

Symmetry and Potential Energy Surfaces

In this chapter two points are considered: (1) the information provided by the shape and topology of a surface and (2) how the shape of the surface makes the nuclei (molecular framework) move in a way that might lower the symmetry of the molecule.

In general, a potential energy surface is a function of $3N - 5$ or $3N - 6$ internal coordinates. For example, for HCN these coordinates could be r_{CH} , r_{CN} , and θ_{HCN} . At local minima on the energy surface small displacements of any of these internal coordinates $\{X_i\}$ increase the electronic energy. (Note that more than one minimum might be present, as, in the case of HCN and HNC.) Hence, at the local minima, the slopes or gradients vanish,

$$\left(\frac{\partial E}{\partial X_i}\right)_{\min} = 0, \quad (2.1)$$

and the curvatures are positive, that is,

$$\left(\frac{\partial^2 E}{\partial X_i^2}\right)_{\min} > 0, \quad (2.2)$$

and

$$\det \left(\frac{\partial^2 E}{\partial X_i \partial X_j}\right)_{\min} > 0. \quad (2.3)$$

An alternative statement is that the gradients vanish and the eigenvalues of the Hessian matrix $(\partial^2 E / \partial X_i \partial X_j)$ are positive. Notice that it is possible that although equations 2.1-2.3 are obeyed, the potential well located at this minimum may not be deep enough to hold a bound vibrational state (if the zero-point vibrational energy is greater than the dissociation energy of the well).

At an activated complex or transition state, equation 2.1 is still valid for *all* coordinates, but along *one* special direction (which generally will be some

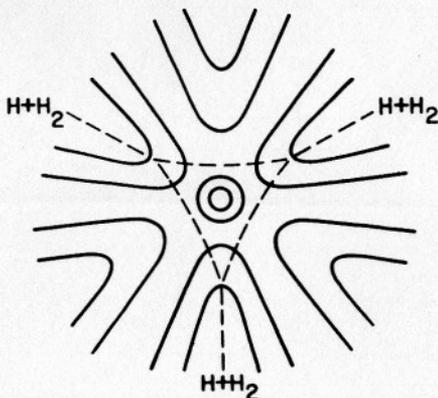


Figure 2-1

Schematic plot of potential surfaces for the exchange reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$. The central point is symmetric H_3 , which is at a maximum in energy. The dashed lines are the reaction coordinates actually followed.

combination of all of the X_i —that is, $Q_r = \sum a_{ir} X_i$) the curvature is negative, $\partial^2 E / \partial Q_r^2 < 0$, with all other curvatures being positive. This direction is called the *reaction coordinate*. If this direction is followed away from the transition state, the slope $\partial E / \partial Q_r$ becomes nonzero. In particular, if we move along Q_r in a manner that maintains all other slopes at zero, namely $\partial E / \partial X_i = 0$ and $\partial^2 E / \partial X_i^2 > 0$, then it is said that one is “walking along a reaction path.” There may, of course, be more than one reaction path and more than one transition state on the potential energy surface of a molecule, which simply means that there is more than one reaction event that this molecule (or “super” molecule) can undergo. By super molecule is meant the total system consisting of all atoms involved in the reaction. For example, H_2CO can undergo decomposition to yield either $\text{H}_2 + \text{CO}$ or $\text{H} + \text{HCO}$. Hence, H_2CO , $\text{H}_2 + \text{CO}$, and $\text{H} + \text{HCO}$ all consist of the same super molecule.

From the above discussion, we see that the reaction coordinate Q_r traces out the “valley floor,” defining the reaction path that connects the reactants to the activated complex (where even $\partial E / \partial Q_r = 0$). Because a “mountain pass” such as that described above for the activated complex has only one direction of negative curvature, it cannot connect more than two valleys, and hence the reaction coordinate Q_r must be nondegenerate at the activated complex. Figure 2-1 illustrates this situation; it should be clear that the top of the mountain cannot be an activated complex. Lower-energy pathways exist for getting from one valley to another, and along these lower-energy paths there are nondegenerate motions with negative curvatures that have a point at which $\partial E / \partial Q_r = 0$.

It is *not* true that the coordinates of a molecule actually move *only* along

potential surface; the internal motion of a molecule depends both upon the surface and upon how the collision occurs (initial molecular orientations, velocities, etc.). However, it is still useful to learn how to follow the reaction coordinate from local minima characterizing reactants through the activated complex to products. If this path can be followed, one might be able to predict whether the energy of the activated complex is high (i.e., if a large activation energy is expected). Hence, even though we are primarily interested in *energetics* (in contrast to the actual *dynamics* that the molecule undergoes on the surface), knowledge of the shape of the potential surface is important. To carry out *dynamic* studies of reaction mechanisms requires knowledge of the potential energy surface(s) at all geometries that are energetically accessible—not only along Q_r . Although such studies are becoming common in modern research in chemical dynamics, we shall focus on considerations of energetics and hence be satisfied to walk along or near Q_r .

From the slopes and curvatures of a potential energy surface at some starting geometry $\{\mathbf{R}_a^0\}$, automated algorithms (Cerjan and Miller, 1981; Simons, Jørgensen, Taylor, and Ozment, 1983) can be used to walk along Q_r from $\{\mathbf{R}_a^0\}$ to some new geometry $\{\mathbf{R}_a^1\}$. Continuing this step-by-step procedure, a transition state can eventually be reached. Further walking leads to the product state determined by this particular transition state. Such step-by-step walks are now routinely carried out in theoretical studies of chemical reactions. In this book, such walks will be conceptualized but not performed quantitatively.

The concepts just described relating to the shape of a potential energy surface can be used to determine whether an electronic wavefunction ϕ_0 , which has energy E_0 at a starting geometry $\{Q^0\}$, corresponds to a local minimum (e.g., stable conformer), to a transition state, or to some point lying along the reaction coordinate. These conclusions can be made more quantitative. To do so, the dependence of the *electronic* Hamiltonian, which determines the energy surfaces, on the internal coordinates of the molecule must be examined.

The only term in $h_e(\mathbf{r}_i | \mathbf{R}_a)$ that is an electronic operator and depends on \mathbf{R}_a is the electron-nuclear coulomb interaction

$$V_{en} \equiv - \sum_{i,a} Z_a e^2 |\mathbf{r}_i - \mathbf{R}_a|^{-1}.$$

Consider now how this interaction energy would change if some geometrical coordinates were changed by a small amount. The coordinate Q that is changed may be some combination of the x , y , and z position coordinates of each of the nuclei ($Q = \sum_a C_a \cdot \mathbf{R}_a$). The change in V_{en} caused by a small change in Q can be expressed as

$$\frac{\partial V_{en}}{\partial Q} = \nabla (\nabla V_{en}) \cdot (\frac{\partial \mathbf{R}_a}{\partial Q}) \quad (7.4)$$

The derivative $\nabla_{\mathbf{R}} V_{\text{en}}$ is a vector containing the X_a , Y_a , and Z_a derivatives of V_{en} . For example,

$$\frac{\partial}{\partial X_a} V_{\text{en}} = - \sum_i Z_a e^2 |\mathbf{r}_i - \mathbf{R}_a|^{-3} (X_i - X_a), \quad (2.5)$$

in which X_i and X_a are the x coordinates of the i th electron and the a th nucleus, respectively. Notice that $\partial V_{\text{en}}/\partial X_a$ has X -symmetry as an operator in the space of the electrons, so $\nabla_{\mathbf{R}} V_{\text{en}}$ is a vector whose three components have x , y , and z symmetry as electronic operators. The $\partial \mathbf{R}_a/\partial Q$ term is nothing but the change in \mathbf{R}_a accompanying a unit change in Q . The reaction coordinate can also be written as a linear combination of the elementary nuclear coordinate displacements. In fact, the elementary displacements, which are $3N - 6$ or $3N - 5$ in number, can be combined (see Wilson, Decius, and Cross, 1955) to give an equal number of symmetry coordinates (Q_i):

$$Q_i = \sum_j C_{ij} R_j, \quad (2.6)$$

in which the $\{R_j\}$ are the x , y , or z displacement coordinates. Conversely, it is also possible to express the displacements in terms of the symmetry coordinates, namely,

$$R_j = \sum_i (C^{-1})_{ji} Q_i. \quad (2.7)$$

As will be seen shortly, only distortions that are totally symmetric contribute to the *slope* of the potential energy surface when one is on the reaction coordinate. Hence, for motions along the (symmetric) reaction coordinate Q_r , the derivative term appearing in equation 2.4 can be related to the symmetry coefficients C_{ij} ,

$$\frac{\partial R_j}{\partial Q_r} = (C^{-1})_{jr}. \quad (2.8)$$

That is, $\partial R_j/\partial Q_r$ is merely the element of the inverse transformation matrix. For example, in H_2O there are two stretching coordinates

$$Q_{\pm} = \frac{1}{\sqrt{2}} (\Delta r_{\text{OH}_1} \pm \Delta r_{\text{OH}_2}). \quad (2.9)$$

The inverse transformation is

$$\Delta r_{\text{OH}_{1,2}} = \frac{1}{\sqrt{2}} (Q_+ \pm Q_-). \quad (2.10)$$

Hence,

$$\frac{\partial \Delta r_{\text{OH}_{1,2}}}{\partial Q_+} = \frac{1}{\sqrt{2}}; \quad (2.11)$$

since Q_+ is the reaction coordinate (at the equilibrium geometry of H_2O), these derivatives are the values needed in equation 2.4. For the treatment of more complicated symmetry coordinates, see Wilson, Decius, and Cross (1955).

An important point is that $\partial V_{\text{en}}/\partial Q$ has the same symmetry (when considered to be an *electronic* operator) as Q itself has (when considered as a function of nuclear positions). How is this fact useful? Let us assume that we have an electronic wavefunction, which from now on we denote as ψ_0 , that obeys the relation

$$h_e(\mathbf{r}_i | \mathbf{R}_a^0) \psi_0 = E_0(\mathbf{R}_a^0) \psi_0 \quad (2.12)$$

(i.e., the electronic Schrödinger equation at a geometry $\mathbf{R}_a^0 \equiv Q^0$). *Perturbation theory* will first be used to compute the change in the electronic energy E_0 that accompanies a small change in some coordinate Q . The perturbation is the change in h_e brought about by a small movement in the Q direction

$$\begin{aligned} h_e(\mathbf{r}_i | Q) &= h_e(\mathbf{r}_i | Q^0) + (\partial h_e / \partial Q) \Delta Q + \frac{1}{2} (\partial^2 h_e / \partial Q^2) \Delta Q^2 + \dots \\ &\equiv h_e^0 + V. \end{aligned} \quad (2.13)$$

The change in the electronic energy E_0 can be expressed (through second order in ΔQ) using conventional perturbation theory (Eyring, Walter, and Kimball, 1944) as

$$E_0(Q) = E_0(Q^0) + \langle \psi_0 | V | \psi_0 \rangle_{Q^0} + \sum_{k \neq 0} \frac{|\langle \psi_k | V | \psi_0 \rangle_{Q^0}|^2}{E_0(Q^0) - E_k(Q^0)}, \quad (2.14)$$

in which the ψ_k are the other eigenfunctions of h_e at Q^0 .

2.1 Slope of the Energy Surface: First-Order Jahn-Teller Effect

Clearly the only term that is linear in ΔQ appears in the $\langle \psi_0 | V | \psi_0 \rangle_{Q^0}$ factor and gives our approximation to the *slope* of the potential surface along the Q direction

$$\begin{aligned}
 (\partial E_0 / \partial Q)_{Q^0} &= \langle \psi_0 | \partial h_c / \partial Q | \psi_0 \rangle_{Q^0} \\
 &= \sum_a (\partial \mathbf{R}_a / \partial Q) \cdot \langle \psi_0 | - \sum_i Z_a e^2 / |\mathbf{r}_i - \mathbf{R}_a|^3 (\mathbf{r}_i - \mathbf{R}_a) | \psi_0 \rangle \\
 &\quad + \sum_a (\partial \mathbf{R}_a / \partial Q) \cdot \sum_b \frac{Z_a Z_b e^2}{|\mathbf{R}_b - \mathbf{R}_a|^3} (\mathbf{R}_b - \mathbf{R}_a) \quad (2.15)
 \end{aligned}$$

The second term in equation 2.15 comes from taking the derivative with respect to Q of the nuclear-nuclear coulomb repulsion terms (V_{nn}) that were also included in h_c (these terms are not functions of the electronic coordinates). Because V_{nn} is a totally symmetric function of the nuclear positions (i.e., it displays the symmetry of the nuclear framework), any distortion Q that is not totally symmetric yields $\partial V_{nn} / \partial Q = 0$. For example, the antisymmetric stretching coordinate of H_2O does not change V_{nn} , since it moves one H atom closer to the O while the other moves farther away (the H—H distance remains constant). Thus, V_{nn} contributes to the slope of the surface only for totally symmetric distortions.

What about the symmetry effects in V_{en} ? We saw earlier that $\partial V_{en} / \partial Q$ has the same symmetry as Q . If ψ_0 is nondegenerate (i.e., not *symmetry degenerate*), the product $\psi_0^* \psi_0$ is totally symmetric, and thus the integral $\langle \psi_0 | \partial V_{en} / \partial Q | \psi_0 \rangle$ will vanish unless $\partial V_{en} / \partial Q$, and hence Q , is also totally symmetric. Therefore, for nondegenerate states only totally symmetric distortions contribute to the slope of the potential surface; other kinds of motion automatically yield $\partial V_{en} / \partial Q = 0$ and $\langle \psi_0 | \partial V_{en} / \partial Q | \psi_0 \rangle = 0$. At a minimum or at a saddle point, even the symmetric distortions give a total slope of zero, since

$$\partial V_{nn} / \partial Q = - \langle \psi_0 | \partial V_{en} / \partial Q | \psi_0 \rangle$$

at these special points. From the definition of Q_r , the reaction coordinate has to be totally symmetric if ψ_0 is nondegenerate, because the slope of the potential surface along Q_r is assumed to be nonzero except at local minima or at activated complexes.

What if ψ_0 is degenerate? In this case, the symmetry of $\psi_0^* \psi_0$ contains at least one element that is not totally symmetric and that itself may or may not be degenerate. (This result is a simple and well-known result that is treated in

$\langle \psi_0 | \partial V_{en} / \partial Q | \psi_0 \rangle$ (but not to $\partial V_{nn} / \partial Q$) is also possible. Moreover, motion along such nonsymmetric directions (in one or the other \pm sense) will lower the electronic energy, so such degenerate points on the surface are generally not activated complexes (since the slope is nonzero at degenerate points). Hence we conclude that a degenerate state will generally be unstable to distortion along a nonsymmetric direction (which thereby lowers the overall symmetry of the molecule). If this nonsymmetric distortion is itself degenerate then, though some of the original symmetry of the molecule may be lost, it is possible that not all of the symmetry is broken (by these linear $\langle \psi_0 | \partial V_{en} / \partial Q | \psi_0 \rangle$ terms). Molecules for which these slope terms are nonvanishing for degenerate states are said to be unstable with respect to first-order Jahn-Teller (FOJT) distortion. Of course, the symmetry of $\psi_0^* \psi_0$ also contains A_1 (the totally symmetric element), so symmetric distortions also give rise to nonvanishing slopes for degenerate states. However, such symmetric distortions will generally preserve the degeneracy of the state ψ_0 .

At this stage of the analysis of movement along the reaction coordinate, the following points have been established about the potential surface: (1) At the activated complex, Q_r cannot be degenerate because a mountain pass can connect only two valleys; that is, the surface can have only one direction of negative curvature. (2) If ψ_0 is nondegenerate, Q_r must be totally symmetric. (3) If a point is reached at which ψ_0 is degenerate, a nonsymmetric motion will distort the molecule, thereby lowering its energy (remaining in the valley) and lowering its symmetry (so this motion is now symmetric in this lower-symmetry point group). This behavior of the reaction coordinate—that is, totally symmetric—makes the symmetry of ψ_0 unchanged (except when ψ_0 is degenerate) and leads to the concept of connecting states by symmetry (symmetry conservation).

2.2 Surface Curvature: Second-Order Jahn-Teller Effect

The effects of terms that determine the *slope* of the potential energy surface have just been described; now, curvature terms—those quadratic in Q_r —will be examined.

The quadratic terms are mainly of concern in regions of the potential surface at which the slopes are zero but at which the system might be unstable because it is at a saddle point—for example, at the activated complex. Equation 2.8 has two such terms. The first term

$$\langle \psi_0 | \partial^2 V / \partial Q_r^2 | \psi_0 \rangle_{Q_r}$$

concerns the response of the “frozen” charge density of ψ_0 to a change in

symmetry), and $\partial^2 V / \partial Q_r^2$ has the same symmetry as Q_r^2 . Hence, the term $\langle \psi_0 | \partial^2 V / \partial Q_r^2 | \psi_0 \rangle$ is generally nonzero; in fact, it is also positive. This can be seen by evaluating $\partial^2 V / \partial Q^2$:

$$\frac{\partial^2 V}{\partial Q^2} = \sum_{a,b} \frac{\partial \mathbf{R}_a}{\partial Q} \cdot \frac{\partial^2 V}{\partial \mathbf{R}_a \partial \mathbf{R}_b} \cdot \frac{\partial \mathbf{R}_b}{\partial Q}. \quad (2.16)$$

Recall that V contains V_{nn} and V_{en} terms. Because

$$d^2/dx^2 |x-y|^{-1} = -4\pi\delta(x-y),$$

(see page 69 of Arfken, 1970) the expression can be evaluated. For V_{nn} , note that $Z_a Z_b |\mathbf{R}_a - \mathbf{R}_b|^{-1}$ contains $\mathbf{R}_a - \mathbf{R}_b$ in a symmetrical fashion; thus,

$$\partial / \partial \mathbf{R}_b |\mathbf{R}_a - \mathbf{R}_b|^{-1} = -\partial / \partial \mathbf{R}_a |\mathbf{R}_a - \mathbf{R}_b|^{-1}.$$

Therefore,

$$\frac{\partial^2 V_{nn}}{\partial \mathbf{R}_a \partial \mathbf{R}_a} = -4\pi \sum_{b \neq a} Z_a Z_b e^2 \delta(\mathbf{R}_a - \mathbf{R}_b) \quad (2.17)$$

and

$$\frac{\partial V_{nn}}{\partial \mathbf{R}_a \partial \mathbf{R}_b} = 4\pi Z_a Z_b e^2 \delta(\mathbf{R}_a - \mathbf{R}_b), \text{ for } a \neq b. \quad (2.18)$$

Since the nuclei never are located at the same position, these δ functions vanish.

Using the above δ -function identity, $\partial^2 V_{en} / \partial Q^2$ can be evaluated as

$$\frac{\partial V_{en}}{\partial \mathbf{R}_a \partial \mathbf{R}_a} = \sum_i (-Z_a e^2) (-4\pi) \delta(\mathbf{r}_i - \mathbf{R}_a) \text{ and } \frac{\partial^2 V_{en}}{\partial \mathbf{R}_a \partial \mathbf{R}_b} = 0.$$

Thus,

$$\frac{\partial^2 V_{en}}{\partial Q^2} = \sum_i \sum_a (\partial \mathbf{R}_a / \partial Q)^2 4\pi e^2 Z_a \delta(\mathbf{r}_i - \mathbf{R}_a). \quad (2.19)$$

The expectation value of this term gives the first term in the curvature, namely,

$$\psi_0 | (\partial^2 V_{en} / \partial Q^2) | \psi_0 = \sum 4\pi Z_a e^2 (\partial \mathbf{R}_a / \partial Q)^2 \rho(\mathbf{R}_a) \quad (2.20)$$

in which $\rho(\mathbf{R}_a)$ is the electron density in state ψ_0 at the nucleus at \mathbf{R}_a . Clearly, this contribution to the curvature is always positive and will be nonzero for any symmetry of ψ_0 , since $\partial^2 V/\partial Q^2$ is totally symmetric. The negative curvature of the surface at an activated complex is a result of a second contribution to the curvature. This is given by

$$\sum_{k \neq 0} |\langle \psi_k | (\partial V/\partial Q) | \psi_0 \rangle|^2 (E_0 - E_k)^{-1}$$

and is always negative (if ψ_0 is the ground state) because $E_0 - E_k$ is negative. Earlier, it was shown that $\partial V/\partial Q$ has the same symmetry as Q . Therefore, if Q is totally symmetric (as it is along the reaction coordinate where ψ_0 is nondegenerate), the excited state ψ_k must have the same symmetry as ψ_0 . On the other hand, if Q is not symmetric, which might occur at a minimum or maximum point at which *all* $\partial E/\partial Q = 0$ (and hence consideration of the quadratic terms in $E_0(Q)$ becomes essential), or if ψ_0 were degenerate, so that Q leads to distortion of the molecule, then the symmetry of ψ_k is dictated by the direct product of the Q and ψ_0 symmetries. Notice that because the slope of E_0 is zero at the activated complex, the energy variation is now dictated by the quadratic terms, which can *now* allow Q_r to be nonsymmetric.

Clearly, for these negative curvature terms to become important (and even dominant, as they are at an activated complex), the symmetry of ψ_k must be correct *and* the energy splitting $E_0 - E_k$ must be small. This situation occurs when a chemical bond is broken. For example, at large internuclear distances the σ^2 and $\sigma^1\sigma^{*1}$ configurations of HCl are reasonably close together in energy. Because $\partial V/\partial Q$ is a one-electron operator, the excited states ψ_k that can couple most strongly with ψ_0 are those that are singly excited relative to ψ_0 (Condon and Shortley, 1957; Cook, 1978). As a result, negative curvature along the reaction path should be possible when there are low-lying excited states that involve single promotions of electrons from bonding orbitals in ψ_0 to antibonding orbitals in ψ_k .

To gain more insight into why ψ_k and ψ_0 should be related in this antibonding/bonding manner, recall that we are looking (using perturbation theory) at the response of the system (ψ_0, E_0) to a small displacement of the nuclei (Jørgensen and Simons, 1981). The energy response has already been discussed above. The change in the wavefunction caused by the perturbation V is given by

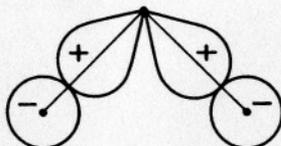
$$\psi_0 \rightarrow \psi_0 + \sum_{k \neq 0} \langle \psi_k | V | \psi_0 \rangle (E_0 - E_k)^{-1} \psi_k \quad (2.21)$$

(Eyring, Walter, and Kimball, 1944). Thus, the electron density $\psi_0^* \psi_0$ changes (through first order in the change in Q) by an amount

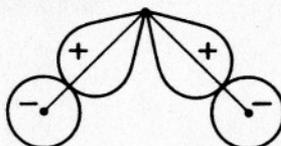
$$\sum_{k \neq 0} 2\psi_0^* \psi_k \langle \psi_k | \partial V / \partial Q | \psi_0 \rangle (E_0 - E_k)^{-1} \equiv \sum_{k \neq 0} \delta \rho_{0k}. \quad (2.22)$$

Where $\delta \rho_{0k}$ is positive, the electron density increases as the motion along Q occurs; where it is negative, electron density decreases. The symmetry (i.e., the nodal pattern) of $\delta \rho_{0k}$ can be determined by looking at the symmetry of $\psi_0^* \psi_k$. If ψ_0 and ψ_k are approximated by Slater determinants (Cook, 1978) that differ by a single orbital replacement ($\phi_0 \rightarrow \phi_k$), the nodal pattern is that of the orbital products $\phi_0^* \phi_k$. The positive nuclei will move to regions at which $\delta \rho_{0k}$ is positive (i.e., in which electron density piles up) and will leave regions in which $\delta \rho_{0k}$ is negative.

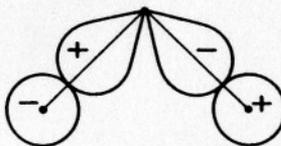
Consider, for example, the H_2O molecule at its equilibrium geometry. Since ψ_0 is nondegenerate, all of the slope terms vanish. What about the curvatures? Excitation of an electron from the bonding a_1 OH orbital to its antibonding a_1 partner gives a $\phi_0^* \phi_k$ pattern of the form



which is consistent (according to the above analysis of the integrals arising in the curvature terms) with a symmetric stretch distortion. The bonding b_2 to antibonding $b_2 \delta \rho_{0k}$ also looks like



which is also consistent with a symmetric stretch. On the other hand, the $a_1 \rightarrow b_2$ or $b_2 \rightarrow a_1$ excitations have a $\delta \rho_{0k}$ of the form



which is consistent with an antisymmetric b_2 stretch. Of course, we do not expect any of these excitations to give rise to large (negative) contributions to the curvatures in this particular (H_2O) case. Their excitation energies, which occur

excitations are more than outweighed by the positive contributions arising from the terms shown in equation 2.20. This is, of course, expected here, since we are considering H_2O at its equilibrium geometry and negative curvature is not anticipated.

Before proceeding to the application of the ideas presented in the first two chapters, it is useful to review the facts that have been established about the reaction coordinate, the activated complex, and the slope and curvature of the surface along Q_r . Remember that the goal is to be able to use this information to move along Q_r from reactants, through an activated complex, to products in order to estimate the activation energy for a reaction. As this path is taken, the symmetry of the wavefunction remains conserved except when the state becomes degenerate (first-order Jahn-Teller) or when low-lying singly excited states come into play and give rise to second-order Jahn-Teller distortions.