# Chapter 3. Characteristics of Energy Surfaces

*Born-Oppenheimer energy surfaces (or the empirical functions often used to represent them) possess important critical points that detail the properties of stable molecular structures, transition states, intersection seams, and reaction paths, all of which play central roles in the theoretical description of chemical reactions and molecular properties. In this Chapter, you will learn about these special points on the surfaces, how to find them, and what to do with them once you know them.*

## 3.1. Strategies for Geometry Optimization and Finding Transition States

*The extension of the harmonic and Morse vibrational models to polyatomic 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, but first it is important to describe how one locates the minimum-energy and transition-state geometries on such surfaces.*

### 3.1.1 Finding Local Minima

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 or a geometry that you guessed as a reasonable one for the minimum or transition state that you are seeking):

$$V (q_k) = V(0) + \Sigma_k (\partial V/\partial q_k) q_k + 1/2 \Sigma_{j,k} q_j H_{j,k} q_k + ... \ .$$

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 the Figure 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.
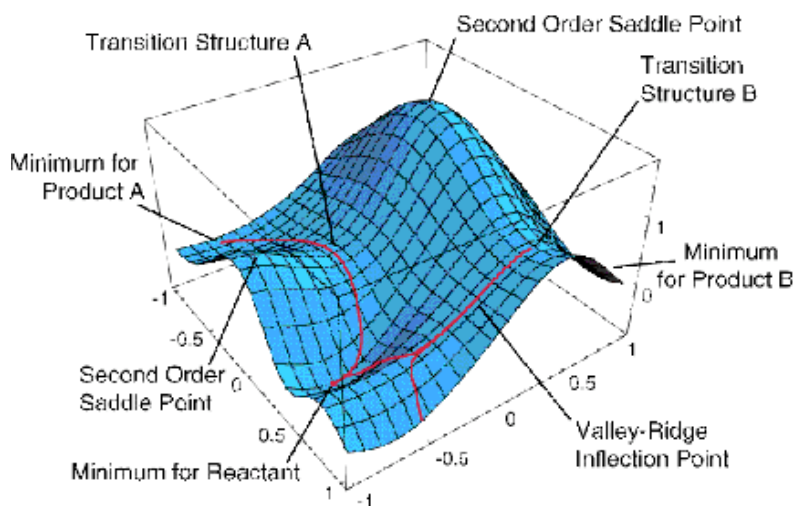


Figure 3.1. Two-dimensional potential surface showing minima, transition states, and paths connecting them.

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, so one is often forced to work without knowing the Hessian matrix elements), the linear approximation

$$V\,(q_k) = V(0) + \Sigma_k\,g_K\,q_k$$

suggests that one should choose "step" elements $q_k$ that are opposite in sign from that of the corresponding gradient elements $g_k = (\partial V/\partial q_k)$ if one wishes to move "downhill" toward a minimum. The magnitude of 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 (i.e., one wants to assure that $\Sigma_k\,g_K\,q_k$ is not too large).

When second derivative data is available, there are different approaches to predicting what step $\{q_k\}$ to take in search of a minimum, and it is within such Hessian-based strategies that the concept of stepping along 3N-6 independent modes arises. We first write the quadratic Taylor expansion

$$V(q_k) = V(0) + \Sigma_k\ g_k\ q_k + 1/2\ \Sigma_{j,k}\ q_j\ H_{j,k}\ q_k$$

in matrix-vector notation

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

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

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

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

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

where $\lambda_k$ are the eigenvalues of the Hessian matrix. 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 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. It can be difficult to properly identify the 5 or 6 translation and rotation eigenvalues of the Hessian because numerical precision issues often cause them to occur as very small positive or negative eigenvalues. If the molecule being studied actually does possess internal (i.e., vibrational) eigenvalues that are very small (e.g., the torsional motion of the methyl group in ethane has a very small energy barrier as a result of which the energy is very weakly dependent on this coordinate), one

has to be careful to properly identify the translation-rotation and internal eigenvalues. By examining the eigenvectors corresponding to all of the low Hessian eigenvalues, one can identify and thus separate the former from the latter. In the remainder of this discussion, I will assume that the rotations and translations have been properly identified and the strategies I discuss will refer to utilizing the remaining 3N-5 or 3N-6 eigenvalues and eigenvectors to carry out a series of geometry "steps" designed to locate energy minima and transition states.

The eigenvectors of $\mathbf{H}$ form the columns of the array $\mathbf{U}$ that brings $\mathbf{H}$ to diagonal form:

$$\Sigma_\lambda \, H_{k,l} \, U_{l,m} = \lambda_m \, U_{k,m}$$

Therefore, if we define

$$Q_m = \Sigma_k \, U^T_{m,k} \, q_k \text{ and } G_m = \Sigma_k \, U^T_{m,k} \, g_k$$

to be the component of the step $\{q_k\}$ and of the gradient along the $m^{th}$ 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:

$$V \, (q_k) = V(0) + \Sigma_m \, G^T_m \, Q_m + 1/2 \, \Sigma_m \, Q_m \, \lambda_m \, Q_m.$$

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 when we are searching for minima (strategies for finding a transition state will be discussed below).

For each eigenmode direction, one can ask for what size 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

$$Q_m = - G_m/\lambda_m \ ;$$

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 $\lambda_m$ values, this indicates that one may be "close" to a minimum on the energy surface (because all $\lambda_m$ 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, much like the gradient-based strategy discussed earlier suggested. 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:

$$V(\text{after step}) = V(0) + \Sigma_m\, G^T_m\, (- G_m/\lambda_m) + 1/2\, \Sigma_m\, \lambda_m\, (- G_m/\lambda_m)^2$$

$$= V(0) -\ 1/2\, \Sigma_m\, \lambda_m\, (- G_m/\lambda_m)^2.$$

This clearly suggests that the step will lead "downhill" in energy along each eigenmode as long as all of the $\lambda_m$ values are positive. For example, if one were to begin with a good estimate for the equilibrium geometries of ethylene and propene, one could place these two molecules at a distance $R_0$ longer than the expected inter-fragment equilibrium distance $R_{vdW}$ in the van der Waals complex formed when they interact. Because both fragments are near their own equilibrium geometries and at a distance $R_0$ at which long-range attractive forces will act to draw them together, a strategy such as outlined above could be employed to locate the van der Waals minimum on their energy surface. This minimum is depicted qualitatively in Fig. 3.1a.
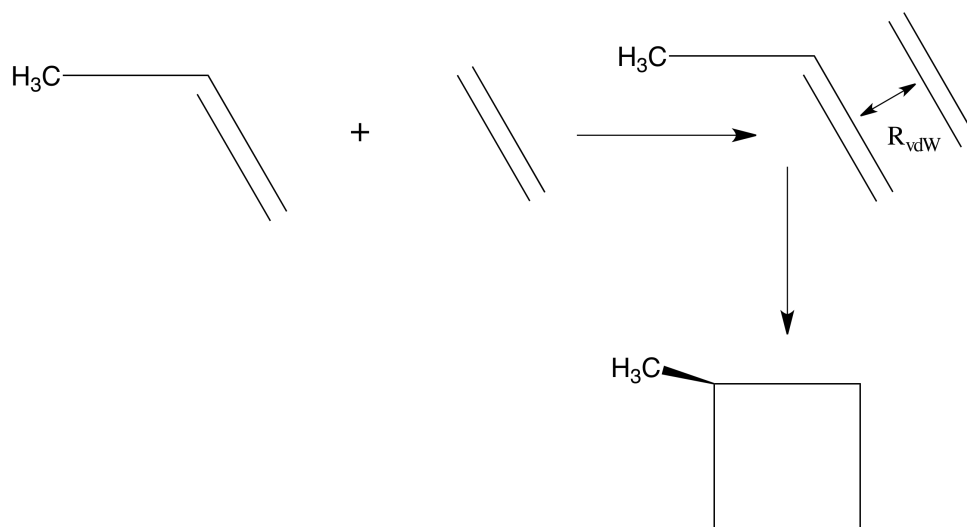
Figure 3.1a Van der Waals complex (upper right) formed between ethylene and propene whose geometry might be located using the prescription outlined above. Product of the [2+2] cyclo-addition reaction, methyl-cyclobutane (lower right).

Beginning at $R_0$, one would find that 3N-6 = 39 of the eigenvalues of the Hessian matrix are non-zero, where N = 15 is the total number of atoms in the ethylene-propene complex. Of these 39 non-zero eigenvalues, three will have eigenvectors describing radial and angular displacements of the two fragments relative to one another; the remaining 36 will describe internal vibrations of the complex. The eigenvalues belonging to the inter-fragment radial and angular displacements may be positive or negative (because you made no special attempt to orient the molecules at optimal angles and you may not have guessed very well at optimal the equilibrium inter-fragment distance), so it would probably be wisest to begin the energy-minimization process by using gradient information to step downhill in energy until one reaches a geometry $R_1$ at which all 39 of the Hessian matrix eigenvalues are positive. From that point on, steps determined by both the gradient and Hessian (i.e., $Q_m = - G_m/\lambda_m$) can be used unless one encounters a geometry at which one of the eigenvalues $\lambda_m$ is very small, in which case the step $Q_m = - G_m/\lambda_m$ along this eigenmode could be unrealistically large. In this case, it would be better to not take $Q_m = - G_m/\lambda_m$ for the step along this particular direction but to take a small step in the direction opposite to the gradient to improve chances of moving downhill. Such small-eigenvalue issues could arise, for example, if the torsion angle of propene's methyl

group happened, during the sequence of geometry steps, to move into a region where eclipsed rather than staggered geometries are accessed. Near eclipsed geometries, the Hessian eigenvalue describing twisting of the methyl group is negative; near staggered geometries, it is positive.

Whenever one or more of the $\lambda_m$ are negative at the current geometry, one is in a region of the energy surface that is not sufficiently close to a minimum to blindly follow the prescription $Q_m = - G_m/\lambda_m$ along all modes. If only one $\lambda_m$ is negative, one anticipates being near a transition state (at which all gradient components vanish and all but one $\lambda_m$ are positive with one $\lambda_m$ 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 $\lambda_m$, but taking a step of opposite direction (e.g., $Q_n = + G_n/\lambda_n$ unless $\lambda_n$ is very small in which case a small step opposite $G_n$ is best) along the direction having negative $\lambda_n$ <u>if</u> one is attempting to move toward a minimum. This is what I recommended in the preceding paragraph when an eclipsed geometry (which is a transition state for rotation of the methyl group) is encountered if one is seeking an energy minimum.

### 3.1.2 Finding Transition States

On the other hand, if one is in a region where one Hessian eigenvalues is negative (and the rest are positive) and if one is seeking to find a transition state, then taking steps $Q_m = - G_m/\lambda_m$ along all of the modes Having positive eigenvalues and taking $Q_n = - G_n/\lambda_n$ along the mode having negative eigenvalue is appropriate. The steps $Q_m = - G_m/\lambda_m$ will act to keep the energy near its minimum along all but one direction, and the step $Q_n = - G_n/\lambda_n$ will move the system uphill in energy along the direction having negative curvature, exactly as one desires when "walking" uphill in a streambed toward a mountain pass.

However, even the procedure just outlined for finding a transition state can produce misleading results unless some extent of chemical intuition is used. Let me give an example to illustrate this point. Let's assume that one wants to find begin near the geometry of the van der Waals complex involving ethylene and propene and to then locate the transition state on the reaction path leading to the [2+2] cyclo-addition products methyl-cyclobutane as also shown in Fig. 3.1a. Consider employing either of

two strategies to begin the "walk" leading from the van der Waals complex to the desired transition state (TS):

1. One could find the lowest (non-translation or non-rotation) Hessian eigenvalue and take a small step uphill along this direction to begin a streambed walk that might lead to the TS. Using the smallest Hessian eigenvalue to identify a direction to explore makes sense because it is along this direction that the energy surface rises least abruptly (at least near the geometry of the reactants).

2. One could move the ethylene radially a bit (say 0.2 Å) closer to the propene to generate an initial geometry to begin the TS search. This makes sense because one knows the reaction must lead to inter-fragment carbon-carbon distances that are much shorter in the methyl-cyclobutane products than in the van der Waals complex.

The first strategy suggested above will likely fail because the series of steps generated by walking uphill along the lowest Hessian eigenmode will produce a path leading from eclipsed to staggered orientation of propene's methyl group. Indeed, this path leads to a TS, but it is not the [2+2] cyclo-addition TS that we want. The take-home lesson here is that uphill streambed walks beginning at a minimum on the reactants' potential energy surface may or may not lead to the desired TS. Such walks are not foolish to attempt, but one should examine the nature of the eigenmode being followed to judge whether displacements along this mode make chemical sense. Clearly, only rotating the methyl group is not a good way to move from ethylene and propene to methyl-cyclobutane.

The second strategy suggested above might succeed, but it would probably still need to be refined. For example, if the displacement of the ethylene toward the propene were too small, one would not have distorted the system enough to move it into a region where the energy surface has negative curvature along the reaction path as it must have as one approaches the TS. So, if the Hessian eigenmodes whose eigenvectors possess substantial inter-fragment radial displacements are all positive, one has probably not moved the two fragments close enough together. Probably the best way to then proceed would be to move the two fragments even closer (or, to move them along a linear

synchronous path[1] connecting the reactants and products) until one finds a geometry at which a negative Hessian eigenvalue's eigenmode has substantial components along what appears to be reasonable for the desired reaction path (i.e., substantial displacements leading to shorter inter-fragment carbon-carbon distances). Once one has found such a geometry, one can use the strategies detailed earlier (e.g., $Q_m = - G_m/\lambda_m$) to then walk uphill along one mode while minimizing along the other modes to move toward the TS. If successful, such a process will lead to the TS at which all components of the gradient vanish and all but one eigenvalue of the Hessian is positive. The take-home lesson of the example is it is wise to try to first find a geometry close enough to the TS to cause the Hessian to have a negative eigenvalue whose eigenvector has substantial character along directions that make chemical sense for the reaction path.

In either a series of steps toward a minimum or toward a TS, 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 the would simply translate or rotate the molecule), one must compute the $\{q_k\}$. To do so, we use the relationship

$$Q_m = \Sigma_k U^T_{m,k} q_k$$

and write its inverse (using the unitary nature of the $\mathbf{U}$ matrix):

$$q_k = \Sigma_m U_{k,m} Q_m$$

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

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[1] This is a series of geometries $\mathbf{R}_x$ defined through a linear interpolation (using a parameter $0 < x < 1$) between the 3N Cartesian coordinates $\mathbf{R}_{reactants}$ belonging to the

i. one has a molecule containing "soft modes" (i.e., degrees of freedom along which the energy varies little), or

ii. as one moves from a region of negative curvature into a region of positive curvature (or vice versa)- in such cases, the 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.

### 3.1.3 Energy Surface Intersections

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. Later in this Chapter, and again 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.

It is sometimes important to find geometries at which two Born-Oppenheimer energy surfaces $V_1(\mathbf{q})$ and $V_2(\mathbf{q})$ intersect because such regions often serve as efficient funnels for trajectories or wave packets evolving on one surface to undergo so-called non-adiabatic transitions to the other surface. Let's spend a few minutes thinking about under what circumstances 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 $\Phi_1$ and $\Phi_2$ 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 $\Psi_1$ and $\Psi_2$ that more accurately represent the eigenstates, one usually forms linear combinations of $\Phi_1$ and $\Phi_2$,

$$\Psi_K = C_{K,1} \Phi_1 + C_{K,2} \Phi_2$$

from which a 2x2 matrix eigenvalue problem arises:

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equilibrium geometry of the reactants and the corresponding coordinates $\mathbf{R}_{products}$ of the products: $\mathbf{R}_x = \mathbf{R}_{reactants} x + (1-x) \mathbf{R}_{products}$

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

This quadratic equation has two solutions

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

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 <u>two</u> identities hold simultaneously (i.e., at the same geometry):

$$H_{1,1} = H_{2,2}$$

and

$$H_{1,2} = 0.$$

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 (e.g., one is a singlet and the other a triplet), 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. For a triatomic molecule with 3N-6 = 3 internal degrees of freedom, this means that surfaces of the same symmetry can cross in a space of dimension 1 (i.e., along

a line) while those of different symmetry can cross in a space of dimension 2 (i.e., in a plane). An example of such a surface intersection is shown in Fig. 3.1c.
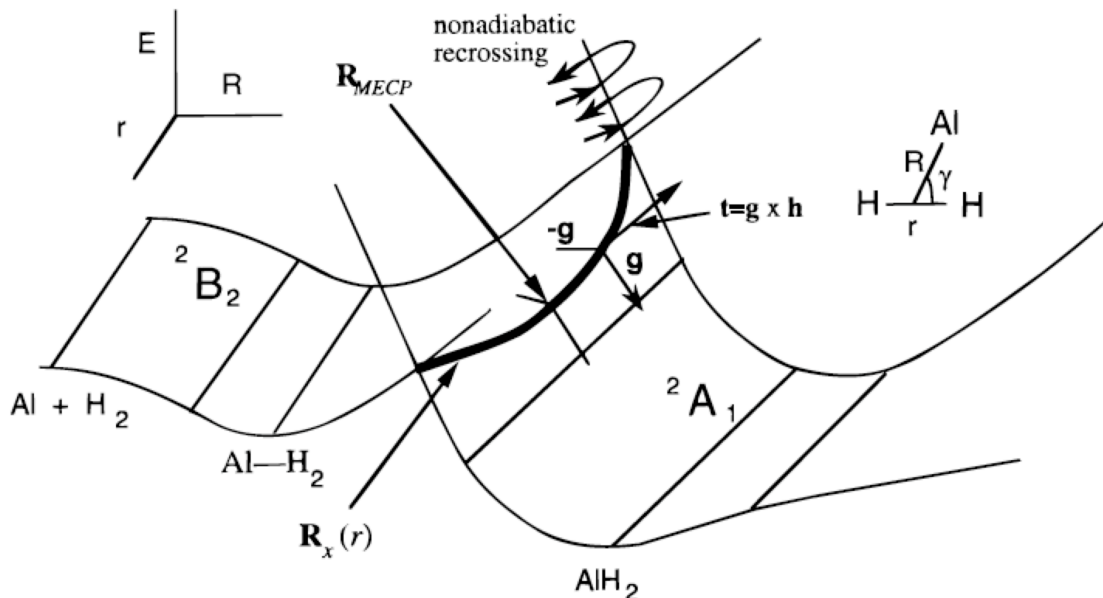


Figure 3.1c Depiction of the $^2A_1$ and $^2B_2$ Born-Oppenheimer surfaces arising when Al $(3s^2\,3p^1;\,^2P)$ combines with $H_2\,(\sigma_g^2;\,^1\Sigma_g^+)$ to form $AlH_2(^2A_1)$.

First considering the reaction of Al $(3s^2\,3p^1;\,^2P)$ with $H_2\,(\sigma_g^2;\,^1\Sigma_g^+)$ to form $AlH_2(^2A_1)$ as if it were to occur in $C_{2v}$ symmetry, the Al atom's occupied 3p orbital can be directed in either of three ways. If it is directed toward the midpoint of the H-H bond, it produces an electronic state of $^2A_1$ symmetry. If it is directed out of the plane of the $AlH_2$, it gives a state of $^2B_1$ symmetry, and if it is directed parallel to the H-H bond, it generates a state of $^2B_2$ symmetry. The $^2A_1$ state is, as shown in the upper left of Fig. 3.1c, repulsive as the Al atom's 3s and 3p orbitals begin to overlap with the hydrogen molecule's $\sigma_g$ orbital at large R-values. The $^2B_2$ state, in which the occupied 3p orbital is directed sideways parallel to the H-H bond, leads to a shallow van der Waals well at long-R but also moves to higher energy at shorter R-values.

The ground state of the $AlH_2$ molecule has its five valence orbitals occupied as follows: (i) two electrons occupy a bonding Al-H orbital of $a_1$ symmetry, (ii) two electrons occupy a bonding Al-H orbital of $b_2$ symmetry, and (iii) the remaining electron

occupies a non-bonding orbital of $sp^2$ character localized on the Al atom and having $a_1$ symmetry. This $a_1{}^2 b_2{}^2 a_1{}^1$ orbital occupancy of the $AlH_2$ molecule's ground state does not correlate directly with any of the three degenerate configurations of the ground state of Al + $H_2$ which are $a_1{}^2 a_1{}^2 a_1{}^1$, $a_1{}^2 a_1{}^2 b_1{}^1$, and $a_1{}^2 a_1{}^2 b_2{}^1$ as explained earlier. It is this lack of direct configuration correlation that generates the reaction barrier show in Fig. 3.1c.

Let us now return to the issue of finding the lower-dimensional (3N-8 or 3N-7) space in which two surfaces cross, assuming one has available information about the gradients and Hessians of both of these energy surfaces $V_1$ and $V_2$. There are two components of characterizing the intersection space within which $V_1 = V_2$:

(1) One has to first locate one geometry $\mathbf{q}_0$ lying within this space and then,

(2) one has to sample nearby geometries (e.g., that might have lower total energy) lying within this subspace where $V_1 = V_2$.

To locate a geometry at which the difference function $F = [V_1 - V_2]^2$ passes through zero, one can employ conventional functional minimization methods, such as those detailed earlier when discussing how to find energy minima, to locate where $F = 0$, but now the function one is seeking to locate a minimum on is the potential energy surface difference.

Once one such geometry ($\mathbf{q}_0$) has been located, one subsequently tries to follow the seam (i.e., for a triatomic molecule, this is the one-dimensional line of crossing; for larger molecules, it is a 3N-8 dimensional space) within which the function F remains zero. Professor [David Yarkony](http://www.jhu.edu/~chem/yarkony/) (http://www.jhu.edu/~chem/yarkony/) has developed efficient routines for characterizing such subspaces (D. R. Yarkony, Acc. Chem. Res. 31, 511-518 (1998)). The basic idea is to parameterize steps away from ($\mathbf{q}_0$) in a manner that constrains such steps to have no component along either the gradient of ($H_{1,1} - H_{2,2}$) or along the gradient of $H_{1,2}$. Because $V_1 = V_2$ requires having both $H_{1,1} = H_{2,2}$ and $H_{1,2} = 0$, taking steps obeying these two constraints allows one to remain within the subspace where $H_{1,1} = H_{2,2}$ and $H_{1,2} = 0$ are simultaneously obeyed. Of course, it is a formidable task to map out the entire 3N-8 or 3N-7 dimensional space within which the two surfaces intersect, and this is essentially never done. Instead, it is common to try to find, for example, the point within this subspace at which the two surfaces have their lowest energy. An example of such a point is labeled $R_{MECP}$ in Fig. 3.1c, and would be of special interest when studying reactions taking place on the lower-energy surface that have to

access the surface-crossing seam to evolve onto the upper surface. The energy at $R_{MECP}$ reflects the lowest energy needed to access this surface crossing.

Such intersection seam location procedures are becoming more commonly employed, but are still under very active development, so I will refer the reader to Prof. Yarkony's paper cited above for further guidance. For now, it should suffice to say that locating such surface 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, or thermal reactions that require the system to evolve onto an excited state through a surface crossing.

## 3.2. Normal Modes of Vibration

*Having seen how one can use information about the gradients and Hessians on a Born-Oppenheimer surface to locate geometries corresponding to stable species and transition states, let us now move on to see how this same data is used to treat vibrations on this surface.*

For a polyatomic molecule whose electronic energy's dependence 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:

$$V(q_k) = V(0) + \Sigma_k (\partial V/\partial q_k) q_k + 1/2\ \Sigma_{j,k}\ q_j\ H_{j,k}\ q_k + ...\ ,$$

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 geometry corresponds to a minimum or transition state, the gradient terms will all vanish, 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) for a minimum and one negative eigenvalues and 3N-6 or 3N-7 positive eigenvalues for a transition state.

**3.2.1. 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:

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

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:

$$T = 1/2\ \Sigma_j\ m_j \left( \frac{dq_j}{dt} \right)^2,$$

where $\dfrac{dq_j}{dt}$ is 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:

$$m_j\ \frac{d^2 q_j}{dt^2} = -\Sigma_k H_{j,k} q_k$$

where the force along the $j^{th}$ coordinate is given by minus the derivative of the potential V along this coordinate $(\partial V/\partial q_j) = \Sigma_k\ H_{j,k}\ q_k$ 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 above Newton equations become

$$\frac{d^2 x_j}{dt^2} = -\Sigma_k H'_{j,k} x_k$$

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:

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

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

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

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. 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 $\omega_j^2$ as well as the corresponding eigenvectors $x_k^{(j)}$.

It is useful to note that, if this same kind of analysis were performed at a geometry corresponding to a transition state, 3N-6 or 3N-7 of the $\omega_j^2$ values would be positive, but one of them would be negative. The eigenvector corresponding to the negative eigenvalue of the mass-weighted Hessian points along a very important direction that we will discuss later; it is the direction of the so-called intrinsic reaction coordinate (IRC).

When reporting the eigenvalues $\omega_j^2$ at such a transition-state geometry, one often says that there is one imaginary frequency because one of the $\omega_j^2$ values is negative; this value of $\omega_j^2$ characterizes the curvature of the energy surface along the IRC at the transition state. The positive vibrational eigenvalues of transition-state geometries are used, as discussed in Chapter 8, to evaluate statistical mechanics partition functions for reaction rates, and the negative $\omega_j^2$ value plays a role in determining the extent of tunneling through the barrier on the reaction surface.

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

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

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

$$\Psi = \Pi_{j=1,3N-5 \text{ or } 6} \; \psi_{v_j} (x^{(j)})$$

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

$$\Delta E_{v_j \rightarrow v_j + 1} = \hbar \, \omega_j$$

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

One might wonder whether mass-weighted Cartesian coordinates would be better or more appropriate to use when locating minima and transition states on Born-Oppenheimer energy surfaces. Although mass-weighted coordinates are indeed essential
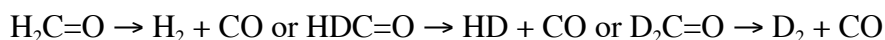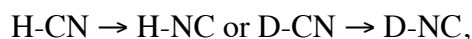
for evaluating harmonic vibrational frequencies and, as we will see later, for tracing out so-called intrinsic reaction paths, their use produces the same minima and transition states as one finds using coordinates that are mass-weighted. This is because the condition that all components of the gradient

$$\frac{\partial V}{\partial q_j} = 0$$

of the energy surface vanish at a minimum or at a transition state will automatically be obeyed when expressed in terms of mass-weighted coordinates since

$$\frac{\partial V}{\partial q_j} = \frac{\partial V}{\partial x_j} \frac{\partial x_j}{\partial q_j} = \frac{\partial V}{\partial x_j} \sqrt{m_j} \;.$$

Notice that this means the geometries of all local minima and transition states on a given Born-Oppenheimer surface will be exactly the same regardless of what isotopes appear in the molecule. For example, for the reactions

$$H\text{-}CN \rightarrow H\text{-}NC \text{ or } D\text{-}CN \rightarrow D\text{-}NC,$$

$$H_2C=O \rightarrow H_2 + CO \text{ or } HDC=O \rightarrow HD + CO \text{ or } D_2C=O \rightarrow D_2 + CO$$

the geometries of the reactants, products, and transition states (for each of the distinct reactions) will not depend on the identity of the hydrogen isotopes. However, the harmonic vibrational frequencies will depend on the isotopes because the mass-weighted Hessian differs from the Hessian expressed in terms of non-mass-weighted coordinates.

**3.2.2. The Use of Symmetry**

1. Symmetry Adapted Modes

It is often possible to simplify the calculation of the normal mode harmonic 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 ($\Delta x_L$) 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 ($\Delta y_L$) produces an energy change identical to movement of the right H in the positive y direction ($\Delta y_R$).
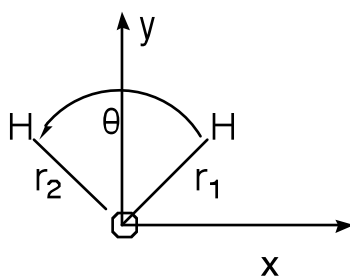


Figure 3.2. Water molecule showing its two bond lengths and angle

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 $\Delta x_L$ through the yz plane (the two planes are depicted in Fig. 3.3) produces - $\Delta x_R$, and reflection of $\Delta y_L$ through this same plane yields $\Delta y_R$.
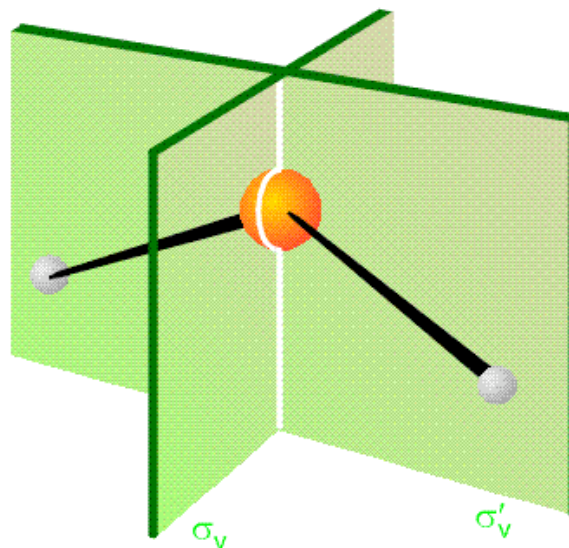
Figure 3.3. Two planes of symmetry of the water molecule.

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 $\Gamma$ labels the irreducible  representation in the appropriate point group and j labels the particular combination of that symmetry (i.e., there may be more than one kind of displacement that has a given symmetry $\Gamma$).  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 four projection operators:

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

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

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

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

to each of the 9 original coordinates (the symbol $\sigma$ denotes reflection through a plane and $C_2$ means rotation about the molecule's $C_2$ axis). Of course, one will <u>not</u> 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 $a_1$ <u>symmetry</u> (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 $b_2$ 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 symmetry-adapted coordinates $Q_{\Gamma,j}$ are expressed as unitary transformations of the original mass-weighted Cartesian coordinates:

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

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

$$H^{\Gamma}_{j,l} = \sum_{kk'} C_{\Gamma,j,k} \; H_{k,k'} \; (m_k \, m_{k'})^{-1/2} \; C_{\Gamma,l,k'}$$

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

$$H^{\Gamma\,\Gamma'}_{j\,l} = \Sigma_{k,k'} \; C_{\Gamma,j,k} \; H_{k,k'} \; (m_k \, m_{k'})^{-1/2} \; C_{\Gamma',l,k'}$$

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 $H^{a_1}_{j\,l}$ is formed as follows:

$$
\begin{bmatrix} \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \\[2mm] \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \\[2mm] & 001 & \end{bmatrix}
\begin{bmatrix} m_H^{-1/2}\dfrac{\partial^2 V}{\partial x_L^2}m_H^{-1/2} & m_H^{-1/2}m_H^{-1/2}\dfrac{\partial^2 V}{\partial x_L \partial x_R} & m_H^{-1/2}m_H^{-1/2}\dfrac{\partial^2 V}{\partial x_L \partial y_O}m_O^{-1/2} \\[3mm] m_H^{-1/2}\dfrac{\partial^2 V}{\partial x_R \partial x_L}m_H^{-1/2}m_H^{-1/2}\dfrac{\partial^2 V}{\partial x_R^2}m_H^{-1/2} & m_H^{-1/2}m_H^{-1/2}\dfrac{\partial^2 V}{\partial x_R \partial y_O}m_O^{-1/2} \\[3mm] m_O^{-1/2}\dfrac{\partial^2 V}{\partial y_O \partial x_L}m_H^{-1/2}m_O^{-1/2}\dfrac{\partial^2 V}{\partial y_O \partial x_R} & m_H^{-1/2}m_O^{-1/2}\dfrac{\partial^2 V}{\partial y_O^2}m_O^{-1/2} \end{bmatrix}
\begin{bmatrix} \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \\[2mm] -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \\[2mm] & 001 & \end{bmatrix}
$$

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 coefficients $\{C_{\Gamma,j,k}\}$ of the $j^{th}$ normal mode of symmetry $\Gamma$ in terms of the mass-weighted Cartesian coordinates $\{X_k\}$. The relationship $X_k = q_k\,(m_k)^{1/2}$ can then be used to express these coefficients in terms of the original Cartesian coordinates $\{q_k\}$.

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, when expressed in terms of the original (i.e., non-mass-weighted) Cartesian coordinates

$$\frac{1}{\sqrt{3}}\;[x_L + x_R + x_O]$$

$$\frac{1}{\sqrt{3}}\;[y_L + y_R + y_O]$$

$$\frac{1}{\sqrt{3}}\;[z_L + z_R + z_O]$$

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 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 two rotations are of $b_1$ and $b_2$ symmetry and involve spinning of the molecule about the x- and z- axes of the Fig. 3.2, 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 in Fig. 3.4.
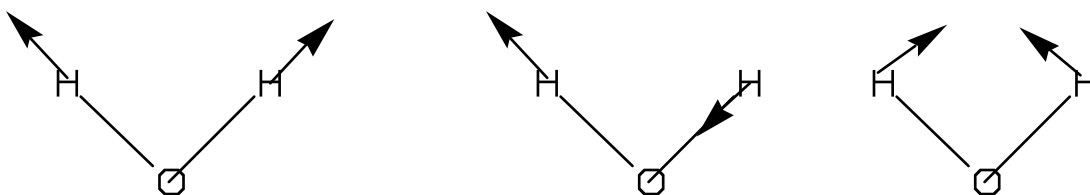
Figure 3.4. Symmetric and asymmetric stretch modes and bending mode of water

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 modes' harmonic 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 $CF_4$ molecule in tetrahedral symmetry.
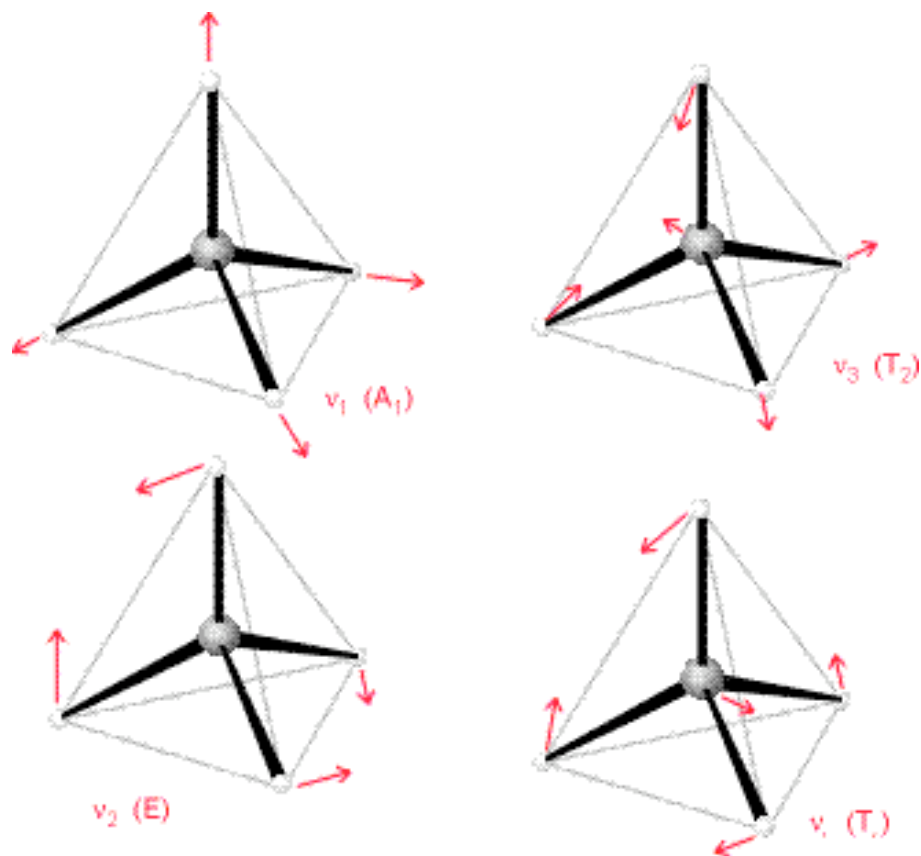
Figure 3.5. Symmetries of vibrations of methane

## 3.3 Intrinsic Reaction Paths

As we will discuss in more detail in Chapter 8, there is a special path connecting reactants, transition states, and products that is especially useful to characterize in terms of energy surface gradients and Hessians. This is the Intrinsic Reaction Path (IRP). To construct an IRP, one proceeds as follows:

a. Once a transition state (TS) has been located, its mass-weighted Hessian matrix is formed and diagonalized. The normalized eigenvector **s** belonging to the one negative eigenvalue of this matrix defines the initial direction(s) leading from the TS to either reactants or products (a unit vector along **s** is one direction; a unit vector along –**s** is the second).

b. One takes a small step (i.e., a displacement of the Cartesian coordinates $\{q_j\}$ of the nuclei having a total length L) along the direction **s**, and this direction is taken to define

the first step along the intrinsic reaction coordinate (IRC) that will eventually lead to the IRP. When **s** is expressed in terms of the its components $\{s_j\}$ along the Cartesian coordinates $\{q_j\}$

$$\mathbf{s} = \Sigma_j \, s_j \, q_j$$

the displacements $\{\delta q_j\}$ can be expressed as

$$\delta q_j = L \, s_j.$$

c. One re-evaluates the gradient and Hessian at this new geometry (call it $\{\mathbf{q}^0\}$), forms the mass-weighted Hessian at $\{\mathbf{q}^0\}$, and identifies the eigenmode having negative curvature. The gradient along this direction will no longer vanish (as it did at the TS), and the normalized eigenvector of this mode is now used to define the continuation of the direction **s** along the IRC.

d.  One then minimizes the energy along the 3N-6 or 3N-7 coordinates transverse to **s**. This can be done by expressing the energy in terms of the corresponding eigenmodes $\{Q_k\}$ of the mass-weighted Hessian

$$V = \sum_{k=1}^{3N-6 \, or \, 3N-7} [g_k \delta Q_k + \frac{1}{2} \omega_k^2 \delta Q_k^2]$$

where $g_k$ is the component of the gradient of the energy along the eigenmode $Q_k$ and $\omega_k^2$ is the eigenvalue of the mass-weighted Hessian for this mode. This energy minimization transverse to **s** is designed to constrain the "walk" downhill from the TS at (or near) the minimum in the streambed along which the IRC is evolving. After this energy minimization step, the Cartesian coordinates will be defined as $\{\mathbf{q}^1\}$.

e. At $\{\mathbf{q}^1\}$, one re-evaluates the gradient and Hessian, and proceeds as in step (c) above. This process is continued, generating a series of geometries $\{\mathbf{q}^0, \mathbf{q}^1, \mathbf{q}^2, \ldots \mathbf{q}^K\}$ that define points on the IRC. At each of these geometries, the gradient will have its largest component (excluding at the TS, where all components vanish) along the direction of **s**

because the energy minimization process will cause its components transverse to **s** to (at least approximately) vanish.

f. Eventually, a geometry will be reached at which all 3N-5 or 3N-6 of the eigenvalues of the mass-weighted Hessian are positive; here, one is evolving into a region where the curvature along the IRC is positive and suggests one may be approaching a minimum. However, at this point, there will be one eigemode (the one whose eigenvalue just changed from negative to positive) along which the gradient has its largest component. This eigenmode will continue to define the IRC's direction **s**.

g. One continues by taking a small step along **s** downhill in energy, after which the energy is minimized along the modes transverse to **s**. This process is continued until the magnitude of the gradient (which always points along **s**) becomes small enough that one can claim to have reached a minimum.

h. The process described above will lead from the TS to either the reactants or products, and will define one branch of the IRP. To find the other branch, one returns to step (b) and begins the entire process again but now taking the first small step in the opposite direction (i.e., along the negative of the eigenvector of the mass-weighted Hessian at the TS). Proceeding along this path, one generates the other branch of the IRP; the series of geometries leading from reactants, through the TS, to products defines the full IRP. At any point along this path, the direction **s** is the direction of the IRC.

This process for generating the IRP can be viewed as generating a series of Cartesian coordinates $\{\mathbf{q}^k\}$ lying along a continuous path $\{\mathbf{q}(s)\}$ that is the solution of the following differential equation

$$\frac{dq_j(s)}{ds} = -\frac{g_j(s)}{|g(s)|}$$

where $q_j$ is the $j^{th}$ Cartesian coordinate, $g_j$ is the energy gradient along this Cartesian coordinate, $|g|$ is the norm of the total energy gradient, and s is the continuous parameter describing movement along the IRC. The initial condition appropriate to solving this differential equation is that the initial step (i.e., at s = 0) is to be directed along (for one

branch of the IRP) or opposed to (for the other branch) the eigenmode of the mass-weighted Hessian having negative eigenvalue at the TS.

**3.4 Chapter Summary**

In this Chapter, you should have learned about the following things:

1. Characteristics of Born-Oppenheimer energy surfaces, and how to find local minima, transition states, intrinsic reaction paths, and intersection seams on them.

2. The harmonic normal modes of vibration extracted from the mass weighted Hessian matrix, and how symmetry can be used to simplify the problem.