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Finding Transition States When Second-Order Jahn–Teller Instability Occurs

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Abstract

When second-order Jahn–Teller couplings become strong along "streambeds" on potential energy surfaces, instability reflected in negative curvature along a symmetry-lowering distortion coordinate can take place. The point where such negative curvature sets in is usually *not* a transition state because the gradient of the potential is usually large there. In this paper, it is demonstrated how to use the local energy, local gradient, local Hessian, *and* knowledge of how quickly the curvature for the symmetry-breaking mode evolves along the streambed (i.e., the derivative of this curvature) to predict how far to move in the symmetry-breaking mode in search of the desired transition state. It is shown that the Hessian matrix evaluated at the symmetry-broken geometry suggested by this analysis has only one negative eigenvalue. Because this analysis is based on a local approximation to the potential, its predictions are, of course, approximate. As such, they only "suggest" the proper direction and magnitude that one should "step" to move toward a transition state. © 1993 John Wiley & Sons, Inc.

I. Introduction

After years of experience [1] studying potential energy surfaces for a variety of chemical reactions, we decided to explore in further detail the local topologies of potential energy surfaces that are affected by second-order Jahn–Teller (SOJT) instabilities [2]. We have found it especially challenging to locate and characterize, via local harmonic vibrational frequencies, true transition states in such situations. We offer the approach described in this paper as a tool for moving away from points when SOJT instability sets in and toward possible nearby transition states.

The particular issue addressed in this paper can be illustrated by considering a potential energy surface V that is a function of two types of internal molecular coordinates—those denoted **x** that preserve the point-group symmetry and others denoted **y** that alter the point-group symmetry. For example, when considering [1f, 1n] the C_{2v} insertion of B^+ into H_2, the distance R from B^+ to the center of the H—H bond and r, the H—H bond length compose **x** and the asymmetric stretch coordinate of the B^+H_2 moiety is **y** (see Fig. 1).

It is common [1]* when exploring potential surfaces in search of transition states (i.e., points at which the derivatives of V along all internal coordinates vanish and

*Many different approaches to the problem of finding transition states are summarized in the selected references in [3].

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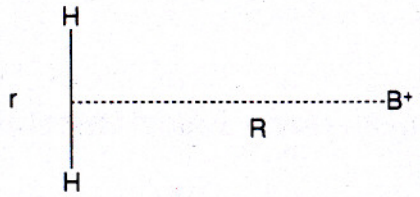

Figure 1. Coordinate system used to label C_{2v} geometries for $B^+ + H_2$.

where only one direction has negative curvature) to use *local* information about V to approximate its dependence on $\mathbf{x}$ and $\mathbf{y}$. Specifically, one often uses the local gradient $\mathbf{F}$ and Hessian $\mathbf{H}$ to write

$$V(\mathbf{x},\mathbf{y}) \cong \mathbf{F}_x\delta\mathbf{x} + \mathbf{F}_y\delta\mathbf{y} + \frac{1}{2}\delta_{\mathbf{x}}\mathbf{H}_{\mathbf{x}}\delta\mathbf{x} + \frac{1}{2}\delta\mathbf{y}\mathbf{H}_{\mathbf{y}}\delta\mathbf{y} + V(\mathbf{x}_0,\mathbf{y}_0), \qquad (1)$$

where $\mathbf{x}_0, \mathbf{y}_0$ is the point at which the gradient and Hessian are computed. The cross terms $\mathbf{H}_{\mathbf{xy}} = \partial^2 E/\partial\mathbf{x}\partial\mathbf{y}$ vanish because the coordinates $\mathbf{x}$ and $\mathbf{y}$ are of different symmetry.

When searching for transition states (TS), it is common to "step" along a series of geometries at which (i) the gradient along all but one internal Hessian eigenmode† coordinate (denoted x_r) vanishes and (ii) all or all but one of the eigenvalues of the Hessian matrix $\mathbf{H}$ are positive. Following such a "streambed" *away from* a local minimum (at which all gradient elements vanish and all Hessian eigenvalues are positive) is a popular strategy [1]* for finding transition states. In many cases, such a strategy does indeed produce a series of points (referred to as "steps") along which the gradient has vanishing components along all but one of the eigenvectors of the (local) Hessian and along which one of the Hessian eigenvalues evolves from positive to negative at which time its eigenvector is parallel to the gradient. Such a "walk" often converges to a TS with the last change in geometry (i.e., the last "step") being (nearly) parallel to the negative Hessian eigenvalue's eigenvector.

II. The Appearance of SOJT Instability

However, along such an exploration of a potential energy surface, another electronic state may approach the state whose surface V is being explored. If the other state's spatial symmetry is different from that of the state of interest, the two states can be mixed (thereby lowering the energy of the lower state) if a nonsymmetry preserving

†The $3N \times 3N$ Hessian matrix (N is the number of atoms in the system) has six (for nonlinear molecules) or five (for linear species) zero eigenvalues that correspond to translation or (infinitesimal) rotation of the molecule. There are procedures (see, e.g., [4]) for removing these degrees of freedom and focusing on the Hessian eigenvalues and eigenvectors corresponding to true *internal* motions. In this paper, we assume that a separation has been effected, and we make reference only to the remaining $3N$-6 or $3N$-5 internal-motion eignevalues.

*Many different approaches to the problem of finding transition states are summarized in the selected references in [3].

distortion of the molecular structure takes place; this is the origin of so-called [2] SOJT coupling.

For example, in the $Al^+ + H_2$ C_{2v} surface discussed above, the ground electronic state has $^1A_1$ symmetry. Along the streambed shown in Figure 2, all Hessian eigenvalues are positive until the point denoted A is reached; here, the eigenvalue whose eigenvector is (nearly) parallel to the gradient vector becomes negative. Following this same streambed further leads to a point (denoted B) at which the Hessian eigenvalue corresponding to the asymmetric stretch *also* becomes negative. Until reaching B, this eigenvalue is positive, as a result of which C_{2v} symmetry is preserved in the streambed walking strategy designed to move "uphill" along one eigenmode while minimizing V along all *other* eigenmodes. The asymmetric stretch eigenvalue evolves from positive to negative as point B is passed because an excited state of $^1B_2$ symmetry (derived from the $3s^1 3p^1$ configuration of Al^+) approaches the $^1A_1$ state closely. Once the two states have similar energies, a distortion of $A_1 \times B_2 = B_2$ symmetry causes them to undergo an avoided crossing with the (lower) $^1A_1$ state pushed to lower energy. The asymmetric distortion has B_2 symmetry and thus can induce such SOJT instability along this mode.

What is perplexing about the above situation is that prior to reaching the point of onset of SOJT instability, only one Hessian eigenvalue is negative and the streambed exploration progresses normally, but suddenly a second Hessian eigenvalue becomes negative. In Figure 3 we illustrate how the asymmetric stretching mode's Hessian eigenvalue changes rapidly in the onset region for SOJT instability. The focus of this paper is to identify the proper "next step" to take in such cases, because *the point of onset of SOJT instability is not a TS* since it has two directions of negative curvature.

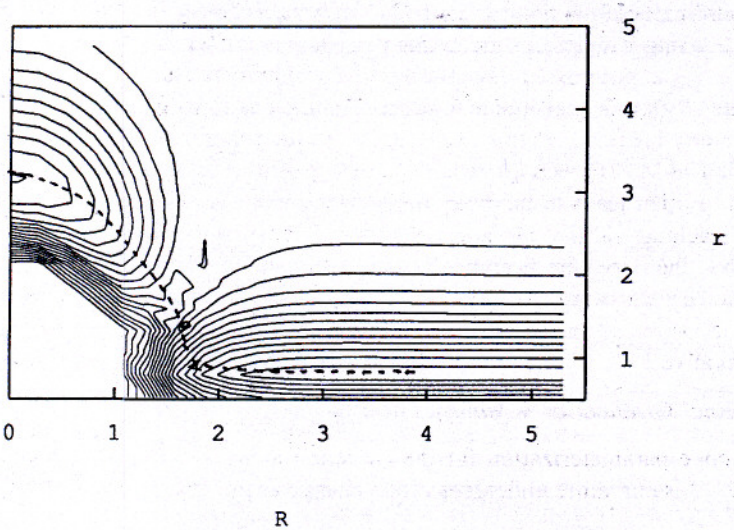

Figure 2. C_{2v} symmetry contour plot of the ($^1A_1$) ground-state energy of $Al^+ + H_2$. The R (distance of Al^+ to the center of H—H) and r (H—H distance) axes are in Å, and the contours are spaced by 10.0 kcal/mol.

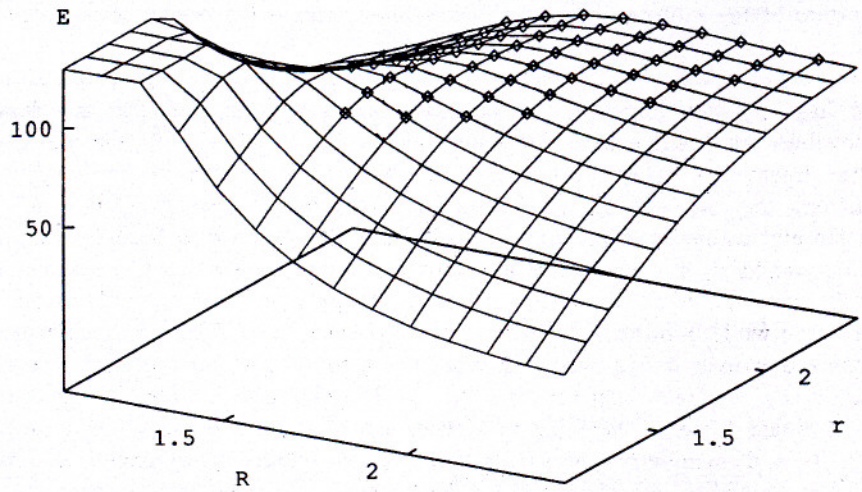

Figure 3. The $^1A_1$ surface in a region where the $^1B_2$ surface is very close to it. At grid points marked by the diamond shape, the b_2 mode's Hessian eigenvalue is negative; at the other points, it is positive.

III. An Extension of the Local Quadratic Potential Model

To this end, let us model, *local* to the point B, whose components we denote $(\mathbf{x}_B, \delta y = 0)$, where SOJT instability first sets in, the potential surface as

$$V = V(\mathbf{x}_B, \delta y = 0) + \mathbf{F}\delta\mathbf{x} + \frac{1}{2}\delta\mathbf{x}H_x\delta\mathbf{x} + (x_r - x_{rB})A_y\delta y^2. \qquad (2)$$

The $\mathbf{x}$ coordinates at the point B are collectively $\mathbf{x}_B$, whereas the value of the "special" coordinate along which steps are taking place and along which the gradient is strongly nonzero is x_{rB} at point B. For simplicity, we consider only a single symmetry-breaking coordinate (δy); this is adequate to describe situations in which SOJT coupling induces any symmetry breaking. In this expansion of V, the curvature along this δy coordinate is modeled as $A_y\ (x_r - x_{rB})$, where $x_r - x_{rB}$ is the displacement along the "step direction" x_r that leads to the point of SOJT instability. In the $Al^+ + H_2$ example, just prior to reaching $\mathbf{x}_B$, the curvature along δy is positive, and upon moving (slightly) through $\mathbf{x}_B$, the curvature becomes negative. In general, if moving to larger x_r values causes the δy curvature to move from negative to positive, then A_y is positive; if moving to larger x_r causes this curvature to move from positive to negative, then A_y is negative.‡

A. *The Total Gradient of* V *Vanishes at a* TS

The above parameterization for the curvature along δy is based upon knowledge about how this curvature undergoes a sign change as the onset point for SOJT instability

‡In the $Al^+ + H_2$ example, if we denote $x_r = 0$ as the $Al^+ + H_2$ asymptote, then one is moving to larger x_r as point B is approached and eventually traversed. Therefore, A_y is negative. Because V increases as one moves from small x_r to larger x_r, in like manner, $F_r = (\partial V)/(\partial x_r)$ is positive.

is reached. Clearly, this information represents partial knowledge of third-order derivatives of V (i.e., $A_y = (\partial^3 V/\partial x_r \partial^2 y)$). Let us now explore the implications of the sign change in the δy curvature by seeking conditions under which this approximate[§] V exhibits a stationary point at which *all* first-order derivatives vanish:

$$0 = \frac{\partial V}{\partial x_i} = F_i + \sum_j H_{ij}\delta x_j + \delta_{ir} A_y \delta y^2 \tag{3a}$$

$$0 = \frac{\partial V}{\partial y} = 2\delta y(x_r - x_{rB})A_y\,. \tag{3b}$$

These conditions are those that characterize a TS, which is precisely what such surface walking strategies are designed to locate.

B. The Newton–Raphson Solution Is Not Useful

There are two options to pursue as solutions to Eqs. (3). If $\delta y = 0$, then all of the $\{\delta x_j\}$ must obey the Newton–Raphson condition $\delta x_j = -\sum_i H_{ji}^{-1} F_i$. This "step" is not acceptable; it simply causes the walk to proceed along the same direction that it had been moving, thus progressing even further into the region of negative δy curvature where the curvature along x_r remains negative in the $Al^+ + H_2$ example above.

C. Breaking Symmetry Is Useful

The second option is more fruitful. Taking $x_r = x_{rB}$, $\delta y = \pm\sqrt{-F_r/A_y}$, and $\delta x_j = -\sum_i H_{ji}^{-1} F_i$ for $j \neq r$ causes

(i) Newton–Raphson steps along all **x** coordinates except the direction x_r along which the streambed lies (this simply causes these directions to be constrained to minima, thereby remaining at the bottom of the streambed).

(ii) No movement along the streambed direction (i.e., $x_r - x_{rB} = 0$).

(iii) Transverse movement in either the $\pm\delta y$ direction with magnitude $\sqrt{-F_r/A_y}$.

It is interesting to note that knowledge of how the δy curvature varies along x_r [i.e., $(\partial(\partial^2 V/\partial^2 y)/\partial x_r)$] is, because of the analytic nature of V, equivalent to knowledge of how the gradient along x_r varies with δy [i.e., $\partial^2(\partial V/\partial x_r)/\partial y^2)$]. It is for this reason that A_y, evaluated by detecting the evolution of the δy curvature, can be used to locate where the gradient along x_r vanishes.

D. The Hessian at the Symmetry–broken Geometry Has Only One Negative Eigenvalue

At the point recommended by the above analysis, *all* elements of the gradient vanish and the Hessian matrix has the following elements:

[§]This entire derivation is based on the local approximation to V given in Eq. (2). As such, conclusions drawn must be viewed as approximations that represent the best that can be made given the local energy and local derivative data that are available.

$$\frac{\partial^2 V}{\partial y^2} = 0 \tag{4a}$$

$$\frac{\partial^2 V}{\partial y \partial x_r} = 2\delta y A_y = \pm 2\sqrt{-F_r A_y} \tag{4b}$$

$$\frac{\partial^2 V}{\partial y \partial x_i} = 0 \qquad \text{for } i \neq r \tag{4c}$$

$$\frac{\partial^2 V}{\partial x_i \partial x_j} = H_{ij}\,. \tag{4d}$$

The coupling between the δy and x_r directions causes the Hessian evaluated at $(x_r = x_{rB}, \delta y = \pm\sqrt{-F_r/A_y},\ \delta x_j = -\sum_i H_{ji}^{-1} F_i;\ j \neq r)$ to be identical to the Hessian evaluated at the SOJT instable point $(x_r = x_{rB},\ \delta y = 0,\ \delta x_j = 0,\ j \neq r)$ *except* for the coupling terms $(\partial^2 V)/(\partial y \partial x_r) = \pm 2\sqrt{-F_r A_y}$. The uncoupled Hessian that applies at the SOJT point has one zero eigenvalue (for the δy coordinate), one negative eigenvalue (along the x_r coordinate), and positive eigenvalues for the remaining coordinates. Therefore, the Hessian that has the coupling present *must* have one negative eigenvalue with all of the remaining being positive; i.e., the zero and the one negative eigenvalue of the uncoupled Hessian are coupled by the $\pm 2\sqrt{-F_r A_y}$ terms and "repel" one another, thereby producing one eigenvalue larger than zero and the second more negative than that of the uncoupled Hessian.

In the situation where $\mathbf{H}_x$ has no negative eigenvalues in the region where SOJT instability sets in, a similar analysis can be performed. In this case, $(\partial^2 V)/(\partial y^2) = 0$, $(\partial^2 V)/(\partial y \partial x_r) = 2\delta y A_y = \pm 2\sqrt{-F_r A_y}$, and $(\partial^2 V)/(\partial y \partial x_i) = 0$ for $i \neq r$ still hold. However, the coupling $(\partial^2 V)/(\partial y \partial x_r)$ now causes the zero eigenvalue of the uncoupled Hessian to be shifted to a lower (i.e., negative) value and the remaining (positive) eigenvalues of $\mathbf{H}_x$, on average, to be shifted upward. The net result is that again there is *one* negative eigenvalue and all the rest are positive.

In the latter case, the negative eigenvalue's eigenvector will lie primarily along the δy direction because this eigenvalue derives from the (assumed small) shift of the δy curvature to a negative value. In the first case treated above, the δy curvature shifts upward to a positive value, and the one negative eigenvalue of $\mathbf{H}_x$ shifts to an even more negative value, in which case the eigenvector belonging to the negative curvature direction will lie primarily along the x_r direction.

IV. Overview

To summarize, at the onset of SOJT instability, knowledge of how the curvature along the symmetry-breaking coordinate varies along the streambed walk $[(\partial^2 V)/(\partial x_r \partial y^2)]$ allows one to locate a point $(x_r = x_{rB},\ \delta x_i = -\sum_j H_{ij}^{-1} F_j,\ i \neq r,\ \delta y = \pm\sqrt{-F_r/A_y})$ at which $\nabla V = 0$ and at which there exists *only one* direction of negative curvature. The direction of negative curvature at this new point will lie primarily along δy if $\mathbf{H}_x$ has no negative eigenvalues; it will lie primarily along x_r if $\mathbf{H}_x$ has one negative eigenvalue. The point described above is therefore a TS! The energy V_{TS} at this TS is predicted to be *identical* to that at the point of onset of

SOJT instability V_{SOJT}, which can be demonstrated by simply substituting $x_r = x_{rB}$, $\delta y = \pm\sqrt{-F_r/A_y}$ $\delta x_i = -\sum_j H_{ij}^{-1} F_j$, $i \neq r$ into Eq. (2).

In [5a], Valtazanos and Ruedenberg provide an analysis close to that described here, in particular for situations when the two states involved in the SOJT interaction are of different symmetry. Also, Quapp [5b] examined bifurcations of model two-dimensional surfaces in some detail. In the former development, the potential V is modeled as also containing a term $A_4\delta y^4$; no cubic term of the type $A_3\delta y^3$ is included because the plane of symmetry under which $\delta y \rightarrow -\delta y$ is assumed[‖] to be a symmetry plane of the molecule prior to onset of SOJT instability. If the $\delta y = \pm\sqrt{-F_r/A_y}$ displacement obtained in our analysis is large, it would be necessary to use a more complicated expression for V analogous to that given in [5a]:

$$V = V_{SOJT} + \mathbf{F}\delta\mathbf{x} + \frac{1}{2}\delta\mathbf{x}\mathbf{H}_x\delta\mathbf{x} + (x_r - x_{rB})A_y\delta y^2 + A_4\delta y^4. \qquad (5)$$

Requiring the gradient of this V to vanish produces equations analogous to Eqs. (3), but the solutions no longer give $x_r - x_{rB} = 0$, but are more complicated; a step involving components along *both* δy and x_r is now required.

We will not explore this more complex approximation further here. We prefer to stop at the more straightforward analysis provided earlier because this *suggests a step* away from the onset point for SOJT instability that can be undertaken *given only the knowledge that is already available* when the potential surface walk encounters the SOJT difficulty V_{SOJT}, the gradient ∇V, and the Hessian $\mathbf{H}$ and how the δy curvature varies along x_r (as embodied in A_y). To use Eq. (5), one would also need to obtain, either from analytical derivatives of V or by pointwise analyzing the y dependence of $\partial^2 V/\partial y^2$, the A_4 coefficient. The approach advocated here is based upon the analyticity of the potential energy surface as a function of nuclear positions, which implies that knowledge of $A_y = [\partial(\partial^2 V/\partial^2 y)]/(\partial x_r)$, obtained by monitoring how the δy curvature evolves along x_r, is equivalent to knowledge of the δy dependence of the off-diagonal Hessian matrix elements coupling x_r and δy: $[\partial(\partial^2 V/\partial y \partial x_r)]/(\partial y)$, which is also equivalent to knowing the second-order derivatives along δy of the gradient along x_r: $[\partial^2(\partial V/\partial x_r)]/(\partial y^2)$. It is knowledge of such matrix elements that allows us, in this work, to obtain information about how far to "step" in the δy direction to cause the gradient $(\partial V)/(\partial x_r)$ along x_r to vanish.

The findings described in this paper show how to move *past* geometries at which SOJT instability begins (and which are *not* TSs) and move to nearby lower-symmetry geometries that are possible TSs. Even though $V_{TS} = V_{SOJT}$, the geometries and local harmonic vibrational frequencies of the TS are *not* the same as those of the SOJT point. It is therefore essential to find the TS geometries and use these geometries and frequencies to compute, e.g., chemical reaction rate coefficients via TS or variational

[‖]It is possible that two states of the same symmetry approach one another along a streambed on, e.g., the lower-energy surface. In such cases, the degree of freedom transverse to the gradient needs not contain any components that alter the molecule's symmetry. Thus, the assumption that V is an even function of δy would not be valid in such cases, and it would be appropriate to use a term of form $A_3\delta y^3$ as the lowest-order correction to our Eq. (2).

TS formulae [6]. The methods used to derive the results given here can also be used to analyze potential energy surfaces in regions of conical intersections [7].

Acknowledgments

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