Part 1. Background Material

In this portion of the text, most of the topics that are appropriate to an undergraduate reader are covered. Many of these subjects are subsequently discussed again in Chapter 5, where a broad perspective of what theoretical chemistry is about is offered. They are treated again in greater detail in Chapters 6-8 where the three main disciplines of theory, electronic structure, chemical dynamics, and statistical mechanics, are covered in depth appropriate to a graduate-student reader.

Chapter 1. The Basics of Quantum Mechanics

1.1 Why Quantum Mechanics is Necessary for Describing Molecular Properties.

The field of theoretical chemistry deals with the structures, bonding, reactivity, and physical properties of atoms, molecules, radicals, and ions all of whose sizes range from ca. 1 Å for atoms and small molecules to a few hundred Å for polymers and biological molecules such as DNA and proteins. Sometimes these building blocks combine to form nanoscopic materials (e.g., quantum dots, graphene sheets) whose dimensions span up to thousands of Å, making them amenable to detection using specialized microscopic tools. However, description of the motions and properties of the particles comprising such small systems has been found to not be amenable to treatment using classical mechanics. Their structures, energies, and other properties have only been successfully described within the framework of quantum mechanics. This is why quantum mechanics has to be mastered as part of learning theoretical chemistry.

We know that all molecules are made of atoms that, in turn, contain nuclei and electrons. As I discuss in this Chapter, the equations that govern the motions of electrons and of nuclei are not the familiar Newton equations

$$\mathbf{F} = m\,\mathbf{a}$$

but a new set of equations called Schrödinger equations. When scientists first studied the behavior of electrons and nuclei, they tried to interpret their experimental findings in terms of classical Newtonian motions, but such attempts eventually failed. They found that such small light particles behaved in a way that simply is not consistent with the Newton equations. Let me now illustrate some of the experimental data that gave rise to these paradoxes and show you how the scientists of those early times then used these data to suggest new equations that these particles might obey. I want to stress that the Schrödinger equation was not derived but postulated by these scientists. In fact, to date, to the best of my knowledge, no one has been able to derive the Schrödinger equation.

From the pioneering work of Bragg on diffraction of x-rays from planes of atoms or ions in crystals, it was known that peaks in the intensity of diffracted x-rays having wavelength λ would occur at scattering angles θ determined by the famous Bragg equation:

$$n \lambda = 2 d \sin\theta,$$

where d is the spacing between neighboring planes of atoms or ions. These quantities are illustrated in Fig. 1.1 shown below. There are may such diffraction peaks, each labeled by a different value of the integer n (n = 1, 2, 3, …). The Bragg formula can be derived by considering when two photons, one scattering from the second plane in the figure and the second scattering from the third plane, will undergo constructive interference. This condition is met when the extra path length covered by the second photon (i.e., the length from points A to B to C) is an integer multiple of the wavelength of the photons.

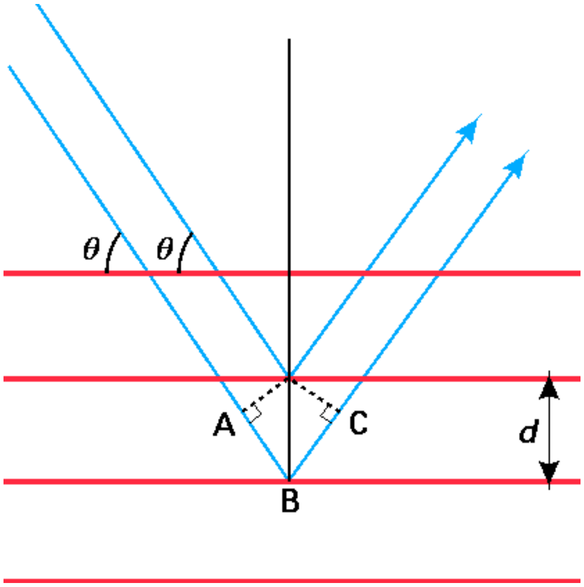


Figure 1.1. Scattering of two beams at angle θ from two planes in a crystal spaced by d.

The importance of these x-ray scattering experiments to electrons and nuclei appears in the experiments of Davisson and Germer in 1927 who scattered electrons of (reasonably) fixed kinetic energy E from metallic crystals. These workers found that plots of the number of scattered electrons as a function of scattering angle θ displayed peaks at angles θ that obeyed a Bragg-like equation. The startling thing about this observation is that electrons are particles, yet the Bragg equation is based on the properties of waves. An important observation derived from the Davisson-Germer experiments was that the scattering angles θ observed for electrons of kinetic energy E could be fit to the Bragg $n \lambda = 2d \sin\theta$ equation if a wavelength were ascribed to these electrons that was defined by

$$\lambda = h/(2m_e E)^{1/2},$$

where m_e is the mass of the electron and h is the constant introduced by Max Planck and Albert Einstein in the early 1900s to relate a photon's energy E to its frequency ν via $E = h\nu$. These amazing findings were among the earliest to suggest that electrons, which had always been viewed as particles, might have some properties usually ascribed to waves. That is, as de Broglie has suggested in 1925, an electron seems to have a wavelength inversely related to its momentum, and to display wave-type diffraction. I should mention that analogous diffraction was also observed when other small light particles (e.g., protons, neutrons, nuclei, and small atomic ions) were scattered from crystal planes. In all such cases, Bragg-like diffraction is observed and the Bragg equation is found to govern the scattering angles if one assigns a wavelength to the scattering particle according to

$$\lambda = h/(2\ m\ E)^{1/2}$$

where m is the mass of the scattered particle and h is Planck's constant ($6.62\ x10^{-27}$ erg sec).

The observation that electrons and other small light particles display wave like behavior was important because these particles are what all atoms and molecules are made of. So, if we want to fully understand the motions and behavior of molecules, we must be sure that we can adequately describe such properties for their constituents. Because the classical Newtonian equations do not contain factors that suggest wave properties for electrons or nuclei moving freely in space, the above behaviors presented significant challenges.

Another problem that arose in early studies of atoms and molecules resulted from the study of the photons emitted from atoms and ions that had been heated or otherwise excited (e.g., by electric discharge). It was found that each kind of atom (i.e., H or C or O) emitted photons whose frequencies ν were of very characteristic values. An example of such emission spectra is shown in Fig. 1.2 for hydrogen atoms.

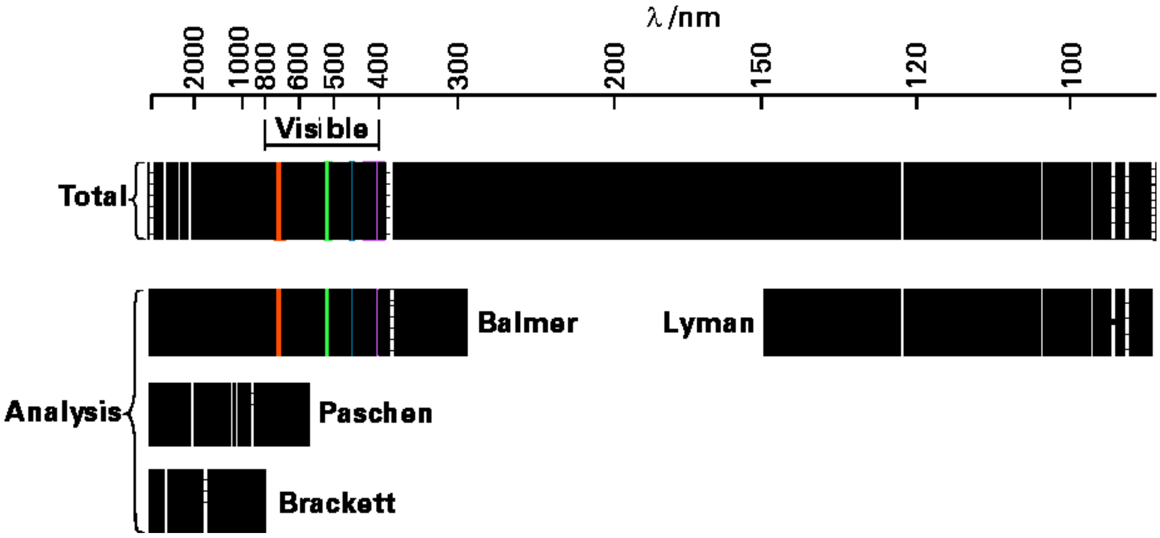
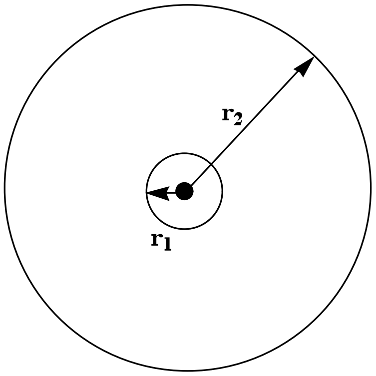


Figure 1.2. Emission spectrum of atomic hydrogen with some lines repeated below to illustrate the series to which they belong.

In the top panel, we see all of the lines emitted with their wave lengths indicated in nanometers. The other panels show how these lines have been analyzed (by scientists whose names are associated) into patterns that relate to the specific energy levels between which transitions occur to emit the corresponding photons.

In the early attempts to rationalize such spectra in terms of electronic motions, one described an electron as moving about the atomic nuclei in circular orbits such as shown in Fig. 1. 3.



Two circular orbits of radii r_1 and r_2.

Figure 1. 3. Characterization of small and large stable orbits for an electron moving around a nucleus.

A circular orbit was thought to be stable when the outward centrifugal force characterized by radius r and speed v ($m_e\ v^2/r$) on the electron perfectly counterbalanced the inward attractive Coulomb force (Ze^2/r^2) exerted by the nucleus of charge Z:

$$m_e\ v^2/r = Ze^2/r^2$$

This equation, in turn, allows one to relate the kinetic energy $1/2\ m_e\ v^2$ to the Coulombic energy Ze^2/r, and thus to express the total energy E of an orbit in terms of the radius of the orbit:

$$E = 1/2\ m_e\ v^2 - Ze^2/r = -1/2\ Ze^2/r.$$

The energy characterizing an orbit or radius r, relative to the E = 0 reference of energy at $r \rightarrow \infty$, becomes more and more negative (i.e., lower and lower) as r becomes smaller. This relationship between outward and inward forces allows one to conclude that the electron should move faster as it moves closer to the nucleus since $v^2 = Ze^2/(r\ m_e)$. However, nowhere in this model is a concept that relates to the experimental fact that each atom emits only certain kinds of photons. It was believed that photon emission occurred when an electron moving in a larger circular orbit lost energy and moved to a smaller circular orbit. However, the Newtonian dynamics that produced the above equation would allow orbits of any radius, and hence any energy, to be followed. Thus, it would appear that the electron should be able to emit photons of any energy as it moved from orbit to orbit.

The breakthrough that allowed scientists such as Niels Bohr to apply the circular-orbit model to the observed spectral data involved first introducing the idea that the electron has a wavelength and that this wavelength λ is related to its momentum by the de Broglie equation $\lambda = h/p$. The key step in the Bohr model was to also specify that the radius of the circular orbit be such that the circumference of the circle 2π r be equal to an integer (n) multiple of the wavelength λ. Only in this way will the electron's wave experience constructive interference as the electron orbits the nucleus. Thus, the Bohr relationship that is analogous to the Bragg equation that determines at what angles constructive interference can occur is

$$2 \pi r = n \lambda.$$

Both this equation and the analogous Bragg equation are illustrations of what we call boundary conditions; they are extra conditions placed on the wavelength to produce some desired character in the resultant wave (in these cases, constructive interference). Of course, there remains the question of why one must impose these extra conditions when the Newton dynamics do not require them. The resolution of this paradox is one of the things that quantum mechanics does.

Returning to the above analysis and using $\lambda = h/p = h/(m_e v)$, $2\pi r = n\lambda$, as well as the force-balance equation $m_e v^2/r = Ze^2/r^2$, one can then solve for the radii that stable Bohr orbits obey:

$$r = (nh/2\pi)^2 \, 1/(m_e Z e^2)$$

and, in turn for the velocities of electrons in these orbits

$$v = Z e^2/(nh/2\pi).$$

These two results then allow one to express the sum of the kinetic ($1/2\ m_e v^2$) and Coulomb potential ($-Ze^2/r$) energies as

$$E = -1/2\ m_e Z^2 e^4/(nh/2\pi)^2.$$

Just as in the Bragg diffraction result, which specified at what angles special high intensities occurred in the scattering, there are many stable Bohr orbits, each labeled by a value of the integer n. Those with small n have small radii (scaling as n^2), high velocities (scaling as 1/n) and more negative total energies (n.b., the reference zero of energy corresponds to the electron at $r = \infty$, and with $v = 0$). So, it is the result that only certain orbits are allowed that causes only certain energies to occur and thus only certain energies to be observed in the emitted photons.

It turned out that the Bohr formula for the energy levels (labeled by n) of an electron moving about a nucleus could be used to explain the discrete line emission spectra of all one-electron atoms and ions (i.e., H, He^+, Li^{+2}, etc., sometimes called hydrogenic species) to very high precision. In such an interpretation of the experimental data, one claims that a photon of energy

$$h\nu = R\,(1/n_i^2 - 1/n_f^2)$$

is emitted when the atom or ion undergoes a transition from an orbit having quantum number n_i to a lower-energy orbit having n_f. Here the symbol R is used to denote the following collection of factors:

$$R = 1/2\ m_e Z^2 e^4/(h/2\pi)^2$$

and is called the Rydberg unit of energy and is equal to 13.6 eV.

The Bohr formula for energy levels did not agree as well with the observed pattern of emission spectra for species containing more than a single electron. However, it does give a reasonable fit, for example, to the Na atom spectra if one examines only transitions involving only the single 3s valence electron. Moreover, it can be greatly improved if one introduces a modification designed to treat the penetration of the Na atom’s 3s and higher orbitals within the regions of space occupied by the 1s, 2s, and 2p orbitals. Such a modification to the Bohr model is achieved by introducing the idea of a so-called quantum defect δ into the principal quantum number n so that the expression for the n-dependence of the orbitals changes to

$$E = -R/(n-\delta)^2$$

For example, choosing δ equal to 0.41, 1.37, 2.23, 3.19, or 4.13 for Li, Na, K, Rb, and Cs, respectively, in this so-called Rydberg formula, one finds decent agreement between the n-dependence of the energy spacings of the singly excited valence states of these atoms. The fact that δ is larger for Na than for Li and largest for Cs reflects that fact that the 3s orbital of Na penetrates the 1s, 2s, and 2p shells while the 2s orbital of Li penetrates only the 1s shell and the 6s orbital of Cs penetrates n = 1, 2, 3, 4, and 5 shells.

It turns out this Rydberg formula can also be applied to certain electronic states of molecules. In particular, for closed-shell cations such as NH_4^+, H_3O^+, protonated alcohols and protonated amines (even on side chains of amino acids), an electron can be attached into a so-called Rydberg orbital to form corresponding neutral radicals such as NH_4, H_3O, R-NH_3, or R-OH_2. For example, in NH_4, the electron bound to an underlying NH_4^+ cation core. The lowest-energy state of this Rydberg species is often labeled 3s because NH_4^+ is isoelectronic with the Na^+ cation which binds an electron in its 3s orbital in its ground state. As in the cases of alkali atoms, these Rydberg molecules also possess excited electronic states. For example, the NH_4 radical has states labeled 3p, 3d, 4s, 4p, 4d, 4f, etc. By making an appropriate choice of the quantum defect parameter d, the energy spacings among these states can be fit reasonably well to the Rydberg formula $E = -R/(n-\delta)^2$. In Fig. 1.3.a several Rydberg orbitals of NH_4 are shown

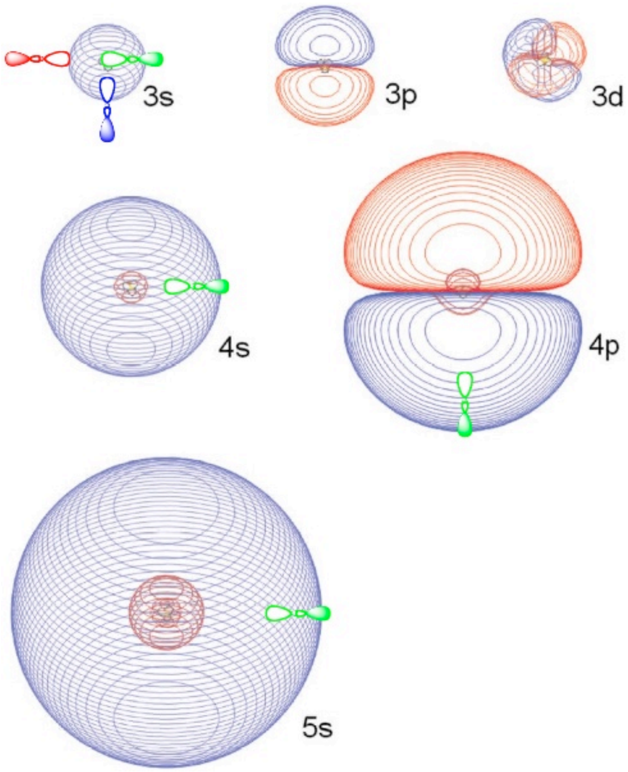


Figure 1.3. a. The n = 3, 4, and 5 Rydberg orbitals of NH_4 with their outermost contours containing 60% of their electron density. The smaller orbitals are supposed to depict C-C, C-N, or C-O σ^* orbitals to give perspective of the Rydberg orbitals' sizes.

These Rydberg orbitals can be quite large (their sizes scale as n^2), clearly have the s, p, or d angular shapes, and possess the expected number of radial nodes. However, for molecular Rydberg orbital's, and unlike atomic Rydberg orbitals, the three p, five d, seven f, etc. orbitals are not degenerate; instead they are split in energy in a manner reflecting the symmetry of the underlying cation's symmetry. For example, for NH_4, the three 3p orbitals are degenerate and belong to t_2 symmetry in the T_d point group; the five 3d orbitals are split into three degenerate t_2 and two degenerate e orbitals.

So, the Bohr model works well for one-electron atoms or ions and the quantum defect-modified Bohr equation describes reasonably well some states of alkali atoms and of Rydberg molecules. The primary reason for the breakdown of the Bohr formula is the neglect of electron-electron Coulomb repulsions in its derivation, which are qualitatively corrected for by using the quantum defect parameter for Rydberg atoms and molecules. Nevertheless, the success of the Bohr model made it clear that discrete emission spectra could only be explained by introducing the concept that not all orbits were allowed. Only special orbits that obeyed a constructive-interference condition were really accessible to the electron's motions. This idea that not all energies were allowed, but only certain quantized energies could occur was essential to achieving even a qualitative sense of agreement with the experimental fact that emission spectra were discrete.

In summary, two experimental observations on the behavior of electrons that were crucial to the abandonment of Newtonian dynamics were the observations of electron diffraction and of discrete emission spectra. Both of these findings seem to suggest that electrons have some wave characteristics and that these waves have only certain allowed (i.e., quantized) wavelengths.

So, now we have some idea about why Newton's equations fail to account for the dynamical motions of light and small particles such as electrons and nuclei. We see that extra conditions (e.g., the Bragg condition or constraints on the de Broglie wavelength) could be imposed to achieve some degree of agreement with experimental observation. However, we still are left wondering what equations can be applied to properly describe such motions and why the extra conditions are needed. It turns out that a new kind of equation based on combining wave and particle properties needed to be developed to address such issues. These are the so-called Schrödinger equations to which we now turn our attention.

As I said earlier, no one has yet shown that the Schrödinger equation follows deductively from some more fundamental theory. That is, scientists did not derive this equation; they postulated it. Some idea of how the scientists of that era dreamed up the Schrödinger equation can be had by examining the time and spatial dependence that characterizes so-called traveling waves. It should be noted that the people who worked on these problems knew a great deal about waves (e.g., sound waves and water waves) and the equations they obeyed. Moreover, they knew that waves could sometimes display the characteristic of quantized wavelengths or frequencies (e.g., fundamentals and overtones in sound waves). They knew, for example, that waves in one dimension that are constrained at two points (e.g., a violin string held fixed at two ends) undergo oscillatory motion in space and time with characteristic frequencies and wavelengths. For example, the motion of the violin string just mentioned can be described as having an amplitude

A(x,t) at a position x along its length at time t given by

$$A(x,t) = A(x,o) \cos(2\pi \nu t),$$

where ν is its oscillation frequency. The amplitude's spatial dependence also has a sinusoidal dependence given by

$$A(x,0) = A \sin (2\pi x/\lambda)$$

where λ is the crest-to-crest length of the wave. Two examples of such waves in one dimension are shown in Fig. 1. 4.

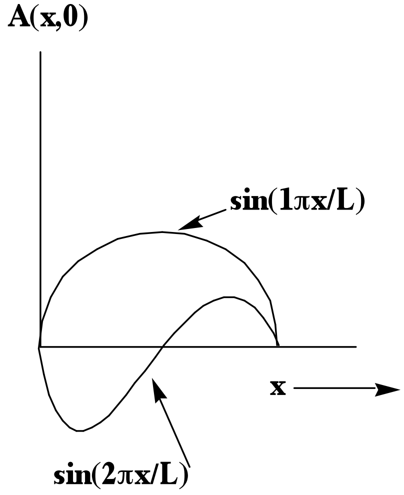


Figure 1.4. Fundamental and first overtone notes of a violin string of length L.

In these cases, the string is fixed at x = 0 and at x = L, so the wavelengths belonging to the two waves shown are $\lambda = 2L$ and $\lambda = L$. If the violin string were not clamped at x = L, the waves could have any value of λ. However, because the string is attached at x = L, the allowed wavelengths are quantized to obey

$$\lambda = 2L/n,$$

where $n = 1, 2, 3, 4, \ldots$ .The equation that such waves obey, called the wave equation, reads:

$$d^2A(x,t)/dt^2 = c^2\ d^2A/dx^2$$

where c is the speed at which the wave travels. This speed depends on the composition of the material from which the violin string is made; stiff string material produces waves with higher speeds than for softer material. Using the earlier expressions for the x- and t-dependences of the wave A(x,t), we find that the wave's frequency and wavelength are related by the so-called dispersion equation:

$$\nu^2 = (c/\lambda)^2,$$

or

$$c = \lambda\ \nu.$$

This relationship implies, for example, that an instrument string made of a very stiff material (large c) will produce a higher frequency tone for a given wavelength (i.e., a given value of n) than will a string made of a softer material (smaller c).

For waves moving on the surface of, for example, a rectangular two-dimensional surface of lengths L_x and L_y, one finds

$$A(x,y,t) = \sin(n_x\ \pi x/L_x)\ \sin(n_y\ \pi y/L_y)\ \cos(2\pi\ \nu t).$$

Hence, the waves are quantized in two dimensions because their wavelengths must be constrained to cause A(x,y,t) to vanish at $x = 0$ and $x = L_x$ as well as at $y = 0$ and $y = L_y$ for all times t.

It is important to note, in closing this discussion of waves on strings and surfaces, that it is not being a solution to the Schrödinger equation that results in quantization of the wavelengths. Instead, it is the condition that the wave vanish at the boundaries that generates the quantization. You will see this trend time and again throughout this text; when a wave function is subject to specific constraints at its inner or outer boundary (or both), quantization will result; if these boundary conditions are not present, quantization will not occur. Let us now return to the issue of waves that describe electrons moving.

The pioneers of quantum mechanics examined functional forms similar to those shown above. For example, forms such as $A = \exp[\pm 2\pi i(\nu t - x/\lambda)]$ were considered because they correspond to periodic waves that evolve in x and t under no external x- or t- dependent forces. Noticing that

$$d^2A/dx^2 = - (2\pi/\lambda)^2 A$$

and using the de Broglie hypothesis $\lambda = h/p$ in the above equation, one finds

$$d^2A/dx^2 = - p^2 (2\pi/h)^2 A.$$

If A is supposed to relate to the motion of a particle of momentum p under no external forces (since the waveform corresponds to this case), p^2 can be related to the energy E of the particle by $E = p^2/2m$. So, the equation for A can be rewritten as:

$$d^2A/dx^2 = - 2m E (2\pi/h)^2 A,$$

or, alternatively,

$$- (h/2\pi)^2 (1/2m) d^2A/dx^2 = E A.$$

Returning to the time-dependence of A(x,t) and using $\nu = E/h$, one can also show that

$$i\,(h/2\pi)\, dA/dt = E\, A,$$

which, using the first result, suggests that

$$i\,(h/2\pi)\, dA/dt = -\,(h/2\pi)^2\,(1/2m)\, d^2A/dx^2.$$

This is a primitive form of the Schrödinger equation that we will address in much more detail below. Briefly, what is important to keep in mind that the use of the de Broglie and Planck/Einstein connections ($\lambda = h/p$ and $E = h\,\nu$), both of which involve the constant h, produces suggestive connections between

$$i\,(h/2\pi)\, d/dt \text{ and } E$$

and between

$$p^2 \text{ and } -\,(h/2\pi)^2\, d^2/dx^2$$

or, alternatively, between

$$p \text{ and } -\,i\,(h/2\pi)\, d/dx.$$

These connections between physical properties (energy E and momentum p) and differential operators are some of the unusual features of quantum mechanics.

The above discussion about waves and quantized wavelengths as well as the observations about the wave equation and differential operators are not meant to provide or even suggest a derivation of the Schrödinger equation. Again the scientists who invented quantum mechanics did not derive its working equations. Instead, the equations and rules of quantum mechanics have been postulated and designed to be consistent with laboratory observations. My students often find this to be disconcerting because they are hoping and searching for an underlying fundamental basis from which the basic laws of quantum mechanics follow logically. I try to remind them that this is not how theory works. Instead, one uses experimental observation to postulate a rule or equation or theory, and one then tests the theory by making predictions that can be tested by further experiments. If the theory fails, it must be refined, and this process continues until one has a better and better theory. In this sense, quantum mechanics, with all of its unusual mathematical constructs and rules, should be viewed as arising from the imaginations of scientists who tried to invent a theory that was consistent with experimental data and which could be used to predict things that could then be tested in the laboratory. Thus far, this theory has proven to be reliable, but, of course, we are always searching for a new and improved theory that describes how small light particles move.

If it helps you to be more accepting of quantum theory, I should point out that the quantum description of particles reduces to the classical Newton description under certain circumstances. In particular, when treating heavy particles (e.g., macroscopic masses and even heavier atoms), it is often possible to use Newton dynamics. Soon, we will discuss in more detail how the quantum and classical dynamics sometimes coincide (in which case one is free to use the simpler Newton dynamics). So, let us now move on to look at this strange Schrödinger equation that we have been digressing about for so long.

1.2 The Schrödinger Equation and Its Components

It has been well established that electrons moving in atoms and molecules do not obey the classical Newton equations of motion. People long ago tried to treat electronic motion classically, and found that features observed clearly in experimental measurements simply were not consistent with such a treatment. Attempts were made to supplement the classical equations with conditions that could be used to rationalize such observations. For example, early workers required that the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ be allowed to assume only integer multiples of $h/2\pi$ (which is often abbreviated as $\hbar$), which can be shown to be equivalent to the Bohr postulate $n \lambda = 2 \pi r$. However, until scientists realized that a new set of laws, those of quantum mechanics, applied to light microscopic particles, a wide gulf existed between laboratory observations of molecule-level phenomena and the equations used to describe such behavior.

Quantum mechanics is cast in a language that is not familiar to most students of chemistry who are examining the subject for the first time. Its mathematical content and how it relates to experimental measurements both require a great deal of effort to master. With these thoughts in mind, I have organized this material in a manner that first provides a brief introduction to the two primary constructs of quantum mechanics- operators and wave functions that obey a Schrödinger equation. Next, I demonstrate the application of these constructs to several chemically relevant model problems. By learning the solutions of the Schrödinger equation for a few model systems, the student can better appreciate the treatment of the fundamental postulates of quantum mechanics as well as their relation to experimental measurement for which the wave functions of the known model problems offer important interpretations.

1.2.1 Operators

Each physically measurable quantity has a corresponding operator. The eigenvalues of the operator tell the only values of the corresponding physical property that can be observed in an experimental probe of that property. Some operators have a continuum of eigenvalues, but others have only discrete quantized eigenvalues.

Any experimentally measurable physical quantity F (e.g., energy, dipole moment, orbital angular momentum, spin angular momentum, linear momentum, kinetic energy) has a classical mechanical expression in terms of the Cartesian positions $\{q_i\}$ and momenta $\{p_i\}$ of the particles that comprise the system of interest. Each such classical expression is assigned a corresponding quantum mechanical operator **F** formed by replacing the $\{p_i\}$ in the classical form by the differential operator $-i\hbar\partial/\partial q_j$ and leaving the coordinates q_j that appear in F untouched. If one is working with a classical quantity expressed in terms of curvilinear coordinates, it is important that this quantity first be rewritten in Cartesian coordinates. The replacement of the Cartesian momenta by $-i\hbar\partial/\partial q_j$ can then be made and the resultant expression can be transformed back to the curvilinear coordinates if desired.

For example, the classical kinetic energy of N particles (with masses m_l) moving in a potential field containing both quadratic and linear coordinate-dependence can be written as

$$F=\Sigma_{l=1,N} (p_l^2/2m_l + 1/2\ k(q_l-q_l^0)^2 + L(q_l-q_l^0)).$$

The quantum mechanical operator associated with this F is

$$\mathbf{F}=\Sigma_{l=1,N} (- \hbar^2/2m_l\ \partial^2/\partial q_l^2 + 1/2\ k(q_l-q_l^0)^2 + L(q_l-q_l^0)).$$

Such an operator would occur when, for example, one describes the sum of the kinetic energies of a collection of particles (the $\Sigma_{l=1,N} (p_l^2/2m_l)$ term), plus the sum of "Hookes' Law" parabolic potentials (the $1/2\ \Sigma_{l=1,N}\ k(q_l-q_l^0)^2$), and (the last term in F) the interactions of the particles with an externally applied field whose potential energy varies linearly as the particles move away from their equilibrium positions $\{q_l^0\}$.

Let us try more examples. The sum of the z-components of angular momenta (recall that vector angular momentum **L** is defined as **L** = **r** x **p**) of a collection of N particles has the following classical expression

$$F=\Sigma_{j=1,N} (x_jp_{yj} - y_jp_{xj}),$$

and the corresponding operator is

$$\mathbf{F}=-i\hbar\ \Sigma_{j=1,N} (x_j\partial/\partial y_j - y_j\partial/\partial x_j).$$

If one transforms these Cartesian coordinates and derivatives into polar coordinates, the above expression reduces to

$$\mathbf{F} = -i\ \hbar\ \Sigma_{j=1,N}\ \partial/\partial\phi_j$$

where ϕ_j is the azimuthal angle of the j^{th} particle.

The x-component of the dipole moment for a collection of N particles has a classical form of

$$F=\Sigma_{j=1,N}\ Z_j e x_j,$$

for which the quantum operator is

$$\mathbf{F}=\Sigma_{j=1,N}\ Z_j e x_j\ ,$$

where $Z_j e$ is the charge on the j^{th} particle. Notice that in this case, classical and quantum forms are identical because F contains no momentum operators.

Remember, the mapping from F to **F** is straightforward only in terms of Cartesian coordinates. To map a classical function F, given in terms of curvilinear coordinates (even if they are orthogonal), into its quantum operator is not at all straightforward. The mapping can always be done in terms of Cartesian coordinates after which a transformation of the resulting coordinates and differential operators to a curvilinear system can be performed.

The relationship of these quantum mechanical operators to experimental measurement lies in the eigenvalues of the quantum operators. Each such operator has a corresponding eigenvalue equation

$$\mathbf{F}\ \chi_j = \alpha_j\ \chi_j$$

in which the χ_j are called eigenfunctions and the (scalar numbers) α_j are called eigenvalues. All such eigenvalue equations are posed in terms of a given operator (**F** in this case) and those functions $\{\chi_j\}$ that **F** acts on to produce the function back again but multiplied by a constant (the eigenvalue). Because the operator **F** usually contains differential operators (coming from the momentum), these equations are differential equations. Their solutions χ_j depend on the coordinates that **F** contains as differential operators. An example will help clarify these points. The differential operator d/dy acts on what functions (of y) to generate the same function back again but multiplied by a constant? The answer is functions of the form exp(ay) since

$$d(\exp(ay))/dy = a \exp(ay).$$

So, we say that exp(ay) is an eigenfunction of d/dy and a is the corresponding eigenvalue.

As I will discuss in more detail shortly, the eigenvalues of the operator **F** tell us the <u>only</u> values of the physical property corresponding to the operator **F** that can be observed in a laboratory measurement. Some **F** operators that we encounter possess eigenvalues that are discrete or quantized. For such properties, laboratory measurement will result in only those discrete values. Other **F** operators have eigenvalues that can take on a continuous range of values; for these properties, laboratory measurement can give any value in this continuous range.

An important characteristic of the quantum mechanical operators formed as discussed above for any measureable property is the fact that they are Hermitian. An operator **F** that acts on coordinates denoted q is Hermitian if

$$\int \phi_I^* \mathbf{F} \phi_J \, dq = \int [\mathbf{F} \phi_I]^* \phi_J \, dq$$

or, equivalently,

$$\int \phi_I^* \mathbf{F} \phi_J \, dq = [\int \phi_J^* \mathbf{F} \phi_I \, dq]^*$$

for any functions $\phi_I(q)$ and $\phi_J(q)$. The operator corresponding to any power of the coordinate q itself is easy to show obeys this identity, but what about the corresponding momentum operator $-i\hbar \, \partial/\partial q$? Let's take the left hand side of the above identity for $\mathbf{F} = -i\hbar \, \partial/\partial q$ and rewrite it using integration by parts as follows:

$$\int_{-\infty}^{\infty}\phi_I^*(q)[-i\hbar\frac{\partial\phi_J(q)}{\partial q}]dq = -\,i\hbar\int_{-\infty}^{\infty}\phi_I^*(q)[\frac{\partial\phi_J(q)}{\partial q}]dq = -i\hbar\{-\int_{-\infty}^{\infty}\frac{\partial\phi_I^*(q)}{\partial q}\phi_J(q)dq + \phi_I^*(\infty)\phi_J(\infty) - \phi_I^*(-\infty)\phi_J(-\infty)\}$$

If the functions $\phi_I(q)$ and $\phi_J(q)$ are assumed to vanish at ±∞, the right-hand side of this equation can be rewritten as

$$i\hbar\int_{-\infty}^{\infty}\frac{\partial\phi_I^*(q)}{\partial q}\phi_J(q)dq = \int_{-\infty}^{\infty}[-i\hbar\frac{\partial\phi_I(q)}{\partial q}]^*\phi_J(q)dq = [\int_{-\infty}^{\infty}\phi_J^*(q)[-i\hbar\frac{\partial\phi_I(q)}{\partial q}]dq]^*.$$

So, $-i\hbar\,\partial/\partial q$ is indeed a Hermitian operator. Moreover, using the fact that q_j and p_j are Hermitian, one can show that any operator **F** formed using the rules described above is also Hermitian.

One thing you need to be aware of concerning the eigenfunctions of any Hermitian operator is that each pair of eigenfunctions ψ_n and $\psi_{n'}$ belonging to different eigenvalues display a property termed orthonormality. This property means that not only may ψ_n and $\psi_{n'}$ each normalized so their probability densities integrate to unity

$$1=\int |\psi_n|^2\,dx = \int |\psi_{n'}|^2\,dx,$$

but they are also orthogonal to each other

$$0 = \int \psi_n{}^*\,\psi_{n'}\,dx$$

where the complex conjugate * of the first function appears only when the ψ solutions contain imaginary components (e.g., the functions $\exp(im\phi)$, which eigenfunctions of the z-component of angular momentum $-i\hbar\,\partial/\partial\phi$). The orthogonality condition can be viewed as similar to the condition of two vectors $\mathbf{v_1}$ and $\mathbf{v_2}$ being perpendicular, in which case their scalar (sometimes called dot) product vanishes $\mathbf{v}_1 \bullet \mathbf{v}_2 = 0$. I want you to keep this property in mind because you will soon see that it is a characteristic of all eigenfunctions of any Hermitian operator.

It is common to write the integrals displaying the normalization and orthogonality conditions in the following so-called Dirac notation

$$1 = <\psi_n | \psi_n> \qquad\qquad 0 = <\psi_n | \psi_{n'}>,$$

where the $| >$ and $< |$ symbols represent ψ and ψ^*, respectively, and putting the two together in the $< | >$ construct implies the integration over the variables that ψ depends upon. The Hermitian character of an operator **F** means that this operator forms a Hermitian matrix when placed between pairs of functions and the coordinates are integrated over. For example, the matrix representation of an operator **F** when acting on a set of functions denoted $\{\phi_J\}$ is:

$$F_{I,J} = <\phi_I | \mathbf{F} | \phi_J> = \int \phi_I^* \, \mathbf{F} \, \phi_J \, dq.$$

For all of the operators formed following the rules stated earlier, one finds that these matrices have the following property:

$$F_{I,J} = F_{J,I}^*$$

which makes the matrices what we call Hermitian. If the functions upon which **F** acts and **F** itself have no imaginary parts (i.e., are real), then the matrices turn out to be symmetric:

$$F_{I,J} = F_{J,I} .$$

The importance of the Hermiticity or symmetry of these matrices lies in the fact that it can be shown that such matrices have all real (i.e., not complex) eigenvalues and have eigenvectors that are orthogonal (or, in the case of degenerate eigenvalues, can be chosen to be orthogonal). Let's see how these conditions follow from the Hermiticity property.

If the operator **F** has two eigenfunctions ψ_1 and ψ_2 having eigenvalues λ_1 and λ_2, respectively, then

$$\mathbf{F}\,\psi_1 = \lambda_1\,\psi_1.$$

Multiplying this equation on the left by ψ_2^* and integrating over the coordinates (denoted q) that **F** acts on gives

$$\int \psi_2^*\mathbf{F}\,\psi_1\,dq = \lambda_1\int \psi_2^*\psi_1\,dq.$$

The Hermitian nature of **F** allows us to also write

$$\int \psi_2^*\mathbf{F}\,\psi_1\,dq = \int (\,\mathbf{F}\,\psi_2)^*\,\psi_1\,dq,$$

which, because

$$\mathbf{F}\,\psi_2 = \lambda_2\,\psi_2$$

gives

$$\lambda_1\int \psi_2^*\psi_1\,dq = \int \psi_2^*\mathbf{F}\,\psi_1\,dq = \int (\,\mathbf{F}\,\psi_2)^*\,\psi_1\,dq = \lambda_2\int \psi_2^*\psi_1\,dq.$$

If λ_1 is not equal to λ_2, the only way the left-most and right-most terms in this equality can be equal is if

$$\int \psi_2^*\psi_1\,dq = 0,$$

which means the two eigenfunctions are orthogonal. If the two eigenfunctions ψ_1 and ψ_2 have equal eigenvalues, the above derivation can still be used to show that ψ_1 and ψ_2 are orthogonal to the other eigenfunctions $\{\psi_3, \psi_4$, etc.$\}$ of **F** that have different eigenvalues. For the eigenfunctions ψ_1 and ψ_2 that are degenerate (i.e., have equal eigenvalues), we cannot show that they are orthogonal (because they need not be so). However, because any linear combination of these two functions is also an eigenfunction of **F** having the same eigenvalue, we can always choose a combination that makes ψ_1 and ψ_2 orthogonal to one another.

Finally, for any given eigenfunction ψ_1, we have

$$\int \psi_1^* \mathbf{F}\, \psi_1\, dq = \lambda_1 \int \psi_1^* \psi_1\, dq$$

However, the Hermitian character of **F** allows us to rewrite the left hand side of this equation as

$$\int \psi_1^* \mathbf{F}\, \psi_1\, dq = \int [\mathbf{F}\psi_1]^* \psi_1\, dq = [\lambda_1]^* \int \psi_1^* \psi_1\, dq.$$

These two equations can only remain valid if

$$[\lambda_1]^* = \lambda_1,$$

which means that λ_1 is a real number (i.e., has no imaginary part).

So, all quantum mechanical operators have real eigenvalues (this is good since these eigenvalues are what can be measured in any experimental observation of that property) and can be assumed to have orthogonal eigenfunctions. It is important to keep these facts in mind because we make use of them many times throughout this text.

1.2.2 Wave functions

The eigenfunctions of a quantum mechanical operator depend on the coordinates upon which the operator acts. The particular operator that corresponds to the total energy of the system is called the Hamiltonian operator. The eigenfunctions of this particular operator are called wave functions

A special case of an operator corresponding to a physically measurable quantity is the Hamiltonian operator H that relates to the total energy of the system. The energy eigenstates of the system Ψ are functions of the coordinates $\{q_j\}$ that H depends on and of time t. The function $|\Psi(q_j,t)|^2 = \Psi^*\Psi$ gives the probability density for observing the coordinates at the values q_j at time t. For a many-particle system such as the H_2O molecule, the wave function depends on many coordinates. For H_2O, it depends on the x, y, and z (or r,θ, and ϕ) coordinates of the ten electrons and the x, y, and z (or r,θ, and ϕ) coordinates of the oxygen nucleus and of the two protons; a total of thirty-nine coordinates appear in Ψ.

If one is interested in what the probability distribution is for finding the corresponding momenta p_j at time t, the wave function $\Psi(q_j, t)$ has to first be written as a combination of the eigenfunctions of the momentum operators $-i\hbar\,\partial/\partial q_j$. Expressing $\Psi(q_j,t)$ in this manner is possible because the momentum operator is Hermitian and it can be shown that the eigenfunctions of any Hermitian operator form a complete set of functions. The momentum operator's eigenfunctions are

$$(1/2\pi\hbar)^{1/2} \exp(ip_j q_j/\hbar),$$

and they obey

$$-i\hbar\, \partial/\partial q_j\, (1/2\pi\hbar)^{1/2} \exp(ip_j q_j/\hbar) = p_j\, (1/2\pi\hbar)^{1/2} \exp(ip_j q_j/\hbar).$$

These eigenfunctions can also be shown to be orthonormal

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dq_j \exp^{-i\frac{p_j q_j}{\hbar}} \exp^{i\frac{p'_j q_j}{\hbar}} = \delta(p_j - p'_j).$$

Expanding $\Psi(q_j,t)$ in terms of these normalized momentum eigenfunctions gives

$$\Psi(q_j,t) = \int_{-\infty}^{\infty} C(p_j,t)\frac{1}{\sqrt{2\pi\hbar}}\exp(i\frac{p_j q_j}{\hbar})dp_j$$

We can find the expansion coefficients $C(p_j,t)$ by multiplying the above equation by the complex conjugate of another (labeled p_j') momentum eigenfunction and integrating over q_j

$$C(p'_j,t) = \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi\hbar}} \exp(-i\frac{p'_j q_j}{\hbar}) \Psi(q_j,t) dq_j$$

The quantities $|C(p'_j,t)|^2$ then give the probability of finding momentum p'_j at time t.

In classical mechanics, the coordinates q_j and their corresponding momenta p_j are functions of time. The state of the system is then described by specifying $q_j(t)$ and $p_j(t)$. In quantum mechanics, the concept that q_j is known as a function of time is replaced by the concept of the probability density for finding coordinate q_j at a particular value at a particular time $|\Psi(q_j,t)|^2$ or the probability density $|C(p'_j,t)|^2$ for finding momentum p'_j at time t.

The Hamiltonian eigenstates are especially important in chemistry because many of the tools that chemists use to study molecules probe the energy states of the molecule. For example, most spectroscopic methods are designed to determine which energy state (electronic, vibrational, rotational, nuclear spin, etc.) a molecule is in. However, there are other experimental measurements that measure other properties (e.g., the z-component of angular momentum or the total angular momentum).

As stated earlier, if the state of some molecular system is characterized by a wave function Ψ that happens to be an eigenfunction of a quantum mechanical operator **F**, one can immediately say something about what the outcome will be if the physical property F corresponding to the operator **F** is measured. In particular, since

$$\mathbf{F}\, \chi_j = \lambda_j\, \chi_j,$$

where λ_j is one of the eigenvalues of **F**, we know that the value λ_j will be observed if the property F is measured while the molecule is described by the wave function $\Psi = \chi_j$. In fact, once a measurement of a physical quantity F has been carried out and a particular eigenvalue λ_j has been observed, the system's wave function Ψ becomes the eigenfunction χ_j that corresponds to that eigenvalue. That is, the act of making the measurement causes the system's wave function to become the eigenfunction of the property that was measured. This is what is meant when one hears that the act of making a measurement can change the state of the system in quantum mechanics.

What happens if some other property G, whose quantum mechanical operator is **G** is measured in a case where we have already determined $\Psi = \chi_j$? We know from what was said earlier that some eigenvalue μ_k of the operator **G** will be observed in the measurement. But, will the molecule's wave function remain, after G is measured, the eigenfunction $\Psi = \chi_j$ of **F**, or will the measurement of G cause Ψ to be altered in a way that makes the molecule's state no longer an eigenfunction of **F**? It turns out that if the two operators **F** and **G** obey the condition

$$\mathbf{F}\,\mathbf{G} = \mathbf{G}\,\mathbf{F},$$

then, when the property G is measured, the wave function $\Psi = \chi_j$ will remain unchanged. This property that the order of application of the two operators does not matter is called commutation; that is, we say the two operators commute if they obey this property. Let us see how this property leads to the conclusion about Ψ remaining unchanged if the two operators commute. In particular, we apply the **G** operator to the above eigenvalue equation from which we concluded that $\Psi = \chi_j$:

$$\mathbf{G}\,\mathbf{F}\,\chi_j = \mathbf{G}\,\lambda_j\,\chi_j.$$

Next, we use the commutation to re-write the left-hand side of this equation, and use the fact that λ_j is a scalar number to thus obtain:

$$\mathbf{F}\,\mathbf{G}\,\chi_j = \lambda_j\,\mathbf{G}\,\chi_j.$$

So, now we see that ($\mathbf{G}\chi_j$) itself is an eigenfunction of **F** having eigenvalue λ_j. So, unless there are more than one eigenfunction of **F** corresponding to the eigenvalue λ_j (i.e., unless this eigenvalue is degenerate), $\mathbf{G}\chi_j$ must itself be proportional to χ_j. We write this proportionality conclusion as

$$\mathbf{G}\,\chi_j = \mu_j\,\chi_j,$$

which means that χ_j is also an eigenfunction of **G**. This, in turn, means that measuring the property G while the system is described by the wave function $\Psi = \chi_j$ does not change the wave function; it remains χ_j.

If there are more than one function $\{\chi_{j1}, \chi_{j2, \ldots}\chi_{jM}\}$ that are eigenfunctions of **F** having the same eigenvalue λ_j, then the relation $\mathbf{F}\,\mathbf{G}\,\chi_j = \lambda_j\,\mathbf{G}\,\chi_j$ only allows us to conclude that $\mathbf{G}\,\chi_j$ is some combination of these degenerate functions

$$\mathbf{G}\,\chi_j = \Sigma_{k=1,M}\, C_k\,\chi_{jk}.$$

Below, I offer some examples that I hope will clarify what these rules mean and how the relate to laboratory measurements.

In summary, when the operators corresponding to two physical properties commute, once one measures one of the properties (and thus causes the system to be an eigenfunction of that operator), subsequent measurement of the second operator will (if the eigenvalue of the first operator is not degenerate) produce a unique eigenvalue of the second operator and will not change the system wave function. If either of the two properties is subsequently measured (even over and over, again), the wave function will remain unchanged and the value observed for the property being measured will remain the same as the original eigenvalue observed.

However, if the two operators do not commute, one simply cannot reach the above conclusions. In such cases, measurement of the property corresponding to the first operator will lead to one of the eigenvalues of that operator and cause the system wave function to become the corresponding eigenfunction. However, subsequent measurement of the second operator will produce an eigenvalue of that operator, but the system wave function will be changed to become an eigenfunction of the second operator and thus no longer the eigenfunction of the first.

I think an example will help clarify this discussion. Let us consider the following orbital angular momentum operators for N particles

$$\mathbf{L} = \mathbf{\Sigma}_{\mathbf{j=1,N}} (\mathbf{r}_\mathbf{j} \, \mathbf{x} \, \mathbf{p}_\mathbf{j}) \text{ or}$$

$$\mathbf{L}_\mathbf{z} = -i\hbar \, \Sigma_{j=1,N} (x_j \, \partial/\partial y_j - y_j \, \partial/\partial x_j)$$

$$\mathbf{L}_\mathbf{x} = -i\hbar \, \Sigma_{j=1,N} (y_j \, \partial/\partial x_j - x_j \, \partial/\partial y_j)$$

$$\mathbf{L}_\mathbf{y} = -i\hbar \, \Sigma_{j=1,N} (z_j \, \partial/\partial x_j - x_j \, \partial/\partial z_j)$$

and

$$\mathbf{L}^2 = \mathbf{L}_\mathbf{x}^2 + \mathbf{L}_\mathbf{y}^2 + \mathbf{L}_\mathbf{z}^2$$

It turns out that the operator $\mathbf{L}^2$ can be shown to commute with any one of $\mathbf{L}_\mathbf{z}$**,** $\mathbf{L}_\mathbf{x}$, or $\mathbf{L}_\mathbf{y}$, but $\mathbf{L}_\mathbf{z}$**,** $\mathbf{L}_\mathbf{x}$**,** or $\mathbf{L}_\mathbf{y}$ do not commute with one another (we will discuss these operators in considerably more detail in Chapter 2 section 2.7; for now, please accept these statements).

Let us assume a measurement of $\mathbf{L}_\mathbf{z}$ is carried out and one obtains the value $2\hbar$. Thus far, all one knows is that the system can be described by a wave function that is some combination of D, F, G, H, etc. angular momentum functions $|L, m=2>$ having different L-values but all having m = 2

$$\Psi = \Sigma_{L>2} C_L |L, m=2>,$$

but one does not know the amplitudes C_L telling how much a given L-value contributes to Ψ. One can express Ψ as such a linear combination because the Hermitian quantum mechanical operators formed as described above can be shown to possess complete sets of eigenfunctions; this means that any function (of the appropriate variables) can be written as a linear combination of these eigenfunctions as done above.

If one subsequently carries out a measurement of $\mathbf{L}^2$, the fact that $\mathbf{L}^2$ and $\mathbf{L}_\mathbf{z}$ commute means that this second measurement will not alter the fact that Ψ contains only contributions with m =2, but it will result in observing only one specific L-value. The probability of observing any particular L-value will be given by $|C_L|^2$. Once this measurement is realized, the wave function will contain only terms having that specific L-value and m = 2. For example, if L = 3 is found, we know the wave function has L = 3 and m = 2, so we know it is a F-symmetry function with m = 2, but we don't know any more. That is, we don't know if it is an n = 4, 5, 6, etc. F-function.

What now happens if we make a measurement of $\mathbf{L}_x$ when the system is in the L = 3, m=2 state (recall, this m = 2 is a value of the $\mathbf{L}_z$ component of angular momentum)? Because $\mathbf{L}_x$ and $\mathbf{L}^2$ commute, the measurement of $\mathbf{L}_x$ will not alter the fact that Ψ contains only L = 3 components. However, because $\mathbf{L}_x$ and $\mathbf{L}_z$ do not commute, we can not assume that Ψ is still an eigenfunction of $\mathbf{L}_x$; it will be a combination of eigenfunctions of $\mathbf{L}^2$ having L = 3 but having m-values between -3 and 3, with m now referring to the eigenvalue of $\mathbf{L}_x$ (no longer to $\mathbf{L}_z$)

$$\Psi = \Sigma_{m=-3,3} C_m |L=3, m>.$$

When $\mathbf{L}_x$ is measured, the value $m\hbar$ will be found with probability $|C_m|^2$, after which the wave function will be the |L=3, m> eigenfunction of $\mathbf{L}^2$ and $\mathbf{L}_x$ (and no longer an eigenfunction of $\mathbf{L}_z$)

I understand that these rules of quantum mechanics can be confusing, but I assure you they are based on laboratory observations about how atoms, ions, and molecules behave when subjected to state-specific measurements. So, I urge you to get used to the fact that quantum mechanics has rules and behaviors that may be new to you but need to be mastered by you.

1.2.3 The Schrödinger Equation

This equation is an eigenvalue equation for the energy or Hamiltonian operator; its eigenvalues provide the only allowed energy levels of the system

1. The Time-Dependent Equation

If the Hamiltonian operator contains the time variable explicitly, one must solve the time-dependent Schrödinger equation

Before moving deeper into understanding what quantum mechanics means, it is useful to learn how the wave functions Ψ are found by applying the basic equation of quantum mechanics, the Schrödinger equation, to a few exactly soluble model problems. Knowing the solutions to these 'easy' yet chemically very relevant models will then facilitate learning more of the details about the structure of quantum mechanics.

The Schrödinger equation is a differential equation depending on time and on all of the spatial coordinates necessary to describe the system at hand (thirty-nine for the H_2O example cited above). It is usually written

$$\mathbf{H}\,\Psi = i\,\hbar\,\partial\Psi/\partial t$$

where $\Psi(q_j,t)$ is the unknown wave function and **H** is the operator corresponding to the total energy of the system. This Hermitian operator is called the Hamiltonian and is formed, as stated above, by first writing down the classical mechanical expression for the total energy (kinetic plus potential) in Cartesian coordinates and momenta and then replacing all classical momenta p_j by their quantum mechanical operators $p_j = - i\hbar\partial/\partial q_j$.

For the H_2O example used above, the classical mechanical energy of all thirteen particles is

$$E = \Sigma_{i=1,30}\, p_i^2/2m_e + 1/2\, \Sigma_{j\neq i=1,10}\, e^2/r_{i,j} - \Sigma_{a=1,3;i=1,10}\, Z_a e^2/r_{i,a}$$

$$+ \Sigma_{a=1,9}\, p_a^2/2m_a + 1/2\, \Sigma_{b\neq a=1,3}\, Z_a Z_b e^2/r_{a,b}\ ,$$

where the indices i and j are used to label the ten electrons whose thirty Cartesian coordinates and thirty Cartesian momenta are $\{q_i\}$ and $\{p_j\}$, and a and b label the three nuclei whose charges are denoted $\{Z_a\}$ and whose nine Cartesian coordinates and nine Cartesian momenta are $\{q_a\}$ and $\{p_a\}$. The electron and nuclear masses are denoted m_e and $\{m_a\}$, respectively. The corresponding Hamiltonian operator is

$$\mathbf{H} = \Sigma_{i=1,30}\, [- (\hbar^2/2m_e)\, \partial^2/\partial q_i^2\,]+ 1/2\, \Sigma_{j\neq i=1,10}\, e^2/r_{i,j} - \Sigma_{a=1,3;i=1,10}\, Z_a e^2/r_{i,a}$$

$$+ \Sigma_{a=1,9}\, [- (\hbar^2/2m_a)\, \partial^2/\partial q_a^2\,]+ 1/2\, \Sigma_{b\neq a=1,3}\, Z_a Z_b e^2/r_{a,b}$$

where $r_{i,j}$, $r_{i,a}$, and $r_{a,b}$ denote the distances between electron pairs, electrons and nuclei, and nuclear pairs, respectively.

Notice that **H** is a second order differential operator in the space of the thirty-nine Cartesian coordinates that describe the positions of the ten electrons and three nuclei. It is a second order operator because the momenta appear in the kinetic energy as p_j^2 and p_a^2, and the quantum mechanical operator for each momentum $p = -i\hbar\, \partial/\partial q$ is of first order. The Schrödinger equation for the H_2O example at hand then reads

$$\{\Sigma_{i=1,30} [- (\hbar^2/2m_e)\, \partial^2/\partial q_i^2]+ 1/2\, \Sigma_{j\neq i}\, e^2/r_{i,j} - \Sigma_{a=1,3;i=1,10}\, Z_a e^2/r_{i,a} \}\, \Psi$$

$$+ \{\Sigma_{a=1,9} [- (\hbar^2/2m_a)\, \partial^2/\partial q_a^2]+ 1/2\, \Sigma_{b\neq a}\, Z_a Z_b e^2/r_{a,b} \}\, \Psi = i\, \hbar\, \partial\Psi/\partial t.$$

The Hamiltonian in this case contains t nowhere. An example of a case where H does contain t occurs, for example, when the an oscillating electric field **E** cos(ωt) along the x-axis interacts with the electrons and nuclei and a term

$$\Sigma_{a=1,3}\, Z_z e\, X_a\, \mathbf{E} \cos(\omega t) - \Sigma_{j=1,10}\, e\, x_j\, \mathbf{E} \cos(\omega t)$$

is added to the Hamiltonian. Here, X_a and x_j denote the x coordinates of the a^{th} nucleus and the j^{th} electron, respectively.

2. The Time-Independent Equation

If the Hamiltonian operator does not contain the time variable explicitly, one can solve the time-independent Schrödinger equation

In cases where the classical energy, and hence the quantum Hamiltonian, do not contain terms that are explicitly time dependent (e.g., interactions with time varying external electric or magnetic fields would add to the above classical energy expression time dependent terms), the separations of variables techniques can be used to reduce the Schrödinger equation to a time-independent equation. In such cases, **H** is not explicitly time dependent, so one can assume that $\Psi(q_j,t)$ is of the form (n.b., this step is an example of the use of the separations of variables method to solve a differential equation)

$$\Psi(q_j,t) = \Psi(q_j)\ F(t).$$

Substituting this 'ansatz' into the time-dependent Schrödinger equation gives

$$\Psi(q_j)\ i\ \hbar\ \partial F/\partial t = F(t)\ \ \mathbf{H}\ \Psi(q_j)\ .$$

Dividing by $\Psi(q_j)$ F(t) then gives

$$F^{-1}\ (i\ \hbar\ \partial F/\partial t) = \Psi^{-1}\ (\mathbf{H}\ \Psi(q_j)\ ).$$

Since F(t) is only a function of time t, and $\Psi(q_j)$ is only a function of the spatial coordinates $\{q_j\}$, and because the left hand and right hand sides must be equal for all values of t and of $\{q_j\}$, both the left and right hand sides must equal a constant. If this constant is called E, the two equations that are embodied in this separated Schrödinger equation read as follows:

$$\mathbf{H}\ \Psi(q_j) = E\ \Psi(q_j),$$

$$i\hbar\ dF(t)/dt = E\ F(t).$$

The first of these equations is called the time-independent Schrödinger equation; it is an eigenvalue equation in which one is asked to find functions that yield a constant multiple of themselves when acted on by the Hamiltonian operator. Such functions are called eigenfunctions of **H** and the corresponding constants are called eigenvalues of **H**. For example, if **H** were of the form $(-\ \hbar^2/2I)\ \partial^2/\partial\phi^2 = \mathbf{H}$, then functions of the form $\exp(i\ m\phi)$ would be eigenfunctions because

$$\{-\hbar^2/2I\ \partial^2/\partial\phi^2\}\ \exp(i\ m\phi) = \{\ m^2 \hbar^2\ /2I\ \}\ \exp(i\ m\phi).$$

In this case, $m^2 \hbar^2 /2I$ is the eigenvalue. In this example, the Hamiltonian contains the square of an angular momentum operator (recall earlier that we showed the z-component of angular momentum $\mathbf{L}_z$ for a single particle is to equal – i $\hbar$ d/dϕ).

When the Schrödinger equation can be separated to generate a time-independent equation describing the spatial coordinate dependence of the wave function, the eigenvalue E must be returned to the equation determining F(t) to find the time dependent part of the wave function. By solving

$$i\hbar\ dF(t)/dt = E\ F(t)$$

once E is known, one obtains

$$F(t) = \exp(\ -i\ Et/\ \hbar),$$

and the full wave function can be written as

$$\Psi(q_j,t) = \Psi(q_j)\ \exp\ (-i\ Et/\ \hbar).$$

For the above example, the time dependence is expressed by

$$F(t) = \exp\ (\ -i\ t\ \{\ m^2 \hbar^2\ /2M\ \}/\ \hbar).$$

In such cases, the spatial probability density $|\Psi(q_j,t)|^2$ does not depend upon time because the product exp (-i Et/ $\hbar$) exp (i Et/ $\hbar$) reduces to unity.

In summary, whenever the Hamiltonian does not depend on time explicitly, one can solve the time-independent Schrödinger equation first and then obtain the time dependence as exp(-i Et/ $\hbar$) once the energy E is known. In the case of molecular structure theory, it is a quite daunting task even to approximately solve the full

Schrödinger equation because it is a partial differential equation depending on all of the coordinates of the electrons and nuclei in the molecule. For this reason, there are various approximations that one usually implements when attempting to study molecular structure using quantum mechanics.

It should be noted that it is possible to prepare in the laboratory, even when the Hamiltonian contains no explicit time dependence, wave functions that are time dependent and that have time-dependent spatial probability densities. For example, one can prepare a state of the Hydrogen atom that is a superposition of the 2s and $2p_z$ wave functions

$$\Psi(\mathbf{r},t=0) = C_1 \Psi_{2s}(\mathbf{r}) + C_2 \Psi_{2pz}(\mathbf{r})$$

where the two eigenstates obey

$$\mathbf{H}\, \Psi_{2s}(\mathbf{r}) = E_{2s} \Psi_{2s}(\mathbf{r})$$

and

$$\mathbf{H}\, \Psi_{2pz}(\mathbf{r}) = E_{2pz} \Psi_{2pz}(\mathbf{r}).$$

When **H** does not contain t explicitly, it is possible to then express $\Psi(\mathbf{r},t)$ in terms of $\Psi(\mathbf{r},t=0)$ as follows:

$$\Psi(\mathbf{r},t) = \exp(-i\mathbf{H}\mathbf{t}/\hbar)[\, C_1 \Psi_{2s}(\mathbf{r}) + C_2 \Psi_{2pz}(\mathbf{r})]$$

$$= [\, C_1 \Psi_{2s}(\mathbf{r}) \exp(-itE_{2s}/\hbar) + C_2 \Psi_{2pz}(\mathbf{r}) \exp(-itE_{2pz}/\hbar)].$$

This function, which is a superposition of 2s and $2p_z$ functions, does indeed obey the full time-dependent Schrödinger equation $\mathbf{H}\, \Psi = i\, \hbar\, \partial\Psi/\partial t$. The probability of observing the system in the 2s state if a measurement capable of making this determination were carried out is

$$|C_1 \exp(-itE_{2s}/\hbar)|^2 = |C_1|^2$$

and the probability of finding it in the 2pz state is

$$|C_2 \exp(-itE_{2pz}/\hbar)|^2,$$

both of which are independent of time. This does not mean that Ψ or the spatial probability density Ψ describes is time-independent because the product

$$[C_1 \Psi_{2s} (\mathbf{r}) \exp(-itE_{2s}/\hbar)+C_2 \Psi_{2pz} (\mathbf{r})\exp(-itE_{2pz}/\hbar)]^* [C_1 \Psi_{2s} (\mathbf{r})\exp(-itE_{2s}/\hbar)+C_2 \Psi_{2pz} (\mathbf{r}) \exp(-itE_{2pz}/\hbar)]$$

contains cross terms that depend on time.

It is important to note that applying $\exp(-i\mathbf{H}t/\hbar)$ to such a superposition state in the manner shown above, which then produces a superposition of states each of whose amplitudes carries its own time dependence, only works when **H** has no time dependence. If **H** were time-dependent, $i \hbar \partial/\partial t$ acting on $\exp(-i\mathbf{H}t/\hbar)\, \Psi(\mathbf{r},t=0)$ would contain an additional factor involving $\partial\mathbf{H}/\partial t$ as a result of which one would not have $\mathbf{H}\, \Psi = i \hbar\, \partial\Psi/\partial t$.

3. The Born-Oppenheimer Approximation

One of the most important approximations relating to applying quantum mechanics to molecules and molecular ions is known as the Born-Oppenheimer (BO) approximation. The basic idea behind this approximation involves realizing that in the full electrons-plus-nuclei Hamiltonian operator introduced above

$$\mathbf{H} = \Sigma_i [- (\hbar^2/2m_e)\, \partial^2/\partial q_i^2]+ 1/2\, \Sigma_{j\neq i}\, e^2/r_{i,j} - \Sigma_{a,i}\, Z_a e^2/r_{i,a}$$

$$+ \Sigma_a [- (\hbar^2/2m_a)\, \partial^2/\partial q_a^2]+ 1/2\, \Sigma_{b\neq a}\, Z_a Z_b e^2/r_{a,b}$$

the time scales with which the electrons and nuclei move are usually quite different. In particular, the heavy nuclei (i.e., even a H nucleus weighs nearly 2000 times what an electron weighs) move (i.e., vibrate and rotate) more slowly than do the lighter electrons. For example, typical bond vibrational motions occur over time scales of ca. 10^{-14} s, molecular rotations require 10-100 times as long, but electrons undergo periodic motions within their orbits on the 10^{-17} s timescale if they reside within core or valence orbitals. Thus, we expect the electrons to be able to promptly "adjust" their motions to the much more slowly moving nuclei.

This observation motivates us to consider solving the Schrödinger equation for the movement of the electrons in the presence of fixed nuclei as a way to represent the fully adjusted state of the electrons at any fixed positions of the nuclei. Of course, we then have to have a way to describe the differences between how the electrons and nuclei behave in the absence of this approximation and how they move within the approximation. These differences give rise to so-called non-Born-Oppenheimer corrections, radiationless transitions, surface hops, and non-adiabatic transitions, which we will deal with later.

It should be noted that this separation of time scales between fast electronic and slow vibration and rotation motions does not apply as well to, for example, Rydberg states of atoms and molecules. As discussed earlier, in such states, the electron in the Rydberg orbital has much lower speed and much larger radial extent than for typical core or valence orbitals. For this reason, corrections to the BO model are usually more important to make when dealing with Rydberg states.

The electronic Hamiltonian that pertains to the motions of the electrons in the presence of clamped nuclei

$$\mathbf{H} = \Sigma_i \,[- (\hbar^2/2m_e)\, \partial^2/\partial q_i^2\,] + 1/2\, \Sigma_{j\neq i}\, e^2/r_{i,j} - \Sigma_{a,i}\, Z_a e^2/r_{i,a} \quad 1/2\, \Sigma_{b\neq a}\, Z_a Z_b e^2/r_{a,b}$$

produces as its eigenvalues through the equation

$$\mathbf{H}\, \psi_J(q_j|q_a) = E_J(q_a)\, \psi_J(q_j|q_a)$$

energies $E_K(q_a)$ that depend on where the nuclei are located (i.e., the $\{q_a\}$ coordinates). As its eigenfunctions, one obtains what are called electronic wave functions $\{\psi_K(q_i|q_a)\}$ which also depend on where the nuclei are located. The energies $E_K(q_a)$ are what we usually call potential energy surfaces. An example of such a surface is shown in Fig. 1.5.

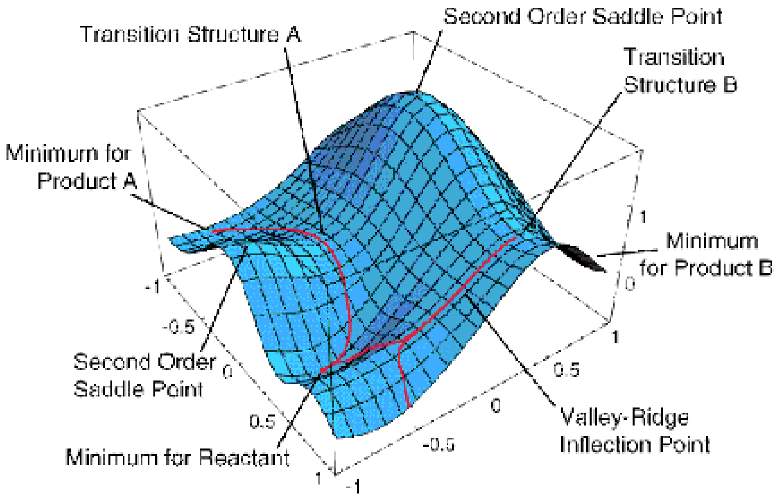


Figure 1. 5. Two dimensional potential energy surface showing local minima, transition states and paths connecting them.

This surface depends on two geometrical coordinates $\{q_a\}$ and is a plot of one particular eigenvalue $E_J(q_a)$ vs. these two coordinates.

Although this plot has more information on it than we shall discuss now, a few features are worth noting. There appear to be three minima (i.e., points where the derivative of E_J with respect to both coordinates vanish and where the surface has positive curvature). These points correspond, as we will see toward the end of this introductory material, to geometries of stable molecular structures. The surface also displays two first-order saddle points (labeled transition structures A and B) that connect the three minima. These points have zero first derivative of E_J with respect to both coordinates but have one direction of negative curvature. As we will show later, these points describe transition states that play crucial roles in the kinetics of transitions among the three stable geometries.

Keep in mind that Fig. 1. 5 shows just one of the E_J surfaces; each molecule has a ground-state surface (i.e., the one that is lowest in energy) as well as an infinite number of excited-state surfaces. Let's now return to our discussion of the BO model and ask what one does once one has such an energy surface in hand.

The motion of the nuclei are subsequently, within the BO model, assumed to obey a Schrödinger equation in which $\Sigma_a [- (\hbar^2/2m_a) \partial^2/\partial q_a^2]+ 1/2 \Sigma_{b\neq a} Z_aZ_be^2/r_{a,b} + E_K(q_a)$ defines a rotation-vibration Hamiltonian for the particular energy state E_K of interest. The rotational and vibrational energies and wave functions belonging to each electronic state (i.e., for each value of the index K in $E_K(q_a)$) are then found by solving a Schrödinger equation with such a Hamiltonian.

This BO model forms the basis of much of how chemists view molecular structure and molecular spectroscopy. For example as applied to formaldehyde $H_2C=O$, we speak of the singlet ground electronic state (with all electrons spin paired and occupying the lowest energy orbitals) and its vibrational and rotational states as well as the $n\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic states and their vibrational and rotational levels. Although much more will be said about these concepts later in this text, the student should be aware of the concepts of electronic energy surfaces (i.e., the $\{E_K(q_a)\}$) and the vibration-rotation states that belong to each such surface.

I should point out that the 3N Cartesian coordinates $\{q_a\}$ used to describe the positions of the molecule's N nuclei can be replaced by 3 Cartesian coordinates (X,Y,Z) specifying the center of mass of the N nuclei and 3N-3 other so-called internal coordinates that can be used to describe the molecule's orientation (these coordinates appear in the rotational kinetic energy) and its bond lengths and angles (these coordinates appear in the vibrational kinetic and potential energies). When center-of-mass and internal coordinates are used in place of the 3N Cartesian coordinates, the Born-Oppenheimer energy surfaces $\{E_K(q_a)\}$ are seen to depend only on the internal coordinates. Moreover, if the molecule's energy does not depend on its orientation (e.g., if it is moving freely in the gas phase), the $\{E_K(q_a)\}$ will also not depend on the 3 orientational coordinates, but only on the 3N-6 vibrational coordinates.

Having been introduced to the concepts of operators, wave functions, the Hamiltonian and its Schrödinger equation, it is important to now consider several examples of the applications of these concepts. The examples treated below were chosen to provide the reader with valuable experience in solving the Schrödinger equation; they were also chosen because they form the most elementary chemical models of electronic motions in conjugated molecules and in atoms, rotations of linear molecules, and vibrations of chemical bonds.

1.3 Your First Application of Quantum Mechanics- Motion of a Particle in One Dimension.

This is a very important problem whose solutions chemists use to model a wide variety of phenomena.

Let's begin by examining the motion of a single particle of mass m in one direction which we will call x while under the influence of a potential denoted V(x). The classical expression for the total energy of such a system is $E = p^2/2m + V(x)$, where p is the momentum of the particle along the x-axis. To focus on specific examples, consider how this particle would move if V(x) were of the forms shown in Fig. 1. 6, where the total energy E is denoted by the position of the horizontal line.

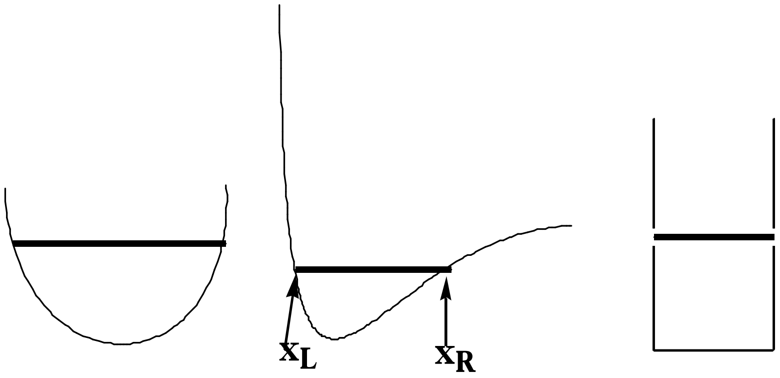


Figure 1. 6. Three characteristic potentials showing left and right classical turning points at energies denoted by the horizontal lines.

1.3.1 The Classical Probability Density

I would like you to imagine what the probability density would be for this particle moving with total energy E and with V(x) varying as the above three plots illustrate. To conceptualize the probability density, imagine the particle to have a blinking lamp attached to it and think of this lamp blinking say 100 times for each time it takes for the particle to complete a full transit from its left turning point, to its right turning point and back to the former. The turning points x_L and x_R are the positions at which the particle, if it were moving under Newton's laws, would reverse direction (as the momentum changes sign) and turn around. These positions can be found by asking where the momentum goes to zero:

$$0 = p = (2m(E-V(x))^{1/2}.$$

These are the positions where all of the energy appears as potential energy E = V(x) and correspond in the above figures to the points where the dark horizontal lines touch the V(x) plots as shown in the central plot.

The probability density at any value of x represents the fraction of time the particle spends at this value of x (i.e., within x and x+dx). Think of forming this density by allowing the blinking lamp attached to the particle to shed light on a photographic plate that is exposed to this light for many oscillations of the particle between x_L and x_R. Alternatively, one can express the probability P(x) dx that the particle spends between x and x + dx by dividing the spatial distance dx by the velocity (p/m) of the particle at the point x:

$$P(x)dx = (2m(E-V(x))^{-1/2}\ m\, dx.$$

Because E is constant throughout the particle's motion, P(x) will be small at x values where the particle is moving quickly (i.e., where V is low) and will be high where the particle moves slowly (where V is high). So, the photographic plate will show a bright region where V is high (because the particle moves slowly in such regions) and less brightness where V is low. Note, however, that as x approaches the classical turning points, the velocity approaches zero, so the above expression for P(x) will approach infinity. It does not mean the probability of finding the particle at the turning point is infinite; it means that the probability density is infinite there. This divergence of P(x) is a characteristic of the classical probability density that will be seen to be very different from the quantum probability density.

The bottom line is that the probability densities anticipated by analyzing the classical Newtonian dynamics of this one particle would appear as the histogram plots shown in Fig. 1.7 illustrate.

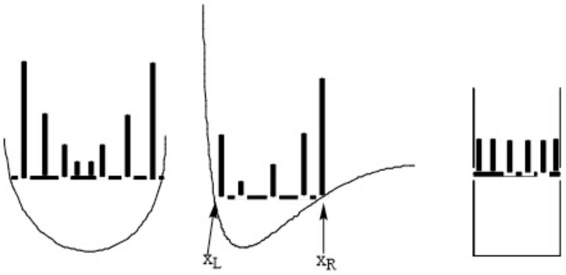


Figure 1. 7 Classical probability plots for the three potentials shown

Where the particle has high kinetic energy (and thus lower V(x)), it spends less time and P(x) is small. Where the particle moves slowly, it spends more time and P(x) is larger. For the plot on the right, V(x) is constant within the "box", so the speed is constant, hence P(x) is constant for all x values within this one-dimensional box. I ask that you keep these plots in mind because they are very different from what one finds when one solves the Schrödinger equation for this same problem. Also please keep in mind that these plots represent what one expects if the particle were moving according to classical Newtonian dynamics (which we know it is not!).

1.3.2 Quantum Treatment

To solve for the quantum mechanical wave functions and energies of this same kind of problem, we first write the Hamiltonian operator as discussed above by replacing p by $-i \hbar\, d/dx$:

$$H = - \hbar^2/2m\, d^2/dx^2 + V(x).$$

We then try to find solutions $\psi(x)$ to $H\psi = E\psi$ that obey certain conditions. These conditions are related to the fact that $|\psi (x)|^2$ is supposed to be the probability density for finding the particle between x and x+dx. To keep things as simple as possible, let's focus on the box potential V shown in the right side of Fig. 1. 7. This potential, expressed as a function of x is:$V(x) = \infty$ for $x< 0$ and for $x> L$; $V(x) = 0$ for x between 0 and L.

The fact that V is infinite for $x< 0$ and for $x> L$, and that the total energy E must be finite, says that ψ must vanish in these two regions ($\psi = 0$ for $x< 0$ and for $x> L$). This condition means that the particle cannot access regions of space where the potential is infinite. The second condition that we make use of is that $\psi (x)$ must be continuous; this means that the probability of the particle being at x cannot be discontinuously related to the probability of it being at a nearby point. It is also true that the spatial derivative $d\psi/dx$ must be continuous except at points where the potential V(x) has an infinite discontinuity like it does in the example shown on the right in Fig. 1.7. The continuity of $d\psi/dx$ relates to continuity of momentum (recall, $-i\hbar\partial/\partial x$ is a momentum operator). When a particle moves under, for example, one of the two potential shown on the left or middle of Fig. 1.7, the potential smoothly changes as kinetic and potential energy interchange during the periodic motion. In contrast, when moving under the potential on the right of Fig. 1.7, the potential undergoes a sudden change of direction when the particle hits either wall. So, even classically, the particle's momentum undergoes a discontinuity at such hard-wall turning points. These conditions of continuity of ψ (and its spatial first derivative) and that ψ must vanish in regions of space where the potential is extremely high were postulated by the pioneers of quantum mechanics so that the predictions of the quantum theory would be in line with experimental observations.

1.3.3 Energies and Wave functions

The second-order differential equation

$$-\hbar^2/2m\, d^2\psi/dx^2 + V(x)\, \psi = E\, \psi$$

has two solutions (because it is a second order equation) in the region between x= 0 and x= L where V(x) = 0:

$$\psi = \sin(kx) \text{ and } \psi = \cos(kx),$$

where k is defined as

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

Hence, the most general solution is some combination of these two:

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

We could, alternatively use exp(ikx) and exp(-ikx) as the two independent solutions (we do so later in Sec. 1.4 to illustrate) because sin(kx) and cos(kx) can be rewritten in terms of exp(ikx) and exp(-ikx); that is, they span exactly the same space.

The fact that ψ must vanish at x= 0 (n.b., ψ vanishes for x< 0 because V(x) is infinite there and ψ is continuous, so it must vanish at the point x= 0) means that the weighting amplitude of the cos(kx) term must vanish because cos(kx) = 1 at x = 0. That is,

$$B = 0.$$

The amplitude of the sin(kx) term is not affected by the condition that ψ vanish at x= 0, since sin(kx) itself vanishes at x= 0. So, now we know that ψ is really of the form:

$$\psi(x) = A \sin(kx).$$

The condition that ψ also vanish at x= L (because it vanishes for $x < 0$ where V(x) again is infinite) has two possible implications. Either A = 0 or k must be such that sin(kL) = 0. The option A = 0 would lead to an answer ψ that vanishes at all values of x and thus a probability that vanishes everywhere. This is unacceptable because it would imply that the particle is never observed anywhere.

The other possibility is that sin(kL) = 0. Let's explore this answer because it offers the first example of energy quantization that you have probably encountered. As you know, the sin function vanishes at integral multiples of π. Hence kL must be some multiple of π; let's call the integer n and write $L\,k = n\,\pi$ (using the definition of k) in the form:

$$L\,(2mE/\hbar^2)^{1/2} = n\,\pi.$$

Solving this equation for the energy E, we obtain:

$$E = n^2\,\pi^2\,\hbar^2/(2mL^2)$$

This result says that the only energy values that are capable of giving a wave function ψ (x) that will obey the above conditions are these specific E values. In other words, not all energy values are allowed in the sense that they can produce ψ functions that are continuous and vanish in regions where V(x) is infinite. If one uses an energy E that is not one of the allowed values and substitutes this E into sin(kx), the resultant function will not vanish at x = L. I hope the solution to this problem reminds you of the violin string that we discussed earlier. Recall that the violin string being tied down at x = 0 and at x = L gave rise to quantization of the wavelength just as the conditions that ψ be continuous at x = 0 and x = L gave energy quantization.

Substituting $k = n\pi/L$ into $\psi = A \sin(kx)$ gives

$$\psi\,(x) = A\,\sin(n\pi x/L).$$

The value of A can be found by remembering that $|\psi|^2$ is supposed to represent the probability density for finding the particle at x. Such probability densities are supposed to be normalized, meaning that their integral over all x values should amount to unity. So, we can find A by requiring that

$$1 = \int |\psi(x)|^2\ dx = |A|^2 \int \sin^2(n\pi x/L)\ dx$$

where the integral ranges from x = o to x = L. Looking up the integral of $\sin^2(ax)$ and solving the above equation for the so-called normalization constant A gives

$$A = (2/L)^{1/2} \text{ and so}$$

$$\psi(x) = (2/L)^{1/2}\ \sin(n\pi x/L).$$

The values that n can take on are n = 1, 2, 3, ….; the choice n = 0 is unacceptable because it would produce a wave function $\psi(x)$ that vanishes at all x.

The full x- and t- dependent wave functions are then given as

$$\Psi(x,t) = (2/L)^{1/2}\ \sin(n\pi x/L)\ \exp[-it\ n^2\ \pi^2\ \hbar^2/(2mL^2)/\hbar].$$

Notice that the spatial probability density $|\Psi(x,t)|^2$ is not dependent on time and is equal to $|\psi(x)|^2$ because the complex exponential disappears when $\Psi^*\Psi$ is formed. This means that the probability of finding the particle at various values of x is time-independent.

Another thing I want you to notice is that, unlike the classical dynamics case, not all energy values E are allowed. In the Newtonian dynamics situation, E could be specified and the particle's momentum at any x value was then determined to within a sign. In contrast, in quantum mechanics, one must determine, by solving the Schrödinger equation, what the allowed values of E are. These E values are quantized, meaning that they occur only for discrete values $E = n^2\pi^2\hbar^2/(2mL^2)$ determined by a quantum number n, by the mass of the particle m, and by characteristics of the potential (L in this case).

1.3.4 Probability Densities

Let's now look at some of the wave functions ψ (x) and compare the probability densities $|\psi(x)|^2$ that they represent to the classical probability densities discussed earlier. The n = 1 and n = 2 wave functions are shown in the top of Fig. 1.8. The corresponding quantum probability densities are shown below the wave functions in two formats (as x-y plots and shaded plots that could relate to the flashing light way of monitoring the particle's location that we discussed earlier).

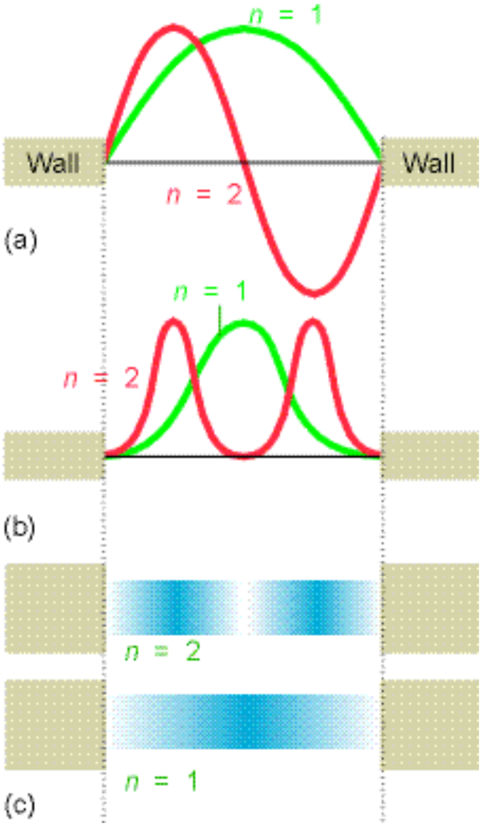


Figure 1. 8. The two lowest wave functions and probability densities

A more complete set of wave functions (for n ranging from 1 to 7) are shown in Fig. 1. 9.

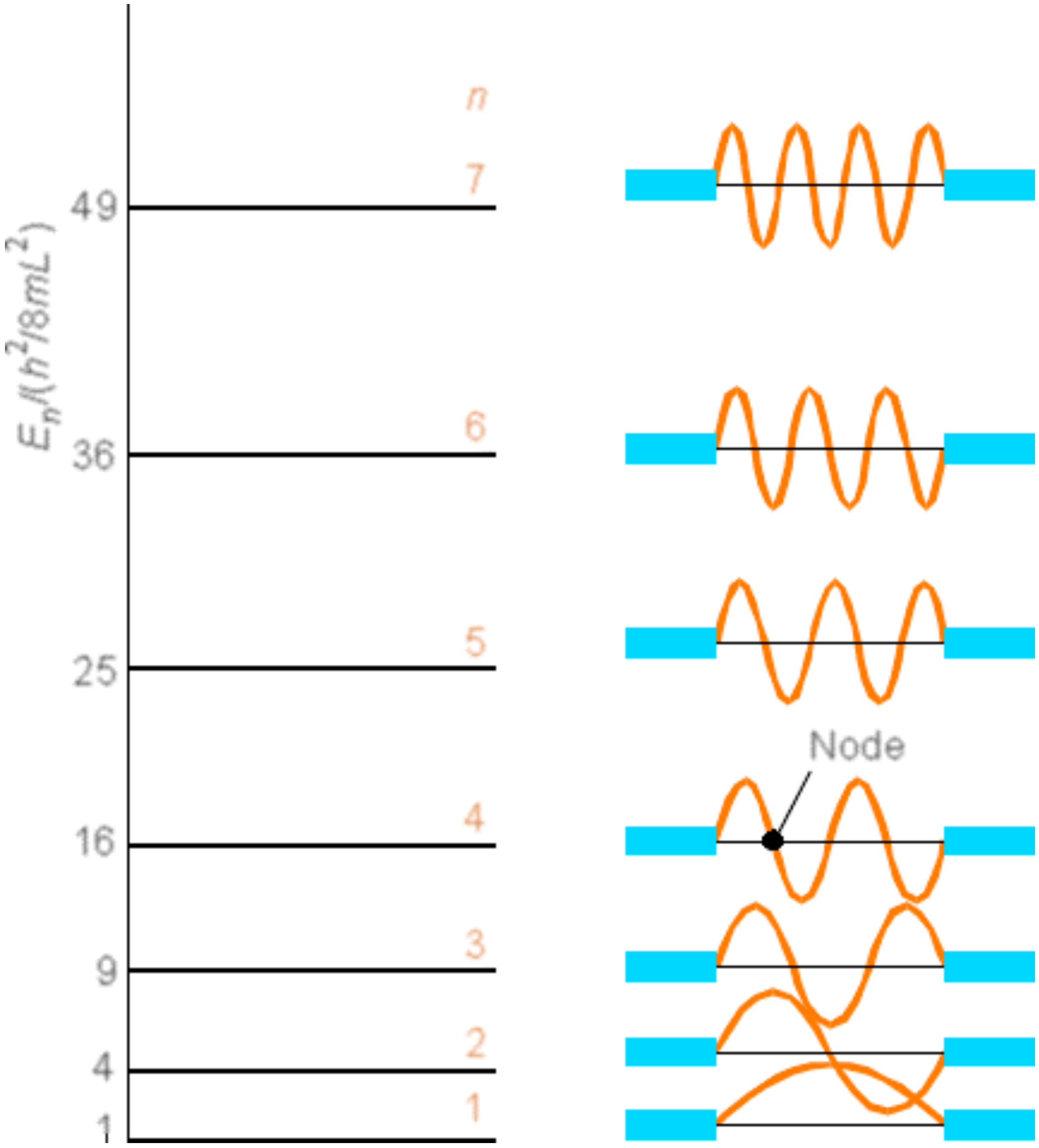


Figure 1. 9. Seven lowest wave functions and energies

Notice that as the quantum number n increases, the energy E also increases (quadratically with n in this case) and the number of nodes in ψ also increases. Also notice that the probability densities are very different from what we encountered earlier for the classical case. For example, look at the n = 1 and n = 2 densities and compare them to the classical density illustrated in Fig. 1.10.

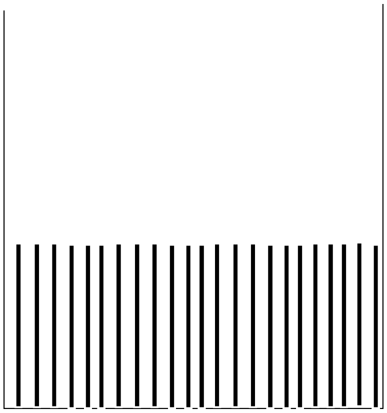


Figure 1. 10. Classical probability density for potential shown

The classical density is easy to understand because we are familiar with classical dynamics. In this case, we say that P(x) is constant within the box because the fact that V(x) is constant causes the kinetic energy and hence the speed of the particle to remain constant, and this is true for any energy E. In contrast, the n = 1 quantum wave function's P(x) plot is peaked in the middle of the box and falls to zero at the walls. The n = 2 density P(x) has two peaks (one to the left of the box midpoint, and one to the right), a node at the box midpoint, and falls to zero at the walls. One thing that students often ask me is "how does the particle get from being in the left peak to being in the right peak if it has zero chance of ever being at the midpoint where the node is?" The difficulty with this question is that it is posed in a terminology that asks for a classical dynamics answer. That is, by asking "how does the particle get..." one is demanding an answer that involves describing its motion (i.e., it moves from here at time t_1 to there at time t_2). Unfortunately, quantum mechanics does not deal with issues such as a particle's trajectory (i.e., where it is at various times) but only with its probability of being somewhere (i.e., $|\psi|^2$). The next section will treat such paradoxical issues even further.

1.3.5 Classical and Quantum Probability Densities

As just noted, it is tempting for most beginning students of quantum mechanics to attempt to interpret the quantum behavior of a particle in classical terms. However, this adventure is full of danger and bound to fail because small light particles simply do not move according to Newton's laws. To illustrate, let's try to understand what kind of (classical) motion would be consistent with the n = 1 or n = 2 quantum P(x) plots shown in Fig. 1. 8. However, as I hope you anticipate, this attempt at gaining classical understanding of a quantum result will not work in that it will lead to nonsensical results. My point in leading you to attempt such a classical understanding is to teach you that classical and quantum results are simply different and that you must resist the urge to impose a classical understanding on quantum results at least until you understand under what circumstances classical and quantum results should or should not be comparable.

For the n = 1 case in Fig. 1.8, we note that P(x) is highest at the box midpoint and vanishes at x = 0 and x = L. In a classical mechanics world, this would mean that the particle moves slowly near x = L/2 and more quickly near x = 0 and x = L. Because the particle's total energy E must remain constant as it moves, in regions where it moves slowly, the potential it experiences must be high, and where it moves quickly, V must be small. This analysis (n.b., based on classical concepts) would lead us to conclude that the n =1 P(x) arises from the particle moving in a potential that is high near x = L/2 and low as x approaches 0 or L.

A similar analysis of the P(x) plot for n = 2 would lead us to conclude that the particle for which this is the correct P(x) must experience a potential that is high midway between x = 0 and x = L/2, high midway between x = L/2 and x = L, and low near x = L/2 and near x = 0 and x = L. These conclusions are crazy because we know that the potential V(x) for which we solved the Schrödinger equation to generate both of the wave functions (and both probability densities) is constant between x = 0 and x = L. That is, we know the <u>same</u> V(x) applies to the particle moving in the n = 1 and n = 2 states, whereas the classical motion analysis offered above suggests that V(x) is different for these two cases.

What is wrong with our attempt to understand the quantum P(x) plots? The mistake we made was in attempting to apply the equations and concepts of classical dynamics to a P(x) plot that did not arise from classical motion. Simply put, one cannot ask how the particle is moving (i.e., what is its speed at various positions) when the particle is undergoing quantum dynamics. Most students, when first experiencing quantum wave functions and quantum probabilities, try to think of the particle moving in a classical way that is consistent with the quantum P(x). This attempt to retain a degree of classical understanding of the particle's movement is almost always met with frustration, as I illustrated with the above example and will illustrate later in other cases.

Continuing with this first example of how one solves the Schrödinger equation and how one thinks of the quantized E values and wave functions ψ, let me offer a little more optimistic note than offered in the preceding discussion. If we examine the $\psi(x)$ plot shown in Fig. 1.9 for n = 7, and think of the corresponding $P(x) = |\psi(x)|^2$, we note that the P(x) plot would look something like that shown in Fig. 1. 11.

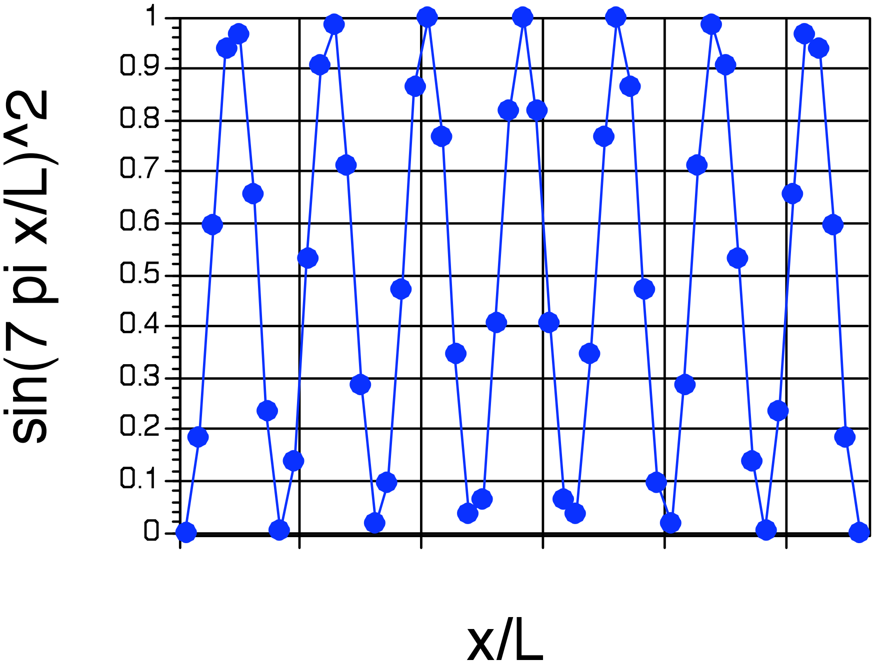


Figure 1. 11. Quantum probability density for n = 7 showing seven peaks and six nodes

It would have seven maxima separated by six nodes. If we were to plot $|\psi(x)|^2$ for a very large n value such as n = 55, we would find a P(x) plot having 55 maxima separated by 54 nodes, with the maxima separated approximately by distances of (1/55L). Such a plot, when viewed in a coarse-grained sense (i.e., focusing with somewhat blurred vision on the positions and heights of the maxima) looks very much like the classical P(x) plot in which P(x) is constant for all x. Another way to look at the difference between the low-n and high-n quantum probability distributions is reflected in the so-called local de Broglie wavelength

$$\lambda_{local}(x) = \frac{h}{\sqrt{2m(E - V(x))}}.$$

It can be shown that the classical and quantum probabilities will be similar in regions of space where

$$|d\lambda_{local}/dx| << 1.$$

This inequality will be true when E is much larger than V, which is consistent with the view that high quantum states behave classically, but it will not hold when E is only slightly above V (i.e., for low-energy quantum states and for any quantum state near classical turning points) or when E is smaller than V (i.e., in classically forbidden regions).

In summary, it is a general result of quantum mechanics that the quantum P(x) distributions for large quantum numbers take on the form of the classical P(x) for the same potential V that was used to solve the Schrödinger equation except near turning points and in classically forbidden regions. It is also true that, at any specified energy, classical and quantum results agree better when one is dealing with heavy particles than for light particles. For example, a given energy E corresponds to a higher n quantum number in the particle-in-a-box formula $E_n = n^2\hbar^2/(2mL^2)$ for a heavier particle than for a lighter particle. Hence, heavier particles, moving with a given energy E, have more classical probability distributions.

To gain perspective about this matter, in the table shown below, I give the energy levels $E_n = n^2\pi^2\hbar^2/(2mL^2)$ in kcal mol^{-1} for a particle whose mass is 1, 2000, 20,000, or 200,000 times an electron's mass constrained to move within a one-dimensional region of length L (in Bohr units denoted a_0; 1 a_0 =0.529 Å).

Energies E_n (kcal mol^{-1}) for various m and L combinations

	L = 1 a_0	L = 10 a_0	L = 100 a_0	L = 1000 a_0
m = 1 m_e	$3.1 \times 10^{3} n^2$	$3.1 \times 10^{1} n^2$	$3.1 \times 10^{-1} n^2$	$3.1 \times 10^{-3} n^2$
m = 2000 m_e	$1.5 \times 10^{0} n^2$	$1.5 \times 10^{-2} n^2$	$1.5 \times 10^{-4} n^2$	$1.5 \times 10^{-6} n^2$
m = 20,000 m_e	$1.5 \times 10^{-1} n^2$	$1.5 \times 10^{-3} n^2$	$1.5 \times 10^{-5} n^2$	$1.5 \times 10^{-7} n^2$
m = 200,000 m_e	$1.5 \times 10^{-2} n^2$	$1.5 \times 10^{-4} n^2$	$1.5 \times 10^{-6} n^2$	$1.5 \times 10^{-8} n^2$

Clearly, for electrons, even when free to roam over 50-500 nanometers (e.g., L = 100 a_0 or L = 1000 a_0), one does not need to access a very high quantum state to reach 1 kcal mol^{-1} of energy (e.g., n = 3 would be adequate for L =100 a_0). Recall, it is high quantum states where one expects the classical and quantum spatial probability distribution to be similar. So, when treating electrons, one is probably (nearly) always going to have to make use of quantum mechanics and one will not be able to rely on classical mechanics.

For light nuclei, with masses near 2000 times the electron's mass, if the particle is constrained to a small distance range (e.g., 1-10 a_0), again even low quantum states will have energies in excess of 1 kcal mol^{-1}. Only when free to move over of 100 to 1000 a_0 does 1 kcal mol^{-1} correspond to relatively large quantum numbers for which one expects near-classical behavior. The data shown in the above table can also be used to estimate when quantum behavior such as Bose-Einstein condensation can be expected. When constrained to 100 a_0, particles in the 1 amu mass range have translational energies in the 0.15 n^2 cal mol^{-1} range. Realizing that RT = 1.98 cal mol^{-1} K^{-1}, this means that translational temperatures near 0.1 K would be needed to cause these particles to occupy their n = 1 ground state.

In contrast, particles with masses in the range of 100 amu, even when constrained to distances of ca. 5 Å, require n to exceed ca. 10 before having 1 kcal mol^{-1} of translational energy. When constrained to 50 Å, 1 kcal mol^{-1} requires n to exceed 1000. So, heavy particles will, even at low energies, behave classically except if they are constrained to very short distances.

We will encounter this so-called quantum-classical correspondence principal again when we examine other model problems. It is an important property of solutions to the Schrödinger equation because it is what allows us to bridge the gap between using the

Schrödinger equation to treat small light particles and the Newton equations for macroscopic (big, heavy) systems.

1.3.6 Time Propagation of Wave functions

For a particle in a box system that exists in an eigenstate $\psi(x) = (2/L)^{1/2} \sin(n\pi x/L)$ having an energy $E_n = n^2\pi^2\hbar^2/(2mL^2)$, the time-dependent wave function is

$$\Psi(x,t) = (2/L)^{1/2} \sin(n\pi x/L) \exp(-itE_n/\hbar),$$

that can be generated by applying the so-called time evolution operator U(t,0) to the wave function at t = 0:

$$\Psi(x,t) = U(t,0)\, \Psi(x,0),$$

where an explicit form for U(t,t') is:

$$U(t,t') = \exp[-i(t-t')\mathbf{H}/\hbar].$$

The function $\Psi(x,t)$ has a spatial probability density that does not depend on time because

$$\Psi^*(x,t)\, \Psi(x,t) = (2/L) \sin^2(n\pi x/L) = \Psi^*(x,0)\, \Psi(x,0)$$

since $\exp(-itE_n/\hbar) \exp(itE_n/\hbar) = 1$. However, it is possible to prepare systems (even in real laboratory settings) in states that are not single eigenstates; we call such states superposition states. For example, consider a particle moving along the x- axis within the box potential but in a state whose wave function at some initial time t = 0 is

$$\Psi(x,0) = 2^{-1/2} (2/L)^{1/2} \sin(1\pi x/L) - 2^{-1/2} (2/L)^{1/2} \sin(2\pi x/L).$$

This is a superposition of the n =1 and n = 2 eigenstates. The probability density associated with this function is

$$|\Psi(x,0)|^2 = 1/2\{(2/L)\sin^2(1\pi x/L) + (2/L)\sin^2(2\pi x/L) - 2(2/L)\sin(1\pi x/L)\sin(2\pi x/L)\}.$$

The n = 1 and n = 2 components, the superposition Ψ, and the probability density at t = 0 are shown in the first three panels of Fig. 1.12.

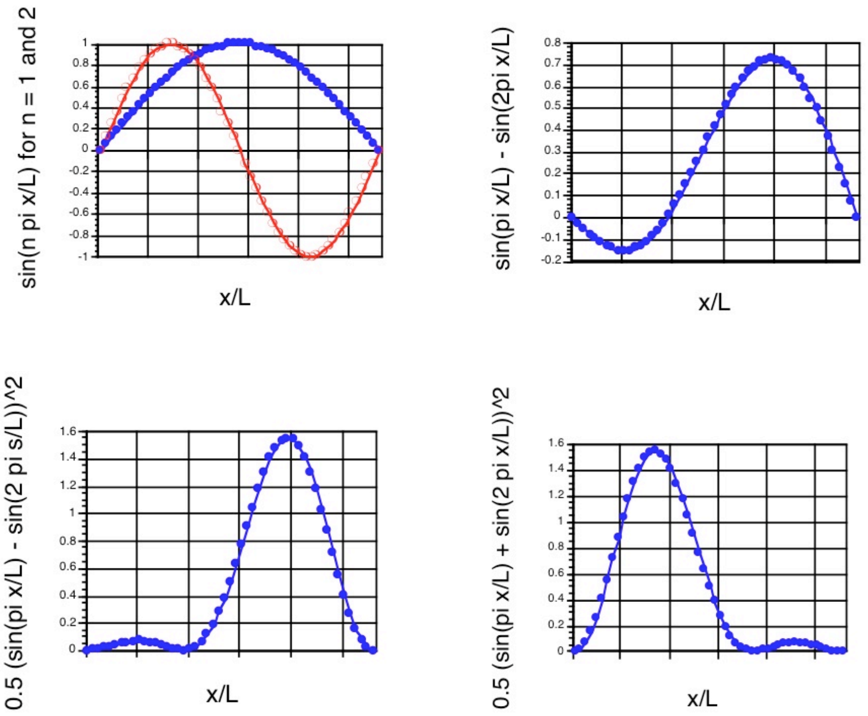


Figure 1. 12. The n = 1 and n = 2 wave functions (upper left), their superposition (upper right), and the t = 0 (bottom left) and time-evolved (bottom right) probability densities of the superposition

It should be noted that the probability density associated with this superposition state is not symmetric about the x=L/2 midpoint even though the n = 1 and n = 2 component wave functions and densities are. Such a density describes the particle localized more strongly in the large-x region of the box than in the small-x region at t = 0.

Now, let's consider the superposition wave function and its density at later times. Applying the time evolution operator exp(-it**H**/ħ) to $\Psi(x,0)$ generates this time-evolved function at time t:

$$\Psi(x,t) = \exp(-it\mathbf{H}/\hbar)\ \{2^{-1/2}\ (2/L)^{1/2}\ \sin(1\pi x/L) - 2^{-1/2}\ (2/L)^{1/2}\ \sin(2\pi x/L)\}$$

$$= \{2^{-1/2}\ (2/L)^{1/2}\ \sin(1\pi x/L)\ )\ \exp(-itE_1/\hbar).\ - 2^{-1/2}\ (2/L)^{1/2}\ \sin(2\pi x/L)\ )\ \exp(-itE_2/\hbar)\ \}.$$

The spatial probability density associated with this Ψ is:

$$|\Psi(x,t)|^2 = 1/2\{(2/L)\ \sin^2(1\pi x/L) + (2/L)\ \sin^2(2\pi x/L)$$

$$-2(2/L)\ \cos(E_2-E_1)t/\hbar)\ \sin(1\pi x/L)\sin(2\pi x/L)\}.$$

At t = 0, this function clearly reduces to that written earlier for $\Psi(x,0)$. Notice that as time evolves, this density changes because of the $\cos(E_2-E_1)t/\hbar)$ factor it contains. In particular, note that as t moves through a period of time $\delta t = \pi\ \hbar/(E_2-E_1)$, the cos factor changes sign. That is, for t = 0, the cos factor is +1; for $t = \pi\ \hbar/(E_2-E_1)$, the cos factor is –1; for $t = 2\ \pi\ \hbar/(E_2-E_1)$, it returns to +1. The result of this time-variation in the cos factor is that $|\Psi|^2$ changes in form from that shown in the bottom left panel of Fig. 1. 12 to that shown in the bottom right panel (at $t = \pi\ \hbar/(E_2-E_1)$) and then back to the form in the bottom left panel (at $t = 2\ \pi\ \hbar/(E_2-E_1)$). One can interpret this time variation as describing the particle's probability density (not its classical position!), initially localized toward the right side of the box, moving to the left and then back to the right. Of course, this time evolution will continue over more and more cycles as time evolves further.

This example illustrates once again the difficulty with attempting to localize particles that are being described by quantum wave functions. For example, a particle that is characterized by the eigenstate $(2/L)^{1/2}\ \sin(1\pi x/L)$ is more likely to be detected near x = L/2 than near x = 0 or x = L because the square of this function is large near x = L/2. A particle in the state $(2/L)^{1/2}$ $\sin(2\pi x/L)$ is most likely to be found near x = L/4 and x = 3L/4, but not near x = 0, x = L/2, or x =L. The issue of how the particle in the latter state moves from being near x = L/4 to x = 3L/4 is not something quantum mechanics deals with. Quantum mechanics does not allow us to follow the particle's trajectory which is what we need to know when we ask how it moves from one place to another. Nevertheless, superposition wave functions can offer, to some extent, the opportunity to follow the motion of the particle.

For example, the superposition state written above as $2^{-1/2}$ $(2/L)^{1/2}$ $\sin(1\pi x/L)$ – $2^{-1/2}$ $(2/L)^{1/2}$ $\sin(2\pi x/L)$ has a probability amplitude that changes with time as shown in Fig. 1.12. Moreover, this amplitude's major peak does move from side to side within the box as time evolves. So, in this case, we can say with what frequency the major peak moves back and forth. In a sense, this allows us to follow the particle's movements, but only to the extent that we are satisfied with ascribing its location to the position of the major peak in its probability distribution. That is, we can not really follow its precise location, but we can follow the location of where it is very likely to be found. However, notice that the time it takes the particle to move from right to left $t = \pi \hbar/(E_2-E_1)$ is dependent upon the energy difference between the two states contributing to the superposition state, not to the energy of either of these states, which is very different from what would expect if the particle were moving classically.

These are important observation that I hope the student will keep fresh in mind. They are also important ingredients in modern quantum dynamics in which localized wave packets, which are similar to superposed eigenstates discussed above, are used to detail the position and speed of a particle's main probability density peak.

The above example illustrates how one time-evolves a wave function that is expressed as a linear combination (i.e., superposition) of eigenstates of the problem at hand. There is a large amount of current effort in the theoretical chemistry community aimed at developing efficient approximations to the $\exp(-it\mathbf{H}/\hbar)$ evolution operator that do not require $\Psi(x,0)$ to be explicitly written as a sum of eigenstates. This is important because, for most systems of direct relevance to molecules, one can not solve for the eigenstates; it is simply too difficult to do so. You can find a significantly more detailed treatment of the research-level treatment of this subject in my Theory Page web site (http://simons.hec.utah.edu/TheoryPage/index.html) and my QMIC textbook (http://simons.hec.utah.edu/TheoryPage/BookPDF/TableofContents.html). However, let's spend a little time on a brief introduction to what is involved.

The problem is to express exp(-it**H**/$\hbar$) $\Psi(q_j)$, where $\Psi(q_j)$ is some initial wave function but not an eigenstate, in a manner that does not require one to first find the eigenstates $\{\psi_J\}$ of H and to expand Ψ in terms of these eigenstates:

$$\Psi\ (t=0) = \Sigma_J\, C_J\, \psi_J$$

after which the desired function is written as

$$\exp(-it\mathbf{H}/\hbar)\ \Psi(q_j) = \Sigma_J\, C_J\, \psi_J\, \exp(-itE_J/\hbar).$$

The basic idea is to break the operator **H** into its kinetic **T** and potential **V** energy components and to realize that the differential operators appear in **T** only. The importance of this observation lies in the fact that **T** and **V** do not commute which means that **TV** is not equal to **VT** (n.b., recall that for two quantities to commute means that their order of appearance does not matter). Why do they not commute? Because **T** contains second derivatives with respect to the coordinates $\{q_j\}$ that **V** depends on, so, for example, $d^2/dq^2(V(q)\ \Psi(q))$ is not equal to $V(q)d^2/dq^2\Psi(q)$. The fact that **T** and **V** do not commute is important because the most obvious attempt to approximate exp(-it**H**/$\hbar$) is to write this single exponential in terms of exp(-it**T**/$\hbar$) and exp(-it**V**/$\hbar$). However, the identity

$$\exp(-it\mathbf{H}/\hbar) = \exp(-it\mathbf{V}/\hbar)\ \exp(-it\mathbf{T}/\hbar)$$

is not fully valid as one can see by expanding all three of the above exponential factors as $\exp(x) = 1 + x + x^2/2! + ...$, and noting that the two sides of the above equation only agree if one can assume that **TV** = **VT**, which, as we noted, is not true.

In most modern approaches to time propagation, one divides the time interval t into many (i.e., P of them) small time slices $\tau = t/P$. One then expresses the evolution operator as a product of P short-time propagators (the student should by now be familiar with the fact that **H**, **T**, and **V** are operators, so, from now on I will no longer necessarily use bold lettering for these quantities):

$$\exp(-itH/\hbar) = \exp(-i\tau H/\hbar)\ \exp(-i\tau H/\hbar)\ \exp(-i\tau H/\hbar)\ \ldots = [\exp(-i\tau H/\hbar)\ ]^P.$$

If one can then develop an efficient means of propagating for a short time τ, one can then do so over and over again P times to achieve the desired full-time propagation.

It can be shown that the exponential operator involving H can better be approximated in terms of the T and V exponential operators as follows:

$$\exp(-i\tau H/\hbar) \approx \exp(-\tau^2\ (TV-VT)/\hbar^2)\ \exp(-i\tau V/\hbar)\ \exp(-i\tau T/\hbar).$$

So, if one can be satisfied with propagating for very short time intervals (so that the τ^2 term can be neglected), one can indeed use

$$\exp(-i\tau H/\hbar) \approx \exp(-i\tau V/\hbar)\ \exp(-i\tau T/\hbar)$$

as an approximation for the propagator $U(\tau,0)$. It can also be shown that the so-called split short-time expression

$$\exp(-i\tau H/\hbar) \approx \exp(-i\tau V/2\hbar)\ \exp(-i\tau T/\hbar)\ \exp(-i\tau V/2\hbar)$$

provides an even more accurate representation of the short-time propagator (because expansions of the left- and right-hand sides agree to higher orders in $\tau/\hbar$).

To progress further, one then expresses $\exp(-i\tau T/\hbar)$ acting on $\exp(-i\tau V/2\hbar)\ \Psi(q)$ in terms of the eigenfunctions of the kinetic energy operator T. Note that these eigenfunctions do not depend on the nature of the potential V, so this step is valid for any and all potentials. The eigenfunctions of $T = -\ \hbar^2/2m\ d^2/dq^2$ are the momentum eigenfunctions that we discussed earlier

$$\psi_p(q) = (1/2\pi)^{1/2} \exp(ipq/\hbar)$$

and they obey the following orthogonality

$$\int \psi_{p'}^*(q)\, \psi_p(q)\, dq = \delta(p'-p)$$

and completeness relations

$$\int \psi_p(q)\, \psi_p^*(q')\, dp = \delta(q-q').$$

Writing $\exp(-i\tau V/2\hbar)\, \Psi(q)$ as

$$\exp(-i\tau V/2\hbar)\Psi(q) = \int dq'\ \delta(q-q')\, \exp(-i\tau V(q')/2\hbar)\Psi(q'),$$

and using the above expression for $\delta(q-q')$ gives:

$$\exp(-i\tau V/2\hbar)\Psi(q) = \iint \psi_p(q)\, \psi_p^*(q')\, \exp(-i\tau V(q')/2\hbar)\Psi(q')\, dq'\, dp.$$

Then inserting the explicit expressions for $\psi_p(q)$ and $\psi_p^*(q')$ in terms of

$\psi_p(q) = (1/2\pi)^{1/2} \exp(ipq/\hbar)$ gives

$$\exp(-i\tau V/2\hbar)\Psi(q)$$

$$= \iint (1/2\pi)^{1/2} \exp(ipq/\hbar)\, (1/2\pi)^{1/2} \exp(-ipq'/\hbar)\, \exp(-i\tau V(q')/2\hbar)\Psi(q')\, dq'\, dp.$$

Now, allowing $\exp(-i\tau T/\hbar)$ to act on $\exp(-i\tau V/2\hbar)\, \Psi(q)$ produces

$$\exp(-i\tau T/\hbar)\, \exp(-i\tau V/2\hbar)\Psi(q) =$$

$$\iint \exp(-i\tau p^2\hbar^2/2m\hbar)\ (1/2\pi)^{1/2} \exp(ip(q-q')/\hbar)\ (1/2\pi)^{1/2} \exp(-i\tau V(q')/2\hbar)\Psi(q')\ dq'\ dp.$$

The integral over p above can be carried out analytically and gives

$$\exp(-i\tau T/\hbar) \exp(-i\tau V/2\hbar)\Psi(q) =$$

$$(m/2i\pi\tau\hbar)^{1/2} \int \exp(im(q-q')^2/2\tau\hbar) \exp(-i\tau V(q')/2\hbar)\ \Psi(q')\ dq'.$$

So, the final expression for the short-time propagated wave function is:

$$\Psi(q.\tau) = (m/2i\pi\tau\hbar)^{1/2}\exp(-i\tau V(q)/2\hbar)\int\exp(im(q-q')^2/2\tau\hbar) \exp(-i\tau V(q')/2\hbar)\Psi(q')\ dq',$$

which is the working equation one uses to compute $\Psi(q,\tau)$ knowing $\Psi(q)$. Notice that all one needs to know to apply this formula is the potential V(q) at each point in space. One does not need to know any of the eigenfunctions of the Hamiltonian to apply this method. This is especially attractive when dealing with very large molecules or molecules in condensed media where it is essentially impossible to determine any of the eigenstates and where the energy spacings between eigenstates is extremely small. However, one does have to use this formula over and over again to propagate the initial wave function through many small time steps τ to achieve full propagation for the desired time interval t = P τ.

Because this type of time propagation technique is a very active area of research in the theory community, it is likely to continue to be refined and improved. Further discussion of it is beyond the scope of this book, so I will not go further into this direction. The web site of Professor Nancy Makri (http://www.chemistry.illinois.edu/faculty/Nancy_Makri.html) provides access to further information about the quantum time propagation research area.

1.4 Free Particle Motions in More Dimensions

The number of dimensions depends on the number of particles and the number of spatial (and other) dimensions needed to characterize the position and motion of each particle. The number of dimensions also affects the number of quantum numbers that may be used to label eigenstates of the Hamiltonian.

1.4.1 The Schrödinger Equation

Consider an electron of mass m and charge e moving on a two-dimensional surface that defines the x,y plane (e.g., perhaps an electron is constrained to the surface of a solid by a potential that binds it tightly to a narrow region in the z-direction but allows it to roam freely over a rectangular area in the x, y, plane), and assume that the electron experiences a constant and not time-varying potential V_0 at all points in this plane. For example, if V_0 is negative, it could reflect the binding energy of the electron relative to its energy in vacuum.

The pertinent time independent Schrödinger equation is:

$$- \hbar^2/2m\, (\partial^2/\partial x^2 + \partial^2/\partial y^2)\psi(x,y) + V_0\psi(x,y) = E\, \psi(x,y).$$

The task at hand is to solve the above eigenvalue equation to determine the allowed energy states for this electron. Because there are no terms in this equation that couple motion in the x and y directions (e.g., no terms of the form $x^a y^b$ or $\partial/\partial x\ \partial/\partial y$ or $x\partial/\partial y$), separation of variables can be used to write ψ as a product $\psi(x,y)=A(x)B(y)$. Substitution of this form into the Schrödinger equation, followed by collecting together all x-dependent and all y-dependent terms, gives;

$$- \hbar^2/2m\, A^{-1}\partial^2A/\partial x^2 - \hbar^2/2m\, B^{-1}\partial^2B/\partial y^2 = E-V_0.$$

Since the first term contains no y-dependence and the second contains no x-dependence, and because the right side of the equation is independent of both x and y, both terms on the left must actually be constant (these two constants are denoted E_x and E_y, respectively, realizing that they have units of energy). This observation allows two separate Schrödinger equations to be written:

$$-\hbar^2/2m\ A^{-1}\partial^2 A/\partial x^2 = E_x, \text{ and}$$

$$-\hbar^2/2m\ B^{-1}\partial^2 B/\partial y^2 = E_y.$$

The total energy E can then be expressed in terms of these separate energies E_x and E_y from $E_x + E_y = E-V_0$. Solutions to the x- and y- Schrödinger equations are easily seen to be:

$$A(x) = \exp(ix(2mE_x/\hbar^2)^{1/2}) \text{ and } \exp(-ix(2mE_x/\hbar^2)^{1/2})\ ,$$

$$B(y) = \exp(iy(2mE_y/\hbar^2)^{1/2}) \text{ and } \exp(-iy(2mE_y/\hbar^2)^{1/2}).$$

Two independent solutions are obtained for each equation because the x- and y-space Schrödinger equations are both second order differential equations (i.e., a second order differential equation has two independent solutions).

1.4.2 Boundary Conditions

The boundary conditions, not the Schrödinger equation, determine whether the eigenvalues will be discrete or continuous

If the electron is entirely unconstrained within the x,y plane, the energies E_x and E_y can assume any values; this means that the experimenter can inject the electron onto the x,y plane with any total energy E and any components E_x and E_y along the two axes as long as $E_x + E_y = E$. In such a situation, one speaks of the energies along both coordinates as being in the continuum or not quantized.

In contrast, if the electron is constrained to remain within a fixed area in the x,y plane (e.g., a rectangular or circular region), then the situation is qualitatively different. Constraining the electron to any such specified area gives rise to boundary conditions that impose additional requirements on the above A and B functions. These constraints can arise, for example, if the potential V(x,y) becomes very large for x,y values outside the region, in which case, the probability of finding the electron outside the region is very small. Such a case might represent, for example, a situation in which the molecular structure of the solid surface changes outside the enclosed region in a way that is highly repulsive to the electron (e.g., as in the case of molecular corrals on metal surfaces). This case could then represent a simple model of so-called corrals in which the particle is constrained to a finite region of space.

For example, if motion is constrained to take place within a rectangular region defined by $0 \le x \le L_x$; $0 \le y \le L_y$, then the continuity property that all wave functions must obey (because of their interpretation as probability densities, which must be continuous) causes A(x) to vanish at 0 and at L_x. That is, because A must vanish for $x < 0$ and must vanish for $x > L_x$, and because A is continuous, it must vanish at $x = 0$ and at $x = L_x$. Likewise, B(y) must vanish at 0 and at L_y. To implement these constraints for A(x), one must linearly combine the above two solutions $\exp(ix(2mE_x/\hbar^2)^{1/2})$ and $\exp(-ix(2mE_x/\hbar^2)^{1/2})$ to achieve a function that vanishes at x=0:

$$A(x) = \exp(ix(2mE_x/\hbar^2)^{1/2}) - \exp(-ix(2mE_x/\hbar^2)^{1/2}).$$

One is allowed to linearly combine solutions of the Schrödinger equation that have the same energy (i.e., are degenerate) because Schrödinger equations are linear differential equations. An analogous process must be applied to B(y) to achieve a function that vanishes at y=0:

$$B(y) = \exp(iy(2mE_y/\hbar^2)^{1/2}) - \exp(-iy(2mE_y/\hbar^2)^{1/2}).$$

Further requiring A(x) and B(y) to vanish, respectively, at $x=L_x$ and $y=L_y$, respectively, gives equations that can be obeyed only if E_x and E_y assume particular values:

$$\exp(iL_x(2mE_x/\hbar^2)^{1/2}) - \exp(-iL_x(2mE_x/\hbar^2)^{1/2}) = 0, \text{ and}$$

$$\exp(iL_y(2mE_y/\hbar^2)^{1/2}) - \exp(-iL_y(2mE_y/\hbar^2)^{1/2}) = 0.$$

These equations are equivalent (i.e., using $\exp(ix) = \cos(x) + i \sin(x)$) to

$$\sin(L_x(2mE_x/\hbar^2)^{1/2}) = \sin(L_y(2mE_y/\hbar^2)^{1/2}) = 0.$$

Knowing that $\sin(\theta)$ vanishes at $\theta = n\pi$, for n=1,2,3,..., (although the $\sin(n\pi)$ function vanishes for n=0, this function vanishes for all x or y, and is therefore unacceptable because it represents zero probability density at all points in space) one concludes that the energies E_x and E_y can assume only values that obey:

$$L_x(2mE_x/\hbar^2)^{1/2} = n_x\pi,$$

$$L_y(2mE_y/\hbar^2)^{1/2} = n_y\pi, \text{ or}$$

$$E_x = n_x^2\pi^2 \hbar^2/(2mL_x^2), \text{ and}$$

$$E_y = n_y^2\pi^2 \hbar^2/(2mL_y^2), \text{ with } n_x \text{ and } n_y = 1,2,3, \ldots$$

and

$$E = V_0 + E_x + E_y.$$

It is important to stress that it is the imposition of boundary conditions, expressing the fact that the electron is spatially constrained, that gives rise to quantized energies. In the absence of spatial confinement, or with confinement only at x = 0 or L_x or only at y = 0 or L_y, quantized energies would not be realized.

In this example, confinement of the electron to a finite interval along both the x and y coordinates yields energies that are quantized along both axes. If the electron were confined along one coordinate (e.g., between $0 \le x \le L_x$) but not along the other (i.e., B(y) is either restricted to vanish only at y=0 or at y=L_y or at neither point), then the total energy E lies in the continuum; its E_x component is quantized but E_y is not. Analogs of such cases arise, for example, for a triatomic molecule containing one strong and one weak bond. If the bond with the higher dissociation energy is excited to a level that is not enough to break it but that is in excess of the dissociation energy of the weaker bond, one has a situation that is especially interesting. In this case, one has two degenerate states

(1) one with the strong bond having high internal energy and the weak bond having low energy (ψ_1), and

(2) a second with the strong bond having little energy and the weak bond having more than enough energy to rupture it (ψ_2).

Although an experiment may prepare the molecule in a state that contains only the former component (i.e., $\Psi(t=0)= C_1\psi_1 + C_2\psi_2$ with $C_1 = 1, C_2 = 0$), coupling between the two degenerate functions (induced by terms in the Hamiltonian **H** that have been ignored in defining ψ_1 and ψ_2) can cause the true wave function $\Psi = \exp(-it\mathbf{H}/\hbar)\ \Psi(t=0)$ to acquire a component of the second function as time evolves. In such a case, one speaks of internal vibrational energy relaxation (IVR) giving rise to unimolecular decomposition of the molecule.

1.4.3 Energies and Wave Functions for Bound States

For discrete energy levels, the energies are specified functions that depend on quantum numbers, one for each degree of freedom that is quantized

Returning to the situation in which motion is constrained along both axes, the resultant total energies and wave functions (obtained by inserting the quantum energy levels into the expressions for A(x) B(y)) are as follows:

$$E_x = n_x{}^2\pi^2 \hbar^2/(2mL_x{}^2), \text{ and}$$

$$E_y = n_y{}^2\pi^2 \hbar^2/(2mL_y{}^2),$$

$$E = E_x + E_y \ +V_0$$

$$\psi(x,y) = (1/2L_x)^{1/2} (1/2L_y)^{1/2}[\exp(in_x\pi x/L_x) -\exp(-in_x\pi x/L_x)]$$

$$[\exp(in_y\pi y/L_y) -\exp(-in_y\pi y/L_y)], \text{ with } n_x \text{ and } n_y =1,2,3, \ldots \ .$$

The two $(1/2L)^{1/2}$ factors are included to guarantee that ψ is normalized:

$$\int |\psi(x,y)|^2 \, dx \, dy = 1.$$

Normalization allows $|\psi(x,y)|^2$ to be properly identified as a probability density for finding the electron at a point x, y.

Shown in Fig. 1. 13 are plots of four such two dimensional wave functions for n_x and n_y values of (1,1), (2,1), (1.2) and (2,2), respectively.

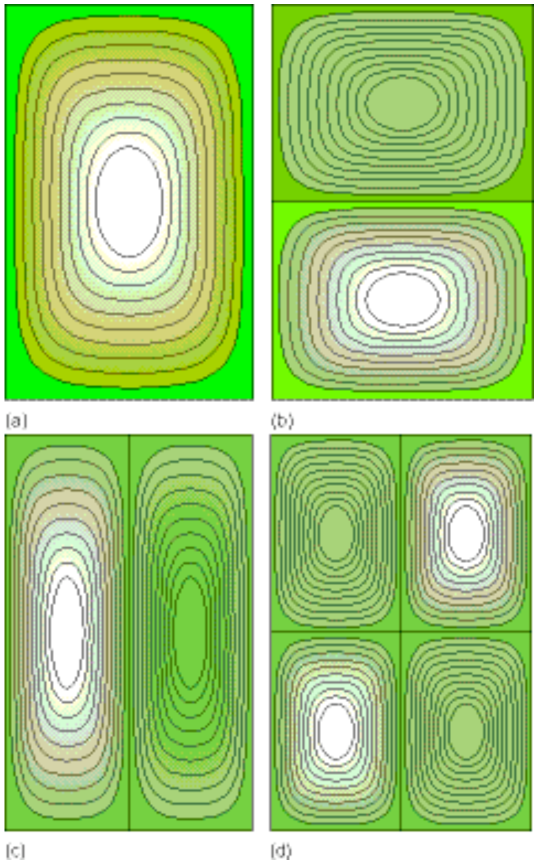


Figure 1. 13. Plots of the (1,1), (2,1), (1,2) and (2,2) wave functions

Note that the functions vanish on the boundaries of the box, and notice how the number of nodes (i.e., zeroes encountered as the wave function oscillates from positive to negative) is related to the n_x and n_y quantum numbers and to the energy. This pattern of more nodes signifying higher energy is one that we encounter again and again in quantum mechanics and is something the student should be able to use to guess the relative energies of wave functions when their plots are at hand. Finally, you should also notice that, as in the one-dimensional box case, any attempt to classically interpret the probabilities P(x,y) corresponding to the above quantum wave functions will result in failure. As in the one-dimensional case, the classical P(x,y) would be constant along slices of fixed x and varying y or slices of fixed y and varying x within the box because the speed is constant there. However, the quantum P(x,y) plots, at least for small quantum numbers, are not constant. For large n_x and n_y values, the quantum P(x,y) plots will again, via the quantum-classical correspondence principle, approach the (constant) classical P(x,y) form except near the classical turning points (i.e., near the edges of the two-dimensional box).

If, instead of being confined to a rectangular corral, the electron were constrained to lie within a circle of radius R, the Schrödinger equation is more favorably expressed in polar coordinates (r, θ). Transforming the partial derivatives appearing in the Schrödinger equation

$$- \hbar^2/2m\ (\partial^2/\partial x^2 + \partial^2/\partial y^2)\psi(x,y) + V(x,y)\ \psi(x,y) = E\ \psi(x,y)$$

into polar coordinates and realizing that the potential depends on r but not on θ gives

$$- \hbar^2/2m\ (r^{-1}\partial/\partial r(r\partial/\partial r) + r^{-2}\ \partial^2/\partial\theta^2)\ \psi(r,\theta) + V(r)\ \psi(r,\theta) = E\ \psi(r,\theta).$$

Again using separation of variables to substitute

$$\psi(r,\theta) = A(r)\ B(\theta)$$

into the Schrödinger equation and dividing by AB, we obtain

$$- A^{-1}\ \hbar^2/2m\ (r^{-1}\partial/\partial r(r\partial/\partial r)A(r)) + V_0 - B^{-1}\ \hbar^2/2m\ (r^{-2}\partial^2 B(\theta)/\partial\theta^2) = E$$

where V_0 is the value of the potential inside the circular region. The first two terms on the left and the E on the right side contain no reference to θ, so the quantity $B^{-1}\ \partial^2 B(\theta)/\partial\theta^2$ must be independent of θ:

$$B^{-1}\ \partial^2 B(\theta)/\partial\theta^2 = c$$

Moreover, because the coordinates (r, θ) and (r, θ +2 π) describe the same point in space, B(θ) must obey

$$B(\theta) = B(\theta + 2\pi).$$

The solutions to the above differential equation for $B(\theta)$ subject to the periodicity condition are

$$B(\theta) = (2\pi)^{-1/2} \exp(\pm in\theta);\ n = 0, 1, 2, \ldots.$$

This means that the equation for the radial part of the wave function is

$$- A^{-1}\hbar^2/2m\,(r^{-1}\partial/\partial r(r\partial/\partial r)A(r)) + V_0 - \hbar^2/2m\,(r^{-2}n^2) = E$$

or

$$r^2\, d^2A/dr^2 + r\, dA/dr - n^2 A + 2mr^2/\hbar^2\,(E-V_0)A = 0\ .$$

This differential equation is probably not familiar to you, but it turns out this is the equation obeyed by so-called Bessel functions. The Bessel functions labeled $J_n(ax)$ obey

$$x^2\, d^2J/dx^2 + x\, dJ/dx - n^2 J + a^2 x^2 J = 0$$

so, our A function is

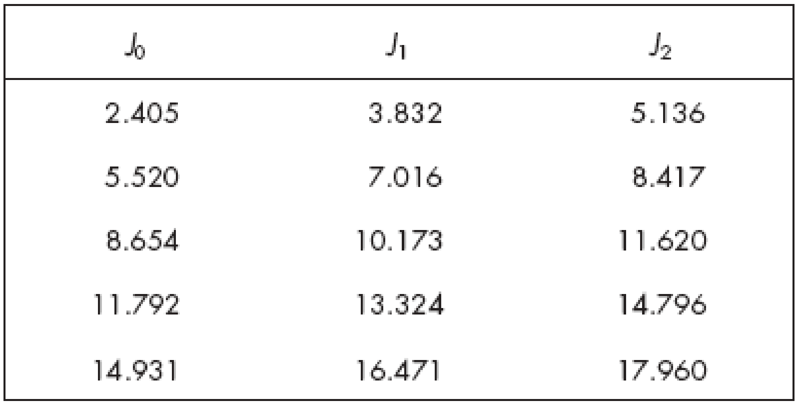
$$A(r) = J_n([2m/\hbar^2\,(E-V_0)]^{1/2} r).$$

The full wave functions are then

$$\psi(r, \theta) = A(r)\, B(\theta) = N\, J_n([2m/\hbar^2\,(E-V)]^{1/2} r)\,(2\pi)^{-1/2} \exp(\pm in\theta)$$

where N is a normalization constant. The energy eigenvalues $E_{j,n}$ cannot be expressed analytically as in the particle-in-a box system (where we used knowledge of the zeros of the sin function to determine E_n). However, knowing that $A(r)$ must vanish at $r = R$, we can use tables (for example, see Kreyszig, E. Advanced Engineering Mathematics, 8th ed.; John Wiley and Sons, Inc.: New York, 1999) that give the values of x at which $J_n(x)$ vanishes to determine the set of eigenvalues associated with each value of the angular momentum quantum number n. In the table shown below, we list the first five values at which J_0 , J_1, and J_2 vanish.

Values of x at which $J_n(x)$ vanish for n = 0, 1, and 2



J_0	J_1	J_2
2.405	3.832	5.136
5.520	7.016	8.417
8.654	10.173	11.620
11.792	13.324	14.796
14.931	16.471	17.960

If we call the values at which $J_n(x)$ vanishes $z_{n,j}$, then the energies are given as

$$E_{n,j} = V_0 + (z_{n,j})^2 \hbar^2/2mR^2.$$

From the ordering of the $z_{n,j}$ values shown in the table above, we can see that the ordering of the energy levels will be $z_{0.1}$, $z_{1,1}$, $z_{1,2}$, $z_{1,0}$, $z_{1,1}$, $z_{1,2}$, and so forth, regardless of the size of the circle R or the mass of the particle m.

The state with n = -1 has the same energy as that with n = 1; likewise, n = -2 has the same energy as n = 2. So, all but the n = 0 states are doubly degenerate; the only difference between such pairs of states is the sense of the angular momentum terms $\exp(\pm ni\theta)$. These energy levels depend on both the angular momentum quantum number n, as well as the radial quantum number j and they depend upon R much like the particle-in-a-box energies depend on the box length L. In Fig. 1.13a we show plots of the probability densities $|\psi(r,\theta)|^2$ for n = 0, 1, and 2 and for j = 1, 3, and 5 to illustrate how the number of radial nodes increases as j increases.

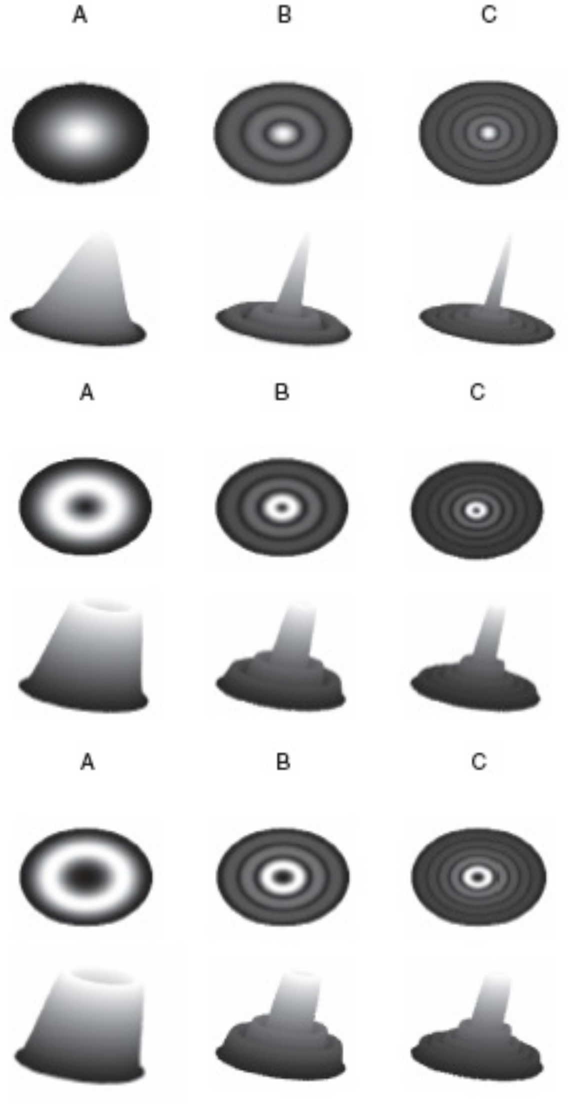


Figure 1.13a Plots of $|\psi(r,\theta)|^2$ for n = 0; j = 1, 3, 5 (top); n = 1; j = 1, 3, 5 (middle); and n = 2; j = 1, 3, 5 (bottom). Taken from Ellison, M. D. *J. Chem. Educ.* **2008,** *85,* 1282–1287.

The character of $|\psi(r,\theta)|^2$ also changes with n. For n = 0, there is high amplitude for the particle being in the center of the circle, but for n > 0, there is no amplitude in the center. This is analogous to what one finds for atomic orbitals; s orbitals have non-zero amplitude at the nucleus, but p, d, and higher orbitals do not.

Let's examine a few more easy problems that can be solved analytically to some degree. This will help illustrate how boundary conditions generate quantization and how the number of quantum numbers depends on the dimensionality of the problem. When considering a particle of mass m moving in three dimensions but constrained to remain within a sphere of radius R, we replace the three Cartesian coordinates x, y, and z by the spherical coordinates r, θ, and φ. Doing so, changes the Schrödinger equation's kinetic energy terms into what we show below

$$-\frac{\hbar^2}{2m\mathbf{r}^2}\left(\frac{\partial}{\partial\mathbf{r}}\left(\mathbf{r}^2\frac{\partial\psi}{\partial\mathbf{r}}\right)\right)-\frac{\hbar^2}{2m}\frac{1}{\mathbf{r}^2\mathbf{Sin}\theta}\frac{\partial}{\partial\theta}\left(\mathbf{Sin}\theta\frac{\partial\psi}{\partial\theta}\right)-\frac{\hbar^2}{2m}\frac{1}{\mathbf{r}^2\mathbf{Sin}^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\mathrm{V(r)}\psi = \mathrm{E}\psi.$$

Taking the potential to be V_0 (a constant) for $0 \le r \le R$, and infinite for $r > R$, we can again use separation of variables to progress in solving this three dimensional differential equation. We substitute

$$\psi(r,\theta,\phi) = Y_{L,M}(\theta,\phi)\, F(r)$$

into the Schrödinger equation and taking into account that the so-called spherical harmonic functions $Y_{L,M}(\theta,\phi)$ obey the following:

$$\frac{1}{\mathbf{Sin}\theta}\frac{\partial}{\partial\theta}\left(\mathbf{Sin}\theta\frac{\partial Y_{L,M}}{\partial\theta}\right)+\frac{1}{\mathbf{Sin}^2\theta}\frac{\partial^2 Y_{L,M}}{\partial\phi^2} = -\,L(L+1)\,Y_{\mathbf{L,M}}.$$

This reduces the Schrödinger equation to an equation for the radial function F(r):

$$-\frac{\hbar^2}{2m\mathbf{r}^2}\left(\frac{\partial}{\partial\mathbf{r}}\left(\mathbf{r}^2\frac{\partial F}{\partial\mathbf{r}}\right)\right)+\frac{\hbar^2}{2mr^2}L(L+1)F + V_0\,F = E\,F.$$

Again, this equation is probably not familiar to you, but it can be recast in a way that makes it equivalent to the equation obeyed by so-called spherical Bessel functions

$$x^2 d^2 j_L(x)/dx^2 + 2x\, dj_L(x)/dx + [x^2 - L(L+1)]\, j_L(x) = 0$$

by taking

$$x = [2m(E-V_0)/\hbar^2]^{1/2}\, r.$$

The result is that the wave functions for this problem reduce to

$$\psi(r,\theta,\phi) = N\, Y_{L,M}(\theta,\phi)\, j_L([2m(E-V_0)/\hbar^2]^{1/2} r)$$

where N is a normalization constant. The energies are determined by requiring $\psi(r,\theta,\phi)$ to vanish at $r = R$, which is analogous to insisting that the spherical Bessel function vanish at $r = R$ in the earlier problem we studied. The values of x ($z_{L,n}$) at which $j_L(x)$ vanish again can be found in various tabulations, including that cited earlier. Several of these values are tabulated below for illustration.

Values of x at which $j_L(x)$ vanish for L = 0, 1, 2, 3, and 4

	n=1	n=2	n=3	n=4
L=0	3.142	6.283	9.425	12.566
L=1	4.493	7.725	10.904	14.066
L=2	5.763	9.095	12.323	15.515
L=3	6.988	10.417	13.698	16.924
L=4	8.183	11.705	15.040	18.301

From the values of $z_{L,n}$, one finds the energies from

$$E_{L,n} = V_0 + (z_{L,n})^2\, \hbar^2/2mR^2.$$

Again, we see how the energy depends on the size of the constraining region (characterized by R) very much in the same way as in the earlier systems. We also see that E depends on the angular momentum quantum number L (much as it did in the preceding example) and on the mass of the particle. However, the energy ordering of these levels is different from what we have seen earlier as reflected in the ordering of the $z_{L,n}$ values shown in the above table. The energies appear in the order (L=0 n =1; L-2 n =1; L=2 n =1; L=0 n = 2; L = 3 n =1; L =1 n = 2, and so on, and this is true for any size sphere R and any particle mass m.

If, instead of being constrained to move within a spherical volume, the particle is constrained to move on the surface of a sphere or radius R, the variable r is fixed (at r = R) and the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{1}{R^2\mathbf{Sin}\theta}\frac{\partial}{\partial\theta}\left(\mathbf{Sin}\theta\frac{\partial\psi}{\partial\theta}\right) - \frac{\hbar^2}{2m}\frac{1}{R^2\mathbf{Sin}^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + V_0\,\psi = E\psi.$$

Using

$$\frac{1}{\mathbf{Sin}\theta}\frac{\partial}{\partial\theta}\left(\mathbf{Sin}\theta\frac{\partial Y_{L,M}}{\partial\theta}\right) + \frac{1}{\mathbf{Sin}^2\theta}\frac{\partial^2 Y_{L,M}}{\partial\phi^2} = -\,L(L+1)\,Y_{\mathbf{L,M}}$$

we can see that the wave functions are the spherical harmonics and the energies are given by

$$E_{L,M} = V_0 + \frac{L(L+1)\hbar^2}{2mR^2}$$

Note that the energies depend on L but not on the M quantum number. So, each state belonging to level L is 2L+1 fold degenerate because M ranges from –L to L.

Finally, if instead of being constrained to move within a circle of radius R, the particle were constrained to move on the surface of the circle, the two-dimensional Schrödinger equation treated earlier would reduce to

$$-\hbar^2/2mR^2\,\partial^2\psi(\theta)/\partial\theta^2 + V_0\,\psi(\theta) = E\,\psi(\theta).$$

The solutions are the familiar functions

$$\psi(\theta) = (1/2\,\pi)^{1/2} \exp(in\theta);\ n = 0, \pm 1, \pm 2, \ldots$$

and the energies are

$$E_n = n^2\hbar^2/2mR^2 + V_0.$$

Note that the quantization of energy arises because the angular momentum is quantized to be $n\hbar$; this condition arose, in turn, by the condition that

$$\psi(\theta) = \psi(\theta + 2\,\pi).$$

As with the case of a particle moving within the circular region, the states with $n > 0$ are doubly degenerate; the difference between pairs of such states reflecting the sense of their angular momentum.

These model problems will be seen in Chapter 2 to be very useful representations of situations that arise when an electron is constrained within or on the surface of various nanoscopic particles. For now, they were discussed to illustrate how separations of variables can sometimes be used to decompose the Schrödinger equation into one-dimensional ordinary differential equations and to show how it is the boundary conditions (either constraining ψ to vanish at certain distances or insisting that ψ be periodic when appropriate) that produce the quantization. It is important to note that it is when a particle is spatially constrained (e.g., when its wave function was forced to vanish at two locations $x = 0$ and $x = L_x$) that quantized energy levels result. When the particle is not so spatially trapped, its energy will not be quantized. You will see this behavior over and over as we explore other models for electronic, vibrational, and rotational motions in molecules.

1.4.4 Quantized Action Can Also be Used to Derive Energy Levels

There is another approach that can be used to find energy levels and is especially straightforward to use for systems whose Schrödinger equations are separable. The so-called classical action (denoted S) of a particle moving with momentum **p** along a path leading from initial coordinate $\mathbf{q}_i$ at initial time t_i to a final coordinate $\mathbf{q}_f$ at time t_f is defined by:

$$S = \int_{\mathbf{q}_i;t_i}^{\mathbf{q}_f;t_f} \mathbf{p} \bullet \mathbf{dq} .$$

Here, the momentum vector **p** contains the momenta along all coordinates of the system, and the coordinate vector **q** likewise contains the coordinates along all such degrees of freedom. For example, in the two-dimensional particle-in-a-box problem considered above, **q** = (x, y) has two components as does **p** = (p_x, p_y), and the action integral is:

$$S = \int_{x_i;y_i;t_i}^{x_f;y_f;t_f} (p_x \, dx + p_y \, dy) .$$

In computing such actions, it is essential to keep in mind the sign of the momentum as the particle moves from its initial to its final positions. The examples given below will help clarify these matters and will show how to apply the idea.

For systems for which the Hamiltonian is separable, the action integral decomposes into a sum of such integrals, one for each degree of freedom. In the two-dimensional example, the additivity of H:

$$H = H_x + H_y = p_x^2/2m + p_y^2/2m + V(x) + V(y)$$

$$= - \hbar^2/2m\ \partial^2/\partial x^2 + V(x) - \hbar^2/2m\ \partial^2/\partial y^2 + V(y)$$

means that p_x and p_y can be independently solved for in terms of the potentials V(x) and V(y) as well as the energies E_x and E_y associated with each separate degree of freedom:

$$p_x = \pm \sqrt{2m(E_x - V(x))}$$

$$p_y = \pm \sqrt{2m(E_y - V(y))} \;;$$

the signs on p_x and p_y must be chosen to properly reflect the motion that the particle is actually undergoing at any instant of time. Substituting these expressions into the action integral yields:

$$S = S_x + S_y$$

$$= \int_{x_i;t_i}^{x_f;t_f} \pm\sqrt{2m(E_x - V(x))}\, dx \; + \int_{y_i;t_i}^{y_f;t_f} \pm\sqrt{2m(E_y - V(y))}\, dy \;.$$

The relationship between these classical action integrals and the existence of quantized energy levels has been shown to involve equating the classical action for motion that is periodic between a left and right turning point, as for a classical particle undergoing periodic vibrational motion, to the following multiple of Planck's constant:

$$S_{\text{closed}} = \int_{\mathbf{q}_i;t_i}^{\mathbf{q}_f=\mathbf{q}_i;t_f} p\,dq = (n + 1/2)\, h,$$

where the quantization index n ranges from 0 to ∞ in steps of unity. Alternatively, for motion in a closed angular path, as for a particle moving on a circular or elliptical path, the action quantization condition reads:

$$S_{\rm closed} = \int_{\mathbf{q}_i;t_i}^{\mathbf{q}_f=\mathbf{q}_i;t_f} p dq = \text{n h},$$

where again n ranges from 0 to ∞ in steps of unity.

When action-quantization as described above is applied to the so-called harmonic oscillator problem (this serves as the simplest reasonable model for vibration of a diatomic molecule AB) that we will study in quantum form later, one expresses the total energy as the sum of kinetic and potential energies

$$E = p^2/2\mu + k/2\ x^2$$

where $\mu = m_A m_B/(m_A + m_B)$ is the reduced mass of the AB diatomic molecule, k is the force constant describing the bond between A and B, x is the bond-length displacement, and p is the momentum associated with the bond length. The quantized action requirement then reads

$$(n + 1/2)\ h = \int p\ dx = \int [2\mu(E - k/2\ x^2)]^{1/2} dx.$$

This integral is carried out between $x = -(2E/k)^{1/2}$ and $(2E/k)^{1/2}$ the left and right turning points of the oscillatory motion and back again to form a closed path. Carrying out this integral and equating it to (n +1/2) h gives the following expression for the energy E:

$$E = (n + 1/2)\ (h/2\pi)\ [k/\mu]^{1/2}\ .$$

If the quantum number n is allowed to assume integer values ranging from n = 0, 1, 2, to infinity, these energy levels agree with the full quantum treatment's results that we will obtain later.

For an example of applying this approach to a problem involving motion along a closed loop, let's consider the free (i.e., with no potential affecting its angular motion) rotation of a diatomic molecule AB having fixed bond length R. The rotational energy can be written as

$$E = \frac{p_\phi^2}{2\mu R^2}$$

where p_ϕ is the momentum associated with rotation and μ is the reduced mass of the AB molecule. Solving for p_ϕ and inserting this into the action-quantization equation appropriate for motion along a closed loop gives

$$\int_{\phi=0}^{\phi=2\pi} p_\phi d\phi = \int_{\phi=0}^{\phi=2\pi} \sqrt{2\mu R^2 E}\, d\phi = \sqrt{2\mu R^2 E}\,(2\pi) = nh .$$

Solving for the energy E then gives

$$E = \frac{(nh)^2}{(2\pi)^2 2\mu R^2} = \frac{n^2\hbar^2}{2\mu R^2},$$

which is exactly the same result as we obtained earlier when solving the Schrödinger equation for the motion of a particle moving on a circle.

Now, let's apply action quantization to each of the independent coordinates of the two-dimensional particle in a box problem. The two separate action quantization conditions read:

$$(n_x + 1/2)\, h = \int_{x=0}^{x=L_x} \sqrt{2m(E_x - V(x))}\, dx \; + \int_{x=L_x}^{x=0} -\sqrt{2m(E_x - V(x))}\, dx$$

$$(n_y + 1/2)\, h = \int_{y=0}^{y=L_y} \sqrt{2m(E_y - V(y))}\, dy \; + \int_{y=L_y}^{y=0} -\sqrt{2m(E_y - V(y))}\, dy \quad .$$

Notice that the sign of the momenta are positive in each of the first integrals appearing above (because the particle is moving from x = 0 to x = L_x, and analogously for y-motion, and thus has positive momentum) and negative in each of the second integrals (because the motion is from $x = L_x$ to $x = 0$ (and analogously for y-motion) and thus the particle has negative momentum). Within the region bounded by $0 \le x \le L_x$; $0 \le y \le L_y$, the potential is constant and can be taken as zero (this just gives our reference point for total energy). Using this fact, and reversing the upper and lower limits, and thus the sign, in the second integrals above, one obtains:

$$(n_x + 1/2)\, h = 2 \int_{x=0}^{x=L_x} \sqrt{2mE_x}\, dx = 2\sqrt{2mE_x}\; L_x$$

$$(n_y + 1/2)\, h = 2 \int_{y=0}^{y=L_y} \sqrt{2mE_y}\, dy = 2\sqrt{2mE_y}\; L_y.$$

Solving for E_x and E_y, one finds:

$$E_x = \frac{[(n_x + 1/2)h]^2}{8mL_{x^2}}$$

$$E_y = \frac{[(n_y + 1/2)h]^2}{8mL_{y^2}}.$$

These are not the same quantized energy levels that arose when the wave function boundary conditions were matched at $x = 0$, $x = L_x$ and $y = 0$, $y = L_y$. In the Schrödinger equation approach, the energy expressions did not have the + ½ factor that appears in the above action-based result. It turns out that, for potentials that are defined in a piecewise manner, as the particle-in-a-box potential is (i.e., the potential undergoes an infinite jump at $x = 0$ and $x = L$), the action quantization condition has to be modified. An example of how and why one has to make this modification is given in a paper from Prof. Bill Miller's group (J. E. Adams and W. H. Miller, J. Chem. Phys. 67, 5775-5778 (1977)), but

I will not discuss it further here because its details are beyond the level of this text. Suffice it to say that for periodic motion between two turning points on a smooth (i.e., non-piecewise) potential, (n+1/2)h is the correct action quantization value. For angular motion on a closed loop, nh is the proper value. But, for periodic motion between turning points on a piecewise potential, the modifications discussed in the above reference must be applied to cause action quantization to reproduce the correct quantum result.

The use of action quantization as illustrated above has become a very important tool. It has allowed scientists to make great progress toward bridging the gap between classical and quantum descriptions of molecular dynamics. In particular, by using classical concepts such as trajectories and then imposing quantized-action conditions, people have been able to develop so-called semi-classical models of molecular dynamics. In such models, one is able to retain a great deal of classical understanding while building in quantum effects such as energy quantization, zero-point energies, and interferences. Both at my Theory Page web site (http://simons.hec.utah.edu/TheoryPage/index.html) and from papers accessed on the web site of one of the pioneers of semi-classical theory as applied to chemistry, Professor William H. Miller (http://chem.berkeley.edu/faculty/miller/index.php), you can learn more about this subject.

Before leaving this section, it is worth discussing a bit more the energy and angular momentum quantization that occurs when treating free one-dimensional rotational motion of a particle on a circle or a linear rigid molecule constrained to lie on a plane. When we used action quantization to address this kind of problem, we obtained quantized energies

$$E = \frac{n^2\hbar^2}{2\mu R^2}$$

which, through the energy expression given in terms of angular momentum

$$E = \frac{p_\phi^2}{2\mu R^2},$$

implies that the angular momentum itself is quantized

$$p_\phi = \pm n\hbar .$$

This is the same result we obtain when we seek eigenfunctions and eigenvalues the quantum mechanics L_z angular momentum operator. As we showed earlier, this operator, when computed as the z-component of **r x p**, can be written in polar (r, θ, ϕ) coordinates as

$$L_z = - i \hbar \, d/d\phi.$$

The eigenfunctions of this operator have the form exp(iaϕ), and the eigenvalues are a ħ. Because geometries with azimuthal angles equal to ϕ or equal to ϕ + 2π are exactly the same geometries, the function exp(iaϕ) should be exactly the same as exp(ia(ϕ+2π)). This can only be the case if a is an integer. Thus, one concludes that only integral multiples of ħ can be allowed values of the z-component of angular momentum.

Experimentally, one measures the z-component of an angular momentum by placing the system possessing the angular momentum in a magnetic field of strength B and observing how many z-component energy states arise. This splitting in energy levels is termed the Zeeman effect. For example, a boron atom with one unpaired electron its 2p orbital has one unit of orbital angular momentum, so one finds three separate z-component values which are usually denoted m = -1, m=0, and m=1. Another example is offered by the scandium atom with one unpaired electron in a d orbital; this atom's states split into five (m = -2, -1, 0, 1, 2) z-component states. In each case, one finds 2L + 1 values of the m quantum number, and, because L is an integer, 2L + 1 is an odd integer. Both of these observations are consistent with the expectation that only integer values can occur for L_z eigenvalues as obtained from action quantization and from the boundary condition exp(iaϕ) = exp(ia(ϕ+2π)).

However, it has been observed that some species do not possess 3 or 5 or 7 or 9 z-component states but an even number of such states. In particular, electrons, protons, or neutrons are observed to have only two z-component eigenvalues. This also is observed in, for example, the Boron atom mentioned above, if one examines the further splittings of the 2p (m = -1, 0, and 1) levels caused by the magnetic field's action on the unpaired electron's spin. Because, as we discuss later in this text, all angular momenta have z-component eigenvalues that are separated from one another by unit multiples of $\hbar$, one is forced to conclude that these three fundamental building-block particles (electrons, protons, and neutrons) have z-component eigenvalues of 1/2 $\hbar$ and – 1/2 $\hbar$. The appearance of half-integral angular momenta is not consistent with the action-quantization result or the observation made earlier that ϕ and $\phi + 2\pi$ correspond to exactly the same physical point in coordinate space, which, in turn, implies that only full-integer angular momenta are possible.

The resolution of the above paradox (i.e., how can half-integer angular momenta exist?) involves realizing that some angular momenta correspond not to the **r x p** angular momenta of a physical mass rotating, but, instead, are intrinsic properties of certain particles. That is, the intrinsic angular momenta of electrons, protons, and neutrons can not be viewed as arising from rotation of some mass that comprises these particles. Instead, such intrinsic angular momenta are fundamental built in characteristics of these particles. For example, the two 1/2 $\hbar$ and – 1/2 $\hbar$ angular momentum states of an electron, usually denoted α and β, respectively, are two internal states of the electron that are degenerate in the absence of a magnetic field but which represent two distinct states of the electron. Analogously, a proton has 1/2 $\hbar$ and – 1/2 $\hbar$ states, as do neutrons. All such half-integral angular momentum states cannot be accounted for using classical mechanics but are known to arise in quantum mechanics. This means that, when we teach introductory chemistry to young students, it is not correct to say that the up and down (α and β) spin states of an electron can be viewed in terms of the electron's mass spinning clockwise or counterclockwise around some axis. Such spinning-mass angular momenta can only possess integer values; half-integer angular momenta cannot and should not be described in terms of spinning masses.

1.4.5 Action Can Also be Used to Generate Wave Functions

Action integrals computed from classical descriptions of motion on potential energy surfaces can also be used to generate approximate quantum wave functions. So doing offers yet another avenue for making connection between the classical and quantum worlds. To see how such a connection can arise directly from the Schrödinger equation, we begin with the time-independent Schrödinger equation for a single particle of mass m moving on a potential V(r) that depends on the particle's position coordinates r:

$$E\Psi(r) = -\frac{\hbar^2}{2m}\nabla^2\Psi(r) + V(r)\Psi(r).$$

Then, we express the complex wave function as a constant real amplitude A multiplied by a complex phase which we write as:

$$\Psi(r) = A\exp(iW(r)/\hbar).$$

Substituting this expression for $\Psi(r)$ into the Schrödinger equation gives an equation for W:

$$E = V + \frac{(\nabla W)^2}{2m} - i\hbar\frac{\nabla^2 W}{2m}.$$

This equation contains both real and imaginary components (n.b., W itself is complex). It is usually solved by assuming W(r) can be expanded in a power series in the variable $\hbar$. This expansion is motivated by noting that if the $i\hbar\frac{\nabla^2 W}{2m}$ factor in the above equation is neglected, the resulting equation

$$0 = V - E + \frac{(\nabla W)^2}{2m}$$

would make sense if $\nabla W(r)$ were equal to the classical momentum of the particle. So, taking the $\hbar \rightarrow 0$ limit of the equation for W(r) appears to reduce this quantum mechanics equation to a classical result in which $\nabla W(r)$ = p(**r**).

So, substituting

$$W(r) = W_0(r) + \hbar W_1(r) + \hbar^2 W_2(r) + \ldots$$

into the above equation for W(r) and gathering together all terms of a given power in $\hbar$ produces equations for the various $W_n(r)$, the first two of which read:

$$0 = 2m(V - E) + (\nabla W_0)^2$$

and

$$0 = 2\nabla W_0 \cdot \nabla W_1 - i\nabla^2 W_0.$$

To simplify further discussion of this so-called semi-classical wave function theory, let us restrict attention to the case in which there is only one spatial coordinate. For the two- or three-dimensional cases, ∇W_0 and ∇W_1 are vector quantities, and the solution of these equations is considerably more complicated, especially if the potential V(**r**) can not be separated into additive contributions from each of the variables. When there is only one spatial coordinate, ∇W_0 and ∇W_1 are scalar quantities.

The first equation can be solved for $W_0(r)$ and gives two independent solutions (i.e., those corresponding to the ± sign):

$$W_0(r) = \pm \int^r \sqrt{2m(E - V(r'))} dr',$$

each of which will be real when E > V(r) (i.e., in classically allowed regions of space) and imaginary when E < V(r) (i.e., in classically forbidden regions). Notice that W_0(r) contains an integrand equal to the classical momentum $p(r) = \sqrt{2m(E - V(r))}$.

The equation for W_1(r) can also be solved:

$$W_1(r) = \frac{i}{2}\ln[\sqrt{2m(E - V(r))}].$$

So, through first-order in $\hbar$, the semi-classical wave functions are

$$\Psi(r) = A\exp(\pm\frac{i}{\hbar}\int^r \sqrt{2m(E - V(r'))}dr')\exp(\frac{i\hbar}{2\hbar}i\ln[\sqrt{2m(E - V(r))}])$$

$$= \frac{1}{\sqrt{\sqrt{2m(E - V(r))}]}}A\exp(\pm\frac{i}{\hbar}\int^r \sqrt{2m(E - V(r'))}dr').$$

These pairs of wave functions are often expressed as

$$\Psi = \frac{1}{\sqrt{\sqrt{2m(E - V(r))}]}}A\exp(\pm\frac{i}{\hbar}\int^r \sqrt{2m(E - V(r'))}dr')$$

in regions of space where E > V, and

$$\Psi = \frac{1}{\sqrt{\sqrt{2m(-E + V(r))}]}}A\exp(\pm\frac{1}{\hbar}\int^r \sqrt{2m(-E + V(r'))}dr')$$

in the classically forbidden regions where V > E. Notice that the wave functions in the classically allowed regions have probability densities given by

$$\Psi^*\Psi = \frac{A^2}{\sqrt{2m(E - V(r))}}$$

which is exactly the classical probability density we discussed earlier in this Chapter. The probability is inversely proportional to the speed of the particle at location r, and has the same singularity as the classical probability at turning points (where V = E). In contrast, the probability densities in regions where V > E either grow or decay exponentially within these classically forbidden regions.

Let's see how these semi-classical wave functions can be applied to some of the model problems we discussed earlier. For the one dimensional particle-in-a-box problem, the two exponentially growing and decaying functions are not needed because in the regions r < 0 and r > L, the wave function can be taken to vanish. Within the region 0 ≤ r ≤ L, there are two independent wave functions

$$\Psi = \frac{1}{\sqrt{\sqrt{2m(E-V(r))}]}} A\exp(\pm\frac{i}{\hbar}\int^{r}\sqrt{2m(E-V(r'))}dr'),$$

and the potential V(r') is constant (let's call the potential in this region V_0). So, the integration appearing in these two wave functions can be carried out to give

$$\Psi = \frac{1}{\sqrt{\sqrt{2m(E-V_0)}]}} A\exp(\pm\frac{ir}{\hbar}\sqrt{2m(E-V_0)}).$$

We can combine these two functions to generate a function that will vanish at r = 0 (as it must for this particle-in-a-box problem):

$$\Psi = \frac{1}{\sqrt{\sqrt{2m(E-V_0)}]}} A[\exp(\frac{ir}{\hbar}\sqrt{2m(E-V_0)}) - \exp(-\frac{ir}{\hbar}\sqrt{2m(E-V_0)})].$$

We can then use the condition that Ψ must also vanish at r = L to obtain an equation that specifies the energies E that are allowed:

$$0 = [\exp(\frac{iL}{\hbar}\sqrt{2m(E-V_0)}) - \exp(-\frac{iL}{\hbar}\sqrt{2m(E-V_0)})] = 2i\sin(\frac{L}{\hbar}\sqrt{2m(E-V_0)}),$$

which means that

$$E = V_0 + \frac{n^2\pi^2\hbar^2}{2mL^2}.$$

These energies are exactly the same as we found when we solved the Schrödinger equation for this model problem.

It is informative to note that these semi-classical wave functions, which are not exact because they were obtained by retaining only terms up to the first power of $\hbar$, were able to generate quantum nodal patterns (i.e., interferences) and quantized energy levels even though they contained classical concepts such as the momentum at various positions in space. It was by superimposing two functions having the same energy that nodal patterns were obtained.

Let's now consider what happens when we apply the semi-classical wave function to the harmonic oscillator problem also discussed earlier. In this case, there are two classical turning points r_1 and r_2 at which E = V(r). The semi-classical wave functions appropriate to the three regions (two classically forbidden and one classically allowed) are:

$$\Psi_1 = \frac{1}{\sqrt{\sqrt{2m(-E+V(r))}]}}A_1\exp(-\frac{1}{\hbar}\int_{r_2}^{r}\sqrt{2m(-E+V(r'))}dr'), r \ge r_2$$

$$\Psi_2 = \frac{1}{\sqrt{\sqrt{2m(-E+V(r))}]}}A_2\exp(\frac{1}{\hbar}\int_{r_1}^{r}\sqrt{2m(-E+V(r'))}dr'), r \le r_1$$

$$\Psi_3 = \frac{1}{\sqrt{\sqrt{2m(E-V(r))}]}}[A_3\exp\int_{r_1}^{r}(\frac{i}{\hbar}\sqrt{2m(E-V(r'))}dr') - A_{3'}\exp\int_{r}^{r_2}(-\frac{i}{\hbar}\sqrt{2m(E-V(r'))}dr')], r_1 \le r \le r_2$$

.

The first two decay exponentially within the two classically forbidden regions. The third is a combination of the two independent solutions within the classically allowed region, with the amplitudes of the two solutions defined by the coefficients A_3 and $A_{3'}$. The amplitudes A_1 and A_2 multiply the wave functions in the two classically forbidden regions, and all four amplitudes as well as the energy E must be determined by (i) normalizing the total wave function to obey

$$\int_{-\infty}^{\infty} \Psi^* \Psi dr = 1$$

and (2) by matching the wave functions Ψ_1 and Ψ_3 and their first derivatives at $r = r_1$, and the wave functions Ψ_2 and Ψ_3 and their first derivatives at $r = r_2$.

Before addressing how this wave function matching might be accomplished, let me point out an interesting property of the factor entering into the exponential of the semi-classical wave function. We first use the two expressions

$$\frac{dW_0}{dr} = \pm\sqrt{2m(E - V(r))}$$

and

$$\frac{dW_1}{dr} = \frac{i\dfrac{d\sqrt{2m(E-V)}}{dr}}{2\sqrt{2m(E-V)}}$$

given above for the first two components of W(r) and then make use of the harmonic form of V(r)

$$V(r) = \frac{1}{2}kr^2 .$$

Next, we evaluate the integral of dW/dr for a closed classical path in which the system moves from the left turning point

$$r_1 = -\sqrt{\frac{2E}{k}}$$

to the right turning point

$$r_2 = \sqrt{\frac{2E}{k}}$$

and back again to the left turning point. The contribution from integrating dW_0/dr along this closed path is (n.b., the + sign is used for the first part of the path because the particle has positive momentum, and the – sign applies to the return part of the path when the particle has negative momentum):

$$W_0 = \int_{r_1}^{r_2} \sqrt{2m(E - \frac{1}{2}kr^2)}dr - \int_{r_2}^{r_1} \sqrt{2m(E - \frac{1}{2}kr^2)}dr$$

which is exactly the action integral we treated earlier in this Chapter when we computed $\int p(r)dr$ for the classical harmonic oscillator. The contribution from integrating dW_1/dr along this closed path can be evaluated by first writing

$$\frac{dW_1}{dr} = \frac{\pm i\frac{d\sqrt{2m(E - 1/2kr^2)}}{dr}}{\pm 2\sqrt{2m(E - 1/2kr^2)}} = \frac{-ikr}{4(E - 1/2kr^2)}.$$

The integral from r_1 to r_2 of this quantity can be carried out (using the substitution $r = (2E/k)^{1/2} y$) as

$$\frac{-ik}{4}\int_{-\sqrt{\frac{2E}{k}}}^{\sqrt{\frac{2E}{k}}}\frac{rdr}{(E-1/2kr^2)}=\frac{-ik}{4}\int_{-1}^{1}\frac{\frac{2E}{k}ydy}{E(1-y^2)}=\frac{-i}{4}\int_{-1}^{1}\frac{ydy}{(1-y)(1+y)}.$$

The evaluation of the integral remaining on the right-hand side can be done using contour integration (undergraduate students may not have encountered this subject within complex variable theory; I refer them to pp. 367-377 *Methods of Theoretical Physics*, P. M. Morse and H. Feshabach, McGraw-Hill, New York (1953) or p. 113 *Applied Complex Variables*, J. W. Dettman, Macmillan Co. New York (1965)). The basic equation from contour integration says that an integral of the form $\int\frac{f(z)}{(z-a)}dz$, where z = a is a singularity, is equal to $2\pi i f(a)$. Our integral has singularities at y = 1 and at y = -1, so there are two such contributions. The net result is that our integral reduces to

$$\frac{-i}{4}\int_{-1}^{1}\frac{ydy}{(1-y)(1+y)}=\frac{i}{4}2\pi i[\frac{1}{2}+\frac{-1}{-2}]=-\frac{\pi}{2}.$$

So, the contribution to the integral of dW_1/dr arising from r_1 to r_2 is equal to $-\pi/2$. The integral from r_2 back to r_1 gives another factor or $-\pi/2$. Combining the integral of dW_0/dr and the integral of dW_1/dr (multiplied by $\hbar$ because $W = W_0 + \hbar W_1 + \ldots$) gives the following final result

$$W=\int_{r_1}^{r_2}\sqrt{2m(E-\frac{1}{2}kr^2)}dr-\int_{r_2}^{r_1}\sqrt{2m(E-\frac{1}{2}kr^2)}dr-\pi\hbar.$$

If the original Bohr quantization is applied to the integral of dW/dr along a closed classical path:

$$W=nh, n=0,1,2,...$$

our result above then says that

$$nh = \int_{r_1}^{r_2} \sqrt{2m(E - \frac{1}{2}kr^2)}dr - \int_{r_2}^{r_1} \sqrt{2m(E - \frac{1}{2}kr^2)}dr - 1/2h$$

which is the same as

$$\int p(r)dr = (n + 1/2)h .$$

This means that the ½ factor that arises in the action quantization condition for periodic motions between two turning points can be viewed as arising from the first quantum correction (i.e., the term first order in $\hbar$) to the semi-classical wave function. Recall that equating this classical action integral to (n+1/2) h gave the correct (i.e., quantum) energies for this harmonic oscillator problem.

We have seen how a semi-classical wave function can be defined, what its spatial probability density is, how it can build in interference (to achieve proper nodal patterns), and how quantizing its action can give the correct allowed energy levels. However, there is one issue we have not fully addressed. To solve for the coefficients (A_1, … A_3,) multiplying the semi-classical wave functions in the classically allowed and forbidden regions, the wave functions Ψ_1 and Ψ_3 and their first derivatives must be matched at r = r_1, and the wave functions Ψ_2 and Ψ_3 and their first derivatives must be matched at r = r_2. Unfortunately, the details of this matching process are rather complicated and require examining in more detail the nature of the wave functions near the classical turning points where each of Ψ_1, Ψ_2, and Ψ_3 contain factors of the form $\sqrt{\sqrt{2m(-E + V(r))]}}$ in their denominators. It should be clear that matching functions and their derivatives that contain such singularities pose special challenges. I will not go further into this matter here; rather, I refer the interested reader to pp. 268-279 of Quantum Mechanics, 3rd Ed., L. I. Schiff, McGraw-Hill, New York (1968) for a good treatment of this so-called WKB approach to the matching issue.

1.5 Chapter Summary

In this Chapter, you should have learned about the following things:

1. Why quantum mechanics is needed; that is, what things classical mechanics does not describe correctly. How quantum and classical descriptions can sometimes agree and when they will not. How certain questions can only be asked when classical mechanics applies, not when quantum mechanics is needed.
2. The Schrödinger equation, operators, wave functions, eigenvalues and eigenfunctions and their relations to experimental observations.
3. Time propagation of wave functions.
4. Free particle motion and corresponding eigenfunctions in one, two, and three dimensions and the associated energy levels, and the relevance of these models to various chemistry issues.
5. Action quantization and the resulting semi-classical wave functions and how this point of view offers connections between classical and quantum perspectives.