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THEORETICAL MODELS FOR REACTION DYNAMICS IN POLYATOMIC MOLECULAR SYSTEMS

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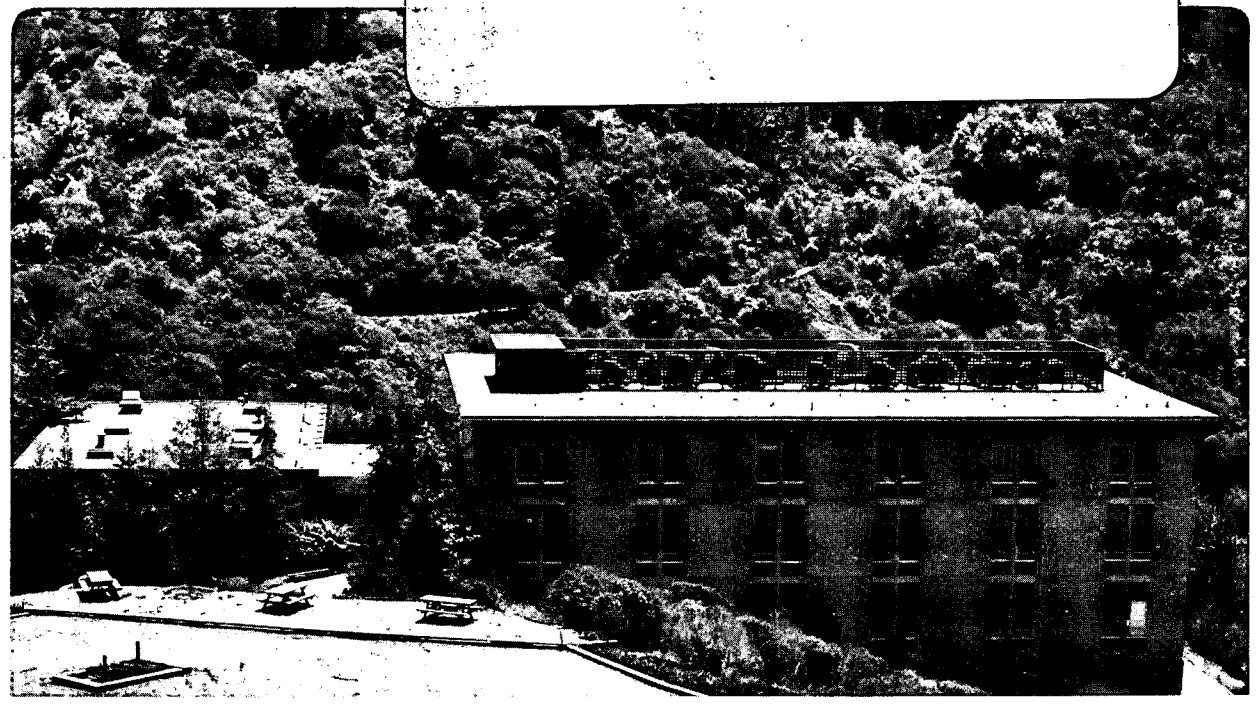## Materials & Chemical Sciences Division

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Theoretical Models for Reaction Dynamics in Polyatomic Molecular Systems

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Theoretical Models for Reaction Dynamics in Polyatomic Molecular Systems

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ABSTRACT. The reaction path Hamiltonian based on the minimum energy reaction path is reviewed. Another reaction path Hamiltonian, this one based on a straight line path from reactants to products, is also introduced. It is argued that the latter model provides a better description of H-atom transfer reactions, a process for which the former one is poor. A variety of quantum and classical dynamical approaches based on these Hamiltonians are surveyed.

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 $\sim10^{3N-6}$ 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.

To deal with this situation one introduces the idea of a

reaction path.[5-7] Section 2 utilizes 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. Section 2 describes this model more completely.

The practically important feature of this reaction path model is that the necessary quantum chemistry calculations are quite feasible by exploiting the analytic gradient methodology[8] that has been developed in recent years. One thus begins the reaction path calculation at the saddle point of the PES - whose location, in fact, is made efficient by using analytic gradient calculations - and then follows the (negative) gradient vector step-by-step down to reactants and to products. Along this steepest descent path one also computes the force constant matrix. The important point is that this is a one dimensional process; i.e., one is computing the potential energy along a one-dimensional curve that snakes its way through a 3N-6 dimensional space. The effort in doing this thus does not increase dramatically as the number of atoms in the system increases.

Section 2 describes how a complete Hamiltonian can be constructed in terms of a reaction coordinate, the distance along the MEP, and local normal coordinates for vibration perpendicular to the MEP (together with momentum variables conjugated to these coordinates). This is the reaction path Hamiltonian.[5a]

Although a reaction path Hamiltonian based on the minimum energy reaction path is often an appropriate description of the reaction of interest, 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. Section 3 shows how a straight line reaction path[9] is appropriate for these situations.

Finally, Section 4 considers some of the dynamical treatments that can be based on these reaction path Hamiltonians. Statistical approximations, i.e., transition state-like theories, are the simplest, and they are easily applied in terms of the reaction path Hamiltonian. Several more dynamically rigorous approaches are also described.

2.   THE REACTION PATH HAMILTONIAN[5a]

If $\{x_{i\gamma}\} \equiv \underline{x}$, $i = 1,....,N$, $\gamma = x,y,z$, denote the 3N mass-weighted cartesian coordinates of the N atoms, then the steepest descent

path $\underline{x}_0(s)$ is determined by starting at the transition state (s=0) and integrating the following equation

$$\frac{d}{ds} \underline{x}(s) = \underline{x}'(s) = - \frac{\partial V(\underline{x})}{\partial \underline{x}} / \left| \frac{\partial V}{\partial \underline{x}} \right| , \qquad (2.1)$$

the solution of which is $\underline{x}_0(s)$. The parameter s is the reaction coordinate, the distance along the path. (This is clear since it follows from Eq. (2.1) that

$$ds = |d\underline{x}| = \sqrt{\sum_{i\gamma} (dx_{i\gamma})^2} , \qquad (2.2)$$

which is the usual definition of arc length.)[10]
There have recently been several papers[10] that have explored in detail the mechanics of determining minimum energy reactions paths. With the advent of analytic gradient methods[8] in _ab initio_ quantum chemistry it is rapidly becoming practical to carry out these calculations for quite complex molecular systems.

For positions $\underline{x}$ close to the reaction path one uses a standard Taylor's series expansion to approximate the potential energy

$$V(\underline{x}) = V_0(s) + \underline{D}(s)\cdot\left(\underline{x}-\underline{x}_0(s)\right) + \tfrac{1}{2}\left(\underline{x}-\underline{x}_0(s)\right)\cdot\underline{K}(s)\cdot\left(\underline{x}-\underline{x}_0(s)\right) + \ldots \quad (2.3)$$

where

$$V_0(s) = V\left(\underline{x}_0(s)\right) \qquad (2.4a)$$

$$\underline{D}(s) = \left(\frac{\partial V}{\partial \underline{x}}\right)_{\underline{x}\, =\, x_0(s)} \qquad (2.4b)$$

$$\underline{K}(s) = \left(\frac{\partial^2 V}{\partial \underline{x}\partial \underline{x}}\right)_{\underline{x}\, =\, \underline{x}_0(s)} . \qquad (2.4c)$$

To define coordinates properly one must insure that the displacements $\underline{x}-\underline{x}_0(s)$ are perpendicular to the reaction path, and furthermore, conservation of total angular (and linear) momentum requires that they also be orthogonal to the directions which correspond to pure rotations (and translations). This is accomplished by introducing the projector $\underline{P}(s)$ that, at position s on the reaction path, projects onto the 7 directions that corresponds to the 3 pure translations of the N atom system, the 3 pure rotations of the N atom system, and the direction along the reaction path,

$$P_{i\gamma,i'\gamma'}(s) = \sum_{k=3N-6}^{3N} L_{i\gamma,k}(s)\, L_{i'\gamma',k}(s), \qquad (2.5)$$

where $\{L_{i\gamma,k}(s)\}$ are the orthonormal vectors for these 7 directions; $k=3N-6$ is chosen to be the direction along the reaction path, so that

$$\underline{L}_{3N-6}(s) = \underline{x}'(s); \qquad (2.6)$$

explicit formulae for the vectors $\underline{L}_k(s)$, $k=3N-7,\ldots,3N$ for pure rotations and translations have been given.[5a]

One then diagonalizes the <u>projected force constant matrix</u>,

$$\bigl(\underline{1}-\underline{P}(s)\bigr)\cdot\underline{K}(s)\cdot\bigl(\underline{1}-\underline{P}(s)\bigr); \qquad (2.7)$$

there are 7 zero eigenvalues, with the 7 eigenvectors given above, and $3N-7$ non-zero eigenvalues, denoted $\{\omega_k(s)^2\}$, with eigenvectors $\{\underline{L}_k(s)\}$, $k=1,\ldots,3N-7$. Displacements away from the reaction path, $\underline{x}-\underline{x}_0(s)$, are then expressed as

$$\underline{x}-\underline{x}_0(s) = \sum_{k=1}^{3N-7} \underline{L}_k(s)Q_k, \qquad (2.8)$$

which guarantees that they are orthogonal to the reactive path and to the directions that are pure rotations and translations. The <u>normal coordinates</u> $\{Q_k\}$, $k=1,\ldots,3N-7$, are the amounts of displacement away from the reaction path in the $3N-7$ independent directions that are perpendicular to it. The coordinates $(s,Q_1,\ldots,Q_{3N-7})$ are thus the $3N-6$ coordinates that characterize the internal motion of the N atom system. In terms of them the potential energy of Eq. (2.3) takes the form

$$V(s,\{Q_k\}) = V_0(s) + \sum_{k=1}^{3N-7} \tfrac{1}{2}\omega_k(s)^2 Q_k^2 + \ldots . \qquad (2.9)$$

The term $V_0(s)$ is often referred to as the <u>reaction profile</u>, i.e., the potential energy along the reaction path. The latter terms clearly have the form of a harmonic valley in displacements away from the reaction path, the frequencies of which vary with position along the path.

In terms of the original 3N mass-weighted cartesian coordinates the Hamiltonian of the N atom system is

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$$H(\underline{p},\underline{x}) = \sum_{i\gamma} \tfrac{1}{2}p_{i\gamma}{}^2 + V(\underline{x}), \qquad (2.10)$$

where $\{p_{i\gamma}\} = \underline{p}$ are the momenta conjugated to $\underline{x}$. One wishes to express H in terms of the $3N-6$ reaction path coordinates $(s,\{Q_k\}$, $k=1,\ldots,3N-7)$ and momenta $(p_s,\{P_k\}\ k=1,\ldots,3N-7)$ conjugate to them, and also the 6 coordinates and momenta that describe pure rotations and translations. This is a tedious procedure, the details for which the reader is referred to the original paper.[5a] For the case of total angular momentum $J=0$ the result is

$$H(p_s,s,\underline{P},\underline{Q}) = \tfrac{1}{2}\Big[p_s - \sum_{k,k'=1}^{F-1} Q_k P_{k'} B_{k,k'}(s)\Big]^2 \Big/ \Big[1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)\Big]^2$$

$$+ \sum_{k=1}^{F-1} \tfrac{1}{2}P_k{}^2 + V_0(s) + \sum_{k=1}^{F-1} \tfrac{1}{2}\omega_k(s)^2 Q_k{}^2, \qquad (2.11)$$

where $F = 3N-6$ is the number of internal degrees of freedom, and the coupling functions are given in terms of the eigenvectors of the projected force constant matrix (and their derivative with respect to s)

$$B_{k,k'}(s) = \underline{L}'_k(s)^T \cdot \underline{L}_k(s) = \sum_{i\gamma} L'_{i\gamma,k}(s)\, L_{i\gamma,k'}(s), \qquad (2.12)$$

where the prime denotes $(\frac{\partial}{\partial s})$ and "T" transpose. $B_{k,k'}(s)$ is a skew-symmetric matrix

$$B_{k,k'}(s) = -B_{k',k}(s), \qquad (2.13)$$

a consequence of which is that its diagonal elements are zero.

Eqs. (2.11)-(2.13) fully specify the reaction path Hamiltonian.[5a] If all the coupling functions were ignored, it would have the simple form of a one-dimensional Hamiltonian for motion along the reaction path,

$$\tfrac{1}{2}p_s{}^2 + V_0(s), \qquad (2.14)$$

plus a sum of harmonic oscillators for motion perpendicular to it. (The s-dependence of the frequencies $\{\omega_k(s)\}$, however, causes coupling between these motions.) The coupling functions $B_{k,k'}(s)$ are

the primary cause of coupling, i.e., energy transfer, between the various degrees of freedom. Most important among these are the curvature coupling's $B_{k,F}(s)$ that occur in the denomination of Eq. (2.11) and couple normal mode k directly to the reaction coordinate (labeled as mode F). Since

$$\underline{L}_F(s) = \underline{L}_{3N-6}(s) = \underline{x}'(s), \qquad (2.15)$$

one can show that

$$\sum_{k=1}^{F} B_{k,F}(s)^2 = \sum_{k=1}^{F} \underline{L}_F'(s)^T \cdot \underline{L}_k(s) \; \underline{L}_k(s)^T \cdot \underline{L}_F'(s)$$

$$= \underline{L}_F'(s)^T \cdot \underline{L}_F'(s) = \underline{x}''(s) \cdot \underline{x}''(s)$$

$$= \kappa(s)^2, \qquad (2.16)$$

where $\kappa(s)$ is the curvature of the reaction path at position s along it. Thus $B_{k,F}(s)$ is essentially a measure of how the total curvature $\kappa(s)$ projects onto the various normal modes k, i.e., of which modes k the reaction path is "curving into" as one moves along it. The modes k for which $B_{k,F}(s)$ is large are strongly coupled to motion along the reaction path and exchange energy with it freely, and vice-versa if $B_{k,F}(s)$ is small. The values of s for which $B_{k,F}(s)$ is large also tell one _where_ along the reaction path the energy transfer will take place.

The coupling functions $B_{k,k'}(s)$ for k and k' < F couple modes k and k' directly. As seen from the definition, Eq. (2.12), $B_{k,k'}(s)$ is the amount that the _change_ in $\underline{L}_k(s)$ with s projects onto $\underline{L}_{k'}(s)$; i.e., it is a kind of coriolis-like interaction caused by the spiraling of the eigenvectors $\underline{L}_k(s)$ about the reaction path.

The reaction path Hamiltonian of Eq. (2.11) can be generalized to deal with non-zero total angular momentum.[5a] The rotational Hamiltonian which is added to Eq. (2.11) is

$$H_{rot}^J(K, q_K) = A(s)(J^2-K^2)\cos^2 q_K + B(s)(J^2-K^2)\sin^2 q_K + C(s)K^2, \quad (2.17)$$

where A(s), B(s), and C(s) are the three rotation constants of the N-atom system at position s along the reaction path; K and q_K are the action-angle variables which characterize the internal rotation degree of freedom, and J is the (conserved) total angular momentum. There are also rotation-vibration coupling terms that are not given here.

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$$\sum_{k=1}^{F} B_{k,F}(s)^2 = \sum_{k=1}^{F} \underline{L}'_F(s)^T \cdot \underline{L}_k(s) \, \underline{L}_k(s)^T \cdot \underline{L}'_F(s)$$

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where $A(s)$, $B(s)$, and $C(s)$ are the three rotation constants of the N-atom system at position s along the reaction path; K and q_K are the action-angle variables which characterize the internal rotation degree of freedom, and J is the (conserved) total angular momentum. There are also rotation-vibration coupling terms that are not given here.

Often it is adequate to make an "almost symmetric top" approximation to the rotational Hamiltonian. This corresponds to averaging Eq. (2.17) over the angle variable, giving

$$H_{rot}^{J} = \frac{1}{2}\left(A(s)+B(s)\right)\left(J^2-K^2\right) + C(s)K^2, \qquad (2.18)$$

so that K, as well as J, is now a conserved quantity (assuming that the rotation-vibration coupling terms are also neglected). Within this approximation Eq. (2.18) simply adds a centrifugal potential to Eq. (2.11); i.e., Eq. (2.11) is modified only by the replacement

$$V_0(s) \rightarrow V_{JK}(s) = V_0(s) + \frac{1}{2}\left(A(s)+B(s)\right)\left(J^2-K^2\right) + C(s)K^2. \qquad (2.19)$$

This permits angular momentum effects to be accounted for (approximately) in a very simple way.

3. LINEAR REACTION PATH

For many purposes the minimum energy reaction path described in the previous Section is excellent. It has been successfully applied to a large number of reactions,[11-12] and will undoubtedly be the method of choice in the future in many situations.

There is one process, however, for which the minimum energy path is not a good description, namely an H-atom transfer process. This is the polyatomic version of a heavy + light-heavy mass combination,[13] e.g.,

$$C\ell + HC\ell \rightarrow C\ell H + C\ell, \qquad (3.1)$$

for which the minimum energy path is extremely sharply curved in the appropriately mass-weighted coordinates. A very curved reaction path means that the curvature coupling elements $\{B_{kF}(s)\}$ in Eq. (2.11) are very large for some modes k, and this causes singularities in the Hamiltonian because the denominator in the first term can vanish for small displacements Q_k away from the reaction path.

The situation is even more severe for a polyatomic system than it is for the simple atom-diatom system Eq. (3.1) This is because there will be many modes that are lower in frequency than H-atom motion, and one can prove in general that the minimum energy path always approaches a potential minimum along the normal mode of lowest frequency (of the appropriate symmetry).[9] For an H-atom transfer, therefore, the minimum energy path begins at the transition state being primarily H-atom motion, but abruptly switches to heavy atom motion further down the path. In general, many of these abrupt

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switches (local Fermi resonances) occur, so that the minimum energy path will have many "kinks" on its journey from the transition state to the reactant (and product) potential minimum. This is clearly not a useful path on which to base the reaction dynamics.
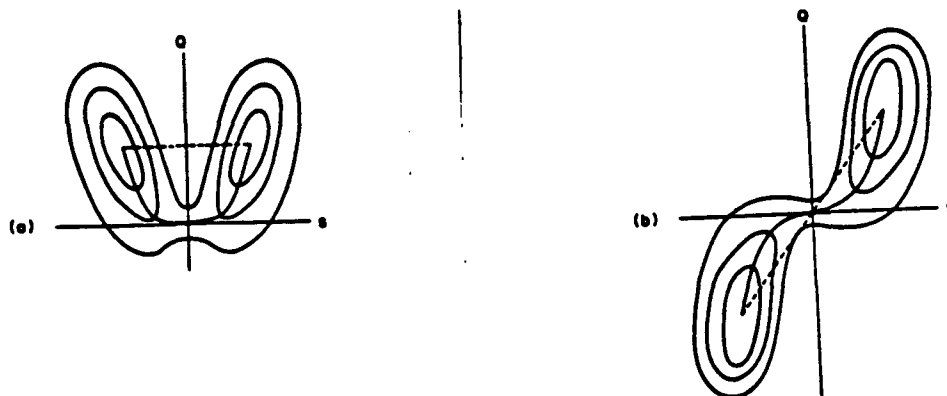

Figure 1. Sketch of contour plots for two characteristic potential energy surfaces. The solid lines indicate the minimum energy path from the transition state down to reactants and to products, and the broken line is the straight line path from reactants to products.

As an alternative a <u>linear</u> reference path between the reactant and product potential minima has been suggested.[9] Fig. 1 shows a sketch of two potential surfaces for a two-dimensional model of a symmetric H-atom transfer. Fig. 1a applies qualitatively to H-atom transfer in malonaldehyde

(3.2)
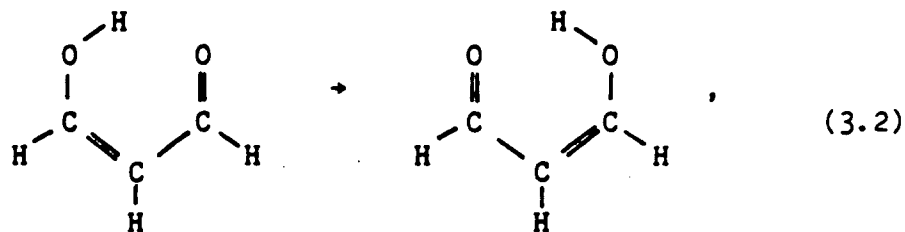
where the two modes are the H-atom motion (s) and the O-O stretch (Q), while Fig. 1b is illustrated by the double H-atom transfer in the formic acid dimer,

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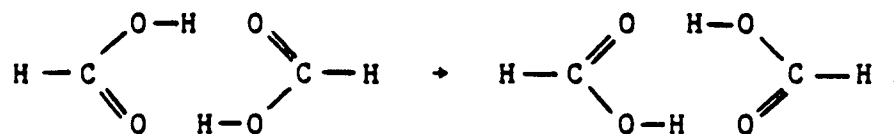
where the two relevant modes for the picture are the asymmetric H-atom motion (s) and the asymmetric O-C-O vibration (Q). In both cases the solid curves indicate the minimum energy path and the broken curve the straight line path. In the case of the Fig. 1a the straight line path misses the transition state by a large distance, but this is actually physically correct; i.e., the most important path for tunneling in this situation "cuts the corner"[14] of the potential surface. For the case in Fig. 1b the straight line path actually passes through the transition state.

The form of Hamiltonian based on this straight line reaction path is constructed in a similar way as that in Section II. The reaction, or reference path $\underline{x}_0(s)$ is now, however, given by (again in mass-weighted cartesian coordinates)

$$\underline{x}_0(s) = \tfrac{1}{2}(\underline{x}_p + \underline{x}_r) + s(\underline{x}_p - \underline{x}_r)/|\underline{x}_p - \underline{x}_r|, \qquad (3.4)$$

rather than by following the minimum energy path, where $\underline{x}_p$ and $\underline{x}_r$ are the (mass-weighted) cartesian coordinates of the products and reactants, respectively (i.e., the geometries of these local minima on the potential energy surface). For Eq. (3.4) to apply it is necessary that the 3N cartesian coordinates $\underline{x}_p$ and $\underline{x}_r$ be defined in consistent coordinate systems. These conditions have been worked out and are easy to insure.[15]

The Hamiltonian for this linear reaction path is now constructed in precisely the same manner as Section II; the projected force constant matrix is diagonalized to obtain the 3N-7 non-zero frequencies $\{\omega_k(s)\}$ and corresponding eigenvectors $\{\underline{L}_k(s)\}$, $k=1,\ldots,3N-7$. The resulting Hamiltonian differs from Eq. (2.11) in only two ways. First, since the reaction path is <u>straight</u>, the curvature coupling element $B_{k,F}(s)$ are all zero. Second, since the linear path is not the minimum energy path, the linear term in the potential, Eq. (2.3), is not zero,

$$\underline{D}(s) \cdot \left(\underline{x} - \underline{x}_0(s)\right) = -\underline{f}(s) \cdot \underline{Q}, \qquad (3.5a)$$

$$f_k(s) = -\sum_{i\gamma} D_{i\gamma}(s)\, L_{i\gamma,k}(s). \qquad (3.5b)$$

The Hamiltonian is thus given by

$$H(p_s, s, \underline{P}, \underline{Q}) = \tfrac{1}{2}\left[p_s - \sum_{k,k'=1}^{F-1} Q_k P_{k'} B_{k,k'}(s)\right]^2 + \sum_{k=1}^{F-1} \tfrac{1}{2}P_k^{\,2} + V_0(s)$$

$$- \sum_{k=1}^{F-1} f_k(s) \, Q_k + \sum_{k=1}^{F-1} \tfrac{1}{2}\omega_k(s)^2 \, Q_k^2 . \qquad (3.6)$$

Finally, in this case it is also possible to eliminate the coriolis coupling elements $B_{k,k'}(s)$ in Eq. (3.6) by making a linear transformation of the coordinates $\{Q_k\}$ amongst themselves.[5b] The price paid for this is that the quadratic term in the potential involving the coordinate $\{Q_k\}$, the last term in Eq. (3.6), becomes non-diagonal. The details of this derivation are omitted here, but the final result for the Hamiltonian is[15]

$$H(p_s,s,\underline{P},\underline{Q}) = \tfrac{1}{2}p_s^2 + \sum_{k=1}^{F-1} \tfrac{1}{2}P_k^2 + V_0(s) - \sum_{k=1}^{F-1} f_k(s) \, Q_k$$

$$+ \sum_{k,k'=1}^{F-1} \tfrac{1}{2} Q_k Q_{k'} \, K_{k,k'}(s) . \qquad (3.7)$$

Here $\underline{P}$ and $\underline{Q}$ are actually not the same quantities as in Eq. (3.6), but related to them by a linear transformation; $\underline{f}(s)$ and $\underline{K}(s)$ in Eq. (3.7) are similarly related by a linear transformation to those in Eq. (3.6).

The advantage of Eq. (3.7) over (3.6) is that the coupling between modes k and k' is in the potential energy in Eq. (3.7) (via the $k \neq k'$ elements of $K_{k,k'}(s)$), while it occurs in the kinetic energy (via the $B_{k,k'}(s)$ elements) in Eq. (3.6). Eqs. (3.6) and (3.7) may thus be termed "adiabatic" and "diabatic" representations, respectively, of the vibrational modes, in analogy with the situation for vibronic Hamiltonians.[16]

4. DYNAMICAL MODELS

With a Hamiltonian one can begin to describe dynamics, and this section considers some of the dynamical models that have been based on the reaction path Hamiltonian, beginning with the simplest approaches and proceeding to more rigorous ones.

4.1. Transition State Theory and Related Models

The simplest dynamical models are statistical ones, and to define them in the most general way it is useful to introduce the microcanonical flux, i.e., the average flux for a given total energy (and, more generally, for a given total angular momentum). For the reaction path Hamiltonian of Section 2, the microcanonical flux

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through a dividing surface that is perpendicular to the reaction path at distance s_0 along it is defined by

$$N(E,s_0) = \frac{2\pi\hbar}{(2\pi\hbar)^F} \int ds \int dp_s \int d\underline{P} \int d\underline{Q} \; \delta(E-H) \; \delta(s-s_0)\dot{s}h(\dot{s}) \quad (4.1)$$

where $\dot{s}$, the velocity along the reaction path, is given by Hamilton's equations

$$\dot{s} = \partial H/\partial p_s; \quad\quad\quad (4.2)$$

the step function $h(\dot{s})$

$$h(\dot{s}) = \begin{cases} 1 & \dot{s} > 0 \\ 0 & \dot{s} < 0 \end{cases}$$

ensures that Eq. (4.1) is the "one-way flux" through the dividing surface. With the reaction path Hamiltonian it is a straightforward calculation to show that Eq. (4.1) and (4.2) give

$$N(E,s) = [E-V_0(s)]^{F-1}/\left\{(F-1)! \prod_{k=1}^{F-1} \omega_k(s)\right\} \quad (4.3)$$

where s_0 has now been replaced simply by s. Remarkably, therefore, none of the coupling functions $B_{k,k'}(s)$ appear in the microcanonical flux; they have not been neglected in the calculation, they simply do not appear in the final result. (If the minimum energy path is not the reference path for the reaction path Hamiltonian, as for the linear reference path considered in the latter path of Section 3, then Eq. (4.3) is modified by the replacement

$$V_0(s) \rightarrow V_0(s) - \sum_{k=1}^{F-1} \frac{f_k(s)^2}{2\omega_k(s)^2}, \quad (4.4)$$

where $\{f_k(s)\}$ are the coefficients of the terms in the potential energy that are linear in the coordinates $\{Q_k\}$.)

Transition state theory corresponds to looking for the minimum (with respect to s) flux,[17] the main bottleneck to the reaction,

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$$N_{TST}(E) = \min_s N(E,s) \qquad (4.5)$$

The microcanonical rate constant, for example, is given in terms of $N(E)$, the cumulative reaction probability - which is approximated in transition state theory by the minimum of the microcanonical flux - by

$$k(E) = N(E)/[2\pi\hbar\rho(E)], \qquad (4.6a)$$

where $\rho(E)$ is the density of reactant states

$$\rho(E) = (2\pi\hbar)^{-F} \int ds \int dp_s \int d\underline{P} \int d\underline{Q} \; \delta(E-H). \qquad (4.6b)$$

A calculation similar to that which leads to Eq. (4.3) gives $\rho(E)$ as

$$\rho(E) = (2\pi\hbar)^{-1}\left(\sqrt{2\pi}/\Gamma(F-\tfrac{1}{2})\right) \int ds \; [E-V_0(s)]^{F-3/2}/ \prod_{k=1}^{F-1} \hbar\omega_k(s), \qquad (4.7)$$

where the limits of the s integration are the classical turning points (the roots of $V_0(s) = E$).

The canonical, i.e., thermally averaged rate constant, is given by the ratio of the Boltzmann averages of $N(E)$ and $\rho(E)$,

$$k(T) = \bar{N}(T)/2\pi\hbar Q_0(T), \qquad (4.8)$$

where

$$\bar{N}(T) = \int^{\infty} dE \; \exp(-E/kT)N(E) \qquad (4.9a)$$

$$Q_0(T) = \int^{\infty} dE \; \exp(-E/kT) \; \rho(E); \qquad (4.9b)$$

$Q_0(T)$, of course, is the reactant partition function. From Eq. (4.7) one can obtain the following expressing for $Q_0(T)$,

$$Q_0(T) = \left(\frac{kT}{2\pi\hbar^2}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} ds \, \exp(-V_0(s)/kT) \prod_{k=1}^{F-1} \frac{kT}{\hbar\omega_k(s)}. \quad (4.10)$$

A useful, though somewhat less rigorous result can be obtained by computing $\bar{N}(T,s)$, i.e., the Boltzmann average of $N(E,s)$, Eq. (4.1) – (4.3), before one minimizes this quantity with respect to s, and then minimizing $\bar{N}(T,s)$ with respect to s. The Boltzmann average of Eq. (4.3) can be evaluated explicitly, giving

$$\bar{N}(T,s) = kT \, \exp\left(-\beta V_0(s)\right) \prod_{k=1}^{F-1} \frac{kT}{\hbar\omega_k(s)}, \quad (4.11)$$

where s is now chosen to be the value which minimizes $\bar{N}(T,s)$. This result, combined with Eq. (4.8), gives the well-known Eyring version of transition state theory

$$k(T) = \frac{kT}{h} \frac{Q^{\ddagger}(T)}{Q_0(T)} \exp(-V^{\ddagger}/kT), \quad (4.12)$$

where

$$V^{\ddagger} = V_0(s)$$

$$Q^{\ddagger}(T) = \prod_{k=1}^{F-1} \frac{kT}{\hbar\omega(s)},$$

s being chosen as the value which minimizes the rate.

If there are several local minima of $N(E,s)$ as a function of s, then this corresponds to several "bottlenecks" of the reactive flux. If one assumes that microcanonical equilibrium is established locally in the regions between these bottlenecks - e.g., by the existence of long-lived intermediates - then one can derive a "unified" statistical model.[18,5b] This model approximates the cumulative reaction probability as

$$N(E) = \left[\sum_{k=1,3...}^{2M+1} \frac{1}{N_k(E)} - \sum_{k=2,4...}^{2M} \frac{1}{N_k(E)} \right]^{-1} \quad (4.13)$$

where for $k=1,3,5,...., 2M+1$, $\{N_k(E)\}$ are the local minima of $N(E,s)$,

and for k=2,4,..., 2M they are the local maxima separating the local minima.

To apply these statistical theories one thus only needs the potential energy along the reaction path $V_0(s)$ and the frequencies $\{\omega_k(s)\}$ of the transverse modes. To locate the extrema of the flux $N(E,s)$ as a function of s one can show[5b] that the equation

$$\partial N(E,s)/\partial s = 0 \qquad (4.14)$$

is equivalent to the following one

$$E = W(s) \qquad (4.15a)$$

which involves the energy-independent function

$$W(s) = V_0(s) - V_0'(s)(F-1)/ \sum_{k=1}^{F-1} \frac{\omega_k'(s)}{\omega_k(s)}. \qquad (4.15b)$$

To find the various extrema of the microcanonical flux one thus needs only to plot the function $W(s)$ and look to see where it is equal to the energy E. This is a simple way to see how the reaction "mechanism" changes with energy. Typically, for example, at low energy E there is only one bottleneck, i.e., one minimum in the flux, so that ordinary transition state theory is a good approximation, while at higher energies there may be several minima. This latter situation is a herald, even within this statistical description, of more complex dynamics, i.e., "recrossing trajectories", which cause the breakdown of simple transition state theory.[17]

4.2 Semiclassical Perturbation-Infinite Order Sudden Approximation

Going beyond statistical approximations to more dynamically based treatments opens the door to a wide variety of possibilities, from simple approximate models to more accurate treatments that are capable (with sufficient effort) of arbitrary accuracy. Here I note one particularly simple approximate model that has been developed and applied to a variety of different dynamical phenomena, namely the semiclassical perturbation-infinite order sudden (SCP-IOS) model.[19]

The SCP-IOS model is the semiclassical approximation of Miller and Smith[20] applied to the reaction-path Hamiltonian. It has the appealing feature that it behaves qualitatively correctly both in the adiabatic limit, which is the situation if the transverse vibrational motion is much faster than motion along the reaction coordinate, and also in the sudden limit, which is the case if reaction-coordinate

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motion is much faster than transverse vibrational motion. For the case of a collinear atom-diatom reaction it becomes the Hofacker-Levine model.[21]

To illustrate how simple it is to apply, e.g., the probability of the vibrational transition $(n_1,...,n_{F-1}) \rightarrow (n'_1,...,n'_{F-1})$ in the transverse vibrational modes during motion from s_1 to s_2 along the reaction path is given by

$$P_{\underset{\sim}{n}_2 \leftarrow \underset{\sim}{n}_1}(E) = \sum_{k=1}^{F-1} |J_{\Delta n_k}(\gamma_k)|^2 \qquad (4.16a)$$

where $J_{\Delta n_k}$ is the regular Bessel function of order Δn_k, and the "collision integrals" γ_k are given by

$$\gamma_k = \left| \int_{s_1}^{s_2} ds \, B_{k,F}(s) \, \{2[E-V_n(s)]\}^{\frac{1}{2}} [(2n_k+1)/\omega_k(s)]^{\frac{1}{2}} e^{i\delta_k(s)} \right|$$

with

$$V_{\underset{\sim}{n}}(s) = V_0(s) + \sum_{k=1}^{F-1} (n_k+\frac{1}{2}) \, \omega_k(s)$$

$$\delta_k(s) = \int_{s_1}^{s} ds' \, \omega_k(s')/\{2[E-V_{\underset{\sim}{n}}(s')]\}^{\frac{1}{2}}$$

$$\underset{\sim}{n} = \frac{1}{2}(\underset{\sim}{n}_1 + \underset{\sim}{n}_2). \qquad (4.16b)$$

The collision integral γ_k is a measure of how much vibrational excitation is induced in mode k during motion from s_1 to s_2: the Bessel function $J_{\Delta n_k}(\gamma_k)^2$ has its maximum at $\Delta n_k = \gamma_k$, so that γ_k is the most probable vibrational quantum number change. A typical application of this expression would be to predict the product state distribution of an exothermic chemical reaction: with $\underset{\sim}{n}_1 = 0$, $s_1 = 0$, and $s_2 = \infty$, Eq. (4.16) gives the distribution of product internal degrees of freedom. Clearly the modes with the larger coupling element $B_{k,F}$ will be the ones excited most during motion from the transition state ($s_1 = 0$) to products ($s_2 = \infty$). Conversely, $s_1 = -\infty$ and $s_2 = 0$ and $\underset{\sim}{n}_2 = 0$ corresponds to the time-reversed situation. In this case the modes k for which γ_k is large are the most effective promoting modes for the reaction; i.e., vibrational energy initially in such a mode will be converted with high probability into energy along the reaction coordinate at the transition state.
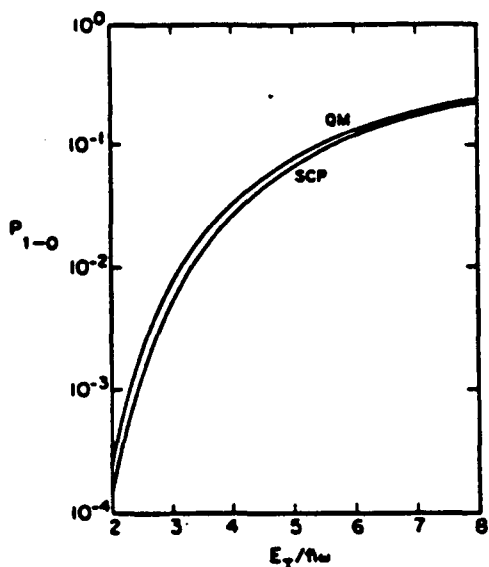
Figure 2. Transition probability for the 0 → 1 vibrational excitation of H_2 by collision with He, as a function of total energy. H_2 is modeled as a Morse oscillator. QM and SCP denote the essentially exact quantum mechanical results computed for this collinear system, and the present results of the SCP-IOS reaction path model.

Fig. 2 shows an example of the SCP-IOS model, i.e., Eq. (4.16), applied to vibrational excitation of H_2 by collision with He atoms.[19] One sees that this simple dynamical model based on the reaction path Hamiltonian does an extremely good job of describing vibrational inelasticity.

The SCP-IOS approximation has also been used to describe the effects of the curvature coupling elements on tunneling probabilities in chemical reactions. For example, the probability of tunneling through a simple barrier is given within the SCP-IOS model by

$$P = P_0 \prod_{k=1}^{F-1} I_0(\theta_k)^2 \qquad (4.17a)$$

where

$$P_0 = e^{-2\theta_0} \qquad (4.17b)$$

$$\theta_0 = \int ds \, \sqrt{2[V_{eff}(s) - E}} \qquad (4.17c)$$

$$\theta_k = \int ds \ \sqrt{2[V_{eff}(s)-E]} \ \frac{B_{k,F}(s)}{\sqrt{\omega_k(s)}} \ \cosh\delta_k(s). \qquad (4.17d)$$

P_0 is the usual one-dimensional WKB tunneling probability, and the effect of curvature coupling is contained in the multiplicative factors $I_0(\theta_k)^2$, one for each mode k. I_0 is the Bessel function of imaginary argument which is an exponentially increasing function; i.e.,

$$I_0(0)^2 = 1$$

$$I_0(\theta_k)^2 \sim e^{2\theta_k}/(2\pi\theta_k) \qquad (4.18)$$

for $\theta_k \gg 0$. Curvature coupling thus <u>increases</u> the tunneling probability.
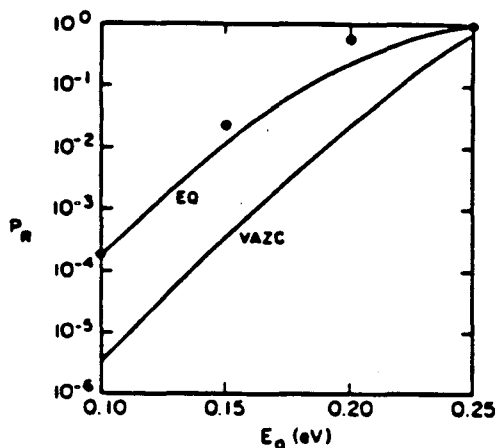

Figure 3. Reaction probability for collinear $H+H_2 \rightarrow H_2+H$ on the Porter-Karplus potential energy surface. EQ denotes the exact quantum mechanical values, VAZC the results of the vibrationally adiabatic zero curvature approximation, and the points the results of the present SCP-IOS reaction path model.

For the well-studied test case, the collinear $H+H_2$ reaction, for example, Fig. 3 shows the reaction probability as a function of initial translational energy.[5c] One sees that P_0 (i.e., VAZC) is a factor of ~50-100 too small, but the SCP-IOS model, i.e., Eq. (4.17), brings it to within a factor of 2 of the correct value.

The SCP-IOS model has also been used to determine the degree of mode specificity in state-selected unimolecular decomposition.[22,23]

If there were no coupling between the various modes of the polyatomic system, then the unimolecular decomposition would clearly be mode specific: i.e., different initial states with essentially the same total energy would decay at different rates because they would have various amount of energy in the reaction coordinate and there would be no energy transfer among the various degrees of freedom. Conversely, to the extent that coupling between the modes causes efficient energy transfer among them, one expects more statistical behavior, i.e., the rate of decomposition depending essentially only on the total energy of the initial state and not on the particular initial state that is prepared. The degree of mode specificity in the state-specific unimolecular decay rates is thus a sensitive measure of the intermode coupling and thus a direct test of the way that the SCP-IOS, or any other model, is able to describe this.

4.3 Dynamical Methods for 'System' Coupled to a Harmonic 'Bath'

The Hamiltonian that results with the linear reaction path described in Section 3, namely that given by Eq. (3.7), is sufficiently simple that it lends itself to special dynamical treatments. It has the generic form

$$H = H_{sys} + H_{bath} + H_{coupling}, \qquad (4.19a)$$

where H_{sys} is the Hamiltonian for the "system" of interest, i.e., the reaction coordinate,

$$H_{sys} = \tfrac{1}{2}p_s^2 + V_0(s), \qquad (4.19b)$$

H_{bath} is the Hamiltonian of a harmonic "bath" that is of less interest,

$$H_{bath} = \sum_{k=1}^{F-1} (\tfrac{1}{2}P_k^2 + \tfrac{1}{2}\omega_k^2 Q_k^2), \qquad (4.19c)$$

where the force constant matrix has here been assumed to be independent of the reaction coordinate, and $H_{coupling}$ is the term that couples the system and bath,

$$H_{coupling} = -\sum_{k=1}^{F-1} f_k(s)Q_k. \qquad (4.19d)$$

All strategies for dealing with such Hamiltonians involve trying to eliminate the bath to as large an extent as possible and concentrate

attention on the system, while not altogether neglecting the effect of the bath on the system.

At the level of classical mechanics, for example, it is possible to solve the equations of motion for the bath exactly and obtain the following <u>generalized Langevin equation</u>[24] for the system,

$$\ddot{s}(t) = - V_0{}'(s(t))$$

$$+ \sum_{k=1}^{F-1} f_k{}'(s(t))[Q_k(0)\cos(\omega_k t)+P_k(0)\sin(\omega_k t)/\omega_k]$$

$$+ \sum_{k=1}^{F-1} f_k{}'(s(t)) \int_0^t dt' f_k(s(t'))\sin(\omega_k(t-t'))/\omega_k, \qquad (4.20)$$

where the first term is the force originating from the local potential $V_0(s)$, the second term is the so-called "random force" that involves the initial conditions of the bath degrees of freedom, and the third term is the non-local "friction" on the reaction coordinate. Eq. (4.20) is dynamically <u>exact</u>, i.e., one has "eliminated" the bath and obtained a one-dimensional equation of motion for the system alone (albeit a complicated equation because it includes the effect of the bath on the system).

To carry out an analogous procedure in quantum mechanics requires use of the Feynman path integral[25] version of quantum mechanics. I will mention here only schematically how this is done. The path integral is an expression for the kernel of the time evolution operator

$$\langle s_2 Q_2| e^{-iH(t_2-t_1)/\hbar} |s_1 Q_1\rangle = \int_{s_1}^{s_2} Ds(t)\, e^{i\phi[s(t),Q(t)]}. \qquad (4.21)$$

The integration symbols in Eq. (4.21) indicate a functional integral over all paths $s(t)$ and $Q(t)$ with the boundary conditions $s(t_1) = s_1$, $s(t_2) = s_2$, $Q(t_1) = Q_1$, and $Q(t_2) = Q_2$, respectively. $\phi[s,Q]$ is the classical action functional for a path $s(t),Q(t)$. Because the Hamiltonian has the simple form of Eq. (4.19), the action functional has the analogous form

$$\phi[s(t),Q(t)] = \phi_{sys}[s(t)]+\phi_{bath}[Q(t)]+\phi_{coupling}[s(t),Q(t)]. \qquad (4.22)$$

Furthermore, because the Schrödinger equation for the time-dependent forced harmonic oscillator is analytically solvable, one can evaluate

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the $\int D\underset{\sim}{Q}$ path integral analytically, so that Eq. (4.21) takes the form

$$\langle s_2 \underset{\sim}{Q}_2 | e^{-iH(t_2-t_1)/\hbar} | s_1 \underset{\sim}{Q}_1 \rangle = \int_{s_1}^{s_2} Ds(t) e^{i\phi_{sys}[s(t)]} K_{s_2 \underset{\sim}{Q}_2, s_1 \underset{\sim}{Q}_1}[s(t)],$$

(4.23a)

where the influence functional K,

$$K_{s_2 \underset{\sim}{Q}_2, s_1 \underset{\sim}{Q}_1}[s(t)] \equiv \int_{\underset{\sim}{Q}_1}^{\underset{\sim}{Q}_2} D\underset{\sim}{Q}(t) e^{i\phi_{bath}[\underset{\sim}{Q}(t)]} e^{i\phi_{coupling}[s(t),\underset{\sim}{Q}(t)]},$$

(4.23b)

is a known[25] exactly calculable functional of the path s(t). Eq.
(4.23a) is thus a path integral for only one degree of freedom –
analogous to Eq. (4.20), the classical equation of motion for only
one degree of freedom – though it is a complicated one-dimensional
quantum mechanical problem because it includes the effects of the
bath on the system (through the influence functional K).

There is currently a great deal of effort being expended (and
progress being made!) in learning how to carry out quantum
calculations using path integral methods.[26-28] As has been
indicated, this progress is all very relevant to the linear reaction
path model described in Section 3. Using path integrals, for
example, allows one to evaluate the flux-flux autocorrelation
function[29a] $C_f(t)$,

$$C_f(t) = tr\{F \exp[-(\beta/2-it/\hbar)H]F \exp[-(\beta/2+it/\hbar)H]\} \quad (4.24a)$$

where F is the "flux-through-a-surface" operator; the Boltzmann rate
constant is given (exactly!) by the integral of this correlation
function,

$$k(T) = Q_0(T)^{-1} \int_0^\infty dt\, C_f(t), \quad (4.24b)$$

$Q_0(T)$ being the reactant partition function. Several applications
using this methodology to compute thermal rate constants have been
reported, some for simple A+BC gas phase reactions and some for
diffusion of H atoms on solid surfaces.[29b,c,d,e]

Other, less rigorous theoretical treatments can also be usefully
applied to the system-bath Hamiltonian of Eq. (4.19). One of the
most useful of these is the time-dependent self consistent field

(TDSCF) approximation.[30-34] Here the time dependent wave function is written as a product of factors ("orbitals"), one for each degree of freedom,

$$\psi(s,\underline{Q},t) = \chi(s,t) \prod_{k=1}^{F-1} \phi_k(Q_k,t). \qquad (4.25)$$

Substituting this ansatz for the wavefunction into the time-dependent Schrödinger equation leads to equations for the bath orbitals $\phi_k(Q_k,t)$ that can be solved exactly, and to the following one-dimensional Schrödinger equation for the system orbital,[34]

$$i\hbar \frac{\partial\chi(s,t)}{\partial t} = \{H_{sys} - \sum_{k=1}^{F-1} f_k(s)[\bar{Q}_k\cos(\omega_k t) + \bar{P}_k\sin(\omega_k t)/\omega_k]$$

$$- \sum_{k=1}^{F-1} f_k(s) \int_0^t dt'\bar{f}_k(t')\sin(\omega_k(t-t'))/\omega_k\}\chi(s,t), \qquad (4.26)$$

where

$$\bar{Q}_k = \langle\phi_k(0)|Q_k|\phi_k(0)\rangle \qquad (4.27a)$$

$$\bar{P}_k = \langle\phi_k(0)|P_k|\phi_k(0)\rangle \qquad (4.27b)$$

$$\bar{f}(t) = \langle\chi(t)|f_k|\chi(t)\rangle. \qquad (4.27c)$$

One recognizes Eq. (4.26), the one-dimensional Schrödinger equation for the system orbital $\chi(s,t)$, to be directly analogous to the classical equation of motion, Eq. (4.20); in Eq. (4.27) $\bar{Q}_k$ and $\bar{P}_k$ are the expectation values of the coordinate and momentum operators with the initial orbital for mode k, $\phi_k(Q_k,0)$, and $\bar{f}(t)$ is the expectation value of the operator $f_k(s)$ with the system orbital $\chi(s,t)$. Note that Eq. (4.26) is a non-linear Schrödinger equation because the function $\chi(s,t)$ appears in the definition of $\bar{f}(t')$; Eq. (4.26) would thus have to be solved iteratively.

An even better approximation is the multiconfiguration TDSCF approach[34] which expands the wavefunction as sums of products of the type in Eq. (4.25). This is particularly necessary if the wavefunction is composed of physically distinct parts as, for example, for the case a (multidimensional) double well potential function characteristic of an isomerization reaction.

Another very useful way of treating the system-bath Hamiltonian of Eq. (4.19) is via a basis set of shifted oscillator wavefunctions.[35] This has been seen to give an excellent description of coupling effects on double well isomerization reactions. The reader is referred to the original papers for the specifics of this approach.

5. CONCLUDING REMARKS

Use of a reaction path, either the minimum energy path or the linear path, with a local harmonic approximation to the potential energy about it allows one to overcome the intimidating problem of dealing with a potential energy surface in 3N-6 dimensional space. The minimum energy path will be useful for describing many, but not all reactions. It is not useful, for example, for H-atom transfer reactions, but the linear reaction path described in Section 3 should treat these processes quite well.

With either of these model Hamiltonians there may be cases when the local harmonic approximation to modes away from the reaction path may fail. If this happens for only a few of the modes then one can readily correct the situation simply by including higher order terms (i.e., cubic, quartic, etc.) in the potential in these few coordinates.

A variety of dynamical approaches are available for determining the reaction dynamics that result from these Hamiltonians. Section 4 has surveyed some of these, concentrating primarily on quantum mechanical methods. Classical trajectory methods are also always possible, and for other than H-atom transfer reactions should be adequate for most phenomena. The trajectories may be determined by "integrating out" the harmonic bath, i.e., Eq. (4.20), or probably simpler by integrating the trajectories in the full F=3N-6 dimensional space.

These two types of reaction path Hamiltonians, and a large array of dynamical tools should allow one to carry out realistic calculations to model a variety of dynamical processes in polyatomic systems.

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