for which the quantum of energy is equal to Φ (Equation 1.3.1). Light below that frequency, no matter how bright, will not eject electrons.

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

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

photoelectrons are observed. This frequency is measured in units of Hertz (1/second) in honor of the discoverer of the photoelectric effect.

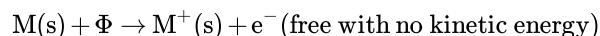
Einstein's Equation 1.3.1 explains the properties of the photoelectric effect quantitatively. A strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy $E = h\nu$ can be transferred to an actual particle (an electron), imparting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

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

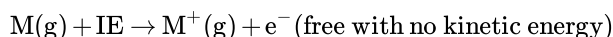
Einstein's simple explanation (Equation 1.3.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also led to the creation of a 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**).



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.



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

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

Strategy

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

Solution for (a)

Photon energy is given by

$$E = h\nu$$

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

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

Combining these two equations gives the useful relationship

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

Now substituting known values yields

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

Converting to eV, the energy of the photon is

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

Solution for (b)

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

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

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.

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1.4: The Atomic Emission 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.
- Describe Rydberg's theory for the hydrogen spectra.
- Interpret the hydrogen spectrum in terms of the energy states of electrons.

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 Spectrum

The spectrum of *hydrogen*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Angstrom in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Angstrom, 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).

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 ([blackbody radiation](#), for example, 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.

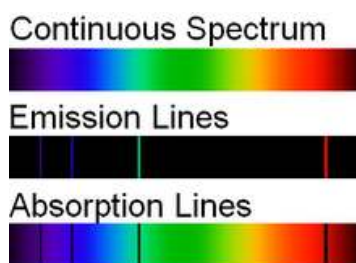


Figure 1.4.1 : Continuous spectrum and two types of line spectra. from Wikipedia.

In 1802, William Wollaston in England had discovered (perhaps by using a thinner slit or a better prism) that in fact the solar spectrum itself 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. Fraunhofer 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

Designation	Element	Wavelength (nm)
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

Fraunhofer Absorption Lines

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.

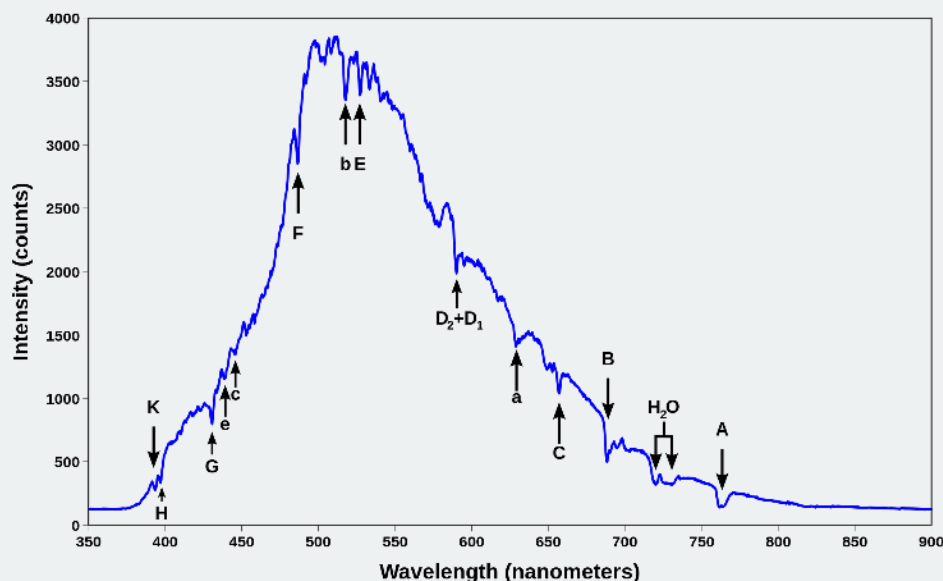


Figure 1.4.2: Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. from Wikipedia.

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, Kirchhoff 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.

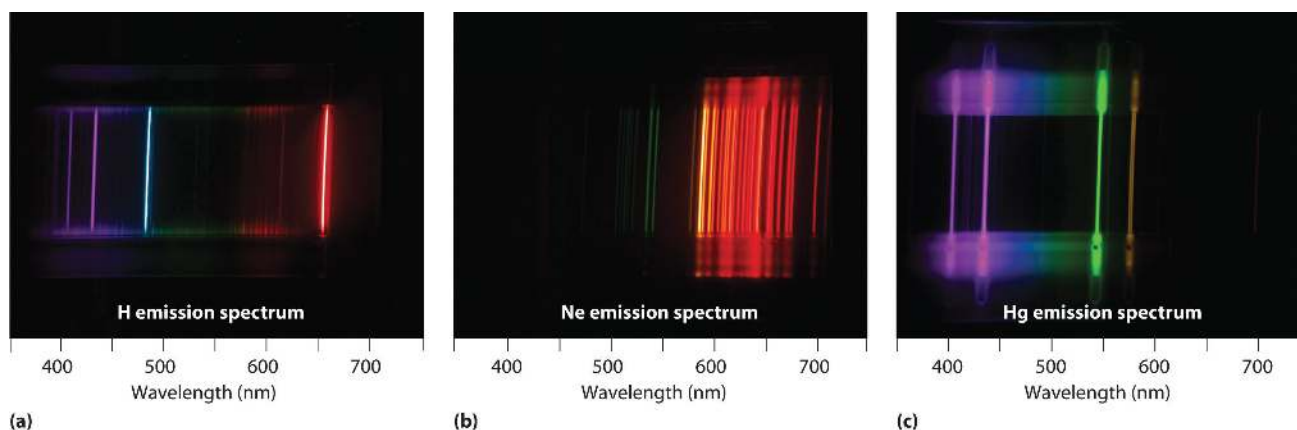


Figure 1.4.3: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) helium; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below.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

The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specific atom (in contrast 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: The visible hydrogen emission spectrum lines in the Balmer series. The red line at the right is the H_{α} line and the two leftmost lines are considered to be ultraviolet as they have wavelengths less than 400 nm. from Wikipedia.

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Angstrom 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 formula:

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

where

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

The first four wavelengths of Equation 1.4.1 (with $n_2=3,4,5,6$) were in excellent agreement with the experimental lines from Angstrom (Table 1.4.2). Balmer predicted that other lines exist in the infrared that correspond to $n = 7, 8$, etc., 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 resents 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 (Figure 1.4.4). This behavior converges to a highest possible energy as Example 1.4.1 demonstrates. If the lines are

plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure 1.4.4; these lines are called the **Balmer series**.

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

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \quad (1.4.2)$$

where

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

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.

📌 Wavenumbers

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda \nu = c \quad (1.4.3)$$

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 $1/\text{s}$ - 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

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \quad (1.4.4)$$

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

$$E = \frac{hc}{\lambda} \quad (1.4.5)$$

$$E = hc \times \frac{1}{\lambda} \quad (1.4.6)$$

$$E = hc\tilde{\nu} \quad (1.4.7)$$

$$E \propto \tilde{\nu} \quad (1.4.8)$$

✓ Balmer Series

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

Solution

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

$$\lambda_{\text{longest}} = (364.56 \text{ nm}) \left(\frac{9}{9-4} \right) \quad (1.4.9)$$

$$\lambda_{\text{longest}} = (364.56 \text{ nm}) (1.8) = 656.2 \text{ nm} \quad (1.4.10)$$

This is also known as the H_α line of atomic hydrogen and is bright red (Figure 1.4.4).

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

$$\lambda_{shortest} = \lim_{n_2 \rightarrow \infty} (364.56 \text{ nm}) \left(\frac{n_2^2}{n_2^2 - 4} \right) \quad (1.4.11)$$

This can be solved via [L'Hôpital's Rule](#), or alternatively the limit can be expressed via the equally useful energy expression (Equation 1.4.2) and simply solved:

$$\tilde{\nu}_{greatest} = \lim_{n_2 \rightarrow \infty} R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \quad (1.4.12)$$

$$\tilde{\nu}_{greatest} = \lim_{n_2 \rightarrow \infty} R_H \left(\frac{1}{4} \right) = 27,434 \text{ cm}^{-1} \quad (1.4.13)$$

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.

The Generalized Rydberg Equation

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 (Equation 1.4.2). 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 general equation is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1.4.14)$$

where

- R_H is the *Rydberg* constant and is equal to $109,737 \text{ cm}^{-1}$.
- 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 $n_1^2 = 2$. Is there a different series with the following formula (e.g., $n_1 = 1$)?

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad (1.4.15)$$

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

Table 1.4.3: The Lyman Series of Hydrogen Emission Lines ($n_1 = 1$)

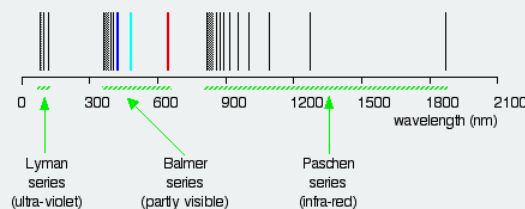
n_2	2	3	4	5	...
λ (nm)	121	102	97	94	...
$\tilde{\nu}$ (cm ⁻¹)	82,2291	97,530	102,864	105,332	...

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 $n_2^2 = 3$ and $n_1^2 = 4, 5, 6, 7, \dots$ is called **Paschen series**.

Note

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 $n_1 = 6$



The spectral series of hydrogen based of the Rydberg Equation (on a logarithmic scale).

✓ Example 1.4.2: 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:

- Substitute the appropriate values into Equation 1.5.1 (the Rydberg equation) and solve for λ .
- Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = \mathfrak{R} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1.4.16)$$

A For the Lyman series, $n_1 = 1$.

$$\frac{1}{\lambda} = \mathfrak{R} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.097 \times m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) = 8.228 \times 10^6 m^{-1} \quad (1.4.17)$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly $200 - 5,000 \text{ cm}^{-1}$, the visible from $11,000$ to $25,000 \text{ cm}^{-1}$ and the UV between $25,000$ and $100,000 \text{ cm}^{-1}$. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1} .

$$\tilde{\nu} = \frac{1}{\lambda} = 8.228 \times 10^6 \text{ m}^{-1} \left(\frac{m}{100 \text{ cm}} \right) = 82,280 \text{ cm}^{-1} \quad (1.4.18)$$

and

$$\lambda = 1.215 \times 10^{-7} \text{ m} = 122 \text{ nm} \quad (1.4.19)$$

This emission line is called Lyman alpha. It 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 O₂ molecules to O atoms which react with other O₂ molecules to form stratospheric ozone

B This wavelength is in the ultraviolet region of the spectrum.

? Exercise 1.4.2: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $(n_1 = 5)$ orbit. 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: $4.65 \times 10^3 \text{ nm}$; 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.

Contributors and Attributions

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1.5: de Broglie's Postulate

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:

$$\lambda = \frac{h}{p} \quad (1.5.1)$$

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 relativity](#). In general, a particle of mass m and momentum p has an energy

$$E = \sqrt{p^2 c^2 + m^2 c^4} \quad (1.5.2)$$

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

$$h\nu = \frac{hc}{\lambda} = pc \quad (1.5.3)$$

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 $9.109383 \times 10^{-31} \text{ g}$ and the velocity is obtained from the given kinetic energy of 1000 eV:

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

Solve for momentum

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

convert to SI units

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

expanding definition of joule into base SI units and cancel

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

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

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

? Exercise 1.6.1 : Baseball Waves

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

Answer

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

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

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

The de Broglie wavelength of this fast ball is:

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

? 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?

- The electron
- The proton
- 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: The Heisenberg Uncertainty Principle

Learning Objectives

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

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

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

Probability

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

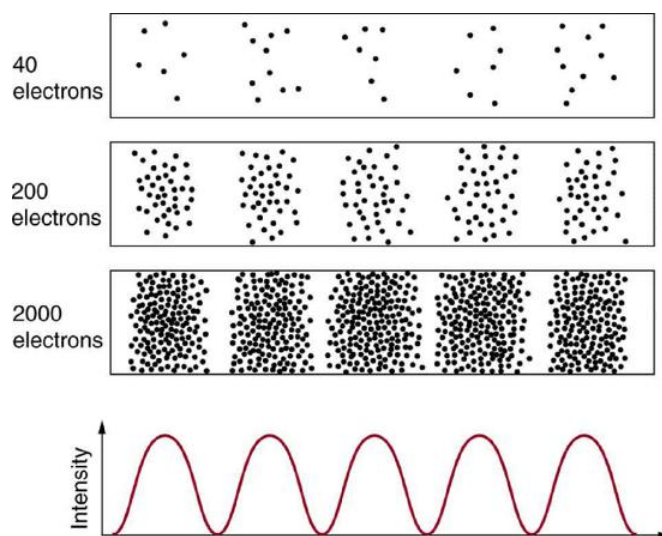


Figure 1.9.1 : The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength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

After de Broglie proposed the wave nature of matter, many physicists, including Schrödinger and Heisenberg, explored the consequences. The idea quickly emerged that, *because of its wave character, a particle's trajectory and destination cannot be precisely predicted for each particle individually*. However, each particle goes to a definite place (Figure 1.9.1). After compiling enough data, you get a distribution related to the particle's wavelength and diffraction pattern. There is a certain *probability* of finding the particle at a given location, and the overall pattern is called a **probability distribution**. Those who developed quantum mechanics devised equations that predicted the probability distribution in various circumstances.

It is somewhat disquieting to think that you cannot predict exactly where an individual particle will go, or even follow it to its destination. Let us explore what happens if we try to follow a particle. Consider the double-slit patterns obtained for electrons and

photons in Figure 1.9.2 . The interference patterns build up statistically as individual particles fall on the detector. This can be observed for photons or electrons—for now, let us concentrate on electrons. You might imagine that the electrons are interfering with one another as any waves do. To test this, you can lower the intensity until there is never more than one electron between the slits and the screen. The same interference pattern builds up!

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

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

Heisenberg's Uncertainty Principle

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

$$\Delta p = \frac{h}{\lambda} \quad (1.6.1)$$

$$\Delta x = \lambda \quad (1.6.2)$$

By substituting Δx for λ into Equation 1.6.1, we derive

$$\Delta p = \frac{h}{\Delta x} \quad (1.6.3)$$

or,

$$\Delta p \Delta x = h \quad (1.6.4)$$

early form of uncertainty principle

A Common Trend in Quantum Systems

Equation 1.6.4 can be derived by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let $\Delta p = mv$, and $\Delta x = h/(mv)$ (from De Broglie's expression for the wavelength of a particle). Substituting in Δp for mv in the second equation leads to Equation 1.6.4.

Equation 1.6.4 was further refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

$$\Delta p_x \Delta x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \quad (1.6.5)$$

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

Equation 1.6.5 reveals that the more accurately a particle's position is known (the smaller Δx is), the less accurately the momentum of the particle in the x direction (Δp_x) is known. Mathematically, this occurs because the smaller Δx becomes, the

larger Δp_x must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known (Figure 1.9.2).

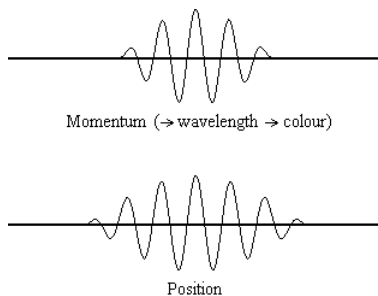


Figure 1.9.2 : The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength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

What is the Proper Definition of Uncertainty?

Equation 1.6.5 relates the uncertainty of momentum and position. An immediate questions that arise is if Δx represents the full range of possible x values or if it is half (e.g., $\langle x \rangle \pm \Delta x$). Δx is the standard deviation and is a statistic measure of the spread of x values. The use of half the possible range is more accurate estimate of Δx . As we will demonstrated later, once we construct a wavefunction to describe the system, then both x and Δx can be explicitly derived. However for now, Equation 1.6.5 will work.

For example: If a problem argues a particle is trapped in a box of length, L , then the uncertainty of it position is $\pm L/2$. So the value of Δx used in Equation 1.6.5 should be $L/2$, not L .

✓ Example 1.9.1

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

Solution

The uncertainty principle (Equation 1.6.5):

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

can be written

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

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

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

the relevant parameters are

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

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

? Exercise 1.9.1

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

Answer

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

Understanding the Uncertainty Principle through Wave Packets and the Slit Experiment

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



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

✓ Example 1.9.2

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

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

Solution a

From Equation 1.6.5, the $\Delta p_x = m\Delta v_x$ with $m = 1.0 \text{ g}$. Solving for Δx to get

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

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

Solution b

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

? Exercise 1.9.2

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

Answer

We need to quantify the uncertainty of the electron in position. We can estimate that as $\pm 5 \times 10^{-10} \text{ m}$. Hence, substituting the relevant numbers into Equation 1.6.5 and solving for Δv we get

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

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

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

📌 Humor: Heisenberg and the Police

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

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CHAPTER OVERVIEW

2: The Schrödinger equation

[2.1: The Schrödinger Wave Equation](#)

[2.2: The Schrödinger Equation is an Eigenvalue Problem](#)

[2.3: The Postulates of Quantum Mechanics](#)

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2.1: The Schrödinger Wave Equation

Beginning in the early 20th century, physicists began to acknowledge that matter--much like electromagnetic radiation--possessed wave-like behaviors. While electromagnetic radiation were well understood to obey Maxwell's Equations, matter obeyed no known equations.

Introduction

In 1926, the Austrian physicist Erwin Schrödinger formulated what came to be known as the (time-dependent) Schrödinger Equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \frac{-\hbar^2}{2m} \nabla^2 \Psi(x, t) + V(x) \Psi(x, t) \quad (2.1.1)$$

Equation 2.1.1 effectively describes matter as a wave that fluctuates with both displacement and time. Since the imaginary portion of the equation dictates its time dependence, it is sufficed to say that for most purposes it can be treated as time-independent. The result is seen in Equation 2.1.2:

$$\frac{-\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x) \quad (2.1.2)$$

Although this time-independent Schrödinger Equation can be useful to describe a matter wave in free space, we are most interested in waves when confined to a small region, such as an electron confined in a small region around the nucleus of an atom. Several different models have been developed that provide a means by which to study a matter-wave when confined to a small region: the particle in a box (infinite well), finite well, and the Hydrogen atom. We will discuss each of these in order to develop a greater understanding for how a wave behaves when it is in a bound state.

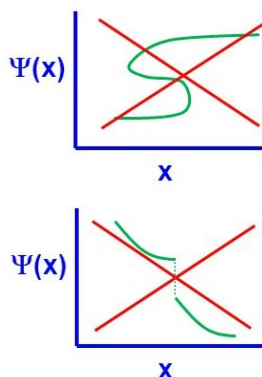


Figure 2.1.1 : Two unacceptable wavefunctions. (left) This is not a single-valued function and (right) this is a non-continuous function

There are four general aspects that are applicable to an acceptable wavefunction

1. An acceptable wavefunction will be the solution of the Schrödinger equation (either Equations 2.1.1 or 2.1.2).
2. An acceptable wavefunction must be normalizable so will approach zero as position approaches infinity.
3. An acceptable wavefunction must be a continuous function of position.
4. An acceptable wavefunction will have a continuous slope (Figure 2.1.1).

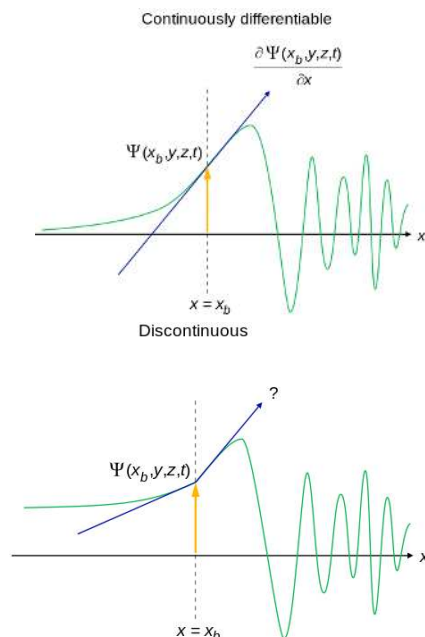


Figure 2.1.2 : Wavefunction continuity in space

Interpretation of the Wavefunction

Since wavefunctions can in general be complex functions, the physical significance cannot be found from the function itself because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the square of the modulus.

$$\psi^*(r, t)\psi(r, t) = |\psi(r, t)|^2 \quad (2.1.3)$$

where r is a vector (x, y, z) specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field. At one time it was thought that for an electron described by the wavefunction $\psi(r)$, the quantity $e\psi^*(r_i)\psi(r_i)d\tau$ was the amount of charge to be found in the volume $d\tau$ located at r_i . However, Max Born found this interpretation to be inconsistent with the results of experiments.

The Born interpretation, which generally is accepted today, is that $\psi^*(r_i)\psi(r_i)d\tau$ is the probability that the electron is in the volume $d\tau$ located at r_i . The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the probability density, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability. The idea that we can understand the world of atoms and molecules only in terms of probabilities is disturbing to some, who are seeking more satisfying descriptions through ongoing research.

Normalization of the Wavefunction

A probability is a real number between 0 and 1. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. The probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x \in -\infty: \infty}(t) = \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx. \quad (2.1.4)$$

However, a measurement of x *must* yield a value between $-\infty$ and $+\infty$, since the particle has to be located somewhere. It follows that $P_{x \in -\infty: \infty}(t) = 1$, or

$$\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1, \quad (2.1.5)$$

which is generally known as the *normalization condition* for the wavefunction.

✓ Example 2.1.1: Normalizing a Gaussian wavefunction

Normalize the wavefunction of a Gaussian wave packet, centered on $x = x_0$, and of characteristic width σ : i.e.,

$$\psi(x) = \psi_0 e^{-(x-x_0)^2/(4\sigma^2)}. \quad (2.1.6)$$

Solution

To determine the normalization constant ψ_0 , we simply substitute Equation 2.1.6 into Equation 2.1.5, to obtain

$$|\psi_0|^2 \int_{-\infty}^{\infty} e^{-(x-x_0)^2/(2\sigma^2)} dx = 1. \quad (2.1.7)$$

Changing the variable of integration to $y = (x - x_0)/(\sqrt{2}\sigma)$, we get

$$|\psi_0|^2 \sqrt{2}\sigma \int_{-\infty}^{\infty} e^{-y^2} dy = 1. \quad (2.1.8)$$

However,

$$\int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\pi}, \quad (2.1.9)$$

which implies that

$$|\psi_0|^2 = \frac{1}{(2\pi\sigma^2)^{1/2}}. \quad (2.1.10)$$

Hence, a general **normalized** Gaussian wavefunction takes the form

$$\psi(x) = \frac{e^{i\phi}}{(2\pi\sigma^2)^{1/4}} e^{-(x-x_0)^2/(4\sigma^2)} \quad (2.1.11)$$

where ϕ is an arbitrary real phase-angle.

Contributors and Attributions

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

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2.2: The Schrödinger Equation is an Eigenvalue Problem

Learning Objectives

- To recognize that each quantum mechanical observable is determined by solve by an eigenvalue problem with different operators for different observable
- Confirm if a specific wavefunction is an eigenfunction of a specific operation and extract the corresponding observable (the eigenvalue)
- To recognize that the Schrödinger equation, just like all measurable, is also an eigenvalue problem with the eigenvalue ascribed to total energy
- Identify and manipulate several common quantum mechanical operators

As per the definition, an operator acting on a function gives another function, however a special case occurs when the generated function is proportional to the original

$$\hat{A}\psi \propto \psi \quad (2.2.1)$$

This case can be expressed in terms of an equality by introducing a proportionality constant k

$$\hat{A}\psi = k\psi \quad (2.2.2)$$

Not all functions will solve an equation like in Equation 2.2.2. If a function does, then ψ is known as an **eigenfunction** and the constant k is called its **eigenvalue** (these terms are hybrids with German, the purely English equivalents being "characteristic function" and "characteristic value", respectively). Solving **eigenvalue problems** are discussed in most linear algebra courses.

In quantum mechanics, every experimental measurable a is the eigenvalue of a specific operator ($\hat{A}$):

$$\hat{A}\psi = a\psi \quad (2.2.3)$$

The a eigenvalues represents the possible measured values of the $\hat{A}$ operator. Classically, a would be allowed to vary continuously, but in quantum mechanics, a typically has only a sub-set of allowed values (hence the quantum aspect). Both time-dependent and time-independent Schrödinger equations are the best known instances of an eigenvalue equations in quantum mechanics, with its eigenvalues corresponding to the allowed energy levels of the quantum system.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}) \quad (2.2.4)$$

The object on the left that acts on $\psi(x)$ is an example of an **operator**.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \quad (2.2.5)$$

In effect, what it says to do is "take the second derivative of $\psi(x)$, multiply the result by $-(\hbar^2/2m)$ and then add $V(x)\psi(x)$ to the result of that." Quantum mechanics involves many different types of operators. This one, however, plays a special role because it appears on the left side of the Schrödinger equation. It is called the **Hamiltonian operator** and is denoted as

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \quad (2.2.6)$$

Therefore, the time-dependent Schrödinger equation can be (and it more commonly) written as

$$\hat{H}\psi(x, t) = i\hbar \frac{\partial}{\partial t} \psi(x, t) \quad (2.2.7)$$

and the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \quad (2.2.8)$$

Note that the functional form of Equation 2.2.8 is the same as the general eigenvalue equation in Equation 2.2.2 where the eigenvalues are the (allowed) total energies (E).

The **Hamiltonian**, named after the Irish mathematician Hamilton, comes from the formulation of Classical Mechanics that is based on the total energy, $H = T + V$, rather than Newton's second law, $F = ma$. Equation 2.2.8 says that the Hamiltonian operator operates on the wavefunction to produce the energy E , which is a scalar (e.g., expressed in Joules) times the wavefunction.

Correspondence Principle

Note that $\hat{H}$ is derived from the classical energy $p^2/2m + V(x)$ simply by replacing $p \rightarrow -i\hbar(d/dx)$. This is an example of the **Correspondence Principle** initially proposed by Niels Bohr that states that the behavior of systems described by quantum theory reproduces classical physics in the limit of large quantum numbers.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is then the eigenvalue, and the system is said to be in an eigenstate. Equation 2.2.8 states this principle mathematically for the case of energy as the observable. If the wavefunction is not the eigenfunction of the operation, then the measurement will give an eigenvalue (by definition), but not necessarily the same one for each measurement (this will be discussed in more detail in later section).

2.2.1: Common Operators

Although we could theoretically come up with an infinite number of operators, in practice there are a few which are much more important than any others.

- **Linear Momentum:**

The linear momentum operator of a particle moving in one dimension (the x -direction) is

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad (2.2.9)$$

and can be generalized in three dimensions:

$$\hat{\vec{p}} = -i\hbar \nabla \quad (2.2.10)$$

- **Position**

The position operator of a particle moving in one dimension (the x -direction) is

$$\hat{x} = x \quad (2.2.11)$$

and can be generalized in three dimensions:

$$\hat{\vec{r}} = \vec{r} \quad (2.2.12)$$

where $\vec{r} = (x, y, z)$.

- **Kinetic Energy**

Classically, the kinetic energy of a particle moving in one dimension (the x -direction), in terms of momentum, is

$$KE_{classical} = \frac{p_x^2}{2m} \quad (2.2.13)$$

Quantum mechanically, the corresponding kinetic energy operator is

$$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (2.2.14)$$

and can be generalized in three dimensions:

$$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m} \nabla^2 \quad (2.2.15)$$

- **Angular Momentum:**

Angular momentum requires a more complex discussion, but is the cross product of the position operator $\hat{\vec{r}}$ and the momentum operator $\hat{\vec{p}}$

$$\hat{\vec{L}} = -i\hbar(\vec{r} \times \nabla) \quad (2.2.16)$$

- **Hamiltonian:**

The Hamiltonian operator corresponds to the total energy of the system

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (2.2.17)$$

and it represents the total energy of the particle of mass m in the potential $V(x)$. The Hamiltonian in three dimensions is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \quad (2.2.18)$$

- **Total Energy:**

The energy operator from the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \hat{H} \Psi(x, t) \quad (2.2.19)$$

The right hand side of Equation 2.2.6 is the Hamiltonian Operator. In addition determining system energies, the Hamiltonian operator dictates the time evolution of the wavefunction

$$\hat{H} \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (2.2.20)$$

This aspect will be discussed in more detail elsewhere.

2.2.2: Eigenstate, Eigenvalues, Wavefunctions, Measurables, and Observables

In general, the **wavefunction** gives the "state of the system" for the system under discussion. It stores all the information available to the observer about the system. Often in discussions of quantum mechanics, the terms *eigenstate* and *wavefunction* are used interchangeably. The term *eigenvalue* is used to designate the value of measurable quantity associated with the wavefunction.

- If you want to measure the energy of a particle, you have to operate on the wavefunction with the Hamiltonian operator (Equation 2.2.6).
- If you want to measure the momentum of a particle, you have to operate on wavefunction with the momentum operator (Equation 2.2.9).
- If you want to measure the position of a particle, you have to operate on wavefunction with the position operator (Equation 2.2.11).
- If you want to measure the kinetic energy of a particle, you have to operate on wavefunction with the kinetic energy operator (Equation 2.2.14).

When discussing the eigenstates of the Hamiltonian ($\hat{H}$), the associated eigenvalues represent energies and within the context of the momentum operators, the associated eigenvalues refer to the momentum of the particle. However, not all wavefunctions (ψ) are eigenstates of an operator (ϕ) – and if they are not, they can be usually be written as superpositions of eigenstates.

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

This will be discussed in more detail in later sections.

While the wavefunction may not be the eigenstate of an observable, when that operator operates on that wavefunction, the wavefunction **becomes** an eigenstate of that observable and only eigenvalues can be observed. Another way to say this is that the wavefunction "collapses" into an eigenstate of the observable. Because quantum mechanical operators have different forms, their associated eigenstates are similarly often (i.e., most of the time) different. For example, when a wavefunction is an eigenstate of total energy, it will **not** be an eigenstate of momentum.

If a wavefunction is an eigenstate of one operator, (e.g., momentum), that state is not necessarily an eigenstate of a different operator (e.g., energy), although not always.

The wavefunction immediately after a measurement is an eigenstate of the operator associated with this measurement. What happens to the wavefunction after the measurement is a different topic.

✓ Example 3.3.1

Confirm that the following wavefunctions are eigenstates of linear momentum and kinetic energy (or neither or both):

- $\psi = A \sin(ax)$
- $\psi = N e^{-ix/\hbar}$

Strategy

This question is asking if the eigenvalue equation holds for the operators and these wavefunctions. This is just asking if these wavefunctions are solutions to Equation 2.2.2 using the operators in Equations 2.2.9 and 2.2.14, i.e., are these equations true:

$$\hat{p}_x \psi = p_x \psi \quad (2.2.21)$$

$$\hat{K}E \psi = KE \psi \quad (2.2.22)$$

where p_x and KE are the measurables (eigenvalues) for these operators.

Solution a

Let's evaluate the left side of the linear momentum eigenvalue problem (Equation 2.2.21)

$$-i\hbar \frac{\partial}{\partial x} A \sin(ax) = -i\hbar A a \cos(ax)$$

and compare to the the right side of Equation 2.2.21

$$p_x A \sin(ax)$$

These are **not** the same so this wavefunction is not an eigenstate of momentum.

Let's look at the left side of the kinetic energy eigenvalue problem (Equation 2.2.22)

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} A \sin(ax) &= -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} A a \cos(ax) \\ &= +\frac{\hbar^2}{2m} A a^2 \sin(ax) \end{aligned}$$

and compare to the right side

$$KE A \sin(ax)$$

These are same, so this specific wavefunction is an eigenstate of kinetic energy. Moreover, the measured kinetic energy will be

$$KE = +\frac{\hbar^2}{2m} a^2$$

Solution b

Let's look at the left side of Equation 2.2.21 for linear momentum

$$-i\hbar \frac{\partial}{\partial x} N e^{-ix/\hbar} = -N e^{-ix/\hbar}$$

and the right side of Equation 2.2.21

$$p_x N e^{-ix/\hbar}$$

These are the same so this wavefunction is an eigenstate of momentum with momentum $p_x = -N$.

Let's look at the left side of Equation 2.2.22 for kinetic energy

$$\begin{aligned}
 -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} N e^{-ix/\hbar} &= +i \frac{\hbar}{2m} \frac{\partial}{\partial x} N e^{-ix/\hbar} \\
 &= +\frac{1}{2m} N e^{-ix/\hbar}
 \end{aligned}$$

and the right side

$$K E N e^{-ix/\hbar}$$

These are same so this wavefunction is an eigenstate of kinetic energy. And the measured kinetic energy will be

$$K E = \frac{1}{2m}$$

This wavefunction is an eigenstate of both momentum and kinetic energy.

Exercise 3.3.1

Are $\psi = M e^{-bx}$ functions eigenstates of linear momentum and kinetic energy (or neither or both)?

Answer

ψ is an eigenstate of linear momentum with a eigenvalue of $b i \hbar$ and also an eigenstate of kinetic energy with an eigenvalue of b^2 .

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2.3: The Postulates of Quantum Mechanics

There are only a small number of postulates of quantum mechanics. Upon them is built all of the conclusions of this powerful theory.

Postulate 1

The state of a quantum-mechanical system is completely specified by a function $\Psi(\mathbf{r}, t)$ that depends on the coordinates of the particle ($\mathbf{r}$) and the time (t). This function, called the wavefunction has the important property that

$$\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)dxdydz$$

is the probability of finding the particle within the infinitesimally small volume element $dxdydz$ located at position $\mathbf{r}$ at time t .

Postulate 2

To every physical observable in classical mechanics, there corresponds an operator in quantum mechanics. This operator will be both linear and Hermitian.

Postulate 3

In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a which satisfy the eigenvalue equation

$$\hat{A}\phi = a\phi$$

It is important to note that the wavefunction describing the particle need not be an eigenfunction of the operator $\hat{A}$. However, well defined wavefunctions (those meeting the requirements of all of the postulates of quantum mechanics) will have the possibility of being described as a linear combination of eigenfunctions of any of the needed operators. The Superposition Principle is invaluable in working with this concept.

Postulate 4

If a system is in a state described by a normalized wavefunction (Ψ) then the average measured value of the observable corresponding to $\hat{A}$ is given by

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi d\tau \quad \text{or} \quad \langle a \rangle = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

Postulate 5

The wavefunction of a system evolves in time according to the time dependent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t)$$

Each of these postulates has important consequences and ramifications as to what quantum theory can (and cannot) tell us about a particle or system. In the remainder of this section, we will explore each postulate individually in order to lay a foundation of what quantum mechanics can predict for us about the nature of matter.

Postulate 1: a Squared Wavefunction is a Probability Distribution

This postulate describes the commonly accepted interpretation of a wavefunction. First and foremost, a wavefunction is a mathematical function. It must be single valued in that for each point in space, there is only one value that can be calculated from the function. When considering all space which a particle may occupy, the squared wavefunction must create a smooth¹ and continuous probability distribution describing where the particle might be observed to be located. (for our purposes, "smooth" means that the first derivative of the function must be continuous.) Since the square of the wavefunction is a probability distribution for the location of the particle, any location in space where the squared wavefunction is zero, has a corresponding probability of zero that the particle will be observed at that location.

✓ Example 2.3.1

Consider a particle of mass m in box of length a that is prepared such that its wave function is given by

$$\psi(x) = \sqrt{\frac{30}{a^5}} \cdot x(a-x)$$

Calculate the probability that the particle will have a position measurement reveal the particle to be in the middle half of the box (with the measured position satisfying $a/4 \leq x \leq 3a/4$.)

Solution

The squared wavefunction gives the probability distribution for where the particle's position will be measured to be.

$$(\psi(x))^2 = \frac{30}{a^5} (a^2 x^2 - 2ax^3 + x^4)$$

The total probability will be given by the following integral.

$$\begin{aligned} P &= \int_{a/4}^{3a/4} [\psi(x)]^2 dx \\ &= \frac{30}{a^5} \int_{a/4}^{3a/4} (a^2 x^2 - 2ax^3 + x^4) dx \\ &= \frac{30}{a^5} \left[\frac{a^2 x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5} \right]_{a/4}^{3a/4} \\ &= \frac{30}{a^5} \left(\frac{27a^5}{192} - \frac{162a^5}{1024} + \frac{243a^5}{5120} - \frac{a^5}{192} + \frac{2a^5}{1024} - \frac{a^5}{5120} \right) \\ &= \frac{30}{a^5} \left(\frac{26a^5}{192} - \frac{164a^5}{1024} + \frac{242a^5}{5120} \right) \\ &= 0.520 \end{aligned}$$

Note that the final probability is unitless!

¹ The wavefunction will be smooth provided that the potential energy function is not discontinuous. A discontinuous potential energy function (such as a step function) will lead to a wavefunction that which single-valued, will not have a continuous first derivative, and therefore, not be "smooth" in the strictest sense.

The wavefunction contains all of the information about a system that is needed to understand how the system behaves and how it will behave in the future, at least within the limits of the quantum theory! Information on such properties as energy, momentum and position are all contained in the wavefunction.

Postulate 2: Quantum Mechanical Operators

The second postulate describes the nature of quantum mechanical operators and their relationship to those properties of a system which we can observe. The operators are the tools that pull physical information from the wavefunction and reveal the properties of the quantum mechanical system. The following table shows some operators and their corresponding physically observable quantities.

	Physical Observable	One Dimension	Three Dimensions
$\hat{x}$	Position	x	$\mathbf{r}$
$\hat{p}$	Momentum	$-i\hbar \frac{d}{dx}$	$-i\hbar \vec{\nabla}$
$\hat{H}$	Energy	$\hat{T} + \hat{U}$	
$\hat{T}$	Kinetic	$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$	$-\frac{\hbar^2}{2m} \nabla^2$

	Physical Observable	One Dimension	Three Dimensions
$\hat{U}$	Potential	$U(x)$	$U(\mathbf{r})$

Each of these operators will have two very important properties. 1) Each is **linear** and 2) each is **Hermitian**. In one dimension, an operator ($\hat{A}$) is defined to be linear if the following condition holds:

$$\hat{A}(af(x) + bg(x)) = a\hat{A}f(x) + b\hat{A}g(x)$$

where a and b are scalar values. An example of a linear operator is multiplication by a constant or a function. Taking a derivative (or integrating) is also a linear operation, as is adding a constant or a function. An example of a non-linear operator is taking a logarithm or raising a function to a power other than one.

The Hermitian nature of quantum mechanical operators has many important consequences. An operator ($\hat{A}$) is Hermitian if it satisfies the following relationship:

$$\int g^* \hat{A} f d\tau = \int f \hat{A}^* g^* d\tau$$

for well-behaved ² functions f and g , where the asterisk (*) indicated the complex conjugate of the function or operator. Hermitian operators have the important properties that 1) their

² A well-behaved function is one that is normalizable and continuous over the relevant space of the problem.

✓ Example 2.3.1

Is the operator $\frac{d}{dx}$ a Hermitian operator?

Solution

For an operator $\hat{A}$ to be Hermitian, the following relationship must hold (for wellbehaved functions f and g :

$$\int g^* \hat{A} f d\tau = \int f \hat{A}^* g^* d\tau$$

So if we choose arbitrary functions f and g , we can evaluate the left-hand side of the above relationship by noting the pattern $d(uv) = u dv + v du$ and integrating by parts. Using this approach

$$\int u dv = uv - \int v du$$

Making the substitutions that

$$u = g^* \\ dv = \frac{d}{dx} f dx$$

it should be clear that

$$du = \frac{d}{dx} g^* dx \\ v = f$$

So

$$\int g^* \frac{d}{dx} f dx = g^* f|_{-\infty}^{\infty} - \int f \frac{d}{dx} g^* dx$$

In order for f and g to meet the criteria that they are normalizable, they must vanish as x approaches $\pm\infty$. As such,

$$g^* f|_{-\infty}^{\infty} = 0$$

And we are left with

$$\int g^* \frac{d}{dx} f dx = - \int f \frac{d}{dx} g^* dx$$

Which clearly can not be true. Therefore, the operator $\frac{d}{dx}$ is not Hermitian. You should, however, be able to use the same method to show that the operator $\hat{A} = i \frac{d}{dx}$ is in fact Hermitian!

Postulate 3: Measurable Values

Postulate three states that the only measurable values for a system are those values that are eigenvalues of the corresponding quantum mechanical operator. The first measurable value which we will explore is the energy of the system (see below.) Because the wavefunction provides a probability distribution, it also provides a means of predicting the statistics for a theoretical infinite set of measurements on a system. The ramifications of that point are developed in the discussion of the fourth postulate.

Postulate 4: Expectation Values

An expectation value is an average value that would be expected based on an infinite number of measurements. Since wavefunctions give us probability information, it stands to reason that we can calculate a great deal of statistical information about a system based on the wavefunction and the corresponding operators. This will be discussed in detail in section D with regards to expectation values calculated for position, momentum and energy. It is important to note that the expectation value does not indicate the most probable measurement or observation that will be made, nor must it even give a value that can ever be measured; it just gives the average.

This postulate has very important (and controversial) ramifications. It forms the basis for how the Heisenberg Uncertainty Principle can be discussed. The problem is that quantum mechanics cannot tell you what will be measured, but rather only the probability that a certain value can be measured for a specific property. While a subtle point, it shakes the very nature of our intuition as to what it means for a system to have a certain property. In most cases, the properties we associate with classical particles do not even exist in quantum mechanical particles (at least in any sense to which we are accustomed) until those properties are measured. This has led to numerous debates as to the validity of quantum mechanics as a model, and even led one of the original developers of quantum theory (Erwin Schrödinger) to change his mind completely on the model.

Postulate 5: the evolution of a system in time

The 5th postulate indicates how a system will evolve in time. It also gives the definition of the time dependent Schrödinger equation.

We will explore many of these properties based on the particle in a box problem in order to gain some insight into what quantum mechanics can and can not tell us about a system. The particle in a box problem actually has limited physical application (although it does have some), but does provide a "thought sandbox" in which we can explore the concepts, powers and limitations of the quantum theory. Hopefully then when we apply the theory to problems of greater chemical interest, we can focus more on the conclusions than on the specific mathematics.

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CHAPTER OVERVIEW

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3.2: The One-Dimensional Particle in a Box

3.3: Particle in a 2-Dimensional Box

3.4: A Particle in a Three-Dimensional Box

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

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3.1: Particle in a One-Dimensional Box

A particle in a 1-dimensional box is a fundamental quantum mechanical approximation describing the translational motion of a single particle confined inside an infinitely deep well from which it *cannot* escape.

Introduction

The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of E and ψ that the particle can possess. E represents allowed energy values and $\psi(x)$ is a wavefunction, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

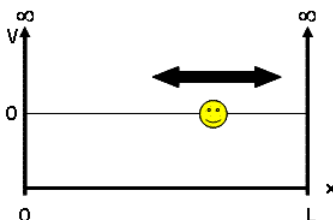
Recipe for Quantum Mechanics

To solve the problem for a particle in a 1-dimensional box, we must follow our *Big, Big recipe for Quantum Mechanics*:

1. Define the Potential Energy, V
2. Solve the Schrödinger Equation
3. Solve for the wavefunctions
4. Solve for the allowed energies

Step 1: Define the Potential Energy V

The potential energy is 0 inside the box ($V=0$ for $0 < x < L$) and goes to infinity at the walls of the box ($V=\infty$ for $x < 0$ or $x > L$). We assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box. Doing so significantly simplifies our later mathematical calculations as we employ these **boundary conditions** when solving the Schrödinger Equation.



Step 2: Solve the Schrödinger Equation

The time-independent Schrödinger equation for a particle of mass m moving in one direction with energy E is

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

with

- $\hbar$ is the reduced Planck constant where $\hbar = \frac{h}{2\pi}$
- m is the mass of the particle
- $\psi(x)$ is the stationary time-independent wavefunction
- $V(x)$ is the potential energy as a function of position
- E is the energy, a real number

This equation can be modified for a particle of mass m free to move parallel to the x -axis with zero potential energy ($V = 0$ everywhere) resulting in the quantum mechanical description of free motion in one dimension:

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

This equation has been well studied and gives a general solution of:

$$\psi(x) = A \sin(kx) + B \cos(kx)$$

where A , B , and k are constants.

Step 3: Define the Wavefunction

The solution to the Schrödinger equation we found above is the general solution for a 1-dimensional system. We now need to apply our **boundary conditions** to find the solution to our particular system. According to our boundary conditions, the probability of finding the particle at $x = 0$ or $x = L$ is zero. When $x = 0$, then $\sin(0) = 0$ and $\cos(0) = 1$; therefore, B must equal 0 to fulfill this boundary condition giving:

$$\psi(x) = A \sin(kx) \quad (3.1.2)$$

We can now solve for our constants (A and k) systematically to define the wavefunction.

Solving for k

Differentiate the wavefunction with respect to x :

$$\frac{d\psi}{dx} = kA \cos(kx)$$

Differentiate the wavefunction again with respect to x :

$$\frac{d^2\psi}{dx^2} = -k^2 A \sin(kx)$$

Since $\psi(x) = A \sin(kx)$, then

$$\frac{d^2\psi}{dx^2} = -k^2 \psi$$

If we then solve for k by comparing with the Schrödinger equation above, we find:

$$k = \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2}$$

Now we plug k into our wavefunction (Equation 3.1.2):

$$\psi = A \sin \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} x$$

Solving for A

To determine A , we have to apply the boundary conditions again. Recall that the *probability of finding a particle at $x = 0$ or $x = L$ is zero*.

When $x = L$:

$$0 = A \sin \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} L$$

This is only true when

$$\left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} L = n\pi$$

where $n = 1, 2, 3, \dots$

Plugging this back in gives us:

$$\psi = A \sin \frac{n\pi}{L} x$$

To determine A , recall that the total probability of finding the particle inside the box is 1, meaning there is no probability of it being outside the box. When we find the probability and set it equal to 1, we are *normalizing* the wavefunction.

$$\int_0^L \psi^2 dx = 1$$

For our system, the normalization looks like:

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

Using the solution for this integral from an integral table, we find our normalization constant, A :

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

Which results in the normalized wavefunctions for a particle in a 1-dimensional box:

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \quad (3.1.3)$$

where $n = 1, 2, 3, \dots$

Step 4: Determine the Allowed Energies

Solving for the energy of each ψ requires substituting Equation 3.1.3 into Equation 3.1.1 to get the allowed energies for a particle in a box:

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (3.1.4)$$

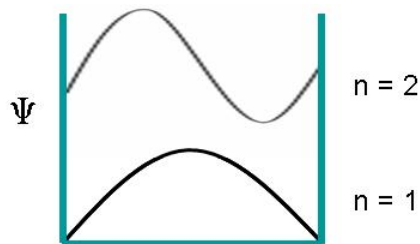
Equation 3.1.4 is a very important result and tells us that:

1. The energy of a particle is quantized.
2. The lowest possible energy of a particle is **NOT** zero. This is called the **zero-point energy** and means the particle can never be at rest because it always has some kinetic energy.

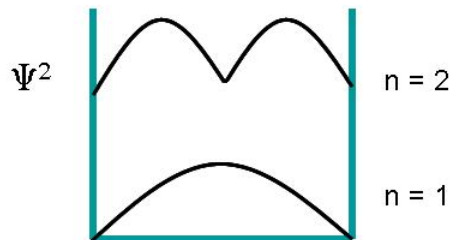
This is also consistent with the [Heisenberg Uncertainty Principle](#): if the particle had zero energy, we would know where it was in both space and time.

What does all this mean?

The wavefunction for a particle in a box at the $n = 1$ and $n = 2$ energy levels look like this:



The probability of finding a particle at a certain spot in the box is determined by squaring ψ . The probability distribution for a particle in a box at the $n = 1$ and $n = 2$ energy levels looks like this:



Notice that the number of **nodes** (places where the particle has zero probability of being located) increases with increasing energy n . Also note that as the energy of the particle becomes greater, the quantum mechanical model breaks down as the energy levels get closer together and overlap, forming a continuum. This continuum means the particle is free and can have any energy value. At such high energies, the classical mechanical model is applied as the particle behaves more like a continuous wave. Therefore, the particle in a box problem is an example of [Wave-Particle Duality](#).

✓ Example 3.1.1

What is the ΔE between the $n = 4$ and $n = 5$ states for an F_2 molecule trapped within in a one-dimension well of length 3.0 cm? At what value of n does the energy of the molecule reach $1/4k_B T$ at 450 K, and what is the separation between this energy level and the one immediately above it?

Solution

Since this is a one-dimensional particle in a box problem, the particle has only kinetic energy ($V = 0$), so the permitted energies are:

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

with $n = 1, 2, \dots$

The energy difference between $n = 4$ and $n = 5$ is then

$$\begin{aligned}\Delta E &= E_5 - E_4 \\ &= \frac{5^2 h^2}{8mL^2} - \frac{4^2 h^2}{8mL^2}\end{aligned}$$

Using Equation 3.1.4 with the mass of F_2 ($37.93 \text{ amu} = 6.3 \times 10^{-26} \text{ kg}$) and the length of the box ($L = 3 \times 3.0 \times 10^{-2} \text{ m}^2$):

$$\begin{aligned}\Delta E &= \frac{9h^2}{8mL^2} \\ &= \frac{9(6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})^2}{8(6.30938414 \times 10^{-26} \text{ kg})(3.0 \times 10^{-2} \text{ m}^2)^2} \\ &= 8.70 \times 10^{-39} \text{ J}\end{aligned}$$

The n value for which the energy reaches $\frac{1}{4}k_B T$:

$$\begin{aligned}\frac{n^2 h^2}{8mL^2} &= \frac{1}{4}k_B T \\ n &= 1.79 \times 10^9\end{aligned}$$

The separation between $n + 1$ and n :

$$\begin{aligned}\Delta E &= E_{n+1} - E_n \\ &= \frac{(n+1)^2 h^2 - (n)^2 h^2}{8mL^2} \\ &= \frac{(2n+1)h^2}{8mL^2} \\ &= 3.47 \times 10^{-30} \text{ J}\end{aligned}$$

Important Facts to Learn from the Particle in the Box

- The energy of a particle is quantized. This means it can only take on discrete energy values.
- The lowest possible energy for a particle is **NOT** zero (even at 0 K). This means the particle *always* has some kinetic energy.
- The square of the wavefunction is related to the probability of finding the particle in a specific position for a given energy level.

- The probability changes with increasing energy of the particle and depends on the position in the box you are attempting to define the energy for
- In classical physics, the probability of finding the particle is independent of the energy and the same at all points in the box

References

1. Chang, Raymond. *Physical Chemistry for the Biosciences*. Sansalito, CA: University Science, 2005.

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3.2: The One-Dimensional Particle in a Box

Imagine a particle of mass m constrained to travel back and forth in a one dimensional box of length a . For convenience, we define the endpoints of the box to be located at $x = 0$ and $x = a$. The derivation of wavefunctions and energy levels and the properties of the system using the tools of quantum mechanics will be instructive as we move forward in our studies of quantum mechanics.

The Hamiltonian

Whenever we begin a new quantum mechanical problem, the first challenge is to write the **Hamiltonian** that describes the system. This always has two parts - a **Kinetic Energy** term (which is always the same for each particle) and a **Potential Energy** term (that is different for each new system.)

The kinetic energy term in one dimension for a single particle is always given by

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

This operator can be derived from the momentum operator based on the relationship between momentum and kinetic energy that comes from classical physics. Namely

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

As such,

$$\begin{aligned}\hat{T} &= \frac{p^2}{2m} \\ &= \frac{1}{2m} \left(-i\hbar \frac{d}{dx} \right) \\ &= \frac{(-i\hbar)^2}{2m} \frac{d^2}{dx^2} \\ &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\end{aligned}$$

The potential energy function is also fairly simple for this problem. The potential energy is infinite outside of the box ($x < 0$ and $x > a$) and zero every place else. This forces the particle to be in the box at all times. It also limits the relevant space of the problem to lie between $x = 0$ and $x = a$ since the infinite potential energy precludes the particle from ever existing outside of the limits of $x = 0$ and $x = a$.

$$U(x) = \begin{cases} \infty & \text{if } x < 0 \\ 0 & \text{if } 0 \leq x \leq a \\ \infty & \text{if } x > a \end{cases}$$

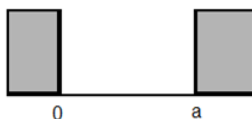


Figure 3.2.1

So for the problem, limited to the space inside the box, the Hamiltonian can be written

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

And the Schrödinger equation can be written as

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

where $\psi(x)$ is the wavefunction describing the state of the particle. There are a number of approaches that can be used to solve this equation to find the wavefunctions $\psi(x)$ which satisfy the differential equation.

The Solution

We will solve this problem two different ways. First, we will solve it using the de Broglie wavelength (an algebraic solution) and then using the Schrödinger equation (an eigenvalue/eigenfunction approach.)

The de Broglie Approach

Before trying to solve the problem using Schrödinger's equation, let's use the de Broglie condition to solve the problem algebraically. Recall that de Broglie suggested that a particle can be treated as a wave, the wavelength of which is given by $\lambda = h/p$, where h is Planck's constant, and p is the momentum of the particle.

The necessary conditions on the de Broglie wave are that the wave itself must vanish at the ends of the box (in order to satisfy the first postulate, since the particle can never escape the box.) This will happen for very specific wavelengths which are dependent on the length of the box itself. This is very common in physics for any system with a wave nature. When the wave is constrained to a specific geometry, the system will "ring" with frequencies (and thus wavelengths) characteristic of the medium and the geometry. Quantum mechanical systems are no different in that regard.

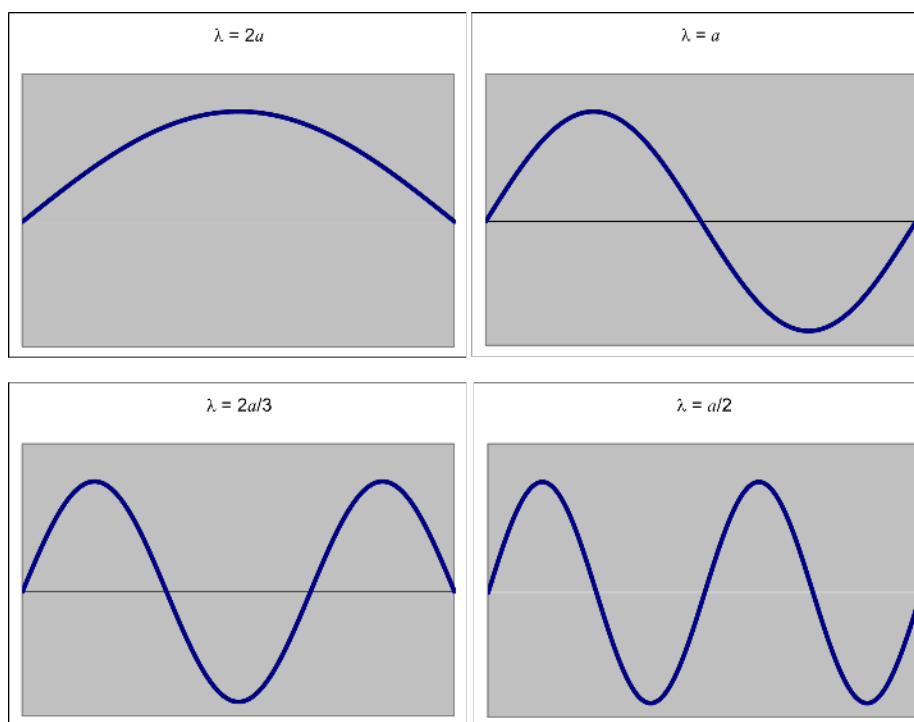


Figure 3.2.2

What will be required in order to create a standing wave is that the length of the box (a) must be an integral multiple of half de Broglie wavelengths ($\lambda/2$).

$$a = n \frac{\lambda}{2}$$

Given that the de Broglie wavelength is related to momentum, it is simple to derive the following relationship, indicating the possible values for momentum.

$$\begin{aligned} a &= n \frac{\lambda}{2} \\ &= \frac{nh}{2p} \\ p &= \frac{nh}{2a} \end{aligned}$$

Given the relationship between momentum and kinetic energy, the expected expression for energy levels can be derived.

$$E = \frac{p^2}{2m} = \frac{1}{2m} \left(\frac{nh}{2a} \right)^2 = \frac{n^2 h^2}{8ma^2}$$

And since the energy depends on n^2 , the spacings between successive energy levels increases as the energy increases.

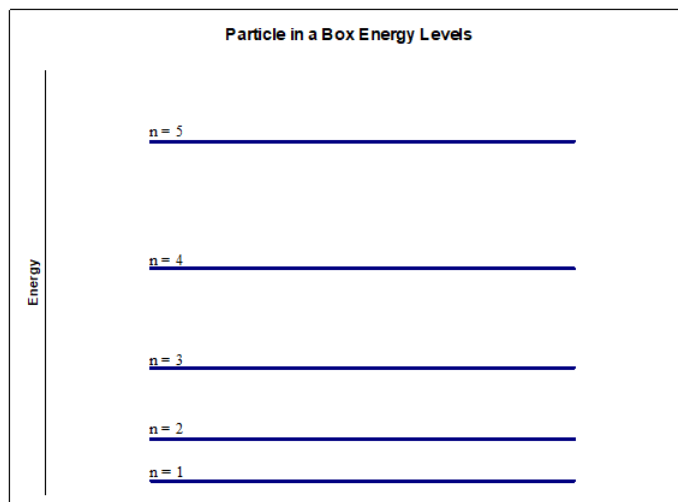


Figure 3.2.3

Now let's see if we can derive this expression based on the Schrödinger equation.

The Schrödinger equation: the wavefunctions

The time-independent Schrödinger equation can be written

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

Where H is the Hamiltonian operator that was derived in section B.2, ψ is the wavefunction describing the system, and E , the eigenvalue of the Hamiltonian, gives the energy. The wavefunctions are derived so that they are eigenfunctions of the Hamiltonian operator. Substituting the specific statement of the Hamiltonian

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi = E\psi$$

For convenience, we can gather all of the constants in one place by making a substitution

$$-k^2 = -\frac{2mE}{\hbar^2}$$

The particular choice of the form of this substitution is made to simplify the solutions by avoiding (for now) imaginary functions. With the substitution, the Schrödinger equation can be rewritten as

$$\frac{d^2}{dx^2} \psi = -k^2 \psi$$

As was the case for the classical wave-on-a-string problem, this is a second order ordinary differential equation, and this has two linearly independent solutions. A general solution is given by a linear combination of two linearly independent solutions, so one way to write a solution is

$$\psi = A \sin(kx) + B \cos(kx)$$

Now we can focus on evaluating A , B and k based on the boundary conditions. The boundary conditions are that the wavefunction must go to 0 at the ends of the box, in accordance with the first postulate.

The first boundary condition, $\psi(0) = 0$, yields the following result:

$$\begin{aligned}\psi(0) &= A \sin(k \cdot 0) + B \cos(k \cdot 0) \\ &= 0 + B = 0\end{aligned}$$

So $B = 0$ and the cosine term must vanish. Focusing only on what has not vanished from the solutions, the second boundary condition, $\psi(a) = 0$, can be applied.

$$\psi(a) = A \sin(k \cdot a) = 0$$

There are two trivial ways to make this true. One is to make $A = 0$ and the other is to make $k = 0$. Both are trivial solutions and unimportant (but fun to mention in class!) The other way to force the function to 0 at $x = a$ is to insure that the sine function is zero by forcing

$$k \cdot a = n\pi$$

where n is an integer ($n = 1, 2, 3 \dots$), since the sine function crosses zero every $n\pi$ radians. This is an important point: the application of a boundary condition leads to the introduction of a quantum number and fixed the results to only functions where that number has a value taken from a very specific list. In fact, the origin of quantum numbers in all problems is the result of the application of boundary conditions.

Solving for k and substituting yields

$$\psi(x) = A \sin\left(\frac{n\pi x}{a}\right)$$

This is as far as the boundary conditions can get us. The value of A is determined based on the first postulate of quantum mechanics, which says that the square of the wavefunction must give a probability distribution as to where the particle can be measured to be. Since all measurements must place the particle in the box, the sum of probabilities at all of the possible locations in the box must equal unity. This implies the condition that

$$\int_0^a (\psi(x))^2 dx = 1$$

Solving for A yields

$$\begin{aligned}\int_0^a (\psi(x))^2 dx &= A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx \\ &= A^2 \left[\frac{x}{2} - \frac{\sin\left(\frac{2n\pi x}{a}\right)}{\left(\frac{4n\pi}{a}\right)} \right]_0^a \\ &= A^2 \left(\frac{a}{2} - 0 - 0 + 0 \right) \\ A &= \sqrt{\frac{2}{a}}\end{aligned}$$

Notice that the value of A did not depend on the quantum number n . Normalization constants usually do have some dependence on the quantum numbers that arise from the application of boundary conditions, but this is one of the rare problems in which the normalization constant does not.

The Schrödinger Equation: the energy levels

Whenever we solve a quantum mechanical problem, there are two important things at which we must look: the energy levels and the wavefunctions. To chemists, the energy levels are the most important part, as the energy levels govern the chemistry the system can do. To a physicist, it is the wavefunctions that are important as they contain all of the information about the physical nature of the system.

The energy levels can be derived using the normalized wavefunctions and the Schrödinger equation.

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

$$\underbrace{-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}}_{\hat{H}} \underbrace{\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)}_{\psi} = \underbrace{\frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2}_{E} \underbrace{\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)}_{\psi}$$

Comparison (or solving for E) yields the following

$$E = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

which looks similar to, but not exactly like the result produced using the de Broglie relationship. In fact, it is the identical result! Making the substitution $\hbar = h/2\pi$, it is easy to show that

$$E = \frac{n^2 h^2}{8ma^2}$$

These energy levels depend on n^2 , and so doubling the quantum number n quadruples the energy. Another way of saying this is that the energy level spacings (the difference in energy between two successive levels) increase with increasing n or energy.

It is also interesting to note that the energy levels are given by a real (non-imaginary) expression. This is to be expected since the energy is the eigenvalue of a Hermitian operator, the Hamiltonian, and thus must be a real value.

Properties of the Wavefunctions

The wavefunctions for the one-dimensional particle in a box problem are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

These wavefunctions have many important properties.

Orthogonality

Similar to the relationship of Hermitian operators having real eigenvalues, the eigenfunctions of Hermitian operators must be orthogonal. Our wavefunctions are actually an infinite set of function, any pair of which must cause the inner product integral to vanish. Mathematically, this looks like

$$\int_0^a \psi_n(x) \cdot \psi_m(x) dx = 0 \quad n \neq m$$

This relationship is easy to verify. To do so, we will make use of the following result taken from a standard table of integrals.

$$\int \sin(\alpha x) \sin(\beta x) dx = \frac{\sin[(\alpha - \beta)x]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)x]}{2(\alpha + \beta)} \quad \alpha \neq \beta$$

Noting that $\alpha = \frac{n\pi}{a}$ and $\beta = \frac{m\pi}{a}$, substitution into the above relationship yields

$$\begin{aligned} \int_0^a \psi_n(x) \cdot \psi_m(x) dx &= \left[\frac{\sin\left[\frac{\pi}{a}(n-m)x\right]}{2\left(\frac{\pi}{a}(n-m)\right)} - \frac{\sin\left[\frac{\pi}{a}(n+m)x\right]}{2\left(\frac{\pi}{a}(n+m)\right)} \right]_0^a \\ &= \left[\frac{\sin[\pi(n-m)]}{2\left(\frac{\pi}{a}(n-m)\right)} - \frac{\sin[\pi(n+m)]}{2\left(\frac{\pi}{a}(n+m)\right)} - 0 + 0 \right] \end{aligned}$$

And since n and m are integer, $n - m$ and $n + m$ must also be integers. And the sine of an integral multiple of π is always zero, it is easy to show that this function vanishes for any $n \neq m$.

Normalization

When $n = m$ the integral becomes

$$\int_0^a [\psi_n(x)]^2 dx = \frac{2}{a} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$

which can be evaluated using the result from a table of integrals

$$\int \sin^2(\alpha x) dx = \frac{x}{2} - \frac{\sin(2\alpha x)}{4\alpha}$$

So making the substitution $\alpha = \frac{n\pi}{a}$

$$\begin{aligned} \frac{2}{a} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx &= \frac{2}{a} \left[\frac{x}{2} - \frac{\sin\left(\frac{2n\pi x}{a}\right)}{4(n\pi/a)} \right]_0^a \\ &= \frac{2}{a} \left[\frac{a}{2} - 0 - 0 + 0 \right] \\ &= 1 \end{aligned}$$

This result shouldn't be surprising since the value $A = \sqrt{\frac{2}{a}}$ was chosen to ensure the result! Specifically, it was chosen so as to normalize the wave functions.

✓ Example 3.2.1

Show that the wavefunction

$$\Psi(x) = \sqrt{\frac{30}{a^5}} \cdot x(a-x)$$

is normalized for a particle in a box of length a .

Solution

The wavefunction is normalized if

$$\int_0^a \Psi(x)\Psi(x)dx = 1$$

This can be demonstrated by plugging the wavefunction into the relationship and testing to see if it is true:

$$\begin{aligned} \int_0^a \sqrt{\frac{30}{a^5}} \cdot x(a-x) \sqrt{\frac{30}{a^5}} \cdot x(a-x) dx &= \frac{30}{a^5} \int_0^a x^2 (a^2 - 2ax + x^2) dx \\ &= \frac{30}{a^5} \int_0^a (a^2 x^2 - 2ax^3 + x^4) dx \\ &= \frac{30}{a^5} \left[\frac{a^2 x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5} \right]_0^a \\ &= \frac{30}{a^5} \left(\frac{a^5}{3} - \frac{a^5}{2} + \frac{a^5}{5} - 0 + 0 - 0 \right) \\ &= \frac{30}{a^5} \left(\frac{10a^5}{30} - \frac{15a^5}{30} + \frac{6a^5}{30} \right) \\ &= \frac{30}{a^5} \left(\frac{a^5}{30} \right) \\ &= 1 \end{aligned}$$

Therefore the wavefunction is normalized!

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3.3: Particle in a 2-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.

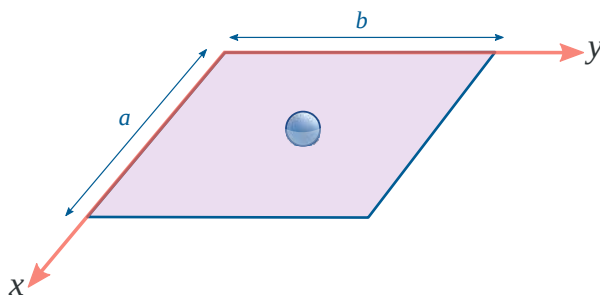


Figure 3.3.1: A particle in a $a \times b$ 2-dimensional box with infinite height can only be found within the box (highlighted). (CC BY-NC; Ümit Kaya)

Extending the (time-independent) Schrödinger equation for a one-dimensional system

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (3.3.1)$$

to a two-dimensional system is not difficult

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2\psi(x, y)}{\partial x^2} + \frac{\partial^2\psi(x, y)}{\partial y^2} \right) + V(x, y)\psi(x, y) = E\psi(x, y). \quad (3.3.2)$$

Equation 3.3.2 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, i.e.

$$V(x, y) = \begin{cases} 0 & 0 \leq x \leq a \text{ and } 0 \leq y \leq b \\ \infty & x < 0 \text{ and } x > a \\ \infty & y < 0 \text{ and } y > b \end{cases}$$

So Equation 3.3.2 becomes

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2\psi(x, y)}{\partial x^2} + \frac{\partial^2\psi(x, y)}{\partial y^2} \right) = E\psi(x, y). \quad (3.3.3)$$

Since the Hamiltonian (i.e. left side of Equation 3.3.3) 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

$$\psi(x, y) = X(x)Y(y). \quad (3.3.4)$$

This ansatz separates Equation 3.3.3 into two independent one-dimensional Schrödinger equations

$$-\frac{\hbar^2}{2m} \left(\frac{d^2X(x)}{dx^2} \right) = \varepsilon_x X(x). \quad (3.3.5)$$

$$-\frac{\hbar^2}{2m} \left(\frac{d^2 Y(y)}{dy^2} \right) = \varepsilon_y Y(y). \quad (3.3.6)$$

where the total energy of the particle is the sum of the energies from each one-dimensional Schrödinger equation

$$E = \varepsilon_x + \varepsilon_y \quad (3.3.7)$$

The differential equations in Equations 3.3.5 and 3.3.6 are familiar as they were found for the particle in a 1-D box [previously](#). They have the general solution

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x) \quad (3.3.8)$$

$$Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y) \quad (3.3.9)$$

Applying Boundary Conditions

The general solutions in Equations 3.3.8 and 3.3.9 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 3.3.8, 3.3.9, and 3.3.4 to construct the wavefunction $\psi(x, y)$ for a particle in a 2D box of the form

$$\psi(x, y) = N \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}} x\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}} y\right) \quad (3.3.10)$$

We still need to satisfy the remaining boundary conditions $\psi(L, y) = 0$ and $\psi(x, L) = 0$

$$N \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}} L\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}} y\right) = 0 \quad (3.3.11)$$

and

$$N \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}} x\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}} L\right) = 0 \quad (3.3.12)$$

Equation 3.3.11 can be satisfied if

$$\sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}} L\right) = 0 \quad (3.3.13)$$

independent of the value of y , while Equation 3.3.12 can be satisfied if

$$\sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}} L\right) = 0 \quad (3.3.14)$$

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

$$\sqrt{\frac{2m\varepsilon_x}{\hbar^2}} L = n_x \pi \quad (3.3.15)$$

and

$$\sqrt{\frac{2m\varepsilon_y}{\hbar^2}} L = n_y \pi \quad (3.3.16)$$

which yield the allowed values of ε_x and ε_y as

$$\varepsilon_{n_x} = \frac{\hbar^2 \pi^2}{2mL^2} n_x^2 \quad (3.3.17)$$

and

$$\varepsilon_{n_y} = \frac{\hbar^2 \pi^2}{2mL^2} n_y^2 \quad (3.3.18)$$

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

$$E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2) \quad (3.3.19)$$

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, ... Note, therefore, that the ground state energy $E_{1,1}$ is

$$E_{1,1} = \frac{\hbar^2 \pi^2}{mL^2} \quad (3.3.20)$$

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 3.3.10, the wavefunctions become

$$\psi_{n_x, n_y}(x, y) = N \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \quad (3.3.21)$$

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

$$\psi_{n_x, n_y}(x, y) = \frac{2}{L} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \quad (3.3.22)$$

The Separability of the Hamiltonian

Because the Hamiltonian in Equation 3.3.3 can be expressed as a simple sum of independent terms, the solutions can be expressed as simple **products** of the one-dimensional solution (Equation 3.3.22) with energies that are expressed as the **sum** of one-dimensional energies (Equation 3.3.19). This observation extends to higher dimensional wavefunctions as demonstrated later.

The wavefunctions in Equation 3.3.22 are somewhat more difficult than 1-D analogs to visualize because they are two dimensional. Nevertheless, we can still visualize them, and Figure 3.3.1 shows the following wavefunctions: $\psi_{1,1}(x, y)$, $\psi_{2,1}(x, y)$ and $\psi_{2,2}(x, y)$.

$$\psi_{n_x, n_y}(x, y)$$

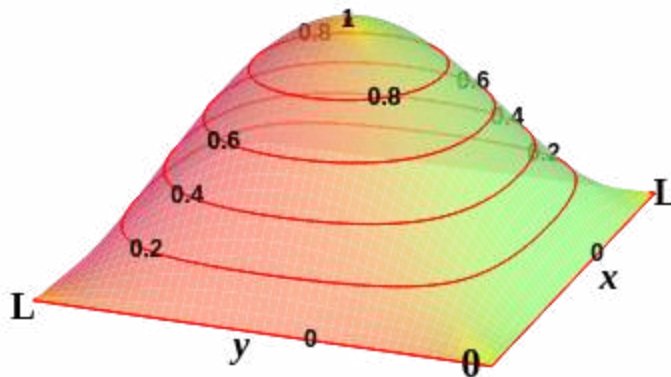


Figure 3.3.1: Visualizing the first six wavefunctions for a particle in a two-dimensional square box ($L_x = L_y = L$). Use the slide bar to independently change either n_x or n_y quantum number and see the changing wavefunction.

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.

$$\psi_{n_x, n_y}(x, y)$$

$$|\psi_{n_x, n_y}(x, y)|^2$$

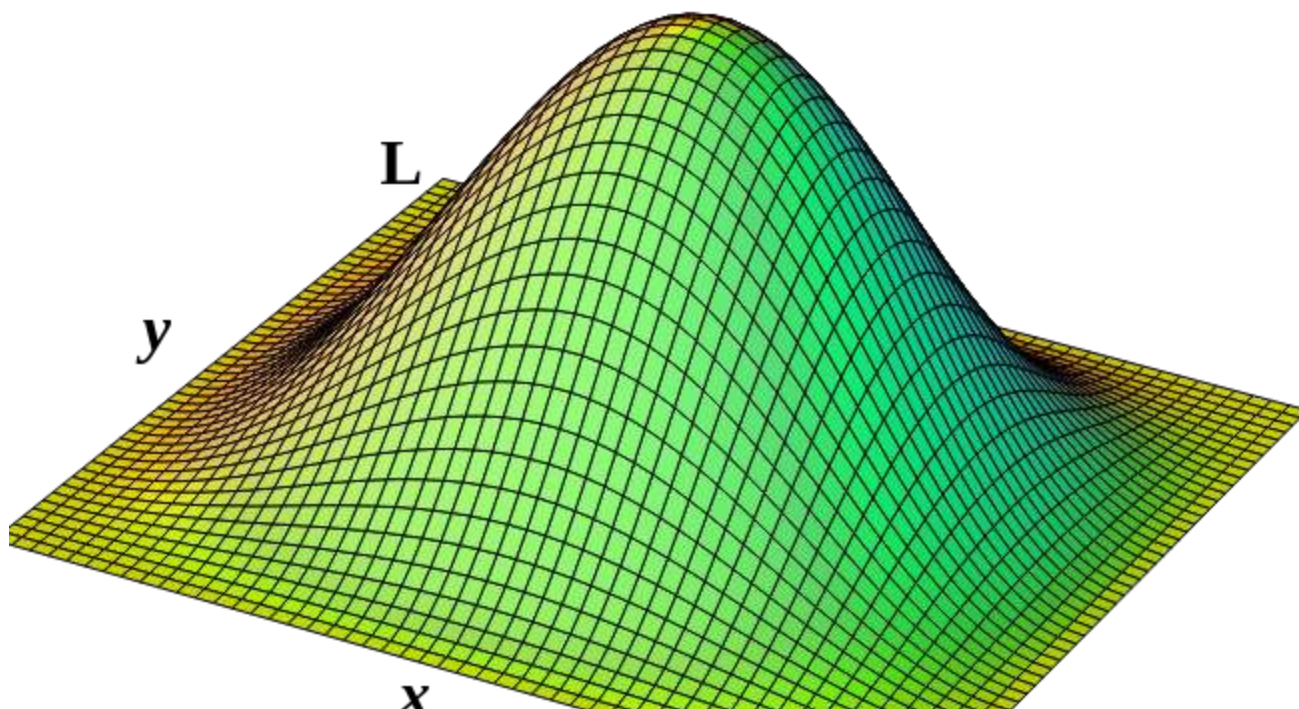


Figure 3.3.2: Visualizing the first six wavefunctions and associated probability densities for a particle in a two-dimensional square box ($L_x = L_y = L$). Use the slide bar to independently change either n_x or n_y quantum number and see the changing wavefunction.

Unlike in the one-dimensional analogue, 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:

$$\psi_{n_x n_y}(x, y) = \psi_{n_x}(x) \psi_{n_y}(y) \quad (3.3.23)$$

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

$$\begin{aligned} P(x \in [a, b] \text{ and } y \in [c, d]) &= \int_a^b dx \int_c^d dy |\psi_{n_x n_y}(x, y)|^2 \\ &= \int_a^b dx \int_c^d dy \psi_{n_x}^2(x) \psi_{n_y}^2(y) \\ &= \left[\int_a^b \psi_{n_x}^2(x) dx \right] \left[\int_c^d \psi_{n_y}^2(y) dy \right] \end{aligned} \quad (3.3.24)$$

✓ Example 3.3.1: 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 3.3.24, we have

$$\begin{aligned} P(x \in [0, L/2] \text{ and } y \in [0, L/2]) &= \left[\int_0^{L/2} \psi_1^2(x) dx \right] \left[\int_0^{L/2} \psi_2^2(y) dy \right] \\ &= \left[\frac{2}{L} \int_0^{L/2} \sin^2\left(\frac{\pi x}{L}\right) dx \right] \left[\frac{2}{L} \int_0^{L/2} \sin^2\left(\frac{2\pi y}{L}\right) dy \right] \\ &= \left[\frac{2}{L} \frac{L}{4} \right] \left[\frac{2}{L} \frac{L}{4} \right] \\ &= \frac{1}{4} \end{aligned}$$

This can be graphically confirmed by exploring the probability densities in Figure 3.3.2 for the $\psi_{1,2}(x, y)$ state.

? Exercise 3.3.1

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 3.3.2 for 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:

$$E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \quad (3.3.25)$$

instead of Equation 3.3.19 and

$$\psi_{n_x, n_y}(x, y) = \frac{2}{\sqrt{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \quad (3.3.26)$$

instead of Equation 3.3.22

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 3.3.3 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.

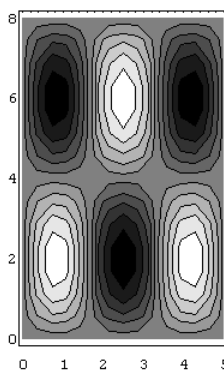


Figure 3.3.2: Contours of the $n_x = 2$ and $n_y = 3$ wavefunction (left) and $n_x = 3$ and $n_y = 2$ wavefunction (right).

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 3.3.25 with $n_x = 1$ and $n_y = 1$. This energy (E_{11}) is hence

$$E_{1,1} = \frac{2\hbar^2\pi^2}{2mL^2} \quad (3.3.27)$$

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* have 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 wavefunction has same energy:

$$E_{2,1} = E_{1,2} = \frac{5\hbar^2\pi^2}{2mL^2} \quad (3.3.28)$$

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

$$n^2 = n_x^2 + n_y^2 \quad (3.3.29)$$

as well as the degree of degeneracy are depicted in Table 3.3.1.

Table 3.3.1: 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:

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}. \quad (3.3.30)$$

✓ Example 3.3.2: 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 3.3.25

$$E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

and for a square well $L_x = L_y = L$ this simplifies to Equation 3.3.19

$$E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2)$$

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 3.3.1 demonstrates) to a higher energetic state, e.g., $(n_x = 2, n_y = 2)$.

The energy of the lowest excited state is $\frac{5\hbar^2}{8mL^2}$ and the energy of the next higher excited state is $\frac{8\hbar^2}{8mL^2}$, 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 expression 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

$$\begin{aligned} L &= \sqrt{\frac{3\hbar \pi}{4mc}} \lambda \\ &= 1.91 \text{ nm} \end{aligned}$$

? Exercise 3.3.2

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.

- What is the length of the box if this potential well is a square ($L_x = L_y = L$)?
- How many wavefunction exist between these two states (do not count the start or ending states)

Answer a

$$L = 3.5 \text{ nm}$$

Answer b

From the energies in Table 3.3.1, 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

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3.4: 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).

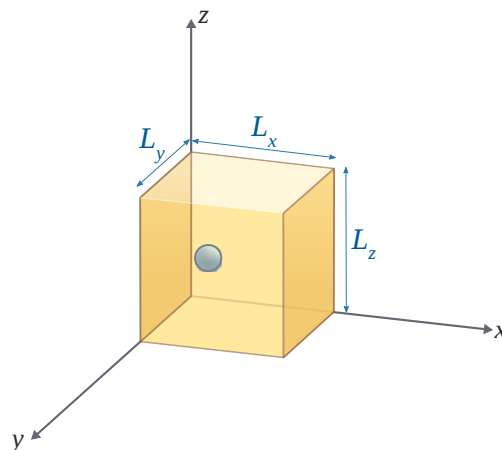


Figure 3.9.1 : A particle in 3D box with three lengths L_x , L_y , and L_z . (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \quad (3.4.1)$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrodinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \quad (3.4.2)$$

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):

$$\psi(x, y, z) = X(x)Y(y)Z(z) \quad (3.4.3)$$

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 3.4.3 into Equation 3.4.2 and divide it by the xyz product:

$$\begin{aligned}\frac{d^2\psi}{dx^2} &= YZ \frac{d^2X}{dx^2} \Rightarrow \frac{1}{X} \frac{d^2X}{dx^2} \\ \frac{d^2\psi}{dy^2} &= XZ \frac{d^2Y}{dy^2} \Rightarrow \frac{1}{Y} \frac{d^2Y}{dy^2} \\ \frac{d^2\psi}{dz^2} &= XY \frac{d^2Z}{dz^2} \Rightarrow \frac{1}{Z} \frac{d^2Z}{dz^2} \\ \left(-\frac{\hbar^2}{2mX} \frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY} \frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ} \frac{d^2Z}{dz^2}\right) &= E\end{aligned}\quad (3.4.4)$$

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 3.4.4 to equal zero:

$$\begin{aligned}\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2} \varepsilon_x X &= 0 \\ \frac{d^2Y}{dy^2} + \frac{2m}{\hbar^2} \varepsilon_y Y &= 0 \\ \frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2} \varepsilon_z Z &= 0\end{aligned}$$

Now we can add all the energies together to get the total energy:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \quad (3.4.5)$$

Do these equations look familiar? They should because we have now reduced the 3D box into three particle in a 1D box problems!

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2} E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad (3.4.6)$$

Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,

$$n = 1, 2, \dots \infty$$

Use the normalization wavefunction equation for each variable:

$$\psi(x) = \begin{cases} \sqrt{\frac{2}{L_x}} \sin \frac{n\pi x}{L_x} & \text{if } 0 \leq x \leq L \\ 0 & \text{if } L < x < 0 \end{cases}$$

Normalization wavefunction equation for each variable (that substitute into Equation 3.4.3):

$$X(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi x}{L_x}\right) \quad (3.4.7)$$

$$Y(y) = \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi y}{L_y}\right) \quad (3.4.8)$$

$$Z(z) = \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_z \pi z}{L_z}\right) \quad (3.4.9)$$

The limits of the three quantum numbers

- $n_x = 1, 2, 3, \dots \infty$
- $n_y = 1, 2, 3, \dots \infty$
- $n_z = 1, 2, 3, \dots \infty$

For each constant use the de Broglie Energy equation:

$$\varepsilon_x = \frac{n_x^2 h^2}{8mL_x^2} \quad (3.4.10)$$

with $n_x = 1 \dots \infty$

Do the same for variables n_y and n_z . Combine Equation 3.4.3 with Equations 3.4.7-3.4.9 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \quad (3.4.11)$$

with

$$V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}}$$

To find the Total Energy, add Equation 3.4.10 and Equation 3.4.5.

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad (3.4.12)$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.4.12) and a 1D box.

3.4.1: 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 3.4.12 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 3.4.11). The particle having a particular value of energy in the excited state *MAY* have 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 3.4.12 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.

- What is the energy of the 7th energy level?
- 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).

3.4.2: References

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

Solutions to select questions can be found online.

3.2

Determine from the following operators which are linear and nonlinear:

- $\hat{A}f(x) = f(x)^2$ [square $f(x)$]
- $\hat{A}f(x) = f^*(x)$ [form the complex conjugate of $f(x)$]
- $\hat{A}f(x) = 0$ [multiply $f(x)$ by zero]
- $\hat{A}f(x) = [f(x)]^{-1}$ [take the reciprocal of $f(x)$]
- $\hat{A}f(x) = f(0)$ [evaluate $f(x)$ at $x=0$]
- $\hat{A}f(x) = \ln f(x)$ [take the log of $f(x)$]

Solution

It is important to note that an operator $\hat{A}$ is *linear* if

$$\underbrace{\hat{A}[c_1 f(x) + c_2 f_2(x)]}_{\text{left side}} = \underbrace{c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x)}_{\text{right side}}$$

and the operator is *nonlinear* if

$$\underbrace{\hat{A}[c_1 f_1(x) + c_2 f_2(x)]}_{\text{left side}} \neq \underbrace{c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x)}_{\text{right side}}$$

a)

Evaluate the left side

$$\begin{aligned} \hat{A}[c_1 f(x) + c_2 f_2(x)] &= [c_1 f(x) + c_2 f_2(x)]^2 \\ &= c_1^2 f(x)^2 + 2c_1 f(x)c_2 f_2(x) + c_2^2 f_2(x)^2 \end{aligned}$$

Evaluate the right side

$$c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x) = c_1 [f_1(x)]^2 + c_2 [f_2(x)]^2 \neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

b)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1^* f_1^*(x) + c_2^* f_2^*(x)$$

Evaluate the right side

$$\begin{aligned} c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x) &= c_1 f_1^*(x) + c_2 f_2^*(x) \\ &= \hat{A}[c_1 f_1(x) + c_2 f_2(x)] \end{aligned}$$

This operator is linear

c)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = 0$$

Evaluate the right side

$$\begin{aligned} c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x) &= c_1 f_1(x) + c_2 f_2(x) = 0 \\ &= \hat{A}[c_1 f_1(x) + c_2 f_2(x)] \end{aligned}$$

This operator is linear

d)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = \frac{1}{c_1 f_1(x) + c_2 f_2(x)}$$

Evaluate the right side

$$c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x) = \frac{c_1}{f_1(x)} + \frac{c_2}{f_2(x)} \\ \neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

e)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 f_1(0) + c_2 f_2(0)$$

Evaluate the right side

$$= c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x)$$

This operator is linear

f)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = \ln[c_1 f_1(x) + c_2 f_2(x)]$$

Evaluate the right side

$$c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x) = c_1 \ln f_1(x) + c_2 \ln f_2(x) \\ \neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

3.8

Show that for a particle in a box with length a with state $n = 3$ that there are 3 locations along the x axis where the probability density is at a maximum.

Solution

The probability density for a particle in a box for state $n = 3$ is

$$\psi^* \psi = \frac{2}{a} \sin^2 \frac{3\pi x}{a}$$

To maximize the probability density, take its derivative and set it equal to zero and solve for x .

$$\begin{aligned} \frac{d}{dx} \left[\frac{2}{a} \sin^2 \frac{3\pi x}{a} \right] &= \frac{2}{a} \cdot 2 \cdot \sin \frac{3\pi x}{a} \cdot \cos \frac{3\pi x}{a} \cdot \frac{3\pi}{a} = 0 \\ \sin \frac{3\pi x}{a} \cos \frac{3\pi x}{a} &= 0 \end{aligned}$$

We want to not choose values of x that make $\sin \frac{3\pi x}{a} = 0$, as that means that the probability density will be zero. We will only choose the zeros of $\cos \frac{3\pi x}{a}$. So the possible values for x which make

$$\cos \frac{3\pi x}{a} = 0$$

are

$$\begin{aligned} \frac{3\pi x}{a} &= \frac{2m+1}{2} \pi \quad m = 0, 1, 2, \dots \\ x &= \frac{(2m+1)a}{6} \end{aligned}$$

We only choose $m = 0, 1, 2$ and not 3 because $m = 3$ would give $x = \frac{7a}{6}$ which is outside the box. So the locations are

$$\begin{aligned} x &= \frac{a}{6} \\ x &= \frac{a}{2} \\ x &= \frac{5a}{6} \end{aligned}$$

3.13

What range for L is possible for σ_x given:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

where L is the length of the 1-D box? Hint: Remember that σ_x is the uncertainty in the position of a particle in a box.

Solution

For a particle in a box:

$$\langle x \rangle = \frac{L}{2}$$

and

$$\begin{aligned} \langle x^2 \rangle &= \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} \\ \sigma_x &= \sqrt{\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \left(\frac{L}{2}\right)^2} \end{aligned}$$

By inspection, only values of σ_x less than L will make this statement true.

3.14

Using the trigonometric identity

$$\cos(2x) = 2 \cos^2 x - 1$$

show that

$$\begin{aligned} \int_0^a 2 \cos^2 \frac{n\pi x}{a} - 1 dx &= 0 \\ \int_0^a \cos \frac{2n\pi x}{a} dx &= 0 \\ \frac{a}{2n\pi} \sin(2n\pi) &= 0 \end{aligned}$$

3.18

Is the wavefunction $\phi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ orthonormal over $0 \leq x \leq L$. Explain your reasoning.

Solution

For a wavefunction to be orthonormal, it has to satisfy these conditions 1.) it has to be orthogonal and 2.) it has to be normalized.

To show that it is orthogonal:

$$\int_0^L \phi_m \phi_n dx = 0$$

when $m \neq n$

To show that the wavefunction is normalized it must follow that

$$\int_0^L \phi_n \phi_n dx = 1$$

when $m=n$

Because our wavefunction satisfies both conditions, it is an orthonormal function.

We find that

$$\langle \psi_3 | \psi_3 \rangle = \int_{-\infty}^{\infty} \frac{2}{L} \left(\sin \frac{3\pi x}{L} \right)^2 dx = 1$$

and

$$\langle \psi_4 | \psi_4 \rangle = \int_{-\infty}^{\infty} \frac{2}{L} \left(\sin \frac{3\pi x}{L} \right) \left(\sin \frac{4\pi x}{L} \right) dx = 0$$

From orthogonality, we can learn that if n is not equal to m , our dot product will always be zero. But if $n = m$ our dot product will equal 1.

3.22

What is the Heisenberg Uncertainty Principle? Do position and momentum follow the uncertainty principle; why or why not? If they do, what is the minimum uncertainty in the velocity of an electron if it is known to be within 1.5nm of a nucleus?

Solution

The Heisenberg Uncertainty Principle states that two properties that follow cannot be **simultaneously** measured to **arbitrary** precision. Position and momentum follow the principle. If one were to try and commute these two operators, one would not get zero and therefore the properties do not commute. If they do not commute then they cannot be measured to arbitrary precision.

We know that

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

And that $p = mv$. This gives

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

The mass of an electron is known is $m_e \approx 9.1 \times 10^{-31} \text{ kg}$. The problem also gives Δx to be 1.5 nm. From here, it becomes a plug and chug to solve for Δv .

$$\Delta v = 3.86 \times 10^4$$

3.23

Describe the degeneracies of a two-dimensional box whose two sides have different lengths.

Solution

The energies of a two-dimensional box is given by,

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right)$$

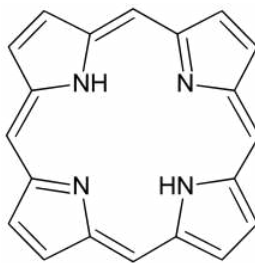
We can see that even if $a \neq b$, the energy levels will not necessarily be degenerate.

3.26

How many degenerate states do the first three energy levels for a three-dimensional particle in a box have if $a = b = c$?

3.27

Metal porphyrin molecules are commonly in many proteins and it has the general structure.



This molecule is planar, so we can approximate π electrons as being confined inside a square. What are energy levels and corresponding degeneracies of a particle in a square of side m ? Porphyrin molecules have 18 π electrons. If the length of the molecule is 850 pm, what is the lowest energy absorption of the porphyrin molecules? (the experimental value $\approx 17,000 \text{ cm}^{-1}$)

Solution

The first energy level is $E_{(1,1,1)}$ which has no degeneracy.

The second energy state is $E_{(2,1,1)} = E_{(1,2,1)} = E_{(1,1,2)}$, therefore it has three degenerate states.

The third energy state is $E_{(2,2,1)} = E_{(2,1,2)} = E_{(1,2,2)}$, therefore it has three degenerate states.

3.26

For a two dimensional box of width w and height $h = \sqrt{a}w$, calculate all possible energy combinations between E_{11} and E_{33} note any degeneracy.

Solution

The energy of a two dimensional particle in the box has the form,

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{w^2} + \frac{n_y^2}{h^2} \right)$$

In this specific case $h = \sqrt{a}w$ so we can simplify the problem to,

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{w^2} + \frac{2n_y^2}{w^2} \right)$$

Now we can tabulate the energy level indicating degeneracy.

E_{xy}	Degeneracy	$\frac{E8mw^2}{h^2}$
E_{11}	1	3
E_{12}, E_{31}	2	5
E_{21}	1	4
E_{22}	1	6
E_{13}, E_{32}	2	7
E_{23}	1	8
E_{33}	1	9

3.32

In this problem, we will explore the quantum-mechanical problem of a free particle that is not restricted to a finite region. Remember quantized energies of a particle in a box is a direct result from the boundary conditions set by the confines of the box.

When the potential energy $V(x)$ is equal to zero and the Schrodinger equation become

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

The two solutions to this Schrodinger equation are

$$\begin{aligned}\psi_1(x) &= A_1 e^{ikx} \\ \psi_2(x) &= A_2 e^{-ikx}\end{aligned}$$

where

$$k = \frac{(2mE)^{1/2}}{\hbar}$$

Show that $\psi_1(x)$ and $\psi_2(x)$ are solution to the Schrodinger equation where the potential energy $V(x)$ is equal to zero

Solution

In order to prove that $\psi_1(x)$ and $\psi_2(x)$ are solutions we need to mention a few values

$$p = \hbar k \rightarrow k = p/\hbar \rightarrow k = \frac{(2mE)^{1/2}}{\hbar}$$

Now we have

$$\begin{aligned}\frac{d^2 A e^{\pm ikx}}{dx^2} + \frac{2mE}{\hbar^2} A e^{\pm ikx} &= 0 \\ A(\pm ik)^2 e^{\pm ikx} + \frac{2mE}{\hbar^2} A e^{\pm ikx} &= 0 \rightarrow -k^2 + \frac{2mE}{\hbar^2} = 0\end{aligned}$$

Cancel the like terms

$$\text{Thus, } k = \frac{(2mE)^{1/2}}{\hbar}, \text{ which equals the original } k \text{ value}$$

3.32

Show that E had to be a positive value, since when E is negative the wave function become unbounded for large x values

Solution

If $E < 0$ then k becomes imaginary, $k = ik$

$$\psi = A e^{\pm ikx} = A e^{\pm i(ik)x} = A e^{\pm kx}$$

For $\psi_1(x) = A_1 e^{-kx}$ this will blow up for $x \rightarrow -\infty$

For $\psi_2(x) = A_2 e^{kx}$ this will blow up for $x \rightarrow \infty$

3.32

With $\hat{P} \psi_1(x)$ and $\hat{P} \psi_2(x)$ as eigenvalue equations, show that

$$\hat{P}\psi_1(x) = -i\hbar \frac{d\psi_1}{dx} = \hbar k \psi_1$$

and

$$\hat{P}\psi_2(x) = -i\hbar \frac{d\psi_2}{dx} = -\hbar k \psi_2$$

Solution

$$\begin{aligned}\hat{P}\psi_1(x) &= -i\hbar \frac{d\psi_1}{dx} = -i\hbar \frac{d}{dx} A_1 e^{+ikx} = -i\hbar A_1 (ik) e^{ikx} = +\hbar k A_1 e^{ikx} = +\hbar k \psi_1 \\ \hat{P}\psi_2(x) &= -i\hbar \frac{d\psi_2}{dx} = -i\hbar \frac{d}{dx} A_2 e^{-ikx} = -i\hbar A_2 (-ik) e^{-ikx} = -\hbar k A_2 e^{-ikx} = -\hbar k \psi_2\end{aligned}$$

Now we can show that

$$E = \frac{p^2}{2m} = \frac{\pm(\hbar)^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

3.32

Show that $\psi_1^* \psi_1(x) = A_1^* A_1 = |A_1|^2$ and that $\psi_2^* \psi_2(x) = A_2^* A_2 = |A_2|^2$

Solution

$$\begin{aligned}\psi_1^* \psi_1(x) &= (A_1 e^{ikx})^* A_1 e^{ikx} \\ &= A_1^* A_1 e^{-ikx} e^{ikx} \\ &= A_1^* A_1 e^{-ikx+ikx} = A_1^* A_1 e^0 \\ &= A_1^* A_1 \\ \psi_2^* \psi_2(x) &= (A_2 e^{-ikx})^* A_2 e^{-ikx} \\ &= A_2^* A_2 e^{ikx} e^{-ikx} \\ &= A_2^* A_2 e^0 = A_2^* A_2\end{aligned}$$

ψ has equal probability to be everywhere when $\Delta x = \infty$ and $\Delta p = 0$

3.33A

Assuming that a particle is characterized by a standing de Broglie wave, come up with an equation for the allowed energies of a particle in a one-dimensional box.

Solution

The de Broglie relationship is

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

Because the waves are standing waves, an integral number of half wave-lengths will fit in the box or:

$$a = \frac{n\lambda}{2}$$

and

$$a = \frac{nh}{2p}$$

Solving for p yields

$$p = \frac{nh}{2a}$$

and the corresponding energy is

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{1}{2m} \frac{n^2 h^2}{4a^2} = \frac{n^2 h^2}{8ma^2}$$

3.33B

Derive the lowest allowed velocity for a proton in a box of length 10^{-14} m (approximate size of nucleus), assuming the particle is described by a standing deBroglie wave.

Solution

The de Broglie wavelength is

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

For a one dimensional wave that has nodes on both ends of a box, an integer number of half wavelengths can fit, so

$$n \left(\frac{\lambda}{2} \right) = L$$

Substituting this wavelength in the de Broglie relationship, one gets

$$\nu = \frac{hn}{2m_L}$$

lowest allowed velocity will have $n = 1$

$$\begin{aligned} \nu &= \frac{(6.626 \times 10^{-34})(1)}{2 \times (1.67 \times 10^{-27})(10^{-14})} \\ &= 19.8 \times 10^6 \text{ m/s} \end{aligned}$$

3.33C

If a particle in a one-dimensional box is described by standing de Broglie waves within the box, derive an equation for the allowed energies. Then use that equation to find the transition energy from $n=1$ to $n=2$ given the length of the box is 350 pm and the mass of an electron is 9.109×10^{-31} kg.

Solution

The de Broglie formula is

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

An integral number of half-wavelengths will fit in the box because the waves are standing waves so

$$\begin{aligned} \frac{n\lambda}{2} &= a \\ \frac{nh}{2p} &= a \end{aligned}$$

Then solving for p

$$p = \frac{nh}{2a}$$

Therefore the energy equation is

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{1}{2m} \frac{n^2 h^2}{4a^2} = \frac{n^2 h^2}{8ma^2}$$

Just plug into the equation to find the transition energy

$$\begin{aligned} \Delta E &= \frac{h^2}{8m_e a^2} (2^2 - 1^2) \\ \Delta E &= \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2 (3)}{8(9.109 \times 10^{-31} \text{ kg})(350 \times 10^{-12} \text{ m})^2} \\ \Delta E &= 1.47 \times 10^{-18} \text{ J} \end{aligned}$$

3.35A

Consider the two wavefunctions

$$\psi_n(x) = \sin \frac{n\pi x}{a}$$

with even n numbers and

$$\psi_n(x) = \cos \frac{n\pi x}{a}$$

with odd n numbers.

Prove that the wavefunctions can be symmetric and antisymmetric by using the operation x to $-x$, a is a constant.

Given that the Schrödinger equation has the expression:

$$\hat{H}(x)\psi_n(x) = E_n\psi_n(x)$$

Through the operation x to $-x$, the equation now becomes:

$$\hat{H}(-x)\psi_n(-x) = E_n\psi_n(-x)$$

Show that

$$\hat{H}(x) = \hat{H}(-x)$$

is true to prove the Schrödinger equation.

Solution

Substituting x by $-x$, for odd n numbers,

$$\hat{\psi}_n(-x) = \cos \frac{-n\pi x}{a} = \cos \frac{n\pi x}{a} = \hat{\psi}_n(x) \quad (3.E.1)$$

For even n numbers,

$$\hat{\psi}_n(-x) = \sin \frac{-n\pi x}{a} = -\sin \frac{n\pi x}{a} = -\hat{\psi}_n(x) \quad (3.E.2)$$

Thus, the wavefunction for odd n number is symmetric and even n numbers is antisymmetric.

And,

$$\hat{H}(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} = \hat{H}(x) \quad (3.E.3)$$

$$\hat{H}(-x) = -\frac{\hbar^2}{2m} \frac{d^2}{d(-x)^2} = \hat{H}(x) \quad (3.E.4)$$

Thus,

$$\hat{H}(x) = \hat{H}(-x)$$

and

$$\hat{H}(x)$$

is an even function of x .

3.35B

Show that the Hamiltonian for a Rigid Rotor Model is odd.

Solution

$$\hat{H}(x) = \hat{H}(-x)$$

so

$$\hat{H} = -\frac{h^2}{4\pi\mu}\nabla^2$$
$$\nabla^2 = \frac{d^2y}{dx^2} + \frac{d^2y}{dy^2} + \frac{d^2y}{dz^2}$$

so

$$\frac{d^2y}{dx^2}(x) = 0$$

and

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

so

$$\hat{H}(x) = 0$$

and

$$\hat{H}(-x) = 0$$

so

$$\hat{H}(x) = \hat{H}(-x)$$

3.E: The Schrödinger Equation and a Particle in a Box (Exercises) is shared under a [CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

4: Second Model, Vibrational Motion

- 4.1: A Harmonic Oscillator Obeys Hooke's Law
- 4.2: The Harmonic Oscillator Energy Levels
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- 4.4: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials
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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.

4.1.1: The Classical Harmonic Oscillator

Simple harmonic oscillators about a potential energy minimum can be thought of as a ball rolling frictionlessly in a curved dish or a pendulum swinging frictionlessly back and forth (Figure 5.1.2). The restoring forces are precisely the same in either horizontal direction.

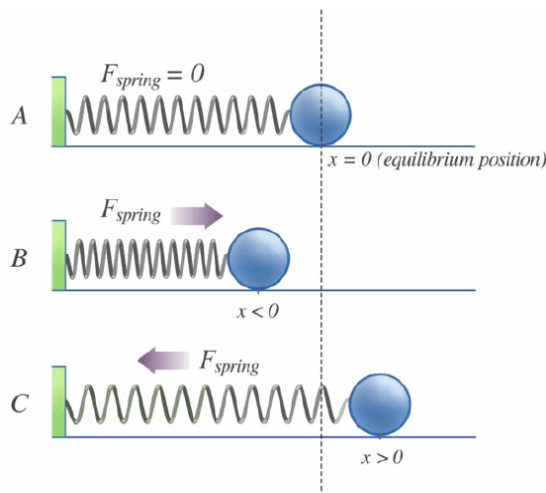


Figure 5.1.2 : A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (CC BY-NC; Ümit Kaya via LibreTexts)

If we consider the bond to behave like a mass on a spring (Figure 5.1.2), then this restoring force (F) is proportional to the displacement (x) from the equilibrium length (x_o) - this is [Hooke's Law](#):

$$F = -kx \quad (4.1.1)$$

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.

$$V(x) = \frac{1}{2}kx^2 \quad (4.1.2)$$

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 .

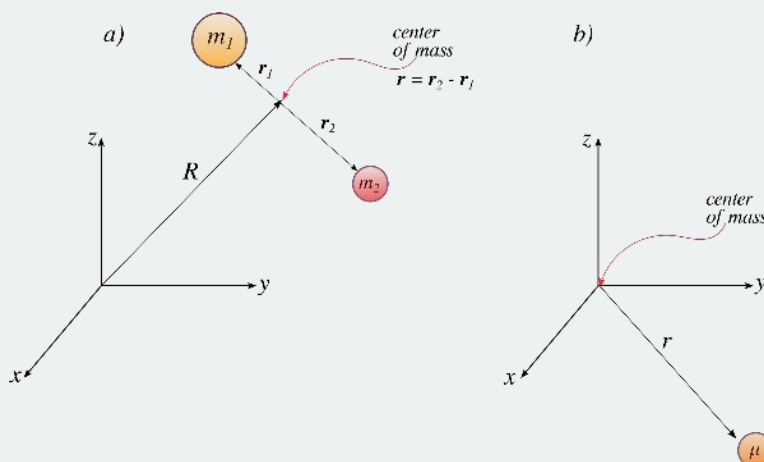


Figure 5.1.3 : Diagrams of the coordinate systems and relevant vectors for the motion of (a) a two-particle diatomic molecule with atoms of mass m_1 and m_2 and (b) the equivalent one-particle pseudo-particle of reduced mass μ . (CC BY-NC; Ümit Kaya via LibreTexts)

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

- 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.
- Show that the second derivative is the force constant, k .
- At what value of x is the potential energy a minimum; at what value of x is the force zero?
- 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

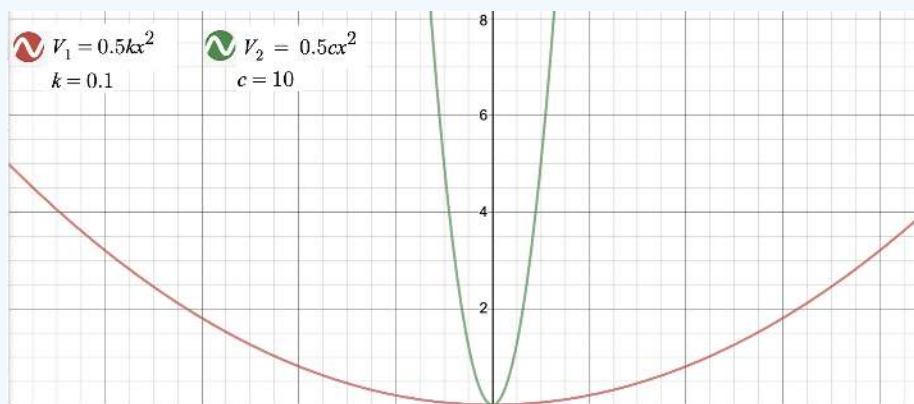
$$V''(x) = \frac{d}{dx} kx = k$$

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.

4.1.2: Solving the Harmonic Oscillator Model

The classical equation of motion for a one-dimensional simple harmonic oscillator with a particle of mass m attached to a spring having spring constant k is

$$m \frac{d^2 x(t)}{dt^2} = -kx(t) \quad (4.1.3)$$

which can be rewritten in the standard form:

$$\frac{d^2 x(t)}{dt^2} + \frac{k}{m} x(t) = 0 \quad (4.1.4)$$

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

$$x(t) = x_o \sin(\omega t + \phi) \quad (4.1.5)$$

with

$$\omega = \sqrt{\frac{k}{m}} \quad (4.1.6)$$

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.

$$\begin{aligned} \frac{d^2 x(t)}{dt^2} + \frac{k}{m} x(t) &= 0 \\ \frac{d^2}{dt^2} (x_0 e^{i\omega t}) + \frac{k}{m} x_0 e^{i\omega t} &= 0 \\ x_0 \frac{d^2}{dt^2} (e^{i\omega t}) + \frac{k}{m} x_0 e^{i\omega t} &= 0 \\ x_0 i^2 \omega^2 (e^{i\omega t}) + \frac{k}{m} x_0 e^{i\omega t} &= 0 \\ x_0 i^2 \omega^2 e^{i\omega t} + \frac{k}{m} x_0 e^{i\omega t} &= 0 \\ x_0 i^2 \omega^2 + \frac{k}{m} x_0 &= 0 \\ -x_0 \frac{k}{m} + \frac{k}{m} x_0 &= 0 \text{ with } \omega = \sqrt{\frac{k}{m}} \end{aligned}$$

Solution b

This requires simply placing the given function $x(t) = x_0 e^{-i\omega t}$ into Equation 4.1.4.

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

? Exercise 5.1.1

Show that sine and cosine functions also are solutions to Equation 4.1.4.

Answer

Using Equation 4.1.4

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

with $\omega = \sqrt{\frac{k}{m}}$.

For

$$x(t) = x_o \sin(\omega t + \phi)$$

Take the second derivative of $x(t)$

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

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.

4.1.3: Harmonic Oscillator Energies

The energy of the vibration is the sum of the kinetic energy and the potential energy. The momentum associated with the harmonic oscillator is

$$p = m \frac{dx}{dt} \quad (4.1.7)$$

so combining Equations 4.1.7 and 4.1.2, the total energy can be written as

$$E = T + V \quad (4.1.8)$$

$$= \frac{p^2}{2m} + \frac{k}{2}x^2 \quad (4.1.9)$$

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.

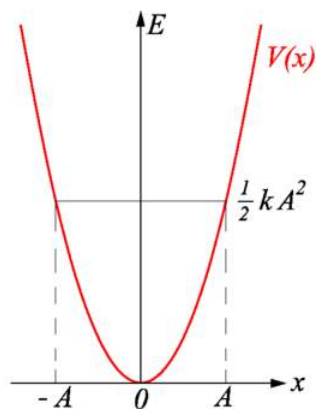


Figure 5.1.5 : The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x . The potential energy $V(x) = \frac{1}{2}kx^2$ is shown in red. (Paul Wormer Wikipedia).

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.)

✓ Example 5.1.3

- What happens to the frequency of the oscillation as the vibration is excited with more and more energy?
- What happens to the maximum amplitude of the vibration as it is excited with more and more energy?

Solution

- Frequency

The energy of the harmonic oscillator can be written as

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

and the frequency of oscillation is $\omega = \sqrt{\frac{k}{m}}$. Notice that the frequency depends only on the stiffness (k) and reduced mass (μ) of the oscillator and not on the energy. Hence, increasing the energy of the vibrations does not affect its frequency.

- 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

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

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 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.

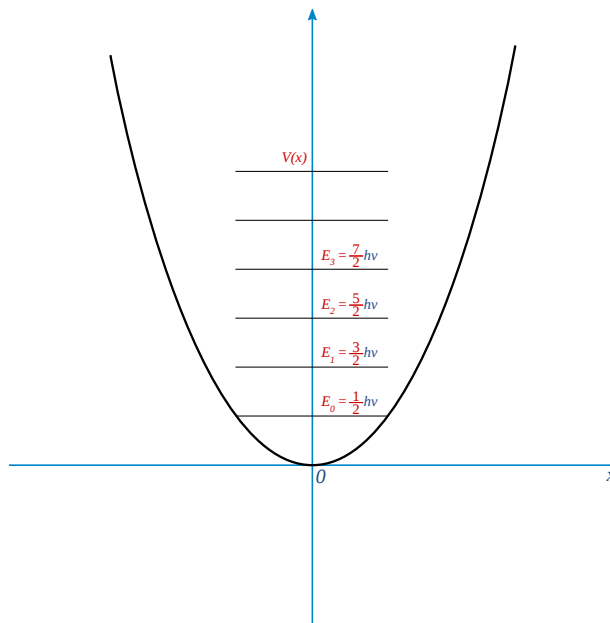


Figure 4.2.1 : Potential energy function and first few energy levels for harmonic oscillator. (CC BY=NC; Ümit Kaya via LibreTexts)

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 4.2.1 and Figure 4.2.1 .

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega = \left(v + \frac{1}{2}\right) h\nu \quad (4.2.1)$$

with

$$v = 0, 1, 2, 3, \dots \infty$$

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

$$P_{Q \rightarrow Q+dQ} = \int_Q^{Q+dQ} \psi_v^*(Q) \psi_v(Q) dQ \quad (4.2.2)$$

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 $\langle P_Q^2 \rangle$, 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 4.2.1

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 of its 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

$$\int_{-\infty}^{\infty} \psi_v^*(x) \psi_v(x) dx = 1 \quad (4.2.3)$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x) \psi_v(x) dx = 0 \quad \text{for } v' \neq v \quad (4.2.4)$$

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

$$\frac{\hbar\omega}{2} = \frac{kQ_0^2}{2} \quad (4.2.5)$$

*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 4.2.1 which is

$$\omega = \sqrt{\frac{k}{\mu}} \quad (4.2.6)$$

Contributors and Attributions

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

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4.3: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For studying the energetics of molecular vibration we take the simplest example, a diatomic heteronuclear molecule AB. Let the respective masses of atoms A and B be m_A and m_B . For diatomic molecules, we define the reduced mass μ_{AB} by:

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \quad (4.3.1)$$

Reduced mass is the representation of a two-body system as a single-body one. When the motion (displacement, vibrational, rotational) of two bodies are only under mutual interactions, the inertial mass of the moving body with respect to the body at rest can be simplified to a reduced mass.

4.3.1: Reduced Mass

Viewing the multi-body system as a single particle allows the separation of the motion: vibration and rotation, of the particle from the displacement of the center of mass. This approach greatly simplifies many calculations and problems.

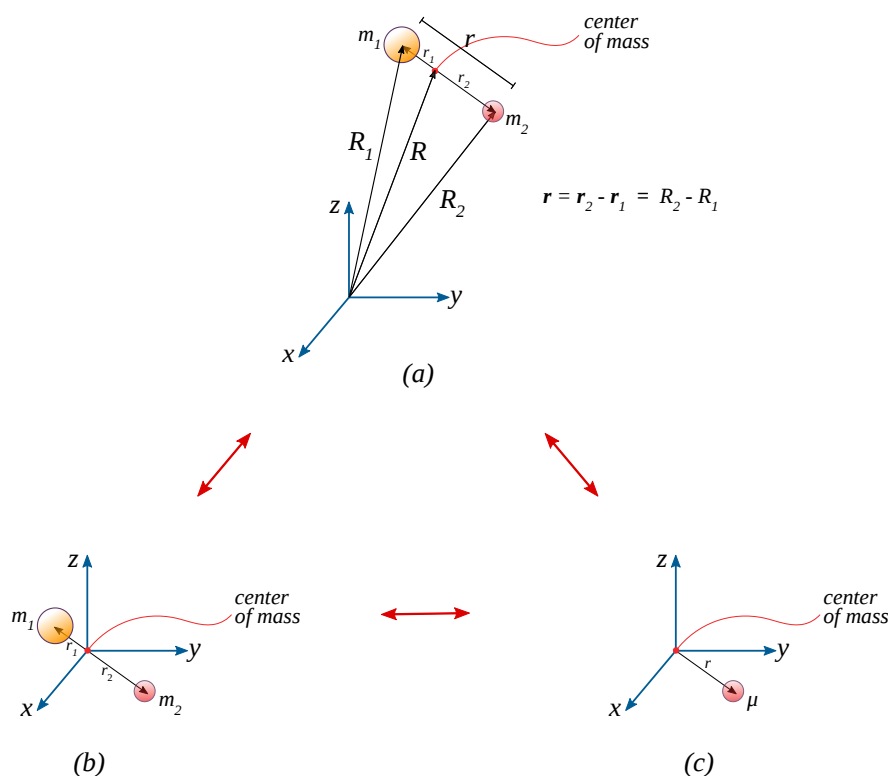


Figure 5.2.1 : a) the individual vectors to the particles m_1 and m_2 in the coordinate space and the resultant vector. b) center of mass. c) reduced mass. (CC BY-NC; Ümit Kaya via LibreTexts)

This concept is readily used in the general motion of diatomics, i.e. simple harmonic oscillator (vibrational displacement between two bodies, following Hooke's Law), the rigid rotor approximation (the moment of inertia about the center of mass of a two-body system), spectroscopy, and many other applications.

✓ Example 5.2.1 : Reduced Mass

Determine the reduced mass of the two body system of a proton and electron with $m_{proton} = 1.6727 \times 10^{-27} \text{ kg}$ and $m_{electron} = 9.110 \times 10^{-31} \text{ kg}$.

Answer

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

4.3.2: The Quantum Harmonic Oscillator

The classical Harmonic Oscillator approximation is a simple yet powerful representation of the energetics of an oscillating spring system. Central to this model is the formulation of the quadratic potential energy

$$V(x) \approx \frac{1}{2} kx^2 \quad (4.3.2)$$

One problem with this classical formulation is that it is not general. We cannot use it, for example, to describe vibrations of diatomic molecules, where quantum effects are important. This requires the formulation for Schrödinger Equation using Equation 4.3.2.

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

Solving this quantum harmonic oscillator is appreciably harder than solving the Schrödinger Equation for the simpler particle-in-the-box model and is outside the scope of this text. However, as with most quantum modules (and in contrast to the classical harmonic oscillator), the energies are quantized in terms of a quantum number (v in this case):

$$E_v = \hbar \left(\sqrt{\frac{k}{\mu}} \right) \left(v + \frac{1}{2} \right) \quad (4.3.3)$$

$$= h\nu \left(v + \frac{1}{2} \right) \quad (4.3.4)$$

with the natural vibrational frequency of the system given as

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (4.3.5)$$

and the mass, μ , is the reduced mass of the system (Equation 4.3.1).

Warning

Be careful to distinguish ν , the symbol for the natural frequency (as a Greek nu) from v the quantum harmonic oscillator quantum number (Latin v).

Caution: Do Not Use Atomic Weights to Calculate Reduced Masses

The vibrational frequencies given by Equation 4.3.5 depend on the force constants (k) and the atomic masses of the vibrating nuclei via the reduced mass (μ). It should be clear that the substitution of one isotope of an atom in a molecule for another isotope will affect the atomic masses and therefore the reduced mass (via Equation 4.3.1) and therefore the vibrational frequencies (via Equation 4.3.5).

It is important to remember that the Periodic Table gives only atomic weights of elements, which are scaled averages of atoms normally encountered in the laboratory (Table 5.2.1). To properly discuss vibrational frequencies of molecules, we need to know (or denote) the specific isotopes in the molecule. Check Table A4 for that information.

Table 5.2.1: Atomic Mass and Isotope Composition. Consult Table A4 for more extensive table.

isotope	atomic mass (in amu)	isotopic abundance (%)
^1H	1.007825	99.985
^2H	2.0140	0.015

isotope	atomic mass (in amu)	isotopic abundance (%)
^{35}Cl	35.968852	75.77
^{37}Cl	36.965903	24.23
^{79}Br	78.918336	50.69
^{81}Br	80.916289	49.31

✓ Example 5.2.1 : Isotope Effect

What are the reduced mass for $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$? If the spring constants for vibrations of both molecules are equal and estimated at 478 N/m , what are the natural vibrational frequencies of these two molecules?

Solution

The periodic table gives an atomic weight of 35.45 amu for chlorine, but remember this is the the average of the natural abundances of different chlorine isotopes which is dictated primary by two isotopes: ^{35}Cl and ^{37}Cl . For this problem, we need the exact mass of the ^1H , ^{35}Cl , and ^{37}Cl isotopes. Check Table A4 for that information.

For $^1\text{H}^{35}\text{Cl}$:

$$\begin{aligned}
 \text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\
 &= \frac{m_{\text{H}} m_{^{35}\text{Cl}}}{m_{\text{H}} + m_{^{35}\text{Cl}}} \\
 &= \frac{(1.0078)(34.9688)}{1.0078 + 34.9688} \text{ amu} \\
 &= 0.9796 \text{ amu}
 \end{aligned}$$

or when converted into kg is $1.629 \times 10^{-27} \text{ kg}$.

For $^1\text{H}^{37}\text{Cl}$:

$$\begin{aligned}
 \text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\
 &= \frac{m_{\text{H}} m_{^{37}\text{Cl}}}{m_{\text{H}} + m_{^{37}\text{Cl}}} \\
 &= \frac{(1.0078)(36.965)}{1.0078 + 36.965} \text{ amu} \\
 &= 0.9810 \text{ amu}
 \end{aligned}$$

or when converted into kg is $1.6291 \times 10^{-27} \text{ kg}$. This is only 0.29% bigger.

Equation 4.3.5 is used to predict the respective vibrational frequencies of these two molecules.

For $^1\text{H}^{35}\text{Cl}$:

$$\begin{aligned}
 \nu &= \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \\
 &= \frac{1}{2\pi} \sqrt{\frac{478 \text{ N/m}}{1.629 \times 10^{-27} \text{ kg}}} \\
 &= 8.6394 \times 10^{13} \text{ s}^{-1}
 \end{aligned}$$

For $^1\text{H}^{37}\text{Cl}$:

$$\begin{aligned}\nu &= \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2\pi} \sqrt{\frac{478 \text{ N/m}}{1.629 \times 10^{-27} \text{ kg}}} \\ &= 8.621 \times 10^{13} \text{ s}^{-1}\end{aligned}$$

As with the differences in the reduced masses, the differences in the vibrational frequencies of these two molecules is quite small. However, high resolution IR spectroscopy can easily distinguish the vibrations between these two molecules. Exercise 5.2.1 will demonstrate that this "**isotope effect**" is not always a small effect.

? Exercise 5.2.1 : Hydrogen Chloride

The force constant is weakly sensitive to the specific isotopes in a molecule (and we typically assume it is isotope independent). If the $k = 478 \text{ N/m}$ for both H^{35}Cl and H^{37}Cl . What are the vibration frequencies in these two diatomic molecules.

Answer

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

D^{35}Cl : 2081 cm^{-1}

4.3: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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4.4: 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 polyatomic 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, $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \quad (4.4.1)$$

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero. As shown in Equation 4.4.1, 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,

$$\hat{H}(q) = \frac{1}{2\mu} \hat{P}_q^2 + \frac{k}{2} \hat{q}^2 \quad (4.4.2)$$

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

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu} \frac{d^2}{dq^2} + \frac{k}{2} q^2 \quad (4.4.3)$$

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

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi_v(q)}{dq^2} + \frac{k}{2} q^2 \psi_v(q) = E_v \psi_v(q) \quad (4.4.4)$$

or upon rearranging

$$\frac{d^2\psi_v(q)}{dq^2} + \frac{2\mu}{\hbar^2} \left(E_v - \frac{k}{2} q^2 \right) \psi_v(q) = 0 \quad (4.4.5)$$

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

$$\beta^2 = \frac{\hbar}{\sqrt{\mu k}} \quad (4.4.6)$$

and then changing the variable from q to x where

$$x = \frac{q}{\beta} \quad (4.4.7)$$

so that

$$\frac{d^2}{dq^2} = \frac{1}{\beta^2} \frac{d^2}{dx^2} \quad (4.4.8)$$

After substituting Equations 4.4.6 and 4.4.8 into Equation 4.4.5, the differential equation for the harmonic oscillator becomes

$$\frac{d^2 \psi_v(x)}{dx^2} + \left(\frac{2\mu\beta^2 E_v}{\hbar^2} - x^2 \right) \psi_v(x) = 0 \quad (4.4.9)$$

? Exercise 4.4.1

Make the substitutions given in Equations 4.4.6 and 4.4.8 into Equation 4.4.5 to get Equation 4.4.9.

4.4.1: Solving for the Quantum Wavefunctions

A common strategy for solving differential equations, which is employed here, is to find a solution that is valid for large values of the variable and then develop the complete solution as a product of this asymptotic solution and a power series. Since the potential energy approaches infinity as x and the coordinate q approach infinity, the wavefunctions must approach zero (this is, the wavefunctions must **converge to zero**):

$$\lim_{x \rightarrow \infty} \psi_v(x) = 0 \quad (4.4.10)$$

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

$$\lim_{x \rightarrow \infty} \phi_v(x) \exp\left(\frac{-x^2}{2}\right) = 0 \quad (4.4.11)$$

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

$$\begin{aligned} \phi_v(x) &= \sum_{n=0}^{\infty} c_n(v) x^n \\ &= c_n(v)x + c_n(v)x^2 + c_n(v)x^3 + \dots \end{aligned}$$

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.

$$\sum_{n=0}^v c_n x^n \quad (4.4.12)$$

Each of the truncations of the power series in Equation 4.4.12 can be multiplied by the exponential function in Equation 4.4.11 to create a family of valid solutions to the differential equation in Equation 4.4.9.

$$\psi_v(x) = \sum_{n=0}^v c_n x^n \exp\left(\frac{-x^2}{2}\right) \quad (4.4.13)$$

? Exercise 4.4.2

Write the first four polynomials, $v = 0$ to $v = 1$, $v = 12$, $v = 13$, $v = 14$ for Equation 4.4.12 and use suitable software to prepare plots of these polynomials. Identify the curves in the plots.

? Exercise 4.4.3

Confirm that the wavefunction given by Equation 4.4.13 is a solution to the harmonic oscillator Schrödinger Equation in Equation 4.4.9 for $v = 0$ and $v = 1$.

4.4.1.1: Hermite Polynomials

While polynomials in general approach ∞ (or $-\infty$) as x approaches ∞ , the decreasing exponential term overpowers the polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of x or $-x$. The exact forms

of polynomials that solve Equation 4.4.9 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 4.4.1 . Hermite polynomials will be discussed in more detail in the following Section.

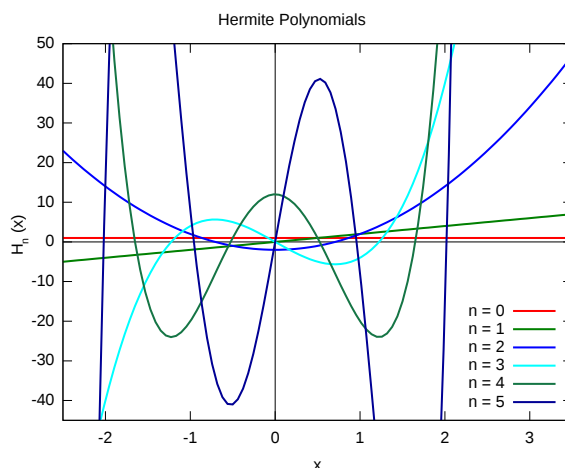


Figure 4.4.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; [Alessio Damato](#), Vulpecula and others via Wikipedia)

? Exercise 4.4.4

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 .

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \quad (4.4.14)$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \quad (4.4.15)$$

📌 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 4.4.7) and a different constant α :

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

so Equation 4.4.15 becomes

$$\psi_v(x) = N_v'' H_v(\sqrt{\alpha}Q) e^{-\alpha Q^2/2}$$

with a slightly different normalization constant

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

? Exercise 4.4.5

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

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \quad (4.4.16)$$

with $v = 0, 1, 2, 3, \dots$

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 4.4.6

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 4.4.16, 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 4.4.2, and the corresponding probability densities are shown in Figure 4.4.3. 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.

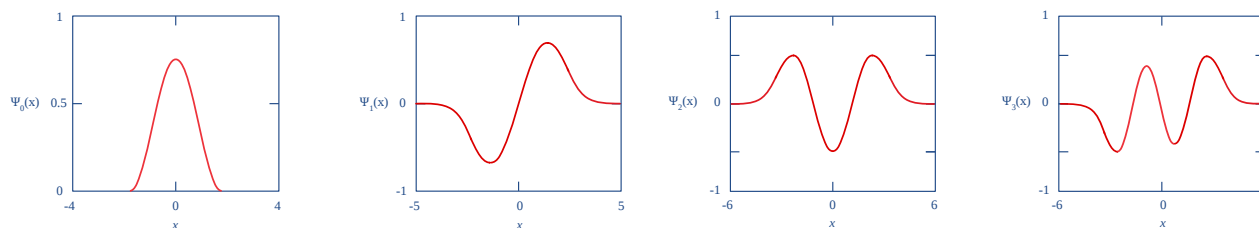


Figure 4.4.2 : The harmonic oscillator wavefunctions describing the four lowest energy states.

? Exercise 4.4.7

Write a few sentences describing and comparing the plots in Figure 4.4.2 . 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?

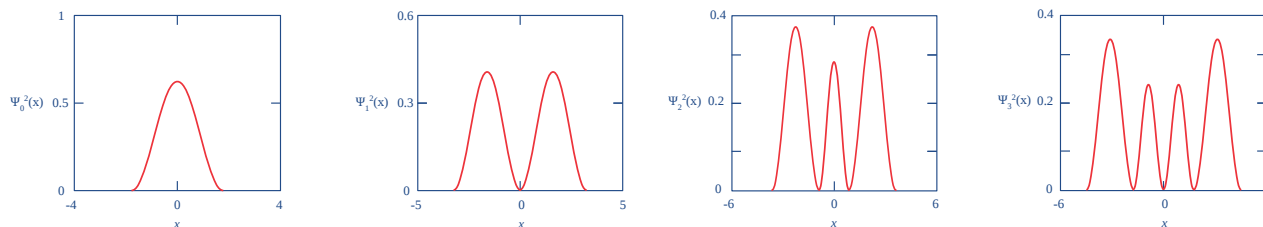


Figure 4.4.3 : The probability densities for the four lowest energy states of the harmonic oscillator.

? Exercise 4.4.8

Explain how Figure 4.4.3 is related to Figure 4.4.2 . Explain the physical significance of the plots in Figure 4.4.3 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 4.4.2 is simply the wavefunction in Figure 4.4.1 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 4.4.9

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 4.4.9 , 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.

4.4.2: Tunneling in the Quantum Harmonic Oscillator

The observation that the wavefunctions are not zero at the classical limit means that the quantum mechanical oscillator has a finite probability of having a displacement that is larger than what is classically possible. The oscillator can be in a region of space where the potential energy is greater than the total energy. Classically, when the potential energy equals the total energy, the kinetic energy and the velocity are zero, and the oscillator cannot pass this point. A quantum mechanical oscillator, however, has a finite probability of passing this point. For a molecular vibration, this property means that the amplitude of the vibration is larger than

what it would be in a classical picture. In some situations, a larger amplitude vibration could enhance the chemical reactivity of a molecule.

? Exercise 4.4.10

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 4.4.3. The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region (Figure 4.4.3). To calculate this probability, we use

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \quad (4.4.17)$$

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

$$P[\text{allowed}] = 2 \int_0^{Q_0} \psi_0^*(Q) \psi_0(Q) dQ \quad (4.4.18)$$

The factor 2 appears in Equation 4.4.18 from the changing 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 4.4.18, 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 4.4.18 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}} \int_0^1 \exp(-x^2) dx \quad (4.4.19)$$

The integral in Equation 4.4.19 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, $\text{ERF}(1) = 0.843$ and $P[\text{forbidden}] = 0.157$. 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 4.4.11

Numerically verify that $P[\text{allowed}]$ in Equation 4.4.19 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

Contributors and Attributions

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

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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](#)

$$V(x) = V(x_0) + \left. \frac{dV(x)}{dx} \right|_{x_0} (x - x_0) + \frac{1}{2!} \left. \frac{d^2V(x)}{dx^2} \right|_{x_0} (x - x_0)^2 + \dots + \frac{1}{n!} \left. \frac{d^n V(x)}{dx^n} \right|_{x_0} (x - x_0)^n \quad (4.5.1)$$

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

$$V(x) = \frac{1}{2} kx^2 + \frac{1}{6} \gamma x^3 \quad (4.5.2)$$

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 4.5.2 demonstrates, the harmonic oscillator (red curve) is a good approximation for the exact potential energy of a vibration (blue curve).

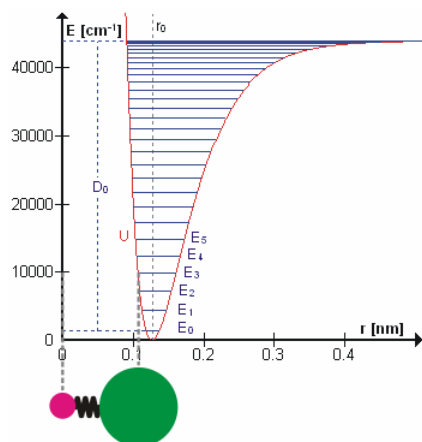


Figure 4.5.1 : The vibration of the HCl molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, HCl is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed 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 4.5.2 ; green curve) improves the harmonic oscillation approximation especially under greater displacement from equilibrium.

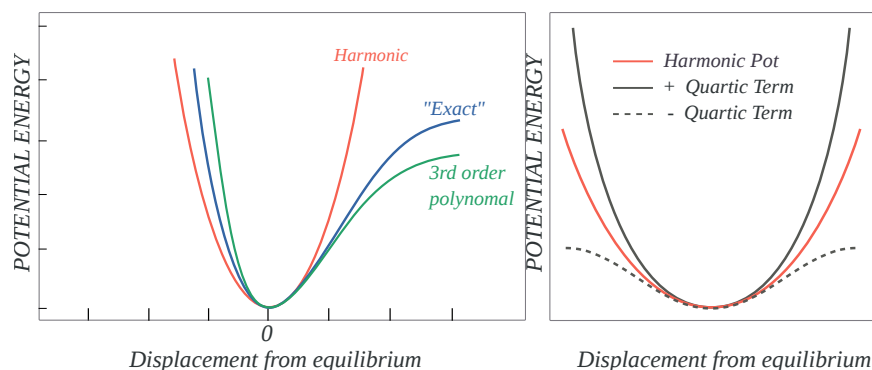


Figure 4.5.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

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 4.5.1 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 4.5.1 with the Schrödinger equation) and have the general form

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + \text{higher terms} \quad (4.5.3)$$

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 4.5.1 ; 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 4.5.4).

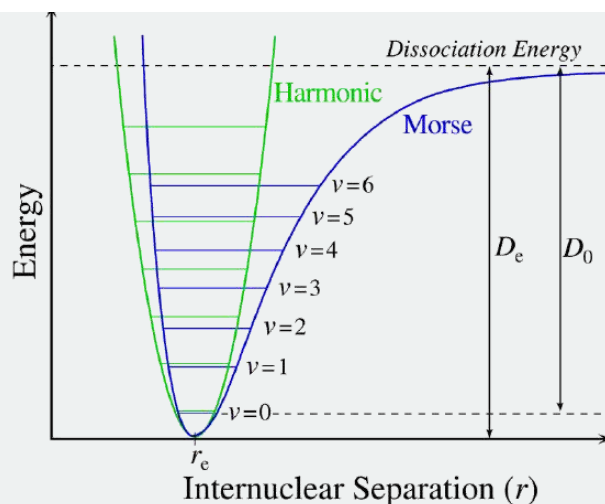


Figure 4.5.4 : The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by $\hbar\omega$, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation 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_0 :

$$V(x) = D(1 - e^{-\beta(x-x_0)})^2 \quad (4.5.4)$$

with $V(x = x_0) = 0$ and $V(x = \infty) = D$.

The Morse Potential (Figure 4.5.4) 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 4.5.4) is not trivial, but can be done analytically.

$$\hat{H}|\psi\rangle = E_n|\psi\rangle$$

with

$$\hat{H} = \hat{T} + \hat{V} \quad (4.5.5)$$

$$= \frac{-\hbar^2 d^2}{2m dx^2} + D(1 - e^{-\beta(x-x_0)})^2 \quad (4.5.6)$$

The solutions and energies for the Morse potential will not be used in this course and will not be discussed in more detail.

Contributors and Attributions

- Peter Kelly (UCDavis)

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4.6: 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.

4.6.1: IR Spectroscopy

Transitions between vibrational energy levels can be induced about by absorption or emission of radiation. To understand this, knowledge of both the initial and final eigenstates is needed. The energy of the v^{th} eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad (4.6.1)$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞ . Equation 4.6.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \quad (4.6.2)$$

where ν_m is the vibrational frequency of the vibration. Equation 4.6.2 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

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v) h\nu_m \end{aligned} \quad (4.6.3)$$

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 4.6.3 simplifies to

$$\begin{aligned} h\nu_{\text{photon}} &= h\nu_m \\ &= \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \end{aligned} \quad (4.6.4)$$

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:

$$\tilde{\nu}(\text{cm}^{-1}) = \frac{1}{\lambda(\mu\text{m})} \times 10^4 \left(\frac{\mu\text{m}}{\text{cm}} \right) \quad (4.6.5)$$

$$= \frac{\nu(\text{Hz})}{c(\text{cm/s})} \quad (4.6.6)$$

Equation 4.6.3 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (4.6.7)$$

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 $\text{N} \cdot \text{m}^{-1}$.

Molecule	HF	HCl	HBr	HI	CO	NO
Force constant, k ($\text{N} \cdot \text{m}^{-1}$)	970	480	410	320	1860	1530

For the diatomic molecules listed above, calculate the following:

- angular frequency ($\text{rad} \cdot \text{s}^{-1}$)
- natural frequency (Hz)
- period (s)
- separation between energy levels
- wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$.

Solution

For HCl:

- angular frequency

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

- natural frequency:

$$\nu = \frac{\omega}{2\pi} = 8.68 \times 10^{13}$$

- period (s):

$$T = \frac{1}{\nu} = 1.15 \times 10^{-14}$$

- separation between energy levels:

$$\Delta E = E_{v=1} - E_{v=0} = \hbar\omega = 5.75 \times 10^{-20} \text{ J}$$

e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$:

$$3.46 \times 10^{-6} \text{ m}$$

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 (ν), HZ
Near	0.78 -2.5	12800 - 4000	3.8×10^{14} - 1.2×10^{14}
Middle	2.5 - 50	4000 - 200	3.8×10^{14} - 1.2×10^{14}
Far	50 -100	200 -10	3.8×10^{14} - 1.2×10^{14}
Most Used	2.5 -15	4000 -670	3.8×10^{14} - 1.2×10^{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 2886 cm^{-1} . Compute the vibrational energy of H^{35}Cl in its lowest state.

- Compute the classical limit for the stretching of the HCl bond from its equilibrium length in this state.
- What percent of the equilibrium bond length is this extension?

Solution

The $\text{H}-\text{Cl}$ bond length is $0.127 \text{ nm} = 1.27 \times 10^{-10} \text{ m}$ and the IR transition is observed at 2886 cm^{-1} . We first convert this to Hertz

$$2886 \text{ cm}^{-1} (3 \times 10^{10} \text{ cm/s}) = 8.646 \times 10^{13} \text{ s}^{-1} = 8.646 \times 10^{13} \text{ Hz}$$

The equations for the energy of the v^{th} eigenstate of a harmonic oscillator is

$$E_v = (v + 1/2)\hbar\omega$$

So the ground state ($v = 0$) energy is

$$E_0 = \frac{1}{2}\hbar\omega$$

with

$$\begin{aligned}\omega &= 2\pi\nu \\ &= 5.54 \times 10^{14} \text{ rad/s}\end{aligned}$$

We can then extra the ground state vibrational energy (aka zero-point energy) from

$$\begin{aligned}
 E_o &= \frac{1}{2} \hbar \omega \\
 &= \frac{1}{2} \hbar (5.54 \times 10^{14} \text{ rad/s}) \\
 &= 2.916 \times 10^{-20} \text{ J}
 \end{aligned}$$

The classical limit of the stretch is denoted as Q_0 , this can be equated as potential energy in relation to the total E_0 found above as, at E_0 , all of the energy would be potential energy in the form of the stretch. In comparison to the classic spring potential

$$V = \frac{1}{2} k Q_0^2$$

As described above, we can relate the two as

$$\frac{1}{2} \hbar \omega = \frac{1}{2} k Q_0^2$$

or,

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

where $Q_0 = 1.10 \times 10^{-11} \text{ m} = 0.0110 \text{ nm}$.

Lastly, this classical limit to length can be compared to the equilibrium bond length by a simple relation of

$$\begin{aligned}
 \text{Percent bond length} &= \frac{Q_0}{x_{eq}} \times 100\% \\
 &= \frac{0.110 \text{ nm}}{0.127 \text{ nm}} \times 100\% \\
 &= 86.6\%
 \end{aligned}$$

4.6.2: Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can transition from one vibrational energy state to another. Which transitions between vibrational states are allowed? When discussing the Bohr hydrogen atom in Chapter 1, we identified multiple transitions between different states as being responsible for the line spectra emission of the hydrogen atom. No limitations were identified so that any transition between any starting state and ending state was possible and this resulted in a complex pattern in the spectra. As we will identify later on, when considering multi-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:

$$\mu_T = \langle \psi_{v'} | \hat{\mu}(x) | \psi_v \rangle \quad (4.6.8)$$

$$= \int_{-\infty}^{\infty} \psi_{v'}^*(x) \hat{\mu}(x) \psi_v(x) dx \quad (4.6.9)$$

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 observed). Transitions with low probabilities are called "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.

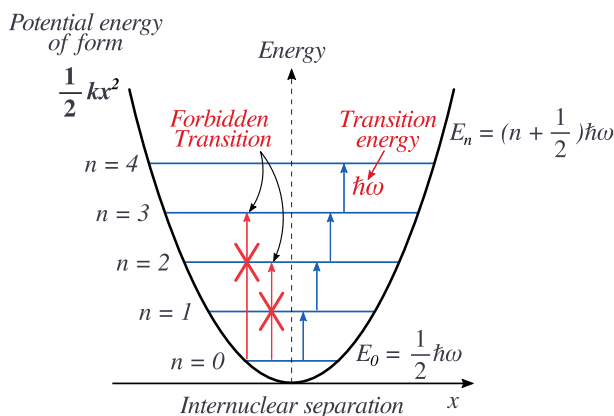


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 4.6.9, 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

$$\hat{\mu} = \sum_{\text{electrons}} e\vec{r} + \sum_{\text{nuclei}} q\vec{R} \quad (4.6.10)$$

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 equilibrium position ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left. \frac{d\mu(x)}{dx} \right|_{x=0} x + \left. \frac{d^2\mu(x)}{dx^2} \right|_{x=0} x^2 + \dots \quad (4.6.11)$$

Retaining only the first two terms and substituting into Equation 4.6.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left. \frac{d\mu(x)}{dx} \right|_{x=0} \int_{-\infty}^{\infty} x\psi_{v'}^*(x)\psi_v(x)dx \quad (4.6.12)$$

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 4.6.11. 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 4.6.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 4.6.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1. Also note that the second term is zero if

$$\left. \frac{d\mu(x)}{dx} \right|_{x=0} = 0 \quad (4.6.13)$$

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 4.6.12 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 4.6.13 **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

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \quad (4.6.14)$$

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 4.6.4. 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

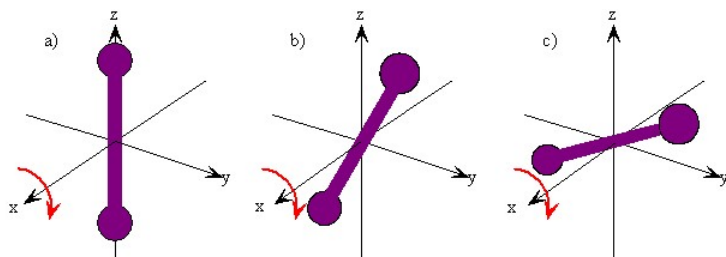
Compute the approximate transition frequencies in wavenumber units for the first and second overtone transitions in HCl given that the fundamental is at $2,886\text{ cm}^{-1}$.

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CHAPTER OVERVIEW

5: 3rd Model: Rotational Motion



[5.1: The Energy Levels of a Rigid Rotor](#)

[5.2: The Rigid Rotator is a Model for a Rotating Diatomic Molecule](#)

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5.1: 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

$$E_{tot} = T + V \quad (5.1.1)$$

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 simplifies our discussion.

Since $V = 0$ then $E_{tot} = T$ and we can also say that:

$$T = \frac{1}{2} \sum m_i v_i^2 \quad (5.1.2)$$

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

$$\omega = \frac{v}{r} \quad (5.1.3)$$

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

$$v_i = \omega X r_i \quad (5.1.4)$$

Thus we can rewrite Equation 5.1.2 as:

$$T = \frac{1}{2} \sum m_i v_i (\omega X r_i) \quad (5.1.5)$$

Since ω is a scalar constant, we can rewrite Equation 5.1.5 as:

$$T = \frac{\omega}{2} \sum m_i (v_i X r_i) = \frac{\omega}{2} \sum l_i = \omega \frac{L}{2} \quad (5.1.6)$$

where l_i is the **angular momentum** of the i^{th} particle, and L is the angular momentum of the *entire system*. Also, we know from physics that,

$$L = I\omega \quad (5.1.7)$$

where I is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite Equation 5.1.2 as

$$T = \omega \frac{I\omega}{2} = \frac{1}{2} I\omega^2 \quad (5.1.8)$$

Equation 5.1.8 shows that the energy of the rigid rotor scales with increasing angular frequency (i.e., the faster it 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).

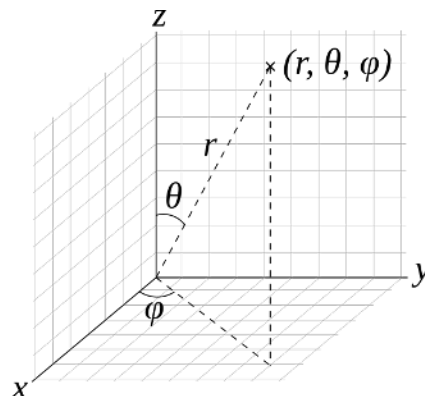


Figure 5.8.1 : The spherical coordinate system in terms of the Cartesian system. (Public Domain; Andeggs via Wikipedia).

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

$$|\psi(\theta, \varphi)\rangle = |\Theta(\theta)\Phi(\varphi)\rangle \quad (5.1.9)$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 5.1.10

$$\hat{H}|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \quad (5.1.10)$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2} \left[\frac{\partial}{\partial r_0} r_0^2 \frac{\partial}{\partial r_0} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] |\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \quad (5.1.11)$$

Since $r = r_0$ is constant for the **rigid rotor** and does not appear as a variable in the functions, the partial derivatives with respect to r are zero; i.e. the functions do not change with respect to r . We also can substitute the symbol I for the moment of inertia, μr_0^2 in the denominator of the left hand side of Equation 5.1.11, to give

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] |\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \quad (5.1.12)$$

To begin the process of the Separating of Variables technique, multiply each side of Equation 5.1.12 by $\frac{2I}{\hbar^2}$ and $\frac{-\sin^2 \theta}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)} \left[\sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \varphi^2} \right] \Theta(\theta)\Phi(\varphi) = \frac{-2IE \sin^2 \theta}{\hbar^2} \quad (5.1.13)$$

Simplify the appearance of the right-hand side of Equation 5.1.13 by defining a parameter λ :

$$\lambda = \frac{2IE}{\hbar^2}. \quad (5.1.14)$$

Note that this λ has no connection to a wavelength; it is merely being used as an algebraic symbol for the combination of constants shown in Equation 5.1.14

Inserting λ , evaluating partial derivatives, and rearranging Equation 5.1.13 produces

$$\frac{1}{\Theta(\theta)} \left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \Theta(\theta) + (\lambda \sin^2 \theta) \Theta(\theta) \right] = -\frac{1}{\Phi(\varphi)} \frac{\partial^2}{\partial \varphi^2} \Phi(\varphi) \quad (5.1.15)$$

? Exercise 5.8.1

Carry out the steps leading from Equation 5.1.13 to Equation 5.1.15. Keep in mind that, if y is not a function of x ,

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

Equation 5.1.15 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

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) \Theta(\theta) + (\lambda \sin^2 \theta - m_J^2) \Theta(\theta) = 0 \quad (5.1.16)$$

and the φ -equation

$$\frac{d^2}{d\varphi^2} \Phi(\varphi) + m_J^2 \Phi(\varphi) = 0 \quad (5.1.17)$$

The partial derivatives have been replaced by total derivatives because only a single variable is involved in each equation.

Often m_J is referred to as just m for convenience.

? Exercise 5.8.2

Show how Equations 5.1.16 and 5.1.17 are obtained from Equation 5.1.15.

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:

$$\Phi_m(\varphi) = N e^{\pm i m_J \varphi} \quad (5.1.18)$$

where we introduce the number m to track how many wavelengths of the wavefunction occur around one rotation (similar to the wavelength description of the Bohr atom).

? Exercise 5.8.3

Substitute Equation 5.1.18 into Equation 5.1.17 to show that it is a solution to that differential equation.

Answer

Substitute

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

into

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

$$\begin{aligned}\frac{d^2}{d\varphi^2} \Phi_m(\varphi) + m_J^2 \Phi_m(\varphi) &= \frac{d}{d\varphi} (N (\pm i m_J) e^{\pm i m_J \varphi}) + m_J^2 \Phi_m(\varphi) \\ &= N (\pm i m_J)^2 e^{\pm i m_J \varphi} + m_J^2 (N e^{\pm i m_J \varphi}) \\ &= -N m_J^2 e^{\pm i m_J \varphi} + N m_J^2 e^{\pm i m_J \varphi} = 0\end{aligned}$$

Thus

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

is a solution to the differential equations.

The normalization condition, Equation 5.1.19 is used to find a value for N that satisfies Equation 5.1.18

$$\int_0^{2\pi} \Phi^*(\varphi) \Phi(\varphi) d\varphi = 1 \quad (5.1.19)$$

The range of the integral is only from 0 to 2π because the angle φ specifies the position of the internuclear axis relative to the x-axis of the coordinate system and angles greater than 2π do not specify additional new positions.

? Exercise 5.8.4

Use the normalization condition in Equation 5.1.19 to demonstrate that $N = 1/\sqrt{2\pi}$.

Answer

We need to evaluate Equation 5.1.19 with $\psi(\varphi) = N e^{\pm i m_J \varphi}$

$$\begin{aligned}\psi^*(\varphi) \psi(\varphi) &= N e^{+i m_J \varphi} N e^{-i m_J \varphi} \\ &= N^2\end{aligned}$$

$$1 = \int_0^{2\pi} N^* N d\varphi = 1$$

$$N^2 (2\pi) = 1$$

$$N = \sqrt{1/2\pi}$$

Values for m are found by using a **cyclic boundary condition**. The cyclic boundary condition means that since φ and $\varphi + 2\pi$ refer to the same point in three-dimensional space, $\Phi(\varphi)$ must equal $\Phi(\varphi + 2\pi)$, i.e.

$$e^{i m_J \varphi} = e^{i m_J (\varphi + 2\pi)} \quad (5.1.20)$$

$$= e^{i m_J \varphi} e^{i m_J 2\pi} \quad (5.1.21)$$

For the equality in Equation 5.1.21 to hold, $e^{i m_J 2\pi}$ must equal 1, which is true only when

$$m_J = \dots, -3, -2, -1, 0, 1, 2, 3, \dots \quad (5.1.22)$$

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 $e^{i m_J 2\pi}$ equals 1 for m_J equal to zero or any positive or negative integer.

Thus, the Φ function is

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

with

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

Solving the $\Theta(\theta)$ Equation

Finding the $\Theta(\theta)$ functions that are solutions to the θ -equation (Equation 5.1.16) is a more complicated process. Solutions are found to be a set of power series called *Associated Legendre Functions* (Table M2), which are power series of trigonometric functions, i.e., products and powers of sine and cosine functions. The $\Theta(\theta)$ functions, along with their normalization constants, are shown in the third column of Table 5.8.1.

Table 5.8.1 : Spherical Harmonic Wavefunctions

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta, \varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}} \cos \theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}} \cos \theta$
1	1	$\sqrt{\frac{3}{4}} \sin \theta$	$\frac{1}{\sqrt{2\pi}} e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}} \sin \theta$	$\frac{1}{\sqrt{2\pi}} e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}} (3 \cos^2 \theta - 1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
1	2	$\sqrt{\frac{15}{4}} \sin \theta \cos \theta$	$\frac{1}{\sqrt{2\pi}} e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}} \sin \theta \cos \theta$	$\frac{1}{\sqrt{2\pi}} e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}} \sin^2 \theta$	$\frac{1}{\sqrt{2\pi}} e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}} \sin^2 \theta$	$\frac{1}{\sqrt{2\pi}} e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\varphi}$

The solution to the θ -equation requires that λ in Equation 5.1.15 be given by

$$\lambda = J(J+1) \quad (5.1.23)$$

where

$$J \geq |m_J| \quad (5.1.24)$$

J can be 0 or any positive integer greater than or equal to m_J . Each pair of values for the quantum numbers, J and m_J , identifies a rotational state with a wavefunction (Equation 5.1.9) and energy (below). Equation 5.1.24 means that J controls the allowed values of m_J .

Each pair of values for the quantum numbers, J and m_J , identifies a rotational state and hence a specific wavefunction with associated energy.

The combination of Equations 5.1.14 and 5.1.23 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2 \lambda}{2I} = J(J+1) \frac{\hbar^2}{2I} \quad (5.1.25)$$

Using Equation 5.1.25, you can construct a rotational energy level diagram (Figure 5.8.2). For simplicity, use energy units of $\frac{\hbar^2}{2I}$.

- $J = 0$: The lowest energy state has $J = 0$ and $m_J = 0$. This state has an energy $E_0 = 0$. There is only **one state** with this energy, i.e. one set of quantum numbers, one wavefunction, and one set of properties for the molecule.
- $J = 1$: The next energy level is $J = 1$ with energy $\frac{2\hbar^2}{2I}$. There are **three states** with this energy because m_J can equal +1, 0, or -1. These different states correspond to different orientations of the rotating molecule in space. States with the same energy are said to be degenerate. The degeneracy of an energy level is the number of states with that energy. The degeneracy of the $J = 1$ energy level is 3 because there are three states with the energy $\frac{2\hbar^2}{2I}$.
- $J = 2$: The next energy level is for $J = 2$. The energy is $\frac{6\hbar^2}{2I}$, and there are **five states** with this energy corresponding to $m_J = +2, +1, 0, -1, -2$. The energy level degeneracy is five. Note that the spacing between energy levels increases as J increases. Also note that the degeneracy increases. The degeneracy is always $2J + 1$ because m_J ranges from $+J$ to $-J$ in integer steps, including 0.

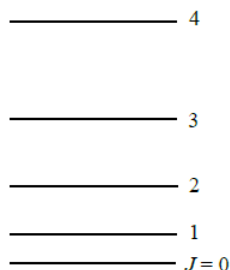


Figure 5.8.2 : Energy spacing for a rigid rotor (in 3D). Notice the energy depends only on J and not depend on m_J . That is, the energy of the rotor is not affected by its orientation.

Each allowed energy of rigid rotor is $(2J + 1)$ -fold degenerate. Hence, there exist $(2J + 1)$ different wavefunctions with that energy.

? Exercise 5.8.6

Compute the energy levels for a rotating molecule for $J = 0$ to $J = 5$ using units of $\frac{\hbar^2}{2I}$.

Answer

This rotating molecule can be assumed to be a rigid rotor molecule. From solving the Schrödinger equation for a rigid rotor we have the relationship for energies of each rotational eigenstate (Equation 5.1.25):

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

Using this equation, we can plug in the different values of the J quantum number so that

$$\text{For } J=0, E = (0)(1)(\hbar^2/2I) = 0 \quad \text{For } J=1, E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$$

This shows that as J increases, the energy levels get farther apart (Figure 5.8.2).

- For $J=2, E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For $J=3, E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For $J=4, E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For $J=5, E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

? Exercise 5.8.7

For $J = 0$ to $J = 5$, identify the degeneracy of each energy level and the values of the m_J quantum number that go with each value of the J quantum number. Construct a rotational energy level diagram including $J = 0$ through $J = 5$. Label each level with the appropriate values for the quantum numbers J and m_J . Describe how the spacing between levels varies with increasing J .

Answer

This rotating molecule can be assumed to be a rigid rotor molecule. From solving the Schrödinger equation for a rigid rotor, we have:

$$\lambda = 2IE/\hbar^2$$

Where λ is an arbitrary parameter not related to wavelength. Additionally, λ is assigned a quantum relation so that

$$\lambda = J(J+1)$$

Thus, combining the two equations and solving for E yields

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

Using this equation, we can plug in the different values of J so that

- For $J=0$, $E = (0)(1)(\hbar^2/2I) = 0$
- For $J=1$, $E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$
- For $J=2$, $E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For $J=3$, $E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For $J=4$, $E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For $J=5$, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

This shows that as J increases, the energy levels get closer and closer together.

📌 Interpretation of Quantum Numbers for a Rigid Rotor

The m_J quantum number reflects the component of the angular momentum along the z direction (and hence is sometimes called the azimuthal quantum number). For a fixed value of J , the different values of m_J reflect the different **directions** the angular momentum vector could be pointing – for large, positive m_J the angular momentum is mostly along $+z$; if m_J is zero the angular momentum is orthogonal to z . Physically, the energy of the rotation does not depend on the direction, which is reflected in the fact that the energy depends only on J (Equation 5.1.25), which measures the length of the vector, not its direction given by m_J .

✓ Example 5.8.7 : Molecular Oxygen

Calculate $J = 0$ to $J = 1$ rotational transition of the O_2 molecule with a bond length of 121 pm.

Solution

$$E = \frac{\hbar^2}{I} = \frac{\hbar^2}{\mu r^2}$$

$$\mu_{O_2} = \frac{m_O m_O}{m_O + m_O} = \frac{(15.9994)(15.9994)}{15.9994 + 15.9994} = 7.9997$$

convert from atomic units to kilogram using the conversion: 1 au = 1.66×10^{-27} kg. Plug and chug.

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

Spherical Harmonics

A wavefunction that is a solution to the rigid rotor Schrödinger Equation (Equation 5.1.9) can be written as a single function $Y(\theta, \varphi)$, which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta) \Phi_{m_J}(\varphi) \quad (5.1.26)$$

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 .

The z axis in this figure is the horizontal, X axis points to the back of the image and the y axis points up in the plane of the page.

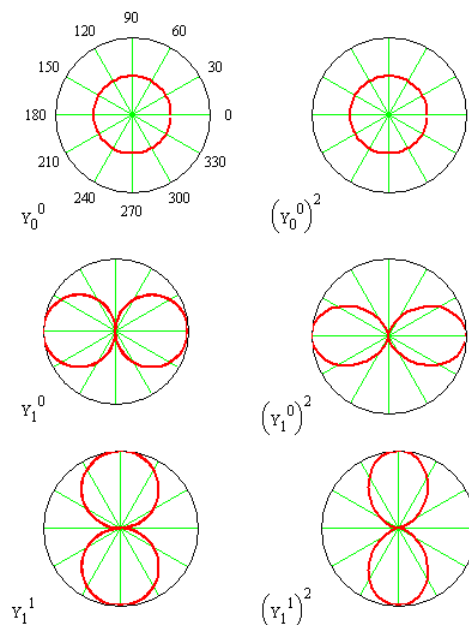


Figure 5.8.3 : Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ .

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 .

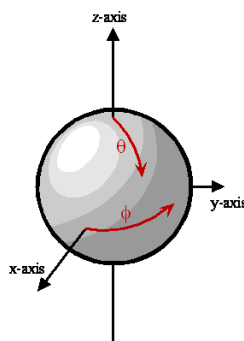


Figure 5.8.4 : Space for a rigid rotor is restricted to the surface of a sphere of radius r_0 . The only degrees of freedom are motions along θ or φ on the surface of the sphere.

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

$$Pr[\theta_0, \varphi_0] = Y_J^{m_J*}(\theta_0, \varphi_0) Y_J^{m_J}(\theta_0, \varphi_0) ds \quad (5.1.27)$$

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

$$ds = \sin \theta d\theta d\varphi \quad (5.1.28)$$

? 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 φ 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

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta \quad (5.1.29)$$

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 $\theta = 90^\circ$. 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 φ .

? Exercise 5.8.10

Write a paragraph describing the information about a rotating molecule that is provided in the polar plot of $Pr[\theta, \varphi]$ 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-dimensions: 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.

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- Mark Tuckerman (New York University)
- MIT OpenCourseWare (Robert Guy Griffin and Troy Van Voorhis)

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

Learning Objectives

- Demonstrate how to use the 3D rigid rotor to describe a rotating diatomic molecules
- Demonstate how microwave spectroscopy can get used to characterize rotating diatomic molecules
- Interpret 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.

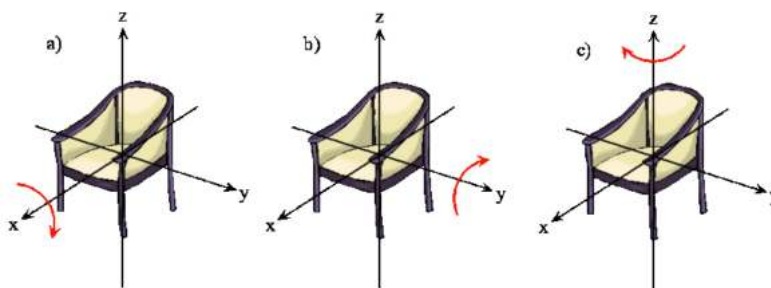


Figure 5.9.1 : Cartesian rotations of a chair. Rotations about the (a) x axis, (b) y axis, and (c) z axis.

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?

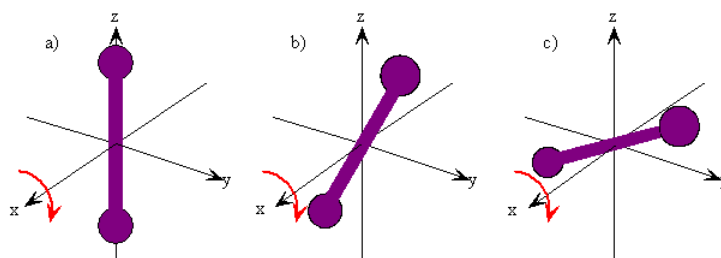


Figure 5.9.2 : Rotation of a diatomic molecule about the x axis.

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 $3 - 40 \text{ cm}^{-1}$.

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, $\hat{\mu}$.

$$\mu_T = \int Y_{J_f}^{m_f*} \hat{\mu} Y_{J_i}^{m_i} \sin \theta d\theta d\varphi \quad (5.2.1)$$

or in bracket notation

$$\mu_T = \langle Y_{J_f}^{m_f} | \hat{\mu} | Y_{J_i}^{m_i} \rangle \quad (5.2.2)$$

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,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \quad (5.2.3)$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \quad (5.2.4)$$

and

$$\Delta m_J = 0, \pm 1 \quad (5.2.5)$$

A photon is absorbed for $\Delta J = +1$ and emitted for $\Delta J = -1$.

? Exercise 5.9.1

Explain why your microwave oven heats water, but not air. Hint: draw and compare Lewis structures for components of air and for water.

The energies of the J^{th} rotational levels are given by

$$E_J = J(J+1) \frac{\hbar^2}{2I} \quad (5.2.6)$$

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

Microwave Transition Energies

The transition energies for absorption of radiation are given by

$$E_{\text{photon}} = \Delta E \quad (5.2.7)$$

$$= E_f - E_i \quad (5.2.8)$$

$$= h\nu \quad (5.2.9)$$

$$= hc\bar{\nu} \quad (5.2.10)$$

Substituting the relationship for energy (Equation 5.2.6) into Equation 5.2.8 results in

$$E_{\text{photon}} = E_f - E_i \quad (5.2.11)$$

$$= J_f(J_f+1) \frac{\hbar^2}{2I} - J_i(J_i+1) \frac{\hbar^2}{2I} \quad (5.2.12)$$

with J_i and J_f representing the rotational quantum numbers of the initial (lower) and final (upper) levels involved in the absorption transition.

Since microwave spectroscopists use frequency units and infrared spectroscopists use wavenumber units when describing rotational spectra and energy levels, both ν and $\bar{\nu}$ are important to calculate. When we add in the constraints imposed by the selection rules to identify possible transitions, J_f in Equation 5.2.12 can be replaced by $J_i + 1$, since the selection rule requires $J_f - J_i = 1$ for the absorption of a photon (Equation 5.2.4). The equation for absorption transitions (Equation 5.2.12) then can be written in terms of the only the quantum number J_i of the initial state.

$$E_{\text{photon}} = h\nu \quad (5.2.13)$$

$$= hc\bar{\nu} \quad (5.2.14)$$

$$= 2(J_i + 1) \frac{\hbar^2}{2I} \quad (5.2.15)$$

Equation 5.2.15 can be rewritten as

$$E_{\text{photon}} = 2B(J_i + 1)$$

where B is the **rotational constant** for the molecule and is defined in terms of the *energy* of the absorbed photon

$$B = \frac{\hbar^2}{2I} \quad (5.2.16)$$

Often spectroscopists want to express the rotational constant in terms of *frequency* of the absorbed photon and do so by dividing Equation 5.2.16 by h

$$B(\text{in freq}) = \frac{B}{h} \quad (5.2.17)$$

$$= \frac{h}{8\pi^2\mu r_0^2} \quad (5.2.18)$$

More often, spectroscopists want to express the rotational constant in terms of *wavenumbers* ($\bar{\nu}$) of the absorbed photon by dividing Equation 5.2.16 by hc ,

$$\tilde{B} = \frac{B}{hc} = \frac{h}{8\pi^2 c \mu r_0^2} \quad (5.2.19)$$

The rotational constant depends on the distance (R) and the masses of the atoms (via the reduced mass) of the nuclei in the diatomic molecule.

? Exercise 5.9.2

Construct a rotational energy level diagram for $J = 0, 1$, and 2 and add arrows to show all the allowed transitions between states that cause electromagnetic radiation to be absorbed or emitted.

? Exercise 5.9.3

Complete the steps going from Equation 5.2.12 to Equation 5.2.16 and identify the units of B at the end.

Answer

$$\Delta E_{\text{photon}} = E_f - E_i$$

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

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

$$J_f - J_i = 1$$

$$J_f = 1 + J_i$$

$$\begin{aligned} E_{\text{photon}} = h\nu = hc\tilde{\nu} &= (1 + J_i)(2 + J_i) \frac{\hbar^2}{2I} - J_i(J_i + 1) \frac{\hbar^2}{2I} \\ &= \frac{\hbar^2}{2I} [2 + 3J_i + J_i^2 - J_i^2 - J_i] \\ &= \frac{\hbar^2}{2I} 2(J_i + 1) \\ &= 2B(J_i + 1) \end{aligned}$$

Now we do a standard dimensional analysis

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

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

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

? Exercise 5.9.4

Infrared spectroscopists use units of wavenumbers. Rewrite the steps going from Equation 5.2.12 to Equation 5.2.16 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 .

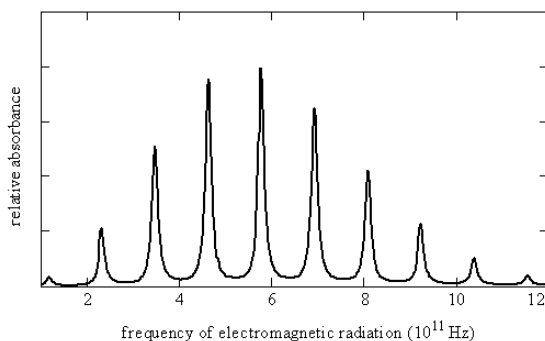


Figure 5.9.3: The rotation spectrum of $^{12}\text{C}^{16}\text{O}$ at 40 K. The peaks are tabulated in Table 5.9.1.

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 $^{12}\text{C}^{16}\text{O}$ 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 5.2.19 predicts a pattern of exactly equally spaced lines. The lowest energy transition is between $J_i = 0$ and $J_f = 1$ so the first line in the spectrum appears at a frequency of $2B$. The next transition is from $J_i = 1$ to $J_f = 2$ so the second line appears at $4B$. The spacing of these two lines is $2B$. In fact the spacing of all the lines is $2B$, which is consistent with the experimental data in Table 5.9.1 showing that the lines are very nearly equally spaced. The difference between the first spacing and the last spacing is less than 0.2%.

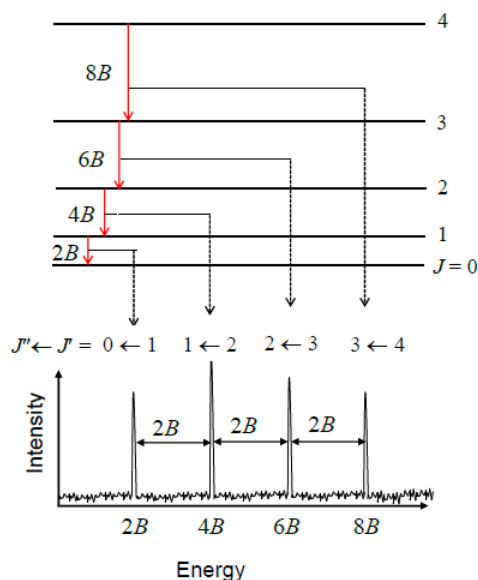


Figure 5.9.4 : Energy levels and line positions calculated in the rigid rotor approximation. (CC BY-SA 3.0; Nrrw via Wikipedia)

? Exercise 5.9.5

Use Equation 5.2.19 to prove that the spacing of any two lines in a rotational spectrum is $2B$, i.e. derive:

$$\nu_{J_i+1} - \nu_{J_i} = 2B$$

Answer

To prove the relationship, evaluate the LHS. First, define the terms:

$$\nu_{J_i} = 2B(J_i + 1), \nu_{J_i+1} = 2B((J_i + 1) + 1)$$

Substitute into the equation and evaluate:

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

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

$$2B = 2B$$

LHS equals RHS. Therefore, the spacing between any two lines is equal to $2B$.

✓ Example 5.9.1 : Rotation of Sodium Hydride

The molecule NaH undergoes a rotational transition from $J = 0$ to $J = 1$ when it absorbs a photon of frequency $2.94 \times 10^{11} \text{ Hz}$. 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 $1 \text{ au} = 1.66 \times 10^{-27} \text{ kg}$. Multiplying this by 0.9655 gives a reduced mass of $1.603 \times 10^{-27} \text{ kg}$. Substituting in for R_e gives

$$\begin{aligned}R_e &= \sqrt{\frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})}{2\pi(1.603 \times 10^{-27} \text{ kg})(2.94 \times 10^{11} \text{ Hz})}} \\ &= 1.899 \times 10^{-10} \text{ m} \\ &= 1.89 \text{ \AA}\end{aligned}$$

? 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 $^{12}\text{C}^{16}\text{O}$.

Solution

- $J=0$: $\nu_0 = 115271.21 \text{ MHz}$
- $J=1$: $\nu_1 = 230538.01 \text{ MHz}$

$$\begin{aligned}\Delta\nu &= 230538.01 \text{ MHz} - 115271.21 \text{ MHz} \\ &= 115266.8 \text{ MHz} \\ &= 1.153 \times 10^{11} \text{ Hz} \\ &= \frac{\hbar}{2\pi\mu R_e^2}\end{aligned}$$

The reduced mass is

$$\begin{aligned}\mu &= \frac{m_C m_O}{m_C + m_O} \\ &= \frac{12.01 \times 16.00}{12.01 + 16.00} \\ &= 6.86 \text{ amu}\end{aligned}$$

Convert to kg

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

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

Advanced: Non-Rigid Rotors

Centrifugal stretching of the bond as J increases causes the decrease in the spacing between the lines in an observed spectrum (Table 5.9.1). This decrease shows that the molecule is not really a rigid rotor. As the rotational angular momentum increases with increasing J , the bond stretches. This stretching increases the moment of inertia and decreases the rotational constant (Figure 5.9.5).



Figure 5.9.5 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY 3.0; www.cleonis.nl).

The effect of centrifugal stretching is smallest at low J values, so a good estimate for B can be obtained from the $J = 0$ to $J = 1$ transition. From B , a value for the bond length of the molecule can be obtained since the moment of inertia that appears in the definition of B (Equation 5.2.16) 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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CHAPTER OVERVIEW

6: The Hydrogen Atom

The solution of the Schrödinger equation (wave equation) for the hydrogen atom uses the fact that the Coulomb potential produced by the nucleus is isotropic (it is radially symmetric in space and only depends on the distance to the nucleus). Although the resulting energy eigenfunctions (the orbitals) are not necessarily isotropic themselves, their dependence on the angular coordinates follows completely generally from this isotropy of the underlying potential: the eigenstates of the Hamiltonian (that is, the energy eigenstates) can be chosen as simultaneous eigenstates of the angular momentum operator. This corresponds to the fact that angular momentum is conserved in the orbital motion of the electron around the nucleus. Therefore, the energy eigenstates may be classified by two angular momentum quantum numbers, ℓ and m (both are integers). The angular momentum quantum number $\ell = 0, 1, 2, \dots$ determines the magnitude of the angular momentum. The magnetic quantum number $m = -\ell, \dots, +\ell$ determines the projection of the angular momentum on the (arbitrarily chosen) z -axis.

[6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly](#)

[6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics](#)

[6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision](#)

[6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers](#)

[6.5: s-orbitals are Spherically Symmetric](#)

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[6.7: The Helium Atom Cannot Be Solved Exactly](#)

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

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass. This reduced particle is located at r , where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume throughout this chapter that the reduced mass equals the electron mass and the proton is located at the center of mass.

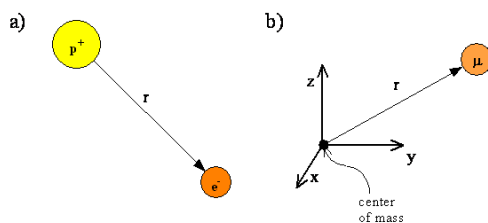


Figure 6.1.1 : (a) The proton (p^+) and electron (e^-) of the hydrogen atom. (b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

? Exercise 6.1.1

- Assuming the Bohr radius gives the distance between the proton and electron, calculate the distance of the proton from the center of mass, and calculate the distance of the electron from the center of mass.
- Calculate the reduced mass of the electron-proton system.
- In view of your calculations in (a) and (b), comment on the validity of a model in which the proton is located at the center of mass and the reduced mass equals the electron mass.

Since the internal motion of any two-particle system can be represented by the motion of a single particle with a reduced mass, the description of the hydrogen atom has much in common with the description of a diatomic molecule discussed previously. The time-independent Schrödinger Equation for the hydrogen atom

$$\hat{H}(r, \theta, \varphi)\psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi) \quad (6.1.1)$$

employs the same kinetic energy operator, $\hat{T}$, written in spherical coordinates. For the hydrogen atom, however, the distance, r , between the two particles can vary, unlike the diatomic molecule where the bond length was fixed and the **rigid rotor** model was applicable. The hydrogen atom Hamiltonian also contains a potential energy term, $\hat{V}$, to describe the attraction between the proton and the electron. This term is the Coulomb potential energy,

$$\hat{V}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (6.1.2)$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a **central potential**.

The full expression for $\hat{H}$ in spherical coordinates is

$$\hat{H}(r, \theta, \varphi) = -\frac{\hbar^2}{2\mu r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \quad (6.1.3)$$

The contributions from rotational and radial components of the motion become clearer if we write out the complete Schrödinger equation,

$$\left\{ -\frac{\hbar^2}{2\mu r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \right\} \psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi) \quad (6.1.4)$$

multiply both sides of Equation 6.1.4 by $2\mu r^2$, and rearrange to obtain

$$\begin{aligned} \hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \psi(r, \theta, \varphi) \right) + 2\mu r^2 \left[E + \frac{e^2}{4\pi\epsilon_0 r} \right] \psi(r, \theta, \varphi) = \\ -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] \psi(r, \theta, \varphi) \end{aligned} \quad (6.1.5)$$

Manipulating the Schrödinger equation in this way helps us recognize the square of the angular momentum operator in Equation 6.1.5. The square of the angular momentum operator in Equation 6.1.6.

$$\hat{M}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] \quad (6.1.6)$$

Substituting Equation 6.1.6 into Equation 6.1.5 produces

$$\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \psi(r, \theta, \varphi) \right) + 2\mu r^2 [E - \hat{V}] \psi(r, \theta, \varphi) = \hat{M}^2 \psi(r, \theta, \varphi) \quad (6.1.7)$$

? Exercise 6.1.2

Show the algebraic steps going from Equation 6.1.4 to 6.1.5 and finally to 6.1.7. Justify the statement that the rotational and radial motion are separated in Equation 6.1.7.

Since the angular momentum operator does not involve the radial variable, r , we can separate variables in Equation 6.1.7 by using a product wavefunction, as we did previously for rigid rotors. We know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions (Table M4), $Y(\theta, \varphi)$, so a good choice for a product function is

$$\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi) \quad (6.1.8)$$

The Spherical Harmonic functions provide information about where the electron is around the proton, and the radial function $R(r)$ describes how far the electron is away from the proton.

To separate variables, substitute the product function, Equation 6.1.8 into Equation 6.1.7, evaluate partial derivatives, divide each side by $R(r)Y(\theta, \varphi)$, and set each side of that resulting equation equal to a constant λ .

$$\frac{\hbar^2}{R(r)} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R(r) + \frac{2\mu r^2}{R(r)} [E - V] R(r) = \lambda \quad (6.1.9)$$

$$\frac{1}{Y(\theta, \varphi)} \hat{M}^2 Y(\theta, \varphi) = \lambda \quad (6.1.10)$$

Equations 6.1.9 and 6.1.10 represent the radial differential equation and the angular differential equation, respectively. As we describe below, they are solved separately to give the $Y(\theta, \varphi)$ angular functions and the $R(r)$ radial functions.

? Exercise 6.1.3

Complete the steps leading from Equations 6.1.7 to 6.1.9 and 6.1.10.

Rearranging Equation 6.1.10 yields

$$\hat{M}^2 Y_l^{m_l}(\theta, \varphi) = \lambda Y_l^{m_l}(\theta, \varphi) \quad (6.1.11)$$

where we have added the indices l and m_l to identify a particular spherical harmonic function. Note that the notation has changed from that used with the Rigid Rotor; it is customary to use J and m_J to represent the angular momentum quantum numbers for rotational states, but for electronic states, it is customary to use l and m_l to represent the same thing. Furthermore, the electronic angular momentum is designated by L and the corresponding operator is called $\hat{L}$. In complete electronic notation, Equation 6.1.11 is

$$\hat{L}^2 Y_l^{m_l}(\theta, \varphi) = \lambda Y_l^{m_l}(\theta, \varphi) \quad (6.1.12)$$

Equation 6.1.12 says that $Y_l^{m_l}(\theta, \varphi)$ must be an eigenfunction of the angular momentum operator $\hat{L}^2$ with eigenvalue λ . We know from the discussion of the Rigid Rotor that the eigenvalue λ is $J(J+1)\hbar^2$, or in electronic notation, $l(l+1)\hbar^2$. Consequently, Equation 6.1.12 becomes

$$\hat{L}^2 Y_l^{m_l}(\theta, \varphi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta, \varphi) \quad (6.1.13)$$

Using this value for λ and rearranging Equation 6.1.9, we obtain

$$-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R(r) + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) - E \right] R(r) = 0 \quad (6.1.14)$$

? Exercise 6.1.4

Write the steps leading from Equation 6.1.9 to Equation 6.1.14.

The details for solving Equation 6.1.14 are provided elsewhere, but the procedure and consequences are similar to previously examined cases. As for the harmonic oscillator, an asymptotic solution (valid at large r) is found, and then the complete solutions are written as products of the asymptotic solution and polynomials arising from sequential truncations of a power series expansion.

Contributors and Attributions

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

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6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

The solutions to the hydrogen atom Schrödinger equation are functions that are products of a spherical harmonic function and a radial function:

$$\psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r)Y_l^{m_l}(\theta, \phi) \quad (6.2.1)$$

The wavefunctions for the hydrogen atom depend upon the three variables r , θ , and ϕ and the three quantum numbers n , l , and m_l . The variables give the position of the electron relative to the nucleus in spherical coordinates. The absolute square of the wavefunction, $|\psi(r, \theta, \phi)|^2$, evaluated at r , θ , and ϕ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r , θ , and ϕ .

? Exercise 6.2.1

What is the value of the integral (in bracket 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 $m = 0, \pm 1, \pm 2, \dots, \pm \infty$. 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 $Y_l^m(\theta, \phi)$.

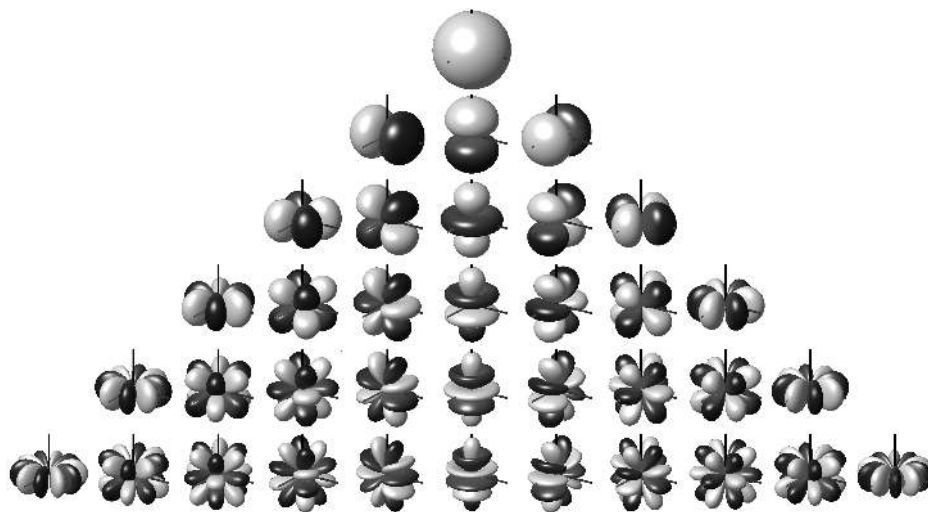


Figure 6.2.1: Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.

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.

- What are the values for n and l ?
- 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:

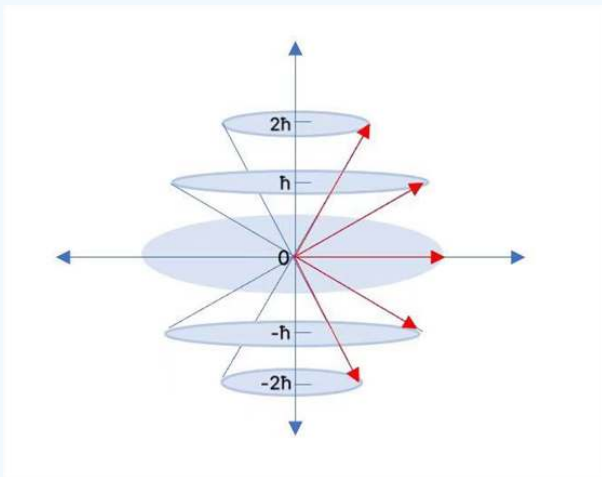
$$E_n = \frac{E_1}{n^2} = \frac{-13.6\text{eV}}{9} = -1.51\text{eV}$$

and angular momentum

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

- 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	$m_l = 0$	$\frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0} \right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \cos \theta$
$\psi_{21\pm 1}$	2	1	$m_l = \pm 1$	$\frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0} \right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin \theta e^{\pm i\phi}$
ψ_{300}	3	0	$m_l = 0$	$\frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} \left(27 - 18 \frac{Zr}{a_0} + 2 \frac{Z^2 r^2}{a_0^2} \right) e^{-\frac{Zr}{3a_0}}$
ψ_{310}	3	1	$m_l = 0$	$\frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0} \right) e^{-\frac{Zr}{3a_0}}$

	n	l	m_l	ψ_{n,l,m_l}
$\psi_{31\pm1}$	3	1	$m_l = \pm 1$	$\frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}};$
ψ_{320}	3	2	$m_l = 0$	$\frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} (3\cos^2\theta)$
$\psi_{32\pm1}$	3	2	$m_l = \pm 1$	$\frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin\theta \cos\theta$
$\psi_{32\pm2}$	3	2	$m_l = \pm 2$	$\frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta e^{\pm 2i\phi}$

We can take superposition states of the solutions to obtain real wavefunctions that do not have any imaginary components:

Table 6.2.2 : The real solutions to the Schrödinger equation for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	m_l	$\psi_{n,l}$
ψ_{1s}	1	0	0	$\frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
ψ_{2s}	2	0	0	$\frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
ψ_{2p_z}	2	1	0	$\frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \cos\theta$
ψ_{2p_x}	2	1	± 1	$\frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta \cos\phi$
ψ_{2p_y}	2	1	± 1	$\frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta \sin\phi$
ψ_{3s}	3	0	0	$\frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-\frac{Zr}{3a_0}}$
ψ_{3p_z}	3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}};$
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	$\frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} (3\cos^2\theta)$
$\psi_{3d_{xz}}$	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	$\frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta \cos 2\phi$
$\psi_{3d_{xy}}$	3	2	± 2	$\frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta \sin 2\phi$

These are the wavefunctions that are most often depicted. Visualizing the variation of an electronic wavefunction with r , θ , and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron-deficient part of one molecule is attracted to an electron-rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately do not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$. Do not confuse such plots with polar plots, which look similar. Probability densities also can be represented by contour maps, as shown in Figure 6.2.2 .

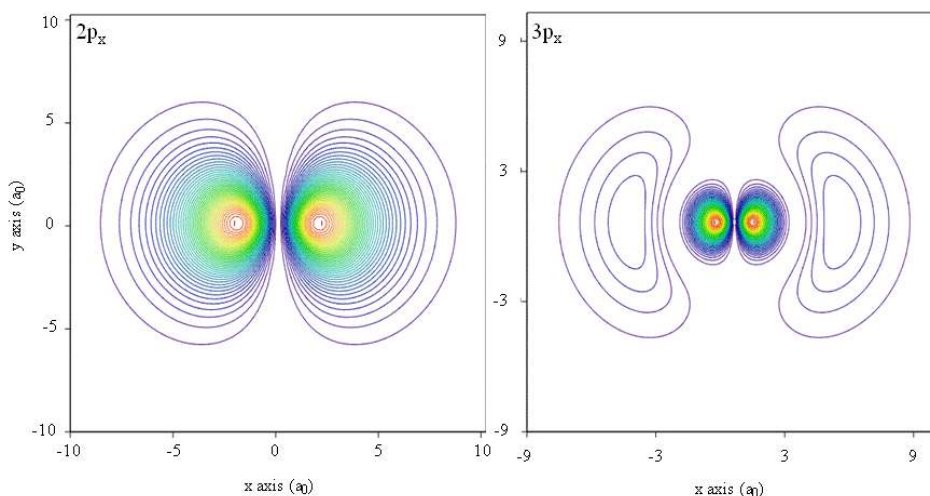


Figure 6.2.2: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical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

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s, 2s, and 2p orbitals plotted in Figure 6.2.3.

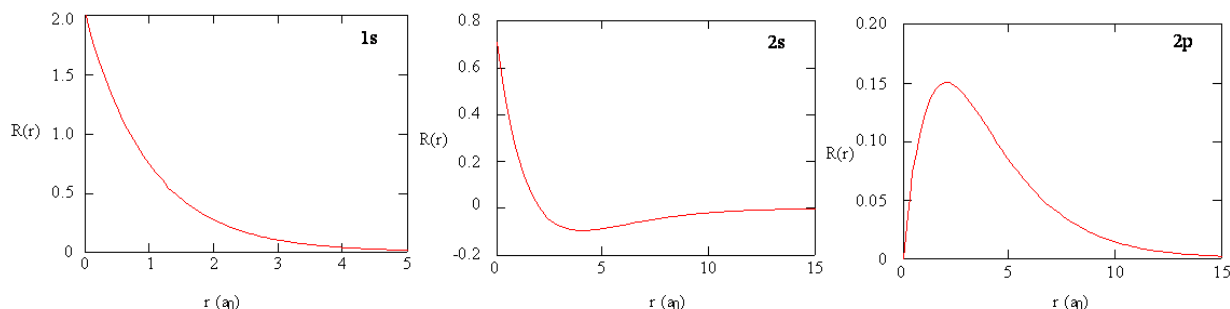


Figure 6.2.3: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

The 1s function in Figure 6.2.3 starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

Next notice how the radial function for the 2s orbital, Figure 6.2.3, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$, but p, d, f and all other functions go to zero at the origin. It is useful to remember that there are $n - 1 - l$ radial nodes in a wavefunction, which means that a 1s orbital has no radial nodes, a 2s has one radial node, and so on.

? Exercise 6.2.5

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

? Exercise 6.2.6

What mathematical feature of each of the radial functions controls the number of radial nodes?

Answer

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

? Exercise 6.2.7 : Radial Node

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

Answer

A node exists when the radial portion of the wavefunction equals 0. The radial portion of the 2s wavefunction is:

$$R(r) = \left(\frac{1}{2\sqrt{2}} \right) \left(\frac{Z}{\alpha_0} \right)^{\frac{3}{2}} (2 - \rho) e^{-\frac{\rho}{2}}$$

where $\rho = \frac{Zr}{\alpha_0}$, $Z = 1$ for the hydrogen atom and α_0 is the Bohr radius.

Therefore:

$$R(r) = \left(\frac{1}{2\sqrt{2}} \right) \left(\frac{1}{\alpha_0} \right)^{\frac{3}{2}} \left(2 - \frac{r}{\alpha_0} \right) e^{-\frac{r}{2\alpha_0}}$$

For this wavefunction:

- $\left(\frac{1}{\alpha_0} \right)^{\frac{3}{2}}$ is a constant and will never equal 0.
- $e^{-\frac{r}{2\alpha_0}}$ 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.

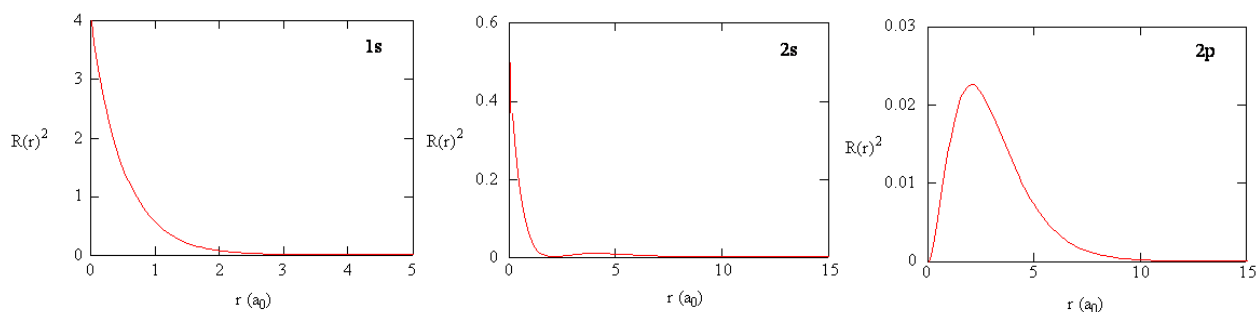


Figure 6.2.4: Radial probability densities for the 1s, 2s, and 2p orbitals.

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.

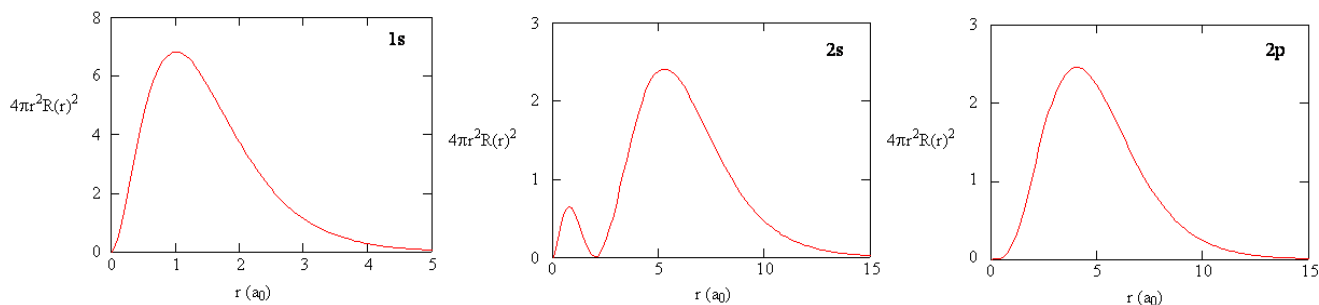


Figure 6.2.5: The radial distribution function for the 1s, 2s, and 2p orbitals.

? 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 .

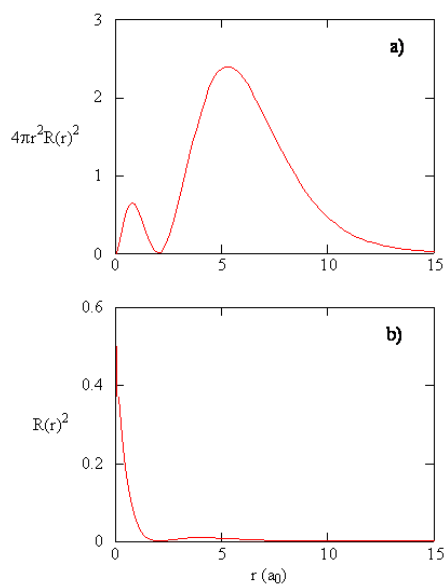


Figure 6.2.6: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

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6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

Learning Objectives

- Understand how to measure the orbital angular momentum of an electron around a nucleus.
- Understand how the Heisenburgh Uncertainty Principle extends to orbital angular momenta.
- Manipulate the angular momenta cyclic permutations that allow two of the three projects to be simultaneous measured

Consider a particle described by the Cartesian coordinates $(x, y, z) \equiv \vec{r}$ and their conjugate momenta $(p_x, p_y, p_z) \equiv \vec{p}$. The classical definition of the *orbital angular momentum* of such a particle about the origin is (i.e., via the [vector cross product](#)):

$$\vec{L} = \vec{r} \times \vec{p}$$

which can be separated into projections into each of the primary axes :

$$L_x = y p_z - z p_y,$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

Extending this discussion to the quantum mechanics, we can assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \vec{\hat{L}}$ - 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

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (6.3.1)$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad (6.3.2)$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (6.3.3)$$

These can be transforming to operators in standard spherical polar coordinates,

$$x = r \sin \theta \cos \varphi$$

$$y = r \sin \theta \sin \varphi$$

$$z = r \cos \theta$$

we obtain

$$\hat{L}_x = i\hbar \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right)$$

$$\hat{L}_y = -i\hbar \left(\cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

We can introduce a new operator $\hat{L}^2$:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (6.3.4)$$

$$= -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \quad (6.3.5)$$

The eigenvalue problem for $\hat{L}^2$ takes the form

$$\hat{L}^2 |\psi\rangle = \lambda \hbar^2 |\psi\rangle \quad (6.3.6)$$

where $\psi(r, \theta, \varphi)$ is the wavefunction, and λ is a number. Let us write

$$\psi(r, \theta, \varphi) = R(r) Y(\theta, \varphi) \quad (6.3.7)$$

By definition,

$$\boxed{L^2 Y_l^{m_l} = l(l+1) \hbar^2 Y_l^{m_l}} \quad (6.3.8)$$

where l is an integer. This is an important conclusion that argues the angular momentum is quantized with the square of the magnitude of the angular momentum only capable of assume one of the discrete set of values (Equation 6.3.8). From this, the **amplitude** of angular momentum can be expressed

$$\boxed{|\vec{L}| = \sqrt{L^2} = \sqrt{l(l+1)} \hbar} \quad (6.3.9)$$

Warning

We often refer to a particle in a state with angular momentum quantum number l as having angular momentum l , rather than saying that it has angular momentum of $\sqrt{l(l+1)} \hbar$ magnitude, primarily since it is awkward to say quickly.

The properties of spherical harmonics that the z-component of the angular momentum (L_z) is also quantized and can only assume a one of a discrete set of values

$$L_z Y_l^{m_l} = m_l \hbar Y_l^{m_l} \quad (6.3.10)$$

where m_l is an integer lying in the range $-l \leq m_l \leq l$.

- l is sometimes called "azimuthal quantum number" or "orbital quantum number"
- m_l is sometimes called "magnetic quantum number"

Simultaneous Measurements

Note that observables associated with $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ can, in principle, be measured. However, to determine if they can be measured *simultaneously* with infinite precision, the corresponding operators must **commute**. Remember that the fundamental commutation relations satisfied by the position and linear momentum operators are:

$$[\hat{x}_i, \hat{x}_j] = 0$$

$$[\hat{p}_i, \hat{p}_j] = 0$$

$$[\hat{x}_i, \hat{p}_j] = i \hbar \delta_{ij}$$

where i and j stand for either x , y , or z . Consider the commutator of the operators $\hat{L}_x$ and $\hat{L}_z$:

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= [(y p_z - z p_y), (z p_x - x p_z)] \\ &= y [p_z, z] p_x + x p_y [z, p_z] \\ &= i \hbar (-y p_x + x p_y) \\ &= i \hbar \hat{L}_z \end{aligned}$$

The **cyclic permutations** of the above result yield the fundamental commutation relations satisfied by the components of an orbital angular momentum:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \quad (6.3.11)$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \quad (6.3.12)$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y \quad (6.3.13)$$

The three commutation relations (Equations 6.3.11 - 6.3.13) are the foundation for the whole theory of angular momentum in quantum mechanics. Whenever we encounter three operators having these commutation relations, we know that the dynamical variables that they represent have identical properties to those of the components of an angular momentum (which we are about to derive). In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 6.3.11 - 6.3.13) represent the components of some sort of angular momentum.

Any three operators that satisfy the cyclic commutation relations represent the components of some sort of angular momentum.

✓ Example 6.3.1 : Commutators

Show that the $\hat{L}^2$ and $\hat{L}_x$ operators commute.

Solution

We want to confirm that $[\hat{L}^2, \hat{L}_x] = 0$ that from Equation 6.3.4 this can be expanded

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x]$$

from the properties of commutators, this can be expanded

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]$$

However,

$$[\hat{L}_x^2, \hat{L}_x] = \hat{L}_x^2 \hat{L}_x - \hat{L}_x \hat{L}_x^2 = \hat{L}_x \hat{L}_x \hat{L}_x - \hat{L}_x \hat{L}_x \hat{L}_x = 0$$

So

$$\begin{aligned} [\hat{L}^2, \hat{L}_x] &= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\ &= \hat{L}_y^2 \hat{L}_x - \hat{L}_x \hat{L}_y^2 + \hat{L}_z^2 \hat{L}_x - \hat{L}_x \hat{L}_z^2 \\ &= \hat{L}_y \hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y \hat{L}_y + \hat{L}_z \hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z \hat{L}_z \end{aligned}$$

Lets look at some related forms which can be used to simplify the above expression. The first two terms can and final two terms can be rewritten as different commutators

$$\begin{aligned} [\hat{L}_y, \hat{L}_x] &= \hat{L}_y + \hat{L}_y [\hat{L}_y, \hat{L}_x] \\ &= (\hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y) \hat{L}_y + \hat{L}_y (\hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y) \\ &= \hat{L}_y \hat{L}_x \hat{L}_y - \hat{L}_x \hat{L}_y \hat{L}_y + \hat{L}_y \hat{L}_y \hat{L}_x - \hat{L}_y \hat{L}_x \hat{L}_y \end{aligned}$$

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,

$$[\hat{L}_z, \hat{L}_x] \hat{L}_z + \hat{L}_z [\hat{L}_z, \hat{L}_x] = \hat{L}_z \hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z \hat{L}_z$$

So,

$$\begin{aligned}
 [\hat{L}^2, \hat{L}_x] &= [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\
 &= -i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_z\hat{L}_y \\
 &= 0
 \end{aligned}$$

One can also show similarly that

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

Example 6.3.1 shows that while L_z can be known with certainty, L_x and L_y would **unknown**. This means that every vector with the appropriate length and z-component can be 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).

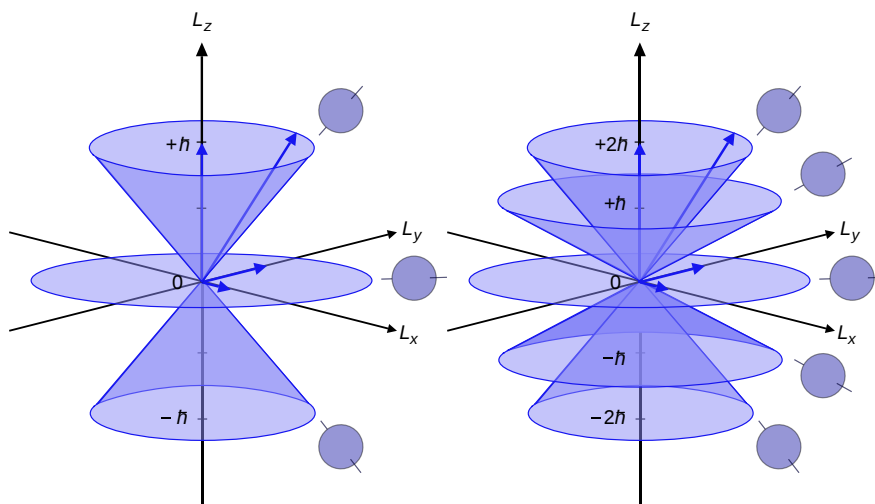


Figure 6.3.1 : Illustration of the vector model of orbital angular momentum. (left) A set of states with quantum numbers $l = 1$, and $m_l = -1, 0, +1$. (right) A set of states with quantum numbers $l = 2$, and $m_l = -2, -1, 0, +1, +2$. (Public Domain; Maschen via Wikipedia)

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 not need to solve two eigenvalue 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 $l = 0, 1, 2, \dots$

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 $m_l = -l, 0 - 1, \dots, 0, \dots, +l + 1, l$ for a given value of l . Hence, l and m_l are the *angular momentum quantum number* and the *magnetic quantum number*, respectively.

Contributors and Attributions

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6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

Learning Objectives

- Recognize how the hydrogen atomic orbitals vary as a function of the three primary quantum numbers

The solutions to the hydrogen atom Schrödinger equation discussed previously are functions that are products of a **spherical harmonic function** and a **radial function**.

$$\psi_{n,l,m_l}(r, \theta, \varphi) = \underbrace{R_{n,l}(r)}_{\text{radial}} \underbrace{Y_l^{m_l}(\theta, \varphi)}_{\text{angular}} \quad (6.4.1)$$

The wavefunctions for the hydrogen atom depend upon the three variables r , θ , and φ and the three quantum numbers n , l , and m_l . The variables give the position of the electron relative to the proton in spherical coordinates. The absolute square of the wavefunction, $|\psi(r, \theta, \varphi)|^2$, evaluated at r , θ , and φ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r , θ , and φ .

? Exercise 6.4.1

Evaluate the following integrals

- $\langle \psi(r, \theta, \varphi) | \psi(r, \theta, \varphi) \rangle$
- $\langle \psi(r, \theta, \varphi) | \psi(r', \theta', \varphi') \rangle$

Answer

- This integral is equal to one since $\psi(r, \theta, \varphi)$ are normalized eigenstates.
- However, we can explicitly evaluate this integral for any arbitrary pair of eigenstates

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

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

$$R_{\text{asymptotic}}(r) \sim \exp\left(-\frac{r}{n}a_0\right) \quad (6.4.2)$$

where n will turn out to be a quantum number and a_0 is the Bohr radius (~ 52.9 pm). Note that this function decreases exponentially with distance, in a manner similar to the decaying exponential portion of the harmonic oscillator wavefunctions, but with a different distance dependence, r vs. r^2 .

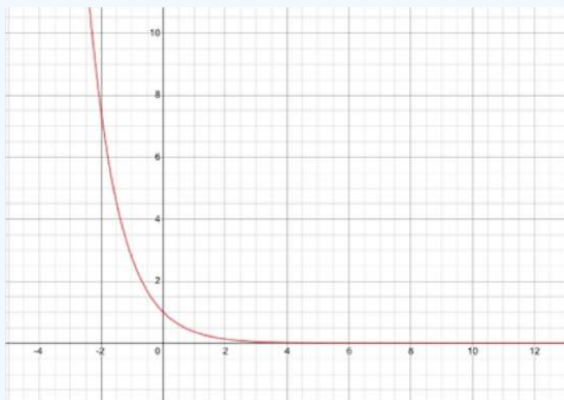
? Exercise 6.4.2

What happens to the magnitude of $R_{\text{asymptotic}}(r)$ as the distance r from the proton approaches infinity? Sketch a graph of the function, $R_{\text{asymptotic}}(r)$. Why might this behavior be expected for an electron in a hydrogen atom?

Answer

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

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.

$$L_{n,l}(r) = \sum_{i=0}^{n-l-1} c_i r^i \quad (6.4.3)$$

These polynomials are identified by two indices or quantum numbers, n and l . Physically acceptable solutions require that n must be greater than or equal to $l + 1$. The smallest value for l is zero, so the smallest value for n is 1. The angular momentum quantum number affects the solution to the radial equation because it appears in the radial differential equation, (Equation 6.4.1).

The $R(r)$ functions that solve the radial differential Equation 6.4.1, are products of the associated Laguerre polynomials and the exponential factor, multiplied by a normalization factor ($N_{n,l}$) and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,l} \left(\frac{r}{a_0}\right)^l L_{n,l}(r) e^{-\frac{r}{na_0}} \quad (6.4.4)$$

The decreasing exponential term overpowers the increasing polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of r . The first six radial functions are provided in Table 6.4.1. Note that the functions in the table exhibit a dependence on Z , the atomic number of the nucleus. As discussed later in this chapter, other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$.

Table 6.4.3 : Radial functions for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	$R_{n,l}(\rho)$
R_{10}	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$
R_{20}	2	0	$\frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \rho) e^{-\rho/2}$
R_{21}	2	1	$\frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2}$
R_{30}	3	0	$\frac{2}{81\sqrt{3}} \left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\rho + 2\rho^2) e^{-\rho/3}$
R_{31}	3	1	$\frac{1}{81\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} (6\rho + \rho^2) e^{-\rho/3}$
R_{32}	3	2	$\frac{1}{81\sqrt{30}} \left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}$

The constraint that n be greater than or equal to $l + 1$ also turns out to quantize the energy, producing the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2}$$

Bohr Theory vs. Schrödinger Theory

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger and Bohr models differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $\sqrt{l(l+1)} \hbar$.

3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

? Exercise 6.4.3

Explain how the Schrödinger equation leads to the conclusion that the angular momentum of the hydrogen atom can be zero, and explain how the existence of such states with zero angular momentum contradicts Bohr's idea that the electron is orbiting around the proton in the hydrogen atom.

Contributors and Attributions

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

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6.5: s-orbitals are Spherically Symmetric

The hydrogen atom wavefunctions, $\psi(r, \theta, \varphi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1, l = 0$ is called the 1s orbital, and an electron that is described by this function is said to be "in" the 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.

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

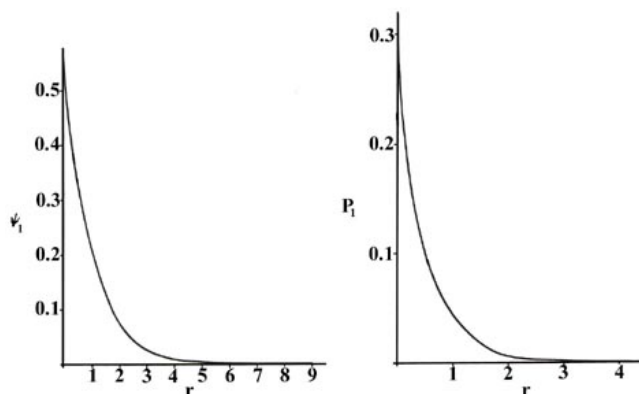


Figure 6.5.1 : The wavefunction and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

Two interpretations can again be given to the P_1 curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Figure 6.5.1 for P_1 . That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing r . The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than 10^{-8} cm will be greater than K , the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret P_1 as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of P_n for every small volume element over all space adds up to unity, i.e., one electron and one electronic charge.)

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately does not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^* \psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^* \psi$.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane (Figure 6.5.2), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line (Figure 6.5.2). Since the electron density depends only on r , the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.

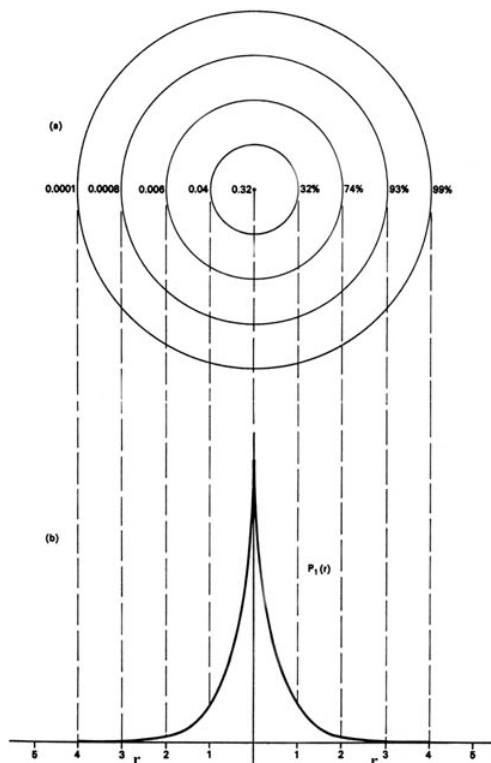


Figure 6.5.2 : (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter = 4.2×10^{-8} cm). (b) This is a profile of the contour map along a line through the nucleus. It is, of course, the same as that given previously in Figure 6.5.1 for P_1 , but now plotted from the nucleus in both directions.

When the electron is in a definite energy level we shall refer to the P_n distributions as **electron density distributions**, since they describe the manner in which the total electronic charge is distributed in space. The electron density is expressed in terms of the number of electronic charges per unit volume of space, e/V . The volume V is usually expressed in atomic units of length cubed, and one atomic unit of electron density is then e/a_0^3 . To give an idea of the order of magnitude of an atomic density unit, 1 au of charge density $e/a_0^3 = 6.7$ electronic charges per cubic Ångström. That is, a cube with a length of 0.52917×10^{-8} cm, if uniformly filled with an electronic charge density of 1 au, would contain 6.7 electronic charges.

For every value of the energy E_n , for the hydrogen atom, there is a degeneracy equal to n^2 . Therefore, for $n = 1$, there is but one atomic orbital and one electron density distribution. However, for $n = 2$, there are four different atomic orbitals and four different electron density distributions, all of which possess the same value for the energy, E_2 . Thus for all values of the principal quantum number n there are n^2 different ways in which the electronic charge may be distributed in three-dimensional space and still possess the same value for the energy. For every value of the principal quantum number, **one** of the possible atomic orbitals is independent of direction and gives a spherical electron density distribution which can be represented by circular contours as has been exemplified above for the case of $n = 1$. The other atomic orbitals for a given value of n exhibit a directional dependence and predict density distributions which are not spherical but are concentrated in planes or along certain axes. The angular dependence of the atomic orbitals for the hydrogen atom and the shapes of the contours of the corresponding electron density distributions are intimately connected with the angular momentum possessed by the electron.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s and 2s orbitals plotted in Figure 6.5.3. The 1s function in Figure 6.5.3; *left* starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

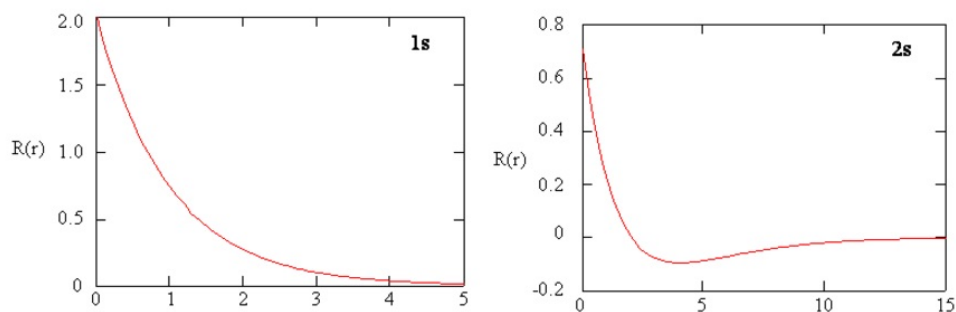


Figure 6.5.3 : Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click [here](#).

Next notice how the radial function for the 2s orbital, Figure 6.5.3; *right*, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$.

? Exercise 6.5.1

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

? Exercise 6.5.2

What mathematical feature of each of the radial functions controls the number of radial nodes?

? Exercise 6.5.3 : Radial Nodes

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

? Exercise 6.5.4

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Answer

	Energy 1. Particle in a Box ($\frac{h^2 n^2}{8m_e L^2}$) 2. Harmonic Oscillator($(n+0.5)\hbar\omega$) 3. Hydrogen ($-13.6\text{eV}/n^2$)	Number of Radial Nodes ($n-1$)	Number of Angular Nodes $l = (n-1)$ $l: s=0$ $p=1$ $d=2$	Total Number of Nodes
$n = 1$	1. $6.02 \times 10^{-38} \text{ J/L}^2$ 2. $1.5\hbar\omega$ 3. -13.6 eV	-	0	0

	Energy	Number of		Angular	Total Number of Nodes
	1. Particle in a Box ($\frac{h^2 n^2}{8m_e L^2}$) 2. Harmonic Oscillator($(n+0.5)\hbar\omega$) 3. Hydrogen ($-13.6\text{eV}/n^2$)	Nodes	Radial	Nodes	
		(n-1)		$l = (n-1)$ $l: s=0$ $p=1$ $d=2$	
$n = 2$	1. $6.02 \times 10^{-38} \text{ J/L}^2$ 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. $6.02 \times 10^{-38} \text{ J/L}^2$ 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 .

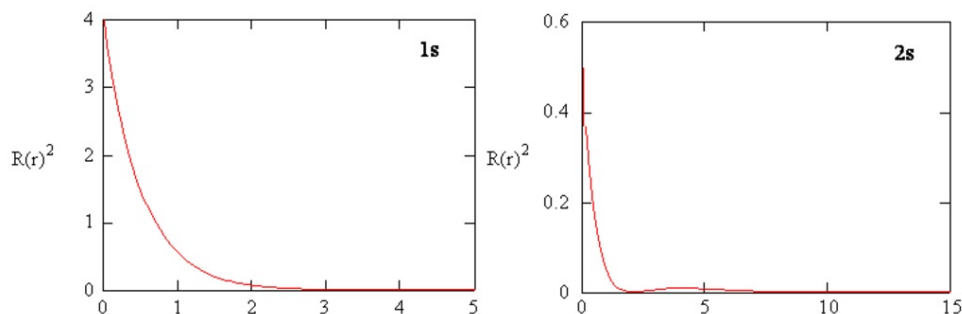


Figure 6.5.4 : Radial densities ($R(r) \cdot R(r)$) for the 1s and 2s orbitals.

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:

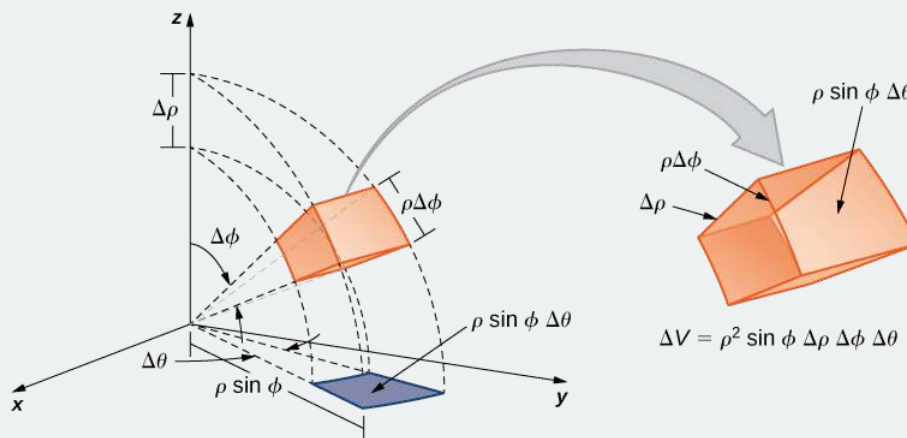
$$\frac{4}{3}\pi [(r + \Delta r)^3 - r^3]$$

the difference in volume between two concentric spheres. When this expression for the volume is expanded, we obtain

$$\frac{4}{3}\pi (3r^2 \Delta r + 3r \Delta r^2 + \Delta r^3)$$

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.

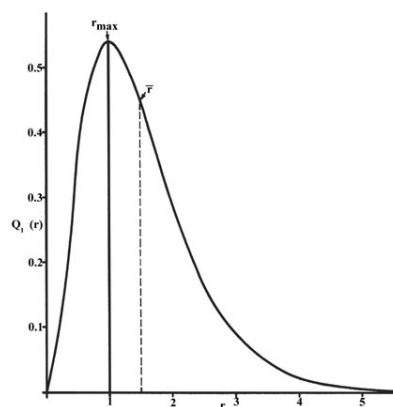


Figure 6.5.5 : The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r + \delta r$.

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_0 , 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.

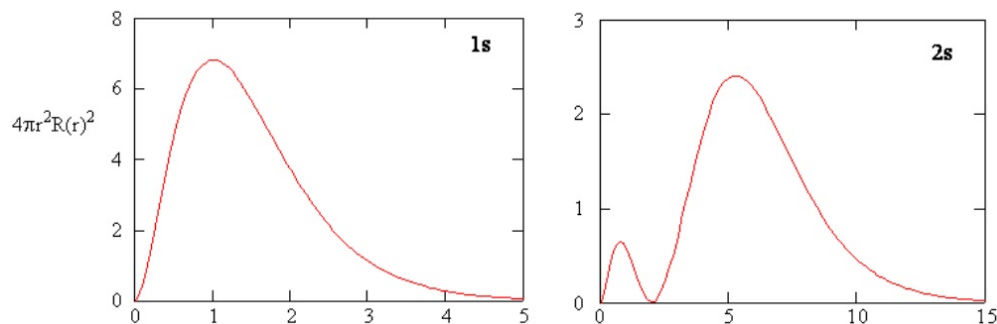


Figure 6.5.6 : The radial distribution function ($4\pi r^2 R(r)^2$) for the 1s and 2s orbitals. Compare to the radial functions in Figure 6.5.3 or the radial densities in Figure 6.5.4 . For an interactive graph click [here](#).

✓ Example 6.5.1 :

Calculate the probability of finding a 1s hydrogen electron being found within distance $2a_0$ from the nucleus.

Solution

Note the wavefunction of hydrogen 1s orbital which is

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-\rho}$$

with $\rho = \frac{r}{a_0}$.

The probability of finding the electron within $2a_0$ distance from the nucleus will be:

$$prob = \underbrace{\int_0^\pi \sin \theta d\theta}_{\text{over } \theta} \underbrace{\frac{1}{\pi a_0^3} \int_0^{2a_0} r^2 e^{-2r/a_0} dr}_{\text{over } r} \underbrace{\int_0^{2\pi} d\phi}_{\text{over } \phi}$$

Since $\int_0^\pi \sin \theta d\theta = 2$ and $\int_0^{2\pi} d\phi = 2\pi$, we have

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

There is a 76.2% probability that the electrons will be within $2a_0$ 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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6.6: Orbital Angular Momentum and the p-Orbitals

Learning Objectives

- To relate the classical orbital angular momentum for an particle to the quantum equivalent
- Characterize the magnitude 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.

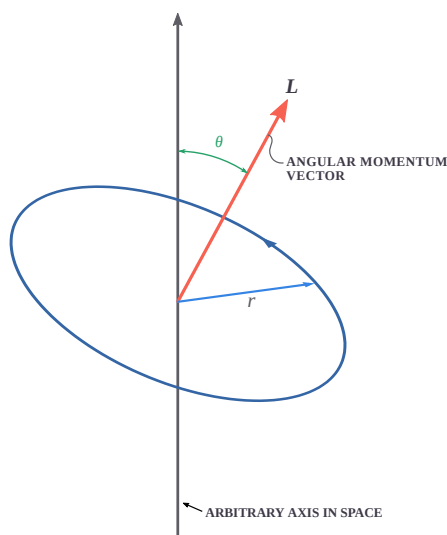


Figure 6.6.1 : The angular momentum vector for a classical model of the atom. (CC BY-NC; Ümit Kaya via LibreTexts)

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:

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

The angular momentum vector $\vec{L}$ is directed along the axis of rotation. From the definition it is evident that the angular momentum vector will remain constant as long as the speed of the electron in the orbit is constant ($|\vec{v}|$ remains unchanged) and the plane and radius of the orbit remain unchanged. Thus for a given orbit, the angular momentum is constant as long as the angular velocity of the particle in the orbit is constant. In an atom the only force on the electron in the orbit is directed along r ; it has no component in the direction of the motion. The force acts in such a way as to change only the linear momentum. Therefore, while the linear momentum is not constant during the circular motion, the angular momentum is. A force exerted on the particle in the direction of the vector $\vec{v}$ would change the angular velocity and the angular momentum. When a force is applied which does change $\vec{L}$, a **torque**

is said to be acting on the system. Thus angular momentum and torque are related in the same way as are linear momentum and force.

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:

$$|L| = \sqrt{l(l+1)}\hbar \quad (6.6.1)$$

with $l = 0, 1, 2, 3, \dots, n - 1$.

Furthermore, the value of n limits the maximum value of the angular momentum as the value of l cannot be greater than $n - 1$. For the state $n = 1$ discussed above, l may have the value of zero only. When $n = 2$, l may equal 0 or 1, and for $n = 3$, $l = 0$ or 1 or 2, etc. When $l = 0$, it is evident from Equation 6.6.1 that the angular momentum of the electron is zero. The atomic orbitals which describe these states of zero angular momentum are called s orbitals. The s orbitals are distinguished from one another by stating the value of n , the principal quantum number. They are referred to as the $1s$, $2s$, $3s$, etc., atomic orbitals.

The preceding discussion referred to the $1s$ orbital since for the ground state of the hydrogen atom $n = 1$ and $l = 0$. This orbital, and all s orbitals in general, predict spherical density distributions for the electron as discussed previously.

It is common usage to refer to an electron as being "in" an orbital even though an orbital is, but a mathematical function with no physical reality. To say an electron is in a particular orbital is meant to imply that the electron is in the quantum state which is described by that orbital. For example, when the electron is in the $2s$ orbital the hydrogen atom is in a state for which $n = 2$ and $l = 0$.

Comparing these results with those for the $1s$ orbital in Figure 6.6.2 we see that as n increases the average value of r increases. This agrees with the fact that the energy of the electron also increases as n increases. The increased energy results in the electron being on the average pulled further away from the attractive force of the nucleus. As in the simple example of an electron moving on a line, nodes (values of r for which the electron density is zero) appear in the probability distributions. The number of nodes increases with increasing energy and equals $n - 1$.

When the electron possesses angular momentum the density distributions are no longer spherical. In fact for each value of l , the electron density distribution assumes a characteristic shapes in Figure 6.6.2 .

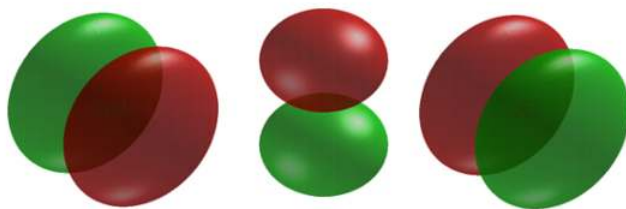


Figure 6.6.2 : The appearance of the three $2p$ orbitals in three-dimensional space. (CC BY-SA 3.0; I, Sarxos).

When $l = 1$, the orbitals are called p orbitals. In this case the orbital and its electron density are concentrated along a line (axis) in space. The $2p$ 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 $2p$ orbital does not place any electronic charge density at the nucleus. The electron density of a $1s$ orbital, on the other hand, is a maximum at the nucleus. The same diagram for the $2p$ 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.

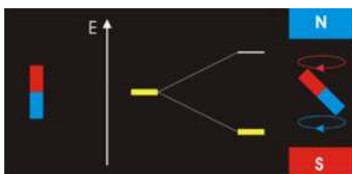


Figure 6.6.3 : The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left). However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative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

$$|\psi_{2,1,0}\rangle = r \cos \theta R(r) \quad (6.6.2)$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2} \sin \theta e^{i\phi} R(r) \quad (6.6.3)$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2} \sin \theta e^{-i\phi} R(r) \quad (6.6.4)$$

The notation is $|\psi_{n,l,m_l}\rangle$ with $R(r)$ is the radial component of this wavefunction, θ is the angle with respect to the z -axis and ϕ is the angle with respect to the xz -plane.

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

in which Z is the atomic number (or probably better nuclear charge) and a_0 is the Bohr radius.

In switching from spherical to Cartesian coordinates, we make the substitution $z = r \cos \theta$, so:

$$|\psi_{2,1,0}\rangle = zR(r)$$

This is ψ_{2p_z} since the value of ψ is dependent on z : when $z = 0$; $\psi = 0$, which is expected since $z = 0$ describes the xy -plane. The other two wavefunctions are degenerate in the xy -plane. An equivalent statement is that these two orbitals do not lie on the x - and y -axes, but rather bisect them. Thus it is typical to take linear combinations of them to make the equation look prettier. If any set of wavefunctions is a solution to the Schrödinger equation, then any set of linear combinations of these wavefunctions must also be a solution (Section 2.4). We can do this because of the linearity of the Schrödinger equation.

In the equations below, we're going to make use of some trigonometry, notably Euler's formula:

$$e^{i\phi} = \cos \phi + i \sin \phi \quad (6.6.5)$$

$$\sin \phi = \frac{e^{i\phi} - e^{-i\phi}}{2i} \quad (6.6.6)$$

$$\cos \phi = \frac{e^{i\phi} + e^{-i\phi}}{2} \quad (6.6.7)$$

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

$$\psi_{2p_x} = \frac{1}{\sqrt{2}}(\psi_{2,1,+1} - \psi_{2,1,-1})$$

$$= \frac{1}{2}(e^{i\phi} + e^{-i\phi}) r \sin \theta f(r)$$

$$= r \sin \theta \cos \phi f(r) = x f(r)$$

$$\psi_{2p_y} = \frac{i}{\sqrt{2}}(\psi_{2,1,+1} + \psi_{2,1,-1})$$

$$= \frac{1}{2i}(e^{i\phi} - e^{-i\phi}) r \sin \theta f(r)$$

$$= r \sin \theta \sin \phi f(r) = y f(r)$$

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 *3d* 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.

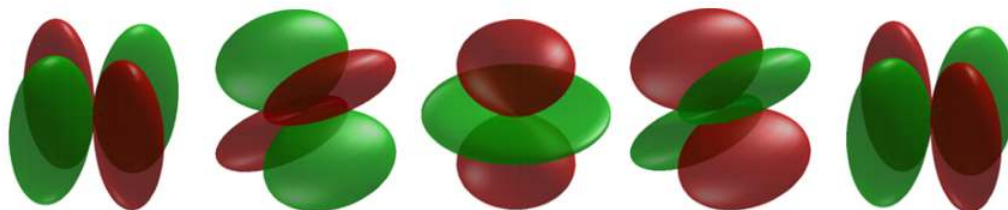


Figure 6.6.4 : The appearance of the 3d electron density distribution in three-dimensional space. (CC BY-SA 3.0; I, [Sarxos](#))

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 $l = 4, 5, 6 \rightarrow g, h, i, \dots$

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

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6.7: The Helium Atom Cannot Be Solved Exactly

Learning Objectives

- Adding electrons to the quantum hydrogen atom results in analytically unsolvable Schrödinger Equations (they exist, we just do not have analytical forms for them)
- A basic aspect of the corresponding multi-electron Hamiltonians is that they are NOT separable with respect to the spatial coordinate of each electron
- The solutions to multi-electron Schrödinger Equations are called multi-electron wavefunctions and they are often approximated as a product of single-electron wavefunctions (called the orbital approximation).

Multi-electron Hamiltonians

The second element in the periodic table provides our first example of a quantum-mechanical problem which *cannot* be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

Figure 6.7.1 shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors r_1 and r_2 . The electrons are separated by a distance $r_{12} = |r_1 - r_2|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

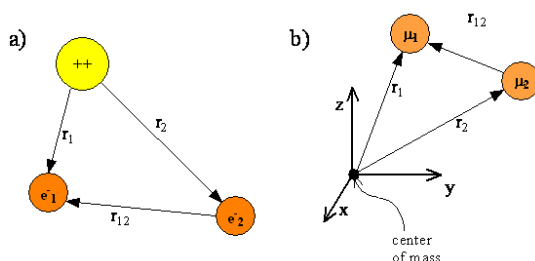


Figure 6.7.1 : (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Hamiltonian operator for the hydrogen atom serves as a reference point for writing the Hamiltonian operator for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} \quad (6.7.1)$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \quad (6.7.2)$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \quad (6.7.3)$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \quad (6.7.4)$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (6.7.5)$$

The two-electron Hamiltonian in Equation 6.7.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z ; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \quad (6.7.6)$$

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

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e} \sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i \neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \quad (6.7.7)$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 6.7.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 6.7.3 and 6.7.4). The other big difference between single electron systems and multi-electron systems is the presence of the $V_{ij}(r_{ij})$ terms which contain $1/r_{ij}$, where r_{ij} is the distance between electrons i and j . These terms account for the electron-electron repulsion that we expect between like-charged particles.

? Exercise 6.7.1 : Multi-electron atom Hamiltonians

For the generalized multi-electron atom Hamiltonian (Equation 6.7.7):

- Explain the origin of each of the three summations.
- What do these summations over (i.e., what is the origin of the summing index)?
- 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.

- Write the multi-electron Hamiltonian for a ^{11}B atom.
- Would it be any different for a $^{11}\text{B}^+$ ion?
- Would it be any different for a ^{10}B atom?

Answer

a.

$$\hat{H}_B(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \vec{r}_5) = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

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, $^{11}\text{B}^+$ has one less electron than ^{11}B . Its Hamiltonian is

$$\hat{H}_{B^+}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i \frac{-4e^2}{4\pi\epsilon_0 r_i} + \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

or expanded to 14 terms

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

c. No effect. Changing the number of neutrons in the nucleus does not affect kinetic nor potential energies of the electrons. The Hamiltonian for ^{10}B is identical to ^{11}B . This is technically correct for this level of discussion, but as 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 6.7.7 would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their Coulomb repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends *simultaneously* upon the coordinates of all the electrons; i.e., **a multi-electron wavefunction**,

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \dots \vec{r}_n)$$

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.

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

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.

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

Unfortunately, the Coulomb repulsion terms (Equation 6.7.5) make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms and molecules even for two electrons atoms. We have to rely on approximations and the *orbital approximation* is central to basic chemistry concepts.

The Orbital Approximation

The most basic approximations to the exact solutions to a multi-electron atom Hamiltonian, $\hat{H}$, (Equation 6.7.7) involve writing a multi-electron wavefunction ($\psi(r_1, r_2, \dots, r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1, r_2, \dots, r_n) \approx \varphi_1(r_1)\varphi_2(r_2) \dots \varphi_n(r_n) \quad (6.7.8)$$

or in Dirac notation

$$|\psi(r_1, r_2, \dots, r_n)\rangle \approx |\varphi_1(r_1)\rangle |\varphi_2(r_2)\rangle \dots |\varphi_n(r_n)\rangle \quad (6.7.9)$$

The energy of the atom in the state associated with a specific multi-electron wavefunction (E) is obtained from the multi-electron Schrödinger Equation

$$\hat{H}\psi(r_1, r_2, \dots, r_n) = E\psi(r_1, r_2, \dots, r_n)$$

Within the approximation in Equation 6.7.8, E can be expressed sum of the energies of the one-electron components (ϵ_i).

$$E \approx \sum_i \epsilon_i$$

This is called the **orbital approximation**.

By writing the multi-electron wavefunction as a product of single-electron functions (Equations 6.7.8 or 6.7.9), we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be separately identified. For atoms, these single-electron wavefunctions are called *atomic orbitals* and resemble the wavefunctions for hydrogen-like atoms. For molecules, as we will see in the following chapters, these are called *molecular orbitals*. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

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CHAPTER OVERVIEW

7: Multielectron Atoms

Electrons with more than one atom, such as Helium (He), and Nitrogen (N), are referred to as multi-electron atoms. Hydrogen is the only atom in the periodic table that has one electron in the orbitals under ground state. We will learn how additional electrons behave and affect a certain atom.

[7.1: Atomic and Molecular Calculations are Expressed in Atomic Units](#)

[7.2: Perturbation Theory and the Variational Method for Helium](#)

[7.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method](#)

[7.4: Hartree-Fock Calculations Give Good Agreement with Experimental Data](#)

Thumbnail: Neon Atom. (CC BY 3.0 Unported; [BruceBlaus](#) via [Wikipedia](#))

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7.1: Atomic and Molecular Calculations are Expressed in Atomic Units

Learning Objectives

- Demonstrate how solving electron structure problems are less cluttered by switching to atomic units instead of SI units.

Atomic units (au or a.u.) form a system of natural units which is especially convenient for atomic physics calculations. Atomic units, like SI units, have a unit of mass, a unit of length, and so on. However, the use and notation is somewhat different from SI. Suppose a particle with a mass of m has 3.4 times the mass of electron. The value of mass m can be written in three ways:

- $m = 3.4 m_e$: This is the clearest notation (but least common), where the atomic unit is included explicitly as a symbol.
- $m = 3.4 a. u.$: This notation is ambiguous, but is common. Here, it means that the mass m is 3.4 times the atomic unit of mass. If considering a length L of 3.4 times the atomic unit of length, the equation would look the same, $L = 3.4 a. u.$ The dimension needs to be inferred from context, which is sloppy.
- $m = 3.4$: This notation is similar to the previous one, and has the same dimensional ambiguity. It comes from formally setting the atomic units to 1 (Table 8.1.1).

This article deals with "Hartree type" of atomic units, where the numerical values of the following four fundamental physical constants are all unity by definition:

Table 8.1.1 : Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units	Value in Atomic Units
mass	electron rest mass	m_e	$9.109 \times 10^{-31} \text{ kg}$	1
charge	elementary charge	e	$1.602 \times 10^{-19} \text{ C}$	1
action	reduced Planck's constant	$\hbar = \frac{h}{2\pi}$	$1.054 \times 10^{-34} \text{ J}\cdot\text{s}$	1
electric constant ⁻¹	Coulomb force constant	$k_e = \frac{1}{4\pi\epsilon_0}$	$8.987 \times 10^9 \text{ kg}\cdot\text{m}^3\cdot\text{s}^{-2}\cdot\text{C}^{-2}$	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	$4\pi\epsilon_0\hbar^2/(m_e e^2) = \hbar/(m_e \alpha c)$	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			$\hbar/E_h$	2.418×10^{-17} s	
velocity			$a_0 E_h / \hbar = \alpha c$	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 = $\frac{1}{2}$
- Electric field (due to nucleus) = 1
- Electrical attractive force (due to nucleus) = 1

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7.2: Perturbation Theory and the Variational Method for Helium

Learning Objectives

- Demonstrate that both perturbation theory and variational methods can be used to solve the electron structure of the helium atom.

Both perturbation theory and variation method (especially the linear variational method) provide good results in approximating the energy and wavefunctions of multi-electron atoms. Below we address both approximations with respect to the helium atom.

Perturbation Theory of the Helium Atom

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a **zero-order Hamiltonian**. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. For example, we call the simplified or starting Hamiltonian, $\hat{H}^0$, the zero order term, and the correction term $\hat{H}^1$.

$$\hat{H} = \hat{H}^0 + \hat{H}^1 \quad (7.2.1)$$

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

$$\hat{H}^0 = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}}_{\text{H atom Hamiltonian}} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}}_{\text{H atom Hamiltonian}} \quad (7.2.2)$$

$$\hat{H}^1 = \frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \quad (7.2.3)$$

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

$$\begin{aligned} E^1 &= \langle \psi^0 | \hat{H}^1 | \psi^0 \rangle \\ &= \int \psi^{0*} \hat{H}^1 \psi^0 d\tau \end{aligned} \quad (7.2.4)$$

Equation 7.2.4 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 7.2.2) is the product of two single-electron hydrogen wavefunctions (scaled by the increased nuclear charge) since $\hat{H}^0$ can be separated into independent functions of each electron (i.e., [Separation of Variables](#)).

$$|\psi^0\rangle = |\varphi_{1s}(r_1)\varphi_{1s}(r_2)\rangle$$

So the integral in Equation 7.2.4 is

$$E^1 = \iint \varphi_{1s}(r_1)\varphi_{1s}(r_2) \frac{1}{r_{12}} \varphi_{1s}(r_1)\varphi_{1s}(r_2) d\tau_1 d\tau_2 \quad (7.2.5)$$

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

$$E_{approx2} = E^0 + E^1 = -74.8 \text{ eV} \quad (7.2.6)$$

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy:

$$E^0 = \frac{2}{n^2} + \frac{2}{n^2} = 4 \underbrace{E_h}_{\text{hartrees}} = 108.8 \text{ eV}$$

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,

$$E^0 + E^1 + E^2 = -79.2 \text{ eV}.$$

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. We 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.

$$\begin{aligned} E_h &= 4.359 \times 10^{-18} \text{ J} \\ &= 27.21 \text{ eV}. \end{aligned}$$

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.

$$E_{\text{trial}} = \frac{\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle} \quad (7.2.7)$$

$$= \frac{\int_0^\infty \psi_{\text{trial}}^* \hat{H} \psi_{\text{trial}} d\tau}{\int_0^\infty \psi_{\text{trial}}^2 d\tau} \quad (7.2.8)$$

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 7.2.7, 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.

$$|\psi(1, 2)\rangle_{\text{trial}} = \phi(1)\phi(2) \quad (7.2.9)$$

$$= \exp[-\alpha(r_1 + r_2)] \quad (7.2.10)$$

The variational energy obtained after minimizing Equation 7.2.8 after substituting the trial wavefunction (Equation 7.2.10) by varying α is

$$E_{\text{trial}} = -2.84766 E_h$$

and the experimentally determined ground-state energy for the helium atom is the sum of first and second ionization energies

$$E_{\text{exp}} = I_1 + I_2 = -2.90372 E_h \quad (7.2.11)$$

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

$$\left| \frac{E_{\text{trial}}(\alpha) - E_{\text{exp}}}{E_{\text{exp}}} \right| = \left| \frac{-2.84766 E_h + 2.90372 E_h}{-2.90372 E_h} \right| \quad (7.2.12)$$

$$= 1.93\% \quad (7.2.13)$$

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.

$$\phi(r_1) = \exp(-\alpha r_1) + \exp(-\beta r_1) \quad (7.2.14)$$

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

$$|\psi(1, 2)\rangle_{\text{trial}} = \phi(1)\phi(2) \quad (7.2.15)$$

$$= \exp(-\alpha r_1) \exp(-\alpha r_2) + \exp(-\alpha r_1) \exp(-\beta r_2) + \exp(-\beta r_1) \exp(-\alpha r_2) + \exp(-\beta r_1) \exp(-\beta r_2) \quad (7.2.16)$$

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 7.2.8). 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 7.2.8 after substituting the trial wavefunction (Equation 7.2.16) by varying α and β is

$$E_{\text{trial}} = -2.86035 E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 7.2.11) is

$$\left| \frac{E_{\text{trial}}(\alpha, \beta) - E_{\text{exp}}}{E_{\text{exp}}} \right| = \left| \frac{-2.86035 E_h + 2.90372 E_h}{-2.90372 E_h} \right| \quad (7.2.17)$$

$$= 1.49\% \quad (7.2.18)$$

Clearly introducing some electron-electron interactions into the trial wavefunction has improved the agreement between theory and experiment (Equation 7.2.13 vs. 7.2.18).

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 7.2.16). This yields a multi-electron wavefunction of the form,

$$|\psi(1, 2)\rangle_{\text{trial}} = \exp(-\alpha r_1) \exp(-\beta r_2) + \exp(-\beta r_1) \exp(-\alpha r_2) \quad (7.2.19)$$

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 7.2.8 after substituting the trial wavefunction (Equation 7.2.19) by varying α and β is

$$E_{\text{trial}} = -2.87566 E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 7.2.11) is

$$\left| \frac{E_{\text{trial}}(\alpha, \beta) - E_{\text{exp}}}{E_{\text{exp}}} \right| = \left| \frac{-2.87566 E_h + 2.90372 E_h}{-2.90372 E_h} \right| \quad (7.2.20)$$

$$= 0.97\% \quad (7.2.21)$$

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.

$$|\psi_{trial}(1, 2)\rangle = (\exp[-\alpha(r_1 + r_2)])(1 + \beta r_{12}) \quad (7.2.22)$$

In the trial multi-electron wavefunction of Equation 7.2.22, 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 7.2.8 after substituting the trial wavefunction (Equation 7.2.22) 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 7.2.11) is

$$\left| \frac{E_{trial}(\alpha, \beta) - E_{exp}}{E_{exp}} \right| = \left| \frac{-2.89112 E_h + 2.90372 E_h}{-2.90372 E_h} \right| \quad (7.2.23)$$

$$= 0.43\% \quad (7.2.24)$$

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 7.2.19) as shown here.

$$|\psi(1, 2)\rangle_{trial} = [\exp(-\alpha r_1) \exp(-\beta r_2) + \exp(-\beta r_1) \exp(-\alpha r_2)] [1 + \gamma r_{12}] \quad (7.2.25)$$

Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground-state energy. The variational energy obtained after minimizing Equation 7.2.8 after substituting the trial wavefunction (Equation 7.2.25) 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 7.2.11) is

$$\left| \frac{E_{trial}(\alpha, \beta, \gamma) - E_{exp}}{E_{exp}} \right| = \left| \frac{-2.90143 + 2.90372 E_h}{-2.90372 E_h} \right| \quad (7.2.26)$$

$$= 0.0789\% \quad (7.2.27)$$

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

Learning Objectives

- Show how the Hartree approximation can be used to solve for the wavefunctions and energies of multi-electron atoms.
- Understand the orbital approach of independent orbitals is an approximation to a multi-electron system with the motions of all electrons coupled together.
- Demonstrate how the Self-Consistent 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-of-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.

$$V_{\text{nuclear-electron}}(r_1) = -\frac{Z}{|\mathbf{r} - \mathbf{R}|} \quad (7.3.1)$$

in atomic units with $|\mathbf{r} - \mathbf{R}|$ is the distance between the electron and the nucleus, The Hamiltonian must also have terms for electron-electron repulsion (also in atomic units)

$$V_{\text{electron-electron}}(r_{12}) = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

with $|\mathbf{r} - \mathbf{r}'|$ is the distance between electron 1 and electron 2. So the proper multi-electron Hamiltonian can be constructed

$$\hat{H}(r_1, r_2, \dots, r_n) = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{\text{nuclear-electron}}(r_i) + \sum_{i \neq j} V_{\text{electron-electron}}(r_{ij}) \quad (7.3.2)$$

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their electron-electron repulsion (final term in Equation 7.3.2) means that an exact wavefunction for a multi-electron system would be a single function that depends **simultaneously** upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:

$$|\psi(r_1, r_2, \dots, r_i)\rangle \quad (7.3.3)$$

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

The Hartree Approximation

The method for finding best possible one-electron wavefunctions that was published by Douglas Hartree in 1948 and improved two years later by Vladimir Fock. For the Schrödinger equation to be analytically solvable, the variables must be separable - the variables are the coordinates of the electrons. To separate the variables in a way that retains information about electron-electron interactions, the electron-electron term (Equation 7.3.1) must be approximated so it depends only on the coordinates of one electron. Such an approximate Hamiltonian can account for the interaction of the electrons in **an average way**. The exact one-electron eigenfunctions of this approximate Hamiltonian then can be found by solving the Schrödinger equation. These functions are the best possible **one-electron functions**.

The Hartree approximation starts by invoking an initial *ansatz* that the multi-electron wavefunction in Equation 7.3.3 can be expanded as a product of single-electron wavefunctions (i.e., orbitals)

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

from which it follows that the electrons are *independent*, and interact only via the mean-field Coulomb potential. This yields one-electron Schrödinger equations of the form

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

or

$$H_e(r)\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

where $V(r)$ is the potential in which the electron moves; this includes both the nuclear-electron interaction

$$V_{nucleus}(\mathbf{r}) = -Ze^2 \sum_R \frac{1}{|\mathbf{r} - \mathbf{R}|}$$

and the mean field arising from the $N - 1$ other electrons. We smear the other electrons out into a smooth negative charge density $\rho(\mathbf{r}')$ leading to a potential of the form

$$V_{electron}(\mathbf{r}) = -e \int d\mathbf{r}' \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

where

$$\rho(\mathbf{r}) = \sum_i^{\text{occupied}} |\psi(\mathbf{r})|^2.$$

The sum over runs over all occupied states; i.e., only the states of electrons that exist in the atom. The wavefunctions that from this approach with the Hamiltonian $H_e(r)$ involve possess three kinds of energies discussed below.

Three Energies within the Hartree Approximation

The total energy ϵ_j of the orbital ϕ_j , is the sum of the above three contributions:

1. **Kinetic Energy:** The Kinetic energy of the electron has an average value is computed by taking the expectation value of the kinetic energy operator

$$\frac{-\hbar^2}{2m} \nabla^2$$

with respect to any particular solution $\phi_j(r)$ to the Schrödinger equation:

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

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

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

3. **Electron-Electron Coulombic Repulsion Energy:** Coulomb repulsion energies with all of the $N - 1$ other electrons, which are assumed to occupy other atomic orbitals denoted ϕ_K , with this energy computed as

$$\sum_{j \neq k} \langle \phi_j(r)\phi_k(r') | \frac{e^2}{|r - r'|} | \phi_j(r)\phi_k(r') \rangle. \quad (7.3.4)$$

The Dirac notation $\langle \phi_j(r)\phi_k(r') | \frac{e^2}{|r - r'|} | \phi_j(r)\phi_k(r') \rangle$ is used to represent the two-electron (six-dimensional) Coulomb integral

$$J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr'$$

that describes the Coulomb repulsion between the charge density $|\phi_j(r)|^2$ for the electron in ϕ_j and the charge density $|\phi_k(r')|^2$ for the electron in ϕ_k . Of course, the sum over k must be limited to exclude $k = j$ to avoid counting a “self-interaction” of the electron in orbital ϕ_j with itself.

Adding these all together to get the total energy ϵ_j of the orbital ϕ_j :

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

This treatment of the electrons and their orbitals is referred to as the **Hartree-level of theory**.

When screened hydrogenic atomic orbitals are used to approximate the ϕ_j and ϕ_K orbitals, the resultant ϵ_j values do **not** produce accurate predictions. For example, the negative of ϵ_j should approximate the ionization energy for removal of an electron from the orbitals ϕ_j . Such ionization potentials (IP s) can be measured, and the measured values do not agree well with the theoretical values when a crude screening approximation is made for the atomic orbitals.

The Self-Consistent 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).

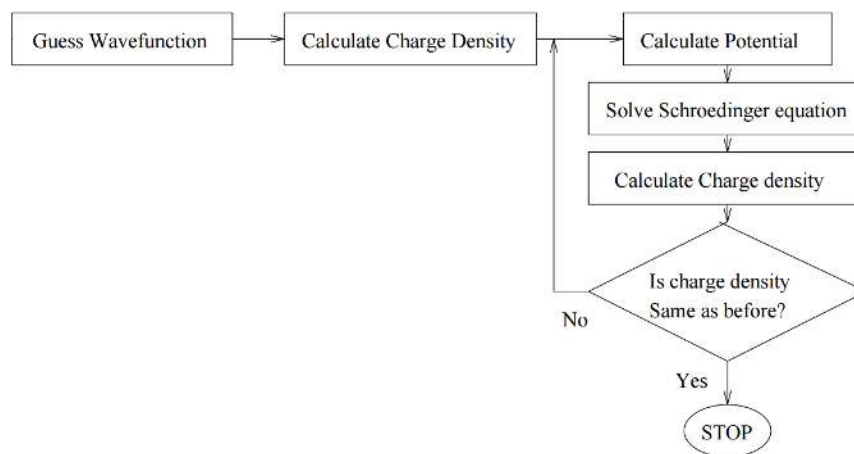


Figure 8.3.1 : Algorithm for Self-consistent field theory.

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

$$|\psi(1, 2, \dots, 6)\rangle = |\psi_{1s}(1)\psi_{1s}(2)\psi_{2s}(3) \dots \psi_{1p}(6)\rangle. \quad (7.3.5)$$

However, such approximate orbitals are not sufficiently accurate to be of use in quantitative simulations of atomic and molecular structure. In particular, their energies do not properly follow the trends in atomic orbital (AO) energies that are taught in introductory chemistry classes (Figure 8.3.2).

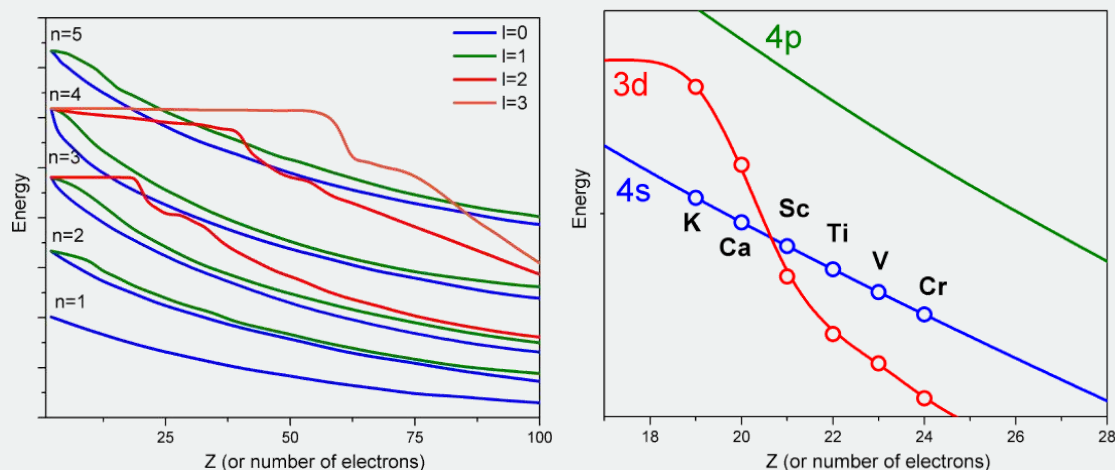


Figure 8.3.2 : Energies of Atomic Orbitals as Functions of the number of electrons in Neutral Atoms. (CC BY 4.0; Delmar Larsen).

For example, the relative energies of the $3d$ and $4s$ orbitals are not adequately described in a model that treats electron repulsion effects in terms of a simple screening factor. So, now it is time to examine how we can move beyond the screening model and take the electron repulsion effects, which cause the inter-electronic couplings that render the Schrödinger equation insolvable, into account in a more reliable manner.

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

Learning Objectives

- Understand how the Hartree method is expanded to include symmetrized multi-electron determinantal wavefunctions via the Hartree-Fock equations.
- Understand how to calculate the orbital energies from HF theory.
- Apply HF theory with Koopman's theory to estimate ionization energies and electron affinities.

The Hartree method discussed previously is useful as an introduction to the solution of many-particle system and to the concepts of self-consistency and of the self-consistent-field calculations, but its importance is confined to the history of physics. In fact the Hartree method is not just approximate, it is fundamentally wrong since its wavefunction is not antisymmetric to electron permutation! The Hartree-Fock approach discussed below is a better approach, which correctly takes into account the antisymmetric character of the trial wavefunctions.

Although the *Hartree equations* are numerically tractable via the self-consistent field method, it is not surprising that such a crude approximation fails to capture elements of the essential physics. The Pauli exclusion principle demands that the many-body wavefunction be antisymmetric with respect to interchange of any two electron coordinates, e.g.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) \quad (7.4.1)$$

which clearly cannot be satisfied by the multi-electron wavefunctions of the form used in the Hartree Approximation, i.e., the orbital approximation (Equation 7.4.2).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N) \quad (7.4.2)$$

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

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} |\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \dots \psi(\mathbf{r}_N)| \quad (7.4.3)$$

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

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})}_{\text{kinetic energy}} + \underbrace{V_{\text{nucleus}}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{electron-nucleus potential}} + \underbrace{V_{\text{electron}}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{Hartree Term}} - \sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}). \quad (7.4.4)$$

As with the *Hartree equations*, the first term is the kinetic energy of the i^{th} electron

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

and the second term is the electron-nucleus potential between the i^{th} electron and nucleus

$$V_{\text{nucleus}}(\mathbf{r})\psi_i(\mathbf{r})$$

The third term (sometimes called the “Hartree” term) is the electrostatic potential between the i^{th} electron and the **average** charge distribution of the other $N - 1$ electrons.

$$V_{\text{electron}}(\mathbf{r})\psi_i(\mathbf{r}) = J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr' \quad (7.4.5)$$

These three terms are identical to Hartree Equations with the product wavefunction ansatz (i.e., orbital approximation). The fourth term of Equation 7.4.4 is not in the Hartree Equations:

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

and is the *exchange* term. This term resembles the direct Coulomb term, but for the exchanged indices. It is a manifestation of the Pauli exclusion principle, and acts so as to separate electrons of the same spin. This “exchange” term acts only on electrons with

the same spin and comes from the Slater determinant form of the wavefunction (Equation 7.4.3). Physically, the effect of exchange is for like-spin electrons to avoid each other. The exchange term adds considerably to the complexity of these equations.

The Hartree-Fock Equations in Equation 7.4.4 can be recast as series of Schrödinger-like equations:

$$\hat{F}|\varphi_i\rangle = \epsilon_i|\varphi_i\rangle \quad (7.4.6)$$

where $\hat{F}$ is called the **Fock operator** and $\{|\varphi_i\rangle\}$ are the Hartree-Fock orbitals with corresponding energies ϵ_i .

The Fock operator is a one-electron operator and solving a Hartree-Fock equation gives the energy and Hartree-Fock orbital for one electron. For a system with $2N$ electrons, the variable i will range from 1 to N ; i.e. there will be one equation for each orbital. The reason for this is that only the spatial wavefunctions are used in Equation 7.4.6. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving Equation 7.4.6 will be used to describe two electrons.

The nature of the Fock operator reveals how the Hartree-Fock (HF) or Self-Consistent Field (SCF) Method accounts for the electron-electron interaction in atoms and molecules while preserving the idea of **independent atomic orbitals**. The wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\begin{aligned} \hat{F} &= \hat{H}^0 + \sum_{j=1}^N (2\hat{J}_j - \hat{K}_j) \\ &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^N (2\hat{J}_j - \hat{K}_j) \end{aligned} \quad (7.4.7)$$

As shown by the expanded version on the far right, the first term in this equation, $\hat{H}^0$, is the familiar hydrogen-like operator that accounts for the kinetic energy of an electron and the potential energy of this electron interacting with the nucleus. The next term accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The $\hat{J}$ and $\hat{K}$ operators result from the electron-electron repulsion terms in the full Hamiltonian for a multi-electron system. These operators involve the one-electron orbitals as well as the electron-electron interaction energy.

The Fock operator (Equation 7.4.7) depends on **all occupied** orbitals (because of the exchange and Coulomb operators). Therefore, a specific orbital can only be determined if all the others are known. One must use iterative methods to solve the HF equations like the Self-consistent field method discussed previously for the Hartree Approximation.

Exchange Energy

The exchange interaction is a quantum mechanical effect that only occurs between identical particles. Despite sometimes being called an exchange force in analogy to classical force, **it is not a true force**, as it lacks a force carrier. The effect is due to the wavefunction of indistinguishable particles being subject to exchange symmetry, that is, either remaining unchanged (symmetric) or changing its sign (antisymmetric) when two particles are exchanged. Both bosons and fermions can experience the exchange interaction. For fermions, it is sometimes called Pauli repulsion and related to the Pauli exclusion principle. For bosons, the exchange interaction takes the form of an effective attraction that causes identical particles to be found closer together, as in Bose–Einstein condensation.

Example 8.7.1 : Hartree-Fock Energy of Helium

For example, the electron 1 in helium (with $Z = 2$), then

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}$$

The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we will call electron 1 throughout the following discussion), and the **average field created by all the other electrons** in the system is built in terms of the coordinates of a generic “other electron” (which we’ll call electron 2) that is considered to occupy each orbital in turn during the summation over the N spatial orbitals. The best possible one-electron wavefunctions, by definition, will give the **lowest possible total energy** for a multi-electron system used with the complete multielectron Hamiltonian to calculate the expectation

value for the total energy of the system. These wavefunctions are called the **Hartree-Fock wavefunctions** and the calculated total energy is the Hartree-Fock energy of the system.

As with the Hartree Equations, solving the Hartree-Fock Equations is mathematically equivalent to assuming each electron interacts only with the average charge cloud of the other electrons. This is how the electron-electron repulsion is handled. This also why this approach is also called the **Self-Consistent Field (SCF)** approach.

Hartree-Fock Energy

The Hartree-Fock equations $h_e \phi_i = \epsilon_i \phi_i$ imply that the orbital energies ϵ_i can be written as:

$$\begin{aligned}\epsilon_i &= \langle \phi_i | h_e | \phi_i \rangle \\ &= \langle \phi_i | T + V | \phi_i \rangle + \sum_{j(\text{occupied})} \langle \phi_i | J_j - K_j | \phi_i \rangle \\ &= \langle \phi_i | T + V | \phi_i \rangle + \sum_{j(\text{occupied})} [J_{i,j} - K_{i,j}],\end{aligned}$$

where $T + V$ represents the kinetic (T) and nuclear attraction (V) energies, respectively. Thus, ϵ_i is the average value of the kinetic energy plus Coulombic attraction to the nuclei for an electron in ϕ_i plus the sum over all of the spin-orbitals occupied in ψ of Coulomb minus Exchange interactions of these electrons with the electron in ϕ_i .

If ϕ_i is an occupied spin-orbital, the $j = i$ term $[J_{i,i} - K_{i,i}]$ disappears in the above sum and the remaining terms in the sum represent the Coulomb minus exchange interaction of ϕ_i with all of the $N - 1$ other occupied spin-orbitals. If ϕ_i is a virtual spin-orbital, this cancelation does not occur because the sum over j does not include $j = i$. So, one obtains the Coulomb minus exchange interaction of ϕ_i with all N of the occupied spin-orbitals in ψ . Hence the energies of occupied orbitals pertain to interactions appropriate to a total of N electrons, while the energies of virtual orbitals pertain to a system with $N + 1$ electrons. This difference is very important to understand and to keep in mind.

To give an idea of how well HF theory can predict the ground state energies of several atoms, consider Table 8.7.1 below:

Table 8.7.1 : Hartree-Fock Calculations of Ground Energies of Select Atoms (all energies are in R_H)

Atom	Hartree-Fock Energy	Experiment
<i>He</i>	-5.72	-5.80
<i>Li</i>	-14.86	-14.96
<i>Ne</i>	-257.10	-257.88
<i>Ar</i>	-1053.64	-1055.20

Koopmans' Theorem

Koopmans' theorem states that the first ionization energy is equal to the negative of the orbital energy of the highest occupied molecular orbital. Hence, the ionization energy required to generated a cation and detached electron is represented by the removal of an electron from an orbital without changing the wavefunctions of the other electrons. This is called the "frozen orbital approximation." Let us consider the following model of the detachment or attachment of an electron in an N -electron system.

1. In this model, both the parent molecule and the species generated by adding or removing an electron are treated at the single-determinant level.
2. The Hartree-Fock orbitals of the parent molecule are used to describe both species. It is said that such a model neglects orbital relaxation (i.e., the re-optimization of the spin-orbitals to allow them to become appropriate to the daughter species).

Within this model, the energy difference between the daughter and the parent can be written as follows (ϕ_k represents the particular spin-orbital that is added or removed):

- for electron detachment (vertical ionization energies)

$$E_{N-1} - E_N = -\epsilon_k \quad (7.4.8)$$

- and for electron attachment (electron affinities)

$$E_N - E_{N+1} = -\epsilon_k. \quad (7.4.9)$$

The Hartree-Fock equations deal with exchange exactly; however, the equations neglect more detailed correlations due to many-body interactions. The effects of electronic correlations are not negligible; indeed the failure of Hartree-Fock theory to successfully incorporate correlation leads to one of its most celebrated failures.

✓ Example 8.7.2 : Electron Affinity

Let's derive this result for the case in which an electron is added to the $N + 1^{st}$ spin-orbital. The energy of the N -electron determinant with spin-orbitals ϕ_1 through ϕ_N occupied is

$$E_N = \sum_{i=1}^N \langle \phi_i | T + V | \phi_i \rangle + \sum_{i=1}^N [J_{i,i} - K_{i,i}]$$

which can also be written as

$$E_N = \sum_{i=1}^N \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N [J_{i,j} - K_{i,j}].$$

Likewise, the energy of the $N + 1$ -electron determinant wavefunction is

$$E_{N+1} = \sum_{i=1}^{N+1} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N+1} [J_{i,j} - K_{i,j}].$$

The difference between these two energies is given by

$$\begin{aligned} E_N - E_{N+1} &= -\langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \frac{1}{2} \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ &\quad - \frac{1}{2} \sum_{j=1}^{N+1} [J_{N+1,j} - K_{N+1,j}] \\ &= -\langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ &= -\epsilon_{N+1}. \end{aligned}$$

That is, the energy difference is equal to minus the expression for the energy of the $N + 1^{st}$ spin-orbital, which was given earlier.

🔧 Advanced: Electron Correlation and the "Exchange Hole"

In the Copenhagen Interpretation, the squared modulus of the wavefunction gives the probability of finding a particle in a given place. The many-body wavefunction gives the N -particle distribution function, i.e. $|\Phi(r_1, \dots, r_N)|^2$ is the probability density that particle 1 is at r_1 , ..., and particle N is at r_N . However, when trying to work out the interaction between electrons, what we want to know is the probability of finding an electron at r , given the positions of all the other electrons $\{r_i\}$. This implies that the electron behaves quantum mechanically when we evaluate its wavefunction, but as a classical point particle when it contributes to the potential seen by the other electrons.

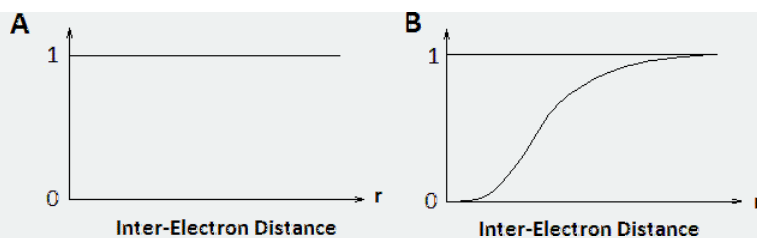


Figure 8.7.2 : Normalized Conditional Probability for from electron-electron interactions (excluding coulomb effects) in (A) the Hartree approximation and (B) the Hartree-Fock approximation.

The contributions of electron-electron interactions in N -electron systems within the Hartree and Hartree-Fock methods are shown in Figure 8.7.2 . The conditional electron probability distributions $n(r)$ of $N - 1$ electrons around an electron with given spin situated at $r = 0$. Within the Hartree approximation, all electrons are treated as independent, therefore $n(r)$ is structureless. However, within the Hartree-Fock approximation, the N -electron wavefunction reflects the Pauli exclusion principle and near the electron at $r = 0$ the exchange hole can be seen where the the density of spins equal to that of the central electron is reduced. Electrons with opposite spins are **unaffected** (not shown).

Summary

So, within the limitations of the HF, frozen-orbital model, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to as Koopmans' theorem; it is used extensively in quantum chemical calculations as a means of estimating ionization potentials (Equation 7.4.8) and Electron Affinities (Equation 7.4.9) and often yields results that are qualitatively correct (i.e., ± 0.5 eV). In general Hartree-Fock theory gives a great first order solution (99%) to describing multi-electron systems, but that last 1% is still too great for quantitatively describing many aspects of chemistry and more sophisticated approaches are necessary. These are discussed elsewhere.

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CHAPTER OVERVIEW

8: Chemical Bonding in Diatomic Molecules

Our basis for understanding chemical bonding and the structures of molecules is the electron orbital description of the structure and valence of atoms, as provided by quantum mechanics. We assume an understanding of the periodicity of the elements based on the nuclear structure of the atom and our deductions concerning valence based on electron orbitals.

[8.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules](#)

[8.2: The \$H_2^+\$ Prototypical Species](#)

[8.3: The Overlap Integral](#)

[8.4: Chemical Bond Stability](#)

[8.5: Bonding and Antibonding Orbitals](#)

[8.6: A Simple Molecular-Orbital Treatment of \$H_2\$ Places Both Electrons in a Bonding Orbital](#)

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[8.11: Photoelectron Spectra Support the Existence of Molecular Orbitals](#)

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[8.13: Molecular Term Symbols Describe Electronic States of Molecules](#)

[8.14: Molecular Term Symbols Designate Symmetry](#)

Thumbnail: A covalent bond forming H_2 where two hydrogen atoms share the two electrons. (CC BY-SA 3.0; [Jacek FH](#) via [Wikipedia](#); modified by LibreTexts)

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

Learning Objectives

- Understand the need to introduce an approximation like the Born-Oppenheimer approximation to solve multi-electron systems
- Understand the basis of parameterization involved in using the Born-Oppenheimer approximation

Using quantum mechanics to predict the chemical bonding patterns, optimal geometries, and physical and chemical properties of molecules is a large and active field of research known as *molecular quantum mechanics* or more commonly as *quantum chemistry*. The density functional theory referred to in the previous lecture, for which the chemistry Nobel prize was given in 1998, has had a tremendous impact in quantum chemistry, with some of the papers in this subject having acquired some 10,000 citations each since their publication. In fact, the 1998 chemistry Nobel prize was shared between Walter Kohn, one of the inventors of density functional theory and John Pople, the developer of a commonly used quantum chemistry software package.

Quantum chemistry calculations allow the geometries of molecules to be computed as well as a wide range of properties. Quantum chemistry can also be used in a novel way, in which the electrons are treated using quantum mechanics but the nuclei are treated as classical particles. We use quantum mechanics to calculate the internuclear forces but then use these forces in Newton's Second Law to study the motion of the nuclei during chemical reactions. This gives us a microscopic window into the specific motions, the complex dance, executed by the nuclei during a simple or complex chemical process.

The methods of quantum chemistry have become very sophisticated, and there are various software packages that can be downloaded for carrying out the calculations of quantum chemistry. It should be noted that these packages use a series of approximations to solve the Schrödinger equation because for all but the simplest of molecules, exact solutions are not available. We will discuss some of these methods, but first we need to introduce some of the underlying theory.

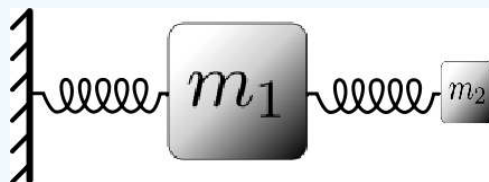
The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. We already made use of this approximation in the particle-in-a-box model when we explained the electronic absorption spectra of cyanine dyes without considering the motion of the nuclei. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. In this chapter we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times). Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of Ze^2/r^2 acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, $a = F/m$, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 2000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are not. You can imagine running a 100-yard dash against someone whose acceleration is a 2000 times greater than yours. That person could literally run circles around you.

✓ Example 9.1.1 : Coupled Oscillators with Dissimilar Masses

If two particles interact in some way, and one is much heavier than the other, the light particle will move essentially as a "slave" of the heavy particle. That is, it will simply follow the heavy particle wherever it goes, *and*, it will move rapidly in response to the heavy particle motion. As an illustration of this phenomenon, consider the simple mechanical system pictured below:



(CC BY-SA 3.0 Unported; Jim.belk via [Wikipedia](#)).

Considering this as a classical system, we expect that the motion will be dominated by the large heavy particle (m_1), which is attached to a fixed wall by a spring. The small, light particle (m_2), which is attached to the heavy particle by a spring will simply follow the heavy particle

and execute rapid oscillations around it.

So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei are not moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wavefunction can depend on the positions of the nuclei even though their motion is neglected.

Now we look at the mathematics to see what is done in solving the Schrödinger equation after making the Born-Oppenheimer approximation. For a diatomic molecule as an example, the Hamiltonian operator is grouped into three terms

$$\hat{H}(r, R) = \hat{T}_{nuc}(R) + \frac{e^2}{4\pi\epsilon_0} \frac{Z_A Z_B}{R} + \hat{H}_{elec}(r, R) \quad (8.1.1)$$

where

$$\hat{T}_{nuc}(R) = -\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 \quad (8.1.2)$$

and

$$\hat{H}_{elec}(\vec{r}, \vec{R}) = \frac{-\hbar^2}{2m} \sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left(-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}} \right) \quad (8.1.3)$$

In Equation 8.1.1, the first term represents the kinetic energy of the nuclei, the second term represents the Coulomb repulsion of the two nuclei, and the third term represents the contribution to the energy from the electrons, which consists of their kinetic energy, mutual repulsion for each other, and attraction for the nuclei. $\vec{r}$ and $\vec{R}$ are vectors specifying the positions of all the electrons and all the nuclei, respectively.

? Exercise 9.1.1

Define all the symbols in Equations 8.1.1 through 8.1.3.

Answer

$$\begin{aligned} \hat{H}(r, R) &= \underbrace{\hat{T}_{nuc}(R)}_{\text{Kinetic Energy Term for nuclei}} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{Z_A Z_B}{R}}_{\text{Repulsion Term for nuclei}} + \underbrace{\hat{H}_{elec}(r, R)}_{\text{Hamiltonian for electrons}} \\ \hat{T}_{nuc}(R) &= \underbrace{\frac{\hbar^2}{2m_A} \nabla_A^2}_{\text{Kinetic Energy Term for nuclei A}} - \underbrace{\frac{\hbar^2}{2m_b} \nabla_B^2}_{\text{Kinetic Energy Term for nuclei B}} \\ \hat{H}_{elec}(\vec{r}, \vec{R}) &= \underbrace{\frac{-\hbar^2}{2m} \sum_i \nabla_i^2}_{\text{Kinetic Energy Term for electrons}} \\ &\quad + \frac{e^2}{4\pi\epsilon_0} \left(-\underbrace{\sum_i \frac{Z_A}{r_{Ai}}}_{\text{Attraction Term between nuclei A and electron i}} - \underbrace{\sum_i \frac{Z_B}{r_{Bi}}}_{\text{Attraction Term between nuclei B and electron i}} + \underbrace{\frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}}}_{\text{Repulsion Term between electrons}} \right) \end{aligned}$$

where, Z_x is the charge of particle x, m_x is the mass of particle x and r_{xz} is the distance between particle x and z.

? Exercise 9.1.2

Explain why the factor of 1/2 appears in the last term in Equation 8.1.3.

Answer

The 1/2 term is there to make sure we do not double count the potential energies via the two summations. Otherwise, we would independently add the potential energy of electron 1 with electron 2 and the potential energy of electron 2 with electron 1. These are the same and hence one has to be removed.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation 8.1.1, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction $\varphi_e(r, R)$ is found as a solution to the electronic Schrödinger equation

$$\hat{H}_{elec}(r, R)\varphi_e(r, R) = E_e(R)\varphi_e(r, R) \quad (8.1.4)$$

Even though the nuclear kinetic energy terms are neglected, the Born-Oppenheimer approximation still takes into account the variation in the positions of the nuclei in determining the electronic energy and the resulting electronic wavefunction depends upon the nuclear positions, R . As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product

$$\psi_{ne}(r, R) = X_{ne}(R)\varphi_e(r, R) \quad (8.1.5)$$

This product wavefunction is called the Born-Oppenheimer wavefunction. The function $X_{ne}(R)$ is the vibrational wavefunction, which is a function of the nuclear coordinates R and depends upon both the vibrational and electronic quantum numbers or states, n and e , respectively. The electronic function, $\varphi_e(r, R)$, is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, e . Translational and rotational motion is not included here. The translational and rotational wavefunctions simply multiply the vibrational and electronic functions in Equation 8.1.5 to give the complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

In the *Crude Born-Oppenheimer Approximation*, R is set equal to R_0 , the equilibrium separation of the nuclei, and the electronic wavefunctions are taken to be the same for all positions of the nuclei (i.e., the nuclei never move). The electronic energy, $E_e(R)$, in Equation 8.1.4 combines with the repulsive Coulomb energy of the two nuclei, to form the potential energy function that controls the nuclear motion as shown in Figure 9.1.1.

$$V_e(R) = E_e(R) + \frac{e^2}{4\pi\epsilon_0} \frac{Z_A Z_B}{R} \quad (8.1.6)$$

Consequently the Schrödinger equation for the vibrational motion is

$$(\hat{T}_{nuc}(R) + V(R))X_{ne}(R) = E_{ne}X_{ne}(R) \quad (8.1.7)$$

Potential Energy Curves and Surfaces

Previously, the potential energy was approximated as a harmonic potential or Morse potential depending on the displacement, R , of the nuclei from their equilibrium positions.

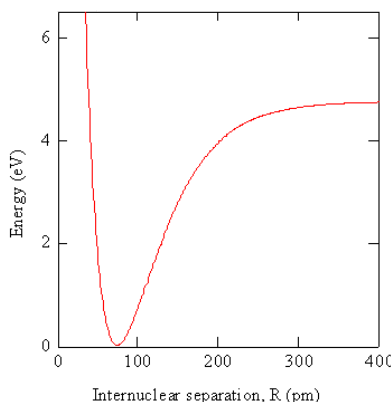


Figure 9.1.1 : The potential energy function for a diatomic molecule.

In practice the electronic Schrödinger equation is solved using approximations at particular values of R to obtain the wavefunctions $\varphi_e(r, R)$ and potential energies $V_e(R)$. The potential energies can be graphed as illustrated in Figure 9.1.1.

The graph in Figure 9.1.1 is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When R is very large there are two atoms that are weakly interacting. As R becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of R , the internuclear repulsion is very large so the energy is large and positive. This energy function controls the motion of the nuclei. Previously, we approximated this function by a harmonic potential to obtain the description of vibrational motion in terms of the harmonic oscillator model. Other approximate functional forms could be used as well, e.g. the Morse potential. The equilibrium position of the nuclei is where this function is a minimum, i.e. at $R = R_0$. If we obtain the wavefunction at $R = R_0$ and use this function for all values of R , we have employed the *Crude Born-Oppenheimer approximation*.

? Exercise 9.1.3

Relate Equation 8.1.7 to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

While the potential energy function, $V_e(R)$, for a diatomic molecule is a 1-D curve (Figure 9.1.1), molecules with more than two atoms will have multi-dimensional **potential energy surfaces** with $3N-6$ (or $3N-5$ for linear molecule) dimensions for the number of internal degrees of freedom.

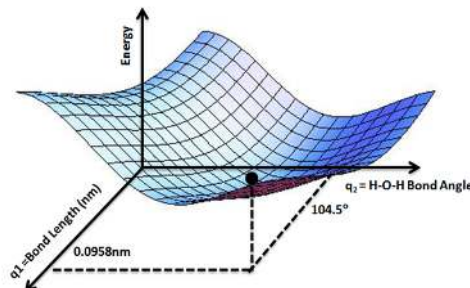


Figure 9.1.2 : The potential energy surface for a water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°. from Wikipeda (AimNature)

The potential energy surface concept can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction. Qualitatively the reaction coordinate diagrams (one-dimensional slices through the potential energy surfaces) have numerous applications. Chemists use reaction coordinate diagrams as both an analytical and pedagogical aid for rationalizing and illustrating kinetic and thermodynamic events. The purpose of energy profiles and surfaces is to provide a qualitative representation of how potential energy varies with molecular motion for a given reaction or process.

? Exercise 9.1.4

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

Summary

In this section we started with the Schrödinger equation for a diatomic molecule and separated it into two equations, an electronic Schrödinger equation and a nuclear Schrödinger equation. In order to make the separation, we had to make an approximation. We had to neglect the effect of the nuclear kinetic energy on the electrons. The fact that this assumption works can be traced to the fact that the nuclear masses are much larger than the electron mass. We then used the solution of the electronic Schrödinger equation to provide the potential energy function for the nuclear motion. The solution to the nuclear Schrödinger equation provides the vibrational wavefunctions and energies.

Contributors and Attributions

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

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8.2: The H_2^+ Prototypical Species

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion 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, repel 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.

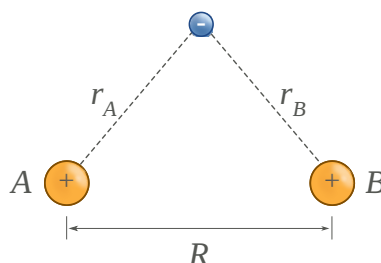


Figure 9.2.1 : Hydrogen molecular ion H_2^+ with fixed nuclei A and B , internuclear distance R . (CC BY-NC; Ümit Kaya via LibreTexts)

The electronic Hamiltonian for H_2^+ is

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

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

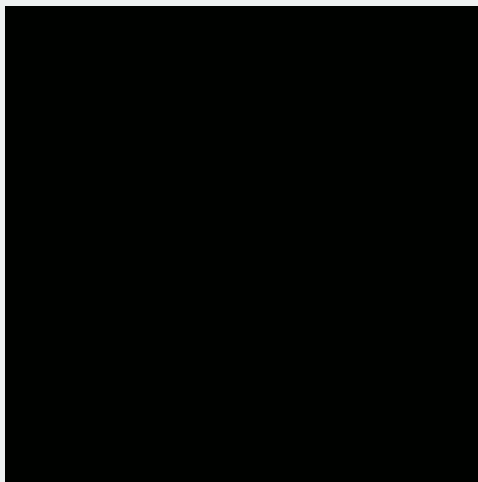
$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \quad (8.2.2)$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals $1s_A$ and $1s_B$.

The Linear Combination of Atomic Orbitals (LCAO) Approximation and Interference

The LCAO approximation is an example of the linear variational method discussed previously with the true molecular orbital wavefunction approximated as an expansion of a basis set of atomic orbitals on each atom of the molecule with variable coefficients that can be optimized (e.g., via the secular equations). As discussed previously, the number of wavefunctions (solutions) extracted from solving the secular determinant is equal the number of elements in the expansion. So for the expansion in Equation 8.2.2 with two atomic orbitals contributing result in two molecule orbitals.

This method yields a approximate picture of the molecular orbitals in a molecules. The figure below shows two atoms approaching along the axis of one of their $2p$ states. In the top row, the two lobes facing one another have the same sign; in the bottom row they have opposite sign. These are two different linear combinations of the same two atomic states, on different atoms and with difference phases (i.e., signs of C_A vs. C_B in the expansion). In the first example, the electron density increases between the nuclei and in the second example, a very steep-sided node between the two nuclei causes all the probability density to face away from the atom opposite.



For H_2^+ , the simplest molecule, the starting function is given by Equation 8.2.2. We must determine the values for the coefficients, C_A and C_B . We could use the variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B . These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition $|C_A|^2 = |C_B|^2$; namely, $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \quad (8.2.3)$$

$$\psi_- = C_-(1s_A - 1s_B) \quad (8.2.4)$$

The probability density for finding the electron at any point in space is given by $|\psi|^2$ and the electronic charge density is just $e|\psi|^2$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced (Figure 9.2.2 (bottom) between the two protons, whereas it is diminished for ψ_- as shown in Figures 9.2.2 (top). ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons.

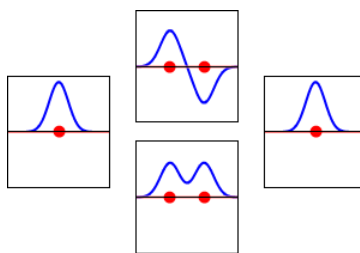


Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional.)

So ψ_+ is called a **bonding molecular orbital**. If the electron were described by ψ_- , the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an **antibonding molecular orbital**.

Contributors and Attributions

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

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8.3: The Overlap Integral

For H_2^+ , the simplest molecule, we must determine the values for the coefficients, C_A and C_B for the LCAO approximation for the molecular orbital as a linear combination of the two atomic orbitals

$$|\psi(r)\rangle = C_A 1s_A(r) + C_B 1s_B(r)$$

We could use the linear variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B . These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition

$$|C_A|^2 = |C_B|^2$$

so $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

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

and

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

The probability density for finding the electron at any point in space is given by $|\psi|^2$ and the electronic charge density is just $e|\psi|^2$. The important difference between ψ_+ and ψ_- is that the charge density for $|\psi_+\rangle$ is enhanced between the two protons, whereas it is diminished for $|\psi_-\rangle$ as shown in Figures 9.3.1. ψ_- has a node in the middle while $|\psi_+\rangle$ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So $|\psi_+\rangle$ is called a *bonding molecular orbital*. If the electron were described by $|\psi_-\rangle$, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so $|\psi_-\rangle$ is called an *antibonding molecular orbital*.

Now we want to evaluate C_+ and C_- and then calculate the energy. The bonding and antibonding character of ψ_+ and ψ_- also should be reflected in the energy. If $|\psi_+\rangle$ indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts H_2^+ to be stable or not and also how much energy is required to dissociate this molecule.

The constants C_+ and C_- are evaluated from the standard normalization condition:

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

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

$$|C_{\pm}|^2 \left[\underbrace{\langle 1s_A | 1s_A \rangle}_1 + \underbrace{\langle 1s_B | 1s_B \rangle}_1 \pm \underbrace{\langle 1s_B | 1s_A \rangle}_S \pm \underbrace{\langle 1s_A | 1s_B \rangle}_{S^*} \right] = 1 \quad (8.3.5)$$

Since the atomic orbitals are normalized, the first two integrals are just 1. The last two integrals are called *overlap integrals* and are symbolized by S and S^* , respectively, since one is the complex conjugate of the other.

The overlap integrals are telling us to take the value of $1s_B$ at a point multiply by the value of $1s_A$ at that point and sum (integrate) such a product over all of space (Figure 9.3.1). If the functions do not overlap, i.e. if one is zero when the other one is not and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancelation of positive and negative contributions.

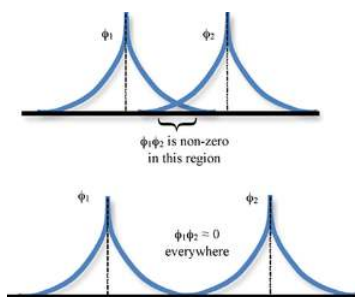


Figure 9.3.1 : The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close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

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from $R = \infty$ to $R = 0$. Clearly when the protons are infinite distance apart, there is no overlap, and when $R = 0$ both functions are centered on one nucleus and $\langle 1s_A | 1s_B \rangle$ becomes identical to $\langle 1s_B | 1s_A \rangle$, which is normalized to 1, because $1s_A = 1s_B$.

With these considerations and using the fact that 1s wavefunctions are real so

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle = S \quad (8.3.6)$$

Equation 8.3.5 becomes

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

The solution to Equation 8.3.7 is given by

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

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

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

and

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

The energies associated with these wavefunctions requires a bit more effort to calculate though as demonstrated in the following section.

For the overlap integral of two 1s orbitals from the hydrogen dimer discussed above is difficult to evaluate analytically and is explained here. The final answer is:

$$S(R) = \langle 1s_A | 1s_B \rangle \quad (8.3.11)$$

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

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

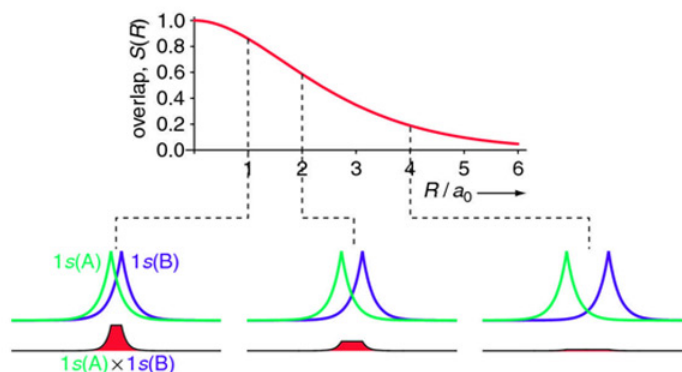


Figure 9.3.2 : The overlap integral at different proton separations.

✓ Example 9.3.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for H_2^+ for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

Solution

The electronic charge density is calculated with the formula $|e\psi^2|$ where $e = 1.602 \times 10^{-19} C$

a: Bonding Molecular Orbital

First, squaring the bonding molecular orbital (Equation 8.3.9) gives us:

$$\begin{aligned}\psi_+^2 &= \frac{1}{2(1+S)}(1s_A + 1s_B)^2 \\ &= \frac{1}{2(1+S)} \frac{1}{\pi a_0^3} \left(e^{-r_A/a_0} + e^{-r_B/a_0} \right)^2 \\ &= \frac{1}{2(1+S)} \frac{1}{\pi a_0^3} \\ &= (0.561)^2 \times \left(\frac{1}{\pi \times (52.9 \text{ pm})^3} \right) = 6.7672 \times 10^{-7} \text{ pm}^{-3}\end{aligned}$$

(Note: The value of C^2 is obtained from equation 9.3.12 and the value of S is from Equation 8.3.12)

To find the density at halfway between A and B for the bonding orbital evaluate at $1/2 R$,

$$\begin{aligned}r_A &= \frac{1}{2}R \text{ and } r_B = \frac{1}{2}R \\ \psi_+^2 &= 3.7 \times 10^{-7} \text{ pm}^{-3}\end{aligned}$$

Now multiply this answer by e to generate the electronic charge density,

$$P = (3.7 \times 10^{-7} \text{ pm}^{-3}) \times (1.602 \times 10^{-19}) C = 5.93 \times 10^{-26} C/pm^3$$

b: Antibonding Molecular Orbital

To find the halfway between A and B for the anti-bonding orbital at $r_A = \frac{1}{2}R$ and $r_B = \frac{1}{2}R$. However, simple inspection of Equation 8.3.10 or Figure 9.3.1 shows this will be zero.

$$e\psi_-^2 = 0$$

Obviously, when multiplied by e , the answer is still zero. This makes logical sense as there would be no charge density between the two atoms as there lies a node with no probability of finding an electron.

? Exercise 9.3.1

Show that for two arbitrary functions $\langle \varphi_B | \varphi_A \rangle$ is the complex conjugate of $\langle \varphi_A | \varphi_B \rangle$ and that these two integrals are equal if the functions are real.

Contributors and Attributions

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

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8.4: Chemical Bond Stability

Learning Objectives

- Identify the nature of the energy of molecular orbitals of a diatomic as a function of intermolecular distance
- Identify the three integrals involved in calculation the total Molecular Orbital Energy: coulomb Integral, exchange integral, and overlap integral

As shown previously, we can construct two molecular orbitals for the H_2^+ system using the LCAO approximation with a basis set of two 1s atomic orbitals (i.e., the 1s orbitals on hydrogen A ($1s_A$) and hydrogen B ($1s_B$)):

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

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

$$E_{\pm} = \langle \psi_{\pm} | \hat{H}_{elec} | \psi_{\pm} \rangle \quad (8.4.2)$$

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

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[\underbrace{\langle 1s_A | \hat{H}_{elec} | 1s_A \rangle}_{H_{AA}} + \underbrace{\langle 1s_B | \hat{H}_{elec} | 1s_B \rangle}_{H_{BB}} \pm \underbrace{\langle 1s_A | \hat{H}_{elec} | 1s_B \rangle}_{H_{AB}} \pm \underbrace{\langle 1s_B | \hat{H}_{elec} | 1s_A \rangle}_{H_{BA}} \right] \quad (8.4.3)$$

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

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

? Exercise 9.4.1

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

Answer

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

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}}(1s_a \pm 1s_b)$$

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

$$E_{\pm} = \langle \psi_{\pm} | \hat{H} | \psi_{\pm} \rangle = N^2 \langle (1s_a \pm 1s_b) | \hat{H} | (1s_a \pm 1s_b) \rangle$$

We can see from above that the normalization constant squared results in:

$$N^2 = \frac{1}{2(1 \pm S)}$$

We now FOIL the multiple (i.e., expanded term by term):

$$\langle 1s_a | \hat{H} | 1s_a \rangle + \langle 1s_b | \hat{H} | 1s_b \rangle \pm \langle 1s_a | \hat{H} | 1s_b \rangle \pm \langle 1s_b | \hat{H} | 1s_a \rangle$$

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

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

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.

$$H_{AA} = H_{BB} \quad (8.4.5)$$

and since the wavefunctions are real

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

so

$$H_{AB} = H_{BA} \quad (8.4.6)$$

These two equalities simplify Equation 8.4.4:

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

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

$$H_{AA} = \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_A \right\rangle}_{E_H} + \frac{e^2}{4\pi\epsilon_0 R} \underbrace{\langle 1s_A | 1s_A \rangle}_1 - \underbrace{\left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle}_{J_{AB}} \quad (8.4.8)$$

- The first term is just the integral for the energy of the hydrogen atom of the 1s orbital, E_H .
- The second integral is equal to 1 by normalization; the prefactor is just the Coulomb repulsion of the two protons.
- The last integral, including the minus sign, is represented by J and is called the **Coulomb integral**.

Physically J_{AB} is the potential energy of interaction of the electron located around proton A with proton B . It is negative because it is an attractive interaction. It is the average interaction energy of an electron described by the $1s_A$ function with proton B .

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 electron with the electron density function $1s_B$

Now consider H_{AB} .

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

- In the first integral we have the hydrogen atom Hamiltonian and the H atom function $1s_B$. The function $1s_B$ is an eigenfunction of the operator with eigenvalue E_H . Since E_H is a constant it factors out of the integral, which then becomes the overlap integral, S . The first integral therefore reduces to $E_H S$.
- The second term is just the Coulombic energy of the two protons times the overlap integral.
- The third term, including the minus sign, is given the symbol K and is called the *exchange integral* because the electron is described by the $1s_A$ orbital on one side and by the $1s_B$ orbital on the other side of the operator. The electron changes or exchanges position in the molecule.

The Exchange Integral ()

In a **coulomb integral**, the electron always is in the same orbital; whereas, in an *Exchange Integral*, the electron is in one orbital on one side of the operator and in a different orbital on the other side.

Using the expressions for H_{AA} (Equation 8.4.8) and H_{AB} (Equation 8.4.9) and substituting into Equation 8.4.7 produces:

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

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

Equation 8.4.11 tells us that the energy of the H_2^+ molecule is the energy of a hydrogen atom plus the repulsive energy of two protons plus some additional electrostatic interactions of the electron with the protons. These additional interactions are given by the last term

$$\frac{J \pm K}{1 \pm S}.$$

If the protons are infinitely far apart then only E_H is nonzero, which we can set to zero by subtracting off:

$$\Delta E_{\pm} = E_{\pm} - E_H \quad (8.4.12)$$

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

To get a chemical bond and a stable H_2^+ molecule $\Delta E_{\pm}$ must be less than zero and have a minimum, i.e. $\frac{J \pm K}{1 \pm S}$ must be sufficiently negative to overcome the positive repulsive energy of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ for some value of R . For large R , these terms are zero, and for small R , the **Coulomb repulsion of the protons rises to infinity**.

? Exercise 9.4.2

Show that Equation 9.2.1 follows from Equation 8.4.7

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

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

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

Figure 9.4.2 shows graphs of the four terms contributing to the energy of H_2^+ (Equation 8.4.13). In Figure 9.4.2, you can see that as the internuclear distance R approaches zero,

- the Coulomb repulsion of the two protons goes from near zero to a large positive number,
- the overlap integral goes for zero to one, and
- J and K become increasingly negative.

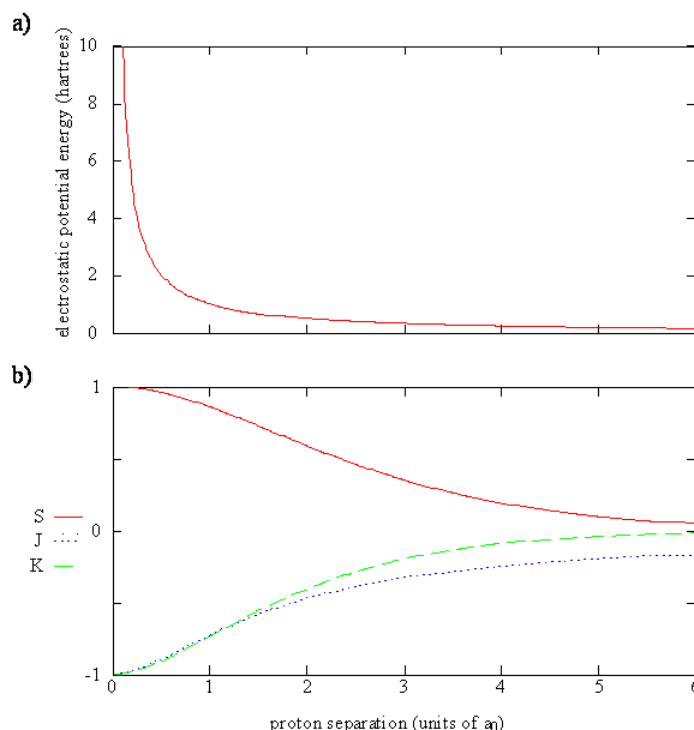


Figure 9.4.2 : (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). (b) The overlap (S), Coulomb (J), and exchange (K) integrals at different proton separations. The units for J and K are hartrees; S has no units. (CC BY-SA-NC;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

Note that both J and K integrals are **negative** since all quantities in the integrands of Equation 8.4.14 and 8.4.15 are positive. In the Coulomb integral, $e\varphi_{1s_A}^*(r)\varphi_{1a_A}(r)$ is the charge density of the electron around proton A, since $\mathbf{r}$ 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 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 to the build-up of electron charge density between the two protons.

? Exercise 9.4.3

Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for H_2^+ .

Figure 9.4.3 shows the energy of H_2^+ relative to the energy of a separated hydrogen atom and a proton as given by Equation 8.4.11. For the electron in the ψ_- orbital, the energy of the molecule, $E_{el}(R)$, **always** is greater than the energy of the separated atom and proton.

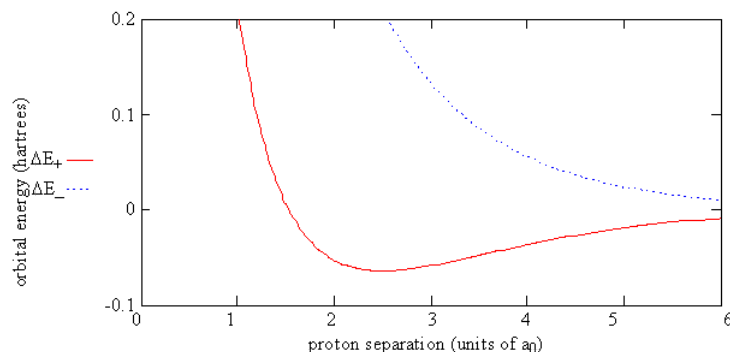


Figure 9.4.3 : Energy of the H_2^+ bonding molecular orbital ΔE_+ and the molecular orbital ΔE_- , relative to the energy of a separated hydrogen atom and proton.

For the electron in the ψ_+ orbital, you can see that the big effect for the energy of the bonding orbital, $E_+(R)$, is the balance between the repulsion of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ and J and K, which are both negative. J and K manage to compensate for the repulsion of the two protons until their separation is less than 100 pm (i.e the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. This minimum represents the formation of a chemical bond. The effect of S is small. It only causes the denominator in Equation 8.4.11 to increase from 1 to 2 as R approaches 0.

For the antibonding orbital, $-K$ is a positive quantity and essentially cancels J so there is not sufficient compensation for the Coulomb repulsion of the protons. The effect of the $-K$ in the expression, Equation 8.4.11, for E_- is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for ψ_- is even lower than that given by the atomic orbitals.

Contributors and Attributions

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

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8.5: Bonding and Antibonding Orbitals

Learning Objectives

- Characterize the bonding and anti-bonding molecular orbitals in H^+

The two molecular orbitals of the H^+ ion were created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the j^{th} molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$|\psi_J\rangle = \sum_i^N c_{J,i} |\phi_i\rangle \quad (8.5.1)$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 8.5.1). Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1s orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 9.5.1).

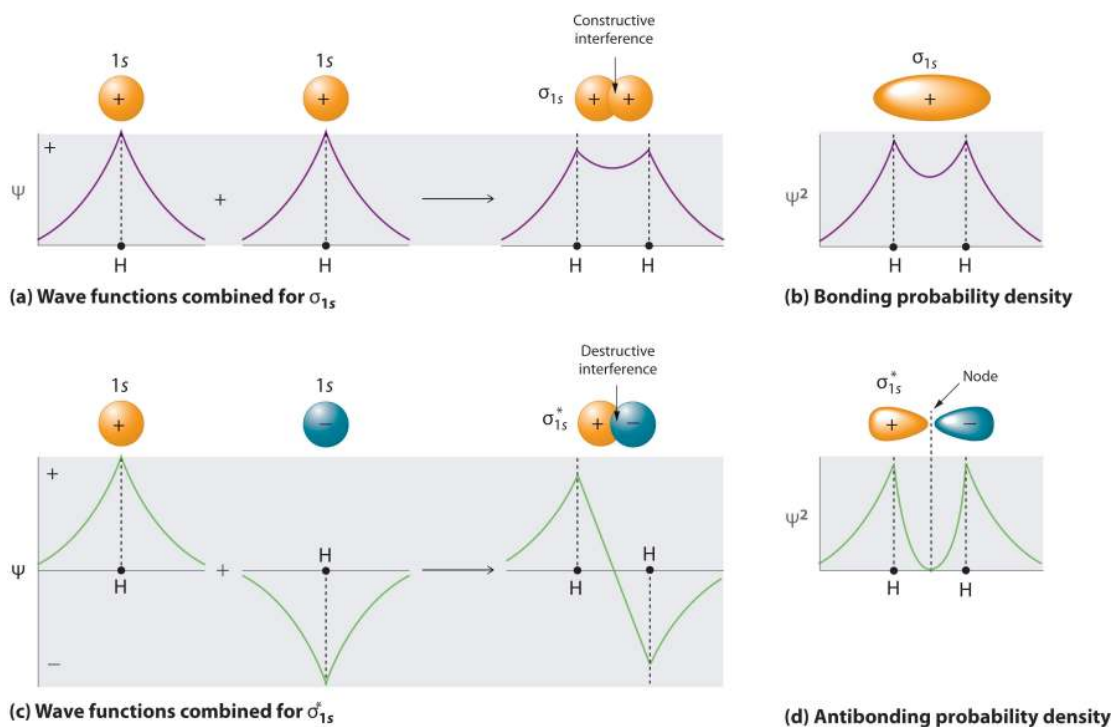


Figure 9.5.1 : Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wavefunctions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wavefunction (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates 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 (Ψ^2) for the σ_{1s}^* antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei. (CC BY-SA-NC; anonymous).

In the sigma (σ) orbital, the electron density along the internuclear axis and between the nuclei has *cylindrical symmetry*; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1s denotes the atomic orbitals from which the molecular orbital was derived.

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

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 9.5.1). The

resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ_{1s}^* and has a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$|\sigma_{1s}^*\rangle = \frac{1}{\sqrt{2(1-S)}}(|1s_A\rangle - |1s_B\rangle) \quad (8.5.3)$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wavefunctions. In contrast, electrons in the σ_{1s}^* orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ_{1s}^* orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wavefunctions).

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1s atomic orbitals. Conversely, electrons in the σ_{1s}^* orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1s atomic orbitals. Consequently, the σ_{1s}^* molecular orbital has a *higher* energy than either of the hydrogen 1s atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1s atomic orbitals, and the σ_{1s}^* (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 9.5.2

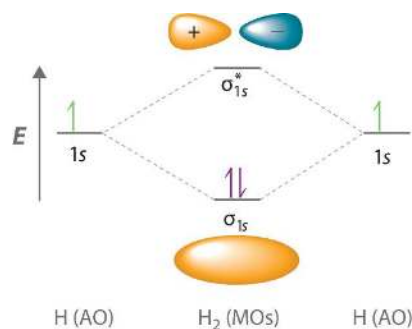


Figure 9.5.2 : Molecular Orbital Energy-Level Diagram for H₂. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H₂ molecule is more stable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

$$E_J = \frac{\langle \psi_J | \hat{H}_{elec} | \psi_J \rangle}{\langle \psi_J | \psi_J \rangle} \quad (8.5.4)$$

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

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

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

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

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

$$\frac{\partial E_J}{\partial c_k} = 0 \quad (8.5.8)$$

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

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

These equations are the **secular equations** and were discussed previously in the context of the linear variational method approximation. For the two basis set expansion (N) in Figure 9.5.1, these are

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

where c_1 and c_2 are the coefficients in the linear combination of the atomic orbitals used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

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

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

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0 \quad (8.5.12)$$

Each molecular orbital ($|\psi_J\rangle$) from this treatment has an energy E_J that is given by a different set of coefficients, $\{c_{ij}\}$ where i runs over all N functions in the basis (i.e., number of the atomic orbitals in the LCAO approximation of Equation 8.5.1), and J runs over molecular orbitals. Solve the set of linear equations using that specific E_J to determine c_{ij} values.

Steps in a Solving the Secular Equations

1. Select a set of N basis functions
2. Determine all $N(N-1)/2$ values of both H_{ij} and S_{ij}
3. Form the secular determinant; determine N roots E_j of secular equation
4. For each E_j solve the set of linear equations to determine the basis set coefficients $\{c_{ij}\}$ for the j -th molecular orbital

For more information on solving the Secular equations check [here](#).

The greater the number of atomic orbitals N that combine to generate the molecular orbitals (Equation 8.5.1), the more accurate the LCAO approximation is. This is expected based on our discussions of the variational method examples. Hence, the ψ_+ and ψ_- molecular orbitals for H_2^+ are better expressed with higher energy hydrogenic wavefunctions

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

The reasons that only the p_z atomic orbitals are included in this expansion are discussed later.

Contributors and Attributions

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

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8.6: A Simple Molecular-Orbital Treatment of H₂ 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.

$$|\psi_i\rangle = \sum_j c_{ij} \varphi_j \quad (8.6.1)$$

where

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

The variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. Just as for atoms, each electron in a molecule can be described by a product of spin-orbitals. Since electrons are fermions, the electronic wavefunction must be **antisymmetric** with respect to the permutation of any two electrons. A Slater determinant containing the molecular spin orbitals produces the antisymmetric wavefunction. For example for two electrons,

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

Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, ϵ . Following the Aufbau Principle, two electrons with different spins (α and β , consistent with the Pauli Exclusion Principle discussed for multi-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 $\psi_1^2 \psi_2^2 \psi_3^2 \dots \psi_n^2$. 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.

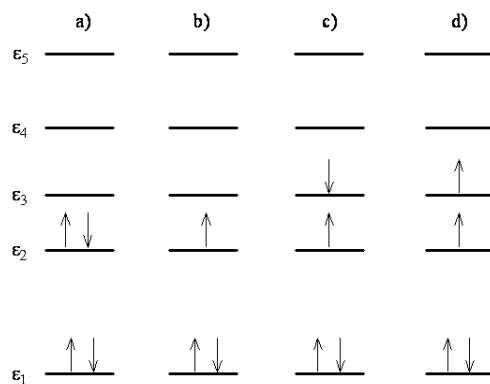


Figure 9.6.1 : a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

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

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \quad (8.6.3)$$

Contrasting LCAO with other Quantum Chemistry Methods

As we have already seen, the LCAO approach is very approximate, yielding only qualitative results. It should be noted that the Hartree-Fock method discussed earlier for atoms can also be used for molecules. For example, the molecule He_2^+ has three electrons, and the Li atom also has three electrons. As usual with Hartree-Fock, the idea is to optimize the shapes of the single-electron orbitals $\psi_1(r)$, $\psi_2(r)$ and $\psi_3(r)$ by minimizing the guess to the ground state energy E_g . Of course, we will not get the same answer as for Li because there is a different V_{en} energy for He_2^+ due to the presence of two positively charge nuclei ($charge = +2e$) separated by a distance R in contrast to the single $+3e$ charged nucleus for Li . When the shapes of the orbitals are optimized, we also obtain three energy ε_1 , ε_2 and ε_3 . Not unexpectedly, we find that two of the HF orbitals resemble $1\sigma_g$ while the third resembles $1\sigma_u^*$ and the first two energies ε_1 and ε_2 will be nearly equal, while the third ε_3 will be noticeably higher. To contrast with the LCAO approach, in LCAO, we do not optimize the shapes of the orbitals (these are assumed *a priori* to be $1s$ shaped). All we do is choose the mixing coefficients so as to minimize the guess to the ground-state energy E_g .

We note, finally, that the density functional theory alluded to earlier can also be used for molecules. It is often the case that density functional theory yields a more accurate description than Hartree-Fock, but this depends on the molecule. In any case, both are more accurate than LCAO. There is also a hierarchy of methods called *post Hartree-Fock* methods, all of which are based on the wavefunction rather than the electron density, that can be used to improve upon the HF approximation systematically. The greater the accuracy that is desired for the calculation, the more costly computationally the post HF methods become, so quantum chemistry is often a trade-off between accuracy and efficiency, an issue that becomes more critical to take into account when calculations on large molecules must be carried out!

Contributors and Attributions

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

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8.7: Molecular Orbitals Can Be Ordered According to Their Energies

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they are often ignored in constructing molecular orbitals. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

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.

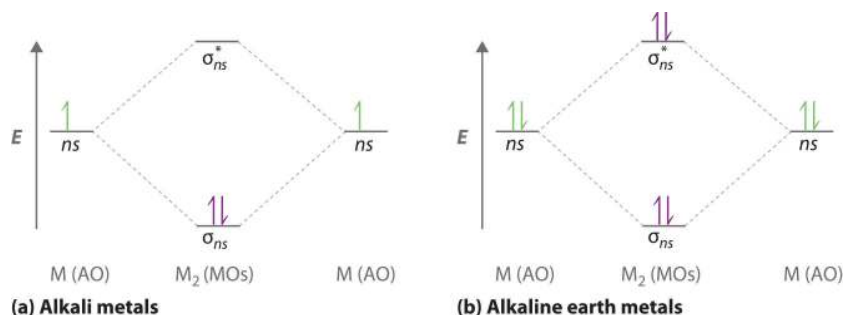


Figure 9.7.1 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}^* (nonbonding) levels, leading to a predicted bond order of 0. (CC BY-SA-NC; anonymous).

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule. As shown in Figure 8.7.1b this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}^* antibonding orbital and give a bond order of 0. Thus Be_2 , Mg_2 , Ca_2 , Sr_2 , and Ba_2 are all expected to be unstable, in agreement with experimental data. In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

✓ Example 9.7.1 : Sodium Dimer Ion

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

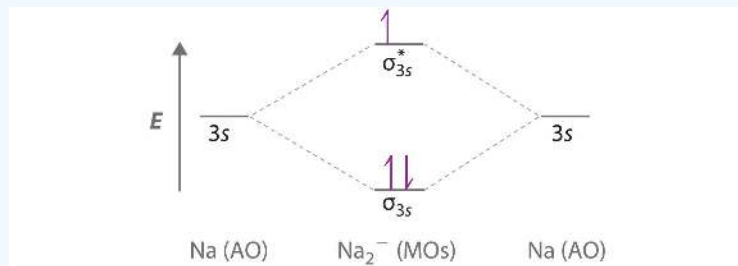
Strategy

- Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
- 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.
- Calculate the bond order and predict whether the species is stable.

Solution

A Because sodium has a $[\text{Ne}]3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two $1s$ atomic orbitals.

B The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s}^* and a $(\sigma_{3s})^2(\sigma_{3s}^*)^1$ electron configuration.



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C The bond order is $(2-1) \div 2 = 1/2$. With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

? Exercise 9.7.1 : Calcium Dimer Cation

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

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

Molecular Orbitals Formed from np 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.

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

Just as with ns orbitals, we can form molecular orbitals from np orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 9.7.2, it is the mathematical *difference* of their wavefunctions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the z -axis):

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

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

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

In this combination, shown in part (b) in Figure 9.7.2, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

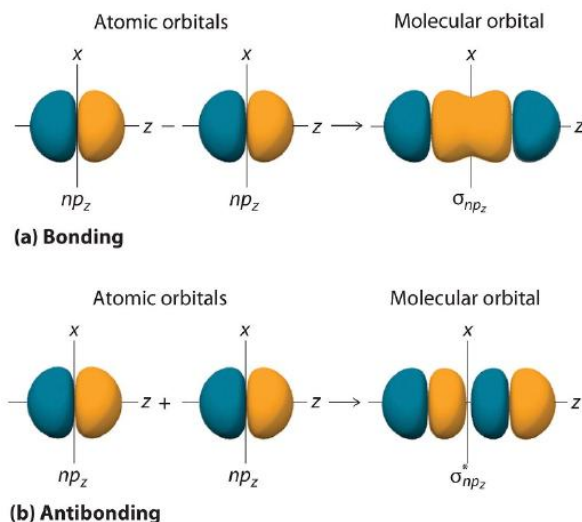


Figure 9.7.2 : Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms. (a) By convention, in a linear molecule or ion, the z -axis always corresponds to the internuclear axis, with $+z$ to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate $- + - +$, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ^* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

The remaining p orbitals on each of the two atoms, np_x and np_y , do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 9.7.3, we see that we have two pairs of np orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π^*) orbital. An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel np atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x(A) + np_x(B) \quad (8.7.4)$$

$$\pi_{np_x}^* = np_x(A) - np_x(B) \quad (8.7.5)$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi_{np_y}^*$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi_{np_x}^*$ and $\pi_{np_y}^*$ molecular orbitals.

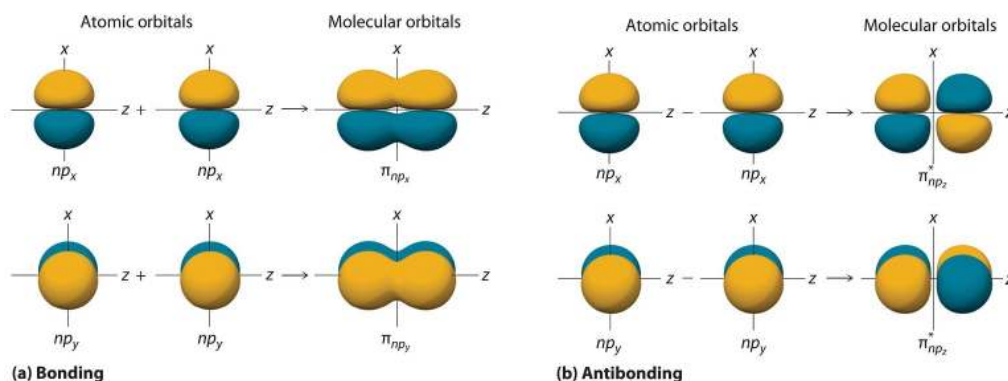


Figure 9.7.3 : Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms. (a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) 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.

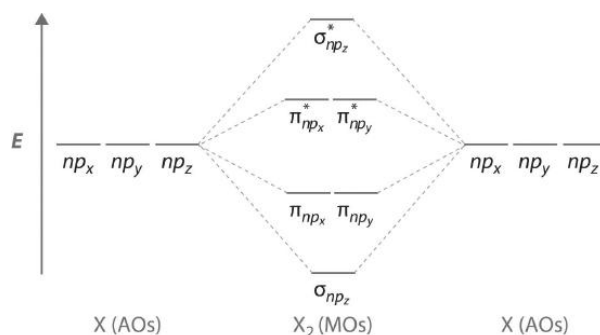


Figure 9.7.4 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x , np_y , and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ^* molecular orbitals 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 8.7.5a; the $n = 1$ orbitals (σ_{1s} and σ_{1s}^*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the

diagram, the σ_{2s} and σ_{2s}^* molecular orbitals are much lower in energy than the molecular orbitals derived from the $2p$ atomic orbitals because of the large difference in energy between the $2s$ and $2p$ atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three $2p$ orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y} . For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma_{2p_z}^*$ orbital is higher in energy than either of the degenerate $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rules. Two electrons each fill the σ_{2s} and σ_{2s}^* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons.

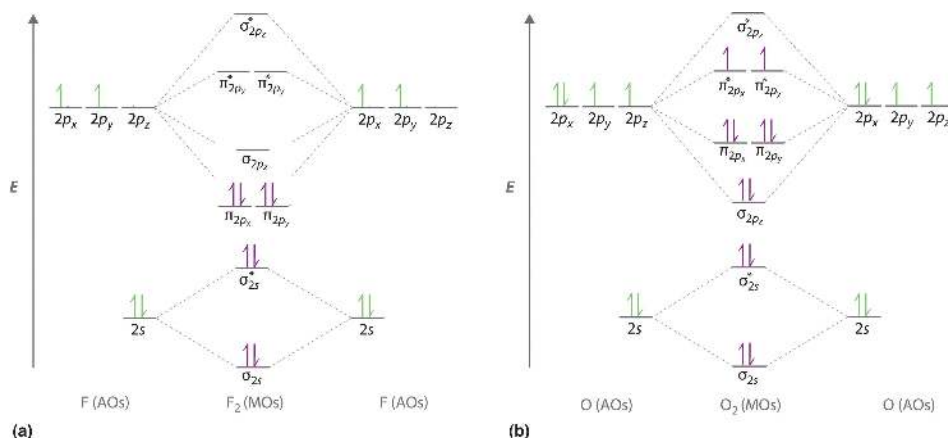


Figure 9.7.5 : Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2 , with 8 valence electrons (4 from each C atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2 , with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $(\pi_{2p_x}^*, \pi_{2p_y}^*)$ 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 $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ orbitals. The difference in energy between the $2s$ and $2p$ atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the $2s$ electrons by electrons in the $2p$ subshell. The bonding interaction between the $2s$ 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 π_{2p_x} and π_{2p_y} 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.

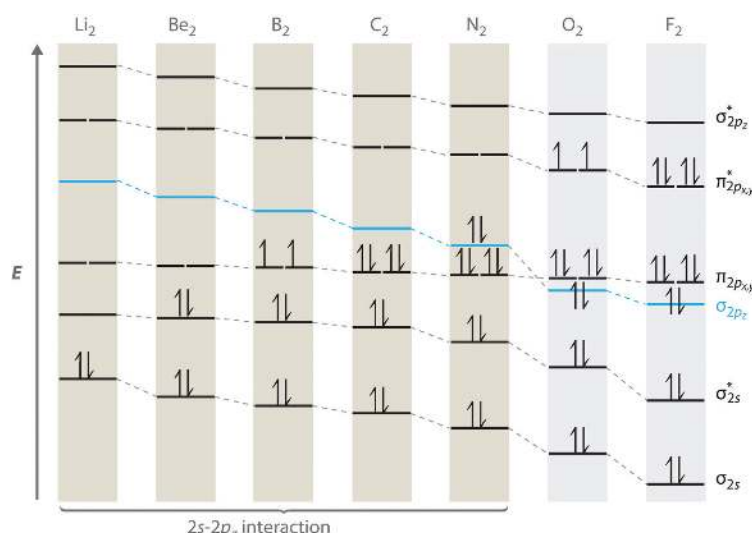


Figure 9.7.6 : Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For 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 $2p$ 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

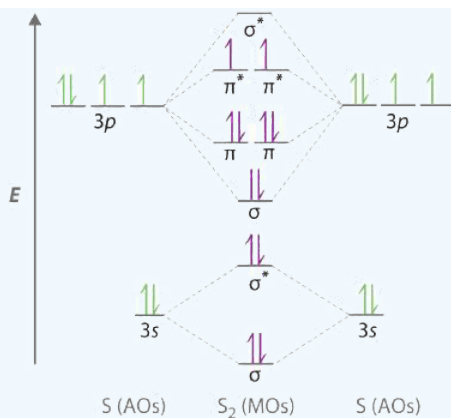
Strategy:

- 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.
- Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2 .
- Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
- Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[\text{Ne}]3s^23p^4$ 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 $3s$ and $3p$ 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 $\pi_{3p_x}^*$ and $\pi_{3p_y}^*$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p_{x,y}}^*)^2$ with 2 unpaired electrons. The bond order is $(8 - 4) \div 2 = 2$, so we predict an S=S double bond.

? Exercise 9.7.2

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi_{2p_{x,y}}^*)^4$ bond order of 1; no unpaired electrons

Molecular Orbitals Formed from ns with np Orbitals

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an ns atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 9.7.7, the sum of the two atomic wavefunctions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ^* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

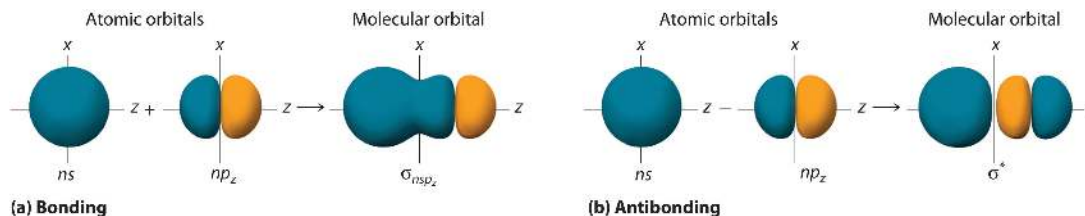


Figure 9.7.7 : Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ^* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

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

Learning Objectives

- Using bond order as a metric for the existence of molecules

Bond Order

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. Within the molecular orbital approach, *bond order* is defined as one-half the *net* number of bonding electrons:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \quad (8.8.1)$$

To calculate the bond order of H_2 , we know that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ_{1s}^* (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\text{bond order} = \frac{2 - 0}{2} = 1 \quad (8.8.2)$$

This result corresponds to the single covalent bond; double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams to describe the bonding in other pairs of atoms and ions where $n = 1$, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's Rules.

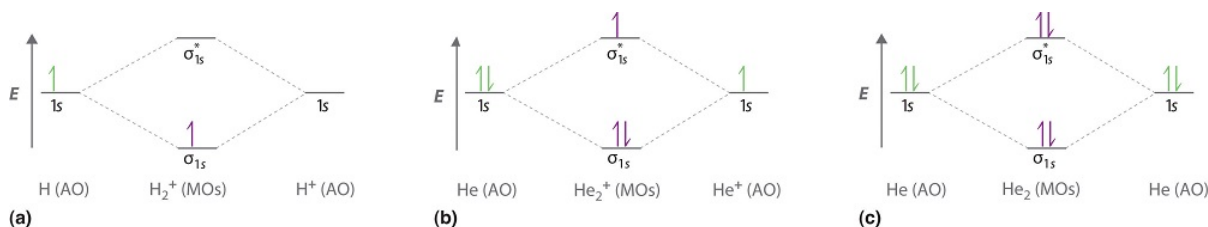


Figure 9.8.1 : Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. (CC BY-SA-NC; anonymous)

Figure 8.8.1a shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (via Equation 8.8.1)

$$\text{bond order} = \frac{1 - 0}{2} = 1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+ . With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 9.8.1, these predictions agree with the experimental data.

Table 9.8.1 : Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Species	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	5,500	4.6×10^{-5}

Figure 8.8.1b is the molecular orbital energy-level diagram for He_2^{2+} . This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the σ_{1s}^* antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration. This electron configuration gives a bond order (via Equation 8.8.1) of

$$\text{bond order} = \frac{2 - 1}{2} = 1/2$$

As with H_2^+ , the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2 . In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 9.8.1).

✓ Example 9.8.1 : The ion

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the He_2^{2+} ion.

Given: chemical species

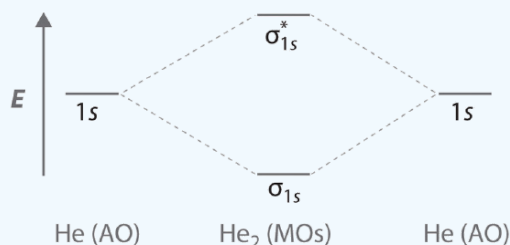
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

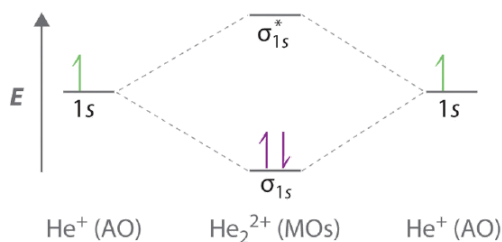
- Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
- Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
- Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1s atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ_{1s}^* antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1s atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired.

C So the bond order is (via Equation 8.8.1)

$$\frac{2 - 0}{2} = 1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

? Exercise 9.8.1 : The Ion

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure 8.8.1c is the molecular orbital energy-level diagram for He_2 . With a total of four valence electrons, both the σ_{1s} bonding and σ_{1s}^* antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ electron configuration, with a predicted bond order (via Equation 8.8.1) of

$$\text{bond order} = \frac{2 - 2}{2} = 0 \quad (8.8.3)$$

which indicates that the He_2 molecule has no net covalent bond and is not a stable species.

The ability to track bond order to bond strength is due to the fact that the energy difference between the anti-bonding σ_{1s}^* molecular orbital and the original $1s$ atomic orbital is *larger* than the energy difference between the bonding σ_{1s} molecular orbital and the $1s$ atomic orbitals. This was derived previously where the stabilization energy (ΔE_+) of the σ_{1s} molecular orbital is less than the destabilization energy (ΔE_-) of the anti-bonding σ_{1s}^* molecular orbital:

$$\Delta E_{\pm} = E_{\pm} - E_H \quad (8.8.4)$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \quad (8.8.5)$$

Hence, the anti-bonding σ_{1s}^* molecular orbital is more destabilized relative to the atomic orbitals than the bonding σ_{1s} molecular orbital is stabilized relative to the $1s$ atomic orbitals (E_H).

The fact that the anti-bonding MO energy difference is larger than the bonding σ_{1s} molecular orbital energy difference is the true reason that helium dimer is not predicted to exist with a covalent bond. Of the four valence electrons in helium dimer, two will fill the bonding σ_{1s} molecular orbital, and the other two will fill the anti-bonding σ_{1s}^* molecular orbital. The two electrons in the bonding σ_{1s} molecular orbital will achieve some stabilization relative to the $1s$ atomic orbitals, but the two electrons in the anti-bonding σ_{1s}^* molecular orbital will achieve *greater* de-stabilization relative to their position in the atomic orbitals. The net result is a less stable molecule than if the electrons remained in their respective $1s$ atomic orbitals.

The electrons in antibonding orbitals cancel (and exceed) the stabilization resulting from electrons in bonding orbitals. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature (at least as a covalently bonding complex).

📌 However, Van der Waals Helium Dimers do exist

Based on molecular orbital theory discussed above, the He_2 molecule should not exist since no covalent bond formed between the helium atoms (Equation 8.8.3). However, the molecular orbital description above neglects the van der Waals force that exists between the atoms as demonstrated by the existence of liquid helium (at 4 K). So a "molecule" composed of two helium atoms bound by the van der Waals force may exist by this attractive force instead - and it does.

A helium dimer molecule bound by Van der Waals forces was first proposed by John Clarke Slater in 1928 and observed in 1993 by Gentry and coworkers. Interestingly, He_2 is the largest known molecule of two atoms when in its ground state with an extremely long bond length with a separation of about 5,200 pm. The binding energy is only $4.6 \times 10^{-5} \text{ kJ/mol}$, so the He–He bond is 5,000 times weaker than the covalent bond in the hydrogen molecule (Table 9.8.1).

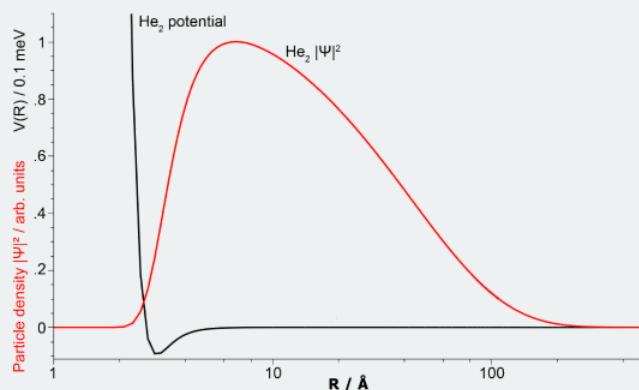


Figure 9.8.2 : The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i.e., tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses (He_2 potential and wavefunction taken from Przybytek 2010), while the classical turning point is located at 13.6 Å, the overall wavefunction extends to more than 200 Å. (Inspire; <http://inspirehep.net/record/1415151/plots>)

Conclusion

The decrease in energy caused by the bonding orbital (constructive interference of the atomic orbitals) is canceled by the increase in energy caused by the antibonding orbital (destructive interference of the atomic orbitals), so it is not energetically favorable for the helium atoms to be in such proximity, so if that situation arises, they'll separate quickly since there's no force keeping them there.

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

The Pauli exclusion principle plays as important a role in the understanding of the electronic structure of molecules as it does in the case of atoms. The end result of the Pauli principle is to limit the amount of electronic charge density that can be placed at any one point in space. For example, the Pauli principle prevents the 1s orbital in an atom from containing more than two electrons. Since the 1s orbital places most of its charge density in regions close to the nucleus, the Pauli principle, by limiting the occupation of the 1s orbital, limits the amount of density close to the nucleus. Any remaining electrons must be placed in orbitals which concentrate their charge density further from the nucleus.

In an earlier discussion we pointed out that the reason the electron doesn't fall onto the nucleus is because it must possess kinetic energy if Heisenberg's uncertainty principle is not to be violated. This is one reason why matter doesn't collapse. The Pauli principle is equally important in this regard. The electron density of the outer electrons in an atom cannot collapse and move closer to the nucleus since it can do so only if the electrons occupy an orbital with a lower n value. If, however, the inner orbital contains two electrons, then the Pauli principle states that the collapse cannot occur. We must be careful in our interpretation of this aspect of the Pauli principle. The density from a 2s orbital has a small but finite probability of being found well within the density of the 1s orbital. Do not interpret the Pauli principle as implying that the density from an occupied orbital has a clearly defined and distinct region in real space all to its own. This is not the case. The operation of the Pauli principle is more subtle than this. In some simple cases, such as the ones we wish to discuss below, the limiting effect of the Pauli principle on the density distribution can, however, be calculated and pictured in a very direct manner.

The Pauli principle demands that when two electrons are placed in the same orbital their spins must be paired. What restriction is placed on the spins of the electrons during the formation of a molecule, when two orbitals, each on a different atom, overlap one another? For example, consider the approach of two hydrogen atoms to form a hydrogen molecule. Consider atom A to have the configuration $1s^1\alpha$ and atom B the configuration $1s^1\beta$. Even when the atoms approach very close to one another the Pauli principle would be satisfied as the spins of the two electrons are opposed. This is the situation we have tacitly assumed in our previous discussion of the hydrogen molecule. However, what would occur if two hydrogen atoms approached one another and both had the same configuration and spin, say $1s^1\alpha$? When two atoms are relatively close together the electrons become **indistinguishable**. It is no longer possible to say which electron is associated with which atom as both electrons move in the vicinity of both nuclei. Indeed this is the effect which gives rise to the chemical bond. In so far as we can still regard the region around each atom to be governed by its own atomic orbital, distorted as it may be, two electrons with the same spin will not be able to concentrate their density in the binding region. This region is common to the orbitals on both atoms, and since the electrons possess the same spin they cannot both be there simultaneously. In the region of greatest overlap of the orbitals, the binding region, the presence of one electron will tend to exclude the presence of the other if their spins are parallel. Instead of density accumulating in the binding region as two atoms approach, electron density is removed from this region and placed in the antibonding region behind each nucleus where the overlap of the orbitals is much smaller. Thus the approach of two hydrogen atoms with parallel spins does not result in the formation of a stable molecule. This repulsive state of the hydrogen molecule, in which both electrons have the same spin and atomic orbital quantum numbers, can be detected spectroscopically.

We can now give the general requirements for the formation of a chemical bond. Electron density must be accumulated in the region between the nuclei to an extent greater than that obtained by allowing the original atomic density distributions to overlap. In general, the increase in charge density necessary to balance the nuclear force of repulsion requires the presence of two electrons.

We are now in a position to build up and determine the electronic configurations of the homonuclear diatomic molecules by adding electrons two at a time to the molecular orbitals with the spins of the electrons paired, always filling the orbitals of lowest energy first. We shall, at the same time, discuss the effectiveness of each orbital in binding the nuclei and make qualitative predictions regarding the stability of each molecular configuration.

The Pauli Exclusion Principle in Hydrogen Dimer

The two electrons in the hydrogen molecule may both be accommodated in the $1s_g$ orbital if their spins are paired and the molecular orbital configuration for H_2 is $1s_g^2$. Since the $1s_g$ orbital is the only occupied orbital in the ground state of H_2 , the density distribution shown previously in Figure 9.9.2 for H_2 is also the density distribution for the $1s_g$ orbital when occupied by two

electrons. The remarks made previously regarding the binding of the nuclei in H_2 by the molecular charge distribution apply directly to the properties of the $1s_g$ charge density.

The Pauli Exclusion Principle in Helium Dimer

The electronic configuration of He_2 is $1s_g^2 1s_u^2$. A s_u orbital, unlike a s_g orbital, possesses a node in the plane midway between the nuclei and perpendicular to the bond axis. The $1s_u$ orbital and all s_u orbitals in general, because of this nodal property, cannot concentrate charge density in the binding region. It is instead concentrated in the antibinding region behind each nucleus (Figure 9.9.3).

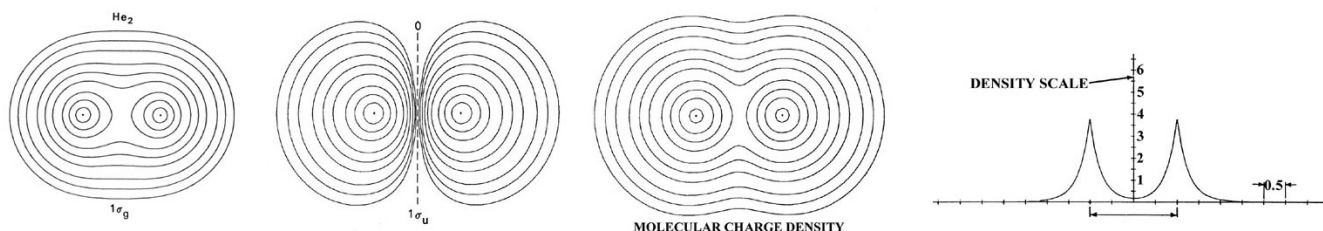


Figure 9.9.3 : Contour maps of the doubly-occupied $1s_g$ and $1s_u$ molecular orbital charge densities and of the total molecular charge distribution of He_2 at $R = 2.0$ au. A profile of the total charge distribution along the internuclear axis is also shown.

The s_u orbitals are therefore classified as **antibonding**. It is evident from the form of density distribution for the $1s_u$ orbital that the charge density in this orbital pulls the nuclei apart rather than drawing them together. Generally, the occupation of an equal number of s_g and s_u orbitals results in an unstable molecule. The attractive force exerted on the nuclei by the charge density in the s_g orbitals is not sufficient to balance both the nuclear force of repulsion and the antibinding force exerted by the density in the s_u orbitals. Thus molecular orbital theory ascribes the instability of He_2 to the equal occupation of bonding and antibonding orbitals. Notice that the Pauli exclusion principle is still the basic cause of the instability. If it were not for the Pauli principle, all four electrons could occupy a s_g -type orbital and concentrate their charge density in the region of low potential energy between the nuclei. It is the Pauli principle, and not a question of energetics, which forces the occupation of the $1s_u$ antibonding orbital.

The total molecular charge distribution is obtained by summing the individual molecular orbital densities for single or double occupation numbers as determined by the electronic configuration of the molecule. Thus the total charge distribution for He_2 (Figure 9.9.3) is given by the sum of the $1s_g$ and $1s_u$ orbital densities for double occupation of both orbitals. The adverse effect which the nodal property of the $1s_u$ orbital has on the stability of He_2 is very evident in the total charge distribution. Very little charge density is accumulated in the central portion of the binding region. The value of the charge density at the mid-point of the bond in He_2 is only 0.164 au compared to a value of 0.268 au for H_2 .

We should reconsider in the light of molecular orbital theory the stability of He_2^+ and the instability of the hydrogen molecule with parallel spins. He_2^+ will have the configuration $1s_g^2 1s_u^1$. Since the $1s_u$ orbital is only singly occupied in He_2^+ , less charge density is accumulated in the antibinding regions than is accumulated in these same regions in the neutral molecule. Thus the binding forces of the doubly-occupied $1s_g$ density predominate and He_2^+ is stable. The electron configuration of (triplet) H_2 is $1s_g^1(\alpha)1s_u^1(\alpha)$ when the electronic spins are parallel. The electrons **must** occupy separate orbitals because of the Pauli exclusion principle. With equal occupation of bonding and antibonding orbitals, the triplet H_2 species is predicted to be unstable.

Contributors and Attributions

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8.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

Learning Objectives

- To describe the connection between bond order, bond length and bond energy in diatomic molecules
- To explain the observed paramagnetic properties of molecular oxygen with Molecular Orbital theory

In general chemistry courses, students learn that covalent bonds can come as either single, double or triple bonds, which are identified by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases (Table 9.10.1).

Table 9.10.1 : General Correlation between Bond Strength, length and order in Covalent bonds

Bond	Bond Order	Bond Enthalpy (kJ/mol)	Bond Length (Å)
C–C	1	348	1.54
C=C	2	614	1.34
C≡C	3	839	1.20
N–N	1	163	1.47
N=N	2	418	1.24
N≡N	3	941	1.10

The above trend can be observed in the first row diatomics in Figure 9.10.1 . The bond order can be determined directly from the molecular orbital electron configurations. For diatomics, the occupations can correlate to bond length, bond energies (Figure 9.10.1).

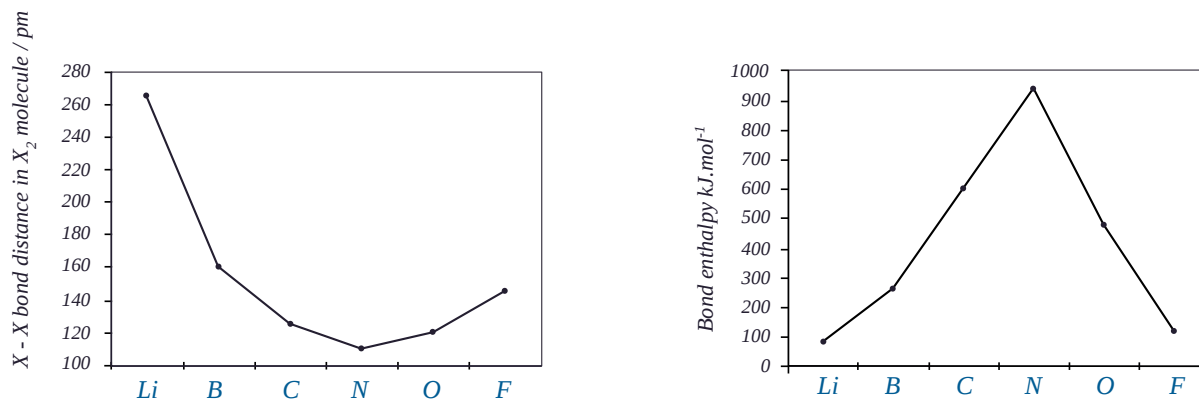


Figure 9.10.1 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

The trends in Figure 9.10.1 and Table 9.10.1 extend to molecular ions.

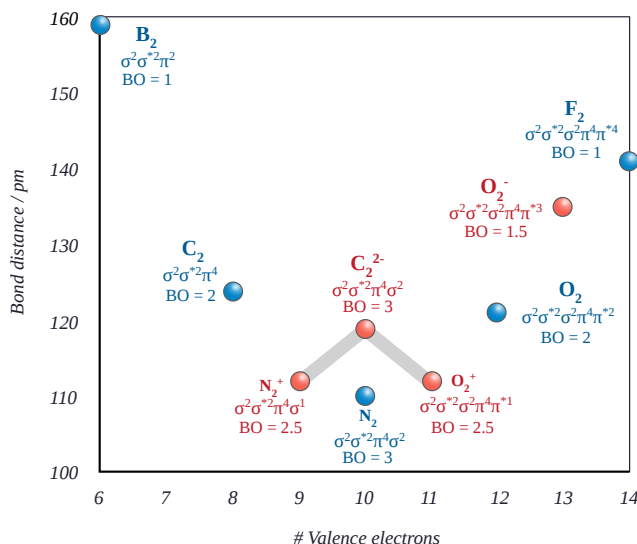


Figure 9.10.2 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

✓ Example 9.10.1 : Molecular Oxygen

Arrange the following four molecular oxygen species in order of increasing bond length: O_2^+ , O_2 , O_2^- , and O_2^{2-} .

Solution

The bond length in the oxygen species can be explained by the positions of the electrons in molecular orbital theory. To obtain the molecular orbital energy-level diagram for O_2 , we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in Figure 9.10.1 . We again fill the orbitals according to Hund's rules and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}^* orbitals, two more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ orbitals. According to Hund's first rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving a multiplicity of 3 (a triplet state) with two unpaired electrons. This leads to a predicted bond order of

$$\frac{8 - 4}{2} = 2$$

which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

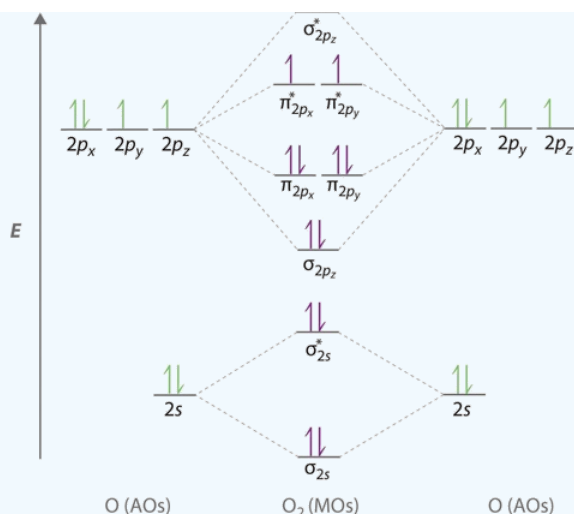


Figure 9.10.3 : Molecular Orbital Energy-Level Diagrams for O_2 . With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $(\pi_{2p_x}^*, \pi_{2p_y}^*)$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; Anonymous by request).

The bond order is determined from the the electron configurations. The electron configurations for the four species are contrasted below.

- O_2 :

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^{*1} \pi_{2p_x}^{*1}$$

From Equation ???, the bond order for O_2 is 2 (i.e., a double bond).

- O_2^+ :

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^{*0} \pi_{2p_x}^{*0}$$

From Equation ???, the bond order for O_2^+ is 2.5. An alternative and equally valid configuration is

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^{*0} \pi_{2p_x}^{*1}$$

- O_2^- :

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^{*2} \pi_{2p_x}^{*1}$$

From Equation ???, the bond order for O_2^- is 1.5. An alternative and equally valid configuration is

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^{*1} \pi_{2p_x}^{*2}$$

- O_2^{2-} :

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_x}^2 \pi_{2p_y}^{*2} \pi_{2p_x}^{*2}$$

From Equation ???, the bond order for O_2^{2-} is 1.

The bond order decreases and the bond length increases in the order. The predicted order of increasing bondlength then is $O_2^+ < O_2 < O_2^- < O_2^{2-}$. This trend is confirmed experimentally with O_2^+ (112.2 pm), O_2 (121 pm), O_2^- (128 pm) and O_2^{2-} (149 pm).

Molecular Oxygen is Paramagnetic

We now turn to a molecular orbital description of the bonding in O_2 . It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory or Lewis bonding) can predict the presence of two unpaired electrons in O_2 .

Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Video 9.10.1, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.



Video 9.10.1 : Liquid O_2 Suspended between the Poles of a Magnet. Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

Advanced: Spin Barriers

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O , CO_2 , and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O , CO_2 , and N_2 , have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O , CO_2 , and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*.

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8.11: Photoelectron Spectra Support the Existence of Molecular Orbitals

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx ; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp .

$$\Delta p \Delta x \geq \frac{\hbar}{2} \quad (8.11.1)$$

You can see from Equation 8.11.1 that as Δp approaches 0, Δx must approach ∞ , which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 8.11.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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8.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a “skewed” molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 8.12.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

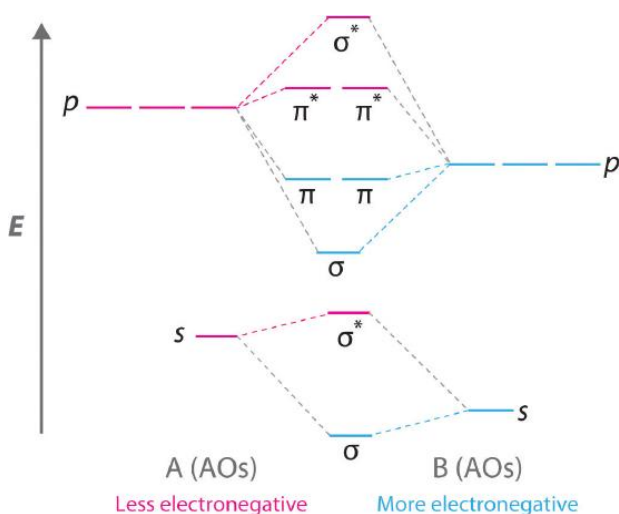


Figure 8.12.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

📌 An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2 , which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 8.12.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 8.12.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from $2p$ atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore $(8-3) \div 2 = 2 \frac{1}{2}$. 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.

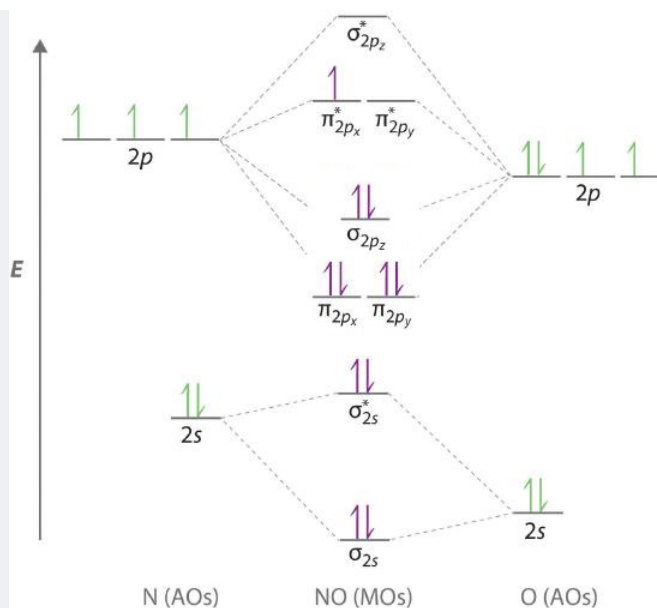


Figure 8.12.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $(\pi_{2p_x}^*, \pi_{2p_y}^*)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_{x,y}})^4(\sigma_{2p_z})^2(\pi_{2p_{x,y}}^*)^1$ 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 8.12.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 8.12.13 NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an $N \equiv O$ 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 8.12.6 that the 1s orbital of atomic hydrogen is closest in energy to the 3p orbitals of chlorine. Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3p orbitals. Of the three p orbitals, only one, designated as $3p_z$, can interact with the H 1s orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1s orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3s, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is $(2 - 0) \div 2 = 1$. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1s atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+} - Cl^{\delta-}$.

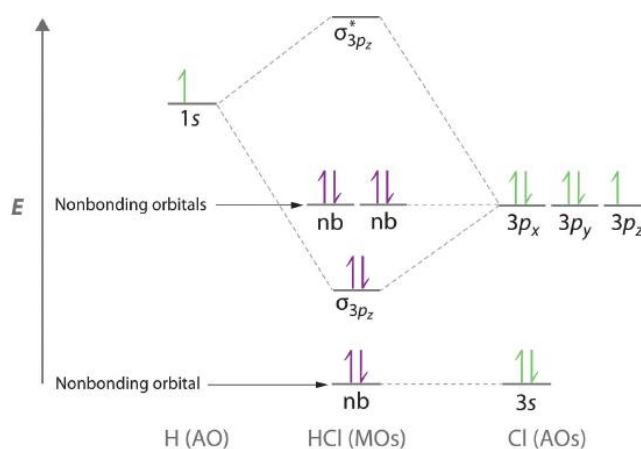


Figure 8.12.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Electrons in nonbonding molecular orbitals have no effect on bond order.

✓ Example 8.12.4: The Cyanide Ion

Use a “skewed” molecular orbital energy-level diagram like the one in Figure 8.12.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

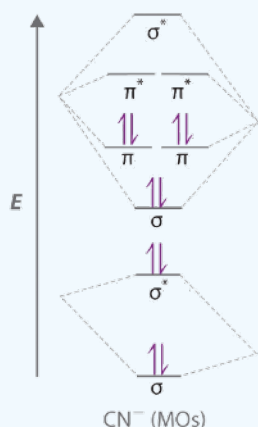
Asked for: “skewed” molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

- Calculate the total number of valence electrons in CN^- . Then place these electrons in a molecular orbital energy-level diagram like Figure 8.12.4 in order of increasing energy. Be sure to obey the [Pauli principle](#) and [Hund's rule](#) while doing so.
- 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 8.12.4 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2 .

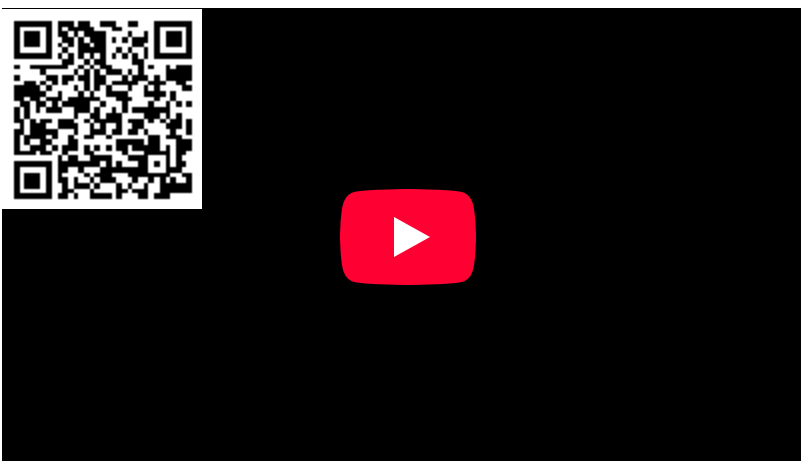
? Exercise 8.12.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

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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8.13: 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 deduced from molecular term symbols following selection rules. For multi-atomic molecules, symmetry labels play most of term symbols' roles.

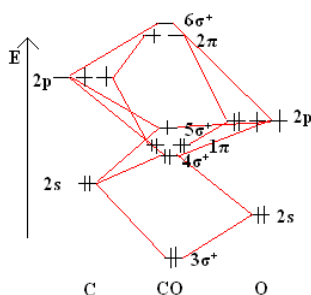
For homonuclear diatomics, the term symbol has the following form:

$$^{2S+1}\Lambda_{\Omega, (g/u)}^{(+/-)} \quad (8.13.1)$$

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: $\Sigma \Pi \Delta \Phi \dots$ when $\Lambda = 0, 1, 2, 3, \dots$, respectively. For heteronuclear diatomics, the term symbol does not include the g/u part, for there is not inversion center in the molecule.

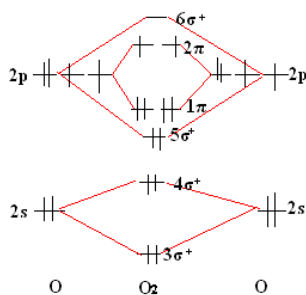
Determining term symbols of diatomics

Let's start with CO again. As we have seen before, the molecule has a close-shell configuration. Its ground state is a totally symmetric singlet, $^1\Sigma^+$, since the only possible values of (S, Λ) are $(0, 0)$. If one of the HOMO electrons on the $5\sigma^+$ orbital has jumped to the LUMO, this molecule will be in an excited state as follows.



Suppose a CO molecule is in the excited state shown above. In order to know the term symbol of this state, a direct product of the labels is required for the two MO's with unpaired electrons. The multiplication is such as $\Pi \times \Sigma^+ = \Pi$. According to Pauli's exclusion rule, these two unpaired electrons can never share the same set of quantum numbers, therefore the spin degeneracy S can reach its maximum 3. The resulting term symbols are $^1\Pi$ and $^3\Pi$.

Now if we look at O_2 , it does not have a close-shell configuration at its ground state. There are two unpaired electrons each occupying one of the two degenerate 2π orbitals, which can be seen in the diagram below.



The term symbol for oxygen molecule at its ground state is therefore derived such as $\Pi \times \Pi = \Sigma^+ + \Sigma^- + [\Delta]$, as the symbol in brackets does not allow the oxygen atoms to commute.

Transition between electronic states of diatomics

We'll focus on selection rules. Like atomic electronic states, different selection rules apply when differently incurred transitions occur. Usually for electric dipole field induced transitions, the selection rules are the same as for atoms.

1. $\Delta\Lambda = 0, \pm 1$ except $\Lambda = 0 \nrightarrow \Lambda' = 0$
2. $\Delta S = 0$
3. $\Delta\Omega = 0; \pm 1$ except $\Omega = 0 \nrightarrow \Omega' = 0$

References

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2. D. J. Willock (2009). *Molecular Symmetry*. John Wiley & Sons Ltd. ISBN 0-470-85348-4

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8.14: 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:

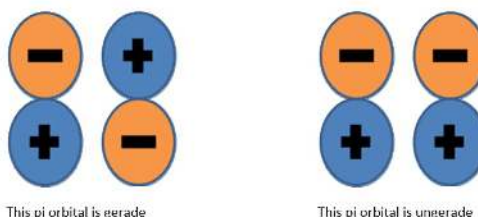
- $\Lambda = 0 \rightarrow \Sigma$
- $\Lambda = 1 \rightarrow \Pi$
- $\Lambda = 2 \rightarrow \Delta$
- $\Lambda = 3 \rightarrow \Phi$

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 **g** and **u** 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.



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 pi 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:

- $(+)(+) \rightarrow +$

- $(+)(-) \rightarrow -$
- $(-)(-) \rightarrow +$

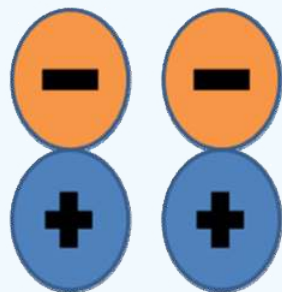
Reflection only applies to Σ states! For $\Lambda > 0$, there are no reflection labels! If you experiment with the rules, you will quickly realize why this is the case.

✓ Example 9.15.2

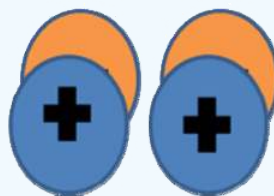
What is the reflection of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

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 selected, but the orthogonal plane would have worked just as well.



The "vertical" orbital is +



The "horizontal" orbital is -

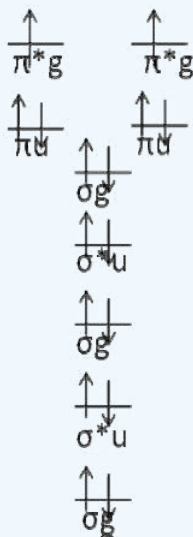
The "vertical" orbital is + The "horizontal" orbital is - Since one is + and one is - , the overall reflection is - . Try using the orthogonal plane and convince yourself that you still get the same answer.

✓ Example 9.15.3: Oxygen

What are the term symbols for O_2 ?

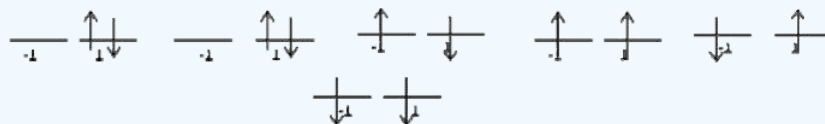
Solution

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

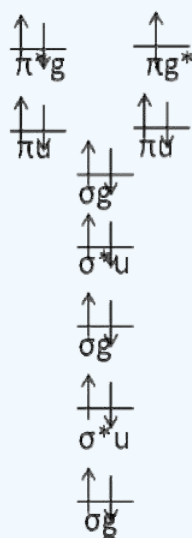
This is a $\Lambda = 0$ state with three possible spin configurations, so it is $^3\Sigma$. We know that the electrons are in different sub-orbitals (if you cannot see this, try drawing all of the possible combinations that give $\Lambda = 0$). Both of the orbitals are gerade, so the overall parity is gerade. One of the orbitals will be +, the other will be - . The final answer is $^1\Delta_g$ and $^3\Sigma_g^+$

? 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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