QUANTUM STATES OF ATOMS AND MOLECULES

Zielinksi et al.
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Licensing

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1: Spectroscopy

Spectroscopy generally is defined as the area of science concerned with the absorption, emission, and scattering of electromagnetic radiation by atoms and molecules, which may be in the gas, liquid, or solid phase. Visible electromagnetic radiation is called light, although the terms light, radiation, and electromagnetic radiation can be used interchangeably. You will discover some properties of electromagnetic radiation in Activities 1 and 2.

Spectroscopy played a key role in the development of quantum mechanics and is essential to understanding molecular properties and the results of spectroscopic experiments. It is used as a "stepping stone" to take us to the concepts of quantum mechanics and the quantum mechanical description of molecular properties in order to make the discussion more concrete and less abstract and mathematical. A spectrum is a graph that shows the intensity of radiation at different wavelengths or the response of the atomic or molecular system to different wavelengths of the radiation. Examples of absorption and fluorescence spectra are shown in Figures 1.1 and 1.2.

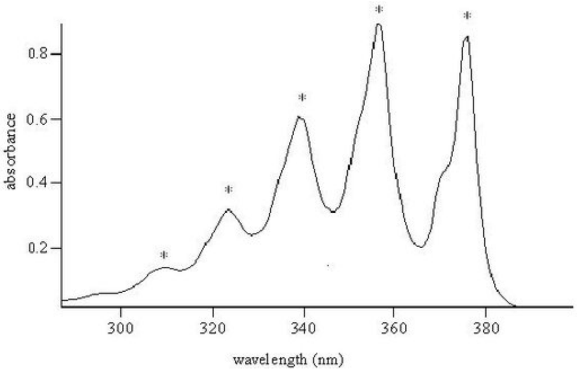

Figure 1.1: An absorption spectrum of anthracene.

An absorption spectrum shows how much light is absorbed by a sample at each wavelength of the radiation. Absorption spectra generally are displayed in one of three different ways: as a plot of either the transmission (T), absorbance (A), or the absorption coefficient (ε) on the y-axis with the wavelength on the x-axis. Sometimes the absorbance is called the optical density (OD). If we define I0 as the intensity of light incident on a sample, I as the intensity of the light transmitted by the sample, d as the thickness of the sample, and c as the concentration of the absorbing species in the sample, then

$$T = \frac{I}{I_0} \tag{1.1}$$

$$A = log \frac{I_0}{I} \tag{1.2}$$

$$\epsilon = \frac{1}{dc} log_{10} \left(\frac{I_0}{I} \right) \tag{1.3}$$

Equation 1.3 is a rearranged form of Beer's law, as developed in a Problem at the end of this chapter. Each of the quantities I, I_0, and ε are functions of the wavelength of the light being used.

Three different ways of plotting absorption spectra are used because each has particular advantages. The transmission function is simple. The absorbance condenses large variations by using a logarithm so reasonably-sized graphs show both large and small variations in light intensity. Also, the absorbance is proportional to a fundamental property, which is the absorption coefficient. The absorption coefficient is of interest because it can be calculated from the transition moment, which is a quantum mechanical quantity. In Chapter 4, we will use quantum mechanics to calculate transition moments for some molecules.

Energy often is released from atoms, molecules, and solids as light. This light is called luminescence in general and fluorescence and phosphorescence in particular situations that are identified by the decay time of the luminescence and the nature of the excited state. The decay time is the characteristic time it takes for the luminescence to disappear after the source of energy is removed or turned off. Fluorescence decays quickly (in microseconds or faster), and phosphorescence decays slowly (milliseconds to minutes). The concepts of angular momentum and a transition moment that are developed in other chapters will help you understand why these decay times are so different and depend on the nature of the excited state. The fluorescence spectrum in Figure 1.2. shows how the intensity of the light emitted by fluorescein varies with wavelength. This spectrum is an example of a distribution function. It shows how the fluorescence intensity is distributed over a range of wavelengths.

The idea of a distribution function is an important one that you may have encountered previously (e.g. the Maxwell-Boltzmann velocity distribution) and will encounter again. The term spectroscopy also is used in electron spectroscopy and mass spectroscopy where the energy distribution of electrons and the mass distribution of ions are the quantities of interest. These distributions give the absolute or relative number of particles with a given energy or mass. In general, any function that shows how some property is distributed (i.e. a distribution function) can be called a spectrum.

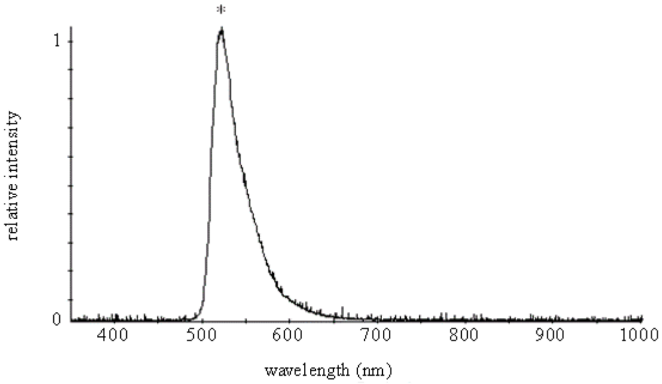

Figure 1.2: A fluorescence spectrum of fluorescein.

In scattering, light incident on an atomic or molecular system is deflected to some other direction, and in the process the wavelength of the light may or may not change. When the wavelength does not change, the scattering is called elastic or Rayleigh scattering, and when the wavelength does change, it is called inelastic scattering or Raman scattering. Scattering spectra show the intensity of radiation that is scattered in some direction as a function of the wavelength of the scattered radiation. Rather than plotting the absolute wavelength on the x-axis, it is common to plot the change in wavenumber value for the radiation, because this quantity is proportional to the energy left behind in the molecule during the scattering process.

The spectra in Figures 1.1 and 1.2 are characterized by intense features, which are called spectral bands or lines, at some points on the x-axis. The peaks of spectral bands are indicated by a star in Figures 1.1 and 1.2. The spectral bands are characterized by three quantities: their location on the x-axis, their intensity or height, and their width or shape. Quantum mechanics is needed to understand and explain these characteristics. From this book, you will learn how to interpret and calculate the positions of the bands on the x-axis in terms of the energy level structure of molecules and the intensities in terms of the transition moments. The band widths and shapes are due to dynamical effects that are unfortunately beyond the scope of this book.

The above discussion of spectroscopy brings us to the question: What is electromagnetic radiation? During the nineteenth century, research in the areas of optics, electricity, and magnetism and the unification of the resulting concepts by Maxwell provided convincing evidence that electromagnetic radiation consists of two sinusoidally oscillating fields or waves, an electric field and a magnetic field. In the simplest situation, which is radiation in a vacuum, these fields oscillate perpendicular to each other and perpendicular to the direction of propagation of the wave.

Various units are used in discussing electromagnetic radiation, and you must be familiar with conversions between them. Tables 3-5 provide the most frequently used units and their relationships. These units include hertz, joules, electron volts, wavenumbers, Angstroms, and nanometers. Any of these units, not just wavelength, can be used when plotting a spectrum.

The electromagnetic spectrum commonly is viewed as split into different regions. These regions are classified by the nature of the instrumentation (sources, wavelength selectors and detectors) that are used in the different frequency ranges. The different radiation frequencies correspond to different kinds of motions or degrees of freedom within a molecule, e.g. rotational motion (microwave region), vibrational motion (infrared region), electronic motion (generally visible through soft x-ray regions) and nuclear and electron spin motion (radio and microwave regions). After a description of the historical development of quantum mechanics and the introduction of some key concepts associated with it, this book uses quantum mechanics to account for the spectra associated with these motions and identify what can be learned about these degrees of freedom from the spectra.

Table 2 lists the parameters that characterize electromagnetic radiation. As you can see from this table, Greek letters often are used to represent physical quantities. The use of symbols makes writing equations and derivations and showing relationships much shorter and quicker than using words, but we pay a price for this convenience. We have to remember what the symbols mean, and since there are more quantities than there are symbols, even with the use of both Latin and Greek letters, some symbols mean more than one thing. Consequently, we must deduce their meaning from the context. Tables at the end of this chapter provide you with information about Greek letters and other items such as units and physical constants that will prove useful to you.

While spectra often are plotted with the wavelength, and sometimes with the wavenumber values or the frequency, on the x-axis, usually the energy associated with a photon at a particular wavelength is needed in order to relate spectra to the energy level structure of molecules. The following relationships convert wavelength λ, wavenumbers $\bar{\nu}$, and frequency ν to photon energy E.

$$E = \frac{hc}{\lambda} \tag{1.4}$$

$$E = hc\bar{\nu} \tag{1.5}$$

$$E = h\nu \tag{1.6}$$

where c is the speed of light in a vacuum.

Since wavenumbers and frequency are proportional to energy, sometimes spectroscopists measure energy in these units for convenience.

CHAPTER OVERVIEW

2: Foundations of Quantum Mechanics

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

2.1: Prelude to the Foundations of Quantum Mechanics

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

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

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

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

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

2.2: Black-Body Radiation

One experimental phenomenon that could not be adequately explained by classical physics was black-body radiation. Hot objects emit electromagnetic radiation. The burners on most electric stoves glow red at their highest setting. If we take a piece of metal and heat it in a flame, it begins to glow, dark red at first, then perhaps white or even blue if the temperature is high enough. A very hot object would emit a significant amount of energy in the ultraviolet region of the spectrum, and people are emitters of energy on the other end of the spectrum. We can see this infrared energy by using night vision goggles. The exact spectrum depends upon properties of the material and the temperature. A black-body is an ideal object that emits all frequencies of radiation with a spectral distribution that depends only on the temperature and not on its composition. The radiation emitted by such an object is called black-body radiation. Black-body radiation can be obtained experimentally from a pinhole in a hollow cavity that is held at a constant temperature.

It was found that the observed intensity of black-body radiation as a function of wavelength varies with temperature. 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.” There was no agreement between theory and experiment in the ultraviolet region of the black-body spectrum. This is shown in Figure $2.2.1$.

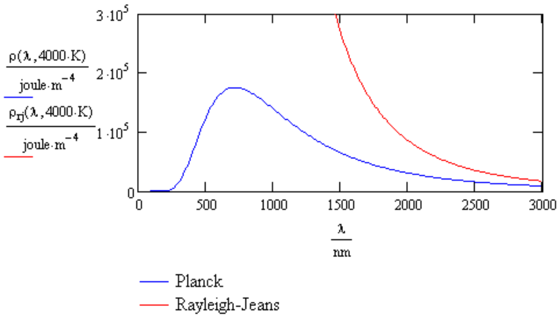

Figure $2.2.1$: Planck and experimental (blue) and Rayleigh-Jeans (red) radiation distribution curves show the radiation density for each model at 4000 K as a function of wavelength.

Max Planck was the first to successfully explain the spectral distribution of black-body radiation. He said that the radiation resulted from oscillations of electrons. Similarly, oscillations of electrons in an antenna produce radio waves. With revolutionary insight and creativity, Planck realized that in order to explain the spectral distribution, he needed to assume that the energy E of the oscillating electrons was quantized and proportional to integer multiples of the frequency ν

$$E = nh\nu \tag{2.2.1}$$

where n is an integer and h is a proportionality constant. He then was able to derive an equation (Equation $2.2.2$) that gave excellent agreement with the experimental observations for all temperatures provided that the value of 6.62618×10^{-34} Joule.sec was used for h. This new fundamental constant, which is an essential component of Quantum Mechanics, now is called Planck’s constant. The Boltzmann constant, k_B, and the speed of light (c), also appear in the equation.

$$\rho(\lambda, T)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{\frac{hc}{\lambda k_B T}} - 1} \tag{2.2.2}$$

Example $2.2.1$

Use Equation to show that the units of ρ(λ,T)dλ are J/m^3 as expected for an energy density.

Equation $2.2.2$ gives ρ(λ,T)dλ, the radiation density (J/m^3) between λ and λ + dλ inside the cavity from which the black-body radiation is emitted. The parameters in the equation are Planck’s constant, the speed of light, Boltzmann’s constant, the temperature, and the wavelength. The agreement between Planck’s theory and the experimental observation provided strong evidence that the energy of electron motion in matter is quantized. In the next two sections, we will see that the energy carried by light also is quantized in units of h $\bar{\nu}$. These packets of energy are called “photons.”

Example $2.2.2$

Use Planck's equation to prepare computer-generated graphs showing how ρ(λ,T), which is the black-body radiation density per nm, varies with wavelength at various temperatures. Use these graphs to explain why white hot is hotter than red hot. A Mathcad file link is provided as a head start for this exercise.

Example $2.2.3$

Use the results from Exercise $2.2.2$ to prepare a computer-generated graph of λ_{max}, which is the peak (or maximum) of the functions plotted in Exercise $2.2.1$, as a function of T. Describe how the color of the light emitted from the black-body varies with temperature.

Example $2.2.4$

Use the results from Exercise $2.2.4$ to estimate the color temperature of sunlight (that has a maximum at 480 nm) and the temperature of a tungsten light bulb (that has a maximum at 1035 nm.)

2.3: Photoelectric Effect

In the photoelectric effect, light incident on the surface of a metal causes electrons to be ejected. The number of emitted electrons and their kinetic energy can be measured as a function of the intensity and frequency of the light. One might expect, as did the physicists at the beginning of the Twentieth Century, that the energy in the light wave (its intensity in $J/m^2 s$) should be transferred to the kinetic energy of the emitted electrons. Also, the number of electrons that break away from the metal should change with the frequency of the light wave. This dependence on frequency was expected because the oscillating electric field of the light wave causes the electrons in the metal to oscillate back and forth, and the electrons in the metal respond at different frequencies. In other words, it was expected that the number of emitted electrons should depend upon the frequency, and their kinetic energy should depend upon the intensity of the light wave (at fixed wavelength).

> *The classical expectation of the photoelectric effect was that the number of emitted electrons would depend upon the frequency, and their kinetic energy should depend upon the intensity of the light wave.*

As shown in Figure 2.3.1, just the opposite behavior is observed in the photoelectric effect. 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.
- the number of electrons (i.e. the electric current) is proportional to the light intensity (at a fixed wavelength) and independent of the frequency of the incident radiation above the threshold value of ν_0 (no current is observed below ν_0).

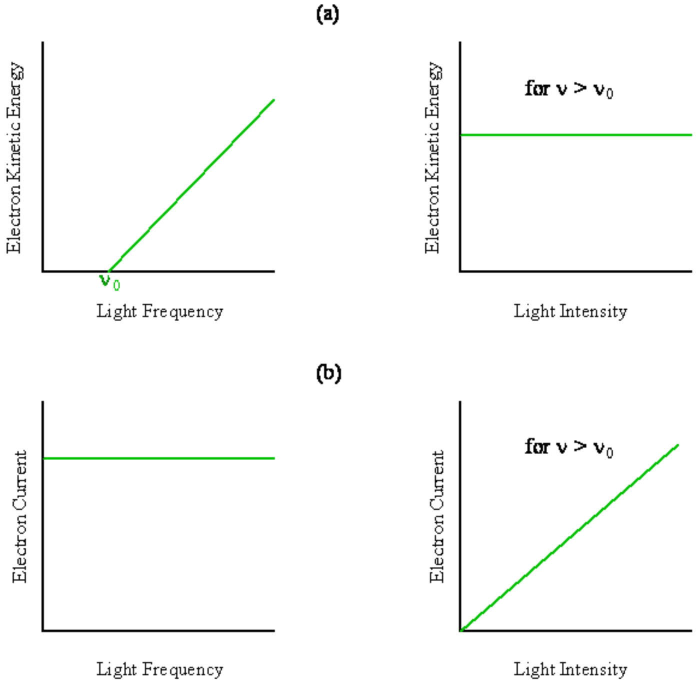

Figure 2.3.1: Schematic drawings showing the characteristics of the photoelectric effect. (a) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value and is independent of the light intensity. (b) The number of electrons emitted per second (i.e. the electric current) is independent of frequency and increases linearly with the light intensity.

In 1905, Albert Einstein explained the observations shown in Figure 2.3.1 with the bold hypothesis that energy carried by light existed in packets of an amount $h\nu$. Each packet or photon could cause one electron to be ejected, which is like having a moving particle collide with and transfer energy to a stationary particle. The number of electrons ejected therefore depends upon the number of photons, i.e. the intensity of the light. Some of the energy in the packet is used to overcome the binding energy of the electron in the metal. This binding energy is called the work function, Φ. The remaining energy appears as the kinetic energy, $\frac{1}{2}mv^2$, of the emitted electron.

Equations 2.3.1 and 2.3.2 express the conservation of energy for the photoelectric process

$$E_{photon} = K_{Eelectron} + W_{electron} \tag{2.3.1}$$

$$h\nu = \frac{1}{2}mv^2 + \Phi \tag{2.3.2}$$

Rearranging this equation reveals the linear dependence of kinetic energy on frequency as shown in Figure $2.3.1$.

$$\frac{1}{2}mv^2 = h\nu - \Phi \tag{2.3.3}$$

The slope of the straight line obtained by plotting the kinetic energy as a function of frequency above the threshold frequency is just Planck's constant, and the x-intercept, where $\frac{1}{2}mv^2 = 0$, is just the work function of the metal, $\Phi = h\nu_0$.

Example 2.3.1

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

With such an analysis Einstein obtained a value for h in agreement with the value Planck deduced from the spectral distribution of black-body radiation. The fact that the same quantization constant could be derived from two very different experimental observations was very impressive and made the concept of energy quantization for both matter and light credible. In the next sections we will see that wavelength and momentum are properties that also are related for both matter and light.

2.4: The Compton Effect

The Compton effect concerns the inelastic scattering of x-rays by electrons. Scattering means dispersing in different directions, and inelastic means that energy is lost by the scattered object in the process. The intensity of the scattered x-ray is measured as a function of the wavelength shift $\Delta\lambda$, where

$$\lambda' = \lambda + \Delta\lambda \tag{2.4.1}$$

and the scattering angle θ.

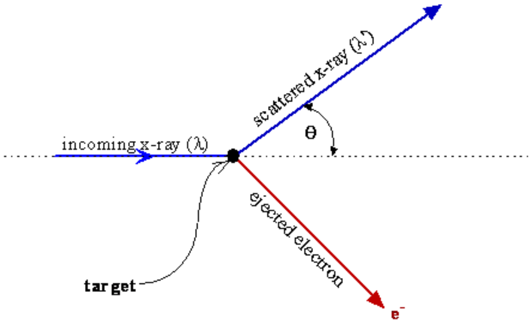

Figure 2.4.1: The Compton Effect. X-rays scattered from a target at an angle have a different wavelength from the incident x-ray, and produce an ejected electron.

To explain the experimental observations, it is necessary to describe the situation just as one would when discussing two particles, e.g. marbles, colliding and scattering from each other. The x-ray scatters (changes direction) and causes an electron with mass me to be ejected from the object with a direction that conserves the momentum of the system. Momentum and energy conservation equations then explain the scattering angles and the observed wavelength shift of the x-ray when the momentum of the x-rays is taken to be equal to h/λ and the energy is $h\nu$.

These considerations lead to Equation 2.4.2, which describes the experimental data for the variation of $\Delta\lambda$ with θ. The success of using energy and momentum conservation for two colliding particles to explain the experimental data for the Compton effect is powerful evidence that electromagnetic radiation has momentum just like a particle and that the momentum and energy are given by h/λ and $h\nu$, respectively.

$$\Delta\lambda = \frac{h}{m_e c}(1 - \cos\theta) \tag{2.4.2}$$

Example 2.4.1

For Compton scattering, determine the wavelength shift at a scattering angle of 90^o, and identify the scattering angles where the wavelength shift is the smallest and the largest.

2.5: Hydrogen Luminescence

The luminescence spectrum of the hydrogen atom reveals light being emitted at discrete frequencies. These spectral features appear so sharp that they are called lines. These lines, occurring in groups, are found in different regions of the spectrum; some are in the visible, some in the infrared, and some in the vacuum ultraviolet. The occurrence of these lines was very puzzling in the late 1800's. Spectroscopists approach this type of problem by looking for some regularity or pattern in the observations. Johannes Rydberg recognized a pattern and expressed it in terms of the following formula,

$$\bar{\nu} = R_H \left(\frac{1}{f^2} - \frac{1}{i^2} \right) \tag{2.5.1}$$

Here $\bar{\nu}$ is the "frequency" of the line in wavenumber units

$$\bar{\nu} = \frac{\nu}{c} \tag{2.5.2}$$

R_H is a constant equal to 109,677.581 cm^{-1}, now called the Rydberg constant, and f and i are positive integers with $i > f$. Different groups of lines, called Rydberg series, are obtained for different values of f. The lines in each series arise from a range of values for i. This analysis by Rydberg was pretty amazing. It pictured the hydrogen atom as some sort of counting machine that utilized integer numbers for some unknown reason.

Example 2.5.1

Calculate the wavelength of a line in the hydrogen atom luminescence spectrum corresponding to f = 7 and i = 8. In which region of the electromagnetic spectrum will this line appear?

Since the Rydberg equation was derived empirically (i.e., invented to describe experimental data), the next question was, "Can the Rydberg equation and the origin of the integer values for f and i be obtained from theoretical considerations?" This question was enormously difficult for scientists at the time because the nature of the spectrum, discrete lines rather than a continuous frequency distribution, and the very existence of atoms, was not consistent with existing physical theories.

Example 2.5.2

Explain what it means to say a constant or an equation is empirical. Give an example of a value that is determined empirically.

2.6: Early Models of the Hydrogen Atom

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

There are some basic problems with the Rutherford model. The Coulomb force that exists between oppositely charge particles means that a positive nucleus and negative electrons should attract each other, and the atom should collapse. To prevent the collapse, the electron was postulated to be orbiting the positive nucleus. The Coulomb force is used to change the direction of the velocity, just as a string pulls a ball in a circular orbit around your head or the gravitational force holds the moon in orbit around the Earth.

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

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

Niels Bohr approached this problem by proposing that we simply must invent new physical laws since experimental observations are inconsistent with the known physical laws. Bohr therefore proposed in 1913 that

1. The electron could orbit the nucleus in a stationary state without collapsing.
2. These orbits have discrete energies and radiation is emitted at a discrete frequency when the electron makes a transition from one orbit to another.
3. The energy difference between the orbits is proportional to the frequency of radiation emitted

$$E_f - E_i = \Delta E_{fi} = h\nu \tag{2.6.1}$$

   where the constant of proportionality, h, is Planck's constant. Note that $E_f - E_i$ is the difference between energy levels and $h\nu$ is the energy of the emitted photon.
4. The angular momentum, M, of the orbiting electron is a positive integer multiple of $h/2\pi$, which often is written as $\hbar$ and called h-bar.

$$M = n\hbar \tag{2.6.2}$$

- where $n = 1, 2, 3, \ldots$

Bohr's revolutionary proposal was taken seriously because with these ideas, he could derive Rydberg's formula and calculate a value for the Rydberg constant, which up to this point had only been obtained empirically by fitting the Rydberg equation to the luminescence data.

Example 2.6.1

Make four sketches to illustrate Bohr's four propositions

2.7: Derivation of the Rydberg Equation from Bohr's Model

Bohr postulated that electrons existed in orbits or states that had discrete energies. We therefore want to calculate the energy of these states and then take the differences in these energies to obtain the energy that is released as light when an electron makes a transition from one state to a lower energy one.

Because the proton is so much more massive than the electron, we can consider the proton to be fixed and the electron to be rotating around it. For the general case, two particles rotate about their center of mass, and this rotation can be described as the rotation of a single particle with a reduced mass.

To explain the hydrogen luminescence spectrum, we write the energy, E, of an orbit or state of the hydrogen atom as the sum of the kinetic energy, T, and potential energy, V, of the rotating electron. The potential energy is just the Coulomb energy for two particles with charges q_1 and q_2.

$$E = T + V \tag{2.7.1}$$

$$T = \frac{1}{2} m_e v^2 \tag{2.7.2}$$

and

$$V = \frac{q_1 q_2}{4\pi\epsilon_0 r} = \frac{(Ze)(-e)}{4\pi\epsilon_0 r} = \frac{-Ze^2}{4\pi\epsilon_0 r} \tag{2.7.3}$$

In general the charge on an atomic nucleus is Ze, where Z is the number of protons in the nucleus. The charge on a single proton is simply the fundamental constant for the unit charge, e, and the charge on an electron is $-e$. The factor $4\pi\varepsilon_0$ is due to the use of SI units, and ε is the permittivity of free space ($8.85419 \times 10^{-12} C^2 N^{-1} m^{-2}$).

Even though $Z = 1$ for the hydrogen atom, Z is retained in Equation 2.7.3 and subsequent equations so the results apply to any one-electron ion as well (e.g., He^+, Li^{2+}, etc.).

Example 2.7.1

Show that 1 $C^2 N^{-1} m^{-2}$ is equivalent to 1 F/m.

By invoking the **Virial Theorem** for electrostatic forces, we can determine the radii of the orbit and the energy of the rotating electron, derive the Rydberg equation, and calculate a value for the Rydberg constant. This theorem says that the total energy of the system is equal to half of its potential energy and also equal to the negative of its kinetic energy.

$$E = \frac{V}{2} = -T \tag{2.7.4}$$

The Virial Theorem has fundamental importance in both classical mechanics and quantum mechanics. It has many applications in chemistry beyond its use here. The word virial comes from the Latin word for force, vires, and the Virial Theorem results from an analysis of the forces acting on a system of charged particles. A proof of the validity of this theorem for the hydrogen atom is available.

The Virial Theorem makes it possible to obtain the total energy from the potential energy if we have the radius, r, of the orbit in Equation 2.7.3. We can obtain the radius of the orbit by first expressing the kinetic energy T in terms of the angular momentum M,

$$T = \frac{M^2}{2m_e r^2} \tag{2.7.5}$$

where $M = m_e v r$.

Using the Virial Theorem, Equation 2.7.4, to equate the expressions for $V/2$ and $-T$ (Equations 2.7.3 and 2.7.5), introducing Bohr's proposal that angular momentum M is quantized, $M = nhbar$, and solving for r gives

$$r_n = \frac{\pi\epsilon_0 \hbar^2 n^2}{m_e Z e^2} \tag{2.7.6}$$

Notice in equation 2.7.6 how the quantization of angular momentum results in the quantization of the radii of the orbits. The smallest radius, for the orbit with $n = 1$, is called the Bohr radius and is denoted by a_0.

$$a_0 = 52.92\, pm = 0.5292\, \text{Å} \tag{2.7.7}$$

Substituting Equations 2.7.3 and 2.7.6 into Equation $2-15$ for the total energy gives

$$E_n = \frac{-m_e Z^2 e^4}{8\epsilon_0^2 h^2 n^2} \tag{2.7.8}$$

which shows that the energy of the electron also is quantized. Equation 2.7.8 gives the energies of the electronic states of the hydrogen atom. It is very useful in analyzing spectra to represent these energies graphically in an energy-level diagram. An energy-level diagram has energy plotted on the vertical axis with a horizontal line drawn to locate each energy level.

Example 2.7.2

Calculate the potential energy, the kinetic energy, and the total energy for hydrogen when r = 52.92 pm.

Example 2.7.3

Sketch an energy level diagram for the hydrogen atom. Label each energy level with the quantum number n and the radius of the corresponding orbit.

Example 2.7.4

Calculate a value for the Bohr radius using Equation 2.7.6 to check that this equation is consistent with the value 52.9 pm. What would the radius be for n = 1 in the Li^{2+} ion.

Example 2.7.5

How do the radii of the hydrogen orbits vary with n? Prepare a graph showing r as a function of n. To which family of curves does this plot belong? States of hydrogen atoms with n = 200 have been prepared. What is the diameter of the atoms in these states? Identify something else this size.

To explain the hydrogen atom luminescence spectrum, Bohr said that light of frequency vif is produced when an electron goes from an orbit with n = i (“i” represents “initial”) to a lower energy orbit with n = f (“f” represents “final”), with i > f. In other words, the energy of the photon is equal to the difference in energies of the two orbits or hydrogen atom states associated with the transition.

$$E_{photon} = h\nu_{if} = E_i - E_f = \Delta E_{if} = \frac{me^4}{8\epsilon_0^2 h^2}\left(\frac{1}{f^2} - \frac{1}{i^2}\right) \tag{2.7.9}$$

Using $\nu_{if} = c\bar{\nu}_{if}$ converts Equation (2.20) from frequency to wave number units,

$$\bar{\nu}_{if} = \frac{me^4}{8\epsilon_0^2 h^3}\left(\frac{1}{f^2} - \frac{1}{i^2}\right) \tag{2.7.10}$$

When we identify R_H with the ratio of constants on the right hand side of Equation (2-21), we obtain the Rydberg equation with the Rydberg constant as in Equation (2-22).

$$R_H = \frac{me^4}{8\epsilon_0^2 h^3} \tag{2.7.11}$$

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

Example 2.7.6

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

2.8: Summary of Bohr's Contribution

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

How might one have been so clever as to propose that angular momentum is quantized in units of $\hbar$? Possibly, by using unit analysis.

Example 2.8.1

Show that the units of Planck’s constant (J s) are the same as angular momentum (mvr = kgm^2/s).

Example 2.8.2

Why do you suppose Bohr did not include the possibility of no angular momentum for the electron, i.e. n = 0?

The factor of $\frac{1}{2\pi}$ is needed to obtain the experimental value for RH from the theory. Without this factor Bohr would have calculated a value for RH that was smaller than the experimental value by a factor of $(2\pi)^2$.

Example 2.8.3

Calculate a value for R_H using fundamental Constants. Repeat the calculation assuming that angular momentum is quantized in units of h rather than ħ. Show that the value you calculate differs from the value obtained by Rydberg from the hydrogen atom data by a factor of $(2\pi)^2$.

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

> *Bohr’s ideas successfully explained the hydrogen spectrum, but they failed when applied to the spectra of other atoms.*

Bohr’s idea that the absorption or emission of light corresponds to an electron jumping from one orbit to another also is not entirely accurate. When light is absorbed or emitted by an atom or molecule, the atom or molecule makes a transition from one energy state to another. If there is more than one state associated with each energy level, the energy level is said to be degenerate. Bohr’s analysis produced the correct energy level spacing for the hydrogen atom and therefore could explain the luminescence spectrum, but the analysis did not identify all the possible electronic states of the hydrogen atom, as we shall see later in Chapter 8 with the Zeeman effect. The Bohr model also did not predict the electronic states of multielectron atoms. This spurred a long period of development culminating in quantum mechanics as we are studying in this text.

Contributors and Attributions

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2.9: The Wave Properties of Matter

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

$$\lambda = \frac{\hbar}{p} \tag{2.9.1}$$

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

$$p = \hbar k \tag{2.9.2}$$

Example 2.9.1

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

Example 2.9.2

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

The validity of de Broglie’s proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. The interference pattern was just like that produced when water waves pass through two holes in a barrier to generate separate wave fronts that combine and interfere with each other. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both electrons and electromagnetic radiation. Diffraction patterns are obtained if the wavelength is comparable to the spacing between scattering centers. Immediately below in the box are two hyperlinks that show you patterns obtained by electron diffraction and by x-ray diffraction. You can find others on the Internet by searching x-ray diffraction pattern and electron diffraction pattern to see how electron and x-ray diffraction are being used in modern research.

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

$$2\pi r = n\lambda \tag{2.9.3}$$

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

$$rp = \frac{nh}{2\pi} \tag{2.9.4}$$

Since rp equals the angular momentum, we have

$$M = n\hbar \tag{2.9.5}$$

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

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

Example 2.9.3

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

2.E: Foundations of Quantum Mechanics (Exercises)

Q2.1

Construct graphs from the following data to illustrate the key features of the photoelectric effect. Determine the work function for Ni and a value for Planck's constant from the data.

Photoelectric Effect for a Nickel Metal Film

wavelength(nm)	relative light intensity	relative electron current	electron kinetic energy (eV)
400	1	0	0.00
350	1	0	0.00
300	1	0	0.00
250	1	0	0.00
200	1	1	0.98
150	1	1	3.05
100	1	1	7.19
50	1	1	19.60
150	1	1	3.05
150	2	2	3.05
150	3	3	3.05
150	4	4	3.05
150	5	5	3.05
150	6	6	3.05
150	7	7	3.05
150	8	8	3.05
150	9	9	3.05

Q2.2

Suppose you need to take an absorption spectrum of a naphthalene sample in the near-UV region, around 320 nm. How much intensity is gained in this region by using an expensive tungsten filament lamp ($75) with a color temperature of 3400 K compared to an inexpensive lamp ($7.50) with a color temperature of 2800 K? Which lamp would you purchase and why? List all of the assumptions you made in formulating your answer.

Q2.3

Calculate the de Broglie wavelength for an electron in the first Bohr orbit of the hydrogen atom and compare this wavelength with the circumference of the orbit. What insight do you gain from this comparison?

Q2.4

Neutrons as well as electrons and x-rays are used to obtain information about molecular structure through diffraction patterns. What must the velocity of a neutron be for its de Broglie wavelength to be about five times smaller than a bond length? Do you consider this velocity to be large or small? Two typical bond lengths are: C-C = 1.54Å and C-H 1.08 Å.

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

2.S: Foundations of Quantum Mechanics (Summary)

Around 1900 several experimental observations were made that could not be explained, not even qualitatively, by existing physical laws. It therefore was necessary to invent (create) new concepts: quantization of energy and momentum, and a momentum-wavelength relation. In 1900 Planck proposed that electron oscillations in matter were quantized, and their energy was related by E = hν to the frequency of radiation emitted by a hot object. In 1905 Einstein proposed that electromagnetic radiation, light, also was quantized, consisting of photons, each with energy E = hν. In 1914 Bohr used this energy-frequency relationship together with the quantization of angular momentum, $M = n\hbar$, to construct a model of the hydrogen atom that was consistent with its luminescence spectrum. In 1922 Compton explained the inelastic scattering of x-rays by matter by treating the x-rays as particles with momentum p = h/λ. In 1924 de Broglie argued that particles should then have the properties of waves with a wavelength λ. This suggestion led Schrödinger to develop the general underlying theory of Quantum Wave Mechanics in 1925. The wave-like properties of electrons and the validity of the de Broglie relationship were demonstrated directly by Thomson’s and Davisson and Germer’s diffraction experiments in 1926 and 1927.

CHAPTER OVERVIEW

3: The Schrödinger Equation

The discussion in this chapter constructs the ideas that lead to the postulates of quantum mechanics, which are given at the end of the chapter. The overall picture is that quantum mechanical systems such as atoms and molecules are described by mathematical functions that are solutions of a differential equation called the Schrödinger equation. In this chapter we want to make the Schrödinger equation and other postulates of Quantum Mechanics seem plausible. We follow a train-of-thought that could resemble Schrödinger's original thinking. The discussion is not a derivation; it is a plausibility argument. In the end we accept and use the Schrödinger equation and associated concepts because they explain the properties of microscopic objects like electrons and atoms and molecules.

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

3.1: Introduction to the Schrödinger Equation

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

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

✓ Example 3.1.1

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

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

$$\frac{dC(t)}{dt} = -kC(t) \tag{3.1.1}$$

$$C(t) = C_0 e^{-kt} \tag{3.1.2}$$

✓ Example 3.1.2

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

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

$$\frac{d^2\psi(x)}{dx^2} = k\psi(x) \tag{3.1.3}$$

✓ Example 3.3

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

✓ Example 3.1.4

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

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

3.2: A Classical Wave Equation

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

$$A(x) = A_0 \sin\left(\frac{2\pi x}{\lambda}\right) \tag{3.2.1}$$

or upon time, t,

$$A(t) = A_0 \sin(2\pi\nu t) \tag{3.2.2}$$

or upon both space and time,

$$A(x,t) = A_0 \sin\left(\frac{2\pi x}{\lambda} - 2\pi\nu t\right) \tag{3.2.3}$$

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

$$A(x,t) = A_0 \sin(kx - \omega t) \tag{3.2.4}$$

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

$$\frac{\partial^2 A(x,t)}{\partial x^2} = -k^2 A_0 \sin(kx - \omega t) = -k^2 A(x,t) \tag{3.2.5}$$

$$\frac{\partial^2 A(x,t)}{\partial t^2} = -\omega^2 A_0 \sin(kx - \omega t) = -\omega^2 A(x,t) \tag{3.2.6}$$

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

$$k^{-2}\frac{\partial^2 A(x,t)}{\partial x^2} = -A(x,t) = \omega^{-2}\frac{\partial^2 A(x,t)}{\partial t^2} \tag{3.2.7}$$

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

$$\omega = \frac{2\pi\nu}{\lambda} = \nu k \tag{3.2.8}$$

and Equation 3.2.7 can be rewritten to give what is known as the classical wave equation in one dimension. This equation is very important. It is a differential equation whose solution describes all waves in one dimension that move with a constant velocity (e.g. the vibrations of strings in musical instruments) and it can be generalized to three dimensions. The classical wave equation in one-dimension is

$$\frac{\partial^2 A(x,t)}{\partial x^2} = \nu^{-2}\frac{\partial^2 A(x,t)}{\partial t^2} \tag{3.2.9}$$

Example 3.2.1

Complete the steps leading from Equation 3.2.3 to Equations 3.2.5 and 3.2.6 and then to Equation 3.2.9.

3.3: Invention of the Schrödinger Equation

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

$$\frac{\partial^2 A(x,t)}{\partial x^2} = \nu^{-2} \frac{\partial^2 A(x,t)}{\partial t^2} \tag{3.3.1}$$

Although we used a sine function to obtain the classical wave equation, functions other than the sine function can be substituted for A in Equation 3.3.1. Our goal as chemists is to seek a method for finding the wavefunctions that are appropriate for describing electrons, atoms, and molecules. In order to reach this objective, we need the appropriate wave equation.

Exercise 3.3.1

Show that the functions $e^{i(kx+\omega t)}$ and $\cos(k\,x - \omega\,t)$ also satisfy the classical wave equation (Equation 3.3.1). Note that i is a constant equal to $\sqrt{-1}$.

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

For the classical wave equation, Equation 3.3.1, separating variables is very easy because x and t do not appear together in the same term in the differential equation. In fact, they are on opposite sides of the equation. The variables already have been separated, and we only have to see what happens when we substitute a product function into this equation. It is common in Quantum Mechanics to symbolize the functions that are solutions to Schrödinger's equation as ψ, ψ, or ϕ, so we use $\Phi(x)$ as the x-function, and examine the consequences of using $\cos(\omega t)$ as one possibility for the t-function.

$$\psi(x,t) = \psi(x) cos(\omega t) \tag{3.3.2}$$

After substituting Equation 3.3.2 into the classical wave Equation 3.3.1 and differentiating, we obtain

$$\cos(\omega t) \frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{\omega^2}{\nu^2} \psi(x) \cos(\omega t) \tag{3.3.3}$$

which yields, after simplifying and rearranging,

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{\omega^2}{\nu^2} \psi(x) = 0 \tag{3.3.4}$$

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

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{p^2}{\hbar^2} \psi(x) = 0 \tag{3.3.5}$$

Exercise 3.3.2

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

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

$$E = T + V(x) = \frac{p^2}{2m} + V(x) \tag{3.3.6}$$

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

Solving Equation 3.3.6 for p^2 and substituting it into Equation 3.3.5 gives us **the Schrödinger Equation**,

$$\frac{\partial^2\psi(x)}{\partial x^2}+\frac{2m}{\hbar^2}(E-V(x))\psi(x)=0 \tag{3.3.7}$$

which usually is written in rearranged form,

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x) \tag{3.3.8}$$

Notice that the left side of Equation 3.3.8 consists of the two terms corresponding to the kinetic energy and the potential energy. When we look at the left side of Equation 3.3.8, we can deduce a method of extracting the total energy from a known wavefunction, or we can use Equation 3.3.8) to find the wavefunction. Finding wavefunctions for models of interesting chemical phenomena will be one of the tasks we will accomplish in this text.

Exercise 3.3.3

Show the steps that lead from Equations 3.3.1 and 3.3.2 to Equation 3.3.8.

More precisely, Equation 3.3.8 is the Schrödinger equation for a particle of mass m moving in one dimension (x) in a potential field specified by $V(x)$. Since this equation does not contain time, it often is called the Time-Independent Schrödinger Equation. As mentioned previously, functions like ψ(x) are called wavefunctions because they are solutions to this wave equation. The term, wave, simply denotes oscillatory behavior or properties. The significance of the wavefunction will become clear as we proceed. For now, ψ(x) is the wavefunction that accounts for or describes the wave-like properties of particles.

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

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z) \tag{3.3.9}$$

Exercise 3.3.4

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

$$V(x,y)=-\frac{(x^2+y^2)}{2}. \tag{3.3.10}$$

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

$$\nabla^2=\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) \tag{3.3.11}$$

with the del operator,

$$\nabla=\left(\vec{x}\frac{\partial}{\partial x}+\vec{y}\frac{\partial}{\partial y}+\vec{z}\frac{\partial}{\partial z}\right) \tag{3.3.12}$$

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

Exercise 3.3.5

Write the del-operator and the Laplacian operator for two dimensions and rewrite your answer to Exercise 3.3.4 in terms of the Laplacian operator.

3.4: Operators, Eigenfunctions, Eigenvalues, and Eigenstates

The Laplacian operator is called an operator because it does something to the function that follows: namely, it produces or generates the sum of the three second-derivatives of the function. Of course, this is not done automatically; you must do the work, or remember to use this operator properly in algebraic manipulations. Symbols for operators are often (although not always) denoted by a hat ^ over the symbol, unless the symbol is used exclusively for an operator, e.g. ∇ (del/nabla), or does not involve differentiation, e.g.r for position.

Recall, that we can identify the total energy operator, which is called the Hamiltonian operator, $\hat{H}$, as consisting of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{3.4.1}$$

Using this notation we write the Schrödinger Equation as

$$\hat{H}\psi(x,y,z) = E\psi(x,y,z) \tag{3.4.2}$$

The Hamiltonian

The term Hamiltonian, named after the Irish mathematician Hamilton, comes from the formulation of Classical Mechanics that is based on the total energy,

$$H = T + V \tag{3.4.3}$$

rather than Newton's second law,

$$\vec{F} = m\vec{a} \tag{3.4.4}$$

Equation 3.4.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a number, (a quantity of Joules), times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an eigenvalue equation. The function is called an eigenfunction, and the resulting numerical value is called the eigenvalue. Eigen here is the German word meaning self or own.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is the eigenvalue, and the system is said to be in an eigenstate. Equation 3.4.2 states this principle mathematically for the case of energy as the observable.

3.5: Momentum Operators

One of the tasks we must be able to do as we develop the quantum mechanical representation of a physical system is to replace the classical variables in mathematical expressions with the corresponding quantum mechanical operators. In the preceding section, operators were identified for the total energy and the kinetic energy. Potential energy operators will be introduced case by case in the following chapters. In the remaining paragraphs, we will focus on the momentum operator.

Momentum operators now can be obtained from the kinetic energy operator. Since the classical expression for the kinetic energy of a particle moving in one dimension, along the x-axis, is

$$T_x = \frac{P_x^2}{2m} \tag{3.5.1}$$

we expect that

$$\hat{T}_x = \frac{P_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{3.5.2}$$

so we can identify the operator for the square of the x-momentum as

$$\hat{P}_x^2 = -\hbar^2 \frac{\partial^2}{\partial x^2} \tag{3.5.3}$$

Since $\hat{P}_x^2$, can be interpreted to mean $\hat{P}_x \cdot \hat{P}_x$, there are two possibilities for $\hat{P}_x$, namely

$$\hat{P}_x = i\hbar \frac{\partial}{\partial x} \tag{3.5.4}$$

or

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x} \tag{3.5.5}$$

where $i = \sqrt{-1}$. The second possibility is the best choice, as explained below.

In making this choice, consider the e^{ikx} function. This function is an eigenfunction of both possible forms for the momentum operator. This fact can be used to choose which form of the momentum operator to use.

Problems

Exercise 3.5.11 Demonstrate that the function e^{ikx} is an eigenfunction of either momentum operator.

Plan: Start with $\hat{P}_x \psi(x) = P_x \psi(x)$ where $\psi(x) = e^{ikx}$.

Operate on $\psi(x) = e^{ikx}$ with $\pm i\hbar \frac{\partial}{\partial x}$ to show that $P_x = \mp \hbar k$.

Which do you prefer, $p_x = +\hbar k$ or $p_x = -\hbar k$?

If we use the momentum operator that has the - sign, we get the momentum and the wave vector pointing in the same direction, $p_x = +\hbar k$, which is the preferred result corresponding to the de Broglie relation.

The review of vectors and scalar products may help you with the following exercises.

Exercise 3.5.12 Show graphically, using a unit vector diagram, that $\vec{x} \cdot \vec{x} = 1 \text{and} \vec{x} \cdot \vec{y} = 0$.

Exercise 3.5.13 Consider a particle moving in three dimensions. The total momentum, which is a vector, is $p = \vec{x} P_x + \vec{y} P_y + \vec{z} P_z$

where $\vec{x}, \vec{y}, and \vec{z}$ are unit vectors pointing in the x, y, and z directions, respectively. Write the operators for the momentum of this particle in the x, y, and z directions, and show that the total momentum operator is $-i\hbar\nabla = -i\hbar\left(\vec{x}\frac{\partial}{\partial x} + \vec{y}\frac{\partial}{\partial y} + \vec{z}\frac{\partial}{\partial z}\right)$ is the vector operator called del(nabla). Show that the scalar product $\nabla \cdot \nabla$ produces the Laplacian operator.

Exercise 3.5.14 Following Exercise 3.5.11, show that the de Broglie relation $p = \frac{h}{\lambda}$ follows from the definition of the momentum operator and the momentum eigenfunction for a one-dimensional space.

Exercise 3.5.15 Write the wavefunction for an electron moving in the z-direction with an energy of 100 eV. The form of the wavefunction is e^{ikz}. You need to find the value for k. Obtain the electron’s momentum by operating on the wavefunction with the momentum operator.

3.6: The Time-Dependent Schrodinger Equation

The time-dependent Schrödinger equation, is used to find the time dependence of the wavefunction. This equation relates the energy to the first time derivative analogous to the classical wave equation that involved the second time derivative. This equation,

$$\hat{H}(r,t)\psi(r,t) = i\hbar\frac{\partial}{\partial t}\psi(r,t) \tag{3.6.1}$$

where r represents the spatial coordinates (x, y, z), must be used when the Hamiltonian operator depends on time, e.g. when a time dependent external field causes the potential energy to change with time.

Even if the Hamiltonian does not depend on time, we can use this equation to find the time dependence $\varphi(t)$ of the eigenfunctions of $\hat{H}(r)$. First we write the wavefunction $\Psi(r,t)$ as a product of a space function ($\psi(r)$) and a time function ($\varphi(t)$) and substitute into Equation 3.6.1.

$$\Psi(r,t) = \psi(r)\varphi(t) \tag{3.6.2}$$

We use a product function because the space and time variables are separated in Equation 3.6.1 when the Hamiltonian operator does not depend on time. Since $\psi(r)$ is an eigenfunction of $\hat{H}(r)$ with eigenvalue E, this substitution leads to Equation 3.6.5

$$\hat{H}(r)\psi(r)\varphi(t) = i\hbar\frac{\partial}{\partial t}\psi(r)\varphi(t) \tag{3.6.3}$$

$$E\psi(r)\varphi(t) = i\hbar\psi(r)\frac{\partial}{\partial t}\psi(t) \tag{3.6.4}$$

which rearranges to

$$\frac{d\varphi(t)}{\varphi(t)} = \frac{-iE}{\hbar}dt \tag{3.6.5}$$

Integration gives

$$\varphi(t) = e^{-i\omega t} \tag{3.6.6}$$

by setting the integration constant to 0 and using the definition $\omega = \frac{E}{\hbar}$. Thus, we see the time dependent Schrödinger equation contains the condition $E = \hbar\omega$ proposed by Planck and Einstein.

The eigenfunctions of a time-independent Hamiltonian therefore have an oscillatory time dependence given by a complex function, i.e. a function that involves $\sqrt{-1}$.

$$\Psi(r,t) = \psi(r)e^{-i\omega t} \tag{3.6.7}$$

When molecules are described by such an eigenfunction, they are said to be in an eigenstate of the time-independent Hamiltonian operator. We will see that all observable properties of a molecule in an eigenstate are constant or independent of time because the calculation of the properties from the eigenfunction is not affected by the time dependence of the eigenfunction. A wavefunction with this oscillatory time dependence e-iωt therefore is called a stationary-state function.

When a system is not is a stationary state, the wavefunction can be represented by a sum of eigenfunctions like those above. In this situation, the oscillatory time dependence does not cancel out in calculations, but rather accounts for the time dependence of physical observables. Examples are provided in Chapter 4, Activity 2, and Chapter 5, Activity 1.

Example 3.6.16

Complete the steps leading from Equation 3.6.1 to Equation 3.6.7.

Example 3.6.17

Show that Equation 3.6.7 is a solution to Equation 3.6.1 when the Hamiltonian operator does not depend on time and $\psi(r)$ is an eigenfunction of the Hamiltonian operator.

This might be a good time to review complex numbers

3.7: Meaning 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.

$$\psi^*(r,t)\psi(r,t) = |\psi(r,t)|^2 \tag{3.7.1}$$

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 $e\psi^*(ri)\psi(r_i)d\tau$ 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 scattering 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 dτ 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.

Example $3.7.1$

Show that the square of the modulus of $\psi(r,t) = \psi(r)e^{-i\omega-t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Example $3.7.2$

Show that the square of the modulus

Example $3.7.3$

Show that the square of the modulus

Example $3.7.4$

According to the Born interpretation, what is the physical significance of $e\psi^*(r_0)(r_0)d\tau$?

3.8: Expectation Values

An important deduction can be made if we multiply the left-hand side of the Schrödinger equation by $\psi^*(x)$, integrate over all values of x, and examine the potential energy term that arises. We can deduce that the potential energy integral provides the average value for the potential energy. Likewise we can deduce that the kinetic energy integral provides the average value for the kinetic energy. This is shown in Equation 3.8.1. If we generalize this conclusion, such integrals give the average value for any physical quantity by using the operator corresponding to that physical observable in the integral. In the equation below, the symbol $\langle H\rangle$ is used to denote the average value for the total energy.

$$\langle H\rangle = \int_{-\infty}^{\infty} \psi^*(x)\hat{H}\psi(x)dx = \underbrace{\int_{-\infty}^{\infty} \psi^*(x)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x)dx}_{\text{kinetic energy term}} + \underbrace{\int_{-\infty}^{\infty} \psi^*(x)V(x)\psi(x)dx}_{\text{Potential energy term}} \tag{3.8.1}$$

Example 3.8.1

Evaluate the two integrals in Equation 3.8.1 for the wavefunction $\psi(x)=\sin(kx)$ and the potential function $V(x)=x$.

The Hamiltonian operator consists of a kinetic energy term and a potential energy term. The kinetic energy operator involves differentiation of the wavefunction to the right of it. This step must be completed before multiplying by the complex conjugate of the wavefunction. The potential energy, however, usually depends only on position and not momentum. The potential energy operator therefore only involves the coordinates of a particle and does not involve differentiation. For this reason we do not need to use a caret over V in Equation 3.8.1. For example, the harmonic potential in one dimension is ½kx^2. (Note: here k is the force constant and not the wave vector. Unfortunately just like words, a symbol can have more than one meaning, and the meaning must be gotten from the context.) The potential energy integral then involves only products of functions, and the order of multiplication does not affect the result, e.g. 6×4 = 4×6 = 24. This property is called the commutative property. The potential energy integral therefore can be written as

$$\langle V\rangle = \int_{-\infty}^{\infty} V(x)\psi^*(x)\psi(x)dx \tag{3.8.2}$$

This integral is telling us to take the probability that the particle is in the interval dx at x, which is $\psi^*(x)\psi(x)dx$, multiply this probability by the potential energy at x, and sum (i.e. integrate) over all possible values of x. This procedure is just the way to calculate the average potential energy $\langle V\rangle$ of the particle. This integral therefore is called the average-value integral or the expectation-value integral because it gives the average result of a large number of measurements of the particle's potential energy.

When an operator involves differentiation, it does not commute with the wavefunctions, e.g.

$$\psi^*(x)\frac{\partial^2}{\partial x^2}\psi(x) \neq \psi^*(x)\psi(x)\frac{\partial^2}{\partial x^2} \neq \frac{\partial^2}{\partial x^2}(\psi^*(x)\psi(x)) \tag{3.8.3}$$

but the interpretation of the kinetic energy integral in Equation 3.8.1 is the same as for the potential energy. This integral gives the average kinetic energy of the particle.

These expectation value integrals are very important in Quantum Mechanics. They provide us with the average values of physical properties (e.g. like energy, momentum, or position) because in many cases precise values cannot, even in principle, be determined. If we know the average of some quantity, it also is important to know whether the distribution is narrow, i.e. all values are close to the average, or broad, i.e. many values differ considerably from the average. The width of a distribution is characterized by its variance.

3.9: Postulates of Quantum Mechanics

We now summarize the postulates of Quantum Mechanics that have been introduced. The application of these postulates will be illustrated in subsequent chapters.

Postulate 1

The properties of a quantum mechanical system are determined by a wavefunction Ψ(r,t) that depends upon the spatial coordinates of the system and time, r and t. For a single particle system, r is the set of coordinates of that particle $r = (x_1, y_1, z_1)$. For more than one particle, r is used to represent the complete set of coordinates $r = (x_1, y_1, z_1, x_2, y_2, z_2, \dots x_n, y_n, z_n)$. Since the state of a system is defined by its properties, ψ specifies or identifies the state and sometimes is called the state function rather than the wavefunction.

Postulate 2

The wavefunction is interpreted as probability amplitaude with the absolute square of the wavefunction, $\Psi^*(r,t)\Psi(r,t)$ interpreted at the probability density at time t. A probability density times a volume is a probability, so for one particle

$$\psi^*(x_1, y_1, z_1, t)\psi(x_1, y_1, z_1, t)dx_1dy_1dz_1 \tag{3.9.1}$$

is the probability that the particle is in the volume $dx\ dy\ dz$ located at x_l, y_l, z_l at time t.

For a many particle system, we write the volume element as $d\tau = dx_1dy_1dz_1 \dots dx_ndy_ndz_n$; and $\Psi^*(r,t)\Psi(r,t)d\tau$ is the probability that particle 1 is in the volume $dx_ldy_ldz_1$ at $x_ly_lz_l$ and particle 2 is in the volume $dx_2dy_2dz_2$ at $x_2y_2z_2$, etc.

Because of this probabilistic interpretation, the wavefunction must be *normalized*.

$$\int\limits_{all space} \psi^*(r,t)\psi(r,t)d\tau = 1 \tag{3.9.2}$$

The integral sign here represents a multi-dimensional integral involving all coordinates: $x_l \dots z_n$. For example, integration in three-dimensional space will be an integration over dV, which can be expanded as:

- $dV = dx\, dy\, dz$ in Cartesian coordinates or
- $dV = r^2 \sin\phi\, dr\, d\theta\, d\phi$ in spherical coordinates or
- $dV = r\, dr\, d\theta\, dz$ in cylindrical coordinates.

Postulate 3

For every observable property of a system there is a quantum mechanical operator. The operator for position of a particle in three dimensions is just the set of coordinates x, y, and z, which is written as a vector

$$r = (x, y, z) = x\vec{i} + y\vec{j} + z\vec{k} \tag{3.9.3}$$

The operator for a component of momentum is

$$\hat{P}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.9.4}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = -\left(\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \tag{3.9.5}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \tag{3.9.6}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2 \tag{3.9.7}$$

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

Postulate 4

The time-independent wavefunctions of a time-independent Hamiltonian are found by solving the time-independent Schrödinger equation.

$$\hat{H}(r)\psi(r) = E\psi(r) \tag{3.9.8}$$

These wavefunctions are called stationary-state functions because the properties of a system in such a state, i.e. a system described by the function $\psi(r)$, are time independent.

Postulate 5

The time evolution or time dependence of a state is found by solving the time-dependent Schrödinger equation.

$$\hat{H}(r,t)\psi(r,t) = i\hbar\frac{\partial}{\partial t}\psi(r,t) \tag{3.9.9}$$

For the case where $\hat{H}$ is independent of time, the time dependent part of the wavefunction is $e^{-i\omega t}$ where $\omega = \frac{E}{\hbar}$ or equivalently $\nu = \frac{E}{h}$, which shows that the energy-frequency relation used by Planck, Einstein, and Bohr results from the time-dependent Schrödinger equation. This oscillatory time dependence of the probability amplitude does not affect the probability density or the observable properties because in the calculation of these quantities, the imaginary part cancels in multiplication by the complex conjugate.

Postulate 6

If a system is described by the eigenfunction ψ of an operator $\hat{A}$ then the value measured for the observable property corresponding to $\hat{A}$ will always be the eigenvalue a, which can be calculated from the eigenvalue equation.

$$\hat{A}\psi = a\psi \tag{3.9.10}$$

Postulate 7

If a system is described by a wavefunction ψ, which is not an eigenfunction of an operator $\hat{A}$, then a distribution of measured values will be obtained, and the average value of the observable property is given by the expectation value integral,

$$\langle A \rangle = \frac{\int \psi^* \hat{A}\psi d\tau}{\int \psi^* \psi d\tau} \tag{3.9.11}$$

where the integration is over all coordinates involved in the problem. The average value $\langle A \rangle$, also called the expectation value, is the average of many measurements. If the wavefunction is normalized, then the normalization integral in the denominator of Equation (3-47) equals 1.

Problems

- Exercise 3.9.21 What does it mean to say a wavefunction is normalized? Why must wavefunctions be normalized?
- **Exercise 3.9.22** Rewrite Equations(3-42) and (3-43) using the definitions of $\hbar$, ∇, and ∇_2.
- **Exercise 3.9.23** Write a definition for a stationary state. What is the time dependence of the wavefunction for a stationary state?
- **Exercise 3.9.24** Show how the energy-frequency relation used by Planck, Einstein, and Bohr results from the time-dependent Schrödinger equation.
- **Exercise 3.9.25** Show how the de Broglie relation follows from the postulates of Quantum Mechanics using the definition of the momentum operator.
- **Exercise 3.9.26** What quantity in Quantum Mechanics gives you the probability density for finding a particle at some specified position in space? How do you calculate the average position of the particle and the uncertainty in the position of the

particle from the wavefunction?

3.E: The Schrödinger Equation (Exercises)

Q3.1

Prove **Euler's formula** is correct by expanding $e^{\pm i\theta}$, $\cos\theta$, and $\sin\theta$ each in terms of a **Maclaurin series** and showing that corresponding terms are identical.

Q3.2

The following table gives the results of many measurements of the length of a laser cavity. Complete the table by calculating the probability for each value. Use the probabilities that you calculated to compute the average value for the length, the average of the length squared, the variance, and the standard deviation in the measurements.

length (cm)	number of times the value was obtained	probability
100.05	4	
100.04	3	
100.03	6	
100.02	9	
100.01	8	
100.00	9	
99.99	9	
99.98	8	
99.97	2	
99.96	3	

Q3.3

Consider an electron trapped by a positively charged point defect in a one-dimensional world. The following wavefunction with α = 20/nm describes the distance x of the electron from the point defect located at x=0. Note that in 1, 2, and 3 dimensions, r = |x|, $(x^2+y^2)^{1/2}$, and $(x^2+y^2+z^2)^{1/2}$, respectively.

$$\psi(r) = Ne^{-\alpha|x|} \tag{3.E.1}$$

1. Evaluate the normalization constant N.
2. Graph the probability density for this electron.
3. Calculate the expectation value for x and |x|.
4. If the electron were in a two or three-dimensional world, such as on the surface of a crystal or in a free atom, would the average distance of the electron from the origin <r> be less, the same, or larger than the value you found for one dimension?
5. Determine whether the expectation value for r depends upon the dimensionality of the world (1, 2, or 3) in which the atom lives.

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

CHAPTER OVERVIEW

4: Electronic Spectroscopy of Cyanine Dyes

Our first chemical application of Quantum Mechanics is directed at obtaining a description of the electronic spectra of a class of molecules called cyanine dyes. We start with this set of molecules because we can use a particularly simple model, the particle-in-a-box model, to describe their electronic structure. This simple model applied to a real molecular system will further develop our “sense of Quantum Mechanics.” We also will discover rules, called selection rules, that are used to tell whether a transition between two energy levels will occur in an absorption or emission spectrum. Later we will learn about more sophisticated and general methods for describing the electronic states of atoms and molecules.

Topic hierarchy

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

4.1: Introduction

Overview of key concepts and equations for the particle in a box

Potential energy	V = 0 inside box ($0 < x < L$) V = ∞ outside box
Hamiltonian	$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$
Wavefunctions	$(\frac{2}{L})^{1/2}\sin(\frac{n\pi}{L}x)$
Quantum Numbers	n = 1, 2, 3, …
Energies	$E = n^2(\frac{h^2}{8mL^2})$
Spectroscopic Selection Rules	Δn = odd integer
Angular Momentum Properties	none

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

4.2: Cyanine Dyes

Cyanine dye molecules, which have the general structure shown in Figure 4.2.1, are planar cations. The number of carbon atoms in the chain can vary, as can the nature of the end groups containing the nitrogen atoms. The R groups in the diagram represent H, CH_3, CH_3CH_2, or many other moieties including ring structures. Since these dyes are cations, they can be paired with many anions, e.g. I^-, iodide. The position (wavelength) and strength (absorption coefficient) of the absorption band depends upon the length of the carbon chain between the nitrogen atoms but is not affected very much by the nature of the end groups beyond the nitrogen atoms.

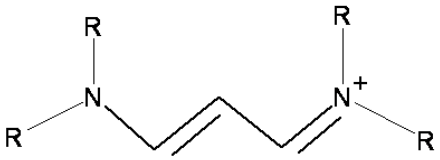

Figure 4.2.2 if $R = CH_3$).

These molecules are called dye molecules because they have very intense absorption bands in the visible region of the spectrum as shown in Figure 4.2.2. This strong absorption of light at particular wavelengths makes solutions of these molecules brightly colored. A solution of a dye shows the color of the light that is not absorbed. The strong absorption leads to many applications in technology. For example, dyes are used to color plastics, fabrics, and hair. They also can be used as filters to produce colored light and as a laser medium in medical applications.

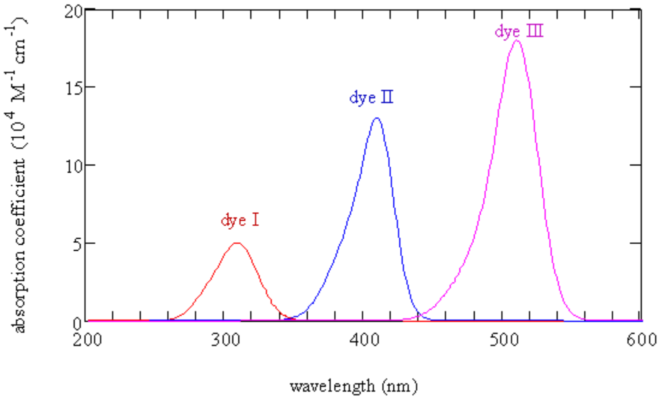

Figure 4.2.2: Absorption spectra of 3 cyanine dyes constructed from data in the paper by W.T. Simpson, J. Chem. Phys. Series A, 1948, 16, p 1124. $R = CH_3$ for each dye. Dye I has 3 carbon atoms and the absorption maximum is at 309 nm, dye II has 5 carbon atoms and the absorption maximum, λ_{max}, is at 409 nm, and dye III has 7 carbon atoms and the absorption maximum is at 512 nm.

Example 4.2.1

Draw the Lewis electron dot structure of dye I that produced the spectrum shown in Figure 4.2.2 with the maximum absorption at 309 nm. Examine the resonance structures and determine whether all the carbon-carbon bonds are identical or whether some are single bonds and some are double bonds.

Example 4.2.2

Use Figure 4.2.2 to describe what happens to the maximum absorption coefficient and the wavelength of the peak absorption as the length of a cyanine dye molecule increases.

Example 4.2.3

The decadic molar absorption coefficient for dye III at λ = 512 nm is almost 200,000 in units of $1000 cm^2/mol$. If 0.1 gram of dye III (very small) were dissolved in 10 liters of water (very large), what fraction of light at 512 nm would be absorbed in a path length of 1 mm (very small)? What is the concentration of this solution? What insight do you gain from your results? (Note: the molar mass is 179 g/mol.)

The electrons and bonds in the cyanine dyes can be classified as sigma or pi. The probability densities for the sigma electrons are large along the lines connecting the nuclei, while the probability densities for the pi electrons are large above and below the plane containing the nuclei. In molecular orbital theory, the π electrons can be described by wavefunctions composed from p_z atomic orbitals, shown in Figure $4.2.3$.

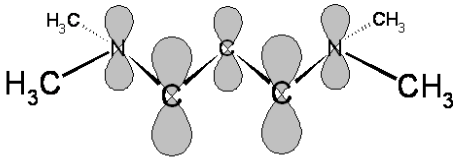

Figure $4.2.3$: Carbon and nitrogen p_z-orbitals of a cyanine dye (dye I in Figure $4.2.2$).

Example $4.2.4$

Determine the number of pi electrons in each of the three molecules described in Figure $4.2.2$.

The pi electrons in these molecules, one from each carbon atom and three from the two nitrogen atoms, are delocalized over the length of the molecule between the nitrogen atoms. When ultraviolet and visible light is absorbed by the cyanine dyes, the energy is used to cause transitions of the pi electrons from one energy level to another, as sketched in Figure $4.2.4$. The longest wavelength transition occurs from the highest-energy occupied level to the lowest-energy unoccupied level. We will use Quantum Mechanics and a simple model, called the particle-in-a-box model, to explain why the longer molecules absorb at longer wavelengths and have larger absorption coefficients. This analysis will demonstrate that Quantum Mechanics is a quantitative theory. It provides both a qualitative understanding of chemical systems and numerical values for the properties of interest. Both are important for understanding molecules and their chemistry.

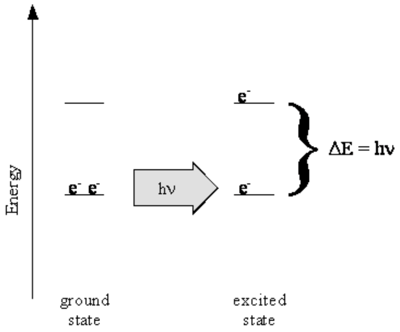

Figure $4.2.4$: The transition of an electron from a lower energy level to a higher one absorbs energy and produces the observed absorption spectrum.

You can visualize the absorption of energy and the promotion of an electron from a lower energy level to a higher one like throwing a shirt from your closet floor to a shelf. There is an important difference however. You can see the shirt on the way from the floor to the shelf. You can tell when it left the floor, and when it arrived on the shelf. Such precise information cannot be obtained for the electron. We only know the probability that the electron is in the lower level and the probability that it is in the higher level as a function of time. We do not know exactly when during this period that the electron makes the transition from one energy level to the other.

We can imagine that the potential energy experienced by the pi electron varies along the chain as shown in Figure $4.2.5$ effectively trapping the electron in the pi region of the molecule, i.e. in a one-dimensional box. At the end of the chain the potential energy rises to a large value. The particle-in-a-box model essentially consists of three approximations to the actual potential energy.

1. The chain of carbon atoms forms a one-dimensional space of some length L for the pi electrons.
2. The potential energy is constant along the chain; i.e. the oscillations are ignored.
3. The potential energy becomes infinite at some point slightly past the nitrogen atoms.

Since only changes in energy are meaningful, and an absolute zero of energy does not exist, the constant potential energy of the electron along the chain between the nitrogen atoms can be defined as zero. The particle-in-a-box potential energy also is shown in Figure $4.2.5$.

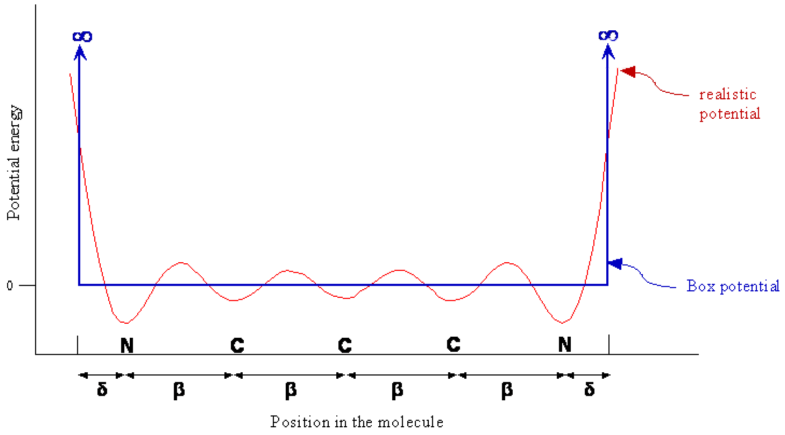

Figure 4.2.5: A diagram of the particle-in-a-box potential energy superimposed on a somewhat more realistic potential. The bond length is given by β, the overshoot by δ, and the length of the box by L = bβ + 2δ, where b is the number of bonds. For this example, dye I in Figure 4.2.1, L = 4β + 2δ.

The particle-in-a-box model allows us to relate the transition energy obtained from the position of the absorption maximum to the length of the conjugated part of the molecule, i.e. distance L between the infinite potential barriers at the ends of the molecule. From this distance for different series of dyes, we can obtain the average bond length β and the distance δ the box extends beyond a nitrogen atom for each series. If this model is reasonable, we expect the average bond lengths to be similar for each series and δ to vary from one series to another due to differences in the end groups attached to the nitrogen atoms. Some end groups might, due to their polarizability or electronegativity, allow the electrons to penetrate further past the nitrogen atoms than others. Analyzing the data in this way rather than using estimated bond lengths to predict transition energies was suggested by R.S. Moog. (J. Chem Educ. 1991, 68, 506-508.)

Example 4.2.5

In Figure 4.2.5, why does a realistic potential energy dip at each atom? Why is the dip larger for nitrogen than for carbon? Why does the potential energy increase sharply at the ends of the molecule?

4.3: The Particle-in-a-Box Model

The particle-in-a box model is used to approximate the Hamiltonian operator for the π electrons because the full Hamiltonian is quite complex. The full Hamiltonian operator for each electron consists of the kinetic energy term $\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$ and the sum of the Coulomb potential energy terms $\frac{q_1 q_2}{4\pi\epsilon_0 r_{12}}$ for the interaction of each electron with all the other electrons and with the nuclei (q is the charge on each particle and r is the distance between them). Considering these interactions, the Hamiltonian for electron i given below.

$$\hat{H}_i = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \underbrace{\sum_j \frac{e^2}{4\pi\epsilon_0 r_{i,j}}}_{\text{sum over electrons}} - \underbrace{\sum_n \frac{e^2 Z_n}{4\pi\epsilon_0 r_{i,n}}}_{\text{sum over nuclei}} \tag{4.3.1}$$

The Schrödinger equation obtained with this Hamiltonian cannot be solved analytically by anyone because of the electron-electron interaction terms. Some approximations for the potential energy must be made.

We want a model for the dye molecules that has a particularly simple potential energy function because we want to be able to solve the corresponding Schrödinger equation easily. The particle-in-a-box model has the necessary simple form. It also permits us to get directly at understanding the most interesting feature of these molecules, their absorption spectra.

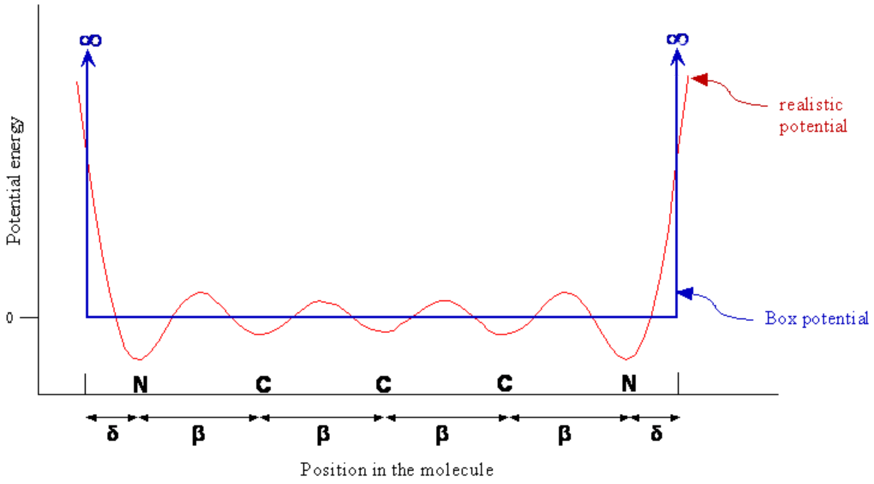

Figure 4.3.1: A diagram of the particle-in-a-box potential energy superimposed on a somewhat more realistic potential. The bond length is given by β, the overshoot by δ, and the length of the box by L = bβ + 2δ, where b is the number of bonds.

As mentioned in the previous section, we assume that the π-electron motion is restricted to left and right along the chain in one dimension. The average potential energy due to the interaction with the other electrons and with the nuclei is taken to be a constant except at the ends of the molecule. At the ends, the potential energy increases abruptly to a large value; this increase in the potential energy keeps the electrons bound within the conjugated part of the molecule. Figure $4.3.1$ shows the classical particle-in-a-box potential function and the more realistic potential energy function. We have defined the constant potential energy for the electrons within the molecule as the zero of energy. One end of the molecule is set at $x = 0$, the other at $x = L$, and the potential energy is goes to infinity at these points.

For one electron located within the box, i.e. between $x = 0$ and $x = L$, the Hamiltonian is

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} \tag{4.3.2}$$

because $V = 0$, and the (time-independent) Schrödinger equation that needs to be solved is then

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \tag{4.3.3}$$

We need to solve this differential equation to find the wavefunction and the energy. In general, differential equations have multiple solutions (solutions that are families of functions), so actually by solving this equation, we will find all the wavefunctions and all the energies for the particle-in-a-box. There are many ways of solving differential equations, and you will see some of them illustrated here and in subsequent chapters. One way is to recognize functions that might satisfy the equation. This equation says that differentiating the function twice produces the function times a constant. What kinds of functions have you seen that regenerate the function after differentiating twice? Exponential functions and sine and cosine functions come to mind.

Example 4.3.1

Use $\sin(kx)$, $\cos(kx)$, and e^{ikx} for the possible wavefunctions in Equation 4.3.3 and differentiate twice to demonstrate that each of these functions satisfies the Schrödinger equation for the particle-in-a-box.

Exercise $4.3.1$ leads you to the following three equations.

$$\frac{\hbar^2 k^2}{2m}\sin(kx) = E\sin(kx) \tag{4.3.4}$$

$$\frac{\hbar^2 k^2}{2m}\cos(kx) = E\cos(kx) \tag{4.3.5}$$

$$\frac{\hbar^2 k^2}{2m}e^{ikx} = Ee^{ikx} \tag{4.3.6}$$

For the equalities expressed by these equations to hold, E must be given by

$$E = \frac{\hbar^2 k^2}{2m} \tag{4.3.7}$$

Kinetic energy is the momentum squared divided by twice the mass $p^2/2m$, so we conclude from Equation 4.3.7 that $\hbar^2 k^2 = p^2$.

> *Solutions to differential equations that describe the real world also must satisfy conditions imposed by the physical situation. These conditions are called boundary conditions.*

For the particle-in-a-box, the particle is restricted to the region of space occupied by the conjugated portion of the molecule, between $x = 0$ and $x = L$. If we make the large potential energy at the ends of the molecule infinite, then the wavefunctions must be zero at $x = 0$ and $x = L$ because the probability of finding a particle with an infinite energy should be zero. Otherwise, the world would not have an energy resource problem. This boundary condition therefore requires that $\psi(0) = \psi(L) = 0$.

Example 4.3.2

Which of the functions $sin(kx)$, $cos(kx)$, or e^{ikx} is 0 when x = 0?

As you discovered in Exercise $4.3.2$ for these three functions, only $sin(kx) = 0$ when $x = 0$. Consequently only $sin(kx)$ is a physically acceptable solution to the Schrödinger equation.

The boundary condition described above also requires us to set $\psi(L) = 0$.

$$\psi(L) = \sin(kL) = 0 \tag{4.3.8}$$

The sine function will be zero if $kL = n\pi$ with $n = 1, 2, 3, \cdots$. In other words,

$$k = \frac{n\pi}{L} \tag{4.3.9}$$

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

Note that $n = 0$ is **not acceptable** here because this makes the wave vector zero $k = 0$, so $\sin(kx) = 0$, and thus $\psi(x)$ is zero everywhere. If the wavefunction were zero everywhere, it means that the probability of finding the electron is zero. This clearly is not acceptable because it means there is no electron.

Example 4.3.3

Show that $\sin(kx)=0$ at $x=L$ if $k=n\pi/L$ and n is an integer.

Negative Quantum Numbers

It appears that a negative integer also would work for n because

$$\sin\left(\frac{-n\pi}{L}x\right)=-\sin\left(\frac{n\pi}{L}x\right) \tag{4.3.10}$$

which also satisfies the boundary condition at $x=L$. The reason negative integers are not used is a bit subtle. Changing n to $-n$ just changes the sign (also called the phase) of the wavefunction from + to -, and does not produce a function describing a new state of the particle. Note that the probability density for the particle is the absolute square of the function, and the energies are the same for n and $-n$. Also, since the wave vector k is associated with the momentum (p = ħk), n > 0 means k > 0 corresponding to momentum in the positive direction, and $n<0$ means $k<0$ corresponding to momentum in the negative direction. By using Euler's formula one can show that the sine function incorporates both k and $-k$ since

$$\sin(kx)=\frac{1}{2i}(e^{ikx}-e^{-ikx}) \tag{4.3.11}$$

so changing n to $-n$ and k to $-k$ does not produce a function describing new state, because both momentum states already are included in the sine function.

The set of wavefunctions that satisfies both boundary conditions is given by

$$\psi_n(x)=N\sin\left(\frac{n\pi}{L}x\right)\text{with } n=1,2,3,\cdots \tag{4.3.12}$$

The normalization constant N is introduced and evaluated to satisfy the normalization requirement.

$$\int_0^L \psi^*(x)\psi(x)dx=1 \tag{4.3.13}$$

$$N^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx=1 \tag{4.3.14}$$

$$N=\sqrt{\frac{1}{\int_0^L \sin^2\frac{n\pi x}{L}dx}} \tag{4.3.15}$$

$$N=\sqrt{\frac{2}{L}} \tag{4.3.16}$$

Finally we write the wavefunction:

$$\psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \tag{4.3.17}$$

Example 4.3.4

Evaluate the integral in Equation 4.3.14 and show that $N=(2/L)^{1/2}$.

By finding the solutions to the Schrödinger equation and imposing boundary conditions, we have found a whole set of wavefunctions and corresponding energies for the particle-in-a box. The wavefunctions and energies depend upon the number n, which is called a quantum number. In fact there are an infinite number of wavefunctions and energy levels, corresponding to the infinite number of values for n $n=1\rightarrow\infty$. The wavefunctions are given by Equation 4.3.17 and the energies by Equation 4.3.7. If we substitute the expression for k from Equation 4.3.9 into Equation 4.3.7, we obtain the equation for the energies E_n

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = n^2\left(\frac{h^2}{8mL^2}\right) \tag{4.3.18}$$

Example 4.3.4

Substitute the wavefunction, Equation 4.3.17, into Equation ??? and differentiate twice to obtain the expression for the energy given by Equation 4.3.18.

From Equation 4.3.18 we see that the energy is quantized in units of $\frac{h^2}{8mL^2}$; i.e. only certain values for the energy of the particle are possible. This quantization, the dependence of the energy on integer values for n, results from the boundary conditions requiring that the wavefunction be zero at certain points. We will see in other chapters that quantization generally is produced by boundary conditions and the presence of Planck's constant in the equations.

The lowest-energy state of a system is called the ground state. Note that the ground state ($n = 1$) energy of the particle-in-a-box is not zero. This energy is called the zero-point energy.

Example 4.3.5

Here is a neat way to deduce or remember the expression for the particle-in-a-box energies. The momentum of a particle has been shown to be equal to $\hbar k$. Show that this momentum, with k constrained to be equal to $n\pi/L$, combined with the classical expression for the kinetic energy in terms of the momentum $(p^2/2m)$ produces Equation ???. Determine the units for $\frac{h^2}{8mL^2}$ from the units for h, m, and L.

Example 4.3.6

Why must the wavefunction for the particle-in-a-box be normalized? Show that φ(x) in Equation 4.3.17 is normalized.

Example 4.3.6

Use a spreadsheet program, Mathcad, or other suitable software to construct an accurate energy level diagram and to plot the wavefunctions and probability densities for a particle-in-a-box with $n = 1$ to 6. You can make your graphs universal, i.e. apply to any particle in any box, by using the quantity $(h^2/8mL^2)$ as your unit of energy and L as your unit of length. To make these universal graphs, plot n^2 on the y-axis of the energy-level diagram, and plot x/L from 0 to 1 on the x-axis of your wavefunction and probability density graphs.

Example 4.3.7

How does the energy of the electron depend on the size of the box and the quantum number n? What is the significance of these variations with respect to the spectra of cyanine dye molecules with different numbers of carbon atoms and pi electrons? Plot $E(n_2)$, $E(L_2)$, and $E(n)$ on the same figure and comment on the shape of each curve.

The quantum number serves as an index to specify the energy and wavefunction or state. Note that E_n for the particle-in-a-box varies as n^2 and as $1/L^2$, which means that as n increases the energies of the states get further apart, and as L increases the energies get closer together. How the energy varies with increasing quantum number depends on the nature of the particular system being studied; be sure to take note of the relationship for each case that is discussed in subsequent chapters.

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

4.4: Spectroscopy of the Particle-in-a-Box Model

The wavefunctions that describe electrons in atoms and molecules are called orbitals. An orbital is a wavefunction for a single electron. When we say an electron is in orbital n, we mean that it is described by a particular wavefunction Ψ_n and has energy E_n. All the properties of this electron can be calculated from Ψ_n as described in Chapter 3.

We will now use the particle-in-a-box model to explain the absorption spectra of the cyanine dyes. When an atom or molecule absorbs a photon, the atom or molecule goes from one energy level, designated by quantum number n_i, to a higher energy level, designated by n_f. We can also say that the molecule goes from one electronic state to another. This change is called a transition. Sometimes it is said that an electron goes from one orbital to another in a transition, but this statement is not general. It is valid for a particle-in-a-box, but not for real atoms and molecules, which are more complicated than the simple particle-in-a-box model.

The energy of the photon absorbed ($E_{photon} = h\nu$) matches the difference in the energy between the two states involved in the transition (ΔE_{states}). In general, the observed frequency or wavelength for a transition is calculated from the change in energy using the following equalities,

$$\Delta E_{states} = E_f - E_i = E_{photon} = h\nu = hc\bar{\nu} \tag{4.4.1}$$

Then, for the specific case of the particle-in-a-box,

$$E_{photon} = \Delta E_{states} = E_f - E_i = \frac{(n_f^2 - n_i^2)h^2}{8mL^2} \tag{4.4.2}$$

where n_f is the quantum number associated with the final state and n_i is the quantum number for the initial state. A negative value for E_{photon} means the photon is emitted as a result of the transition in states; a positive value means the photon is absorbed.

Generally the transition energy, E_{photon} or ΔE_{states}, is taken to correspond to the peak in the absorption spectrum. When high accuracy is needed for the electronic transition energy, the spectral line shape must be analyzed to account for rotational and vibrational motion as well as effects due to the solvent or environment. Contributions of rotational and vibrational motion to an absorption spectrum will be discussed in later chapters.

In a cyanine dye molecule that has three carbon atoms in the chain, there are six π-electrons. When light is absorbed, one of these electrons increases its energy by an amount $h\nu$ and jumps to a higher energy level. In order to use Equation 4.4.1, we need to know which energy levels are involved.

We assign the electrons to the lowest energy levels to create the ground-state lowest-energy electron configuration. We could put all six electrons in the $n = 1$ level, or we could put one electron in each of $n = 1$ through $n = 6$, or we could pair the electrons in $n = 1$ through $n = 3$, etc.

The Pauli Exclusion Principle says that each spatial wavefunction can describe, at most, two electrons, or in other words, that each energy level can have only two electrons assigned to it. Spatial refers to our 3-dimensional space, and a spatial wavefunction depends upon the spatial coordinates x, y, or z. We will discuss the Pauli Exclusion Principle more fully later, but you probably have encountered it in other courses.

Rather than appeal to the Pauli Exclusion Principle to assign the electrons to the energy levels, let's try an empirical approach and discover the Pauli Exclusion Principle as a result. Assign the electrons to the energy levels in different ways until you find an assignment that agrees with experiment.

When there is an even number of electrons, the lowest-energy transition is the energy difference between the highest occupied level (HOMO) and the lowest unoccupied level (LUMO). HOMO designates the highest-energy occupied molecular orbital, and LUMO designates the lowest-energy unoccupied molecular orbital. The term orbital refers to the wavefunction or energy level for one electron. All other transitions have a higher energy. For the case with all the electrons in the first energy level, the lowest-energy transition energy would be $h\nu = E_2 - E_1$. With one electron in each of the first six levels, $h\nu = E_7 - E_6$, and with the electrons paired, $h\nu = E_4 - E_3$.

Example 4.4.1

Draw energy level diagrams indicating the HOMO, the LUMO, the electrons and the lowest energy transition for each of the three cases mentioned in the preceding paragraph.

Example 4.4.2

For the three ways of assigning the 6 electrons to the energy levels in Exercise 4.4.17, calculate the peak absorption wavelength λ for a cyanine dye molecule with 3 carbon atoms in the chain using a value for L of 0.849 nm, which is obtained by estimating bond lengths. Which wavelength agrees most closely with the experimental value of 309 nm for this molecule?

It turns out that the assignment that gives a reasonable wavelength for the absorption of a cyanine dye with 6 π electrons is $h\nu = E_4 - E_3$ as you concluded from Exercise 4.4.2. In this way we have “discovered” the Pauli Exclusion Principle, electrons should be paired in the same energy level whenever possible, and we accept it for now because it agrees with the experimental observations of the cyanine dye spectra.

In molecules with an odd number of electrons, it is possible to have transitions between the doubly occupied molecular orbitals and the singly occupied molecular orbital as well as from the singly occupied orbital to an unoccupied orbital.

4.5: The Transition Dipole Moment and Spectroscopic Selection Rules

Once we know what energy a given transition would have, we can ask, “Which transitions between energy levels or states are possible?” In answering this question, we also will learn why the longer cyanine dye molecules have stronger absorptions, or larger absorption coefficients.

Clearly the transitions cannot violate the Pauli Exclusion Principle; that is, they cannot produce an electron configuration with three electrons in the same orbital. Besides the Pauli Exclusion Principle, there are additional restrictions that result from the nature of the interaction between electromagnetic radiation and matter. These restrictions are summarized by spectroscopic selection rules. These rules tell whether or not a transition from one state to another state is possible.

To obtain these selection rules, we consider light as consisting of perpendicular oscillating electric and magnetic fields. The magnetic field interacts with magnetic moments and causes transitions seen in electron spin resonance and nuclear magnetic resonance spectroscopies. The oscillating electric field interacts with electrical charges, i.e. the positive nuclei and negative electrons that comprise an atom or molecule, and cause the transitions seen in UV-Visible, atomic absorption, and fluorescence spectroscopies.

The energy of interaction, E, between a system of charged particles and an electric field ϵ is given by the scalar product of the electric field and the dipole moment, μ, for the system. Both of these quantities are vectors.

$$E = -\mu \cdot \epsilon \tag{4.5.1}$$

The dipole moment is defined as the summation of the product of the charge q_j times the position vector r_j for all charged particles j.

$$\mu = \sum_j q_j r_j \tag{4.5.2}$$

Example 4.5.1

Calculate the dipole moment of HCl from the following information. The position vectors below use Cartesian coordinates (x, y, z), and the units are pm. What fraction of an electronic charge has been transferred from the chlorine atom to the hydrogen atom in this molecule? $r_H = (124.0, 0, 0)$, $r_{Cl} = (-3.5, 0, 0)$, $q_H = 2.70x10^{-20}C$, $q_{Cl} = -2.70x10^{-20}C$.

Example 4.5.2

Sketch a diagram for Exercise $4.5.1$ showing the coordinate system, the HCl molecule and the dipole moment.

To calculate an expectation value for this interaction energy, we need to evaluate the expectation value integral.

$$\langle E \rangle = \int \psi_n^* (-\hat{\mu} \cdot \hat{\epsilon}) \psi_n d\tau \tag{4.5.3}$$

The $\int d\tau$ symbol simply means integrate over all coordinates. The operators $\hat{\mu}$ and $\hat{\epsilon}$ are vectors and are the same as the classical quantities, μ and ϵ.

Usually the wavelength of light used in electronic spectroscopy is very long compared to the length of a molecule. For example, the wavelength of green light is 550 nm, which is much larger than molecules, which are closer to 1 nm in size. The magnitude of electric field then is essentially constant over the length of the molecule, and ϵ can be removed from the integration since it is constant wherever ψ is not zero. In other words, ψ is finite only over the volume of the molecule, and the electric field is constant over the volume of the molecule. What remains for the integral is the expectation value for the permanent dipole moment of the molecule in state n, namely,

$$\langle \mu \rangle = \int \psi_n^* \hat{\mu} \psi_n d\tau \tag{4.5.4}$$

so

$$E = -\langle \mu \rangle \cdot \epsilon \tag{4.5.5}$$

Example 4.5.3

Verify that the vectors in the scalar product in Equation 4.5.5 commute by expanding $\mu \cdot \epsilon$ and $\epsilon \cdot \mu$. Use particle-in-a-box wave functions with HCl charges and coordinates.

Equation 4.5.5 shows that the strength or energy of the interaction between a charge distribution and an electric field depends on the dipole moment of the charge distribution.

To obtain the strength of the interaction that causes transitions between states, the transition dipole moment is used rather than the dipole moment. The transition dipole moment integral is very similar to the dipole moment integral in Equation 4.5.4 except the two wavefunctions are different, one for each of the states involved in the transition. Two different states are involved in the integral because the transition dipole moment integral has to do with the magnitude of the interaction with the electric field that causes a transition between the two states. For a transition where the state changes from ψi to ψf, the transition dipole moment integral is

$$\langle \mu \rangle_T = \int \psi_f^* \hat{\mu} \psi_i d\tau = \mu_T \tag{4.5.6}$$

Just like the probability density is given by the absolute square of the wavefunction, the probability for a transition as measured by the absorption coefficient is proportional to the absolute square $\mu_T^* \mu_T$ of the transition dipole moment, which is calculated using Equation 4.5.6. Since taking the absolute square always produces a positive quantity, it does not matter whether the transition moment itself is positive, negative, or imaginary. The transition dipole moment integral and its relationship to the absorption coefficient and transition probability can be derived from the time-dependent Schrödinger equation. Here we only want to introduce the concept of the transition dipole moment and use it to obtain selection rules and relative transition probabilities for the particle-in-a-box. Later it will be applied to other systems that we will be considering.

If $\mu_T = 0$ then the interaction energy is zero and no transition occurs or is possible between states characterized by ψ_i and ψ_f. Such a transition is said to be forbidden, or more precisely, electric-dipole forbidden. In fact, the electric-dipole electric-field interaction is only the leading term in a multipole expansion of the interaction energy, but the higher order terms in this expansion usually are not significant. If μ_T is large, then the probability for a transition and the absorption coefficient are large.

It is very useful to be able to tell whether a transition is possible, $\mu_T \neq 0$, or not possible, $\mu_T = 0$, without having to evaluate integrals. Properties of the wavefunctions such as symmetry or angular momentum can be used to determine the conditions that must exist for the transition dipole moment to be finite, i.e. not zero. Statements called spectroscopic selection rules summarize these conditions. Selection rules do not tell us how probable or intense a transition is. They only tell us whether a transition is possible or not possible.

For the particle-in-a-box model, as applied to dye molecules and other appropriate molecular systems, we need to consider the transition moment integral for one electron. According to Equation 4.5.2, the dipole moment operator for an electron in one dimension is –ex since the charge is –e and the electron is located at x.

$$\mu_T = -e \int_0^L \psi_f^*(x) x \psi_i(x) dx \tag{4.5.7}$$

This is the integral that must be evaluated for various particle-in-a-box wavefunctions to see which transitions are allowed (i.e. $\mu_T \neq 0$) and forbidden ($\mu_T = 0$) and to determine the relative strengths of the allowed transitions.

4.6: Selection Rules for the Particle-in-a-Box

This section explores the use of symmetry to determine selection rules. Here we derive an analytical expression for the transition dipole moment integral for the particle-in-a-box model. The result that the magnitude of this integral increases as the length of the box increases explains why the absorption coefficients of the longer cyanine dye molecules are larger. We use the transition moment integral and the trigonometric forms of the particle-in-a-box wavefunctions to get Equation 4.6.2 for an electron making a transition from orbital i to orbital f.

$$\mu_T = \frac{-2e}{L} \int_0^L \sin\left(\frac{f\pi x}{L}\right) x \sin\left(\frac{i\pi x}{L}\right) dx \tag{4.6.1}$$

$$= \frac{-2e}{L} \int_0^L x \sin\left(\frac{f\pi x}{L}\right) \sin\left(\frac{i\pi x}{L}\right) dx \tag{4.6.2}$$

Exercise 4.6.1

Why is there a factor $2/L$ in Equation 4.6.2? What are the units associated with the dipole moment and the transition dipole moment?

Simplify the integral in Equation 4.6.2 by substituting the product-to-sum trigonometric identity

$$\sin\psi \sin\theta = \frac{1}{2}[\cos(\psi-\theta) - \cos(\psi+\theta)] \tag{4.6.3}$$

and also redefine the sum and difference terms:

$$\Delta n = f - i$$

and

$$n_T = f + i$$

So Equation 4.6.2

$$\mu_T = \frac{-e}{L} \int_0^L x \left[\cos\left(\frac{\Delta n \pi x}{L}\right) - \cos\left(\frac{n_T \pi x}{L}\right)\right] dx \tag{4.6.4}$$

$$= \frac{-e}{L} \left[\int_0^L x \cos\left(\frac{\Delta n \pi x}{L}\right) dx - \int_0^L x \cos\left(\frac{n_T \pi x}{L}\right) dx\right] \tag{4.6.5}$$

These two definite integrals can be directly evaluated using this relationship

$$\int_0^L x\cos(ax)dx = \left[\frac{1}{a^2}\cos(ax) + \frac{x}{a}\sin(ax)\right]_0^L \tag{4.6.6}$$

where a is any nonzero constant. Using Equation 4.6.6 in Equation 4.6.5 produces

$$T = \frac{-e}{L}\left(\frac{L}{\pi}\right)^2 \left[\frac{1}{\Delta n^2}(\cos(\Delta n\pi) - 1) - \frac{1}{n_T^2}(\cos(n_T\pi) - 1) + \frac{1}{\Delta n}\sin(\Delta n\pi) - \frac{1}{n_T}\sin(n_T\pi)\right] \tag{4.6.7}$$

Exercise 4.6.2

Show that if Δn is an even integer, then n_T must be an even integer and $\mu_T = 0$.

Exercise 4.6.3

Show that if i and f are both even or both odd integers then Δn is an even integer and $\mu_T = 0$.

Exercise 4.6.4

Show that if Δn is an odd integer, then n_T must be an odd integer and μ_T is given by Equation 4.6.8.

$$\mu_T = \frac{-2eL}{\pi^2}\left(\frac{1}{n_T^2} - \frac{1}{\Delta n^2}\right) = \frac{8eL}{\pi^2}\left(\frac{f_i}{\left(f^2 - i^2\right)^2}\right) \tag{4.6.8}$$

Exercise 4.6.5

Show that the two expressions for the transition moment in Equation 4.6.8 are in fact equivalent.

Example 4.6.1

What is the value of the transition moment integral for transitions 1 → 3 and 2 → 4?

Solution

For these two transitions, either n and f are both odd or they are both even integers. In either case, Δn and n_T are even integers. The cosine of an even integer multiple of π is +1 so the cosine terms in Equation 4.6.7 become (1-1) = 0. The sine terms are zero because the sine of an even integer multiple of π is zero. Therefore, $\mu_T = 0$ for these transitions and they are forbidden. The same reasoning applies to any transitions that have both i and f as even or as odd integers.

Exercise 4.6.1

What is the value of the transition moment for the n = 8 to f = 10 transition?

Example 4.6.2

What is the value of the transition moment integral for transitions 1 → 2 and 2 → 3?

Solution

For these two transitions Δn = 1 and nT = 3 and 5, respectively, all odd integers. The cosine of an odd-integer multiple of π is -1 so the cosine terms in Equation 4.6.7 become (-1-1) = -2. The sine terms in Equation 4.6.7 are zero because the sine of an odd integer multiple of π is zero. Therefore, μ_T has some finite value given by Equation 4.6.8. The same reasoning is used to evaluate the transition moment integral for any transitions that have Δn and nT as odd integers, e.g. 2 → 7 and 3 → 8. In these cases Δn = 5 and nT = 9 and 11, respectively. Again the transition moment integral for each of these transitions is finite.

Exercise 4.6.2

Explain why one of the following transitions occurs with excitation by light and the other does not: $i = 1$ to $f = 7$ and $i = 3$ to $f = 6$.

From Examples 4.6.1 and 4.6.2, we can formulate the selection rules for the particle-in-a-box model: Transitions are forbidden if $\Delta n = f - i$ is an even integer. Transitions are allowed if $\Delta n = f - i$ is an odd integer. In the next section we will see that these selection rules can be understood in terms of the symmetry of the wavefunctions.

Through the evaluation of the transition moment integral, we can understand why the spectra of cyanine dyes are very simple. The spectrum for each dye consists only of a single peak because other transitions have very much smaller transition dipole moments. We also see that the longer molecules have the larger absorption coefficients because the transition dipole moment increases with the length of the molecule.

Exercise 4.6.6

The lowest energy transition is from the HOMO to the LUMO, which were defined previously. Compute the value of the transition moment integral for the HOMO to LUMO transition $E_3 \rightarrow E_4$ for a cyanine dye with 3 carbon atoms in the conjugated chain. What is the next lowest energy transition for a particle-in-a-box? Compute the value of the transition moment integral for the next lowest energy transition that is allowed for this dye. What are the quantum numbers for the energy levels associated with this transition? How does the probability of this transition compare in magnitude with that for 3→4?

4.7: Using Symmetry to Identify Integrals that are Zero

It generally requires much work and time to evaluate integrals analytically or even numerically on a computer. Our time, computer time, and work can be saved if we can identify by inspection when integrals are zero. The determination of when integrals are zero leads to spectroscopic selection rules and provides a better understanding of them. Here we use graphs to examine properties of the wavefunctions for a particle-in-a-box to determine when the transition dipole moment integral is zero and thereby obtain the spectroscopic selection rules for this system. These considerations are completely general and can be applied to any integrals. We essentially determine whether integrals are zero or not by drawing pictures and thinking. What could be easier?

Consider the case for a transition from orbital $n = 1$ to orbital $n = 2$ of a molecule described by the particle-in-a-box model. These two wavefunctions are shown in Figure 4.7.1 as $f1$ and $f2$, respectively. For the curves shown on the left in the figure, we defined the box to have unit length, L = 1, and infinite potential barriers at $x = 0$ and $x = L$ as we did previously, so the particle is trapped between 0 and L. For the curves shown on the right, $g1$ and $g2$, we put the origin of the coordinate system halfway between the potential barriers, i.e. at the center of the box. The barriers have not moved and the particle has not changed, but our description of the position of the barriers and the particle has changed. We now say the barriers are located at $x = -L/2$ and $x = +L/2$, and the particle is trapped between $-L/2$ and $+L/2$.

Clearly the wavefunctions in Figure 4.7.1 look the same for these two choices of coordinate systems. The appearance of the wavefunctions doesn't depend on the coordinate system we have chosen or on our labels since the wavefunctions tell us about the probability of finding the particle. This probability does not change when we change the coordinate system or relabel the axis. The names of these functions do change, however. In Figure 4.7.1a, they both are sine functions. In Figure 4.7.1b, one is a cosine function and the other is a sine function multiplied by -1.

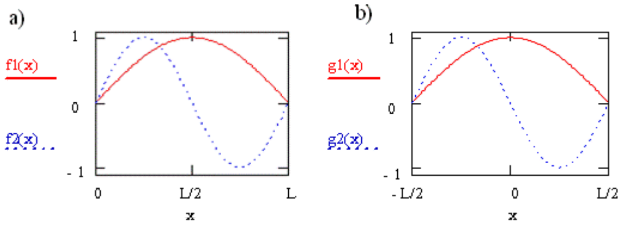

Figure 4.7.1: Wavefunctions for quantum state n=1 and quantum state n=2 in the two different coordinate systems.

Exercise 4.7.1

Sketch $(f_1(x))^2$ and $(g_1(x))^2$. What do you observe? Sketch $(f_2(x))^2$ and $(g_2(x))^2$. What do you observe? What is the significance with respect to the probability given by both f(x) and g(x)?

We moved the origin of the coordinate system to the center of the box to take advantage of the symmetry properties of these functions. By symmetry, we mean the correspondence in form on either side of a dividing point, line, or plane. As we shall see, the analysis of the symmetry is straightforward if the origin of the coordinate systems coincides with the dividing point, line, or plane. Since the right and left halves of the box or molecule represented by the box are the same, the square of the wavefunction for x > 0 must be the same as the square of the wavefunction for x < 0. Since the box is symmetrical, the probability density, Ψ2, for the particle distribution also must be symmetrical because there is no reason for the particle to be located preferentially on one side or the other.

The transition moment integral for the particle-in-a-box involves three functions (ψ_f, ψ_i, and x) that are multiplied together at each point x to form the integrand. These three functions for i = 1 and f = 2 are plotted on the left in Figure 4.7.2. The integrand is the product of these three functions and is shown on the right in the figure. The integral is the area between the integrand and the zero on the y-axis. Clearly this area and thus also the value of the integral is not zero. The integral is negative because ψ_2 is negative for x > 0 and x is negative for x < 0. Since $\mu_T \neq 0$, the transition from ψ_1 to ψ_2 is allowed. As we previously mentioned in this chapter, and will see again later, the absorption coefficient is proportional to the absolute square of μ_T so it is acceptable for the transition moment integral to be negative. It even could involve $\sqrt{-1}$. Taking the absolute square makes both negative and imaginary quantities positive.

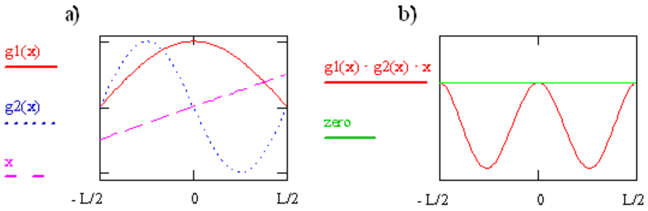

Figure 4.7.2: Functions (a) and integrand (b) of the transition moment integral for the transition from quantum state n = 1 to quantum state n = 2.

Exercise 4.7.2

Write the expression or function for the integrand that is plotted on the right side of Figure 4.7.7 in terms of x, sine, and cosine functions. Use your function to explain why the integrand is 0 at x = 0 and has minima at x = + 0.25L and - 0.25L. Sketch the corresponding probability function.Where are the peaks in the probability function?

Now consider the transition moment integral for quantum state n = 1 to quantum state n = 3. In Figure 4.7.3, the wavefunctions and the x operator are shown on the left side, and the integrand is shown on the right side. For this case we see that the integrand for x < 0 is the negative of the integrand for x > 0. This difference in sign means the net positive area for x > 0 is canceled by the net negative area for x < 0, so the total area and the transition moment integral are zero. We therefore conclude that the transition from n = 1 to n = 3 is forbidden.

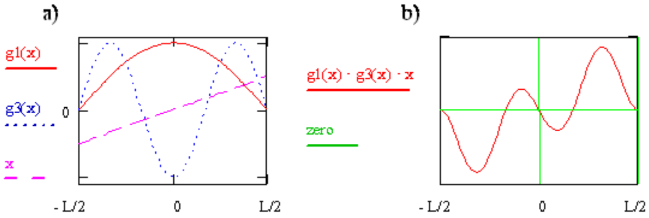

Figure 4.7.3: Functions (a) and integrand (b) of the transition moment integral for the transition from quantum state n = 1 to quantum state n = 3.

Exercise 4.7.3

Write the expression or function for the integrand that is plotted on the right side of Figure 4.7.8 in terms of x and cosine functions. Use your function to explain why the integrand is zero at x = 0, why is it negative just above x = 0, and why as x goes from 0 to –0.5, the integrand first is positive and then negative.

In spectroscopy some special terms are used to describe the symmetry properties of wavefunctions. The terms symmetric, **gerade**, and even describe functions like $f(x)=x^2$ and $\psi_1(x)$ for the particle-in-a-box that have the property $f(x)=f(-x)$, i.e. the function has the same values for x > 0 and for x < 0. The terms antisymmetric, **ungerade**, and odd describe functions like $f(x)=x$ and $\psi_2(x)$ for the particle-in-a-box that have the property $f(x)=-f(-x)$, i.e. the function for $x>0$ is has values that are opposite in sign compared to the function for x < 0. Gerade and ungerade are German words meaning even and odd and are abbreviated as g and u. Note that antisymmetric does not mean non-symmetric.

If an integrand is u, then the integral is zero! It is zero because the contribution from $x>0$ is cancelled by the contribution from $x<0$, as shown by the example in Figure 4.7.8. An integrand will be u if the product of the functions comprising it is u. The following rules make it possible to quickly identify whether a product of two functions is u.

$$g\cdot g=g, u\cdot u=g, g\cdot u=u \tag{4.7.1}$$

These rules are the same as those for multiplying +1 for g and -1 for u. The validity of these rules can be seen by examining Figures 4.7.1 and 4.7.1. If an integrand consists of more than two functions, the rules are applied to pairs of functions to obtain the symmetry of their product, and then applied to pairs of the product functions, and so forth, until one obtains the symmetry of the integrand.

Exercise 4.7.4

Use Mathcad or some other software to draw graphs of $x^2, -x^2, x^3, and - x^3$ as a function of x. Which of these functions are g and which are u? Is the product function $x^2 \cdot x^3 g$ or u? How about $x^2 \cdot -x^2 \cdot x^3 \text{and} x^2 \cdot x^3 \cdot -x^3$?

Exercise 4.7.5

Label each function in Figures Figure $4.7.2$ and Figure $4.7.3$ as g or u. Also label the integrands.

Exercise 4.7.6

Use symmetry arguments to determine which of the following transitions between quantum states are allowed for the particle-in-a-box:

a. $n = 2$ to $n = 3$
b. $n = 2$ to $n = 4$.

Symmetry properties of functions allow us to identify when the transition moment integral and other integrals are zero. This symmetry-based approach to integration can be generalized and becomes even more powerful when concepts taken from mathematical Group Theory are used. With the tools of Group Theory, one can examine symmetry properties in three-dimensional space for complicated molecular structures. A group-theoretical analysis helps understand features in molecular spectra, predict products of chemical reactions, and simplify theoretical calculations of molecular structures and properties.

4.8: Other Properties of the Particle-in-a-Box

Now that we have mathematical expressions for the wavefunctions and energies for the particle-in-a-box, we can answer a number of interesting questions. The answers to these questions use quantum mechanics to predict some important and general properties for electrons, atoms, molecules, gases, liquids, and solids.

What is the lowest energy for an electron? The lowest energy level is E_1, and it is important to recognize that this lowest energy is not zero. This finite (meaning neither zero nor infinite) energy is called the zero-point energy, and the motion associated with this energy is called the zero-point motion. Any system that is restricted to some region of space is said to be bound. The zero-point energy and motion are manifestations of the wave properties and the Heisenberg Uncertainty Principle, and are general properties of bound quantum mechanical systems. The position and momentum of the particle cannot be determined exactly. According to the Heisenberg Uncertainty Principle, the product of the uncertainties, i.e. standard deviations in these quantities, must be greater than or equal to ħ/2. If the energy were zero, then the momentum would be exactly zero, which would violate the Heisenberg Uncertainty Principle unless the uncertainty in position were infinite. The system then would not be localized in space to any extent at all, which we will find to be true for the case of a free particle, which is not bound. The uncertainty in the position of a bound system is not infinite, so the uncertainty in the momentum cannot be zero, as it would be if the energy were zero.

Where is the electron?

Exercise 4.8.1

Use your solution to Exercise $4.8.15$ to write a few sentences answering this question about the location of the electron. What insight do you gain from the graphs you made for the probability distribution at very large n compared to n = 1?

Exercise 4.8.2

Use the general form of the particle-in-a-box wavefunction sin(kx) for any n to find the mathematical expression for the position expectation value $\langle x\rangle$ for a box of length L. How does $\langle x\rangle$ depend on n? Evaluate the integral.

Exercise 4.8.3

Calculate the probability of finding an electron at L/2 in an interval ranging from $\frac{L}{2}-\frac{L}{200}$ to $\frac{L}{2}+\frac{L}{200}$ for n = 1 and n = 2. Since the length of the interval, L/100, is small compared to L, you can get an approximate answer without integrating.

What is the momentum of an electron in the box?

The particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator.

Exercise 4.8.4

Show that the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator.

Example 4.8.1

Even though the wavefunctions are not momentum eigenfunctions, we can calculate the expectation value for the momentum. Show that the expectation or average value for the momentum of an electron in the box is zero in every state.

Solution

First write the expectation value integral for the momentum. Then insert the expression for the wavefunction and evaluate the integral as shown here.

$$\langle P\rangle=\int_0^L \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)dx \tag{4.8.1}$$

$$= \int_0^L \left(\frac{2}{L}\right)^{1/2} \sin(\frac{n\pi x}{L}) \left(-i\hbar\frac{d}{dx}\right) \left(\frac{2}{L}\right)^{1/2} \sin(\frac{n\pi x}{L}) dx \tag{4.8.2}$$

$$= -i\hbar \left(\frac{2}{L}\right) \int_0^L \sin(\frac{n\pi x}{L}) \left(\frac{d}{dx}\right) \sin(\frac{n\pi x}{L}) dx \tag{4.8.3}$$

$$= -i\hbar \left(\frac{2}{L}\right) \left(\frac{n\pi}{L}\right) \int_0^L \sin(\frac{n\pi x}{L}) \cos(\frac{n\pi x}{L}) dx \tag{4.8.4}$$

$$= 0 \tag{4.8.5}$$

It may seem that the electron does not have any momentum, which is not correct because we know the energy is never zero. In fact, the energy that we obtained for the particle-in-a-box is entirely kinetic energy because we set the potential energy at 0.

Since the kinetic energy is the momentum squared divided by twice the mass, it is easy to understand how the average momentum can be zero and the kinetic energy finite. It must be equally likely for the particle-in-a-box to have a momentum -p as +p. The average of +p and –p is zero, yet p^2 and the average of p^2 are not zero.

The information that the particle is equally likely to have a momentum of +p or –p is contained in the wavefunction. The sine function is a representation of the two momentum eigenfunctions e^{ikx} and e^{-ikx} as shown by Exercise 4.8.5.

Exercise 4.8.5

Write the particle-in-a-box wavefunction as a normalized linear combination of the momentum eigenfunctions e^{ikx} and e^{-ikx} by using Euler’s formula. Show that the momentum eigenvalues for these two functions are p = +ħk and -ħk.

The interpretation of these results is physically interesting. The exponential wavefunctions in the linear combination for the sine function represent the two opposite directions in which the electron can move. One exponential term represents movement to the left and the other term represents movement to the right. The electrons are moving, they have kinetic energy and momentum, yet the average momentum is zero.

> *Does the fact that the average momentum of an electron is zero and the average position is L/2 violate the Heisenberg Uncertainty Principle? No, of course not, because the Heisenberg Uncertainty Principle pertains to the uncertainty in the momentum and in the position, not to the average values.*

Quantitative values for these uncertainties can be obtained to compare with the limit set by the Heisenberg Uncertainty Principle for the product of the uncertainties in the momentum and position. First, we need a quantitative definition of uncertainty. Here, just like in experimental measurements, a good definition of uncertainty is the standard deviation or the root mean square deviation from the average. It can be shown by working Problem 6 at the end of this chapter that the standard deviation in the position of the particle-in-a-box is given by

$$\sigma_x = \frac{L}{2\pi n}\sqrt{\frac{\pi^2}{3}n^2 - 2} \tag{4.8.6}$$

and the standard deviation in the momentum by

$$\sigma_p = \frac{n\pi\hbar}{L} \tag{4.8.7}$$

Even for n = 1, the lowest value for n, σx is finite and proportional to L. As L increases the uncertainty in position of the electron increases. On the other hand, as L increases, σp decreases, but the product is never zero; and the uncertainty principle holds.

Exercise 4.8.6

Evaluate the product σx σp for n = 1 and for general n. Is the product greater than ħ/2 for all values of n and L as required by the Heisenberg Uncertainty Principle?

Are the eigenfunctions of the particle-in-a-box Hamiltonian orthogonal?

Two functions Ψ_A and Ψ_B are orthogonal if

$$\int_{all space} \psi_A^* \psi_B d\tau = 0 \tag{4.8.8}$$

In general, eigenfunctions of a quantum mechanical operator with different eigenvalues are orthogonal.

Exercise 4.8.7

Evaluate the integral $\int \psi_1^* \psi_3 dx$ and as many other pairs of particle-in-a-box eigenfunctions as you wish (use symmetry arguments whenever possible) and explain what the results say about orthogonality of the functions.

Exercise 4.8.8

What happens to the energy level spacing for a particle-in-a-box when mL^2 becomes much larger than h^2? What does this result imply about the relevance of quantization of energy to baseballs in a box between the pitching mound and home plate? What implications does quantum mechanics have for the game of baseball in a world where h is so large that baseballs exhibit quantum effects?

- Is quantization important for macroscopic objects?
- How can one determine the relative energies of wavefunctions by examination?

The first derivative of a function is the rate of change of the function, and the second derivative is the rate of change in the rate of change, also known as the curvature. A function with a large second derivative is changing very rapidly. Since the second derivative of the wavefunction occurs in the Hamiltonian operator that is used to calculate the energy by using the Schrödinger equation, a wavefunction that has sharper curvatures than another, i.e. larger second derivatives, should correspond to a state having a higher energy. A wavefunction with more nodes than another over the same region of space must have sharper curvatures and larger second derivatives, and therefore should correspond to a higher energy state.

Exercise 4.8.9

Identify a relationship between the number of nodes in a wavefunction and its energy by examining the graphs you made in Exercise 4.8.15. A node is the point where the amplitude passes through zero. What does the presence of many nodes mean about the shape of the wavefunction?

4.9: Properties of Quantum Mechanical Systems

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

Hermitian Theorem

Since the eigenvalues of a quantum mechanical operator correspond to measurable quantities, the eigenvalues must be real, and consequently a quantum mechanical operator must be Hermitian.

Proof

We start with the premises that ψ and φ are functions, $\int d\tau$ represents integration over all coordinates, and the operator Â is Hermitian by definition if

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{4.9.1}$$

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

$$\hat{A}\psi = a\psi \tag{4.9.2}$$

$$\hat{A}^* \psi^* = a^* \psi^* = a\psi^* \tag{4.9.3}$$

Note that a* = a because the eigenvalue is real. Multiply Equations 4.9.2 and 4.9.3 from the left by ψ* and ψ, respectively, and integrate over all the coordinates. Note that ψ is normalized. The results are

$$\int \psi^* \hat{A} \psi d\tau = a \int \psi^* \psi d\tau = a \tag{4.9.4}$$

$$\int \psi \hat{A}^* \psi^* d\tau = a \int \psi \psi^* d\tau = a \tag{4.9.5}$$

Since both integrals equal a, they must be equivalent.

$$\int \psi^* \hat{A} \psi d\tau = \int \psi \hat{A}^* \psi^* d\tau \tag{4.9.6}$$

The operator acting on the function, $\hat{A}^* \int \psi^* \hat{A} \psi d\tau = \int \psi \hat{A}^* \psi^* d\tau_*$, produces a new function. Since functions commute, Equation 4.9.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{4.9.7}$$

This equality means that Â is Hermitian.

Orthogonality Theorem

Eigenfunctions of a Hermitian operator are orthogonal if they have different eigenvalues. Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.

Proof

ψ and φ are two eigenfunctions of the operator Â with real eigenvalues a_1 and a_2, respectively. Since the eigenvalues are real, $a_1^* = a_1$ and $a_2^* = a_2$.

$$\hat{A}\psi = a_1 \psi \tag{4.9.8}$$

$$\hat{A}^*\psi^* = a_2\psi^* \tag{4.9.9}$$

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

$$\int \psi^*\hat{A}\psi d\tau = a_1\int \psi^*\psi d\tau \tag{4.9.10}$$

$$\int \psi\hat{A}^*\psi^* d\tau = a_2\int \psi\psi^* d\tau \tag{4.9.11}$$

Subtract the two equations in (4-45)to obtain

$$\int \psi^*\hat{A}\psi d\tau - \int \psi\hat{A}^*\psi^* d\tau = (a_1 - a_2)\int \psi^*\psi d\tau \tag{4.9.12}$$

The left-hand side of (4-46) is zero because Â is Hermitian yielding

$$0 = (a_1 - a_2)\int \psi^*\psi d\tau \tag{4.9.13}$$

If a1 and a2 in (4-47) are not equal, then the integral must be zero. This result proves that nondegenerate eigenfunctions of the same operator are orthogonal.

Exercise 4.9.44

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

Schmidt Orthogonalization Theorem

If the eigenvalues of two eigenfunctions are the same, then the functions are said to be degenerate, and linear combinations of the degenerate functions can be formed that will be orthogonal to each other. Since the two eigenfunctions have the same eigenvalues, the linear combination also will be an eigenfunction with the same eigenvalue. Degenerate eigenfunctions are not automatically orthogonal but can be made so mathematically. The proof of this theorem shows us one way to produce orthogonal degenerate functions.

Proof

If ψ and φ are degenerate but not orthogonal, define $\Phi = \varphi - S\psi$ where S is the overlap integral $\int \psi^*\psi d\tau$, then ψ and Φ will be orthogonal.

$$\int \psi^*\phi d\tau = \int \psi^*(\varphi - S\psi)d\tau = \int \psi^*\psi d\tau - S\int \psi^*\psi d\tau \tag{4.9.14}$$

$$= S - S = 0 \tag{4.9.15}$$

Exercise 4.9.45

Find N that normalizes Φ if $\Phi = N(\varphi - S\psi)$ where ψ and φ are normalized and S is their overlap integral.

Commuting Operator Theorem

If two operators commute, then they can have the same set of eigenfunctions. By definition, two operators $\hat{A}$ and $\hat{B}$commute if the effect of applying $\hat{A}$ then $\hat{B}$ is the same as applying $\hat{B}$ then $\hat{A}$, i.e. $\hat{A}\hat{B} = \hat{B}\hat{A}$. For example, the operations brushing-your-teeth and combing-your-hair commute, while the operations getting-dressed and taking-a-shower do not. This theorem is very important. If two operators commute and consequently have the same set of eigenfunctions, then the corresponding physical quantities can be evaluated or measured exactly simultaneously with no limit on the uncertainty. As mentioned previously, the eigenvalues of the operators correspond to the measured values.

Proof

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

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \tag{4.9.16}$$

Equation (4-49) says that $\hat{A}\psi$ is an eigenfunction of $\hat{B}$ with eigenvalue b, which means that when $\hat{A}$ operates on ψ, it cannot change ψ. At most, $\hat{A}$ operating on ψ can produce a constant times ψ.

$$\hat{A}\psi = a\psi \tag{4.9.17}$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \tag{4.9.18}$$

Equation 4.9.18 shows that Equation 4.9.17 is consistent with Equation 4.9.16. Consequently ψ also is an eigenfunction of $\hat{A}$ with eigenvalue a.

Exercise 4.9.46

Write definitions of the terms orthogonal and commutation.

Exercise 4.9.47

Show that the operators for momentum in the x-direction and momentum in the y-direction commute, but operators for momentum and position along the x-axis do not commute. Since differential operators are involved, you need to show whether

$$\hat{P}_x\hat{P}_y f(x,y) = \hat{P}_y\hat{P}_x f(x,y) \tag{4.9.19}$$

$$\hat{P}_x\hat{x}f(x) = \hat{x}\hat{P}_x f(x) \tag{4.9.20}$$

where f is an arbitrary function, or you could try a specific form for f, e.g. f = 6xy.

General Heisenberg Uncertainty Principle

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

$$\sigma_A\sigma_B \geq |\int \psi^*[\hat{A}\hat{B} - \hat{B}\hat{A}]\psi d\tau \tag{4.9.21}$$

where the integral inside the square brackets is called the commutator, and $|\;|$ signifies the modulus or absolute value. If $\hat{A}$ and $\hat{B}$ commute, then the right-hand-side of equation (4-52) is zero, so either or both σA and σ B could be zero, and there is no restriction on the uncertainties in the measurements of the eigenvalues a and b. If $\hat{A}$ and $\hat{B}$ do not commute, then the right-hand-side of equation (4-52) will not be zero, and neither σA nor σB can be zero unless the other is infinite. Consequently, both a and b cannot be eigenvalues of the same wavefunctions and cannot be measured simultaneously to arbitrary precision.

Exercise 4.9.48

Show that the commutator for position and momentum in one dimension equals –i ħ and that the right-hand-side of Equation (4-52) therefore equals ħ/2 giving $\sigma_x\sigma_{px} \geq \frac{\hbar}{2}$

Exercise 4.9.49

In a later chapter you will learn that the operators for the three components of angular momentum along the three directions in space (x, y, z) do not commute. What is the relevance of this mathematical property to measurements of angular momentum in atoms and molecules?

Exercise 4.9.50

Write the definition of a Hermitian operator and statements of the Orthogonality Theorem, the Schmidt Orthogonalization Theorem, and the Commuting Operator Theorem.

Exercise 4.9.51

Reconstruct proofs for the Orthogonality Theorem, the Schmidt Orthogonalization Theorem, and the Commuting Operator Theorem.

Exercise 4.9.52

Write a paragraph summarizing the connection between the commutation property of operators and the uncertainty principle.

4.E: Electronic Spectroscopy of Cyanine Dyes (Exercises)

Q4.1

Write the Schrödinger equation for a particle in a two dimensional box with infinite potential barriers and adjacent sides of unequal length (a rectangle). Solve the equation by separating variables with a product function X(x)Y(y) to obtain the wavefunctions X(x) and Y(y) and energy eigenvalues. How many different sets of quantum numbers are needed for this case? Sketch an energy level diagram to illustrate the energy level structure. What happens to the energy levels when the box is a square? When two or more states have the same energy, the states and the energy level are said to be degenerate. What is the zero point energy for an electron in a square box of length 0.05 nm?

Q4.2

A materials scientist is trying to fabricate a novel electronic device by constructing a two dimensional array of small squares of silver atoms. She thinks she has managed to produce an array with each square consisting of a monolayer of 25 atoms. You are an optical spectroscopist and want to test this conclusion. Use the particle-in-a-box model to predict the wavelength of the lowest energy electronic transition for these quantum dots. Which electrons do you want to describe by the particle-in-a-box model, or do you think you can apply this model to all the electrons in silver and get a reasonable prediction? In which spectral region does this transition lie? What instrumentation would you need to observe this transition?

Q4.3

Model the pi electrons of benzene by adapting the electron in a box model. Consider benzene to be a ring of radius r and circumference 2πr. You can find r by using the bond length of benzene (0.139 nm) and some trigonometry. Show how the electron on a ring is analogous to the electron in a linear box. Derive this analogy by thinking, not by copying from some book. What is the boundary condition for the case of the particle on a ring? Find mathematical expressions for the energy and the wavefunctions. Draw an energy level diagram. What is the physical reason that the energy levels are degenerate for this situation? Predict the wavelength of the lowest energy electronic transition for benzene. Compare your prediction with the experimental value (256 nm). What insight do you gain from this comparison?

Q4.4

Explain how and why the following two sets of selection rules for the particle-in-a-box are related to each other: (1) If Δn is even, the transition is forbidden; if Δn is odd, the transition is allowed. (2) If the transition is g to g or u to u, it is forbidden; if the transition is g to u or u to g, it is allowed.

Q4.5

The factor $fi/(f^2 - i^2)^2$ in Equation (4-32) determines the relative intensity of transitions in the particle-in-a-box model. Make plots of $[fi/(f^2-i^2)^2]$ vs f for several values of i with f starting at i+1 and increasing. What conclusions can you make about particle-in-a-box spectra from your plots?

Q4.6

Starting with the mathematical definition of uncertainty as the standard or root mean square deviation σ from the average, show by evaluating the appropriate expectation value integrals that

$$\sigma_x = \frac{L}{2\pi n}\left(\frac{\pi^2 n^2}{3} - 2\right) \text{and} \sigma_p = \frac{n\pi\hbar}{L} \tag{4.E.1}$$

for a particle in a one-dimensional box of length L as given in the chapter. Then show that the product $\sigma_x \sigma_p \geq \frac{\hbar}{2}$.

Q4.7

Use the symbolic processor in Mathcad to help you carry out the steps leading from Equation (4-27) to Equation (4-31). See Activity 4.3 for an introduction to the symbolic processor.

Q4.8

An electron is confined to a one-dimensional space with infinite potential barriers at x = 0 and x = L and a constant potential energy between 0 and L. The electron is described by the wavefunction $\psi(x) = N(Lx - x^2)$

In responding to the following questions (a through g), do not leave your answers in the form of integrals, i.e. do the integrals. Note:

$$\text{Note}: \int x^n dx = \frac{1}{n+1} x^{n+1} + C \text{for} x \neq 0 \tag{4.E.2}$$

1. Explain why this wavefunction must be normalized, and find an expression for N that normalizes the wavefunction.
2. Define what is meant by the expectation value, and find the expectation value for the position of the electron and the momentum of the electron.
3. Find the expectation value for the energy of the electron.
4. Is your energy expectation value consistent with your momentum expectation value? Explain.
5. What is the energy of the n = 1 state for the one-dimensional particle-in-a-box model? How does the energy obtained in (c) compare with this value? Explain why these two energies must have such a relationship to each other.
6. Does the wavefunction, $\psi(x) = N(Lx - x^2)$, for this electron represent a stationary state of the electron?
7. What is the probability that the electron will be located at x = L/3 in an interval of length L/100? Explain why you expect this probability to be time dependent or time independent.

Q4.9

How does choosing the potential energy inside the box to be –100 eV rather than 0 modify the description of the particle-in-a-box?

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

4.S: Electronic Spectroscopy of Cyanine Dyes (Summary)

In this chapter we used a very simple model called the particle-in-a-box model or the infinite-potential-well model to obtain very crude approximate wavefunctions for pi electrons in cyanine dye molecules. With the particle in the box model, we can estimate the wavelengths at which the peaks occur in the absorption spectra from estimated bond lengths, or we can use the wavelength information to determine average bond lengths in a series of dye molecules. By evaluating the transition moment integral, we can explain the relative intensities of these peaks and obtain selection rules for the spectroscopic transitions. The selection rules also can be deduced from qualitative symmetry considerations.

This model assumes the electrons are independent of each other and uses a particularly simple form for the potential energy of the electrons. The model also assumes that the atomic nuclei are fixed in space, i.e. the molecule is not vibrating or rotating. This latter assumption, which is known as the Crude Born-Oppenheimer Approximation, will be discussed in a later chapter. The physical basis for this approximation is the fact that the mass of the electron is much smaller than the mass of an atomic nucleus. The electrons therefore respond to forces or are accelerated by forces much faster than the nuclei (remember $a = f/m$) so the electron motion in a molecule can be examined by assuming that the nuclei are stationary.

We did not discuss the widths and shapes of the peaks. Contributions to the line widths and shapes come from motion of the nuclei; which we will consider later. Nuclei in a molecule vibrate, i.e. move relative to each other, and rotate around the center of mass of the molecule. The rotational and vibrational motion, as well as interaction with the solvent, which also is neglected, produce the spectral band widths and shapes and even affect the position of the absorption maximum. When light is absorbed the vibrational and rotational energy of the molecule can change along with the change in the electronic energy. Line widths and shapes therefore depend upon the absorption of different amounts of vibrational and rotational energy. Actually, in a condensed phase, molecular rotation is hindered. This hindered rotation is called libration.

An outcome of our examination of the cyanine dye wavefunctions was a glimpse at three fundamental properties of quantum mechanical systems: orthogonality of wavefunctions, the Heisenberg Uncertainty Principle, and the zero-point energy of bound systems. We also observed that quantum numbers result from the boundary conditions used to describe the physical system. Another observation was that the energy levels for the particle in the box get further apart as the quantum number n increases, but closer together as the size of the box increases. Lastly, the spectra we observe occur because of the interaction of molecules with electromagnetic radiation and the resulting transition of the molecule from one energy level to a higher energy level.

Questions for Thought

1. What is the difference between the spectroscopic wavelength and the wavefunction wavelength?
2. What is the total probability of finding any pi electron on one half-side of a cyanine dye molecule?
3. What is a molecular orbital and how is it related to visible-ultraviolet spectroscopy?
4. Why does a series of conjugated dye molecules, such as the cyanines, have colors ranging from red to blue?
5. Write a few paragraphs describing the origins of the absorption spectra for conjugated dye molecules using the particle-in-a-box model and the terms HOMO and LUMO.
6. Write a paragraph discussing the feasibility of determining the ionization potential for a dye molecule using the particle-in-a-box model.

Contributors and Attributions

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CHAPTER OVERVIEW

5: Translational States

In this chapter we apply the principles of Quantum Mechanics to the simplest possible physical system, a free particle in one dimension. This particle could be an electron or, if we only consider translational motion, an atom or a molecule. Free means that no forces are acting on the particle. Since a force is produced by a change in the potential energy, the potential energy must be constant if there is no force. This constant can be taken to be zero because energy is relative not absolute. By saying energy is relative, we mean we are concerned with adding and removing energy from systems not with the absolute value of the energy content. The discussion of the free particle in this chapter further illustrates the fundamental ideas of Quantum Mechanics and introduces solutions to new problems. Specifically the energy, momentum and probability density for a free particle are discussed, and a connection is made between the wave property of matter and the uncertainty principle.

5.1: The Free Particle

We obtain the Schrödinger equation for the free particle using the following steps. First write

$$\hat{H}\psi = E\psi \tag{5.1.1}$$

Next define the Hamiltonian,

$$\hat{H} = \hat{T} + \hat{V} \tag{5.1.2}$$

and substitute the potential energy operator

$$\hat{V} = 0 \tag{5.1.3}$$

and the kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{5.1.4}$$

to obtain the Schrödinger equation for a free particle

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{5.1.5}$$

A major problem in Quantum Mechanics is finding solutions to differential equations, e.g. Equation 5.1.5. Differential equations arise because the operator for kinetic energy includes a second derivative. We will solve the differential equations for some of the more basic cases, but since this is not a course in Mathematics, we will not go into all the details for other more complicated cases. The solutions that we consider in the greatest detail will illustrate the general procedures and show how the physical concept of quantization arises mathematically.

We already encountered Equation 5.1.5 in the last chapter Chapter 4. There, we used our knowledge of some basic functions to find the solution. Now we solve this equation by using some algebra and mathematical logic. First we rearrange Equation 5.1.5 and make the substitution

$$k^2 = \frac{2mE}{\hbar^2}. \tag{5.1.6}$$

> The substitution in Equation 5.1.6 is only one way of making a simplification. You could also use a different formulation for the substitution
>
> $$\alpha = \frac{2mE}{\hbar^2}$$
>
> but then you would find later that $(\alpha)^{1/2}$ corresponds to the wavevector k which equals $\frac{2\pi}{\lambda}$ and $\frac{P}{\hbar}$. So choosing a squared variable like k^2 in Equation 5.1.6 is a choice made with foresight. Trial-and-error is one method scientists use to solve problems, and the results often look sophisticated and insightful after they have been found, like choosing k^2 rather than α.

Since E is the kinetic energy,

$$E = \frac{p^2}{2m} \tag{5.1.7}$$

and we saw in previous chapters that the momentum p and the wavevector k are related,

$$p = \hbar k \tag{5.1.8}$$

we also could recognize that $\frac{2mE}{\hbar^2}$ is just k^2 as shown here in Equation 5.1.11.

$$\frac{2mE}{\hbar^2} = \left(\frac{2m}{\hbar^2}\right)\left(\frac{p^2}{2m}\right) \tag{5.1.9}$$

$$= \left(\frac{2\cancel{m}}{\cancel{\hbar^2}}\right)\left(\frac{\cancel{\hbar^2}k^2}{2\cancel{m}}\right) \tag{5.1.10}$$

$$= k^2 \tag{5.1.11}$$

The result for Equation 5.1.5 after rearranging and substitution of result from Equation 5.1.11 is

$$\left(\frac{d^2}{dx^2} + k^2\right)\psi(x) = 0 \tag{5.1.12}$$

This linear second-order differential equation can be solved in the same way that a algebraic quadratic equation is solved. It is separated into two factors, and each is set equal to 0. This factorization produces two first-order differential equations that can be integrated. The details are shown in the following equations.

$$\left(\frac{d^2}{dx^2} + k^2\right)\psi(x) = \left(\frac{d}{dx} + ik\right)\left(\frac{d}{dx} - ik\right)\psi(x) = 0 \tag{5.1.13}$$

Equation 5.1.13 will be true if either

$$\left(\frac{d}{dx} + ik\right)\psi(x) = 0 \tag{5.1.14}$$

or

$$\left(\frac{d}{dx} - ik\right)\psi(x) = 0 \tag{5.1.15}$$

Rearranging and designating the two equations and the two solutions simultaneously by a + sign and a – sign produces

$$\frac{d\psi_\pm(x)}{\psi_\pm(x)} = \pm ik\,dx \tag{5.1.16}$$

which leads to

$$\ln\psi_\pm(x) = \pm ikx + C_\pm \tag{5.1.17}$$

and finally

$$\psi_\pm(x) = A_\pm e^{\pm ikx} \tag{5.1.18}$$

The constants A_+ and A_- result from the constant of integration. The values of these constants are determined by some physical constraint that is imposed upon the solution. Such a constraint is called a boundary condition. For the particle in a box, discussed previously, the boundary condition is that the wavefunction must be zero at the boundaries where the potential energy is infinite. The free particle does not have such a boundary condition because the particle is not constrained to any one place. Another constraint is normalization, and here the integration constants serve to satisfy the normalization requirement.

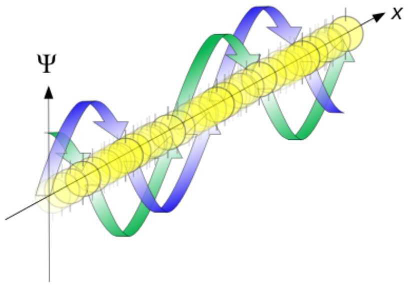

Figure 5.1.1: Propagation of free particle waves in 1d - real part of the complex amplitude is blue, imaginary part is green. The probability (shown as the color opacity) of finding the particle at a given point x is spread out like a waveform, there is no definite position of the particle. (public domain).

? Exercise 5.1.1

Show that the operator $\left(\frac{d^2}{dx^2}+k^2\right)$ equals $\left(\frac{d}{dx}+ik\right)\left(\frac{d}{dx}-ik\right)$ and that the two factors commute since k does not depend on x. The answer is Equation 5.1.13.

✓ Example 5.1.1: Normalizing the wavefunction of a free particle

Use the normalization constraint to evaluate $A_{\pm}$ in Equation 5.1.18.

Solution

Since the integral of $|\psi|^2$ over all values of x from $-\infty$ to $+\infty$ is infinite, it appears that the wavefunction ψ cannot be normalized. We can circumvent this difficulty if we imagine the particle to be in a region of space ranging from $-L$ to $+L$ and consider L to approach infinity.

The normalization then proceeds in the usual way as shown below. Notice that the normalization constants are **real** even though the wavefunctions are complex.

$$\int_{-L}^{+L}\psi^*(x)\psi(x)dx = A_{\pm}^*A_{\pm}\int_{-L}^{L}e^{\mp ikx}e^{\pm ikx}dx = 1$$

$$|A_{\pm}|^2\int_{-L}^{+L}dx = |A_{\pm}|^2 2L = 1$$

$$A_{\pm} = [2L]^{-1/2}$$

? Exercise 5.1.2

Write the wavefunctions, ψ^+ and ψ^-, for the free particle, explicitly including the normalization factors found in Example 5.1.1.

? Exercise 5.1.3

Find solutions to each of the following differential equations.

$$\frac{d^2y(x)}{dx^2}+25y(x)=0$$

$$\frac{d^2y(x)}{dx^2}-3y(x)=0$$

A neat property of linear differential equations is that sums of solutions also are solutions, or more generally, linear combinations of solutions are solutions. A linear combination is a sum with constant coefficients where the coefficients can be positive, negative, or imaginary. For example

$$\psi(x)=C_1\psi_+(x)+C_2\psi_-(x) \tag{5.1.19}$$

where C_1 and C_2 are the constant coefficients. Inserting the functions from Equation 5.1.18, one gets

$$\psi(x)=\frac{C_1}{\sqrt{2L}}e^{+ikx}+\frac{C_2}{\sqrt{2L}}e^{-ikx} \tag{5.1.20}$$

By using Euler's formula,

$$e^{\pm ikx}=\cos(kx)\pm i\sin(kx) \tag{5.1.21}$$

Equation 5.1.19 is transformed into

$$\psi(x) = C\cos(kx) + D\sin(kx) \tag{5.1.22}$$

where we see that k is just the wavevector $\dfrac{2\pi}{\lambda}$ in the trigonometric form of the solution to the Schrödinger equation. This result is consistent with our previous discussion regarding the choice of k^2 to represent $\dfrac{2mE}{\hbar^2}$.

? Exercise 5.1.4

Find expressions for C and D in Equation 5.1.22 for two cases: when $C_1 = C_2$ = +1 and when C_1 = +1 and C_2 = -1.

? Exercise 5.1.5

Verify that Equations 5.1.20 and 5.1.22 are solutions to the Schrödinger Equation (Equation 5.1.5) with the eigenvalue $E = \dfrac{\hbar^2 k^2}{2m}$.

? Exercise 5.1.6

Demonstrate that the wavefunctions you wrote for Exercise 5.1.2 are eigenfunctions of the momentum operator with eigenvalues $\hbar k$ and $-\hbar k$.

? Exercise 5.1.7

Determine whether $\psi(x)$ in Equation 5.1.20 is an eigenfunction of the momentum operator.

? Exercise 5.1.8

The probability density for finding the free particle at any point in the segment $-L$ to $+L$ can be seen by plotting $\psi^*\psi$ from -L to +L. Sketch these plots for the two wavefunctions, ψ_+ and ψ_-, that you wrote for Exercise 5.1.2. Demonstrate that the area between $\psi^*\psi$ and the x-axis equals 1 for any value of L. Why must this area equal 1 even as L approaches infinity? Are all points in the space equally probable or are some positions favored by the particle?

We found wavefunctions that describe the free particle, which could be an electron, an atom, or a molecule. Each wavefunction is identified by the wavevector k. A wavefunction tells us three things about the free particle: the energy of the particle, the momentum of the particle, and the probability density of finding the particle at any point. You have demonstrated these properties in Exercises 5.1.5, 5.1.6, and 5.1.8. These ideas are discussed further in the following paragraphs.

We first find the momentum of a particle described by $\psi_+(x)$. We also can say that the particle is in the state $\psi_+(x)$. The value of the momentum is found by operating on the function with the momentum operator. Remember this problem is one-dimensional so vector quantities such as the wavevector or the momentum appear as scalars. The result is shown in Example 5.1.1.

✓ Example 5.1.2

Extract the momentum from the wavefunction for a free electron.

Solution

First we write the momentum operator and wavefunction as shown by I and II. The momentum operator tells us the mathematical operation to perform on the function to obtain the momentum. Complete the operation shown in II to get III, which simplifies to IV.

$$\underset{I}{-i\hbar\frac{d}{dx}}\psi_+(x) = \underset{II}{-i\hbar\frac{d}{dx}A_+e^{ikx}} = \underset{III}{(-i\hbar)(ik)A_+e^{ikx}} = \underset{IV}{\hbar k\psi_+(x)}$$

Example 5.1.2 is another way to conclude that the momentum of this particle is

$$p = \hbar k. \tag{5.1.23}$$

Here the Compton-de Broglie momentum-wavelength relation $p = \hbar k$ appears from the solution to the Schrödinger equation and the definition of the momentum operator! For an electron in the state $\psi_-(x)$, we similarly find $p = -\hbar k$. This particle is moving in the minus x direction, opposite from the particle with momentum $+\hbar k$.

Since $k = \dfrac{2\pi}{\lambda}$, what then is the meaning of the wavelength for a particle, e.g. an electron? The wavelength is the wavelength of the wavefunction that describes the properties of the electron. We are not saying that an electron is a wave in the sense that an ocean wave is a wave; rather we are saying that a wavefunction is needed to describe the wave-like properties of the electron. Why the electron has these wave-like properties, remains a mystery.

We find the energy of the particle by operating on the wavefunction with the Hamiltonian operator as shown next in Equation 5.1.26. Examine each step and be sure you see how the eigenvalue is extracted from the wavefunction.

$$\hat{H}\psi_\pm(x) = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}A_\pm e^{\pm ikx} \tag{5.1.24}$$

$$= \frac{-\hbar^2}{2m}(\pm ik)^2 A_\pm e^{\pm ikx} \tag{5.1.25}$$

$$= \frac{\hbar^2 k^2}{2m} A_\pm e^{\pm ikx} \tag{5.1.26}$$

Notice again how the operator works on the wavefunction to extract a property of the system from it. We conclude that the energy of the particle is

$$E = \frac{\hbar^2 k^2}{2m} \tag{5.1.27}$$

Which is just the classical relation between energy and momentum of a free particle, $E = \dfrac{p^2}{2m}$. Note that an electron with momentum +ħk has the same energy as an electron with momentum -ħk. When two or more states have the same energy, the states and the energy level are said to be degenerate.

We have not found any restrictions on the momentum or the energy. These quantities are not quantized for the free particle because there are no boundary conditions. Any wave with any wavelength fits into an unbounded space. Quantization results from boundary conditions imposed on the wavefunction, as we saw for the particle-in-a-box.

? Exercise 5.1.9

Describe how the wavelength of a free particle varies with the energy of the particle.

? Exercise 5.1.10

Summarize how the energy and momentum information is contained in the wavefunction and how this information is extracted from the wavefunction.

The probability density of a free particle at a position in space x_0 is

$$\psi^*_\pm(x_0)\psi_\pm(x_0) = (2L)^{-1} e^{\mp ikx_0} e^{\pm ikx_0} = (2L)^{-1} \tag{5.1.28}$$

From this result we see that the probability density has units of 1/m; it is the probability per meter of finding the electron at the point x_0. This probability is independent of x_0, the electron can be found any place along the x axis with equal probability. Although we have no knowledge of the position of the electron, we do know the electron momentum exactly. This relationship between our knowledge of position and momentum is a manifestation of the Heisenberg Uncertainty Principle, which says that as the uncertainty in one quantity is reduced, the uncertainty in another quantity increases. For this case, we know the momentum exactly and have no knowledge of the position of the particle. The uncertainty in the momentum is zero; the uncertainty in the position is infinite.

5.2: The Uncertainty Principle

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{5.2.1}$$

You can see from Equation 5.2.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 5.2.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

5.3: Linear Combinations of Eigenfunctions

It is not necessary that an electron be described by an eigenfunction of the Hamiltonian operator. Many problems encountered by quantum chemists and computational chemists lead to wavefunctions that are not eigenfunctions of the Hamiltonian operator. Science is like that; interesting problems are not simple to solve. They require adaptation of current techniques, creative energy, and a good set of skills developed by studying solutions to previously solved interesting problems.

Consider a free electron in one dimension that is described by the wavefunction

$$\psi(x) = C_1\psi_1(x) + C_2\psi_2(x) \tag{5.3.1}$$

with

$$\psi_1(x) = \left(\frac{1}{2L}\right)^{1/2} e^{ik_1x} \tag{5.3.2}$$

$$\psi_2(x) = \left(\frac{1}{2L}\right)^{1/2} e^{ik_2x} \tag{5.3.3}$$

where k_1 and k_2 have different magnitudes. Although such a function is not an eigenfunction of the momentum operator or the Hamiltonian operator, we can calculate the average momentum and average energy of an electron in this state from the expectation value integral. (Note: "in-this-state" means "described-by-this-wavefunction".)

? Exercise 5.3.1

Show that the function $\psi(x)$ defined by Equation 5.3.1 is not an eigenfunction of the momentum operator or the Hamiltonian operator for a free electron in one dimension.

The function shown in Equation 5.3.1 belongs to a class of functions known as **superposition functions**, which are linear combinations of eigenfunctions. A linear combination of functions is a sum of functions, each multiplied by a weighting coefficient, which is a constant. The adjective linear is used because the coefficients are constants. The constants, e.g. C_1 and C_2 in Equation 5.3.1, give the weight of each component (ψ_1 and ψ_2) in the total wavefunction. Notice from the discussion previously that each component in Equation 5.3.1 is an eigenfunction of the momentum operator and the Hamiltonian operator although the linear combination function (i.e., $\psi(x)$) is **not**.

The expectation value, i.e. average value, of the momentum operator is found as follows. First, write the integral for the expectation value and then substitute into this integral the superposition function and its complex conjugate as shown below. Since we are considering a free particle in one dimension, the limits on the integration are $-L$ and $+L$ with L going to infinity.

$$\langle p \rangle = \int \psi^*(x) \left(-i\hbar \frac{d}{dx}\right) \psi(x) dx \tag{5.3.4}$$

$$= \frac{-i\hbar}{2L} \int\limits_{-L}^{+L} \left(C_1^* e^{-ik_1x} + C_2^* e^{-ik_2x}\right) \frac{d}{dx} \left(C_1 e^{ik_1x} + C_2 e^{ik_2x}\right) dx \tag{5.3.5}$$

$$= \frac{-i\hbar}{2L} \int\limits_{-L}^{+L} \left(C_1^* e^{-ik_1x} + C_2^* e^{-ik_2x}\right) \left((ik_1)C_1 e^{ik_1x} + (ik_2)C_2 e^{ik_2x}\right) dx \tag{5.3.6}$$

Cross-multiplying the two factors in parentheses yields four terms.

$$\langle p \rangle = I_1 + I_2 + I_3 + I_4$$

with

$$I_1 = \frac{\hbar k_1}{2L} C_1^* C_1 \int_{-L}^{+L} dx = C_1^* C_1 \hbar k_1 \tag{5.3.7}$$

$$I_2 = \frac{\hbar k_2}{2L} C_2^* C_2 \int_{-L}^{+L} dx = C_2^* C_2 \hbar k_2 \tag{5.3.8}$$

$$I_3 = \frac{\hbar k_1}{2L} C_1^* C_2 \int_{-L}^{+L} e^{i(k_2-k_1)x} dx \tag{5.3.9}$$

$$I_4 = \frac{\hbar k_1}{2L} C_2^* C_1 \int_{-L}^{+L} e^{i(k_1-k_2)x} dx \tag{5.3.10}$$

An integral of two different functions, e.g. $\int \psi_1^* \psi_2 dx$, is called an **overlap integral** or **orthogonality integral**. When such an integral equals zero, the functions are said to be orthogonal. The integrals in I_3 and I_4 are zero because the functions ψ_1 and ψ_2 are orthogonal. We know ψ_1 and ψ_2 are orthogonal because of the Orthogonality Theorem, described previously, that states that eigenfunctions of any Hermitian operator, such as the momentum operator or the Hamiltonian operator, with different eigenvalues, which is the case here, are orthogonal. Also, by using Euler's formula and following Example 5.3.1 below, you can see why these integrals are zero.

✓ Example 5.3.1

For the integral part of I_3 obtain

$$\int \cos[(k_2-k_1)x]dx + i\int \sin[(k_2-k_1)x]dx$$

from Euler's formula.

Solution

Here we have the integrals of a cosine and a sine function along the x-axis from minus infinity to plus infinity. Since these integrals are the area under the cosine and sine curves, they must be zero because the positive lobes are canceled by the negatives lobes when the integration is carried out from $-\infty$ to $+\infty$.

As a result of this orthogonality, $\langle p \rangle$ is just $I_1 + I_2$, which is

$$\langle p \rangle = C_1^* C_1 \hbar k_1 + C_2^* C_2 \hbar k_2 \tag{5.3.11}$$

$$= C_1^* C_1 p_1 + C_2^* C_2 p_2 \tag{5.3.12}$$

where $\hbar k_1$ is the momentum p_1 of state ψ_1, and $\hbar k_2$ is the momentum p_2 of state ψ_2. As explained in Chapter 3, an average value can be calculated by summing, over all possibilities, the possible values times the probability of each value. Equation 5.3.12 has this form if we interpret $C_1^* C_1$ and $C_2^* C_2$ as the probability that the electron has momentum p_1 and p_2, respectively. These coefficients therefore are called probability amplitude coefficients, and their absolute value squared gives the probability that the electron is described by ψ_1 and ψ_2, respectively. This interpretation of these coefficients as probability amplitudes is very important.

? Exercise 5.3.2A

Find the expectation value for the energy $\langle E \rangle$ for the superposition wavefunction given by Equation 5.3.3.

? Exercise 5.3.2B

Explain why $C_1^*C_1$ is the probability that the electron has energy $\dfrac{\hbar^2k_1^2}{2m}$ and $C_2^*C_2$ is the probability that the electron has energy $\dfrac{\hbar^2k_2^2}{2m}$.

? Exercise $5.3.2C$

What is the expectation value for the energy when both components have equal weights in the superposition function, i.e. when $C_1 = C_2 = 2^{-1/2}$?

5.E: Translational States (Exercises)

Q5.1

Write the Schrödinger equation for a free particle in three-dimensional space.

Q5.2

Solve the Schrödinger equation to find the wavefunctions for a free particle in three-dimensional space.

Q5.3

Show that these functions are eigenfunctions of the momentum operator in three-dimensional space.

Q5.4

If you have not already done so, use vector notation for the wave vector and position of the particle.

Q5.5

Write the wavefunctions using vector notation for the wave vector and the position.

Q5.6

Write the momentum operator in terms of the del-operator, which is defined as $\hat{\nabla} = \vec{x}\frac{\partial}{\partial x} + \vec{y}\frac{\partial}{\partial y} + \vec{z}\frac{\partial}{\partial z}$ where the arrow caps on x, y, and z designate unit vectors.

Q5.7

Write the Laplacian operator in terms of partial derivatives with respect to x, y, and z. The Laplacian operator is defined as the scalar product of del with itself, $\hat{\partial}^2 = \hat{\partial} \cdot \hat{\partial}$.

Q5.8

Write the kinetic energy operator in terms of the Laplacian operator.

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

5.S: Translational States (Summary)

In this chapter we applied the principles of quantum mechanics to the simplest physical system, a free particle in one dimension, which could be an electron, an atom, or a molecule. We wrote the Schrödinger equation for the system and then solved this equation to obtain the wavefunctions, ψk(x), describing the system. Each wavefunction is identified by the magnitude of the wave vector, k, as a subscript. We observed that the wavefunctions are not quantized because there are no boundary conditions for this system. By “not quantized,” we mean that the wave vector, momentum, and energy can have any values. We determined the constants of integration for our solutions by using the normalization condition. By using the wavefunction and the momentum operator to obtain the momentum of the particle, we discovered that the momentum was related to the wave vector and wavelength just as Compton and de Broglie proposed. Note that the momentum and energy of the free particle are related just as they are classically. The position of the particle is completely undetermined by the wavefunction because the momentum is given exactly. The particle could be anywhere. This relationship between momentum and position is a manifestation of the Heisenberg Uncertainty Principle. The momentum is known exactly because the wavefunction is an eigenfunction of the momentum operator.

The concepts of overlap, orthogonality, and linear combination or superposition of functions appeared in the discussion. These concepts will be useful later when we discuss bonding and the mathematical representations of bonding in semi-empirical and ab initio molecular orbital theories. Linear combinations of atomic orbitals and other functions are used to describe bonds in molecules, and the overlap and orthogonality of these functions are important there.

Exercise $5.S.14$ Complete the table below. For an example of a completed table, see the overview table at the end of Chapter 4.

Overview of key concepts and equations for the free particle

Potential energy	V =
Hamiltonian	
Wavefunctions	Ψ =
Quantum Numbers	
Energies	E =
Spectroscopic Selection Rules	
Angular Momentum Properties	

Contributors and Attributions

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CHAPTER OVERVIEW

6: Vibrational States

In this chapter we use the harmonic oscillator model and a combination of classical and quantum mechanics to learn about the vibrational states of molecules. The first section of the chapter introduces the concepts of normal modes and normal coordinates in order to deal with the complexity of vibrational motion found in polyatomic molecules. The second section of the chapter reviews the classical treatment of the harmonic oscillator model, which is very general. Anything with a potential energy that depends quadratically on position, or equivalently experiences a linear restoring force, is a harmonic oscillator. In addition to vibrating molecules, the harmonic oscillator model therefore describes physical systems such as a pendulum, a weight hanging from a spring, or weights connected by springs.

The remainder of the chapter treats the vibrational states of molecules using quantum mechanics, starting with the solutions to the Schrödinger equation. Quantum mechanics provides the probability density function for positions of the atomic nuclei and the vibrational energy level structure, and is used to calculate spectroscopic selection rules, explain intensities in spectra, and calculate the vibrational force constants. Our analysis will identify the molecular properties that determine the frequency of radiation that is absorbed, determine which vibrations appear in the infrared spectrum (and which do not), and determine why some vibrations absorb radiation strongly (and others do not).

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6.1: Spatial Degrees of Freedom, Normal Coordinates and Normal Modes

To deal with the complexity of the vibrational motion in polyatomic molecules, we need to utilize the three important concepts listed as the title of this section. By a spatial degree of freedom, we mean an independent direction of motion. A single atom has three spatial degrees of freedom because it can move in three independent or orthogonal directions in space, i.e. along the x, y, or z-axes of a Cartesian coordinate system. Motion in any other direction results from combining velocity components along two or three of these directions. Two atoms have six spatial degrees of freedom because each atom can move in any of these three directions independently.

Equivalently, we also can say one atom has three spatial degrees of freedom because we need to specify the values of three coordinates (x_1, y_1, z_1) to locate the atom. Two atoms have six spatial degrees of freedom because we need to specify the values of six coordinates, (x_1, y_1, z_1) and (x_2, y_2, z_2), to locate two atoms in space. In general, to locate N atoms in space, we need to specify 3N coordinates, so a molecule comprised of N atoms has 3N spatial degrees of freedom.

Exercise 6.1.1

Identify the number of spatial degrees of freedom for the following molecules: Cl_2, CO_2, H_2O, CH_4, C_2H_2, C_2H_4, C_6H_6.

The motion of the atomic nuclei in a molecule is not as simple as translating each of the nuclei independently along the x, y, and z axes because the nuclei, which are positively charged, are coupled together by the electrostatic interactions with the electrons, which are negatively charged. The electrons between two nuclei effectively attract them to each other, forming a chemical bond.

Consider the case of a diatomic molecule, which has six degrees of freedom. The motion of the atoms is constrained by the bond. If one atom moves, a force will be exerted on the other atom because of the bond. The situation is like two balls coupled together by a spring. There are still six degrees of freedom, but the motion of atom 1 along x, y, and z is not independent of the motion of atom 2 along x, y, and z because the atoms are bound together.

It therefore is not very useful to use the six Cartesian coordinates, (x_1, y_1, z_1) and (x_2, y_2, z_2), to describe the six degrees of freedom because the two atoms are coupled together. We need new coordinates that are independent of each other and yet account for the coupled motion of the two atoms. These new coordinates are called normal coordinates, and the motion described by a normal coordinate is called a normal mode.

A normal coordinate is a linear combination of Cartesian displacement coordinates. A linear combination is a sum of terms with constant weighting coefficients multiplying each term. The coefficients can be imaginary or any positive or negative number including +1 and -1. For example, the point or vector r = (1, 2, 3) in three-dimensional space can be written as a linear combination of unit vectors.

$$r = 1\bar{x} + 2\bar{y} + 3\bar{z} \tag{6.1.1}$$

A Cartesian displacement coordinate gives the displacement in a particular direction of an atom from its equilibrium position. The equilibrium positions of all the atoms are those points where no forces are acting on any of the atoms. Usually the displacements from equilibrium are considered to be small. For illustration, the Cartesian displacement coordinates for HCl are defined in Table 6.1.1, and they are illustrated in Figure 6.1.1.

Table 6. Cartesian displacement coordinates for HCl.*

$$q_1 = X_H - X_H^e \tag{6.1.2}$$

$$q_2 = y_H - y_H^e \tag{6.1.3}$$

$$q_3 = z_H - z_H^e \tag{6.1.4}$$

$$q_4 = x_{Cl} - x_{Cl}^e \tag{6.1.5}$$

$$q_5 = y_{Cl} - y_{Cl}^e \tag{6.1.6}$$

$$q_6 = z_{Cl} - z_{Cl}^e \tag{6.1.7}$$

*The superscript e designates the coordinate value at the equilibrium position.

Note that the position of one atom can be written as a vector r_1 where $r_1 = (x_1, y_1, z_1)$, and the positions of two atoms can be written as two vectors r_1 and r_2 or as a generalized vector that contains all six components $r = (x_1, y_1, z_1, x_2, y_2, z_2)$. Similarly the six Cartesian displacement coordinates can be written as such a generalized vector $q = (q_1, q_2, q_3, q_4, q_5, q_6)$.

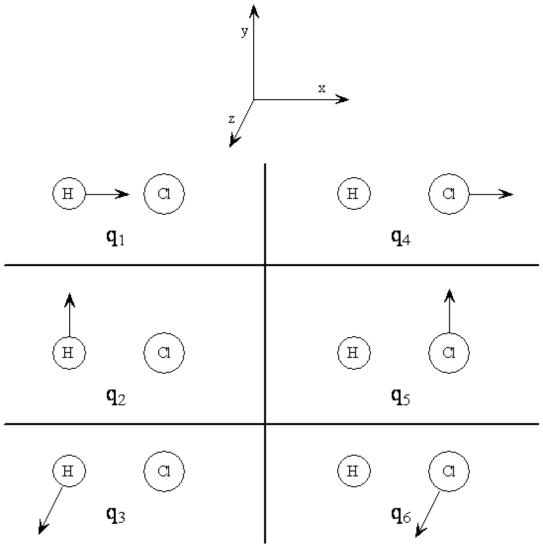

Figure 6.1.1: The Cartesian displacement coordinates for HCl. Note that the internuclear axis is the x-axis.

For a diatomic molecule it is easy to find the linear combinations of the Cartesian displacement coordinates that form the normal coordinates and describe the normal modes. Just take sums and differences of the Cartesian displacement coordinates. Refer to Table 6.1.1 and Figure 6.1.4. for the definition of the q's. The combination q1 + q4 corresponds to translation of the entire molecule in the x direction; call this normal coordinate Tx. Similarly we can define Ty = q2 + q5 and Tz = q3 + q6 as translations in the y and z directions, respectively. Now we have three normal coordinates that account for three of the degrees of freedom, the three translations of the entire molecule.

What do we do about the remaining three degrees of freedom? Here let's use a simple rule for doing creative science: if one thing works, try something similar and examine the result. In this case, if adding quantities works, try subtracting them. Examine the combination q2 - q5. This combination means that H is displaced in one direction and Cl is displaced in the opposite direction. Because of the bond, the two atoms cannot move completely apart, so this small displacement of each atom from equilibrium is the beginning of a rotation about the z-axis. Call this normal coordinate Rz. Similarly define Ry = q3 - q6 to be rotation about the y-axis. We now have found two rotational normal coordinates corresponding to two rotational degrees of freedom.

The remaining combination, q1 - q4, corresponds to the atoms moving toward each other along the x-axis. This motion is the beginning of a vibration, i.e. the oscillation of the atoms back and forth along the x-axis about their equilibrium positions, and accounts for the remaining sixth degree of freedom. We use Q for the vibrational normal coordinate.

$$Q = q_1 - q_4 \tag{6.1.8}$$

To summarize: a normal coordinate is a linear combination of atomic Cartesian displacement coordinates that describes the coupled motion of all the atoms that comprise a molecule. A normal mode is the coupled motion of all the atoms described by a normal coordinate. While diatomic molecules have only one normal vibrational mode and hence one normal vibrational coordinate, polyatomic molecules have many.

Exercise 6.1.2

Draw and label six diagrams, each similar to Figure 6.1.1, to show the 3 translational, 2 rotational and 1 vibrational normal coordinates of a diatomic molecule.

Exercise 6.1.3

Vibrational normal modes have several distinguishing characteristics. Examine the animations for the normal modes of benzene shown in Figure 6.1.3 to identify and make a list of these characteristics. Use a molecular modeling program to calculate and visualize the normal modes of another molecule.

The list of distinguishing characteristics of normal modes that you compiled in Exercise $6.1.4$ should include the following four properties. If not, reexamine the animations to confirm that these characteristics are present.

1. In a particular vibrational normal mode, the atoms move about their equilibrium positions in a sinusoidal fashion with the same frequency.
2. Each atom reaches its position of maximum displacement at the same time, but the direction of the displacement may differ for different atoms.
3. Although the atoms are moving, the relationships among the relative positions of the different atoms do not change.
4. The center of mass of the molecule does not move.

For the example of HCl, see Table $6.1.1$, the first property, stated mathematically, means

$$q_1 = A_1 \sin(\omega t) \text{and} q_4 = A_4 \sin(\omega t) \tag{6.1.9}$$

The maximum displacements or amplitudes are given by A1 and A4, and the frequency of oscillation (in radians per second) is ω for both displacement coordinates involved in the normal vibrational mode of HCl. Substitution of Equations (6-3) for the displacement coordinates into the expression determined above for the vibrational normal coordinate, Equation (6-2), yields

$$Q = q_1 - q_4 = A_1 \sin(\omega t) - A_4 \sin(\omega t) \tag{6.1.10}$$

This time-dependent expression describes the coupled motions of the hydrogen and chlorine atoms in a vibration of the HCl molecule. In general for a polyatomic molecule, the magnitude of each atom's displacement in a vibrational normal mode may be different, and some can be zero. If an amplitude, the A, for some atom in some direction is zero, it means that atom does not move in that direction in that normal mode. In different normal modes, the displacements of the atoms are different, and the frequencies of the motion generally are different. If two or more vibrational modes have the same vibrational frequency, these modes are called degenerate.

You probably noticed in Exercise $6.1.4$ that the atoms reached extreme points in their motion at the same time but that they were not all moving in the same direction at the same time. These characteristics are described by the second and third properties from the list above. For the case of HCl, the two atoms always move in exactly opposite directions during the vibration. Mathematically, the negative sign in Equation that we developed for the normal coordinate, Q, accounts for this relationship.

This timing with respect to the direction of motion is called the phasing of the atoms. In a normal mode, the atoms move with a constant phase relationship to each other. The phase relationship is represented by a phase angle φ in the argument of the sine function that describes the time oscillation, sin(ωt + φ). The angle is called a phase angle because it shifts the sine function on the time axis. We can illustrate this phase relationship for HCl. Use the trigonometric identity

$$-\sin\theta = \sin(\theta + 180^0) \tag{6.1.11}$$

in Equation 6.1.10 to obtain

$$Q = A_1 \sin(\omega t) + A_4 \sin(\omega t + 180^0) \tag{6.1.12}$$

to see that that the phase angle for this case is 180^o.

The phase angle φ accounts for the fact that the H atom and the Cl atom reach their maximum displacements in the positive x-direction, +A1 and +A4, at different times. Generally in a normal mode the phase angle φ is 0o or 180o. If φ = 0o for both atoms, the atoms move together, and they are said to be in-phase. For the vibration of a diatomic molecule such as HCl, the phase angle for one atom is φ = 0o, and the phase angle for the other atom is φ = 180o. The atoms therefore move in opposite directions any time, and the atoms are said to be 180o out-of-phase. When φ is 180o, two atoms reach the extreme points in their motion at the same time, but one is in the positive direction and the other is in the negative direction.

Phase relationships can be seen by watching a marching band. All the players are executing the same marching motion at the same frequency, but a few may be ahead or behind the rest. You might say, "They are out-of-step." You also could say, "They are out-of-phase."

To illustrate the fourth property for HCl, recall that the center of mass for a diatomic molecule is defined as the point where the following equation is satisfied.

$$m_H d_H = m_{Cl} d_{Cl} \tag{6.1.13}$$

The masses of the atoms are given by m_H and m_Cl, and d_H and d_{Cl} are the distances of these atoms from the center of mass.

Exercise 6.1.4

Find the distances, dH and dCl, of the H and Cl atoms from the center of mass in HCl given that the bond length is 0.13 nm. In general for a diatomic molecule, AB, what determines the ratio dA/dB, and which atom moves the greater distance in the vibration?

In general, to satisfy the center of mass condition, a light atom is located further from the center of mass than a heavy atom. To keep the center of mass fixed during a vibration, the amplitude of motion of an atom must depend inversely on its mass. In other words, a light atom is located further from the center of mass and moves a longer distance in a vibration than a heavy atom.

Exercise 6.1.5

Find the ratio of A1 to A4 from Equation that keeps the HCl center of mass stationary during a vibration. Find values for A1 and A4 that satisfy the condition

$$A12 + A42 = 1. \tag{6.1.14}$$

Exercise 6.1.6

For a vibrating HCl molecule, use the four properties of a normal vibrational mode, listed previously, to sketch a graph showing the position of the H atom (plot 1) and the position of the Cl atom (plot 2) as a function of time. Both plots should be on the same scale. Hint: place x on the vertical axis and time on the horizontal axis.

In general, a molecule with 3N spatial degrees of freedom has 3 translational normal modes (along each of the three axes), 3 rotational normal modes (around each of the three axes), and 3N-6 (the remaining number) different vibrational normal modes of motion. A linear molecule, as we have just seen, only has two rotational modes, so there are 3N-5 vibrational normal modes. Rotational motion about the internuclear axis in a linear molecule is not one of the 3N spatial degrees of freedom derived from the translation of atoms in three-dimensional space. Rather, such motion corresponds to other degrees of freedom, rotational motion of the electrons and a spinning motion of the nuclei. Indeed, the electronic wavefunction for a linear molecule is characterized by some angular momentum (rotation) about this axis, and nuclei have a property called spin.

Exercise 6.1.7

Identify the number of translational, rotational, and vibrational normal modes for the following molecules: $Cl_2, CO_2, H_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, C_6H_6$. Using your intuition, draw diagrams similar to the ones in Exercise $6.1.3$ to show the normal modes of H_2O and C_2H_4. It is difficult to identify the normal modes of triatomic and larger molecules by intuition. A mathematical analysis is essential. It is easier to see the normal modes if you use a molecular modeling program like Spartan or Gaussian to generate and display the normal modes.

You probably found in trying to complete Exercise $6.1.7$ that it is difficult to identify the normal modes and normal coordinates of triatomic and large molecules by intuition. A mathematical analysis is essential. A general analysis based on the Lagrangian formulation of classical mechanics is described separately.

6.2: Classical Description of the Vibration of a Diatomic Molecule

A classical description of the vibration of a diatomic molecule is needed because the quantum mechanical description begins with replacing the classical energy with the Hamiltonian operator in the Schrödinger equation. It also is interesting to compare and contrast the classical description with the quantum mechanical picture.

The motion of two particles in space can be separated into translational, vibrational, and rotational motions. The internal motions of vibration and rotation for a two-particle system can be described by a single reduced particle with a reduced mass μ located at r.

For a diatomic molecule, Figure $6.2.1$, the vector 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 normal vibrational coordinate Q for a diatomic molecule.

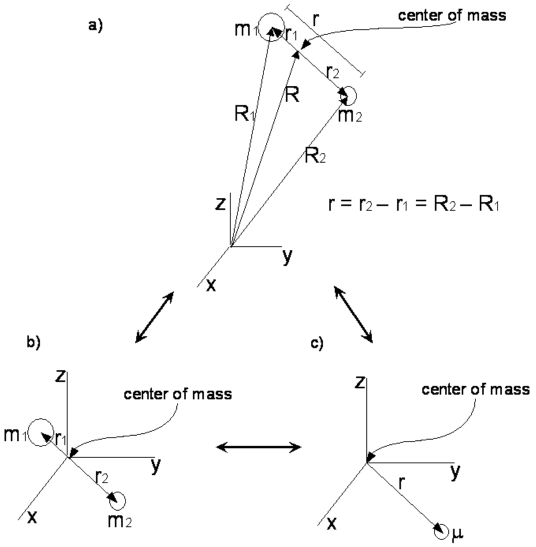

Figure $6.2.1$: The diagram shows the coordinate system for a reduced particle. R_1 and R_2 are vectors to m_1 and m_2. R is the resultant and points to the center of mass. (b) Shows the center of mass as the origin of the coordinate system, and (c) expressed as a reduced particle.

We can use Newton's equation of motion

$$\vec{F} = m\vec{a} \tag{6.2.1}$$

to obtain a classical description of how a diatomic molecule vibrates. In this equation, the mass, m, is the reduced mass μ of the molecule, the acceleration, a, is d^2Q/dt^2, and the force, f, is the force that pulls the molecule back to its equilibrium bond length. If we consider the bond to behave like a spring, then this restoring force is proportional to the displacement from the equilibrium length, which is Hooke's Law

$$F = -kQ \tag{6.2.2}$$

where k is the **force constant**. Hooke's Law says that the force is proportional to, but in opposite direction to, the displacement, Q. The force constant, k, 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. (See Exercise $6.2.9$ below.)

$$V(Q) = \frac{1}{2}kQ^2 \tag{6.2.3}$$

Hooke's Law or the harmonic (i.e. quadratic) potential given by Equation $6.2.3$ is a common 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. In fact IR and other vibrational spectra provide information about the molecular composition of substances and about the bonding structure of molecules because of this relationship between the electron density in the bond and the bond force constant. Note that a stiff bond with a large force constant is not necessarily a strong bond with a large dissociation energy.

Example 6.2.1

a. Show that minus the first derivative of the harmonic potential energy function in Equation 6.2.3 with respect to Q is the Hooke's Law force.
b. Show that the second derivative is the force constant, k.
c. At what value of Q is the potential energy a minimum; at what value of Q is the force zero?
d. Sketch graphs to compare the potential energy and the force for a system with a large force constant to one with a small force constant.

In view of the above discussion, Equation 6.2.1 can be rewritten as

$$\frac{d^2Q(t)}{dt^2}+\frac{k}{\mu}Q(t)=0 \tag{6.2.4}$$

Equation 6.2.4 is the equation of motion for a classical harmonic oscillator. It is a linear second-order differential equation that can be solved by the standard method of factoring and integrating as described in Chapter 5.

Example 6.2.2

Substitute the following functions into Equation 6.2.4 to show that they are both possible solutions to the classical equation of motion.

$$Q(t)=Q_0e^{i\omega t} \text{and} Q(t)=Q_0e^{-i\omega t} \tag{6.2.5}$$

where

$$\omega=\sqrt{\frac{k}{\mu}} \tag{6.2.6}$$

Note that the Greek symbol ω for frequency represents the angular frequency $2\pi\nu$.

Example 6.2.3

Show that sine and cosine functions also are solutions to Equation 6.2.4.

Example 6.2.4

Using the sine function, sketch a graph showing the displacement of the bond from its equilibrium length as a function of time. Such motion is called **harmonic**. Show how your graph can be used to determine the frequency of the oscillation. Obtain an equation for the velocity of the object as a function of time, and plot the velocity on your graph also. Note that momentum is mass times velocity so you know both the momentum and position at all times.

Example 6.2.5

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 by 9 times and the mass is increased by 4 times, by what factor does the frequency change?

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

$$P_Q = \mu \frac{dQ}{dt} \tag{6.2.7}$$

so the energy can be written as

$$E = T + V = \frac{P_Q^2}{2\mu} + \frac{k}{2} Q^2 \tag{6.2.8}$$

Example 6.2.6

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?

Example 6.2.7

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?

We can generalize this discussion to any normal mode in a polyatomic molecule. The normal coordinate associated with a normal mode can be thought of as a vector Q, with each component giving the displacement amplitude of a particular atom in a particular direction. Equation 6.2.4 then applies to the length of this vector $Q = |Q|$. As Q increases, it means the displacements of all the atoms that move in that normal mode increase, and the restoring force increases as well.

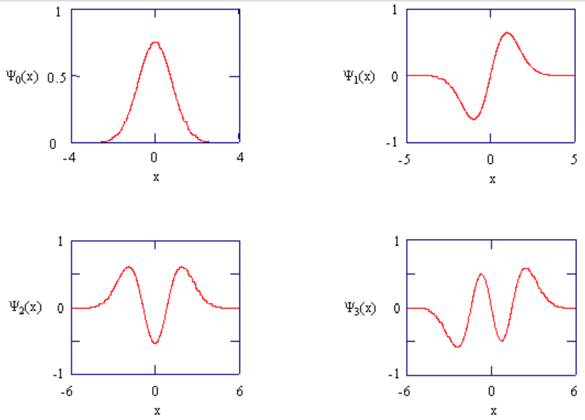

***Figure 6.3.3.6:** The harmonic oscillator wavefunctions describing the four lowest energy states.*

In completing Exercise 6.3.23, 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?

6.4: Harmonic Oscillator Properties

In this section we contrast the classical and quantum mechanical treatments of the harmonic oscillator, and we describe some of the properties that can be calculated using the quantum mechanical harmonic oscillator model. The problems at the end of the chapter require that you do some of these calculations, which involve the evaluation of non-trivial integrals. Methods for evaluating such integrals are provided in a detailed math supplement. These integrals are important. They also will appear in later chapters on electronic structure. Working through the problems with the support of the link will give you the opportunity to engage the mathematics on your own terms and deepen your understanding of the material in this section.

For a classical oscillator as described in Section 6.2 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 effective mass M 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.

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 6.4.1.

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega \tag{6.4.1}$$

with

$$v = 0, 1, 2, 3, \cdots \tag{6.4.2}$$

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

$$Pr[Q \text{to} Q + dQ] = \psi_v^*(Q)\psi_v(Q)dQ \tag{6.4.3}$$

We can, however, calculate the average displacement and the mean square displacement of the atoms relative to their equilibrium positions. This average is just $\langle Q \rangle$, the expectation value for Q, and the mean square displacement is $\langle Q^2 \rangle$, the expectation value for Q_2. Similarly we can calculate the average momentum $\langle P_Q \rangle$, and the mean square momentum $\left\langle P_Q^2 \right\rangle$, but we cannot specify the momentum as a function of time.

Physically what do we expect to find for the average displacement and the average momentum? Since the potential energy function is symmetric around Q = 0, we expect values of Q > 0 to be equally as likely as Q < 0. The average value of Q therefore should be zero.

These results for the average displacement and average momentum do not mean that the harmonic oscillator is sitting still. As for the particle-in-a-box case, we can imagine the quantum mechanical harmonic oscillator as moving back and forth and therefore having an average momentum of zero. Since the lowest allowed harmonic oscillator energy, E_0, is $\frac{\hbar\omega}{2}$ and not 0, the atoms in a molecule must be moving even in the lowest vibrational energy state. This phenomenon is called the zero-point energy or the zero-point motion, and it stands in direct contrast to the classical picture of a vibrating molecule. Classically, the lowest energy available to an oscillator is zero, which means the momentum also is zero, and the oscillator is not moving.

Exercise 6.4.23b

Compare the quantum mechanical harmonic oscillator to the classical harmonic oscillator at v=1 and v=50.

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. These uncertainties are calculated in Problem 3 at the end of this chapter. 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.

In Problem 2, we show that the product of the standard deviations for the displacement and the momentum, σ_Q and σ_p, satisfies the **Heisenberg Uncertainty Principle**.

$$\sigma_Q \sigma_p \geq \frac{\hbar}{2} \tag{6.4.4}$$

The harmonic oscillator wavefunctions form an **orthonormal set,** which means that all functions in the set are normalized individually

$$\int_{-\infty}^{\infty} \psi_v^*(x)\psi_v(x)dx = 1 \tag{6.4.5}$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x)\psi_v(x)dx = 0 \tag{6.4.6}$$

for $v' \neq v$.

The fact that a family of wavefunctions forms an orthonormal set is often helpful in simplifying complicated integrals. We will use these properties in Section 6.6, for example, when we determine the harmonic oscillator selection rules for vibrational transitions in a molecule and calculate the absorption coefficients for the absorption of infrared radiation.

Finally, we can calculate the probability that a harmonic oscillator is in the classically forbidden region. What does this tantalizing statement mean? Classically, the maximum extension of an oscillator is obtained by equating the total energy of the oscillator to the potential energy, because at the maximum extension all the energy is in the form of potential energy. If all the energy weren't in the form of potential energy at this point, the oscillator would have kinetic energy and momentum and could continue to extend further away from its rest position. Interestingly, as we show below, the wavefunctions of the quantum mechanical oscillator extend beyond the classical limit, i.e. beyond where the particle can be according to classical mechanics.

The lowest allowed energy for the quantum mechanical oscillator is called the zero-point energy, $E_0 = \frac{\hbar\omega}{2}$. Using the classical picture described in the preceding paragraph, this total energy must equal the potential energy of the oscillator at its maximum extension. We define this classical limit of the amplitude of the oscillator displacement as Q_0. When we equate the zero-point energy for a particular normal mode to the potential energy of the oscillator in that normal mode, we obtain

$$\frac{\hbar\omega}{2} = \frac{KQ_0^2}{2} \tag{6.4.7}$$

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 6.4.8 which is

$$\omega = \sqrt{\frac{K}{M}} \tag{6.4.8}$$

Solving for Q0 in Equation 6.4.7 by substituting for ω and rearranging, we obtain the very interesting result

$$Q_0^2 = \frac{\hbar\omega}{K} = \frac{\hbar}{M\omega} = \frac{\hbar}{\sqrt{KM}} = \beta^2 \tag{6.4.9}$$

Here we see that β, the parameter we introduced in Equation 6-20, is more than just a way to collect variables; β has physical significance. It is the classical limit to the amplitude (maximum extension) of an oscillator with energy $E_0 = \frac{\hbar\omega}{2}$. Because β has this meaning, the variable x gives the displacement of the oscillator from its equilibrium position in units of the maximum classically allowed displacement for the v = 0 state (lowest energy state). In other words, x = 1 means the oscillator is at this classical limit, and x = 0.5 means it is halfway there.

Exercise 6.4.24

The HCl 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 HCl 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?

The classical limit, Q_0, for the lowest-energy state is given by Equation 6.4.9; i.e., $Q_0 = \pm\beta$ or $x = \dfrac{Q_0}{\beta} = \pm 1$. Examination of the quantum mechanical wavefunction for the lowest-energy state reveals that the wavefunction Ψ0(x) extends beyond these points. Higher energy states have higher total energies, so the classical limits to the amplitude of the displacement will be larger for these states.

Exercise 6.4.25

Mark x = +1 and x = - 1 on the graph for $|\psi_0(x)^2|$ in Figure 6.4.7 and note whether the wavefunction is zero at these points.

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 6.4.26

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.

The fact that a quantum mechanical oscillator has a finite probability to enter the classically forbidden region of space is a consequence of the wave property of matter and the Heisenberg Uncertainty Principle. A wave changes gradually, and the wavefunction approaches zero gradually as the potential energy approaches infinity.

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, the state with v = 0. The classically forbidden region is shown by the shading of the regions beyond Q0 in the graph you constructed for Exercise 6.4.26. The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region. To calculate this probability, we use

$$Pr[\text{forbidden}] = 1 - Pr[\text{allowed}] \tag{6.4.10}$$

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, Pr[allowed], to evaluate is

$$Pr[\text{allowed}] = 2\int_0^{Q_0} \psi_0^*(Q)\psi_0(Q)dQ \tag{6.4.11}$$

The factor 2 appears in Equation 6.4.11 from the symmetry of the wavefunction, which extends from $-Q_0 to + Q_0$. To evaluate the integral in Equation 6.4.11, use the wavefunction and do the integration in terms of x, Equation (6-29). Recall that for v = 0, Q = Q0 corresponds to x = 1. Including the normalization constant, Equation ??? produces

$$Pr[\text{allowed}] = \frac{2}{\sqrt{\pi}} \int_0^1 exp(-x^2) dx \tag{6.4.12}$$

The integral in Equation 6.4.12 is called an error function (ERF), and can only be evaluated numerically. Values can be found in books of mathematical tables or obtained with Mathcad. When the limit of integration is 1, ERF(l) = 0.843 and Pr[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 6.4.27

Numerically Verify that Pr[allowed] in Equation (6-39) equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

6.5: Quantum Mechanical Tunneling

Quantum mechanical tunneling is a consequence of the fact that a vibrating molecule has a significant probability to be in the classically forbidden region of space, i.e. beyond the classical limit. Suppose that rather than having a harmonic potential for the displacement of an atom from its equilibrium position, one has a double well potential with a finite potential-energy barrier between the two sides as shown in Figure $6.5.1$.

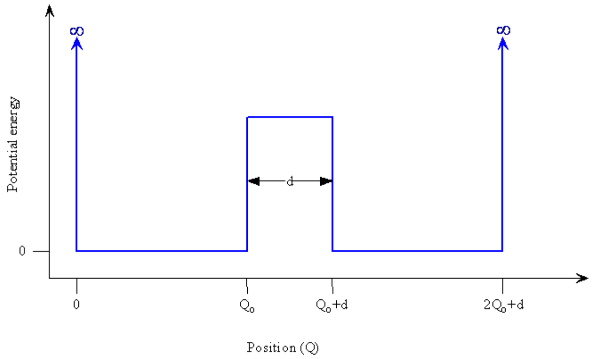

Figure $6.5.1$: A double-well potential. The potential energy of an atom as a function of its position in space.

How might the wavefunctions for the position of the atom, or other particle such as an electron, with this type of potential look? A reasonable starting approximation would be to consider a harmonic oscillator wavefunction in each well. Because of their asymptotic approach to zero, the functions extend into the region of the barrier, i.e. into the classically forbidden region. These functions can even connect up with each other if the barrier is not too high or too wide. The connection of the two functions means that a particle starting out in the well on the left side has a finite probability of tunneling through the barrier and being found on the right side even though the energy of the particle is less than the barrier height. According to classical mechanics, the particle would be trapped on the left side if it did not have enough energy to go over the barrier. In quantum mechanics, the particle can tunnel through the barrier. An energy barrier does not necessarily restrict a quantum mechanical system to a certain region of space because the wavefunctions can penetrate through the barrier region. Tunneling has been proposed to explain electron transfer in some enzyme reactions and to account for mutations of DNA base pairs as a hydrogen atom in a hydrogen bond tunnels through the barrier from the electronegative atom of one base to the electronegative atom in the partner base.

What do we mean when we say that something like tunneling occurs quantum mechanically but not classically? We mean that classical mechanics is not an adequate description of the way the atomic world behaves. Classical mechanics works fine for macroscopic objects but not for nanoscopic objects. The importance of the mass and Planck's constant in determining whether an object can be described classically or not can be illustrated by the Uncertainty Principle. When the Uncertainty Principle,

$$\Delta x \Delta p > \frac{\hbar}{2}, \tag{6.5.1}$$

and the relationship between momentum and wavelength,

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

was applied to macroscopic objects like a baseball. It was found that the uncertainties and wavelength are so small compared to macroscopic dimensions that the wave properties of these objects are not detectable. Large masses can be described classically because Planck's constant is so small. The situations examined in the following paragraphs consider tunneling along these same lines.

We first look at the case of a proton. Is it reasonable to think that a proton can tunnel through a potential barrier? Consider a hydrogen bond between two paired bases in a nucleic acid helix and the resulting double-well potential-energy function similar to the one illustrated in Figure $6.5.1$.

Exercise 6.5.1

Sketch potential-energy functions for each of the hydrogen bonds in a guanine-cytosine base pair. Describe how your drawings reflect the nature of the base pairing shown in standard biochemistry textbooks.

We want to compare Q_0, the maximum classical displacement of the proton, with the separation of the potential wells, d, which we take as the width of the potential barrier at half its height. If d is much larger than Q_0, tunneling would not be probable because the wavefunction, which falls off very rapidly (exponentially), would become extremely small, essentially zero within the barrier as Q increases beyond Q_0. On the other hand, if d is not too much larger than Q_0, then the wavefunction will still have a significant non-zero value at the further side of the barrier and tunneling will be probable.

The rate at which the wavefunction approaches zero in the barrier region depends upon both the *height* and *width* of the barrier. As the barrier height increases, the width must become smaller for tunneling to be significant, but we can still get a feeling for whether tunneling is reasonable or not by comparing the separation of the potential wells with Q_0. For a hydrogen-bonded proton between two electronegative centers, d has been calculated to be approximately 0.1 nm (about 10% of a N-H bond length) and $Q_0^2 = \frac{\hbar}{m\omega}$ giving Q_0 = 0.01 nm. Since d is only 10 times larger than Q0 in this estimate, tunneling cannot be excluded as a real possibility.

Exercise 6.5.2

Obtain a value for Q_0 by using the mass of a proton and a characteristic vibrational frequency for a NH or OH bond (3300 cm^{-1}).

Exercise 6.5.3

Identify what happens to Q_0, the ratio $\frac{d}{Q_0}$, and your expectations for tunneling as the mass of the particle increases, e.g. if the proton were replaced by a deuteron.

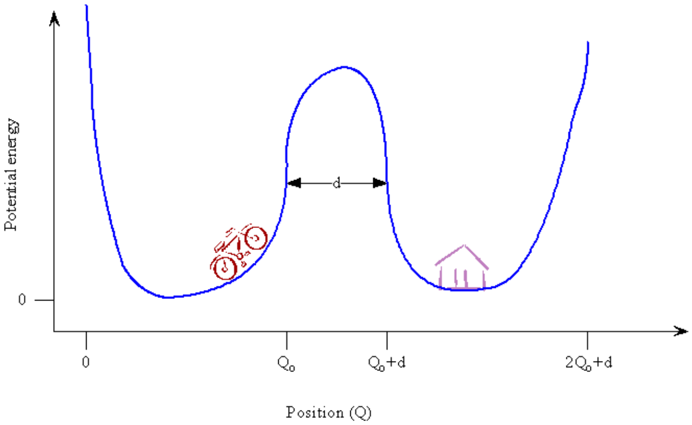

Figure 6.5.2: A macroscopic example of a double-well potential.

Now consider a macroscopic system for comparison. Assume that you and your bicycle are stuck in a valley one hill away from your home in the next valley. You are in your lowest energy state, and you have 1000 m to go. What conclusion do we reach if we apply the above estimates for the probability of tunneling to you? We want to use $Q_0^2 \approx \frac{\hbar}{m\omega}$ to estimate your maximum displacement from the bottom of the valley and compare it to the distance to your home valley. For example, we can give you a mass of 100 kg and a frequency of oscillation between the two hills that form the valley of ω = 2π / 100 s. Your mass is 29 orders of magnitude (factors of ten) greater than that of a proton, and your oscillation frequency is 16 orders of magnitude smaller than that of a proton. This frequency means that it takes 100 s for you to complete one cycle rolling back and forth between the two hills that form the valley in which you are located. The larger mass dominates the smaller frequency with the result that your Q0 is 10^{-18} m, and the hill you need to cross is 1000 m wide, $d \approx 10^3$ m. A bicyclist in the lowest energy quantum state has a maximum displacement of 10-18 nm (10^{-27} m) and a distance to tunnel of about 103 m. Tunneling under these conditions is not a probable event because the distance to go is so much larger than the maximum displacement. A bicyclist wouldn't have a chance in a lifetime of getting home without generating sufficient energy to ride over the hill. What would happen if Planck's constant were much larger? If h were 10^7 J s, then tunneling also would be important for massive objects like people, and it would make our lives easier and more interesting.

Exercise 6.5.4

Verify that if h = 10^7 J s then tunneling would be important for people.

6.6: Harmonic Oscillator Selection Rules

Photons can be absorbed or emitted, and the harmonic oscillator can go from one vibrational energy state to another. Which transitions between vibrational states are allowed? If we take an infrared spectrum of a molecule, we see numerous absorption bands, and we need to relate these bands to the allowed transitions involving different normal modes of vibration.

The selection rules are determined by the transition moment integral.

$$\mu_T = \int_{-\infty}^{\infty} \psi_{v'}^*(Q)\hat{\mu}(Q)\psi_v(Q)dQ \tag{6.6.1}$$

To evaluate this integral we need to express the dipole moment operator, $\hat{\mu}$, in terms of the magnitude of the normal coordinate Q. The dipole moment operator is defined as

$$\hat{\mu} = \sum_{electrons} er + \sum_{nuclei} qR \tag{6.6.2}$$

where the two sums are over all the electrons and nuclei and involve the particle charge (-e or q) multiplying the position vector (r or R). We can obtain this dipole moment operator in terms of the magnitude of the normal coordinate, Q, in a simple way by using a Taylor series expansion for the dipole moment.

$$\mu(Q) = \mu_{Q=0} + \left(\frac{d\mu(Q)}{dQ}\right)_{Q=0} Q + \left(\frac{d^2\mu(Q)}{dQ^2}\right)_{Q=0} Q^2 + \cdots \tag{6.6.3}$$

Retaining only the first two terms and substituting into Equation 6.6.1 produces

$$\mu_T = \mu_{Q=0} \int_{-\infty}^{\infty} \psi_{v'}(Q)\psi_v(Q)dQ + \left(\frac{d\mu(Q)}{dQ}\right)_{Q=0} \int_{-\infty}^{\infty} Q\psi_{v'}^*(Q)\psi_v(Q)dQ \tag{6.6.4}$$

In the above expressions, μQ = 0 is the dipole moment of the molecule when the nuclei are at their equilibrium positions, and $\left(\frac{d\mu(Q)}{dQ}\right)_{Q=0}$ 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 Q and not a higher power of Q in Equation 6.6.3. Both μ and $\left(\frac{d\mu(Q)}{dQ}\right)_{Q=0}$ are moved outside of the integral because they are constants that no longer depend on Q because they are evaluated at Q = 0.

The integral in the first term in Equation6.6.4) is 0 because any two harmonic oscillator wavefunctions are orthogonal. The integral in the second term of Equation is zero except when $v' = v \pm 1$ as demonstrated in Exercise $6.6.32$ Also note that the second term is zero if

$$\left(\frac{d\mu(Q)}{dQ}\right)_{Q=0} = 0 \tag{6.6.5}$$

Exercise 6.6.1

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation 6.6.4 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 6.6.5 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.

$$\text{For allowed transitions} \Delta v = \pm 1 \tag{6.6.6}$$

Consider oxygen and nitrogen molecules. Because they are symmetrical, their dipole moments are zero, μ = 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, $\dfrac{d\mu(Q)}{dQ} = 0$. Consequently, oxygen and nitrogen cannot absorb infrared radiation as a result of vibrational motion.

This result has important practical consequences. Chemists can do infrared spectroscopy in the air. The spectrometer need not be evacuated to eliminate the absorption due to oxygen and nitrogen. This situation greatly simplifies the spectrometer design, lowers the cost of the instrument, and makes it more convenient to use.

Exercise 6.6.2

Explain why the absorption coefficient in Beer's Law is larger for some normal modes than for others.

The case $v' = v + 1$ corresponds to going from one vibrational state to a higher energy one by absorbing a photon with energy hν. The case v' = v − 1 corresponds to a transition that emits a photon with energy hν. 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 ???). 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.

$$\Delta E = E_{final} - E_{initial} = h v_{photon} = \hbar \omega_{oscillator} \tag{6.6.7}$$

In a perfect harmonic oscillator, the only possibilities are $\Delta = \pm 1$; all others are forbidden. This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of only one strong line, as shown in Figure 6.6.1, because as you showed in your energy level diagram in Exercise 6.6.20, the energy levels are equally spaced in the harmonic oscillator model. If the levels were not equally spaced, then transitions from v = 0 to 1 and from v = 1 to 2, etc. would occur at different frequencies.

The actual 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, Δv = 2, generally appears at a frequency slightly less than twice that of the fundamental, i.e. the frequency due to the Δv = 1 transition.

Exercise 6.6.2

Compute the approximate transition frequencies in wavenumber units for the first and second overtone transitions in HCl given that the fundamental is at 2886 cm^{-1}.

Also note that hot bands, those involving transitions from thermally populated states having v>0, can be present in the spectra. The number density of molecules, nv, in a particular energy level, v, at any temperature is proportional to the Boltzmann factor.

$$n_v \propto e^{-\frac{E_v}{k_B T}} \tag{6.6.8}$$

For molecules at room temperature or below, the v = 0 vibrational state is the one that is most heavily populated.

Exercise 6.6.3

Using the Boltzmann distribution, determine the ratio of the number of HCl molecules in the v = 1 vibrational state compared to the v = 0 state at room temperature. Comment on the expected intensity of the hot-band transition from the v = 1 state at room temperature. At what temperature might the hot band for HCl have an intensity that is 25% of the fundamental band at that temperature?

These considerations explain the low-resolution absorption spectrum of a diatomic molecule shown in Figure 6.6.1. Such spectra are simple because only the fundamental (v = 0 to 1) is intense. The overtones (v = 0 to v > 1) are very weak and are not shown in the spectrum. They only appear at all because the actual molecular potential is slightly anharmonic, making the harmonic oscillator model and selection rules only an approximation. This anharmonicity becomes more important for the higher energy states (v >> 0) that involve larger displacements from equilibrium, i.e. larger values of Q. We conclude that the harmonic oscillator approximation is very good because the forbidden overtone transitions are indeed weak.

Generally each intense peak that is seen in an infrared spectrum of a polyatomic molecule corresponds to the fundamental transition of a different normal mode because the overtones are forbidden in the harmonic approximation and hot bands are weak at room temperature. However in a polyatomic molecule, combination bands that involve the excitation of two normal modes also can be intense. They arise from a higher order term in the expansion of μ(Q); namely,

$$\left(\frac{\partial^2 \mu}{\partial Q_A \partial Q_B}\right)_{Q=0} Q_A Q_B \tag{6.6.9}$$

This derivative gives the change in the dipole moment due to the motion of two normal modes simultaneously.

6.S: Vibrational States (Exercises)

Q6.1

Demonstrate for one or two cases that the harmonic oscillator wavefunctions form an orthonormal set.

Q6.2

Show that the behavior of the harmonic oscillator for the v = 0 state is consistent with the Heisenberg Uncertainty Principle by computing the product of the standard deviations for displacement and momentum, i.e. $\sigma_Q \sigma_P$. You can express $\sigma_Q \sigma_P$ in terms of <Q>,

, <Q2>, and <p2>.

Q6.3

Complete the following:

a. For v = 0 vibrations of HF, HCl, and HBr compute the standard deviations for the displacements from equilibrium. The vibrational frequencies are given by 4139, 2886, and 2559 cm^{-1}.
b. Use the standard deviation in the displacement as well as the classical maximum possible displacement (Q_0) to characterize the ground state vibrational amplitude and compare these quantities to an estimate of the bond lengths in these molecules obtained from the atomic covalent radii for H (37 pm), F (72 pm), Cl (99 pm), and Br (114 pm).
c. What percent of the original bond length are these characteristic displacements? Is this bond length changing significantly during a vibration?
d. What molecular properties determine the vibrational amplitude? How does the vibrational amplitude depend on these properties?
e. Explain the differences in the vibrational amplitudes for these three molecules.

Q6.4

Complete the following:

1. Use the harmonic oscillator model to describe the vibration of nitrogen, and prepare a Mathcad graph showing the potential energy function. The vibrational frequency is given by 2360 cm^{-1}.
2. Mark the energy of the v = 8 state on your graph of the potential energy with a horizontal line. Prepare another graph showing the v = 8 harmonic oscillator wavefunction and probability density function.
3. On both graphs, mark the classical limit to the displacement of the oscillator with the energy in (b) from its equilibrium position.
4. Describe the probability of finding the oscillator at various distances away from the equilibrium position. How does the quantum mechanical oscillator differ from the classical oscillator in this regard?

Q6.5

Complete the following

a. Do unwanted bands due to oxygen, nitrogen, water, and carbon dioxide in the air appear in infrared spectra of chemical samples?
b. How many normal modes are there for H_2O? How many of these are infrared active?
c. How many normal modes and infrared active modes are there for CO_2?
d. Look up the vibrational frequencies of water and carbon dioxide in library books on spectroscopy and make sketches of the low-resolution IR spectra that you would expect. Include overtone, combination, and hot bands. Key references on molecular vibrations are Molecular Vibrations by Wilson, Decius, and Cross and Infrared and Raman Spectra by Herzberg.

Q6.6

1. Complete the following:
    1. Compare the potentials and the wavefunctions for the harmonic oscillator and the particle in a box. Summarize the similarities and the differences.

2. Is the harmonic oscillator selection rule Δv = ±1 almost or approximately true also for the particle in a box?
3. Why would you expect this selection rule to be approximately valid or to fail completely for the particle in a box?

Q6.7

Another model that often is applied to molecules is the Morse oscillator. The potential energy for the Morse oscillator has the following form:

$$V(x) = D_e(1 - e^{-\beta x})^2, \tag{6.S.1}$$

where x is the displacement of the oscillator from its equilibrium position, and D_e and β are constants or parameters.

a. At what value of x is $V(x)$ a minimum?
b. What is $V(x)$ when x becomes very large?
c. What happens to $V(x)$ as x becomes a large negative number?
d. Based on your answers to a, b, and c, sketch a graph of $V(x)$ vs x.
e. From your graph, identify the parameter in the Morse potential that you would call the equilibrium dissociation energy.
f. How does the equilibrium dissociation energy in the Morse potential differ from the actual bond dissociation energy at 0 K?
g. Mark, using arrows and labels, the equilibrium dissociation energy and the bond dissociation energy on your graph.
h. Expand $V(x)$ in a power series and show that the force constant for a corresponding harmonic potential is given by $k = 2D_e\beta^2$.
i. The parameters D_e and β generally are evaluated for specific molecules from observed vibrational frequencies. Using values obtained for HCl ($D_e = 7.31 \times 10^{-19}$ J, β= $1.82 \times 10^{10} m^{-1}$), plot on the same graph both the Morse potential and the harmonic potential for HCl. In making your plot, use $x = R - R_e$, where R is the internuclear separation, and Re is the equilibrium bond length, 127.5 pm.
j. What insights, especially regarding the idea of anharmonicity, do you gain by comparing the plots that you constructed in the previous part (above) of the Morse potential and the harmonic potential?

Q6.8

1. Sketch a double well potential for the hydrogen bond found between oxygen and nitrogen in a G-C base pair of DNA. On which side of the diagram is the nitrogen? Sketch the wavefunction with v = 0 for the N-proton bond. Draw a continuation of the wavefunction into the forbidden region and beyond into the oxygen side of the bond. How do you think the wavefunction on the oxygen side of the bond will look? Use the relative amplitudes as predicted by the probability distribution for the wavefunction to predict the likelihood for finding the proton on the oxygen side of the hydrogen bond. If the DNA double strand separated at just the moment when the proton was on the oxygen side of the molecule, and this situation were stable for a period of time that is longer than required for most biochemical reactions, what might be the consequences for replication or transcription using this mutated strand of DNA? You may need to review some biochemistry, especially the structures of hydrogen-bonded base pairs to complete this problem.

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6.S: Vibrational States (Summary)

In this chapter we developed the quantum mechanical description of the harmonic oscillator for a diatomic molecule and applied it to the normal modes of molecular vibrations. We examined the functional form of the wavefunctions and the associated energy level structure. We can calculate expectation values (average values) and standard deviations for the displacement, the momentum, the square of the displacement, and the square of the momentum. The wavefunctions, which form an orthonormal set, were used to determine electric dipole selection rules for spectroscopic transitions, and in the problems at the end of the chapter, they are used to calculate several properties of the harmonic oscillator. The phenomenon of quantum mechanical tunneling through a potential-energy barrier was introduced and its relationship to real chemical phenomena was illustrated by consideration of hydrogen bonding in DNA. We finally looked at the nature of low-resolution IR spectra and introduced the anharmonicity concept to account for forbidden overtone transitions in spectra. The presence of combination bands in spectra was attributed to second derivative terms in the expansion of the dipole moment operator in terms of the normal coordinates. The simple harmonic oscillator model works well for molecules at room temperature because the molecules are in the lower vibrational levels where the effects of anharmonicity are small.

Self-Assessment Quiz

1. Write a definition of a normal vibrational mode.
2. Write a definition of a normal vibrational coordinate.
3. List the steps in a methodology for finding the normal vibrational coordinates and frequencies.
4. What is a harmonic oscillator?
5. How is the harmonic oscillator relevant to molecular properties?
6. Write the Hamiltonian operator for a one-dimensional harmonic oscillator.
7. What are the major steps in the procedure to solve the Schrödinger equation for the harmonic oscillator?
8. What are the three parts of a harmonic oscillator wavefunction?
9. How is the quantum number v produced in solving the Schrödinger equation for the harmonic oscillator?
10. What are the allowed energies for a quantum harmonic oscillator?
11. What determines the frequency of a quantum harmonic oscillator?
12. What information about a molecular vibration is provided by the harmonic oscillator wavefunction for a normal coordinate?
13. Sketch graphs of the harmonic oscillator potential energy and a few wavefunctions.
14. Draw the harmonic oscillator energy level diagram.
15. Why is the lowest possible energy of the quantum oscillator not zero?
16. Compute the approximate energy for the first overtone transition in HBr given that the fundamental is 2564 cm-1.
17. If a transition from vibrational energy level v = 3 to v = 4 were observed in an infrared spectrum, where would that spectral line appear relative to the one for the transition from v = 0 to v = 1?
18. What is the harmonic oscillator selection rule for vibrational excitation by infrared radiation?
19. Explain why the infrared absorption coefficient is larger for some normal modes than for others.
20. Why is it possible for quantum particles to tunnel through potential barriers?
21. What are the values of integrals like $\int\limits_{-\infty}^{\infty} \psi_n^*(Q)\psi_m(Q)dQ$ using harmonic oscillator wavefunctions?

CHAPTER OVERVIEW

7: Rotational States

Molecules rotate as well as vibrate. Transitions between rotational energy levels in molecules generally are found in the far infrared and microwave regions of the electromagnetic spectrum.

7.1: Introduction to Rotation

Molecules rotate as well as vibrate. Transitions between rotational energy levels in molecules generally are found in the far infrared and microwave regions of the electromagnetic spectrum. A rotational spectrum of a simple diatomic molecule is illustrated in Figure $7.1.1$ and quantitative information about this spectrum is given in Table $7.1.2$ near the end of this chapter. Notice that the lines are nearly equally spaced and vary in intensity. In this chapter, we will see that the magnitude of the molecule's moment of inertia causes rotational transitions to lie in these spectral regions. We also will learn why the lines are nearly equally spaced and vary in intensity. Such spectra can be used to determine bond lengths, and even bond angles in polyatomic molecules.

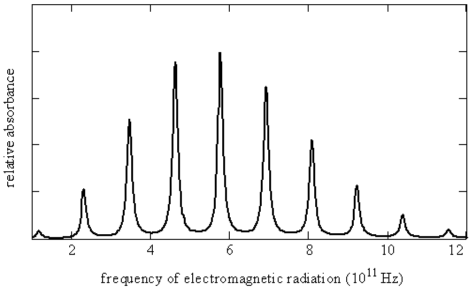

Figure $7.1.1$: The rotation spectrum of $^{12}C^{16}O$ at 40 K.

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; see Figures $7.1.2$ and $7.1.3$. The 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 a rotation.

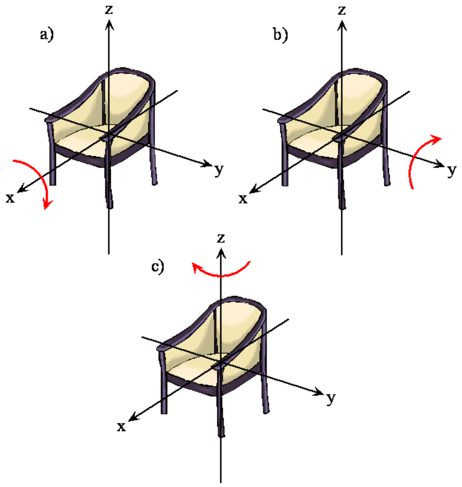

Figure $7.1.2$: Cartesian rotations of a chair. Rotations about the a) x axis, b) y axis and c) z axis.

In this chapter we consider the case of a diatomic molecule. Solving the Schrödinger equation for rotational motion will give us the rotational energies and angular momenta, the wavefunctions associated with these energy levels and angular momenta, and the quantum numbers that serve to label the energy levels, angular momenta, and wavefunctions. The quantum numbers appear because of boundary conditions imposed on the wavefunctions.

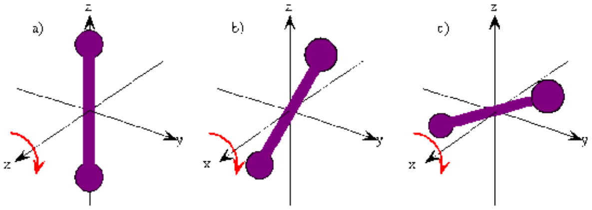

Figure $7.1.3$: Rotation of a diatomic molecule about the x axis.

We will find that the energy of rotation is quantized. This quantization and the selection rules for spectroscopic transitions between the various energy levels lead to the absorption lines seen in the rotational spectrum in Figure $7.1.1$. The angular momentum also is quantized, which means that only certain values of the angular momentum are possible, and, when some direction is uniquely defined by an electric or magnetic field, only certain orientations of the rotating molecule in space are possible. This restriction on orientation is called space quantization.

As you can see in Figure $7.1.4$ and Exercise $7.1.1$, the angular momentum vector for a classical rotating system is perpendicular to the plane of rotation. The direction of the vector is given by applying the right-hand rule to the direction of rotation. The orientation of a classical rotating diatomic molecule therefore is defined by the plane in which the internuclear axis lies during rotation or by the direction of the angular momentum vector, which is perpendicular to this plane. The direction of the angular momentum vector is called the axis-of-rotation. Angular momentum vectors are useful because they provide a shorthand way to represent the classical motion of a rotating diatomic molecule. Given only an angular momentum vector, it is possible to reconstruct the direction and plane of rotation in addition to the magnitude of the angular momentum, which is in turn a function of the reduced mass, bond length, and angular velocity of the rotating molecule.

The material in this chapter is very important because the wavefunctions obtained by solving the Schrödinger equation for rotational motion also will be used to describe the hydrogen atom in the next chapter. The hydrogen atom wavefunctions, in turn, are the key to understanding atomic and molecular structure and chemical reactivity.

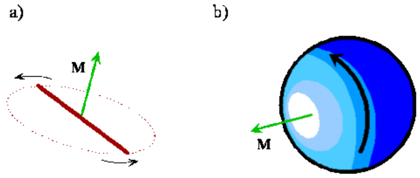

Figure $7.1.4$: The angular momentum vector (M) for a rotating system is perpendicular to the plane of rotation, parallel to the axis of rotation.

Exercise $7.1.1$

To visualize these different orientations and the axis-of-rotation, use your pencil to represent the internuclear axis of a diatomic molecule, rotate it in different planes and align another pencil along the axis-of-rotation in each case.

7.2: The Hamiltonian Operator for Rotational Motion

We start our consideration of rotational motion with a system consisting of two atoms connected by a rigid bond, shown in Figure 7.2.1. Translational motion can be separated from rotational motion if we specify the position of the center of mass by a vector R, and the positions of each atom relative to the center of mass by vectors r_1 and r_2. The positions of the atoms then are given by $R+r_1$ and $R+r_2$. The motion of the two particles is described as the translational motion of the center of mass plus the rotational motion of the two particles around the center of mass.

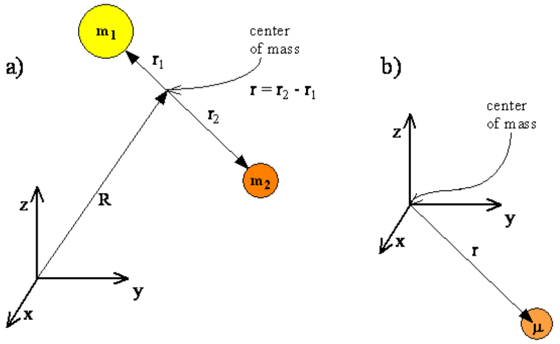

Figure 7.2.1 Diagrams of the coordinate systems and relevant vectors for a) a diatomic molecule with atoms of mass m_1 and m_2 and b) the equivalent reduced particle of reduced mass μ.

The quantum mechanical description of translational motion, which corresponds to a free particle with total mass m_1+m_2, was described in Chapter 5. Since translational motion and rotational motion are separable, i.e. independent, the translational and rotational energies will add, and the total wavefunction will be a product of a translational function and a rotational function.

Exercise 7.2.1

What do you need to know in order to write the Hamiltonian for the rigid rotor?

We start our quantum mechanical description of rotation with the Hamiltonian:

$$\hat{H}=\hat{T}+\hat{V} \tag{7.2.1}$$

To explicitly write the components of the Hamiltonian operator, first consider the classical energy of the two rotating atoms and then transform the classical momentum that appears in the energy equation into the equivalent quantum mechanical operator. In the classical analysis the rotational motion of two particles separated by a distance r can be treated as a single particle with reduced mass μ at a distance r from the center of rotation, which is the center of mass.

The kinetic energy of the reduced particle is

$$T=\frac{p^2}{2\mu} \tag{7.2.2}$$

where

$$P^2=P_x^2+P_y^2+P_z^2 \tag{7.2.3}$$

Transforming T to a quantum-mechanical operator yields

$$\hat{T}=-\frac{\hbar^2\nabla^2}{2\mu} \tag{7.2.4}$$

where ∇^2 is the Laplacian operator.

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \tag{7.2.5}$$

The rigid rotor model does not include the presence of electric or magnetic fields, or any other external force. Since there are no forces acting on the rotating particle, the potential energy is constant, and we can set it to zero or to any other value because only changes in energy are significant, and there is no absolute zero of energy.

$$\hat{V} = 0 \tag{7.2.6}$$

Therefore, the Hamiltonian operator for the Schrödinger equation describing this system consists only of the kinetic energy term.

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2 \nabla^2}{2\mu} \tag{7.2.7}$$

In Equation 7.2.5 we wrote the Laplacian operator in Cartesian coordinates. Cartesian coordinates (x, y, z) describe position and motion relative to three axes that intersect at 90º. They work fine when the geometry of a problem reflects the symmetry of lines intersecting at 90º, but the Cartesian coordinate system is not so convenient when the geometry involves objects going in circles as in the rotation of a molecule. In this case, spherical coordinates $(r,\ \theta,\ \phi)$ shown in Figure $7.2.2$ are better.

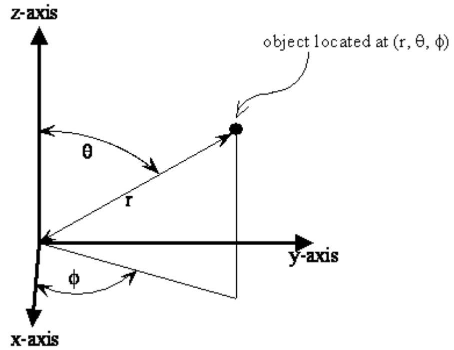

Figure $7.2.2$: Location of a point in three-dimensional space using both Cartesian and spherical coordinates. The variable ranges given in Equation define all of space in the spherical coordinate system.

The limits of these coordinnates are

- $0 \le r < \infty$
- $0 \le \theta < \pi$
- $0 \le \varphi < 2\pi$

Spherical coordinates are better because they reflect the spherical symmetry of a rotating molecule. Spherical coordinates have the advantage that motion in a circle can be described by using only a single coordinate. For example, as shown in Figure $7.2.2$, changing φ describes rotation around the z-axis. Changing θ also is very simple. It describes rotation in any plane containing the z-axis, and r describes the distance from the origin for any value of θ and φ.

This situation is analogous to choosing Cartesian or spherical coordinates to locate rooms in a building. Cartesian coordinates are excellent if the building is designed with hallways intersecting at 90º and with an elevator running perpendicular to the floors. Cartesian coordinates would be awkward to use for addresses in a spherical satellite space station with spherical hallways at various distances from the center.

Exercise 7.2.2

Imagine and draw a sketch of a spherical space station with spherical shells for hallways. Show how three spherical coordinates can be used to specify the address of a particular room in terms of values for r, θ, and φ.

In order to use spherical coordinates, we need to express ∇^2 in terms of r, θ and θ and φ. The result of the coordinate transformation is

$$\nabla^2 = \frac{1}{r^2}\left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) \tag{7.2.8}$$

The Hamiltonian operator in spherical coordinates now becomes

$$\hat{H} = \frac{-\hbar^2}{2\mu r^2}[\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}] \tag{7.2.9}$$

This version of the Hamiltonian looks more complicated than Equation 7.2.7, but it has the advantage of using variables that are separable (see Separation of Variables). As you may recall, when the variables are separable, the Schrödinger equation can be written as a sum of terms, with each term depending only on a single variable, and the wavefunction solutions are products of functions that each depend on only one variable.

7.3: Solving the Rigid Rotor Schrödinger Equation

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 ϕ-function depending only on φ

$$\psi(\theta,\varphi)=\Theta(\theta)\Phi(\varphi) \tag{7.3.1}$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 7.3.2:

$$\hat{H}\psi(\theta,\varphi)=E\psi(\theta,\varphi) \tag{7.3.2}$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{\partial}{\partial r_0}r_0^2\frac{\partial}{\partial r_0}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi)=E\Theta(\theta)\Phi(\varphi) \tag{7.3.3}$$

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 7.3.3, to give

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi)=E\Theta(\theta)\Phi(\varphi) \tag{7.3.4}$$

To begin the process of separating the variables in Equation 7.3.4, multiply each side of the equation by $\frac{2I}{\hbar^2}$ and $\frac{-\sin^{\theta}}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi)=\frac{-2IE\sin^2\theta}{\hbar^2} \tag{7.3.5}$$

Simplify the appearance of the right-hand side of Equation 7.3.5 by defining a parameter λ:

$$\lambda=\frac{2IE}{\hbar^2} \tag{7.3.6}$$

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 7.3.6.

Inserting λ, evaluating partial derivatives, and rearranging Equation 7.3.5 produces

$$\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta\right)\Theta(\theta)\right]=-\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) \tag{7.3.7}$$

Exercise 7.3.1

Carry out the steps leading from Equation 7.3.5 to Equation 7.3.7. Keep in mind that, if y is not a function of x,

$$\frac{dy}{dx}=y\frac{d}{dx} \tag{7.3.8}$$

Equation 7.3.7 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^2 because soon we will need the square root of it. The two differential equations to solve are the θ -equation

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta-m^2\right)\Theta(\theta)=0 \tag{7.3.9}$$

and the φ -equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m^2\Phi(\varphi)=0 \tag{7.3.10}$$

The partial derivatives have been replaced by total derivatives because only a single variable is involved in each equation.

Exercise 7.3.2

Show how Equations 7.3.9 and 7.3.10 are obtained from Equation 7.3.7.

The φ-equation is similar to the Schrödinger equation for the free particle. Since we already solved this differential equation in Chapter 5, we immediately write the solutions:

$$\Phi_m(\varphi)=Ne^{\pm im\varphi} \tag{7.3.11}$$

Exercise 7.3.3

Substitute Equation 7.3.11 into Equation 7.3.10 to show that it is a solution to that differential equation.

The normalization condition, Equation 7.3.12, is used to find a value for N that satisfies Equation 7.3.11.

$$\int_0^{2\pi}\Phi^*(\varphi)\Phi(\varphi)d\varphi=1 \tag{7.3.12}$$

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 7.3.4

Use the normalization condition, Equation 7.3.11 to show that

$$N=(2\pi)-\frac{1}{2}. \tag{7.3.13}$$

Values for m are found by using a **cyclic boundary condition**. The cyclic boundary condition means that since φ and $\varphi+2\varphi$ refer to the same point in three-dimensional space, $\Phi(\varphi)$ must equal $\Phi(\varphi+2\varphi)$, i.e.

$$e^{im\varphi}=e^{im(\varphi+2\pi)} \tag{7.3.14}$$

$$=e^{im\varphi}e^{im2\pi} \tag{7.3.15}$$

For the equality in Equation 7.3.15 to hold, $e^{im2\pi}$ must equal 1, which is true only when

$$m=\cdots,-3,-2,-1,0,1,2,3,\cdots \tag{7.3.16}$$

In other words m can equal any positive or negative integer or zero.

Exercise 7.3.5

Use Euler's Formula to show that $e^{im2\pi}$ equals 1 for m equal to zero or any positive or negative integer.

Thus, the Φ function is

$$\Phi_m(\varphi)=(2\pi)^{-1/2}e^{\pm im\varphi} \tag{7.3.17}$$

$$\text{with } m=0,\pm1,\pm2,\cdots \tag{7.3.18}$$

Finding the $\Theta(\theta)$ functions that are solutions to the θ-equation, Equation 7.3.9, is a more complicated process. Solutions are found to be a set of power series called Associated Legendre Functions, 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 7.3.1.

Table 7.3.1: Spherical Harmonic Wavefunctions

m	J	$\Theta_J^m(\theta)$	$\Phi(\varphi)$	$Y_J^m(\theta,\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
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 7.3.7 be given by

$$\lambda = J(J+1) \tag{7.3.19}$$

where

$$J \geq |m| \tag{7.3.20}$$

J can be 0 or any positive integer greater than or equal to m. Each pair of values for the quantum numbers, J and m, identifies a rotational state and a wavefunction. For clarity in remembering that J controls the allowed values of m, m is often referred to as m_J, and we will now use that notation.

The combination of Equations 7.3.6 and 7.3.19 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2\lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{7.3.21}$$

Exercise 7.3.6

Compute the energy levels for a rotating molecule for J = 0 to J = 5 using units of $\frac{\hbar^2}{2I}$.

Using Equation 7.3.21, you can construct a rotational energy level diagram. For simplicity, use energy units of $\frac{\hbar^2}{2I}$. 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.

The next energy level is $J=l$ 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. These states are discussed in detail in Sections

7.3 and 7.4. 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 $J = l$ energy level is 3 because there are three states with the energy $\frac{2\hbar^2}{2I}$.

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.

Exercise 7.3.7

For $J = 0$ to $J = 5$, identify the degeneracy of each energy level and the values of the mJ quantum number that go with each value of the J quantum number. Construct a rotational energy level diagram (see Drawing Energy Level Diagrams) including J = 0 through 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.

A wavefunction that is a solution to the rigid rotor Schrödinger equation (defined in Equation 7.3.1) can be written as a single function Yθ, φ), which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{7.3.22}$$

The spherical harmonic wavefunction is labeled with mJ 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 Table 7.3.1 plots of some of the θ-functions are shown in Figure 7.3.1.

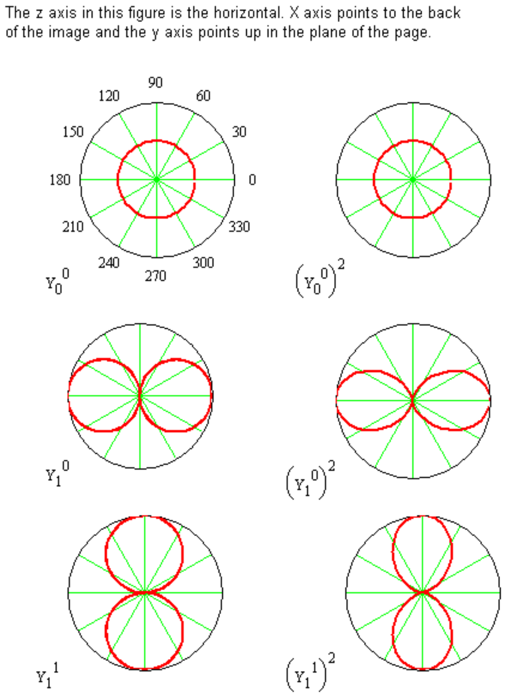

Figure 7.3.1: Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

The two-dimensional space for a rigid rotor is defined as the surface of a sphere of radius r_0, as shown in Figure 7.3.2.

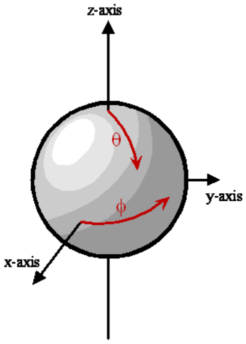

Figure $7.3.2$: Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

The probability of finding the internuclear axis at specific coordinates θ_0 and φ_0 within an infinitesimal area ds on this curved surface is given by

$$Pr\left[\theta_0,\varphi_0\right]=Y_J^{m_J*}(\theta_0,\varphi_0)Y_J^{m_J}(\theta_0,\varphi_0)ds \tag{7.3.23}$$

where the area element ds is centered at θ_0 and φ_0. 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, and in spherical coordinates the area element used for integrating θ and φ is

$$ds=\sin\theta d\theta d\varphi \tag{7.3.24}$$

Exercise $7.3.8$

Use calculus to evaluate the probability of finding the internuclear axis of a molecule described by the $J=1$, $m_J=0$ wavefunction somewhere in the region defined by a range in θ of 0° to 45°, and a range in of 0° to 90°. Note that a double integral will be needed. Sketch this region as a shaded area on Figure $7.3.1$.

Consider the significance of the probability density function by examining the J = 1, mJ = 0 wavefunction. The Spherical Harmonic for this case is

$$Y_1^0=\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta \tag{7.3.25}$$

The polar plot of $(Y_1^0)^2$ is shown in Figure $7.3.1$. For $J=1$ and $m_J=0$, the probability of finding the internuclear axis is independent of the angle φ from the x-axis, and greatest for finding the internuclear axis along the z-axis, but there also is a probability for finding it at other values of θ as well. So, although the internuclear axis is not always aligned with the z-axis, the probability is highest for this alignment. Also, since the probability is independent of the angle φ, the internuclear axis can be found in any plane containing the z-axis with equal probability.

The $J=1$, $m_J=0$ function is 0 when θ = 90°. Therefore, the entire xy-plane is a node. This fact means the probability of finding the internuclear axis in this particular horizontal plane is 0 in contradiction to our classical picture of a rotating molecule. In the classical picture, a molecule rotating in a plane perpendicular to the xy-plane must have the internuclear axis lie in the xy-plane twice every revolution, but the quantum mechanical description says that the probability of being in the xy-plane is zero. This conclusion means that molecules are not rotating in the classical sense, but they still have some, but not all, of the properties associated with classical rotation. The properties they retain are associated with angular momentum.

Exercise $7.3.9$

For each state with $J=0$ and $J=1$, use the function form of the Y spherical harmonics and Figure $7.3.1$ to determine the most probable orientation of the internuclear axis in a diatomic molecule, i.e. the most probable values for θ and θ.

Exercise 7.3.10

Write a paragraph describing the information about a rotating molecule that is provided in the polar plot of $Pr[\theta, \theta]$ for the $J = 1$, $m_J = \pm 1$ state in Figure $7.3.1$. Compare this information to the classical picture of a rotating object.

7.4: Angular Momentum Operators and Eigenvalues

Angular momentum is a key component in the physical descriptions of rotating systems. It is important because angular momentum, just like energy and linear momentum, must be conserved in any process. Consequently angular momentum is used to derive selection rules for spectroscopic transitions, determine which states of atoms and molecules can be affected by various perturbations, and identify possible and forbidden mechanisms in chemical reactions. Rotational angular momentum also explains the splitting of spectral lines in electric and magnetic fields and the angular distributions of gas-phase reaction products.

Now that we have the rotational wavefunctions that describe the rotational states, we need the angular momentum operators that enable us to extract the angular momentum properties from the wavefunctions. In this section we develop the operators for total angular momentum and the z-component of angular momentum, and use these operators to learn about the quantized nature of angular momentum for a rotating diatomic molecule.

Since the energy of a rotating object is related to its total angular momentum M and moment of inertia I,

$$M^2 = 2IE \tag{7.4.1}$$

the quantization of energy arising from the quantum-mechanical treatment of rotation, given by Equation 7.4.1, means that the total angular momentum also is quantized.

$$M^2 = J(J+1)\hbar^2 \tag{7.4.2}$$

Consequently, J is called the rotational angular momentum quantum number. In the equation above, M^2 is a scalar quantity corresponding to the square of the length of the angular momentum vector, M. From this equation, we can learn something about the magnitude of the angular momentum of the rotating molecule, but nothing about the orientation.

Exercise 7.4.1

Show that the combination of Equations 7.4.1 and ??? lead to Equation 7.4.2.

Just as there is an operator for the energy, $\hat{H}$, there also is an operator for the square of the angular momentum. We can discover this operator if we make some substitutions and rewrite Equation ???. Start with Equation ???, and use the spherical harmonic function in place of the product function $\Theta(\theta)\psi(\varphi)$ to obtain

$$-\frac{\hbar^2}{2I}\left[\frac{\partial}{\partial r_0} r_0^2 \frac{\partial}{\partial r_0} + \frac{1}{\sin\theta}\frac{\partial}{d\partial}\sin\theta\frac{\partial}{d\partial} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] Y_J^{mJ}(\theta,\varphi) = EY_J^{mJ}(\theta,\varphi) \tag{7.4.3}$$

Multiplying both sides by 2I and then using Equation 7.4.1 to replace 2IE on the right-hand side with M^2 yields

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{d\partial}\sin\theta\frac{\partial}{d\partial} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] Y(\theta,\varphi) = M^2 Y(\theta,\varphi) \tag{7.4.4}$$

Equation 7.4.4 is an eigenvalue equation. The operator on the left operates on the spherical harmonic function to give a value for M^2, the square of the rotational angular momentum, times the spherical harmonic function. This operator thus must be the operator for the square of the angular momentum.

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{d\partial}\sin\theta\frac{\partial}{d\partial} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{7.4.5}$$

The spherical harmonics therefore are eigenfunctions of $\hat{M}^2$ with eigenvalues given by Equation 7.4.2, where J is the angular momentum quantum number. The magnitude of the angular momentum, i.e. the length of the angular momentum vector, $\sqrt{M^2}$, varies with the quantum number J. The classical interpretation of this fact is that the molecule rotates with higher angular velocity in a state with higher J since neither the mass nor the radius of rotation can change.

The m_J quantum number is associated with the φ-equation, Equation ???. Figure 7.4.8 shows that φ describes rotation about the z-axis. Since angular momentum results from rotation about an axis, it seems plausible that the mJ quantum number is related to the z-component of angular momentum. To demonstrate that this association of m with the z-component of angular momentum is indeed correct, we need to write an operator for the z-component of angular momentum. When we operate on the Φ function with this operator, we expect to get an eigenvalue for the z-component of angular momentum.

We create an angular momentum operator by changing the classical expression for angular momentum into the corresponding quantum mechanical operator. The classical expression for the z-component of angular momentum is

$$M_z = xp_y - yp_x \tag{7.4.6}$$

By substituting the equivalents for the coordinates and momenta we obtain

$$\hat{M}_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \tag{7.4.7}$$

After changing to spherical coordinates by using the chain rule and trigonometric identities , $\hat{M}_z$ becomes

$$\hat{M}_z = i\hbar \frac{\partial}{\partial \varphi} \tag{7.4.8}$$

Exercise 7.4.2

Start with $\dfrac{\partial}{\partial \varphi}$ and change to Cartesian coordinates by using the chain rule to prove that

$$\frac{\partial}{\partial \varphi} = x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}. \tag{7.4.9}$$

Exercise 7.4.3

Use the operator $\hat{M}_z$ to operate on the general form of the wavefunction $\phi_m(\varphi)$ given in Equation ???. Based on your result, what are the possible values for the z-component of the angular momentum?

In Exercise 7.4.15we did indeed produce an eigenvalue equation that tells us that the z-component of angular momentum is

$$M_z = m_J\hbar \tag{7.4.10}$$

The z-component of the angular momentum is very useful because it provides information about the orientation of the total angular momentum vector, M. The magnitude of the total angular momentum vector, M, can be determined from M^2, but it is only through the value of M_z that we know anything about the orientation of M.

Exercise 7.4.4

Determine the lengths of the angular momentum vectors, M, for $J = 0$, 1, and 2 and the lengths of their projections on the z-axis.

One might expect from classical mechanics to be able to obtain the other two components of angular momentum, M_x and M_y, as well. These components are the projections of the angular momentum vector onto the x- and y-axes. In order for the rigid rotor wavefunctions to be eigenfunctions of $\hat{M}_x$ and $\hat{M}_y$ as well as $\hat{M}_z$, these operators must commute with $\hat{M}_z$. They do not **commute**. Since the rigid rotor wavefunctions are not eigenfunctions of $\hat{M}_x$ and $\hat{M}_y$, we cannot obtain their eigenvalues, which is another way of saying that we cannot know anything about the x and y components of angular momentum. Only the z component of the angular momentum can be determined in the quantum mechanical system. This limitation is a manifestation of the Heisenberg Uncertainty Principle. Since we know M_z exactly (there is no uncertainty), we can have no knowledge of M_x or M_y (the uncertainty must be infinite). This conclusion means that the angular momentum vector can be pointing with equal probability anywhere on a circle around the z-axis, giving all possible projections on the x and y axes. See Figure 7.4.1 for an illustration with J = 1 and $m_J = -1$, 0, and +1.

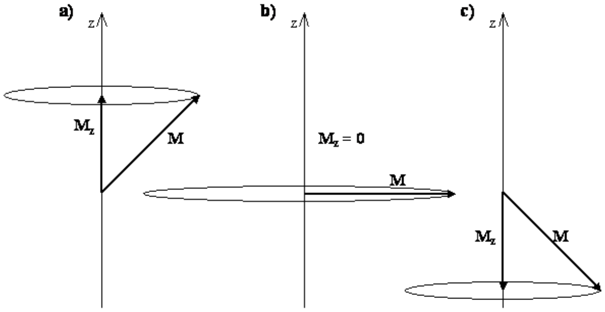

Figure 7.4.1: The three possible orientations of the angular momentum vector M relative to the z axis for the J = 1 states. a) $m_J = 1$, b) $m_J = 0$ and c) $m_J = -1$. The lengths of the vectors are determined by Exercise 7.4.16 and the orientation angle is discussed below. The end of the M vector can lie at any point on the circle perpendicular to the z axis.

As we saw in Exercise 7.4.16, the quantum mechanical results for a rotating diatomic molecule provide us with the magnitudes of the angular momentum vector for each state, along with the projection of the vector for that state along the z-axis. We can get no information about the projection of the vector on the other two axes. Using this collection of results and a little trigonometry, we can construct the quantitative physical picture of the angular momentum vector for each of the rotational states that is shown in Figure 7.4.1. If α is the angle between the angular momentum vector and the z-axis, then in general

$$\cos\alpha = \frac{m_J\hbar}{\sqrt{J(J+1)\hbar^2}} \tag{7.4.11}$$

where α can be obtained using the inverse cosine (arccos)

$$\alpha = arccos\left[\frac{m_J}{\sqrt{J(J+1)}}\right] \tag{7.4.12}$$

Exercise 7.4.5

Calculate the possible angles a $J = 1$ angular momentum vector can have with respect to the z-axis.

Exercise 7.4.6

What is the rotational energy and angular momentum of a molecule in the state with $J = 0$? Describe the rotation of a molecule in this state.

Classically the plane of rotation is perpendicular to the angular momentum vector. We can locate angular momentum vectors shown in Figure 7.4.1 for any rotational state by calculating the value of α using the appropriate quantum numbers for that state in Equation ???. If we then impose the classical interpretation of the angular momentum vector, we can construct a physical picture of a rotating diatomic molecule associated with the angular momentum vector for each rotational state, as discussed in the next section of this chapter.

7.5: Quantum Mechanical Properties of Rotating Diatomic Molecules

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?

Introduction

In isotropic space, meaning all directions are equivalent, any given molecule can have any orientation. The z-axis can have any orientation. Since we cannot distinguish different directions in isotropic space, different molecules will have different angular momentum vectors and all orientations of these vectors in space will be equally probable. Thus for example, even though our quantum mechanical description says that only three states with different angular momentum and internuclear axis orientations are allowed for the $J = 1$ energy level ($m_J = 0, 1, -1$), there are no practical consequences of this fact in isotropic space.

We can make space anisotropic by applying an external field, e.g. an electric field or a magnetic field. The field direction is a unique direction in space, and it is most convenient to assign the z-axis to that direction. Our rotational wavefunctions and operators implicitly are designed to have z be the special axis because of the relationships between the spherical coordinates and the Cartesian coordinates. The effects of external electric and magnetic fields on atomic and molecular spectra is an active area of research that has provided much insight into the properties of atoms and molecules and the use of quantum mechanics to describe them. For example, magnetic field effects on atomic spectra contributed to the discovery of electron spin and are discussed in the next chapter. These effects are known as Stark effects (electric field) and Zeeman effects (magnetic field) after the pioneers who discovered them.

For the ground state, J = 0, the rotational energy and angular momentum are zero. With no rotational energy or angular momentum, the molecule cannot be rotating! It may be vibrating and translating, but it is not rotating. What is its orientation in space? Examine the wavefunction in Figure $7.5.9$. All values of θ and φ are equally probable; we have no information about the orientation of the molecule in this state. The fact that there is no uncertainty in the angular momentum (it is exactly zero), and no information about the orientation (the uncertainty is infinite) is consistent with the Heisenberg Uncertainty Principle.

The space for a rigid rotor is defined by all the values for the variables θ and φ. Since a rigid rotor is not constrained to any region of this space by a potential boundary, the energy and angular momentum can be zero because the uncertainty in the location of the rotor in this space is infinite. The rotor can be anywhere; θ and φ can have any values. This situation is analogous to the free particle, where we knew the momentum exactly but had no knowledge of the particle's position. When J is different from 0, the uncertainty in the location of the rotor decreases. It is more likely to be found in some regions of space than in others. This decrease in uncertainty about the location of the rotor is accompanied by an increase in the uncertainty in the angular momentum as required by the Uncertainty Principle. We still know the magnitude of the angular momentum vector exactly, but its direction in space is uncertain.

Next consider the case $J = l$ with $m_J = +1, 0, -1$. The length of the angular momentum vectors for all of these states is $\sqrt{2}\hbar$, see Exercise $7.5.16$ and Figure $7.5.11$. From a classical perspective, the non-zero value for angular momentum means that the molecule must be rotating. The projections of the vectors onto the z-axis are ħ, 0, and -ħ for the $m_J = +1, 0, -1$ states, respectively. The classical interpretation of this result is that, while the plane of rotation of the molecule, which is perpendicular to the angular momentum vector describing each state, is confined to a specific orientation with respect to the z-axis, it is not confined with respect to the x- and y- axes.

The classical picture of rotation and interpretation of the angular momentum vector for the J = 1, $m_J = 0$ state places the internuclear axis in the positions shown in Figure $7.5.1$, rotating with equal probability in any plane containing the z-axis but unconstrained with respect to the angle φ.

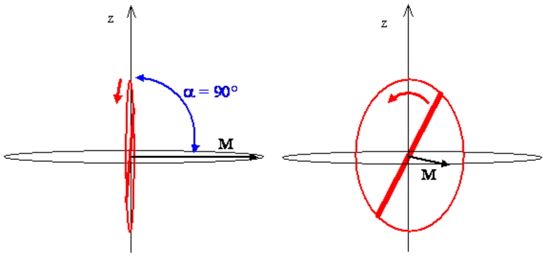

Figure 7.5.1: The plane of rotation of the diatomic molecule (red) can have any orientation in space that includes the z axis. The angular momentum vector M is always oriented perpendicular to the z axis.

For the $J = 1$, $m_J = 1$ and $m_J = -1$ states, the wavefunctions are given by

$$Y_1^1 = \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\varphi} \tag{7.5.1}$$

$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\varphi} \tag{7.5.2}$$

The imaginary component in these wavefunctions is somewhat disconcerting until we realize that the modulus squared of the wavefunction has the physical interpretation of a probability density, and the imaginary component disappears in the modulus.

$$|Y_1^1|^2 = |Y_1^{-1}|^2 = \frac{3}{8\pi}\sin^2\theta \tag{7.5.3}$$

In these expressions, which are identical, the angle φ again does not appear. There are no constraints on the wavefunctions with respect to the angle φ; i.e., the probability density is spread evenly over all values of φassociated with a particular θ. The θ dependence is a $\sin^2$ function, which has a maximum at 90° and goes to 0° as θ goes to 0° and 180° for both of these rotational states as shown in Figure 7.5.3.

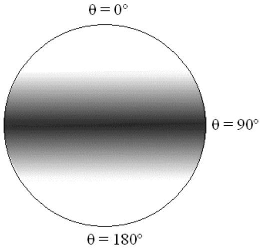

Figure 7.5.3: A map of the probability density associated with the Y_{11} and Y_{1-1} spherical harmonics, mapped onto a sphere. The intensity of color is proportional to the probability density.

The classical interpretation of the rotation associated with the angular momentum vector for the $m_J = 1$ state, which is tilted at an angle of 45° from the z-axis, says that the possible planes of rotation containing the internuclear axis of the molecule are aligned perpendicular to the angular momentum vector, as shown in Figure 7.5.4a. The molecule is rotating in any of these planes with equal probability.

For the $m_J = -1$ state, the angular momentum vector is at an angle α = 135° from the z-axis, and the possible planes of rotation containing the internuclear axis are perpendicular to it, as shown in Figure 7.5.4b. Using the right hand rule, the direction of rotation is clockwise for the $m_J = -1$ state and counterclockwise for the $m_J = 1$ state.

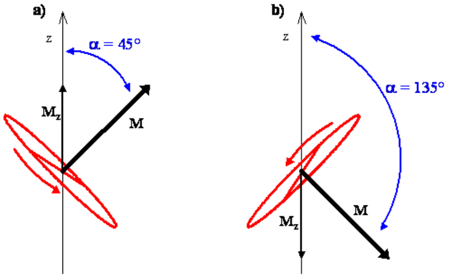

Figure 7.5.4: The orientation of the plane of rotation and the angular momentum vectors for J = 1 and a) $m_J = +1$ and b) $m_J = -1$. Looking at the planes of motion from above, the $m_J = 1$ rotation appears counterclockwise and the $m_J = -1$ rotation appears clockwise.

Exercise 7.5.19

Five states have $J = 2$. Calculate the angles the angular momentum vectors for these states make with respect to the z-axis. Sketch a diagram similar to Figure 7.5.4 in which all five angular momentum vectors for the $J = 2$ energy level are placed on the same diagram. Describe how the molecule rotates relative to one of these vectors.

7.6: Rotational Spectroscopy of Diatomic Molecules

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 shown at the beginning of the chapter in Figure 7.6.1.1 spans a frequency range of 100 to 1200 GHz, which corresponds to 3 - 40 cm^{-1}.

The selection rules for the rotational transitions are derived from the transition moment integral by using the spherical harmonic functions and the appropriate dipole moment operator, $\hat{\mu}$.

$$\mu_T = \int Y_{J_f}^{m_f *} \hat{\mu} Y_{J_i}^{m_i} \sin\theta \, d\theta \, d\varphi \tag{7.6.1}$$

Evaluating the transition moment integral involves a bit of mathematical effort. This evaluation reveals that the transition moment depends on the square of the dipole moment of the molecule, μ^2 and the rotational quantum number, J, of the initial state in the transition,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \tag{7.6.2}$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \tag{7.6.3}$$

$$\Delta m_J = 0, \pm 1 \tag{7.6.4}$$

For $\Delta J = +1$, a photon is absorbed; for $\Delta J = -1$ a photon is emitted.

Exercise 7.6.1

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 rotational levels are given by Equation 7.6.5,

$$E = J(J+1)\frac{\hbar^2}{2I} \tag{7.6.5}$$

and each energy level has a degeneracy of $2J+1$ due to the different m_J values.

Exercise 7.6.2

Use the rotational energy level diagram for $J = 0$, $J = 1$, and $J = 2$ that you produced in Exercise 7.6.9, and add arrows to show all the allowed transitions between states that cause electromagnetic radiation to be absorbed or emitted.

Transition Energies

The transition energies for absorption of radiation are given by

$$E_{photon} = \Delta E_{states} \tag{7.6.6}$$

$$= E_f - E_i \tag{7.6.7}$$

$$= h\nu \tag{7.6.8}$$

$$= hc\bar{\nu} \tag{7.6.9}$$

Substituted Equation 7.6.5 into Equation 7.6.9

$$h\nu = hc\bar{\nu} \tag{7.6.10}$$

$$= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \tag{7.6.11}$$

Since microwave spectroscopists use frequency, and infrared spectroscopists use wavenumber units when describing rotational spectra and energy levels, both ν and $\bar{\nu}$ are included in Equation 7.6.11, and J_i and J_f are the rotational quantum numbers of the initial (lower) and final (upper) levels involved in the absorption transition. When we add in the constraints imposed by the selection rules, J_f is replaced by $J_i + 1$, because the selection rule requires $J_f - J_i = 1$ for absorption. The equation for absorption transitions then can be written in terms of the quantum number J_i of the initial level alone.

$$h\nu = hc\bar{\nu} = 2(J_i + 1)\frac{\hbar^2}{2I} \tag{7.6.12}$$

Divide Equation 7.6.12 by h to obtain the frequency of the allowed transitions,

$$\nu = 2B(J_i + 1) \tag{7.6.13}$$

where B, the rotational constant for the molecule, is defined as

$$B = \frac{\hbar^2}{2hI} \tag{7.6.14}$$

Exercise 7.6.3

Complete the steps going from Equation 7.6.11 to Equation 7.6.14 and identify the units of B at the end.

Exercise 7.6.4

Infrared spectroscopists use units of wave numbers. Rewrite the steps going from Equation 7.6.11 to Equation 7.6.14 to obtain expressions for $\hbar\nu$ and B in units of wave numbers. Note that to convert B in Hz to B in cm^{-1}, you simply divide the former by c.

Figure 7.6.1 shows the rotational spectrum of $^{12}C^{16}O$ 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 7.6.1.

Table 7.6.1: Rotational Transitions in $^{12}C^{16}O$ at 40 K

J	ν_J(MHz)	Spacing from previous line(MHz)	γ_{max}
0	115,271.21	0	0.0082
1	230,538.01	115,266.80	0.0533
2	345,795.99	115,257.99	0.1278
3	461,040.76	115,244.77	0.1878
4	576,267.91	115,227.15	0.1983
5	691,473.03	115,205.12	0.1618
6	806,651.78	115,178.68	0.1064
7	921,799.55	115,147.84	0.0576
8	1,036,912.14	115,112.59	0.0262
9	1,151,985.08	115,072.94	0.0103

Let's try to reproduce Figure 7.6.1 from the data in Table 7.6.1 by using the quantum theory that we have developed so far. Equation 7.6.13 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 $2B$ according to this equation, which is consistent with the data in Table 7.6.1 showing that the lines are very nearly equally spaced. The difference between the first spacing and the last spacing is less than 0.2%.

Exercise 7.6.5

Use Equation 7.6.13 to prove that the spacing of any two lines in a rotational spectrum is $2B$. That is, derive $\nu_{J_i+1} - \nu_{J_i} = 2B$.

Non-Rigid Rotor Effects

Centrifugal stretching of the bond as J increases causes the decrease in the spacing between the lines in an observed spectrum. 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. Centrifugal stretching is exactly what you see if you swing a ball on a rubber band in a circle (Figure 7.6.1).

Figure 7.6.1: In the absence of the spring, the particles would fly apart. However, the force exerted by the extended spring pulls the particles onto a periodic, oscillatory path. (CC BY-SA 3.0; Cleonis).

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 7.6.14, is the reduced mass times the bond length squared.

Exercise 7.6.6

Use the frequency of the $J = 0$ to $J = 1$ transition observed for carbon monoxide to determine a bond length for carbon monoxide.

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 7.6.1.1 and Table 7.6.1. The maximum absorption coefficient for each line, γ_{max}, is proportional to the magnitude of the transition moment, μ_T which is given by Equation 7.6.2, and to the population difference between the initial and final states, Δn. Since Δn is the difference in the number of molecules present in the two states per unit volume, it is actually a difference in number density.

$$\gamma_{max} = C_{\mu T} \cdot \Delta n \tag{7.6.15}$$

where $C_{\mu T}$ includes constants obtained from a more complete derivation of the interaction of radiation with matter.

The dependence on the number of molecules in the initial state is easy to understand. For example, if no molecules were in the $J = 7, m_J = 0$ state, no radiation could be absorbed to produce a $J = 7, m_J = 0$ to $J = 8, m_J = 0$ transition. The dependence of the line intensity on the population of the final state is explained in the following paragraphs.

When molecules interact with an electromagnetic field (i.e., a photon), they can be driven from one state to another with the absorption or emission of energy. Usually there are more molecules in the lower energy state and the absorption of radiation is observed as molecules go from the lower state to the upper state. This situation is the one we have encountered up to now. In some situations, there are more molecules in the upper state and the emission of radiation is observed as molecules are driven from the upper state to the lower state by the electromagnetic field. This situation is called population inversion, and the process is called stimulated emission. Stimulated emission is the reason lasers are possible. Laser is an acronym for light amplification by stimulated emission of radiation. Even in the absence of an electromagnetic field, atoms and molecules can lose energy spontaneously and decay from an upper state to a lower energy state by emitting a photon. This process is called spontaneous emission. Stimulated emission therefore can be thought of as the inverse of absorption because both processes are driven by electromagnetic radiation, i.e. the presence of photons.

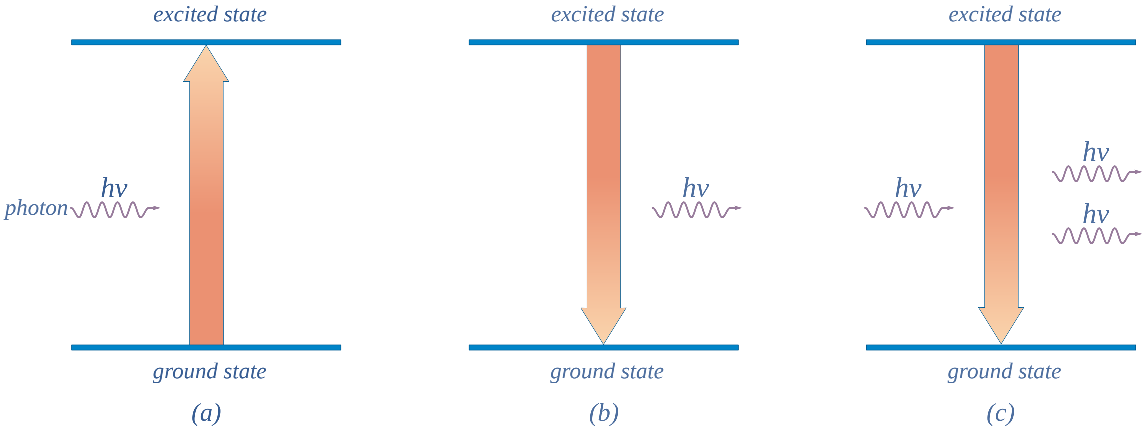

Figure 7.6.2: a) In absorption, an incident photon $h\nu$ is absorbed by the system and drives the system from the ground state to an excited state. b) In spontaneous emission, a photon is produced when the system goes from an excited state to the ground state. c) In stimulated emission, an incident photon is not absorbed, but drives the system from an excited state to the ground state, accompanied by release of a second photon.

Whether absorption or stimulated emission is observed when electromagnetic radiation interacts with a sample depends upon the population difference, Δn, of the two states involved in the transition. For a rotational transition,

$$\Delta n = n_J - n_{J+1} \tag{7.6.16}$$

where n_J represents the number of molecules in the lower state and n_{J+1} represents the number in the upper state per unit volume. If this difference is 0, there will be no net absorption or stimulated emission because they exactly balance. If this difference is positive, absorption will be observed; if it is negative, stimulated emission will be observed.

We can develop an expression for Δn that uses only the population of the initial state, n_J, and the Boltzmann factor. The Boltzmann factor allows us to calculate the population of a higher state given the population of a lower state, the energy gap between the states and the temperature. Multiply the right-hand side of Equation 7.6.16 by n_J/n_J to obtain

$$\Delta n = \left(1 - \frac{n_{J+1}}{n_J}\right) n_J \tag{7.6.17}$$

Next recognize that the ratio of populations of the states is given by the Boltzmann factor which when substituted into yields

$$\Delta n = \left(1 - e^{\frac{-h\nu_J}{kT}}\right) n_J \tag{7.6.18}$$

where $h\nu_J$ is the energy difference between the two states. For the rigid rotor model

$$\nu_J = 2B(J+1) \tag{7.6.19}$$

so Equation 7.6.18 can be rewritten as

$$\Delta n = \left(1 e^{\frac{-2hB(J+1)}{kT}}\right) n_J \tag{7.6.20}$$

Equation expresses the population difference between the two states involved in a rotational transition in terms of the population of the initial state, the rotational constant for the molecule, B, the temperature of the sample, and the quantum number of the initial state.

To get the number density of molecules present in the initial state involved in the transition, n_J, we multiply the fraction of molecules in the initial state, F_J, by the total number density of molecules in the sample, n_{total}.

$$n_J = F_J \cdot n_{total} \tag{7.6.21}$$

The fraction F_J is obtained from the rotational partition function.

$$F_J = (2J+1)\left(\frac{hB}{kT}\right)\left(e^{\frac{-2hB(J+1)}{kT}}\right) \tag{7.6.22}$$

The exponential is the Boltzmann factor that accounts for the thermal population of the energy states. The factor $2J+1$ in this equation results from the degeneracy of the energy level. The more states there are at a particular energy, the more molecules will be found with that energy. The (hB/kT) factor results from normalization to make the sum of F_J over all values of J equal to 1. At room temperature and below only the ground vibrational state is occupied; so all the molecules (n_{total}) are in the ground vibrational state. Thus the fraction of molecules in each rotational state in the ground vibrational state must add up to 1.

Exercise 7.6.7

Show that the numerator, $J(J+1)hB$ in the exponential of Equation 7.6.22 is the energy of level J.

Exercise 7.6.8: Hydrogen Chloride

Calculate the relative populations of the lowest $(J=0)$ and second $(J=1)$ rotational energy level in the HCl molecule at room temperature. Do the same for the lowest and second vibrational levels of HCl. Compare the results of these calculations. Are Boltzmann populations important to vibrational spectroscopy? Are Boltzmann populations important for rotational spectroscopy?

Now we put all these pieces together and develop a master equation for the maximum absorption coefficient for each line in the rotational spectrum, which is identified by the quantum number, J, of the initial state. Start with Equation 7.6.15 and replace μ_T using Equation 7.6.2.

$$\gamma_{max} = C\left(\mu^2 \frac{J+1}{2J+1}\right)\cdot \Delta n \tag{7.6.23}$$

Then replace Δn using Equation 7.6.20.

$$\gamma_{max} = C\left(\mu^2 \frac{J+1}{2J+1}\right)\left(e^{\frac{-2hB(J+1)}{kT}}\right) n_J \tag{7.6.24}$$

Finally replace nJ using Equations 7.6.21 and 7.6.22 to produce

$$\gamma_{max} = C\left[\mu^2 \frac{J+1}{2J+1}\right]\left[e^{\frac{-2hB(J+1)}{kT}}\right]\left[(2J+1)\left(\frac{hB}{kT}\right)\left(e^{\frac{-2hB(J+1)}{kT}}\right)\right] n_{total} \tag{7.6.25}$$

Equation 7.6.25 enables us to calculate the relative maximum intensities of the peaks in the rotational spectrum shown in Figure 7.6.2, assuming all molecules are in the lowest energy vibrational state, and predict how this spectrum would change with temperature. The constant C includes the fundamental constants ϵ_o, c and h, that follow from a more complete derivation of the interaction of radiation with matter. The complete theory also can account for the line shape and width and includes an additional radiation frequency factor.

$$C = \frac{2\pi}{3\epsilon_0 ch} \tag{7.6.26}$$

In the spectrum shown in Figure 7.6.1.1, the absorption coefficients for each peak first increase with increasing J because the difference in the populations of the states increases and the factor $(J+1)$ increases. Notice that the denominator in the factor resulting from the transition moment cancels the degeneracy factor $2J+1$. After the maximum the second Boltzmann factor, which is a decreasing exponential as J increases, dominates, and the intensity of the peaks drops to zero. Exploration of how well Equation 7.6.25 corresponds to the data in Table 7.6.1 and discovering how a rotational spectrum changes with temperature are left to an end-of-the-chapter activity.

Exercise 7.6.9

Why does not the first Boltzmann factor in Equation 7.6.25 cause the intensity to drop to zero as J increases.

7.7: Overview of the Rigid Rotor

We found that the rotational wavefunctions are functions called the Spherical Harmonics, and that these functions are products of Associated Legendre Functions and the $e^{im}\varphi$ function. Two quantum numbers, J and m_J, are associated with the rotational motion of a diatomic molecule. The quantum numbers identify or specify the particular functions that describe particular rotational states. The functions are written as

$$\psi_{J,m_J}(\theta,\varphi)=Y_{J,m_J}(\theta,\varphi)=\Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{7.7.1}$$

The absolute square of the wavefunction evaluated at a particular (θ,φ) gives the probability density for finding the internuclear axis aligned at these angles.

Constraints on the wavefunctions arose from boundary conditions, the requirement that the functions be single valued, and the interpretation of the functions as probability amplitudes. The Spherical Harmonic functions for the rigid rotor have these necessary properties only when $|m_J|\le J$ and mJ is an integer. J is the upper limit to the value of mJ, but there is no upper limit to the value for J. The subscript J is added to mJ as a reminder that J controls the allowed range of mJ.

The angular momentum of a rotating diatomic molecule is quantized by the same constraints that quantize the energy of a rotating system. As summarized in the table below, the rotational angular momentum quantum number, J, specifies both the energy and the square of the angular momentum. The z-component of the angular momentum is specified by mJ.

Rotational spectra consist of multiple lines spaced nearly equally apart because many rotational levels are populated at room temperature and the rotational energy level spacing increases by approximately $2B$ with each increase in J. The rotational constant, B, can be used to calculate the bond length of a diatomic molecule. The spectroscopic selection rules for rotation, shown in the Overview table, allow transitions between neighboring J states with the constraint that mJ change by 0 or 1 unit. Additionally, the molecule must have a non-zero dipole moment in order to move from one state to another by interacting with electromagnetic radiation. The factors that interact to control the line intensities in rotational spectra (γ_{max}) include the magnitude of the transition moment, μ_T, and the population difference between the initial and final states involved in the transition, Δn.

So far you have seen three different quantum mechanical models (the particle-in-a-box, the harmonic oscillator, and the rigid rotor) that can be used to describe chemically interesting phenomena (absorption of light by cyanine dye molecules, the vibration of molecules to determine bond force constants, and the rotation of molecules to determine bond lengths). For these cases, you should remember the chemical problem, the form of the Hamiltonian, and the characteristics of the wavefunctions (i.e. the names of the functions, and their mathematical and graphical forms). Also remember the associated energy level structure, values for the quantum numbers, and selection rules for electric-dipole transitions.

As we shall see in the following chapter, the selection rules for the rigid rotor also apply to the hydrogen atom and other atoms because the atomic wavefunctions include the same spherical harmonic angular functions, eigenfunctions of the angular momentum operators $\hat{M}^2$ and $\hat{M}_z$. The selection rules result from transition moment integrals that involve the same angular wavefunctions and therefore are the same for rotational transitions in diatomic molecules and electronic transitions in atoms.

Exercise 7.7.1

Complete the table below. For an example of a completed table, see Chapter 4.

Overview of key concepts and equations for the Rigid Rotor

- Potential energy
- Hamiltonian
- Wavefunctions
- Quantum Numbers
- Energies
- Spectroscopic Selection Rules
- Angular Momentum Properties

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7.E: Rotational States (Exercises)

Q7.1

Consider a homonuclear diatomic molecule described by the rotational wavefunction $Y_1^0(\theta, \varphi)$.

a. Sketch graphical representations of this function by plotting the amplitude of the function vs. some coordinate with all other coordinates held constant.
b. Sketch a three-dimensional polar plot of this function where the three dimensions are x, y, and z.
c. Sketch a picture to show how this molecule is rotating in space.

Q7.2

Consider a homonuclear diatomic molecule of mass M and bond length D described by the rotational wavefunction $Y_2^{-1}(\theta, \varphi)$.

a. What is the rotational energy of this molecule?
b. What is the rotational angular momentum?
c. What is the z-component of the angular momentum?
d. What angle does the angular momentum vector make with respect to the z-axis?
e. If the molecule is oxygen, what are the numerical answers to 1) – 4)?

Q7.3

Develop an equation for the stimulated emission of a photon. Compare your result to Equation (7-58).

Q7.4

When centrifugal stretching is included in the energy for the states of the rigid rotor, equation has an extra term $v_{allowed} = 2B(J_i + 1) - 4D(J_i + 1)^3$, Equation (7-67), where J is the quantum number for the initial rotational state, B is the rotational constant and D is the centrifugal distortion constant. Use the data in Table 7.2 to determine both B and D graphically. Be careful how you use units. Compare the magnitudes of B and D. What is the percent difference between B determined without centrifugal stretching and that found here including centrifugal stretching? What would be the corresponding percent error in the bond length computed from B?

Q7.5

Write a paragraph explaining why you might expect the same functions involving spherical coordinates to describe both the rigid rotor and the hydrogen atom.

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

CHAPTER OVERVIEW

8: The Hydrogen Atom

The hydrogen atom is of special interest because the hydrogen atom wavefunctions obtained by solving the hydrogen atom Schrödinger equation are a set of functions called atomic orbitals that can be used to describe more complex atoms and even molecules. This feature is particularly useful because, as we shall see in Chapters 9 and 10, the Schrödinger equation for more complex chemical systems cannot be solved analytically. By using the atomic orbitals obtained from the solution of the hydrogen atom Schrödinger equation, we can describe the structure and reactivity of molecules and the nature of chemical bonds. The spacings and intensities of the spectroscopic transitions between the electronic states of the hydrogen atom also are predicted quantitatively by the quantum treatment of this system.

8.1: The Schrödinger Equation

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.

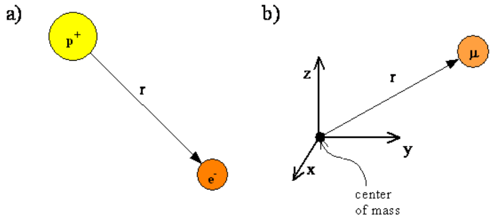

Figure 8.1.1: a) The proton (p^+) and electron (e^-) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Exercise 8.1.1

a. Assuming the Bohr radius gives the distance between the proton and electron, calculate the distance of the proton from the center of mass, and calculate the distance of the electron from the center of mass.
b. Calculate the reduced mass of the electron-proton system.
c. In view of your calculations in (a) and (b), comment on the validity of a model in which the proton is located at the center of mass and the reduced mass equals the electron mass.

Since the internal motion of any two-particle system can be represented by the motion of a single particle with a reduced mass, the description of the hydrogen atom has much in common with the description of a diatomic molecule that we considered in Chapter 7. The Schrödinger Equation for the hydrogen atom

$$\hat{H}(r,\theta,\varphi)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{8.1.1}$$

employs the same kinetic energy operator, $\hat{T}$, written in spherical coordinates as developed in Chapter 7. 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 used. The hydrogen atom Hamiltonian also contains a potential energy term, $\hat{V}$, to describe the attraction between the proton and the electron. This term is the Coulomb potential energy,

$$\hat{V}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{8.1.2}$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a **central potential**.

The full expression for $\hat{H}$ in spherical coordinates is

$$\hat{H}(r,\theta,\varphi) = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r} \tag{8.1.3}$$

The contributions from rotational and radial components of the motion become clearer if we write out the complete Schrödinger equation,

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{8.1.4}$$

multiply both sides of Equation 8.1.4 by $2\mu r$, and rearrange to obtain

$$\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2\left[E + \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(r,\theta,\varphi) = \tag{8.1.5}$$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi) \tag{8.1.6}$$

Manipulating the Schrödinger equation in this way helps us recognize the square of the angular momentum operator in Equation 8.1.6. The square of the angular momentum operator, which was defined in Chapter 7, is repeated here as Equation 8.1.7.

$$\hat{M}^2=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{8.1.7}$$

Substituting Equation 8.1.7 into Equation 8.1.6 produces

$$\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right)+2\mu r^2[E-\hat{V}]\psi(r,\theta,\varphi)=\hat{M}^2\psi(r,\theta,\varphi) \tag{8.1.8}$$

Exercise 8.1.1

Show the algebraic steps going from Equation 8.1.4 to Equation 8.1.6 and finally to Equation 8.1.8. Justify the statement that the rotational and radial motion are separated in Equation 8.1.8.

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 8.1.8 by using a product wavefunction, as we did previously in Chapter 7. From our work on the rigid rotor, Chapter 7, we know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions, $Y(\theta,\varphi)$, so a good choice for a product function is

$$\psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi) \tag{8.1.9}$$

The Spherical Harmonic functions table 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 8.1.9, into Equation 8.1.8, evaluate partial derivatives, divide each side by R(r) $Y(\theta,\varphi)$, and set each side of that resulting equation equal to a constant λ.

$$\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r)+\frac{2\mu r^2}{R(r)}[E-V]R(r)=\lambda \tag{8.1.10}$$

$$\frac{1}{Y(\theta,\varphi)}\hat{M}^2Y(\theta,\varphi)=\lambda \tag{8.1.11}$$

Equations 8.1.10 and 8.1.11 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 8.1.3

Complete the steps leading from Equation 8.1.8 to Equation 8.1.10 and Equation 8.1.11.

Rearranging Equation 8.1.11 yields

$$\hat{M}^2Y_l^{m_l}(\theta,\varphi)=\lambda Y_l^{m_l}(\theta,\varphi) \tag{8.1.12}$$

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 in Chapter 7. 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. Further, the electronic angular momentum is designated by L and the corresponding operator is called $\hat{L}$. In complete electronic notation, Equation 8.1.12 is

$$\hat{L}^2Y_l^{m_l}(\theta,\varphi)=\lambda Y_l^{m_l}(\theta,\varphi) \tag{8.1.13}$$

Equation 8.1.13 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 8.1.13 becomes

$$\hat{L}^2 Y_l^{m_l}(\theta, \varphi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta, \varphi) \tag{8.1.14}$$

Using this value for λ and rearranging Equation 8.1.10, we obtain

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) - E\right]R(r) = 0 \tag{8.1.15}$$

Exercise 8.1.4

Write the steps leading from Equation 8.1.10 to Equation 8.1.15.

The details for solving Equation 8.1.15 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.

The asymptotic solution is

$$R_{asymptotic}(r) = e^{-\frac{r}{n}a_0} \tag{8.1.16}$$

where n will turn out to be a quantum number and a_0 is the Bohr radius. 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 8.1.5

What happens to the magnitude of $R_{asymptotic}(r)$ as the distance r from the proton approaches infinity? Sketch a graph of the function, $R_{asymptotic}(r)$. Why might this behavior be expected for an electron in a hydrogen atom?

ExercisE 8.1.6

Why is exp(-r/na0) used instead of exp(+r/na0) as the exponential component of the hydrogen atom radial function?

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 ci are constant coefficients.

$$L_{n,l}(r) = \sum_{r=0}^{n-l-1} c_i r^i \tag{8.1.17}$$

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 8.1.15.

The $R(r)$ functions, Equation ???, that solve the radial differential Equation 8.1.15, are products of the associated Laguerre polynomials times the exponential factor, multiplied by a normalization factor $(N_{n,l})$ and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,l}\left(\frac{r}{a_0}\right)^l L_{n,l}(r) e^{-\frac{r}{na_0}} \tag{8.1.18}$$

As in Chapter 6, 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 8.1.1. 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 8.1.1: 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	$R_{n,l}(\rho)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$
2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/2}$
3	0	$\frac{1}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\rho+2\rho^2)e^{-\rho/3}$
3	1	$\frac{1}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6\rho-\rho^2)e^{-\rho/3}$
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 discussed in Chapter 2.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{8.1.19}$$

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 model and Bohr model differ. 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. 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 $\sqrt{(l(l+1)}\,\hbar$. 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 8.1.7

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.

8.2: The Wavefunctions

The solutions to the hydrogen atom Schrödinger equation are functions that are products of a **spherical harmonic function** and a **radial function**.

$$\psi_{n,l,m_l}(r,\theta,\varphi) = R_{n,l}(r)Y_l^{m_l}(\theta,\varphi) \tag{8.2.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and φ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the proton in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\varphi)|^2$, evaluated at r, θ, and φ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and φ.

Exercise 8.2.1

What is the value of the integral

$$\int_{\text{all space}} |\psi(r,\theta,\varphi)|^2 d\tau\,?$$

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 in Section 8.4) 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 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 8.2.2

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 8.2.3

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 8.2.4

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? What are the possible values for the magnetic quantum number? What are the possible orientations for the angular momentum vector?

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, $l=1$, and m_l = 0 is called the 1s orbital, and an electron that is described by this function is said to be "in" the ls orbital, i.e. have a 1s orbital state. The constraints on n, l), and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms in Chapter 9 that 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.

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 $\psi^*\psi$. Do not confuse such plots with polar plots, which look similar.

Probability densities also can be represented by contour maps, as shown in Figure $8.2.1$.

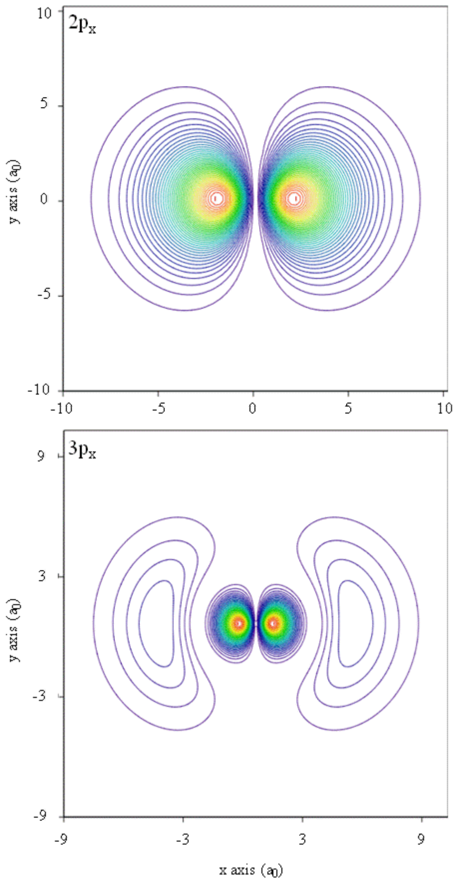

Figure $8.2.1$: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low \(R(r)^{2\)}. The angular function used to create the figure was a linear combination of two Spherical Harmonic functions (see Problem 10 at the end of this chapter.)

Another representational technique, virtual reality modeling, holds a great deal of promise for representation of electron densities. Imagine, for instance, being able to experience electron density as a force or resistance on a wand that you move through three-dimensional space. Devices such as these, called haptic devices, already exist and are being used to represent scientific information. Similarly, wouldn't it be interesting to "fly" through an atomic orbital and experience changes in electron density as color changes or cloudiness changes? Specially designed rooms with 3D screens and "smart" glasses that provide feedback about the direction of the viewer's gaze are currently being developed to allow us to experience such sensations.

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 $8.2.2$.

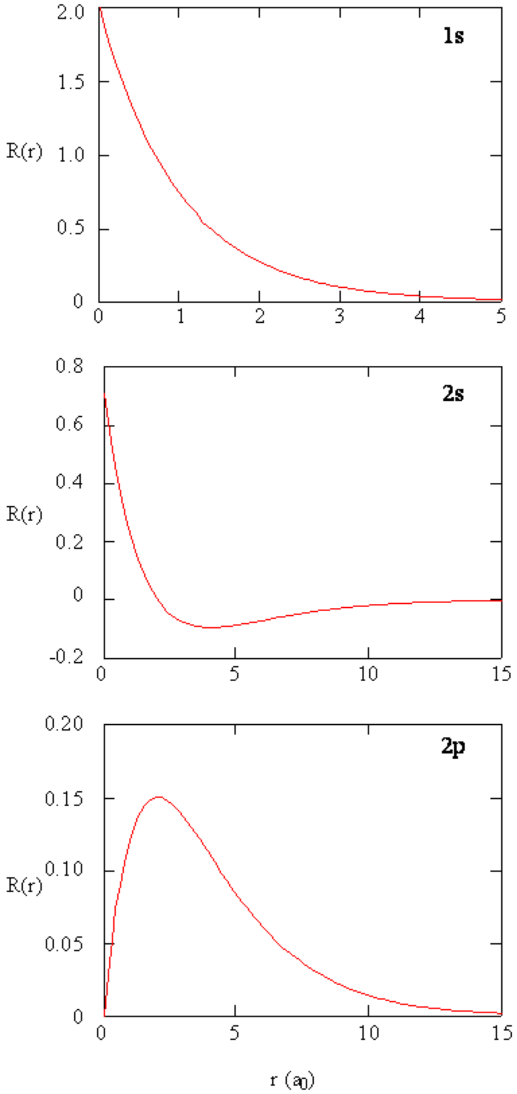

Figure $8.2.2$: Radial function, R(r), for the 1s, 2s, and 2p orbitals.

The 1s function in Figure $8.2.2$ 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 $8.2.2$, 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 $8.2.5$

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 8.2.6

What mathematical feature of each of the radial functions controls the number of radial nodes?

Exercise 8.2.7

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

Exercise 8.2.8

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, 2, and 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.

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 types of atomic orbitals are plotted in Figure (\PageIndex{3}\).

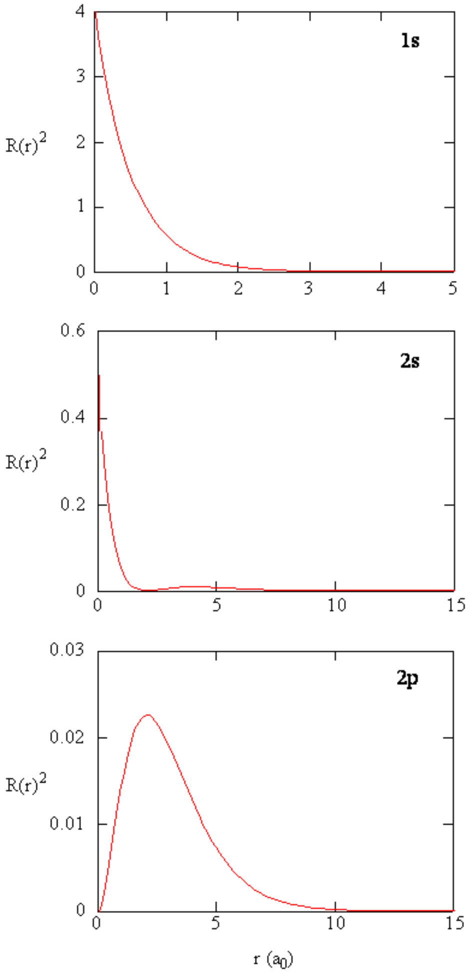

Figure 8.2.3: Radial probability densities for the 1s, 2s, and 2p orbitals.

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 $4\pi r^2 R(r)^* R(r)$.

Radial distribution functions are shown in Figure 8.2.4. 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.

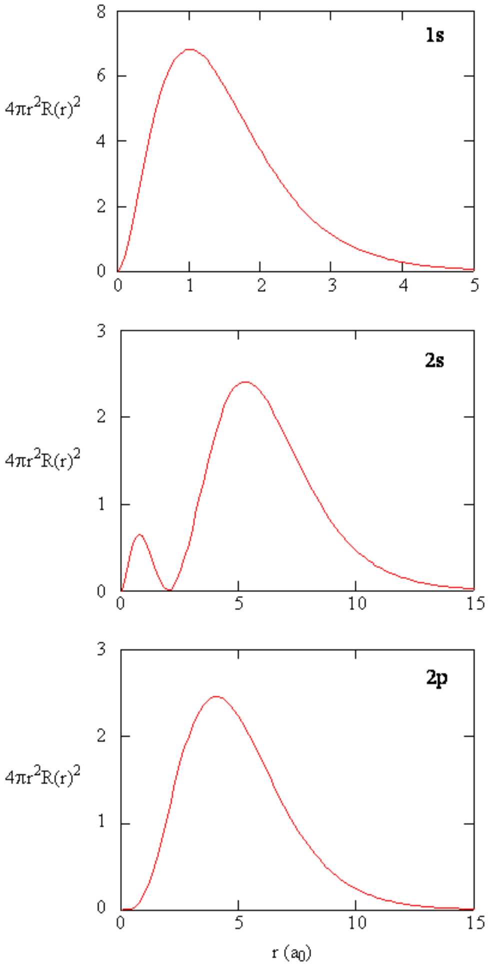

Figure 8.2.4: The radial distribution function for the 1s, 2s, and 2p orbitals.

Exercise 8.2.9

Write a quality comparison of the radial function and radial distribution function for the 2s orbital. See Figure (\PageIndex{5}\)

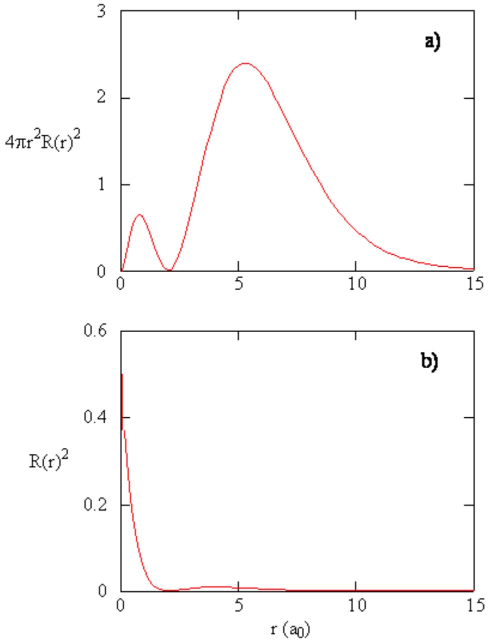

Figure 8.2.5: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

8.3: Orbital Energy Levels, Selection Rules, and Spectroscopy

The orbital energy eigenvalues obtained by solving the hydrogen atom Schrödinger equation are given by

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{8.3.1}$$

where μ is the reduced mass of the proton and electron, n is the principal quantum number and e, ϵ_0 and h are the usual fundamental constants. The energy is negative and approaches zero as the quantum number n approaches infinity. Because the hydrogen atom is used as a foundation for multi-electron systems, it is useful to remember the total energy (binding energy) of the ground state hydrogen atom, $E_H = -13.6\ eV$. The spacing between electronic energy levels for small values of n is very large while the spacing between higher energy levels gets smaller very rapidly. This energy level spacing is a result of the form of the Coulomb potential, and can be understood in terms of the particle in a box model. We saw that as the potential box gets wider, the energy level spacing gets smaller. Similarly in the hydrogen atom as the energy increases, the Coulomb well gets wider and the energy level spacing gets smaller.

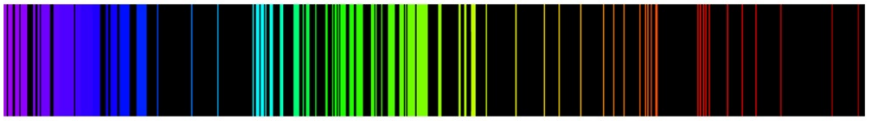

Figure 8.3.1: the emission line spectrum for iron. The discrete lines imply quantized energy states for the atoms that produce them.

The line spectra produced by hydrogen atoms are a consequence of the quantum mechanical energy level expression, Equation 8.3.1. In Chapter 1 we saw the excellent match between the experimental and calculated spectral lines for the hydrogen atom using the Bohr expression for the energy, which is identical to Equation 8.3.1.

Exercise 8.3.1

Using Equation 8.3.1 and a spreadsheet program or other software of your choice, calculate the energies for the lowest 100 energy levels of the hydrogen atom. Also calculate the differences in energy between successive levels. Do the results from these calculations confirm that the energy levels rapidly get closer together as the principal quantum number n increases? What happens to the energy level spacing as the principle quantum number approaches infinity?

The solution of the Schrödinger equation for the hydrogen atom predicts that energy levels with $n > 1$ can have several orbitals with the same energy. In fact, as the energy and n increase, the degeneracy of the orbital energy level increases as well. The number of orbitals with a particular energy and value for n is given by n_2. Thus, each orbital energy level is predicted to be n_2-degenerate. This high degree of orbital degeneracy is predicted only for one-electron systems. For multi-electron atoms, the electron-electron repulsion removes the l degeneracy so only orbitals with the same m_l quantum numbers are degenerate.

Exercise 8.3.2

Use Equation or the data you generated in Exercise 8.3.1 to draw an energy level diagram to scale for the hydrogen atom showing the first three energy levels and their degeneracy. Indicate on your diagram the transition leading to ionization of the hydrogen atom and the numerical value of the energy required for ionization, in eV, atomic units and kJ/mol.

To understand the hydrogen atom spectrum, we also need to determine which transitions are allowed and which transitions are forbidden. This issue is addressed next by using selection rules that are obtained from the transition moment integral. In previous chapters we determined selection rules for the particle in a box, the harmonic oscillator, and the rigid rotor. Now we will apply those same principles to the hydrogen atom case by starting with the transition moment integral.

The transition moment integral for a transition between an initial (i) state and a final (f) state of a hydrogen atom is given by

$$\langle \mu_T \rangle = \int \psi^*_{n_f,l_f,m_{l_f}}(r,\theta,\psi)\hat{\mu}\psi_{n_i,l_i,m_{l_i}}(r,\theta,\psi)d\tau \tag{8.3.2}$$

or in bra ket notation

$$\langle \mu_T \rangle = \langle \psi^*_{n_f,l_f,m_{l_f}} | \hat{\mu} | \psi_{n_i,l_i,m_{l_i}} \rangle \tag{8.3.3}$$

where the dipole moment operator is given by

$$\hat{\mu} = -e\hat{r} \tag{8.3.4}$$

The dipole moment operator expressed in spherical coordinates is

$$\hat{\mu} = -er(\bar{x}\sin\theta\cos\psi + \bar{y}\sin\theta\sin\psi + \bar{z}\cos\theta \tag{8.3.5}$$

The sum of terms on the right hand side of Equation 8.3.5 shows that there are three components of $\langle\mu_T\rangle$ to evaluate in Equation 8.3.2, where each component consists of three integrals: an r integral, a θ integral, and a ψ integral.

Evaluation reveals that the r integral **always differs** from zero so

$$\Delta n = n_f - n_i = \text{not restricted} \tag{8.3.6}$$

There is no restriction on the change in the principal quantum number during a spectroscopic transition; Δn can be anything. For absorption, $\Delta n > 0$, for emission $\Delta n < 0$, and $\Delta n = 0$ when the orbital degeneracy is removed by an external field or some other interaction.

The selection rules for Δl and Δm_l come from the transition moment integrals involving θ and φ in Equation 8.3.2. These integrals are the same ones that were evaluated for the rotational selection rules, and the resulting selection rules are

$$\Delta l = \pm 1 \tag{8.3.7}$$

and

$$\Delta m_l = 0, \pm 1 \tag{8.3.8}$$

Exercise 8.3.3

Write the spectroscopic selection rules for the rigid rotor and for the hydrogen atom. Why are these selection rules the same?

8.4: Magnetic Properties and the Zeeman Effect

Magnetism results from the circular motion of charged particles. This property is demonstrated on a macroscopic scale by making an electromagnet from a coil of wire and a battery. Electrons moving through the coil produce a magnetic field (Figure 8.4.1), which can be thought of as originating from a magnetic dipole or a bar magnet.

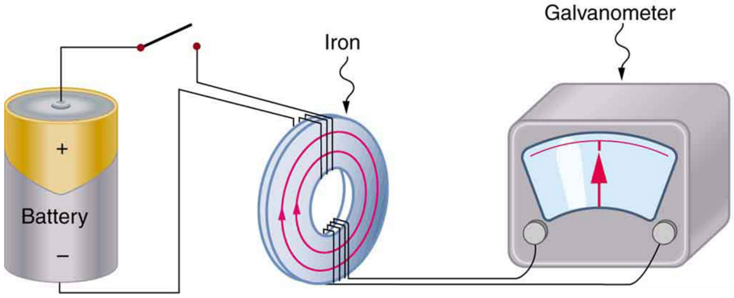

Figure 8.4.1: Faraday's apparatus for demonstrating that a magnetic field can produce a current. A change in the field produced by the top coil induces an emf and, hence, a current in the bottom coil. When the switch is opened and closed, the galvanometer registers currents in opposite directions. No current flows through the galvanometer when the switch remains closed or open. (CC BY 3.0; OpenStax).

> *Magnetism results from the circular motion of charged particles.*

Electrons in atoms also are moving charges with angular momentum so they too produce a magnetic dipole, which is why some materials are magnetic. A magnetic dipole interacts with an applied magnetic field, and the energy of this interaction is given by the scalar product of the magnetic dipole moment, and the magnetic field, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{8.4.1}$$

Magnets are acted on by forces and torques when placed within an external applied magnetic field (Figure 8.4.2). In a uniform external field, a magnet experiences no net force, but a net torque. The torque tries to align the magnetic moment ($\vec{\mu}_m$ of the magnet with the external field $\vec{B}$. The magnetic moment of a magnet points from its south pole to its north pole.

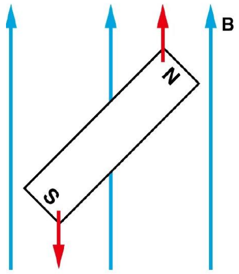

Figure 8.4.2: A magnet will feel a force to realign in an external field, i.e., go from a higher energy to a lower energy. The energy of this system is determined by Equation 8.4.1 and classical can vary since the angle between $\vec{\mu}_m$ and $\vec{B}$ can vary continuously from 0 (low energy) to 180° (high energy).

In a non-uniform magnetic field a current loop, and therefore a magnet, experiences a net force, which tries to pull an aligned dipole into regions where the magnitude of the magnetic field is larger and push an anti-aligned dipole into regions where magnitude the magnetic field is smaller.

Quantum Effects

As expected, the quantum picture is different. Pieter Zeeman was one of the first to observe the splittings of spectral lines in a magnetic field caused by this interaction. Consequently, such splittings are known as the **Zeeman effect**. Let's now use our current knowledge to predict what the Zeeman effect for the 2p to 1s transition in hydrogen would look like, and then compare this prediction with a more complete theory. To understand the Zeeman effect, which uses a magnetic field to remove the degeneracy of different angular momentum states, we need to examine how an electron in a hydrogen atom interacts with an external magnetic field, $\vec{B}$. Since magnetism results from the circular motion of charged particles, we should look for a relationship between the angular momentum $\vec{L}$ and the magnetic dipole moment $\vec{\mu}_m$.

The relationship between the magnetic dipole moment $\vec{\mu}_m$ (also referred to simply as the magnetic moment) and the angular momentum $\vec{L}$ of a particle with mass m and charge q is given by

$$\vec{\mu}_m = \frac{q}{2m}\vec{L} \tag{8.4.2}$$

For an electron, this equation becomes

$$\vec{\mu}_m = -\frac{e}{2m_e}\vec{L} \tag{8.4.3}$$

where the specific charge and mass of the electron have been substituted for q and m. The magnetic moment for the electron is a vector pointing in the direction opposite to $\vec{L}$, both of which classically are perpendicular to the plane of the rotational motion.

Exercise 8.4.1

Will an electron in the ground state of hydrogen have a magnetic moment? Why or why not?

The relationship between the angular momentum of a particle and its magnetic moment is commonly expressed as a ratio, called the gyromagnetic ratio, γ. Gyro is Greek for turn so gyromagnetic simply relates turning (angular momentum) to magnetism. Now you also know why the Greek sandwiches made with meat cut from a spit turning over a fire are called gyros.

$$\gamma = \frac{\mu_m}{L} = \frac{q}{2m} \tag{8.4.4}$$

In the specific case of an electron,

$$\gamma_e = -\frac{e}{2m_e} \tag{8.4.5}$$

Exercise 8.4.2

Calculate the magnitude of the gyromagnetic ratio for an electron.

To determine the energy of a hydrogen atom in a magnetic field we need to include the operator form of the hydrogen atom Hamiltonian. The Hamiltonian always consists of all the energy terms that are relevant to the problem at hand.

$$\hat{H} = \hat{H}^0 + \hat{H}_m \tag{8.4.6}$$

where $\hat{H}^0$ is the Hamiltonian operator in the absence of the field and $\hat{H}_m$ is written using the operator forms of Equations 8.4.1 and 8.4.3),

$$\hat{H}_m = -\hat{\mu}\cdot\vec{B} = \frac{e}{2m_e}\hat{L}\cdot B \tag{8.4.7}$$

The scalar product

$$\hat{L}\cdot\vec{B} = \hat{L}_x B_x + \hat{L}_y B_y + \hat{L}_z B_z \tag{8.4.8}$$

simplifies if the z-axis is defined as the direction of the external field because then B_x and B_y are automatically 0, and Equation 8.4.6 becomes

$$\hat{H} = \hat{H}^0 + \frac{eB_z}{2m_e}\hat{L}_z \tag{8.4.9}$$

where B_z is the magnitude of the magnetic field, which is along the z-axis.

We now can ask, “What is the effect of a magnetic field on the energy of the hydrogen atom orbitals?” To answer this question, we will not solve the Schrödinger equation again; we simply calculate the expectation value of the energy, $\langle E\rangle$, using the existing hydrogen atom wavefunctions and the new Hamiltonian operator.

$$\langle E\rangle = \left\langle \hat{H}^0 \right\rangle + \frac{eB_z}{2m_e}\left\langle \hat{L}_z \right\rangle \tag{8.4.10}$$

where

$$\left\langle \hat{H}^0 \right\rangle = \int \psi^*_{n,l,m_l} \hat{H}^0 \psi_{n,l,m_l} d\tau = E_n \tag{8.4.11}$$

and

$$\left\langle \hat{L}_z \right\rangle = \int \psi^*_{n,l,m_l} \hat{L}_z \psi_{n,l,m_l} d\tau = m_l \hbar \tag{8.4.12}$$

Exercise 8.4.3

Show that the expectation value $\left\langle \hat{L}_z \right\rangle = m_l \hbar$.

The expectation value approach provides an exact result in this case because the hydrogen atom wavefunctions are eigenfunctions of both $\hat{H}^0$ and $\hat{L}_z$. If the wavefunctions were not eigenfunctions of the operator associated with the magnetic field, then this approach would provide a first-order estimate of the energy. First and higher order estimates of the energy are part of a general approach to developing approximate solutions to the Schrödinger equation. This approach, called perturbation theory, is discussed in the next chapter.

The expectation value calculated for the total energy in this case is the sum of the energy in the absence of the field, E_n, plus the Zeeman energy, $\dfrac{e\hbar B_z m_l}{2m_e}$

$$\langle E \rangle = E_n + \frac{e\hbar B_z m_l}{2m_e} \tag{8.4.13}$$

$$= E_n + \mu_B B_z m_l \tag{8.4.14}$$

The factor

$$\frac{e\hbar}{2m_e} = -\gamma_e \hbar = \mu_B \tag{8.4.15}$$

defines the constant μ_B, called the **Bohr magneton**, which is taken to be the fundamental magnetic moment. It has units of 9.2732×10^{-21} erg/Gauss or 9.2732×10^{-24} Joule/Tesla. This factor will help you to relate magnetic fields, measured in Gauss or Tesla, to energies, measured in ergs or Joules, for any particle with a charge and mass the same as an electron.

Equation 8.4.14 shows that the m_l quantum number degeneracy of the hydrogen atom is removed by the magnetic field. For example, the three states ψ_{211}, ψ_{21-1}, and ψ_{210}, which are degenerate in zero field, have different energies in a magnetic field, as shown in Figure 8.4.3.

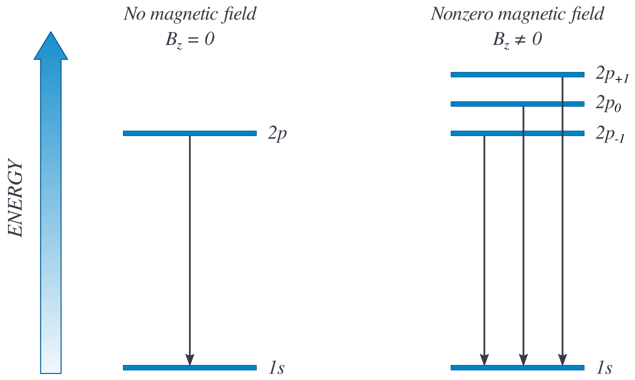

Figure 8.4.3: The Zeeman effect. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field.

The $m_l = 0$ state, for which the component of angular momentum and hence also the magnetic moment in the external field direction is zero, experiences no interaction with the magnetic field. The $m_l = +1$ state, for which the angular momentum in the z-direction is +ħ and the magnetic moment is in the opposite direction, against the field, experiences a raising of energy in the presence of a field. Maintaining the magnetic dipole against the external field direction is like holding a small bar magnet with its poles aligned exactly opposite to the poles of a large magnet (Figure 8.4.5). It is a higher energy situation than when the magnetic moments are aligned with each other.

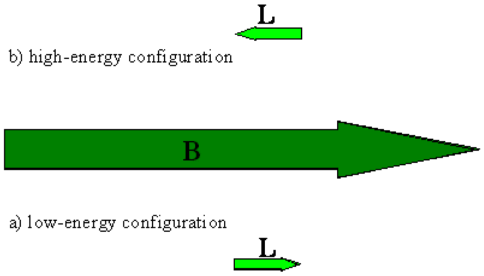

Figure 8.4.4: The effect of an external magnetic field (B) on the energy of a magnetic dipole (L) oriented a) with and b) against the applied magnetic field.

Exercise 8.4.4

Carry out the steps going from Equation 8.4.10 to Equation 8.4.14.

Exercise 8.4.5

Consider the effect of changing the magnetic field on the magnitude of the Zeeman splitting. Sketch a diagram where the magnetic field strength is on the x-axis and the energy of the three 2p orbitals is on the y-axis to show the trend in splitting magnitudes with increasing magnetic field. Be quantitative, calculate and plot the exact numerical values using a software package of your choice.

Exercise 8.4.6

Based on your calculations in Exercise 8.4.2 sketch a luminescence spectrum for the hydrogen atom in the n = 2 level in a magnetic field of 1 Tesla. Provide the numerical value for each of the transition energies. Use cm^{-1} or electron volts for the energy units.

8.5: Discovering Electron Spin

Imagine doing a hypothetical experiment that would lead to the discovery of electron spin. Your laboratory has just purchased a microwave spectrometer with variable magnetic field capacity. We try the new instrument with hydrogen atoms using a magnetic field of 10^4 Gauss and look for the absorption of microwave radiation as we scan the frequency of our microwave generator.

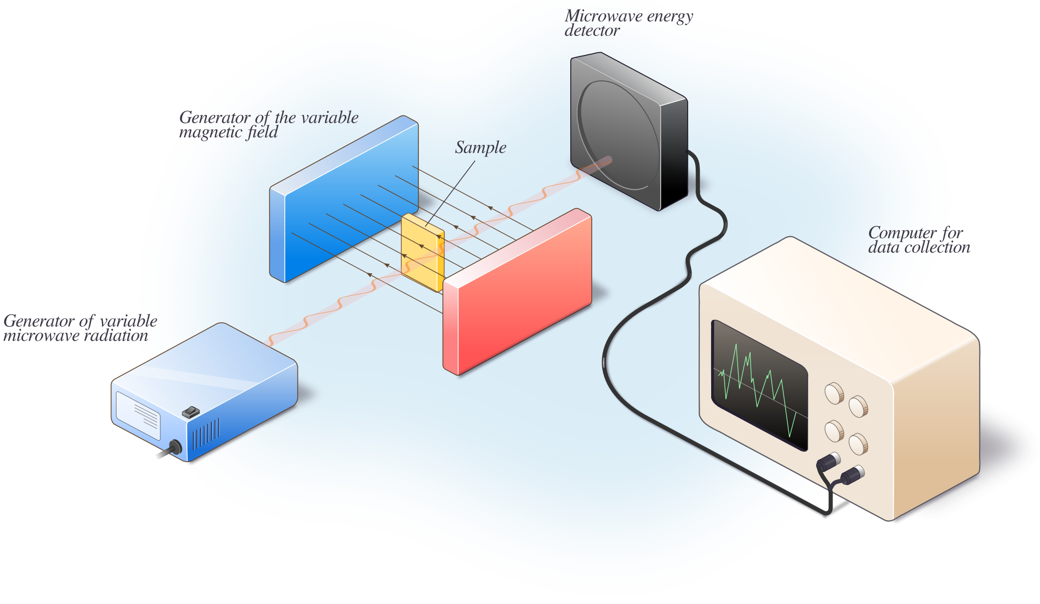

Figure 8.5.1: Schematic diagram of a microwave spectrometer with the sample in a variable magnetic field. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY-NC; Ümit Kaya via LibreTexts)

Finally we see absorption at a microwave photon frequency of $28 \times 10^9\ Hz$ (28 gigahertz). This result is really surprising from several perspectives. Each hydrogen atom is in its ground state, with the electron in a 1s orbital. The lowest energy electronic transition that we predict based on existing theory (the electronic transition from the ground state (ψ_{100} to ψ_{21m}) requires an energy that lies in the vacuum ultraviolet, not the microwave, region of the spectrum. Furthermore, when we vary the magnetic field we note that the frequency at which the absorption occurs varies in proportion to the magnetic field. This effect looks like a Zeeman effect, but if you think about the situation, even if the 1s orbital were doubly degenerate, a $1s$ orbital still has zero orbital angular momentum, no magnetic moment, and therefore no predicted Zeeman effect!

To discover new things, experimentalists sometimes must explore new areas in spite of contrary theoretical predictions. Our theory of the hydrogen atom at this point gives no reason to look for absorption in the microwave region of the spectrum. By doing this crazy experiment, we discovered that when an electron is in the $1s$ orbital of the hydrogen atom, there are two different states that have the same energy. When a magnetic field is applied, this degeneracy is removed, and microwave radiation can cause transitions between the two states. In the rest of this section, we see what can be deduced from this experimental observation. This experiment actually could be done with electron spin resonance spectrometers available today.

In order to explain our observations, we need a new idea, a new model for the hydrogen atom. Our original model for the hydrogen atom accounted for the motion of the electron and proton in our three-dimensional world; the new model needs something else that can give rise to an additional Zeeman-like effect. We need a charged particle with angular momentum to produce a magnetic moment, just like that obtained by the orbital motion of the electron. We can postulate that our observation results from a motion of the electron that wasn't considered in the last section - electron spin. We have a charged particle spinning on its axis. We then have charge moving in a circle, angular momentum, and a magnetic moment, which interacts with the magnetic field and gives us the Zeeman-like effect that we observed.

To describe electron spin from a quantum mechanical perspective, we must have spin wavefunctions and spin operators. The properties of the spin states are deduced from experimental observations and by analogy with our treatment of the states arising from the orbital angular momentum of the electron.

The important feature of the spinning electron is the spin angular momentum vector, which we label S by analogy with the orbital angular momentum L. We define spin angular momentum operators with the same properties that we found for the rotational and orbital angular momentum operators. After all, angular momentum is angular momentum.

We found that (in Bra-ket notation)

$$\hat{L}^2 |Y_l^{m_l}\rangle = l(l+1)\hbar^2 |Y_l^{m_l}\rangle \tag{8.5.1}$$

so by analogy for the spin states, we must have

$$\hat{S}^2 |\sigma_s^{m_s}\rangle = s(s+1)\hbar^2 |\sigma_s^{m_s}\rangle \tag{8.5.2}$$

where σ is a spin wavefunction with quantum numbers s and m_s that obey the same rules as the quantum numbers l and m_l associated with the spherical harmonic wavefunction Y. We also found

$$\hat{L}_z |Y_l^{m_l}\rangle = m_l \hbar |Y_l^{m_l}\rangle \tag{8.5.3}$$

so by analogy, we must have

$$\hat{S}_z |\sigma_s^{m_s}\rangle = m_s \hbar |\sigma_s^{m_s}\rangle \tag{8.5.4}$$

Since m_l ranges in integer steps from $-l$ to $+l$, also by analogy m_s ranges in integer steps from $-s$ to $+s$. In our hypothetical experiment, we observed one absorption transition, which means there are two spin states. Consequently, the two values of m_s must be $+s$ and $-s$, and the difference in m_s for the two states, labeled f and i below, must be the smallest integer step, i.e. 1. The result of this logic is that

$$\begin{aligned} m_{s,f} - m_{s,i} &= 1 \\ (+s) - (-s) &= 1 \\ 2s &= 1 \\ s &= \frac{1}{2} \end{aligned} \tag{8.5.5}$$

Therefore our conclusion is that the magnitude of the spin quantum number is 1/2 and the values for ms are +1/2 and -1/2. The two spin states correspond to spinning clockwise and counter-clockwise with positive and negative projections of the spin angular momentum onto the z-axis. The state with a positive projection, m_s = +1/2, is called α; the other is called β. These spin states are arbitrarily labeled α and β, and the associated spin wavefunctions also are designated by α and β.

From Equation 8.5.4 the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s \hbar \tag{8.5.6}$$

so the value of S_z is $+\hbar/2$ for spin state α and $-\hbar/2$ for spin state β. Using the same line of reasoning we used for the splitting of the m_l states in Section 8.4, we conclude that the α spin state, where the magnetic moment is aligned against the external field direction, has a higher energy than the β spin state.

Even though we don’t know their functional forms, the spin wavefunctions are taken to be normalized and orthogonal to each other.

$$\int \alpha^* \alpha d\tau_s = \int \beta^* \beta d\tau_s = 1 \tag{8.5.7}$$

and

$$\int \alpha^* \beta d\tau_s = \int \beta^* \alpha d\tau_s = 0 \tag{8.5.8}$$

where the integral is over the spin variable τ_s.

Now let's apply these deductions to the experimental observations in our hypothetical microwave experiment. We can account for the frequency of the transition (ν= 28 gigahertz) that was observed in this hypothetical experiment in terms of the magnetic moment of the spinning electron and the strength of the magnetic field. The photon energy, $h\nu$, is given by the difference between the energies of the two states, E_α and E_β

$$\Delta E = h\nu = E_{\alpha} - E_{\beta} \tag{8.5.9}$$

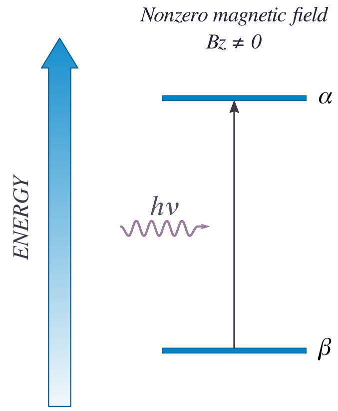

Figure 8.5.2: Absorption of a photon to cause a transition from the β to the α state. (CC BY-NC; Ümit Kaya via LibreTexts)

The energies of these two states consist of the sum of the energy of an electron in a 1s orbital, E_{1s}, and the energy due to the interaction of the spin magnetic dipole moment of the electron, μ_s, with the magnetic field, B (as in Section 8.4). The two states with distinct values for spin magnetic moment μ_s are denoted by the subscripts α and β.

$$E_{\alpha} = E_{1s} - \mu_{s,\alpha} \cdot B \tag{8.5.10}$$

$$E_{\beta} = E_{1s} - \mu_{s,\beta} \cdot B \tag{8.5.11}$$

Substituting the two equations above into the expression for the photon energy gives

$$h\nu = E_{\alpha} - E_{\beta} \tag{8.5.12}$$

$$= (E_{1s} - \mu_{s,\alpha} \cdot B) - (E_{1s} - \mu_{s,\beta} \cdot B) \tag{8.5.13}$$

$$= (\mu_{s,\beta} - \mu_{s,\alpha}) \cdot B \tag{8.5.14}$$

Again by analogy with the orbital angular momentum and magnetic moment discussed in Section 8.4, we take the spin magnetic dipole of each spin state, $\mu_{s,\alpha}$ and $\mu_{s,\beta}$, to be related to the total spin angular momentum of each state, S_{α} and S_{β}, by a constant spin gyromagnetic ratio, γ_s, as shown below.

$$\mu_s = \gamma_s S \tag{8.5.15}$$

$$\mu_{s,\alpha} = \gamma_s S_{\alpha} \tag{8.5.16}$$

$$\mu_{s,\beta} = \gamma_s S_{\beta} \tag{8.5.17}$$

With the magnetic field direction defined as z, the scalar product in Equation 8.5.14 becomes a product of the z-components of the spin angular momenta, $S_{z,\alpha}$ and $S_{z,\beta}$, with the external magnetic field.

Inserting the values for $S_{z,\alpha} = +\dfrac{1}{2}\hbar$ and $S_{z,\alpha} = -\dfrac{1}{2}\hbar$ from Equation 8.5.6 and rearranging Equation 8.5.14 yields

$$\frac{h\nu}{B} = -\gamma_s \hbar \tag{8.5.18}$$

Calculating the ratio $\dfrac{h\nu}{B}$ from our experimental results, $\nu = 28 \times 10^9\ Hz$ when $B = 10^4\ gauss$, gives us a value for

$$-\gamma_s \hbar = 18.5464 \times 10^{-21}\ erg/gauss. \tag{8.5.19}$$

This value is about twice the Bohr magneton, $-\gamma_e \hbar$ with $\gamma_s \hbar = 2.0023, \gamma_e \hbar$, or

$$\gamma_s = 2.0023\gamma_e \tag{8.5.20}$$

The factor of 2.0023 is called the **g-factor** and accounts for the deviation of the spin gyromagnetic ratio from the value expected for orbital motion of the electron. In other words, it accounts for the spin transition being observed where it is instead of where it would be if the same ratio between magnetic moment and angular momentum held for both orbital and spin motions. The value 2.0023 applies to a freely spinning electron; the coupling of the spin and orbital motion of electrons can produce other values for g.

Exercise 8.5.1

Carry out the calculations that show that the g-factor for electron spin is 2.0023.

Interestingly, the concept of electron spin and the value g = 2.0023 follow logically from *Dirac's relativistic quantum theory*, which is beyond the scope of this discussion. Electron spin was introduced here as a postulate to explain experimental observations. Scientists often introduce such postulates parallel to developing the theory from which the property is naturally deduced.

Now that we have discovered electron spin, we need to determine how the electron spin changes when radiation is absorbed or emitted, i.e. what are the selection rules for electron spin of a single electron? Unlike orbital angular momentum, which can have several values, the spin angular momentum can have only the value

$$|S| = \sqrt{s(s+1)\hbar} = \frac{\sqrt{3}}{2}\hbar \tag{8.5.21}$$

Since s = ½, one spin selection rule is

$$\Delta s = 0 \tag{8.5.22}$$

When a magnetic field is applied along the z-axis to remove the m_s degeneracy, another magnetic field applied in the x or y direction exerts a force or torque on the magnetic dipole to turn it. This transverse field can “flip the spin,” and change the projection on the z-axis from $\frac{1}{+2}\hbar$ to $\frac{1}{-2}\hbar$ or from $\frac{1}{-2}\hbar$ to $\frac{1}{+2}\hbar$. So the other spin selection rule for a single electron is

$$\Delta m_s = \pm 1 \tag{8.5.23}$$

8.6: Other One-Electron Systems

The quantum mechanical treatment of the hydrogen atom can be extended easily to other one-electron systems such as He^+, Li^{2+}, etc. The Hamiltonian changes in two places. Most importantly, the potential energy term is changed to account for the charge of the nucleus, which is the atomic number of the atom or ion, Z, times the fundamental unit of charge, e. As shown in Equation 8.6.1, the energy of attraction between the electron and the nucleus increases (i.e., V gets more negative) as the nuclear charge increases.

$$\hat{V}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{8.6.1}$$

The other effect is a very slight change in the reduced mass included in the kinetic energy operator. In fact, the larger the nucleus, the better the approximation that the reduced mass is given by the mass of the electron.

Exercise 8.6.1

Compare the reduced mass of the Li^{+2} ion to that of the hydrogen atom.

The effects of the change in V show up in the wavefunctions and the energy eigenvalues. The expression for the energy becomes

$$E_n = -\frac{Z^2\mu e^4}{8\epsilon_0^2 h^2 n^2} = Z^2 E_{n,H} \tag{8.6.2}$$

where $E_{n,H}$ is the energy of the hydrogen atom. The forms of the wavefunctions are identical to those of the hydrogen atom, except for the fact that Z in the radial functions is no longer equal to 1. The selection rules are unchanged, and the Zeeman effect still occurs.

Exercise 8.6.2

Use the orbital energy level expression in Equation 8.6.2 to predict quantitatively the relative energies (in cm^{-1}) of the spectral lines for H and Li^{2+}.

As the plots in Figure $8.6.1$ reveal, the increased charge on the nucleus creates a stronger attraction for the electron and thus the electron charge density distributions shift to smaller values of r. These other systems look a lot like compressed hydrogen atoms.

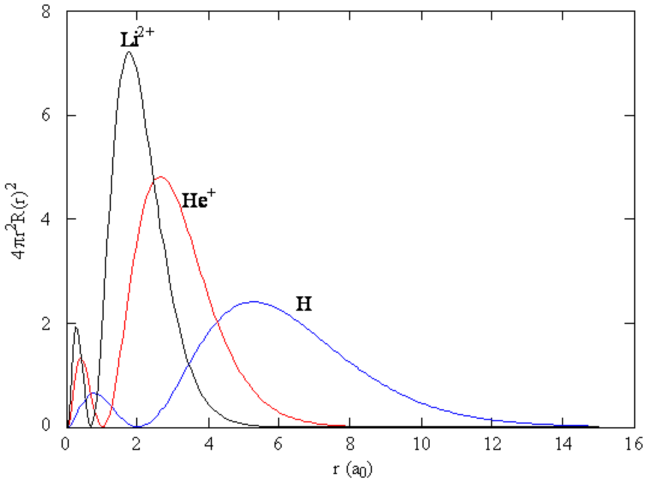

Figure $8.6.1$: Radial distribution functions plotted for the 2s orbitals of H (blue), He^+ (red) and Li^{2+} (black) on the same axis, demonstrating compression of the orbital as Z is increased from 1 to 3.

Exercise 8.6.3

Determine whether or not the angular momentum values, the spherical harmonic functions, and the spectroscopic selection rules that describe the electron in $\hat{H}$ are the same or are different for Li^{2+}. Write a paragraph to justify your answer.

8.7: Spin-Orbitals and Electron Configurations

The wavefunctions obtained by solving the hydrogen atom Schrödinger equation are associated with orbital angular motion and are often called spatial wavefunctions, to differentiate them from the spin wavefunctions. The complete wavefunction for an electron in a hydrogen atom must contain both the spatial and spin components. We refer to the complete one-electron orbital as a spin-orbital and a general form for this orbital is

$$|\varphi_{n,l,m_l,m_s}\rangle = |\psi_{n,l,m_l}(r,\theta,\psi)\rangle |\sigma_s^{m_s}\rangle \tag{8.7.1}$$

A spin-orbital for an electron in the $2p_z$ orbital with $m_s = +\frac{1}{2}$, for example, could be written as

$$|\psi_{2pz_\alpha}\rangle = |\psi_{2,1,0}(r,\theta\psi)\ |\alpha\rangle \tag{8.7.2}$$

A common method of depicting electrons in spin-orbitals arranged by energy is shown in Figure $8.7.1$, which gives one representation of the ground state electron configuration of the hydrogen atom.

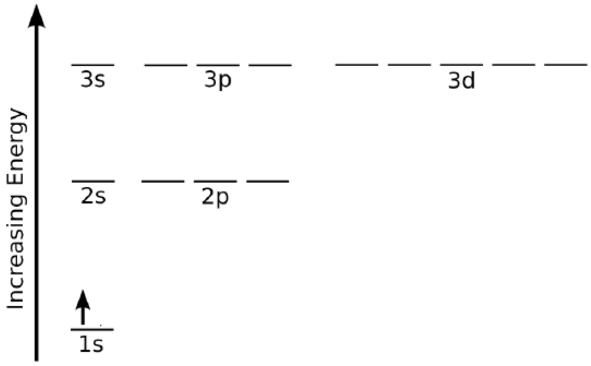

Figure $8.7.1$: Electron configuration of a ground-state hydrogen atom depicted on an energy-level diagram. The electron is represented by an arrow in the 1s orbital.

On the energy level diagram in Figure $8.7.1$, the horizontal lines labeled 1s, 2s, 2p, etc. denote the spatial parts of the orbitals, and an arrow pointing up for spin α and down for spin β denotes the spin part of the wavefunction.

An alternative shorthand notation for electron configuration is the familiar form 1s^1 to denote an electron in the 1s orbital. Note that this shorthand version contains information only about the spatial wavefunction; information about spin is implied. Two electrons in the same orbital have spin α and β, e.g. 1s^2, and one electron in an orbital is assumed to have spin α. Hydrogen atoms can absorb energy and the electron can be promoted to higher energy spin-orbitals. Examples of such excited state configurations are $2p_1$, $3d_1$, etc.

8.8: Coupling of Angular Momentum and Spectroscopic Term Symbols

Around 1930 several spectroscopists using high resolution instruments found that lines in the hydrogen atom spectrum actually are not single lines but they are multiplets as shown for an isotopic mixture of hydrogen,(H^1_α) and deuterium, (H^2_α) in Figure 8.8.1. A multiplet consists of two or more closely spaced lines. Two lines together form a doublet, three a triplet, etc. Multiplets also are called fine structure. The term *fine structure* means the lines are spaced close together, i.e. finely spaced. Such fine structure also was found in spectra of one-electron ions such as He^+.

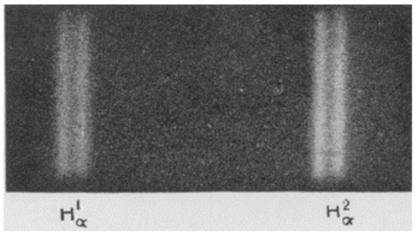

Figure 8.8.1: Photograph of the first line in the Balmer series for atomic hydrogen and deuterium. These lines are identified as H^1_α (hydrogen) and H^2_α (deuterium), respectively. From H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) p. 132 and G.N. Lewis and F.H. Spedding, Phys. Rev. 43, 964 (1933). The doublet splitting for H^1_α at 656.279 nm was measured to be 0.326 cm^{-1}.

You should recall that the H^1_α line in the Balmer series at 656.279 nm was understood as resulting from a single transition of an electron from the n = 3 energy level to the n = 2 level. The observation of fine structure revealed that an orbital energy level diagram does not completely describe the energy levels of atoms. This fine structure also provided key evidence at the time for the existence of electron spin, which was used not only to give a qualitative explanation for the multiplets but also to furnish highly accurate calculations of the multiplet splittings.

Spin-Orbit Coupling

Specifying the orbital configuration of an atom does not uniquely identify the electronic state of the atom because the orbital angular momentum, the spin angular momentum, and the total angular momentum are not precisely specified. For example in the hydrogen $2p^1$ configuration, the electron can be in any of the three p-orbitals, m_l = +1, 0, and –1, and have spins with m_s = +1/2 or –1/2. Thus, there are 3 times 2 different possibilities or states. Also, the orbital and spin angular momentum of the electrons combine in multiple ways to produce angular momentum vectors that are characteristic of the entire atom not just individual electrons, and these different combinations can have different energies. This coupling of orbital and spin angular momentum occurs because both the electron spin and orbital motion produce magnetic dipole moments. As we have seen previously, the relationship between the angular momentum and the magnetic moment is given by the gyromagnetic ratio. These magnetic dipoles interact just like two tiny bar magnets attracting and repelling each other. This interaction is called spin-orbit interaction. The interaction energy is proportional to the scalar product of the magnetic dipole moments, which are proportional to the angular momentum vectors.

$$E_{s-o} = \lambda S \cdot L \tag{8.8.1}$$

$$\hat{H}_{s-o} = \lambda \hat{S} \cdot \hat{L} \tag{8.8.2}$$

where λ represents the constant of proportionality and is called the spin-orbit coupling constant. The spin-orbit interaction couples the spin motion and orbital motion of all the electrons together. This coupling means that exact wavefunctions are not eigenfunctions of the spin and orbital angular momentum operators separately. Rather the total angular momentum J = L+S, the vector sum of the spin and orbital angular momentum, is required to be coupled for a completely accurate description of the system. Trying to describe the coupled system in terms of spin and orbital angular momentum separately is analogous to trying to describe the positions of two coupled bar magnets independently. It cannot be done; their interaction must be taken into account.

We need to be able to identify the electronic states that result from a given electron configuration and determine their relative energies. An electronic state of an atom is characterized by a specific energy, wavefunction (including spin), electron configuration, total angular momentum, and the way the orbital and spin angular momenta of the different electrons are coupled together. There are two descriptions for the coupling of angular momentum. One is called *j-j coupling*, and the other is called *L-S coupling*. The j-j coupling scheme is used for heavy elements (Z > 40), and the L-S coupling scheme is used for the lighter elements. L-S coupling also is called R-S or Russell-Saunders coupling.

L-S Coupling

In L-S coupling, the orbital and spin angular momenta of all the electrons are combined separately

$$L = \sum_i l_i \tag{8.8.3}$$

$$S = \sum_i S_i \tag{8.8.4}$$

The total angular momentum vector then is the sum of the total orbital angular momentum vector and the total spin angular momentum vector.

$$J = L + S \tag{8.8.5}$$

The result of these vector sums is specified in a code that is called a Russell-Saunders term symbol, and each term symbol identifies an energy level of the atom. Consequently, the energy levels also are called terms. A term symbol has the form

$$^{2s+1}L_J \tag{8.8.6}$$

where the code letter that is used for the total orbital angular momentum quantum number L = 0, 1, 2, 3, 4, 5 is S, P, D, F, G, H, respectively. Note how this code matches that used for the atomic orbitals. The superscript $2S+1$ gives the spin multiplicity of the state, where S is the total spin angular momentum quantum number. The spin multiplicity is the number of spin states associated with a given electronic state. In order not to confuse the code letter S for the orbital angular momentum with the spin quantum number S, you must examine the context in which it is used carefully. In the term symbol, the subscript J gives the total angular momentum quantum number. Because of spin-orbit coupling, only J and M_J are valid quantum numbers, but because the spin-orbit coupling is weak L, M_L, S, and M_S still serve to identify and characterize the states for the lighter elements.

For example, the ground state, i.e. the lowest energy state, of the hydrogen atom corresponds to the electron configuration in which the electron occupies the 1s spatial orbital and can have either spin α or spin β. The term symbol for the ground state is $^2S_{1/2}$, which is read as “doublet S 1/2”. The spin quantum number is 1/2 so the superscript $2S+1=2$, which gives the spin multiplicity of the state, i.e. the number of spin states equals 2 corresponding to α and β. The S in the term symbol indicates that the total orbital angular momentum quantum number is 0 (For the ground state of hydrogen, there is only one electron and it is in an s-orbital with $l=0$). The subscript ½ refers to the total angular momentum quantum number. The total angular momentum is the sum of the spin and orbital angular momenta for the electrons in an atom. In this case, the total angular momentum quantum number is just the spin angular momentum quantum number, ½, since the orbital angular momentum is zero. The ground state has a degeneracy of two because the total angular momentum can have a z-axis projection of $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, corresponding to m_J = +1/2 or -1/2 resulting from the two electron spin states α and β. We also can say, equivalently, that the ground state term or energy level is two-fold degenerate.

Exercise 8.8.1

Write the term symbol for a state that has 0 for both the spin and orbital angular momentum quantum numbers.

Exercise 8.8.2

Write the term symbol for a state that has 0 for the spin and 1 for the orbital angular momentum quantum numbers

Russell-Saunders Selection Rules

Higher energy or excited orbital configurations also exist. The hydrogen atom can absorb energy, and the electron can be promoted to a higher energy orbital. The electronic states that result from these excited orbital configurations also are characterized or labeled by term symbols. The details of how to determine the term symbols for multi-electron atoms and for cases where both the orbital and spin angular momentum differ from zero are given elsewhere, along with rules for determining the relative energies of the terms.

We have found that the selection rules for a single electron moving from one atomic orbital to another are

$$\Delta l = \pm 1 \tag{8.8.7}$$

$$\Delta m_l = 0, \pm 1 \tag{8.8.8}$$

For an atom as a whole in the limit of L-S coupling, the Russell-Saunders selection rules are

$$\Delta S = 0 \tag{8.8.9}$$

$$\Delta L = 0, \pm 1 \tag{8.8.10}$$

$$\Delta J = 0, \pm 1 \tag{8.8.11}$$

However, the $J = 0$ to $J = 0$ transition is forbidden

$$\Delta m_J = 0, \pm 1 \tag{8.8.12}$$

However, the $m_J = 0$ to $m_J = 0$ is forbidden if $\Delta J = 0$

These selection rules result from the general properties of angular momentum such as the conservation of angular momentum and commutation relations.

Now we want to apply these ideas to understand why multiplet structure is found in the luminescence spectrum of hydrogen and single electron ions. As we have said, the H_α line in the Balmer series at 656.279 nm can be understood as due to a transition of an electron in a n = 3 atomic orbital to a n = 2 atomic orbital. When this spectral line was examined using high-resolution instruments, it was found actually to be a doublet, i.e. two lines separated by 0.326 cm-1.

There are 9 degenerate orbitals associated with the n = 3 level, and 4 associated with the n = 2 level. Since an electron can be in any orbital with any one of two spins, we expect the total number of states to be twice the number of orbitals. The number of orbitals is given by n2 so there should be 8 states associated with n = 2 and 18 states associated with n = 3. Using the ideas of vector addition of angular momentum, the terms that result from having an electron in any one of these orbitals are given in Table 8.8.1.

Table 8.8.1: H Atom Terms Originating from n = 1, 2, and 3

Orbital Configuration	Term Symbols	Degeneracy
$1s^1$	$^2S_{1/2}$	2
$2s^1$	$^2S_{1/2}$	2
$2p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3s^1$	$^2S_{1/2}$	2
$3p^1$	$^2P_{1/2}$, $2P_{3/2}$	2, 4
$3d^1$	$^2D_{3/2}$, $2D_{5/2}$	4, 6

Table 8.8.1 shows that there are 3 terms associated with n = 2, and 5 terms associated with n = 3. In principle, each term can have a different energy. The degeneracy of each term is determined by the number of projections that the total angular momentum vector has on the z-axis. These projections depend on the mJ quantum number, which ranges from +J to – J in integer steps. J is the total angular momentum quantum number, which is given by the subscript in the term symbol. This relationship between mJ and J (mJ varies from +J to – J in integer steps) is true for any angular momentum vector.

Exercise 8.8.3

Confirm that the term symbols in Table 8. are correct.

Exercise 8.8.4

Confirm that the values for the degeneracy in Table 8.8.1 are correct and that the total number of states add up to 8 for n = 2 and 18 for n = 3.

The energies of the terms depend upon spin-orbit coupling and relativistic corrections that need to be included in the Hamiltonian operator in order to provide a more complete description of the hydrogen atom. As a consequence of these effects, all terms with the same n and J quantum numbers have the same energy while terms with different values for n or J have different energies. The theoretical term splittings as given by H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) pp. 132-137. are shown in Figure 8.8.8.2.

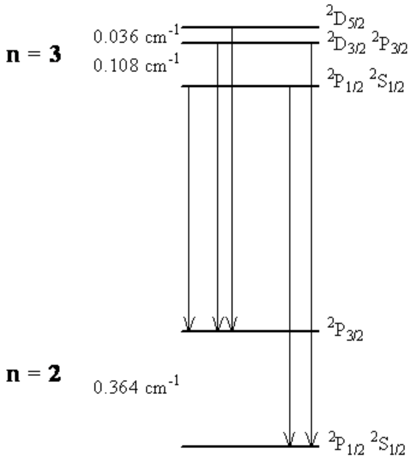

Figure 8.8.8.2 which have a measured separation of 0.326 cm-1.

Figure 8.8.2 shows 5 allowed transitions for the electron in the states associated with n = 3 to the states associated with n = 2. Of these five, two are most intense and are responsible for the doublet structure. These two transitions are indicated by the wide black lines at the bottom of the figure to correspond to the lines observed in the photographic spectrum shown in Figure 8.8.8.2. The other transitions contribute to the width of these lines or are not observed. The theoretical value for the doublet splitting is 0.328 cm-1, which is in excellent agreement with the measured value of 0.326 cm-1. The value of 0.328 cm-1 is obtained by taking the difference, 0.364 – 0.036 cm-1,in the term splittings.

As we have just seen, the electronic states, as identified by the term symbols, are essential in understanding the spectra and energy level structure of atoms, but it also is important to associate the term symbols and states with the orbital electron configurations. The orbital configurations help us understand many of the general or coarse features of spectra and are necessary to produce a physical picture of how the electron density changes because of a spectroscopic transition.

Exercise 8.8.5

Use the Russell-Saunders selection rules to determine which transitions contribute to the H_α line in the hydrogen spectrum.

Magnetic Field Effects

The Zeeman effect that was described in Section 8.4 only considered the orbital motion of the electron and did not include spin angular momentum and the spin magnetic moment. For a more complete analysis of the Zeeman effect associated with the n = 2 to n = 1 transition in the hydrogen atom, we need to use the term symbols for the states, examine how the m_J degeneracy is removed by the magnetic field, and determine which transitions between the states are allowed.

The states involved in a transition of an electron from the 2p atomic orbital to the 1s atomic orbital (where the hydrogen atom goes from the $2p^1$ configuration to the $1s^1$ configuration) are identified in Table 8.8.8.1. The $2p^1$ configuration produces $2P_{3/2}$ and $2P_{1/2}$ terms with the latter being lower in energy by 0.364 cm^{-1} as shown in Figure 8.8.8.2. The $1s^1$ configuration corresponds to a $2S_{1/2}$ term, which also is shown in Figure 8.8.2.

The orbital energy in a magnetic field was given by Equation 8.8.13, which is repeated here.

$$\langle E\rangle = E_0 + \mu_B B_z m_l \tag{8.8.13}$$

This equation can be generalized by changing the angular momentum quantum number to J and adding a g-factor to account for different gyromagnetic ratios

$$\langle E\rangle = E_0 + g m_J \mu_B B_z \tag{8.8.14}$$

While the g-factor equals 2 for a free electron or an electron in an s-orbital, the g-factor of an electron is affected by spin-orbit coupling. For the case of L-S coupling, the g-factor is given by

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \tag{8.8.15}$$

To identify how the energy of states change in an electric field we need only consider the gmJ factor in Equation since μB, which is the Bohr magneton, is a constant and the energy changes just scale with B_z, which is the magnetic field. Consequently we can describe the splittings in terms of gm$_J$ units where one gmJ unit is the product $\mu_B B_z$.

Table $8.8.3$ lists the quantities needed for the Zeeman effect analysis. The information in this table shows that the $2P_{3/2}$ term splits into 4 components. Two components move up in energy 6/3 units and 2/3 units, respectively, and two move down –6/3 and –2/3 units. The 2P$_{1/2}$ term splits into two components. One moves up 1/3 unit, and the other moves down 1/3 unit. The 2S$_{1/2}$ also splits into two components, each moving 1 unit up and down, respectively. The energies of these states in a magnetic field along with the allowed transitions between them are illustrated in Figure $8.8.3$. The addition of spin angular momentum has made the situation much more complicated. Previously we considered a Zeeman effect that produced 3 spectral lines from one, now 2 lines turn into 10 lines in a magnetic field. These 10 lines correspond to 10 different possible transitions of the electron from the 2p^1 configuration to the 1s^1 configuration. These transitions produce two multiplets in the spectrum, one of 6 lines and one of 4 lines.

Table $8.8.3$: Items for the Zeeman Effect Analysis

Term	**J**	**L**	**S**	**g**	**m$_J$**	**g m$_J$**
$2^P_{3/2}$	3/2	1	1/2	4/3	3/2	6/3
					1/2	2/3
					-1/2	-2/3
					-3/2	-6/3
$^2P_{1/2}$	1/2	1	1/2	2/3	1/2	1/3
					-1/2	-1/3
$^2S_{1/2}$	1/2	0	½	2	1/2	1
					-1/2	-1

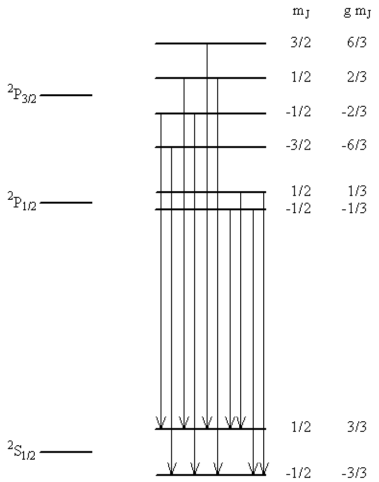

Figure $8.8.3$: Energy level diagram for the low-field Zeeman effect associated with the $2p \rightarrow 1s$ transition in the hydrogen atom, including the allowed transitions.

Exercise $8.8.6$

Using the information in Figure 8.8.8.3,(a) determine the spacing between the lines in the two multiplets in units of $\mu_B B_z$,(b) determine the magnitude of $\mu_B B_z$ </sub>for a field of 10,000 Gauss and for a field of 1 Tesla,(c) approximately what is the separation of the two multiplets in wavenumbers,(d) draw a sketch showing the field-on and field-off spectra you might record in the laboratory for the $2p \rightarrow 1s$ transition, and(e) from the allowed transitions that are shown in the figure and considering the ones that do not occur, determine what the selections rules must be for ΔS, ΔL, ΔJ, and ΔmJ.

8.E: The Hydrogen Atom (Exercises)

Q8.1

Calculate the probability density for a hydrogen 1s electron at a distance 3a$_0$ from the proton along the z-axis (a$_0$ is the Bohr radius).

Q8.2

Calculate the radial probability density for a hydrogen 1s electron to be 3a$_0$ from the proton.

Q8.3

Calculate the probability that a hydrogen 1s electron is within a distance 3a$_0$ from the nucleus.

Q8.4

Calculate and compare the average distances of the electron from the proton for the hydrogen 1s orbital and the 2s orbital. What insight do you gain from this comparison?

Q8.5

What is the percent error in the energy of the 1s orbital if the electron mass is used to calculate the energy rather than the reduced mass?

Q8.6

Calculate the energies (in units of electron volts and wavenumbers) of the three 1s to 2p transitions for a hydrogen atom in a magnetic field of 10 Tesla.

Q8.7

Calculate the frequency of radiation that would be absorbed due to a change in the electron spin state of a hydrogen atom in a magnetic field of 10 Tesla. Compare the energy of this transition to the energy of the 1s to 2p transitions in the previous problem. What insight do you gain from this comparison?

Q8.8

Which is larger for the hydrogen atom, the Zeeman splitting due to spin motion (electron in the 1s orbital) or the Zeeman splitting due to orbital motion (electron in the 2p orbitals neglecting spin)? Why is one larger than the other?

Q8.9

What is the difference between the average value of r and the most probable value of r where r is the distance of the electron from the nucleus?

Q8.10

Show that orbitals directed along the x and y axis can be formed by taking linear combinations of the spherical harmonics Y_1^{+1} and Y_1^{-1}. These orbitals are called p_x and p_y. Why do you think chemists prefer to use px and py rather than the angular momentum eigenfunctions?

Q8.11

What are the expectation values of $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ for the three 2p wavefunctions?

Q8.12

Why can $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$ have the same eigenfunctions?

Q8.13

Derive the selection rules for electronic transitions in the hydrogen atom. See Section 8.3 above and selection rules in Chapter 7. Use Mathcad to generate the radial probability densities for the 3s, 3p, and 3d atomic orbitals of hydrogen. What insight do you gain by comparing these plots?

Q8.14

Examine the Periodic Table and explain the relationship between the number and types of atomic orbitals, including spin, and the columns and rows.

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

8.S: The Hydrogen Atom (Summary)

The Schrödinger equation for one-electron atoms and ions such as H, He^+, Li^{2+}, etc. is constructed using a Coulombic potential energy operator and the three-dimensional kinetic energy operator written in spherical coordinates. Because the radial and angular motions are separable, solutions to the Schrödinger equation consist of products $R(r)Y(\theta,\varphi)$ of radial functions $R(r)$ and angular functions $Y(\theta,\varphi)$ that are called atomic orbitals. Three quantum numbers, n, l, and m_l are associated with the orbitals. Numerous visualization methods are available to enhance our understanding of the orbital shapes and sizes represented by the modulus squared of the wavefunctions. The orbital energy eigenvalues depend only on the n quantum number and match the energies found using the Bohr model of the hydrogen atom. Because all orbitals with the same principal quantum number have the same energy in one-electron systems, each orbital energy level is n2-degenerate. For example, the n = 3 level contains 9 orbitals (one 3s, three 3p's and five 3d's.)

Atomic spectra measured in magnetic fields have more spectral lines than those measured in field-free environments. This Zeeman effect is caused by the interaction of the imposed magnetic field with the magnetic dipole moment of the electrons, which removes the m_l quantum number degeneracy.

In addition to the orbital wavefunctions obtained by solving the Schrödinger equation, electrons in atoms possess a quality called spin that has associated wavefunctions σ, quantum numbers s and ms, spin angular momentum S and spectroscopic selection rules. Interaction with a magnetic field removes the degeneracy of the two spin states, which are labeled α and β, and produces additional fine structure in atomic spectra. While spin does not appear during the solution of the hydrogen atom presented in this text, spin is presented as a postulate because it is necessary to explain experimental observations about atoms.

Single-electron wavefunctions that incorporate both the orbital (spatial) and spin wavefunctions are called spin-orbitals. The occupancy of spin-orbitals is called the electron configuration of an atom. The lowest energy configuration is called the ground state configuration and all other configurations are called excited state configurations. To fully understand atomic spectroscopy, it is necessary to specify the total electronic state of an atom, rather than simply specifying the orbital configuration. An electronic state, or term, is characterized by a specific energy, total angular momentum and coupling of the orbital and spin angular momenta, and can be represented by a term symbol of the form ${}^{2s+1}L_J$ where S is the total spin angular momentum quantum number, L is the total orbital angular momentum quantum number and J is the sum of L and S. One term may include several degenerate electron configurations. The degeneracy of a term is determined by the number of projections of the total angular momentum vector on the z-axis. The degeneracy of a term can be split by interaction with a magnetic field.

Overview of key concepts and equations for the hydrogen atom

- Potential energy
- Hamiltonian
- Wavefunctions
- Quantum Numbers
- Energies
- Spectroscopic Selection Rules
- Angular Momentum Properties

Contributors and Attributions

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CHAPTER OVERVIEW

9: The Electronic States of the Multielectron Atoms

Multi-electron systems, including both atoms and molecules, are central to the study of chemistry. While we can write the Schrödinger equations for a two-electron atom and for many-electron atoms, the Schrödinger equations for atoms (and molecules too) with more than one electron cannot be solved because of electron-electron Coulomb repulsion terms in the Hamiltonian. These terms make it impossible to separate the variables and solve the Schrödinger equation. Fortunately, reasonably good approximate solutions can be found, and an active area of research for physical chemists involves finding methods to make them even better.

In this chapter you will learn several key techniques for approximating wavefunctions and energies, and you will apply these techniques to multi-electron atoms such as helium. You also will learn how to use the theoretical treatment of the electronic states of matter to account for experimental observations about multi-electron systems. For example, the periodic trends in ionization potential and atomic size that are presented in introductory chemistry texts and reproduced here in Figure 9.1 arise directly from the nature of the electronic states of the atoms in the periodic table.

9.1: The Schrödinger Equation For Multi-Electron Atoms

In this chapter, we will use the helium atom as a specific example of a multi-electron atom. Figure 9.1.1 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.

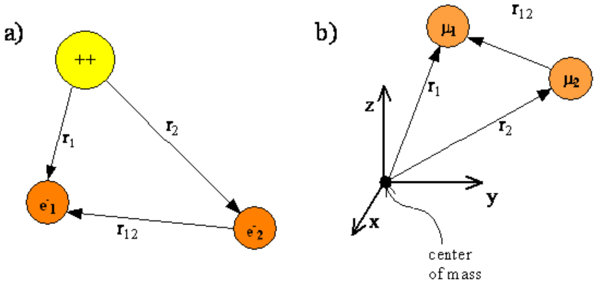

Figure 9.1.1: a) The nucleus (++) and electrons (e-) of the helium atom. b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that $\mu_1 \approx m_e$ and $\mu_2 \approx m_e$.

The Hamiltonian operator for the hydrogen atom serves as a reference point for writing the Hamiltonian operator for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} \tag{9.1.1}$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) + V(r_{12}) \tag{9.1.2}$$

where

$$V(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{9.1.3}$$

$$V(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{9.1.4}$$

$$V(r_{12}) = +\frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{9.1.5}$$

Equation 9.1.2 can be extended to any atom or ion by including terms for the additional electrons and replacing the He nuclear charge +2 with a general charge Z; e.g.

$$V(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{9.1.6}$$

Equation 9.1.2 then becomes

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i \neq j} V(r_{ij}) \tag{9.1.7}$$

Exercise 9.1.1

Referring to Equation 9.1.7, explain the meaning of the three summations and write expressions for the $V(r_i)$ and $V(r_{ij})$ terms.

Exercise 9.1.2

Write the multi-electron Hamiltonian (e.g. Equation 9.1.2) for a boron atom.

Each electron has its own kinetic energy term in Equations 9.1.2 and 9.1.7. For an atom like sodium there would be $\nabla_1^2, \nabla_2^2, \cdot, \nabla_{11}^2$. The other big difference between single electron systems and multi-electron systems is the presence of the $V(r_{ij})$ 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.

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 9.1.7 would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their Coulomb repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends simultaneously upon the coordinates of all the electrons; i.e., a multi-electron wavefunction, $\psi(r_1, r_2, \cdots r_i)$. The modulus squared of such a wavefunction would describe the probability of finding the electrons (though not specific ones) at a designated location in the atom. Alternatively, $ne|\psi|^2$ would describe the total amount of electron density that would be present at a particular spot in the multi-electron atom. 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.

> *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.*

Unfortunately, the Coulomb repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms and molecules even if there are only two electrons. The most basic approximations to the exact solutions involve writing a multi-electron wavefunction as a simple product of single-electron wavefunctions, and obtaining the energy of the atom in the state described by that wavefunction as the sum of the energies of the one-electron components.

$$\psi(r_1, r_2, \cdots, r_i) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_i(r_i) \tag{9.1.8}$$

By writing the multi-electron wavefunction as a product of single-electron functions, 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. For molecules, as we will see in the next chapter, they 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.

9.2: Solution of the Schrödinger Equation for Atoms- The Independent Electron Approximation

In this section we will see a useful method for approaching a problem that cannot be solved analytically and in the process we will learn why a product wavefunction is a logical choice for approximating a multi-electron wavefunction.

The helium atom Hamiltonian is re-written below with the kinetic and potential energy terms for each electron followed by the potential energy term for the electron-electron interaction. The last term, the electron-electron interaction, is the one that makes the Schrödinger equation impossible to solve.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_1 2} \tag{9.2.1}$$

To solve the Schrödinger Equation using this Hamiltonian, we need to make an assumption that allows us to find an approximate solution. The approximation that we consider in this section is the complete neglect of the electron-electron interaction term. Odd though it seems, this assumption corresponds mathematically to treating the helium atom as two non-interacting helium ions (with one electron each) that happen to share the same nucleus.

This approximation is called the independent-electron assumption. While this assumption might seem very drastic, it is worth trying since it also presents a straightforward path to a solution. A general strategy when solving difficult problems is to make an assumption and see how the results turn out. In this case we can compare the results we obtain using the assumption to what is known experimentally about the quantum states of helium, like the ionization energies. Are we a factor of 10 off? 10000? The latter result would probably indicate that we have hit a dead end with this method, while the former might indicate a method worth refining.

Neglecting the electron repulsion term simplifies the helium atom Hamiltonian to a sum of two hydrogen-like Hamiltonians that can be solved exactly.

$$\hat{H}(r_1, r_2) = \hat{H}(r_1) + \hat{H}(r_2) \tag{9.2.2}$$

The variables (the positions of the electrons, r_1 and r_2) in the Schrödinger equation separate, and we end up with two independent Schrödinger equations that are exactly the same as that for the hydrogen atom, except that the nuclear charge is +2e rather than +1e.

$$\hat{H}(r_1)\varphi(r_1) = E_1\varphi(r_1) \tag{9.2.3}$$

$$\hat{H}(r_2)\varphi(r_2) = E_2\varphi(r_2) \tag{9.2.4}$$

Exercise 9.2.1

What is the specific mathematical form for $\hat{H}(r_1)$ in Equation 9.2.2?

Using our previous experiences with separation of variables, we realize that the wavefunction can be approximated as a product of two **single-electron** hydrogen-atom wavefunctions with a nuclear charge $Z = +2e$,

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{9.2.5}$$

Exercise 9.2.2

Write the explicit mathematical expression for the ground state wavefunction for the helium atom shown in Equation 9.2.5.

Binding Energy

As we will show below, the energy eigenvalue associated with the product wavefunction is the sum of the one-electron energies associated with the component single-electron hydrogen-atom wavefunctions.

$$E_{He} = E_1 + E_2 \tag{9.2.6}$$

The energy calculated using the Schrödinger equation is also called the total energy or the binding energy. Binding energy is the energy required to separate the particles of a system (in this case the two electrons and the nucleus) to an infinite distance apart. The binding energy should not be confused with the ionization energy, IP, which is the energy required to remove only one electron from the helium atom. Binding energies can be measured experimentally by sequentially ionizing the atom and summing all the ionization energies. hence for the lithium atom with three electrons, the binding energy is

$$E_{He} = IP_1 + IP_2 + IP_3 \tag{9.2.7}$$

> *The binding energy (or total energy) should not be confused with the ionization energy, IP, which is the energy required to remove a single electron from the atom.*

Exercise 9.2.3

Why was it unnecessary to differentiate the terms binding energy and ionization energy for the hydrogen atom and other one-electron systems?

To calculate binding energies using the approximate Hamiltonian with the missing electron-electron repulsion term, we use the expectation value integral, Equation 9.2.8. This is a general approach and we've used it in earlier chapters. The notation $\int d\tau$ is used to represent integration over the three-dimensional space in spherical coordinates for electrons 1 and 2.

$$\langle E\rangle = \int \varphi_{1s}^*(r_1)\varphi_{1s}^*(r_2)[H(r_1) + H(r_2)]\varphi_{1s}(r_1)\varphi_{1s}(r_2)d\tau \tag{9.2.8}$$

The wavefunctions in Equation 9.2.8 are the hydrogen atom functions with a nuclear charge of +2e. The resulting energy for the helium ground state is

$$E_{approx} = 2Z^2E_H = -108\, eV \tag{9.2.9}$$

where $Z = +2$ and E_H is the binding energy of the hydrogen atom (-13.6 eV). The calculated result for the binding energy can be compared to the experimental value of -78.9 eV. The difference is due to the electron-electron interaction. The experimental and calculated binding and ionization energies are listed in Table 9.2.1.

Table 9.2.1: Spectroscopic and Calculated Energies for Helium

	Experimental	
E (energy to remove all electrons from nucleus)	-79.0 eV	
IP (energy to remove weakest electron from nucleus)	24.6 eV	

Exercise 9.2.4

Start with Equation 9.2.8 and show that E in fact equals -108 eV. Rather than evaluating integrals, derive that

$$E = 2Z^2E_H$$

and substitute the value for E_H.

The deviation of the calculated binding energy from the experimental value can be recognized as being good or bad depending on your point of view. It is bad because a 38% error is nothing to “brag about”; on the other hand, the comparison is good because the calculated value is close to the experimental value. Both the experiment and the calculation give an answer of about -100 eV for the binding energy of helium. This comparison tells you that although the electron repulsion term is important, the idea that the electrons are independent is reasonable. An independent-electron picture is reasonable because you can completely neglect the electron-electron interaction and you get a reasonable value for the binding energy, although it is not particularly accurate.

This observation is important because we can now feel justified in using the idea of independent electrons as a starting point for improved approximate solutions to the Schrödinger equation for multi-electron atoms and molecules. To find better approximate solutions for multi-electron systems, we start with wavefunctions that depend only on the coordinates of a single electron, and then take into account the electron-electron repulsion to improve the accuracy.

Getting highly accurate energies and computed properties for many-electron systems is not an impossible task. In subsequent sections of this chapter we approximate the helium atom using several additional widely applicable approaches, perturbation theory, the variational method, self consistent field theory and the Hartree-Fock approach (SCF-HF), and configuration interaction (CI). These basic computational chemistry tools are used to treat other multi-electron systems, both atomic and molecular, for applications ranging from interpretation of spectroscopy to predictions of chemical reactivity.

Contributors and Attributions

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9.3: Perturbation Theory

Perturbation theory is a method for continuously improving a previously obtained approximate solution to a problem, and it is an important and general method for finding approximate solutions to the Schrödinger equation. We discussed a simple application of the perturbation technique previously with the Zeeman effect.

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 $\hat{H}^1$, the first order term. In the general expression below, there can be an infinite number of correction terms of increasingly higher order,

$$\hat{H} = \hat{H}^0 + \hat{H}^1 + \hat{H}^2 + \cdots \tag{9.3.1}$$

but usually it is not necessary to have more terms than $\hat{H}^0$ and $\hat{H}^1$. For the helium atom,

$$\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \tag{9.3.2}$$

$$\hat{H}^1 = \frac{2e^2}{4\pi\epsilon_0 r_{12}} \tag{9.3.3}$$

In the general form of perturbation theory, the wavefunctions are also built as a sum of terms, with the zero-order terms denoting the exact solutions to the zero-order Hamiltonian and the higher-order terms being the corrections.

$$\psi = \psi^0 + \psi^1 + \psi^2 + \cdots \tag{9.3.4}$$

Similarly, the energy is written as a sum of terms of increasing order.

$$E = E^0 + E^1 + E^2 + \cdots \tag{9.3.5}$$

To solve a problem using perturbation theory, you start by solving the zero-order equation. This provides an approximate solution consisting of E_0 and ψ^0. The zero-order perturbation equation for the helium atom is

$$\hat{H}^0 \psi^0 = E^0 \psi^0 \tag{9.3.6}$$

We already solved this equation for the helium atom and found that E_0 = -108 eV by using the product of two hydrogen atom wavefunctions for ψ^0 and omitting the electron-electron interaction from $\hat{H}^0$.

The next step is to improve upon the zero-order solution by including$\hat{H}^1$, $\hat{H}^2$ etc. and finding ψ^1 and E_1, ψ^2 and E_2, etc. The solution is improved through the stepwise addition of other functions to the previously found result. These functions are found by solving a series of Schrödinger-like equations, the higher-order perturbation equations.

The first-order perturbation equation includes all the terms in the Schrödinger equation $\hat{H}\psi = E\psi$ that represent the first order approximations to $\hat{H}, \psi$ and E. This equation can be obtained by truncating $\hat{H}, \psi$ and E after the first order terms.

$$(\hat{H}^0 + \hat{H}^1)(\psi^0 + \psi^1) = (E^0 + E^1)(\psi^0 + \psi^1) \tag{9.3.7}$$

Now clear the parentheses to get

$$\hat{H}^0\psi^0 + \hat{H}^0\psi^1 + \hat{H}^1\psi^0 + \hat{H}^1\psi^1 = E^0\psi^0 + E^0\psi^1 + E^1\psi^0 + \hat{E}^1\psi^1 \tag{9.3.8}$$

The order of the perturbation equation matches the sum of the superscripts for a given term in the equation above. To form the first-order perturbation equation, we can drop the $\hat{H}^0\varphi^0$ and $E^0\psi^0$ terms because they are zero-order terms and because they cancel each other out, as shown by Equation 9.3.6 We can also drop the $\hat{H}\psi^1$ and $\hat{E}^1\varphi^1$ terms because they are second-order corrections formed by a product of two first-order corrections. The first order perturbation equation thus is

$$\hat{H}^0 \psi^1 + \hat{H}^1 \psi^0 = E^0 \psi^1 + E^1 \psi^0 \tag{9.3.9}$$

To find the first order correction to the energy take the first-order perturbation equation, multiply from the left by ψ^{0*} and integrate over all the coordinates of the problem at hand.

$$\int \psi^{0*} \hat{H}^0 \psi^1 d\tau + \int \psi^{0*} \hat{H}^1 \psi^0 d\tau = E^0 \int \psi^{0*} \psi^1 d\tau + E^1 \int \psi^{0*} \psi^0 d\tau \tag{9.3.10}$$

The integral in the last term on the right hand side of Equation 9.3.10 is equal to one because the wavefunctions are normalized. Because $\hat{H}^0$ is Hermitian, the first integral in Equation 9.3.10 can be rewritten to make use of Equation 9.3.6,

$$\int \psi^{0*} \hat{H}^0 \psi^1 d\tau = \int (\hat{H}^{0*} \varphi^{0*}) \varphi^1 d\tau = E^0 \int \varphi^{0*} \varphi^1 d\tau \tag{9.3.11}$$

which is the same as and therefore cancels the first integral on the right-hand side. Thus we are left with an expression for the first-order correction to the energy

$$E^1 = \int \psi^{0*} \hat{H}^1 \psi^0 d\tau \tag{9.3.12}$$

Since the derivation above was completely general, Equation 9.3.12 is a general expression for the first-order perturbation energy, which provides an improvement or correction to the zero-order energy we already obtained. The integral on the right is in fact an expectation value integral in which the zero-order wavefunctions are operated on by $\hat{H}^1$, the first-order perturbation term in the Hamiltonian, to calculate the expectation value for the first-order energy. This derivation justifies, for example, the method we used for the Zeeman effect to approximate the energies of the hydrogen atom orbitals in a magnetic field. Recall that we calculated the expectation value for the interaction energy (the first-order correction to the energy) using the exact hydrogen atom wavefunctions (the zero-order wavefunctions) and a Hamiltonian operator representing the magnetic field perturbation (the first-order Hamiltonian term.)

Exercise 9.3.7

Without using mathematical expressions, explain how you would solve Equation 9.3.12 for the first-order energy.

For the helium atom, the integral in Equation 9.3.12 is

$$E^1 = \int \int \varphi_{1s}(r_1) \varphi_{1s}(r_2) \frac{1}{r_{12}} \varphi_{1s}(r_1) \varphi_{1s}(r_2) d\tau_1 d\tau_2 \tag{9.3.13}$$

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

$$E_{approx2} = E^0 + E^1 = -74.8 eV \tag{9.3.14}$$

E^1 is the **average interaction energy** of the two electrons calculated using wavefunctions that assume there is no interaction.

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy, so the interaction of the two electrons is an important part of the total energy of the helium atom. We can continue with perturbation theory and find the additional corrections, E^2, E^3, etc. For example, $E^0 + E^1 + E^2$ = -79.2 eV. So with two corrections to the energy, the calculated result is within 0.3% of the experimental value of -79.00 eV. It takes thirteenth-order perturbation theory (adding E1 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 because we are left with the original zero-order wavefunctions. In the next section we will employ an approximation that modifies zero-order wavefunctions in order to address one of the ways that electrons are expected to interact with each other.

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9.4: The Variational Method

In this section we introduce the powerful and versatile variational method and use it to improve the approximate solutions we found for the helium atom using the independent electron approximation. One way to take electron-electron repulsion into account is to modify the form of the wavefunction. A logical modification is to change the nuclear charge, Z, in the wavefunctions to an effective nuclear charge, from +2 to a smaller value, ζ (called zeta) or Z_{eff}. The rationale for making this modification is that one electron partially shields the nuclear charge from the other electron, as shown in Figure $9.4.1$.

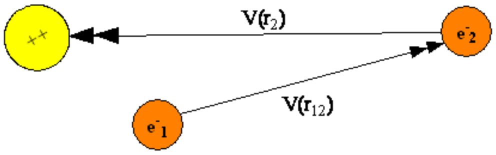

Figure $9.4.1$: Electron-electron shielding leading to a reduced effective nuclear charge. The attractive force of the nucleus on electron 2,$V(r_2)$, is partially countered by the repulsive force between electron 1 and electron 2, $V(r_{12})$.

A region of negative charge density between one of the electrons and the +2 nucleus makes the potential energy between them more positive (decreases the attraction between them). We can effect this change mathematically by using $\zeta < 2$ in the wavefunction expression. If the shielding were complete, then ζ would equal 1. If there is no shielding, then $\zeta = 2$. So a way to take into account the electron-electron interaction is by saying it produces a shielding effect. The shielding isn't zero, and it isn't complete, so the effective nuclear charge is between one and two.

In general, a theory should be able to make predictions in advance of knowledge of the experimental result. Consequently, a principle and method for choosing the best value for ζ or any other adjustable parameter that is to be optimized in a calculation is needed. The Variational Principle provides the required criterion and method. The Variational Principle says that the best value for any variable parameter in an approximate wavefunction is the value that gives the lowest energy for the ground state; i.e., the value that minimizes the energy. The variational method is the procedure that is used to find the lowest energy and the best values for the variable parameters.

The variational principle means that the expectation value for the binding energy obtained using an approximate wavefunction and the exact Hamiltonian operator will be higher than or equal to the true energy for the system. This idea is really powerful. When implemented, it permits us to find the best approximate wavefunction from a given wavefunction that contains one or more adjustable parameters, called a trial wavefunction. A mathematical statement of the variational principle is

$$\langle E_{trial} \rangle \ge E_{true} \tag{9.4.1}$$

where

$$\langle E_{trial} \rangle = \frac{\int \psi^*_{trial} \hat{H} \psi_{trial} \, d\tau}{\int \psi^*_{trial} \psi_{trial} \, d\tau} \tag{9.4.2}$$

Often the expectation value and normalization integrals in Equation 9.4.2 can be evaluated analytically. For the case of He described above, the trial wavefunction is the product wavefunction given by Equation 9.4.3:

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{9.4.3}$$

the adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ, and the Hamiltonian is the complete form given below.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2_1 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla^2_2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_1 2} \tag{9.4.4}$$

When the expectation value for the trial energy is calculated for helium, the result is a function that depends on the adjustable parameter, ζ.

$$E_{trial}(\zeta) = \frac{\mu e^4}{4\epsilon_0^2 h}\left(\zeta^2 - \frac{27}{8}\zeta\right) \tag{9.4.5}$$

This function is shown in Figure $9.4.2$. According to the variation principle, the minimum value of the energy on this graph is the best approximation of the true energy of the system, and the associated value of ζ is the best value for the adjustable parameter.

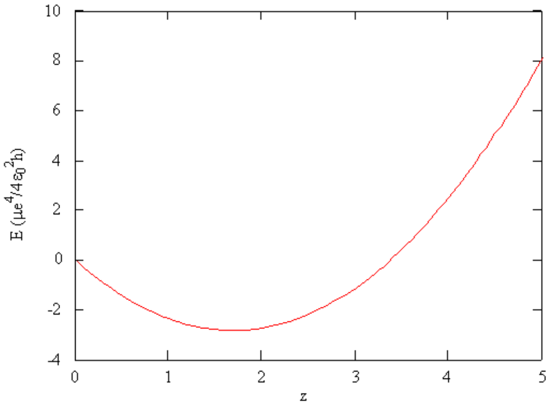

Figure $9.4.2$: Graph of trial energies for helium atom as a function of the adjustable parameter ζ, which represents the effective nuclear charge felt by the electrons. See Equation (9-33)

> *According to the variation principle, the minimum value of the variational energy (Equation 9.4.2) of a trial wavefunction is the best approximation of the true energy of the system.*

Using the mathematical function for the energy of a system, the minimum energy with respect to the adjustable parameter can be found by taking the derivative of the energy with respect to that parameter, setting the resulting expression equal to zero, and solving for the parameter, in this case ζ. This is a standard method in calculus for finding maxima and minima.

Exercise $9.4.2$

Find the value for ζ that minimizes the helium binding energy and compare the binding energy to the experimental value. What is the percent error in the calculated value?

When this procedure is carried out for He, we find $\zeta = 1.6875$ and the approximate energy we calculate using this third approximation method, $E \approx = -77.483\ eV$. Table $9.4.1$ show that a substantial improvement in the accuracy of the computed binding energy is obtained by using shielding to account for the electron-electron interaction. Including the effect of electron shielding in the wavefunction reduces the error in the binding energy to about 2%. This idea is very simple, elegant, and significant.

Table $9.4.1$: Comparison of the results of three approximation methods to experiment.

Method	He binding energy (eV)
Neglect repulsion between electrons	-108.8
First-order Perturbation	-74.8
Variation	-77.483
Experimental	-79.0

The improvement we have seen in the total energy calculations using a variable parameter ζ indicates that an important contribution of electron-electron interaction or repulsion to the total binding energy arises from the fact that each electron shields the nuclear charge from the other electron. It is reasonable to assume the electrons are independent; i.e., that they move independently, but the shielding must be taken into account in order to fine-tune the wavefunctions. The inclusion of optimizable parameters in the wavefunction allows us to develop a clear physical image of the consequences of our variation calculation. Calculating energies correctly is important, and it is also important to be able to visualize electron densities for multi-electron systems. In the next two sections, we take a temporary break from our consideration of approximation methods in order to examine multi-electron wavefunctions more closely.

9.5: Single-electron Wavefunctions and Basis Functions

Finding the most useful single-electron wavefunctions to serve as building blocks for a multi-electron wavefunction is one of the main challenges in finding approximate solutions to the multi-electron Schrödinger Equation. The functions must be different for different atoms because the nuclear charge and number of electrons are different. The attraction of an electron for the nucleus depends on the nuclear charge, and the electron-electron interaction depends upon the number of electrons.

As we saw in our initial approximation methods, the most straightforward place to start in finding reasonable single-electron wavefunctions for multi-electron atoms is with the atomic orbitals produced in the quantum treatment of hydrogen, the so-called “hydrogenic” spin-orbitals. These traditional atomic orbitals, with a few modifications, give quite reasonable calculated results and are still in wide use for conceptually understanding multi-electron atoms. In this section and in Chapter 10 we will explore some of the many other single-electron functions that also can be used as atomic orbitals.

Hydrogenic spin-orbitals used as components of multi-electron systems are identified in the same way as they are for the hydrogen atom. Each spin-orbital consists of a spatial wavefunction, specified by the quantum numbers (n, l, m_l) and denoted ls, 2s, 2p, 3s, 3p, 3d, etc, multiplied by a spin function, specified by the quantum number m_s and denoted α or β. In our initial approximation methods, we ignored the spin components of the hydrogenic orbitals, but they must be considered in order to develop a complete description of multi-electron systems. The subscript on the argument of the spatial function reveals which electron is being described (r_1 is a vector that refers to the coordinates of electron 1, for example.) No argument is given for the spin function. An example of a spin-orbital for electron 2 in a $3p_z$ orbital:

$$|\varphi_{3p_z}\alpha(r_2)\rangle = \varphi_{3,1,0}(r_2)\alpha \tag{9.5.1}$$

In the alternative shorthand notation for this spin-orbital shown below, the coordinates for electron 2 in the spatial function are abbreviated simply by the number “2,” and the spatial function is represented by “$3p_z$” rather than "$\varphi_{3,1,0}$". The argument “2” given for the spin function refers to the unknown spin variable for electron 2. Many slight variations on these shorthand forms are in use in this and other texts, so flexibility and careful reading are important.

$$|\varphi_{3p_z}\alpha(2)\rangle = 3p_z(2)\alpha(2) \tag{9.5.2}$$

In this chapter we will continue the trend of moving away from writing specific mathematical functions and toward a more symbolic, condensed representation. Your understanding of the material in this and future chapters requires that you keep in mind the form and properties of the specific functions denoted by the symbols used in each equation.

Exercise 9.5.1

Write the full mathematical form of $\varphi_{3pz\alpha}$ using as much explicit functional detail as possible.

The basic mathematical functions and thus the general shapes and angular momenta for hydrogenic orbitals are the same as those for hydrogen orbitals. The differences between atomic orbitals for the hydrogen atom and those used as components in the wavefunctions for multi-electron systems lie in the radial parts of the wavefunctions and in the energies. Specifically, the differences arise from the replacement of the nuclear charge Z in the radial parts of the wavefunctions by an adjustable parameter ζ that is allowed to vary in approximation calculations in order to model the interactions between the electrons. We discussed such a procedure for helium The Variational Method previously. The result is that electrons in orbitals with different values for the angular momentum quantum number, l, have different energies. Figure $9.5.1$ shows the results of a quantum mechanical calculation on argon in which the degeneracy of the 2s and 2p orbitals is found to be removed, as is the degeneracy of the 3s, 3p, and 3d orbitals.

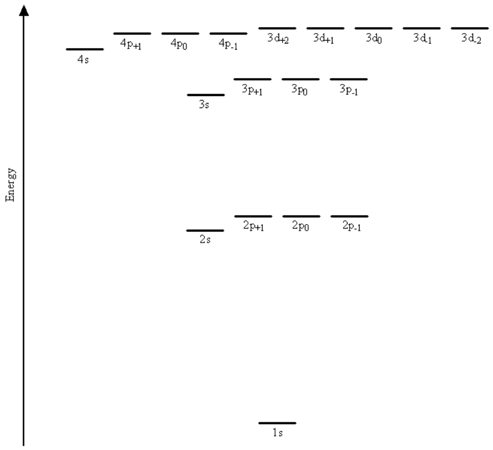

Figure 9.5.1: Ordering of energy levels for Ar. Energy level differences are not to scale.

The energy of each electron now depends not only on its principal quantum number, n, but also on its angular momentum quantum number, l.

The presence of ζ in the radial portions of the wavefunctions also means that the electron probability distributions associated with hydrogenic atomic orbitals in multi-electron systems are different from the exact atomic orbitals for hydrogen. Figure 9.5.2 compares the radial distribution functions for an electron in a 1s orbital of hydrogen (the ground state), a 2s orbital in hydrogen (an excited configuration of hydrogen) and a 1s orbital in helium that is described by the best variational value of ζ. Our use of hydrogen-like orbitals in quantum mechanical calculations for multi-electron atoms helps us to interpret our results for multi-electron atoms in terms of the properties of a system we can solve exactly.

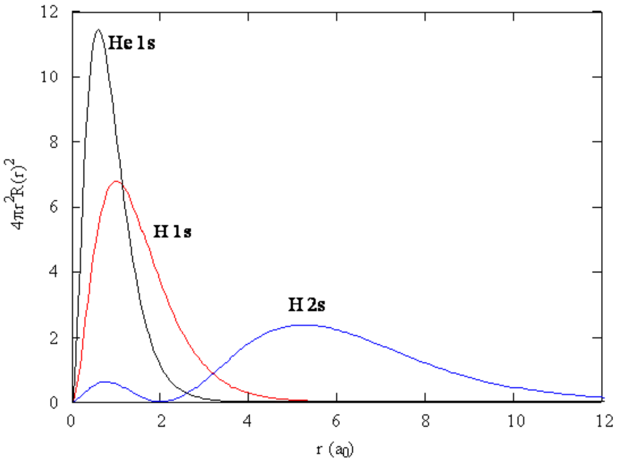

Figure 9.5.2: Radial distribution functions for 1s of hydrogen (red, ζ = 1), 2s of hydrogen (blue, ζ = 1) and 1s of helium (black, ζ = 1.6875).

Exercise 9.5.2

Analyze Figure 9.5.2 and write a paragraph about what you can discern about the relative sizes of ground state hydrogen, excited state hydrogen and ground state helium atoms.

While they provide useful stepping off points for understanding computational results, nothing requires us to use the hydrogenic functions as the building blocks for multi-electrons wavefunctions. In practice, the radial part of the hydrogenic atomic orbital presents a computational difficulty because the radial function has nodes, positive and negative lobes, and steep variations that make accurate evaluation of integrals by a computer slow. Consequently other types of functions are generally used in building multi-electron functions. These usually are related to the hydrogenic orbitals to aid in the analysis of molecular electronic structure. For example, Slater-type atomic orbitals (STO's), designated below as $S_{nlm}(r, \theta, \varphi)$, avoid the difficulties imposed by the hydrogenic functions. The STO's, named after their creator, John Slater, were the first alternative functions that were used extensively in computations. STO's do not have any radial nodes, but still contain a variational parameter ζ (zeta), that corresponds to the effective nuclear charge in the hydrogenic orbitals. In Equation 9.5.3 and elsewhere in this chapter, the distance, r, is measured in units of the Bohr radius, a_0.

$$S_{nlm}(r,\theta,\varphi)=\frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}}r^{n-1}e^{-\zeta r}Y_l^{\;m}(\theta,\varphi) \tag{9.5.3}$$

Exercise 9.5.3

a. Write the radial parts of the 1s, 2s, and 2p atomic orbitals for hydrogen.
b. Write the radial parts of the n = 1 and n = 2 Slater–type orbitals (STO).
c. Check that the above five functions are normalized.
d. Graph these five functions, measuring r in units of the Bohr radius.
e. Graph the radial probability densities for these orbitals. Put the hydrogen orbital and the corresponding STO on the same graph so they can be compared easily.
f. Adjust the zeta parameter ζ in each case to give the best match of the radial probability density for the STO with that of the corresponding hydrogen orbital.
g. Comment on the similarities and differences between the hydrogen orbitals and the STOs and the corresponding radial probability densities.

Linear Variational Method

An alternative approach to the general problem of introducing variational parameters into wavefunctions is the construction of a single-electron wavefunction as a linear combination of other functions. For hydrogen, the radial function decays, or decreases in amplitude, exponentially as the distance from the nucleus increases. For helium and other multi-electron atoms, the radial dependence of the total probability density does not fall off as a simple exponential with increasing distance from the nucleus as it does for hydrogen. More complex single-electron functions therefore are needed in order to model the effects of electron-electron interactions on the total radial distribution function. One way to obtain more appropriate single-electron functions is to use a sum of exponential functions in place of the hydrogenic spin-orbitals.

An example of such a wavefunction created from a sum or linear combination of exponential functions is written as

$$\varphi_{1s}(r_1)=\sum_j c_j e^{-\zeta_j r_j/a_o} \tag{9.5.4}$$

The linear combination permits weighting of the different exponentials through the adjustable coefficients (cj) for each term in the sum. Each exponential term has a different rate of decay through the zeta-parameter ζ_j. The exponential functions in Equation 9.5.4 are called basis functions. Basis functions are the functions used in linear combinations to produce the single-electron orbitals that in turn combine to create the product multi-electron wavefunctions. Originally the most popular basis functions used were the STO's, but today STO's are not used in most quantum chemistry calculations. However, they are often the functions to which more computationally efficient basis functions are fitted.

Physically, the ζ_j parameters account for the effective nuclear charge (often denoted with Z_{eff}. The use of several zeta values in the linear combination essentially allows the effective nuclear charge to vary with the distance of an electron from the nucleus. This variation makes sense physically. When an electron is close to the nucleus, the effective nuclear charge should be close to the actual nuclear charge. When the electron is far from the nucleus, the effective nuclear charge should be much smaller. See Slater's rules for a rule-of-thumb approach to evaluate Z_{eff} values.

A term in Equation 9.5.4 with a small ζ will decay slowly with distance from the nucleus. A term with a large ζ will decay rapidly with distance and not contribute at large distances. The need for such a linear combination of exponentials is a consequence of the electron-electron repulsion and its effect of screening the nucleus for each electron due to the presence of the other electrons.

Exercise 9.5.4

Make plots of φ in Equation 9.5.4 using three equally weighted terms with ζ = 1.0, 2.0, and 5.0. Also plot each term separately.

Computational procedures in which an exponential parameter like ζ is varied are more precisely called the Nonlinear Variational Method because the variational parameter is part of the wavefunction and the change in the function and energy caused by a change in the parameter is not linear. The optimum values for the zeta parameters in any particular calculation are determined by doing a variational calculation for each orbital to minimize the ground-state energy. When this calculation involves a nonlinear variational calculation for the zetas, it requires a large amount of computer time. The use of the variational method to find values for the coefficients, $\{c_j\}$, in the linear combination given by Equation $9.5.4$ above is called the Linear Variational Method because the single-electron function whose energy is to be minimized (in this case φ_{1s}) depends linearly on the coefficients. Although the idea is the same, it usually is much easier to implement the linear variational method in practice.

Nonlinear variational calculations are extremely costly in terms of computer time because each time a zeta parameter is changed, all of the integrals need to be recalculated. In the linear variation, where only the coefficients in a linear combination are varied, the basis functions and the integrals do not change. Consequently, an optimum set of zeta parameters were chosen from variational calculations on many small multi-electron systems, and these values, which are given in Table $9.5.1$, generally can be used in the STOs for other and larger systems.

Table $9.5.1$: Orbital Exponents for Slater Orbitals

Atom	ζ_{1s}	$\zeta_{2s,2p}$
H	1.24	
He	1.69	
Li	2.69	0.80
Be	3.68	1.15
B	4.68	1.50
C	5.67	1.72
N	6.67	1.95
O	7.66	2.25
F	8.56	2.55
Ne	9.64	2.88

Exercise $9.5.5$

Compare the value ζ_{1s} = 1.24 in Table $9.5.1$ for hydrogen with the value you obtained in Exercise $9.5.3$. and comment on possible reasons for any difference. Why are the zeta values larger for 1s than for 2s and 2p orbitals? Why do the ζ_{1s} values increase by essentially one unit for each element from He to Ne while the increase for the $\zeta_{2s,2p}$ values is much smaller?

The discussion above gives us some new ideas about how to write flexible, useful single-electron wavefunctions that can be used to construct multi-electron wavefunctions for variational calculations. Single-electron functions built from the basis function approach are flexible because they have several adjustable parameters, and useful because the adjustable parameters still have clear physical interpretations. Such functions will be needed in the Hartree-Fock method discussed elsewhere.

9.6: Electron Configurations, The Pauli Exclusion Principle, The Aufbau Principle, and Slater Determinants

To discuss the electronic states of atoms we need a system of notation for multi-electron wavefunctions. As we saw in Chapter 8, the assignment of electrons to orbitals is called the electron configuration of the atom. One creates an electronic configuration representing the electronic structure of a multi-electron atom or ion in its ground or lowest-energy state as follows. First, obey the Pauli Exclusion Principle, which requires that each electron in an atom or molecule must be described by a different spin-orbital. Second, assign the electrons to the lowest energy spin-orbitals, then to those at higher energy. This procedure is called the Aufbau Principle (which translates from German as build-up principle). The mathematical analog of this process is the construction of the approximate multi-electron wavefunction as a product of the single-electron atomic orbitals.

For example, the configuration of the boron atom, shown schematically in the energy level diagram in Figure $9.6.1$, is written in shorthand form as $1s^2 2s^2 2p^1$. As we saw in previously, the degeneracy of the 2s and 2p orbitals is broken by the electron-electron interactions in multi-electron systems.

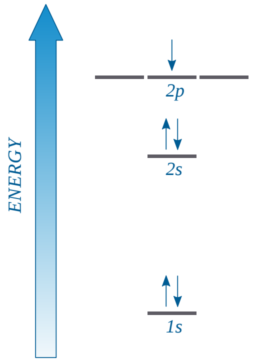

Figure $9.6.1$: Orbital energy level diagram that represents the electron configuration of the boron atom. Orbital energy differences are approximately to scale. (CC BY-SA; Ümit Kaya)

Rather than showing the individual spin-orbitals in the diagram or in the shorthand notation, we commonly say that up to two electrons can be described by each spatial orbital, one with spin function α (electron denoted by an arrow pointing up) and the other with spin function β (arrow pointing down). This restriction is a manifestation of the Pauli Exclusion Principle mentioned above. An equivalent statement of the Pauli Exclusion Principle is that each electron in an atom has a unique set of quantum numbers (n,l, m_l, m_s). Since the two spin functions are degenerate in the absence of a magnetic field, the energy of the two electrons with different spin functions in a given spatial orbital is the same, and they are shown on the same line in the energy diagram.

Exercise $9.6.1$

Write the electronic configuration of the carbon atom and draw the corresponding energy level diagram.

Exercise $9.6.2$

Write the values for the quantum numbers (n, l, m_l, m_s) for each of the six electrons in carbon.

We can deepen our understanding of the quantum mechanical description of multi-electron atoms by examining the concepts of electron indistinguishability and the Pauli Exclusion Principle in detail. We will use the following statement as a guide to keep our explorations focused on the development of a clear picture of the multi-electron atom: “When a multi-electron wavefunction is built as a product of single-electron wavefunctions, the corresponding concept is that exactly one electron’s worth of charge density is described by each atomic spin-orbital.”

A subtle, but important part of the conceptual picture is that the electrons in a multi-electron system are not distinguishable from one another by any experimental means. Since the electrons are indistinguishable, the probability density we calculate by squaring the modulus of our multi-electron wavefunction also cannot change when the electrons are interchanged (permuted) between different orbitals. In general, if we interchange two identical particles, the world does not change. As we will see below, this requirement leads to the idea that the world can be divided into two types of particles based on their behavior with respect to permutation or interchange.

For the probability density to remain unchanged when two particles are permuted, the wavefunction itself can change only by a factor of $e^{i\varphi}$, which represents a complex number, when the particles described by that wavefunction are permuted. As we will show below, the $e^{i\varphi}$ factor is possible because the probability density depends on the absolute square of the function and all expectation values involve $\psi\psi^*$. Consequently $e^{i\varphi}$ disappears in any calculation that relates to the real world because $e^{i\varphi}e^{-i\varphi}=1$.

We could symbolically write an approximate two-particle wavefunction as $\psi(r_1,r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_l) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_1,r_2)$. This new wavefunction must have the property that

$$|\psi(r_1,r_2)|^2=\psi(r_2,r_1)^*\psi(r_2,r_1)=\psi(r_1,r_2)^*\psi(r_1,r_2) \tag{9.6.1}$$

since the probability density of the electrons in the atom does not change upon permutation of the electrons.

Exercise 9.6.3

Permute the electrons in Equation ??? (the product function for He wavefunction.)

Equation 9.6.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1,r_2)=e^{i\varphi}\psi(r_1,r_2) \tag{9.6.2}$$

so that

$$\left(e^{-i\varphi}\psi(r_1,r_2)^*\right)\left(e^{i\varphi}\psi(r_1,r_2)^*\right)=\psi(r_1,r_2)^*\psi(r_1,r_2) \tag{9.6.3}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi}e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi}e^{i\varphi}=e^{i2\varphi}=1 \tag{9.6.4}$$

which is true only if $\varphi=0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi=0$) or -1 (when $\varphi=\pi$). Both possibilities are found in nature.

Exercise 9.6.4

Use Euler's Equality to show that $e^{12\varphi}=1$ when $\varphi=0$ or $n\pi$ and consequently $e^{i\varphi}=\pm1$.

Wavefunctions for which $e^{i\varphi}=+1$ are defined as symmetric with respect to permutation, because the wavefunction is identical before and after a single permutation. Wavefunctions that are symmetric with respect to interchange of the particles obey the following mathematical relationship:

$$e^{i\varphi}e^{i\varphi}=e^{i2\varphi}=1 \tag{9.6.5}$$

The behavior of some particles requires that the wavefunction be symmetric with respect to permutation. These particles are called bosons and have integer spin such as deuterium nuclei, photons, and gluons.

The behavior of other particles requires that the wavefunction be antisymmetric with respect to permutation $(e^{i\varphi}=-1)$. A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below:

$$\psi(r_2,r_1)=e^{i\varphi}\psi(r_1,r_2)=-\psi(r_1,r_2) \tag{9.6.6}$$

These particles, called fermions, have half-integer spin and include electrons, protons, and neutrinos.

Exercise 9.6.5

Explain without any equations why there are only two kinds of particles in the world: bosons and fermions.

In fact, an elegant statement of the Pauli Exclusion Principle is simply “electrons are fermions.” This statement means that any wavefunction used to describe multiple electrons must be antisymmetric with respect to permutation of the electrons, providing yet another statement of the Pauli Exclusion Principle. The requirement that the wavefunction be antisymmetric applies to all multi-electron functions $\psi(r_1, r_2, \cdots r_i)$, including those written as products of single electron functions $\varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_i(r_i)$.

> *Another way to simply restate the Pauli Exclusion Principle is that “electrons are fermions.”*

The first statement of the Pauli Exclusion Principle was that two electrons could not be described by the same spin orbital. To see the relationship between this statement and the requirement that the wavefunction be antisymmetric for electrons, try to construct an **antisymmetric wavefunction** for two electrons that are described by the same spin-orbital. We can try to do so for helium. Write the He approximate two-electron wavefunction as a product of identical 1s spin-orbitals for each electron,$\varphi_{1s_\alpha}(r_1)$ and $\varphi_{1s_\alpha}(r_2)$:

$$\psi(r_1, r_2) = \varphi_{1s\alpha}(r_1)\varphi_{1s\alpha}(r_2) \tag{9.6.7}$$

To permute the electrons in this two-electron wavefunction, we simply substitute the coordinates of electron 1 (r_l) for the coordinates of electron 2 (r_2) and vice versa, to get

$$\psi(r_2, r_1) = \varphi_{1s\alpha}(r_2)\varphi_{1s\alpha}(r_1) \tag{9.6.8}$$

This is identical to the original function (Equatin 9.6.7) since the two single-electron component functions **commute**. The two-electron function has not changed sign, as it must for fermions. We can construct a wavefunction that is antisymmetric with respect to permutation symmetry only if each electron is described by a different function.

Exercise 9.6.6

What is meant by the term permutation symmetry?

Exercise 9.6.7

Explain why the product function $\varphi(r_1)\varphi(r_2)$ could describe two bosons (deuterium nuclei) but can not describe two fermions (e.g. electrons).

Let’s try to construct an antisymmetric function that describes the two electrons in the ground state of helium. Blindly following the first statement of the Pauli Exclusion Principle, that each electron in a multi-electron atom must be described by a different spin-orbital, we try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$\psi(r_1, r_2) = \varphi_{1s\alpha}(r_1)\varphi_{1s\beta}(r_2) \tag{9.6.9}$$

After permutation of the electrons, this becomes

$$\psi(r_2, r_1) = \varphi_{1s\alpha}(r_2)\varphi_{1s\beta}(r_1) \tag{9.6.10}$$

which is different from the starting function (Equation 9.6.9) since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are **different** functions. However, an antisymmetric function must produce the same function multiplied by (–1) after permutation, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make a linear combination of functions. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 9.6.10 from the right-hand side of Equation 9.6.9 has the desired antisymmetric behavior.

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(r_1)\varphi_{1s\beta}(r_2) - \varphi_{1s\alpha}(r_2)\varphi_{1s\beta}(r_1)] \tag{9.6.11}$$

The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

Exercise 9.6.8

Show that the linear combination in Equation 9.6.11 is antisymmetric with respect to permutation of the two electrons. Replace the minus sign with a plus sign (i.e. take the positive linear combination of the same two functions) and show that the resultant linear combination is symmetric.

Exercise 9.6.9

Write a similar linear combination to describe the $1s^1 2s^1$ excited configuration of helium.

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a **Slater determinant**.

The Slater determinant for the two-electron wavefunction of helium is

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) \end{vmatrix} \tag{9.6.12}$$

and a shorthand notation for this determinant is

$$\psi(r_1, r_2) = 2^{-\frac{1}{2}} Det|\varphi_{1s}(r_1)\varphi_{1s}(r_2)| \tag{9.6.13}$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is $(N!)^{-\frac{1}{2}}$ for N electrons.

Exercise 9.6.10

Show that the determinant form is the same as the form for the helium wavefunction that is given in Equation 9.6.11.

Exercise 9.6.11

Expand the Slater determinant in Equation 9.6.12 for the He atom.

Exercise 9.6.12

Write and expand the Slater determinant for the electronic wavefunction of the Li atom.

Exercise 9.6.13

Write the Slater determinant for the carbon atom. If you expanded this determinant, how many terms would be in the linear combination of functions?

Exercise 9.6.14

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

Now that we have seen how acceptable multi-electron wavefunctions can be constructed, it is time to revisit the "guide" statement of conceptual understanding with which we began our deeper consideration of electron indistinguishability and the Pauli Exclusion

Principle. What does a multi-electron wavefunction constructed by taking specific linear combinations of product wavefunctions mean for our physical picture of the electrons in multi-electron atoms? Overall, the antisymmetrized product function describes the configuration (the orbitals, regions of electron density) for the multi-electron atom. Because of the requirement that electrons be indistinguishable, we can't visualize specific electrons assigned to specific spin-orbitals. Instead, we construct functions that allow each electron's probability distribution to be dispersed across each spin-orbital. The total charge density described by any one spin-orbital cannot exceed one electron's worth of charge, and each electron in the system is contributing a portion of that charge density.

Exercise $9.6.13$

Critique the energy level diagram and shorthand electron configuration notation from the perspective of the indistinguishability criterion. Can you imagine a way to represent the wavefunction expressed as a Slater determinant in a schematic or shorthand notation that more accurately represents the electrons? (This is not a solved problem!)

9.7: The Self-Consistent Field Approximation (Hartree-Fock Method)

In this section we consider a method for finding the best possible one-electron wavefunctions that was published by Hartree in 1948 and improved two years later by Fock. For the Schrödinger equation to be solvable, the variables must be separable. The variables are the coordinates of the electrons. In order to separate the variables in a way that retains information about electron-electron interactions, the Coulomb repulsion term, e.g. $\dfrac{e^2}{4\pi\epsilon_0 r_{12}}$ for helium, 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 best possible one-electron wavefunctions, by definition, will give the lowest possible total energy for a multi-electron system when combined into a Slater determinant and 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. Application of the variational method to the problem of minimizing the total energy leads to the following set of Schrödinger-like equations called Hartree-Fock equations,

$$\hat{F}\varphi_i = \epsilon_i \varphi_i \tag{9.7.1}$$

where $\hat{F}$ is called the Fock operator. 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 9.7.1. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving 9.7.1 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 atomic and molecular orbitals. The full antisymmetrized wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\hat{F} = \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \tag{9.7.2}$$

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. For electron 1 in helium, for example,

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \tag{9.7.3}$$

The second term in Equation 9.7.2, $\sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)$, accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we'll 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 operators $\hat{j}$ and $\hat{K}$ 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, $\dfrac{e^2}{4\pi\epsilon_0 r_{12}}$, which in atomic units simplifies to 1/r12. Atomic units are used in the rest of this discussion to simplify the notation by removing fundamental constants.

The operators $\hat{J}$ and $\hat{K}$ are most conveniently defined by examining how they operate on a wavefunction, φ_i, which describes electron 1.

$$\hat{J}_j(1)\varphi_i(1) = \left[\int \varphi_i^*(2)\frac{1}{r_{12}}\varphi_i(2)d\tau_2\right]\varphi_i(1) \tag{9.7.4}$$

$$\hat{K}_j(1)\varphi_i(1) = \left[\int \varphi_j^*(2)\frac{1}{r_{12}}\varphi_i(2)d\tau_2\right]\varphi_j(1) \tag{9.7.5}$$

$\hat{J}$ is called a Coulomb operator. As mentioned above, the specific coordinates 1 and 2 are used here to underline the fact that $\hat{J}$ operates on a function of one electron in an orbital (here, electron 1 in φ_i using the results of an expectation value integral over the coordinates of a different electron (electron 2 in φ_j. The second electron can be described by the same spatial orbital (if i = j) or by a different spatial orbital (if i ≠ j). $\hat{J}$ takes the complex conjugate of an orbital describing electron 2, $\varphi_j^*(2)\varphi_j(2)$, multiplies by 1/r12, and integrates over the coordinates of electron 2. The quantity $d\tau_2\varphi_j^*(2)\varphi_j(2)$ represents the charge distribution in space due to electron 2 in orbital j. The quantity $d\tau_2\varphi_j^*(2)\varphi_j(2)\frac{1}{r_{12}}$ thus represents the potential energy at r_1 due to the charge density at r_2 where r_{12} is the distance between r_1 and r_2. Evaluation of the integral gives the total potential energy at r1 due to the overall, or average, charge density produced by electron 2 in orbital j. Since the part of the Fock operator containing $\hat{J}$ involves a sum over all the orbitals, and a multiplicative factor of 2 to account for the presence of two electrons in each orbital, solution of the Hartree-Fock equation produces a spatial orbital φ_i that is determined by the average potential energy or Coulomb field of all the other electrons.

The other operator under the summation in the Fock operator is $\hat{K}$, the exchange operator. Equation 9.7.5 reveals that this operator involves a change in the labels on the orbitals. In analogy with the Coulomb operator, $d\tau_2\varphi_j^*(2)\varphi_i(2)\frac{1}{r_{12}}$ represents the potential energy at r_1 due to the overlap charge distribution at r_2 associated with orbitals i and j. The integral is the potential energy due to the total overlap charge density associated with electron 2. The term exchange operator is used because the electron is exchanged between the two orbitals i and j. This overlap contribution to the charge density and potential energy is a quantum mechanical effect. It is a consequence of the wave-like properties of electrons. Wave-like properties means the electrons are described by wavefunctions. While difficult to understand in a concrete physical way, the effects of the exchange operator are important contributors to the total energy of the orbitals and the system as a whole. There is no classical analog to this interaction energy, and a classical theory is unable to calculate correctly the energies of multi-electron systems.

For the ground state of helium, electrons 1 and 2 are both described by spatial orbital φ_i, so N = 1 and the sum in Equation 9.7.2 includes only j = 1. Furthermore, since i = j = 1, the exchange and Coulomb integrals are identical in this case. As a result, the summation in the Fock operator takes a very simple form and the complete Fock operator for electron 1 in helium is given by

$$\hat{F}(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} + \hat{U}(1) \tag{9.7.6}$$

where $\hat{U}(1)$ is given by the summation in the Fock operator.

$$\hat{U}(1) = \sum_{j=1}^{1}(2\hat{j}_j - \hat{K}_j) = \int \varphi_1(2)\frac{1}{r_{12}}\varphi_1(2)d\tau_2 \tag{9.7.7}$$

Exercise 9.7.30

Show that $\sum_{j=1}^{1}(2\hat{j}_j - \hat{K}_j) = \int \varphi_1(2)\frac{1}{r_{12}}\varphi_1(2)d\tau_2$ by substituting the definitions of $\hat{J}(1)$ and $\hat{K}(1)$ for helium into the summation and evaluating the summation over the only occupied spatial orbital.

The interaction of electron 1 with electron 2 is averaged over all positions of electron 2 to produce $\hat{U}(1)$. By integrating over the coordinates of electron 2, the explicit dependence of the potential energy on the coordinates of electron 2 is removed. This approach makes it possible to account for the electron-electron repulsion in terms of the spatial distribution of the two electrons using only single-electron terms in the Fock operator and one-electron wavefunctions.

Since both electrons in helium are described by the same spatial wavefunction, the Fock equation given by 9.7.8 and 9.7.6 describes either electron equally well. Solving the Fock equation therefore will give us the spatial wavefunction and the one-electron energy associated with either of the electrons.

The energy of an electron in the spatial orbital φ_1 can be calculated either by solving the Fock equation

$$\hat{F}(1)\varphi_1(1) = \epsilon_1(1)\varphi_1(1) \tag{9.7.8}$$

or by using an expectation value expression.

$$\epsilon_1(1) = \int \varphi_1^*(r_1)\hat{F}(r_1)\varphi_1(r_1)d\tau \tag{9.7.9}$$

In order to solve either of these equations for the energy ϵ_1, we need to evaluate the potential energy function $\hat{U}(1)$ that is part of the Fock operator $\hat{F}(1)$. In order to evaluate $\hat{U}(1)$, the forms of all of the occupied spatial orbitals, $\varphi_i(2)$ must be known. For the simple case of helium, only the $\varphi_1(2)$ function is required, but for larger multi-electron systems, the forms of occupied orbitals ϵ_1, ϵ_2 etc. will be needed to specify $\hat{U}(1)$. For helium, we know that $\varphi_1(2)$ will have the same form as $\varphi_1(1)$, and the φ_1 functions can be obtained by solving the Fock equation (9-58). However, we are now caught in a circle because the Fock operator depends upon the φ_1 function.

The problem with solving Equation 9.7.8 to obtain the Fock orbitals is that the Fock operator, as we have seen, depends on the Fock orbitals. In other words, we need to know the solution to this equation in order to solve the equation. We appear to be between a rock and a hard place. A procedure has been invented to wiggle out of this situation. One makes a guess at the orbitals, e.g. one inserts some adjustable parameters into hydrogenic wavefunctions, for example. These orbitals are used to construct the Fock operator that is used to solve for new orbitals. The new orbitals then are used to construct a new Fock operator, and the process is repeated until no significant change in the orbital energies or functions occurs. At this end point, the orbitals produced by the Fock operator are the same as the orbitals that are used in the Fock operator to describe the average Coulomb and overlap (or exchange) potentials due to the electron-electron interactions. The solution therefore is self-consistent, and the method therefore is called the self-consistent field (SCF) method.

The objective of the Hartree-Fock method is to produce the best possible one-electron wavefunctions for use in approximating the exact wavefunction for a multi-electron system, which can be an atom or a molecule. So what kind of guess functions should we write to get the best possible one-electron wavefunctions? Answers to this question have spawned a huge area of research in computation chemistry over the past 40 years, including a Nobel Prize in 1998. In Chapter 10 we examine in detail the various alternatives for constructing one-electron wavefunctions from basis functions.

Exercise 9.7.31

Write a paragraph without using any equations that describes the essential features of the Hartree-Fock method. Create a block diagram or flow chart that shows the steps involved in the Hartree-Fock method.

The expectation value of the Fock operator gives us the energy of an electron in a particular orbital.

$$\epsilon_i(1) = \int d\tau_1 \varphi_i^*(1)\hat{F}(1)\varphi_i(1) \tag{9.7.10}$$

Using the definition of the Fock operator and representing the integrals with bracket notation gives

$$\epsilon_i(1) = \langle H_i^0 \rangle + \sum_{j=1}^{N} (2J_{ij} - K_{ij}) \tag{9.7.11}$$

where

$$\langle H_i^0 \rangle = \left\langle \varphi_i | -\frac{1}{2}\nabla_1^2 | \varphi_i \right\rangle - \left\langle \varphi_i | \frac{Z}{r_1} | \varphi_i \right\rangle \tag{9.7.12}$$

The kinetic and potential energy terms in the operator $\hat{H}^0$, defined in Equation 9.7.3, are written here in atomic units for simplicity of notation. The sum involving the Coulomb and exchange integrals, J and K, accounts for the electron-electron interaction energy between the electron in orbital i and all the other electrons in the system. We now want to examine the meaning and the nature of the sum over all the orbitals in Equation 9.7.11.

Exercise 9.7.32

Describe the contributions to the orbital energy or single-electron energy $epsilon$ in words as represented by Equation 9.7.11.

For the case j = k one has for $2J_{ik} - K_{ik}$

$$2\left\langle \varphi_i(1)\varphi_k(2)|\frac{1}{r_{12}}|\varphi_i(1)\varphi_k(2)\right\rangle - \left\langle \varphi_i(1)\varphi_k(2)|\frac{1}{r_{12}}|\varphi_k(1)\varphi_i(2)\right\rangle \tag{9.7.13}$$

The first term with the factor of 2 is the average potential energy due to the charge distribution caused by an electron in orbital i with the charge distribution caused by the two electrons in orbital k. The factor of 2 accounts for the two electrons in orbital k. The second term is the average potential energy due to the overlap charge distribution caused by electrons 1 and 2 in orbitals i and k. The second term appears only once, i.e. without a factor of 2, because only one of the electrons in orbital k has the same spin as the electron in orbital i and can exchange with it. The minus sign results from the wavefunction being antisymmetric with respect to electron exchange.

Exercise 9.7.33

Rewrite Equation 9.7.13 including the spin functions α and β explicitly for each electron. Since these two spin functions form an orthonormal set and factor out of the spatial integrals, show that that the exchange integral is zero if the two electrons have different spin.

For the case j = i one has

$$2\left\langle \varphi_i(1)\varphi_i(2)|\frac{1}{r_{12}}|\varphi_i(1)\varphi_i(2)\right\rangle - \left\langle \varphi_i(1)\varphi_i(2)|\frac{1}{r_{12}}|\varphi_i(1)\varphi_i(2)\right\rangle \tag{9.7.14}$$

revealing that $J_{ii} = K_{ii}$, and $2J_{ii} - K_{ii} = J_{ii}$, which corresponds to the *Coulomb repulsion* between the two electrons in orbital i. Because these electrons have opposite spin, there is no exchange energy. This was the case for our helium example, above.

If the single-electron orbital energies are summed to get the total electronic energy, the Coulomb and exchange energies for each pair of electrons are counted twice: once for each member of the pair. These additional $2J - K$ contributions to the single-electron energies must be subtracted from the sum of the single-electron energies to get the total electronic energy, as shown in Equation 9.7.15. The factor of 2 accounts for the fact that two electrons occupy each spatial orbital, and {{\varepsilon }_{i}}\, is the energy of a single electron in a spatial orbital.

$$E_{elec} = \sum_{i=1}^{N}\left[2\epsilon_i - \sum_{j=1}^{N}(2J_{ii} - K_{ij})\right] \tag{9.7.15}$$

Exercise 9.7.34

Use Equations 9.7.11 and 9.7.15 to show that the total electronic energy also can be expressed in the following

$$E_{elec} = \sum_{i=1}^{N}\left[2\left\langle H_i^0\right\rangle - \sum_{j=1}^{N}(2J_{ii} - K_{ij})\right] \tag{9.7.16}$$

$$E_{elec} = \sum_{i=1}^{N}\left(\epsilon_i + \left\langle H_i^0\right\rangle\right) \tag{9.7.17}$$

forms.

Exercise 9.7.35

Write out all the terms in Equation 9.7.15 for the case of 4 electrons in 2 orbitals with different energies.

As we increase the flexibility of wavefunctions by adding additional parameters to the guess orbitals used in Hartree-Fock calculations, we expect to get better and better energies. The variational principle says that any approximate energy calculated using the exact Hamiltonian is an upper bound to the exact energy of a system, so the lowest energy that we calculate using the Hartree-Fock method will be the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single Slater determinant wavefunction. This limit is called the Hartree-Fock limit, the energy is the Hartree-Fock energy, the orbitals producing this limit are by definition the best single-electron orbitals that can be constructed and are called Hartree-Fock orbitals, and the Slater determinant is the Hartree-Fock wavefunction.

Contributors and Attributions

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

9.8: Configuration Interaction

The best energies obtained at the Hartree-Fock level are still not accurate, because they use an average potential for the electron-electron interactions. Configuration interaction (CI) methods help to overcome this limitation. Because electrons interact and repel each other, their motion in atoms is correlated. When one electron is close to the nucleus, the other tends to be far away. When one is on one side, the other tends to be on the other side. This motion is related to that of two people playing tag around a house. As we said before, the exact wavefunction must depend upon the coordinates of both electrons simultaneously. We have shown that it is a reasonable approximation in calculating energies to neglect this correlation and use wavefunctions that only depend upon the coordinates of one electron, which assumes the electrons move independently. This "orbital approximation" is similar to playing tag without keeping track of the other person. This independent-electron approximation gives reasonable, even good values, for the energy, and correlation can be taken into account to improve this description even more. The method for taking correlation into account is called **Configuration Interaction**.

In describing electrons in atoms, it is not necessary to be restricted to only a single orbital configuration given by a Slater determinant. We developed the Slater determinant as a way to create correctly antisymmetrized product wavefunctions that approximate the exact multi-electron function for an atom. By using more than one configuration and putting electrons in different orbitals, spatial correlations in the electron motion can be taken into account. This procedure is called Configuration Interaction (CI).

For example, for the two-electron Slater determinant wavefunction of helium, we could write

$$\psi(r_1, r_2) = \underbrace{c_1 Det|\varphi_{1s}(r_1)\varphi_{1s}(r_2)|}_{\text{ground state: } 1s^2} + \underbrace{c_2 Det|\varphi_{1s}(r_1)\varphi_{2s}(r_2)|}_{\text{excited state: } 1s^1 2s^1} \tag{9.8.1}$$

where c_1 and \(c_2) are coefficients (that can be varied in variational method). This wavefunction adds the excited (higher energy) configuration $1s^12s^1$ to the ground (lowest energy) configuration $1s^2$. The lowest energy configuration corresponds to both electrons being in the same region of space at the same time; the higher energy configuration represents one electron being close to the nucleus and the other electron being further away. This makes sense because the electrons repel each other. When one electron is in one region of space, the other electron will be in another region. Configuration interaction is a way to account for this correlation.

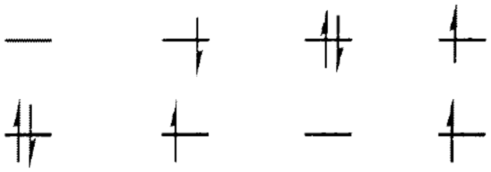

Figure 9.8.1: Within the CI approach the wavefunction for helius is a combination of all possible configurations (themselves described by Slater determinants. The wavefunction in Equation 9.8.1 would be the two left configurations

Exercise 9.8.1

Write a paragraph without using any equations that describes the essential features of configuration interaction.

SECTION OVERVIEW

9.9: Chemical Applications of Atomic Structure Theory

In this section we examine how the results of the various approximation methods considered in this chapter can be used to understand and predict the physical properties of multi-electron atoms. Our results include total electronic energies, orbital energies and single-electron wavefunctions that describe the spatial distribution of electron density. Physical properties that can be used to describe multi-electron atoms include total energies, atomic sizes and electron density distributions, ionization energies and electron affinities. Trends in these properties as Z increases form the basis of the periodic table and, as we see in Chapter 10, control chemical reactivity. Spectroscopic properties are considered in a link that includes a development of term symbols for multi-electron systems.

9.9.9A: Total Electronic Energies

9.9.9B: Orbital Energies

9.9.9C: Atomic Sizes and Electron Density Distributions

9.9.9D: Ionization Potentials

9.9.9E: Electron Affinity

9.9.9A: Total Electronic Energies

Experimental values of the total energy for helium have been used throughout the chapter to gauge the accuracy of our approximation methods. The variation theorem allows us to predict the total energies of atoms by solving for the lowest possible calculated energy. Using the results of variation calculations, perturbation theory, Hartree-Fock calculations, and/or configuration interaction, we can solve for the total energies of atoms with excellent accuracy.

9.9.9B: Orbital Energies

Orbital energies are not physical properties. They are constructs that arise from our approximate approach to a true multi-electron wavefunction using products of single-electron wavefunctions called atomic orbitals. Nevertheless, a great deal can be learned by considering orbital energies.

Our use of orbital energy level diagrams and the Aufbau principle to create electron configurations is based on the idea that the electrons fill the orbitals in order of increasing orbital energy. The implicit assumption is that the sum of the atomic orbital energies represents the total energy of the molecule. This assumption ignores electron correlation effects that arise when two electrons are in the same orbital. For example, electron configurations exhibit periodic trends in the number of electrons present in the atomic orbitals with the highest principal quantum number, n. These electrons are called valence electrons. The periodic table is arranged so that atoms with the same distributions of valence electrons are arranged in columns. Trends in physical properties track the trends in valence electron configurations and thus are called periodic properties.

We know how to calculate orbital energies from first principles. A single table or orbital energy level diagram that is valid for all elements does not suffice because the orbital energies depend on the electron-electron interactions that in turn depend on the number of electrons in the atom and the orbitals they occupy. Consequently, the orbital energies need to be specified for each element, which can be done most conveniently in graphical form.

The diagram/table reveals general trends as well as exceptions to these trends. A careful examination of the diagram reveals the basis for the electron configuration mnemonics or guides given in most introductory chemistry courses:

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p

For example the 1s orbital is always lowest in energy, followed by the 2s, 2p and 3s orbitals. The 4s is lower than the 3d orbital between elements 7 and 20, so the potassium and calcium electron configurations (Z = 19 and 20, respectively) have electrons in the 4s orbital rather than the 3d, and scandium (Z = 21) has the expected configuration [Ar]4s^{2}3d^1. For elements with very small and very large atomic numbers, the energies of all orbitals of a given n tend to converge.

Exercise 9.9.9$B.1B$

Predict the configurations of K, Sc, Ni, Sb, I and Xe.

The ground-state electron configurations of the elements are listed in Table 9.9.9$B.1$. The “exceptions” to the simple mnemonic noted in general chemistry texts are partly a consequence of the inadequacy of a “one-orbital order-fits-all” model. For example, copper has an electron configuration of [Ar]4s^{1}d^{10}. This configuration, which is at odds with the simple mnemonic, would be predicted successfully by the orbital ordering for copper given in an orbital energy diagram.

Table 9.9.9$B.1$: The ground-state electron configurations of the elements.

Atomic Symbol	Atomic Number	Configuration
H	1	1s^1
He	2	1s^2
Li	3	1s2 2s^1
Be	4	1s^2 2s^2
B	5	1s^2 2s^2 2p^1
C	6	1s^2 2s^2 2p^2
N	7	1s^2 2s^2 2p^3
O	8	1s2 2s2 2p4
F	9	1s2 2s2 2p5
Ne	10	1s2 2s2 2p6
Na	11	[Ne] 3s^1

Atomic Symbol	Atomic Number	Configuration
Mg	12	[Ne] $3s^2$
Al	13	[Ne] $3s^2$ $3p^1$
Si	14	[Ne] $3s^2$ $3p^2$
P	15	[Ne] $3s^2$ $3p^3$
S	16	[Ne] $3s^2$ $3p^4$
Cl	17	[Ne] $3s^2$ $3p^5$
Ar	18	[Ne] $3s^2$ $3p^6$
K	19	[Ar] $4s^1$
Ca	20	[Ar] $4s^2$
Sc	21	[Ar] $3d^1$ $4s^2$
Ti	22	[Ar] $3d^2$ $4s^2$
V	23	[Ar] $3d^3$ $4s^2$
Cr	24	[Ar] $3d^5$ $4s^1$
Mn	25	[Ar] $3d^5$ $4s^2$
Fe	26	[Ar] $3d^6$ $4s^2$
Co	27	[Ar] $3d^7$ $4s^2$
Ni	28	[Ar] $3d^8$ $4s^2$
Cu	29	[Ar] $3d^{10}$ $4s^1$
Zn	30	[Ar] $3d^{10}$ $4s^2$
Ga	31	[Ar] $3d^{10}$ $4s^2$ 4^{p1}
Ge	32	[Ar] $3d^{10}$ $4s^2$ $4p^2$
As	33	[Ar] $3d^{10}$ $4s^2$ $4p^3$
Se	34	[Ar] $3d^{10}$ $4s^2$ $4p^4$
Br	35	[Ar] $3d^{10}$ $4s^2$ $4p^5$
Kr	36	[Ar] $3d^{10}$ $4s^2$ $4p^6$

Even with our best calculations, however, we can’t successfully predict electron configurations for all elements using the ordering of orbital energies. For instance, orbital energy diagrams show that the 3d orbital energies are lower than the 4s orbital energies for all known elements with $Z > 20$. However, most of the elements in the first transition series have electron configurations with one or two electrons in the 4s orbital. The reason is that the sum of the orbital energies does not adequately describe the total energy of a multielectron system. Configuration interaction produces our best calculated values for the total energies of multi-electron systems, but the cost is that it wipes out the familiar conceptual picture of atomic orbitals and orbital energies.

9.9.9C: Atomic Sizes and Electron Density Distributions

Knowledge of the relative sizes of atoms is important because their chemistry often correlates with size. For example, substituting one element for another in a crystal to modify the properties of the crystal often works if the two elements have essentially the same atomic size. Understanding electron density distributions is also important in understanding chemical properties.

An approximate but reasonably accurate theoretical understanding of electron density patterns in multi-electron atoms can be built from an examination of the individual atomic orbitals. Thus, for the neon atom, for example, we can create a map of total electron density that can be used to produce pictures like the one shown in Figure $9.9.9C.8$, where colored contours represent different probability density isosurfaces. We create such a map by superimposing the contributions to the electron probability density that arise from each of the spin-orbitals used to construct the multi-electron wavefunction. Maps like this help us to understand the meaning of the size or spatial extent of an atom or molecule and are particularly useful when the degree of diffuseness of electron density needs to be understood. Electron diffraction experiments produce similar maps that can be compared to the theoretical results.

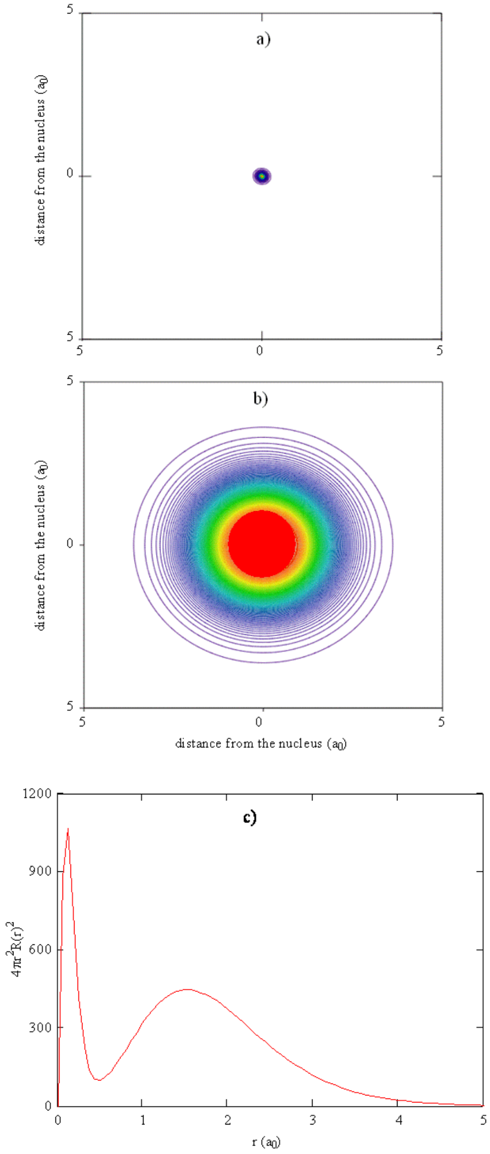

Figure $9.9.9C.1$: Representation of the total electron density map for neon, using the z values in Table $9.9.9C.3$. a) a contour map of the electron probability on the x-y plane b) the same figure as a) but with the high-density area near the nucleus truncated to show farther-out electron density c) the probability distribution function for the total electron density.

Although the size of an atom is not precisely defined because the positions of the electrons are given by probability density functions, various criteria have been proposed for characterizing atomic sizes. An empirical criterion, which originally was used by Pauling, is to take the atomic radius as half the bond length in a diatomic molecule of the element, e.g. C2 for carbon. This distance is called the covalent radius. It also can be determined indirectly by measuring the bond length for an atom of known covalent radius and subtracting this value from the bond length. X-ray crystallography and gas-phase microwave spectroscopy (rotational spectra) are powerful methods for providing such data.

Since the radial functions we obtain for the wavefunctions show electron density decaying exponentially with distance from the nucleus, there is no obvious end to an atom. To relate calculated probability densities to trends in atomic size, it is necessary to choose a cutoff point that can be applied consistently for different atoms. Various methods for doing so include drawing an edge for the atom so that a certain percentage, typically 95%, of the electron density is enclosed. Alternatively, the outside of the atom can be given by an isosurface of some specified total electron probability density. Another criterion that we could use to define the size is the position of the maximum in the radial function or the radial distribution function for the outermost electron. The outermost electron for a particular atom can be defined as the electron that has its maximum in the radial distribution function at the largest value of r.

The major periodic trends in the experimentally-measured atomic radii found in Figure $9.9.9C.1$ at the beginning of the chapter can be modeled with varying degrees of accuracy using the Hartree-Fock wavefunctions with any of the methods described above.

Exercise $9.9.9C.1C$

Predict the relative sizes of Li, Be, B, Al, Ca, Sr and Rh.

9.9.9D: Ionization Potentials

The energy it takes to remove an electron from an atom to infinity is called the ionization potential or the ionization energy. Ionization energy (IP) is the energy change of the following reaction, where the energy of the infinitely separated electron, called the free electron, is defined as zero.

$$A \rightarrow A^{+} + e^{-} \tag{9.9.9D.1}$$

with

$$\Delta E = E_f - E_i = IP_1 \tag{9.9.9D.2}$$

Since the chemical reaction of one element with another involves transferring or sharing electrons, the ionization energies of the electrons affect the chemical reactivity and bonding characteristics of the elements.

The first ionization energies of the elements are illustrated in Figure $9.9.9D.1$ and available in tabulated form (Table A6). The table also includes the second ionization energies

$$A^{+} \rightarrow A^{2+} + e^{-} \tag{9.9.9D.3}$$

with

$$\Delta E = E_f - E_i = IP_2 \tag{9.9.9D.4}$$

and third ionization energies

$$A^{2+} \rightarrow A^{3+} + e^{-} \tag{9.9.9D.5}$$

with

$$\Delta E = E_f - E_i = IP_3 \tag{9.9.9D.6}$$

for some elements.

In general, ionization energy increases across a period (a horizontal row of the periodic table) and decreases down a family (a vertical column of the periodic table.) These trends are often rationalized by assuming that the ionization energy is given by the negative of the orbital energy of the highest filled orbital. This assumption, called **Koopman's theorem**, correctly predicts most of the trends in ionization energy when the Hartree-Fock orbital energies are used. The extent to which ionization energies can be predicted by orbital energies is one measure of how well the product function approximates the true multi-electron wavefunction. The applicability of Koopman's theorem also depends on the similarity between the neutral atom and the positive ion. For example, the formation of a positive ion by removing an electron reduces the total electron-electron repulsion interactions, which in turn can change the relative ordering of energy levels in the neutral and positive ion. This effect can be seen for ions in the transition elements. The electron configurations of the first row transition element ions have electrons in the 3d orbitals and no electrons in the 4s orbital. The s and d orbitals are close in energy for the transition elements, and the effect of ionization is to lower the total energy of a configuration that contains occupied 3d orbitals relative to a configuration in which some of the electrons are in the 4s orbital.

When very careful values are required to explain discrepancies between theory and experiment in ionization energies, configuration interaction is used to calculate the total energy of the neutral and, in a separate calculation, the total energy of the positive ion. The two energies are then subtracted to give the ionization energy. This is akin to what we would do to calculate ionization energies if we were able to solve the multi-electron Schrödinger equation exactly. In that case, we would know the total energy eigenvalues of the multi-electron atom and ion and there would be no single-electron atomic orbital energies to worry about.

Exercise $9.9.9D.3$

How can the data in Figure $9.9.9D.1$ explain why the noble gases form few compounds?

Exercise $9.9.9D.4$

Use ionization energy data to explain why higher oxidation states of Mo might be found more readily than those of Cr.

Exercise $9.9.9D.5$

How can ionization energy data be used to explain why Cu^{2+} is common, but Ag^{2+} is not?

Exercise $9.9.9D.6$

Predict the relative first ionization potentials of Ba, Pb, At, Rn and Fr.

9.9.9E: Electron Affinity

The inverse of ionization, i.e. bringing an electron from infinity to occupy the lowest-energy vacancy in an atomic orbital, produces an energy change called the electron affinity.

$$A + e^- \rightarrow A^- \tag{9.9.9E.1}$$

with

$$\Delta E = E_f - E_i = EA \tag{9.9.9E.2}$$

Negative electron affinities, meaning that the above reaction is exothermic, are found for neutral atoms that are actually higher in energy than the corresponding anion, such as the halogens. The electron affinities of elements, just like their ionization potentials, are important in understanding their chemical reactivity and bonding characteristics. The electron affinity of a neutral atom is actually just the negative of an ionization energy for an anion (i.e, the reverse reaction for Equation 9.9.9E.1).

$$A^- \rightarrow A + e^- \tag{9.9.9E.3}$$

with

$$\Delta E = E_f - E_i = IP_A = -EA_A \tag{9.9.9E.4}$$

As above, the best values for electron affinities are obtained by calculating the difference in total binding energy between an anion and a neutral atom.

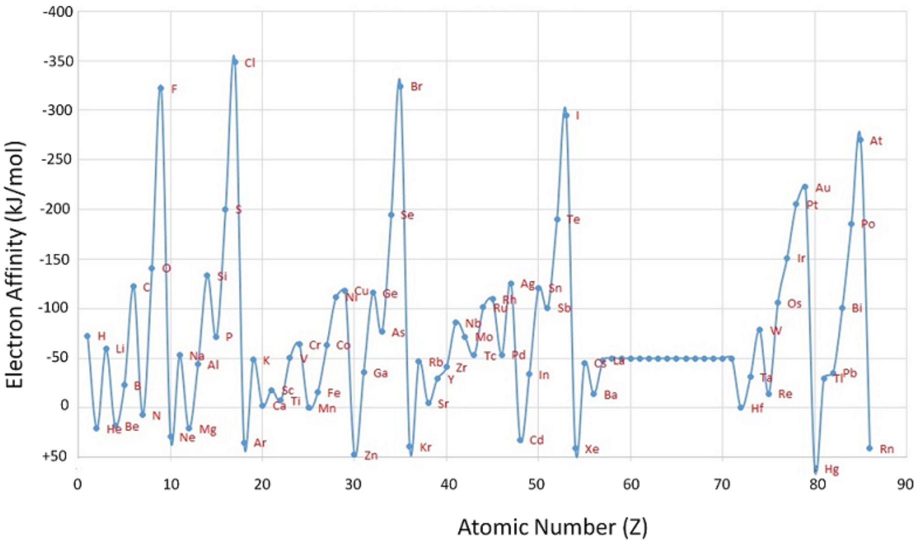

Figure 9.9.9E.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).

9.E: The Electronic States of the Multielectron Atoms (Exercises)

Q9.1

In the hydrogen atom, what is the energy of the *[Math Processing Error]* configuration? How many states result from this configuration? What are the term symbols for these states?

Q9.2

Determine the term symbols for the *[Math Processing Error]* electron configuration of carbon.

Q9.3

Determine the term symbol for the ground state of the sodium atom. Write the term symbols for the excited state where the valence electron is in a 3p orbital. Use this information to account for the appearance of the doublet known as the sodium D-line.

Q9.4

A helium atom is in a *[Math Processing Error]* electron configuration. What are the term symbols for the states that result from this configuration? Write antisymmetric (with respect to permutation symmetry) wavefunctions for these states. Show that only a transition from the ground state to one of these states is allowed through the electric-dipole-field interaction.

Q9.5

Rewrite Equation (9-13) so the wavefunction is antisymmetric with respect to permutation of the two electrons. Repeat Exercise 9.6 using your antisymmetric wavefunction to show that the same result is obtained, and, in because the electron-electron interaction is neglected, the energy does not depend on whether the wavefunction is symmetric or antisymmetric.

Q9.6

An ionization energy or ionization potential is the difference in energy between the energy of an atom and the energy of the corresponding ion. It also can be the difference in energy between an ion and the next higher charged ion. These different possibilities are referred to as the first, second, third, etc. ionization energies.

a. Calculate the ground state energy of He^+ and show that the calculated value of 54.4 eV in Table 9.1 for the first ionization energy is correct.
b. Use your insight to explain why the first ionization energy is just half the helium binding energy.

Q9.7

Compute the second ionization energy for Li (*[Math Processing Error]*) neglecting the electron-electron potential energy term in the Hamiltonian. The experimental value is 75.6 eV. Explain why the computed value differs from the experimental value.

Q9.8

For the ground state of hydrogen, the electron is in a 1s orbital where *[Math Processing Error]* so the Hamiltonian operator is *[Math Processing Error]*

Q9.9

Obtain an expression for the energy of the ground state of the hydrogen atom as a function of *[Math Processing Error]*, where *[Math Processing Error]* is an adjustable parameter in the trial wavefunction *[Math Processing Error]*, which is a Gaussian function.

Q9.10

Find the value for that minimizes the energy and calculate a value for the energy.

Q9.11

Compare this minimum energy with the exact value. What is the percent error?

Q9.12

Do you consider this Gaussian function to be a reasonable approximation to the exact hydrogen 1s atomic orbital?

Q9.13

What is the difference between this Gaussian function and the exact hydrogen 1s function? Illustrate the difference with a computer-generated graph.

Q9.14

Consider a one-dimensional anharmonic oscillator for which the potential function is *[Math Processing Error]*

a. Write the full Hamiltonian for this oscillator.
b. What system would serve as the most reasonable zero-order approximation for this oscillator in order to use perturbation theory most efficiently and effectively?
c. Identify the zero and first order perturbation terms in your Hamiltonian.
d. What is the zero order energy of the lowest energy state for this oscillator?
e. Write the integral for evaluating the first order correction to this energy and compute the first order correction to this energy.

Q9.15

Consider the particle in a box. Use first-order perturbation theory to determine how much the energy levels are shifted by an external electric field of V volts/cm.

Q9.16

Consider two electrons in a one-dimensional box.

a. What is the zero order energy of the lowest energy state for these electrons?
b. What is the first order correction to this energy due to the electron-electron interaction?

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

9.S: The Electronic States of the Multielectron Atoms (Summary)

In this chapter we have used the independent particle model for electrons (i.e, the idea that multi-electron wavefunctions can be approximated as products of single-electron wavefunctions) to approximate multi-electron atoms. State energies are calculated to be as accurate as possible through use of the Variational Method and Perturbation Theory. A large number of basis functions can be used with the SCF method to get the best possible one-electron functions. Although we only considered the helium atom explicitly, the method has been applied to all atoms of the Periodic Table.

We also introduced the idea of configuration interaction to account for electron correlation. Configuration interaction gives us a mathematical way to describe the electrons as they try to avoid each other. In the CI method excited state electron configurations are used to let the electrons avoid each other.

The various ideas presented here require computers to evaluate all the variational parameters and integrals. Many person-years of time and energy were required to write the computer code to do the calculations and assess the results. At this point in time, only the speed and capacity of the computers, our financial resources to pay for them, and the person-time to write the code limit the accuracy of the energies and wavefunctions. Once these demands were severe, and only dedicated experts could carry out such calculations. Today meaningful calculations can be done with desktop PC's or relatively inexpensive workstations using software that can be obtained commercially at little cost.

As we have seen, the single electron orbitals have associated energies and physically interpretable parameters such as the effective nuclear charge. It is precisely this independent particle picture that leads to an understanding of the ordering of atomic orbitals of atoms, the structure of the periodic table, the periodic trends in ionization energies and other properties of atoms, the chemical properties of the elements, and the nature of the chemical bond.

In modern quantum mechanical calculations in chemistry, the focus of research is primarily on molecules and their electronic properties and how the electronic properties determine chemical reactivity and molecular structure. Undergraduate students can do today with small computers what research scientists were doing a mere 10 years ago.

The following chapter will focus on the quantum mechanical concepts used in calculations to study molecules. We include an older method, the Hückel Molecular Orbital method, because it contains the elements found in more sophisticated computational approaches and provides the insight needed to relate the results of calculations to molecular properties.

Some Key Questions for Self Study

- What is a Slater determinant and why is it useful?
- What is the independent electron approximation?
- Why must each electron in an atom have a different set of quantum numbers (*[Math Processing Error]*)?
- How do you add angular momentum to obtain term symbols?
- How do you use term symbols to decide on the relative energies of states?
- How may states result from the carbon configuration *[Math Processing Error]*? What are the term symbols for these states?
- How many states result from the carbon configuration *[Math Processing Error]*? What is the term symbol for the ground state of carbon?
- What happens to the energies of states of an atom in a magnetic field and why? Describe an example.

CHAPTER OVERVIEW

10: Theories of Electronic Molecular Structure

Solving the Schrödinger equation for a molecule first requires specifying the Hamiltonian and then finding the wavefunctions that satisfy the equation. Since the wavefunctions involve the coordinates of all the nuclei and electrons that comprise the molecule, the complete molecular Hamiltonian consists of several terms. The nuclear and electronic kinetic energy operators account for the motion of all of the nuclei and electrons. The Coulomb potential energy terms account for the interactions between the nuclei, the electrons, and the nuclei and electrons.

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10.1: 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

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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 1000. 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 1000 times greater than yours. That person could literally run circles around you. So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei aren't 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

[Math Processing Error]

where

[Math Processing Error]

and

[Math Processing Error]

In Equation *[Math Processing Error]*, 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. Bold-face type is used to represent that *[Math Processing Error]* and *[Math Processing Error]* are vectors specifying the positions of all the electrons and all the nuclei, respectively.

Exercise *[Math Processing Error]*

Define all the symbols in Equations *[Math Processing Error]* through *[Math Processing Error]*.

Exercise *[Math Processing Error]*

Explain why the factor of 1/2 appears in the last term in Equation *[Math Processing Error]*.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation *[Math Processing Error]*, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction *[Math Processing Error]* is found as a solution to the electronic Schrödinger equation:

[Math Processing Error]

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, *[Math Processing Error]*.

As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product the Born-Oppenheimer Approximation

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This product wavefunction is called the Born-Oppenheimer wavefunction. The function [Math Processing Error] is the vibrational wavefunction, which is a function of the nuclear coordinates [Math Processing Error] and depends upon both the vibrational and electronic quantum numbers or states, [Math Processing Error] and [Math Processing Error], respectively. The electronic function, [Math Processing Error], is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, [Math Processing Error]. Translational and rotational motion is not included here. The translational and rotational wavefunctions simply multiply the vibrational and electronic functions in Equation [Math Processing Error] to give he complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

Crude Born-Oppenheimer Approximation

In the *Crude Born-Oppenheimer Approximation*, [Math Processing Error] is set equal to [Math Processing Error], the equilibrium separation of the nuclei, and the electronic wavefunctions are taken to be the same for all positions of the nuclei.

The electronic energy, [Math Processing Error], in Equation [Math Processing Error] 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 [Math Processing Error].

[Math Processing Error]

Consequently the Schrödinger equation for the vibrational motion is

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In Chapter 6, the potential energy was approximated as a harmonic potential depending on the displacement, [Math Processing Error], of the nuclei from their equilibrium positions.

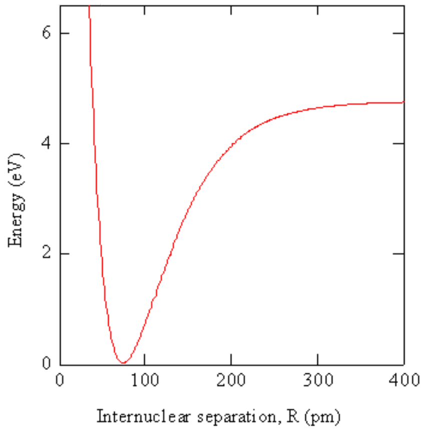

Figure [Math Processing Error]: The potential energy function for a diatomic molecule.

In practice the electronic Schrödinger equation is solved using approximations at particular values of [Math Processing Error] to obtain the wavefunctions [Math Processing Error] and potential energies [Math Processing Error]. The potential energies can be graphed as illustrated in Figure [Math Processing Error].

The graph in Figure [Math Processing Error] is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When [Math Processing Error] is very large there are two atoms that are weakly interacting. As [Math Processing Error] 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 [Math Processing Error], 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 [Math Processing Error]. If we obtain the wavefunction at [Math Processing

Error], and use this function for all values of *[Math Processing Error]*, we have employed the *Crude Born-Oppenheimer* approximation.

Exercise *[Math Processing Error]*

Relate Equation *[Math Processing Error]* to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

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.

Exercise *[Math Processing Error]*

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

10.2: The Orbital Approximation and Orbital Configurations

You should be able to recognize from the form of the electronic Hamiltonian, Equation that the electronic Schrödinger equation, Equation, cannot be solved. The problem, as for the case of atoms, is the electron-electron repulsion terms. Approximations must be made, and these approximations are based on the idea of using one-electron wavefunctions to describe multi-electron systems, in this case molecules just as is done for multi-electron atoms. Initially two different approaches were developed. Heitler and London originated one in 1927, called the **Valence Bond Method**, and Robert Mulliken and others developed the other somewhat later, called the **Molecular Orbital Method**. By using configuration interaction, both methods can provide equivalent electronic wavefunctions and descriptions of bonding in molecules, although the basic concepts of the two methods are different. We will develop only the molecular orbital method because this is the method that is predominantly employed now. The wavefunction for a single electron in a molecule is called a molecular orbital in analogy with the one-electron wavefunctions for atoms being called atomic orbitals.

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, *[Math Processing Error]*, as a linear combination of other functions, *[Math Processing Error]*, which are called basis functions because they provide the basis for representing the molecular orbital.

[Math Processing Error]

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: *[Math Processing Error]* is a general spin function (can be either *[Math Processing Error]* or *[Math Processing Error]*), *[Math Processing Error]* is the basis function (this usually represents an atomic orbital), *[Math Processing Error]* is a molecular orbital, and *[Math Processing Error]* is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in chemical structure.

Just as for atoms, each electron in a molecule can be described by a product of a spatial orbital and a spin function. These product functions are called 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,

[Math Processing Error]

Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, *[Math Processing Error]*. Following the Aufbau Principle, 2 electrons with different spins (*[Math Processing Error]* and *[Math Processing Error]*, consistent with the Pauli Exclusion Principle) 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 *[Math Processing Error]*. The electron configuration also can be specified by an orbital energy level diagram as shown in Figure *[Math Processing Error]*. Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure *[Math Processing Error]*.

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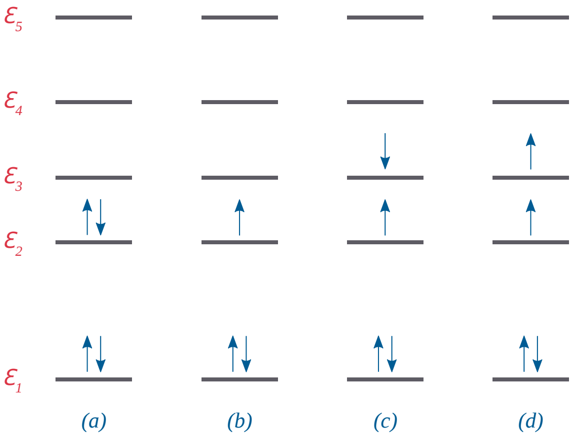


Figure *[Math Processing Error]*: a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration. (CC BY-SA 4.0; Ümit Kaya via LibreTexts)

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 *[Math Processing Error]*. 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. *[Math Processing Error]* or *[Math Processing Error]*, encodes this information, as well as information about the symmetry of the orbital. A *[Math Processing Error]* 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 *[Math Processing Error]* 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 *[Math Processing Error]* with the origin at the inversion center. Inversion takes you from *[Math Processing Error]* to *[Math Processing Error]*. 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 *[Math Processing Error]* is

[Math Processing Error]

10.3: Basis Functions

The molecular spin-orbitals that are used in the Slater determinant usually are expressed as a linear combination of some chosen functions, which are called *basis functions*. This set of functions is called the *basis set*. The fact that one function can be represented by a linear combination of other functions is a general property. All that is necessary is that the basis functions *span-the-space*, which means that the functions must form a complete set and must be describing the same thing. For example, spherical harmonics cannot be used to describe a hydrogen atom radial function because they do not involve the distance r, but they can be used to describe the angular properties of anything in three-dimensional space.

This span-the-space property of functions is just like the corresponding property of vectors. The unit vectors *[Math Processing Error]* describe points in space and form a complete set since any position in space can be specified by a linear combination of these three unit vectors. These unit vectors also could be called **basis vectors**.

Exercise *[Math Processing Error]*

Explain why the unit vectors *[Math Processing Error]* do not form a complete set to describe your classroom.

Just as we discussed for atoms, parameters in the basis functions and the coefficients in the linear combination can be optimized in accord with the Variational Principle to produce a self-consistent field (SCF) for the electrons. This optimization means that the ground state energy calculated with the wavefunction is minimized with respect to variation of the parameters and coefficients defining the function. As a result, that ground state energy is larger than the exact energy, but is the best value that can be obtained with that wavefunction.

Slater-type atomic orbitals (STOs)

Intuitively one might select hydrogenic atomic orbitals as the basis set for molecular orbitals. After all, molecules are composed of atoms, and hydrogenic orbitals describe atoms exactly if the electron-electron interactions are neglected. At a better level of approximation, the nuclear charge that appears in these functions can be used as a variational parameter to account for the shielding effects due to the electron-electron interactions. Also, the use of atomic orbitals allows us to interpret molecular properties and charge distributions in terms of atomic properties and charges, which is very appealing since we picture molecules as composed of atoms. As described in the previous chapter, calculations with hydrogenic functions were not very efficient so other basis functions, **Slater-type atomic orbitals (STOs)**, were invented.

A minimal basis set of STOs for a molecule includes only those STOs that would be occupied by electrons in the atoms forming the molecule. A larger basis set, however, improves the accuracy of the calculations by providing more variable parameters to produce a better approximate wavefunction, but at the expense of increased computational time.

For example, one can use more than one STO to represent one atomic orbital, as shown in Equation *[Math Processing Error]*, and rather than doing a nonlinear variational calculation to optimize each zeta, use two STOs with different values for zeta. The linear variation calculation then will produce the coefficients (*[Math Processing Error]* and *[Math Processing Error]*) for these two functions in the linear combination that best describes the charge distribution in the molecule. The function with the large zeta accounts for charge near the nucleus, while the function with the smaller zeta accounts for the charge distribution at larger values of the distance from the nucleus. This expanded basis set is called a **double-zeta basis set**.

[Math Processing Error]

Example *[Math Processing Error]*

- Plot the normalized radial probability density for a 2s hydrogenic orbital for lithium using an effective nuclear charge of 1.30.
- Fit that radial probability density with the radial probability density for 1 STO by varying the zeta parameter in the STO.
- Also fit the radial probability density for the hydrogenic orbital with that for the sum of 2 STOs, as in Equation (*[Math Processing Error]*), by varying the zeta parameters for each and their coefficients in the sum.
- Report your values for the zeta parameters and the coefficients and provide graphs of these functions and the corresponding radial probability densities. What are your conclusions regarding the utility of using STOs with single or double zeta values to describe the charge distributions in atoms and molecules?

The use of double zeta functions in basis sets is especially important because without them orbitals of the same type are constrained to be identical even though in the molecule they may be chemically inequivalent. For example, in acetylene the p_z orbital along the internuclear axis is in a quite different chemical environment and is being used to account for quite different bonding than the p_x and p_y orbitals. With a double zeta basis set the p_z orbital is not constrained to be the same size as the p_x and p_y orbitals.

Example *[Math Processing Error]*

Explain why the *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]* orbitals in a molecule might be constrained to be the same in a single-zeta basis set calculation, and how the use of a double-zeta basis set would allow the *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]* orbitals to differ.

The use of a minimal basis set with fixed zeta parameters severely limits how much the electronic charge can be changed from the atomic charge distribution in order to describe molecules and chemical bonds. This limitation is removed if STOs with larger n values and different spherical harmonic functions, the *[Math Processing Error]* in the definition of STO's in Chapter 9, are included. Adding such functions is another way to expand the basis set and obtain more accurate results. Such functions are called polarization functions because they allow for charge polarization away form the atomic distribution to occur.

Gaussian Basis Function

While the STO basis set was an improvement over hydrogenic orbitals in terms of computational efficiency, representing the STOs with Gaussian functions produced further improvements that were needed to accurately describe molecules. A **Gaussian basis function** has the form shown in Equation *[Math Processing Error]*. Note that in all the basis sets, only the radial part of the orbital changes, and the spherical harmonic functions are used in all of them to describe the angular part of the orbital.

[Math Processing Error]

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at $r = 0$, and they fall off more rapidly at large values of r.

Example *[Math Processing Error]*

Make plots of the following two functions

- *[Math Processing Error]*
- *[Math Processing Error]*

to illustrate how Gaussian functions differ from hydrogenic orbitals and Slater-type orbitals. The constants multiplying the exponentials normalize these functions. Describe the differences you observe between a Gaussian and a Slater-type function.

To compensate for this problem, each STO is replaced with a number of Gaussian functions with different values for the exponential parameter *[Math Processing Error]*. These Gaussian functions form a *primitive Gaussian basis set*. Linear combinations of the primitive Gaussians are formed to approximate the radial part of an STO. This linear combination is not optimized further in the energy variational calculation but rather is frozen and treated as a single function. The linear combination of *primitive Gaussian functions* is called a *contracted Gaussian function*. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials so there is a net gain in the efficiency of the calculation.

Gaussian basis sets are identified by abbreviations such as N-MPG*. N is the number of Gaussian primitives used for each inner-shell orbital. The hyphen indicates a split-basis set where the valence orbitals are double zeta. The M indicates the number of primitives that form the large zeta function (for the inner valence region), and P indicates the number that form the small zeta function (for the outer valence region). G identifies the set a being Gaussian. The addition of an asterisk to this notation means that a single set of Gaussian 3d polarization functions is included. A double asterisk means that a single set of Gaussian 2p functions is included for each hydrogen atom.

For example, 3G means each STO is represented by a linear combination of three primitive Gaussian functions. 6-31G means each inner shell (1s orbital) STO is a linear combination of 6 primitives and each valence shell STO is split into an inner and outer part (double zeta) using 3 and 1 primitive Gaussians, respectively.

Example [Math Processing Error]

The 1s Slater-type orbital [Math Processing Error] with [Math Processing Error] is represented as a sum of three primitive Gaussian functions,

[Math Processing Error]

This sum is the contracted Gaussian function for the STO.

a. Make plots of the STO and the contracted Gaussian function on the same graph so they can be compared easily. All distances should be in units of the Bohr radius. Use the following values for the coefficients, C, and the exponential parameters, [Math Processing Error].
b.

index j	[Math Processing Error]	Cj
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

c. Change the values of the coefficients and exponential parameters to see if a better fit can be obtained.
d. Comment on the ability of a linear combination of Gaussian functions to accurately describe a STO.

10.4: The Case of H₂⁺

One can develop an intuitive sense of molecular orbitals and what a chemical bond is by considering the simplest molecule, H_2^+. This ion consists of two protons held together by the electrostatic force of a single electron. Clearly the two protons, two positive charges, repeal each other. The protons must be held together by an attractive Coulomb force that opposes the repulsive Coulomb force. A negative charge density between the two protons would produce the required counter-acting Coulomb force needed to pull the protons together. So intuitively, to create a chemical bond between two protons or two positively charged nuclei, a high density of negative charge between them is needed. We expect the molecular orbitals that we find to reflect this intuitive notion.

The electronic Hamiltonian for H_2^+ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{10.4.1}$$

where r gives the coordinates of the electron, and R is the distance between the two protons. Although the Schrödinger equation for H_2^+ can be solved exactly 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.

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 $1s_B(r)$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{10.4.2}$$

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 ls_B.

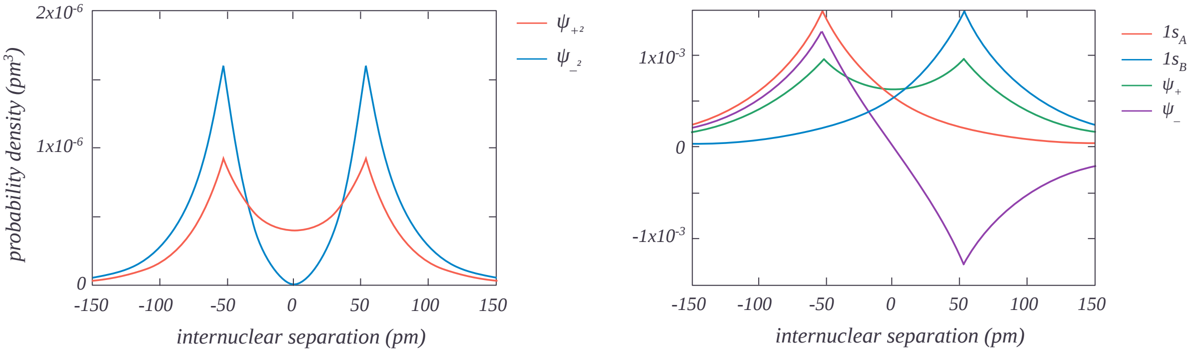
For H_2^+, the simplest molecule, the starting function is given by Equation 10.4.2. We must determine values for the coefficients, C_A and C_B. We could use the variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons 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, $C_A = C_B = C_+ \text{and} C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{10.4.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{10.4.4}$$

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 between the two protons, whereas it is diminished for ψ_- as shown in Figures 10.4.1. 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. 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**.

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 ψ_+ 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.



(b)

(a)

Figure 10.4.1: a) The 1s basis functions and bonding and antibonding molecular orbitals plotted along the internuclear axis, which is defined as the z-axis, for H_2^+. The protons are located at $\pm 53\,pm$, which corresponds to the experimental bond length. b) The electron probability density for the bonding and antibonding molecular orbitals

Exercise 10.4.1

From the information in Figure 10.4.1 for H_2^+, calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

The constants C_+ and C_- are evaluated from the normalization condition. Bracket notation, $< | >$, is used in Equation 10.4.5to represent integration over all the coordinates of the electron for both functions ψ_+ and ψ_-. The right bracket represents a function, the left bracket represents the complex conjugate of the function, and the two together mean integrate over all the coordinates.

$$\int \psi^*_\pm \psi_\pm d\tau = \langle \psi_\pm | \psi_\pm \rangle = 1 \tag{10.4.5}$$

$$\langle C_\pm [1s_A \pm 1s_B] | C_\pm [1s_A \pm 1s_B] \rangle = 1 \tag{10.4.6}$$

$$|C_\pm|^2 [(1s_A|1s_A) + (1s_B|1s_B) \pm (1s_B|1s_A) \pm (1s_A|1s_B)] = 1 \tag{10.4.7}$$

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.

Exercise 10.4.2

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.

The overlap integrals are telling us to take the value of ls$_B$ at a point multiply by the value of ls$_A$ at that point and sum (integrate) such a product over all of space. If the functions don't overlap, i.e. if one is zero when the other one isn't 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 cancellation of positive and negative contributions, as was discussed in Section 4.4.

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 $\langle 1s_A | 1s_B \rangle$, which is normalized to 1, because then $1s_A = 1s_B$.

With these considerations and using the fact that $1s$ wavefunctions are real so

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle = S \tag{10.4.8}$$

Equation 10.4.7becomes

$$|C_\pm|^2 (2 \pm 2S) = 1 \tag{10.4.9}$$

The solution to Equation 10.4.9is given by

$$C_{\pm}=[2(1\pm S)]^{-1/2} \tag{10.4.10}$$

The energy is calculated from the expectation value integral,

$$E_{\pm}=\left\langle\psi_{\pm}|\hat{H}_{elec}|\psi_{\pm}\right\rangle \tag{10.4.11}$$

which expands to give

$$E_{\pm}=\frac{1}{2(1\pm s)}[\left\langle 1s_A|\hat{H}_{elec}|1s_A\right\rangle+\left\langle 1s_B|\hat{H}_{elec}|1s_B\right\rangle\pm\left\langle 1s_A|\hat{H}_{elec}|1s_B\right\rangle\pm\left\langle 1s_B|\hat{H}_{elec}|1s_A\right\rangle] \tag{10.4.12}$$

Exercise 10.4.3

Show that Equation 10.4.11expands to give Equation 10.4.12

The four integrals in Equation 10.4.12 can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively. Notice that A and B appear equivalently in the Hamiltonian operator, Equation 10.4.1. This equivalence means that integrals involving $1s_A$ must be the same as corresponding integrals involving ls_B, i.e.

$$H_{AA}=H_{BB} \tag{10.4.13}$$

and since the wavefunctions are real,

$$H_{AB}=H_{BA} \tag{10.4.14}$$

giving

$$E_{\pm}=\frac{1}{1\pm S}(H_{AA}\pm H_{AB}) \tag{10.4.15}$$

Now examine the details of H_{AA} after inserting Equation 10.4.1for the Hamiltonian operator.

$$H_{AA}=\left\langle 1s_A|-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{4\pi\epsilon_0 r_A}|1s_A\right\rangle+\frac{e^2}{4\pi\epsilon_0 R}\langle 1s_A|1s_A\rangle-\left\langle 1s_A|\frac{e^2}{4\pi\epsilon_0 r_B}|1s_A\right\rangle \tag{10.4.16}$$

The first term is just the integral for the energy of the hydrogen atom, 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 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.

Now consider H_{AB}.

$$H_{AB}=\left\langle 1s_A|-\frac{\hbar^2}{1m}\nabla^2-\frac{e^2}{4\pi\epsilon_0 r_B}|1s_B\right\rangle+\frac{e^2}{4\pi\epsilon_0 R}\langle 1s_A|1s_B\rangle-\left\langle 1s_A|\frac{e^2}{4\pi\epsilon_0 r_A}|1s_B\right\rangle \tag{10.4.17}$$

In the first integral we have the hydrogen atom Hamiltonian and the H atom function $1s_B$. The function ls_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_HS. The second term is just the Coulomb 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**. It is called an exchange integral because the electron is described by the $1s_A$ orbital on one side and by the ls_B orbital on the other side of the operator. The electron changes or exchanges position in the molecule. 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} and HAB and substituting into Equation 10.4.15produces:

$$E_{\pm} = \frac{1}{1\pm S}\left[(E_H + \frac{e^2}{4\pi\epsilon_0 R})(1\pm S) + J \pm K\right] \tag{10.4.18}$$

$$= \underbrace{E_H}_{\text{H Atom Energy}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R}}_{\text{Proton-Proton repulsion}} + \underbrace{\frac{J\pm K}{1\pm S}}_{\text{Bonding Energy}} \tag{10.4.19}$$

The difference in energies of the two states $\Delta E_{\pm}$ is then:

$$\Delta E_{\pm} = E_{\pm} - E_H \tag{10.4.20}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J\pm K}{1\pm S} \tag{10.4.21}$$

Equation 10.4.19 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

$$\frac{J\pm K}{1\pm S} \tag{10.4.22}$$

If the protons are infinitely far apart then only E_H is nonzero. To get a chemical bond and a stable H_2^+ molecule, $\Delta E_{\pm}$ (Equation 10.4.20) must be less than zero and have a minimum, i.e.

$$\frac{J\pm K}{1\pm S} \tag{10.4.23}$$

must be sufficiently negative to overcome the positive repulsive energy of the two protons

$$\frac{e^2}{4\pi\epsilon_0 R} \tag{10.4.24}$$

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 10.4.4

Show that Equation 10.4.1 follows from Equation 10.4.15.

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.

Both J and K have been defined as

$$J = \left\langle 1s_A \middle| \frac{-e^2}{4\pi\epsilon_0 r_B} \middle| 1s_A \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_A}(r)\frac{e^2}{4\pi\epsilon_0 r_B}d\tau \tag{10.4.25}$$

$$K = \left\langle 1s_A \middle| \frac{-e^2}{4\pi\epsilon_0 r_A} \middle| 1s_B \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_B}(r)\frac{e^2}{4\pi\epsilon_0 r_A}d\tau \tag{10.4.26}$$

Note that both integrals are negative since all quantities in the integrand are positive. In the Coulomb integral, $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the charge density of the electron around proton A, since **r** represents the coordinates of the electron relative to proton A. Since r_B is the distance of this electron to proton B, the Coulomb integral gives the potential energy of the charge density around proton A interacting with proton B. J can be interpreted as an average potential energy of this interaction because $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the probability density for the electron at point **r**, and $\frac{e^2}{4\pi\epsilon_0 r_B}$ is the potential energy of the electron at that point due to the interaction with proton B. Essentially, J accounts for the attraction of proton B to the electron density of hydrogen atom A. As the two protons get further apart, this integral goes to zero because all values for r_B become very large and all values for $1/r_B$ become very small.

In the exchange integral, K, the product of the two functions is nonzero only in the regions of space where the two functions overlap. If one function is zero or very small at some point then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the 1/r values become zero. The product $e\varphi^*_{1s_A}(r)\varphi_{1a_B}(r)$ is called the *overlap charge density*. Since the overlap charge density is significant in the region of space between the two nuclei, it makes an important contribution to the chemical bond. The exchange integral, K, is the potential energy due to the interaction of the overlap charge density with one of the protons. While J accounts for the attraction of proton B to the electron density of hydrogen atom A, K accounts for the added attraction of the proton due the build-up of electron charge density between the two protons.

Exercise 10.4.5

Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for H_2^+.

Figure 10.4.2 shows graphs of the terms contributing to the energy of H_2^+. In this figure 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.

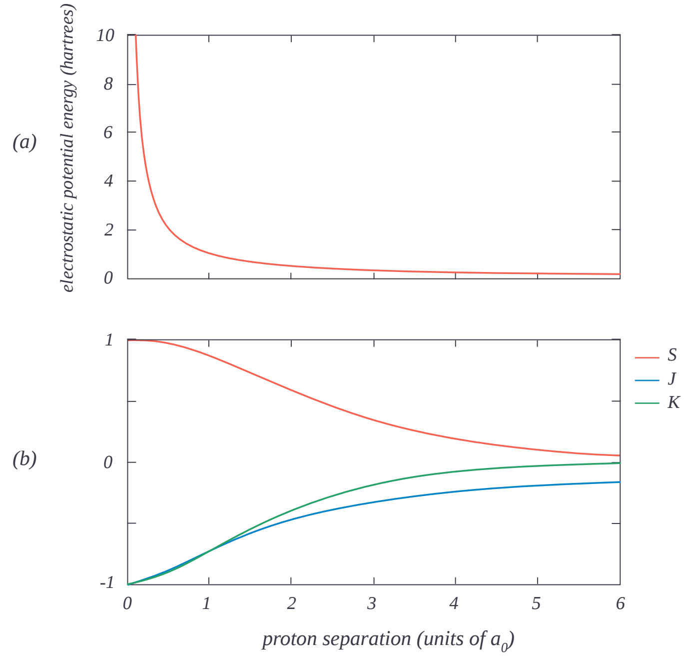


Figure 10.4.2 a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). b) The overlap, Coulomb, and exchange integrals at different proton separations. The units for J and K are hartrees; S has no units.

Figure 10.4.3 shows the energy of H_2^+ relative to the energy of a separated hydrogen atom and a proton as given by Equation 10.4.19. For the electron in the antibonding orbital, the energy of the molecule, $E_H(R)$, always is greater than the energy of the separated atom and proton.

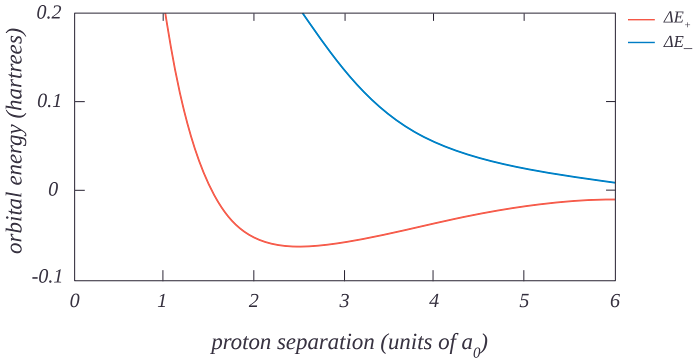


Figure 10.4.3: Energy of the H_2^+ bonding molecular orbital ΔE_+ and the antibonding molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

For the electron in the bonding 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 10.4.19to 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 10.4.19, 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.

This picture of bonding in H_2^+ 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).

Exercise 10.4.6

Write the final expressions for the energy of ψ_- and ψ_-, explain what these expressions mean, and explain why one describes the chemical bond in H2+and the other does not.

Exercise 10.4.7

Figure 10.4.2shows that $S = 1$ and $J = K = 1$ hartree when $R = 0$. Explain why S equals 1 and J and K equal -1 hartree when $R = 0$.

10.5: Homonuclear Diatomic Molecules

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. Quantitative theories are described in subsequent sections.

First consider diatomic carbon, C_2. The first question to ask is, “Are the electrons paired or unpaired?” For example, if we start with acetylene and remove 2 hydrogen atoms, we get C_2 with an unpaired electron on each carbon. On the other hand, it might be possible for these electrons to pair up and give C_2 with a quadruple bond. Let's examine the molecular orbital theory of C_2 to see what that theory predicts.

Just as for the hydrogen molecule, we combine the two corresponding atomic orbitals from each atom. We are using the smallest possible basis set for this discussion. From each combination, we get a bonding molecular orbital and an antibonding molecular orbital. We expect the p_z orbitals on the two atoms to have more overlap than the p_x and p_y orbitals. We therefore expect the exchange integrals to be larger and the resulting molecular orbital $2p_z\sigma_g$ to have a lower energy, i.e. be more bonding, than the $2p_x\pi_u$ and $2p_y\pi_u$, which are degenerate since the x and y directions are equivalent. Using the Aufbau Principle, we assign 2 electrons to each orbital as shown in Figure $10.5.1$, and end up with two electrons to put in two degenerate orbitals. Because of electron-electron repulsion, the lowest energy state will have each electron in a different degenerate orbital where they can be further apart than if they were in the same orbital. This separation reduces the repulsive Coulomb potential energy. Thus in C_2 we have 2 unpaired electrons, each in a bonding molecular orbital. The bond order, which is given by the number of electrons in bonding molecular orbitals minus the number of electrons in antibonding molecular orbitals divided by 2, is however 2, and each unpaired electron is not localized on a single C atom. So we see that the electronic structure of

$$C_2(1s\sigma_g^2, 1s\sigma_u^2, 2s\sigma_g^2, 2s\sigma_u^2, 2p\sigma_g^2, 2p\pi_u^2)$$

is quite different from what we would expect by thinking it is acetylene without the two H atoms. The acetylene structure naively predicts a triple bond and two nonbonded electrons on each carbon atom.

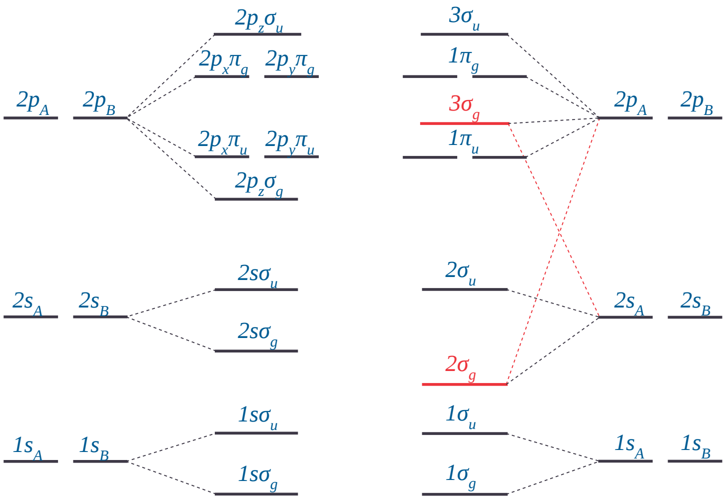


Figure 10.5.1: Ordering of molecular orbitals by energy for homonuclear diatomic molecules with (right side) and without (left side) significant mixing of molecular orbitals. The vertical energy axis is not to scale. (CC BY-NC; Ümit Kaya)

The two unpaired electrons in the two $2p\pi_u$ orbitals of C_2 predicted by this simple theory produce a singlet or a triplet ground state. The singlet ground state results if the electron spins are antiparallel $(\alpha\beta)$, and the triplet ground state results if the electron spins are parallel (the three triplet spin functions are $\alpha\alpha$ $\alpha\beta$ and $\beta\beta$). Hund’s rules predict the triplet state to have the lower energy, but the ground state of C_2 is known experimentally to be a singlet state. The singlet state results from a configuration where the $2p\sigma_g$ orbital has a higher energy than the $2p\pi_u$ orbitals, and all electrons are paired $(1s\sigma_g^2, 1s\sigma_u^2, 2s\sigma_g^2, 2s\sigma_u^2, 2p\pi_u^4, 2p\sigma_g^0)$. The bond order is still 2, but there are no unpaired electrons. All the molecular orbitals are doubly occupied.

This configuration is accounted for theoretically by a more complete theory that allows the molecular orbitals to be written as linear combinations of all the valence atomic orbitals not just a pair of atomic orbitals. The $2\sigma_g$ molecular orbital, which in the simple scheme is $2s_A + 2s_B$, is stabilized by mixing with $2p_{zA} + 2p_{zB}$, which is the $3\sigma_g$ orbital. As a result of this mixing, the $3\sigma_g$ orbital is destabilized and pushed to higher energy, above the $2p\pi_u$ orbitals. This mixing is just an example of hybridization. Better wavefunctions and better energies are obtained by using hybrid functions, which in this case is a linear combination of 1s and $2p_z$ functions. The relative energies of these hybrid orbitals also are shown on the right hand side of Figure $10.5.1$.

For such mixing to be important, the orbitals must have the same symmetry and be close to each other in energy. Because of these constraints, this mixing is most important for the $2s\sigma_g$ and $2p\sigma_g$ orbitals, both of which have symmetry. This ordering is found for all the diatomic molecules of the first row elements except O_2 and F_2. For these two molecules, the energy separation between the 2s and 2p orbitals is larger, and consequently the mixing is not strong enough to alter the energy level structure from that predicted by using the simple two-function basis set.

10.6: Semi-Empirical Methods- Extended Hückel

An electronic structure calculation from first principles (*ab initio*) presents a number of challenges. Many integrals must be evaluated followed by a self-consistent process for assessing the electron-electron interaction and then electron correlation effects must be taken into account. Semi-empirical methods do not proceed analytically in addressing these issues, but rather uses experimental data to facilitate the process. Several such methods are available. These methods are illustrated here by the approaches built on the work of Hückel.

Extended Hückel Molecular Orbital Method (EH)

One of the first semi-empirical methods to be developed was Hückel Molecular Orbital Theory (HMO). HMO was developed to describe molecules containing conjugated double bonds. HMO considered only electrons in π orbitals and ignored all other electrons in a molecule. It was successful because it could address a number of issues associated with a large group of molecules at a time when calculations were done on mechanical calculators.

The **Extended Hückel Molecular Orbital Method (EH)** grew out of the need to consider all valence electrons in a molecular orbital calculation. By considering all valence electrons, chemists could determine molecular structure, compute energy barriers for rotation about bonds, and even determine energies and structures of transition states for reactions. The computed energies could be used to choose between proposed transitions states to clarify reaction mechanisms.

In the EH method, only the n valence electrons are considered. The total valence electron wavefunction is described as a product of the one-electron wavefunctions.

$$\psi_{valence} = \psi_1(1)\psi_2(2)\psi_3(3)\psi_3(3)\ldots\psi_j(n) \tag{10.6.1}$$

where n is the number of electrons and j identifies the molecular orbital. Each molecular orbital is written as an linear combination of atomic orbitals (LCAO).

$$\psi_j = \sum_{r=1}^{N} c_{jr}\varphi_j \tag{10.6.2}$$

where now the φ_j are the valance atomic orbitals chosen to include the 2s, $2p_x$, $2p_y$, and $2p_z$ of the carbons and heteroatoms in the molecule and the 1s orbitals of the hydrogen atoms. These orbitals form the *basis set*. Since this basis set contains only the atomic-like orbitals for the valence shell of the atoms in a molecule, it is called a *minimal basis set*.

Each ψ_j, with $j = 1 \ldots N$, represents a molecular orbital, i.e. a wavefunction for one electron moving in the electrostatic field of the nuclei and the other electrons. Two electrons with different spins are placed in each molecular orbital so that the number of occupied molecular orbitals N is half the number of electrons, n, i.e. $N = n/2$.

The number of molecular orbitals that one obtains by this procedure is equal to the number of atomic orbitals. Consequently, the indices j and r both run from 1 to N. The c_{jr} are the weighting coefficients for the atomic orbitals in the molecular orbital. These coefficients are not necessarily equal, or in other words, the orbital on each atom is not used to the same extent to form each molecular orbital. Different values for the coefficients give rise to different net charges at different positions in a molecule. This charge distribution is very important when discussing spectroscopy and chemical reactivity.

The energy of the j^{th} molecular orbital is given by a one-electron Schrödinger equation using an effective one electron Hamiltonian, h_{eff}, which expresses the interaction of an electron with the rest of the molecule.

$$h_{eff}\psi_j = \epsilon_j\psi_j \tag{10.6.3}$$

is the energy eigenvalue of the j^{th} molecular orbital, corresponding to the eigenfunction ψ_j. The beauty of this method, as we will see later, is that the exact form of h_{eff} is not needed. The total energy of the molecule is the sum of the single electron energies.

$$E_\pi = \sum_j n_j\epsilon_j \tag{10.6.4}$$

where n_j is the number of electrons in orbital j.

The expectation value expression for the energy for each molecular orbital is used to find and then E_π

$$\epsilon_j = \frac{\int \psi_j \times h_{eff} \psi_j d\tau}{\int \psi_j \times \psi_j d\tau} = \frac{\langle \psi_j | h_{eff} | \psi_j \rangle}{\langle \psi_j | \psi_J \rangle} \tag{10.6.5}$$

The notation $\langle || \rangle$, which is called a bra-ket, just simplifies writing the expression for the integral. Note that the complex conjugate now is identified by the left-side position and the bra notation $< |$ and not by an explicit *.

After substituting Equation 10.6.2 into 10.6.5, we obtain for each molecular orbital

$$\epsilon_j = \frac{\left\langle \sum_{r=1}^{N} c_{jr} \psi_r | h_{eff} | \sum_{s=1}^{N} c_{js} \psi_s \right\rangle}{\left\langle \sum_{r=1}^{N} c_{jr} \psi_r | \sum_{s=1}^{N} c_{js} \psi_s \right\rangle} \tag{10.6.6}$$

which can be rewritten as

$$\epsilon = \frac{\sum_{r=1}^{N} \sum_{s=1}^{N} c_r^* c_s \langle \psi_r | h_{eff} | \psi_s \rangle}{\sum_{r=1}^{N} \sum_{s=1}^{N} c_r^* c_s \langle \psi_r | \psi_s \rangle} \tag{10.6.7}$$

where the index j for the molecular orbital has been dropped because this equation applies to any of the molecular orbitals.

Exercise 10.6.1

Consider a molecular orbital made up of three atomic orbitals, e.g. the three carbon $2p_z$ orbitals of the allyl radical, where the internuclear axes lie in the xy-plane. Write the LCAO for this MO. Derive the full expression, starting with Equation 10.6.5 and writing each term explicitly, for the energy expectation value for this LCAO in terms of heff. Compare your result with Equation 10.6.7 to verify that Equation 10.6.7 is the general representation of your result.

Exercise 10.6.2

Write a paragraph describing how the Variational Method could be used to find values for the coefficients cjr in the linear combination of atomic orbitals.

To simplify the notation we use the following definitions. The integrals in the denominator of Equation 10.6.7 represent the overlap between two atomic orbitals used in the linear combination. The overlap integral is written as S_{rs}. The integrals in the numerator of Equation 10.6.7 are called either resonance integrals or coulomb integrals depending on the atomic orbitals on either side of the operator h_{eff} as described below.

- $S_{Rs} = \langle \psi_r | \psi_s \rangle$ is the overlap integral. $S_{rr} = 1$ because we use normalized atomic orbitals. For atomic orbitals r and s on different atoms, S_{rs} has some value between 1 and 0: the further apart the two atoms, the smaller the value of S_{rs}.
- $H_{rr} = \langle \psi_r | h_{eff} | \psi_s \rangle$ is the **Coulomb Integral**. It is the kinetic and potential energy of an electron in, or described by, an atomic orbital, φ_r, experiencing the electrostatic interactions with all the other electrons and all the positive nuclei.
- $H_{rs} = \langle \psi_r | h_{eff} | \psi_s \rangle$ is the **Resonance Integral** or **Bond Integral**. This integral gives the energy of an electron in the region of space where the functions φ_r and φ_s overlap. This energy sometimes is referred to as the energy of the overlap charge. If r and s are on adjacent bonded atoms, this integral has a finite value. If the atoms are not adjacent, the value is smaller, and assumed to be zero in the Hückel model.

In terms of this notation, Equation 10.6.18 can be written as

$$\epsilon = \frac{\sum_{r=1}^{N} \sum_{s=1}^{N} c_r^* c_s H_{rs}}{\sum_{r=1}^{N} \sum_{s=1}^{N} c_r^* c_s S_{rs}} \tag{10.6.8}$$

We now must find the coefficients, the c's. One must have a criterion for finding the coefficients. The criterion used is the *Variational Principle*. Since the energy depends linearly on the coefficients in Equation 10.6.8, the method we use to find the best set of coefficients is called the **Linear Variational Method**.

Linear Variational Method

The task is to minimize the energy with respect to all the coefficients by solving the N simultaneous equations produced by differentiating Equation 10.6.8 with respect to each coefficient.

$$\frac{\partial \epsilon}{\partial c_t} = 0 \tag{10.6.9}$$

for $t = 1, 2, 3, \dots N$

Actually we also should differentiate Equation 10.6.8 with respect to the c_t^*, but this second set of N equations is just the complex conjugate of the first and produces no new information or constants.

To carry out this task, rewrite Equation 10.6.8 to obtain Equation 10.6.10 and then take the derivative of Equation 10.6.10 with respect to each of the coefficients.

$$\epsilon \sum_r \sum_s c_r^* c_s S_{rs} = \sum_r \sum_s c_r^* c_s H_{rs} \tag{10.6.10}$$

Actually we do not want to do this differentiation N times, so consider the general case where the coefficient is. Here t represents any number between 1 and N.

This differentiation is relatively easy, and the result, which is shown by Equation 10.6.12, is relatively simple because some terms in Equation 10.6.10 do not involve and others depend linearly on. The derivative of the terms that do not involve c_t is zero (e.g.

$$\frac{\partial c_3^* c_4 H_{34}}{\partial c_2} = 0. \tag{10.6.11}$$

The derivative of terms that contain is just the constant factor that multiples the, (e.g. $\dfrac{\partial c_3^* c_2 H_{32}}{\partial c_2} = c_3^* H_{32}$). Consequently, only terms in Equation 10.6.10 that contain contribute to the result, and whenever a term contains, that term appears in Equation 10.6.12 without the because we are differentiating with respect to. The result after differentiating is

$$\epsilon \sum_r c_r^* S_{rt} = \sum_r c_r^* H_{rt} \tag{10.6.12}$$

If we take the complex conjugate of both sides, we obtain

Since

$$\epsilon = \epsilon^*, S_{rt}^* = S_{tr} \tag{10.6.13}$$

and

$$H_{rt}^* = H_{tr}, \tag{10.6.14}$$

then Equation ??? can be reversed and written as

$$\sum_r c_r H_{tr} = \epsilon \sum_r c_r S_{tr} \tag{10.6.15}$$

or upon rearranging as

$$\sum_r c_r (H_{tr} - S_{tr} \epsilon) = 0 \tag{10.6.16}$$

There are N simultaneous equations that look like this general one; N is the number of coefficients in the LCAO. Each equation is obtained by differentiating Equation 10.6.10 with respect to one of the coefficients.

Exercise 10.6.3

Explain why the energy $\epsilon = \epsilon^*$, show that $S_{rt}^* = S_{tr}$ (write out the integral expressions and take the complex conjugate of , and show that $H_{rt}^* = H_{tr}$ (write out the integral expressions, take the complex conjugate of , and use the Hermitian property of quantum mechanical operators).

Exercise 10.6.4

Rewrite your solution to Exercise 10.6.3 for the 3-carbon π system found in the allyl radical in the form of Equation 10.6.10 and then derive the set of three simultaneous equations for the coefficients. Compare your result with Equation 10.6.16 to verify that Equation 10.6.16 is a general representation of your result.

This method is called the **linear variational method** because the variable parameters affect the energy linearly unlike the shielding parameter in the wavefunction that was discussed in Chapter 9. The shielding parameter appears in the exponential part of the wavefunction and the effect on the energy is nonlinear. A nonlinear variational calculation is more laborious than a linear variational calculation.

Equations 10.6.15 and 10.6.16 represent a set of homogeneous linear equations. As we discussed for the case of **normal mode analysis** in Chapter 6, a number of methods can be used for solving these equations to obtain values for the energies, $\epsilon' s$, and the coefficients, the $c_r' s$.

Matrix methods are the most convenient and powerful. First we write more explicitly the set of simultaneous equations that is represented by Equation . The first equation has t = 1, the second t = 2, *etc*. N represents the index of the last atomic orbital in the linear combination.

$$\begin{aligned} c_1 H_{11} + c_2 H_{12} + \dots c_n H_{1N} &= c_1 S_{11}\epsilon + c_2 S_{12}\epsilon + \dots c_N S_{1N}\epsilon \\ c_1 H_{21} + c_2 H_{22} + \dots c_n H_{2N} &= c_1 S_{21}\epsilon + c_2 S_{22}\epsilon + \dots c_N S_{2N}\epsilon \\ \vdots\vdots &= \vdots\vdots \\ c_1 H_{N1} + c_2 H_{N22} + \dots c_n H_{NN} &= c_1 S_{N1}\epsilon + c_2 S_{N2}\epsilon + \dots c_N S_{NN}\epsilon \end{aligned} \tag{10.6.17}$$

This set of equations can be represented in matrix notation.

$$HC' = SC'\epsilon \tag{10.6.18}$$

Here we have square matrix **H** and **S** multiplying a column vector **C'** and a scalar ϵ. Rearranging produces

$$HC' - SC'\epsilon = 0 \tag{10.6.19}$$

$$(H - S\epsilon)C' = 0 \tag{10.6.20}$$

Exercise 10.6.5

For the three atomic orbitals you used in Exercises ??? and ???, write the Hamiltonian matrix H, the overlap matrix S, and the vector C'. Show by matrix multiplication according to Equation 10.6.18 that you produce the same Equations that you obtained in Exercise 10.6.21.

The problem is to solve these simultaneous equations, or the matrix equation, and find the orbital energies, which are the $\epsilon' s$, and the atomic orbital coefficients, the $c' s$, that define the molecular orbitals.

Exercise 10.6.6

Identify two methods for solving simultaneous equations and list the steps in each.

In the EH method we use an effective one electron Hamiltonian, and then proceed to determine the energy of a molecular orbital where $H_{rs} = \langle \psi_r | h_{eff} | \psi_s \rangle$ and $S_{rs} = \langle \psi_r | \psi_s \rangle$.

Minimization of the energy with respect to each of the coefficients again yields a set of simultaneous equations just like Equation 10.6.16.

$$\sum_r c_r (H_{tr} - S_{tr}\epsilon) = 0 \tag{10.6.21}$$

As before, these equations can be written in matrix form in Equation 10.6.18

Equation 10.6.18 accounts for one molecular orbital. It has energy ϵ, and it is defined by the elements in the **C'** column vector, which are the coefficients that multiply the atomic orbital basis functions in the linear combination of atomic orbitals.

We can write one matrix equation for all the molecular orbitals.

$$HC = SCE \tag{10.6.22}$$

where **H** is a square matrix containing the H_{rs}, the one electron energy integrals, and **C** is the matrix of coefficients for the atomic orbitals. Each column in **C** is the **C'** that defines one molecular orbital in terms of the basis functions. In extended Hückel theory, the overlap is not neglected, and **S** is the matrix of overlap integrals. **E** is the diagonal matrix of orbital energies. All of these are square matrices with a size that equals the number of atomic orbitals used in the LCAO for the molecule under consideration.

Equation 10.6.22 represents an eigenvalue problem. For any extended Hückel calculation, we need to set up these matrices and then find the eigenvalues and eigenvectors. The eigenvalues are the orbital energies, and the eigenvectors are the atomic orbital coefficients that define the molecular orbital in terms of the basis functions.

Exercise 10.6.7

What is the size of the H matrix for HF? Write out the matrix elements in the H matrix using symbols for the wavefunctions appropriate to the HF molecule. Consider this matrix and determine if it is symmetric by examining pairs of off-diagonal elements. In a symmetric matrix, pairs of elements located by reflection across the diagonal are equal, i.e. Hrc = Hcr where r and c represent the row and column, respectively. Why are such pairs of elements equal? Write out the S matrix in terms of symbols, showing the diagonal and the upper right portion of the matrix. This matrix also is symmetric, so if you compute the diagonal and the upper half of it, you know the values for the elements in the lower half. Why are pairs of S matrix elements across the diagonal equal?

The elements of the **H** matrix are assigned using experimental data. This approach makes the extended Hückel method a *semi-empirical* molecular orbital method. The basic structure of the method is based on the principles of physics and mathematics while the values of certain integrals are assigned by using educated guesses and experimental data. The H_{rr} are chosen as valence state ionization potentials with a minus sign to indicate binding. The values used by R. Hoffmann when he developed the extended Hückel technique were those of H.A. Skinner and H.O. Pritchard (Trans. Faraday Soc. **49** (1953), 1254). These values for C and H are listed in Table 10.6.1. The values for the heteroatoms (N, O, and F) are taken from Pople and Beveridge (*Approximate Molecular Orbital Theory*, McGraw-Hill Book Company, New York, 1970).

Table 10.6.1: Ionization potentials of various atomic orbitals.

Atomic orbital	Ionization potential (eV)
H 1s	13.6
C 2s	21.4
C 2p	11.4
N 2s	25.58
N 2p	13.9
O 2s	32.38
O 2p	15.85
F 2s	40.20
F 2p	18.66

The H_{rs} values are computed from the ionization potentials according to

$$H_{rs} = \frac{1}{2}K(H_{rr} + H_{ss})S_{rs} \tag{10.6.23}$$

The rationale for this expression is that the energy should be proportional to the energy of the atomic orbitals, and should be greater when the overlap of the atomic orbitals is greater. The contribution of these effects to the energy is scaled by the parameter K. Hoffmann assigned the value of K after a study of the effect of this parameter on the energies of the occupied orbitals of ethane. The conclusion was that a good value for K is $K = 1.75$.

Exercise 10.6.8

Fill in numerical values for the diagonal elements of the Extended Hückel Hamiltonian matrix for HF using the ionization potentials given in Table $10.6.1$.

The overlap matrix also must be determined. The matrix elements are computed using the definition $S_{rs} = \langle\psi_r|\psi_s\rangle$ where φ_k and ψ_s are the atomic orbitals. *Slater-type orbitals* (STO’s) are used for the atomic orbitals rather than hydrogenic orbitals because integrals involving STO's can be computed more quickly on computers. Slater type orbitals have the form

$$\phi_{1s}(r) = 2\zeta^{3/2}\exp(-\zeta r) \tag{10.6.24}$$

$$\phi_{2s}(r) = \phi_2 p(r) = \left(\frac{4\zeta^5}{3}\right)^{1/2} r\exp(-\zeta r) \tag{10.6.25}$$

where zeta, ζ, is a parameter describing the screened nuclear charge. In the extended Hückel calculations done by Hoffmann, the Slater orbital parameter ζ was 1.0 for the H_{1s} and 1.652 for the C_{2s} and C_{2p} orbitals.

Exercise 10.6.9

Describe the difference between Slater-type orbitals and hydrogenic orbitals.

Overlap integrals involve two orbitals on two different atoms or centers. Such integrals are called two-center integrals. In such integrals there are two variables to consider, corresponding to the distances from each of the atomic centers, r_A and r_B. Such integrals can be represented as

$$S_{A_{2s}B_{2s}} = \left(\frac{4\zeta^5}{3}\right)\int r_A\exp(-\zeta r_A) r_B\exp(-\zeta r_B)d\tau \tag{10.6.26}$$

but elliptical coordinates must be used for the actual integration. Fortunately the software that does extended Hückel calculations contains the programming code to do overlap integrals. The interested reader will find sufficient detail on the evaluation of overlap integrals and the creation of the programmable mathematical form for any pair of Slater orbitals in Appendix B4 (pp. 199 - 200) of the book *Approximate Molecular Orbital Theory* by Pople and Beveridge. The values of the overlap integrals for HF are given in Table $10.6.2$.

Exercise 10.6.10

Using the information in Table $10.6.2$, identify which axis (x, y, or z) has been defined as the internuclear axis. Fill in the missing values in Table $10.6.2$. This requires no calculation, only insight.

Table 10.6.2: Overlap Integrals for HF

	F 2s	F $2p_x$	F $2p_y$	F $2p_z$	H 1s
F 2s					0.47428
F $2p_x$					0
F $2p_y$					0.38434
F $2p_z$					0
H 1s					

Exercise 10.6.11: Hydrogen Fluoride

Using the information in Tables $10.6.1$ and $10.6.2$, write the full Hückel H matrix and the S matrix that appears in Equation 10.6.22 for HF.

Our goal is to find the coefficients in the linear combinations of atomic orbitals and the energies of the molecular orbitals. For these results, we need to transform Equation 10.6.22

$$HC = SCE$$

into a form that allows us to use matrix diagonalization techniques. We are hampered here by the fact that the overlap matrix is not diagonal because the orbitals are not orthogonal. Mathematical methods do exist that can be used to transform a set of functions into an orthogonal set. Essentially these methods apply a transformation of the coordinates from the local coordinate system describing the molecule into one where the atomic orbitals in the LCAO are all orthogonal. Such a transformation can be accomplished through matrix algebra, and computer algorithms for this procedure are part of all molecular orbital programs. The following paragraph describes how this transformation can be accomplished.

If the matrix M has an inverse M^{-1} Then

$$MM^{-1} = 1 \tag{10.6.27}$$

and we can place this product in a matrix equation without changing the equation. When this is done for Equation 10.6.22, we obtain

$$HMM^{-1}C = SMM^{-1}CE \tag{10.6.28}$$

Next multiply on the left by M^{-1} and determine M so the product $M^{-1}SM$ is the identity matrix, i.e. a matrix that has 1's on the diagonal and 0's off the diagonal is the case for an orthogonal basis set.

$$M^{-1}HMM^{-1}C = M^{-1}SMM^{-1}CE \tag{10.6.29}$$

which then can be written as

$$H''C'' = C''E'' \tag{10.6.30}$$

where

$$C' = M^{-1}C \tag{10.6.31}$$

The identity matrix is not included because multiplying by the identity matrix is just like multiplying by the number 1. It doesn't change anything. The H'' matrix can be diagonalized by multiplying on the left by the inverse of C'' to find the energies of the molecular orbitals in the resulting diagonal matrix E.

$$E = C''^{-1}H''C'' \tag{10.6.32}$$

The matrix C'' obtained in the diagonalization step is finally back transformed to the original coordinate system with the M matrix, $C = MC''$ since $C'' = M^{-1}C$.

Fortunately this process is automated in some computer software. For example, in Mathcad, the command genvals(H,S) returns a list of the eigenvalues for Equation 10.6.22. These eigenvalues are the diagonal elements of E. The command genvecs(H,S) returns a matrix of the normalized eigenvectors corresponding to the eigenvalues. The i$^{\text{th}}$ eigenvalue in the list goes with the i$^{\text{th}}$ column in the eigenvector matrix. This problem, where S is not the identity matrix, is called a general eigenvalue problem, and *gen* in the Mathcad commands refers to *general*.

Exercise 10.6.12

Using your solution to Exercise $10.6.11$, find the orbital energies and wavefunctions for HF given by an extended Hückel calculation. Construct an orbital energy level diagram, including both the atomic and molecular orbitals, and indicate the atomic orbital composition of each energy level. Draw lines from the atomic orbital levels to the molecular orbital levels to show which atomic orbitals contribute to which molecular orbitals. What insight does your calculation provide regarding the ionic or covalent nature of the chemical bond in HF?

10.7: Mulliken Populations

Mulliken populations (R.S. Mulliken, J. Chem. Phys. 23, 1833, 1841, 23389, 2343 (1955)) can be used to characterize the electronic charge distribution in a molecule and the bonding, antibonding, or nonbonding nature of the molecular orbitals for particular pairs of atoms. To develop the idea of these populations, consider a real, normalized molecular orbital composed from two normalized atomic orbitals.

$$\psi_i = c_{ij}\phi_j + c_{ik}\phi_k \tag{10.7.1}$$

The charge distribution is described as a probability density by the square of this wavefunction.

$$\psi_i^2 = c_{ij}^2\phi_j^2 + c_{ik}^2\phi_k^2 + 2c_{ik}\phi_i\phi_j \tag{10.7.2}$$

Integrating over all the electronic coordinates and using the fact that the molecular orbital and atomic orbitals are normalized produces

$$1 = c_{ij}^2 + c_{ik}^2 + 2C_{ij}c_{ik}S_{jk} \tag{10.7.3}$$

where S_{jk} is the overlap integral involving the two atomic orbitals.

Mulliken's interpretation of this result is that one electron in molecular orbital ψ_t contributes c_{ij}^2 to the electronic charge in atomic orbital φ_j, c_{ik}^2 to the electronic charge in atomic orbital φ_k, and $2c_{ij}c_{ik}S_{jk}$ to the electronic charge in the overlap region between the two atomic orbitals. He therefore called c_{ij}^2 and c_{ik}^2, the *atomic-orbital populations*, and $2c_{ij}c_{ik}S_{jk}$, the *overlap population*. The overlap population is >0 for a bonding molecular orbital, <0 for an antibonding molecular orbital, and 0 for a nonbonding molecular orbital.

It is convenient to tabulate these populations in matrix form for each molecular orbital. Such a matrix is called the *Mulliken population matrix*. If there are two electrons in the molecular orbital, then these populations are doubled. Each column and each row in a population matrix is corresponds to an atomic orbital, and the diagonal elements give the atomic-orbital populations, and the off-diagonal elements give the overlap populations. For our example, Equation 10.7.1, the population matrix is

$$P_i = \begin{pmatrix} c_{ij}^2 & 2c_{ij}c_{ik}S_{jk} \\ 2c_{ij}c_{ik}S_{jk} & c_{ik}^2 \end{pmatrix} \tag{10.7.4}$$

Since there is one population matrix for each molecular orbital, it generally is difficult to deal with all the information in the population matrices. Forming the *net population matrix* decreases the amount of data. The net population matrix is the sum of all the population matrices for the occupied orbitals.

$$NP = \sum_{i=occupied} P_i \tag{10.7.5}$$

The net population matrix gives the atomic-orbital populations and overlap populations resulting from all the electrons in all the molecular orbitals. The diagonal elements give the total charge in each atomic orbital, and the off-diagonal elements give the total overlap population, which characterizes the total contribution of the two atomic orbitals to the bond between the two atoms.

The *gross population matrix* condenses the data in a different way. The net population matrix combines the contributions from all the occupied molecular orbitals. The gross population matrix combines the overlap populations with the atomic orbital populations for each molecular orbital. The columns of the gross population matrix correspond to the molecular orbitals, and the rows correspond to the atomic orbitals. A matrix element specifies the amount of charge, including the overlap contribution, that a particular molecular orbital contributes to a particular atomic orbital. Values for the matrix elements are obtained by dividing each overlap population in half and adding each half to the atomic-orbital populations of the participating atomic orbitals. The matrix elements provide the gross charge that a molecular orbital contributes to the atomic orbital. *Gross* means that overlap contributions are included. The gross population matrix therefore also is called the *charge matrix for the molecular orbitals*. An element of the gross population matrix (in the jth row and ith column) is given by

$$GP_{ji} = Pi_{jj} + \frac{1}{2}\sum_{k\neq j} Pi_{jk} \tag{10.7.6}$$

where P_i is the population matrix for the i^th^ molecular orbital, Pi_{jj} is the atomic-orbital population and the Pi_{jk} is the overlap population for atomic orbitals j and k in the i^th^ molecular orbital.

Further condensation of the data can be obtained by considering atomic and overlap populations by atoms rather than by atomic orbitals. The resulting matrix is called the *reduced-population matrix*. The reduced population is obtained from the net population matrix by adding the atomic orbital populations and the overlap populations of all the atomic orbitals of the same atom. The rows and columns of the reduced population matrix correspond to the atoms.

Atomic-orbital charges are obtained by adding the elements in the rows of the gross population matrix for the occupied molecular orbitals. Atomic charges are obtained from the atomic orbital charges by adding the atomic-orbital charges on the same atom. Finally, the net charge on an atom is obtained by subtracting the atomic charge from the nuclear charge adjusted for complete shielding by the 1s electrons.

Exercise 10.7.1

Using your results from Exercise $10.7.29$for HF, determine the Mulliken population matrix for each molecular orbital, the net population matrix, the charge matrix for the molecular orbitals, the reduced population matrix, the atomic orbital charges, the atomic charges, the net charge on each atom, and the dipole moment. Note: The bond length for HF is 91.7 pm and the experimental value for the dipole moment is $6.37 \times 10^{-30}\, C \cdot m$.

10.8: The Self-Consistent Field and the Hartree-Fock Limit

In a modern *ab initio* electronic structure calculation on a closed shell molecule, the electronic Hamiltonian is used with a single determinant wavefunction. This wavefunction, ψ, is constructed from molecular orbitals, ψ that are written as linear combinations of contracted Gaussian basis functions, φ

$$\varphi_j = \sum_k c_{jk}\psi_k \tag{10.8.1}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals (STOs). The exponential parameters in the STOs are optimized by calculations on small molecules using the nonlinear variational method and then those values are used with other molecules. The problem is to calculate the electronic energy from

$$E = \frac{\displaystyle\int \psi^* \hat{H}\psi d\tau}{\displaystyle\int \psi^* \psi d\tau} \tag{10.8.2}$$

and find the optimum coefficients c_{jk} for each molecular orbital in Equation 10.8.1 by using the Self Consistent Field Method and the Linear Variational Method to minimize the energy as was described in the previous chapter for the case of atoms.

To obtain the total energy of the molecule, we need to add the internuclear repulsion to the electronic energy calculated by this procedure. The total energy of the molecule can be calculated for different geometries (i.e. bond lengths and angles) to find the minimum energy configuration. Also, the total energies of possible transition states can be calculated to find the lowest energy pathway to products in chemical reactions.

$$V_{rs} = \sum_{r=1}^{N-1} \sum_{s=r+1}^{N} \frac{Z_r Z_s}{r_{rs}} \tag{10.8.3}$$

Exercise 10.8.1

For a molecule with three nuclei, show that the sums in Equation 10.8.3 correctly include all the pairwise potential energy terms without including any twice.

As we improve the basis set used in calculations by adding more and better functions, we expect to get better and better energies. The variational principle says an approximate energy is an upper bound to the exact energy, so the lowest energy that we calculate is the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single determinant wavefunction. This limit is called the *Hartree-Fock limit*, the energy is the *Hartree-Fock energy*, the molecular orbitals producing this limit are called *Hartree-Fock orbitals*, and the determinant is the *Hartree-Fock wavefunction*.

Exercise 10.8.2

Write a one-sentence definition of the Hartree-Fock wavefunction that captures all the essential features of this function.

Restricted vs. Unrestricted Hartree-Fock

You may encounter the terms *restricted* and *unrestricted* Hartree-Fock. The above discussion pertains to a restricted HF calculation. In a restricted HF calculation, electrons with α spin are restricted or constrained to occupy the same spatial orbitals as electrons with β spin. This constraint is removed in an unrestricted calculation. For example, the spin orbital for electron 1 could be $\psi_A(r_1)\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(r_2)\beta(2)$, where both the spatial molecular orbital and the spin function differ for the two electrons. Such spin orbitals are called *unrestricted*. If both electrons are constrained to have the same spatial orbital, e.g. $\psi_A(r_1)\alpha(1)$ and $\psi_A(r_2)\beta(2)$, then the spin orbital is said to be *restricted*. While unrestricted spin orbitals can provide a better description of the electrons, twice as many spatial orbitals are needed, so the demands of the calculation are much higher. Using unrestricted orbitals is particular beneficial when a molecule contains an odd number of electrons because there are more electrons in one spin state than in the other.

Carbon Dioxide

Now consider the results of a self-consistent field calculation for carbon monoxide, CO. It is well known that carbon monoxide is a poison that acts by binding to the iron in hemoglobin and preventing oxygen from binding. As a result, oxygen is not transported by the blood to cells. Which end of carbon monoxide, carbon or oxygen, do you think binds to iron by donating electrons? We all know that oxygen is more electron-rich than carbon (8 vs 6 electrons) and more electronegative. A reasonable answer to this question therefore is *oxygen*, but experimentally it is carbon that binds to iron.

A quantum mechanical calculation done by Winifred M. Huo, published in J. Chem. Phys. 43, 624 (1965), provides an explanation for this counter-intuitive result. The basis set used in the calculation consisted of 10 functions: the ls, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of C and O. Ten molecular orbitals (mo's) were defined as linear combinations of the ten atomic orbitals, which are written as

$$\psi_k = \sum_{j=1}^{10} C_{kj}\varphi_j \tag{10.8.4}$$

where k identifies the mo and j identifies the atomic orbital basis function. The ground state wavefunction ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 10.8.5gives the energy of the ground state,

$$E = \frac{\left\langle \psi|\hat{H}|\psi \right\rangle}{\langle \psi|\psi \rangle} \tag{10.8.5}$$

where the denominator accounts for the normalization requirement. The coefficients C_{kj} in the linear combination are determined by the variational method to minimize the energy. The solution of this problem gives the following equations for the molecular orbitals. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

- $1s \approx 0.941 s_o$. The 1 says this is the first σ orbital. The σ says it is symmetric with respect to reflection in the plane of the molecule. The large coefficient, 0.94, means this is essentially the 1s atomic orbital of oxygen. The oxygen 1s orbital should have a lower energy than that of carbon because the positive charge on the oxygen nucleus is greater.
- $2s \approx 0.921 s_c$. This orbital is essentially the 1s atomic orbital of carbon. Both the 1σ and 2σ are "nonbonding" orbitals since they are localized on a particular atom and do not directly determine the charge density between atoms.
- $3s \approx (0.722 s_o + 0.182 p_{zo}) + (0.282 s_c + 0.162 p_{zc})$. This orbital is a "bonding" molecular orbital because the electrons are delocalized over C and O in a way that enhances the charge density between the atoms. The 3 means this is the third σ orbital. This orbital also illustrates the concept of hybridization. One can say the 2s and 2p orbitals on each atom are hybridized and the molecular orbital is formed from these hybrids although the calculation just obtains the linear combination of the four orbitals directly without the *à priori* introduction of hybridization. In other words, hybridization just falls out of the calculation. The hybridization in this bonding LCAO increases the amplitude of the function in the region of space between the two atoms and decreases it in the region of space outside of the bonding region of the atoms.
- $4s \approx (0.372 s_c + 0.12 p_{zc}) + (0.542 p_{zo} - 0.432 s_0)$. This molecular orbital also can be thought of as being a hybrid formed from atomic orbitals. The hybridization of oxygen atomic orbitals, because of the negative coefficient with $2s_O$, decreases the electron density between the nuclei and enhances electron density on the side of oxygen facing away from the carbon atom. If we follow how this function varies along the internuclear axis, we see that near carbon the function is positive whereas near oxygen it is negative or possibly small and positive. This change means there must be a node between the two nuclei or at the oxygen nucleus. Because of the node, the electron density between the two nuclei is low so the electrons in this orbital do not serve to shield the two positive nuclei from each other. This orbital therefore is called an "antibonding" mo and the electrons assigned to it are called antibonding electrons. This orbital is the antibonding partner to the 3σ orbital.
- $1\pi \approx 0.322 p_{xc} + 0.442 p_{xo} \text{and} 2\pi \approx 0.322 p_{yc} + 0.442 p_{yo}$ These two orbitals are degenerate and correspond to bonding orbitals made up from the p_x and p_y atomic orbitals from each atom. These orbitals are degenerate because the x and y directions are equivalent in this molecule. π tells us that these orbitals are antisymmetric with respect to reflection in a plane containing the nuclei.
- $5\sigma \approx 0.382_{sC} - 0.382_{pC} - 0.292 p_{zO}$. This orbital is the sp hybrid of the carbon atomic orbitals. The negative coefficient for $2p_C$ puts the largest amplitude on the side of carbon away from oxygen. There is no node between the atoms. We conclude this is a nonbonding orbital with the nonbonding electrons on carbon. This is not a "bonding" orbital because the electron density between the nuclei is lowered by hybridization. It also is not an antibonding orbital because there is no node between the nuclei. When carbon monoxide binds to Fe in hemoglobin, the bond is made between the C and the Fe. This bond involves the

donation of the 5σ nonbonding electrons on C to empty d orbitals on Fe. Thus mo theory allows us to understand why the C end of the molecule is involved in this electron donation when we might naively expect O to be more electron-rich and capable of donating electrons to iron.

Exercise 10.8.3

Summarize how Quantum Mechanics is used to describe bonding and the electronic structure of molecules.

Exercise 10.8.4

Construct an energy level diagram for CO that shows both the atomic orbitals and the molecular orbitals. Show which atomic orbitals contribute to each molecular orbital by drawing lines to connect the mo's to the ao's. Label the molecular orbitals in a way that reveals their symmetry. Use this energy level diagram to explain why it is the carbon end of the molecule that binds to hemoglobin rather than the oxygen end.

10.9: Correlation Energy and Configuration Interaction

The Hartree-Fock energy is not as low as the exact energy. The difference is due to electron correlation effects and is called the **correlation energy**. The Hartree-Fock wavefunction does not include these correlation effects because it describes the electrons as moving in the average potential field of all the other electrons. The instantaneous influence of electrons that come close together at some point is not taken into account. Electrons repel each other, and they will try to stay away from each other. Their motion therefore is correlated, and this correlation reduces the energy of the system because it reduces the electron-electron repulsion. The Hartree-Fock wavefunction does not account for this correlation and therefore produces an energy that is too high.

One method for accounting for these correlation effects and the correlation energy is called **configuration interaction (CI)**. In configuration interaction, Slater determinants are formed from two or more orbital occupation configurations. The CI wavefunction then is written as a linear combination of these determinants, and the coefficients are determined to minimize the energy.

$$\psi_{CI} = c_1 D_1 + c_2 D_2 \tag{10.9.1}$$

Good quality one-electron molecular orbitals are obtained by using a large basis set, by optimizing the parameters in the functions with the variational method, and by accounting for the electron-electron repulsion using the self-consistent field method. Electron correlation effects are taken into account with configuration interaction. The CI methodology means that a wavefunction is written as a series of Slater Determinants involving different configurations, just as we discussed for the case of atoms. The limitation in this approach is that computer speed and capacity limit the size of the basis set and the number of configurations that can be used.

Exercise 10.9.1

Define correlation energy and explain why it is omitted in a SCF calculation and how it is included in a CI calculation.

Exercise 10.9.2

Write a CI wavefunction for helium using Slater determinants for the 1s2 and 1s12s1 configurations. Explain how addition of the $1s^1 2s^1$ configuration to the wavefunction accounts for electron correlation in terms of keeping the electrons apart in different regions of space

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10.E: Theories of Electronic Molecular Structure (Exercises)

Q10.1

1. Plot the amplitude of the atomic and molecular orbitals along the inter-nuclear axis (defined as the z-axis) of the H_2^+ molecule.
   a. Plot the four basis functions for the H_2^+ molecule:

$$\varphi_{1sA}, \varphi_{1sB}, \varphi_{2p_zA}, \varphi_{2p_zB} \tag{10.E.1}$$

   b. Construct and graph a bonding molecular orbital using these basis functions with a parameter λ multiplying the $2p_z$ functions, for a few values of the parameter λ between 0 and 1. Determine the normalization constant N for each value of λ by assuming that the atomic overlap integrals are either 0 or 1.

$$\psi = \frac{1}{N}[\varphi_{1sA} + \varphi_{1sB} + \lambda(\varphi_{2p_zA} + \varphi_{2p_zB})] \tag{10.E.2}$$

   c. Explain why the molecular orbital you graphed is a bonding orbital.
   d. Explain why a value for λ greater than 0 should improve the description of a bonding orbital.

Q10.2

Construct energy level diagrams for B_2 and O_2 that show both the atomic orbitals and the molecular orbitals and use these diagrams to explain why both molecules are paramagnetic. Label the molecular orbitals to reveal both their symmetry and their atomic orbital parentage. Note: one diagram and labeling does not apply to both molecules.

Q10.3

Defend or shoot down the following statement. The Born-Oppenheimer approximation predicts that vibrational frequencies, vibrational force constants, and bond dissociation energies should be independent of isotopic substitution.

Q10.4

Explain in terms of both the electronic charge density and the electronic energy, why chemists describe the overlap of atomic orbitals as being important for bond formation.

Q10.5

Compare the extended Hückel calculation on HF with the SCF calculation reported in B.j. Ransil, Rev. Mod. Phys. 32, 239, 245 (1960) in J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory (McGraw-Hill, 1970) pp. 46-51.

Q10.6

From the following bond lengths and dipole moments, compute the charges on the hydrogen atom and the halide atom. Compare the results with the electronegativities predicted from the order of these elements in the Periodic Table. What do these charges tell you about the contribution of the hydrogen 1s atomic orbital to the molecular orbitals for each molecule? Use the insight you gained from this problem, to define ionic and covalent bonding.

Molecule	R_0 in pm	μ in 10^{-30} C m
HF	91.7	6.37
HCl	127.5	3.44
HBr	141.4	2.64
HI	160.9	1.40

10.S: Theories of Electronic Molecular Structure (Summary)

Other terms account for the interactions between all the magnetic dipole moments and the interactions with any external electric or magnetic fields. The charge distribution of an atomic nucleus is not always spherical and, when appropriate, this asymmetry must be taken into account as well as the relativistic effect that a moving electron experiences as a change in mass. This complete Hamiltonian is too complicated and is not needed for many situations. In practice, only the terms that are essential for the purpose at hand are included. Consequently in the absence of external fields, interest in spin-spin and spin-orbit interactions, and in electron and nuclear magnetic resonance spectroscopy (ESR and NMR), the molecular Hamiltonian usually is considered to consist only of the kinetic and potential energy terms, and the Born-Oppenheimer approximation is made in order to separate the nuclear and electronic motion.

In general, electronic wavefunctions for molecules are constructed from approximate one-electron wavefunctions. These one-electron functions are called molecular orbitals. The expectation value expression for the energy is used to optimize these functions, i.e. make them as good as possible. The criterion for quality is the energy of the ground state. According to the Variational Principle, an approximate ground state energy always is higher than the exact energy, so the best energy in a series of approximations is the lowest energy. In this chapter we describe how the variational method, perturbation theory, the self-consistent field method, and configuration interaction all are used to describe the electronic states of molecules. 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, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in their chemical structure.

Study Guide

- What is meant by the expression *ab initio* calculation?
- List all the terms in a complete molecular Hamiltonian.
- Why are calculations on closed-shell systems more easily done than on open-shell systems?
- How is it possible to reduce a multi-electron Hamiltonian operator to a single-electron Fock operator?
- Why is the calculation with the Fock operator called a self-consistent field calculation?
- What is the physical meaning of a SCF one-electron energy?
- Why is the nonlinear variational method not used in every case to optimize basis functions, and what usually is done instead?
- Why is it faster for a computer to use the variational principle to determine the coefficients in a linear combination of functions than to determine the parameters in the functions?
- Identify the characteristics of hydrogenic, Slater, and Gaussian basis sets.
- What is meant by the Hartree-Fock wavefunction and energy?
- What is the difference between a restricted and unrestricted Hartree-Fock calculation?
- What is neglected that makes the Hartree-Fock energy necessarily greater than the exact energy?
- What is meant by correlation energy?
- What purpose is served by including configuration interaction in a calculation?

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

10.10: Electronic States

The electronic configuration of an atom or molecule is a concept imposed by the orbital approximation. Spectroscopic transitions and other properties of atoms and molecules result from the states and not from the configurations, although it is useful to think about both the configuration and the state whenever possible. While a single determinant wavefunction generally is adequate for closed-shell systems (i.e. all electrons are paired in spatial orbitals), the best descriptions of the electronic states, especially for excited states and free radicals that have unpaired electrons, involve configuration interaction using multiple determinants. In these descriptions different configurations are mixed together and the picture of an orbital configuration disintegrates, and other properties, such as orbital and spin angular momentum and symmetry, are needed to identify and characterize the electronic states of molecules.

While a component of orbital angular momentum is preserved along the axis of a linear molecule, generally orbital angular momentum is quenched due to the irregular shapes of molecules. Angular momentum is quenched because circular motion is not possible when the potential energy function does not have circular symmetry.

The spin orbitals, however, still can be eigenfunctions of the spin angular momentum operators because the spin-orbit coupling usually is small. The resulting spin state depends on the orbital configuration. For a closed-shell configuration, the spin state is a singlet and the spin angular momentum is 0 because the contributions from the α and β spins cancel. For an open shell configuration, which is characteristic of free radicals, there is an odd number of electrons and the spin quantum number $s = \frac{1}{2}$. This configuration produces a doublet spin state since $2S + 1 = 2$. Excited configurations result when electromagnetic radiation or exposure to other sources of energy promotes an electron from an occupied orbital to a previously unoccupied orbital. An excited configuration for a closed shell system produces two states, a singlet state $(2S + 1 = 0)$ and a triplet state $(2S + 1 = 3)$ depending on how the electron spins are paired. The z-components of the angular momentum for 2 electrons can add to give +1, 0, or –1 in units of ħ. The three spin functions for a triplet state are

$$\alpha(1)\alpha(2) \tag{10.10.1}$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \tag{10.10.2}$$

$$\beta(1)\beta(2) \tag{10.10.3}$$

and the singlet spin function is

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \tag{10.10.4}$$

The singlet and triplet states differ in energy even though the electron configuration is the same. This difference results from the antisymmetry condition imposed on the wavefunctions. The antisymmetry condition reduces the electron-electron repulsion for triplet states, so triplet states have the lower energy.

The electronic states of molecules therefore are labeled and identified by their spin and orbital angular momentum and symmetry properties, as appropriate. For example, the ground state of the hydrogen molecule is designated as $X^1\sum_g^+$. In this symbol, the X identifies the state as the ground state, the superscript 1 identifies it as a singlet state, the sigma says the orbital angular momentum is 0, and the g identifies the wavefunction as symmetric with respect to inversion. Other states with the same symmetry and angular momentum properties are labeled as A, B, C, etc in order of increasing energy or order of discovery. States with different spin multiplicities from that of the ground state are labeled with lower case letters, a, b, c, etc.

For polyatomic molecules the symmetry designation and spin multiplicity are used. For example, an excited state of naphthalene is identified as $^1B_{1u}$. The superscript 1 identifies it as a singlet state, The letter B and subscript 1 identifies the symmetry with respect to rotations, and the subscript u says the wavefunction is antisymmetric with respect to inversion.

Good quality descriptions of the electronic states of molecules are obtained by using a large basis set, by optimizing the parameters in the functions with the variational method, and by accounting for the electron-electron repulsion using the self-consistent field method. Electron correlation effects are taken into account with configuration interaction (CI). The CI methodology means that a wavefunction is written as a series of Slater Determinants involving different configurations, just as we discussed for the case of atoms. The limitation in this approach is that computer speed and capacity limit the size of the basis set and the number of configurations that can be used.

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Glossary

angular node | An angular node will occur where the angular part of the electronic wavefunction equals zero.

ansatz | An educated guess or an additional assumption made to help solve a problem, and which is later verified to be part of the solution by its results.

atomic orbitals | Atomic orbital is a mathematical function describing the location and wave-like behavior of a single electron in an atom. This function can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus.

Beer's Law | The Beer-Lambert law relates the optical attenuation of a physical material containing a single attenuating species of uniform concentration to the optical path length through the sample and absorptivity of the species.

Bohr magneton | A physical constant and the natural unit for expressing the magnetic moment of an electron caused by either its orbital or spin angular momentum. ($\mu_{B} = e\hbar/2m_e$)

Bosons | Bosons are particles with integer spin (s = 0, 1, 2, ...).

Bound state | A state is called bound state if its position probability density at infinite tends to zero for all the time. Roughly speaking, we can expect to find the particle(s) in a finite size region with certain probability.

Bra–ket notation | The bra–ket notation is a way to represent the states and operators of a system by angle brackets and vertical bars, for example, |α> and |α><β|.

Collapse | "Collapse" means the sudden process which the state of the system will "suddenly" change to an eigenstate of the observable during measurement.

commutator | The commutator of two operators elements **a** and **b** is defined by **[a,b]=ab-ba**. The commutator is zero if and only if **a** and **b** commute.

commute | The commutator of two operators elements **a** and **b** is defined by **[a,b]=ab-ba**. The commutator is zero if and only if **a** and **b** commute.

Correspondence principle | For every observable property of a system there is a corresponding quantum mechanical operator.

cyclic boundary condition | A boundary condition associated with regularly repeating intervals. For quantum rigid rotors, this implied the wavefunction must equal itself upon a full rotation, i.e., ψ(0º)=ψ(360º).

Degeneracy | If the energy of different states (wavefunctions that are not scalar multiple of each other) are the same, the states are called **degenerate**.

Degenerate energy level | If the energy of different state (wave functions which are not scalar multiple of each other) is the same, the energy level is called degenerate. There is no degeneracy in 1D system.

Density matrix | Physically, the density matrix is a way to represent pure states and mixed states. The density matrix of pure state whose ket is |α> is |α><α|.

Density operator | Physically, the density matrix is a way to represent pure states and mixed states. The density matrix of pure state whose ket is |α> is |α><α|.

dipole moment | The electric dipole moment is a measure of the separation of positive and negative electrical charges within a system and is a measure of the system's overall polarity.

Dirac notation | The bra–ket notation is a way to represent the states and operators of a system by angle brackets and vertical bars, for example, |α> and |α><β|.

Eigenstates | An eigenstate of an operator A is a vector satisfied the eigenvalue equation: A | a > = λ | a >, where λ is a scalar (the eigenvalue).

eigenvalue | Any value of λ that is is a solution to the eigenvalue problem (A·v=λ·v) is known as an eigenvalue of the matrix A.

eigenvalue equation | An eigenvalue problem is A·v=λ·v, where A is an n-by-n matrix, v is a non-zero n-by-1 vector and λ is a scalar (that can be real or complex).

eigenvector | Any value of v that is is a solution to the eigenvalue problem (A·v=λ·v) is known as an eigenvevctor of the matrix A.

Energy spectrum | The energy spectrum refers to the possible energy of a system.
For bound system (bound states), the energy spectrum is discrete; for unbound system (scattering states), the energy spectrum is continuous.

even function | A function is even if f(x)=f(-x)

Expectation value | The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It can be thought of as an average of all the possible outcomes of a measurement as weighted by their likelihood, and as such it is not the most probable value of a measurement; indeed the expectation value may have zero probability of occurring

Fermions | Fermions are particles with half-integer spin (s = 1/2, 3/2, 5/2, ...).

Fine Structure Constant | 1/137 . The fine structure constant is a mathematical constant that is given as the ratio of the classical and quantum electromagnetic constants. It is also known as **Sommerfeld's constant.**

forbidden transition | A eigentstate to eigenstate transition with zero probability of being observed. This is determined by the relevant transition moment integral

g-factor | A dimensionless quantity that characterizes the magnetic moment and angular momentum of an atom, a particle or the nucleus. It is essentially a proportionality constant that relates the observed magnetic moment μ of a particle to its angular momentum quantum number and a unit of magnetic moment. (also known as spin gyromagnetic ratio)

gyromagnetic ratio | The ratio of its magnetic moment to its angular momentum, and it is often denoted by the symbol γ, gamma (also known as magnetogyric ratio)

Hamiltonian | The operator represents the total energy of the system.

Hermite polynomials | A family of orthogonal polynomials. In quantum mechanics, they results from solving the harmonic oscillator model.

Hermitian | A Hermitian matrix is a complex square matrix that is equal to its own conjugate transpose—that is, the element in the i-th row and j-th column is equal to the complex conjugate of the element in the j-th row and i-th column, for all indices i and j. aij=aji* . Hermitian matrices always have real eigenvalues. Operators connected to physical observable are Hermitian since observables must be real.

Hermitian operator | An operator satisfying A = $A^{\dagger}$.

Hilbert space | Given a system, the possible pure state can be represented as a vector in a Hilbert space. Each ray (vectors differ by phase and magnitude only) in the corresponding Hilbert space represent a state.

Identity operator | Operator that does not change the elements it operates on.

Indistinguishable particles | If a system shows measurable differences when one of its particles is replaced by another particle, these two particles are called distinguishable.

Ket | A wave function expressed in the form $|a\rangle$ is called a ket.

Lambshift | Relativistic correction of the difference in energy levels of the $^2S_{1/2}$ and $^2P_{1/2}$ hydrogen atom not predicted by the Dirac equation

Laplacian | The Laplacian is a differential operator that is given by the divergence of the gradient.

LCAO | This is is a simple method of quantum chemistry that yields a qualitative picture of the molecular orbitals in a molecule.

Legendre polynomials | A family of complete and orthogonal polynomials with numerous applications. In quantum mechanics, they results from solving the rigid rotor model.

Linear combination of atomic orbitals | This is is a simple method of quantum chemistry that yields a qualitative picture of the molecular orbitals in a molecule.

Maclaurin series | The Maclaurin series is an expansion of a function in an infinite sum of polynomial terms that are expressed in terms of the function's derivatives at **zero**.

magnetogyric ratio | The ratio of its magnetic moment to its angular momentum, and it is often denoted by the symbol γ, gamma (also known as magnetogyric ratio

Mixed state | A mixed state is a statistical ensemble of pure state.

molecular orbitals | A molecular orbital is a mathematical function describing the location and wave-like behavior of a single electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region. The LCAO approximation is often used to approximate molecular orbitals as a series of atomic orbitals

node | Location where the quantum mechanical wavefunction is zero and therefore, with no probability amplitude.

Normalized wave function | A wave function |a > is said to be normalized if < a | a> = 1.

Observable | Mathematically, it is represented by a Hermitian operator.

observer effect | When an observed system is disturbed by the act of observation. This is often the result of instruments that, by necessity, alter the state of what they measure in some manner.

odd function | A function is odd if -f(x)=f(-x)

operator | A mathematical entity that transforms one function into another [Richard Fitzpatrick]

orbital angular momentum | The classical definition of angular momentum is $L = r \times p$. The quantum-mechanical counterparts of these objects share the same relationship where r is the quantum position operator, p is the quantum momentum operator, × is cross product, and L is the orbital angular momentum operator. L (just like p and r) is a vector operator whose components operators are L_x, L_y, L_z, which are the projection of L on the x, y, and z axis, respectively

overtone | A band that occurs in a vibrational spectrum of molecule that is associated with the transition from the ground state (v=0) to the second excited state (v=2).

Pauli exclusion principle | The principle that two or more identical fermions (e.g., electrons) cannot occupy the same quantum state within the same quantum system simultaneously. An alternative formulation is that no two fermions can have the same set of quantum numbers in a system

Pure state | A state which can be represented as a wave function / ket in Hilbert space / solution of Schrödinger equation is called pure state. See "mixed state".

Quantum numbers | A way of representing a state by several numbers

Radial distribution function | The square of the radial distribution function describes the probability of finding an a electron a given distance from the nucleus. This is related to the radial probability density by adding a factor of $4\pi r^2$ (the volumen element of a sphere). The radial distribution functions depend on both n and l.

radial node | A radial node will occur where the radial part of the electronic wavefunction equals zero.

radial probability density | The probability density for the electron to be at a point located the distance r from the nucleus. The radial radial probability density depend on both n and l.

reduced mass | The "effective" inertial mass appearing in the two-body problems. It is a quantity which allows two-body problems to be solved as if they were one-body problems.

rotational constant | A constant commonly used to describe molecular free rotation that depends on the distribution of mass within the molecule (i.e, moment of inertia, I) and other constants: $B=h/(8\pi^2 cI)$

selection rule | Selection rules describes when the probability of transitioning from one level to another cannot be zero. They explicitly come from evaluating the relevant transition moment integral

selection rules | Selection rules describes when the probability of transitioning from one level to another cannot be zero. They explicitly come from evaluating the relevant transition moment integral

spherical harmonics | Spherical harmonics are functions of the spherical polar angles θ and φ and appear as eigenfunctions of (squared) orbital angular momentum. They form an orthogonal and complete set. Any harmonic is a function that satisfies Laplace's differential equation.

spin | Spin is a quantized property of all particles, both matter and force, in the Universe. Matter particles have half-integer spin (1/2, 3/2,…) and force particles integer spin (0, 1, 2,…). Spin is intrinsic angular momentum possessed by the particles. The spin of a particle is sort of analogous to that of a spinning top, except that the particle can only spin at one speed, can't stop or even slow down, and is infinitesimally small. It is important to note that in no way are the particles actually spinning. [CC-BY-SA]

spin gyromagnetic ratio | A dimensionless quantity that characterizes the magnetic moment and angular momentum of an atom, a particle or the nucleus. It is essentially a proportionality constant that relates the observed magnetic moment μ of a particle to its angular momentum quantum number and a unit of magnetic moment. (also known as g-factor)

square-integrable | A square-integrable function is a real- or complex-valued measurable function for which the integral of the **square** of the absolute value is finite.

State vector | synonymous to "wave function".

Stationary state | A stationary state of a bound system is an eigenstate of Hamiltonian operator. Classically, it corresponds to standing wave.

stationary states | This is a quantum state with all observables independent of time. It is an eigenvector of the Hamiltonian.

Taylor series | The Taylor series is an expansion of a function in an infinite sum of polynomial terms that are expressed in terms of the function's derivatives at a single point.

Time-Independent Schrödinger Equation | A modification of the Time-Dependent Schrödinger equation as an eigenvalue problem. The solutions are energy eigenstate of the system.

transition moment integral | The integral representing the probability for a transition between an initial eigenstate and a final eignestate by the absorption or emission of photon(s)

uncertainty principle | The uncertainty principle (put forward by Werner Heisenberg) states that there will always be an intrinsic uncertainty in determining both a particle's position and momentum (i.e., you cannot know both exactly at the same time). This has nothing to do with science's ability to detect the properties of momentum and position. [CC-BY-SA]

wavenumber | The wavenumber is a unit of frequency that is equal to the frequency (in Hertz) divided by the speed of light. This is typically in unit of cm^{-1}. Since wavenumbers are proportional to frequency, and to photon energy (by $E=h\nu$), it is also a unit of energy.

zero point motion | Fluctuation in the position of an object necessitated by having zero point energy. This is a consequence of the Heisenberg uncertainty principle.

Zero-point energy | Zero-point energy (ZPE) is the lowest possible energy that a quantum mechanical system may have.

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