Chapter 3
Characteristics of energy surfaces

3.1 Strategies for geometry optimization

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

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

$$V(q_k) = V(0) + \sum_k (\partial V/\partial q_k)q_k + 1/2 \sum_{j,k} q_j H_{j,k} q_k + \cdots. \tag{3.1}$$

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

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

$$V(q_k) = V(0) + \sum_k g_K q_k \tag{3.2}$$

suggests that one should choose "step" elements q_k that are opposite in sign from that of the corresponding gradient elements $g_k = (\partial V/\partial q_k)$. The magnitude of
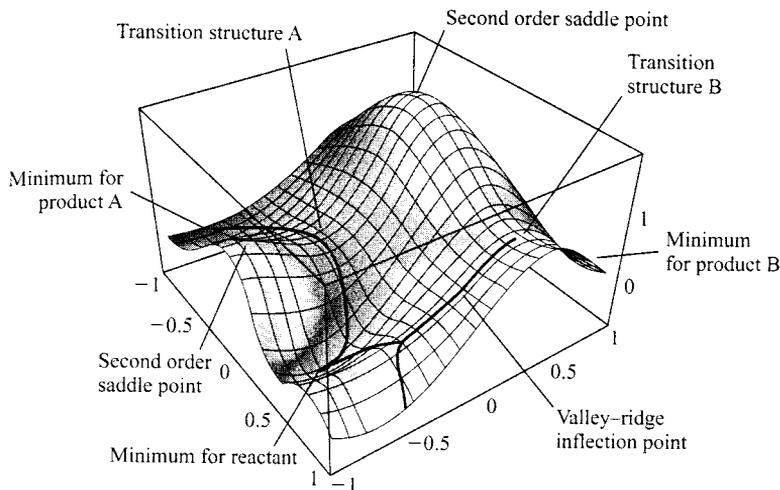
Transition structure A

Second order saddle point

Transition structure B

Minimum for product A

Minimum for product B

Second order saddle point

Valley–ridge inflection point

Minimum for reactant

-1

-0.5

0

0.5

1

1

0.5

0

-0.5

-1

1

0

Figure 3.1

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

the step elements is usually kept small in order to remain within the "trust radius" within which the linear approximation to V is valid to some predetermined desired precision.

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

$$V(q_k) = V(0) + \sum_k g_k q_k + 1/2 \sum_{j,k} q_j H_{j,k} q_k \qquad (3.3)$$

in matrix-vector notation

$$V(\mathbf{q}) = V(0) + \mathbf{q}^T \cdot \mathbf{g} + 1/2 \mathbf{q}^T \cdot \mathbf{H} \cdot \mathbf{q} \qquad (3.4)$$

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

$$V(\mathbf{q}) = V(0) + \mathbf{g}^T \mathbf{U} \mathbf{U}^T \mathbf{q} + 1/2 \mathbf{q}^T \mathbf{U} \mathbf{U}^T \mathbf{H} \mathbf{U} \mathbf{U}^T \mathbf{q}. \qquad (3.5)$$

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

$$(\mathbf{U}^T \mathbf{H} \mathbf{U})_{k,l} = \delta_{k,l} \lambda_k \qquad (3.6)$$

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

the array $\mathbf{U}$ that brings $\mathbf{H}$ to diagonal form:

$$\sum_l H_{k,l} U_{l,m} = \lambda_m U_{k,m}. \tag{3.7}$$

Therefore, if we define

$$Q_m = \sum_k U_{m,k}^\mathrm{T} q_k \quad \text{and} \quad G_m = \sum_k U_{m,k}^T g_k \tag{3.8}$$

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

$$V(q_k) = V(0) + \sum_m G_m^\mathrm{T} Q_m + 1/2 \sum_m Q_m \lambda_m Q_m. \tag{3.9}$$

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

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

$$Q_m = -G_m/\lambda_m; \tag{3.10}$$

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

$$V(\text{after step}) = V(0) + \sum_m G_m^\mathrm{T}(-G_m/\lambda_m) + 1/2 \sum_m \lambda_m(-G_m/\lambda_m)^2$$
$$= V(0) - 1/2 \sum_m \lambda_m(-G_m/\lambda_m)^2. \tag{3.11}$$

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

However, if one or more of the λ_m are negative at the current geometry, one is in a region of the energy surface that is not close to a minimum. In fact, if only one λ_m is negative, one anticipates being near a transition state (at which all gradient components vanish and all but one λ_m are positive with one λ_m negative). In such

a case, the above analysis suggests taking a step $Q_m = -G_m/\lambda_m$ along all of the modes having positive λ_m, but taking a step of opposite direction $Q_n = +G_n/\lambda_n$ along the direction having negative λ_n.

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

$$Q_m = \sum_k U_{m,k}^T q_k \qquad (3.12)$$

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

$$q_k = \sum_m U_{k,m} Q_m \qquad (3.13)$$

to compute the desired Cartesian step components.

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

(i)   one has a molecule containing "soft modes" (i.e., degrees of freedom along which the energy varies little), or
(ii) one moves from a region of negative curvature into a region of positive curvature (or vice versa) – in such cases, the curvature must move through or near zero.

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

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

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

functions Ψ_1 and Ψ_2 that more accurately represent the eigenstates. one usually forms linear combinations of Φ_1 and Φ_2,

$$\Psi_K = C_{K,1}\Phi_1 + C_{K,2}\Phi_2 \qquad (3.14)$$

from which a 2×2 matrix eigenvalue problem arises:

$$\begin{vmatrix} H_{1,1} - E & H_{1,2} \\ H_{2,1} & H_{2,2} - E \end{vmatrix} = 0. \qquad (3.15)$$

This quadratic equation has two solutions

$$2E_\pm = (H_{1,1} + H_{2,2}) \pm \sqrt{(H_{1,1} - H_{2,2})^2 + 4H_{1,2}^2}. \qquad (3.16)$$

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

$$H_{1,1} = H_{2,2} \qquad (3.17)$$

and

$$H_{1,2} = 0. \qquad (3.18)$$

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

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

very active development. Locating these intersections is an important ingredient
when one is interested in studying, for example, photochemical reactions in which
the reactants and products may move from one electronic surface to another.

3.2 Normal modes of vibration

Having seen how one can use information about the gradients and Hes-
sians on a Born–Oppenheimer surface to locate geometries correspond-
ing to stable species, let us now move on to see how this same data are
used to treat vibrations on this surface.

For a polyatomic molecule whose electronic energy depends on the $3N$
Cartesian coordinates of its N atoms, the potential energy V can be expressed
(approximately) in terms of a Taylor series expansion about any of the local
minima. Of course, different local minima (i.e., different isomers) will have
different values for the equilibrium coordinates and for the derivatives of the
energy with respect to these coordinates. The Taylor series expansion of the
electronic energy is written as

$$V(q_k) = V(0) + \sum_k (\partial V / \partial q_k) q_k + 1/2 \sum_{j,k} q_j H_{j,k} q_k + \cdots, \qquad (3.19)$$

where $V(0)$ is the value of the electronic energy at the stable geometry under study,
q_k is the displacement of the kth 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 di-
rections, $H_{j,k} = (\partial^2 V / \partial q_j \partial q_k)$. If the geometry corresponds to a stable species,
the gradient terms will all vanish (meaning this geometry corresponds to a min-
imum, 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 geom-
etry corresponds to a transition state. From now on, we assume that the geometry
under study corresponds to that of a stable minimum about which vibrational
motion occurs. The treatment of unstable geometries is of great importance to
chemistry, but this material will be limited to vibrations of stable species.

3.2.1 The Newton equations of motion for vibration

The kinetic and potential energy matrices

Truncating the Taylor series at the quadratic terms (assuming these terms dom-
inate because only small displacements from the equilibrium geometry are of

interest), one has the so-called harmonic potential:

$$V(q_k) = V(0) + 1/2 \sum_{j,k} q_j H_{j,k} q_k. \tag{3.20}$$

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

$$T = 1/2 \sum_j m_j \dot{q}_j^2, \tag{3.21}$$

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 jth Cartesian coordinate resides. The Newton equations thus obtained are

$$m_j \ddot{q} = -\sum_k H_{j,k} q_k, \tag{3.22}$$

where the force along the jth 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

$$x_j = q_j (m_j)^{1/2}. \tag{3.23}$$

in terms of which the above Newton equations become

$$\ddot{x}_j = -\sum_k H'_{j,k} x_k \tag{3.24}$$

and the mass-weighted Hessian matrix elements are

$$H'_{j,k} = H_{j,k} (m_j m_k)^{-1/2}. \tag{3.25}$$

The harmonic vibrational energies and normal mode eigenvectors

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

$$x_j(t) = x_j(0) \cos(\omega t), \tag{3.26}$$

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

$$\omega^2 x_j = \sum_k H'_{j,k} x_k \tag{3.27}$$

in which the eigenvalues are the squares of the so-called normal mode vibrational frequencies and the eigenvectors give the amplitudes of motion along each of the $3N$ mass-weighted Cartesian coordinates that belong to each mode. Hence, to perform a normal-mode analysis of a molecule, one forms the mass-weighted

Hessian matrix and then finds the $3N - 5$ or $3N - 6$ non-zero eigenvalues ω_j^2 as well as the corresponding eigenvectors $x_k^{(j)}$.

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

$$E(v_1, v_2, \ldots, v_{3N-5 \text{ or } 6}) = \sum_{j=1}^{3N-5 \text{ or } 6} \hbar\omega_j(v_j + 1/2), \tag{3.28}$$

a sum of $3N - 5$ or $3N - 6$ independent contributions, one for each normal mode. The corresponding total vibrational wave function

$$\Psi = \prod_{j=1.3N-5 \text{ or } 6} \psi_{v_j}\left(x^{(j)}\right) \tag{3.29}$$

is a product of $3N - 5$ or $3N - 6$ harmonic oscillator functions $\psi_{v_j}(x^{(j)})$, one for each normal mode. The energy gap between one vibrational level and another in which one of the v_j quantum numbers is increased by unity (i.e., for fundamental vibrational transitions) is

$$\Delta E_{v_j \to v_j - 1} = \hbar\omega_j. \tag{3.30}$$

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

3.2.2 The use of symmetry

Symmetry adapted modes

It is often possible to simplify the calculation of the normal mode frequencies and eigenvectors by exploiting molecular point group symmetry. For molecules that possess symmetry at a particular stable geometry, the electronic potential $V(q_j)$ displays symmetry with respect to displacements of symmetry equivalent Cartesian coordinates. For example, consider the water molecule at its C_{2v} equilibrium geometry as illustrated in Fig. 3.2. A very small movement of the H_2O molecule's left H atom in the positive x direction (Δx_L) produces the same change in the potential V as a correspondingly small displacement of the right H atom in the negative x direction ($-\Delta x_R$). Similarly, movement of the left H in the positive y direction (Δy_L) produces an energy change identical to movement of the right H in the positive y direction (Δy_R).

The equivalence of the pairs of Cartesian coordinate displacements is a result of the fact that the displacement vectors are connected by the point group operations of the C_{2v} group. In particular, reflection of Δx_L through the yz plane (the two planes are depicted in Fig. 3.3) produces $-\Delta x_R$, and reflection of Δy_L through this same plane yields Δy_R.
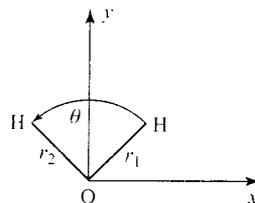

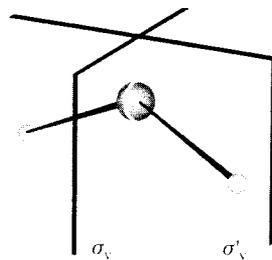**Figure 3.2** Water molecule showing its two bond lengths and bond angle.

Figure 3.3 Two planes of symmetry of the water molecule.

More generally, it is possible to combine sets of Cartesian displacement coordinates $\{q_k\}$ into so-called symmetry adapted coordinates $\{Q_{\Gamma,j}\}$, where the index Γ labels the irreducible representation in the appropriate point group and j labels the particular combination of that symmetry. These symmetry adapted coordinates can be formed by applying the point group projection operators (that are treated in detail in Chapter 4) to the individual Cartesian displacement coordinates.

To illustrate, again consider the H_2O molecule in the coordinate system described above. The $3N = 9$ mass weighted Cartesian displacement coordinates $(X_L, Y_L, Z_L, X_O, Y_O, Z_O, X_R, Y_R, Z_R)$ can be symmetry adapted by applying the following 4 projection operators:

$$P_{a_1} = 1 + \sigma_{yz} + \sigma_{xy} + C_2, \tag{3.31}$$
$$P_{b_1} = 1 + \sigma_{yz} - \sigma_{xy} - C_2, \tag{3.32}$$
$$P_{b_2} = 1 - \sigma_{yz} + \sigma_{xy} - C_2, \tag{3.33}$$
$$P_{a_2} = 1 - \sigma_{yz} - \sigma_{xy} + C_2, \tag{3.34}$$

to each of the 9 original coordinates (the symbol σ denotes reflection through a plane and C_2 means rotation about the molecule's C_2 axis). Of course, one will *not* obtain $9 \times 4 = 36$ independent symmetry adapted coordinates in this manner; many identical combinations will arise, and only 9 will be independent.

The independent combinations of a_1 *symmetry* (normalized to produce vectors of unit length) are

$$Q_{a_1,1} = 2^{-1/2}[X_L - X_R], \tag{3.35}$$
$$Q_{a_1,2} = 2^{-1/2}[Y_L + Y_R], \tag{3.36}$$
$$Q_{a_1,3} = [Y_O]. \tag{3.37}$$

Those of b_2 symmetry are

$$Q_{b_2,1} = 2^{-1/2}[X_L + X_R], \tag{3.38}$$
$$Q_{b_2,2} = 2^{-1/2}[Y_L - Y_R], \tag{3.39}$$
$$Q_{b_2,3} = [X_O], \tag{3.40}$$

and the combinations

$$Q_{b_1,1} = 2^{-1/2}[Z_L + Z_R], \tag{3.41}$$
$$Q_{b_1,2} = [Z_O] \tag{3.42}$$

are of b_1 symmetry, whereas

$$Q_{a_2,1} = 2^{-1/2}[Z_L - Z_R] \tag{3.43}$$

is of a_2 symmetry.

Point group symmetry of the harmonic potential

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

$$Q_{\Gamma,j} = \sum_k C_{\Gamma,j,k} X_k. \tag{3.44}$$

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

$$H_{j,l}^{\Gamma} = \sum_{k,k'} C_{\Gamma,j,k} H_{k,k'} (m_k m_{k'})^{-1/2} C_{\Gamma,l,k'} \tag{3.45}$$

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

$$H_{j,l}^{\Gamma\Gamma'} = \sum_{k,k'} C_{\Gamma,j,k} H_{k,k'} (m_k m_{k'})^{-1/2} C_{\Gamma,l,k'} \tag{3.46}$$

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 9×9 mass-weighted Hessian eigenvalue problem can be subdivided into two 3×3 matrix problems (of a_1 and b_2 symmetry), one 2×2 matrix of b_1 symmetry and one 1×1 matrix of a_2 symmetry. The eigenvalues of each of these blocks provide the squares of the harmonic vibrational frequencies, the eigenvectors provide the normal mode displacements as linear combinations of the symmetry adapted $\{Q_{\Gamma,j}\}$.

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

$$\frac{1}{\sqrt{3}}[X_L + X_R + X_O], \tag{3.47}$$

$$\frac{1}{\sqrt{3}}[Y_L + Y_R + Y_O], \tag{3.48}$$

$$\frac{1}{\sqrt{3}}[Z_L + Z_R + Z_O] \tag{3.49}$$

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

$$\frac{1}{\sqrt{2}}(Z_L - Z_R) \tag{3.50}$$

is a rotation (about the y-axis in Fig. 3.2) of a_2 symmetry. This rotation vector can be generated by applying the a_2 projection operator to Z_L or to Z_R. The other

Figure 3.4 Symmetric and asymmetric stretch modes and bending mode of water.
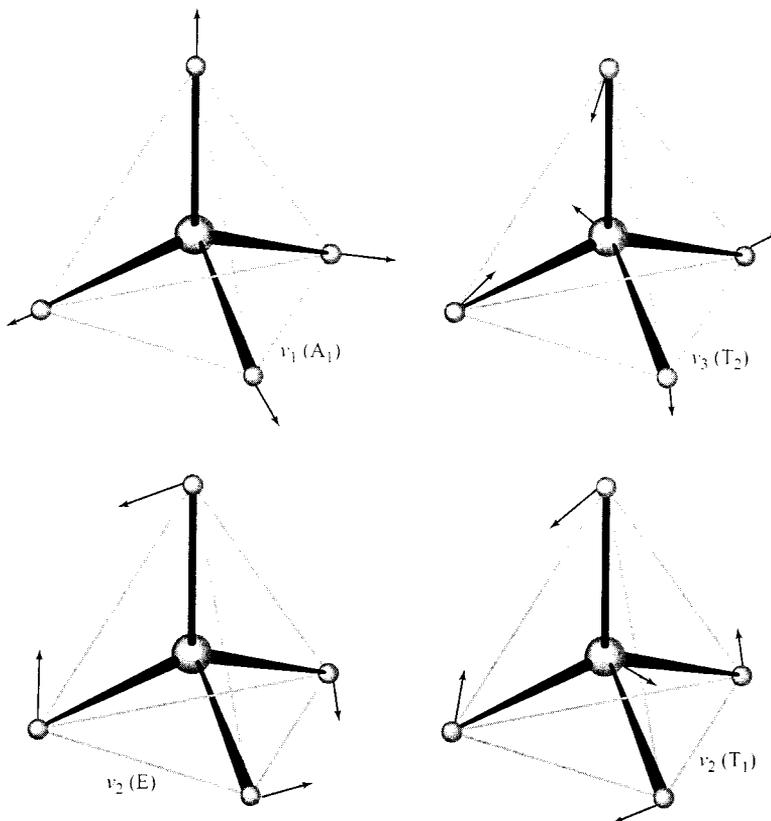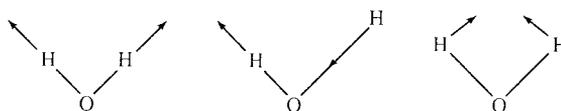

Figure 3.5 Symmetries of vibrations of methane.

two rotations are of b_1 and b_2 symmetry and involve spinning of the molecule about the x- and z-axes of Fig. 3.2, respectively.

So, of the nine Cartesian displacements, three are of a_1 symmetry, three of b_2, two of b_1, and one of a_2. Of these, there are three translations (a_1, b_2, and b_1) and three rotations (b_2, b_1, and a_2). This leaves two vibrations of a_1 and one of b_2 symmetry. For the H_2O example treated here, the three non-zero eigenvalues of the mass-weighted Hessian are therefore of a_1, b_2, and a_1 symmetry. They describe the symmetric and asymmetric stretch vibrations and the bending mode, respectively, as illustrated in Fig. 3.4.

The method of vibrational analysis presented here can work for any polyatomic molecule. One knows the mass-weighted Hessian and then computes the non-zero eigenvalues, which then provide the squares of the normal mode vibrational frequencies. Point group symmetry can be used to block diagonalize this Hessian and to label the vibrational modes according to symmetry as we show in Fig. 3.5 for the CH_4 molecule in tetrahedral symmetry.