

## 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  $H = E$ , 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

$$T = \sum_{a=1,M} \left( -\frac{\hbar^2}{2m_a} \right) \nabla_a^2,$$

$$H = H_e + T$$

$$H_e = \sum_j \left\{ \left( -\frac{\hbar^2}{2m_e} \right) \nabla_j^2 - \sum_a Z_a e^2 / r_{j,a} \right\} + \sum_{j < k} e^2 / r_{j,k} \\ + \sum_{a < b} Z_a Z_b e^2 / R_{a,b}.$$

Here,  $m_a$  is the mass of the nucleus  $a$ ,  $Z_a e^2$  is its charge, and  $\nabla_a^2$  is the Laplacian with respect to the three cartesian coordinates of this nucleus (this operator  $\nabla_a^2$  is given in spherical polar coordinates in Appendix A);  $r_{j,a}$  is the distance between the  $j^{\text{th}}$  electron and the  $a^{\text{th}}$  nucleus,  $r_{j,k}$  is the distance between the  $j^{\text{th}}$  and  $k^{\text{th}}$  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 not 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  $\psi_i(r|\mathbf{R})$  obey  $H_e \psi_i(r|\mathbf{R}) = E_i(\mathbf{R}) \psi_i(r|\mathbf{R})$

for any values of the R-variables, and form a complete set of functions of r for any values of R. These eigenfunctions and their eigenvalues  $E_i(\mathbf{R})$  depend on R only because the potentials appearing in  $H_e$  depend on R. The  $\psi_i$  and  $E_i$  are the electronic wavefunctions and electronic energies 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  $\Psi$  to have its r-dependence expanded in terms of the  $\psi_i$ :

$$\Psi(r, \mathbf{R}) = \sum_i \psi_i(r|\mathbf{R}) \chi_i(\mathbf{R}).$$

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

$$(H_e + T - E) \Psi = 0.$$

Projecting this equation against  $\langle \psi_j(r|\mathbf{R}) |$  (integrating only over the electronic coordinates because the  $\psi_j$  are orthonormal only when so integrated) gives:

$$[ (E_j(\mathbf{R}) - E) \chi_j(\mathbf{R}) + T \chi_j(\mathbf{R}) ] = - \sum_i \{ \langle \psi_j | T | \psi_i \rangle (\mathbf{R}) \chi_i(\mathbf{R}) + \sum_{a=1, M} ( - \hbar^2 / m_a ) \langle \psi_j | \nabla_a | \psi_i \rangle (\mathbf{R}) \cdot \nabla_a \chi_i(\mathbf{R}) \},$$

where the  $(\mathbf{R})$  notation in  $\langle \psi_j | T | \psi_i \rangle (\mathbf{R})$  and  $\langle \psi_j | \nabla_a | \psi_i \rangle (\mathbf{R})$  has been used to remind one that the integrals  $\langle \dots \rangle$  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  $\chi_i(\mathbf{R})$  functions:

$$[ (E_j(\mathbf{R}) - E) \chi_j^0(\mathbf{R}) + T \chi_j^0(\mathbf{R}) ] = 0,$$

where the superscript in  $\psi_i^0(\mathbf{R})$  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'  $E_j(\mathbf{R})$ . That is, within the BO picture, the electronic energies  $E_j(\mathbf{R})$ , considered as functions of the nuclear positions  $\mathbf{R}$ , 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  $\psi_{j,m}^0(\mathbf{R})$  and energy levels  $E_{j,m}^0$  for each surface  $E_j(\mathbf{R})$  because  $T + E_j(\mathbf{R})$  is a Hermitian operator in  $\mathbf{R}$ -space for each surface (labelled  $j$ ):

$$[T + E_j(\mathbf{R})] \psi_{j,m}^0(\mathbf{R}) = E_{j,m}^0 \psi_{j,m}^0.$$

The eigenvalues  $E_{j,m}^0$  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  $\theta$  and  $\phi$  that describe the orientation of the bond axis relative to a laboratory-fixed coordinate system:

$$T_{V/R} = -\frac{\hbar^2}{2\mu} \left\{ \frac{\partial^2}{\partial R^2} + \frac{1}{R} \left( \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \phi^2} \right) - R^{-2} \hbar^{-2} L^2 \right\},$$

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

$$L^2 = \hbar^2 \left\{ (\sin \theta)^{-1} \frac{\partial^2}{\partial \phi^2} + (\sin \theta)^2 \frac{\partial^2}{\partial \theta^2} + 2 \cos \theta \frac{\partial}{\partial \theta} \frac{\partial}{\partial \phi} \right\}.$$

Because the potential  $E_j(\mathbf{R})$  depends on  $R$  but not on  $\theta$  or  $\phi$ , the V/R function  $\psi_{j,m}^0$  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  $T_{V/R}$ ,  $\psi_{j,n}^0$  can be written as

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

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

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

$$-\frac{\hbar^2}{2\mu} \left\{ \frac{\partial^2}{\partial R^2} + \frac{1}{R} \left( \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \phi^2} \right) - R^{-2} \hbar^{-2} J(J+1) \right\} F_{j,J,v}(R)$$

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

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

$$- \hbar^2/2\mu \left\{ \frac{d^2}{dR^2} + \frac{J(J+1)\hbar^2}{2\mu R^2} \right\} F_{j,0,v}(R)$$

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

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

$$- \hbar^2/2\mu \left\{ \frac{d^2}{dR^2} + \frac{J(J+1)\hbar^2}{2\mu R^2} \right\} \psi_{j,0,v}(R) + E_j(R) \psi_{j,0,v}(R) = E_{j,0,v}^0 \psi_{j,0,v} .$$

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):

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

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

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

$$-\frac{\hbar^2}{2\mu} \left\{ \frac{d^2}{dR^2} + \frac{J(J+1)}{R^2} \right\} F_{j,J,v}^0(R) + E_j(R) F_{j,J,v}^0(R) \\ + \frac{\hbar^2 J(J+1)}{2\mu R_e^2} F_{j,J,v}^0 = E_{j,J,v}^0 F_{j,J,v}^0,$$

and have solutions whose energies separate

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

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

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

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:  $E_J = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}$  and  $Y_{J,M}(\theta, \phi)$ ; 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

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

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

$$B = \frac{h}{8\pi^2 c\mu R_e^2}.$$

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:  $M = -J, -J+1, -J+2, \dots, J-2, J-1, J$ .

The explicit form of the zeroth-order vibrational wavefunctions and energy levels,  $F_{j,v}^0$  and  $E_{j,v}^0$ , 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

$$E_j(R) = 1/2 k_j (R-R_e)^2 ;$$

as a consequence, the wavefunctions and energy levels reduce to

$$E_{j,v}^0 = E_j(R_e) + \hbar \omega_j (v + 1/2), \text{ and}$$

$$F_{j,v}^0(R) = [2^v v! ]^{-1/2} ( \mu / \hbar )^{1/4} \exp(- (R-R_e)^2/2) H_v ( \omega_j^{1/2} (R-R_e)),$$

where  $\omega_j = (k_j \mu)^{1/2}/\hbar$  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

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

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

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

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  $\theta$  and  $\phi$ ). For any non-linear molecule, three angles (usually  $\theta$ ,  $\phi$ , and  $\chi$ ) 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  $Y_{J,M}(\theta, \phi)$  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:

$$E_J^0 = J(J+1) \hbar^2/(2I).$$

Here the total moment of inertia  $I$  of the molecule takes the place of  $\mu R_e^2$  in the diatomic molecule case

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

$m_a$  is the mass of atom  $a$  whose distance from the center of mass of the molecule is  $(R_a - R_{\text{CofM}})$ . 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:

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

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

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

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

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  $\mathbf{J}$  along the direction belonging to the  $i^{\text{th}}$  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  $J^2$  :

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

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  $D^J_{M,K}(\alpha, \beta, \gamma)$  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  $I_a \geq I_b \geq I_c$  ). The rotational Hamiltonian can now be written in terms of  $J^2$  and the component of  $\mathbf{J}$  along the unique moment of inertia's axis as:

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

for prolate tops, and

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

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  $\mathbf{J}$  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:

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

for prolate tops, and

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

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.