

# Section 1 The Basic Tools of Quantum Mechanics

## Chapter 1

*Quantum Mechanics Describes Matter in Terms of Wavefunctions and Energy Levels.  
Physical Measurements are Described in Terms of Operators Acting on Wavefunctions*

### I. Operators, Wavefunctions, and the Schrödinger Equation

The trends in chemical and physical properties of the elements described beautifully in the periodic table and the ability of early spectroscopists to fit atomic line spectra by simple mathematical formulas and to interpret atomic electronic states in terms of empirical quantum numbers provide compelling evidence that some relatively simple framework must exist for understanding the electronic structures of all atoms. The great predictive power of the concept of atomic valence further suggests that molecular electronic structure should be understandable in terms of those of the constituent atoms.

Much of quantum chemistry attempts to make more quantitative these aspects of chemists' view of the periodic table and of atomic valence and structure. By starting from 'first principles' and treating atomic and molecular states as solutions of a so-called Schrödinger equation, quantum chemistry seeks to determine what underlies the empirical quantum numbers, orbitals, the *aufbau* principle and the concept of valence used by spectroscopists and chemists, in some cases, even prior to the advent of quantum mechanics.

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, the authors have organized this introductory section in a manner that first provides the student with a brief introduction to the two primary constructs of quantum mechanics, operators and wavefunctions that obey a Schrödinger equation, then demonstrates the application of these constructs to several chemically relevant model problems, and finally returns to examine in more detail the conceptual structure of quantum mechanics.

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 because the wavefunctions of the known model problems can be used to illustrate.

## A. Operators

*Each physically measurable quantity has a corresponding operator. The eigenvalues of the operator tell the values of the corresponding physical property that can be observed*

In quantum mechanics, any experimentally measurable physical quantity  $F$  (e.g., energy, dipole moment, orbital angular momentum, spin angular momentum, linear momentum, kinetic energy) whose classical mechanical expression can be written in terms of the cartesian positions  $\{q_i\}$  and momenta  $\{p_i\}$  of the particles that comprise the system of interest is assigned a corresponding quantum mechanical operator  $\mathbf{F}$ . Given  $F$  in terms of the  $\{q_i\}$  and  $\{p_i\}$ ,  $\mathbf{F}$  is formed by replacing  $p_j$  by  $-i\hbar / q_j$  and leaving  $q_j$  untouched.

For example, if

$$F = \sum_{i=1,N} (p_i^2/2m_i + 1/2 k(q_i - q_i^0)^2 + L(q_i - q_i^0)),$$

then

$$\mathbf{F} = \sum_{i=1,N} (-\hbar^2/2m_i \nabla_i^2 + 1/2 k(q_i - q_i^0)^2 + L(q_i - q_i^0))$$

is the corresponding quantum mechanical operator. Such an operator would occur when, for example, one describes the sum of the kinetic energies of a collection of particles (the  $\sum_{i=1,N} (p_i^2/2m_i)$  term, plus the sum of "Hookes' Law" parabolic potentials (the  $1/2 \sum_{i=1,N} k(q_i - q_i^0)^2$ ), 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  $\{q_i^0\}$ .

The sum of the z-components of angular momenta of a collection of  $N$  particles has

$$F = \sum_{j=1,N} (x_j p_{yj} - y_j p_{xj}),$$

and the corresponding operator is

$$\mathbf{F} = -i\hbar \sum_{j=1,N} (x_j \nabla_j - y_j \nabla_j).$$

The x-component of the dipole moment for a collection of  $N$  particles

has

$$F = \sum_{j=1, N} Z_j e x_j, \text{ and}$$

$$\mathbf{F} = \sum_{j=1, N} Z_j e \mathbf{x}_j ,$$

where  $Z_j e$  is the charge on the  $j^{\text{th}}$  particle.

The mapping from  $F$  to  $\mathbf{F}$  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. Interested readers are referred to Kemble's text on quantum mechanics which deals with this matter in detail. 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 corresponding transformation of the kinetic energy operator to spherical coordinates is treated in detail in Appendix A. The text by EWK also covers this topic in considerable detail.

The relationship of these quantum mechanical operators to experimental measurement will be made clear later in this chapter. For now, suffice it to say that these operators define equations whose solutions determine the values of the corresponding physical property that can be observed when a measurement is carried out; only the values so determined can be observed. This should suggest the origins of quantum mechanics' prediction that some measurements will produce **discrete** or **quantized** values of certain variables (e.g., energy, angular momentum, etc.).

## B. Wavefunctions

*The eigenfunctions of a quantum mechanical operator depend on the coordinates upon which the operator acts; these functions are called wavefunctions*

In addition to operators corresponding to each physically measurable quantity, quantum mechanics describes the state of the system in terms of a wavefunction that is a function of the coordinates  $\{q_j\}$  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  $\text{H}_2\text{O}$  molecule, the wavefunction depends on many coordinates. For the  $\text{H}_2\text{O}$  example, it depends on the  $x$ ,  $y$ , and  $z$  (or  $r$ ,  $\theta$ , and  $\phi$ ) coordinates of the ten

electrons and the x, y, and z (or r,  $\theta$ , and  $\phi$ ) coordinates of the oxygen nucleus and of the two protons; a total of thirty-nine coordinates appear in  $\Psi$ .

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  $t$ :  $|\Psi(q_j, t)|^2$ . 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.

### C. The Schrödinger Equation

*This equation is an eigenvalue equation for the energy or Hamiltonian operator; its eigenvalues provide the 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*

How to extract from  $\Psi(q_j, t)$  knowledge about momenta is treated below in Sec. III. A, where the structure of quantum mechanics, the use of operators and wavefunctions to make predictions and interpretations about experimental measurements, and the origin of 'uncertainty relations' such as the well known Heisenberg uncertainty condition dealing with measurements of coordinates and momenta are also treated.

Before moving deeper into understanding what quantum mechanics 'means', it is useful to learn how the wavefunctions  $\Psi$  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 because these model cases can be used as 'concrete examples'.

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<sub>2</sub>O example cited above). It is usually written

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

where  $\psi(\mathbf{q},t)$  is the unknown wavefunction and  $\mathbf{H}$  is the operator corresponding to the total energy physical property 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  $\mathbf{p}_j = -i\hbar \nabla / q_j$ .

For the H<sub>2</sub>O example used above, the classical mechanical energy of all thirteen particles is

$$E = \sum_i \left\{ \frac{p_i^2}{2m_e} + \frac{1}{2} \sum_j e^2/r_{i,j} - \sum_a Z_a e^2/r_{i,a} \right\} + \sum_a \left\{ \frac{p_a^2}{2m_a} + \frac{1}{2} \sum_b Z_a Z_b e^2/r_{a,b} \right\},$$

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

$$\mathbf{H} = \sum_i \left\{ -(\hbar^2/2m_e) \nabla_i^2 + \frac{1}{2} \sum_j e^2/r_{i,j} - \sum_a Z_a e^2/r_{i,a} \right\} + \sum_a \left\{ -(\hbar^2/2m_a) \nabla_a^2 + \frac{1}{2} \sum_b Z_a Z_b e^2/r_{a,b} \right\}.$$

Notice that  $\mathbf{H}$  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  $\mathbf{p} = -i\hbar \nabla / q$  is of first order.

The Schrödinger equation for the H<sub>2</sub>O example at hand then reads

$$\sum_i \left\{ -(\hbar^2/2m_e) \nabla_i^2 + \frac{1}{2} \sum_j e^2/r_{i,j} - \sum_a Z_a e^2/r_{i,a} \right\} \psi + \sum_a \left\{ -(\hbar^2/2m_a) \nabla_a^2 + \frac{1}{2} \sum_b Z_a Z_b e^2/r_{a,b} \right\} \psi = i\hbar \partial \psi / \partial t.$$

## 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 discussed later in this text), the separations of variables techniques can be used to reduce the Schrödinger equation to a time-independent equation.

In such cases,  $\mathbf{H}$  is not explicitly time dependent, so one can assume that  $\psi(\mathbf{q}_j, t)$  is of the form

$$\psi(\mathbf{q}_j, t) = \psi(\mathbf{q}_j) F(t).$$

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

$$\psi(\mathbf{q}_j) i \hbar \frac{dF}{dt} = \mathbf{H} \psi(\mathbf{q}_j) F(t).$$

Dividing by  $\psi(\mathbf{q}_j) F(t)$  then gives

$$F^{-1} i \hbar \frac{dF}{dt} = -1 (\mathbf{H} \psi(\mathbf{q}_j)).$$

Since  $F(t)$  is only a function of time  $t$ , and  $\psi(\mathbf{q}_j)$  is only a function of the spatial coordinates  $\{\mathbf{q}_j\}$ , and because the left hand and right hand sides must be equal for all values of  $t$  and of  $\{\mathbf{q}_j\}$ , 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:

$$\mathbf{H} \psi(\mathbf{q}_j) = E \psi(\mathbf{q}_j),$$

$$i \hbar \frac{dF(t)}{dt} = i \hbar \frac{dF(t)}{dt} = E F(t).$$

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  $\mathbf{H}$  and the corresponding constants are called eigenvalues of  $\mathbf{H}$ .

For example, if  $\mathbf{H}$  were of the form  $-\hbar^2/2M \nabla^2 = \mathbf{H}$ , then functions of the form  $\exp(i \mathbf{m} \cdot \mathbf{r})$  would be eigenfunctions because

$$\{-\hbar^2/2M \nabla^2\} \exp(i \mathbf{m} \cdot \mathbf{r}) = \{m^2 \hbar^2/2M\} \exp(i \mathbf{m} \cdot \mathbf{r}).$$

In this case,  $\{m^2 \hbar^2/2M\}$  is the eigenvalue.

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

$$\psi(\mathbf{q}_j, t) = \psi(\mathbf{q}_j) \exp(-i Et/\hbar).$$

For the above example, the time dependence is expressed by

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

Having been introduced to the concepts of operators, wavefunctions, 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 learner with valuable experience in solving the Schrödinger equation; they were also chosen because the models they embody 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. Examples of Solving the Schrödinger Equation

### A. Free-Particle Motion in Two 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*

## 1. The Schrödinger Equation

Consider an electron of mass  $m$  and charge  $e$  moving on a two-dimensional surface that defines the  $x,y$  plane (perhaps the 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 potential  $V_0$  at all points in this plane (on any real atomic or molecular surface, the electron would experience a potential that varies with position in a manner that reflects the periodic structure of the surface). The pertinent time independent Schrödinger equation is:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x,y) + V_0 \psi(x,y) = E \psi(x,y).$$

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  $\frac{\partial}{\partial x} \frac{\partial}{\partial y}$  or  $\frac{\partial}{\partial x} \psi$  or  $\frac{\partial}{\partial y} \psi$ ), separation of variables can be used to write  $\psi(x,y)$  as a product  $\psi(x,y) = A(x)B(y)$ . Substitution of this form into the Schrödinger equation, followed by collecting together all  $x$ -dependent and all  $y$ -dependent terms, gives;

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

Since the first term contains no  $y$ -dependence and the second contains no  $x$ -dependence, both must actually be constant (these two constants are denoted  $E_x$  and  $E_y$ , respectively), which allows two separate Schrödinger equations to be written:

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

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

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.

## 2. Boundary Conditions

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

If the electron is entirely unconstrained within the x,y plane, the energies  $E_x$  and  $E_y$  can assume any value; 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 so-called 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.

For example, if motion is constrained to take place within a rectangular region defined by  $0 \leq x \leq L_x$ ;  $0 \leq y \leq L_y$ , then the continuity property that all wavefunctions must obey (because of their interpretation as probability densities, which must be continuous) causes A(x) to vanish at 0 and at  $L_x$ . 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<sub>x</sub> and y=L<sub>y</sub>, gives equations that can be obeyed only if E<sub>x</sub> and E<sub>y</sub> 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 to

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

Knowing that sin( ) vanishes at =n , for n=1,2,3,..., (although the sin(n ) 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<sub>x</sub> and E<sub>y</sub> can assume only values that obey:

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

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

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

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

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<sub>x</sub> or only at y =0 or L<sub>y</sub>, 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 < x < L<sub>x</sub>) 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. 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 ( $\psi_1$ ), and ii. the strong bond having little energy and the weak bond having more than enough energy to rupture it ( $\psi_2$ ). 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  $C_1 \gg C_2$ ), coupling between the two degenerate functions (induced by terms in the Hamiltonian  $\mathbf{H}$  that have been ignored in defining  $\psi_1$  and  $\psi_2$ ) usually causes the true wavefunction  $\psi = \exp(-it\mathbf{H}/\hbar)$  to acquire a component of the second function as time evolves. In such a case, one speaks of internal vibrational energy flow giving rise to unimolecular decomposition of the molecule.

### 3. Energies and Wavefunctions 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 wavefunctions (obtained by inserting the quantum energy levels into the expressions for

$A(x)$   $B(y)$  are as follows:

$$E_x = n_x^2 \frac{\hbar^2}{2mL_x^2}, \text{ and}$$

$$E_y = n_y^2 \frac{\hbar^2}{2mL_y^2},$$

$$E = E_x + E_y ,$$

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

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

The two  $(1/2L)^{1/2}$  factors are included to guarantee that  $\psi$  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  $x, y$ .

#### 4. Quantized Action Can Also be Used to Derive Energy Levels

There is another approach that can be used to find energy levels and is especially straightforward to use for systems whose Schrödinger equations are separable. The so-called classical **action** (denoted  $S$ ) of a particle moving with momentum  $\mathbf{p}$  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:

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

Here, the momentum vector  $\mathbf{p}$  contains the momenta along all coordinates of the system, and the coordinate vector  $\mathbf{q}$  likewise contains the coordinates along all such degrees of freedom. For example, in the two-dimensional particle in a box problem considered above,  $\mathbf{q} = (x, y)$  has two components as does  $\mathbf{p} = (P_x, p_y)$ , 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 decomposed into a sum of such integrals, one for each degree of freedom. In this two-dimensional example, the additivity of  $H$ :

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

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

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 (i.e., a path that starts and ends at the same place after undergoing motion away from the starting point but eventually returning to the starting coordinate at a later time) to an integral multiple of Planck's constant:

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

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 with negative momentum). Within the region bounded by  $0 \leq x \leq L_x$ ;  $0 \leq y \leq L_y$ , 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:

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

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

These are the same quantized energy levels that arose when the wavefunction 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:

$$n h = \int_{\mathbf{q}_i; \mathbf{t}_i}^{\mathbf{q}_f; \mathbf{t}_f} \mathbf{p} \cdot d\mathbf{q}$$

has been used to obtain the result.

## B. Other Model Problems

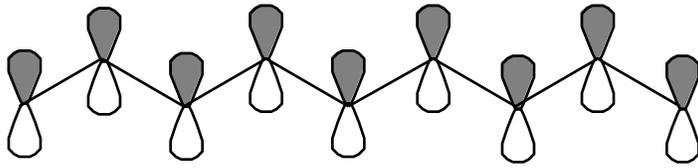
### 1. Particles in Boxes

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

The above 'particle in a box' model for motion in two dimensions 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 crystals, respectively. 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. These orbitals 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  $\theta$  and  $\phi$ . This same spherical box model has been used to describe the orbitals of valence electrons in clusters of mono-valent 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 sufficiently delocalized to render this simple model rather effective (see T. P. Martin, T. Bergmann, H. Göhlich, and T. Lange, J. Phys. Chem. 95, 6421 (1991)).

One-dimensional free particle motion provides a qualitatively correct picture for  $\pi$ -electron motion along the p orbitals of a delocalized polyene. 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  $L=(N-1)R$ . Below, 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 Network with 9 Centers Involved

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

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

A product wavefunction 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

$$H = \sum_j H(j)$$

in which each  $H(j)$  describes the kinetic and potential energy of an individual electron. This (approximate) additivity of  $H$  implies that solutions of  $H \Psi = E \Psi$  are products of solutions to  $H(j) \psi_j(\mathbf{r}_j) = E_j \psi_j(\mathbf{r}_j)$ .

The two lowest  $\psi$ -excited states would correspond to states of the form

$$\psi_1^* \psi_1 \psi_2 \psi_2 \psi_3 \psi_3 \psi_4 \psi_5 \psi_5 , \text{ and}$$

$$\psi_1^* \psi_1 \psi_2 \psi_2 \psi_3 \psi_3 \psi_4 \psi_4 \psi_6 ,$$

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

1 1 2 2 3 3 4 5 5

denotes

1 ( $\mathbf{r}_1$ ) 1 ( $\mathbf{r}_2$ ) 2 ( $\mathbf{r}_3$ ) 2 ( $\mathbf{r}_4$ ) 3 ( $\mathbf{r}_5$ ) 3 ( $\mathbf{r}_6$ ) 4 ( $\mathbf{r}_7$ ) 5  
 ( $\mathbf{r}_8$ ) 5 ( $\mathbf{r}_9$ ).

The electronic excitation energies within this model would be

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

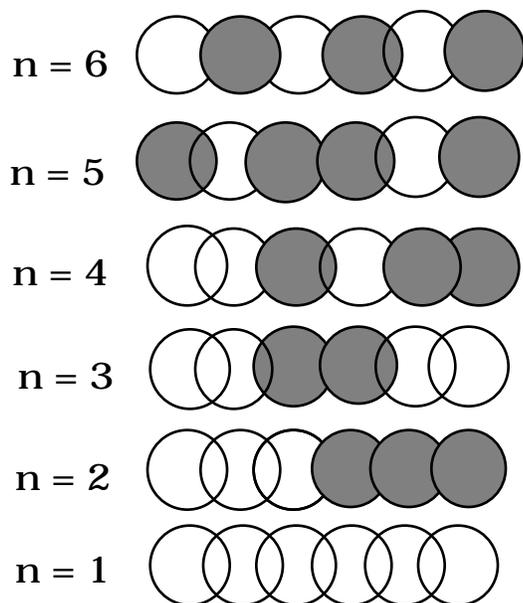
$E^* = \frac{\hbar^2}{2m} [6^2/L^2 - 5^2/L^2]$ , for the two excited-state functions described above. It turns out that this simple model of  $\pi$ -electron energies provides a qualitatively correct picture of such excitation energies.

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  $V_0 + \frac{\hbar^2}{2m} [5^2/L^2]$  is equal to minus the lowest ionization energy of the 1,3,5,7-nonatetraene radical, gives energy levels (as  $E = V_0 + \frac{\hbar^2}{2m} [n^2/L^2]$ ) which then are approximations to ionization energies.

The individual  $\pi$ -molecular orbitals

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

are depicted in the figure below for a model of the 1,3,5 hexatriene  $\pi$ -orbital system for which the 'box length'  $L$  is five times the distance  $R_{CC}$  between neighboring pairs of Carbon atoms.



$$(2/L)^{1/2} \sin(n \ x/L); L = 5 \times R_{CC}$$

In this figure, positive amplitude is denoted by the clear spheres and negative amplitude is shown by the darkened spheres; the magnitude of the  $k^{\text{th}}$  C-atom centered atomic orbital in the  $n^{\text{th}}$  -molecular orbital is given by  $(2/L)^{1/2} \sin(n \ kR_{CC}/L)$ .

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 system described earlier would be more facile for the ground state than for either  $\pi^*$  or  $\sigma^*$ . In the former, the unpaired spin density resides in  $\psi_5$ , which has non-zero amplitude at the  $C_5$  site  $x=L/2$ ; in  $\pi^*$  and  $\sigma^*$ , the unpaired density is in  $\psi_4$  and  $\psi_6$ , respectively, both of which have zero density at  $C_5$ . These densities reflect the values  $(2/L)^{1/2} \sin(n \ kR_{CC}/L)$  of the amplitudes for this case in which  $L = 8 \times R_{CC}$  for  $n = 5, 4,$  and  $6$ , respectively.

## 2. One Electron Moving About a Nucleus

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  $r$ ,  $\theta$ , and  $\phi$  variables

[Suggested Extra Reading- Appendix B: The Hydrogen Atom Orbitals]

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

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

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

$$-\frac{\hbar^2}{2\mu r^2} \left( \frac{\partial^2}{\partial r^2} + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right) \psi + V(r) \psi = E \psi$$

Subtracting  $V(r)$  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

$$\frac{1}{\sin^2 \theta} \left( \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi = -\frac{2\mu r^2}{\hbar^2} (E - V(r)) \psi - \frac{\partial^2 \psi}{\partial r^2} - \frac{2}{r} \frac{\partial \psi}{\partial r}$$

Notice that the right-hand side of this equation is a function of  $r$  only; it contains no  $\theta$  or  $\phi$  dependence. Let's call the entire right hand side  $F(r)$  to emphasize this fact.

To further separate the  $\theta$  and  $\phi$  dependence, we multiply by  $\sin^2 \theta$  and subtract the derivative terms from both sides to obtain

$$\frac{\partial^2 \psi}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} = F(r) \sin^2 \theta \psi - \sin^2 \theta \frac{\partial^2 \psi}{\partial r^2} - 2 \sin^2 \theta \frac{\partial \psi}{\partial r}$$

Now we have separated the  $\theta$  dependence from the  $\phi$  and  $r$  dependence. If we now substitute  $\psi = Q(r) \Theta(\theta) \Phi(\phi)$  and divide by  $Q$ , we obtain

$$\frac{1}{2} \frac{d^2 Q}{dr^2} = \frac{1}{Q} F(r) \sin^2 \theta - \sin^2 \theta - \frac{Q}{r^2}.$$

Now all of the  $\theta$  dependence is isolated on the left hand side; the right hand side contains only  $r$  and  $Q$  dependence.

Whenever one has isolated the entire dependence on one variable as we have done above for the  $\theta$  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  $Q$  dependence and the right hand side contains no  $\theta$  dependence. Because the two sides are equal, they both must actually contain no  $r$ ,  $\theta$ , or  $Q$  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 this form.

#### a. The $\theta$ Equation

The resulting  $\theta$  equation reads

$$\frac{d^2 Q}{d\theta^2} + m^2 Q = 0$$

which has as its most general solution

$$Q = A e^{im\theta} + B e^{-im\theta}.$$

We must require the function  $Q$  to be single-valued, which means that

$$Q(\theta) = Q(\theta + 2\pi) \text{ or,}$$

$$A e^{im\theta} (1 - e^{2im\pi}) + B e^{-im\theta} (1 - e^{-2im\pi}) = 0.$$

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

#### b. The $r$ Equation

Now returning to the equation in which the  $\theta$  dependence was isolated from the  $r$  and  $Q$  dependence, and rearranging the  $\theta$  terms to the left-hand side, we have

$$\frac{1}{\sin^2 \theta} \frac{d^2 Q}{d\theta^2} - \frac{Q}{\sin^2 \theta} = F(r)Q.$$

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

$$\frac{1}{\sin^2 \theta} \frac{d}{d\theta} \left( \sin^2 \theta \frac{dY}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} Y = \frac{F(r)R}{R} = -\lambda,$$

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

We now can write the  $\theta$  equation as

$$\frac{1}{\sin^2 \theta} \frac{d}{d\theta} \left( \sin^2 \theta \frac{dY}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} Y = -\lambda,$$

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

$$\frac{d}{d\theta} = \frac{z}{\sqrt{1-z^2}} \frac{d}{dz} = -\frac{z}{\sqrt{1-z^2}} \frac{d}{dz}.$$

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

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

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

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

Equating like powers of  $z$  gives

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

Note that for large values of  $k$

$$\frac{a_{k+2}}{a_k} = \frac{k^2 - 1 + \frac{1}{k}}{k^2 - 1 + \frac{2}{k} - 1 + \frac{1}{k}} = 1.$$

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 obeys  $l(l+1)$ , where  $l$  is an integer. So, once again, we see that a boundary condition (i.e., that the wavefunction be normalizable in this case) give rise to quantization. In this case, the values of  $l$  are restricted to  $l(l+1)$ ; before, we saw that  $m$  is restricted to  $0, \pm 1, \pm 2, \dots$ .

Since this 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  $P_0(z) = 1$ . For  $l=1$  the same thing applies and  $P_1(z) = z$ . For  $l=2$ ,  $a_2 = -6 \frac{a_0}{2} = -3a_0$ , 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  $\psi$  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  $\psi$  problem for non-zero  $m$  values.

The above  $P$  and  $e^{im\phi}$  functions, when re-expressed in terms of  $\theta$  and  $\phi$ , yield the full angular part of the wavefunction for any centrosymmetric potential. These solutions are usually written as  $Y_{l,m}(\theta, \phi) = P_l^m(\cos \theta) (2\pi)^{\frac{1}{2}} \exp(im\phi)$ , and are called spherical harmonics. They provide the angular solution of the  $r, \theta, \phi$  Schrödinger equation for any problem in which the potential depends only on the radial coordinate. Such situations include all one-electron atoms and ions (e.g., H, He<sup>+</sup>, Li<sup>++</sup>, 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).

c. 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 derived results and specifying  $V(r)$  to be the coulomb potential appropriate for an electron in the field of a nucleus of charge  $+Ze$ , yields:

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

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

$$\rho = \frac{-8\mu E}{\hbar^2} \frac{1}{2} r, \text{ and } \lambda^2 = -\frac{\mu Z^2 e^4}{2E\hbar^2}.$$

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),  $\lambda$  is real. On the other hand, if  $E$  is positive, as it will be for states that lie in the continuum,  $\lambda$  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  $S(\rho) = R(r)$  and substitute  $S$  for  $R$  to obtain:

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

The differential operator terms can be recast in several ways using

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

It is useful to keep in mind these three embodiments of the derivatives that enter into the radial kinetic energy; in various contexts it will be useful to employ various of these.

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  $\rho$  values. Having found solutions at these limits, we will use a power series in  $\rho$  to "interpolate" between these two limits.

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

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

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

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

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

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

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

$$S(\infty) = L e^{-\frac{1}{2}} P(\infty),$$

where the function  $L$  is expanded in an infinite power series in  $L$  as  $P(\infty) = \sum a_k L^k$ . Again substituting this expression for  $S$  into the above equation we obtain

$$P'' + P'(2L+2) + P(-L-1) = 0,$$

and then substituting the power series expansion of  $P$  and solving for the  $a_k$ 's we arrive at:

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

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  $e^{-x}$ . Because the power series expansion of  $P$  describes a function that behaves like  $e^{-x}$  for large  $x$ , the resulting  $S(\infty)$

function would not be normalizable because the  $e^{-\frac{1}{2}}$  factor would be overwhelmed by this  $e^{-x}$  dependence. Hence, the series expansion of  $P$  must truncate in order to achieve a normalizable  $S$  function. Notice that if  $a$  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  $a$  real) and continuum (with  $a$  imaginary) states. In the former case, the boundary condition of non-divergence arises; in the latter, it does not.

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

$P(\rho)$  polynomial  $n' = 0, 1, 2, \dots$  after which the  $l$ -value can run from  $l = 0$ , in steps of unity up to  $l = n - 1$ .

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

$$E = - \frac{\mu Z^2 e^4}{2\hbar^2 n^2} \quad \text{and} \quad r = \frac{Zr_0}{n}.$$

Here, the length  $a_0$  is the so called Bohr radius  $a_0 = \frac{\hbar^2}{\mu e^2}$ ; it appears once the above  $E$ -

expression is substituted into the equation for  $P(\rho)$ . 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  $\rho$  from zero through  $n-l-1$ .

This energy quantization does not arise for states lying in the continuum because the condition that the expansion of  $P(\rho)$  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 treated on p. 90 of EWK.

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

$$R_{n,L}(r) = S(\rho) = L_{n-L-1}^{-L}(\rho) P_{n-L-1}(\rho)$$

depend on the  $n$  and  $l$  quantum numbers and are given in terms of the Laguerre polynomials (see EWK for tabulations of these polynomials).

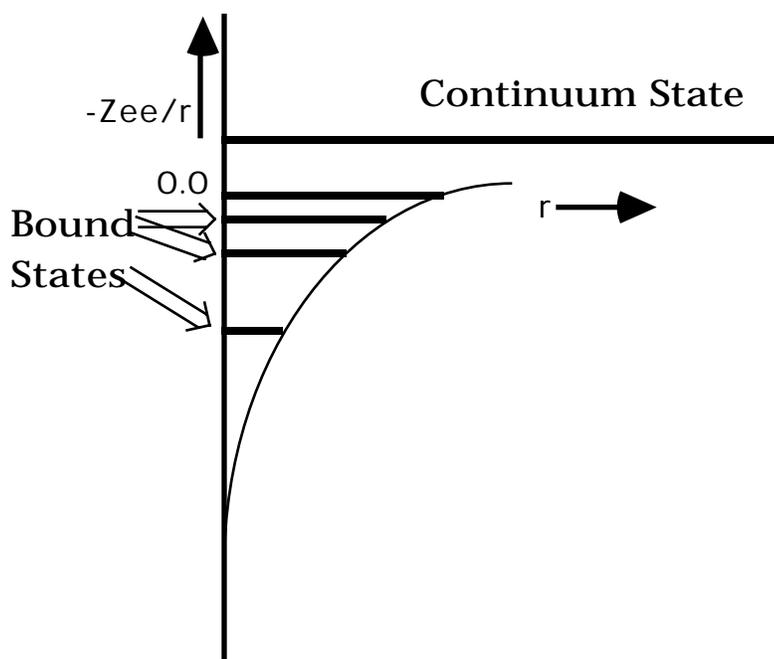
#### d. Summary

To summarize, the quantum numbers  $l$  and  $m$  arise through boundary conditions requiring that  $Y_{l,m}(\theta, \phi)$  be normalizable (i.e., not diverge) and  $Y_{l,m}(\theta, \phi) = Y_{l,m}(\theta + 2\pi, \phi)$ . In the texts by Atkins, EWK, and McQuarrie the differential equations obeyed by the  $\theta$  and  $\phi$  components of  $Y_{l,m}$  are solved in more detail and properties of the solutions are discussed. This differential equation involves the three-dimensional Schrödinger equation's angular kinetic energy operator. That is, the angular part of the above Hamiltonian is equal to  $-\hbar^2 L^2 / 2mr^2$ , where  $L^2$  is the square of the total angular momentum for the electron.

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 wavefunctions (angular and radial) and

energies are summarized in Appendix B for principal quantum numbers  $n$  ranging from 1 to 3 and in Pauling and Wilson for  $n$  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 the figure below).



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 use Appendix B to gain a firmer understanding of the nature of the radial and angular parts of these wavefunctions. 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  $\pi$ -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  $Z_{\text{eff}}$  can be used in place of  $Z$  in the  $\psi_{n,l,m}$  and  $E_{n,l}$  to generate approximate atomic orbitals to be filled by electrons in a many-electron atom. For

example, in the crudest approximation of a carbon atom, the two 1s electrons experience the full nuclear attraction so  $Z_{\text{eff}}=6$  for them, whereas the 2s and 2p electrons are screened by the two 1s electrons, so  $Z_{\text{eff}}= 4$  for them. Within this approximation, one then occupies two 1s orbitals with  $Z=6$ , two 2s orbitals with  $Z=4$  and two 2p orbitals with  $Z=4$  in forming the full six-electron wavefunction of the lowest-energy state of carbon.

### 3. Rotational Motion For a Rigid Diatomic Molecule

*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:

$$\frac{\hbar^2}{2\mu} \left\{ (R^2 \sin^2 \theta)^{-1} \left[ \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + (R^2 \sin^2 \theta)^{-1} \frac{\partial^2}{\partial \phi^2} \right] \right\} \psi = E \psi$$

or

$$L^2 / 2\mu R^2 = E \quad .$$

The angles  $\theta$  and  $\phi$  describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and  $\mu$  is the reduced mass of the diatomic molecule  $\mu=m_1 m_2 / (m_1 + m_2)$ . The differential operators can be seen to be exactly the same as those that arose in the hydrogen-like-atom case, and, as discussed above, these  $\frac{\partial}{\partial \theta}$  and  $\frac{\partial^2}{\partial \phi^2}$  differential operators are identical to the  $L^2$  angular momentum operator whose general properties are analyzed in Appendix G. Therefore, the same spherical harmonics that served as the angular parts of the wavefunction in the earlier case now serve as the entire wavefunction for the so-called rigid rotor:  $\psi = Y_{J,M}(\theta, \phi)$ . As detailed later in this text, the 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  $J$ ). 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 angular momentum selection rules often restrict  $J$  to 1,0, and -1) are given by

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

These energy spacings are of relevance to microwave spectroscopy which probes the rotational energy levels of molecules.

The rigid rotor provides the most commonly employed approximation to the rotational energies and wavefunctions 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.

#### 4. Harmonic Vibrational Motion

*This Schrödinger equation forms the basis for our thinking about bond stretching and angle bending vibrations as well as collective phonon motions in solids*

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

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} \psi(r) + V(r) \psi(r) = E \psi(r),$$

where  $\mu$  is the reduced mass  $\mu = m_1 m_2 / (m_1 + m_2)$  of the two atoms.

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

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

This equation is exactly the same as the equation seen above for the radial motion of the electron in the hydrogen-like atoms except that the reduced mass  $\mu$  replaces the electron mass  $m$  and the potential  $V(r)$  is not the coulomb potential.

If the potential is approximated as a quadratic function of the bond displacement  $x = r - r_e$  expanded about the point at which  $V$  is 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  $-\infty$ , 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 solving the radial differential equation for this potential (see Chapter 5 of McQuarrie), 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  $y = (\mu k/\hbar^2)^{1/4} x$  as a new scaled radial coordinate allows the solution of the large- $r$  equation to be written as:

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

The general solution to the radial equation is then taken to be of the form:

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

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 wavefunction 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:

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

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

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

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.

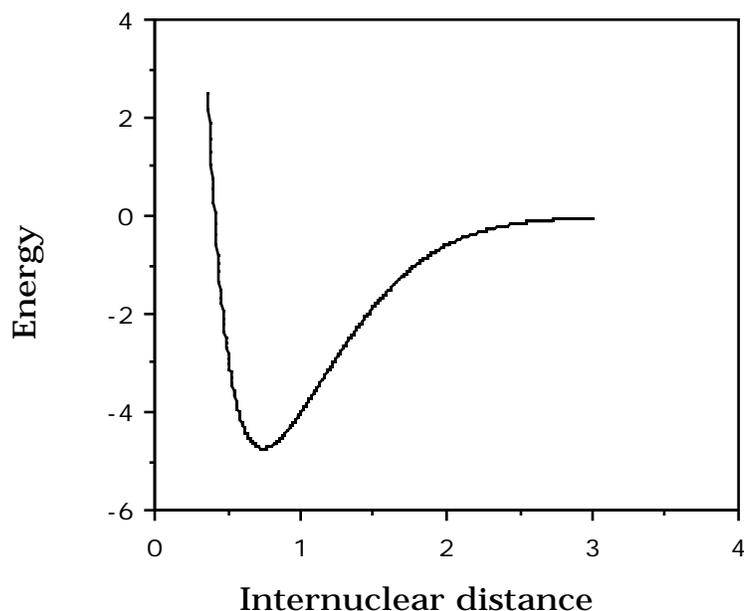
Because the  $H_n$  are odd or even functions of  $x$  (depending on whether  $n$  is odd or even), the wavefunctions  $\psi_n(x)$  are odd or even. This splitting of the solutions into two distinct classes is an example of the effect of symmetry; in this case, the symmetry is caused by the symmetry of the harmonic potential with respect to reflection through the origin along the  $x$ -axis. Throughout this text, many symmetries will arise; in each case, symmetry properties of the potential will 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 wavefunctions and energies can be labeled.

The harmonic oscillator energies and wavefunctions 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 wavefunction 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 the figure below)

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

is often used in this regard.



Here,  $D_e$  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 determines the vibrational frequencies. The advantage of using the Morse potential to improve upon harmonic-oscillator-level predictions is that its energy levels and wavefunctions are also known exactly. The energies are given in terms of the parameters of the potential as follows:

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

where the force constant  $k$  is  $k=2D_e a^2$ . 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  $D_e$ .

### III. The Physical Relevance of Wavefunctions, Operators and Eigenvalues

*Having gained experience on the application of the Schrödinger equation to several of the more important model problems of chemistry, it is time to return to the issue of how the wavefunctions, operators, and energies relate to experimental reality.*

*In mastering the sections that follow the reader should keep in mind that :*

- i. It is the molecular system that possesses a set of characteristic wavefunctions and energy levels, but*
- ii. It is the experimental measurement that determines the nature by which these energy levels and wavefunctions are probed.*

This separation between the 'system' with its intrinsic set of energy levels and 'observation' or 'experiment' with its characteristic interaction with the system forms an important point of view used by quantum mechanics. It gives rise to a point of view in which the measurement itself can 'prepare' the system in a wavefunction that need not be any single eigenstate but can still be represented as a combination of the complete set of eigenstates. For the beginning student of quantum mechanics, these aspects of quantum mechanics are among the more confusing. If it helps, one should rest assured that all of the mathematical and 'rule' structure of this subject was created to permit the predictions of quantum mechanics to replicate what has been observed in laboratory experiments.

### ***Note to the Reader :***

*Before moving on to the next section, it would be very useful to work some of the Exercises and Problems. In particular, Exercises 3, 5, and 12 as well as problems 6, 8, and 11 provide insight that would help when the material of the next section is studied. The solution to Problem 11 is used throughout this section to help illustrate the concepts introduced here.*

#### **A. The Basic Rules and Relation to Experimental Measurement**

*Quantum mechanics has a set of 'rules' that link operators, wavefunctions, and eigenvalues to physically measurable properties. These rules have been formulated not in some arbitrary manner nor by derivation from some higher subject. Rather, the rules were designed to allow quantum mechanics to mimic the experimentally observed facts as revealed in mother nature's data. The extent to which these rules seem difficult to*

*understand usually reflects the presence of experimental observations that do not fit in with our common experience base.*

[Suggested Extra Reading- Appendix C: Quantum Mechanical Operators and Commutation]

The structure of quantum mechanics (QM) relates the wavefunction and operators  $\mathbf{F}$  to the 'real world' in which experimental measurements are performed through a set of rules (Dirac's text is an excellent source of reading concerning the historical development of these fundamentals). Some of these rules have already been introduced above. Here, they are presented in total as follows:

1. The time evolution of the wavefunction is determined by solving the time-dependent Schrödinger equation (see pp 23-25 of EWK for a rationalization of how the Schrödinger equation arises from the classical equation governing waves, Einstein's  $E=h\nu$ , and deBroglie's postulate that  $\lambda=h/p$ )

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

where  $\mathbf{H}$  is the Hamiltonian operator corresponding to the total (kinetic plus potential) energy of the system. For an isolated system (e.g., an atom or molecule not in contact with any external fields),  $\mathbf{H}$  consists of the kinetic and potential energies of the particles comprising the system. To describe interactions with an external field (e.g., an electromagnetic field, a static electric field, or the 'crystal field' caused by surrounding ligands), additional terms are added to  $\mathbf{H}$  to properly account for the system-field interactions.

If  $\mathbf{H}$  contains no explicit time dependence, then separation of space and time variables can be performed on the above Schrödinger equation  $\Psi = \psi \exp(-itE/\hbar)$  to give

$$\mathbf{H} \psi = E \psi.$$

In such a case, the time dependence of the state is carried in the phase factor  $\exp(-itE/\hbar)$ ; the spatial dependence appears in  $\psi(q_j)$ .

The so called time independent Schrödinger equation  $\mathbf{H} \psi = E \psi$  must be solved to determine the physically measurable energies  $E_k$  and wavefunctions  $\psi_k$  of the system. The most general solution to the full Schrödinger equation  $i\hbar \frac{\partial}{\partial t} \Psi = \mathbf{H} \Psi$  is then given by applying  $\exp(-i\mathbf{H}t/\hbar)$  to the wavefunction at some initial time ( $t=0$ )  $\Psi = \sum_k C_k \psi_k$  to obtain

$\psi(\mathbf{q}, t) = \sum_k C_k \psi_k \exp(-itE_k/\hbar)$ . The relative amplitudes  $C_k$  are determined by knowledge of the state at the initial time; this depends on how the system has been prepared in an earlier experiment. Just as Newton's laws of motion do not fully determine the time evolution of a classical system (i.e., the coordinates and momenta must be known at some initial time), the Schrödinger equation must be accompanied by initial conditions to fully determine  $\psi(\mathbf{q}, t)$ .

**Example :**

*Using the results of Problem 11 of this chapter to illustrate, the sudden ionization of  $N_2$  in its  $v=0$  vibrational state to generate  $N_2^+$  produces a vibrational wavefunction*

$$\psi_0 = \frac{1}{\sqrt{\pi}} e^{-x^2/2} = 3.53333 \text{Å}^{-1/2} e^{-(244.83 \text{Å}^{-2})(r-1.09769 \text{Å})^2}$$

*that was created by the fast ionization of  $N_2$ . Subsequent to ionization, this  $N_2$  function is not an eigenfunction of the new vibrational Schrödinger equation appropriate to  $N_2^+$ . As a result, this function will time evolve under the influence of the  $N_2^+$  Hamiltonian.*

*The time evolved wavefunction, according to this first rule, can be expressed in terms of the vibrational functions  $\{\psi_v\}$  and energies  $\{E_v\}$  of the  $N_2^+$  ion as*

$$\psi(\mathbf{q}, t) = \sum_v C_v \psi_v \exp(-i E_v t/\hbar).$$

*The amplitudes  $C_v$ , which reflect the manner in which the wavefunction is prepared (at  $t=0$ ), are determined by determining the component of each  $\psi_v$  in the function  $\psi$  at  $t=0$ . To do this, one uses*

$$C_v = \int \psi_v^* (\mathbf{q}, t=0) \psi(\mathbf{q}, t=0) d\mathbf{q} = C_v,$$

*which is easily obtained by multiplying the above summation by  $\psi_v^*$ , integrating, and using the orthonormality of the  $\{\psi_v\}$  functions.*

*For the case at hand, this results shows that by forming integrals involving products of the  $N_2$   $v=0$  function  $\psi_0$  ( $t=0$ )*

$$\psi_0 = -\frac{1}{4} e^{-x^2/2} = 3.53333 \text{Å}^{-\frac{1}{2}} e^{-(244.83 \text{Å}^{-2})(r-1.09769 \text{Å})^2}$$

and various  $N_2^+$  vibrational functions  $\psi_v$ , one can determine how  $\psi_0$  will evolve in time and the amplitudes of all  $\{\psi_v\}$  that it will contain. For example, the  $N_2$   $v=0$  function, upon ionization, contains the following amount of the  $N_2^+$   $v=0$  function:

$$C_0 = \int \psi_0^*(N_2^+) \psi_0(N_2) dr$$

$$= \int 3.47522 e^{-229.113(r-1.11642)^2} 3.53333 e^{-244.83(r-1.09769)^2} dr$$

As demonstrated in Problem 11, this integral reduces to 0.959. This means that the  $N_2$   $v=0$  state, subsequent to sudden ionization, can be represented as containing  $|0.959|^2 = 0.92$  fraction of the  $v=0$  state of the  $N_2^+$  ion.

This example relates to the well known Franck-Condon principle of spectroscopy in which squares of 'overlaps' between the initial electronic state's vibrational wavefunction and the final electronic state's vibrational wavefunctions allow one to estimate the probabilities of populating various final-state vibrational levels.

In addition to initial conditions, solutions to the Schrödinger equation must obey certain other constraints in form. They must be continuous functions of all of their spatial coordinates and must be single valued; these properties allow  $\psi^*$  to be interpreted as a probability density (i.e., the probability of finding a particle at some position can not be multivalued nor can it be 'jerky' or discontinuous). The derivative of the wavefunction must also be continuous except at points where the potential function undergoes an infinite jump (e.g., at the wall of an infinitely high and steep potential barrier). This condition relates to the fact that the momentum must be continuous except at infinitely 'steep' potential barriers where the momentum undergoes a 'sudden' reversal.

2. An experimental measurement of any quantity (whose corresponding operator is  $\mathbf{F}$ ) must result in one of the eigenvalues  $f_j$  of the operator  $\mathbf{F}$ . These eigenvalues are obtained by solving

$$\mathbf{F} \psi_j = f_j \psi_j,$$

where the  $\psi_j$  are the eigenfunctions of  $\mathbf{F}$ . Once the measurement of  $\mathbf{F}$  is made, for that sub-population of the experimental sample found to have the particular eigenvalue  $f_j$ , the wavefunction becomes  $\psi_j$ .

The equation  $\mathbf{H} \psi_k = E_k \psi_k$  is but a special case; it is an especially important case because much of the machinery of modern experimental chemistry is directed at placing the system in a particular energy quantum state by detecting its energy (e.g., by spectroscopic means).

The reader is strongly urged to also study Appendix C to gain a more detailed and illustrated treatment of this and subsequent rules of quantum mechanics.

3. The operators  $\mathbf{F}$  corresponding to all physically measurable quantities are Hermitian; this means that their matrix representations obey (see Appendix C for a description of the 'bra'  $\langle \psi |$  and 'ket'  $|\psi\rangle$  notation used below):

$$\langle \psi_j | \mathbf{F} | \psi_k \rangle = \langle \psi_k | \mathbf{F} | \psi_j \rangle^* = \langle \mathbf{F} \psi_j | \psi_k \rangle$$

in any basis  $\{\psi_j\}$  of functions appropriate for the action of  $\mathbf{F}$  (i.e., functions of the variables on which  $\mathbf{F}$  operates). As expressed through equality of the first and third elements above, Hermitian operators are often said to 'obey the turn-over rule'. This means that  $\mathbf{F}$  can be allowed to operate on the function to its right or on the function to its left if  $\mathbf{F}$  is Hermitian.

Hermiticity assures that the eigenvalues  $\{f_j\}$  are all real, that eigenfunctions  $\{\psi_j\}$  having different eigenvalues are orthogonal and can be normalized  $\langle \psi_j | \psi_k \rangle = \delta_{j,k}$ , and that eigenfunctions having the same eigenvalues can be made orthonormal (these statements are proven in Appendix C).

4. Once a particular value  $f_j$  is observed in a measurement of  $\mathbf{F}$ , this same value will be observed in all subsequent measurements of  $\mathbf{F}$  as long as the system remains undisturbed by measurements of other properties or by interactions with external fields. In fact, once  $f_j$  has been observed, the state of the system becomes an eigenstate of  $\mathbf{F}$  (if it already was, it remains unchanged):

$$\mathbf{F} \psi_j = f_j \psi_j.$$

This means that the measurement process itself may interfere with the state of the system and even determines what that state will be once the measurement has been made.

**Example:**

Again consider the  $v=0$   $N_2$  ionization treated in Problem 11 of this chapter. If, subsequent to ionization, the  $N_2^+$  ions produced were probed to determine their internal vibrational state, a fraction of the sample equal to  $|\langle (N_2; v=0) | (N_2^+; v=0) \rangle|^2 = 0.92$  would be detected in the  $v=0$  state of the  $N_2^+$  ion. For this sub-sample, the vibrational wavefunction becomes, and remains from then on,

$$\psi(t) = (N_2^+; v=0) \exp(-i t E_{v=0}^+ / \hbar),$$

where  $E_{v=0}^+$  is the energy of the  $N_2^+$  ion in its  $v=0$  state. If, at some later time, this sub-sample is again probed, all species will be found to be in the  $v=0$  state.

5. The probability  $P_k$  of observing a particular value  $f_k$  when  $F$  is measured, given that the system wavefunction is  $\psi$  prior to the measurement, is given by expanding  $\psi$  in terms of the complete set of normalized eigenstates of  $F$

$$\psi = \sum_j |j\rangle \langle j | \psi \rangle$$

and then computing  $P_k = |\langle k | \psi \rangle|^2$ . For the special case in which  $\psi$  is already one of the eigenstates of  $F$  (i.e.,  $\psi = |k\rangle$ ), the probability of observing  $f_j$  reduces to  $P_j = \delta_{j,k}$ . The set of numbers  $C_j = \langle j | \psi \rangle$  are called the expansion coefficients of  $\psi$  in the basis of the  $\{|j\rangle\}$ . These coefficients, when collected together in all possible products as  $D_{j,i} = C_i^* C_j$  form the so-called density matrix  $D_{j,i}$  of the wavefunction  $\psi$  within the  $\{|j\rangle\}$  basis.

**Example:**

If  $F$  is the operator for momentum in the  $x$ -direction and  $\psi(x,t)$  is the wave function for  $x$  as a function of time  $t$ , then the above expansion corresponds to a Fourier transform of

$$\psi(x,t) = \frac{1}{2} \int_{-\infty}^{\infty} \exp(ikx) \exp(-ikx') \psi(x',t) dx' dk.$$

Here  $(1/2)^{1/2} \exp(ikx)$  is the normalized eigenfunction of  $\hat{F} = -i\hbar / x$  corresponding to momentum eigenvalue  $\hbar k$ . These momentum eigenfunctions are orthonormal:

$$\frac{1}{2} \int_{-\infty}^{\infty} \exp(-ikx) \exp(ik'x) dx = \delta(k-k'),$$

and they form a complete set of functions in  $x$ -space

$$\frac{1}{2} \int_{-\infty}^{\infty} \exp(-ikx) \exp(ikx') dk = \delta(x-x')$$

because  $\hat{F}$  is a Hermitian operator. The function  $\int_{-\infty}^{\infty} \exp(-ikx') \psi(x',t) dx'$  is called the momentum-space transform of  $\psi(x,t)$  and is denoted  $\phi(k,t)$ ; it gives, when used as  $|\phi(k,t)|^2$ , the probability density for observing momentum values  $\hbar k$  at time  $t$ .

### Another Example:

Take the initial  $\psi$  to be a superposition state of the form

$$\psi = a(2p_0 + 2p_{-1} - 2p_1) + b(3p_0 - 3p_{-1}),$$

where the  $a$  and  $b$  are amplitudes that describe the admixture of  $2p$  and  $3p$  functions in this wavefunction. Then:

a. If  $L^2$  were measured, the value  $2\hbar^2$  would be observed with probability  $3|a|^2 + 2|b|^2 = 1$ , since all of the functions in  $\psi$  are  $p$ -type orbitals. After said measurement, the wavefunction would still be this same  $\psi$  because this entire  $\psi$  is an eigenfunction of  $L^2$ .

b. If  $L_z$  were measured for this

$$\psi = a(2p_0 + 2p_{-1} - 2p_1) + b(3p_0 - 3p_{-1}),$$

the values  $0\hbar$ ,  $1\hbar$ , and  $-1\hbar$  would be observed (because these are the only functions with non-zero  $C_m$  coefficients for the  $L_z$  operator) with respective probabilities  $|a|^2 + |b|^2$ ,  $|a|^2$ , and  $|a|^2 + |-b|^2$ .

c. After  $L_z$  were measured, if the sub-population for which  $-1\hbar$  had been detected were subjected to measurement of  $L^2$  the value  $2\hbar^2$  would certainly be found because the new wavefunction

$$\psi = \{-a 2p_{-1} - b 3p_{-1}\} (|a|^2 + |b|^2)^{-1/2}$$

is still an eigenfunction of  $L^2$  with this eigenvalue.

d. Again after  $L_z$  were measured, if the sub-population for which  $-1\hbar$  had been observed and for which the wavefunction is now

$$\psi = \{-a 2p_{-1} - b 3p_{-1}\} (|a|^2 + |b|^2)^{-1/2}$$

were subjected to measurement of the energy (through the Hamiltonian operator), two values would be found. With probability

$|a|^2 (|a|^2 + |b|^2)^{-1}$  the energy of the  $2p_{-1}$  orbital would be observed; with probability  $|b|^2 (|a|^2 + |b|^2)^{-1}$ , the energy of the  $3p_{-1}$  orbital would be observed.

If  $\psi$  is a function of several variables (e.g., when  $\psi$  describes more than one particle in a composite system), and if  $F$  is a property that depends on a subset of these variables (e.g., when  $F$  is a property of one of the particles in the composite system), then the expansion  $\psi = \sum_j |j\rangle \langle j| \psi$  is viewed as relating only to  $\psi$ 's dependence on the subset of variables related to  $F$ . In this case, the integrals  $\langle k| \psi \rangle$  are carried out over only these variables; thus the probabilities  $P_k = |\langle k| \psi \rangle|^2$  depend parametrically on the remaining variables.

### **Example:**

Suppose that  $\psi(r, \phi)$  describes the radial ( $r$ ) and angular ( $\phi$ ) motion of a diatomic molecule constrained to move on a planar surface. If an experiment were performed to measure the component of the rotational angular momentum of the diatomic molecule perpendicular to the surface ( $L_z = -i\hbar \frac{\partial}{\partial \phi}$ ), only values equal to  $m\hbar$  ( $m=0, 1, -1, 2, -2, 3, -3, \dots$ ) could be observed, because these are the eigenvalues of  $L_z$ :

$$L_z \psi_m = -i\hbar \frac{\partial}{\partial \phi} \psi_m = m\hbar \psi_m, \text{ where}$$

$$\psi_m = (1/2\pi)^{1/2} \exp(im\phi).$$

The quantization of  $L_z$  arises because the eigenfunctions  $\psi_m(\phi)$  must be periodic in  $\phi$ :

$$\psi(\phi + 2\pi) = \psi(\phi).$$

Such quantization (i.e., constraints on the values that physical properties can realize) will be seen to occur whenever the pertinent wavefunction is constrained to obey a so-called boundary condition (in this case, the boundary condition is  $\psi(\phi + 2\pi) = \psi(\phi)$ ).

Expanding the  $\phi$ -dependence of  $\psi$  in terms of the  $\psi_m$

$$\psi = \sum_{m < m/ > m} \psi_m(\phi)$$

allows one to write the probability that  $m\hbar$  is observed if the angular momentum  $L_z$  is measured as follows:

$$P_m = |\langle m | \psi \rangle|^2 = \left| \int \psi_m^*(\phi) \psi(r, \phi) d\phi \right|^2.$$

If one is interested in the probability that  $m\hbar$  be observed when  $L_z$  is measured regardless of what bond length  $r$  is involved, then it is appropriate to integrate this expression over the  $r$ -variable about which one does not care. This, in effect, sums contributions from all  $r$ -values to obtain a result that is independent of the  $r$  variable. As a result, the probability reduces to:

$$P_m = \int \psi_m^*(\phi) \left\{ \int \psi_m^*(r, \phi) \psi(r, \phi) r dr \right\} d\phi d\phi',$$

which is simply the above result integrated over  $r$  with a volume element  $r dr$  for the two-dimensional motion treated here.

If, on the other hand, one were able to measure  $L_z$  values when  $r$  is equal to some specified bond length (this is only a hypothetical example; there is no known way to perform such a measurement), then the probability would equal:

$$P_m r dr = r dr \int \psi_m^*(\phi) \psi_m^*(r, \phi) \psi(r, \phi) \psi(\phi) d\phi d\phi' = |\langle m | \psi \rangle|^2 r dr.$$

6. Two or more properties F,G, J whose corresponding Hermitian operators **F**, **G**, **J** commute

$$\mathbf{FG}-\mathbf{GF}=\mathbf{FJ}-\mathbf{JF}=\mathbf{GJ}-\mathbf{JG}=0$$

have complete sets of simultaneous eigenfunctions (the proof of this is treated in Appendix C). This means that the set of functions that are eigenfunctions of one of the operators can be formed into a set of functions that are also eigenfunctions of the others:

$$\mathbf{F} \psi = f_j \psi \implies \mathbf{G} \psi = g_j \psi \implies \mathbf{J} \psi = j \psi.$$

**Example:**

The  $p_x$ ,  $p_y$  and  $p_z$  orbitals are eigenfunctions of the  $\mathbf{L}^2$  angular momentum operator with eigenvalues equal to  $L(L+1)\hbar^2 = 2\hbar^2$ . Since  $\mathbf{L}^2$  and  $\mathbf{L}_z$  commute and act on the same (angle) coordinates, they possess a complete set of simultaneous eigenfunctions.

Although the  $p_x$ ,  $p_y$  and  $p_z$  orbitals are not eigenfunctions of  $\mathbf{L}_z$ , they can be combined to form three new orbitals:  $p_0 = p_z$ ,  $p_1 = 2^{-1/2} [p_x + i p_y]$ , and  $p_{-1} = 2^{-1/2} [p_x - i p_y]$  that are still eigenfunctions of  $\mathbf{L}^2$  but are now eigenfunctions of  $\mathbf{L}_z$  also (with eigenvalues  $0\hbar$ ,  $1\hbar$ , and  $-1\hbar$ , respectively).

It should be mentioned that if two operators do not commute, they may still have some eigenfunctions in common, but they will not have a complete set of simultaneous eigenfunctions. For example, the  $\mathbf{L}_z$  and  $\mathbf{L}_x$  components of the angular momentum operator do not commute; however, a wavefunction with  $L=0$  (i.e., an S-state) is an eigenfunction of both operators.

The fact that two operators commute is of great importance. It means that once a measurement of one of the properties is carried out, subsequent measurement of that property or of any of the other properties corresponding to mutually commuting operators can be made without altering the system's value of the properties measured earlier. Only subsequent measurement of another property whose operator does not commute with  $\mathbf{F}$ ,  $\mathbf{G}$ , or  $\mathbf{J}$  will destroy precise knowledge of the values of the properties measured earlier.

**Example:**

Assume that an experiment has been carried out on an atom to measure its total angular momentum  $L^2$ . According to quantum mechanics, only values equal to  $L(L+1)\hbar^2$  will be observed. Further assume, for the particular experimental sample subjected to observation, that values of  $L^2$  equal to  $2\hbar^2$  and  $0\hbar^2$  were detected in relative amounts of 64 % and 36 %, respectively. This means that the atom's original wavefunction could be represented as:

$$\psi = 0.8 P + 0.6 S,$$

where  $P$  and  $S$  represent the  $P$ -state and  $S$ -state components of  $\psi$ . The squares of the amplitudes 0.8 and 0.6 give the 64 % and 36 % probabilities mentioned above.

Now assume that a subsequent measurement of the component of angular momentum along the lab-fixed  $z$ -axis is to be measured for that sub-population of the original sample found to be in the  $P$ -state. For that population, the wavefunction is now a pure  $P$ -function:

$$\psi' = P.$$

However, at this stage we have no information about how much of this  $\psi'$  is of  $m = 1, 0$ , or  $-1$ , nor do we know how much  $2p, 3p, 4p, \dots np$  components this state contains.

Because the property corresponding to the operator  $L_z$  is about to be measured, we express the above  $\psi'$  in terms of the eigenfunctions of  $L_z$ :

$$\psi' = P = \sum_{m=1,0,-1} C'_m P_m.$$

When the measurement of  $L_z$  is made, the values  $1\hbar, 0\hbar$ , and  $-1\hbar$  will be observed with probabilities given by  $|C'_1|^2, |C'_0|^2$ , and  $|C'_{-1}|^2$ , respectively. For that sub-population found to have, for example,  $L_z$  equal to  $-1\hbar$ , the wavefunction then becomes

$$\psi'' = P_{-1}.$$

At this stage, we do not know how much of  $2p_{-1}, 3p_{-1}, 4p_{-1}, \dots np_{-1}$  this wavefunction contains. To probe this question another subsequent measurement of the energy (corresponding to the  $H$  operator) could be made. Doing so would allow the amplitudes in the expansion of the above  $\psi'' = P_{-1}$

$$\psi = \sum_n C_n \psi_n$$

to be found.

The kind of experiment outlined above allows one to find the content of each particular component of an initial sample's wavefunction. For example, the original wavefunction has

$0.64 |C_n|^2 / |C_m|^2$  fractional content of the various  $\psi_n$  functions. It is analogous to the other examples considered above because all of the operators whose properties are measured commute.

### Another Example:

Let us consider an experiment in which we begin with a sample (with wavefunction  $\psi$ ) that is first subjected to measurement of  $L_z$  and then subjected to measurement of  $L^2$  and then of the energy. In this order, one would first find specific values (integer multiples of  $\hbar$ ) of  $L_z$  and one would express  $\psi$  as

$$\psi = \sum_m D_m \psi_m$$

At this stage, the nature of each  $\psi_m$  is unknown (e.g., the  $\psi_1$  function can contain  $\psi_{1,1}$ ,  $\psi_{1,0}$ ,  $\psi_{1,-1}$ , etc. components); all that is known is that  $\psi_m$  has  $m\hbar$  as its  $L_z$  value.

Taking that sub-population ( $|D_m|^2$  fraction) with a particular  $m\hbar$  value for  $L_z$  and subjecting it to subsequent measurement of  $L^2$  requires the current wavefunction  $\psi_m$  to be expressed as

$$\psi_m = \sum_L D_{L,m} \psi_{L,m}$$

When  $L^2$  is measured the value  $L(L+1)\hbar^2$  will be observed with probability  $|D_{L,m}|^2$ , and the wavefunction for that particular sub-population will become

$$\psi = \sum_{L,m} D_{L,m} \psi_{L,m}$$

At this stage, we know the value of  $L$  and of  $m$ , but we do not know the energy of the state. For example, we may know that the present sub-population has  $L=1$ ,  $m=-1$ , but we have no knowledge (yet) of how much  $2p_x$ ,  $3p_x$ , ...  $np_x$  the system contains.

To further probe the sample, the above sub-population with  $L=1$  and  $m=-1$  can be subjected to measurement of the energy. In this case, the function  $\psi_{1,-1}$  must be expressed as

$$\psi_{1,-1} = \sum_n D_n'' \psi_{n,-1}.$$

When the energy measurement is made, the state  $\psi_{n,-1}$  will be found  $|D_n''|^2$  fraction of the time.

The fact that  $L_z$ ,  $L^2$ , and  $H$  all commute with one another (i.e., are mutually commutative) makes the series of measurements described in the above examples more straightforward than if these operators did not commute.

In the first experiment, the fact that they are mutually commutative allowed us to expand the 64 % probable  $L^2$  eigenstate with  $L=1$  in terms of functions that were eigenfunctions of the operator for which measurement was about to be made without destroying our knowledge of the value of  $L^2$ . That is, because  $L^2$  and  $L_z$  can have simultaneous eigenfunctions, the  $L = 1$  function can be expanded in terms of functions that are eigenfunctions of both  $L^2$  and  $L_z$ . This in turn, allowed us to find experimentally the sub-population that had, for example  $-1 \hbar$  as its value of  $L_z$  while retaining knowledge that the state remains an eigenstate of  $L^2$  (the state at this time had  $L = 1$  and  $m = -1$  and was denoted  $\psi_{1,-1}$ ). Then, when this  $\psi_{1,-1}$  state was subjected to energy measurement, knowledge of the energy of the sub-population could be gained without giving up knowledge of the  $L^2$  and  $L_z$  information; upon carrying out said measurement, the state became  $\psi_{1,-1}$ .

We therefore conclude that the act of carrying out an experimental measurement disturbs the system in that it causes the system's wavefunction to become an eigenfunction of the operator whose property is measured. If two properties whose corresponding operators commute are measured, the measurement of the second property does not destroy knowledge of the first property's value gained in the first measurement.

On the other hand, as detailed further in Appendix C, if the two properties ( $F$  and  $G$ ) do not commute, the second measurement destroys knowledge of the first property's value. After the first measurement,  $\psi$  is an eigenfunction of  $F$ ; after the second measurement, it becomes an eigenfunction of  $G$ . If the two non-commuting operators' properties are measured in the opposite order, the wavefunction first is an eigenfunction of  $G$ , and subsequently becomes an eigenfunction of  $F$ .

It is thus often said that 'measurements for operators that do not commute interfere with one another'. The simultaneous measurement of the position and momentum along the

same axis provides an example of two measurements that are incompatible. The fact that  $x$  and  $p_x = -i\hbar \frac{d}{dx}$  do not commute is straightforward to demonstrate:

$$\{x(-i\hbar \frac{d}{dx}) - (-i\hbar \frac{d}{dx})x\} = i\hbar \neq 0.$$

Operators that commute with the Hamiltonian and with one another form a particularly important class because each such operator permits each of the energy eigenstates of the system to be labelled with a corresponding quantum number. These operators are called **symmetry operators**. As will be seen later, they include angular momenta (e.g.,  $L^2, L_z, S^2, S_z$ , for atoms) and point group symmetries (e.g., planes and rotations about axes). Every operator that qualifies as a symmetry operator provides a quantum number with which the energy levels of the system can be labeled.

7. If a property  $F$  is measured for a large number of systems all described by the same  $\psi$ , the average value  $\langle F \rangle$  of  $F$  for such a set of measurements can be computed as

$$\langle F \rangle = \langle \psi | \mathbf{F} | \psi \rangle.$$

Expanding  $\psi$  in terms of the complete set of eigenstates of  $\mathbf{F}$  allows  $\langle F \rangle$  to be rewritten as follows:

$$\langle F \rangle = \sum_j f_j |\langle \psi | j \rangle|^2,$$

which clearly expresses  $\langle F \rangle$  as the product of the probability  $P_j$  of obtaining the particular value  $f_j$  when the property  $F$  is measured and the value  $f_j$  of the property in such a measurement. This same result can be expressed in terms of the density matrix  $D_{i,j}$  of the state  $\psi$  defined above as:

$$\begin{aligned} \langle F \rangle &= \sum_{i,j} \langle \psi | i \rangle \langle i | \mathbf{F} | j \rangle \langle j | \psi \rangle = \sum_{i,j} C_i^* \langle i | \mathbf{F} | j \rangle C_j \\ &= \sum_{i,j} D_{j,i} \langle i | \mathbf{F} | j \rangle = \text{Tr} (DF). \end{aligned}$$

Here,  $DF$  represents the matrix product of the density matrix  $D_{j,i}$  and the matrix representation  $F_{i,j} = \langle i | \mathbf{F} | j \rangle$  of the  $\mathbf{F}$  operator, both taken in the  $\{|j\rangle\}$  basis, and  $\text{Tr}$  represents the matrix trace operation.

As mentioned at the beginning of this Section, this set of rules and their relationships to experimental measurements can be quite perplexing. The structure of quantum mechanics embodied in the above rules was developed in light of new scientific observations (e.g., the photoelectric effect, diffraction of electrons) that could not be interpreted within the conventional pictures of classical mechanics. Throughout its development, these and other experimental observations placed severe constraints on the structure of the equations of the new quantum mechanics as well as on their interpretations. For example, the observation of discrete lines in the emission spectra of atoms gave rise to the idea that the atom's electrons could exist with only certain discrete energies and that light of specific frequencies would be given off as transitions among these quantized energy states took place.

Even with the assurance that quantum mechanics has firm underpinnings in experimental observations, students learning this subject for the first time often encounter difficulty. Therefore, it is useful to again examine some of the model problems for which the Schrödinger equation can be exactly solved and to learn how the above rules apply to such concrete examples.

The examples examined earlier in this Chapter and those given in the Exercises and Problems serve as useful models for chemically important phenomena: electronic motion in polyenes, in solids, and in atoms as well as vibrational and rotational motions. Their study thus far has served two purposes; it allowed the reader to gain some familiarity with applications of quantum mechanics and it introduced models that play central roles in much of chemistry. Their study now is designed to illustrate how the above seven rules of quantum mechanics relate to experimental reality.

## B. An Example Illustrating Several of the Fundamental Rules

The physical significance of the time independent wavefunctions and energies treated in Section II as well as the meaning of the seven fundamental points given above can be further illustrated by again considering the simple two-dimensional electronic motion model.

If the electron were prepared in the eigenstate corresponding to  $n_x = 1$ ,  $n_y = 2$ , its total energy would be

$$E = \frac{\hbar^2}{2m} \left[ \frac{1^2}{L_x^2} + \frac{2^2}{L_y^2} \right].$$

If the energy were experimentally measured, this and only this value would be observed, and this same result would hold for all time as long as the electron is undisturbed.

If an experiment were carried out to measure the momentum of the electron along the y-axis, according to the second postulate above, only values equal to the eigenvalues of  $-\hbar^2 \nabla^2 / y$  could be observed. The  $p_y$  eigenfunctions (i.e., functions that obey  $p_y \psi = -\hbar^2 \nabla^2 / y \psi = c \psi$ ) are of the form

$$(1/L_y)^{1/2} \exp(ik_y y),$$

where the momentum  $\hbar k_y$  can achieve any value; the  $(1/L_y)^{1/2}$  factor is used to normalize the eigenfunctions over the range  $0 \leq y \leq L_y$ . It is useful to note that the y-dependence of  $\psi$  as expressed above [ $\exp(i2\pi y/L_y) - \exp(-i2\pi y/L_y)$ ] is already written in terms of two such eigenstates of  $-\hbar^2 \nabla^2 / y$ :

$$-\hbar^2 \nabla^2 / y \exp(i2\pi y/L_y) = 2\hbar^2 \pi^2 / L_y \exp(i2\pi y/L_y), \text{ and}$$

$$-\hbar^2 \nabla^2 / y \exp(-i2\pi y/L_y) = -2\hbar^2 \pi^2 / L_y \exp(-i2\pi y/L_y).$$

Thus, the expansion of  $\psi$  in terms of eigenstates of the property being measured dictated by the fifth postulate above is already accomplished. The only two terms in this expansion correspond to momenta along the y-axis of  $2\hbar^2 \pi^2 / L_y$  and  $-2\hbar^2 \pi^2 / L_y$ ; the probabilities of observing these two momenta are given by the squares of the expansion coefficients of  $\psi$  in terms of the normalized eigenfunctions of  $-\hbar^2 \nabla^2 / y$ . The functions  $(1/L_y)^{1/2} \exp(i2\pi y/L_y)$  and

$(1/L_y)^{1/2} \exp(-i2\pi y/L_y)$  are such normalized eigenfunctions; the expansion coefficients of these functions in  $\psi$  are  $2^{-1/2}$  and  $-2^{-1/2}$ , respectively. Thus the momentum  $2\hbar^2 \pi^2 / L_y$  will be observed with probability  $(2^{-1/2})^2 = 1/2$  and  $-2\hbar^2 \pi^2 / L_y$  will be observed with probability  $(-2^{-1/2})^2 = 1/2$ . If the momentum along the x-axis were experimentally measured, again only two values  $\hbar^2 \pi^2 / L_x$  and  $-\hbar^2 \pi^2 / L_x$  would be found, each with a probability of 1/2.

The average value of the momentum along the x-axis can be computed either as the sum of the probabilities multiplied by the momentum values:

$$\langle p_x \rangle = 1/2 [\hbar^2 \pi^2 / L_x - \hbar^2 \pi^2 / L_x] = 0,$$

or as the so-called expectation value integral shown in the seventh postulate:

$$\langle p_x \rangle = \int \psi^* (-i\hbar \frac{\partial}{\partial x}) \psi dx dy.$$

Inserting the full expression for  $\psi(x,y)$  and integrating over  $x$  and  $y$  from  $0$  to  $L_x$  and  $L_y$ , respectively, this integral is seen to vanish. This means that the result of a large number of measurements of  $p_x$  on electrons each described by the same  $\psi$  will yield zero net momentum along the  $x$ -axis.; half of the measurements will yield positive momenta and half will yield negative momenta of the same magnitude.

The time evolution of the full wavefunction given above for the  $n_x=1, n_y=2$  state is easy to express because this  $\psi$  is an energy eigenstate:

$$\psi(x,y,t) = \psi(x,y) \exp(-iEt/\hbar).$$

If, on the other hand, the electron had been prepared in a state  $\psi(x,y)$  that is not a pure eigenstate (i.e., cannot be expressed as a single energy eigenfunction), then the time evolution is more complicated. For example, if at  $t=0$   $\psi$  were of the form

$$\begin{aligned} \psi &= (2/L_x)^{1/2} (2/L_y)^{1/2} [a \sin(2\pi x/L_x) \sin(\pi y/L_y) \\ &+ b \sin(\pi x/L_x) \sin(2\pi y/L_y) ], \end{aligned}$$

with  $a$  and  $b$  both real numbers whose squares give the probabilities of finding the system in the respective states, then the time evolution operator  $\exp(-i\mathbf{H}t/\hbar)$  applied to  $\psi$  would yield the following time dependent function:

$$\begin{aligned} \psi &= (2/L_x)^{1/2} (2/L_y)^{1/2} [a \exp(-iE_{2,1} t/\hbar) \sin(2\pi x/L_x) \\ &\sin(\pi y/L_y) + b \exp(-iE_{1,2} t/\hbar) \sin(\pi x/L_x) \sin(2\pi y/L_y) ], \end{aligned}$$

where

$$E_{2,1} = \frac{\hbar^2}{2m} [ \frac{4\pi^2}{L_x^2} + \frac{\pi^2}{L_y^2} ], \text{ and}$$

$$E_{1,2} = \frac{\hbar^2}{2m} [ \frac{\pi^2}{L_x^2} + \frac{4\pi^2}{L_y^2} ].$$

The probability of finding  $E_{2,1}$  if an experiment were carried out to measure energy would be  $|a \exp(-iE_{2,1} t/\hbar)|^2 = |a|^2$ ; the probability for finding  $E_{1,2}$  would be  $|b|^2$ . The spatial probability distribution for finding the electron at points  $x,y$  will, in this case, be given by:

$$|\psi\rangle^2 = |a|^2 |\psi_{2,1}\rangle^2 + |b|^2 |\psi_{1,2}\rangle^2 + 2ab \psi_{2,1} \psi_{1,2} \cos(Et/\hbar),$$

where  $E$  is  $E_{2,1} - E_{1,2}$ ,

$$\psi_{2,1} = (2/L_x)^{1/2} (2/L_y)^{1/2} \sin(2x/L_x) \sin(y/L_y),$$

and

$$\psi_{1,2} = (2/L_x)^{1/2} (2/L_y)^{1/2} \sin(x/L_x) \sin(2y/L_y).$$

This spatial distribution is not stationary but evolves in time. So in this case, one has a wavefunction that is not a pure eigenstate of the Hamiltonian (one says that  $\psi$  is a superposition state or a non-stationary state) whose average energy remains constant ( $E = E_{2,1} |a|^2 + E_{1,2} |b|^2$ ) but whose spatial distribution changes with time.

Although it might seem that most spectroscopic measurements would be designed to prepare the system in an eigenstate (e.g., by focusing on the sample light whose frequency matches that of a particular transition), such need not be the case. For example, if very short laser pulses are employed, the Heisenberg uncertainty broadening ( $\Delta E \Delta t \sim \hbar$ ) causes the light impinging on the sample to be very non-monochromatic (e.g., a pulse time of  $1 \times 10^{-12}$  sec corresponds to a frequency spread of approximately  $5 \text{ cm}^{-1}$ ). This, in turn, removes any possibility of preparing the system in a particular quantum state with a resolution of better than  $30 \text{ cm}^{-1}$  because the system experiences time oscillating electromagnetic fields whose frequencies range over at least  $5 \text{ cm}^{-1}$ ).

*Essentially all of the model problems that have been introduced in this Chapter to illustrate the application of quantum mechanics constitute widely used, highly successful 'starting-point' models for important chemical phenomena. As such, it is important that students retain working knowledge of the energy levels, wavefunctions, and symmetries that pertain to these models.*

Thus far, exactly soluble model problems that represent one or more aspects of an atom or molecule's quantum-state structure have been introduced and solved. For example, electronic motion in polyenes was modeled by a particle-in-a-box. The harmonic oscillator and rigid rotor were introduced to model vibrational and rotational motion of a diatomic molecule.

As chemists, we are used to thinking of electronic, vibrational, rotational, and translational energy levels as being (at least approximately) separable. On the other hand, we are aware that situations exist in which energy can flow from one such degree of freedom to another (e.g., electronic-to-vibrational energy flow occurs in radiationless relaxation and vibration-rotation couplings are important in molecular spectroscopy). It is important to understand how the simplifications that allow us to focus on electronic or vibrational or rotational motion arise, how they can be obtained from a first-principles derivation, and what their limitations and range of accuracy are.