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SOME NEW THEORETICAL METHODS FOR TREATING REACTION DYNAMICS IN POLYATOMIC MOLECULAR SYSTEMS

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ABSTRACT. Many useful descriptions of dynamical processes in polyatomic molecular systems are based on a reaction path approach. I.e., the potential energy surface is approximated as a multidimensional harmonic valley about a (curved) line in the 3N-6 dimensional space of the N atom system along which the motion is thought to be most localized. These lectures briefly review this reaction path methodology, but then focus mainly on some more recent approaches that go beyond the reaction path point of view. In particular, it is shown how empirical potential functions can be combined with selected ab initio calculations within an empirical valence bond model in order to construct a global potential energy surface for polyatomic reactions. Two other topics that are discussed are a new way of handling zero point energy in a classical trajectory simulation of polyatomic dynamics and a new model for including tunneling effects in a trajectory simulation.

1. INTRODUCTION

One of the fundamental goals of theoretical chemistry is the quantitative description of chemical reactions from first principles ("ab initio"). One usually envisions accomplishing this in two steps, (1) determination of the (Born-Oppenheimer) potential energy surface by state-of-the-art ab initio quantum chemistry calculations, and (2) solution of the dynamical equations for nuclear motion on this potential surface. For the simplest chemical reactions A+BC → AB+C, where A, B, and C are all single atoms, this is rapidly becoming a reality: quantum chemistry calculations[1] continue to improve in accuracy, and there have recently been quite dramatic advances[2-4] in quantum mechanical reactive scattering theory that provides the rigorous solution to the nuclear dynamics. The goal of the work described in this paper, however, is to extend these capabilities to polyatomic molecular systems.

The first part of the task, i.e., determination of the potential energy surface, at first seems almost insurmountable for a polyatomic

molecular system because of the high dimensionality of the problem: for an N atom system the potential (i.e., the Born-Oppenheimer electronic energy) depends on 3N-6 independent coordinates. If one were to try to map out the potential function in a straight-forward way on a grid of coordinate values, then $\sim 10^{3N-6}$ points - i.e., this many quantum chemistry calculations of the electronic energy - would be required, clearly an impossible task for N greater than 3 or 4.

One of the ways of dealing with this situation is to introduce the idea of a reaction path.[5-7] The most common choice of reaction path is the minimum energy path (MEP), i.e., the steepest descent path (in mass-weighted cartesian coordinates) that descends from the saddle point (i.e., the transition state) of the potential energy surface forward to products and backward to reactants. It seems intuitively clear that this path, also called the "intrinsic" reaction path, passes through the most important part of the potential energy surface for the reaction through this transition state. A full-dimensional potential energy surface is obtained by computing the force constant matrix along the MEP, so that the model is that of a (multidimensional) harmonic valley about the reaction path in the many directions orthogonal to it.

Although the minimum energy path is often the most appropriate choice for the reaction path, there are cases for which this is not so. A most important example of this is an H-atom transfer reaction. For such reactions the minimum energy path has many sharp kinks as it passes from the transition state to the reactants and products minima; it is thus not a useful path on which to base the reaction path model. In these cases it has been shown that a straight line, or diabatic reaction path[8] is more useful.

For either (or any) type of reaction path it is possible to construct a reaction path Hamiltonian[5a] from which the dynamical motion can be determined. The system corresponds to a reaction coordinate, i.e., the distance along the reaction path, plus harmonic oscillator motion (for the many degrees of freedom) about it.

A wide variety of dynamical treatments can be carried out using the reaction path Hamiltonian (RPH).[5] Statistical theories, e.g., transition state theory and its generalizations, are very easily implemented using the RPH. Inelastic energy transfer among various degrees of freedom induced by motion along the reaction path and also tunneling through reaction barriers are conveniently treated via the RPH. It is even possible to carry out quite rigorous quantum mechanical calculations using the RPH. Many applications using these approaches have been carried out in recent years.[9,10]

This reaction path methodology has all been extensively reviewed in the paper[11] written from lectures presented at a recent NATO Advanced Study Institute on "New Theoretical Concepts for Understanding Organic Reactions". The reader is thus referred to this paper for this part of the present lectures.

The present paper supplements the previous one[11] by describing some non-reaction path approaches to treating reaction dynamics in polyatomic systems. A reaction path model is good if the dynamics of interest is related to motion that deviates not too far from the

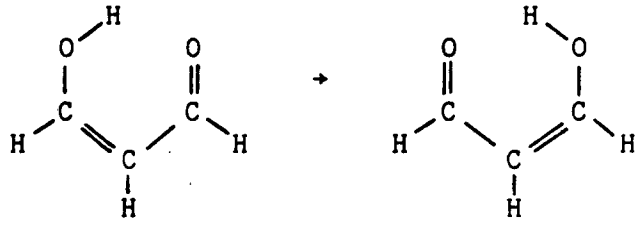
reaction path. Though this may often be true, it is certainly not always the case. In some cases, therefore, it will be necessary to have a global potential energy surface.

Section 2 therefore describes a recent approach we have been pursuing for doing this, namely an empirical valence bond (EVB) model. Warshel,[12] in particular, has utilized this idea to construct potential energy surfaces for truly complex molecules, e.g., proteins. Our interest is in smaller polyatomic systems, but we wish a more quantitative potential surface than biological simulations typically are concerned with. Section 2 describes how we utilize the EVB approach in a more quantitative framework.

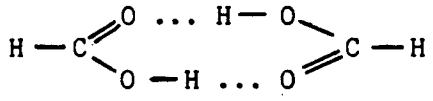
Section 3 then describes some new advances in classical trajectory methodology for use in simulations of polyatomic dynamics. In particular, a recently developed approach is described for handling the zero point energy in a classical trajectory simulation of polyatomic dynamics, and a new model for including tunneling effects in trajectory simulations is presented.

2. Global Potential Energy Surface

To be specific, we consider an isomerization process, e.g.,



(2.1)



(2.2)

for which the potential surface consists of two local minima separated by a saddle point (in many dimensional space). The idea of the empirical valence bond (EVB) model[12] is to express the potential surface $V(\underline{q})$ as the lowest root of a 2x2 secular equation, i.e.,

$$V(\underline{q}) = \tfrac{1}{2}[V_{11}(\underline{q}) + V_{22}(\underline{q})] - \tfrac{1}{2}\{[V_{11}(\underline{q}) - V_{22}(\underline{q})]^2 + 4V_{12}(\underline{q})^2\}^{1/2} . \tag{2.3}$$

In (2.3), $V_{11}(\underline{q})$ is a potential energy function that accurately describes the potential in the vicinity of local minimum 1; it has a single local minimum at this geometry. The simplest approximation

for $V_{11}(\underset{\sim}{q})$ would be a harmonic approximation about the $\underset{\sim}{q}_1$ (the geometry of local minimum 1), or perhaps more accurately, one might use an empirical potential function, such as the MM2 model,[13] that yields an approximate potential energy surface in the vicinity of $\underset{\sim}{q}_1$. $V_{22}(\underset{\sim}{q})$ is a similar function that describes the potential in the region about $\underset{\sim}{q}_2$, the geometry of the second stable isomer.

One thinks of $V_{11}(\underset{\sim}{q})$ and $V_{22}(\underset{\sim}{q})$ as each describing the potential energy surface for one bonding arrangement (i.e., the left and right hand side of Eqs. (2.1) and (2.2)), or one valence bond configuration; they are sometimes referred to as "diabatic" potential functions. $V_{12}(\underset{\sim}{q})$ is a function which describes the coupling between the two configurations. At any geometry for which

$$V_{12}(\underset{\sim}{q}) \ll |V_{11}(\underset{\sim}{q}) - V_{22}(\underset{\sim}{q})| \ , \tag{2.4}$$

Eq. (2.3) gives

$$V(\underset{\sim}{q}) = \mathrm{Min}\ \left(V_{11}(\underset{\sim}{q}),\ V_{22}(\underset{\sim}{q})\right) \ , \tag{2.5}$$

which will be $V_{11}(\underset{\sim}{q})$ or $V_{22}(\underset{\sim}{q})$ for $\underset{\sim}{q}$ near $\underset{\sim}{q}_1$ or $\underset{\sim}{q}_2$, respectively.

As noted above, one has several ways of constructing reasonable approximations to the potential functions V_{11} and V_{22}, each of which corresponds to a single bonding arrangement and thus have only one local minimum. The question is how does one choose the coupling potential $V_{12}(\underset{\sim}{q})$ in a simple, yet accurate fashion. Our answer to this is to choose it so that Eq. (2.3) exactly reproduces an ab initio harmonic approximation about the ab initio transition state geometry. The logic of this prescription is as follows. Empirical approaches (e.g., MM2, etc.) do a reasonably good job of estimating potential functions for stable molecules (and therefore for V_{11} and V_{22}), but they are essentially useless for reactive processes. For medium sized polyatomic systems accurate ab initio calculations are possible for a few selected geometries, even though not at every point in the many dimensional space. The idea is thus to use ab initio input in precisely the region where empirical potential models are unreliable, i.e., the transition state region.

To carry out this idea, note that Eq. (2.3) can be re-written to express $V_{12}(\underset{\sim}{q})$ in terms of $V_{11}(\underset{\sim}{q})$, $V_{22}(\underset{\sim}{q})$, and $V(\underset{\sim}{q})$:

$$V_{12}(\underset{\sim}{q})^2 = [V_{11}(\underset{\sim}{q}) - V(\underset{\sim}{q})][V_{22}(\underset{\sim}{q}) - V(\underset{\sim}{q})] \ . \tag{2.6}$$

It is only necessary to know $V_{12}(\underset{\sim}{q})$ accurately near the transition state (because in other regions Eqs. (2.4) and (2.5) pertain so that $V(\underset{\sim}{q})$ is essentially independent of V_{12}), and about the transition state geometry $\underset{\sim}{q}_0$ one makes the following Taylor's series expansions,

$$V(\underset{\sim}{q}) = V_0 + \tfrac{1}{2}(\underset{\sim}{q}-\underset{\sim}{q}_0)\cdot\underset{\approx}{K}_0\cdot(\underset{\sim}{q}-\underset{\sim}{q}_0) \tag{2.7}$$

$$V_{nn}(\underset{\sim}{q}) = V_n + \underset{\sim}{D}_n\cdot(\underset{\sim}{q}-\underset{\sim}{q}_0) + \tfrac{1}{2}\,(\underset{\sim}{q}-\underset{\sim}{q}_0)\cdot\underset{\approx}{K}_n\cdot(\underset{\sim}{q}-\underset{\sim}{q}_0)\ , \tag{2.8}$$

for n=1, 2, ..., where

$$V_n = V_{nn}(\underset{\sim}{q}_0) \tag{2.9a}$$

$$\underset{\sim}{D}_n = \left(\frac{\partial V_{nn}(\underset{\sim}{q})}{\partial \underset{\sim}{q}}\right)_{\underset{\sim}{q} = \underset{\sim}{q}_0}\ . \tag{2.9b}$$

$$\underset{\approx}{K}_n = \left(\frac{\partial^2 V_{nn}(\underset{\sim}{q})}{\partial \underset{\sim}{q}\partial \underset{\sim}{q}}\right)_{\underset{\sim}{q} = \underset{\sim}{q}_0}\ . \tag{2.9c}$$

The potential and force constant matrix at the transition state, V_0 and $\underset{\approx}{K}_0$, are given by the <u>ab initio</u> calculation, as is the transition state geometry $\underset{\sim}{q}_0$. The values of $V_{nn}(\underset{\sim}{q})$, and its gradient and force constant matrix at the transition state geometry, are evaluated from the empirical functions used for it. Substituting Eqs. (2.7)-(2.9) into (2.6) yields a quadratic approximation for $V_{12}(\underset{\sim}{q})$. We find it useful, furthermore, to exponentiate this expansion, and the result one obtains is

$$V_{12}(\underset{\sim}{q})^2 = A\ \exp[\underset{\sim}{B}\cdot\Delta\underset{\sim}{q} - \tfrac{1}{2}\Delta\underset{\sim}{q}\cdot\underset{\approx}{C}\cdot\Delta\underset{\sim}{q}]\ , \tag{2.10a}$$

where $\Delta\underset{\sim}{q} = \underset{\sim}{q}-\underset{\sim}{q}_0$, and

$$A = (V_1-V_0)(V_2-V_0) \tag{2.10b}$$

$$\underset{\sim}{B} = \frac{\underset{\sim}{D}_1}{(V_1-V_0)} + \frac{\underset{\sim}{D}_2}{(V_2-V_0)}\ , \tag{2.10c}$$

$$\underset{\approx}{C} = \frac{\cdot\underset{\sim}{D}_2\underset{\sim}{D}_2\cdot}{(V_2-V_0)^2} + \frac{\cdot\underset{\sim}{D}_1\underset{\sim}{D}_1\cdot}{(V_1-V_0)^2} + \frac{\underset{\approx}{K}_0-\underset{\approx}{K}_1}{(V_1-V_0)} + \frac{\underset{\approx}{K}_0-\underset{\approx}{K}_2}{(V_2-V_0)}\ . \tag{2.10d}$$

Eq. (2.10) thus gives the coupling potential as a multidimensional Gaussian function. With Eq. (2.10) for V_{12}, $V(\underset{\sim}{q})$ of Eq. (2.3) has a saddle point at $\underset{\sim}{q}=\underset{\sim}{q}_0$, with value $V(\underset{\sim}{q}_0)=V_0$, and

with $\underset{\approx}{K}_0$ as its force constant matrix; i.e., it reproduces the ab initio potential in the vicinity of the ab initio transition state geometry.

It is also clear how one can generalize this procedure to cases where $V(\underset{\sim}{q})$ has more than two local minima: One expresses $V(\underset{\sim}{q})$ as the lowest root of the NxN secular equation (N = number of configurations, i.e., local minima); the diagonal (i.e., diabatic) potential functions $V_{nn}(\underset{\sim}{q})$ are empirical potentials (e.g., MM2) for the various local minima (i.e., bonding arrangements) n=1, ..., N, and the off-diagonal elements $V_{nn'}(\underset{\sim}{q})$ are given by Eq. (2.10) in terms of the ab initio transition state parameters (geometry, barrier height, force constant matrix) for the transition state that connects minimum n to minimum n'.

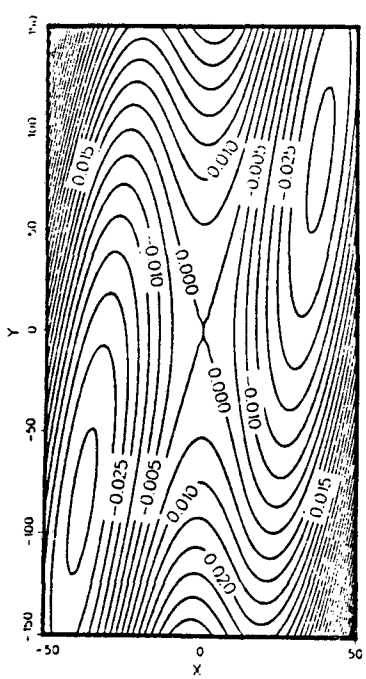
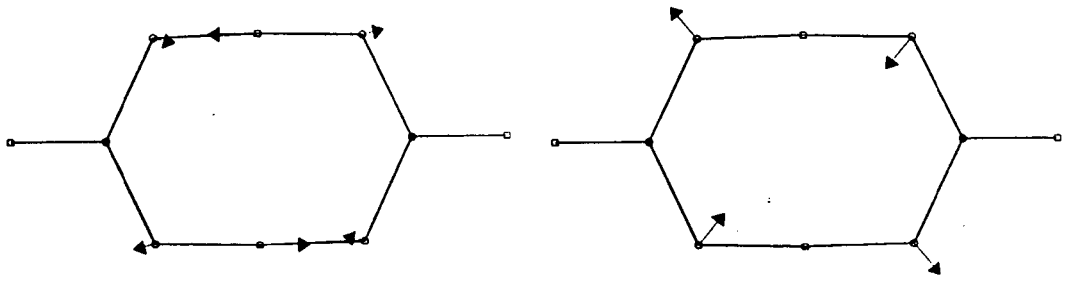


Figure 1. Contour plot of a two dimensional potential surface for formic acid dimer. The energy spacing is 0.005 a.u. The transition state is located at (0,0) with energy set to be 0.0 a.u. The energy of the two minima (locations of the equilibrium state of the two isomers) is about -0.036 a.u. The X axis is the mass-weighted reaction path coordinate which mainly involves the motion of the two tunneling H atoms. The Y axis describes the most strongly coupled normal mode with character of O=C-O motion.

Fig. 1 shows a two-dimensional cut of the EVB potential surface for reaction (2.2), the double H-atom transfer process in formic acid dimer. The normal mode motions for these two degrees of freedom at the transition state are depicted in Figure 2: Figure 2a is mostly motion of the two H atoms that tunnel (the x-coordinate in Fig. 1), and Figure 2b is mostly O=C-O asymmetric stretch and rock (the y-coordinate in Fig 1). This latter mode is the one most strongly coupled to the H atom transfer motion. The diabatic potentials $V_{11}(\underset{\sim}{q})$ and $V_{22}(\underset{\sim}{q})$ in this case are taken simply to be a harmonic normal mode approximation about each local minimum, and $V_{12}(\underset{\sim}{q})$ is given by Eq. (2.10). This EVB potential reproduces the ab initio potential essentially quantitatively over all the relevant region of this two-dimensional configuration space.



(a) (b)

Figure 2. Normal mode representations of the motion of formic acid dimer at the transition state configuration. (a) Motion of the two tunneling H atoms. (b) O=C-O motion: filled circles, open circles and squares stand for C atomc, O atoms, and H atoms, respectively.

3. INCLUDING QUANTUM EFFECTS IN CLASSICAL TRAJECTORY SIMULATIONS

With a global potential surface such as described above, one of the most powerful approaches available to treat dynamics is that of classical trajectory simulations.[14] This is now a widely used technique in many areas of chemistry and biochemistry. There are, however, several serious errors made by these classical methods. In this Section we describe two especially important shortcomings of classical mechanics for polyatomic dynamics and also some recent new work for including the appropriate quantum effects in an approximate framework. The first problem has to do with the zero point vibrational energy and the second with tunneling.

3.1 Simple Model for Handling Zero Point Energy in a Classical Trajectory Simulation

One of the most frustrating shortcomings in using classical mechanics to simulate dynamical processes in polyatomic molecules has to do with a problem involving the zero point energy of vibrational degrees of freedom.[15-17] To describe the problem, recall first the simpler situation of an atom-diatom (gas phase) bimolecular reaction,

$$A + BC(v_i=0) \rightarrow AB(v_f) + C \ , \qquad (3.1)$$

where it is indicated that the reactant diatom BC is initially in its ground vibrational state. It is well-known that a classical trajectory simulation[14] of this process works best if initial conditions for the trajectory are chosen to have the correct zero point vibrational energy in the diatom, with the initial phase of the vibrational motion selected at random (i.e., averaged over), so-called "quasiclassical" initial conditions. Agreement with (the correct) quantum reaction probabilities, or cross sections, would be

much worse if the trajectory were begun with no vibrational energy. A problem can arise even for this simple process if the reaction is endoergic and most of the product is produced in $v_f=0$. It is possible classically to obtain reactive trajectories with less than the zero point vibrational energy in the product molecule AB, clearly an unphysical result since this permits reaction below the quantum threshold for the reaction! This problem is usually dealt with[18] by performing the classical simulation always in the exoergic direction and then using microscopic reversibility to obtain probabilities or cross sections in the reverse direction.

One thus believes that a classical simulation of a polyatomic molecular system will mimic nature (i.e., quantum mechanics) more closely if trajectories are begun with (at least) zero point vibrational energy in all vibrational degrees of freedom, with the phases of the vibrational motion selected at random (i.e., averaged over). To simulate vibrational relaxation of CH local mode overtones in benzene,[19,20] for example, it would seem most reasonable to begin trajectories with the appropriate vibrational energy in the CH stretch and zero point vibrational energy in all the other normal modes.

Since the potential energy function for the polyatomic system is in general anharmonic, energy can flow between various degrees of freedom; often, in fact, it is this intramolecular vibrational energy redistribution (IVR) that one is wishing to simulate. The "zero point energy problem"[19,20] mentioned in the first paragraph is that the energy in some vibrational modes may fall below the (quantum) zero point energy ($\frac{1}{2}\hbar\omega_k$, where ω_k is the harmonic frequency for mode k). This may not at first seem like a serious problem, but even in a medium size polyatomic molecule (e.g., benzene) the zero point energy is a sizeable amount of energy (52.2 kcal/mole in benzene). It is a particularly serious problem if the zero point energy flows out of several modes and "pools" into a specific weak bond. For large molecules it may even happen that the classical mechanics is chaotic at its zero point energy. These are all clearly unphysical effects that arise because classical mechanics cannot prevent the energy in each vibrational mode from dipping below its zero point value.

In a recent paper[21,22] a model has been developed for modifying the classical equations of motion in order to remedy thus situation, i.e., to prevent the vibrational energy in each mode from at any time dipping below its zero point value. The algorithm affects the classical trajectory only when the vibrational energy of a mode attempts to decrease below its zero point value; otherwise the trajectory is the ordinary classical one. It conserves the total energy of the polyatomic system, and since it prevents the energy in each mode from decreasing below its zero point value, there can be no unphysical "energy pooling" of the zero point energy from many modes into one bond. The algorithm is actually quite simple: if the energy in any mode k, say, decreases below its zero point value at time t, then at this time the momentum p_k has its sign changed, and the trajectory continues; this is essentially a time reversal for mode k (only!). One can think of the model as supplying impulsive "quantum

kicks" to a mode whose energy is trying to fall below its zero point value, i.e., a kind of "Planck demon" analogous to a Brownian-like random force.

No attempt will be made to present the derivation of this approach here, but it is perhaps useful to state it more precisely, at least in its simplest version. Thus let $\underset{\sim}{x}=\{x_k\}$ and $\underset{\sim}{p}=\{p_k\}$, k=1, ..., 3N-6 be the normal coordinates and conjugate momenta of the polyatomic system. The Hamiltonian (for zero total angular momentum) is thus of the simple Cartesian form

$$H(\underset{\sim}{p},\underset{\sim}{x}) = \tfrac{1}{2}\, \underset{\sim}{p}^2 + V(\underset{\sim}{x}) \ , \tag{3.2}$$

and the potential energy function consists of a harmonic part plus an anharmonic coupling,

$$V(\underset{\sim}{x}) = V_0(\underset{\sim}{x}) + V_1(\underset{\sim}{x}) \ , \tag{3.3a}$$

where

$$V_0(\underset{\sim}{x}) = \sum_k \tfrac{1}{2}\, \omega_k^{\,2}\, x_k^{\,2} \ . \tag{3.3b}$$

The algorithm may be summarized as follows:

1) Start the trajectory in the appropriate manner (e.g., quasiclassical initial conditions[14]).

2) At the end of each time step in the trajectory, insert the Fortran statement

$$p_k = p_k * \mathrm{Sign}\left(\tfrac{1}{2}\, p_k^{\,2} + \tfrac{1}{2}\omega_k^{\,2} x_k^{\,2} - \tfrac{1}{2}\, \hbar\omega_k\right) \ , \tag{3.4}$$

for all k.

3) Keep on computing!

Eq. (3.4) has no effect on the classical trajectory if the energy in mode k $(\tfrac{1}{2}p_k^{\,2} + \tfrac{1}{2}\omega_k^{\,2}x_k^{\,2})$ stays above its quantum zero point value $(\tfrac{1}{2}\hbar\omega_k)$. If at some time it attempts to dip below this value, though, the sign of p_k is changed, and this has the effect of causing the energy in mode k to increase and thus remain above the zero point value. Since the Hamiltonian involves p_k as $p_k^{\,2}$, this sign change does not change the value of H, i.e., total energy.

The simple version of the model described above pertains to the normal mode vibrational energies. If the dynamics of interest involves motion about a relatively well-defined equilibrium geometry, then this treatment should be adequate. In the more extreme case of

a fragmentation process, e.g., unimolecular decomposition, however, it will not be a reasonable description because the physically relevant modes of the system change radically (the frequencies of some vibrations even going to zero as they evolve into rotations). A more general version[21] of the model corresponds to applying essentially the same procedure as above to the vibrational energies of the instantaneous normal modes.

To conclude this description of the model, we note that imposition of the zero point energy constraint within a harmonic approximation should not be a serious limitation. This is because the algorithm affects the classical mechanics of a vibrational mode only when it is near its zero point level, and most such degrees of freedom are reasonably well-described harmonically at this low level of excitation.

Initial applications[21,22] of this approach show that it does indeed prevent the vibrational energy of each degree of freedom from falling below its zero point value. This thus prevents the total zero point energy from "pooling" into any one degree of freedom. Indications are that the model does indeed give a better description of the dynamics than an unconstrained classical simulation.

3.2 A Semiclassical Tunneling Model for Use in Classical Trajectory Simulation

Another serious limitation of classical mechanics, which hinders its application to many interesting chemical problems, is its inability to describe tunneling effects. However, the quantum mechanical phenomenon of tunneling is often quite prominent in chemical reactions that involve significant motion of light atoms. Typical examples include unimolecular dissociation, e.g.,

$$H_2CO \rightarrow H_2 + CO \ , \tag{3.5}$$

and isomerizations such as Eq. (2.1) and (2.2), as well as bimolecular reactions that involve H atom transfer, e.g.,

$$H_2 + H \rightarrow H + H_2 \ , \tag{3.6a}$$

$$H_2 + F \rightarrow H + HF \ . \tag{3.6b}$$

There do exist "rigorous" semiclassical theories that describe how classical trajectories tunnel, e.g., classical S-matrix theory[23] and the "instanton" (periodic orbit in pure imaginary time) model,[24,25] but they are difficult to apply routinely to sizeable (e.g., more than three atom) molecular systems. There also exist a host of simple tunneling corrections to transition state theory[26] expressions for thermal rate constants; these often work well for this purpose, but they are not applicable to more general dynamical phenomena.

What we seek is a semiclassical model, as generally applicable as possible, for including tunneling in a classical trajectory simulation of the full molecular dynamics; such a model has recently

been presented.[27] The model is similar in spirit to the Tully-Preston[28] surface hopping model for electronically non-adiabatic processes. In the Tully-Preston model a classical trajectory moving on one potential energy surface (i.e., Born-Oppenheimer electronic state) has a probability of making "hops", i.e., instantaneous transitions, to another potential energy surface at certain times. In the present tunneling model[27] the classical trajectory evolving in one classically allowed region of space has, at specific times, a probability for making an instantaneous (in real time) transition to another classically allowed region of space. The model may also be viewed as the classical version of the semiclassical branching model of Waite and Miller,[29] but generalized to allow for a more general tunneling path. This more general tunneling path is very closely related to that used by Heller and Brown[30] in their semiclassical treatment of radiationless transitions.

Again, the reader is referred to the original paper[27] for the detailed development of the model and its application to a variety of examples, including reactions (2.1) and (2.2), and also to unimolecular decomposition. The examples show that the model provides an excellent description of tunneling in multidimensional systems typical of polyatomic molecules. It is also important to emphasize that the model is implementable for truly multidimensional systems. Applicability was, in fact, the essential criterion kept in mind in constructing the model; there do exist more rigorous semiclassical descriptions of multidimensional tunneling,[23-25] but they are not easily implemented within a standard classical trajectory simulation.

4. CONCLUDING REMARKS

This paper has described a variety of approaches for treating dynamical processes in polyatomic molecules that go beyond the reaction path picture. The first step is devising a tractable procedure for obtaining a global potential energy surface, and the empirical valence bond model described in Section 2 shows how this can be done while still incorporating some *ab initio* input. Section 3 then noted two recent advances in classical trajectory simulation methodology, namely a new procedure for dealing more realistically with the quantum zero point energy of vibrational degrees of freedom, and a new quite general semiclassical procedure for including tunneling in a trajectory simulation. Both of these developments should help extend trajectory methods to a wider class of phenomena in the dynamics of polyatomic molecules.

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