Words to the reader about how to use this textbook

I. What This Book Does and Does Not Contain

This text is intended for use by beginning graduate students and advanced upper division undergraduate students in all areas of chemistry.

It provides:

(i) An introduction to the fundamentals of quantum mechanics as they apply to chemistry,

(ii) Material that provides brief introductions to the subjects of molecular spectroscopy and chemical dynamics,

(iii) An introduction to computational chemistry applied to the treatment of electronic structures of atoms, molecules, radicals, and ions,

(iv) A large number of exercises, problems, and detailed solutions.

It does not provide much historical perspective on the development of quantum mechanics. Subjects such as the photoelectric effect, black-body radiation, the dual nature of electrons and photons, and the Davisson and Germer experiments are not even discussed.

To provide a text that students can use to gain introductory level knowledge of quantum mechanics as applied to chemistry problems, such a non-historical approach had to be followed. This text immediately exposes the reader to the machinery of quantum mechanics.

Sections 1 and 2 (i.e., Chapters 1-7), together with Appendices A, B, C and E, could constitute a one-semester course for most first-year Ph. D. programs in the U. S. A. Section 3 (Chapters 8-12) and selected material from other appendices or selections from Section 6 would be appropriate for a second-quarter or second-semester course. Chapters 13- 15 of Sections 4 and 5 would be of use for providing a link to a one-quarter or one-semester class covering molecular spectroscopy. Chapter 16 of Section 5 provides a brief introduction to chemical dynamics that could be used at the beginning of a class on this subject.

There are many quantum chemistry and quantum mechanics textbooks that cover material similar to that contained in Sections 1 and 2; in fact, our treatment of this material is generally briefer and less detailed than one finds in, for example, Quantum Chemistry, H. Eyring, J. Walter, and G. E. Kimball, J. Wiley and Sons, New York, N.Y. (1947), Quantum Chemistry, D. A. McQuarrie, University Science Books, Mill Valley, Ca. (1983), Molecular Quantum Mechanics, P. W. Atkins, Oxford Univ. Press, Oxford, England (1983), or Quantum Chemistry, I. N. Levine, Prentice Hall, Englewood Cliffs,

N. J. (1991), Depending on the backgrounds of the students, our coverage may have to be supplemented in these first two Sections.

By covering this introductory material in less detail, we are able, within the confines of a text that can be used for a one-year or a two-quarter course, to introduce the student to the more modern subjects treated in Sections 3, 5, and 6. Our coverage of modern quantum chemistry methodology is not as detailed as that found in Modern Quantum Chemistry, A. Szabo and N. S. Ostlund, Mc Graw-Hill, New York (1989), which contains little or none of the introductory material of our Sections 1 and 2.

By combining both introductory and modern up-to-date quantum chemistry material in a single book designed to serve as a text for one-quarter, one-semester, two-quarter, or one-year classes for first-year graduate students, we offer a unique product.

It is anticipated that a course dealing with atomic and molecular spectroscopy will follow the student's mastery of the material covered in Sections 1- 4. For this reason, beyond these introductory sections, this text's emphasis is placed on electronic structure applications rather than on vibrational and rotational energy levels, which are traditionally covered in considerable detail in spectroscopy courses.

In brief summary, this book includes the following material:

1. The Section entitled **The Basic Tools of Quantum Mechanics** treats the fundamental postulates of quantum mechanics and several applications to exactly soluble model problems. These problems include the conventional particle-in-a-box (in one and more dimensions), rigid-rotor, harmonic oscillator, and one-electron hydrogenic atomic orbitals. The concept of the Born-Oppenheimer separation of electronic and vibration-rotation motions is introduced here. Moreover, the vibrational and rotational energies, states, and wavefunctions of diatomic, linear polyatomic and non-linear polyatomic molecules are discussed here at an introductory level. This section also introduces the variational method and perturbation theory as tools that are used to deal with problems that can not be solved exactly.

2. The Section **Simple Molecular Orbital Theory** deals with atomic and molecular orbitals in a qualitative manner, including their symmetries, shapes, sizes, and energies. It introduces bonding, non-bonding, and antibonding orbitals, delocalized, hybrid, and Rydberg orbitals, and introduces Hückel-level models for the calculation of molecular orbitals as linear combinations of atomic orbitals (a more extensive treatment of

several semi-empirical methods is provided in Appendix F). This section also develops the Orbital Correlation Diagram concept that plays a central role in using Woodward-Hoffmann rules to predict whether chemical reactions encounter symmetry-imposed barriers.

3. The **Electronic Configurations, Term Symbols, and States** Section treats the spatial, angular momentum, and spin symmetries of the many-electron wavefunctions that are formed as antisymmetrized products of atomic or molecular orbitals. Proper coupling of angular momenta (orbital and spin) is covered here, and atomic and molecular term symbols are treated. The need to include Configuration Interaction to achieve qualitatively correct descriptions of certain species' electronic structures is treated here. The role of the resultant Configuration Correlation Diagrams in the Woodward-Hoffmann theory of chemical reactivity is also developed.

4. The Section on **Molecular Rotation and Vibration** provides an introduction to how vibrational and rotational energy levels and wavefunctions are expressed for diatomic, linear polyatomic, and non-linear polyatomic molecules whose electronic energies are described by a single potential energy surface. Rotations of "rigid" molecules and harmonic vibrations of uncoupled normal modes constitute the starting point of such treatments.

5. The **Time Dependent Processes** Section uses time-dependent perturbation theory, combined with the classical electric and magnetic fields that arise due to the interaction of photons with the nuclei and electrons of a molecule, to derive expressions for the rates of transitions among atomic or molecular electronic, vibrational, and rotational states induced by photon absorption or emission. Sources of line broadening and time correlation function treatments of absorption lineshapes are briefly introduced. Finally, transitions induced by collisions rather than by electromagnetic fields are briefly treated to provide an introduction to the subject of theoretical chemical dynamics.

6. The Section on **More Quantitive Aspects of Electronic Structure Calculations** introduces many of the computational chemistry methods that are used to quantitatively evaluate molecular orbital and configuration mixing amplitudes. The Hartree-Fock self-consistent field (SCF), configuration interaction (CI), multiconfigurational SCF (MCSCF), many-body and Møller-Plesset perturbation theories,

coupled-cluster (CC), and density functional or X_α-like methods are included. The strengths and weaknesses of each of these techniques are discussed in some detail. Having mastered this section, the reader should be familiar with how potential energy hypersurfaces, molecular properties, forces on the individual atomic centers, and responses to externally applied fields or perturbations are evaluated on high speed computers.

II. How to Use This Book: Other Sources of Information and Building Necessary Background

In most class room settings, the group of students learning quantum mechanics as it applies to chemistry have quite diverse backgrounds. In particular, the level of preparation in mathematics is likely to vary considerably from student to student, as will the exposure to symmetry and group theory. This text is organized in a manner that allows students to skip material that is already familiar while providing access to most if not all necessary background material. This is accomplished by dividing the material into sections, chapters and Appendices which fill in the background, provide methodological tools, and provide additional details.

The Appendices covering Point Group Symmetry and Mathematics Review are especially important to master. Neither of these two Appendices provides a first-principles treatment of their subject matter. The students are assumed to have fulfilled normal American Chemical Society mathematics requirements for a degree in chemistry, so only a review of the material especially relevant to quantum chemistry is given in the Mathematics Review Appendix. Likewise, the student is assumed to have learned or to be simultaneously learning about symmetry and group theory as applied to chemistry, so this subject is treated in a review and practical-application manner here. If group theory is to be included as an integral part of the class, then this text should be supplemented (e.g., by using the text Chemical Applications of Group Theory, F. A. Cotton, Interscience, New York, N. Y. (1963)).

The progression of sections leads the reader from the principles of quantum mechanics and several model problems which illustrate these principles and relate to chemical phenomena, through atomic and molecular orbitals, N-electron configurations, states, and term symbols, vibrational and rotational energy levels, photon-induced transitions among various levels, and eventually to computational techniques for treating chemical bonding and reactivity.

At the end of each Section, a set of Review Exercises and fully worked out answers are given. Attempting to work these exercises should allow the student to determine whether he or she needs to pursue additional background building via the Appendices .

In addition to the Review Exercises , sets of Exercises and Problems, and their solutions, are given at the end of each section.

The exercises are brief and highly focused on learning a particular skill. They allow the student to practice the mathematical steps and other material introduced in the section. The problems are more extensive and require that numerous steps be executed. They illustrate application of the material contained in the chapter to chemical phenomena and they help teach the relevance of this material to experimental chemistry. In many cases, new material is introduced in the problems, so all readers are encouraged to become actively involved in solving all problems.

To further assist the learning process, readers may find it useful to consult other textbooks or literature references. Several particular texts are recommended for additional reading, further details, or simply an alternative point of view. They include the following (in each case, the abbreviated name used in this text is given following the proper reference):

1. Quantum Chemistry, H. Eyring, J. Walter, and G. E. Kimball, J. Wiley and Sons, New York, N.Y. (1947)- EWK.
2. Quantum Chemistry, D. A. McQuarrie, University Science Books, Mill Valley, Ca. (1983)- McQuarrie.
3. Molecular Quantum Mechanics, P. W. Atkins, Oxford Univ. Press, Oxford, England (1983)- Atkins.
4. The Fundamental Principles of Quantum Mechanics, E. C. Kemble, McGraw-Hill, New York, N.Y. (1937)- Kemble.
5. The Theory of Atomic Spectra, E. U. Condon and G. H. Shortley, Cambridge Univ. Press, Cambridge, England (1963)- Condon and Shortley.
6. The Principles of Quantum Mechanics, P. A. M. Dirac, Oxford Univ. Press, Oxford, England (1947)- Dirac.
7. Molecular Vibrations, E. B. Wilson, J. C. Decius, and P. C. Cross, Dover Pub., New York, N. Y. (1955)- WDC.
8. Chemical Applications of Group Theory, F. A. Cotton, Interscience, New York, N. Y. (1963)- Cotton.
9. Angular Momentum, R. N. Zare, John Wiley and Sons, New York, N. Y. (1988)- Zare.

10. Introduction to Quantum Mechanics, L. Pauling and E. B. Wilson, Dover Publications, Inc., New York, N. Y. (1963)- Pauling and Wilson.
11. Modern Quantum Chemistry, A. Szabo and N. S. Ostlund, Mc Graw-Hill, New York (1989)- Szabo and Ostlund.
12. Quantum Chemistry, I. N. Levine, Prentice Hall, Englewood Cliffs, N. J. (1991)- Levine.
13. Energetic Principles of Chemical Reactions, J. Simons, Jones and Bartlett, Portola Valley, Calif. (1983),

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 **F**. Given F in terms of the $\{q_i\}$ and $\{p_i\}$, **F** is formed by replacing p_j by $-i\hbar\partial/\partial q_j$ and leaving q_j untouched.

For example, if

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

then

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

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

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

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

and the corresponding operator is

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

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

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

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

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

The mapping from F to **F** is straightforward only in terms of cartesian coordinates. To map a classical function F, given in terms of curvilinear coordinates (even if they are orthogonal), into its quantum operator is not at all straightforward. 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 Ψ 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 H_2O molecule, the wavefunction depends on many coordinates. For the H_2O example, it depends on the x, y, and z (or r,θ, and φ) coordinates of the ten electrons and the x, y, and z (or r,θ, and ϕ) coordinates of the oxygen nucleus and of the two protons; a total of thirty-nine coordinates appear in Ψ.

In classical mechanics, the coordinates q_j and their corresponding momenta p_j are functions of time. The state of the system is then described by specifying $q_j(t)$ and $p_j(t)$. In quantum mechanics, the concept that q_j is known as a function of time is replaced by the concept of the probability density for finding q_j at a particular value at a particular time 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 Ψ are found by applying the basic equation of quantum mechanics, the Schrödinger equation, to a few exactly soluble model problems. Knowing the solutions to these 'easy' yet chemically very relevant models will then facilitate learning more of the details about the structure of quantum mechanics 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_2O example cited above). It is usually written

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

where $\Psi(q_j,t)$ is the unknown wavefunction and **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 $\mathbf{p_j} = - i\hbar\partial/\partial q_j$.

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

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

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

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

The corresponding Hamiltonian operator is

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

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

Notice that **H** is a second order differential operator in the space of the thirty-nine cartesian coordinates that describe the positions of the ten electrons and three nuclei. It is a second order operator because the momenta appear in the kinetic energy as p_j^2 and p_a^2, and the quantum mechanical operator for each momentum $\mathbf{p} = -i\hbar\ \partial/\partial q$ is of first order.

The Schrödinger equation for the H_2O example at hand then reads

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

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

$$= i\ \hbar\ \partial\Psi/\partial t.$$

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, **H** is not explicitly time dependent, so one can assume that $\Psi(q_j,t)$ is of the form

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

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

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

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

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

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

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

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

The first of these equations is called the time-independent Schrödinger equation; it is a so-called eigenvalue equation in which one is asked to find functions that yield a constant multiple of themselves when acted on by the Hamiltonian operator. Such functions are called eigenfunctions of **H** and the corresponding constants are called eigenvalues of **H**.

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

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

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

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

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

For the above example, the time dependence is expressed by

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

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:

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

Because there are no terms in this equation that <u>couple</u> motion in the x and y directions (e.g., no terms of the form x^ay^b or $\partial/\partial x\ \partial/\partial y$ or $x\partial/\partial y$), separation of variables can be used to write ψ as a product $\psi(x,y)=A(x)B(y)$. Substitution of this form into the Schrödinger equation, followed by collecting together all x-dependent and all y-dependent terms, gives;

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

Since the first term contains no y-dependence and the second contains no x-dependence, 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:

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

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

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

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

$B(y) = \exp(iy(2mE_y/\hbar^2)^{1/2})$ 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 $0 \le x \le L_x$; $0 \le y \le L_y$, 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 $x=L_x$ and $y=L_y$, gives equations that can be obeyed only if E_x and E_y assume particular values:

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

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

These equations are equivalent to

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

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

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

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

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

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

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

In this example, confinement of the electron to a finite interval along both the x and y coordinates yields energies that are quantized along both axes. If the electron were confined along one coordinate (e.g., between $0 \le x \le L_x$) but not along the other (i.e., B(y) is either restricted to vanish at y=0 or at $y=L_y$ or at neither point), then the total energy E lies in the continuum; its E_x component is quantized but E_y is not. Such cases arise, for example, when a linear triatomic molecule has more than enough energy in one of its bonds to rupture it but not much energy in the other bond; the first bond's energy lies in the continuum, but the second bond's energy is quantized.

Perhaps more interesting is the case in which the bond with the higher dissociation energy is excited to a level that is not enough to break it but that is in excess of the dissociation energy of the weaker bond. In this case, one has two degenerate states- i. the strong bond having high internal energy and the weak bond having low energy (ψ_1), and ii. the strong bond having little energy and the weak bond having more than enough energy to rupture it (ψ_2). Although an experiment may prepare the molecule in a state that contains only the former component (i.e., $\psi= C_1\psi_1 + C_2\psi_2$ with $C_1>>C_2$), coupling between the two degenerate functions (induced by terms in the Hamiltonian **H** that have been ignored in defining ψ_1 and ψ_2) usually causes the true wavefunction $\Psi = \exp(-it\mathbf{H}/\hbar)\ \psi$ to acquire a component of the second function as time evolves. In such a case, one speaks of internal vibrational energy 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 the 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:

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

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

$$E = E_x + E_y ,$$

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

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

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

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

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

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:

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

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:

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

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

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

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

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

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

$$S = S_x + S_y$$

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

The relationship between these classical action integrals and existence of quantized energy levels has been show to involve equating the classical action for motion on a <u>closed path</u> (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:

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

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

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

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

Notice that the sign of the momenta are positive in each of the first integrals appearing above (because the particle is moving from $x = 0$ to $x = L_x$, and analogously for y-motion, and thus has positive momentum) and negative in each of the second integrals (because the motion is from $x = L_x$ to $x = 0$ (and analogously for y-motion) and thus with negative momentum). Within the region bounded by $0 \le x \le L_x$; $0 \le y \le L_y$, the potential vanishes, so $V(x) = V(y) = 0$. Using this fact, and reversing the upper and lower limits, and thus the sign, in the second integrals above, one obtains:

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

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

Solving for E_x and E_y, one finds:

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

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

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

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

has been used to obtain the result.

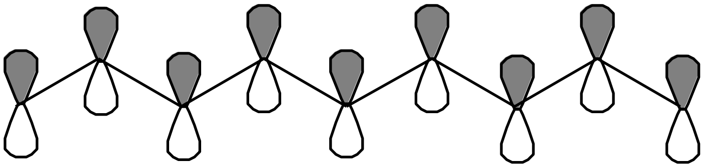
B. Other Model Problems

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 θ and ϕ. 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 π-electron motion along the p_π 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 π 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 π electrons are present (e.g., as in the 1,3,5,7-nonatetraene radical), the ground electronic state would be represented by a total wavefunction consisting of a <u>product</u> in which the lowest four ψ's are doubly occupied and the fifth ψ is singly occupied:

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

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

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

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

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

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

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

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

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

denotes

$\psi_1\alpha(\mathbf{r}_1)\ \psi_1\beta\ (\mathbf{r}_2)\ \psi_2\alpha\ (\mathbf{r}_3)\ \psi_2\beta\ (\mathbf{r}_4)\ \psi_3\alpha\ (\mathbf{r}_5)\ \psi_3\beta\ (\mathbf{r}_6)\ \psi_4\alpha\ (\mathbf{r}_7)\ \psi_5\beta$

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

The electronic excitation energies within this model would be

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

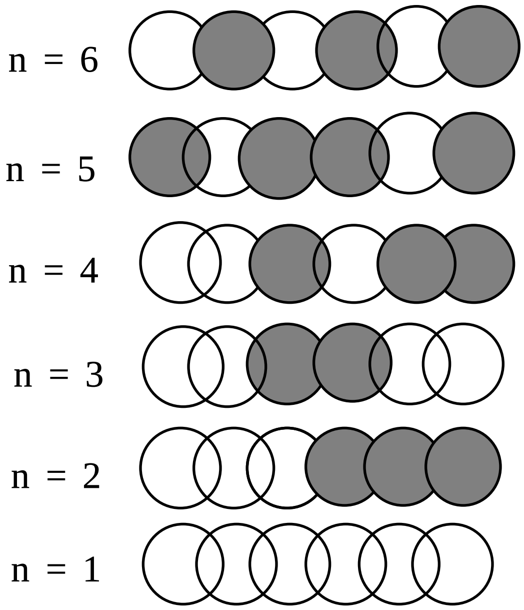
$\Delta E'^* = \pi^2\, \hbar^2/2m\ [\ 6^2/L^2 - 5^2/L^2]$, for the two excited-state functions described above. It turns out that this simple model of π-electron energies provides a qualitatively correct picture of such excitation energies.

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

The individual π-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 π-orbital system for which the 'box length' L is five times the distance R_{CC} between neighboring pairs of Carbon atoms.



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

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^{th} C-atom centered atomic orbital in the n^{th} π-molecular orbital is given by $(2/L)^{1/2} \sin(n\pi k R_{CC}/L)$.

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 Ψ than for either Ψ^* or Ψ'^*. In the former, the unpaired spin density resides in ψ_5, which has non-zero amplitude at the C_5 site $x=L/2$; in Ψ^* and Ψ'^*, the unpaired density is in ψ_4 and ψ_6, respectively, both of which have zero density at C_5. These densities reflect the values $(2/L)^{1/2} \sin(n\pi k R_{CC}/L)$ of the amplitudes for this case in which $L = 8 \text{ x } R_{CC}$ 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, θ, and φ variables

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

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

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

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

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

$$+\frac{1}{r^2\mathrm{Sin}^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+V(r)\psi=E\psi\,.$$

Subtracting $V(r)\psi$ 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

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

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

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

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

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

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

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

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

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

For the above example, we therefore can set both sides equal to a so-called separation constant that we call $-m^2$. It will become clear shortly why we have chosen to express the constant in this form.

a. The Φ Equation

The resulting Φ equation reads

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

which has as its most general solution

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

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

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

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

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

b. The Θ Equation

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

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

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

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

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

We now can write the θ equation as

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

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

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

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

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

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

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

and substitute into the differential equation to obtain

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

Equating like powers of z gives

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

Note that for large values of k

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

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

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

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

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

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

The above P and $e^{im\varphi}$ functions, when re-expressed in terms of θ and φ, yield the full angular part of the wavefunction for any centrosymmetric potential. These solutions are usually written as $Y_{l,m}(\theta,\varphi) = P_l^m(\mathrm{Cos}\theta)\,(2\pi)^{-\frac{1}{2}}\,\exp(im\varphi)$, and are called spherical harmonics. They provide the angular solution of the r,θ, φ Schrödinger equation for 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^+, Li^{++} , etc.), the rotational motion of a diatomic molecule (where the potential depends only on bond length r), the motion of a nucleon in a spherically symmetrical "box" (as occurs in the shell model of nuclei), and the scattering of two atoms (where the potential depends only on interatomic distance).

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:

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

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

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

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

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

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

The differential operator terms can be recast in several ways using

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$E = - \frac{\mu Z^2 e^4}{2\hbar^2 n^2} \text{ and } \rho = \frac{Zr}{a_o n} .$$

Here, the length a_o is the so called Bohr radius $\left(a_o = \frac{\hbar^2}{\mu e^2} \right)$; it appears once the above E-expression is substituted into the equation for ρ. Using the recursion equation to solve for the polynomial's coefficients a_k for any choice of n and l quantum numbers generates a so-called Laguerre polynomial; $P_{n-L-1}(\rho)$. They contain powers of ρ from zero through n-l-1.

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,θ,φ Schrödinger equation for one electron moving about a nucleus of charge Z. The θ and φ solutions are the spherical harmonics $Y_{L,m}(\theta,\varphi)$. The bound-state radial solutions

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

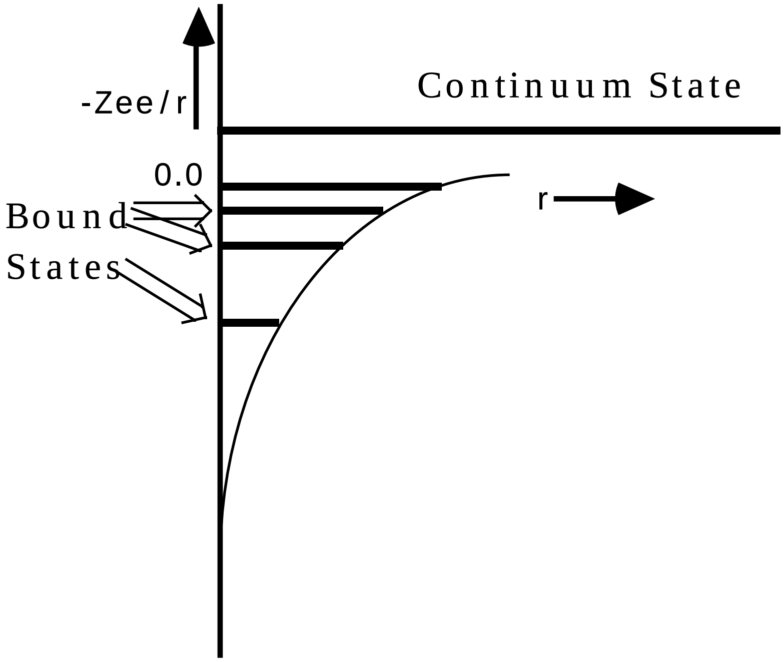
depend on the n and l quantum numbers and are given in terms of the Laguerre polynomials (see EWK for tabulations of these polynomials).

d. Summary

To summarize, the quantum numbers l and m arise through boundary conditions requiring that $\psi(\theta)$ be normalizable (i.e., not diverge) and $\psi(\varphi) = \psi(\varphi+2\pi)$. In the texts by Atkins, EWK, and McQuarrie the differential equations obeyed by the θ and φ 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 π- electrons in conjugated polyenes, these so-called hydrogen-like orbitals provide qualitative descriptions of orbitals of atoms with more than a single electron. By introducing the concept of screening as a way to represent the repulsive interactions among the electrons of an atom, an effective nuclear charge Z_{eff} can be used in place of Z in the $\psi_{n,l,m}$ and $E_{n,l}$ 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 $Z_{eff}=6$ for them, whereas the 2s and 2p electrons are screened by the two 1s electrons, so $Z_{eff}= 4$ for them. Within this approximation, one then occupies two 1s orbitals with Z=6, two 2s orbitals with Z=4 and two 2p orbitals with Z=4 in forming the full six-electron 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:

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

or

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

The angles θ and φ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule $\mu=m_1m_2/(m_1+m_2)$. The differential operators can be seen to be exactly the same as those that arose in the hydrogen-like-atom case, and, as discussed above, these θ and φ 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: $\psi = Y_{J,M}(\theta,\varphi)$. 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 ΔJ to 1,0, and -1) are given by

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

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

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:

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

where μ is the reduced mass $\mu = m_1m_2/(m_1+m_2)$ of the two atoms.
By substituting $\psi = F(r)/r$ into this equation, one obtains an equation for F(r) in which the differential operators appear to be less complicated:

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

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

If the 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 -∞, 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 $\xi = (\mu k/\hbar^2)^{1/4}\ x$ as a new scaled radial coordinate allows the solution of the large-r equation to be written as:

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

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

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

where the C_n are coefficients to be determined. Substituting this expression into the full radial equation generates a set of recursion equations for the C_n amplitudes. As in the solution of the hydrogen-like radial equation, the series described by these coefficients is divergent unless the energy E happens to equal specific values. It is this requirement that the 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:

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

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

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

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

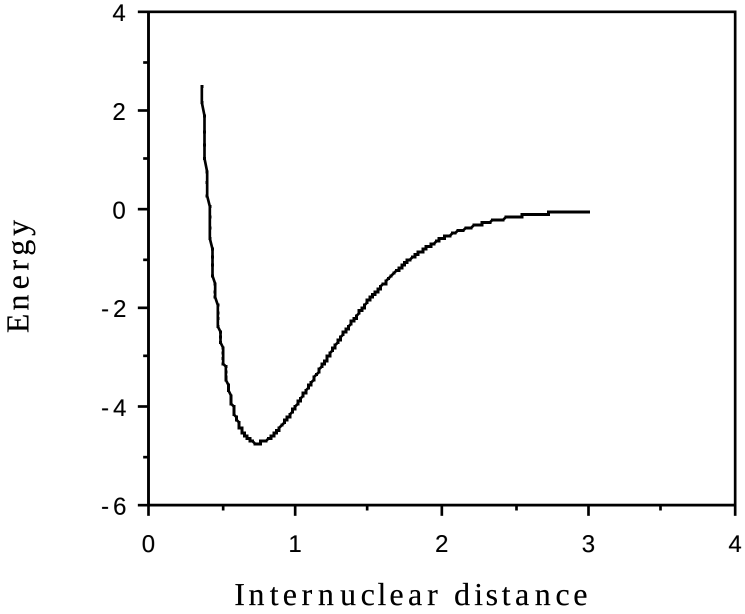
Because the H_n are odd or even functions of x (depending on whether n is odd or even), the wavefunctions $\psi_n(x)$ are odd or even. This splitting of the solutions into two distinct classes is an example of the effect of symmetry; in this case, the symmetry is caused by the symmetry of the harmonic 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:

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

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 Ψ 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 Ψ and operators **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 Ψ 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 $\lambda=h/p$)

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

where **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), **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 **H** to properly account for the system-field interactions.

If **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 ψ_k of the system. The most general solution to the full Schrödinger equation $i\hbar\partial\Psi/\partial t = \mathbf{H}\Psi$ is then given by applying $\exp(-i\mathbf{H}t/\hbar)$ to the wavefunction at some initial time (t=0) $\Psi=\Sigma_k C_k\psi_k$ to obtain

$\Psi(t)=\Sigma_k C_k\psi_k \exp(-itE_k/\hbar)$. 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 $\Psi(q_j,t)$.

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

$$\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} = 3.53333Å^{-\frac{1}{2}} e^{-(244.83Å^{-2})(r-1.09769Å)^2}$$

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

$$\Psi (t) = \Sigma_v C_v \Psi_v \exp(-i E_v t/\hbar).$$

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 Ψ_v in the function Ψ at t=0. To do this, one uses

$$\int \Psi_{v'}^* \Psi(t=0)\, d\tau = C_{v'},$$

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 $\Psi(t=0)$

$$\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} = 3.53333\text{Å}^{-\frac{1}{2}}\, e^{-(244.83\text{Å}^{-2})(r-1.09769\text{Å})^2}$$

and various N_2^+ *vibrational functions* Ψ_v, *one can determine how* Ψ *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:*

$$C_0 = \int \Psi_0^*(N_2^+)\ \Psi_0(N_2)\ d\tau$$

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

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 principal 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 $\Psi^* \Psi$ 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 **F**) must result in one of the eigenvalues f_j of the operator **F**. These eigenvalues are obtained by solving

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

where the φ_j are the eigenfunctions of **F**. Once the measurement of **F** is made, for that sub-population of the experimental sample found to have the particular eigenvalue f_j, the wavefunction becomes φ_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 **F** corresponding to <u>all</u> physically measurable quantities are Hermitian; this means that their matrix representations obey (see Appendix C for a description of the 'bra' | > and 'ket' < | notation used below):

$$<\chi_j|\mathbf{F}|\chi_k> = <\chi_k|\mathbf{F}|\chi_j>^* = <\mathbf{F}\chi_j|\chi_k>$$

in any basis $\{\chi_j\}$ of functions appropriate for the action of **F** (i.e., functions of the variables on which **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 **F** can be allowed to operate on the function to its right or on the function to its left if **F** is Hermitian.

Hermiticity assures that the eigenvalues $\{f_j\}$ are all real, that eigenfunctions $\{\chi_j\}$ having different eigenvalues are orthogonal and can be normalized $<\chi_j|\chi_k>=\delta_{j,k}$, 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 F, this same value will be observed in all subsequent measurements of F as long as the system remains undisturbed by measurements of other properties or by interactions with external fields. In fact, once f_i has been observed, the state of the system becomes an eigenstate of **F** (if it already was, it remains unchanged):

$$\mathbf{F}\Psi = f_i\Psi.$$

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 $|\langle\Psi(N_2; v=0) | \Psi(N_2^+; v=0)\rangle|^2 = 0.92$ *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,*

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

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 Ψ prior to the measurement, is given by expanding Ψ in terms of the complete set of normalized eigenstates of **F**

$$\Psi=\Sigma_j |\varphi_j\rangle \langle\varphi_j|\Psi\rangle$$

and then computing $P_k =|\langle\varphi_k|\Psi\rangle|^2$. For the special case in which Ψ is already one of the eigenstates of **F** (i.e., $\Psi=\varphi_k$), the probability of observing f_j reduces to $P_j =\delta_{j,k}$. The set of numbers $C_j = \langle\varphi_j|\Psi\rangle$ are called the expansion coefficients of Ψ in the basis of the $\{\varphi_j\}$. 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 Ψ within the $\{\varphi_j\}$ 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 Ψ*

$$\Psi(x,t) = 1/2\pi \int \exp(ikx) \int \exp(-ikx') \, \Psi(x',t) \, dx' \; dk.$$

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

$$1/2\pi \int \exp(-ikx) \exp(ik'x) \, dx = \delta(k-k'),$$

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

$$1/2\pi \int \exp(-ikx) \exp(ikx') \, dk = \delta(x-x')$$

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

Another Example:

Take the initial ψ 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 ar amplitudes that describe the admixture of 2p and 3p functions in this wavefunction. Then:

a. If $\mathbf{L^2}$ 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 ψ are p-type orbitals. After said measurement, the wavefunction would still be this same ψ because this entire ψ is an eigenfunction of $\mathbf{L^2}$.

b. If $\mathbf{L_z}$ 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 $\mathbf{L_z}$ operator) with respective probabilities $|\,a\,|^2 + |\,b\,|^2$, $|\,-a\,|^2$, and $|\,a\,|^2 + |\,-b\,|^2$.

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

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

is still an eigenfunction of $\mathbf{L^2}$ with this eigenvalue.

d. Again after $\mathbf{L_z}$ 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 Ψ is a function of several variables (e.g., when Ψ 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 $\Psi=\Sigma_j |\varphi_j\rangle \langle\varphi_j|\Psi\rangle$ is viewed as relating only to Ψ's dependence on the subset of variables related to F. In this case, the integrals $\langle\varphi_k|\Psi\rangle$ are carried out over only these variables; thus the probabilities $P_k = |\langle\varphi_k|\Psi\rangle|^2$ depend parametrically on the remaining variables.

Example:

Suppose that $\Psi(r,\theta)$ describes the radial (r) and angular (θ) 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 ($\mathbf{L}_z = -i\hbar\, \partial/\partial\theta$), only values equal to $m\hbar$ ($m=0,1,-1,2,-2,3,-3,\ldots$) could be observed, because these are the eigenvalues of $\mathbf{L}_z$:

$$\mathbf{L}_z\, \varphi_m = -i\hbar\, \partial/\partial\theta\, \varphi_m = m\hbar\, \varphi_m, \text{ where}$$

$$\varphi_m = (1/2\pi)^{1/2} \exp(im\theta).$$

The quantization of L_z *arises because the eigenfunctions* $\varphi_m(\theta)$ *must be periodic in* θ*:*

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

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 $\varphi(\theta+2\pi) = \varphi(\theta)$*).*

Expanding the θ*-dependence of* Ψ *in terms of the* φ_m

$$\Psi = \Sigma_m <\varphi_m|\Psi> \varphi_m(\theta)$$

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

$$P_m = |<\varphi_m|\Psi>|^2 = |\int\varphi_m{}^*(\theta)\, \Psi(r,\theta)\, d\theta\, |^2.$$

If one is interested in the probability that $m\hbar$ *be observed when* L_z *is measured* <u>*regardless*</u> *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:*

$$P_m = \int \varphi^*(\theta')\, \{\int \Psi^*(r,\theta')\, \Psi(r,\theta)\, r\, dr\}\, \varphi(\theta)\, d\theta'\, d\theta,$$

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:*

$$P_m\, r\, dr = r\, dr \int \varphi_m{}^*(\theta')\Psi^*(r,\theta')\Psi(r,\theta)\varphi_m(\theta) d\theta'\, d\theta = |<\varphi_m|\Psi>|^2\, r\, dr.$$

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:

$$\mathbf{F}\phi_j=f_j\phi_j \Longrightarrow \mathbf{G}\phi_j=g_j\phi_j \Longrightarrow \mathbf{J}\phi_j=j_j\phi_j.$$

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 L_z and 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 **F**, **G**, or **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* ψ *could be represented as:*

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

where P and S represent the P-state and S-state components of ψ*. 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 ψ' *is of* $m = 1, 0,$ *or* -1*, nor do we know how much 2p, 3p, 4p, ... np components this state contains.*

Because the property corresponding to the operator $\mathbf{L_z}$ *is about to be measured, we express the above* ψ' *in terms of the eigenfunctions of* $\mathbf{L_z}$*:*

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

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 $2p_{-1}$*,* $3p_{-1}$*,* $4p_{-1}$*, ...* 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* $\psi''= P_{-1}$

$$\psi'' = P_{-1} = \Sigma_n C''_n \, nP_{-1}$$

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* nP_m *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 ψ*) 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* ψ *as*

$$\psi = \Sigma_m D_m \psi_m.$$

At this stage, the nature of each ψ_m *is unknown (e.g., the* ψ_1 *function can contain* np_1*,* $n'd_1$*,* $n''f_1$*, etc. components); all that is known is that* ψ_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* ψ_m *to be expressed as*

$$\psi_m = \Sigma_L D_{L,m} \psi_{L,m}.$$

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

$$\psi'' = \psi_{L,m}.$$

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 $2p_{-1}$*,* $3p_{-1}$*, ...* np_{-1} *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*

$$\psi_{1,-1} = \Sigma_n D_n'' \, nP_{-1}.$$

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

The fact that $\mathbf{L_z}$, $\mathbf{L^2}$, and $\mathbf{H}$ 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 $\mathbf{L^2}$ 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 $\mathbf{L^2}$ and $\mathbf{L_z}$ can have simultaneous eigenfunctions, the L = 1 function can be expanded in terms of functions that are eigenfunctions of both $\mathbf{L^2}$ and $\mathbf{L_z}$. This in turn, allowed us to find experimentally the sub-population that had, for example -1 ħ as its value of L_z while retaining knowledge that the state remains an eigenstate of $\mathbf{L^2}$ (the state at this time had L = 1 and m = -1 and was denoted P_{-1}). Then, when this P_{-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 nP_{-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, Ψ 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** = x and $\mathbf{p_x} = -i\hbar\, \partial/\partial x$ do not commute is straightforward to demonstrate:

$$\{x(-i\hbar\, \partial/\partial x\,)\, \chi - (-i\hbar\, \partial/\partial x\,)x\, \chi\} = i\hbar\, \chi \neq 0.$$

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 Ψ, the average value <F> of F for such a set of measurements can be computed as

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

Expanding Ψ in terms of the complete set of eigenstates of **F** allows <F> to be rewritten as follows:

$$\langle F\rangle = \Sigma_j\, f_j\, |\langle\varphi_j|\Psi\rangle|^2,$$

which clearly expresses <F> 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 Ψ defined above as:

$$\langle F\rangle = \Sigma_{i,j}\, \langle\Psi|\varphi_i\rangle\, \langle\varphi_i|\mathbf{F}|\varphi_j\rangle\, \langle\varphi_j|\Psi\rangle = \Sigma_{i,j}\, C_i^*\, \langle\varphi_i|\mathbf{F}|\varphi_j\rangle\, C_j$$

$$= \Sigma_{i,j}\, D_{j,i}\, \langle\varphi_i|\mathbf{F}|\varphi_j\rangle = \mathrm{Tr}\ (DF).$$

Here, DF represents the matrix product of the density matrix $D_{j,i}$ and the matrix representation $F_{i,j} = \langle\varphi_i|\mathbf{F}|\varphi_j\rangle$ of the **F** operator, both taken in the $\{\varphi_j\}$ basis, and 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

$$E = \pi^2 \hbar^2/2m \, [\, 1^2/L_x^2 + 2^2/L_y^2 \,].$$

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 $-i\hbar\partial/\partial y$ could be observed. The p_y eigenfunctions (i.e., functions that obey p_y F = $-i\hbar\partial/\partial y$ F = c F) 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 $0 \le y \le L_y$. It is useful to note that the y-dependence of ψ 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 $-i\hbar\partial/\partial y$:

$$-i\hbar\partial/\partial y \exp(i2\pi y/L_y) = 2h/L_y \exp(i2\pi y/L_y) \text{ , and}$$

$$-i\hbar\partial/\partial y \exp(-i2\pi y/L_y) = -2h/L_y \exp(-i2\pi y/L_y) \text{ .}$$

Thus, the expansion of ψ 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 $2h/L_y$ and $-2h/L_y$; the probabilities of observing these two momenta are given by the squares of the expansion coefficients of ψ in terms of the normalized eigenfunctions of $-i\hbar\partial/\partial y$. 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 ψ are $2^{-1/2}$ and $-2^{-1/2}$, respectively. Thus the momentum $2h/L_y$ will be observed with probability $(2^{-1/2})^2 = 1/2$ and $-2h/L_y$ 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 $1h/L_x$ and $-1h/L_x$ 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:

$$\langle p_x \rangle = 1/2\ [1h/L_x - 1h/L_x\ ] = 0,$$

or as the so-called <u>expectation value</u> integral shown in the seventh postulate:

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

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 ψ 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 ψ 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 ψ were of the form

$$\psi = (2/L_x)^{1/2} (2/L_y)^{1/2} [a \sin(2\pi x/L_x) \sin(1\pi y/L_y)$$

$$+ b \sin(1\pi x/L_x) \sin(2\pi y/L_y)],$$

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 ψ would yield the following time dependent function:

$$\Psi = (2/L_x)^{1/2} (2/L_y)^{1/2} [a \exp(-iE_{2,1}\ t/\hbar) \sin(2\pi x/L_x)$$

$$\sin(1\pi y/L_y) + b \exp(-iE_{1,2}\ t/\hbar) \sin(1\pi x/L_x) \sin(2\pi y/L_y)],$$

where

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

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

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:

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

where ΔE is $E_{2,1} - E_{1,2}$,

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

and

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

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 Ψ 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 ($\Delta E \Delta t \geq \hbar$) 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 cm^{-1}). This, in turn, removes any possibility of preparing the system in a particular quantum state with a resolution of better than 30 cm^{-1} because the system experiences time oscillating electromagnetic fields whose frequencies range over at least 5 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.

Chapter 2

Approximation Methods Can be Used When Exact Solutions to the Schrödinger Equation Can Not be Found.

In applying quantum mechanics to 'real' chemical problems, one is usually faced with a Schrödinger differential equation for which, to date, no one has found an analytical solution. This is equally true for electronic and nuclear-motion problems. It has therefore proven essential to develop and efficiently implement mathematical methods which can provide approximate solutions to such eigenvalue equations. Two methods are widely used in this context- the variational method and perturbation theory. These tools, whose use permeates virtually all areas of theoretical chemistry, are briefly outlined here, and the details of perturbation theory are amplified in Appendix D.

I. The Variational Method

For the kind of potentials that arise in atomic and molecular structure, the Hamiltonian H is a Hermitian operator that is bounded from below (i.e., it has a lowest eigenvalue). Because it is Hermitian, it possesses a complete set of orthonormal eigenfunctions $\{\psi_j\}$. Any function Φ that depends on the same spatial and spin variables on which H operates and obeys the same boundary conditions that the $\{\psi_j\}$ obey can be expanded in this complete set

$$\Phi = \Sigma_j \ C_j \psi_j.$$

The expectation value of the Hamiltonian for any such function can be expressed in terms of its C_j coefficients and the <u>exact</u> energy levels E_j of H as follows:

$$<\Phi|H|\Phi> = \Sigma_{ij}\ C_iC_j <\psi_i|H|\psi_j> = \Sigma_j|C_j|^2\ E_j.$$

If the function Φ is normalized, the sum $\Sigma_j\ |C_j|^2$ is equal to unity. Because H is bounded from below, all of the E_j must be greater than or equal to the lowest energy E_0. Combining the latter two observations allows the energy expectation value of Φ to be used to produce a very important inequality:

$$<\Phi|H|\Phi> \geq\ E_0.$$

The equality can hold only if Φ is equal to ψ_0; if Φ contains components along any of the other ψ_j, the energy of Φ will exceed E_0.

This upper-bound property forms the basis of the so-called <u>variational method</u> in which 'trial wavefunctions' Φ are constructed:

i. To guarantee that Φ obeys all of the boundary conditions that the exact ψ_j do and that Φ is of the proper spin and space symmetry and is a function of the same spatial and spin coordinates as the ψ_j;

ii. With parameters embedded in Φ whose 'optimal' values are to be determined by making <Φ|H|Φ> a minimum.

It is perfectly acceptable to vary any parameters in Φ to attain the lowest possible value for <Φ|H|Φ> because the proof outlined above constrains this expectation value to be above the true lowest eigenstate's energy E_0 for <u>any</u> Φ. The philosophy then is that the Φ that gives the lowest <Φ|H|Φ> is the best because its expectation value is closes to the exact energy.

Quite often a <u>trial wavefunction</u> is expanded as a linear combination of other functions

$$\Phi = \Sigma_J\ C_J\ \Phi_J.$$

In these cases, one says that a 'linear variational' calculation is being performed. The set of functions $\{\Phi_J\}$ are usually constructed to obey all of the boundary conditions that the exact state Ψ obeys, to be functions of the the same coordinates as Ψ, and to be of the same spatial and spin symmetry as Ψ. Beyond these conditions, the $\{\Phi_J\}$ are nothing more than members of a set of functions that are convenient to deal with (e.g., convenient to evaluate Hamiltonian matrix elements $<\Phi_I|H|\Phi_J>$) and that can, in principle, be made complete if more and more such functions are included.

For such a trial wavefunction, the energy depends quadratically on the 'linear variational' C_J coefficients:

$$<\Phi|H|\Phi> = \Sigma_{IJ} C_I C_J <\Phi_I |H|\Phi_J>.$$

Minimization of this energy with the constraint that Φ remain normalized ($<\Phi|\Phi> = 1 = \Sigma_{IJ} C_I C_J <\Phi_I|\Phi_J>$) gives rise to a so-called secular or eigenvalue-eigenvector problem:

$$\Sigma_J [<\Phi_I|H|\Phi_J> - E <\Phi_I|\Phi_J>] C_J = \Sigma_J [H_{IJ} - E S_{IJ}]C_J = 0.$$

If the functions $\{\Phi_J\}$ are orthonormal, then the overlap matrix S reduces to the unit matrix and the above generalized eigenvalue problem reduces to the more familiar form:

$$\Sigma_J H_{IJ} C_J = E C_I.$$

The secular problem, in either form, has as many eigenvalues E_i and eigenvectors $\{C_{iJ}\}$ as the dimension of the H_{IJ} matrix as Φ. It can also be shown that between successive pairs of the eigenvalues obtained by solving the secular problem at least one exact eigenvalue must occur (i.e., $E_{i+1} > E_{exact} > E_i$, for all i). This observation is referred to as 'the bracketing theorem'.

Variational methods, in particular the linear variational method, are the most widely used approximation techniques in quantum chemistry. To implement such a method one needs to know the Hamiltonian H whose energy levels are sought and one needs to construct a trial wavefunction in which some 'flexibility' exists (e.g., as in the linear variational method where the C_J coefficients can be varied). In Section 6 this tool will be used to develop several of the most commonly used and powerful molecular orbital methods in chemistry.

II. Perturbation Theory

[Suggested Extra Reading- Appendix D; Time Independent Perturbation Theory]

Perturbation theory is the second most widely used approximation method in quantum chemistry. It allows one to estimate the splittings and shifts in energy levels and changes in wavefunctions that occur when an external field (e.g., an electric or magnetic field or a field that is due to a surrounding set of 'ligands'- a crystal field) or a field arising when a previously-ignored term in the Hamiltonian is applied to a species whose 'unperturbed' states are known. These 'perturbations' in energies and wavefunctions are expressed in terms of the (complete) set of unperturbed eigenstates.

Assuming that all of the wavefunctions Φ_k and energies E_k^0 belonging to the unperturbed Hamiltonian H^0 are known

$$H^0 \Phi_k = E_k^0 \Phi_k ,$$

and given that one wishes to find eigenstates (ψ_k and E_k) of the perturbed Hamiltonian

$$H=H^0+\lambda V,$$

perturbation theory expresses ψ_k and E_k as power series in the perturbation strength λ:

$$\psi_k = \sum_{n=0}^{\infty} \lambda^n \psi_k^{(n)}$$

$$E_k = \sum_{n=0}^{\infty} \lambda^n E_k^{(n)} .$$

The systematic development of the equations needed to determine the $E_k^{(n)}$ and the $\psi_k^{(n)}$ is presented in Appendix D. Here, we simply quote the few lowest-order results.

The zeroth-order wavefunctions and energies are given in terms of the solutions of the unperturbed problem as follows:

$$\psi_k^{(0)} = \Phi_k \text{ and } E_k^{(0)} = E_k^0.$$

This simply means that one must be willing to identify one of the unperturbed states as the 'best' approximation to the state being sought. This, of course, implies that one must therefore strive to find an unperturbed model problem, characterized by H^0 that represents the true system as accurately as possible, so that one of the Φ_k will be as close as possible to ψ_k.

The first-order energy correction is given in terms of the zeroth-order (i.e., unperturbed) wavefunction as:

$$E_k^{(1)} = <\Phi_k| V | \Phi_k>,$$

which is identified as the average value of the perturbation taken with respect to the unperturbed function Φ_k. The so-called first-order wavefunction $\psi_k^{(1)}$ expressed in terms of the complete set of unperturbed functions $\{\Phi_J\}$ is:

$$\psi_k^{(1)} = \sum_{j\neq k} <\Phi_j| V | \Phi_k>/[E_k^0 - E_j^0] \ |\Phi_j> .$$

The second-order energy correction is expressed as follows:

$$E_k^{(2)} = \sum_{j\neq k} |<\Phi_j| V | \Phi_k>|^2/[E_k^0 - E_j^0] ,$$

and the second-order correction to the wavefunction is expressed as

$$\psi_k^{(2)} = \Sigma_{j\neq k} [E_k^0 - E_j^0]^{-1} \Sigma_{l\neq k}\{<\Phi_j| V | \Phi_l> -\delta_{j,l} E_k^{(1)}\}$$

$$<\Phi_l| V | \Phi_k> [E_k^0 - E_l^0]^{-1} |\Phi_j>.$$

An essential point about perturbation theory is that the energy corrections $E_k^{(n)}$ and wavefunction corrections $\psi_k^{(n)}$ are expressed in terms of integrals over the unperturbed wavefunctions Φ_k involving the perturbation (i.e., $<\Phi_j|V|\Phi_l>$) and the unperturbed energies E_j^0. Perturbation theory is most useful when one has, in hand, the solutions to an unperturbed Schrödinger equation that is reasonably 'close' to the full Schrödinger equation whose solutions are being sought. In such a case, it is likely that low-order corrections will be adequate to describe the energies and wavefunctions of the full problem.

It is important to stress that although the solutions to the full 'perturbed' Schrödinger equation are expressed, as above, in terms of sums over all states of the unperturbed Schrödinger equation, it is improper to speak of the perturbation as creating excited-state species. For example, the polarization of the 1s orbital of the Hydrogen atom caused by the application of a static external electric field of strength *E* along the z-axis is described, in first-order perturbation theory, through the sum

$$\Sigma_{n=2,\infty}\ \varphi_{np_0} <\varphi_{np_0} | E\ e\ r\ \cos\theta\ | 1s> [\ E_{1s} - E_{np_0}\ ]^{-1}$$

over all $p_z = p_0$ orbitals labeled by principal quantum number n. The coefficient multiplying each p_0 orbital depends on the energy gap corresponding to the 1s-to-np 'excitation' as well as the electric dipole integral $<\varphi_{np_0} | E\ er\cos\theta\ | 1s>$ between the 1s orbital and the np_0 orbital.

This sum describes the polarization of the 1s orbital in terms of functions that have p_0 symmetry; by combining an s orbital and p_0 orbitals, one can form a 'hybrid-like' orbital that is nothing but a distorted 1s orbital. The appearance of the excited np_0 orbitals has nothing to do with forming excited states; these np_0 orbitals simply provide a set of functions that can describe the response of the 1s orbital to the applied electric field.

The relative strengths and weaknesses of perturbation theory and the variational method, as applied to studies of the electronic structure of atoms and molecules, are discussed in Section 6.

Chapter 3

The Application of the Schrödinger Equation to the Motions of Electrons and Nuclei in a Molecule Lead to the Chemists' Picture of Electronic Energy Surfaces on Which Vibration and Rotation Occurs and Among Which Transitions Take Place.

I. The Born-Oppenheimer Separation of Electronic and Nuclear Motions

Many elements of chemists' pictures of molecular structure hinge on the point of view that separates the electronic motions from the vibrational/rotational motions and treats couplings between these (approximately) separated motions as 'perturbations'. It is essential to understand the origins and limitations of this separated-motions picture.

To develop a framework in terms of which to understand when such separability is valid, one thinks of an atom or molecule as consisting of a collection of N electrons and M nuclei each of which possesses kinetic energy and among which coulombic potential energies of interaction arise. To properly describe the motions of all these particles, one needs to consider the full Schrödinger equation $H\Psi = E\Psi$, in which the Hamiltonian H contains the sum (denoted H_e) of the kinetic energies of all N electrons and the coulomb potential energies among the N electrons and the M nuclei as well as the kinetic energy T of the M nuclei

$$T = \Sigma_{a=1,M} (- \hbar^2/2m_a) \quad {}_a^2,$$

$$H = H_e + T$$

$$H_e = \Sigma_j \{ (- \hbar^2/2m_e) \quad {}_j^2 - \Sigma_a Z_a e^2/r_{j,a} \} + \Sigma_{j<k} e^2/r_{j,k}$$

$$+ \Sigma_{a < b} Z_a Z_b e^2/R_{a,b}.$$

Here, m_a is the mass of the nucleus a, $Z_a e^2$ is its charge, and $\quad {}_a^2$ is the Laplacian with respect to the three cartesian coordinates of this nucleus (this operator $\quad {}_a^2$ is given in spherical polar coordinates in Appendix A); $r_{j,a}$ is the distance between the jth electron and the ath nucleus, $r_{j,k}$ is the distance between the jth and kth electrons, m_e is the electron's mass, and $R_{a,b}$ is the distance from nucleus a to nucleus b.

The full Hamiltonian H thus contains differential operators over the 3N electronic coordinates (denoted r as a shorthand) and the 3M nuclear coordinates (denoted R as a shorthand). In contrast, the electronic Hamiltonian H_e is a Hermitian differential operator in r-space but <u>not</u> in R-space. Although H_e is indeed a function of the R-variables, it is not a differential operator involving them.

Because H_e is a Hermitian operator in r-space, its eigenfunctions Ψ_i (r|R) obey

$$H_e \Psi_i (r|R) = E_i (R) \Psi_i (r|R)$$

for any values of the R-variables, and form a <u>complete set</u> of functions of r for any values of R. These eigenfunctions and their eigenvalues E_i (R) depend on R only because the potentials appearing in H_e depend on R. The Ψ_i and E_i are the <u>electronic wavefunctions</u> and <u>electronic energies</u> whose evaluations are treated in the next three Chapters.

The fact that the set of $\{\Psi_i\}$ is, in principle, complete in r-space allows the full (electronic and nuclear) wavefunction Ψ to have its r-dependence expanded in terms of the Ψ_i:

$$\Psi(r,R) = \Sigma_i \Psi_i (r|R) \Xi_i (R) .$$

The $\Xi_i(R)$ functions, carry the remaining R-dependence of Ψ and are determined by insisting that Ψ as expressed here obey the full Schrödinger equation:

$$(H_e + T - E) \Sigma_i \Psi_i (r|R) \Xi_i (R) = 0.$$

Projecting this equation against $< \Psi_j (r|R)|$ (integrating only over the electronic coordinates because the Ψ_j are orthonormal only when so integrated) gives:

$$[(E_j(R) - E) \Xi_j (R) + T \Xi_j(R)] = - \Sigma_i \{ < \Psi_j | T | \Psi_i > (R) \Xi_i(R)$$

$$+ \Sigma_{a=1,M} (- \hbar^2/m_a) < \Psi_j | \quad _a | \Psi_i >(R) \cdot \quad _a \Xi_i(R) \},$$

where the (R) notation in $< \Psi_j | T | \Psi_i > (R)$ and $< \Psi_j | \quad _a | \Psi_i >(R)$ has been used to remind one that the integrals < ...> are carried out only over the r coordinates and, as a result, still depend on the R coordinates.

In the **Born-Oppenheimer** (BO) approximation, one neglects the so-called non-adiabatic or non-BO couplings on the right-hand side of the above equation. Doing so yields the following equations for the $\Xi_i(R)$ functions:

$$[(E_j(R) - E) \Xi_j^0 (R) + T \Xi_j^0(R)] = 0,$$

where the superscript in $\Xi_i^0(R)$ is used to indicate that these functions are solutions within the BO approximation only.

These BO equations can be recognized as the equations for the translational, rotational, and vibrational motion of the nuclei on the 'potential energy surface' $E_j (R)$. That is, within the BO picture, the electronic energies $E_j(R)$, considered as functions of the nuclear positions R, provide the potentials on which the nuclei move. The electronic and nuclear-motion aspects of the Schrödinger equation are thereby separated.

A. Time Scale Separation

The physical parameters that determine under what circumstances the BO approximation is accurate relate to the motional time scales of the electronic and vibrational/rotational coordinates.

The range of accuracy of this separation can be understood by considering the differences in time scales that relate to electronic motions and nuclear motions under ordinary circumstances. In most atoms and molecules, the electrons orbit the nuclei at speeds much in excess of even the fastest nuclear motions (the vibrations). As a result, the electrons can adjust 'quickly' to the slow motions of the nuclei. This means it should be possible to develop a model in which the electrons 'follow' smoothly as the nuclei vibrate and rotate.

This picture is that described by the BO approximation. Of course, one should expect large corrections to such a model for electronic states in which 'loosely held' electrons exist. For example, in molecular Rydberg states and in anions, where the outer valence electrons are bound by a fraction of an electron volt, the natural orbit frequencies of these electrons are not much faster (if at all) than vibrational frequencies. In such cases, significant breakdown of the BO picture is to be expected.

B. Vibration/Rotation States for Each Electronic Surface

The BO picture is what gives rise to the concept of a manifold of potential energy surfaces on which vibrational/rotational motions occur.

Even within the BO approximation, motion of the nuclei on the various electronic energy surfaces is different because the nature of the chemical bonding differs from surface to surface. That is, the vibrational/rotational motion on the ground-state surface is certainly not the same as on one of the excited-state surfaces. However, there are a complete set of wavefunctions $\Xi^0_{j,m}$ (R) and energy levels $E^0_{j,m}$ for each surface $E_j(R)$ because $T + E_j(R)$ is a Hermitian operator in R-space for each surface (labelled j):

$$[\ T + E_j(R)\ ]\ \Xi^0_{j,m}\ (R) = E^0_{j,m}\ \Xi^0_{j,m}\ .$$

The eigenvalues $E^0_{j,m}$ must be labelled by the electronic surface (j) on which the motion occurs as well as to denote the particular state (m) on that surface.

II. Rotation and Vibration of Diatomic Molecules

For a diatomic species, the vibration-rotation (V/R) kinetic energy operator can be expressed as follows in terms of the bond length R and the angles θ and φ that describe the orientation of the bond axis relative to a laboratory-fixed coordinate system:

$$T_{V/R} = - \hbar^2/2\mu \{ R^{-2} \partial/\partial R(R^2 \partial/\partial R) - R^{-2} \hbar^{-2} L^2 \},$$

where the square of the rotational angular momentum of the diatomic species is

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

Because the potential E_j (R) depends on R but not on θ or φ, the V/R function $\Xi^0_{j,m}$ can be written as a product of an angular part and an R-dependent part; moreover, because L^2 contains the full angle-dependence of $T_{V/R}$, $\Xi^0_{j,n}$ can be written as

$$\Xi^0_{j,n} = Y_{J,M} (\theta,\varphi) F_{j,J,v} (R).$$

The general subscript n, which had represented the state in the full set of 3M-3 R-space coordinates, is replaced by the three quantum numbers J,M, and v (i.e., once one focuses on the three specific coordinates R,θ, and φ, a total of three quantum numbers arise in place of the symbol n).

Substituting this product form for $\Xi^0_{j,n}$ into the V/R equation gives:

$$- \hbar^2/2\mu \{ R^{-2} \partial/\partial R(R^2 \partial/\partial R) - R^{-2} \hbar^{-2} J(J+1) \} F_{j,J,v} (R)$$

$$+ E_j(R) F_{j,J,v} (R) = E^0_{j,J,v} F_{j,J,v}$$

as the equation for the vibrational (i.e., R-dependent) wavefunction within electronic state j and with the species rotating with J(J+1) $\hbar^2$ as the square of the total angular momentum and a projection along the laboratory-fixed Z-axis of M$\hbar$. The fact that the $F_{j,J,v}$ functions do not depend on the M quantum number derives from the fact that the $T_{V/R}$ kinetic energy operator does not explicitly contain J_Z; only J^2 appears in $T_{V/R}$.

The solutions for which J=0 correspond to vibrational states in which the species has no rotational energy; they obey

$$- \hbar^2/2\mu \{ R^{-2} \partial/\partial R(R^2 \partial/\partial R) \} F_{j,0,v} (R)$$

$$+ E_j(R) F_{j,0,v} (R) = E^0_{j,0,v} F_{j,0,v} .$$

The differential-operator parts of this equation can be simplified somewhat by substituting F= $R^{-1}\chi$ and thus obtaining the following equation for the new function χ:

$$- \hbar^2/2\mu \ \partial/\partial R \ \partial/\partial R \ \chi_{j,0,v} (R) + E_j(R) \ \chi_{j,0,v} (R) = E^0_{j,0,v} \ \chi_{j,0,v} .$$

Solutions for which $J \neq 0$ require the vibrational wavefunction and energy to respond to the presence of the 'centrifugal potential' given by $\hbar^2 J(J+1)/(2\mu R^2)$; these solutions obey the full coupled V/R equations given above.

A. Separation of Vibration and Rotation

It is common, in developing the working equations of diatomic-molecule rotational/vibrational spectroscopy, to treat the coupling between the two degrees of freedom using perturbation theory as developed later in this chapter. In particular, one can expand the centrifugal coupling $\hbar^2 J(J+1)/(2\mu R^2)$ around the equilibrium geometry R_e (which depends, of course, on j):

$$\hbar^2 J(J+1)/(2\mu R^2) = \hbar^2 J(J+1)/(2\mu [R_e^2 \ (1+\Delta R)^2])$$

$$= \hbar^2 \ J(J+1)/(2\mu R_e^2) \ [1 - 2 \ \Delta R + \ldots \ ],$$

and treat the terms containing powers of the bond length displacement ΔR^k as perturbations. The zeroth-order equations read:

$$- \hbar^2/2\mu \ \{ \ R^{-2} \ \partial/\partial R(\ R^2 \ \partial/\partial R) \ \} \ F^0_{j,J,v} (R) + \ E_j(R) \ F^0_{j,J,v} (R)$$

$$+ \hbar^2 \ J(J+1)/(2\mu R_e^2) \ F^0_{j,J,v} = E^0_{j,J,v} \ F^0_{j,J,v} ,$$

and have solutions whose energies separate

$$E^0_{j,J,v} = \hbar^2 \ J(J+1)/(2\mu R_e^2) + E_{j,v}$$

and whose wavefunctions are independent of J (because the coupling is not R-dependent in zeroth order)

$$F^0_{j,J,v} (R) = F_{j,v} (R).$$

Perturbation theory is then used to express the corrections to these zeroth order solutions as indicated in Appendix D.

B. The Rigid Rotor and Harmonic Oscillator

Treatment of the rotational motion at the zeroth-order level described above introduces the so-called 'rigid rotor' energy levels and wavefunctions: $E_J = \hbar^2 J(J+1)/(2\mu R_e^2)$ and $Y_{J,M}(\theta,\varphi)$; these same quantities arise when the diatomic molecule is treated as a rigid rod of length R_e. The spacings between successive rotational levels within this approximation are

$$\Delta E_{J+1,J} = 2hcB(J+1),$$

where the so-called rotational constant B is given in cm^{-1} as

$$B = h/(8\pi^2 c\mu R_e^2) .$$

The rotational level J is (2J+1)-fold degenerate because the energy E_J is independent of the M quantum number of which there are (2J+1) values for each J: M= -J, -J+1, -J+2, ... J-2, J-1, J.

The explicit form of the zeroth-order vibrational wavefunctions and energy levels, $F^0_{j,v}$ and $E^0_{j,v}$, depends on the description used for the electronic potential energy surface $E_j(R)$. In the crudest useful approximation, $E_j(R)$ is taken to be a so-called harmonic potential

$$E_j(R) \approx 1/2\, k_j\, (R-R_e)^2 ;$$

as a consequence, the wavefunctions and energy levels reduce to

$$E^0_{j,v} = E_j(R_e) + \hbar \sqrt{k/\mu}\,(v +1/2), \text{ and}$$

$$F^0_{j,v}(R) = [2^v v!]^{-1/2} (\alpha/\pi)^{1/4} \exp(-\alpha(R-R_e)^2/2)\, H_v(\alpha^{1/2} (R-R_e)),$$

where $\alpha = (k_j\, \mu)^{1/2}/\hbar$ and $H_v(y)$ denotes the Hermite polynomial defined by:

$$H_v(y) = (-1)^v \exp(y^2)\, d^v/dy^v \exp(-y^2).$$

The solution of the vibrational differential equation

$$- \hbar^2/2\mu \{ R^{-2} \partial/\partial R(R^2 \partial/\partial R) \} F_{j,v} (R) + E_j(R) F_{j,v} (R) = E_{j,v} F_{j,v}$$

is treated in EWK, Atkins, and McQuarrie.

These harmonic-oscillator solutions predict evenly spaced energy levels (i.e., no anharmonicity) that persist for all v. It is, of course, known that molecular vibrations display anharmonicity (i.e., the energy levels move closer together as one moves to higher v) and that quantized vibrational motion ceases once the bond dissociation energy is reached.

C. The Morse Oscillator

The Morse oscillator model is often used to go beyond the harmonic oscillator approximation. In this model, the potential $E_j(R)$ is expressed in terms of the bond dissociation energy D_e and a parameter a related to the second derivative k of $E_j(R)$ at R_e $k = (d^2E_j/dR^2) = 2a^2D_e$ as follows:

$$E_j(R) - E_j(R_e) = D_e \{ 1 - \exp(-a(R-R_e)) \}^2 .$$

The Morse oscillator energy levels are given by

$$E^0_{j,v} = E_j(R_e) + \hbar \sqrt{k/\mu} (v+1/2) - \hbar^2/4 (k/\mu D_e) (v+1/2)^2;$$

the corresponding eigenfunctions are also known analytically in terms of hypergeometric functions (see, for example, Handbook of Mathematical Functions, M. Abramowitz and I. A. Stegun, Dover, Inc. New York, N. Y. (1964)). Clearly, the Morse solutions display anharmonicity as reflected in the negative term proportional to $(v+1/2)^2$.

D. Perturbative Treatment of Vibration-Rotation Coupling

III. Rotation of Polyatomic Molecules

To describe the orientations of a diatomic or linear polyatomic molecule requires only two angles (usually termed θ *and* φ*). For any non-linear molecule, three angles (usually* α, β*, and* γ*) are needed. Hence the rotational Schrödinger equation for a non-linear molecule is a differential equation in three-dimensions.*

There are 3M-6 vibrations of a non-linear molecule containing M atoms; a linear molecule has 3M-5 vibrations. The linear molecule requires two angular coordinates to describe its orientation with respect to a laboratory-fixed axis system; a non-linear molecule requires three angles.

A. Linear Molecules

The rotational motion of a linear polyatomic molecule can be treated as an extension of the diatomic molecule case. One obtains the $Y_{J,M}$ (θ,φ) as rotational wavefunctions and, within the approximation in which the centrifugal potential is approximated at the equilibrium geometry of the molecule (R_e), the energy levels are:

$$E^0_J = J(J+1)\, \hbar^2/(2I) .$$

Here the total moment of inertia I of the molecule takes the place of μR_e^2 in the diatomic molecule case

$$I = \Sigma_a\, m_a\, (R_a - R_{CofM})^2;$$

m_a is the mass of atom a whose distance from the center of mass of the molecule is $(R_a - R_{CofM})$. The rotational level with quantum number J is (2J+1)-fold degenerate again because there are (2J+1)
M- values.

B. Non-Linear Molecules

For a non-linear polyatomic molecule, again with the centrifugal couplings to the vibrations evaluated at the equilibrium geometry, the following terms form the rotational part of the nuclear-motion kinetic energy:

$$T_{rot} = \Sigma_{i=a,b,c}\, (J_i^2/2I_i).$$

Here, I_i is the eigenvalue of the moment of inertia tensor:

$$I_{x,x} = \Sigma_a m_a [(R_a-R_{CofM})^2 -(x_a - x_{CofM})^2]$$

$$I_{x,y} = \Sigma_a m_a [(x_a - x_{CofM}) (y_a -y_{CofM})]$$

expressed originally in terms of the cartesian coordinates of the nuclei (a) and of the center of mass in an arbitrary molecule-fixed coordinate system (and similarly for $I_{z,z}$, $I_{y,y}$, $I_{x,z}$ and $I_{y,z}$). The operator J_i corresponds to the component of the total rotational angular momentum **J** along the direction belonging to the i^{th} eigenvector of the moment of inertia tensor.

Molecules for which all three principal moments of inertia (the I_i's) are equal are called 'spherical tops'. For these species, the rotational Hamiltonian can be expressed in terms of the square of the total rotational angular momentum J^2 :

$$T_{rot} = J^2 /2I,$$

as a consequence of which the rotational energies once again become

$$E_J = \hbar^2 J(J+1)/2I.$$

However, the $Y_{J,M}$ are not the corresponding eigenfunctions because the operator J^2 now contains contributions from rotations about three (no longer two) axes (i.e., the three principal axes). The proper rotational eigenfunctions are the $D^J_{M,K}$ (α,β,γ) functions known as 'rotation matrices' (see Sections 3.5 and 3.6 of Zare's book on angular momentum) these functions depend on three angles (the three Euler angles needed to describe the orientation of the molecule in space) and three quantum numbers- J,M, and K. The quantum number M labels the projection of the total angular momentum (as $M\hbar$) along the laboratory-fixed z-axis; $K\hbar$ is the projection along one of the internal principal axes (in a spherical top molecule, all three axes are equivalent, so it does not matter which axis is chosen).

The energy levels of spherical top molecules are $(2J+1)^2$ -fold degenerate. Both the M and K quantum numbers run from -J, in steps of unity, to J; because the energy is independent of M and of K, the degeneracy is $(2J+1)^2$.

Molecules for which two of the three principal moments of inertia are equal are called symmetric top molecules. Prolate symmetric tops have $I_a < I_b = I_c$; oblate symmetric tops have $I_a = I_b < I_c$ (it is convention to order the moments of inertia as $I_a \le I_b \le I_c$).

The rotational Hamiltonian can now be written in terms of J^2 and the component of **J** along the unique moment of inertia's axis as:

$$T_{rot} = J_a^2 (1/2I_a - 1/2I_b) + J^2 /2I_b$$

for prolate tops, and

$$T_{rot} = J_c^2 (1/2I_c - 1/2I_b) + J^2/2I_b$$

for oblate tops. Again, the $D^J_{M,K} (\alpha,\beta,\gamma)$ are the eigenfunctions, where the quantum number K describes the component of the rotational angular momentum **J** along the unique molecule-fixed axis (i.e., the axis of the unique moment of inertia). The energy levels are now given in terms of J and K as follows:

$$E_{J,K} = \hbar^2J(J+1)/2I_b + \hbar^2 K^2 (1/2I_a - 1/2I_b)$$

for prolate tops, and

$$E_{J,K} = \hbar^2J(J+1)/2I_b + \hbar^2K^2 (1/2I_c - 1/2I_b)$$

for oblate tops.

Because the rotational energies now depend on K (as well as on J), the degeneracies are lower than for spherical tops. In particular, because the energies do not depend on M and depend on the square of K, the degeneracies are (2J+1) for states with K=0 and 2(2J+1) for states with |K| > 0; the extra factor of 2 arises for |K| > 0 states because pairs of states with K = |K| and K = |-K| are degenerate.

IV. Summary

This Chapter has shown how the solution of the Schrödinger equation governing the motions and interparticle potential energies of the nuclei and electrons of an atom or molecule (or ion) can be decomposed into two distinct problems: (i) solution of the electronic Schrödinger equation for the electronic wavefunctions and energies, both of which depend on the nuclear geometry and (ii) solution of the vibration/rotation Schrödinger equation for the motion of the nuclei on any one of the electronic energy surfaces. This decomposition into approximately separable electronic and nuclear-motion problems remains an important point of view in chemistry. It forms the basis of many of our models of molecular structure and our interpretation of molecular spectroscopy. It also establishes how we approach the computational simulation of the energy levels of atoms and molecules; we first compute electronic energy levels at a 'grid' of different positions of the nuclei, and we then solve for the motion of the nuclei on a particular energy surface using this grid of data.

The treatment of electronic motion is treated in detail in Sections 2, 3, and 6 where molecular orbitals and configurations and their computer evaluation is covered. The vibration/rotation motion of molecules on BO surfaces is introduced above, but should be treated in more detail in a subsequent course in molecular spectroscopy.

Section Summary

This Introductory Section was intended to provide the reader with an overview of the structure of quantum mechanics and to illustrate its application to several exactly solvable model problems. The model problems analyzed play especially important roles in chemistry because they form the basis upon which more sophisticated descriptions of the electronic structure and rotational-vibrational motions of molecules are built. The variational method and perturbation theory constitute the tools needed to make use of solutions of simpler model problems as starting points in the treatment of Schrödinger equations that are impossible to solve analytically.

In Sections 2, 3, and 6 of this text, the electronic structures of polyatomic molecules, linear molecules, and atoms are examined in some detail. Symmetry, angular momentum methods, wavefunction antisymmetry, and other tools are introduced as needed throughout the text. The application of modern computational chemistry methods to the treatment of molecular electronic structure is included. Given knowledge of the electronic energy surfaces as functions of the internal geometrical coordinates of the molecule, it is possible to treat vibrational-rotational motion on these surfaces. Exercises, problems, and solutions are provided for each Chapter. Readers are strongly encouraged to work these exercises and problems because new material that is used in other Chapters is often developed within this context.