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 are covered in depth appropriate to a graduate-student reader.

Chapter 1. The Basics of Quantum Mechanics

Why Quantum Mechanics is Necessary for Describing Molecular Properties.

We know that all molecules are made of atoms which, in turn, contain nuclei and electrons. As I discuss in this introductory section, 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, 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.

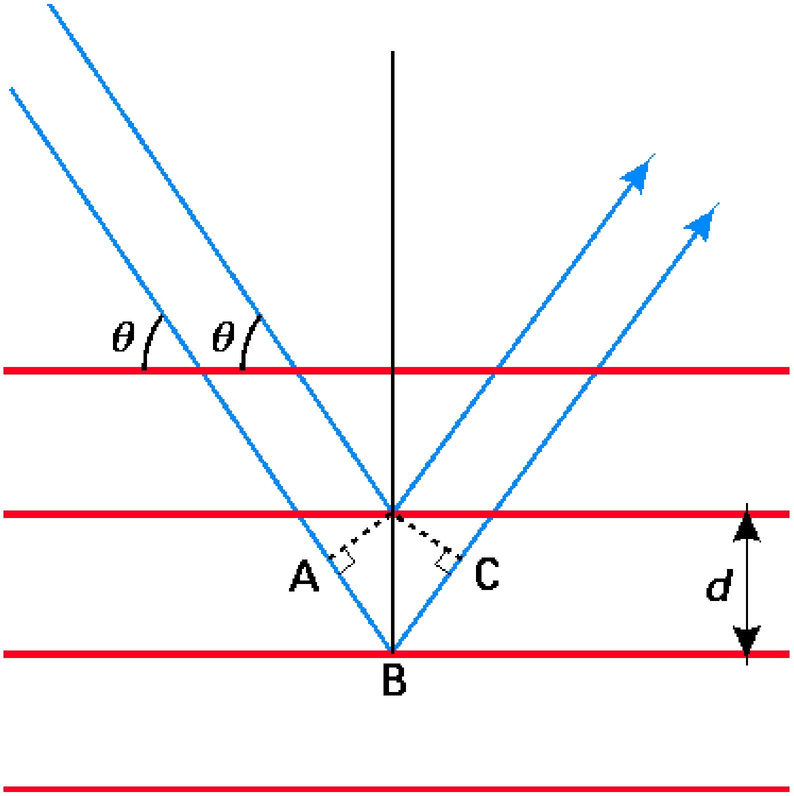


Figure 1.1. Scattering of two beams at angle θ from two planes in a crystal spaced by d.

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 ($6.62\ \text{x}10^{-27}$ 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.

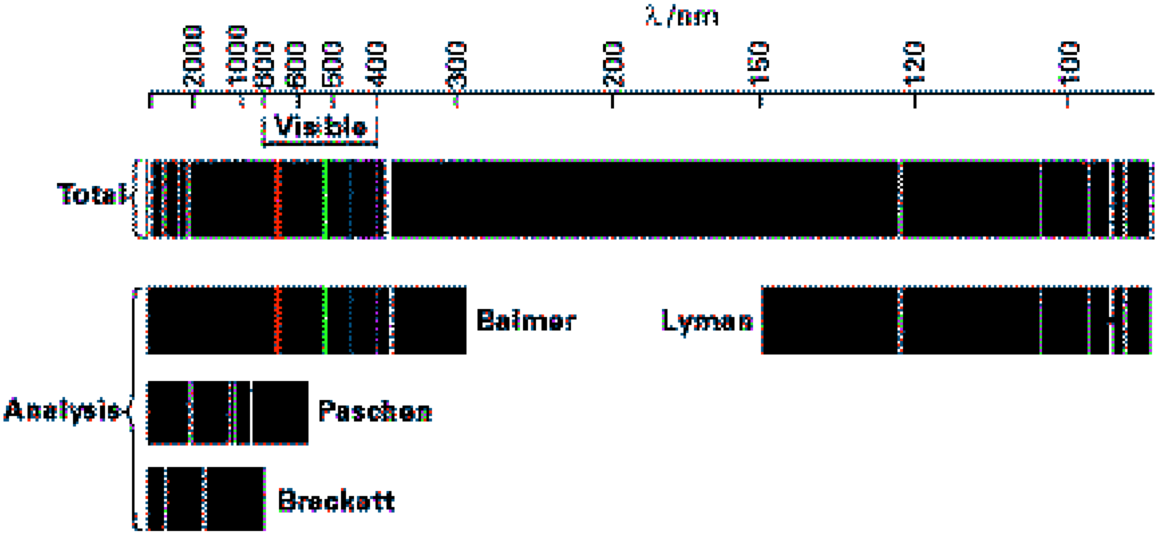
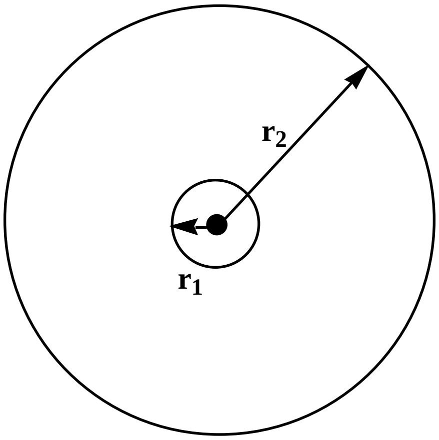


Figure 1.2. Emission spectrum of atomic hydrogen with some lines repeated below to illustrate the series to which they belong.

In the top panel, we see all of the lines emitted with their wave lengths indicated in nano-meters. 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 $r \to \infty$, 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 $2\pi r$ equal 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 $\lambda = h/p = h/(mv)$, $2\pi r = n\lambda$, 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:

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

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, high velocities 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.) to very high precision. In such an interpretation of the experimental data, one claims that a photon of energy

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

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:

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

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 valence electron. The primary reason for the breakdown of the Bohr formula is the neglect of electron-electron Coulomb repulsions in its derivation. Nevertheless, the success of this 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 the equations are that 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 Schrödiger 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 travelling 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.

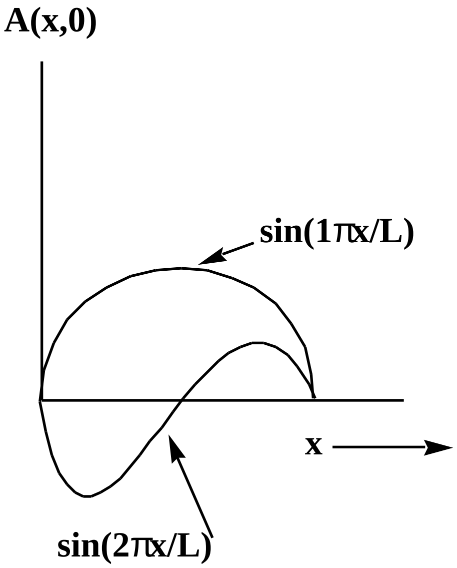


Figure 1.4. Fundamental and first overtone notes of a violin string.

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

$$\lambda = L/n,$$

where n = 1, 2, 3, 4, ...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. 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. 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,

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

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

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

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 uderlying fundamental basis from which the basic laws of quantum mechanics follows 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 will reduce 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. Briefly, 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.

I. 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 mulitples of $h/2\pi$ (which is often abbreviated as $\hbar$), which can be shown to be equivalent to the Borh 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.

A. 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.

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. 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

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

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

$$F=\Sigma_{j=1,N}\,Z_jex_j,$$

for which the quantum operator is

$$\mathbf{F}=\Sigma_{j=1,N}\,Z_jex_j\ ,$$

where Z_je is the charge on the jth particle. Notice that in this case, classical and quantum forms are identical because F contains no momentum operators.

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 only 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.

B. 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.

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 q_j at a particular value at a particular time $|\Psi(q_j,t)|^2$. Knowledge of the corresponding momenta as functions of time is also relinquished in quantum mechanics; again, only knowledge of the probability density for finding p_j with any particular value at a particular time t remains.

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 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.

What happens if some other property G, whose quantum mechanical operator is **G** is measured in such a case? 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 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:

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

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.

So, 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 the two operators do not commute, one simply can not 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 eigenfuction. 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 eigenfuntion of the second operator and thus no longer the eigenfunction of the first.

C. 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 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

$$E = \Sigma_i \{ p_i^2/2m_e + 1/2\ \Sigma_j\ e^2/r_{i,j} - \Sigma_a\ Z_a e^2/r_{i,a} \}$$

$$+ \Sigma_a \{p_a^2/2m_a + 1/2\ \Sigma_b\ Z_a Z_b e^2/r_{a,b} \},$$

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

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

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

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

$$\Sigma_i \{ - (\hbar^2/2m_e)\, \partial^2/\partial q_i^2 + 1/2\, \Sigma_j\, e^2/r_{i,j} - \Sigma_a\, Z_a e^2/r_{i,a} \}\, \Psi$$

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

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

$$\Sigma_a\, Z_z e\, X_a\, \mathbf{E} \cos(\omega t) - \Sigma_j\, e\, x_j\, \mathbf{E} \cos(\omega t)$$

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 a so-called 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 $(-\hbar^2/2M)\,\partial^2/\partial\varphi^2 = \mathbf{H}$, then functions of the form $\exp(i\,m\varphi)$ would be eigenfunctions because

$$\{ -\hbar^2/2M\,\partial^2/\partial\varphi^2\}\exp(i\,m\varphi) = \{ m^2\hbar^2/2M \}\exp(i\,m\varphi).$$

In this case, $m^2\hbar^2/2M$ 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 is to equal $-i\hbar\, d/d\varphi$).

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 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.

3. The Born-Oppenheimer Approximation

One of the most important approximations relating to applying quantum mechanics to molecules 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

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

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

the time scales with which the electrons and nuclei move are generally 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. Thus, we expect the electrons to be able to “adjust” their motions to the much more slowly moving nuclei. This observation motivates us to solve 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.

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

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

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.

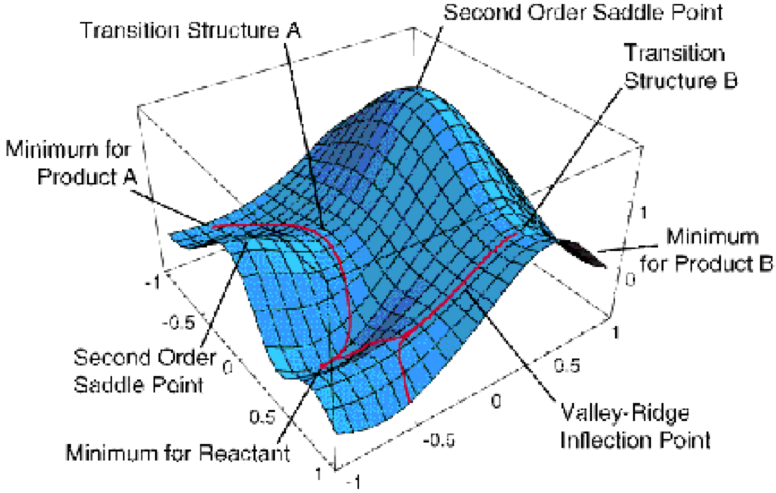


Figure 1. 5. Two dimensional potential energy surface showing local minima, transition states and paths connecting them.

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 $\Sigma_a \{ - (\hbar^2/2m_a) \partial^2/\partial q_a^2 + 1/2 \Sigma_b Z_aZ_be^2/r_{a,b} \} + E_K(q_a)$ 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 states as well as the n→ π* and π → π* electronic states and their vibrational 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.

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.

II. 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.

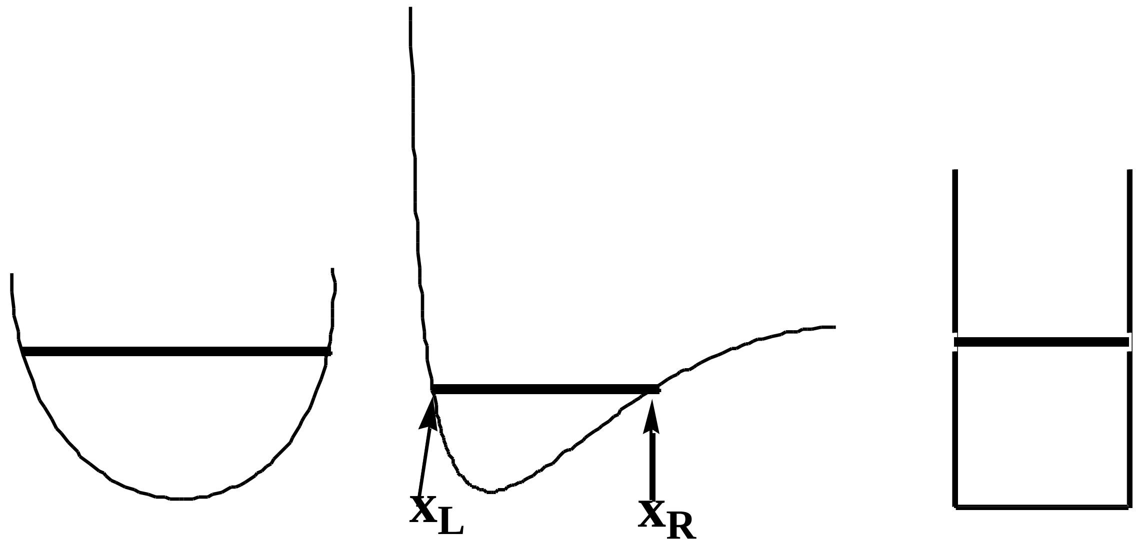


Figure 1. 6. Three characteristic potentials showing left and right classical turning points at energies denoted by the horizontal lines.

A. 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 this probability amplitude P(x) by dividing the spatial distance dx by the velocity of the particle at the point x:

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

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.

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.

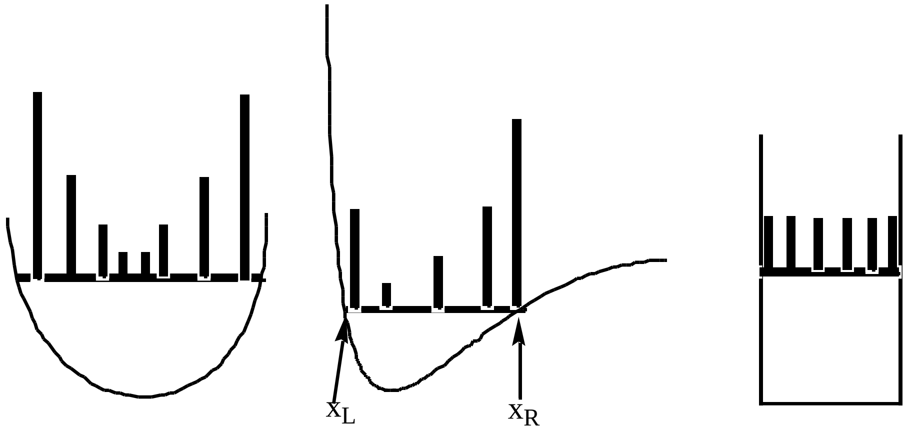


Figure 1. 7 Classical probability plots for the three potentials shown

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!).

B. The Quantum Treatment

To solve for the quantum mechanical wave functions and energies of this same 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. B. 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 can not access these regions 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 can not be discontinuously related to the probability of it being at a nearby point.

C. The 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:

$$\psi = \sin(kx) \text{ and } \psi = \cos(kx), \text{ where k is defined as } k=(2mE/\hbar^2)^{1/2}.$$

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

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

The fact that ψ must vanish at x= 0 (n.b., ψ vanishes for $x< 0$ and 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 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 π (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 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).

D. The Probability Densities

Let's now look at some of the wave functions $\Psi(x)$ 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 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).

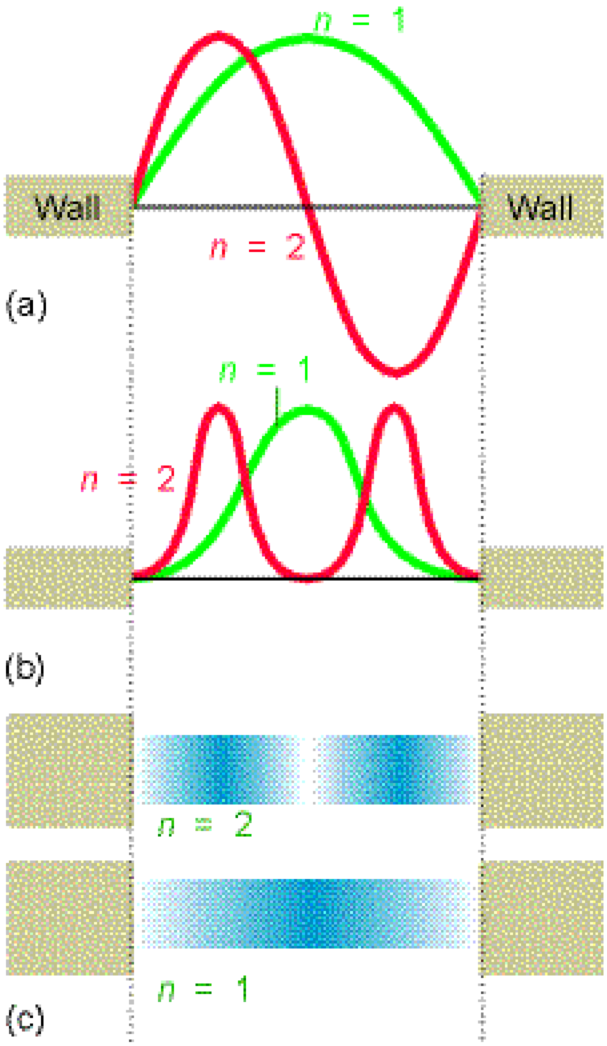


Figure 1. 8. The two lowest wave functions and probability densities

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

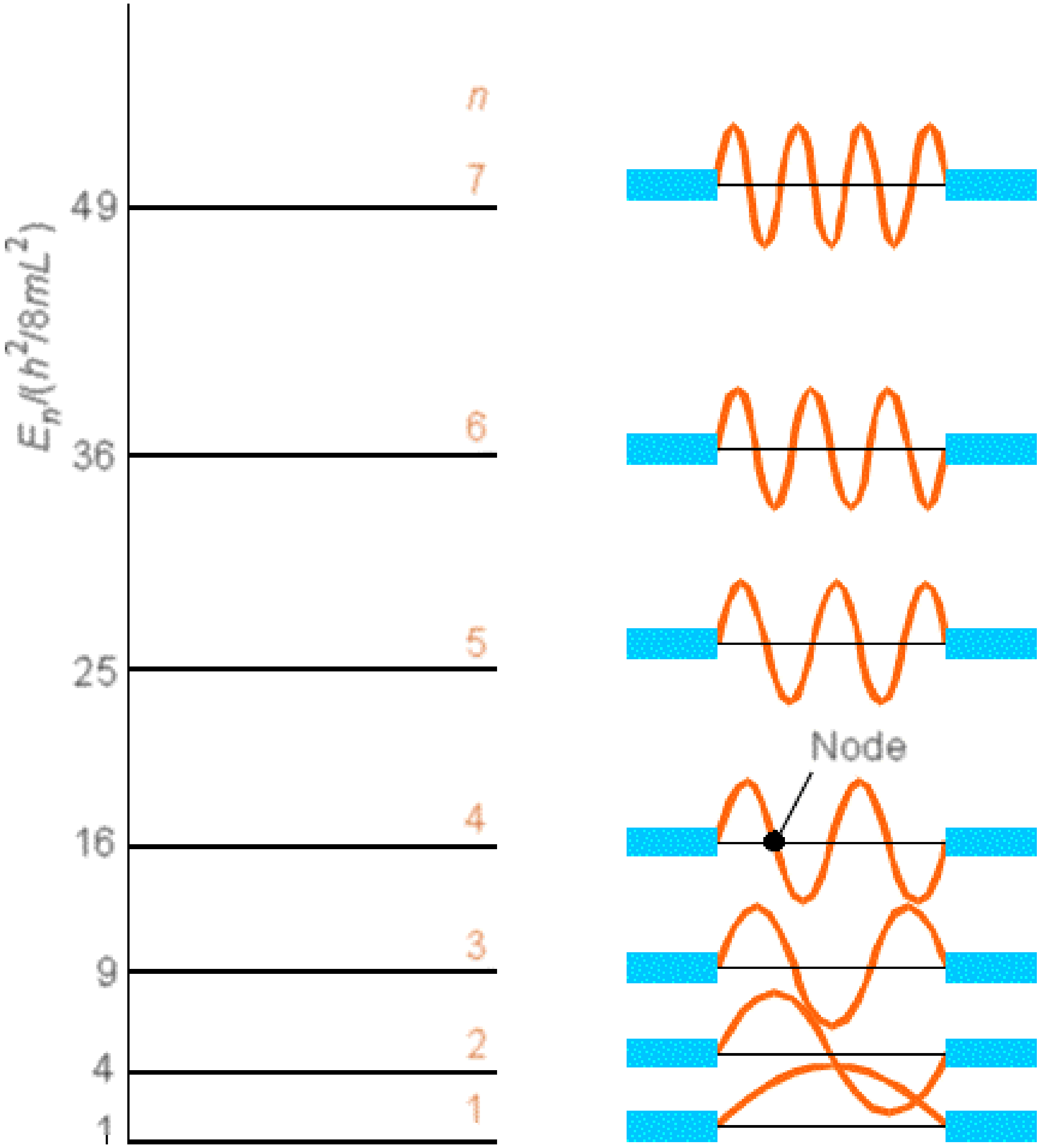


Figure 1. 9. Seven lowest wave functions and energies

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.

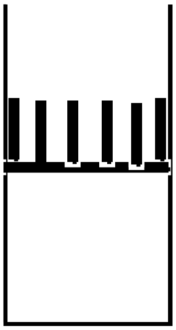


Figure 1. 10. Classical probability density for potential shown

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. 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 probabilty of being somewhere (i.e., $|\Psi|^2$). The next section will treat such paradoxical issues even further.

E. 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. B. 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.

For the n = 1 case, 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 n = 2 P(x) plot 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 very 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 same 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 can not 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 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 Ψ(x) plot shown in Fig. B.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.

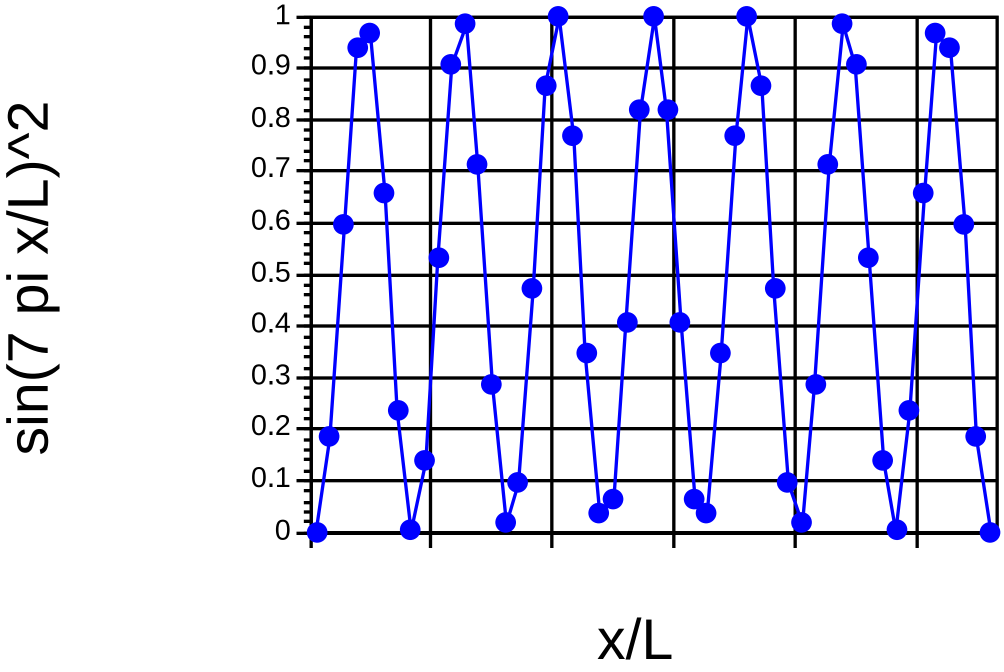


Figure 1. 11. Quantum probability density for n = 7 showing seven peaks and six nodes

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. In fact, 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. It is also true that classical and quantum results agree when one is dealing with heavy particles. For example, a given particle-in-a-box energy $E_n = n^2 \hbar^2/(2mL^2)$ would be achieved for a heavier particle at higher n-values than for a lighter particle. Hence, heavier particles, moving with a given energy E, have higher n and thus more classical probability distributions.

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.

Another thing I would like you to be aware of concerning the solutions ψ and E to this Schrödinger equation is that each pair of wave functions ψ_n and $\psi_{n'}$ belonging to different quantum numbers n and n' (and to different energies) display a property termed orthonormality. This property means that not only are ψ_n and $\psi_{n'}$ each normalized

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

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 (you have only seen one such case thus far- the exp(imφ) eigenfunctions of the z-component of angular momentm). It is common to write the integrals displaying the normalization and orthogonality conditions in the following so-called Dirac notation

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

where the | > and < | symbols represent ψ and ψ^*, respectively, and putting the two together in the < | > construct implies the integration over the variable that ψ depends upon.

The orthogonality conditon 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 $\mathbf{v}_1 \cdot \mathbf{v}_2 = 0$. I want you to keep this property in mind because you will soon see that it is a characteristic not only of these particle-in-a-box wave functions but of all wave functions obtained from any Schrödinger equation.

In fact, the orthogonality property is even broader than the above discussion suggests. It turns out that all quantum mechanical operators formed as discussed earlier (replacing Cartesian momenta p by the corresponding $-i \hbar \partial/\partial q$ operator and leaving all Cartesian coordinates as they are) can be shown to be so-called Hermitian operators. This means that they form Hermitian matrices when they are 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 $\{\varphi_J\}$ is:

$$F_{I,J} = \langle\varphi_I | \mathbf{F} |\varphi_J\rangle = \int \varphi_I^* \mathbf{F} \varphi_J \, dq.$$

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.

So, all quantum mechanical operators, not just the Hamiltonian, have real eigenvalues (this is good since these eigenvalues are what can be measured in any experimental observation of that property) and orthogonal eigenfunctions. It is important to keep these facts in mind because we make use of them many times throughout this text.

F. Time Propagation of Wave functions

For a 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

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

which 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:

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

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

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

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

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

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

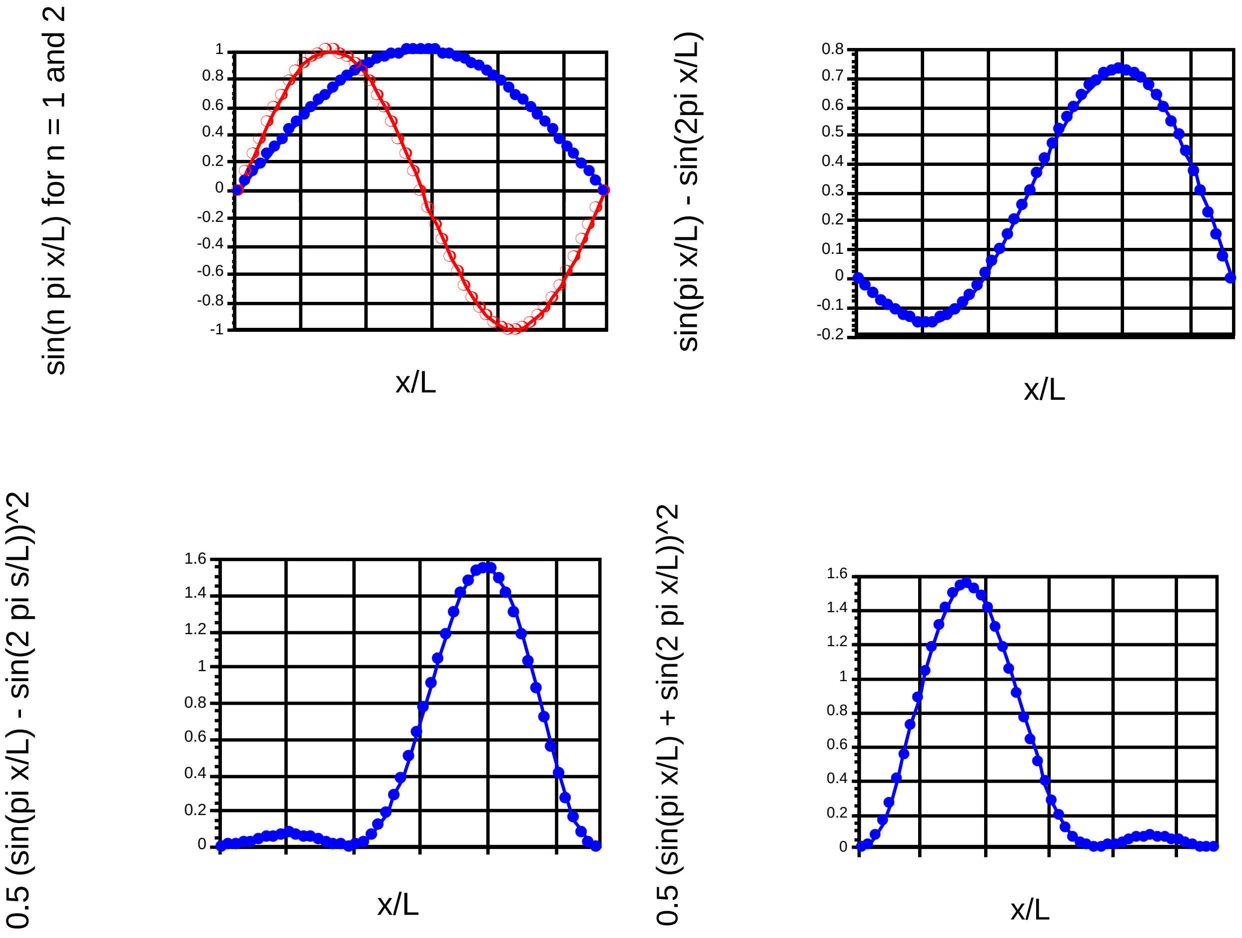


Figure 1. 12. The n = 1 and n = 2 wave functions, their superposition, and the t = 0 and time-evolved probability densities of the superposition

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.

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

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

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

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 length $\delta t = \pi\hbar/(E_2-E_1)$, 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. B. 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 the figure. 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. This is an important observation that I hope the student will keep fresh in mind. It is also an important ingredient in modern quantum dynamics in which localized wave packets, similar to superposed eigenstates, 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 can be expressed as a linear combination (i.e., superposition) of eigenstates of the problem at hand. As noted above, there is a large amount of current effort in the theoretical chemistry community aimed at developing efficient approximations to the $\exp(-itH/\hbar)$ 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 and my QMIC text book. However, let's spend a little time on a brief introduction to what is involved.

The problem is to express exp(-itH/$\hbar$) $\Psi(q_j)$, 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:

$$\Psi = \Sigma_J C_J \Psi_J$$

after which the desired function is written as

$$\exp(-itH/\hbar)\ \Psi(q_j) = \Sigma_J C_J \Psi_J \exp(-itE_J/\hbar).$$

The basic idea is to break 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., 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 common approaches to approximating exp(-itH/$\hbar$) is to write this single exponential in terms of exp(-itT/$\hbar$) and exp(-itV/$\hbar$). However, the identity

$$\exp(-itH/\hbar) = \exp(-itV/\hbar)\ \exp(-itT/\hbar)$$

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:

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

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 $U(\tau,0)$.

To progress further, one then expresses $\exp(-i\tau T/\hbar)$ acting on the initial function $\Psi(q)$ 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

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

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 $\Psi(q)$ as

$$\Psi(q) = \int \delta(q-q')\, \Psi(q'),$$

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

$$\Psi(q) = \iint \psi_p(q)\, \psi_p^*(q')\, \Psi(q')\, dq'\, dp.$$

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

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

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

$$\exp(-i\tau T/\hbar)\ \Psi(q) = \iint \exp(-i\tau p^2\hbar^2/2m\hbar)\ (1/2\pi)^{1/2} \exp(ip(q-q')/\hbar)\ (1/2\pi)^{1/2}\ \Psi(q')\ dq'\ dp.$$

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

$$\exp(-i\tau T/\hbar)\ \Psi(q) = (m/2\pi\tau\hbar)^{1/2} \int \exp(im(q-q')^2/2\tau\hbar)\ \Psi(q')\ dq'.$$

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

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

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 to know any of the eigenfunctions of the Hamiltonian to apply this method. 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 $t = P\,\tau$.

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.

III. 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

A. 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), and assume that the electron experiences a constant and not time-varying potential V_0 at all points in this plane. 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 ψ(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;

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

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). 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 as $E_x + E_y = E-V_0$. 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).

B. 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 $V_0(x,y)$ 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 $y=L_y$, 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:

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

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

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

$E_y = n_y^2\pi^2 \hbar^2/(2mL_y^2)$, with n_x and n_y =1,2,3, ...

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 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, when a linear triatomic molecule has more than enough energy in one of its bonds to rupture it but not much energy in the other bond; the first bond's energy lies in the continuum, but the second bond's energy is quantized.

Perhaps more interesting is the case in which 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. In this case, one has two degenerate states- i. the strong bond having high internal energy and the weak bond having low energy (ψ_1), and ii. 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., $\psi = C_1\psi_1 + C_2\psi_2$ 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) usually causes the true wave function

$\Psi = \exp(-it\mathbf{H}/\hbar)\ \psi$ 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.

C. 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.

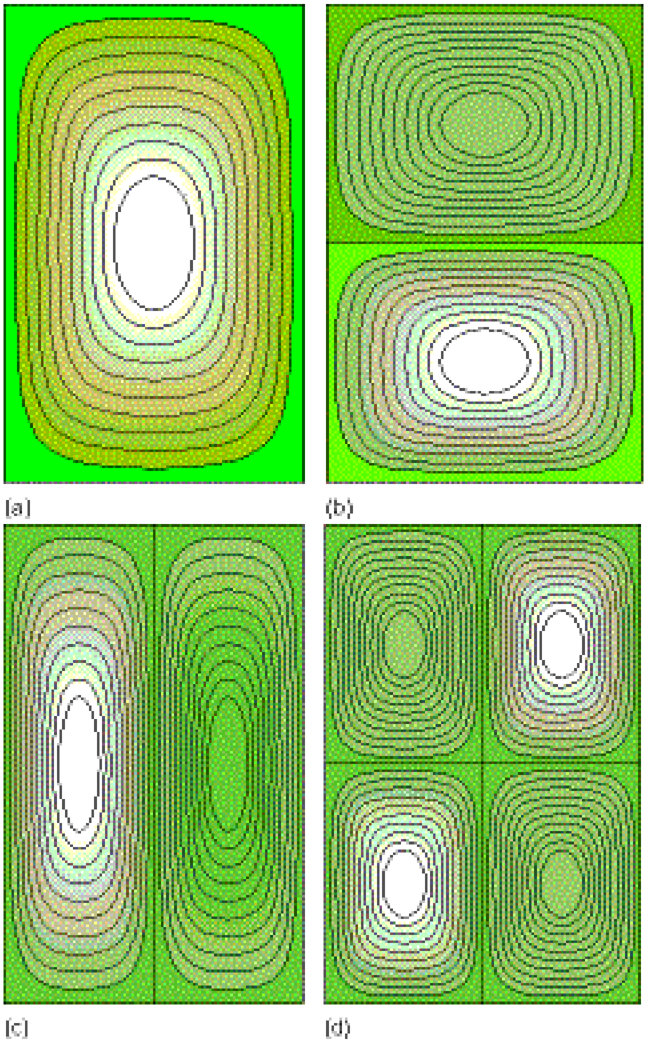


Figure 1. 13. Plots of the (1,1), (2,1), (1,2) and (2,2) wave functions

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.

D. 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:

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

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. An example will help clarify these matters.

For systems such as the above particle in a box example for which the Hamiltonian is separable, the action integral decomposes into a sum of such integrals, one for each degree of freedom. In this 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. 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 existence of quantized energy levels has been shown to involve equating the classical action for motion on a closed path to an integral multiple of Planck's constant:

$$S_{\text{closed}} = \int_{\mathbf{q}_i;t_i}^{\mathbf{q}_f=\mathbf{q}_i;t_f} \mathbf{p}\cdot \mathbf{dq} = n\,h. \qquad (n = 1, 2, 3, 4, ...)$$

Applied to each of the independent coordinates of the two-dimensional particle in a box problem, this expression reads:

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

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

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 vanishes, so $V(x) = V(y) = 0$. Using this fact, and reversing the upper and lower limits, and thus the sign, in the second integrals above, one obtains:

$$n_x h = 2 \int_{x=0}^{x=L_x} \sqrt{2mE_x}\, dx = 2 \sqrt{2mE_x}\; L_x$$

$$n_y h = 2 \int_{y=0}^{y=L_y} \sqrt{2mE_y}\, dy = 2 \sqrt{2mE_y}\; L_y.$$

Solving for E_x and E_y, one finds:

$$E_x = \frac{(n_x h)^2}{8mL_x^2}$$

$$E_y = \frac{(n_y h)^2}{8mL_y^2} \quad .$$

These are 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 this case, one says that the Bohr-Sommerfeld quantization condition:

$$n\, h = \int_{\mathbf{q}_i;t_i}^{\mathbf{q}_f=\mathbf{q}_i;t_f} \mathbf{p}\cdot \mathbf{dq}$$

has been used to obtain the 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 appending quantal 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.

E. Quantized Action Does Not Always Work

Unfortunately, the approach of quantizing the action does not always yield the correct expression for the quantized energies. For example, when applied to the so-called harmonic oscillator problem that we will study in quantum form later, which serves as the simplest reasonable model for vibration of a diatomic molecule AB, one expresses the total energy as

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

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

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

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 h gives the following expression for the energy E:

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

where the quantum number n is allowed to assume integer values ranging from n = 0, 1, 2, to infinity. The problem with this result is that it is wrong! As experimental data clearly show, the lowest-energy level for the vibrations of a molecule do not have E = 0; they have a "zero-point" energy that is approximately equal to $1/2\ (h/2\pi)\ [k/\mu]^{1/2}$. So, although the action quantization condition yields energies whose spacings are reasonably in agreement with laboratory data for low-energy states (e.g., such states have approximately constant spacings), it fails to predict the zero-point energy content of such vibrations. As we will see later, a proper quantum mechanical treatment of the harmonic oscillator yields energies of the form

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

which differs from the action-based result by the proper zero-point energy.

Even with such difficulties known, much progress has been made in extending the most elementary action-based methods to more and more systems by introducing, for example, rules that allow the quantum number n to assume half-integer as well as integer values. Clearly, if n were allowed to equal 1/2, 3/2, 5/2, ..., the earlier action integral would have produced the correct result. However, how does one know when to allow n to assume only integer or only half-integer or both integer and half-integer values. The answers to this question are beyond the scope of this text and constitute an active area of research. For now, it is enough for the student to be aware that one can often find energy levels by using action integrals, but one must be careful in doing so because sometimes the answers are wrong.

Before leaving this section, it is worth noting that the appearance of half-integer quantum numbers does not only occur in the harmonic oscillator case. To illustrate, let us consider the L_z angular momentum operator discussed earlier. As we showed, this operator, when computed as the z-component of **r x p**, can be written in polar (r, θ, φ) coordinates as

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

The eigenfunctions of this operator have the form exp(iaφ), and the eigenvalues are a $\hbar$. 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 $\hbar$ 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. For example, a boron atom with 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.

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, when electrons, protons, or neutrons are subjected to the kind of magnetic field experiment mentioned above, these particles are observed to have only two z-component eigenvalues. Because, as we discuss later in this text, all angular momenta have z-component eigenvalues that are separated from one aother by unit multiples of $\hbar$, one is forced to conclude that these three fundamental building-block particles have z-component eigenvalues of 1/2 $\hbar$ and – 1/2 $\hbar$. The appearance of half-integral angular momenta is not consistent with the observation made earlier that φ and $\varphi + 2\pi$ 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?) involved 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 ħ and – 1/2 ħ 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 ħ and – 1/2 ħ states, as do neutrons. All such half-integral angular momentum states can not be accounted for using classical mechanics but are known to arise in quantum mechanics.

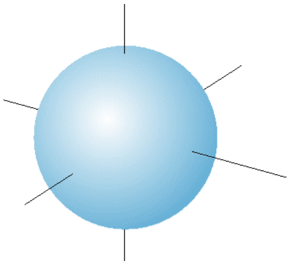
Chapter 2. Model Problems That Form Important Starting Points

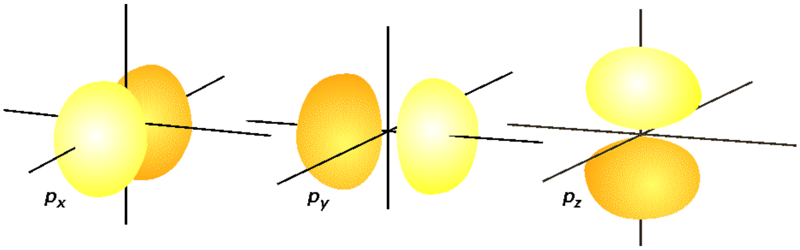
The model problems discussed in this Section form the basis for chemists’ understanding of the electronic states of atoms, molecules, clusters, and solids as well as the rotational and vibrational motions of molecules.

I. Free Electron Model of Polyenes

The particle-in-a-box problem provides an important model for several relevant chemical situations

The 'particle in a box' model for motion in two dimensions discussed earlier can obviously be extended to three dimensions or to one. For two and three dimensions, it provides a crude but useful picture for electronic states on surfaces or in metallic crystals, respectively. I say metallic crystals because it is in such systems that the outermost valence electrons are reasonably well treated as moving freely. Free motion within a spherical volume gives rise to eigenfunctions that are used in nuclear physics to describe the motions of neutrons and protons in nuclei. In the so-called shell model of nuclei, the neutrons and protons fill separate s, p, d, etc. orbitals with each type of nucleon forced to obey the Pauli principle (i.e., to have no more than two nucleons in each orbital because protons and neutrons are Fermions). To remind you, I display in Fig. 2. 1 the angular shapes that characterize s, p, and d orbitals.





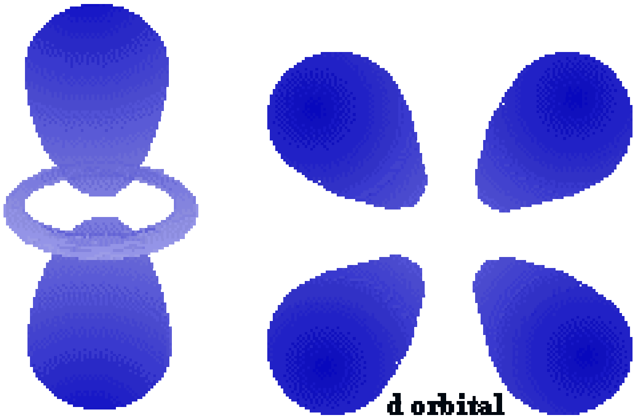
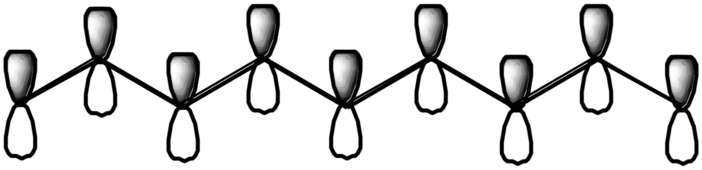


Figure 2.1. The angular shapes of s, p, and d functions

This same spherical box model has also been used to describe the orbitals of valence electrons in clusters of metal atoms such as Cs_n, Cu_n, Na_n and their positive and negative ions. Because of the metallic nature of these species, their valence electrons are essentially free to roam over the entire spherical volume of the cluster, which renders this simple model rather effective. In this model, one thinks of each electron being free to roam within a sphere of radius R (i.e., having a potential that is uniform within the sphere and infinite outside the sphere). Finally, as noted above, this same spherical box model forms the basis of the so-called shell model of nuclear structure. In this model, one assumes that the protons and neutrons that make up a nucleus, both of which are Fermions, occupy spherical-box orbitals (one set of orbitals for protons, another set for neutrons because they are distinguishable from one another). By placing the protons and neutrons into these orbitals, two to an orbital, one achieves a description of the energy levels of the nucleus. Excited states are achieved by promoting a neutron or proton from an occupied orbital to a virtual (i.e., previously unoccupied) orbital. In such a model, especially stable nuclei are achieved when "closed-shell" configurations such as $1s^2$ or $1s^2 2s^2 2p^6$ are realized (e.g., ^{4}He has both neutrons and protons in $1s^2$ configurations).

The orbitals that solve the Schrödinger equation inside such a spherical box are not the same in their radial 'shapes' as the s, p, d, etc. orbitals of atoms because, in atoms, there is an additional radial potential $V(r) = -Ze^2/r$ present. However, their angular shapes are the same as in atomic structure because, in both cases, the potential is independent of θ and ϕ. As the orbital plots shown above indicate, the angular shapes of s, p, and d orbitals display varying number of nodal surfaces. The s orbitals have none, p orbitals have one, and d orbitals have two. Analogous to how the number of nodes related to the total energy of the particle constrained to the x, y plane, the number of nodes in the angular wave functions indicates the amount of angular or rotational energy. Orbitals of s shape have no angular energy, those of p shape have less then do d orbitals, etc.

One-dimensional free particle motion provides a qualitatively correct picture for π-electron motion along the p_π orbitals of delocalized polyenes. The one Cartesian dimension then corresponds to motion along the delocalized chain. In such a model, the box length L is related to the carbon-carbon bond length R and the number N of carbon centers involved in the delocalized network $L=(N-1) R$. In Fig. 2.2, such a conjugated network involving nine centers is depicted. In this example, the box length would be eight times the C-C bond length.



Conjugated π Network with 9 Centers Involved

Figure 2.2. The π atomic orbitals of a conjugated chain of nine carbon atoms

The eigenstates $\psi_n(x)$ and their energies E_n represent orbitals into which electrons are placed. In the example case, if nine π electrons are present (e.g., as in the 1,3,5,7-nonatetraene radical), the ground electronic state would be represented by a total wave function consisting of a product in which the lowest four ψ's are doubly occupied and the fifth ψ is singly occupied:

$$\Psi = \psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\psi_3\alpha\psi_3\beta\psi_4\alpha\psi_4\beta\psi_5\alpha.$$

The z-component angular momentum states of the electrons are labeled α and β as discussed earlier.

A product wave function is appropriate because the total Hamiltonian involves the kinetic plus potential energies of nine electrons. To the extent that this total energy can be represented as the sum of nine separate energies, one for each electron, the Hamiltonian allows a separation of variables

$$H \quad \Sigma_j H(j)$$

in which each H(j) describes the kinetic and potential energy of an individual electron. Recall that when a partial differential equation has no operators that couple its different independent variables (i.e., when it is separable), one can use separation of variables methods to decompose its solutions into products. Thus, the (approximate) additivity of H implies that solutions of $H \Psi = E \Psi$ are products of solutions to

$$H (j) \psi(\mathbf{r}_j) = E_j \psi(\mathbf{r}_j).$$

The two lowest π-excited states would correspond to states of the form

$$\Psi^* = \psi_1\alpha\ \psi_1\beta\ \psi_2\alpha\ \psi_2\beta\ \psi_3\alpha\ \psi_3\beta\ \psi_4\alpha\ \psi_5\beta\ \psi_5\alpha \text{ , and}$$

$$\Psi'^* = \psi_1\alpha\ \psi_1\beta\ \psi_2\alpha\ \psi_2\beta\ \psi_3\alpha\ \psi_3\beta\ \psi_4\alpha\ \psi_4\beta\ \psi_6\alpha \text{ ,}$$

where the spin-orbitals (orbitals multiplied by α or β) appearing in the above products depend on the coordinates of the various electrons. For example,

$$\psi_1\alpha\ \psi_1\beta\ \psi_2\alpha\ \psi_2\beta\ \psi_3\alpha\ \psi_3\beta\ \psi_4\alpha\ \psi_5\beta\ \psi_5\alpha$$

denotes

$$\psi_1\alpha(\mathbf{r}_1)\ \psi_1\beta\ (\mathbf{r}_2)\ \psi_2\alpha\ (\mathbf{r}_3)\ \psi_2\beta\ (\mathbf{r}_4)\ \psi_3\alpha\ \ (\mathbf{r}_5)\ \psi_3\beta\ (\mathbf{r}_6)\ \psi_4\alpha\ (\mathbf{r}_7)$$

$$\psi_5\beta\ (\mathbf{r}_8)\ \psi_5\alpha\ (\mathbf{r}_9).$$

The electronic excitation energies from the ground state to each of the above excited states within this model would be

$$\Delta E^* = \pi^2\ \hbar^2/2m\ [\ 5^2/L^2 - 4^2/L^2]\ \text{and}$$

$$\Delta E'^* = \pi^2\ \hbar^2/2m\ [\ 6^2/L^2 - 5^2/L^2].$$

It turns out that this simple model of π-electron energies provides a qualitatively correct picture of such excitation energies. Its simplicity allows one, for example, to easily suggest how a molecule’s color (as reflected in the complementary color of the light the molecule absorbs) varies as the conjugation length L of the molecule varies. That is, longer conjugated molecules have lower-energy orbitals because L^2 appears in the denominator of the energy expression. As a result, longer conjugated molecules absorb light of lower energy than do shorter molecules.

This simple particle-in-a-box model does not yield orbital energies that relate to ionization energies unless the potential 'inside the box' is specified. Choosing the value of this potential V_0 such that $V_0 + \pi^2\ \hbar^2/2m\ [\ 5^2/L^2]$ is equal to minus the lowest ionization energy of the 1,3,5,7-nonatetraene radical, gives energy levels (as $E = V_0 + \pi^2\ \hbar^2/2m$

[n^2/L^2]) which can then be used as approximations to ionization energies.

The individual π-molecular orbitals

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

are depicted in Fig. 2.3 for a model of the 1,3,5 hexatriene π-orbital system for which the 'box length' L is five times the distance R_{CC} between neighboring pairs of carbon atoms. The magnitude of the k^{th} C-atom centered atomic orbital in the n^{th} π-molecular orbital is given by $(2/L)^{1/2} \sin(n\pi k R_{CC}/L)$.

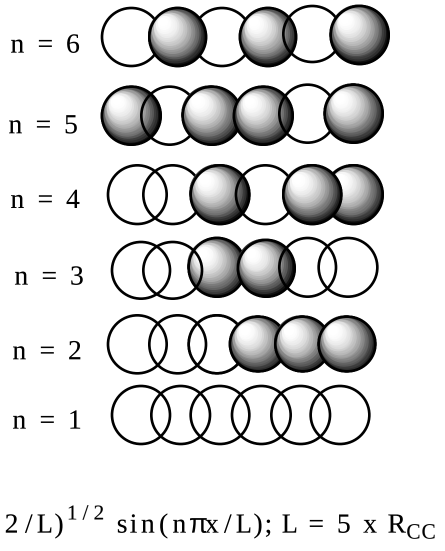


Figure 2.3. The phases of the six molecular orbitals of a chain containing six atoms.

In this figure, positive amplitude is denoted by the clear spheres, and negative amplitude is shown by the darkened spheres. Where two spheres of like shading overlap, the wave function has enhanced amplitude; where two spheres of different shading overlap, a node occurs. Once again, we note that the number of nodes increases as one ranges from the lowest-energy orbital to higher energy orbitals. The reader is once again encouraged to keep in mind this ubiquitous characteristic of quantum mechanical wave functions.

This simple model allows one to estimate spin densities at each carbon center and provides insight into which centers should be most amenable to electrophilic or nucleophilic attack. For example, radical attack at the C_5 carbon of the nine-atom nonatetraene system described earlier would be more facile for the ground state Ψ than for either Ψ* or Ψ'*. In the former, the unpaired spin density resides in ψ_5, which has non-zero amplitude at the C_5 site x=L/2. In Ψ* and Ψ'*, the unpaired density is in ψ_4 and ψ_6, respectively, both of which have zero density at C_5. These densities reflect the values $(2/L)^{1/2}$ $\sin(n\pi kR_{CC}/L)$ of the amplitudes for this case in which L = 8 x R_{CC} for n = 5, 4, and 6, respectively. Plots of the wave functions for n ranging from 1 to 7 are shown in another format in Fig. 2.4 where the nodal pattern is emphasized.

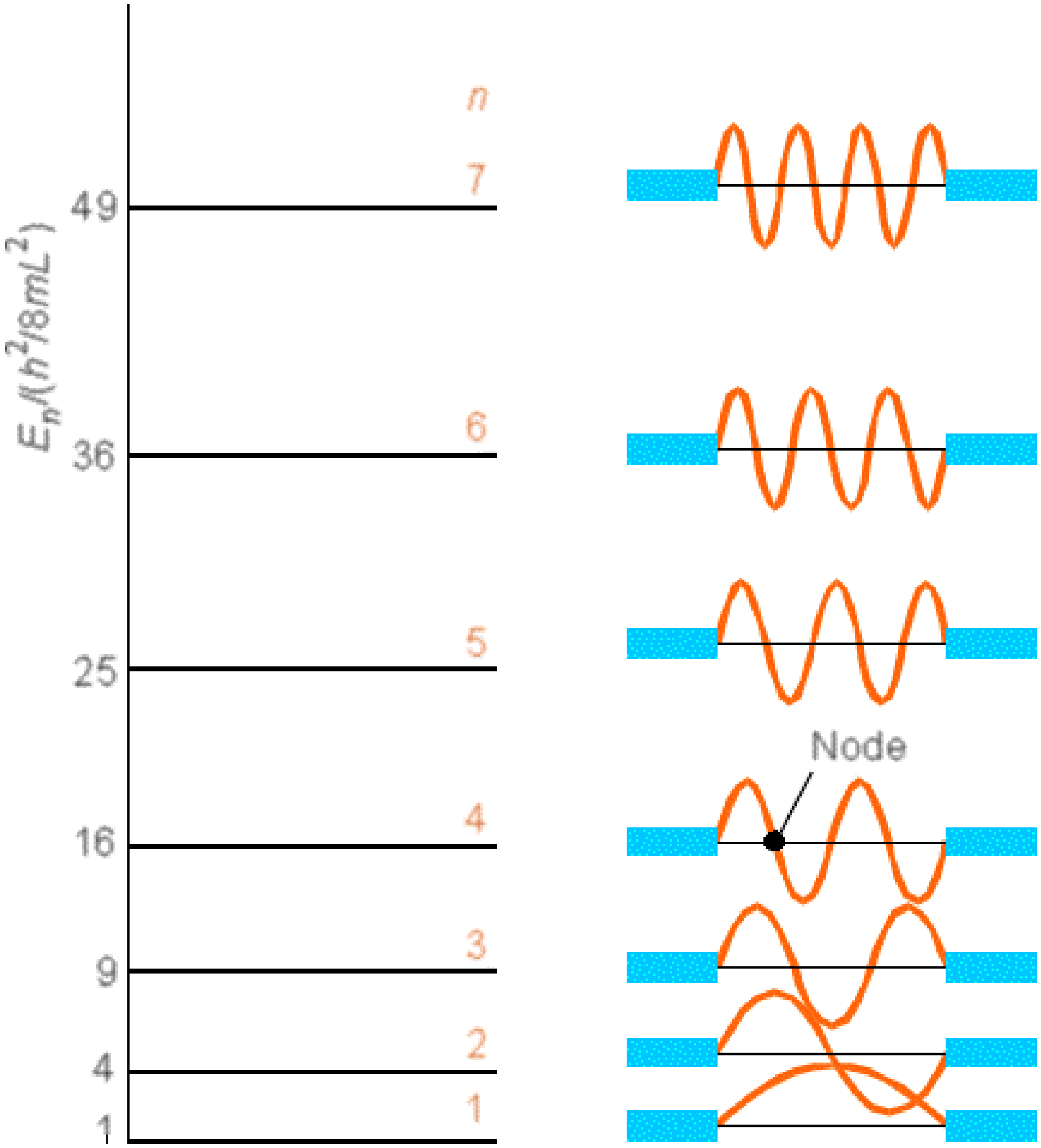


Figure 2.4. The nodal pattern for a chain containing seven atoms

I hope that by now the student is not tempted to ask how the electron "gets" from one region of high amplitude, through a node, to another high-amplitude region. Remember, such questions are cast in classical Newtonian language and are not appropriate when addressing the wave-like properties of quantum mechanics.

II. Bands of Orbitals in Solids

Not only does the particle in a box model offer a useful conceptual representation of electrons moving in polyenes, but it also is the zeroth-order model of band structures in solids. Let us consider a simple one-dimensional “crystal” consisting of a large number of atoms or molecules, each with a single orbital (the blue spheres shown below) that it contributes to the bonding. Let us arrange these building blocks in a regular “lattice” as shown in the Fig. 2.5.

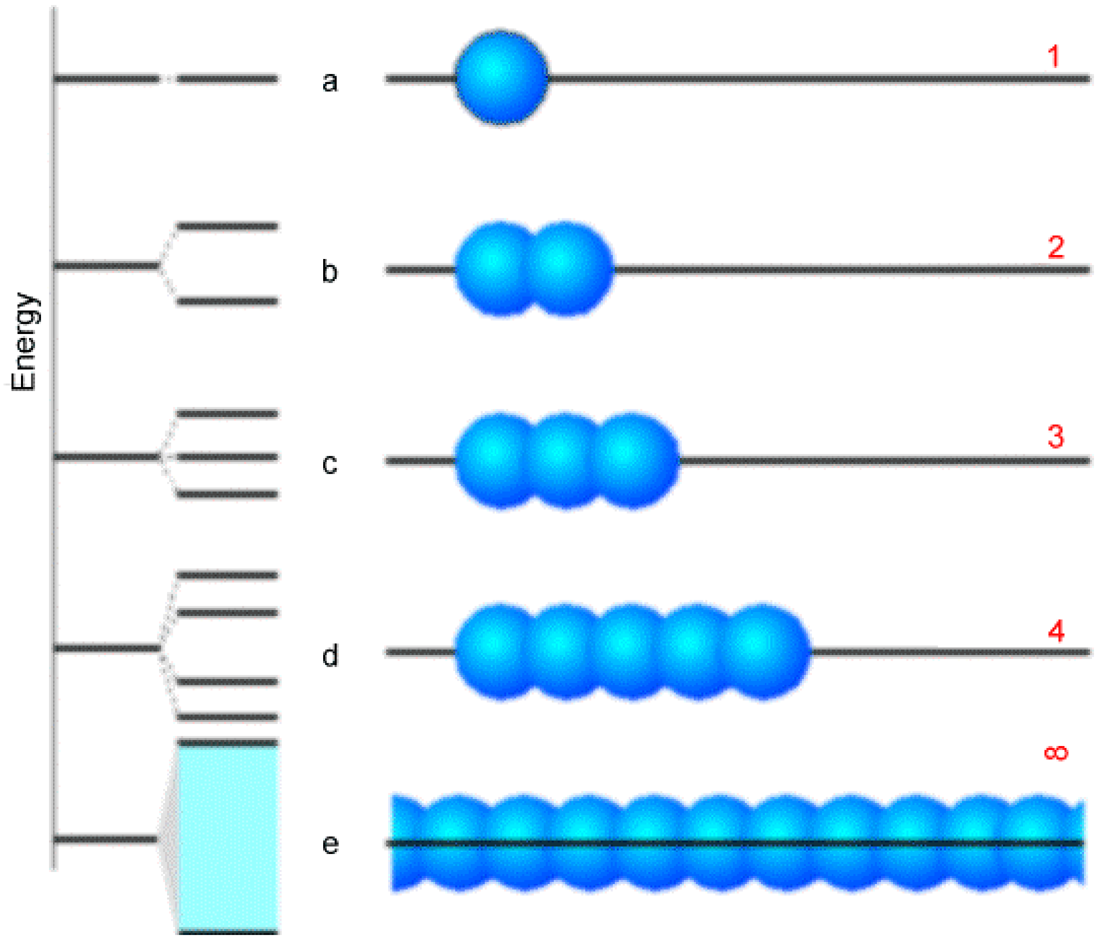


Figure 2.5. The energy levels arising from 1, 2, 3, 4, and an infinite number of orbitals

In the top four rows of this figure we show the case with 1, 2, 3, and 4 building blocks. To the left of each row, we display the energy splitting pattern into which the building blocks' orbitals evolve as they overlap and form delocalized molecular orbitals. Not surprisingly, for n = 2, one finds a bonding and an antibonding orbital. For n = 3, one has a bonding, one non-bonding, and one antibonding orbital. Finally, in the bottom row, we attempt to show what happens for an infinitely long chain. The key point is that the discrete number of molecular orbitals appearing in the 1-4 orbital cases evolves into a continuum of orbitals called a band. This band of orbital energies ranges from its bottom (whose orbital consists of a fully in-phase bonding combination of the building block orbitals) to its top (whose orbital is a fully out-of-phase antibonding combination).

In Fig. 2.6 we illustrate these fully bonding and fully antibonding band orbitals for two cases- the bottom involving s-type building block orbitals, and the top involving p-type orbitals. Notice that when the energy gap between the building block s and p orbitals is larger than is the dispersion (spread) in energy within the band or s or band of p orbitals, a band gap occurs between the highest member of the s band and the lowest member of the p band. The splitting between the s and p orbitals is a property of the individual atoms comprising the solid and varies among the elements of the periodic table. The dispersion in energies that a given band of orbitals is split into as these atomic orbitals combine to form a band is determined by how strongly the orbitals on neighboring atoms overlap. Small overlap produces small dispersion, and large overlap yields a broad band.

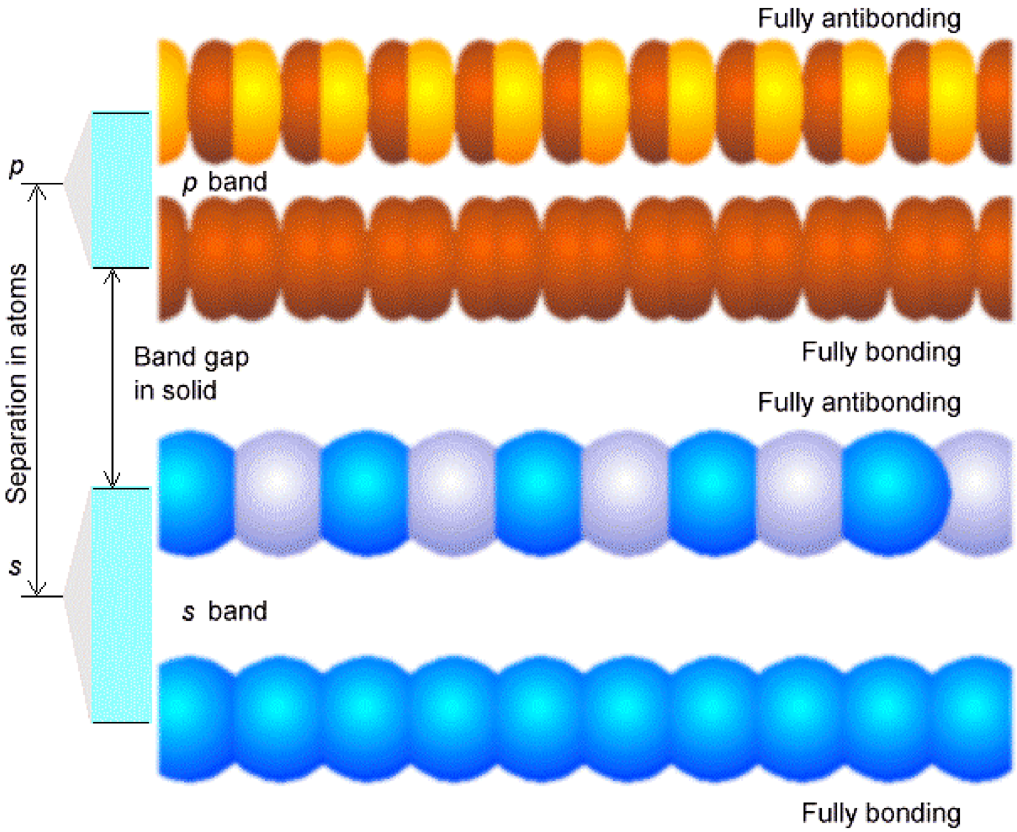


Figure 2.6. The bonding through antibonding energies and band orbitals arising from s and from p orbitals

Depending on how many valence electrons each building block contributes, the various bands formed by overlapping the building-block orbitals of the constituent atoms will be filled to various levels. For example, if each orbital shown above has a single valence electron in an s-orbital (e.g., as in the case of the alkali metals), the s-band will be half filled in the ground state with α and β -paired electrons. Such systems produce very good conductors because their partially filled bands allow electrons to move with very little (e.g., only thermal) excitation among other orbitals in this same band. On the other hand, for alkaline earth systems with two s electrons per atom, the s-band will be completely filled. In such cases, conduction requires excitation to the lowest members of the nearby p-orbital band. Finally, if each building block were an Al ($3s^2\ 3p^1$) atom, the s-band would be full and the p-band would be half filled. Systems whose highest energy occupied band is completely filled and for which the gap in energy to the lowest unfilled band is large are called insulators because they have no way to easily (i.e., with little energy requirement) promote some of their higher-energy electrons from orbital to orbital and thus effect conduction. If the band gap between a filled band and an unfilled band is small, it may be possible for thermal excitation (i.e., collisions with neighboring atoms or molecules) to cause excitation of electrons from the former to the latter thereby inducing conductive behavior. An example of such a case is illustrated in Fig. 2.7.

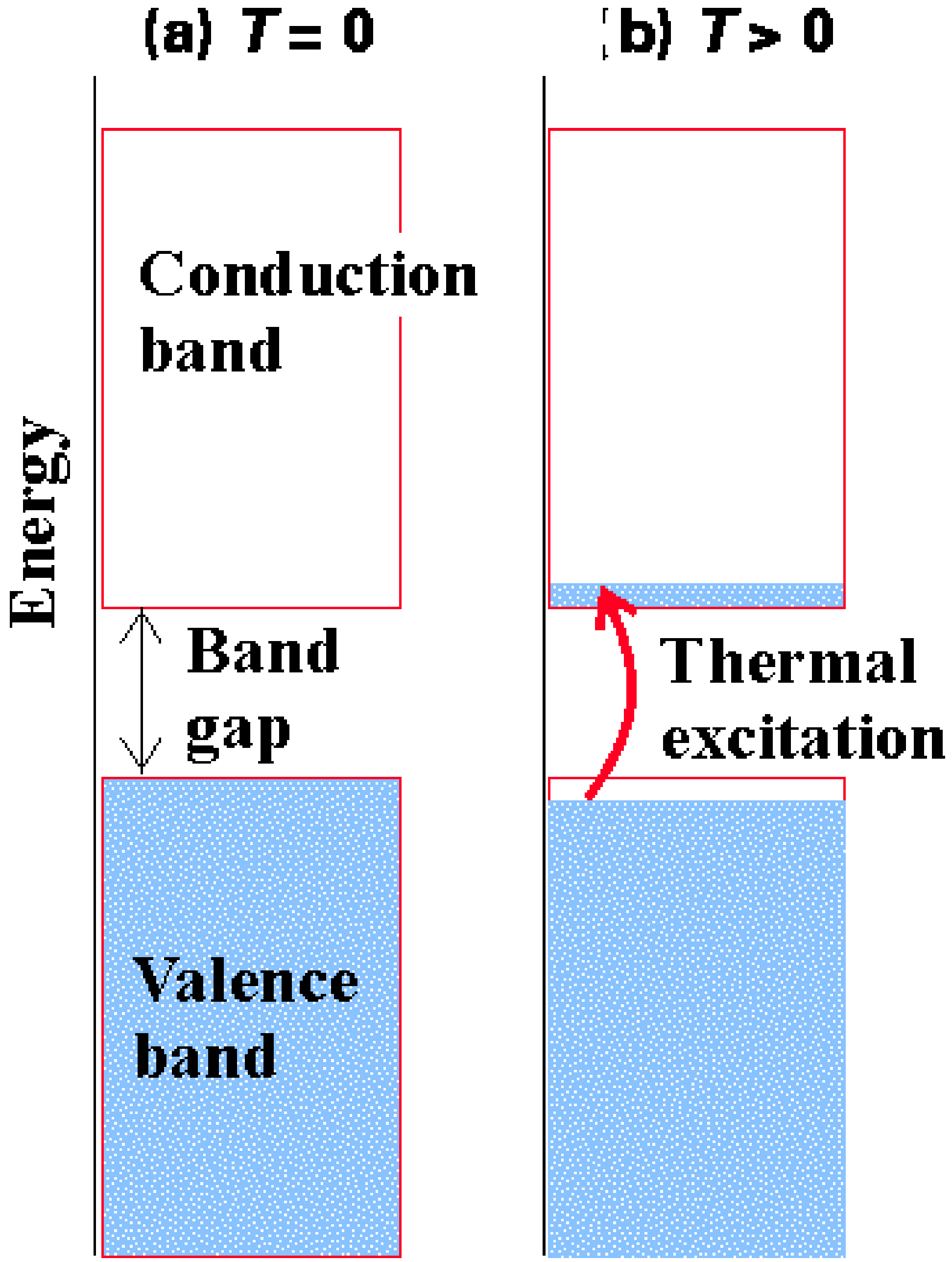


Figure 2.7. The valence and conduction bands and the band gap.

In contrast, systems whose highest energy occupied band is partially filled are conductors because the have little spacing among their occupied and unoccupied orbitals.

To form a semiconductor, one starts with an insulator as shown in Fig.2.8 with its filled (dark) band and a band gap between this band and its empty (clear) upper band.

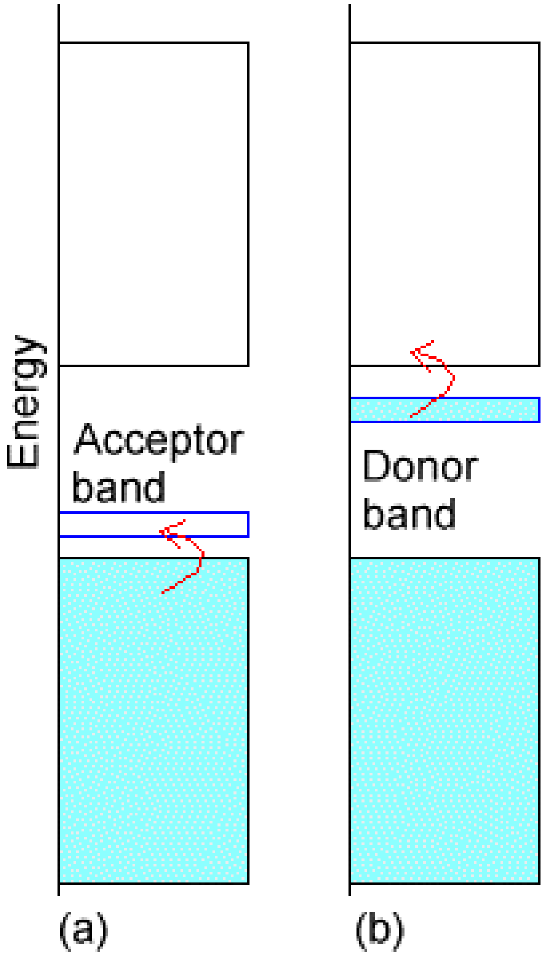


Figure 2.8. The filled and empty bands, the band gap, and exmpty acceptor or filled donor bands.

If this insulator material were synthesized with a small amount of “dopant” whose valence orbitals have energies between the filled and empty bands of the insulator, one may generate a semiconductor. If the dopant species has no valence electrons (i.e., has an empty valence orbital), it gives rise to an empty band lying between the filled and empty bands of the insulator as shown below in case a. In this case, the dopant band can act as an electron acceptor for electrons excited (either thermally or by light) from the filled band into the dopant band. Once electrons enter the dopant band, charge can flow and the system becomes a conductor. Another case is illustrated in the b part of the figure. Here, the dopant has its own band filled but lies close to the empty band of the insulator. Hence excitation of electrons from the dopant band to the empty band can induce current to flow.

III. Densities of States in 1, 2, and 3 dimensions.

When a large number of neighboring orbitals overlap, band are formed. However, the nature of these bands is very different in different dimensions.

Before leaving our discussion of bands of orbitals and orbital energies in solids, I want to address the issue of the density of electronic states and the issue of what determines the energy range into which orbitals of a given band will split. First, let's recall the energy expression for the 1 and 2- dimensional electron in a box case, and let's generalize it to three dimensions. The general result is

$$E = \Sigma_j n_j^2 \pi^2 \hbar^2/(2mL_j^2)$$

where the sum over j runs over the number of dimensions (1, 2, or 3), and L_j is the length of the box along the j^{th} direction. For one dimension, one observes a pattern of energy levels that grows with increasing n, and whose spacing between neighboring energy levels also grows. However, in 2 and 3 dimensions, the pattern of energy level spacing displays a qualitatively different character at high quantum number.

Consider first the 3-dimensional case and, for simplicity, let's use a "box" that has equal length sides L. In this case, the total energy E is $(\hbar^2\pi^2/2mL^2)$ times $(n_x^2 + n_y^2 + n_z^2)$. The latter quantity can be thought of as the square of the length of a vector R having three components n_x, n_y, n_z. Now think of three Cartesian axes labeled n_x, n_y, and n_z and view a sphere of radius R in this space. The volume of the 1/8 th sphere having positive values of n_x, n_y, and n_z and having radius R is $1/8\ (4/3\ \pi R^3)$. Because each cube having unit length along the n_x, n_y, and n_z axes corresponds to a single quantum wave function and its energy, the total number $N_{tot}(E)$ of quantum states with positive n_x, n_y, and n_z and with energy between zero and $E = (\hbar^2\pi^2/2mL^2)R^2$ is

$$N_{tot} = 1/8\ (4/3\ \pi R^3) = 1/8\ (4/3\ \pi\ [2mEL^2/(\hbar^2\pi^2)]^{3/2}$$

The number of quantum states with energies between E and E+dE is $(dN_{tot}/dE)\ dE$, which is the density $\Omega(E)$ of states near energy E:

$$\Omega(E) = 1/8\ (4/3\ \pi\ [2mL^2/(\hbar^2\pi^2)]^{3/2}\ 3/2\ E^{1/2}.$$

Notice that this state density increases as E increases. This means that, in the 3-dimensional case, the number of quantum states per unit energy grows; in other words, the spacing between neighboring state energies decreases, very unlike the 1-dimensioal case where the spacing between neighboring states grows as n and thus E grows. This growth in state density in the 3-dimensional case is a result of the degenacies and near-degenracies that occur. For example, the states with n_x, n_y, n_z = 2,1,1 and 1, 1, 2, and 1, 2, 1 are degenerate, and those with n_x, n_y, n_z = 5, 3, 1 or 5, 1, 3 or 1, 3, 5 or 1, 5, 3 or 3, 1, 5 or 3, 5, 1 are degenerate and nearly degenerate to those having quantum numbers 4, 4, 1 or 1, 4, 4, or 4, 1, 4.

In the 2-dimensional case, degeracies also occur and cause the density of states to possess an interesting E dependence. In this case, we think of states having energy $E = (\hbar^2\pi^2/2mL^2)R^2$, but with $R^2 = n_x^2 + n_y^2$. The total number of states having energy between zero and E is

$$N_{total} = 4\pi R^2 = 4\pi E(2mL^2/\hbar^2\pi^2)$$

So, the density of states between E and E+dE is

$$\Omega(E) = dN_{total}/dE = 4\pi (2mL^2/\hbar^2\pi^2)$$

That is, in this 2-dimensional case, the number of states per unit energy is constant for high E values (where the analysis above applies best).

This kind of analysis for the 1-dimensional case gives

$$N_{total} = R = (2mEL^2/\hbar^2\pi^2)^{1/2}$$

so, the state density between E and E+ dE is:

$$\Omega(E) = 1/2\ (2mL^2/\hbar^2\pi^2)^{1/2}\ E^{-1/2},$$

which clearly shows the widening spacing, and thus lower density, as one goes to higher energies.

These findings about densities of states in 1-, 2-, and 3- dimensions are important because, in various problems one encounters in studying electronic states of extended systems such as solids and surfaces, one needs to know how the number of states available at a given total energy E varies with E. Clearly, the answer to this question depends upon the dimensionality of the problem, and this fact is what I want the students reading this text to keep in mind.

IV. The Most Elementary Model of Orbital Energy Splittings: Hückel or Tight Binding Theory

Now, let's examine what determines the energy range into which orbitals (e.g., p_π orbitals in polyenes or metal s or p orbitals in a solid) split. To begin, consider two orbitals, one on an atom labeled A and another on a neighboring atom labeled B; these orbitals could be, for example, the 1s orbitals of two hydrogen atoms, such as Figure 2.9 illustrates.

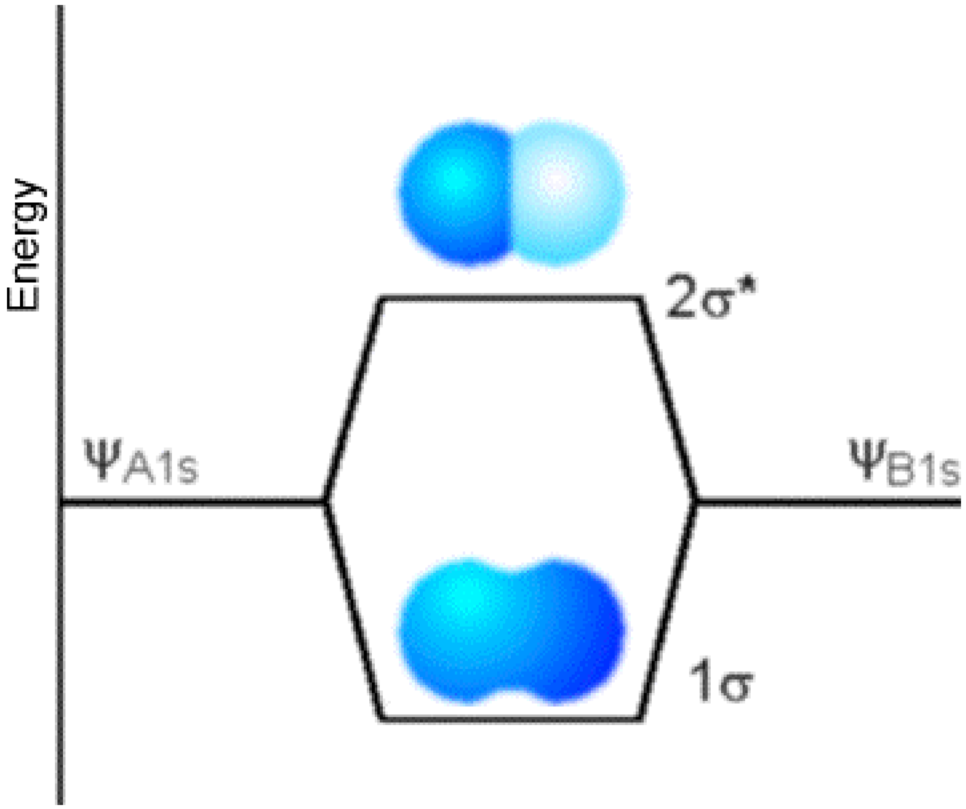


Figure 2.9. Two 1s orbitals combine to produce a σ bonding and a σ* antibonding molecular orbital

However, the two orbitals could instead be two p_π orbitals on neighboring carbon atoms such as are shown in Fig. 2.10 as they form bonding and π* anti-bonding orbitals.

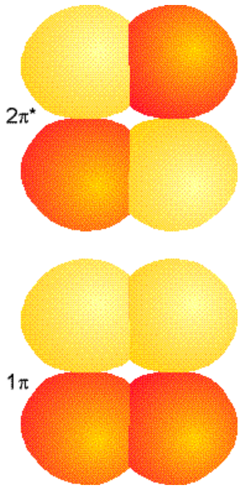


Figure 2.10. Two atomic p_π orbitals form a bonding π and antibonding π* molecular orbital.

In both of these cases, we think of forming the molecular orbitals (MOs) φ_k as linear combinations of the atomic orbitals (AOs) χ_a on the constituent atoms, and we express this mathematically as follows:

$$\varphi_K = \Sigma_a C_{K,a} \chi_a,$$

where the $C_{K,a}$ are called linear combination of atomic orbital to form molecular orbital (LCAO-MO) coefficients. The MOs are supposed to be solutions to the Schrödinger equation in which the Hamiltonian H involves the kinetic energy of the electron as well as the potentials V_L and V_R detailing its attraction to the left and right atomic centers:

$$H = - \hbar^2/2m \quad {}^2 + V_L + V_R.$$

In contrast, the AOs centered on the left atom A are supposed to be solutions of the Schrödinger equation whose Hamiltonian is $H = - \hbar^2/2m \quad {}^2 + V_L$, and the AOs on the right atom B have $H = - \hbar^2/2m \quad {}^2 + V_R$. Substituting $\varphi_K = \Sigma_a C_{K,a} \chi_a$ into the MO's Schrödinger equation $H\varphi_K = \varepsilon_K \varphi_K$ and then multiplying on the left by the complex conjugate of χ_b and integrating over the r, θ and φ coordinates of the electron produces

$$\Sigma_a <\chi_b| - \hbar^2/2m \quad {}^2 + V_L + V_R |\chi_a> C_{K,a} = \varepsilon_K \Sigma_a <\chi_b|\chi_a> C_{K,a}$$

Recall that the Dirac notation <a|b> denotes the integral of a* and b, and <a| op| b> denotes the integral of a* and the operator op acting on b.

In what is known as the Hückel model in organic chemistry or the tight-binding model in solid-state theory, one approximates the integrals entering into the above set of linear equations as follows:

i. The diagonal integral $<\chi_b| - \hbar^2/2m \quad {}^2 + V_L + V_R |\chi_b>$ involving the AO centered on the right atom and labeled χ_b is assumed to be equivalent to $<\chi_b| - \hbar^2/2m \quad {}^2 + V_R |\chi_b>$, which means that net attraction of this orbital to the left atomic center is neglected. Moreover, this integral is approximated in terms of the binding energy (denoted α, not to be confused with the electron spin function α) for an electron that occupies the χ_b orbital: $<\chi_b| - \hbar^2/2m \quad {}^2 + V_R |\chi_b> = \alpha_b$. The physical meaning of α_b is the kinetic energy of the electron in χ_b plus the attraction of this electron to the right atomic center while it resides in χ_b. Of course, an analogous approximation is made for the diagonal integral involving χ_a; $<\chi_a| - \hbar^2/2m \quad {}^2 + V_L |\chi_a> = \alpha_a$.

ii. The off-diagonal integrals $<\chi_b| - \hbar^2/2m \quad {}^2 + V_L + V_R |\chi_a>$ are expressed in terms of a parameter $\beta_{a,b}$ which relates to the kinetic and potential energy of the electron while it resides in the “overlap region” in which both χ_a and χ_b are non-vanishing. This region is shown pictorially above as the region where the left and right orbitals touch or overlap. The magnitude of β is assumed to be proportional to the overlap $S_{a,b}$ between the two AOs : $S_{a,b} = <\chi_a|\chi_b>$. It turns out that β is usually a negative quantity, which can be seen by writing it as $<\chi_b| - \hbar^2/2m \quad {}^2 + V_R |\chi_a> + <\chi_b| \ V_L \ |\chi_a>$. Since χ_a is an eigenfunction of $-\hbar^2/2m \quad {}^2 + \ V_R$ having the eigenvalue α_a, the first term is equal to α_a (a negative quantity) times $<\chi_b|\chi_a>$, the overlap S. The second quantity $<\chi_b| \ V_L \ |\chi_a>$ is equal to the integral of the overlap density $\chi_b(r)\ \chi_a(r)$ multiplied by the (negative) Coulomb potential for attractive interaction of the electron with the left atomic center. So, whenever $\chi_b(r)$ and $\chi_a(r)$ have positive overlap, β will turn out negative.

iii. Finally, in the most elementary Hückel or tight-binding model, the overlap integrals $<\chi_a|\chi_b> = S_{a,b}$ are neglected and set equal to zero on the right side of the matrix eigenvalue equation. However, in some Hückel models, overlap between neighboring orbitals is explictly treated, so, in some of the discussion below we will retain $S_{a,b}$.

With these Hückel approximations, the set of equations that determine the orbital energies ε_K and the corresponding LCAO-MO coefficients $C_{K,a}$ are written for the two-orbital case at hand as in the first 2x2 matrix equations shown below

$$\begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \varepsilon \begin{bmatrix} S & 0 \\ 0 & S \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix}$$

which is sometimes written as

$$\begin{bmatrix} \alpha - \varepsilon & \beta - \varepsilon S \\ \beta - \varepsilon S & \alpha - \varepsilon \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

These equations reduces with the assumption of zero overlap to

$$\begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \varepsilon \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix}$$

The α parameters are identical if the two AOs χ_a and χ_b are identical, as would be the case for bonding between the two 1s orbitals of two H atoms or two $2p_\pi$ orbitals of two C atoms or two 3s orbitals of two Na atoms. If the left and right orbitals were not identical (e.g., for bonding in HeH^+ or for the π bonding in a C-O group), their α values would be different and the Hückel matrix problem would look like:

$$\begin{bmatrix}\alpha & \beta\\ \beta & \alpha'\end{bmatrix}\begin{bmatrix}C_L\\ C_R\end{bmatrix} = \varepsilon \begin{bmatrix}1 & S\\ S & 1\end{bmatrix}\begin{bmatrix}C_L\\ C_R\end{bmatrix}$$

To find the MO energies that result from combining the AOs, one must find the values of ε for which the above equations are valid. Taking the 2x2 matrix consisting of ε times the overlap matrix to the left hand side, the above set of equations reduces to the third set displayed earlier. It is known from matrix algebra that such a set of linear homogeneous equations (i.e., having zeros on the right hand sides) can have non-trivial solutions (i.e., values of C that are not simply zero) only if the determinant of the matrix on the left side vanishes. Setting this determinant equal to zero gives a quadratic equation in which the ε values are the unknowns:

$$(\alpha-\varepsilon)^2 - (\beta-\varepsilon S)^2 = 0.$$

This quadratic equation can be factored into a product

$$(\alpha - \beta - \varepsilon + \varepsilon S)\ (\alpha + \beta - \varepsilon - \varepsilon S) = 0$$

which has two solutions

$$\varepsilon = (\alpha + \beta)/(1 + S), \text{ and } \varepsilon = (\alpha - \beta)/(1 - S).$$

As discussed earlier, it turns out that the β values are usually negative, so the lowest energy such solution is the ε = (α + β)/(1 + S) solution, which gives the energy of the bonding MO. Notice that the energies of the bonding and anti-bonding MOs are not symmetrically displaced from the value α within this version of the Hückel model that retains orbital overlap. In fact, the bonding orbital lies less than β below α, and the antibonding MO lies more than β above α because of the 1+S and 1-S factors in the respective denominators. This asymmetric lowering and raising of the MOs relative to the energies of the constituent AOs is commonly observed in chemical bonds; that is, the antibonding orbital is more antibonding than the bonding orbital is bonding. This is another important thing to keep in mind because its effects pervade chemical bonding and spectroscopy.

Having noted the effect of inclusion of AO overlap effects in the Hückel model, I should admit that it is far more common to utilize the simplified version of the Hückel model in which the S factors are ignored. In so doing, one obtains patterns of MO orbital energies that do not reflect the asymmetric splitting in bonding and antibonding orbitals noted above. However, this simplified approach is easier to use and offers qualitatively correct MO energy orderings. So, let’s proceed with our discussion of the Hückel model in its simplified version.

To obtain the LCAO-MO coefficients corresponding to the bonding and antibonding MOs, one substitutes the corresponding α values into the linear equations

$$\begin{bmatrix} \alpha - \varepsilon & \beta \\ \beta & \alpha - \varepsilon \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

and solves for the C_a coefficients (acutally, one can solve for all but one C_a, and then use normalization of the MO to determine the final C_a). For example, for the bonding MO, we substitute $\varepsilon = \alpha + \beta$ into the above matrix equation and obtain two equations for C_L and C_R:

$$-\beta C_L + \beta C_R = 0$$

$$\beta C_L - \beta C_R = 0.$$

These two equations are clearly not independent; either one can be solved for one C in terms of the other C to give:

$$C_L = C_R,$$

which means that the bonding MO is

$$\varphi = C_L (\chi_L + \chi_R).$$

The final unknown, C_L, is obtained by noting that φ is supposed to be a normalized function $<\varphi|\varphi> = 1$. Within this version of the Hückel model, in which the overlap S is negleted, the normalization of φ leads to the following condition:

$$1 = <\varphi|\varphi> = C_L^2 (<\chi_L|\chi_L> + <\chi_R\chi_R>) = 2 C_L^2$$

with the final result depending on assuming that each χ is itself also normalized. So, finally, we know that $C_L = (1/2)^{1/2}$, and hence the bonding MO is:

$$\varphi = (1/2)^{1/2} (\chi_L + \chi_R).$$

Actually, the solution of $1 = 2 C_L^2$ could also have yielded $C_L = - (1/2)^{1/2}$ and then, we would have

$$\varphi = - (1/2)^{1/2} (\chi_L + \chi_R).$$

These two solutions are not independent (one is just –1 time the other), so only one should be included in the list of MOs. However, either one is just as good as the other because, as shown very early in this text, all of the physical properties that one computes from a wave function depend not on ψ but on $\psi^*\psi$. So, two wave functions that differ from one another by an overall sign factor as we have here have exactly the same $\psi^*\psi$ and thus are equivalent.

In like fashion, we can substitute $\varepsilon = \alpha - \beta$ into the matrix equation and solve for the C_L can C_R values that are appropriate for the antibonding MO. Doing so, gives us:

$$\varphi^* = (1/2)^{1/2} (\chi_L - \chi_R)$$

or, alternatively,

$$\varphi^* = (1/2)^{1/2} (\chi_R - \chi_L).$$

Again, the fact that either expression for φ^* is acceptable shows a property of all solutions to any Scrrödinger equations; any multiple of a solution is also a solution. In the above example, the two “answers” for φ^* differ by a multiplicative factor of (-1).

Let’s try another example to practice using Hückel or tight-binding theory. In particular, I’d like you to imagine two possible structures for a cluster three Na atoms (i.e., pretend that someone came to you and asked what geometry you think such a cluster would assume in its ground electronic state), one linear and one an equilateral triangle. Further, assume that the Na-Na distances in both such clusters are equal (i.e., that the person asking for your theoretical help is willing to assume that variations in bond lengths are not the crucial factor in determining which structure is favored). In Fig. 2.11, I shown the two candidate clusters and their 3s orbitals.

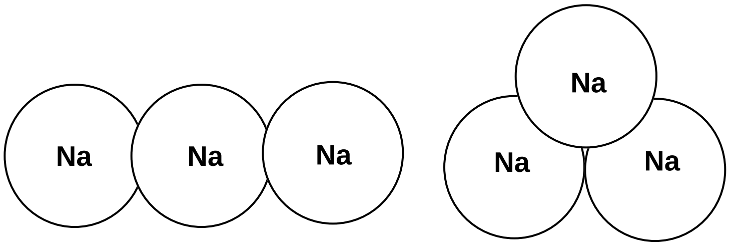


Figure 2.11. Linear and equilateral triangle structures of sodium trimer.

Numbering the three Na atoms' valence 3s orbitals χ_1, χ_2, and χ_3, we then set up the 3x3 Hückel matrix appropriate to the two candidate structures:

$$\begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{bmatrix}$$

for the linear structure (n.b., the zeros arise because χ_1 and χ_3 do not overlap and thus have no β coupling matrix element). Alternatively, for the triangular structure, we find'

$$\begin{bmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{bmatrix}$$

as the Hückel matrix. Each of these 3x3 matrices will have three eigenvalues that we obtain by subtracting ε from their diagonals and setting the determinants of the resulting matrices to zero. For the linear case, doing so generates

$$(\alpha\text{-}\varepsilon)^3 - 2\,\beta^2\,(\alpha\text{-}\varepsilon) = 0,$$

and for the triangle case it produces

$$(\alpha\text{-}\varepsilon)^3 - 3\,\beta^2\,(\alpha\text{-}\varepsilon) + 2\,\beta^2 = 0.$$

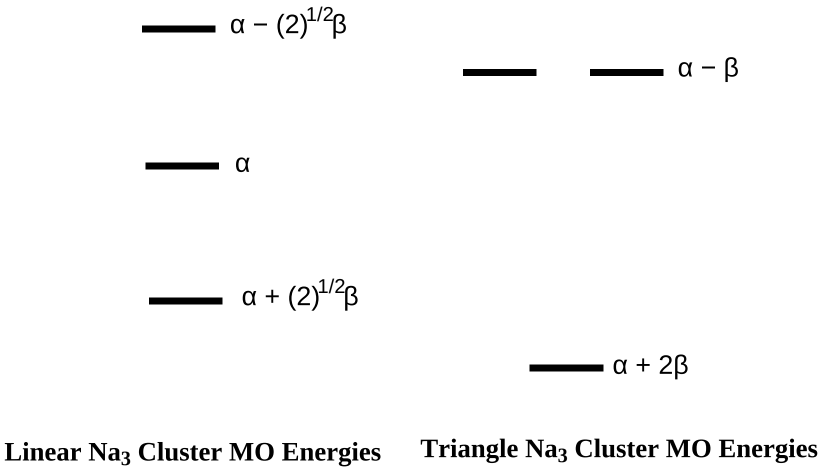
The first cubic equation has three solutions that give the MO energies:

$$\varepsilon = \alpha + (2)^{1/2}\beta, \ \varepsilon = \alpha, \text{ and } \varepsilon = \alpha - (2)^{1/2}\beta,$$

for the bonding, non-bonding and antibonding MOs, respectively. The second cubic equation also has three solutions

$$\varepsilon = \alpha + 2\beta, \ \varepsilon = \alpha - \beta, \text{ and } \varepsilon = \alpha - \beta.$$

So, for the linear and triangular structures, the MO energy patterns are as shown in Fig. 2.12.



Linear Na_3 Cluster MO Energies **Triangle Na_3 Cluster MO Energies**

Figure 2.12. Energy orderings of molecular orbitals of linear and triangular sodium trimer

For the neutral Na_3 cluster about which you were asked, you have three valence electrons to distribute among the lowest available orbitals. In the linear case, we place two electrons into the lowest orbital and one into the second orbital. Doing so produces a 3-electron state with a total energy of $E= 2(\alpha+2^{1/2}\beta) + \alpha = 3\alpha +2\ 2^{1/2}\beta$. Alternatively, for the triangular species, we put two electrons into the lowest MO and one into either of the degenerate MOs resulting in a 3-electron state with total energy $E = 3\alpha + 3\beta$. Because β is a negative quantity, the total energy of the triangular structure is lower than that of the linear structure since $3 > 2\ 2^{1/2}$.

The above example illustrates how we can use Hückel/tight-binding theory to make qualitative predictions (e.g., which of two “shapes” is likely to be of lower energy). Notice that all one needs to know to apply such a model to any set of atomic orbitals that overlap to form MOs is

(i) the individual AO energies α (which relate to the electronegativity of the AOs) and (ii) the degree to which the AOs couple (the β parameters which relate to AO overlaps).

Let's see if you can do some of this on your own. Using the above results, would you expect the cation Na_3^+ to be linear or triangular? What about the anion Na_3^-? Next, I want you to substitute the MO energies back into the 3x3 matrix and find the C_1, C_2, and C_3 coefficients appropriate to each of the 3 MOs of the linear and of the triangular structure. See if doing so leads you to solutions that can be depicted as shown in Fig. 2.13, and see if you can place each set of MOs in the proper energy ordering.

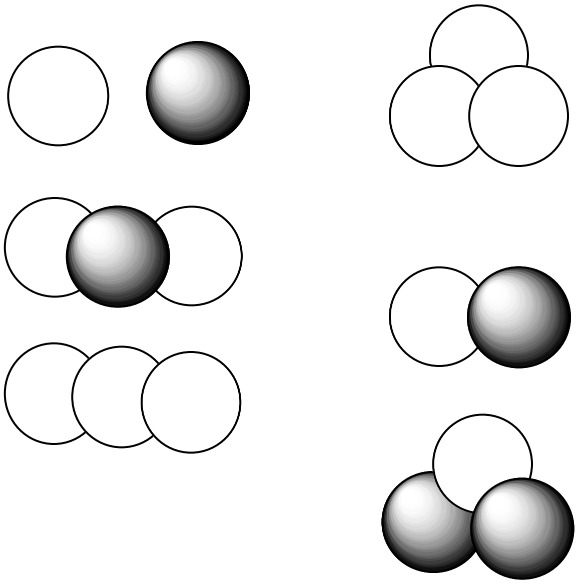


Figure 2.13. The molecular orbitals of linear and triangular sodium trimer (note, they are not energy ordered).

Now, I want to show you how to broaden your horizons and use tight-binding theory to describe all of the bonds in a more complicated molecule such as ethylene shown in Fig. 2.14. Within the model described above, each pair of orbitals that "touch" or overlap gives rise to a 2x2 matrix. More correctly, all n of the constituent AOs form an nxn matrix, but this matrix is broken up into 2x2 blocks whenever each AO touches only one other AO. Notice that this did not happen in the triangular Na_3 case where each AO touched two other AOs. For the ethlyene case, the valence AO's consist of (a) four equivalent C sp^2 orbitals that are directed toward the four H atoms, (b) four H 1s orbitals, (c) two C sp^2 orbitals directed toward one another to form the C-C σ bond, and (d) two C p_π orbitals that will form the C-C π bond. This total of 12 AOs generates 6 Hückel matrices as shown below the ethylene molecule.

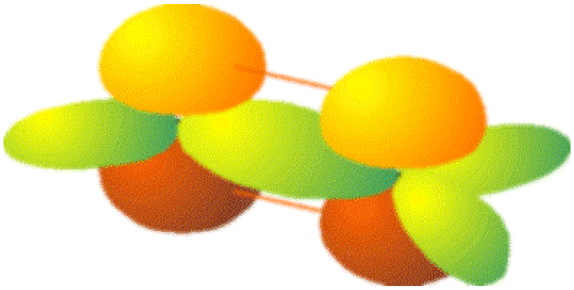


Figure 2.14 Ethylene molecule with four C-H bonds, one C-C σ bond, and one C-C π bond.

We obtain one 2x2 matrix for the C-C σ bond of the form

$$\begin{bmatrix} \alpha_{sp^2} & \beta_{sp^2,sp^2} \\ \beta_{sp^2,sp^2} & \alpha_{sp^2} \end{bmatrix}$$

and one 2x2 matrix for the C-C π bond of the form

$$\begin{bmatrix} \alpha_{p_\pi} & \beta_{p_\pi,p_\pi} \\ \beta_{p_\pi,p_\pi} & \alpha_{p_\pi} \end{bmatrix}$$

Finally, we also obtain four identical 2x2 matrices for the C-H bonds:

$$\begin{bmatrix} \alpha_{sp^2} & \beta_{sp^2,H} \\ \beta_{sp^2,H} & \alpha_H \end{bmatrix}$$

The above matrices will then produce (a) four identical C-H bonding MOs having energies $\varepsilon = 1/2\ \{(\alpha_H + \alpha_C) - [(\alpha_H-\alpha_C)^2 + 4\beta^2]^{1/2}\}$, (b) four identical C-H antibonding MOs having energies $\varepsilon^* = 1/2\ \{(\alpha_H + \alpha_C) + [(\alpha_H - \alpha_C)^2 + 4\beta^2]^{1/2}\}$, (c) one bonding C-C π orbital with $\varepsilon = \alpha_{p\pi} + \beta$, (d) a partner antibonding C-C orbital with $\varepsilon^* = \alpha_{p\pi} - \beta$, (e) a C-C σ bonding MO with $\varepsilon = \alpha_{sp2} + \beta$, and (f) its antibonding partner with $\varepsilon^* = \alpha_{sp2} - \beta$. In all of these expressions, the β parameter is supposed to be that appropriate to the specific orbitals that overlap as shown in the matrices.

If you wish to practice this exercise of breaking a large molecule down into sets of interacting AOs, try to see what Hückel matrices you obtain and what bonding and antibonding MO energies you obtain for the valence orbitals of methane shown in Fig. 2.15.

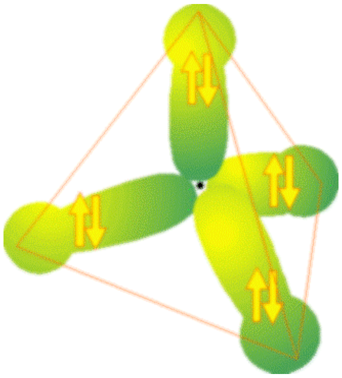


Figure 2.15. Methane molecule with four C-H bonds.

Before leaving this discussion of the Hückel/tight-binding model, I need to stress that it has its flaws (because it is based on approximations and involves neglecting certain terms in the Schrödinger equation). For example, it predicts (see above) that ethylene has four energetically identical C-H bonding MOs (and four degenerate C-H antibonding MOs). However, this is not what is seen when photoelectron spectra are used to probe the energies of these MOs. Likewise, it suggests that methane has four equivalent C-H bonding and antibonding orbitals, which, again is not true. It turns out that, in each of these two cases (ethylene and methane), the experiments indicate a grouping of four <u>nearly</u> iso-energetic bonding MOs and four nearly iso-energetic antibonding MOs. However, there is some "splitting" among these clusters of four MOs. The splittings can be interpreted, within the Hückel model, as arising from couplings or interactions among, for example, one sp^2 or sp^3 orbital on a given C atom and another such orbital on the same atom. Such couplings cause the nxn Hückel matrix to not block-partition into groups of 2x2 sub-matrices because now there exist off-diagonal β factors that couple one pair of directed AOs to another. When such couplings are included in the analysis, one finds that the clusters of MOs expected to be degenerate are not but are split just as the photoelectron data suggest.

V. Hydrogenic Orbitals

The Hydrogenic atom problem forms the basis of much of our thinking about atomic structure. To solve the corresponding Schrödinger equation requires separation of the r, θ, and φ variable.

The Schrödinger equation for a single particle of mass μ moving in a central potential (one that depends only on the radial coordinate r) can be written as

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + V\left(\sqrt{x^2+y^2+z^2}\right)\psi = E\psi.$$

or, introducing the short-hand notation ∇^2**:**

$$-\hbar^2/2m\ \nabla^2\psi + V\psi = E\psi.$$

This equation is not separable in Cartesian coordinates (x,y,z) because of the way x,y, and z appear together in the square root. However, it is separable in spherical coordinates where it has the form

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right) + \frac{1}{r^2\text{Sin}\theta}\frac{\partial}{\partial\theta}\left(\text{Sin}\theta\frac{\partial\psi}{\partial\theta}\right)$$

$$+ \frac{1}{r^2\text{Sin}^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + V(r)\psi = -\hbar^2/2m\ \nabla^2\psi + V\psi = E\psi\ .$$

Subtracting V(r)ψ from both sides of the equation and multiplying by $-\frac{2\mu r^2}{\hbar^2}$ then moving the derivatives with respect to r to the right-hand side, one obtains

$$\frac{1}{\text{Sin}\theta}\frac{\partial}{\partial\theta}\left(\text{Sin}\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\text{Sin}^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}$$

$$= -\frac{2\mu r^2}{\hbar^2}\left(E-V(r)\right)\psi - \frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right).$$

Notice that, except for ψ itself, the right-hand side of this equation is a function of r only;

it contains no θ or φ dependence. Let's call the entire right hand side F(r) ψ to emphasize this fact.

To further separate the θ and φ dependence, we multiply by $\mathrm{Sin}^2\theta$ and subtract the θ derivative terms from both sides to obtain

$$\frac{\partial^2\psi}{\partial\varphi^2} = F(r)\psi\,\mathrm{Sin}^2\theta - \mathrm{Sin}\theta\,\frac{\partial}{\partial\theta}\left(\mathrm{Sin}\theta\,\frac{\partial\psi}{\partial\theta}\right).$$

Now we have separated the φ dependence from the θ and r dependence. We now introduce the procedure used to separate variables in differntial equations and assume ψ can be written as a function of φ times a function of r and θ: $\psi = \Phi(\varphi)Q(r,\theta)$. Dividing by Φ Q, we obtain

$$\frac{1}{\Phi}\,\frac{\partial^2\Phi}{\partial\varphi^2} = \frac{1}{Q}\left(F(r)\mathrm{Sin}^2\theta\; Q - \mathrm{Sin}\theta\,\frac{\partial}{\partial\theta}\left(\mathrm{Sin}\theta\,\frac{\partial Q}{\partial\theta}\right)\right).$$

Now all of the φ dependence is isolated on the left hand side; the right hand side contains only r and θ dependence.

Whenever one has isolated the entire dependence on one variable as we have done above for the φ dependence, one can easily see that the left and right hand sides of the equation must equal a constant. For the above example, the left hand side contains no r or θ dependence and the right hand side contains no φ dependence. Because the two sides are equal, they both must actually contain no r, θ, or φ dependence; that is, they are constant.

For the above example, we therefore can set both sides equal to a so-called separation constant that we call $-m^2$. It will become clear shortly why we have chosen to express the constant in the form of minus the square of an integer. You may recall that we studied this same φ- equation earlier and learned how the integer m arises via. the boundary condition that φ and $\varphi + 2\pi$ represent identical geometries.

1. The Φ Equation

The resulting Φ equation reads (the " symbol is used to represent second derivative)

$$\Phi'' + m^2\Phi = 0 .$$

This equation should be familiar because it is the equation that we treated much earlier when we discussed z-component of angular momentum. So, its further analysis should also be familiar, but for completeness, I repeat much of it. The above equation has as its most general solution

$$\Phi = Ae^{im\varphi} + Be^{-im\varphi} .$$

Because the wave functions of quantum mechanics represent probability densities, they must be continuous and single-valued. The latter condition, applied to our Φ function, means (n.b., we used this in our earlier discussion of z-component of angular momentum) that

$$\Phi(\varphi) = \Phi(2\pi + \varphi) \qquad \text{or,}$$

$$Ae^{im\varphi}\left(1 - e^{2im\pi}\right) + Be^{-im\varphi}\left(1 - e^{-2im\pi}\right) = 0.$$

This condition is satisfied only when the separation constant is equal to an integer m = 0, ±1, ± 2, ... and provides another example of the rule that quantization comes from the boundary conditions on the wave function. Here m is restricted to certain discrete values because the wave function must be such that when you rotate through 2π about the z-axis, you must get back what you started with.

2. The Θ Equation

Now returning to the equation in which the φ dependence was isolated from the r and θ dependence.and rearranging the θ terms to the left-hand side, we have

$$\frac{1}{\mathrm{Sin}\theta}\frac{\partial}{\partial\theta}\left(\mathrm{Sin}\theta\,\frac{\partial Q}{\partial\theta}\right) - \frac{m^2 Q}{\mathrm{Sin}^2\theta} = F(r)Q.$$

In this equation we have separated θ and r variations so we can further decompose the wave function by introducing $Q = \Theta(\theta)\,R(r)$, which yields

$$\frac{1}{\Theta}\frac{1}{\mathrm{Sin}\theta}\frac{\partial}{\partial\theta}\left(\mathrm{Sin}\theta\,\frac{\partial\Theta}{\partial\theta}\right) - \frac{m^2}{\mathrm{Sin}^2\theta} = \frac{F(r)R}{R} = -\lambda,$$

where a second separation constant, -λ, has been introduced once the r and θ dependent terms have been separated onto the right and left hand sides, respectively.

We now can write the θ equation as

$$\frac{1}{\mathrm{Sin}\theta}\frac{\partial}{\partial\theta}\left(\mathrm{Sin}\theta\,\frac{\partial\Theta}{\partial\theta}\right) - \frac{m^2\Theta}{\mathrm{Sin}^2\theta} = -\lambda\,\Theta,$$

where m is the integer introduced earlier. To solve this equation for Θ , we make the substitutions $z = \mathrm{Cos}\theta$ and $P(z) = \Theta(\theta)$, so $\sqrt{1-z^2} = \mathrm{Sin}\theta$, and

$$\frac{\partial}{\partial\theta} = \frac{\partial z}{\partial\theta}\frac{\partial}{\partial z} = -\,\mathrm{Sin}\theta\,\frac{\partial}{\partial z}\ .$$

The range of values for θ was $0 \leq \theta < \pi$, so the range for z is $-1 < z < 1$. The equation for Θ, when expressed in terms of P and z, becomes

$$\frac{d}{dz}\left((1-z^2)\frac{dP}{dz}\right) - \frac{m^2P}{1-z^2} + \lambda P = 0.$$

Now we can look for polynomial solutions for P, because z is restricted to be less than unity in magnitude. If m = 0, we first let

$$P = \sum_{k=0}^{\infty} a_k z^k \ ,$$

and substitute into the differential equation to obtain

$$\sum_{k=0}^{\infty}(k+2)(k+1)\, a_{k+2}\, z^k - \sum_{k=0}^{\infty}(k+1)\, k\, a_k z^k + \lambda \sum_{k=0}^{\infty} a_k z^k = 0.$$

Equating like powers of z gives

$$a_{k+2} = \frac{a_k(k(k+1)-\lambda)}{(k+2)(k+1)} \ .$$

Note that for large values of k

$$\frac{a_{k+2}}{a_k} \rightarrow \frac{k^2\left(1+\frac{1}{k}\right)}{k^2\left(1+\frac{2}{k}\right)\left(1+\frac{1}{k}\right)} = 1.$$

Since the coefficients do not decrease with k for large k, this series will diverge for $z = \pm 1$ unless it truncates at finite order. This truncation only happens if the separation constant λ obeys $\lambda = l(l+1)$, where l is an integer. So, once again, we see that a boundary condition (i.e., that the wave function not diverge and thus be normalizable in this case) give rise to quantization. In this case, the values of λ are restricted to $l(l+1)$; before, we saw that m is restricted to $0, \pm 1, \pm 2, ..$.

Since the above recursion relation links every other coefficient, we can choose to solve for the even and odd functions separately. Choosing a_0 and then determining all of the even a_k in terms of this a_0, followed by rescaling all of these a_k to make the function normalized generates an even solution. Choosing a_1 and determining all of the odd a_k in like manner, generates an odd solution.

For $l= 0$, the series truncates after one term and results in $P_o(z) = 1$. For $l= 1$ the same thing applies and $P_1(z) = z$. For $l= 2$, $a_2 = -6 \frac{a_o}{2} = -3a_o$, so one obtains $P_2 = 3z^2-1$, and so on. These polynomials are called Legendre polynomials.

For the more general case where $m \neq 0$, one can proceed as above to generate a polynomial solution for the Θ function. Doing so, results in the following solutions:

$$P_l^m(z) = (1-z^2)^{\frac{|m|}{2}} \frac{d^{|m|} P_l(z)}{dz^{|m|}} .$$

These functions are called Associated Legendre polynomials, and they constitute the solutions to the Θ problem for non-zero m values.

The above P and $e^{im\varphi}$ functions, when re-expressed in terms of θ and φ, yield the full angular part of the wave function for any centrosymmetric potential. These solutions are usually written as $Y_{l,m}(\theta,\varphi) = P_l^m(\mathrm{Cos}\theta)\,(2\pi)^{-\frac{1}{2}}\,\exp(im\varphi)$, and are called spherical harmonics. They provide the angular solution of the r,θ, φ Schrödinger equation for <u>any</u> problem in which the potential depends only on the radial coordinate. Such situations include all one-electron atoms and ions (e.g., H, He^+, Li^{++} , etc.), the rotational motion of a diatomic molecule (where the potential depends only on bond length r), the motion of a nucleon in a spherically symmetrical "box" (as occurs in the shell model of nuclei), and the scattering of two atoms (where the potential depends only on interatomic distance). The $Y_{l,m}$ functions possess varying number of angular nodes, which, as noted earlier, give clear signatures of the angular or rotational energy content of the wave function. These angular nodes originate in the oscillatory nature of the Legendre and associated Legendre polynomials $P_l^M(\cos\theta)$; the higher l is, the more sign changes occur within the polynomial.

3. The R Equation

Let us now turn our attention to the radial equation, which is the only place that the explicit form of the potential appears. Using our earlier results for the equation obeyed by the R(r) function and specifying V(r) to be the coulomb potential appropriate for an electron in the field of a nucleus of charge +Ze, yields:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{r}\right) - \frac{l(l+1)}{r^2}\right) R = 0.$$

We can simplify things considerably if we choose rescaled length and energy units because doing so removes the factors that depend on μ, $\hbar$, and e. We introduce a new radial coordinate ρ and a quantity σ as follows:

$$\rho = \left(\frac{-8\mu E}{\hbar^2}\right)^{\frac{1}{2}} r, \text{ and } \sigma^2 = -\frac{\mu Z^2 e^4}{2E\hbar^2} .$$

Notice that if E is negative, as it will be for bound states (i.e., those states with energy below that of a free electron infinitely far from the nucleus and with zero kinetic energy), ρ is real. On the other hand, if E is positive, as it will be for states that lie in the continuum, ρ will be imaginary. These two cases will give rise to qualitatively different behavior in the solutions of the radial equation developed below.

We now define a function S such that S(ρ) = R(r) and substitute S for R to obtain:

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dS}{d\rho}\right)+\left(-\frac{1}{4}-\frac{l(l+1)}{\rho^2}+\frac{\sigma}{\rho}\right)S=0.$$

The differential operator terms can be recast in several ways using

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dS}{d\rho}\right)=\frac{d^2S}{d\rho^2}+\frac{2}{\rho}\frac{dS}{d\rho}=\frac{1}{\rho}\frac{d^2}{d\rho^2}(\rho S)\ .$$

The strategy that we now follow is characteristic of solving second order differential equations. We will examine the equation for S at large and small ρ values. Having found solutions at these limits, we will use a power series in ρ to "interpolate" between these two limits.

Let us begin by examining the solution of the above equation at small values of ρ to see how the radial functions behave at small r. As $\rho \to 0$, the second term in the brackets will dominate. Neglecting the other two terms in the brackets, we find that, for small values of ρ (or r), the solution should behave like ρ^L and because the function must be normalizable, we must have $L \geq 0$. Since L can be any non-negative integer, this suggests the following more general form for $S(\rho)$:

$$S(\rho) \approx \rho^L e^{-a\rho}.$$

This form will insure that the function is normalizable since $S(\rho) \to 0$ as $r \to \infty$ for all L, as long as ρ is a real quantity. If ρ is imaginary, such a form may not be normalized (see below for further consequences).

Turning now to the behavior of S for large ρ, we make the substitution of $S(\rho)$ into the above equation and keep only the terms with the largest power of ρ (e.g., the first term in brackets). Upon so doing, we obtain the equation

$$a^2\rho^L e^{-a\rho} = \frac{1}{4}\ \rho^L e^{-a\rho} ,$$

which leads us to conclude that the exponent in the large-ρ behavior of S is $a = \frac{1}{2}$.

Having found the small- and large-ρ behaviors of $S(\rho)$, we can take S to have the following form to interpolate between large and small ρ-values:

$$S(\rho) = \rho^L e^{-\frac{\rho}{2}}\ P(\rho),$$

where the function P is expanded in an infinite power series in ρ as $P(\rho) = \sum a_k \rho^k$.

Again substituting this expression for S into the above equation we obtain

$$P''\rho + P'(2L+2-\rho) + P(\sigma-L-l) = 0,$$

and then substituting the power series expansion of P and solving for the a_k's we arrive at a recursion relation for the a_k coefficients:

$$a_{k+1} = \frac{(k-\sigma+L+l)\, a_k}{(k+1)(k+2L+2)} \ .$$

For large k, the ratio of expansion coefficients reaches the limit $\frac{a_{k+1}}{a_k} = \frac{1}{k}$, which has the same behavior as the power series expansion of e^{ρ}. Because the power series expansion of P describes a function that behaves like e^{ρ} for large ρ, the resulting $S(\rho)$ function would not be normalizable because the $e^{-\frac{\rho}{2}}$ factor would be overwhelmed by this e^{ρ} dependence. Hence, the series expansion of P must truncate in order to achieve a normalizable S function. Notice that if ρ is imaginary, as it will be if E is in the continuum, the argument that the series must truncate to avoid an exponentially diverging function no longer applies. Thus, we see a key difference between bound (with ρ real) and continuum (with ρ imaginary) states. In the former case, the boundary condition of non-divergence arises; in the latter, it does not because $\exp(\rho/2)$ does not diverge if ρ is imaginary.

To truncate at a polynomial of order n', we must have $n' - \sigma + L + l = 0$. This implies that the quantity σ introduced previously is restricted to $\sigma = n' + L + l$, which is certainly an integer; let us call this integer n. If we label states in order of increasing n = 1,2,3,... , we see that doing so is consistent with specifying a maximum order (n') in the $P(\rho)$ polynomial n' = 0,1,2,... after which the L-value can run from L = 0, in steps of unity up to L = n-1.

Substituting the integer n for σ , we find that the energy levels are quantized because σ is quantized (equal to n):

$$E = - \frac{\mu Z^2 e^4}{2\hbar^2 n^2}$$

and the scaled distance turns out to be

$$\rho = \frac{Zr}{a_o n} .$$

Here, the length a_o is the so called Bohr radius $\left(a_o = \frac{\hbar^2}{\mu e^2} \right)$; it appears once the above E-expression is substituted into the equation for ρ. Using the recursion equation to solve for the polynomial's coefficients a_k for any choice of n and l quantum numbers generates a so-called Laguerre polynomial; $P_{n-L-1}(\rho)$. They contain powers of ρ from zero through n-L-1, and they have n-L-1 sign changes as the radial coordinate ranges from zero to infinity. It is these sign changes in the Laguerre polynomials that cause the radial parts of the hydrogenic wave functions to have n-L-1 nodes. For example, 3d orbitals have no radial nodes, but 4d orbitals have one; and, as shown in Fig. 2.16, 3p orbitals have one while 3s orbitals have two. Once again, the higher the number of nodes, the higher the energy in the radial direction.

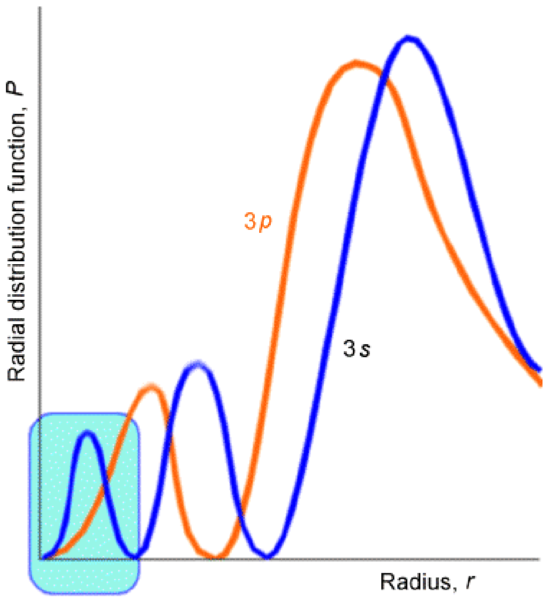


Figure 2.16. Plots of the Radial Parts of the 3s and 3p Orbitals

Let me again remind you about the danger of trying to understand quantum wave functions or probabilities in tems of classical dynamics. What kind of potential V(r) would give rise to, for example, the 3s P(r) plot shown above? Classical mechanics suggests that P should be large where the particle moves slowly and small where it moves quickly. So, the 3s P(r) plot suggests that the radial speed of the electron has three regions where it is low (i.e., where the peaks in P are) and two regions where it is very large (i.e., where the nodes are). This, in turn, suggests that the radial potential V(r) experienced by the 3s electron is high in three regions (near peaks in P) and low in two regions (and at the nucleus). Of course, this conclusion about the form of V(r) is nonsense and again illustrates how one must not be drawn into trying to think of the classical motion of the particle, especially for quantum states with small quantum number. In fact, the low quantum number states of such one-electron atoms and ions have their radial P(r) plots focused in regions of r-space where the potential $-Ze^2/r$ is most attractive (i.e., largest in magnitude).

Finally, we note that the energy quantization does not arise for states lying in the continuum because the condition that the expansion of P(ρ) terminate does not arise. The solutions of the radial equation appropriate to these scattering states (which relate to the scattering motion of an electron in the field of a nucleus of charge Z) are a bit outside the scope of this text, so we will not treat them further here. For the interested student, they are treated on p. 90 of the text by Eyring, Walter, and Kimball.

To review, separation of variables has been used to solve the full r,θ,φ Schrödinger equation for one electron moving about a nucleus of charge Z. The θ and φ solutions are the spherical harmonics $Y_{L,m}$ (θ,φ). The bound-state radial solutions

$$R_{n,L}(r) = S(\rho) = \rho^L e^{-\frac{\rho}{2}} \; P_{n-L-1}(\rho)$$

depend on the n and l quantum numbers and are given in terms of the Laguerre polynomials.

4. Summary

To summarize, the quantum numbers L and m arise through boundary conditions requiring that ψ(θ) be normalizable (i.e., not diverge) and ψ(φ) = ψ(φ+2π). The radial equation, which is the only place the potential energy enters, is found to possess both bound-states (i.e., states whose energies lie below the asymptote at which the potential vanishes and the kinetic energy is zero) and continuum states lying energetically above this asymptote. The resulting hydrogenic wave functions (angular and radial) and energies are summarized on pp. 133-136 in the text by L. Pauling and E. B. Wilson for n up to and including 6 and L up to 5.

There are both bound and continuum solutions to the radial Schrödinger equation for the attractive coulomb potential because, at energies below the asymptote, the potential confines the particle between r=0 and an outer turning point, whereas at energies above the asymptote, the particle is no longer confined by an outer turning point (see Fig. 2.17).

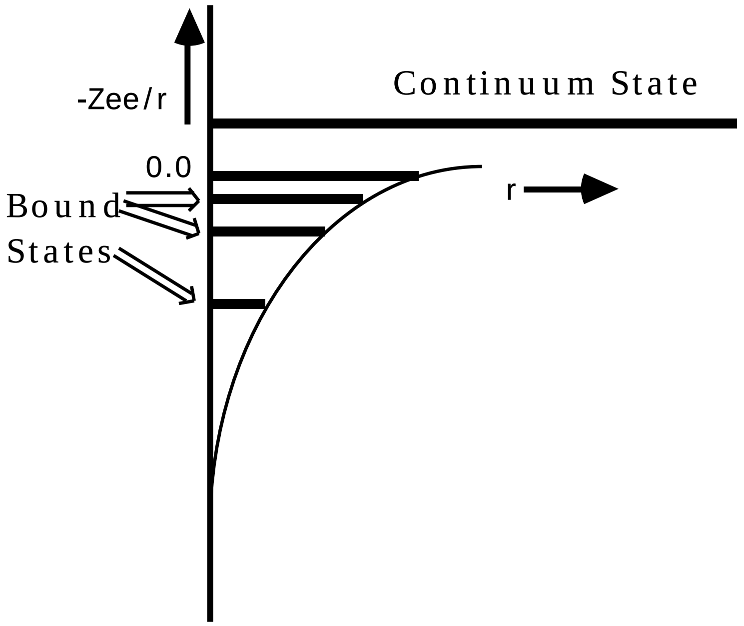


Figure 2.17. Radial Potential for Hydrogenic Atoms and Bound and Continuum Orbital Energies.

The solutions of this one-electron problem form the qualitative basis for much of atomic and molecular orbital theory. For this reason, the reader is encouraged to gain a firmer understanding of the nature of the radial and angular parts of these wave functions. The orbitals that result are labeled by n, L, and m quantum numbers for the bound states and by L and m quantum numbers and the energy E for the continuum states. Much as the particle-in-a-box orbitals are used to qualitatively describe π- electrons in conjugated polyenes, these so-called hydrogen-like orbitals provide qualitative descriptions of orbitals of atoms with more than a single electron. By introducing the concept of screening as a way to represent the repulsive interactions among the electrons of an atom, an effective nuclear charge Z_{eff} can be used in place of Z in the $\psi_{n,L,m}$ and E_n to generate approximate atomic orbitals to be filled by electrons in a many-electron atom. For example, in the crudest approximation of a carbon atom, the two 1s electrons experience the full nuclear attraction so $Z_{eff} = 6$ for them, whereas the 2s and 2p electrons are screened by the two 1s electrons, so $Z_{eff} = 4$ for them. Within this approximation, one then occupies two 1s orbitals with Z = 6, two 2s orbitals with Z = 4 and two 2p orbitals with Z=4 in forming the full six-electron wave function of the lowest-energy state of carbon.

VI. Electron Tunneling

Tunneling is a phenomenon of quantum mechanics, not classical mechanics. It is an extremely important subject that occurs in a wide variety of chemical species.

Solutions to the Schrödinger equation display several properties that are very different from what one experiences in Newtonian dynamics. One of the most unusual and important is that the particles one describes using quantum mechanics can move into regions of space where they would not be “allowed” to go if they obeyed classical equations. Let us consider an example to illustrate this so-called tunneling phenomenon. Specifically, we think of an electron (a particle that we likely would use quantum mechanics to describe) moving in a direction we will call R under the influence of a potential that is:

a. Infinite for $R < 0$ (this could, for example, represent a region of space within a solid material where the electron experiences very repulsive interactions with other electrons);

b. Constant and negative for some range of R between $R = 0$ and R_{max} (this could represent the attractive interaction of the electrons with those atoms or molecules in a finite region of a solid);

c. Constant and repulsive by an amount $\delta V + D_e$ for another finite region from R_{max} to $R_{max} + \delta$ (this could represent the repulsive interactions between the electrons and a layer of molecules of thickness δ lying on the surface of the solid at R_{max});

d. Constant and equal to D_e from $R_{maz} + \delta$ to infinity (this could represent the electron being removed from the solid, but with a “work function energy cost of D_e, and moving freely in the vacuum above the surface and the ad-layer). Such a potential is shown in Fig. 2.18.

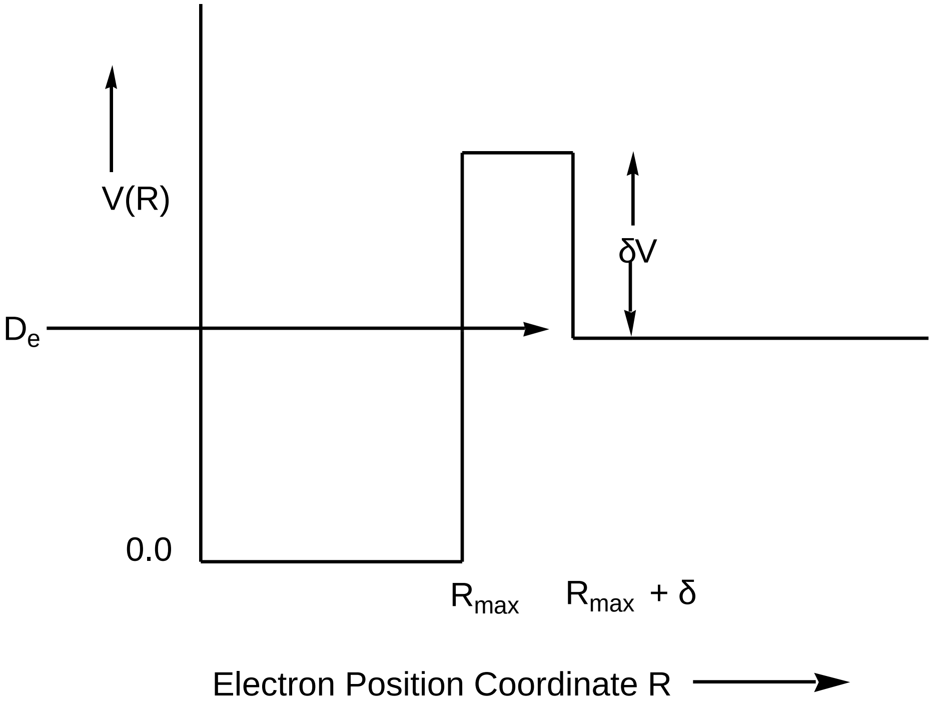


Figure 2.18. One-dimensional potential showing a well, a barrier, and the asymptotic region.

The piecewise nature of this potential allows the one-dimensional Schrödinger equation to be solved analytically. For energies lying in the range $D_e < E < D_e + \delta V$, an especially interesting class of solutions exists. These so-called resonance states occur at energies that are determined by the condition that the amplitude of the wave function within the barrier (i.e., for $0 \le R \le R_{max}$) be large. Let us now turn our attention to this specific energy regime, which also serves to introduce the tunneling phenomenon.

The piecewise solutions to the Schrödinger equation appropriate to the resonance case are easily written down in terms of sin and cos or exponential functions, using the following three definitions:

$$k = \sqrt{2m_e E/\hbar^2}, k' = \sqrt{2m_e(E - D_e)/\hbar^2}, \kappa' = \sqrt{2m_e(D_e + \delta V - E)/\hbar^2}$$

The combination of sin(kR) and cos(kR) that solve the Schrödinger equation in the inner region and that vanish at R=0 (because the function must vanish within the region where V is infinite and because it must be continuous, it must vanish at R=0) is:

$$\Psi = A\sin(kR) \qquad\qquad (\text{for } 0 \le R \le R_{max}).$$

Between R_{max} and $R_{max} + \delta$, there are two solutions that obey the Schrödiger equation, so the most general solution is a combination of these two:

$$\Psi = B^+ \exp(\kappa' R) + B^- \exp(-\kappa' R) \qquad\qquad (\text{for } R_{max} \le R \le R_{max} + \delta).$$

Finally, in the region beyond $R_{max} + \delta$, we can use a combination of either sin(k’R) and cos(k’R) or exp(ik’R) and exp(-ik’R) to express the solution. Unlike the region near R=0, where it was most convenient to use the sin and cos functions because one of them could be “thrown away” since it could not meet the boundary condition of vanishing at R=0, in this large-R region, either set is acceptable. We choose to use the exp(ik’R) and exp(-ik’R) set because each of these functions is an eigenfunction of the momentum operator $-i\hbar\partial/\partial R$. This allows us to discuss amplitudes for electrons moving with positive momentum and with negative momentum. So, in this region, the most general solution is

$$\Psi = C \exp(ik'R) + D \exp(-ik'R) \qquad \text{(for } R_{max} + \delta \leq R < \infty).$$

There are four amplitudes (A, B_+, B_-, and C) that can be expressed in terms of the specified amplitude D of the incoming flux (e.g., pretend that we know the flux of electrons that our experimental apparatus “shoots” at the surface). Four equations that can be used to achieve this goal result when Ψ and $d\Psi/dR$ are matched at R_{max} and at $R_{max} + \delta$ (one of the essential properties of solutions to the Schrödinger equation is that they and their first derivative are continuous; these properties relate to Ψ being a probability and $-ih\partial/\partial R$ being a momentum operator). These four equations are:

$$A\sin(kR_{max}) = B^+ \exp(\kappa' R_{max}) + B^- \exp(-\kappa' R_{max}),$$

$$Ak\cos(kR_{max}) = \kappa' B^+ \exp(\kappa' R_{max}) - \kappa' B^- \exp(-\kappa' R_{max}),$$

$$B^+ \exp(\kappa'(R_{max} + \delta)) + B^- \exp(-\kappa'(R_{max} + \delta))$$

$$= C \exp(ik'(R_{max} + \delta) + D \exp(-ik'(R_{max} + \delta),$$

$$\kappa' B^+ \exp(\kappa'(R_{max} + \delta)) - \kappa' B^- \exp(-\kappa'(R_{max} + \delta))$$

$$= ik'C \exp(ik'(R_{max} + \delta)) - ik' D \exp(-ik'(R_{max} + \delta)).$$

It is especially instructive to consider the value of A/D that results from solving this set of four equations in four unknowns because the modulus of this ratio provides information about the relative amount of amplitude that exists inside the barrier in the attractive region of the potential compared to that existing in the asymptotic region as incoming flux.

The result of solving for A/D is:

$$A/D = 4\, \kappa' \exp(-ik'(R_{max}+\delta))$$

$$\{\exp(\kappa'\delta)(ik'-\kappa')(\kappa'\sin(kR_{max})+k\cos(kR_{max}))/ik'$$

$$+ \exp(-\kappa'\delta)(ik'+\kappa')(\kappa'\sin(kR_{max})-k\cos(kR_{max}))/ik' \}^{-1}.$$

Further, it is instructive to consider this result under conditions of a high (large $D_e + \delta V - E$) and thick (large δ) barrier. In such a case, the "tunneling factor" $\exp(-\kappa'\delta)$ will be very small compared to its counterpart $\exp(\kappa'\delta)$, and so

$$A/D = 4 \frac{ik'\kappa'}{ik'-\kappa'} \exp(-ik'(R_{max}+\delta)) \exp(-\kappa'\delta) \{\kappa'\sin(kR_{max})+k\cos(kR_{max}) \}^{-1}.$$

The $\exp(-\kappa'\delta)$ factor in A/D causes the magnitude of the wave function inside the barrier to be small in most circumstances; we say that incident flux must tunnel through the barrier to reach the inner region and that $\exp(-\kappa'\delta)$ gives the probability of this tunneling.

Keep in mind that, in the energy range we are considering ($E < D_e+\delta$), a classical particle could not even enter the region $R_{max} < R < R_{max} + \delta$; this is why we call this the classically forbidden or tunneling region. A classical particle starting in the large-R region can not enter, let alone penetrate, this region, so such a particle could never end up in the $0 < R < R_{max}$ inner region. Likewise, a classical particle that begins in the inner region can never penetrate the tunneling region and escape into the large-R region. Were it not for the fact that electrons obey a Schrödinger equation rather than Newtonian dynamics, tunneling would not occur and, for example, scanning tunneling microscopy (STM), which has proven to be a wonderful and powerful tool for imaging molecules on and near surfaces, would not exist. Likewise, many of the devices that appear in our modern electronic tools and games, which depend on currents induced by tunneling through various junctions, would not be available. But, or course, tunneling does occur and it can have remarkable effects.

Let us examine an especially important (in chemistry) phenomenon that takes place because of tunneling and that occurs when the energy E assumes very special values. The magnitude of the A/D factor in the above solutions of the Schrödinger equation can become large if the energy E is such that

$$\kappa'\sin(kR_{max})+k\cos(kR_{max})$$

is small. In fact, if

$$\tan(kR_{max}) = -\ k/\kappa'$$

the denominator factor in A/D will vanish and A/D will become infinite. It can be shown that the above condition is similar to the energy quantization condition

$$\tan(kR_{max}) = -\ k/\kappa$$

that arises when bound states of a finite potential well are examined. There is, however, a difference. In the bound-state situation, two energy-related parameters occur

$$k = \sqrt{2\mu E/\hbar^2}$$

and

$$\kappa = \sqrt{2\mu(D_e - E)/\hbar^2}\ .$$

In the case we are now considering, k is the same, but

$$\kappa' = \sqrt{2\mu(D_e + \delta V - E)/\hbar^2}\ )$$

rather than κ occurs, so the two $\tan(kR_{max})$ equations are not identical, but they are quite similar.

Another observation that is useful to make about the situations in which A/D becomes very large can be made by considering the case of a very high barrier (so that κ' is much larger than k). In this case, the denominator that appears in A/D

$$\kappa'\sin(kR_{max})+k\cos(kR_{max}) \quad \kappa' \sin(kR_{max})$$

can become small if

$$\sin(kR_{max}) \quad 0.$$

This condition is nothing but the energy quantization condition that occurs for the particle-in-a-box potential shown in Fig. 2.19.

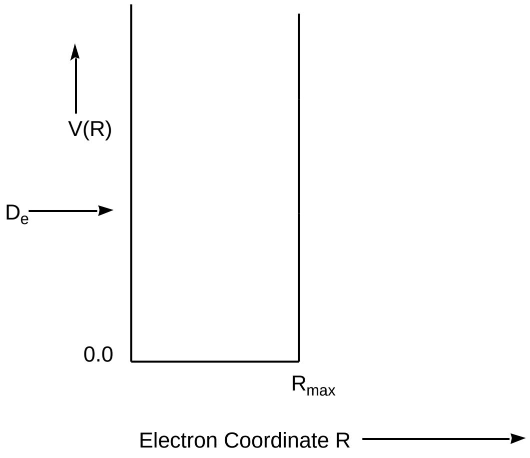


Figure 2.19. One-dimensional potential similar to the tunneling potential but without the barrier and asymptotic region.

This potential is identical to the potential that we were examining for $0 \le R \le R_{max}$, but extends to infinity beyond R_{max} ; the barrier and the dissociation asymptote displayed by our potential are absent.

Let’s consider what this tunneling problem has taught us. First, it showed us that quantum particles penetrate into classically forbidden regions. It showed that, at certain so-called resonance energies, tunneling is much more likely that at energies that are “off resonance”. In our model problem, this means that electrons impinging on the surface with resonance energies will have a very high probability of tunneling to produce an electron that is trapped in the $0 < R < R_{max}$ region.

By the way, we could have solved the four equations for the amplitude C of the outgoing wave in the $R > R_{max}$ region in terms of the A amplitude. We might want to take this approach if wanted to model an experiment in which the electron began in the $0 < R < R_{max}$ region and we wanted to compute the relative amplitude for the electron to escape. However, if we were to solve for C/A and then examined under what conditions the amplitude of this ratio would become small (so the electron can not escape), we would find the same $\tan(kR_{max}) = - k/\kappa'$ resonance condition as we found from the other point of view. This means that the resonance energies tell us for what collision energies the electron will tunnel inward and produce a trapped electron and, at these same energies, an electron that is trapped will not escape quickly.

Whenever one has a barrier on a potential energy surface, at energies above the dissociation asymptote D_e but below the top of the barrier ($D_e + \delta V$ here), one can expect resonance states to occur at "special" scattering energies E. As we illustrated with the model problem, these so-called resonance energies can often be approximated by the bound-state energies of a potential that is identical to the potential of interest in the inner region ($0 \le R \le R_{max}$) but that extends to infinity beyond the top of the barrier (i.e., beyond the barrier, it does not fall back to values below E).

The chemical significance of resonances is great. Highly rotationally excited molecules may have more than enough total energy to dissociate (D_e), but this energy may be "stored" in the rotational motion, and the vibrational energy may be less than D_e. In terms of the above model, high angular momentum may produce a significant centrifugal barrier in the effective potential that characterizes the molecule’s vibration, but the system's vibrational energy may lie significantly below D_e. In such a case, and when viewed in terms of motion on an angular-momentum-modified effective potential such as I show in Fig. 2.20 , the lifetime of the molecule with respect to dissociation is determined by the rate of tunneling through the barrier.

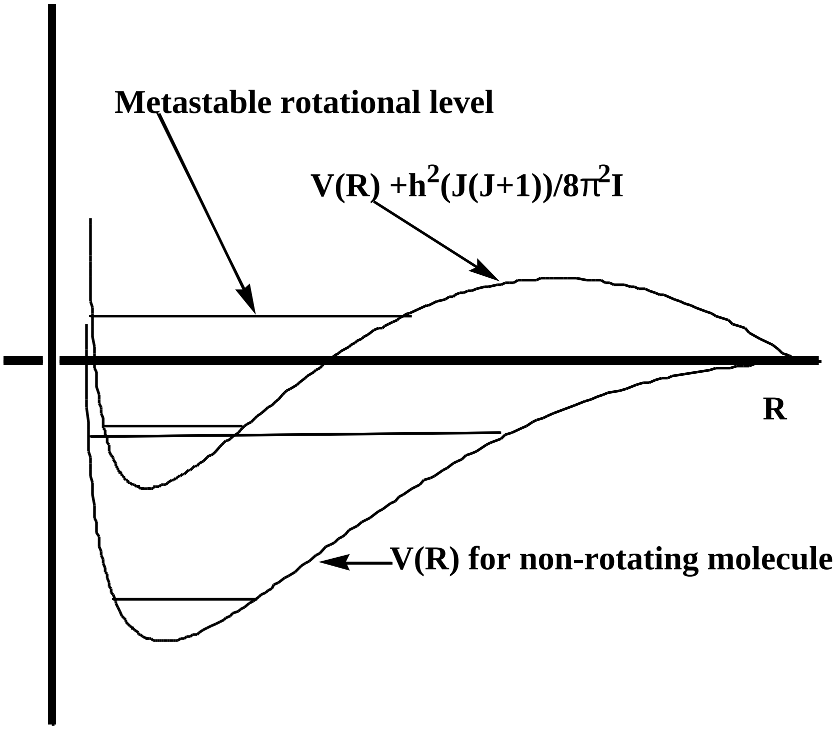


Figure 2.20. Radial potential for non-rotating (J = 0) molecule and for rotating molecule.

In that case, one speaks of "rotational predissociation" of the molecule. The lifetime τ can be estimated by computing the frequency ν at which flux that exists inside R_{max} strikes the barrier at R_{max}

$$\nu = \frac{\hbar k}{2\mu R_{max}} \quad (\text{sec}^{-1})$$

and then multiplying by the probability P that flux tunnels through the barrier from R_{max} to $R_{max} + \delta$:

$$P = \exp(-2\kappa'\delta).$$

The result is that

$$\tau^{-1} = \frac{\hbar k}{2\mu R_{max}} \exp(-2\kappa'\delta)$$

with the energy E entering into k and κ' being determined by the resonance condition: $(\kappa'\sin(kR_{max})+k\cos(kR_{max}))$ = minimum. By looking back at the defintion of κ', we note that the probability of tunneling falls of exponentially with a factor depending on the width δ of the barrier through which the particle must tunnel multiplied by κ', which depends on the height of the barrier $D_e + \delta$ above the energy E available. This exponential dependence on thickness and height of the barriers is something you should keep in mind because it appears in all tunneling rate expressions.

Another important case in which tunneling occurs is in electronically metastable states of anions. In so-called shape resonance states, the anion's "extra" electron experiences

a. an attractive potential due to its interaction with the underlying neutral molecule's dipole, quadrupole, and induced electrostatic moments, as well as

b. a centrifugal potential of the form $L(L+1)h^2/8\pi^2 m_e R^2$ whose magnitude depends on the angular character of the orbital the extra electron occupies.

When combined, the above attractive and centrifugal potentials produce an effective radial potential of the form shown in Fig. 2.21 for the N_2^- case in which the added electron occupies the π^* orbital which has L=2 character when viewed from the center of the N-N bond. Again, tunneling through the barrier in this potential determines the lifetimes of such shape resonance states.

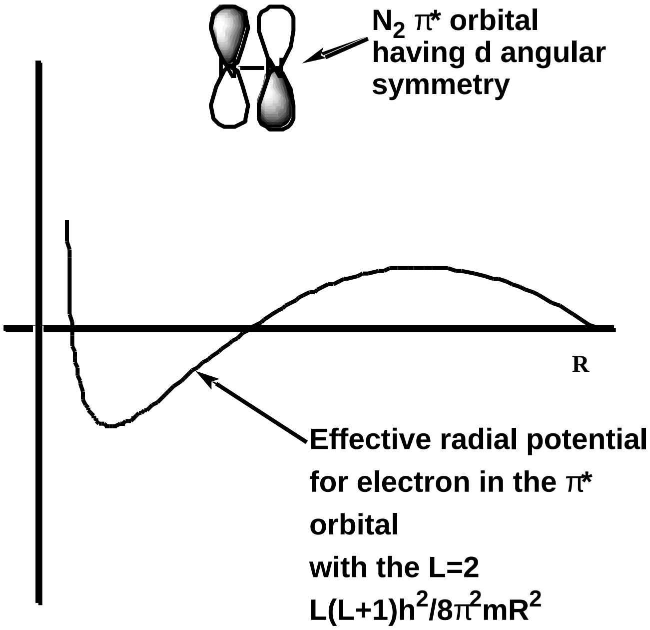


Figure 2.21 Effective radial potential for the excess electron in N_2^- occupying the π^* orbital which has a dominant L = 2 component.

Although the examples treated above involved piecewise constant potentials (so the Schrödinger equation and the boundary matching conditions could be solved exactly), many of the characteristics observed carry over to more chemically realistic situations. In fact, one can often model chemical reaction processes in terms of motion along a "reaction coordinate" (s) from a region characteristic of reactant materials where the potential surface is positively curved in all direction and all forces (i.e., gradients of the potential along all internal coordinates) vanish; to a transition state at which the potential surface's curvature along s is negative while all other curvatures are positive and all forces vanish; onward to product materials where again all curvatures are positive and all forces vanish. A prototypical trace of the energy variation along such a reaction coordinate is in Fig. 2.22.

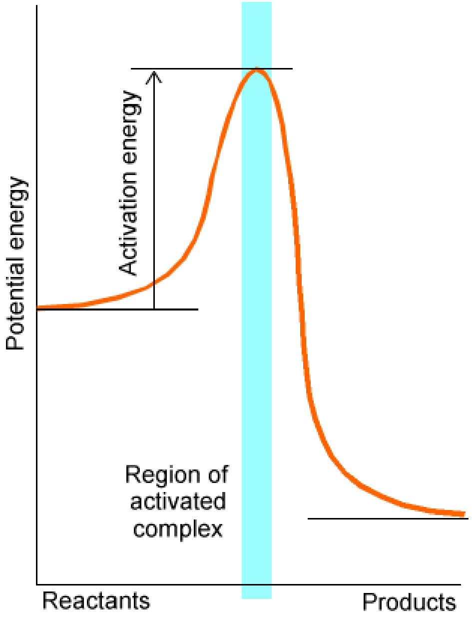


Figure 2.22. Energy profile along a reaction path showing the barrier through which tunneling may occur.

Near the transition state at the top of the barrier on this surface, tunneling through the barrier plays an important role if the masses of the particles moving in this region are sufficiently light. Specifically, if H or D atoms are involved in the bond breaking and forming in this region of the energy surface, tunneling must usually be considered in treating the dynamics.

Within the above "reaction path" point of view, motion transverse to the reaction coordinate s is often modeled in terms of local harmonic motion although more sophisticated treatments of the dynamics is possible. This picture leads one to consider motion along a single degree of freedom (s), with respect to which much of the above treatment can be carried over, coupled to transverse motion along all other internal degrees of freedom taking place under an entirely positively curved potential (which therefore produces restoring forces to movement away from the "streambed" traced out by the reaction path s). This point of view constitutes one of the most widely used and successful models of molecular reaction dynamics and is treated in more detail in Chapter 8 of this text.

VII. Angular Momentum

1. Orbital Angular Momentum

A particle moving with momentum **p** at a position **r** relative to some coordinate origin has so-called orbital angular momentum equal to **L** = **r** x **p** . The three components of this angular momentum vector in a Cartesian coordinate system located at the origin mentioned above are given in terms of the Cartesian coordinates of **r** and **p** as follows:

$$L_z = x\, p_y - y\, p_x ,$$

$$L_x = y\, p_z - z\, p_y ,$$

$$L_y = z\, p_x - x\, p_z .$$

Using the fundamental commutation relations among the Cartesian coordinates and the Cartesian momenta:

$$[q_k,p_j] = q_k\, p_j - p_j\, q_k = i\hbar\, \delta_{j,k} \ (j,k = x,y,z) ,$$

it can be shown that the above angular momentum operators obey the following set of commutation relations:

$$[L_x, L_y] = i\hbar\, L_z ,$$

$$[L_y, L_z] = i\hbar\, L_x ,$$

$$[L_z, L_x] = i\hbar\, L_y .$$

Although the components of **L** do not commute with one another, they can be shown to commute with the operator L^2 defined by

$$L^2 = L_x^2 + L_y^2 + L_z^2 .$$

This new operator is referred to as the square of the total angular momentum operator.

The commutation properties of the components of **L** allow us to conclude that complete sets of functions can be found that are eigenfunctions of L^2 and of one, but not more than one, component of **L**. It is convention to select this one component as L_z, and to label the resulting simultaneous eigenstates of L^2 and L_z as $|l,m>$ according to the corresponding eigenvalues:

$$L^2 \, |l,m> = \hbar^2 \, l(l+1) \, |l,m>, \; l = 0,1,2,3,....$$

$$L_z \, |l,m> = \hbar \, m \, |l,m>, \; m = \pm \, l, \pm(l-1), \pm(l-2), \ldots \pm(l-(l-1)), 0.$$

These eigenfunctions of L^2 and of L_z will not, in general, be eigenfunctions of either L_x or of L_y. This means that any measurement of L_x or L_y will necessarily change the wavefunction if it begins as an eigenfunction of L_z.

The above expressions for L_x, L_y, and L_z can be mapped into quantum mechanical operators by substituting x, y, and z as the corresponding coordinate operators and $-i\hbar\partial/\partial x$, $-i\hbar\partial/\partial y$, and $-i\hbar\partial/\partial z$ for p_x, p_y, and p_z, respectively. The resulting operators can then be transformed into spherical coordinates the results of which are:

$$L_z = -i\hbar\, \partial/\partial\varphi\,,$$

$$L_x = i\hbar\, \{\sin\varphi\, \partial/\partial\theta + \cot\theta\, \cos\varphi\, \partial/\partial\varphi\}\,,$$

$$L_y = -i\hbar\, \{\cos\varphi\, \partial/\partial\theta - \cot\theta\, \sin\varphi\, \partial/\partial\varphi\}\,,$$

$$L^2 = -\hbar^2\, \{(1/\sin\theta)\, \partial/\partial\theta\, (\sin\theta\, \partial/\partial\theta) + (1/\sin^2\theta)\, \partial^2/\partial\varphi^2\}\,.$$

2. Properties of General Angular Momenta

There are many types of angular momenta that one encounters in chemistry. Orbital angular momenta, such as that introduced above, arise in electronic motion in atoms, in atom-atom and electron-atom collisions, and in rotational motion in molecules. Intrinsic spin angular momentum is present in electrons, H^1, H^2, C^{13}, and many other nuclei. In this section, we will deal with the behavior of any and all angular momenta and their corresponding eigenfunctions.

At times, an atom or molecule contains more than one type of angular momentum. The Hamiltonian's interaction potentials present in a particular species may or may not cause these individual angular momenta to be coupled to an appreciable extent (i.e., the Hamiltonian may or may not contain terms that refer simultaneously to two or more of these angular momenta). For example, the NH^- ion, which has a $^2\Pi$

ground electronic state (its electronic configuration is $1s_N{}^2 2\sigma^2 3\sigma^2 2p_{\pi x}{}^2 2p_{py}{}^1$) has electronic spin, electronic orbital, and molecular rotational angular momenta. The full Hamiltonian H contains terms that couple the electronic spin and orbital angular momenta, thereby causing them individually to not commute with H.

In such cases, the eigenstates of the system can be labeled rigorously only by angular momentum quantum numbers j and m belonging to the total angular momentum **J**. The total angular momentum of a collection of individual angular momenta is defined, component-by-component, as follows:

$$J_k = \Sigma_i J_k(i),$$

where k labels x, y, and z, and i labels the constituents whose angular momenta couple to produce **J**.

For the remainder of this Section, we will study eigenfunction-eigenvalue relationships that are characteristic of all angular momenta and which are consequences of the commutation relations among the angular momentum vector's three components. We will also study how one combines eigenfunctions of two or more angular momenta {**J**(i)} to produce eigenfunctions of the the total **J**.

a. Consequences of the Commutation Relations

Any set of three operators that obey

$$[J_x, J_y] = i\hbar J_z ,$$

$$[J_y, J_z] = i\hbar J_x ,$$

$$[J_z, J_x] = i\hbar J_y ,$$

will be taken to define an angular momentum **J**, whose square $J^2 = J_x^2 + J_y^2 + J_z^2$ commutes with all three of its components. It is useful to also introduce two combinations of the three fundamental operators:

$$J_\pm = J_x \pm i J_y ,$$

and to refer to them as raising and lowering operators for reasons that will be made clear below. These new operators can be shown to obey the following commutation relations:

$$[J^2, J_\pm] = 0,$$

$$[J_z, J_\pm] = \pm \hbar J_\pm .$$

Using only the above commutation properties, it is possible to prove important properties of the eigenfunctions and eigenvalues of J^2 and J_z. Let us assume that we have found a set of simultaneous eigenfunctions of J^2 and J_z ; the fact that these two operators commute tells us that this is possible. Let us label the eigenvalues belonging to these functions:

$$J^2 |j,m\rangle = \hbar^2 f(j,m) |j,m\rangle,$$

$$J_z |j,m\rangle = \hbar m |j,m\rangle,$$

in terms of the quantities m and f(j,m). Although we certainly "hint" that these quantities must be related to certain j and m quantum numbers, we have not yet proven this, although we will soon do so. For now, we view f(j,m) and m simply as symbols that represent the respective eigenvalues. Because both J^2 and J_z are Hermitian, eigenfunctions belonging to different f(j,m) or m quantum numbers must be orthogonal:

$$\langle j,m|j',m'\rangle = \delta_{m,m'} \delta_{j,j'} .$$

We now prove several identities that are needed to discover the information about the eigenvalues and eigenfunctions of general angular momenta that we are after. Later in this Section, the essential results are summarized.

i. There is a Maximum and a Minimum Eigenvalue for J_z

Because all of the components of **J** are Hermitian, and because the scalar product of any function with itself is positive semi-definite, the following identity holds:

$$<j,m|J_x^2 + J_y^2|j,m> = <J_x<j,m|\ J_x|j,m> + <J_y<j,m|\ J_y|j,m> \ \geq 0.$$

However, $J_x^2 + J_y^2$ is equal to $J^2 - J_z^2$, so this inequality implies that

$$<j,m|\ J^2 - J_z^2\ |j,m> = \hbar^2\ \{f(j,m) - m^2\} \geq 0,$$

which, in turn, implies that m^2 must be less than or equal to f(j,m). Hence, for any value of the total angular momentum eigenvalue f, the z-projection eigenvalue (m) must have a maximum and a minimum value and both of these must be less than or equal to the total angular momentum squared eigenvalue f.

ii. The Raising and Lowering Operators Change the J_z Eigenvalue but not the J^2 Eigenvalue When Acting on |j,m>

Applying the commutation relations obeyed by $J_\pm$ to |j,m> yields another useful result:

$$J_z\ J_\pm\ |j,m> - J_\pm\ J_z\ |j,m> = \pm\ \hbar\ J_\pm\ |j,m>,$$

$$J^2\ J_\pm\ |j,m> - J_\pm\ J^2\ |j,m> = 0.$$

Now, using the fact that |j,m> is an eigenstate of J^2 and of J_z, these identities give

$$J_z\ J_\pm\ |j,m> \ = (m\hbar \pm \hbar)\ J_\pm\ |j,m> = \hbar\ (m\pm1)\ |j,m>,$$

$$J^2 J_\pm |j,m> = \hbar^2 f(j,m) J_\pm |j,m>.$$

These equations prove that the functions $J_\pm |j,m>$ must either themselves be eigenfunctions of J^2 and J_z, with eigenvalues $\hbar^2 f(j,m)$ and $\hbar (m+1)$ or $J_\pm |j,m>$ must equal zero. In the former case, we see that $J_\pm$ acting on $|j,m>$ generates a new eigenstate with the same J^2 eigenvalue as $|j,m>$ but with one unit of $\hbar$ higher or lower in J_z eigenvalue. It is for this reason that we call $J_\pm$ raising and lowering operators. Notice that, although $J_\pm |j,m>$ is indeed an eigenfunction of J_z with eigenvalue $(m\pm1) \hbar$, $J_\pm |j,m>$ is not identical to $|j,m\pm1>$; it is only proportional to $|j,m\pm1>$:

$$J_\pm |j,m> = C^\pm{}_{j,m} |j,m\pm1>.$$

Explicit expressions for these $C^\pm{}_{j,m}$ coefficients will be obtained below. Notice also that because the $J_\pm |j,m>$, and hence $|j,m\pm1>$, have the same J^2 eigenvalue as $|j,m>$ (in fact, sequential application of $J_\pm$ can be used to show that all $|j,m'>$, for all m', have this same J^2 eigenvalue), the J^2 eigenvalue f(j,m) must be independent of m. For this reason, f can be labeled by one quantum number j.

iii. The J^2 Eigenvalues are Related to the Maximum and Minimum J_z Eigenvalues Which are Related to One Another

Earlier, we showed that there exists a maximum and a minimum value for m, for any given total angular momentum. It is when one reaches these limiting cases that $J_{\pm}$ $|j,m\rangle = 0$ applies. In particular,

$$J_+ |j,m_{max}\rangle = 0,$$

$$J_- |j,m_{min}\rangle = 0.$$

Applying the following identities:

$$J_- J_+ = J^2 - J_z^2 - \hbar J_z ,$$

$$J_+ J_- = J^2 - J_z^2 + \hbar J_z,$$

respectively, to $|j,m_{max}\rangle$ and $|j,m_{min}\rangle$ gives

$$\hbar^2 \{ f(j,m_{max}) - m_{max}^2 - m_{max}\} = 0,$$

$$\hbar^2 \{ f(j,m_{min}) - m_{min}^2 + m_{min}\} = 0,$$

which immediately gives the J^2 eigenvalue $f(j,m_{max})$ and $f(j,m_{min})$ in terms of m_{max} or m_{min}:

$$f(j,m_{max}) = m_{max} (m_{max}+1),$$

$$f(j,m_{min}) = m_{min} (m_{min}-1).$$

So, we now know the J^2 eigenvalues for $|j,m_{max}>$ and $|j,m_{min}>$. However, we earlier showed that $|j,m>$ and $|j,m-1>$ have the same J^2 eigenvalue (when we treated the effect of $J_\pm$ on $|j,m>$) and that the J^2 eigenvalue is independent of m. If we therefore define the quantum number j to be m_{max} , we see that the J^2 eigenvalues are given by

$$J^2 |j,m> = \hbar^2 j(j+1) |j,m>.$$

We also see that

$$f(j,m) = j(j+1) = m_{max} (m_{max}+1) = m_{min} (m_{min}-1),$$

from which it follows that

$$m_{min} = - m_{max} .$$

iv. The j Quantum Number Can Be Integer or Half-Integer

The fact that the m-values run from j to -j in unit steps (because of the property of the $J_\pm$ operators), there clearly can be only integer or half-integer values for j. In the former case, the m quantum number runs over -j, -j+1, -j+2, ..., -j+(j-1), 0, 1, 2, ... j; in the latter, m runs over -j, -j+1, -j+2, ...-j+(j-1/2), 1/2, 3/2, ...j. Only integer and half-interger values can range from j to -j in steps of unity. Species with integer spin are known as Bosons and those with half-integer spin are called Fermions.

v. More on $J_\pm$ |j,m>

Using the above results for the effect of $J_\pm$ acting on |j,m> and the fact that J_+ and J_- are adjoints of one another, allows us to write:

$$<j,m|\, J_-\, J_+\, |j,m> = <j,m|\, (J^2 - J_z^2 - \hbar\, J_z\,)\, |j,m>$$

$$= \hbar^2\, \{j(j+1)-m(m+1)\} = <J_+<j,m|\, J_+|j,m> = (C^+_{j,m})^2,$$

where $C^+_{j,m}$ is the proportionality constant between J_+|j,m> and the normalized function |j,m+1>. Likewise, the effect of J_- can be expressed as

$$<j,m|\, J_+\, J_-\, |j,m> = <j,m|\, (J^2 - J_z^2 + \hbar\, J_z)\, |j,m>$$

$$= \hbar^2\, \{j(j+1)-m(m-1)\} = <J_-<j,m|\, J_-|j,m> = (C^-_{j,m})^2,$$

where $C^-_{j,m}$ is the proportionality constant between J_- |j,m> and the normalized |j,m-1>. Thus, we can solve for $C^\pm_{j,m}$ after which the effect of $J_\pm$ on |j,m> is given by:

$$J_\pm |j,m\rangle = \hbar \{j(j+1) - m(m-1)\}^{1/2} |j,m\pm1\rangle.$$

3. Summary

The above results apply to any angular momentum operators. The essential findings can be summarized as follows:

(i) J^2 and J_Z have complete sets of simultaneous eigenfunctions. We label these eigenfunctions |j,m>; they are orthonormal in both their m- and j-type indices: $\langle j,m| j',m'\rangle = \delta_{m,m'} \delta_{j,j'}$.

(ii) These |j,m> eigenfunctions obey:

$$J^2 |j,m\rangle = \hbar^2 j(j+1) |j,m\rangle, \{ j= \text{integer or half-integer}\},$$

$$J_Z |j,m\rangle = \hbar m |j,m\rangle, \{ m = -j, \text{ in steps of 1 to } +j\}.$$

(iii) The raising and lowering operators $J_\pm$ act on |j,m> to yield functions that are eigenfunctions of J^2 with the same eigenvalue as |j,m> and eigenfunctions of J_z with eigenvalue of (m±1) ħ :

$$J_\pm |j,m> = \hbar \{j(j+1) - m(m\pm1)\}^{1/2} |j,m\pm1>.$$

(iv) When $J_\pm$ acts on the "extremal" states |j,j> or |j,-j>, respectively, the result is zero.

The results given above are, as stated, general. Any and all angular momenta have quantum mechanical operators that obey these equations. It is convention to designate specific kinds of angular momenta by specific letters; however, it should be kept in mind that no matter what letters are used, there are operators corresponding to J^2, J_z, and $J_\pm$ that obey relations as specified above, and there are eigenfunctions and eigenvalues that have all of the properties obtained above. For electronic or collisional orbital angular momenta, it is common to use L^2 and L_z ; for electron spin, S^2 and S_z are used; for nuclear spin I^2 and I_z are most common; and for molecular rotational angular momentum, N^2 and N_z are most common (although sometimes J^2 and J_z may be used). Whenever two or more angular momenta are combined or coupled to produce a "total" angular momentum, the latter is designated by J^2 and J_z.

4. Coupling of Angular Momenta

If the Hamiltonian under study contains terms that couple two or more angular momenta **J**(i), then only the components of the total angular momentum **J** = Σ_i **J**(i) and **J**^{2} will commute with H. It is therefore essential to label the quantum states of the system by the eigenvalues of $\mathbf{J_z}$ and **J**^{2} and to construct variational trial or model wavefunctions that are eigenfunctions of these total angular momentum operators. The problem of angular momentum coupling has to do with how to combine eigenfunctions of the uncoupled angular momentum operators, which are given as simple products of the eigenfunctions of the individual angular momenta $\Pi_i |j_i,m_i>$, to form eigenfunctions of J^2 and J_z.

a. Eigenfunctions of J_z

Because the individual elements of **J** are formed additively, but J^2 is not , it is straightforward to form eigenstates of

$$J_z = \Sigma_i J_z(i);$$

simple products of the form $\Pi_i |j_i,m_i>$ are eigenfunctions of J_z:

$$J_z \Pi_i |j_i,m_i> = \Sigma_k J_z(k) \Pi_i |j_i,m_i> = \Sigma_k \hbar m_k \Pi_i |j_i,m_i>,$$

and have J_Z eigenvalues equal to the sum of the individual $m_k \hbar$ eigenvalues. Hence, to form an eigenfunction with specified J and M eigenvalues, one must combine only those product states $\Pi_i |j_i,m_i>$ whose $m_i\hbar$ sum is equal to the specified M value.

b. Eigenfunctions of J^2; the Clebsch-Gordon Series

The task is then reduced to forming eigenfunctions |J,M>, given particular values for the $\{j_i\}$ quantum numbers. When coupling pairs of angular momenta { |j,m> and |j',m'>}, the total angular momentum states can be written, according to what we determined above, as

$$|J,M> = \Sigma_{m,m'} C^{J,M}_{j,m;j',m'} |j,m> |j',m'>,$$

where the coefficients $C^{J,M}_{j,m;j',m'}$ are called vector coupling coefficients (because angular momentum coupling is viewed much like adding two vectors **j** and **j'** to produce another vector **J**), and where the sum over m and m' is restricted to those terms for which m+m' = M. It is more common to express the vector coupling or so-called Clebsch-Gordon (CG) coefficients as <j,m;j'm'|J,M> and to view them as elements of a "matrix" whose columns are labeled by the coupled-state J,M quantum numbers and whose rows are labeled by the quantum numbers characterizing the uncoupled "product basis" j,m;j',m'. It turns out that this matrix can be shown to be unitary so that the CG coefficients obey:

$$\Sigma_{m,m'} \; \langle j,m;j'm'|J,M\rangle^* \langle j,m;j'm'|J',M'\rangle = \delta_{J,J'} \delta_{M,M'}$$

and

$$\Sigma_{J,M} \; \langle j,n;j'n'|J,M\rangle \langle j,m;j'm'|J,M\rangle^* = \delta_{n,m} \delta_{n',m'}.$$

This unitarity of the CG coefficient matrix allows the inverse of the relation giving coupled functions in terms of the product functions:

$$|J,M\rangle = \Sigma_{m,m'} \langle j,m;j'm'|J,M\rangle \, |j,m\rangle \, |j',m'\rangle$$

to be written as:

$$|j,m\rangle \, |j',m'\rangle = \Sigma_{J,M} \langle j,m;j'm'|J,M\rangle^* \, |J,M\rangle$$

$$= \Sigma_{J,M} \langle J,M|j,m;j'm'\rangle \, |J,M\rangle.$$

This result expresses the product functions in terms of the coupled angular momentum functions.

c. Generation of the CG Coefficients

The CG coefficients can be generated in a systematic manner; however, they can also be looked up in books where they have been tabulated (e.g., see Table 2.4 of Dick Zare's book on angular momentum). Here, we will demonstrate the technique by which the CG coefficients can be obtained, but we will do so for rather limited cases and refer the reader to more extensive tabulations.

The strategy we take is to generate the |J,J> state (i.e., the state with maximum M-value) and to then use J_- to generate |J,J-1>, after which the state |J-1,J-1> (i.e., the state with one lower J-value) is constructed by finding a combination of the product states in terms of which |J,J-1> is expressed (because both |J,J-1> and |J-1,J-1> have the same M-value M=J-1) which is orthogonal to |J,J-1> (because |J-1,J-1> and |J,J-1> are eigenfunctions of the Hermitian operator J^2 corresponding to different eigenvalues, they must be orthogonal). This same process is then used to generate |J,J-2> |J-1,J-2> and (by orthogonality construction) |J-2,J-2>, and so on.

i. The States With Maximum and Minimum M-Values

We begin with the state |J,J> having the highest M-value. This state must be formed by taking the highest m and the highest m' values (i.e., m=j and m'=j'), and is given by:

$$|J,J> = |j,j> |j'j'>.$$

Only this one product is needed because only the one term with m=j and m'=j' contributes to the sum in the above CG series. The state

$$|J,-J\rangle = |j,-j\rangle\, |j',-j'\rangle$$

with the minimum M-value is also given as a single product state.

Notice that these states have M-values given as ±(j+j'); since this is the maximum M-value, it must be that the J-value corresponding to this state is J= j+j'.

ii. States With One Lower M-Value But the Same J-Value

Applying J_- to $|J,J\rangle$, and expressing J_- as the sum of lowering operators for the two individual angular momenta:

$$J_- = J_-(1) + J_-(2)$$

gives

$$J_-|J,J\rangle = \hbar\{J(J+1) -J(J-1)\}^{1/2}\, |J,J-1\rangle$$

$$= (J_-(1) + J_-(2))\, |j,j\rangle\, |j'j'\rangle$$

$$= \hbar\{j(j+1) - j(j-1)\}^{1/2}\, |j,j-1\rangle\, |j',j'\rangle + \hbar\{j'(j'+1)-j'(j'-1)\}^{1/2}\, |j,j\rangle\, |j',j'-1\rangle.$$

This result expresses $|J,J-1\rangle$ as follows:

$$|J,J-1\rangle= [\{j(j+1)-j(j-1)\}^{1/2}\, |j,j-1\rangle\, |j',j'\rangle$$

$$+ \{j'(j'+1)-j'(j'-1)\}^{1/2} |j,j> |j',j'-1>] \{J(J+1) -J(J-1)\}^{-1/2};$$

that is, the |J,J-1> state, which has M=J-1, is formed from the two product states |j,j-1> |j',j'> and |j,j> |j',j'-1> that have this same M-value.

iii. States With One Lower J-Value

To find the state |J-1,J-1> that has the same M-value as the one found above but one lower J-value, we must construct another combination of the two product states with M=J-1 (i.e., |j,j-1> |j',j'> and |j,j> |j',j'-1>) that is orthogonal to the combination representing |J,J-1>; after doing so, we must scale the resulting function so it is properly normalized. In this case, the desired function is:

$$|J-1,J-1>= [\{j(j+1)-j(j-1)\}^{1/2} |j,j> |j',j'-1>$$

$$- \{j'(j'+1)-j'(j'-1)\}^{1/2} |j,j-1> |j',j'>] \{J(J+1) -J(J-1)\}^{-1/2} .$$

It is straightforward to show that this function is indeed orthogonal to |J,J-1>.

iv. States With Even One Lower J-Value

Having expressed |J,J-1> and |J-1,J-1> in terms of |j,j-1> |j',j'> and |j,j> |j',j'-1>, we are now prepared to carry on with this stepwise process to generate the states |J,J-2>, |J-1,J-2> and |J-2,J-2> as combinations of the product states with M=J-2. These product states are |j,j-2> |j',j'>, |j,j> |j',j'-2>, and |j,j-1> |j',j'-1>. Notice that there are precisely as many product states whose m+m' values add up to the desired M-value as there are total angular momentum states that must be constructed (there are three of each in this case).

The steps needed to find the state |J-2,J-2> are analogous to those taken above:

a. One first applies J_- to |J-1,J-1> and to |J,J-1> to obtain |J-1,J-2> and |J,J-2>, respectively as combinations of |j,j-2> |j',j'>, |j,j> |j',j'-2>, and |j,j-1> |j',j'-1>.

b. One then constructs |J-2,J-2> as a linear combination of the |j,j-2> |j',j'>, |j,j> |j',j'-2>, and |j,j-1> |j',j'-1> that is orthogonal to the combinations found for |J-1,J-2> and |J,J-2>.

Once |J-2,J-2> is obtained, it is then possible to move on to form |J,J-3>, |J-1,J-3>, and |J-2,J-3> by applying J_- to the three states obtained in the preceding application of the process, and to then form |J-3,J-3> as the combination of |j,j-3> |j',j'>, |j,j> |j',j'-3>, |j,j-2> |j',j'-1>, |j,j-1> |j',j'-2> that is orthogonal to the combinations obtained for |J,J-3>, |J-1,J-3>, and |J-2,J-3>.

Again notice that there are precisely the correct number of product states (four here) as there are total angular momentum states to be formed. In fact, the product states and the total angular momentum states are equal in number and are both members of orthonormal function sets (because $J^2(1)$, $J_z(1)$, $J^2(2)$, and $J_z(2)$ as well as J^2 and J_z are Hermitian operators). This is why the CG coefficient matrix is unitary; because it maps one set of orthonormal functions to another, with both sets containing the same number of functions.

d. An Example

Let us consider an example in which the spin and orbital angular momenta of the Si atom in its ^3P ground state can be coupled to produce various ^3P_J states. In this case, the specific values for j and j' are j=S=1 and j'=L=1. We could, of course take j=L=1 and j'=S=1, but the final wavefunctions obtained would span the same space as those we are about to determine.

The state with highest M-value is the $^3P(M_s=1, M_L=1)$ state, which can be represented by the product of an $\alpha\alpha$ spin function (representing S=1, M_s=1) and a $3p_1 3p_0$ spatial function (representing L=1, M_L=1), where the first function corresponds to the first open-shell orbital and the second function to the second open-shell orbital. Thus, the maximum M-value is M= 2 and corresponds to a state with J=2:

$$|J=2,M=2\rangle = |2,2\rangle = \alpha\alpha\ 3p_1 3p_0 .$$

Clearly, the state $|2,-2\rangle$ would be given as $\beta\beta\ 3p_{-1}3p_0$.

The states $|2,1\rangle$ and $|1,1\rangle$ with one lower M-value are obtained by applying $J_- = S_- + L_-$ to $|2,2\rangle$ as follows:

$$J_- |2,2\rangle = \hbar\{2(3)-2(1)\}^{1/2} |2,1\rangle$$

$$= (S_- + L_-)\ \alpha\alpha\ 3p_1 3p_0 .$$

To apply S_- or L_- to $\alpha\alpha\ 3p_1 3p_0$, one must realize that each of these operators is, in turn, a sum of lowering operators for each of the two open-shell electrons:

$$S_- = S_-(1) + S_-(2),$$

$$L_- = L_-(1) + L_-(2).$$

The result above can therefore be continued as

$$(S_- + L_-)\ \alpha\alpha\ 3p_1 3p_0 = \hbar\{1/2(3/2)-1/2(-1/2)\}^{1/2}\ \beta\alpha\ 3p_1 3p_0$$

$$+ \hbar\{1/2(3/2)-1/2(-1/2)\}^{1/2}\ \alpha\beta\ 3p_1 3p_0$$

$$+ \hbar\{1(2)-1(0)\}^{1/2}\ \alpha\alpha\ 3p_0 3p_0$$

$$+ \hbar\{1(2)-0(-1)\}^{1/2}\ \alpha\alpha\ 3p_1 3p_{-1}.$$

So, the function $|2,1>$ is given by

$$|2,1> = [\beta\alpha\ 3p_1 3p_0 + \alpha\beta\ 3p_1 3p_0 + \{2\}^{1/2}\ \alpha\alpha\ 3p_0 3p_0$$

$$+ \{2\}^{1/2}\ \alpha\alpha\ 3p_1 3p_{-1}]/2,$$

which can be rewritten as:

$$|2,1> = [(\beta\alpha + \alpha\beta)3p_1 3p_0 + \{2\}1/2\ \alpha\alpha\ (3p_0 3p_0 + 3p_1 3p_{-1})]/2.$$

Writing the result in this way makes it clear that |2,1> is a combination of the product states $|S=1,M_S=0>$ $|L=1,M_L=1>$ (the terms containing $|S=1,M_S=0> = 2^{-1/2}(\alpha\beta+\beta\alpha)$) and $|S=1,M_S=1>$ $|L=1,M_L=0>$ (the terms containing $|S=1,M_S=1> = \alpha\alpha$).

To form the other function with M=1, the |1,1> state, we must find another combination of $|S=1,M_S=0>$ $|L=1,M_L=1>$ and $|S=1,M_S=1>$ $|L=1,M_L=0>$ that is orthogonal to |2,1> and is normalized. Since

$$|2,1> = 2^{-1/2}\ [|S=1,M_S=0>\ |L=1,M_L=1> + |S=1,M_S=1>\ |L=1,M_L=0>],$$

we immediately see that the requisite function is

$$|1,1> = 2^{-1/2}\ [|S=1,M_S=0>\ |L=1,M_L=1> - |S=1,M_S=1>\ |L=1,M_L=0>].$$

In the spin-orbital notation used above, this state is:

$$|1,1> = [(\beta\alpha + \alpha\beta)3p_1 3p_0 - \{2\}^{1/2}\ \alpha\alpha\ (3p_0 3p_0 + 3p_1 3p_{-1})]/2.$$

Thus far, we have found the ^3P_J states with J=2, M=2; J=2, M=1; and J=1, M=1.

To find the ^3P_J states with J=2, M=0; J=1, M=0; and J=0, M=0, we must once again apply the J_- tool. In particular, we apply J_- to |2,1> to obtain |2,0> and we apply J_- to |1,1> to obtain |1,0>, each of which will be expressed in terms of $|S=1,M_S=0>$ $|L=1,M_L=0>$, $|S=1,M_S=1>$ $|L=1,M_L=-1>$, and $|S=1,M_S=-1>$ $|L=1,M_L=1>$. The |0,0> state is then constructed to be a combination of these same product states which is orthogonal to |2,0> and to |1,0>. The results are as follows:

$$|J=2,M=0> = 6^{-1/2}[2\ |1,0>\ |1,0> + |1,1>\ |1,-1> + |1,-1>\ |1,1>],$$

$$|J=1,M=0> = 2^{-1/2}[|1,1>\ |1,-1> - |1,-1>\ |1,1>],$$

$$|J=0, M=0> = 3^{-1/2}[|1,0>\ |1,0> - |1,1>\ |1,-1> - |1,-1>\ |1,1>],$$

where, in all cases, a short hand notation has been used in which the $|S,M_S>$ $|L,M_L>$ product stated have been represented by their quantum numbers with the spin function always appearing first in the product. To finally express all three of these new functions in terms of spin-orbital products it is necessary to give the $|S,M_S>$ $|L,M_L>$ products with M=0 in terms of these products. For the spin functions, we have:

$$|S=1,M_S=1> = \alpha\alpha,$$

$$|S=1,M_S=0> = 2^{-1/2}(\alpha\beta+\beta\alpha).$$

$$|S=1,M_S=-1> = \beta\beta.$$

For the orbital product function, we have:

$$|L=1, M_L=1> = 3p_1 3p_0 ,$$

$$|L=1,M_L=0> = 2^{-1/2}(3p_0 3p_0 + 3p_1 3p_{-1}),$$

$$|L=1, M_L=-1> = 3p_0 3p_{-1}.$$

e. Coupling Angular Momenta of Equivalent Electrons

If equivalent angular momenta are coupled (e.g., to couple the orbital angular momenta of a p^2 or d^3 configuration), one must use the following "box" method to determine which of the term symbols violate the Pauli principle. To carry out this step, one forms all possible unique (determinental) product states with non-negative M_L and M_S values and arranges them into groups according to their M_L and M_S values. For example, the boxes appropriate to the p^2 orbital occupancy are shown below:

	M_L	2	1	0
M_S	1		$\vert p_1\alpha p_0\alpha\vert$	$\vert p_1\alpha p_{-1}\alpha\vert$
	0	$\vert p_1\alpha p_1\beta\vert$	$\vert p_1\alpha p_0\beta\vert$, $\vert p_0\alpha p_1\beta\vert$	$\vert p_1\alpha p_{-1}\beta\vert$, $\vert p_{-1}\alpha p_1\beta\vert$, $\vert p_0\alpha p_0\beta\vert$

There is no need to form the corresponding states with negative M_L or negative M_S values because they are simply "mirror images" of those listed above. For example, the state with $M_L= -1$ and $M_S = -1$ is $|p_{-1}\beta p_0\beta|$, which can be obtained from the $M_L = 1$, $M_S = 1$ state $|p_1\alpha p_0\alpha|$ by replacing α by β and replacing p_1 by p_{-1}.

Given the box entries, one can identify those term symbols that arise by applying the following procedure over and over until all entries have been accounted for:

i. One identifies the highest M_S value (this gives a value of the total spin quantum number that arises, S) in the box. For the above example, the answer is S = 1.

ii. For all product states of this M_S value, one identifies the highest M_L value (this gives a value of the total orbital angular momentum, L, that can arise for this S). For the above example, the highest M_L within the M_S =1 states is $M_L = 1$ (not $M_L = 2$), hence L=1.

iii. Knowing an S, L combination, one knows the first term symbol that arises from this configuration. In the p^2 example, this is ^3P.

iv. Because the level with this L and S quantum numbers contains (2L+1)(2S+1) states with M_L and M_S quantum numbers running from -L to L and from -S to S, respectively, one must remove from the original box this number of product states. To do so, one simply erases from the box one entry with each such M_L and M_S value. Actually, since the box need only show those entries with non-negative M_L and M_S values, only these entries need be explicitly deleted. In the ^3P example, this amounts to deleting nine product states with M_L, M_S values of 1,1; 1,0; 1,-1; 0,1; 0,0; 0,-1; -1,1; -1,0; -1,-1.

v. After deleting these entries, one returns to step 1 and carries out the process again. For the p^2 example, the box after deleting the first nine product states looks as follows (those that appear in italics should be viewed as already cancelled in counting all of the ^3P states):

	M_L	2	1	0
M_S	1		*$\|p_1\alpha p_0\alpha\|$*	*$\|p_1\alpha p_{-1}\alpha\|$*
	0	$\|p_1\alpha p_1\beta\|$	*$\|p_1\alpha p_0\beta\|$*, $\|p_0\alpha p_1\beta\|$	*$\|p_1\alpha p_{-1}\beta\|$*, $\|p_{-1}\alpha p_1\beta\|$, $\|p_0\alpha p_0\beta\|$

It should be emphasized that the process of deleting or crossing off entries in various M_L, M_S boxes involves only counting how many states there are; by no means do we identify the particular L,S,M_L,M_S wavefunctions when we cross out any particular entry in a box. For example, when the $|p_1\alpha p_0\beta|$ product is deleted from the M_L= 1, M_S=0 box in accounting for the states in the ^3P level, we do not claim that $|p_1\alpha p_0\beta|$ itself is a member of the ^3P level; the $|p_0\alpha p_1\beta|$ product state could just as well been eliminated when accounting for the ^3P states.

Returning to the p^2 example at hand, after the ^3P term symbol's states have been accounted for, the highest M_S value is 0 (hence there is an S=0 state), and within this M_S value, the highest M_L value is 2 (hence there is an L=2 state). This means there is a ^1D level with five states having M_L = 2,1,0,-1,-2. Deleting five appropriate entries from the above box (again denoting deletions by italics) leaves the following box:

	M_L	2	1	0
M_S	1		$\mathit{|p_1\alpha p_0\alpha|}$	$\mathit{|p_1\alpha p_{-1}\alpha|}$
	0	$\mathit{|p_1\alpha p_1\beta|}$	$\mathit{|p_1\alpha p_0\beta|}$, $\mathit{|p_0\alpha p_1\beta|}$	$\mathit{|p_1\alpha p_{-1}\beta|}$, $\mathit{|p_{-1}\alpha p_1\beta|}$, $|\mathrm{p}_0\alpha \mathrm{p}_0\beta|$

The only remaining entry, which thus has the highest M_S and M_L values, has M_S = 0 and M_L = 0. Thus there is also a ^1S level in the p^2 configuration.

Thus, unlike the non-equivalent $2p^1 3p^1$ case, in which ^3P, ^1P, ^3D, ^1D, ^3S, and ^1S levels arise, only the ^3P, ^1D, and ^1S arise in the p^2 situation. This "box method" is necessary to carry out whenever one is dealing with equivalent angular momenta.

If one has mixed equivalent and non-equivalent angular momenta, one can determine all possible couplings of the equivalent angular momenta using this method and then use the simpler vector coupling method to add the non-equivalent angular momenta to <u>each</u> of these coupled angular momenta. For example, the p^2d^1 configuration can be handled by vector coupling (using the straightforward non-equivalent procedure) L=2 (the d orbital) and S=1/2 (the third electron's spin) to <u>each</u> of ^3P, ^1D, and ^1S. The result is ^4F, ^4D, ^4P, ^2F, ^2D, ^2P, ^2G, ^2F, ^2D, ^2P, ^2S, and ^2D.

VIII. Rotations of Molecules

1. Rotational Motion For Rigid Diatomic and Linear Polyatomic Molecules

This Schrödinger equation relates to the rotation of diatomic and linear polyatomic molecules. It also arises when treating the angular motions of electrons in any spherically symmetric potential.

A diatomic molecule with fixed bond length R rotating in the absence of any external potential is described by the following Schrödinger equation:

$$\hbar^2/2\mu \, \{(R^2\sin\theta)^{-1}\partial/\partial\theta \, (\sin\theta \, \partial/\partial\theta) + (R^2\sin^2\theta)^{-1} \, \partial^2/\partial\varphi^2 \} \, \psi = E \, \psi$$

or

$$L^2\psi/2\mu R^2 = E\ \psi,$$

where L^2 is the square of the total angular momentum operator $L_x^2 + L_y^2 + L_z^2$ expressed in polar coordinates above. The angles θ and φ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule $\mu=m_1m_2/(m_1+m_2)$. The differential operators can be seen to be exactly the same as those that arose in the hydrogen-like-atom caseas discussed above. Therefore, the same spherical harmonics that served as the angular parts of the wave function in the hydrogen-atom case now serve as the entire wave function for the so-called rigid rotor: $\psi = Y_{J,M}(\theta,\varphi)$. These are exactly the same functions as we plotted earlier when we graphed the s (L=0), p (L=1), and d (L=2) orbitals. As detailed in Chapter 6 of this text, the energy eigenvalues corresponding to each such eigenfunction are given as:

$$E_J = \hbar^2\ J(J+1)/(2\mu R^2) = B\ J(J+1)$$

and are independent of M. Thus each energy level is labeled by J and is 2J+1-fold degenerate (because M ranges from -J to J). Again, this is just like we saw when we looked at the hydrogen orbitals; the p orbitals are 3-fold degenerate and the d orbitals are 5-fold degenerate. The so-called rotational constant B (defined as $\hbar^2/2\mu R^2$) depends on the molecule's bond length and reduced mass. Spacings between successive rotational levels (which are of spectroscopic relevance because, as shown in Chapter 6, angular momentum selection rules often restrict the changes ΔJ in J that can occur upon photon absorption to 1,0, and -1) are given by

$$\Delta E = B\,(J+1)(J+2) - B\,J(J+1) = 2B(J+1).$$

These energy spacings are of relevance to microwave spectroscopy which probes the rotational energy levels of molecules. In fact, microwave spectroscopy offers the most direct way to determine molecular rotational constants and hence molecular bond lengths.

The rigid rotor provides the most commonly employed approximation to the rotational energies and wave functions of linear molecules. As presented above, the model restricts the bond length to be fixed. Vibrational motion of the molecule gives rise to changes in R which are then reflected in changes in the rotational energy levels. The coupling between rotational and vibrational motion gives rise to rotational B constants that depend on vibrational state as well as dynamical couplings, called centrifugal distortions, that cause the total ro-vibrational energy of the molecule to depend on rotational and vibrational quantum numbers in a non-separable manner.

Within this "rigid rotor" model, the absorption spectrum of a rigid diatomic molecule should display a series of peaks, each of which corresponds to a specific J ==> J + 1 transition. The energies at which these peaks occur should grow linearly with J. An example of such a progression of rotational lines is shown in the Fig. 2.23.

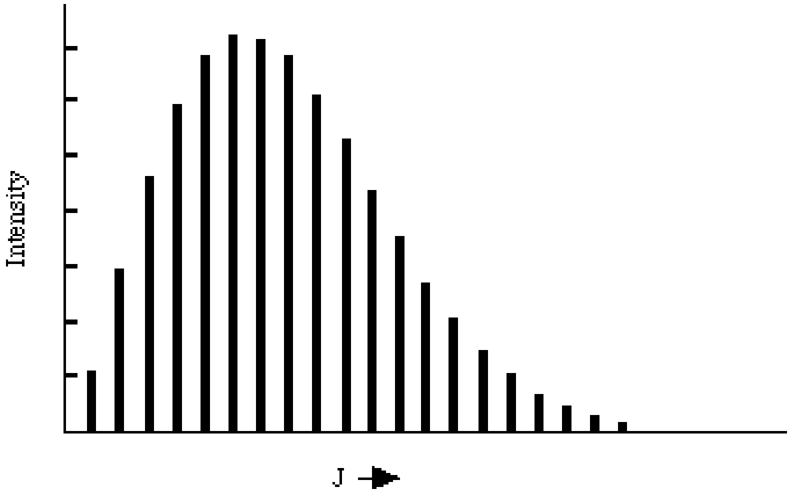


Figure 2.23. Typical rotational absorption profile showing intensity vs. J value of the absorbing level

The energies at which the rotational transitions occur appear to fit the $\Delta E = 2B\,(J+1)$ formula rather well. The intensities of transitions from level J to level J+1 vary strongly with J primarily because the population of molecules in the absorbing level varies with J. These populations P_J are given, when the system is at equilibrium at temperature T, in terms of the degeneracy (2J+1) of the J^{th} level and the energy of this level B J(J+1) by the Boltzmann formula:

$$P_J = Q^{-1}\,(2J+1)\,\exp(-BJ(J+1)/kT),$$

where Q is the rotational partition function:

$$Q = \Sigma_J\,(2J+1)\,\exp(-BJ(J+1)/kT).$$

For low values of J, the degeneracy is low and the exp(-BJ(J+1)/kT) factor is near unity. As J increases, the degeracy grows linearly but the exp(-BJ(J+1)/kT) factor decreases more rapidly. As a result, there is a value of J, given by taking the derivative of (2J+1) exp(-BJ(J+1)/kT) with respect to J and setting it equal to zero,

$$2J_{max} + 1 = \sqrt{2kT/B}$$

at which the intensity of the rotational transition is expected to reach its maximum. This behavior is clearly displayed in the above figure.

The eigenfunctions belonging to these energy levels are the spherical harmonics $Y_{L,M}(\theta,\varphi)$ which are normalized according to

$$\int_0^{\pi} (\int_0^{2\pi} (Y^*_{L,M}(\theta,\varphi)\, Y_{L',M'}(\theta,\varphi) \sin\theta\, d\theta\, d\varphi)) = \delta_{L,L'}\, \delta_{M,M'} .$$

As noted above, these functions are identical to those that appear in the solution of the angular part of Hydrogen-like atoms. The above energy levels and eigenfunctions also apply to the rotation of rigid linear polyatomic molecules; the only difference is that the moment of inertia I entering into the rotational energy expression is given by

$$I = \Sigma_a m_a R_a^2$$

where m_a is the mass of the a^{th} atom and R_a is its distance from the center of mass of the molecule. This moment of inertia replaces μR^2 in the earlier rotational energy level expressions.

2. Rotational Motions of Rigid Non-Linear Molecules

a. The Rotational Kinetic Energy

The rotational kinetic energy operator for a rigid polyatomic molecule is

$$H_{rot} = J_a^2/2I_a + J_b^2/2I_b + J_c^2/2I_c$$

where the I_k (k = a, b, c) are the three principal moments of inertia of the molecule (the eigenvalues of the moment of inertia tensor). This tensor has elements in a Cartesian coordinate system (K, K' = X, Y, Z), whose origin is located at the center of mass of the molecule, that can be computed as:

$$I_{K,K} = \sum_j m_j (R_j^2 - R^2_{K,j}) \qquad \text{(for K = K')}$$

$$I_{K,K'} = - \sum_j m_j R_{K,j} R_{K',j} \qquad \text{(for K} \neq \text{K').}$$

As discussed in more detail in Chapter 6, the components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \,[\cot\theta\, \partial/\partial\chi - (\sin\theta)^{-1}\partial/\partial\varphi\,] - -i\hbar \sin\chi\, \partial/\partial\theta$$

$$J_b = i\hbar \sin\chi \,[\cot\theta\, \partial/\partial\chi - (\sin\theta)^{-1}\partial/\partial\varphi\,] - -i\hbar \cos\chi\, \partial/\partial\theta$$

$$J_c = - i\hbar\, \partial/\partial\chi.$$

The angles θ, φ, and χ are the Euler angles needed to specify the orientation of the rigid molecule relative to a laboratory-fixed coordinate system. The corresponding square of the total angular momentum operator J^2 can be obtained as

$$J^2 = J_a^2 + J_b^2 + J_c^2$$

$$= - \partial^2/\partial\theta^2 - \cot\theta\, \partial/\partial\theta$$

$$+ (1/\sin\theta)\, (\partial^2/\partial\varphi^2 + \partial^2/\partial\chi^2 - 2\cos\theta\,\partial^2/\partial\varphi\partial\chi),$$

and the component along the lab-fixed Z axis J_Z is $- i\hbar\, \partial/\partial\varphi$ as we saw much earlier in this text.

b. The Eigenfunctions and Eigenvalues for Special Cases

i. Spherical Tops

When the three principal moment of inertia values are identical, the molecule is termed a spherical top. In this case, the total rotational energy can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = J^2/2I.$$

As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a as well as J_Z both of which commute with J^2 and with one another. J_Z is the component of **J** along the lab-fixed Z-axis and commutes with J_a because $J_Z = - i\hbar\, \partial/\partial\varphi$ and $J_a = - i\hbar\, \partial/\partial\chi$ act on different angles. The energies associated with such eigenfunctions are

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

for all K (i.e., J_a quantum numbers) ranging from -J to J in unit steps and for all M (i.e., J_Z quantum numbers) ranging from -J to J. Each energy level is therefore $(2J + 1)^2$ degenarate because there are 2J + 1 possible K values and 2J + 1 possible M values for each J.

The eigenfunctions |J,M,K> of J^2, J_Z and J_a , are given in terms of the set of so-called rotation matrices $D_{J,M,K}$:

$$|J,M,K\rangle = \sqrt{\frac{2J + 1}{8\,\pi^2}}\; D^*_{J,M,K}(\theta,\varphi,\chi)$$

which obey

$$J^2 |J,M,K> = \hbar^2 J(J+1) |J,M,K>,$$

$$J_a |J,M,K> = \hbar K |J,M,K>,$$

$$J_Z |J,M,K> = \hbar M |J,M,K>.$$

These $D_{J,M,K}$ functions are propotional to the spherical harmonics $Y_{J,M}(\theta,\phi)$ multiplied by $\exp(iK\chi)$, which reflects its χ-dependence.

ii. Symmetric Tops

Molecules for which two of the three principal moments of inertia are equal are called symmetric tops. Those for which the unique moment of inertia is smaller than the other two are termed prolate symmetric tops; if the unique moment of inertia is larger than the others, the molecule is an oblate symmetric top. An American football is prolate, and a frisbee is oblate.

Again, the rotational kinetic energy, which is the full rotational Hamiltonian, can be written in terms of the total rotational angular momentum operator J^2 and the component of angular momentum along the axis with the unique principal moment of inertia:

$$H_{rot} = J^2/2I + J_a^2\{1/2I_a - 1/2I\}, \text{ for prolate tops}$$

$$H_{rot} = J^2/2I + J_c^2\{1/2I_c - 1/2I\}, \text{ for oblate tops.}$$

Here, the moment of inertia I denotes that moment that is common to two directions; that is, I is the non-unique moment of inertia. As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a or J_c (and of J_Z), and the corresponding energy levels are:

$$E(J,K,M) = \hbar^2 J(J+1)/2I^2 + \hbar^2 K^2 \{1/2I_a - 1/2I\},$$

for prolate tops

$$E(J,K,M) = \hbar^2 J(J+1)/2I^2 + \hbar^2 K^2 \{1/2I_c - 1/2I\},$$

for oblate tops, again for K and M (i.e., J_a or J_c and J_Z quantum numbers, respectively) ranging from -J to J in unit steps. Since the energy now depends on K, these levels are only 2J + 1 degenerate due to the 2J + 1 different M values that arise for each J value. Notice that for prolate tops, because I_a is smaller than I, the energies increase with increasing K for given J. In contrast, for oblate tops, since I_c is larger than I, the energies decrease with K for given J. The eigenfunctions |J, M,K> are the same rotation matrix functions as arise for the spherical-top case, so they do not require any further discussion at this time.

iii. Asymmetric Tops

The rotational eigenfunctions and energy levels of a molecule for which all three principal moments of inertia are distinct (a so-called asymmetric top) can not easily be expressed in terms of the angular momentum eigenstates and the J, M, and K quantum numbers. In fact, no one has ever solved the corresponding Schrödinger equation for this case. However, given the three principal moments of inertia I_a, I_b, and I_c, a matrix representation of each of the three contributions to the rotational Hamiltonian

$$H_{rot} = J_a^2/2I_a + J_b^2/2I_b + J_c^2/2I_c$$

can be formed within a basis set of the {|J, M, K>} rotation-matrix functions discussed earlier. This matrix will not be diagonal because the |J, M, K> functions are not eigenfunctions of the asymmetric top H_{rot}. However, the matrix can be formed in this basis and subsequently brought to diagonal form by finding its eigenvectors $\{C_{n, J,M,K}\}$ and its eigenvalues $\{E_n\}$. The vector coefficients express the asymmetric top eigenstates as

$$\Psi_n (\theta, \varphi, \chi) = \Sigma_{J, M, K}\, C_{n, J,M,K}\, |J, M, K>.$$

Because the total angular momentum J^2 still commutes with H_{rot}, each such eigenstate will contain only one J-value, and hence Ψ_n can also be labeled by a J quantum number:

$$\Psi_{n,J}\ (\theta, \varphi, \chi) = \Sigma_{M,\ K}\ C_{n,\ J,M,K}\ |J, M, K>.$$

To form the only non-zero matrix elements of H_{rot} within the |J, M, K> basis, one can use the following properties of the rotation-matrix functions (see, for example, R. N. Zare, *Angular Momentum*, John Wiley, New York (1988)):

$$<J, M, K|\ J_a^2|\ J, M, K> = <J, M, K|\ J_b^{\ 2}|\ J, M, K>$$

$$= 1/2 <J, M, K|\ J^2 - J_c^2\ |\ J, M, K> = \hbar^2\ [\ J(J+1) - K^2\ ],$$

$$<J, M, K|\ J_c^2|\ J, M, K> = \hbar^2\ K^2,$$

$$<J, M, K|\ J_a^2|\ J, M, K \pm 2> = -\ <J, M, K|\ J_b^{\ 2}|\ J, M, K \pm 2>$$

$$= \ \hbar^2\ [J(J+1) - K(K\pm 1)]^{1/2}\ [J(J+1) -(K\pm 1)(K\pm 2)]^{1/2}$$

$$<J, M, K|\ J_c^2|\ J, M, K \pm 2> = 0.$$

Each of the elements of J_c^2, J_a^2, and J_b^2 must, of course, be multiplied, respectively, by $1/2I_c$, $1/2I_a$, and $1/2I_b$ and summed together to form the matrix representation of H_{rot}. The diagonalization of this matrix then provides the asymmetric top energies and wave functions.

IX. Vibrations of Molecules

This Schrödinger equation forms the basis for our thinking about bond stretching and angle bending vibrations as well as collective vibrations called phonons in solids.

The radial motion of a diatomic molecule in its lowest (J=0) rotational level can be described by the following Schrödinger equation:

$$- (\hbar^2/2\mu)\ r^{-2}\partial/\partial r\ (r^2\partial/\partial r)\ \psi + V(r)\ \psi = E\ \psi,$$

where μ is the reduced mass $\mu = m_1m_2/(m_1+m_2)$ of the two atoms. If the molecule is rotating, then the above Schrödinger equation has an additional term $J(J+1)\hbar^2/2\mu\ r^{-2}\ \psi$ on its left-hand side. Thus, each rotational state (labeled by the rotational quantum number J) has its own vibrational Schrödinger equantion and thus its own set of vibrational energy levels and wave functions. It is common to examine the J=0 vibrational problem and then to use the vibrational levels of this state as approximations to the vibrational levels of states with non-zero J values (treating the vibration-rotation coupling via perturbation theory introduced in Sec. VII.). Let us thus focus on the J=0 situation.

By substituting $\psi = F(r)/r$ into this equation, one obtains an equation for F(r) in which the differential operators appear to be less complicated:

$$-\hbar^2/2\mu\ d^2F/dr^2 + V(r)\ F = E\ F.$$

This equation is exactly the same as the equation seen earlier in this text for the radial motion of the electron in the hydrogen-like atoms except that the reduced mass μ replaces the electron mass m and the potential V(r) is not the Coulomb potential.

If the vibrational potential is approximated as a quadratic function of the bond displacement $x = r-r_e$ expanded about the equilibrium bond length r_e where V has its minimum:

$$V = 1/2\ k(r-r_e)^2,$$

the resulting harmonic-oscillator equation can be solved exactly. Because the potential V grows without bound as x approaches ∞ or -∞, only bound-state solutions exist for this model problem. That is, the motion is confined by the nature of the potential, so no continuum states exist in which the two atoms bound together by the potential are dissociated into two separate atoms.

In solving the radial differential equation for this potential, the large-r behavior is first examined. For large-r, the equation reads:

$$d^2F/dx^2 = 1/2\ k\ x^2\ (2\mu/\hbar^2)\ F,$$

where $x = r-r_e$ is the bond displacement away from equilibrium. Defining $\xi = (\mu k/\hbar^2)^{1/4}\ x$ as a new scaled radial coordinate allows the solution of the large-r equation to be written as:

$$F_{\text{large-r}} = \exp(-\xi^2/2).$$

The general solution to the radial equation is then expressed as this large-r solution multiplied by a power series in the ζ variable:

$$F = \exp(-\xi^2/2) \sum_{n=0}^{\infty} \xi^n C_n ,$$

where the C_n are coefficients to be determined. Substituting this expression into the full radial equation generates a set of recursion equations for the C_n amplitudes. As in the solution of the hydrogen-like radial equation, the series described by these coefficients is divergent unless the energy E happens to equal specific values. It is this requirement that the wave function not diverge so it can be normalized that yields energy quantization. The energies of the states that arise are given by:

$$E_n = \hbar (k/\mu)^{1/2} (n+1/2),$$

and the eigenfunctions are given in terms of the so-called Hermite polynomials $H_n(y)$ as follows:

$$\psi_n(x) = (n!\ 2^n)^{-1/2} (\alpha/\pi)^{1/4} \exp(-\alpha x^2/2)\ H_n(\alpha^{1/2} x),$$

where $\alpha = (k\mu/\hbar^2)^{1/2}$. Within this harmonic approximation to the potential, the vibrational energy levels are evenly spaced:

$$\Delta E = E_{n+1} - E_n = \hbar\,(k/\mu)^{1/2}\ .$$

In experimental data such evenly spaced energy level patterns are seldom seen; most commonly, one finds spacings $E_{n+1} - E_n$ that decrease as the quantum number n increases. In such cases, one says that the progression of vibrational levels displays anharmonicity.

Because the Hermite functions H_n are odd or even functions of x (depending on whether n is odd or even), the wave functions $\psi_n(x)$ are odd or even. This splitting of the solutions into two distinct classes is an example of the effect of symmetry; in this case, the symmetry is caused by the symmetry of the harmonic potential with respect to reflection through the origin along the x-axis (i.e., changing x to –x). Throughout this text, many symmetries arise; in each case, symmetry properties of the potential cause the solutions of the Schrödinger equation to be decomposed into various symmetry groupings. Such symmetry decompositions are of great use because they provide additional quantum numbers (i.e., symmetry labels) by which the wave functions and energies can be labeled.

The basic idea underlying how such symmetries split the solutions of the Schrödinger equation into different classes relates to the fact that a symmetry operator (e.g., the reflection plane in the above example) commutes with the Hamiltonian. That is, the symmetry operator S obeys

$$S\,H\,\Psi = H\,S\,\Psi.$$

So S leaves H unchanged as it acts on H (this allows us to pass S through H in the above equation). Any operator that leaves the Hamiltonian (i.e., the energy) unchanged is called a symmetry operator.

If you have never learned about how point group symmetry can be used to hjelp simplify the solution of the Schrödinger equation, this would be a good time to interrupt your reading and go to Sec. VIII and read the material there.

The harmonic oscillator energies and wave functions comprise the simplest reasonable model for vibrational motion. Vibrations of a polyatomic molecule are often characterized in terms of individual bond-stretching and angle-bending motions, each of which is, in turn, approximated harmonically. This results in a total vibrational wave function that is written as a product of functions, one for each of the vibrational coordinates.

Two of the most severe limitations of the harmonic oscillator model, the lack of anharmonicity (i.e., non-uniform energy level spacings) and lack of bond dissociation, result from the quadratic nature of its potential. By introducing model potentials that allow for proper bond dissociation (i.e., that do not increase without bound as $x \Rightarrow \infty$), the major shortcomings of the harmonic oscillator picture can be overcome. The so-called Morse potential (see Fig. 2.24)

$$V(r) = D_e\,(1-\exp(-a(r-r_e)))^2,$$

is often used in this regard.

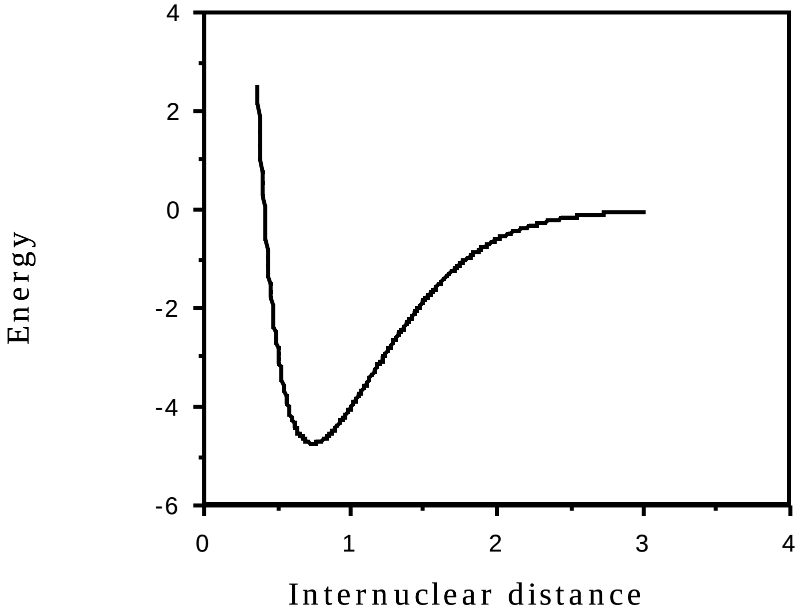


Figure 2.24. Morse potential energy as a function of bond length

In the Morse potential function, D_e is the bond dissociation energy, r_e is the equilibrium bond length, and a is a constant that characterizes the 'steepness' of the potential and thus affects the vibrational frequencies. The advantage of using the Morse potential to improve upon harmonic-oscillator-level predictions is that its energy levels and wave functions are also known exactly. The energies are given in terms of the parameters of the potential as follows:

$$E_n = \hbar(k/\mu)^{1/2} \{ (n+1/2) - (n+1/2)^2 \hbar(k/\mu)^{1/2}/4D_e \},$$

where the force constant is given by $k=2D_e a^2$. The Morse potential supports both bound states (those lying below the dissociation threshold for which vibration is confined by an outer turning point) and continuum states lying above the dissociation threshold. Its degree of anharmonicity is governed by the ratio of the harmonic energy $\hbar(k/\mu)^{1/2}$ to the dissociation energy D_e.

The eigenfunctions of the harmonic and Morse potentials display nodal character analogous to what we have seen earlier in the particle-in-boxes model problems. Namely, as the energy of the vibrational state increases, the number of nodes in the vibrational wave function also increases. The state having vibrational quantum number v has v nodes. I hope that by now the student is getting used to seeing the number of nodes increase as the quantum number and hence the energy grows.

Chapter 3. Characteristics of Energy Surfaces

Born-Oppenheimer energy surfaces (or the empirical functions often used to represent them) possess important critical points that detail the properties of stable molecular structures, transition states, and reaction paths, all of which play central roles in the theoretical description of molecular properties. In this Chapter, you will learn about these special points on the surfaces, how to find them, and what to do with them once you know them.

I. Strategies for Geometry Optimization

The extension of the harmonic and Morse vibrational models to polyatomic molecules requires that the multidimensional energy surface be analyzed in a manner that allows one to approximate the molecule's motions in terms of many nearly independent vibrations. In this Section, we will explore the tools that one uses to carry out such an analysis of the surface.

Many strategies that attempt to locate minima on molecular potential energy landscapes begin by approximating the potential energy V for geometries (collectively denoted in terms of 3N Cartesian coordinates $\{q_j\}$) in a Taylor series expansion about some "starting point" geometry (i.e., the current molecular geometry in an iterative process):

$$V(q_k) = V(0) + \Sigma_k (\partial V/\partial q_k)\, q_k + 1/2\, \Sigma_{j,k}\, q_j\, H_{j,k}\, q_k + \ldots\ .$$

Here, V(0) is the energy at the current geometry, $(\partial V/\partial q_k) = g_k$ is the gradient of the energy along the q_k coordinate, $H_{j,k} = (\partial^2 V/\partial q_j \partial q_k)$ is the second-derivative or Hessian matrix, and q_k is the length of the "step" to be taken along this Cartesian direction. An example of an energy surface in only two dimensions is given in the Figure 3.1 where various special aspects are illustrated. For example, minima corresponding to stable molecular structures, transition states (first order saddle points) connecting such minima, and higher order saddle points are displayed.

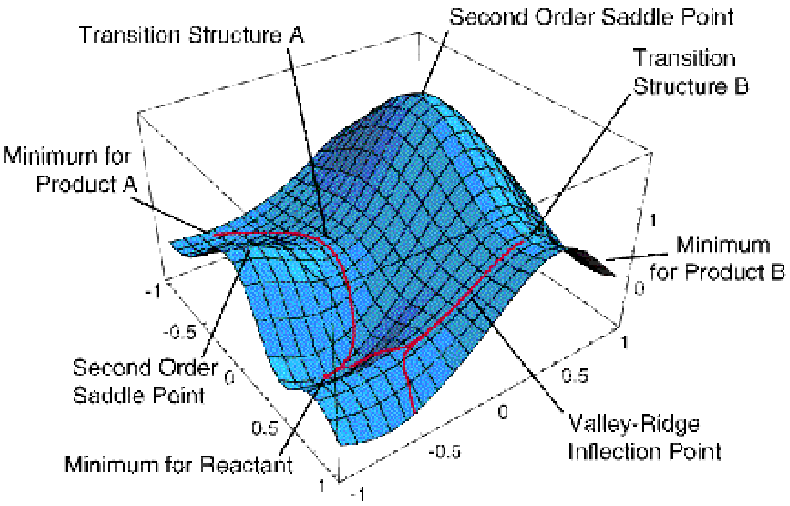


Figure 3.1. Two-dimensional potential surface showing minima, transition states, and paths connecting them.

If the only knowledge that is available is V(0) and the gradient components (e.g., computation of the second derivatives is usually much more computationally taxing than is evaluation of the gradient), the linear approximation

$$V\ (q_k) = V(0) + \Sigma_k\ g_K\ q_k$$

suggests that one should choose “step” elements q_k that are opposite in sign from that of the corresponding gradient elements $g_k = (\partial V/\partial q_k)$. The magnitude of the step elements is usually kept small in order to remain within the “trust radius” within which the linear approximation to V is valid to some predetermined desired precision.

When second derivative data is available, there are different approaches to predicting what step $\{q_k\}$ to take in search of a minimum. We first write the quadratic Taylor expansion

$$V(q_k) = V(0) + \Sigma_k\, g_k\, q_k + 1/2\, \Sigma_{j,k}\, q_j\, H_{j,k}\, q_k$$

in matrix-vector notation

$$V(\mathbf{q}) = V(0) + \mathbf{q}^\mathbf{T} \cdot \mathbf{g} + 1/2\, \mathbf{q}^\mathbf{T} \cdot \mathbf{H} \cdot \mathbf{q}$$

with the elements$\{q_k\}$ collected into the column vector **q** whose transpose is denoted $\mathbf{q}^\mathbf{T}$. Introducing the unitary matrix **U** that diagonalizes the symmetric **H** matrix, the above equation becomes

$$V(\mathbf{q}) = V(0) + \mathbf{g}^\mathbf{T}\, \mathbf{U}\ \mathbf{U}^\mathbf{T}\, \mathbf{q} + \mathbf{1/2}\, \mathbf{q}^\mathbf{T}\ \mathbf{U}\, \mathbf{U}^\mathbf{T}\mathbf{H}\mathbf{U}\, \mathbf{U}^\mathbf{T}\, \mathbf{q}.$$

Because $\mathbf{U}^\mathbf{T}\mathbf{H}\mathbf{U}$ is diagonal

$$(\mathbf{U}^\mathbf{T}\mathbf{H}\mathbf{U})_{k,l} = \delta_{k,l}\ \lambda_k$$

and has eigenvalues λ_k. For non-linear molecules, 3N-6 of these eigenvalues will be non-zero; for linear molecules, 3N-5 will be non-zero. The 5 or 6 zero eigenvalues of H have eigenvectors that describe translation and rotation of the entire molecule; they are zero because the energy surface V does not change if the molecule is rotated or translated. The eigenvectors of **H** form the columns of the array **U** that brings **H** to diagonal form:

$$\Sigma_\lambda H_{k,l} \; U_{l,m} = \lambda_m U_{k,m}$$

Therefore, if we define

$$Q_m = \Sigma_k U^T{}_{m,k} q_k \text{ and } G_m = \Sigma_k U^Y{}_{m,k} g_k$$

to be the component of the step $\{q_k\}$ and of the gradeint along the m^{th} eigenvector of **H**, the quadratic expansion of V can be written in terms of steps along the 3N-5 or 3N-6 $\{Q_m\}$ directions that correspond to non-zero Hessian eigenvalues:

$$V(q_k) = V(0) + \Sigma_m G^T{}_m Q_m + 1/2 \; \Sigma_m Q_m \lambda_m Q_m.$$

The advantage to transforming the gradient, step, and Hessian to the eigenmode basis is that each such mode (labeled m) appears in an independent uncoupled form in the expansion of V. This allows us to take steps along each of the Q_m directions in an independent manner with each step designed to lower the potential energy (as we search for minima).

For each eigenmode direction, one can ask for what step Q would the quantity GQ + 1/2 λ Q^2 be a minimum. Differentiating this quadratic form with respect to Q and setting the result equal to zero gives

$$Q_m = - G_m/\lambda_m \;;$$

that is, one should take a step opposite the gradient but with a magnitude given by the gradient divided by the eigenvalue of the Hessian matrix. If the current molecular geometry is one that has all positive λ_m values, this indicates that one may be “close” to a minimum on the energy surface (because all λ_m are positive at minima). In such case, the step $Q_m = - G_m/\lambda_m$ is opposed to the gradient along all 3N-5 or 3N-6 directions. The energy change that is expected to occur if the step $\{Q_m\}$ is taken can be computed by substituting $Q_m = - G_m/\lambda_m$ into the quadratic equation for V:

$$V(\text{after step}) = V(0) + \Sigma_m G^T_m (- G_m/\lambda_m) + 1/2\ \Sigma_m \lambda_m (- G_m/\lambda_m)^2$$

$$= V(0) - 1/2\ \Sigma_m \lambda_m (- G_m/\lambda_m)^2.$$

This clearly suggests that the step will lead “downhill” in energy as long as all of the λ_m values are positive.

However, if one or more of the λ_m are negative at the current geometry, one is in a region of the energy surface that is not close to a minimum. In fact, if only one λ_m is negative, one anticipates being near a transition state (at which all gradient components vanish and all but one λ_m are positive with one λ_m negative). In such a case, the above analysis suggests taking a step $Q_m = - G_m/\lambda_m$ along all of the modes having positive λ_m, but taking a step of opposite direction $Q_n = + G_n/\lambda_n$ along the direction having negative

λ_n.

In any event, once a step has been suggested within the eigenmode basis, one needs to express that step in terms of the original Cartesian coordinates q_k so that these Cartesian values can be altered within the software program to effect the predicted step. Given values for the 3N-5 or 3N-6 step components Q_m (n.b., the step components Q_m along the 5 or 6 modes having zero Hessian eigenvalues can be taken to be zero because the would simply translate or rotate the molecule), one must compute the $\{q_k\}$. To do so, we use the relationship

$$Q_m = \Sigma_k U^T_{m,k} q_k$$

and write its inverse (using the unitary nature of the **U** matrix):

$$q_k = \Sigma_m U_{k,m} Q_m$$

to compute the desired Cartesian step components.

In using the Hessian-based approaches outlined above, one has to take special care when one or more of the Hessian eigenvalues is small. This often happens when

i. one has a molecule containing “soft modes” (i.e., degrees of freedom along which the energy varies little), or

ii. as one moves from a region of negative curvature into a region of positive curvature (or vice versa)- in such cases, the the curvature must move through or near zero.

For these situations, the expression $Q_m = - G_m/\lambda_m$ can produce a very large step along the mode having small curvature. Care must be taken to not allow such incorrect artificially large steps to be taken.

Before closing this Section, I should note that there are other important regions of potential energy surfaces that one must be able to locate and characterize. Above, we focused on local minima and transition states. In Chapter 8, we will discuss how to follow so-called reaction paths that connect these two kinds of stationary points using the type of gradient and Hessian information that we introduced earlier in this Chapter.

Finally, it is sometimes important to find geometries at which two Born-Oppenheimer energy surfaces $V_1(\mathbf{q})$ and $V_2(\mathbf{q})$ intersect. First, let's spend a few minutes thinking about whether such surfaces can indeed intersect because students often hear that surfaces do not intersect but, instead, undergo "avoided crossings". To understand the issue, let us assume that we have two wave functions Φ_1 and Φ_2 both of which depend on 3N-6 coordinates $\{\mathbf{q}\}$. These two functions are not assumed to be exact eigenfunctions of the Hamiltonian H, but likely are chosen to approximate such eigenfunctions. To find the improved functions Ψ_1 and Ψ_2 that more accurately represent the eigenstates, one usually forms linear combinations of Φ_1 and Φ_2,

$$\Psi_K = C_{K,1}\, \Phi_1 + C_{K,2}\, \Phi_2$$

from which a 2x2 matrix eigenvalue problem arises:

$$\begin{vmatrix} H_{1,1} - E & H_{1,2} \\ H_{2,1} & H_{2,2} - E \end{vmatrix} = 0\,.$$

This quadratic equation has two solutions

$$2E_{\pm} = (H_{1,1} + H_{2,2}) \pm \sqrt{(H_{1,1} - H_{2,2})^2 + 4H_{1,2}{}^2}\ .$$

These two solutions can be equal (i.e., the two state energies can cross) only if the square root factor vanishes. Because this factor is a sum of two squares (each thus being positive quantities), this can only happen if two identities hold:

$$H_{1,1} = H_{2,2}$$

and

$$H_{1,2} = 0.$$

The main point then is that in the 3N-6 dimensional space, the two states will generally not have equal energy. However, in a space of two lower dimensions (because there are two conditions that must simultaneously be obeyed- $H_{1,1} = H_{2,2}$ and $H_{1,2} = 0$), their energies may be equal. They do not have to be equal, but it is possible that they are. It is based upon such an analysis that one usually says that potential energy surfaces in 3N-6 dimensions may undergo intersections in spaces of dimension 3N-8. If the two states are of different symmetry, the off-diagonal element $H_{1,2}$ vanishes automatically, so only one other condition is needed to realize crossing. So, we say that two states of different symmetry can cross in a space of dimension 3N-7.

To find the lower-dimensional space in which two surfaces cross, one must have available information about the gradients and Hessians of both functions V_1 and V_2. One then uses this information to locate a geometry at which the difference function $F = [V_1 - V_2]^2$ passes through zero by using conventional "root finding" methods designed to locate where F = 0. Once one such geometry ($\mathbf{q}_0$) has been located, one subsequently tries to follow the "seam" along which the function F remains zero. This is done by parameterizng steps away from ($\mathbf{q}_0$) in a manner that constrains such steps to have no component along the gradient of F (i.e., to lie in the tangent plane where F is constant). For a system with 3N-6 geometrical degrees of freedom, this seam will be a subsurface of lower dimension (3N-8 or 3N-7 as noted earlier). Such intersection seam location procedures are becoming more commonly employed, but are still under very active development. Locating these intersections is an important ingredient when one is interested in studying, for example, photochemical reactions in which the reactants and products may move from one electronic surface to another.

II. Normal Modes of Vibration

Having seen how one can use information about the gradients and Hessians on a Born-Oppenheimer surface to locate geometries corresponding to stable species, let us now move on to see how this same data is used to treat vibrations on this surface.

For a polyatomic molecule whose electronic energy's dependence on the 3N

Cartesian coordinates of its N atoms, the potential energy V can be expressed (approximately) in terms of a Taylor series expansion about any of the local minima. Of course, different local minima (i.e., different isomers) will have different values for the equilibrium coordinates and for the derivatives of the energy with respect to these coordinates. The Taylor series expansion of the electronic energy is written as:

$$V (q_k) = V(0) + \Sigma_k (\partial V/\partial q_k) q_k + 1/2 \Sigma_{j,k} q_j H_{j,k} q_k + ... \ ,$$

where V(0) is the value of the electronic energy at the stable geometry under study, q_k is the displacement of the k_{th} Cartesian coordinate away from this starting position, $(\partial V/\partial q_k)$ is the gradient of the electronic energy along this direction, and the $H_{j,k}$ are the second derivative or Hessian matrix elements along these directions $H_{j,k} = (\partial^2 V/\partial q_j \partial q_k)$. If the geometry corresponds to a stable species, the gradient terms will all vanish (meaning this geometry corresponds to a minimum, maximum, or saddle point), and the Hessian matrix will possess 3N - 5 (for linear species) or 3N -6 (for non-linear molecules) positive eigenvalues and 5 or 6 zero eigenvalues (corresponding to 3 translational and 2 or 3 rotational motions of the molecule). If the Hessian has one negative eigenvalue, the geometry corresponds to a transition state. From now on, we assume that the geometry under study corresponds to that of a stable minimum about which vibrational motion occurs. The treatment of unstable geometries is of great importance to chemistry, but this material will be limited to vibrations of stable species.

A. The Newton Equations of Motion for Vibration

1. The Kinetic and Potential Energy Matrices

Truncating the Taylor series at the quadratic terms (assuming these terms dominate because only small displacements from the equilibrium geometry are of interest), one has the so-called harmonic potential:

$$V (q_k) = V(0) + 1/2 \Sigma_{j,k} q_j H_{j,k} q_k.$$

The classical mechanical equations of motion for the 3N $\{q_k\}$ coordinates can be written in terms of the above potential energy and the following kinetic energy function:

$$T = 1/2 \Sigma_j m_j \dot{q}_j^2,$$

where $\dot{q}_j$ denotes the time rate of change of the coordinate q_j and m_j is the mass of the atom on which the j^{th} Cartesian coordinate resides. The Newton equations thus obtained are:

$$m_j \ddot{q}_j = - \Sigma_k H_{j,k} q_k$$

where the force along the j^{th} coordinate is given by minus the derivative of the potential V along this coordinate $(\partial V/\partial q_j) = \Sigma_k H_{j,k} q_k$ within the harmonic approximation.

These classical equations can more compactly be expressed in terms of the time evolution of a set of so-called mass weighted Cartesian coordinates defined as:

$$x_j = q_j (m_j)^{1/2},$$

in terms of which the above Newton equations become

$$\ddot{x}_j = - \Sigma_k H'_{j,k} x_k$$

and the mass-weighted Hessian matrix elements are

$$H'_{j,k} = H_{j,k} (m_j m_k)^{-1/2}.$$

2. The Harmonic Vibrational Energies and Normal Mode Eigenvectors

Assuming that the x_j undergo some form of sinusoidal time evolution:

$$x_j(t) = x_j (0) \cos(\omega t),$$

and substituting this into the Newton equations produces a matrix eigenvalue equation:

$$\omega^2 x_j = \Sigma_k H'_{j,k} x_k$$

in which the eigenvalues are the squares of the so-called normal mode vibrational frequencies and the eigenvectors give the amplitudes of motion along each of the 3N mass weighted Cartesian coordinates that belong to each mode. Hence, to perform a normal-mode analysis of a molecule, one forms the mass-weighted Hessian matrix and then finds the 3N-5 or 3N-6 non-zero eigenvalues ω_j^2 as well as the corresponding eigenvectors $x_k^{(j)}$.

Within this harmonic treatment of vibrational motion, the total vibrational energy of the molecule is given as

$$E(v_1, v_2, \cdots v_{3N\text{-}5 \text{ or } 6}) = \sum_{j=1}^{3N\text{-}5or6} \hbar\omega_j \, (v_j + 1/2)$$

a sum of 3N-5 or 3N-6 independent contributions one for each normal mode. The corresponding total vibrational wave function

$$\Psi = \Pi_{j=1,3N\text{-}5or\,6} \; \psi_{v_j} (x^{(j)})$$

is a product of 3N-5 or 3N-6 harmonic oscillator functions $\psi_{v_j} (x^{(j)})$ one for each normal mode. The energy gap between one vibrational level and another in which one of the v_j quantum numbers is increased by unity (i.e., for fundamental vibrational transitions) is

$$\Delta E_{v_j \rightarrow v_j + 1} = \hbar \, \omega_j$$

The harmonic model thus predicts that the "fundamental" (v=0 → v = 1) and "hot band" (v=1 → v = 2) transitions should occur at the same energy, and the overtone (v=0 → v=2) transitions should occur at exactly twice this energy.

B. The Use of Symmetry

1. Symmetry Adapted Modes

It is often possible to simplify the calculation of the normal mode frequencies and eigenvectors by exploiting molecular point group symmetry. For molecules that possess symmetry at a particular stable geometry, the electronic potential $V(q_j)$ displays symmetry with respect to displacements of symmetry equivalent Cartesian coordinates. For example, consider the water molecule at its C_{2v} equilibrium geometry as illustrated in Fig. 3.2. A very small movement of the H_2O molecule's left H atom in the positive x direction (Δx_L) produces the same change in the potential V as a correspondingly small displacement of the right H atom in the negative x direction
($-\Delta x_R$). Similarly, movement of the left H in the positive y direction (Δy_L) produces an energy change identical to movement of the right H in the positive y direction (Δy_R).

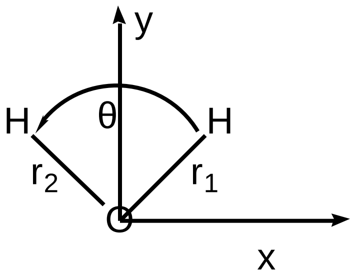


Figure 3.2. Water molecule showing its two bond lengths and angle

The equivalence of the pairs of Cartesian coordinate displacements is a result of the fact that the displacement vectors are connected by the point group operations of the C_{2v} group. In particular, reflection of Δx_L through the yz plane (the two planes are depicted in Fig. 3.3) produces - Δx_R, and reflection of Δy_L through this same plane yields Δy_R.

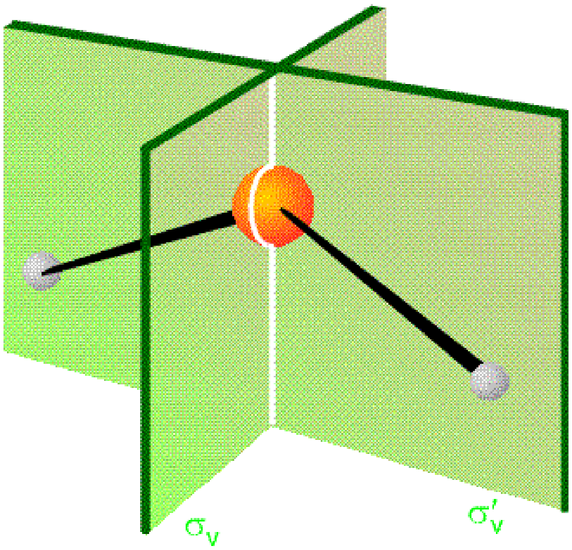


Figure 3.3. Two planes of symmetry of the water molecule.

More generally, it is possible to combine sets of Cartesian displacement coordinates $\{q_k\}$ into so-called symmetry adapted coordinates $\{Q_{\Gamma,j}\}$, where the index Γ labels the irreducible representation in the appropriate point group and j labels the particular combination of that symmetry. These symmetry adapted coordinates can be formed by applying the point group projection operators (that are treated in detail in Sec. VIII) to the individual Cartesian displacement coordinates.

To illustrate, again consider the H_2O molecule in the coordinate system described above. The 3N = 9 mass weighted Cartesian displacement coordinates (X_L, Y_L, Z_L, X_O, Y_O, Z_O, X_R, Y_R, Z_R) can be symmetry adapted by applying the following four projection operators:

$$P_{A_1} = 1 + \sigma_{yz} + \sigma_{xy} + C_2$$

$$P_{b_1} = 1 + \sigma_{yz} - \sigma_{xy} - C_2$$

$$P_{b_2} = 1 - \sigma_{yz} + \sigma_{xy} - C_2$$

$$P_{a_2} = 1 - \sigma_{yz} - \sigma_{xy} + C_2$$

to each of the 9 original coordinates (the symbol σ denotes reflection through a plane and C_2 means rotation about the molecule's C_2 axis). Of course, one will <u>not</u> obtain 9 x 4 = 36 independent symmetry adapted coordinates in this manner; many identical combinations will arise, and only 9 will be independent.

The independent combination of a_1 <u>symmetry</u> (normalized to produce vectors of unit length) are

$$Q_{a_1,1} = 2^{-1/2} [X_L - X_R]$$

$$Q_{a_1,2} = 2^{-1/2} [Y_L + Y_R]$$

$$Q_{a_1,3} = [Y_O]$$

Those of b_2 symmetry are

$$Q_{b_2,1} = 2^{-1/2} [X_L + X_R]$$

$$Q_{b_2,2} = 2^{-1/2} [Y_L - Y_R]$$

$$Q_{b_2,3} = [X_O],$$

and the combinations

$$Q_{b_1,1} = 2^{-1/2} [Z_L + Z_R]$$

$$Q_{b_1,2} = [Z_O]$$

are of b_1 symmetry, whereas

$$Q_{a_2,1} = 2^{-1/2} [Z_L - Z_R]$$

is of a_2 symmetry.

2. Point Group Symmetry of the Harmonic Potential

These nine $Q_{\Gamma,j}$ are expressed as unitary transformations of the original mass weighted Cartesian coordinates:

$$Q_{\Gamma,j} = \sum_{k} C_{\Gamma,j,k} X_k$$

These transformation coefficients $\{C_{\Gamma,j,k}\}$ can be used to carry out a unitary transformation of the 9x9 mass-weighted Hessian matrix. In so doing, we need only form blocks

$$H^{\Gamma}{}_{j,l} = {}_{k\,k'} C_{\Gamma,j,k}\ H_{k,k'}\ (m_k\, m_{k'})^{-1/2}\ C_{\Gamma,l,k'}$$

within which the symmetries of the two modes are identical. The off-diagonal elements

$$H^{\Gamma\,\Gamma'}_{j\,l} = \Sigma_{k,k'}\ C_{\Gamma,j,k}\ H_{k,k'}\ (m_k\, m_{k'})^{-1/2}\ C_{\Gamma',l,k'}$$

vanish because the potential V (q_j) (and the full vibrational Hamiltonian H = T + V) commutes with the C_{2V} point group symmetry operations.

As a result, the 9x9 mass-weighted Hessian eigenvalue problem can be sub divided into two 3x3 matrix problems (of a_1 and b_2 symmetry), one 2x2 matrix of b_1 symmetry and one 1x1 matrix of a_2 symmetry. For example, the a_1 symmetry block $H^{a_1}_{j\,l}$ is formed as follows:

$$\begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} m^{-1}_H \frac{\partial^2 v}{\partial x_L^2} & m^{-1}_H \frac{\partial^2 v}{\partial x_L \partial x_R} & (m_H m_O)^{-1/2} \frac{\partial^2 v}{\partial x_L \partial x_O} \\ m^{-1}_H \frac{\partial^2 v}{\partial x_R \partial x_L} & m^{-1}_H \frac{\partial^2 v}{\partial X^2_R} & (m_H m_O)^{-1/2} \frac{\partial^2 v}{\partial x_R \partial x_O} \\ (m_H m_O)^{-1/2} \frac{\partial^2 v}{\partial x_O \partial x_L} & (m_H m_O)^{-1/2} \frac{\partial^2 v}{\partial x_O \partial x_R} & m^{-1}_O \frac{\partial^2 v}{\partial x_O^2} \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The b_2, b_1 and a_2 blocks are formed in a similar manner. The eigenvalues of each of these blocks provide the squares of the harmonic vibrational frequencies, the eigenvectors provide the normal mode displacements as linear combinations of the symmetry adapted $\{Q^{\Gamma}{}_j\}$.

Regardless of whether symmetry is used to block diagonalize the mass-weighted Hessian, six (for non-linear molecules) or five (for linear species) of the eigenvalues will equal zero. The eigenvectors belonging to these zero eigenvalues describe the 3 translations and 2 or 3 rotations of the molecule. For example,

$$\frac{1}{\sqrt{3}} \; [X_L + X_R + X_O]$$

$$\frac{1}{\sqrt{3}} \; [Y_L + Y_R + Y_O]$$

$$\frac{1}{\sqrt{3}} \; [Z_L + Z_R + Z_O]$$

are three translation eigenvectors of b_2, a_1 and b_1 symmetry, and

$$\frac{1}{\sqrt{2}}(Z_L - Z_R)$$

is a rotation (about the Y-axis in the figure shown above) of a_2 symmetry. This rotation vector can be generated by applying the a_2 projection operator to Z_L or to Z_R. The other two rotations are of b_1 and b_2 symmetry and involve spinning of the molecule about the X- and Z- axes of the Fig. B.39, respectively.

So, of the 9 Cartesian displacements, 3 are of a_1 symmetry, 3 of b_2 , 2 of b_1, and 1 of a_2. Of these, there are three translations (a_1, b_2, and b_1) and three rotations (b_2, b_1, and a_2). This leaves two vibrations of a_1 and one of b_2 symmetry. For the H_2O example treated here, the three non zero eigenvalues of the mass-weighted Hessian are therefore of a_1 b_2 , and a_1 symmetry. They describe the symmetric and asymmetric stretch vibrations and the bending mode, respectively as illustrated in Fig. 3.4.

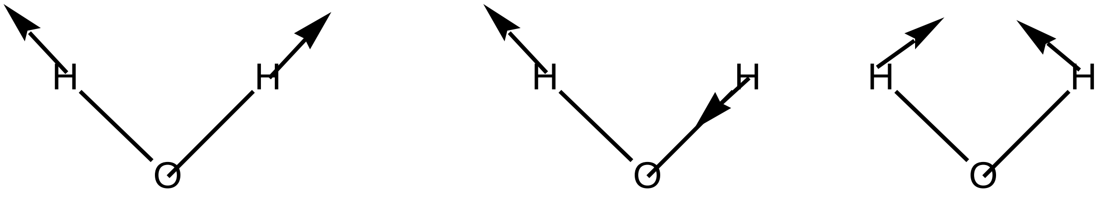


Figure 3.4. Symmetric and asymmetric stretch modes and bending mode of water

The method of vibrational analysis presented here can work for any polyatomic molecule. One knows the mass-weighted Hessian and then computes the non-zero eigenvalues, which then provide the squares of the normal mode vibrational frequencies. Point group symmetry can be used to block diagonalize this Hessian and to label the vibrational modes according to symmetry as we show in Fig. 3.5 for the CF_4 molecule in tetrahedral symmetry.

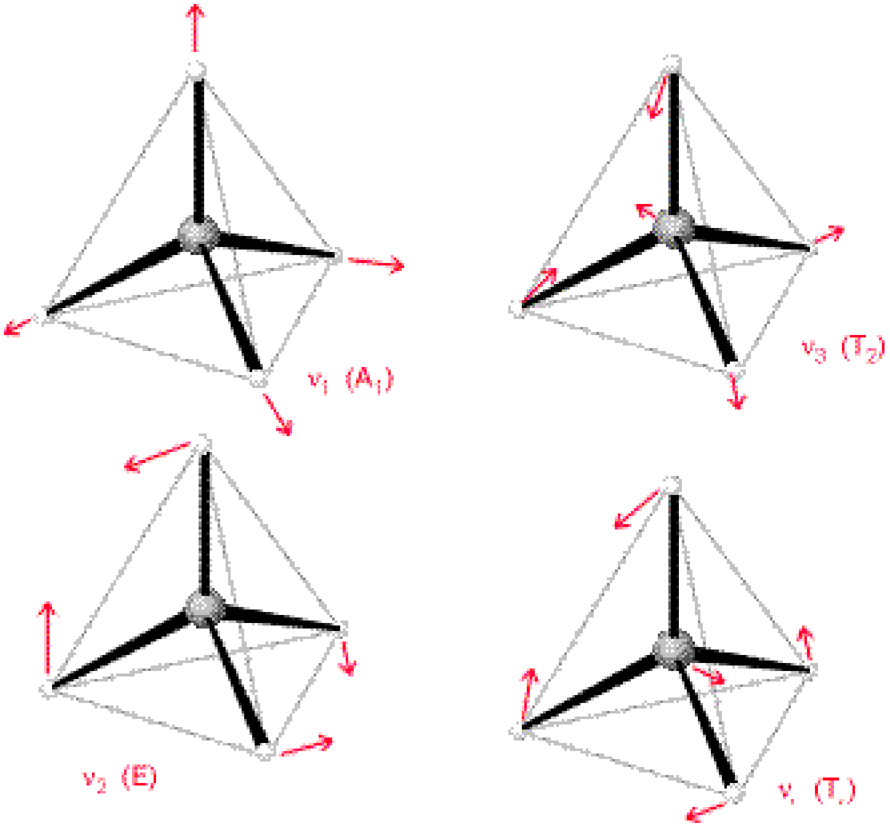


Figure 3.5. Symmetries of vibrations of methane

Chapter 4. Some Important Tools of Theory

For all but the most elementary problems, many of which serve as fundamental approximations to the real behavior of molecules (e.g., the Hydrogenic atom, the harmonic oscillator, the rigid rotor, particles in boxes), the Schrödinger equation can not be solved exactly. It is therefore extremely useful to have tools that allow one to approach these insoluble problems by solving other Schrödinger equations that can be trusted to reasonably describe the solutions of the impossible problem. The tools discussed in this Chapter are the most important tools of this type.

I. Perturbation Theory and the Variational Method

In most practical applications of quantum mechanics to molecular problems, one is faced with the harsh reality that the Schrödinger equation pertinent to the problem at hand can not be solved exactly. To illustrate how desperate this situation is, I note that neither of the following two Schrödinger equations have ever been solved exactly (meaning analytically):

1. The Schrödinger equation for the two electrons moving about the He nucleus:

$$[- \hbar^2/2m_e \nabla_1^2 - \hbar^2/2m_e \nabla_2^2 – 2e^2/r_1 – 2e^2/r_2 + e^2/r_{1,2}]\psi = E \psi,$$

2. The Schrödinger equation for the two electrons moving in an H_2 molecule even if the locations of the two nuclei (labeled A and B) are held clamped:

$$[- \hbar^2/2m_e \nabla_1^2 - \hbar^2/2m_e \nabla_2^2 – e^2/r_{1,A} – e^2/r_{2,A} – e^2/r_{1,B} – e^2/r_{2,B} + e^2/r_{1,2}]\psi = E \psi.$$

These two problems are examples of what is called the “three-body problem” meaning solving for the behavior of three bodies moving relative to one another. Motions of the sun, earth, and moon (even neglecting all the other planets and their moons) constitute another three-body problem. None of these problems, even the classical Newton’s equation for the sun, earth, and moon, have ever been solved exactly. So, what does one do when faced with trying to study real molecules using quantum mechanics?

There are two very powerful tools that one can use to “sneak up” on the solutions to the desired equations by first solving an easier “model” problem and then using the solutions to this problem to approximate the solutions to the real Schrödinger problem of interest. For example, to solve for the energies and wave functions of a boron atom, one could use hydrogenic 1s orbitals (but with $Z = 5$) and hydrogenic 2s and 2p orbitals with $Z = 3$ to account for the screening of the full nuclear charge by the two 1s electrons as a starting point. To solve for the vibrational energies of a diatomic molecule whose energy vs. bond length E(R) is known, one could use the Morse oscillator wave functions as starting points. But, once one has decided on a reasonable “starting point” model to use, how does one connect this model to the real system of interest? Perturbation theory and the variational method are the two tools that are most commonly used for this purpose.

A. Perturbation Theory

In this method, one has available a set of equations for generating a sequence of approximations to the true energy E and true wave function ψ. I will now briefly outline the derivation of these working equations for you. First, one decomposes the true Hamiltonian H into a so-called zeroth-order part H^0 (this is the Hamiltonian of the model problem one has chosen to use to represent the real system) and the difference $(H-H^0)$ which is called the perturbation and often denoted V:

$$H = H^0 + V.$$

The fundamental assumption of perturbation theory is that the wave functions and energies can be expanded in a Taylor series involving various powers of the perturbation. That is, one expands the energy E and the wave function ψ into zeroth-, first-, second, etc, order pieces which form the unknowns in this method:

$$E = E^0 + E^1 + E^2 + E^3 + ...$$

$$\psi = \psi^0 + \psi^1 + \psi^2 + \psi^3 + ...$$

Next, one substitutes these expansions of E of H and of ψ into $H\psi = E\psi$. This produces one equation whose right and left hand sides both contain terms of various “powers” in the perturbation. For example, terms of the form $E^1 \psi^2$ and $V \psi^2$ and $E^0 \psi^3$ are all of third power (also called third order). Next, one equates the terms on the left and right sides that are of the same order. This produces a set of equations, each containing all the terms of a given order. The zeroth, first, and second order such equations are given below:

$$H^0 \psi^0 = E^0 \psi^0,$$

$$H^0 \psi^1 + V \psi^0 = E^0 \psi^1 + E^1 \psi^0$$

$$H^0 \psi^2 + V \psi^1 = E^0 \psi^2 + E^1 \psi^1 + E^2 \psi^0.$$

The zeroth order equation simply instructs us to solve the zeroth-order Schrödinger equation to obtain the zeroth-order wave function ψ^0 and its zeroth-order energy E^0. In the first-order equation, the unknowns are ψ^1 and E^1 (recall that V is assumed to be known because it is the difference between the Hamiltonian one wants to solve and the model Hamiltonian H^0).

To solve the first-order and higher-order equations, one expands each of the corrections to the wave function ψ^K in terms of the complete set of wave functions of the zeroth-order problem $\{\psi^0_J\}$. This means that one must be able to solve $H^0 \psi^0_J = E^0_J \psi^0_J$ not just for the zeroth-order state one is interested in (denoted ψ^0 above) but for all of the other (e.g., excited states if ψ^0 is the ground state) zeroth-order states $\{\psi^0_J\}$. For example, expanding ψ^1 in this manner gives:

$$\psi^1 = \Sigma_J C^1_J \psi^0_J.$$

Now, the unknowns in the first-order equation become E^1 and the C^1_J expansion coefficients. Substituting this expansion into $H^0 \psi^1 + V \psi^0 = E^0 \psi^1 + E^1 \psi^0$ and solving for these unknows produces the following final first-order working equations:

$$E^1 = <\psi^0 | V | \psi^0>$$

$$\psi^1 = \Sigma_J \psi^0{}_J \{<\psi^0 | V | \psi^0{}_J>/(E^0 - E^0{}_J)\},$$

where the index J is restricted such that $\psi_J{}^0$ not equal the state ψ^0 you are interested in. These are the fundamental working equations of first-order perturbation theory. They instruct us to compute the average value of the perturbation taken over a probability distrubution equal to $\psi^{0*} \psi^0$ to obtain the first-order correction to the energy E^1. They also tell us how to compute the first-order correction to the wave function in terms of coefficients multiplying various other zeroth-order wave functions $\psi_J{}^0$.

An analogous approach is used to solve the second- and higher-order equations. Although modern quantum mechanics does indeed use high-order perturbation theory in some cases, much of what the student needs to know is contained in the first- and second-order results to which I will therefore restrict our attention. The expression for the second- order energy correction is found to be:

$$E^2 = \Sigma_J <\psi^0 | V | \psi^0{}_J>^2/(E^0 - E^0{}_J),$$

where again, the index J is restricted as noted above. Let's now consider an example problem that illustrates how perturbation theory is used.

Example Problem for Perturbation Theory

As we discussed earlier, an electron moving in a conjugated bond framework can be modeled as a particle in a box. An externally applied electric field of strength ε interacts with the electron in a fashion that can described by adding the perturbation V = $e\varepsilon\left(x - \frac{L}{2}\right)$ to the zeroth-order Hamiltonian. Here, x is the position of the electron in the box, e is the electron's charge, and L is the length of the box.

First, we will compute the first order correction to the energy of the n=1 state and the first order wave function for the n=1 state. In the wave function calculation, we will only compute the contribution to ψ made by ψ^0_2 (this is just an approximation to keep things simple in this example) . Let me now do all the steps needed to solve this part of the problem. Try to make sure you can do the algebra but also make sure you understand how we are using the first-order perturbation equations.

$$V = e\varepsilon\left(x - \frac{L}{2}\right),\ \Psi^{(0)}_n = \left(\frac{2}{L}\right)^{\frac{1}{2}} \mathrm{Sin}\left(\frac{n\pi x}{L}\right),\ \text{and}$$

$$E^{(0)}_n = \frac{\hbar^2\pi^2 n^2}{2mL^2}\ .$$

$$E^{(1)}_{n=1} = \left\langle \Psi^{(0)}_{n=1} | V | \Psi^{(0)}_{n=1} \right\rangle = \left\langle \Psi^{(0)}_{n=1} | e\varepsilon\left(x - \frac{L}{2}\right) | \Psi^{(0)}_{n=1} \right\rangle$$

$$= \left(\frac{2}{L}\right)\int_0^L \mathrm{Sin}^2\left(\frac{\pi x}{L}\right) e\varepsilon\left(x - \frac{L}{2}\right) dx$$

$$= \left(\frac{2e\varepsilon}{L}\right)\int_0^L \text{Sin}^2\left(\frac{\pi x}{L}\right)x\,dx \;-\; \left(\frac{2e\varepsilon}{L}\right)\left(\frac{L}{2}\right)\int_0^L \text{Sin}^2\left(\frac{\pi x}{L}\right)dx$$

The first integral can be evaluated using the following identity with $a = \frac{\pi}{L}$:

$$\int_0^L \text{Sin}^2(ax)\,xdx = \left[\frac{x^2}{4} - \frac{x\,\text{Sin}(2ax)}{4a} - \frac{\text{Cos}(2ax)}{8a^2}\right]_0^L = \frac{L^2}{4}$$

The second integral can be evaluated using the following identity with $\theta = \frac{\pi x}{L}$

and $d\theta = \frac{\pi}{L}\,dx$:

$$\int_0^L \text{Sin}^2\left(\frac{\pi x}{L}\right)dx = \frac{L}{\pi}\int_0^\pi \text{Sin}^2\theta d\theta$$

$$\int_0^\pi \text{Sin}^2\theta d\theta = \left[-\frac{1}{4}\,\text{Sin}(2\theta) + \frac{\theta}{2}\right]_0^\pi = \frac{\pi}{2}\,.$$

Making all of these appropriate substitutions we obtain:

$$E_{n=1}^{(1)} = \left(\frac{2e\varepsilon}{L}\right)\left(\frac{L^2}{4} - \frac{L}{2}\,\frac{L}{\pi}\,\frac{\pi}{2}\right) = 0$$

$$\Psi^{(1)}_{n=1} = \frac{\left\langle \Psi^{(0)}_{n=2} \middle| e\varepsilon\left(x - \frac{L}{2}\right) \middle| \Psi^{(0)}_{n=1} \right\rangle \Psi^{(0)}_{n=2}}{E^{(0)}_{n=1} - E^{(0)}_{n=2}}$$

$$\Psi^{(1)}_{n=1} = \frac{\left(\frac{2}{L}\right)\int_0^L \text{Sin}\left(\frac{2\pi x}{L}\right) e\varepsilon\left(x - \frac{L}{2}\right)\text{Sin}\left(\frac{\pi x}{L}\right)dx}{\frac{\hbar^2\pi^2}{2mL^2}\left(1^2 - 2^2\right)} \left(\frac{2}{L}\right)^{\frac{1}{2}} \text{Sin}\left(\frac{2\pi x}{L}\right)$$

The two integrals in the numerator need to be evaluated:

$$\int_0^L x\text{Sin}\left(\frac{2\pi x}{L}\right)\text{Sin}\left(\frac{\pi x}{L}\right)dx \text{ , and } \int_0^L \text{Sin}\left(\frac{2\pi x}{L}\right)\text{Sin}\left(\frac{\pi x}{L}\right)dx \text{ .}$$

Using the integral identities $\int x\text{Cos}(ax)dx = \frac{1}{a^2}\text{Cos}(ax) + \frac{x}{a}\text{Sin}(ax)$, and $\int \text{Cos}(ax)dx$

$= \frac{1}{a}\text{Sin}(ax)$, we obtain the following:

$$\int_0^L \text{Sin}\left(\frac{2\pi x}{L}\right)\text{Sin}\left(\frac{\pi x}{L}\right)dx = \frac{1}{2}\left[\int_0^L \text{Cos}\left(\frac{\pi x}{L}\right)dx - \int_0^L \text{Cos}\left(\frac{3\pi x}{L}\right)dx\right]$$

$$= \frac{1}{2}\left[\frac{L}{\pi}\text{Sin}\left(\frac{\pi x}{L}\right)\Big|_0^L - \frac{L}{3\pi}\text{Sin}\left(\frac{3\pi x}{L}\right)\Big|_0^L\right] = 0$$

$$\int_0^L x\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)dx = \frac{1}{2}\left[\int_0^L x\cos\left(\frac{\pi x}{L}\right)dx - \int_0^L x\cos\left(\frac{3\pi x}{L}\right)dx\right]$$

$$= \frac{1}{2}\left[\left(\frac{L^2}{\pi^2}\cos\left(\frac{\pi x}{L}\right) + \frac{Lx}{\pi}\sin\left(\frac{\pi x}{L}\right)\right)\Bigg|_0^L - \left(\frac{L^2}{9\pi^2}\cos\left(\frac{3\pi x}{L}\right) + \frac{Lx}{3\pi}\sin\left(\frac{3\pi x}{L}\right)\right)\Bigg|_0^L\right]$$

$$= \frac{-2L^2}{2\pi^2} - \frac{-2L^2}{18\pi^2} = \frac{L^2}{9\pi^2} - \frac{L^2}{\pi^2} = -\frac{8L^2}{9\pi^2}$$

Making all of these appropriate substitutions we obtain:

$$\Psi^{(1)}_{n=1} = \frac{\left(\frac{2}{L}\right)(e\varepsilon)\left(-\frac{8L^2}{9\pi^2} - \frac{L}{2}(0)\right)}{\frac{-3\hbar^2\pi^2}{2mL^2}}\left(\frac{2}{L}\right)^{\frac{1}{2}}\sin\left(\frac{2\pi x}{L}\right)$$

$$\Psi^{(1)}_{n=1} = \frac{32mL^3e\varepsilon}{27\hbar^2\pi^4}\left(\frac{2}{L}\right)^{\frac{1}{2}}\sin\left(\frac{2\pi x}{L}\right)$$

Now, let's compute the induced dipole moment caused by the polarization of the electron density due to the electric field effect using the equation $\mu_{\text{induced}} = -e\int \Psi^*\left(x - \frac{L}{2}\right)\Psi dx$ with Ψ now being the sum of our zeroth- and first-order wave functions. In computing this integral, we neglect the term proportional to ε^2 because we are interested in only the term linear in ε because this is what gives the dipole moment. Again, allow me to do the algebra and see if you can follow.

$$\mu_{\text{induced}} = -e\int \Psi^*\left(x - \frac{L}{2}\right)\Psi dx\ , \ \text{where, } \Psi = \left(\Psi_1^{(0)} + \Psi_1^{(1)}\right).$$

$$\mu_{\text{induced}} = -e\int_0^L \left(\Psi_1^{(0)} + \Psi_1^{(1)}\right)^*\left(x - \frac{L}{2}\right)\left(\Psi_1^{(0)} + \Psi_1^{(1)}\right)dx$$

$$= -e\int_0^L \Psi_1^{(0)*}\left(x - \frac{L}{2}\right)\Psi_1^{(0)} dx \ - e\int_0^L \Psi_1^{(0)*}\left(x - \frac{L}{2}\right)\Psi_1^{(1)} dx$$

$$- e\int_0^L \Psi_1^{(1)*}\left(x - \frac{L}{2}\right)\Psi_1^{(0)} dx \ - e\int_0^L \Psi_1^{(1)*}\left(x - \frac{L}{2}\right)\Psi_1^{(1)} dx$$

The first integral is zero (see the evaluation of this integral for $E_1^{(1)}$ above). The fourth integral is neglected since it is proportional to ε^2. The second and third integrals are the same and are combined to give:

$$\mu_{\text{induced}} = -2e\int_0^L \Psi_1^{(0)*}\left(x - \frac{L}{2}\right)\Psi_1^{(1)} dx$$

Substituting $\Psi_1^{(0)} = \left(\frac{2}{L}\right)^{\frac{1}{2}}\ \text{Sin}\left(\frac{\pi x}{L}\right)$ and $\Psi_1^{(1)} = \frac{32mL^3e\varepsilon}{27\hbar^2\pi^4}\left(\frac{2}{L}\right)^{\frac{1}{2}}\ \text{Sin}\left(\frac{2\pi x}{L}\right)$, we obtain:

$$\mu_{\text{induced}} = -2e\frac{32mL^3e\varepsilon}{27\hbar^2\pi^4}\left(\frac{2}{L}\right)\int_0^L \text{Sin}\left(\frac{\pi x}{L}\right)\left(x - \frac{L}{2}\right)\text{Sin}\left(\frac{2\pi x}{L}\right)dx$$

These integrals are familiar from what we did to compute Ψ^1; doing them we finally obtain:

$$\mu_{\text{induced}} = -2e\frac{32mL^3e\varepsilon}{27\hbar^2\pi^4}\left(\frac{2}{L}\right)\left(-\frac{8L^2}{9\pi^2}\right)$$

$$\mu_{\text{induced}} = \frac{mL^4e^2\varepsilon}{\hbar^2\pi^6}\frac{2^{10}}{3^5}$$

Now. Let's compute the polarizability, α, of the electron in the n=1 state of the box, and try to undestand physically why α should depend as it does upon the length of the box L. To compute the polarizability, we need to know that $\alpha = \left.\frac{\partial\mu}{\partial\varepsilon}\right|_{\varepsilon=0}$ .Using our induced moment result above, we then find

$$\alpha = \left(\frac{\partial\mu}{\partial\varepsilon}\right)_{\varepsilon=0} = \frac{mL^4e^2}{\hbar^2\pi^6}\frac{2^{10}}{3^5}$$

Notice that this finding suggests that the larger the box (molecule), the more polarizable the electron density. This result also suggests that the polarizability of conjugated polyenes should vary non-linearly with the length of the congugated chain.

B. The Variational Method

Let us now turn to the other method that is used to solve Schrödinger equations approximately, the variational method. In this approach, one must again have some reasonable wave function ψ^0 that is used to approximate the true wave function. Within this approximate wave function, one imbeds one or more variables $\{\alpha_J\}$ that one subsequently varies to achieve a minimum in the energy of ψ^0 computed as an expectation value of the true Hamiltonian H:

$$E(\{\alpha_J\}) = \langle\psi^0| H | \psi^0\rangle/\langle\psi^0 | \psi^0\rangle.$$

The optimal values of the α_J parameters are determined by making

$$dE/d\alpha_J = 0$$

To achieve the desired energy minimum (n.b., we also should verify that the second derivative matrix ($\partial^2E/\partial\alpha_J\partial\alpha_L$) has all positive eigenvalues).

The theoretical basis underlying the variational method can be understood through the following derivation. Suppose the someone knew the exact eigenstates (i.e., true Ψ_K and true E_K) of the true Hamiltonian H. These states obey

$$H \Psi_K = E_K \Psi_K.$$

Because these true states form a complete set (it can be shown that the eigenfunctions of all the Hamiltonian operators we ever encounter have this property), our so-called “trial wave function” ψ^0 can, in principle, be expanded in terms of these Ψ_K:

$$\psi^0 = \Sigma_K C_K \Psi_K.$$

Before proceeding further, allow me to overcome one likely misconception. What I am going through now is only a derivation of the working formula of the variational method. The final formula will not require us to ever know the exact Ψ_K or the exact E_K, but we are allowed to use them as tools in our derivation because we know they exist even if we never know them.

With the above expansion of our trial function in terms of the exact eigenfunctions, let us now substitute this into the quantity $<\psi^0| H | \psi^0>/<\psi^0 | \psi^0>$ that the varitational method instructs us to compute:

$$E = <\psi^0| H | \psi^0>/<\psi^0 | \psi^0> = <\Sigma_K C_K \Psi_K | H | \Sigma_L C_L \Psi_L>/<\Sigma_K C_K \Psi_K|\Sigma_L C_L \Psi_L>.$$

Using the fact that the Ψ_K obey $H\Psi_K = E_K\Psi_K$ and that the Ψ_K are orthonormal (I hope you remember this property of solutions to all Schrödinger equations that we discussed earlier)

$$<\Psi_K|\Psi_L> = \delta_{K.L}$$

the above expression reduces to

$$E = \Sigma_K < C_K \Psi_K | H | C_K \Psi_K >/(\Sigma_K < C_K \Psi_K | C_K \Psi_K >) = \Sigma_K |C_K|^2 E_K/\Sigma_K|C_K|^2.$$

One of the basic properties of the kind of Hamiltonia we encounter is that they have a lowest-energy state. Sometimes we say they are bounded from below, which means their energy states do not continue all the way to minus infinity. There are systems for which this is not the case, but we will now assume that we are not dealing with such systems. This allows us to introduce the inequality $E_K \geq E_0$ which says that all of the energies are higher than or equal to the energy of the lowest state which we denote E_0. Introducing this inequality into the above expression gives

$$E \geq \Sigma_K |C_K|^2 E_0 /\Sigma_K|C_K|^2 = E_0.$$

This means that the variational energy, computed as $<\psi^0| H | \psi^0>/<\psi^0 | \psi^0>$ will lie above the true ground-state energy no matter what trial function ψ^0 we use.

The significance of the above result that $E \geq E_0$ is as follows. We are allowed to imbed into our trial wave function ψ^0 parameters that we can vary to make E, computed as $<\psi^0| H | \psi^0>/<\psi^0 | \psi^0>$ as low as possible because we know that we can never make $<\psi^0| H | \psi^0>/<\psi^0 | \psi^0>$ lower than the true ground-state energy. The philosophy then is to vary the parameters in ψ^0 to render E as low as possible, because the closer E is to E_0 the "better" is our variational wave function. Let me now demonstrate how the variational method is used in such a manner by solving an example problem.

Example Variational Problem

Suppose you are given a trial wave function of the form:

$$\varphi = \frac{Z_e^3}{\pi a_0^3} \exp\left(\frac{-Z_e r_1}{a_0}\right) \exp\left(\frac{-Z_e r_2}{a_0}\right)$$

to represent a two-electron ion of nuclear charge Z and suppose that you are lucky enough that I have already evaluated the $<\psi^0| H | \psi^0>/<\psi^0 | \psi^0>$ integral, which I'll call W, for you and found

$$W = \left(Z_e^2 - 2ZZ_e + \frac{5}{8} Z_e\right)\frac{e^2}{a_0} .$$

Now, let's find the optimum value of the variational parameter Z_e for an arbitrary nuclear charge Z by setting $\frac{dW}{dZ_e} = 0$. After finding the optimal value of Z_e, we'll then find the optimal energy by plugging this Z_e into the above W expression. I'll do the algebra and see if you can follow.

$$W = \left(Z_e^2 - 2ZZ_e + \frac{5}{8} Z_e\right)\frac{e^2}{a_0}$$

$$\frac{dW}{dZ_e} = \left(2Z_e - 2Z + \frac{5}{8}\right)\frac{e^2}{a_0} = 0$$

$$2Z_e - 2Z + \frac{5}{8} = 0$$

$$2Z_e = 2Z - \frac{5}{8}$$

$$Z_e = Z - \frac{5}{16} = Z - 0.3125$$

(n.b., 0.3125 represents the shielding factor of one 1s electron to the other).

Now, using this optimal Z_e in our energy expression gives

$$W = Z_e\left(Z_e - 2Z + \frac{5}{8}\right)\frac{e^2}{a_0}$$

$$W = \left(Z - \frac{5}{16}\right)\left(Z - \frac{5}{16} - 2Z + \frac{5}{8}\right)\frac{e^2}{a_0}$$

$$W = \left(Z - \frac{5}{16}\right)\left(-Z + \frac{5}{16}\right)\frac{e^2}{a_0}$$

$$W = -\left(Z - \frac{5}{16}\right)\left(Z - \frac{5}{16}\right)\frac{e^2}{a_0} = -\left(Z - \frac{5}{16}\right)^2 \frac{e^2}{a_0}$$

$$= -(Z - 0.3125)^2(27.21)\text{ eV}$$

(n.b., since a_0 is the Bohr radius 0.529 Å, e^2/a_0 = 27.21 eV, or one atomic unit of energy).

Is this energy “any good”? The total energies of some two-electron atoms and ions have been experimentally determined to be:

Z = 1	H^-	-14.35 eV
Z = 2	He	-78.98 eV
Z = 3	Li^+	-198.02 eV
Z = 4	Be^{+2}	-371.5 eV
Z = 5	B^{+3}	-599.3 eV
Z = 6	C^{+4}	-881.6 eV
Z = 7	N^{+5}	-1218.3 eV
Z = 8	O^{+6}	-1609.5 eV

Using our optimized expression for W, let's now calculate the estimated total energies of each of these atoms and ions as well as the percent error in our estimate for each ion.

Z	Atom	Experimental	Calculated	% Error
Z = 1	H^-	-14.35 eV	-12.86 eV	10.38%

Z = 2	He	-78.98 eV	-77.46 eV	1.92%
Z = 3	Li^+	-198.02 eV	-196.46 eV	0.79%
Z = 4	Be^{+2}	-371.5 eV	-369.86 eV	0.44%
Z = 5	B^{+3}	-599.3 eV	-597.66 eV	0.27%
Z = 6	C^{+4}	-881.6 eV	-879.86 eV	0.19%
Z = 7	N^{+5}	-1218.3 eV	-1216.48 eV	0.15%
Z = 8	O^{+6}	-1609.5 eV	-1607.46 eV	0.13%

The energy errors are essentially constant over the range of Z, but produce a larger percentage error at small Z.

In 1928, when quantum mechanics was quite young, it was not known whether the isolated, gas-phase hydride ion, H^-, was stable with respect to loss of an electrn ot form a hydrogen atom. Let's compare our estimated total energy for H^- to the ground state energy of a hydrogen atom and an isolated electron (which is known to be -13.60 eV). When we use our expression for W and take Z = 1, we obtain W = -12.86 eV, which is greater than -13.6 eV (H + e^-), so this simple variational calculation erroneously predicts H^- to be unstable. More complicated variational treatments give a ground state energy of H^- of -14.35 eV, in agreement with experiment.

II. Point Group Symmetry

It is assumed that the reader has previously learned, in undergraduate inorganic or physical chemistry classes, how symmetry arises in molecular shapes and structures and what symmetry elements are (e.g., planes, axes of rotation, centers of inversion, etc.). For the reader who feels, after reading this appendix, that additional background is needed, the text by Eyring, Walter, and Kimball or by Atkins and Friedman can be consulted. We review and teach here only that material that is of direct application to symmetry analysis of molecular orbitals and vibrations and rotations of molecules. We use a specific example, the ammonia molecule, to introduce and illustrate the important aspects of point group symmetry.

A. The C_{3v} Symmetry Group of Ammonia - An Example

The ammonia molecule NH_3 belongs, in its ground-state equilibrium geometry, to the C_{3v} point group. Its symmetry operations consist of two C_3 rotations, C_3, C_3^2 (rotations by 120° and 240°, respectively about an axis passing through the nitrogen atom and lying perpendicular to the plane formed by the three hydrogen atoms), three vertical reflections, σ_v, σ_v', σ_v'', and the identity operation. Corresponding to these six operations are symmetry elements: the three-fold rotation axis, C_3 and the three symmetry planes σ_v, σ_v' and σ_v'' that contain the three NH bonds and the z-axis (see Fig. 4.1).

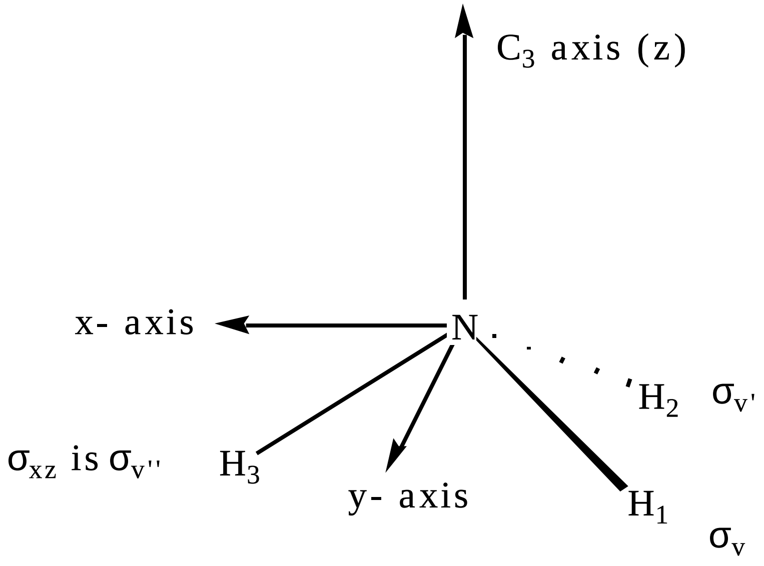


Figure 4.1 Ammonia Molecule and its Symmetry Elements

These six symmetry operations form a mathematical group. A group is defined as a set of objects satisfying four properties.

1. A combination rule is defined through which two group elements are combined to give a result which we call the product. The product of two elements in the group must also be a member of the group (i.e., the group is closed under the combination rule).

2. One special member of the group, when combined with any other member of the group, must leave the group member unchanged (i.e., the group contains an identity element).

3. Every group member must have a reciprocal in the group. When any group member is combined with its reciprocal, the product is the identity element.

4. The associative law must hold when combining three group members (i.e., (AB)C must equal A(BC)).

The members of symmetry groups are symmetry operations; the combination rule is successive operation. The identity element is the operation of doing nothing at all. The group properties can be demonstrated by forming a multiplication table. Let us label the rows of the table by the first operation and the columns by the second operation. Note that this order is important because most groups are not commutative. The C_{3v} group multiplication table is as follows:

	E	C_3	C_3^2	σ_v	σ_v'	σ_v''	second operation
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''	
C_3	C_3	C_3^2	E	σ_v'	σ_v''	σ_v	
C_3^2	C_3^2	E	C_3	σ_v''	σ_v	σ_v'	
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3	
σ_v'	σ_v'	σ_v	σ_v''	C_3	E	C_3^2	
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3	E	
First operation							

Note the reflection plane labels do not move. That is, although we start with H_1 in the σ_v plane, H_2 in σ_v", and H_3 in σ_v", if H_1 moves due to the first symmetry operation, σ_v remains fixed and a different H atom lies in the σ_v plane.

B. Matrices as Group Representations

In using symmetry to help simplify molecular orbital (mo) or vibration/rotation energy level identifications, the following strategy is followed:

1. A set of M objects belonging to the constituent atoms (or molecular fragments, in a more general case) is introduced. These objects are the orbitals of the individual atoms (or of the fragments) in the m.o. case; they are unit vectors along the x, y, and z directions located on each of the atoms, and representing displacements along each of these directions, in the vibration/rotation case.
2. Symmetry tools are used to combine these M objects into M new objects each of which belongs to a specific symmetry of the point group. Because the Hamiltonian (electronic in the m.o. case and vibration/rotation in the latter case) commutes with the symmetry operations of the point group, the matrix representation of **H** within the symmetry adapted basis will be "block diagonal". That is, objects of different symmetry will not interact; only interactions among those of the same symmetry need be considered.

To illustrate such symmetry adaptation, consider symmetry adapting the 2s orbital of N and the three 1s orbitals of the three H atoms. We begin by determining how these orbitals transform under the symmetry operations of the C_{3v} point group. The act of each of the six symmetry operations on the four atomic orbitals can be denoted as follows:

$$(S_N,S_1,S_2,S_3) \xrightarrow{E} (S_N,S_1,S_2,S_3)$$

$$\xrightarrow{C_3} (S_N,S_3,S_1,S_2)$$

$$\xrightarrow{C_3^2} (S_N,S_2,S_3,S_1)$$

$$\xrightarrow{\sigma_v} (S_N,S_1,S_3,S_2)$$

$$\xrightarrow{\sigma_v''} (S_N,S_3,S_2,S_1)$$

$$\xrightarrow{\sigma_v'} (S_N,S_2,S_1,S_3)$$

Here we are using the active view that a C_3 rotation rotates the molecule by 120°. The equivalent passive view is that the 1s basis functions are rotated -120°. In the C_3 rotation, S_3 ends up where S_1 began, S_1, ends up where S_2 began and S_2 ends up where S_3 began.

These transformations can be thought of in terms of a matrix multiplying a vector with elements (S_N,S_1,S_2,S_3). For example, if $D^{(4)}$ (C_3) is the representation matrix giving the C_3 transformation, then the above action of C_3 on the four basis orbitals can be expressed as:

$$D^{(4)}(C_3)\begin{bmatrix} s_N \\ s_1 \\ s_2 \\ s_3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} s_N \\ s_1 \\ s_2 \\ s_3 \end{bmatrix} = \begin{bmatrix} s_N \\ s_3 \\ s_1 \\ s_2 \end{bmatrix}$$

We can likewise write matrix representations for each of the symmetry operations of the C_{3v} point group:

$$D^{(4)}(C_3^2) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix}, \quad D^{(4)}(E) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$$D^{(4)}(\sigma_v) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}, \quad D^{(4)}(\sigma_v') = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$$D^{(4)}(\sigma_v'') = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

It is easy to verify that a C_3 rotation followed by a σ_v reflection is equivalent to a σ_v' reflection alone. In other words

$$\sigma_v C_3 = \sigma_v' \text{ , or, } \quad \begin{array}{ccc} & S_1 & \\ S_2 & & S_3 \end{array} \xrightarrow{C_3} \begin{array}{ccc} & S_3 & \\ S_1 & & S_2 \end{array} \xrightarrow{\sigma_v} \begin{array}{ccc} & S_3 & \\ S_2 & & S_1 \end{array}$$

Note that this same relationship is carried by the matrices:

$$D^{(4)}(\sigma_v)\, D^{(4)}(C_3) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} = D^{(4)}(\sigma_v')$$

Likewise we can verify that $C_3\ \sigma_v = \sigma_{v''}$ directly and we can notice that the matrices also show the same identity:

$$D^{(4)}(C_3)\, D^{(4)}(\sigma_v) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = D^{(4)}(\sigma_v'').$$

In fact, one finds that the six matrices, $D^{(4)}(R)$, when multiplied together in all 36 possible ways obey the same multiplication table as did the six symmetry operations. We say the matrices form a representation of the group because the matrices have all the properties of the group.

1. Characters of Representations

One important property of a matrix is the sum of its diagonal elements which is called the trace of the matrix D and is denoted Tr(D):

$$\mathrm{Tr}(D) = \sum_i D_{ii} = \chi.$$

So, χ is called the trace or character of the matrix. In the above example

$$\chi(E) = 4$$

$$\chi(C_3) = \chi(C_3^2) = 1$$

$$\chi(\sigma_v) = \chi(\sigma_v') = \chi(\sigma_v'') = 2.$$

The importance of the characters of the symmetry operations lies in the fact that they do not depend on the specific basis used to form them. That is, they are invariant to a unitary or orthorgonal transformation of the objects used to define the matrices. As a result, they contain information about the symmetry operation itself and about the space spanned by the set of objects. The significance of this observation for our symmetry adaptation process will become clear later.

Note that the characters of both rotations are the same as are those of all three reflections. Collections of operations having identical characters are called <u>classes</u>. Each operation in a <u>class</u> of operations has the same character as other members of the class. The character of a class depends on the space spanned by the basis of functions on which the symmetry operations act.

2. Another Basis and Another Representation

Above we used (S_N,S_1,S_2,S_3) as a basis. If, alternatively, we use the one-dimensional basis consisting of the 1s orbital on the N-atom, we obtain different characters, as we now demonstrate.

The act of the six symmetry operations on this S_N can be represented as follows:

$S_N \xrightarrow{E} S_N$; $S_N \xrightarrow{C_3} S_N$; $S_N \xrightarrow{C_3^2} S_N$;

$S_N \xrightarrow{\sigma_v} S_N$; $S_N \xrightarrow{\sigma_v'} S_N$; $S_N \xrightarrow{\sigma_v''} S_N$.

We can represent this group of operations in this basis by the one-dimensional set of matrices:

$D^{(1)}(E) = 1$; $D^{(1)}(C_3) = 1$; $D^{(1)}(C_3^2) = 1$,

$D^{(1)}(\sigma_v) = 1$; $D^{(1)}(\sigma_v'') = 1$; $D^{(1)}(\sigma_v') = 1$.

Again we have

$$D^{(1)}(\sigma_v)\, D^{(1)}(C_3) = 1 \quad 1 = D^{(1)}(\sigma_v''), \text{ and}$$

$$D^{(1)}(C_3)\, D^{(1)}(\sigma_v) = 1 \quad 1 = D^{(1)}(\sigma_v').$$

These six matrices form another representation of the group. In this basis, each character is equal to unity. The representation formed by allowing the six symmetry operations to act on the 1s N-atom orbital is clearly not the same as that formed when the same six operations acted on the (S_N,S_1,S_2,S_3) basis. We now need to learn how to further analyze the information content of a specific representation of the group formed when the symmetry operations act on any specific set of objects.

C. Reducible and Irreducible Representations

1. A Reducible Representation

Note that every matrix in the four dimensional group representation labeled $D^{(4)}$ has the so-called block diagonal form

$$\begin{array}{|c|ccc} \hline 1 & 0 & 0 & 0 \\ \hline 0 & \multicolumn{3}{|c|}{} \\ 0 & \multicolumn{3}{|c|}{\text{3 x 3 matrix}} \\ 0 & \multicolumn{3}{|c|}{} \\ \cline{2-4} \end{array}$$

This means that these $D^{(4)}$ matrices are really a combination of two separate group representations (mathematically, it is called a <u>direct sum</u> representation). We say that $D^{(4)}$ is reducible into a one-dimensional representation $D^{(1)}$ and a three-dimensional representation formed by the 3x3 submatrices that we will call $D^{(3)}$.

$$D^{(3)}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \quad D^{(3)}(C_3) = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}; \quad D^{(3)}(C_3{}^2) = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}$$

$$D^{(3)}(\sigma_v) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}; \quad D^{(3)}(\sigma_v') = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}; \quad D^{(3)}(\sigma_v'') = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The characters of $D^{(3)}$ are $\chi(E) = 3$, $\chi(2C_3) = 0$, $\chi(3\sigma_v) = 1$. Note that we would have obtained this $D^{(3)}$ representation directly if we had originally chosen to examine the basis (S_1,S_2,S_3); also note that these characters are equal to those of $D^{(4)}$ minus those of $D^{(1)}$.

2. A Change in Basis

Now let us convert to a new basis that is a linear combination of the original S_1,S_2,S_3 basis:

$$T_1 = S_1 + S_2 + S_3$$

$$T_2 = 2S_1 - S_2 - S_3$$

$$T_3 = S_2 - S_3$$

(Don't worry about how we construct T_1, T_2, and T_3 yet. As will be demonstrated later, we form them by using symmetry projection operators defined below). We determine how the "T" basis functions behave under the group operations by allowing the operations to act on the S_j and interpreting the results in terms of the T_i. In particular,

$$(T_1,T_2,T_3) \xrightarrow{\sigma_v} (T_1,T_2,-T_3); \qquad (T_1,T_2,T_3) \xrightarrow{E} (T_1,T_2,T_3) ;$$

$$(T_1,T_2,T_3) \xrightarrow{\sigma_v'} (S_3+S_2+S_1,2S_3-S_2-S_1,S_2-S_1) = (T_1, -\tfrac{1}{2} T_2 - \tfrac{3}{2} T_3, -\tfrac{1}{2} T_2 + \tfrac{1}{2} T_3);$$

$(T_1,T_2,T_3) \xrightarrow{\sigma_v''} (S_2+S_1+S_3, 2S_2-S_1-S_3, S_1-S_3) = (T_1, -\frac{1}{2} T_2 + \frac{3}{2} T_3, \frac{1}{2} T_2 + \frac{1}{2} T_3);$

$(T_1,T_2,T_3) \xrightarrow{C_3} (S_3+S_1+S_2, 2S_3-S_1-S_2, S_1-S_2) = (T_1, -\frac{1}{2} T_2 - \frac{3}{2} T_3, \frac{1}{2} T_2 - \frac{1}{2} T_3);$

$(T_1,T_2,T_3) \xrightarrow{C_3^2} (S_2+S_3+S_1, 2S_2-S_3-S_1, S_3-S_1) = (T_1, -\frac{1}{2} T_2 + \frac{3}{2} T_3, -\frac{1}{2} T_2 - \frac{1}{2} T_3).$

So the matrix representations in the new T_i basis are:

$$D^{(3)}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}; D^{(3)}(C_3) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{3}{2} \\ 0 & +\frac{1}{2} & -\frac{1}{2} \end{bmatrix};$$

$$D^{(3)}(C_3^2) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & +\frac{3}{2} \\ 0 & -\frac{1}{2} & -\frac{1}{2} \end{bmatrix}; \qquad D^{(3)}(\sigma_v) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix};$$

$$D^{(3)}(\sigma_v') = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{3}{2} \\ 0 & -\frac{1}{2} & +\frac{1}{2} \end{bmatrix}; \qquad D^{(3)}(\sigma_v'') = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & +\frac{3}{2} \\ 0 & +\frac{1}{2} & +\frac{1}{2} \end{bmatrix}.$$

These six matrices can be verified to multiply just as the symmetry operations do; thus they form another three-dimensional representation of the group. We see that in the T_i basis the matrices are block diagonal. This means that the space spanned by the T_i functions, which is the same space as the S_j span, forms a reducible representation that can be decomposed into a one dimensional space and a two dimensional space (via formation of the T_i functions). Note that the characters (traces) of the matrices are not changed by the change in bases.

The one-dimensional part of the above reducible three-dimensional representation is seen to be the same as the totally symmetric representation we arrived at before, $D^{(1)}$. The two-dimensional representation that is left can be shown to be <u>irreducible</u> ; it has the following matrix representations:

$$D^{(2)}(E) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix};\ D^{(2)}(C_3) = \begin{bmatrix} -\frac{1}{2} & -\frac{3}{2} \\ +\frac{1}{2} & -\frac{1}{2} \end{bmatrix};\ D^{(2)}(C_3{}^2) = \begin{bmatrix} -\frac{1}{2} & +\frac{3}{2} \\ -\frac{1}{2} & -\frac{1}{2} \end{bmatrix};$$

$$D^{(2)}(\sigma_v) = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix};\ D^{(2)}(\sigma_v') = \begin{bmatrix} -\frac{1}{2} & -\frac{3}{2} \\ -\frac{1}{2} & +\frac{1}{2} \end{bmatrix};\ D^{(2)}(\sigma_v'') = \begin{bmatrix} -\frac{1}{2} & -\frac{3}{2} \\ -\frac{1}{2} & +\frac{1}{2} \end{bmatrix}$$

The characters can be obtained by summing diagonal elements:

$\chi(E) = 2, \chi\ (2C_3) = -1, \chi\ (3\sigma_v) = 0.$

4. Rotations as a Basis

Another one-dimensional representation of the group can be obtained by taking rotation about the Z-axis (the C_3 axis) as the object on which the symmetry operations act:

$R_Z \xrightarrow{E} R_Z$; $R_Z \xrightarrow{C_3} R_Z$; $R_Z \xrightarrow{C_3^2} R_Z$;

$R_Z \xrightarrow{\sigma_V} -R_Z$; $R_Z \xrightarrow{\sigma_V''} -R_Z$; $R_Z \xrightarrow{\sigma_V'} -R_Z$.

In writing these relations, we use the fact that reflection reverses the sense of a rotation. The matrix representations corresponding to this one-dimensional basis are:

$D^{(1)}(E) = 1$; $D^{(1)}(C_3) = 1$; $D^{(1)}(C_3^2) = 1$;

$D^{(1)}(\sigma_V) = -1$;$D^{(1)}(\sigma_V'') = -1$; $D^{(1)}\ (\sigma_V') = -1$.

These one-dimensional matrices can be shown to multiply together just like the symmetry operations of the C_{3V} group. They form an <u>irreducible</u> representation of the group (because it is one-dimensional, it can not be further reduced). Note that this one-dimensional representation is not identical to that found above for the 1s N-atom orbital, or the T_1 function.

5. Overview

We have found three distinct irreducible representations for the C_{3v} symmetry group; two different one-dimensional and one two dimensional representations. Are there any more? An important theorem of group theory shows that the number of irreducible representations of a group is equal to the number of classes. Since there are three classes of operation (i.e., E, C_3 and σ_v), we have found all the irreducible representations of the C_{3v} point group. There are no more.

The irreducible representations have standard names; the first $D^{(1)}$ (that arising from the T_1 and $1s_N$ orbitals) is called A_1, the $D^{(1)}$ arising from R_z is called A_2 and $D^{(2)}$ is called E (not to be confused with the identity operation E). We will see shortly where to find and identify these names.

Thus, our original $D^{(4)}$ representation was a combination of two A_1 representations and one E representation. We say that $D^{(4)}$ is a direct sum representation: $D^{(4)} = 2A_1 \quad E$. A consequence is that the characters of the combination representation $D^{(4)}$ can be obtained by adding the characters of its constituent irreducible representations.

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_1	1	1	1
E	2	-1	0
$2A_1$ E	4	1	2

6. How to Decompose Reducible Representations in General

Suppose you were given only the characters (4,1,2). How can you find out how many times A_1, E, and A_2 appear when you reduce $D^{(4)}$ to its irreducible parts? You want to find a linear combination of the characters of A_1, A_2 and E that add up (4,1,2). You can treat the characters of matrices as vectors and take the dot product of A_1 with $D^{(4)}$

$$\left[\begin{array}{cccccc}1 & 1 & 1 & 1 & 1 & 1\\ E & C_3 & & \sigma_v & & \end{array}\right]\left[\begin{array}{cc}4 & E\\ 1 & C_3\\ 1 & \\ 2 & \sigma_v\\ 2 & \\ 2 & \end{array}\right] = 4 + 1 + 1 + 2 + 2 + 2 = 12.$$

The vector (1,1,1,1,1,1) is not normalized; hence to obtain the component of (4,1,1,2,2,2) along a unit vector in the (1,1,1,1,1,1) direction, one must divide by the norm of

(1,1,1,1,1,1); this norm is 6. The result is that the reducible representation contains $\frac{12}{6}$ = 2 A_1 components. Analogous projections in the E and A_2 directions give components of 1 and 0, respectively. In general, to determine the number n_Γ of times irreducible representation Γ appears in the reducible representation with characters χ_{red}, one calculates

$$n_\Gamma = \frac{1}{g}\sum_R \chi_\Gamma(R)\chi_{red}(R) ,$$

where g is the order of the group and $\chi_\Gamma(R)$ are the characters of the Γ^{th} irreducible representation.

7. Commonly Used Bases

We could take <u>any</u> set of functions as a basis for a group representation. Commonly used sets include: coordinates (x,y,z) located on the atoms of a polyatomic molecule (their symmetry treatment is equivalent to that involved in treating a set of p orbitals on the same atoms), quadratic functions such as d orbitals - xy,yz,xz,x^2-y^2,z^2, as well as rotations about the x, y and z axes. The transformation properties of these very commonly used bases are listed in the character tables shown at the end of this Section.

8. Summary

The basic idea of symmetry analysis is that any basis of orbitals, displacements, rotations, etc. transforms either as one of the irreducible representations or as a direct sum (reducible) representation. Symmetry tools are used to first determine how the basis transforms under action of the symmetry operations. They are then used to decompose the resultant representations into their irreducible components.

D. Another Example

1. The 2p Orbitals of Nitrogen

For a function to transform according to a specific irreducible representation means that the function, when operated upon by a point-group symmetry operator, yields a linear combination of the functions that transform according to that irreducible representation. For example, a $2p_z$ orbital (z is the C_3 axis of NH_3) on the nitrogen atom belongs to the A_1 representation because it yields unity times itself when C_3, C_3^2, σ_v, σ_v',σ_v'' or the identity operation act on it. The factor of 1 means that $2p_z$ has A_1 symmetry since the characters (the numbers listed opposite A_1 and below E, $2C_3$, and $3\sigma_v$ in the C_{3v} character table shown at the end of this Section) of all six symmetry operations are 1 for the A_1 irreducible representation.

The $2p_x$ and $2p_y$ orbitals on the nitrogen atom transform as the E representation since C_3, C_3^2, σ_v, σ_v', σ_v'' and the identity operation map $2p_x$ and $2p_y$ among one another. Specifically,

$$C_3 \qquad \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix} = \begin{bmatrix} \mathrm{Cos}120^\circ & -\mathrm{Sin}120^\circ \\ \mathrm{Sin}120^\circ & \mathrm{Cos}120^\circ \end{bmatrix} \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix};$$

$$C_3^2 \qquad \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix} = \begin{bmatrix} \mathrm{Cos}240^\circ & -\mathrm{Sin}240^\circ \\ \mathrm{Sin}240^\circ & \mathrm{Cos}240^\circ \end{bmatrix} \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix};$$

$$E \qquad \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix};$$

$$\sigma_v \qquad \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix};$$

$$\sigma_v' \qquad \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix} = \begin{bmatrix} +\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix};$$

$$\sigma_v'' \qquad \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix} = \begin{bmatrix} +\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} 2p_x \\ 2p_y \end{bmatrix}.$$

The 2 x 2 matrices, which indicate how each symmetry operation maps $2p_x$ and $2p_y$ into some combinations of $2p_x$ and $2p_y$, are the representation matrices ($D^{(IR)}$) for that particular operation and for this particular irreducible representation (IR). For example,

$$\begin{bmatrix} +\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} = D^{(E)}(\sigma_v')$$

This set of matrices have the same characters as the $D^{(2)}$ matrices obtained earlier when the T_i displacement vectors were analyzed, but the individual matrix elements are different because we used a different basis set (here $2p_x$ and $2p_y$; above it was T_2 and T_3). This illustrates the invariance of the trace to the specific representation; the trace only depends on the space spanned, not on the specific manner in which it is spanned.

2. A Short-Cut

A short-cut device exists for evaluating the trace of such representation matrices (that is, for computing the characters). The diagonal elements of the representation matrices are the projections along each orbital of the effect of the symmetry operation acting on that orbital. For example, a diagonal element of the C_3 matrix is the component of $C_3 2p_y$ along the $2p_y$ direction. More rigorously, it is $\int 2p_y^* C_3 2p_y d\tau$. Thus, the character of the C_3 matrix is the sum of $\int 2p_y^* C_3 2p_y d\tau$ and $\int 2p_x^* C_3 2p_x d\tau$. In general, the character χ of any symmetry operation S can be computed by allowing S to operate on each orbital φ_i, then projecting $S\varphi_i$ along φ_i (i.e., forming $\int \varphi_i^* S\varphi_i d\tau$), and summing these terms,

$$\sum_i \int \varphi_i^* S\varphi_i d\tau = \chi(S).$$

If these rules are applied to the $2p_x$ and $2p_y$ orbitals of nitrogen within the C_{3v} point group, one obtains

$$\chi(E) = 2, \chi(C_3) = \chi(C_3^2) = -1, \chi(\sigma_v) = \chi(\sigma_v'') = \chi(\sigma_v') = 0.$$

This set of characters is the same as $D^{(2)}$ above and agrees with those of the E representation for the C_{3v} point group. Hence, $2p_x$ and $2p_y$ belong to or transform as the E representation. This is why (x,y) is to the right of the row of characters for the E representation in the C_{3v} character table shown at the end of this Section. In similar fashion, the C_{3v} character table (please refer to this table now) states that $d_{x^2-y^2}$ and d_{xy} orbitals on nitrogen transform as E, as do d_{xy} and d_{yz}, but d_{z^2} transforms as A_1.

Earlier, we considered in some detail how the three $1s_H$ orbitals on the hydrogen atoms transform. Repeating this analysis using the short-cut rule just described, the traces (characters) of the 3 x 3 representation matrices are computed by allowing E, $2C_3$, and $3\sigma_v$ to operate on $1s_{H_1}$, $1s_{H_2}$, and $1s_{H_3}$ and then computing the component of the resulting function along the original function. The resulting characters are $\chi(E) = 3$, $\chi(C_3) = \chi(C_3^2) = 0$, and $\chi(\sigma_v) = \chi(\sigma_v') = \chi(\sigma_v'') = 1$, in agreement with what we calculated before.

Using the orthogonality of characters taken as vectors we can reduce the above set of characters to $A_1 + E$. Hence, we say that our orbital set of three $1s_H$ orbitals forms a reducible representation consisting of the sum of A_1 and E IR's. This means that the three $1s_H$ orbitals can be combined to yield one orbital of A_1 symmetry and a pair that transform according to the E representation.

E. Projector Operators: Symmetry Adapted Linear Combinations of Atomic Orbitals

To generate the above A_1 and E symmetry-adapted orbitals, we make use of so-called symmetry projection operators P_E and P_{A_1}. These operators are given in terms of linear combinations of products of characters times elementary symmetry operations as follows:

$$P_{A_1} = \sum_S \chi_A(S)\, S$$

$$P_E = \sum_S \chi_E(S)\, S$$

where S ranges over C_3, C_3^2, σ_v, σ_v' and σ_v'' and the identity operation. The result of applying P_{A_1} to say $1s_{H_1}$ is

$$P_{A_1}\, 1s_{H_1} = 1s_{H_1} + 1s_{H_2} + 1s_{H_3} + 1s_{H_2} + 1s_{H_3} + 1s_{H_1}$$

$$= 2(1s_{H_1} + 1s_{H_2} + 1s_{H_3}) = \varphi_{A_1},$$

which is an (unnormalized) orbital having A_1 symmetry. Clearly, this same φ_{A_1} would be generated by P_{A_1} acting on $1s_{H_2}$ or $1s_{H_3}$. Hence, only one A_1 orbital exists. Likewise,

$$P_E 1s_{H_1} = 2 \quad 1s_{H_1} - 1s_{H_2} - 1s_{H_3} \equiv \varphi_{E,1}$$

which is one of the symmetry adapted orbitals having E symmetry. The other E orbital can be obtained by allowing P_E to act on $1s_{H_2}$ or $1s_{H_3}$:

$$P_E 1s_{H_2} = 2 \quad 1s_{H_2} - 1s_{H_1} - 1s_{H_3} \equiv \varphi_{E,2}$$

$$P_E 1s_{H_3} = 2 \quad 1s_{H_3} - 1s_{H_1} - 1s_{H_2} = \varphi_{E,3} .$$

It might seem as though three orbitals having E symmetry were generated, but only two of these are really independent functions. For example, $\varphi_{E,3}$ is related to $\varphi_{E,1}$ and $\varphi_{E,2}$ as follows:

$$\varphi_{E,3} = -(\varphi_{E,1} + \varphi_{E,2}).$$

Thus, only $\varphi_{E,1}$ and $\varphi_{E,2}$ are needed to span the two-dimensional space of the E representation. If we include $\varphi_{E,1}$ in our set of orbitals and require our orbitals to be orthogonal, then we must find numbers a and b such that $\varphi'_E = a\varphi_{E,2} + b\varphi_{E,3}$ is orthogonal to $\varphi_{E,1}$: $\int \varphi'_E \, \varphi_{E,1} d\tau = 0$. A straightforward calculation gives $a = -b$ or $\varphi'_E = a\,(1s_{H_2} - 1s_{H_3})$ which agrees with what we used earlier to construct the T_i functions in terms of the S_j functions.

F. Summary

Let us now summarize what we have learned. Any given set of atomic orbitals $\{\varphi_i\}$, atom-centered displacements or rotations can be used as a basis for the symmetry operations of the point group of the molecule. The characters $\chi(S)$ belonging to the operations S of this point group within any such space can be found by summing the integrals $\int \varphi_i{}^* S \varphi_i d\tau$ over all the atomic orbitals (or corresponding unit vector atomic displacements). The resultant characters will, in general, be reducible to a combination of the characters of the irreducible representations $\chi_i(S)$. To decompose the characters $\chi(S)$ of the reducible representation to a sum of characters $\chi_i(S)$ of the irreducible representation

$$\chi(S) = \sum_i n_i \, \chi_i(S) \; ,$$

it is necessary to determine how many times, $n_{i,}$ the i-th irreducible representation occurs in the reducible representation. The expression for n_i is

$$n_i = \frac{1}{g} \sum_S \chi(S) \, \chi_i(S)$$

in which g is the order of the point group- the total number of symmetry operations in the group (e.g., g = 6 for C_{3v}).

For example, the reducible representation $\chi(E) = 3$, $\chi(C_3) = 0$, and $\chi(\sigma_v) = 1$ formed by the three $1s_H$ orbitals discussed above can be decomposed as follows:

$$n_{A_1} = \frac{1}{6} (3 \quad 1 + 2 \quad 0 \quad 1 + 3 \quad 1 \quad 1) \; = 1,$$

$$n_{A_2} = \frac{1}{6}(3 \quad 1 + 2 \quad 0 \quad 1 + 3 \quad 1 \quad (-1)) = 0,$$

$$n_E = \frac{1}{6}(3 \quad 2 + 2 \quad 0 \quad (-1) + 3 \quad 1 \quad 0) = 1.$$

These equations state that the three $1s_H$ orbitals can be combined to give one A_1 orbital and, since E is degenerate, one pair of E orbitals, as established above. With knowledge of the n_i, the symmetry-adapted orbitals can be formed by allowing the projectors

$$P_i = \sum_i \chi_i(S)\ S$$

to operate on each of the primitive atomic orbitals. How this is carried out was illustrated for the $1s_H$ orbitals in our earlier discussion. These tools allow a symmetry decomposition of any set of atomic orbitals into appropriate symmetry-adapted orbitals.

Before considering other concepts and group-theoretical machinery, it should once again be stressed that these same tools can be used in symmetry analysis of the translational, vibrational and rotational motions of a molecule. The twelve motions of NH_3 (three translations, three rotations, six vibrations) can be described in terms of combinations of displacements of each of the four atoms in each of three (x,y,z) directions. Hence, unit vectors placed on each atom directed in the x, y, and z directions form a basis for action by the operations {S} of the point group. In the case of NH_3, the characters of the resultant 12 x 12 representation matrices form a reducible representation in the C_{2v} point group: $\chi(E) = 12$, $\chi(C_3) = \chi(C_3^2) = 0$, $\chi(\sigma_v) = \chi(\sigma_v') = \chi(\sigma_v'') = 2$. For example under σ_v, the H_2 and H_3 atoms are interchanged, so unit vectors on either one will not contribute to the trace. Unit z-vectors on N and H_1 remain unchanged as well as the corresponding y-vectors. However, the x-vectors on N and H_1 are reversed in sign. The total character for σ_v' the H_2 and H_3 atoms are interchanged, so unit vectors on either one will not contribute to the trace. Unit z-vectors on N and H_1 remain unchanged as well as the corresponding y-vectors. However, the x-vectors on N and H_1 are reversed in sign. The total character for σ_v is thus 4 - 2 = 2. This representation can be decomposed as follows:

$$n_{A_1} = \frac{1}{6}\ [1\ \ 1\ \ 12 + 2\ \ 1\ \ 0 + 3\ \ 1\ \ 2] = 3,$$

$$n_{A_2} = \frac{1}{6}\ [1\ \ 1\ \ 12 + 2\ \ 1\ \ 0 + 3\ \ (-1)\ \ 2] = 1,$$

$$n_E = \frac{1}{6}\ [1\ \ 2\ \ 12 + 2\ \ (-1)\ \ 0 + 3\ \ 0\ \ 2] = 4.$$

From the information on the right side of the C_{3v} character table, translations of all four atoms in the z, x and y directions transform as $A_1(z)$ and $E(x,y)$, respectively, whereas rotations about the $z(R_z)$, $x(R_x)$, and $y(R_y)$ axes transform as A_2 and E. Hence, of the twelve motions, three translations have A_1 and E symmetry and three rotations have A_2 and E symmetry. This leaves six vibrations, of which two have A_1 symmetry, none have A_2 symmetry, and two (pairs) have E symmetry. We could obtain symmetry-adapted vibrational and rotational bases by allowing symmetry projection operators of the irreducible representation symmetries to operate on various elementary cartesian (x,y,z) atomic displacement vectors.

G. Direct Product Representations

1. Direct Products in N-Electron Wave functions

We now turn to the symmetry analysis of orbital products. Such knowledge is important because one is routinely faced with constructing symmetry-adapted N-electron configurations that consist of products of N individual spin orbitals, one for each electron. A point-group symmetry operator S, when acting on such a product of orbitals, gives the product of S acting on each of the individual orbitals

$$S(\varphi_1\varphi_2\varphi_3...\varphi_N) = (S\varphi_1)\ (S\varphi_2)\ (S\varphi_3)\ ...\ (S\varphi_N).$$

For example, reflection of an N-orbital product through the σ_v plane in NH_3 applies the reflection operation to all N electrons.

Just as the individual orbitals formed a basis for action of the point-group operators, the configurations (N-orbital products) form a basis for the action of these same point-group operators. Hence, the various electronic configurations can be treated as functions on which S operates, and the machinery illustrated earlier for decomposing orbital symmetry can then be used to carry out a symmetry analysis of configurations.

Another shortcut makes this task easier. Since the symmetry adapted individual orbitals $\{\phi_i, i = 1, ..., M\}$ transform according to irreducible representations, the representation matrices for the N-term products shown above consist of products of the matrices belonging to each ϕ_i. This matrix product is not a simple product but what is called a direct product. To compute the characters of the direct product matrices, one multiplies the characters of the individual matrices of the irreducible representations of the N orbitals that appear in the electron configuration. The direct-product representation formed by the orbital products can therefore be symmetry-analyzed (reduced) using the same tools as we used earlier.

For example, if one is interested in knowing the symmetry of an orbital product of the form $a_1^2a_2^2e^2$ (note: lower case letters are used to denote the symmetry of electronic orbitals, whereas capital letters are reserved to label the overall configuration’s symmetry) in C_{3v} symmetry, the following procedure is used. For each of the six symmetry operations in the C_{2v} point group, the <u>product</u> of the characters associated with each of the <u>six</u> spin orbitals (orbital multiplied by α or β spin) is formed

$$\chi(S) = \prod_i \chi_i(S) = (\chi_{A_1}(S))^2 (\chi_{A_2}(S))^2 (\chi_E(S))^2.$$

In the specific case considered here, $\chi(E) = 4$, $\chi(2C_3) = 1$, and $\chi(3\sigma_v) = 0$. Notice that the contributions of any doubly occupied nondegenerate orbitals (e.g., a_1^2, and a_2^2) to these direct product characters $\chi(S)$ are unity because for <u>all</u> operators $(\chi_k(S))^2 = 1$ for any one-dimensional irreducible representation. As a result, only the singly occupied or degenerate orbitals need to be considered when forming the characters of the reducible direct-product representation $\chi(S)$. For this example this means that the direct-product characters can be determined from the characters $\chi_E(S)$ of the two active (i.e., nonclosed-shell) orbitals - the e^2 orbitals. That is, $\chi(S) = \chi_E(S) \quad \chi_E(S)$.

From the direct-product characters $\chi(S)$ belonging to a particular electronic configuration (e.g., $a_1^2a_2^2e^2$), one must still decompose this list of characters into a sum of irreducible characters. For the example at hand, the direct-product characters $\chi(S)$ decompose into one A_1, one A_2, and one E representation. This means that the e^2 configuration contains A_1, A_2, and E symmetry elements. Projection operators analogous to those introduced earlier for orbitals can be used to form symmetry-adapted orbital products from the individual basis orbital products of the form $a_1^2a_2^2e_x^me_y^{m'}$, where m and m' denote the occupation (1 or 0) of the two degenerate orbitals e_x and e_y. When dealing with indistinguishable particles such as electrons, it is also necessary to further project the resulting orbital products to make them antisymmetric (for Fermions) or symmetric (for Bosons) with respect to interchange of any pair of particles. This step reduces the set of N-electron states that can arise. For example, in the above e^2 configuration case, only $^3A_2$, $^1A_1$, and ^1E states arise; the ^3E, $^3A_1$, and $^1A_2$ possibilities disappear when the antisymmetry projector is applied. In contrast, for an $e^1e'^1$ configuration, all states arise even after the wave function has been made antisymmetric. The steps involved in combining the point group symmetry with permutational antisymmetry are illustrated in Chapter 10 of my QMIC text. In Appendix III of Electronic Spectra and Electronic Structure of Polyatomic Molecules , G. Herzberg, Van Nostrand Reinhold Co., New York, N.Y. (1966) the resolution of direct products among various representations within many point groups are tabulated.

2. Direct Products in Selection Rules

Two states ψ_a and ψ_b that are eigenfunctions of a Hamiltonian $\mathbf{H_o}$ in the absence of some external perturbation (e.g., electromagnetic field or static electric field or potential due to surrounding ligands) can be "coupled" by the perturbation **V** only if the symmetries of **V** and of the two wave functions obey a so-called selection rule. In particular, only if the coupling integral

$$\int \psi_a^* \mathbf{V} \psi_b \, d\tau = V_{a,b}$$

is non-vanishing will the two states be coupled by **V** .

The role of symmetry in determining whether such integrals are non-zero can be demonstrated by noting that the integrand, considered as a whole, must contain a component that is invariant under all of the group operations (i.e., belongs to the totally symmetric representation of the group) if the integral is to not vanish. In terms of the projectors introduced above we must have

$$\sum_{S} \chi_A(S)\ S\ \psi_a^* \mathbf{V}\ \psi_b$$

not vanish. Here the subscript A denotes the totally symmetric representation of whatever point group applies. The symmetry of the product $\psi_a^* \mathbf{V}\ \psi_b$ is, according to what was covered earlier, given by the direct product of the symmetries of ψ_a^* of **V** and of ψ_b. So, the conclusion is that the integral will vanish unless this triple direct product contains, when it is reduced to its irreducible components, a component of the totally symmetric representation.

To see how this result is used, consider the integral that arises in formulating the interaction of electromagnetic radiation with a molecule within the electric-dipole approximation:

$$\int \psi_a^*\ \mathbf{r}\ \psi_b\, d\tau\ .$$

Here, **r** is the vector giving, together with e, the unit charge, the quantum mechanical dipole moment operator

$$\mathbf{r} = e\sum_{n} Z_n \mathbf{R}_n\ - e\sum_{j} \mathbf{r}_j\ ,$$

where Z_n and $\mathbf{R}_n$ are the charge and position of the n^{th} nucleus and $\mathbf{r}_j$ is the position of the j^{th} electron. Now, consider evaluating this integral for the singlet $n \rightarrow \pi^*$ transition in formaldehyde. Here, the closed-shell ground state is of ${}^1A_1$ symmetry and the singlet excited state, which involves promoting an electron from the non-bonding b_2 lone pair orbital on the Oxygen into the π^* b_1 orbital on the CO moiety, is of ${}^1A_2$ symmetry (b_1x $b_2 = a_2$). The direct product of the two wave function symmetries thus contains only a_2 symmetry. The three components (x, y, and z) of the dipole operator have, respectively, b_1, b_2, and a_1 symmetry. Thus, the triple direct products give rise to the following possibilities:

$$a_2 \text{ x } b_1 = b_2,$$

$$a_2 \text{ x } b_2 = b_1,$$

$$a_2 \text{ x } a_1 = a_2 .$$

There is no component of a_1 symmetry in the triple direct product, so the integral vanishes. This allows us to conclude that the $n \rightarrow \pi^*$ excitation in formaldehyde is electric dipole forbidden.

H. Overview

We have shown how to make a symmetry decomposition of a basis of atomic orbitals (or cartesian displacements or orbital products) into irreducible representation components. This tool is very helpful when studying spectroscopy and when constructing the orbital correlation diagrams that form the basis of the Woodward-Hoffmann rules. We also learned how to form the direct-product symmetries that arise when considering configurations consisting of products of symmetry-adapted spin orbitals. Finally, we learned how the direct product analysis allows one to determine whether or not integrals of products of wave functions with operators between them vanish. This tool is of utmost importance in determining selection rules in spectroscopy and for determining the effects of external perturbations on the states of the species under investigation.