

Section 4 Molecular Rotation and Vibration

Chapter 13

Treating the full internal nuclear-motion dynamics of a polyatomic molecule is complicated. It is conventional to examine the rotational movement of a hypothetical "rigid" molecule as well as the vibrational motion of a non-rotating molecule, and to then treat the rotation-vibration couplings using perturbation theory.

I. Rotational Motions of Rigid Molecules

In Chapter 3 and Appendix G the energy levels and wavefunctions that describe the rotation of rigid molecules are described. Therefore, in this Chapter these results will be summarized briefly and emphasis will be placed on detailing how the corresponding rotational Schrödinger equations are obtained and the assumptions and limitations underlying them.

A. Linear Molecules

1. The Rotational Kinetic Energy Operator

As given in Chapter 3, the Schrödinger equation for the angular motion of a rigid (i.e., having fixed bond length R) diatomic molecule is

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

or

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

The Hamiltonian in this problem contains only the kinetic energy of rotation; no potential energy is present because the molecule is undergoing unhindered "free rotation". 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 $\mu = m_1 m_2 / (m_1 + m_2)$.

2. The Eigenfunctions and Eigenvalues

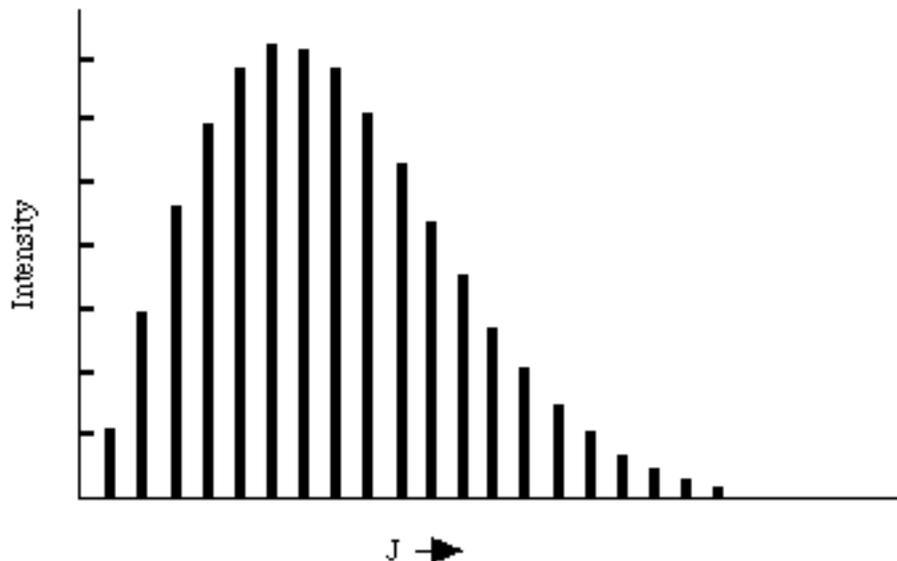
The eigenvalues corresponding to each eigenfunction are straightforward to find because H_{rot} is proportional to the L^2 operator whose eigenvalues have already been determined. The resultant rotational energies are given as:

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

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 rotational constant B (defined as $\hbar^2/2\mu R^2$) depends on the molecule's bond length and reduced mass. Spacings between successive rotational levels (which are of spectroscopic relevance because angular momentum selection rules often restrict J to $1,0$, and -1) are given by

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

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



The energies at which the rotational transitions occur appear to fit the $E = 2B (J+1)$ formula rather well. The intensities of transitions from level J to level $J+1$ vary strongly with J primarily because the population of molecules in the absorbing level varies with J .

These populations P_J are given, when the system is at equilibrium at temperature T , in terms of the degeneracy $(2J+1)$ of the J^{th} level and the energy of this level $B J(J+1)$:

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

where Q is the rotational partition function:

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

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

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

at which the intensity of the rotational transition is expected to reach its maximum.

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

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

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

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

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

B. Non-Linear Molecules

1. The Rotational Kinetic Energy Operator

The rotational kinetic energy operator for a rigid polyatomic molecule is shown in Appendix G to be

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

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

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

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

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos \theta \left[\cot \theta \frac{\partial}{\partial \phi} - (\sin \theta)^{-1} \frac{\partial}{\partial \alpha} \right] - i\hbar \sin \theta \frac{\partial}{\partial \phi}$$

$$J_b = i\hbar \sin \theta \left[\cot \theta \frac{\partial}{\partial \phi} - (\sin \theta)^{-1} \frac{\partial}{\partial \alpha} \right] - i\hbar \cos \theta \frac{\partial}{\partial \phi}$$

$$J_c = -i\hbar \frac{\partial}{\partial \alpha}.$$

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

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

$$= -\frac{2}{\sin^2 \theta} - \cot^2 \theta /$$

$$- (1/\sin^2 \theta) (\frac{2}{\sin^2 \theta} + \frac{2}{\sin^2 \theta} - 2 \cos^2 \theta / \sin^2 \theta),$$

and the component along the lab-fixed Z axis J_Z is $-\hbar^2 / \sin^2 \theta$.

2. The Eigenfunctions and Eigenvalues for Special Cases

a. Spherical Tops

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

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

As a result, the eigenfunctions of H_{rot} are those of J^2 (and J_a as well as J_Z both of which commute with J^2 and with one another; J_Z is the component of \mathbf{J} along the lab-fixed Z-axis and commutes with J_a because $J_Z = -\hbar^2 / \sin^2 \theta$ and $J_a = -\hbar^2 / \sin^2 \theta$ act on different angles).

The energies associated with such eigenfunctions are

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

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

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

$$|J,M,K\rangle = \sqrt{\frac{2J+1}{8}} D_{J,M,K}^*(\theta, \phi, \chi)$$

which obey

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

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

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

b. Symmetric Tops

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

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

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

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

As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a or J_c (and of J_Z), and the corresponding energy levels are:

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

for prolate tops

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

for oblate tops, again for K and M (i.e., J_a or J_c and J_Z quantum numbers, respectively) ranging from $-J$ to J in unit steps. Since the energy now depends on K , these levels are only $2J + 1$ degenerate due to the $2J + 1$ different M values that arise for each J value. The eigenfunctions $|J, M, K\rangle$ are the same rotation matrix functions as arise for the spherical-top case.

c. Asymmetric Tops

The rotational eigenfunctions and energy levels of a molecule for which all three principal moments of inertia are distinct (a so-called **asymmetric top**) can not easily be expressed in terms of the angular momentum eigenstates and the J, M, and K quantum numbers. However, given the three principal moments of inertia I_a , I_b , and I_c , a matrix representation of each of the three contributions to the rotational Hamiltonian

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

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

$$|n\rangle = \sum_{J, M, K} C_{n, J, M, K} |J, M, K\rangle.$$

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

$$|n, J\rangle = \sum_{M, K} C_{n, J, M, K} |J, M, K\rangle.$$

To form the only non-zero matrix elements of H_{rot} within the $|J, M, K\rangle$ basis, one can use the following properties of the rotation-matrix functions (see, for example, Zare's book on Angular Momentum):

$$\langle J, M, K | J_a^2 | J, M, K \rangle = \langle J, M, K | J_b^2 | J, M, K \rangle$$

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

$$\langle J, M, K | J_c^2 | J, M, K \rangle = \hbar^2 K^2,$$

$$\langle J, M, K | J_a^2 | J, M, K \pm 2 \rangle = - \langle J, M, K | J_b^2 | J, M, K \pm 2 \rangle$$

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

$$\langle J, M, K | J_c^2 | J, M, K \pm 2 \rangle = 0.$$

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

II. Vibrational Motion Within the Harmonic Approximation

The simple harmonic motion of a diatomic molecule was treated in Chapter 1, and will not be repeated here. Instead, emphasis is placed on polyatomic molecules whose electronic energy's dependence on the $3N$ Cartesian coordinates of its N atoms can be written (approximately) in terms of a Taylor series expansion about a stable local minimum. We therefore assume that the molecule of interest exists in an electronic state for which the geometry being considered is stable (i.e., not subject to spontaneous geometrical distortion).

The Taylor series expansion of the electronic energy is written as:

$$V(q_k) = V(0) + \sum_k \left(\frac{\partial V}{\partial q_k} \right) q_k + \frac{1}{2} \sum_{j,k} q_j H_{j,k} q_k + \dots$$

where $V(0)$ is the value of the electronic energy at the stable geometry under study, q_k is the displacement of the k_{th} Cartesian coordinate away from this starting position, $(\partial V / \partial q_k)$ is the gradient of the electronic energy along this direction, and the $H_{j,k}$ are the second derivative or Hessian matrix elements along these directions $H_{j,k} = (\partial^2 V / \partial q_j \partial q_k)$. If the starting geometry corresponds to a stable species, the gradient terms will all vanish (meaning this geometry corresponds to a minimum, maximum, or saddle point), and the Hessian matrix will possess $3N - 5$ (for linear species) or $3N - 6$ (for non-linear molecules) positive eigenvalues and 5 or 6 zero eigenvalues (corresponding to 3 translational and 2 or 3 rotational motions of the molecule). If the Hessian has one negative eigenvalue, the geometry corresponds to a transition state (these situations are discussed in detail in Chapter 20).

From now on, we assume that the geometry under study corresponds to that of a stable minimum about which vibrational motion occurs. The treatment of unstable geometries is of great importance to chemistry, but this Chapter deals with vibrations of stable species. For a good treatment of situations under which geometrical instability is expected to occur, see Chapter 2 of the text Energetic Principles of Chemical Reactions by

J. Simons. A discussion of how local minima and transition states are located on electronic energy surfaces is provided in Chapter 20 of the present text.

A. The Newton Equations of Motion for Vibration

1. The Kinetic and Potential Energy Matrices

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

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

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

$$T = \frac{1}{2} \sum_j m_j \dot{q}_j^2,$$

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

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

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

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

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

in terms of which the Newton equations become

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

and the mass-weighted Hessian matrix elements are

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

2. The Harmonic Vibrational Energies and Normal Mode Eigenvectors

Assuming that the x_j undergo some form of sinusoidal time evolution:

$$x_j(t) = x_j(0) \cos(\omega_j t),$$

and substituting this into the Newton equations produces a matrix eigenvalue equation:

$$-\omega_j^2 x_j = \sum_k H'_{j,k} x_k$$

in which the eigenvalues are the squares of the so-called **normal mode** vibrational frequencies and the eigenvectors give the amplitudes of motion along each of the $3N$ mass weighted Cartesian coordinates that belong to each mode.

Within this harmonic treatment of vibrational motion, the total vibrational energy of the molecule is given as

$$E(v_1, v_2, \dots, v_{3N-5 \text{ or } 6}) = \sum_{j=1}^{3N-5 \text{ or } 6} \hbar \omega_j (v_j + 1/2)$$

as sum of $3N-5$ or $3N-6$ independent contributions one for each normal mode. The corresponding total vibrational wavefunction

$$\psi(x_1, x_2, \dots, x_{3N-5 \text{ or } 6}) = \prod_j \psi_{v_j}(x_j)$$

as a product of $3N-5$ or $3N-6$ harmonic oscillator functions $\psi_{v_j}(x_j)$ are for each normal mode within this picture, the energy gap between one vibrational level and another in which one of the v_j quantum numbers is increased by unity (the origin of this "selection rule" is discussed in Chapter 15) is

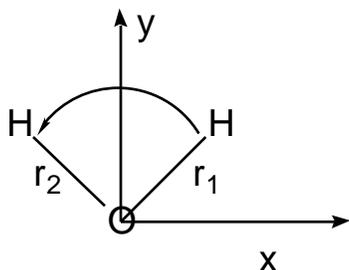
$$E_{v_j+1} - E_{v_j} = \hbar \omega_j$$

The harmonic model thus predicts that the "fundamental" ($v=0 \rightarrow v=1$) and "hot band" ($v=1 \rightarrow v=2$) transition should occur at the same energy, and the overtone ($v=0 \rightarrow v=2$) transitions should occur at exactly twice this energy.

B. The Use of Symmetry

1. Symmetry Adapted Modes

It is often possible to simplify the calculation of the normal mode frequencies and eigenvectors by exploiting molecular point group symmetry. For molecules that possess symmetry, the electronic potential $V(q_j)$ displays symmetry with respect to displacements of symmetry equivalent Cartesian coordinates. For example, consider the water molecule at its C_{2v} equilibrium geometry as illustrated in the figure below. A very small movement of the H_2O molecule's left H atom in the positive x direction (x_L) produces the same change in V as a correspondingly small displacement of the right H atom in the negative x direction ($-x_R$). Similarly, movement of the left H in the positive y direction (y_L) produces an energy change identical to movement of the right H in the positive y direction (y_R).



The equivalence of the pairs of Cartesian coordinate displacements is a result of the fact that the displacement vectors are connected by the point group operations of the C_{2v} group. In particular, reflection of x_L through the yz plane produces $-x_R$, and reflection of y_L through this same plane yields y_R .

More generally, it is possible to combine sets of Cartesian displacement coordinates $\{q_k\}$ into so-called symmetry adapted coordinates $\{Q_{\alpha j}\}$, where the index α labels the irreducible representation and j labels the particular combination of that symmetry. These symmetry adapted coordinates can be formed by applying the point group projection operators to the individual Cartesian displacement coordinates.

To illustrate, again consider the H₂O molecule in the coordinate system described above. The 3N = 9 mass weighted Cartesian displacement coordinates (X_L, Y_L, Z_L, X_O, Y_O, Z_O, X_R, Y_R, Z_R) can be symmetry adapted by applying the following four projection operators:

$$P_{A_1} = 1 + yz + xy + C_2$$

$$P_{b_1} = 1 + yz - xy - C_2$$

$$P_{b_2} = 1 - yz + xy - C_2$$

$$P_{a_2} = 1 - yz - xy + C_2$$

to each of the 9 original coordinates. Of course, one will not obtain 9 x 4 = 36 independent symmetry adapted coordinates in this manner; many identical combinations will arise, and only 9 will be independent.

The independent combination of a₁ symmetry (normalized to produce vectors of unit length) are

$$Q_{a_1,1} = 2^{-1/2} [X_L - X_R]$$

$$Q_{a_1,2} = 2^{-1/2} [Y_L + Y_R]$$

$$Q_{a_1,3} = [Y_O]$$

Those of b₂ symmetry are

$$Q_{b_2,1} = 2^{-1/2} [X_L + X_R]$$

$$Q_{b_2,2} = 2^{-1/2} [Y_L - Y_R]$$

$$Q_{b_2,3} = [X_O],$$

and the combinations

$$Q_{b_1,1} = 2^{-1/2} [Z_L + Z_R]$$

$$Q_{b_1,2} = [Z_O]$$

are of b_1 symmetry, whereas

$$Q_{a_2,1} = 2^{-1/2} [Z_L - Z_R]$$

is of a_2 symmetry.

2. Point Group Symmetry of the Harmonic Potential

These nine $Q_{j,j}$ are expressed as unitary transformations of the original mass weighted Cartesian coordinates:

$$Q_{j,j} = \sum_k C_{j,k} X_k$$

These transformation coefficients $\{C_{j,k}\}$ can be used to carry out a unitary transformation of the 9x9 mass-weighted Hessian matrix. In so doing, we need only form blocks

$$H_{j,l} = \sum_k \sum_{k'} C_{j,k} H_{k,k'} (m_k m_{k'})^{-1/2} C_{l,k'}$$

within which the symmetries of the two modes are identical. The off-diagonal elements

$$H_{j,l} = \sum_k \sum_{k'} C_{j,k} H_{k,k'} (m_k m_{k'})^{-1/2} C_{l,k'}$$

vanish because the potential $V(q_j)$ (and the full vibrational Hamiltonian $H = T + V$) commutes with the C_{2v} point group symmetry operations.

As a result, the 9x9 mass-weighted Hessian eigenvalue problem can be subdivided into two 3x3 matrix problems (of a_1 and b_2 symmetry), one 2x2 matrix of b_1 symmetry

and one 1x1 matrix of a_2 symmetry. For example, the a_1 symmetry block $H_{j,1}^{a_1}$ is formed as follows:

$$\begin{array}{ccccccc}
 \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 & & & & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\
 & m^{-1}H \frac{2v}{x_L^2} & & m^{-1}H \frac{2v}{x_L x_R} & & (m_H m_O)^{-1/2} \frac{2v}{x_L x_O} & & & \\
 & m^{-1}H \frac{2v}{x_R x_L} & & m^{-1}H \frac{2v}{x_R^2} & & (m_H m_O)^{-1/2} \frac{2v}{x_R x_O} & & & \\
 & (m_H m_O)^{-1/2} \frac{2v}{x_O x_L} & & (m_H m_O)^{-1/2} \frac{2v}{x_O x_R} & & m^{-1}O \frac{2v}{x_O^2} & & & \\
 0 & 0 & 1 & & & & & & 0 & 0 & 1
 \end{array}$$

The b_2 , b_1 and a_2 blocks are formed in a similar manner. The eigenvalues of each of these blocks provide the squares of the harmonic vibrational frequencies, the eigenvectors provide the normal mode displacements as linear combinations of the symmetry adapted $\{Q_j\}$.

Regardless of whether symmetry is used to block diagonalize the mass-weighted Hessian, six (for non-linear molecules) or five (for linear species) of the eigenvalues will equal zero. The eigenvectors belonging to these zero eigenvalues describe the 3 translations and 2 or 3 rotations of the molecule. For example,

$$\frac{1}{\sqrt{3}} [X_L + X_R + X_O]$$

$$\frac{1}{\sqrt{3}} [Y_L + Y_R + Y_O]$$

$$\frac{1}{\sqrt{3}} [Z_L + Z_R + Z_O]$$

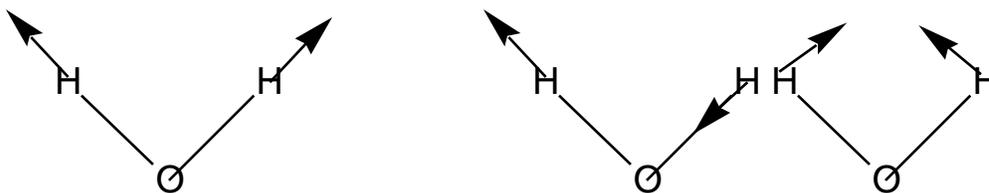
are three translation eigenvectors of b_2 , a_1 and b_1 symmetry, and

$$\frac{1}{\sqrt{2}} (Z_L - Z_R)$$

is a rotation (about the Y-axis in the figure shown above) of a_2 symmetry. This rotation vector can be generated by applying the a_2 projection operator to Z_L or to Z_R . The fact that rotation about the Y-axis is of a_2 symmetry is indicated in the right-hand column of the C_{2v}

character table of Appendix E via the symbol R_Z (n.b., care must be taken to realize that the axis convention used in the above figure is different than that implied in the character table; the latter has the Z -axis out of the molecular plane, while the figure calls this the X -axis). The other two rotations are of b_1 and b_2 symmetry (see the C_{2v} character table of Appendix E) and involve spinning of the molecule about the X - and Z - axes of the figure drawn above, respectively.

So, of the 9 cartesian displacements, 3 are of a_1 symmetry, 3 of b_2 , 2 of b_1 , and 1 of a_2 . Of these, there are three translations (a_1 , b_2 , and b_1) and three rotations (b_2 , b_1 , and a_2). This leaves two vibrations of a_1 and one of b_2 symmetry. For the H_2O example treated here, the three non zero eigenvalues of the mass-weighted Hessian are therefore of a_1 , b_2 , and a_1 symmetry. They describe the symmetric and asymmetric stretch vibrations and the bending mode, respectively as illustrated below.



The method of vibrational analysis presented here can work for any polyatomic molecule. One knows the mass-weighted Hessian and then computes the non-zero eigenvalues which then provide the squares of the normal mode vibrational frequencies. Point group symmetry can be used to block diagonalize this Hessian and to label the vibrational modes according to symmetry.

III. Anharmonicity

The electronic energy of a molecule, ion, or radical at geometries near a stable structure can be expanded in a Taylor series in powers of displacement coordinates as was done in the preceding section of this Chapter. This expansion leads to a picture of uncoupled harmonic vibrational energy levels

$$E(v_1 \cdots v_{3N-5 \text{ or } 6}) = \sum_{j=1}^{3N-5 \text{ or } 6} \hbar \nu_j (v_j + 1/2)$$

and wavefunctions

$$\psi(x_1 \cdots x_{3N-5 \text{ or } 6}) = \prod_{j=1}^{3N-5 \text{ or } 6} \psi_j(x_j).$$

The spacing between energy levels in which one of the normal-mode quantum numbers increases by unity

$$E_{v_j} = E(\cdots v_j+1 \cdots) - E(\cdots v_j \cdots) = \hbar \omega_j$$

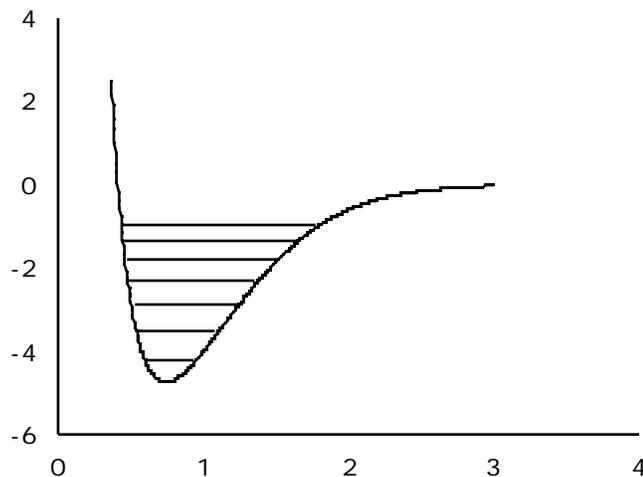
is predicted to be independent of the quantum number v_j . This picture of evenly spaced energy levels

$$E_0 = E_1 = E_2 = \cdots$$

is an incorrect aspect of the harmonic model of vibrational motion, and is a result of the quadratic model for the potential energy surface $V(x_j)$.

A. The Expansion of $E(v)$ in Powers of $(v+1/2)$.

Experimental evidence clearly indicates that significant deviations from the harmonic oscillator energy expression occur as the quantum number v_j grows. In Chapter 1 these deviations were explained in terms of the diatomic molecule's true potential $V(R)$ deviating strongly from the harmonic $1/2k (R-R_e)^2$ potential at higher energy (and hence larger $R-R_e$) as shown in the following figure.



At larger bond lengths, the true potential is "softer" than the harmonic potential, and eventually reaches its asymptote which lies at the dissociation energy D_e above its minimum. This negative deviation of the true $V(R)$ from $1/2 k(R-R_e)^2$ causes the true vibrational energy levels to lie below the harmonic predictions.

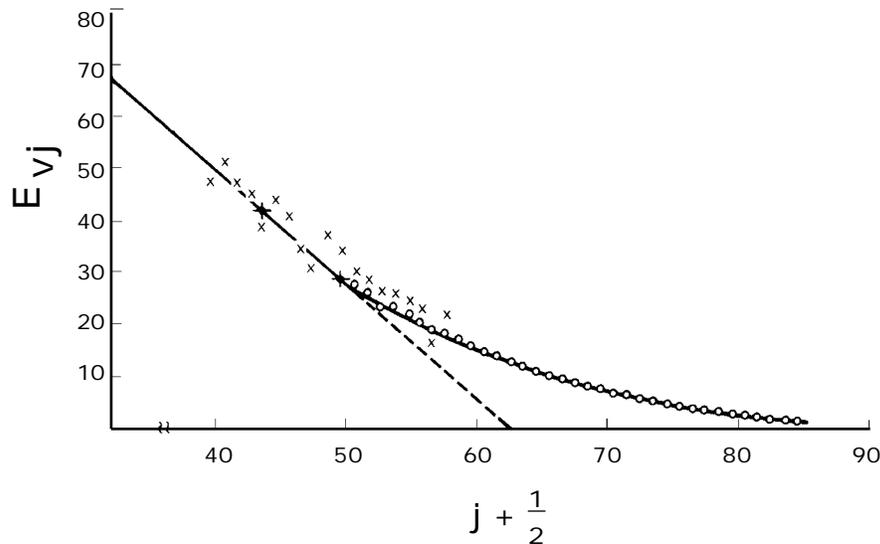
It is convention to express the experimentally observed vibrational energy levels, along each of the $3N-5$ or 6 independent modes, as follows:

$$E(v_j) = \hbar \left[\omega_j (v_j + 1/2) - (x_j) \omega_j (v_j + 1/2)^2 + (y_j) \omega_j (v_j + 1/2)^3 + (z_j) \omega_j (v_j + 1/2)^4 + \dots \right]$$

The first term is the harmonic expression. The next is termed the first anharmonicity; it (usually) produces a negative contribution to $E(v_j)$ that varies as $(v_j + 1/2)^2$. The spacings between successive v_j and $v_j + 1$ energy levels is then given by:

$$\begin{aligned} E_{v_j} &= E(v_j + 1) - E(v_j) \\ &= \hbar \left[\omega_j - 2(x_j) \omega_j (v_j + 1) + \dots \right] \end{aligned}$$

A plot of the spacing between neighboring energy levels versus v_j should be linear for values of v_j where the harmonic and first overtone terms dominate. The slope of such a plot is expected to be $-2\hbar(x_j)\omega_j$ and the small $-v_j$ intercept should be $\hbar[\omega_j - 2(x_j)\omega_j]$. Such a plot of experimental data, which clearly can be used to determine the ω_j and (x_j) parameter of the vibrational mode of study, is shown in the figure below.



B. The Birge-Sponer Extrapolation

These so-called Birge-Sponer plots can also be used to determine dissociation energies of molecules. By linearly extrapolating the plot of experimental E_{v_j} values to large v_j values, one can find the value of v_j at which the spacing between neighboring vibrational levels goes to zero. This value $v_{j, \max}$ specifies the quantum number of the last bound vibrational level for the particular potential energy function $V(x_j)$ of interest. The dissociation energy D_e can then be computed by adding to $1/2\hbar \omega_j$ (the zero point energy along this mode) the sum of the spacings between neighboring vibrational energy levels from $v_j = 0$ to $v_j = v_{j, \max}$:

$$D_e = 1/2\hbar \omega_j + \sum_{v_j = 0}^{v_{j, \max}} E_{v_j}.$$

Since experimental data are not usually available for the entire range of v_j values (from 0 to $v_{j, \max}$), this sum must be computed using the anharmonic expression for E_{v_j} :

$$E_{v_j} = \hbar \left[\omega_j - 2(x_j) \omega_j (v_j + 1/2) + \dots \right].$$

Alternatively, the sum can be computed from the Birge-Sponer graph by measuring the area under the straight-line fit to the graph of E_{v_j} or ν_j from $v_j = 0$ to $v_j = v_{j,\max}$.

This completes our introduction to the subject of rotational and vibrational motions of molecules (which applies equally well to ions and radicals). The information contained in this Section is used again in Section 5 where photon-induced transitions between pairs of molecular electronic, vibrational, and rotational eigenstates are examined. More advanced treatments of the subject matter of this Section can be found in the text by Wilson, Decius, and Cross, as well as in Zare's text on angular momentum.