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Publication Date

1980-07-01



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Materials & Molecular Research Division

Presented at the American Chemical Society Symposium
"Potential Energy Surfaces and Dynamics Calculations"
Las Vegas, NV, August 27-29, 1980

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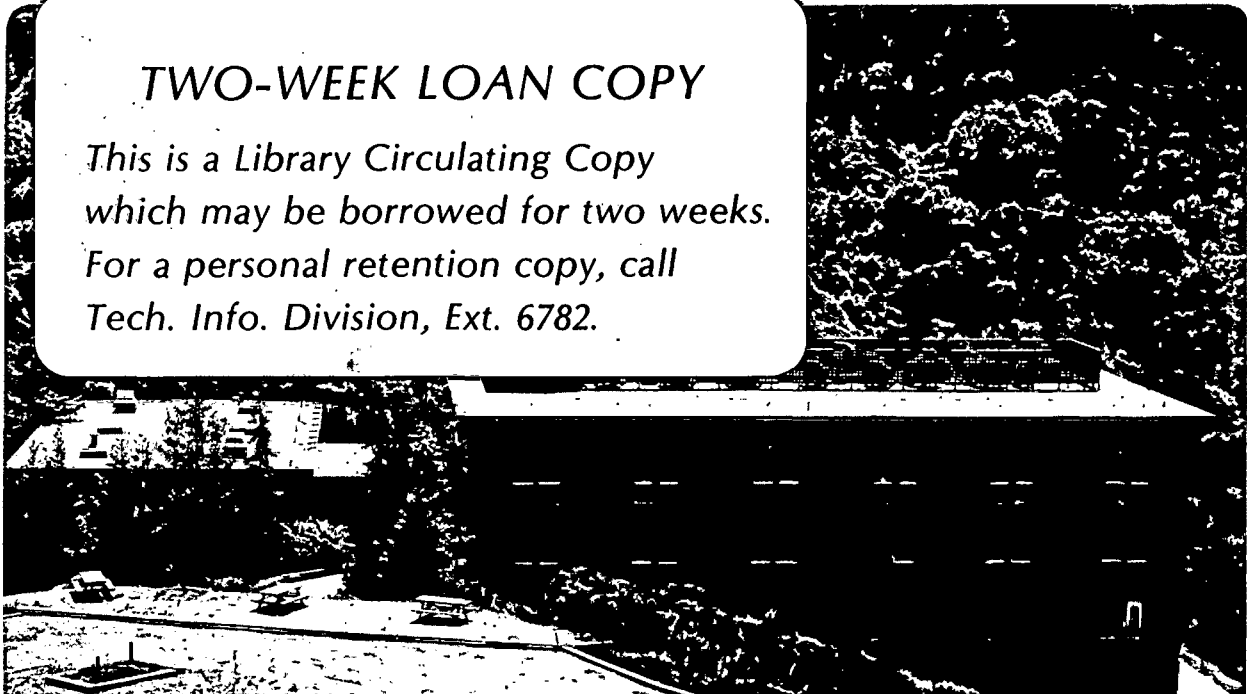
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REACTION PATH HAMILTONIAN FOR POLYATOMIC SYSTEMS:
FURTHER DEVELOPMENTS AND APPLICATIONS

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Abstract

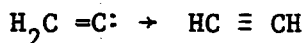
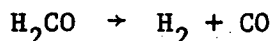
Several developments and new applications of the recently developed reaction path Hamiltonian model for polyatomic reaction dynamics are described. (1) The original form of the Hamiltonian is transformed so that the coupling between vibrational modes normal to the reaction path appears in the potential rather than in the kinetic energy of the Hamiltonian. This is easier to deal with in some applications. (2) It is shown that the unified statistical model takes an extremely simple form within the reaction path Hamiltonian model. Also, a generalized version of the unified statistical model is derived which permits an arbitrary number of "bottlenecks" (flux minima) along the reaction path. (3) A generalized Langevin equation is derived for motion along the reaction path. This is an equation of motion for only one degree of freedom, the reaction coordinate, but it experiences "friction" and "random" forces which are due to coupling with the vibrational modes normal to the reaction path.

I. Introduction.

Ab initio quantum chemistry has made important advances recently in developing methods¹ for the accurate and efficient calculation of the gradient of the potential energy surface, i.e., the derivative of the Born-Oppenheimer electronic energy with respect to nuclear coordinates, for a general molecular system. This has been used most commonly to facilitate the search for transition states, i.e., saddle points on a potential energy surface, but once a saddle point is found it can be used to follow the steepest descent path down from the transition state to reactants and to products. If mass-weighted cartesian coordinates were used, this is the reaction path,² and the distance along it the (mass-weighted) reaction coordinate.

Miller, Handy and Adams³ have recently shown how one can construct a classical Hamiltonian for a general molecular system based on the reaction path and a harmonic approximation to the potential surface about it. The coordinates of this model are the reaction coordinate and normal mode coordinates for vibrations transverse to the reaction path, and are essentially a polyatomic version of the "natural collision coordinates" introduced by Marcus⁴ and by Hofäcker⁵ for $A + BC \rightarrow AB + C$ reactions. One of the important practical aspects of this model is that all of the quantities necessary to define it are obtainable from a relatively modest number of ab initio quantum chemistry calculations, essentially independent of the number of atoms in the system. This thus makes possible an ab initio theoretical description of the reaction dynamics of more than atom-diatom (i.e., $A + BC \rightarrow AB + C$) reactions.

The first application⁶⁻⁸ made of this approach has been to tunneling effects in unimolecular rate constants. Specifically, the microcanonical rates $k(E)$ for the reactions



have been determined in the region below the classical reaction threshold. Somewhat surprisingly perhaps, tunneling is found to have extremely important consequences in these reactions.

This paper describes some new developments and applications based on the reaction path model. In Section II the original form of the reaction path Hamiltonian (cf. Eq. (1.1) below) is transformed to a new representation that has a more desirable structure for some applications. Section III shows how the reaction path model makes application of the unified statistical model⁹ for chemical reactions especially simple, and a generalized version of the unified statistical model is also developed there. Finally, in Section IV the fact that the reaction path model consists of one special degree of freedom--i.e., the reaction coordinate--coupled to a number of harmonic oscillators is exploited to derive a generalized Langevin equation¹⁰ (GLE) for motion along the reaction path. This is a reduced equation of motion for only the reaction coordinate, but it experiences "friction" and a "random force" because of coupling to the transverse vibrational modes.

In concluding this Introduction we summarize the form of the reaction path Hamiltonian³ for a non-rotating system, i.e., zero total angular

momentum, of $F = 3N-6$ ($N =$ number of atoms) degrees of freedom ($F = 3N-5$ if the reaction path corresponds to a linear molecule),

$$\begin{aligned}
 H(p_s, s, P, Q) = & \sum_{k=2}^F \left(\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2 \right) + V_0(s) \\
 & + \frac{\frac{1}{2} \left[p_s - \sum_{k,k'=2}^F Q_k P_{k'} B_{k,k'}(s) \right]^2}{\left[1 + \sum_{k=2}^F Q_k B_{k,1}(s) \right]^2} \quad (1.1)
 \end{aligned}$$

s and p_s are the reaction coordinate and its conjugate momentum, respectively, and $V_0(s)$ the potential energy as a function of s , the mass-weighted distance along the reaction path. Q_k and P_k , $k = 2, \dots, F$ are the normal mode coordinates and momenta for vibrations normal to the reaction path, with frequencies $\omega_k(s)$ that are functions of the reaction coordinate.

The coupling elements $B_{k,k'}(s)$ couple vibrational modes k and k' , and $B_{k,1}(s)$ couples vibrational mode k to the reaction coordinate (which is designated mode $k=1$). The coupling elements $B_{k,1}(s)$ are a measure of how the curvature of the reaction path couples to mode k ; the total curvature of the reaction path, $\kappa(s)$, is related to these elements by³

$$\kappa(s) = \sqrt{\sum_{k=2}^F B_{k,1}(s)^2} \quad (1.2)$$

The coupling functions $B_{k,k'}(s)$ are essentially a Coriolis-like coupling involving the twist of the vibrational modes about the reaction path as a function of s . The coupling functions, as well as $V_0(s)$ and $\{\omega_k(s)\}$,

are obtainable from the ab initio quantum chemistry calculation of the reaction path and the force constant matrix along it. The Hamiltonian for the rotating case, $J \neq 0$, has also been worked out³ but is more complicated than for $J = 0$ because of various kinds of rotation-vibration coupling.

In some applications it is useful to transform from the cartesian variables $\{Q_k, P_k\}$ of the vibrational modes to their action-angle variables¹¹ $\{n_k, q_k\}$, which are related by

$$Q_k = \sqrt{\frac{2n_k + 1}{\omega_k(s)}} \sin q_k \quad (1.3a)$$

$$P_k = \sqrt{(2n_k + 1)\omega_k(s)} \cos q_k \quad (1.3b)$$

$k = 2, \dots, F$. In terms of these variables the Hamiltonian becomes

$$H(p_s, s, \tilde{n}, \tilde{q}) = \frac{\frac{1}{2} [p_s - \sum_{k,k'=2}^F B_{k,k'}(s) \sqrt{(2n_k + 1)(2n_{k'} + 1)} \frac{\sqrt{\omega_k(s)}}{\omega_{k'}(s)} \sin q_k \cos q_{k'}]}{[1 + \sum_{k=2}^F B_{k,1}(s) \sqrt{\frac{2n_k + 1}{\omega_k(s)}} \sin q_k]^2} + V_0(s) + \sum_{k=2}^F (n_k + \frac{1}{2}) \omega_k(s) \quad (1.4)$$

This form is especially useful for semiclassical applications since the action variables $\{n_k\}$ are the classical counterpart to vibrational quantum numbers.

II. Elimination of Coriolis Coupling.

Before considering specific applications of the reaction path model, it is useful to show how a change of canonical variables can be made to eliminate the Coriolis coupling elements $\{B_{k,k'}\}$ from the Hamiltonian. Coupling between the vibrational modes is not eliminated by this transformation, but it is shifted from the kinetic energy, as in Eq. (1.1), to the potential energy (vide infra). Which (equivalent) form of the Hamiltonian is preferred, Eq. (1.1) or Eq. (2.13) below, depends on the application at hand.

The desire is to change from the canonical variables (s, p_s, P, Q) of Eq. (1.1) to new variables $(\bar{s}, \bar{p}_s, \bar{P}, \bar{Q})$ such that (1) the reaction coordinate is unchanged, i.e.,

$$\bar{s} = s \quad , \quad (2.1)$$

(2) in the new variables the kinetic energy associated with the reaction coordinate involves no Coriolis coupling terms, i.e.,

$$\bar{p}_s = p_s - \sum_{k,k'=2}^F Q_k P_{k'} B_{k,k'}(s) \quad , \quad (2.2a)$$

or in matrix notation

$$\bar{p}_s = p_s - \tilde{Q} \cdot \tilde{B}(s) \cdot \tilde{P} \quad ; \quad (2.2b)$$

the numerator in the last term in Eq. (1.1) is then simply $\frac{1}{2} \bar{p}_s^2$. A

third condition we wish to impose is that (3) the kinetic energy of the vibrational modes transverse to the reaction path maintains its diagonal form, i.e.,

$$\frac{1}{2} \sum_{k=2}^F P_k^2 = \frac{1}{2} \sum_{k=2}^F \bar{P}_k^2 \quad (2.3a)$$

or in matrix notation

$$\frac{1}{2} \underline{P} \cdot \underline{P} = \frac{1}{2} \underline{\bar{P}} \cdot \underline{\bar{P}} \quad (2.3b)$$

Equation (2.3) does not necessarily imply that $\underline{\bar{P}} = \underline{P}$, but that one must have

$$\underline{P} = \underline{U}(s) \cdot \underline{\bar{P}} \quad (2.4)$$

where \underline{U} is a unitary matrix that may be a function of s . Equation (2.3) is then fulfilled since

$$\underline{U}^\dagger(s) \cdot \underline{U}(s) = \underline{1} \quad (2.5)$$

Using Eqs. (2.2) and (2.4) in the usual way, one is able to construct the following generating function¹² to effect the transformation:

$$F_2(s, Q; \underline{\bar{p}}_s, \underline{\bar{P}}) = Q \cdot \underline{\bar{P}} + s \underline{\bar{p}}_s + \int_0^s ds' Q \cdot \underline{B}(s') \cdot \underline{U}(s') \underline{\bar{P}} \quad (2.6)$$

The associated differential equations which specify the $(s, p_s, Q, P) \rightarrow (\bar{s}, \bar{p}_s, \bar{Q}, \bar{P})$ transformation are¹²

$$p_s = \frac{\partial F_2}{\partial s} \quad (2.7a)$$

$$P = \frac{\partial F_2}{\partial Q} \quad (2.7b)$$

$$\bar{s} = \frac{\partial F_2}{\partial \bar{p}_s} \quad (2.7c)$$

$$\bar{Q} = \frac{\partial F_2}{\partial \bar{P}} \quad (2.7d)$$

Equations (2.7a) and (2.7c) reproduce the desired results in Eqs. (2.2) and (2.1) above, respectively. Equation (2.7b) leads to the following condition

$$P = \bar{P} + \int_0^s ds' B(s') \cdot U(s') \cdot \bar{P} \quad (2.8)$$

which together with Eq. (2.7) implies that the unitary matrix U must satisfy the equation

$$U(s) = 1 + \int_0^s ds' B(s') \cdot U(s') \quad (2.9)$$

Finally, Eq. (2.7d) defines the new vibrational coordinates in terms of the old,

$$\begin{aligned}\bar{Q} &= Q + \int_0^s ds' Q \cdot B(s') \cdot U(s') \\ &= Q \cdot [1 + \int_0^s ds' B(s') \cdot U(s')]\end{aligned}$$

or in light of Eq. (2.9) this reads

$$\bar{Q} = Q \cdot U(s) \quad (2.10a)$$

and the old coordinates are given in terms of the new ones by

$$Q = \bar{Q} \cdot U^\dagger(s) \quad (2.10b)$$

Equation (2.9) above is the most important relation involved in the transformation to the new variables. Given the Coriolis coupling elements $\{B_{k,k'}(s)\} \equiv B(s)$, Eq. (2.9) is an integral equation for the unitary matrix $U(s)$. By differentiating with respect to s , it is converted into the differential equation

$$U'(s) = B(s) \cdot U(s) \quad (2.11a)$$

with initial condition

$$U(0) = 1 \quad (2.11b)$$

The fact³ that the matrix $B(s)$ is real and skew-symmetric guarantees that U is indeed unitary. To see this, note that the matrix iB is hermitian, so that Eq. (2.11a) may be written as

$$i \frac{d}{ds} \underset{\approx}{U}(s) = [i \underset{\approx}{B}(s)] \cdot \underset{\approx}{U}(s)$$

which has the form of the time dependent (with $s = \text{time}$) Schrödinger equation (with hermitian Hamiltonian iB) for the time evolution operator $\underset{\approx}{U}$, which is well-known to be unitary.¹³ Equation (2.9) is then recognized as the integral form of the time-dependent Schrödinger equation. A formal solution for $\underset{\approx}{U}$ can be given as a power series in $\underset{\approx}{B}$,

$$\underset{\approx}{U}(s) = \underset{\approx}{1} + \int_0^s ds' \underset{\approx}{B}(s') + \int_0^s ds' \int_0^{s'} ds'' \underset{\approx}{B}(s') \cdot \underset{\approx}{B}(s'') + \dots \quad (2.12a)$$

or also as a time-ordered exponential

$$\underset{\approx}{U}(s) = T \exp \left[\int_0^s ds' \underset{\approx}{B}(s') \right] \quad (2.12b)$$

where T is the usual time-ordering operator.¹⁴

Using the above equations, it is easy to show that the Hamiltonian is given in terms of the new variables (from which the over-bars are now dropped) by

$$H(p_s, s, p, Q) = \frac{\frac{1}{2} p_s^2}{[1 + \sum_{k=2}^F Q_k \lambda_k(s)]^2} + \sum_{k=2}^F \frac{1}{2} p_k^2 + V_0(s) + \sum_{k, k'=2}^F \frac{1}{2} Q_k \Lambda_{k, k'}(s) Q_{k'} \quad (2.13a)$$

or in matrix notation

$$H(p_s, s, P, Q) = \frac{\frac{1}{2} p_s^2}{[1 + Q \cdot \lambda(s)]^2} + \frac{1}{2} P \cdot P + V_0(s) + \frac{1}{2} Q \cdot \Lambda(s) \cdot Q, \quad (2.13b)$$

where

$$\Lambda_{k,k'}(s) = \sum_{k''=2}^F U_{k,k''}^\dagger(s) \omega_{k''}(s)^2 U_{k'',k}(s)$$

or

$$\Lambda(s) = U^\dagger(s) \cdot \omega(s)^2 \cdot U(s), \quad (2.14a)$$

where $\omega(s)^2$ is the diagonal matrix of frequency squares, and

$$\lambda_k(s) = \sum_{k'=2}^F U_{k,k'}^\dagger(s) B_{k',1}(s)$$

or

$$\lambda(s) = U^\dagger(s) \cdot B_1(s). \quad (2.14b)$$

As noted at the beginning of this section, the coupling between vibrational modes k and k' now appears in the potential energy, characterized by the coupling element $\Lambda_{k,k'}(s)$. In many applications it is easier to handle this form of coupling than that in the Hamiltonian of Eq. (1.1). Since U is unitary, we note that the elements $\lambda_k(s)$, which couple mode k to the reaction coordinate, are related to the curvature of the reaction path in a similar way as the elements $B_{k,1}(s)$,

$$\kappa(s) = \sqrt{\sum_{k=2}^F \lambda_k(s)^2}$$

III. Unified Statistical Model, Generalization and Applications.

The "unified" statistical model⁹ was introduced originally in order to reconcile, or unify two different kinds of statistical theories, transition state theory¹⁵ which is appropriate for reactions proceeding via a "direct" reaction mechanism, and the phase space theory of Light¹⁶ and Nikitin¹⁷ which is designed to describe reactions proceeding via a long-lived collision complex. It is particularly straightforward to apply this theory within the framework of the reaction path Hamiltonian.

One needs to consider first the microcanonical flux through a sequence of (F-1) dimensional "dividing surfaces" which are normal to the reaction path at position s_0 along it. For total energy E this flux integral is⁹

$$N(s_0, E) = 2\pi\hbar h^{-F} \int ds \int dp_s \int d\tilde{p} \int d\tilde{Q} \delta(E-H) \delta(s-s_0) \dot{s} h(\dot{s}) \quad , \quad (3.1)$$

where H is the reaction path Hamiltonian of Eq. (1.1). The velocity \dot{s} is evaluated via Hamilton equations,

$$\dot{s} = \frac{\partial H}{\partial p_s} \quad , \quad (3.2)$$

where $h(\dot{s})$ is the unit step function,

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

which means that Eq. (3.1) is the "one-way flux" through the surface, i.e., the flux through it in the direction of increasing s . Using Eq. (3.2) and the Hamiltonian in Eq. (3.1), it is not a hard calculation to show that Eq. (3.1) gives the following simple expression,

$$N(s, E) = \frac{[E - V_0(s)]^{F-1}}{(F-1)! \prod_{k=2}^F \hbar \omega_k(s)}, \quad (3.3)$$

where s_0 has been replaced by s . Equation (3.3), which does not require that one neglect the B-coupling functions in Eq. (1.1), is essentially an RRK formula¹⁸ for a fixed value of the reaction coordinate.

The next step in the unified statistical theory⁹ is to look for minima in the flux with respect to s . If only one minimum, or "bottleneck" is found, at s_1 say, then simple transition state theory applies, and the cumulative reaction probability $N(E)$ -- which is defined exactly as

$$N(E) = \sum_{\tilde{n}_2, \tilde{n}_1} |S_{\tilde{n}_2, \tilde{n}_1}(E)|^2, \quad (3.4)$$

where $S_{\tilde{n}_2, \tilde{n}_1}(E)$ are the scattering S-matrix elements for the reaction as $s = -\infty \rightarrow +\infty$ --is given approximately by

$$N(E) = N(s_1, E) \quad (3.5)$$

If two minima are found, at s_1 and s_3 say, separated by a relative maximum at s_2 , then the unified statistical model gives the following

approximation to $N(E)$:

$$N(E) = \frac{N_1(E)N_3(E)}{N_1(E)+N_3(E) - N_1(E)N_3(E)/N_2(E)} \quad (3.6a)$$

where

$$N_i(E) = N(s_i, E) \quad , \quad i = 1, 2, 3 \quad (3.6b)$$

In appropriate limits this reduces to the Light-Nikitin statistical model,

$$N(E) = \frac{N_1(E)N_3(E)}{N_1(E) + N_3(E)}$$

Equation (3.6a) can be re-written in the following equivalent form

$$N(E) = \left[\frac{1}{N_1(E)} + \frac{1}{N_3(E)} - \frac{1}{N_2(E)} \right]^{-1} \quad (3.7)$$

and this is the form that generalizes. Thus suppose that relative minima of flux occur at values $s_1, s_3, s_5, \dots, s_{2M+1}$, and relative maxima of flux occur at s_2, s_4, \dots, s_{2M} . (The first and last flux extrema must always be minima, which can always be achieved by, if necessary, letting $s_1 \rightarrow -\infty$ and/or $s_{2M+1} \rightarrow +\infty$.) The generalized unified statistical model then approximates the cumulative reaction probability by

$$N(E) = \left[\sum_{i=0}^M \frac{1}{N_{2i+1}(E)} - \sum_{i=1}^M \frac{1}{N_{2i}(E)} \right]^{-1}, \quad (3.8)$$

where

$$N_i(E) = N(s_i, E), \quad i = 1, 2, \dots, 2M+1.$$

Equation (3.8) is most easily proved by induction. Thus for $M=2$, so that N_1, N_3 and N_5 are flux minima, and N_2 and N_4 are flux maxima, one considers the region of N_1, N_2 , and N_3 all as one "composite bottleneck" with net flux N_{123} given by Eq. (3.7):

$$\frac{1}{N_{123}(E)} = \frac{1}{N_1(E)} + \frac{1}{N_3(E)} - \frac{1}{N_2(E)}. \quad (3.9)$$

One then has the 3-extrema case again with fluxes N_{123}, N_4 , and N_5 , so that Eq. (3.7) is applied again to give

$$\frac{1}{N(E)} = \frac{1}{N_{123}(E)} + \frac{1}{N_5(E)} - \frac{1}{N_4(E)}, \quad (3.10)$$

which with Eq. (3.9) gives

$$\frac{1}{N(E)} = \frac{1}{N_1} + \frac{1}{N_3} + \frac{1}{N_5} - \frac{1}{N_2} - \frac{1}{N_4},$$

which is Eq. (3.8) for $M=2$. The general case is established by repetition of the argument from the obvious fashion.

Examples

It is interesting to see that this more general situation can arise in some simple applications. Consider first the general condition for an extremum in the flux $N(s,E)$,

$$\frac{\partial N(s,E)}{\partial s} = 0 \quad ; \quad (3.11)$$

from Eq. (3.3) it is not hard to show that this equation can be written in the form

$$V_0'(s) + [E - V_0(s)] \frac{1}{(F-1)} \sum_{k=2}^F \frac{\omega_k'(s)}{\omega_k(s)} . \quad (3.12)$$

If the saddle point $s=0$ is a point of symmetry, as for example in the $H + H_2 \rightarrow H_2 + H$ reaction, then the symmetry dictates that

$$V_0'(0) = 0$$

$$\omega_k'(0) = 0 \quad , \quad k = 2, \dots, F \quad ,$$

so that $s=0$ will always be an extremum in $N(s,E)$. For all the other extrema Eq. (3.13) can be written in the more convenient form

$$E = V(s) \quad , \quad (3.13a)$$

where $V(s)$ is independent of energy

$$V(s) = V_0(s) - \frac{V_0'(s)}{(F-1)^{-1} \sum_{k=2}^F \omega_k'(s)/\omega_k(s)} \quad (3.13b)$$

Collinear H + H₂

For this case F=2, so that Eq. (3.13b) becomes

$$V(s) = V_0(s) - V_0'(s) \omega(s)/\omega'(s) \quad (3.14)$$

and this quantity is plotted in Figure 1 for the Porter-Karplus¹⁹ H₃ potential energy surface. There are several different energy regions to distinguish.

(a) $0 \leq E - V_{sp} \lesssim 0.11$ eV. For energies less than 0.11 eV above the barrier the only extremum in the flux occurs at $s=0$, and it is a minimum. Thus Eq. (3.8) with $M=0$ applies, and this is the case of simple transition state theory. It is known, too, that transition state theory gives essentially exact agreement with classical trajectory calculations for this energy region.

(b) 0.11 eV $\lesssim E - V_{sp} \lesssim 0.25$ eV. Figure 1 shows that for this energy region there will be two roots of Eq. (3.13a) for $s > 0$, and there will be two symmetrically related roots for $s < 0$, as well as the one at $s=0$, for a total of five extrema in $N(s,E)$, two maxima and three minima, so that Eq. (3.8) applies with $M=2$.

(c) 0.25 eV $\lesssim E - V_{sp} \lesssim 0.34$ eV. Figure 1 shows that here there are three roots to Eq. (3.13a) for $s > 0$, and with the three symmetrically

related ones for $s < 0$ and the one at $s = 0$, there are seven flux extrema altogether so that Eq. (3.8) applies with $M = 3$.

(d) $0.34 \text{ eV} \lesssim E - V_{\text{sp}}$. For energies more than 0.34 eV above the saddle point Figure 1 indicates that there is just one root to Eq. (3.13a) for $s > 0$, and with the symmetrically related one for $s < 0$ and the one at $s = 0$, there are three flux extrema, so that Eq. (3.8) applies with $M = 1$.

The appearance and disappearance of various flux extrema as a function of energy is a manifestation of how the reaction mechanism changes as a function of energy; e.g., at low energies there is a single bottleneck to the reactive flux, and simple transition state theory is a good model, but at higher energies other bottlenecks appear. These same phenomena have been seen by Pechukas and Pollack²⁰ in a more dynamically based theory; the dividing surfaces at the flux extrema of the present statistical model become periodic classical trajectories that oscillate across the potential valley, i.e., "trapped trajectories".²⁰ It is interesting to see that many aspects of this more detailed dynamical treatment appear, albeit approximately, in a purely statistical model.

As noted above, the unified statistical model works very well at low energy--where it is simply transition state theory--and though it is an improvement over ordinary transition state theory at higher energies, it is not so accurate as at low energies. This seems to be due to the fact that implicit in the USM is an assumption of micro-canonical equilibrium between the dividing surfaces corresponding to

any two flux minima (i.e., bottlenecks). This is a plausible assumption for the case of a long-lived collision complex, but for the $H + H_2$ system discussed above the "collision complex" caused by the multiple bottlenecks is not sufficiently strongly coupled to make this a good approximation. In their more dynamically based theory, Pechukas et al. have been able to make progress by introducing more dynamical information into the description, but it is not clear how one can do this within a purely statistical model.

$H + H_2$ in 3-d.

Most of the features which complicate the statistical treatment of the collinear $H + H_2$ reaction--or perhaps make it interesting--actually disappear when the reaction is treated in three dimensions. Because the reaction path is linear for this case, $F = 3N-5 = 4$, and Eq. (3.13b) becomes

$$V(s) = V_0(s) - \frac{V_0'(s)}{\frac{1}{3} \left[\frac{\omega_v'(s)}{\omega_v(s)} + 2 \frac{\omega_b'(s)}{\omega_b(s)} \right]}, \quad (3.15)$$

where $\omega_v(s)$ is the stretching frequency normal to the reaction path (it is the symmetric stretch at the saddle point $s = 0$), the same frequency as $\omega(s)$ of the collinear system, and $\omega_b(s)$ is the bending vibrational frequency.

For the same (i.e., Porter-Karplus) potential energy surface, however, $V(s)$ above is negative relative to the saddle point energy for all values of s ; i.e., there are no roots to Eq. (3.13a) for any energy E , so that for all energies the flux minimum at $s=0$ is the only extremum. The unified statistical model is then simple transition

state theory for all energies, and it is indeed true²¹ that transition state theory is in quite good agreement with exact classical trajectory calculations to quite high energies; e.g., transition state theory is only 10% too large at $E - V_{sp} = 1$ eV, while it is a factor of two too large at this energy in the collinear case. The phase space effect of changing dimensionality can thus have dramatic effects on the reaction mechanism and is thus a warning against placing too much reliance on conclusions drawn from collinear studies.

Finally, we note that although all of the discussion in this section has applied to a completely classical mechanical treatment of the reaction, the expression for the cumulative reaction probability can be quantized in the usual ad hoc fashion in statistical theory by replacing the classical flux of Eq. (3.3) by the quantum mechanical integral density of states,

$$N_{QM}(s, E) = \sum_{n_2, n_3, \dots, n_F=0} h[E - V_0(s) - \sum_{k=2}^F (n_k + \frac{1}{2}) \hbar \omega_k(s)] ,$$

where h is again the unit step function. This expression must be modified further if one wishes to take account of tunneling through the bottleneck regions.

IV. Generalized Langevin Model.

In most chemical reactions, particularly those involving large molecular systems, not all modes of the composite system will be strongly coupled to the reaction path. If the reaction is an atom transfer reaction, for example, then modes corresponding to vibrations in regions of the molecules far from the reaction site will clearly be only weakly affected by the reaction. In terms of the reaction path Hamiltonian, this means that for such modes $\omega_k(s)$ will be essentially independent of s and the coupling elements $B_{k,1}(s)$ or $\lambda_k(s)$ will be small.

It seems intuitively reasonable, therefore, that one should be able to partition the complete F degrees of freedom into the reaction coordinate and the few vibrational modes that are strongly coupled to it (the "system"), and the remaining (perhaps very many) modes that are only weakly affected by the reaction (the "bath"). The "system" thus consists of the reaction coordinate, mode 1, and vibrational mode $k = 2, \dots, f$, say, and the "bath" are the remaining modes $k = f+1, \dots, F$. As is customary[‡] in such developments, the Hamiltonian is divided as

$$H = H_{\text{system}} + H_{\text{bath}} + H_{\text{coupling}}, \quad (4.1)$$

where the "system" Hamiltonian is the standard reaction path Hamiltonian for the f strongly coupled degrees of freedom, i.e., Eq. (1.1) or (2.13), with $F \rightarrow f$. The "bath" Hamiltonian is that for the $k = f+1, \dots, F$ uncoupled vibrational modes

[‡] Many references could be given related to generalized Langevin equations. The methodology I follow is very similar to that in reference 10.

$$H_{\text{bath}} = \sum_{k=f+1}^F \left(\frac{1}{2} p_k^2 + \frac{1}{2} \omega_k^2 Q_k^2 \right), \quad (4.2)$$

and H_{coupling} is the interaction coupling the "system" and the "bath". For this generalized Langevin approach to be useful it is necessary that the coupling be only a linear function of the "bath" coordinates $\{Q_k\}$ $k = f+1, \dots, F$. Taking the reaction path Hamiltonian as in Eq. (2.13), the potential energy part of H_{coupling} is of this form, namely

$$\sum_{k'=2}^f \sum_{k=f+1}^F Q_k \Lambda_{k,k'}(s) Q_{k'},$$

but the coupling in the kinetic energy is not, at least not without approximation. Thus the kinetic energy in Eq. (2.13) is linearized in the "bath" coordinates, so that the complete coupling Hamiltonian is taken as

$$H_{\text{coupling}} = \sum_{k'=2}^f \sum_{k=f+1}^F Q_k \Lambda_{k,k'}(s) Q_{k'} - \frac{p_s^2 \sum_{k=f+1}^F Q_k \lambda_k(s)}{\left[1 + \sum_{k=2}^f Q_k \lambda_k(s) \right]^3} \quad (4.3)$$

The next step in the standard generalized Langevin development is to construct the equations of motion for the "bath" variables. These are easily obtained,

$$\ddot{Q}_k(t) + \omega_k^2 Q_k(t) = - \sum_{k'=2}^f \Lambda_{k,k'}(s) Q_{k'} + \frac{p_s^2 \lambda_k(s)}{\left[1 + \sum_{k'=2}^f Q_{k'} \lambda_{k'}(s) \right]^3}, \quad (4.4)$$

and since the RHS is independent of the "bath" variables these equations can be solved immediately to give

$$Q_k(t) = Q_k^{(0)}(t) + \int_0^t dt' \frac{\sin \omega_k(t-t')}{\omega_k} \left[\frac{p_s(t')^2 \lambda_k(s(t'))}{[1 + \sum_{k'=2}^f Q_{k'}(t') \lambda_{k'}(s(t'))]^3} - \sum_{k'=2}^f \Lambda_{k,k'}(s(t')) Q_{k'}(t') \right], \quad (4.5a)$$

$k = f+1, \dots, F,$

where $Q_k^{(0)}$ is the free harmonic oscillator "bath" trajectory,

$$Q_k^{(0)}(t) = \sqrt{\frac{2n_k+1}{\omega_k}} \sin(q_k + \omega_k t) \quad ; \quad (4.5b)$$

(n_k, q_k) are the initial values for the action-angle variables of the "bath". The "bath" trajectory $\{Q_k(t)\}$, $k = f+1, \dots, F$ is now completely known in terms of the "system" trajectory $\{s(t), Q_k(t), k=2, \dots, f\}$, and by substituting it into the equation of motion for the "system" one obtains a generalized Langevin equation for the "system". The overall picture which emerges is then that of the reaction of a small dynamical "system" (of f degrees of freedom) which experiences "friction" and "random" forces from a harmonic bath. If $f = 2$, for example, the "system" consists of the reaction coordinate and one transverse vibrational mode, which is equivalent to a collinear $A + BC \rightarrow AB + C$ reaction system, but it is now a collinear reaction which experiences the additional effects of friction and random forces from the other vibrational modes.

The development is reasonably straight-forward from this point, the only non-standard effects arising because the coupling Hamiltonian of Eq. (4.3) involves one of the "system's" momenta, p_s , in addition

to its coordinates (s, Q_2, \dots, Q_f) . Rather than continuing with the general situation, we thus specialize to the particular case that all the vibrational modes are taken as the "bath"; i.e. the "system" is only the reaction coordinate itself. The picture of the reaction is then essentially that of Brownian motion, i.e., a particle moving in one dimension under the influence of friction and random forces from a surrounding medium (which in the present case is the set of all transverse vibrational modes). If all the vibrational modes are taken as the "bath", then the coupling elements $B_{k,k'}$ and $\Lambda_{k,k'}$ are all zero (by assumption), and $\lambda_k(s) = B_{k,1}(s)$ are the curvature couplings. One then obtains a generalized Langevin equation of the standard form¹⁰ for motion along the reaction coordinate,

$$\ddot{s}(t) + V_0'(s) + \int_0^t dt' \dot{s}(t') M(t, t') + R(t) = 0, \quad (4.6)$$

where the random force $R(t)$ is given by

$$R(t) = \frac{1}{\dot{s}} \sum_{k=2}^F \left[\frac{d(\dot{s}^2 \lambda_k)}{dt} \sqrt{\frac{2n_k+1}{\omega_k}} \sin(q_k + \omega_k t) + 2(\dot{s}^2 \lambda_k) \sqrt{(2n_k+1)\omega_k} \cos(q_k + \omega_k t) \right], \quad (4.7)$$

and M , the memory kernel for the friction force, is

$$\begin{aligned}
 M(t, t') = & \frac{1}{\dot{s}(t) \dot{s}(t')} \sum_{k=2}^F \left\{ \frac{d(\dot{s}^2 \lambda_k)}{dt} \frac{d(\dot{s}^2 \lambda_k)}{dt'} \frac{\cos \omega_k (t-t')}{\omega_k^2} \right. \\
 & + 4(\dot{s}^2 \lambda_k)_t (\dot{s}^2 \lambda_k)_{t'} \cos \omega_k (t-t') \\
 & + 2 \frac{d(\dot{s}^2 \lambda_k)}{dt} (\dot{s}^2 \lambda_k)_{t'} \frac{\sin \omega_k (t-t')}{\omega_k} \\
 & \left. + 2 (\dot{s}^2 \lambda_k)_t \frac{d(\dot{s}^2 \lambda_k)}{dt'} \frac{\sin \omega_k (t'-t)}{\omega_k} \right\} \\
 (\dot{s}^2 \lambda_k)_t = & \dot{s}(t)^2 \lambda_k(s(t)), \text{ etc.} \tag{4.8}
 \end{aligned}$$

We note that, as usual,¹⁰ the memory kernel can be expressed in terms of the Boltzmann average of the autocorrelation function of the random force,

$$M(t, t') = \frac{1}{kT} \langle R(t) R(t') \rangle_T, \tag{4.9}$$

where the Boltzmann average is over the initial values of the action-angle variables of the "bath"

$$\langle (\dots) \rangle_T \equiv \left(\prod_{k=2}^F \frac{\omega_k}{2\pi kT} \right) \int_0^{2\pi} dq \int_0^\infty dn e^{-\omega \cdot n/kT} (\dots), \tag{4.10}$$

where $(\underline{n}, \underline{q}) = n_k, q_k, k = 2, \dots, F$.

Using the above equations, a simple expression can be obtained for the average energy loss experienced by the reaction coordinate for a given time interval $(0, t_f)$,

$$\begin{aligned}
 \overline{\Delta E}_s & \equiv \left\langle \int_0^{t_f} dt \frac{d}{dt} \left[\frac{1}{2} \dot{s}^2 + V_0(s) \right] \right\rangle \\
 & = \left\langle \int_0^{t_f} dt \dot{s}(t) [\ddot{s}(t) + V_0'(s)] \right\rangle, \tag{4.11}
 \end{aligned}$$

where the average here need be only over the angle variables of the "bath". The expression one obtains is

$$\overline{\Delta E_s} = - \sum_{k=2}^F \overline{\Delta E_k} \quad , \quad (4.12a)$$

where $\overline{\Delta E_k}$, the average energy gained by mode k, is given by

$$\overline{\Delta E_k} = \left\langle \frac{1}{2} \left| \int_0^{t_f} dt e^{i\omega_k t} \dot{s}(t)^2 \lambda_k(s(t)) \right|^2 \right\rangle \quad , \quad (4.12b)$$

with the trajectory $s(t)$ determined by the generalized Langevin equation, Eq. (4.6). If, for example, $t=0$ corresponds to the saddle point of the potential surface, $s=0$, and $t_f \rightarrow \infty$ corresponds to the products, $s \rightarrow \infty$, then Eq. (4.12) gives the amount of energy gained by vibrational mode k as the reaction proceeds from transition state to products. If one adds the further approximation that the trajectory $s(t)$ is the zeroth order trajectory determined only by the potential $V_0(s)$, then the following explicit expression is obtained

$$\overline{\Delta E_k} = \frac{1}{2} \left| \int_0^\infty ds \lambda_k(s) \sqrt{2[E_s - V_0(s)]} \exp\left[i\omega_k \int_0^s ds' \sqrt{2[E_s - V_0(s')]} \right] \right|^2 \quad , \quad (4.13)$$

where E_s is the energy available at the transition state. We emphasize, though, that this approximation to the trajectory may be rather severe, so that Eq. (4.13) is probably only of qualitative utility.

Finally, we also emphasize that it is probably not a good idea to take all the vibrational modes as the "bath", for a few of them

will probably be strongly coupled to the reaction coordinate and this would introduce complicated dynamical structure into the "friction" and "random" forces. If one wishes to apply this procedure quantitatively, then it is probably much more realistic to keep at least the one or two modes most strongly coupled to the reaction coordinate--as measured by the size of the coupling elements $\lambda_k(s)$ or $B_{k,1}(s)$ -- as part of the "system", so that the "bath" then truly is a set of free harmonic oscillators only weakly coupled to it.

V. Concluding Remarks.

This paper has considered several formal and practical developments based on the reaction path Hamiltonian for a molecular system. The unified statistical model and its generalizations discussed in Section III and the generalized Langevin description developed in Section IV may find utility as computational techniques and/or conceptual frameworks for understanding various aspects of reaction dynamics in polyatomic systems.

Acknowledgments

This work has been supported by the Division of Chemical Sciences,
Office of Basic Energy Sciences, U.S. Department of Energy under
contract No. W-7405-Eng-48.

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Figure Caption

The quantity $V(s)$, as defined by Eq. (3.14), as a function of the (mass-weighted) reaction coordinate, for the collinear $H + H_2 \rightarrow H_2 + H$ reaction.

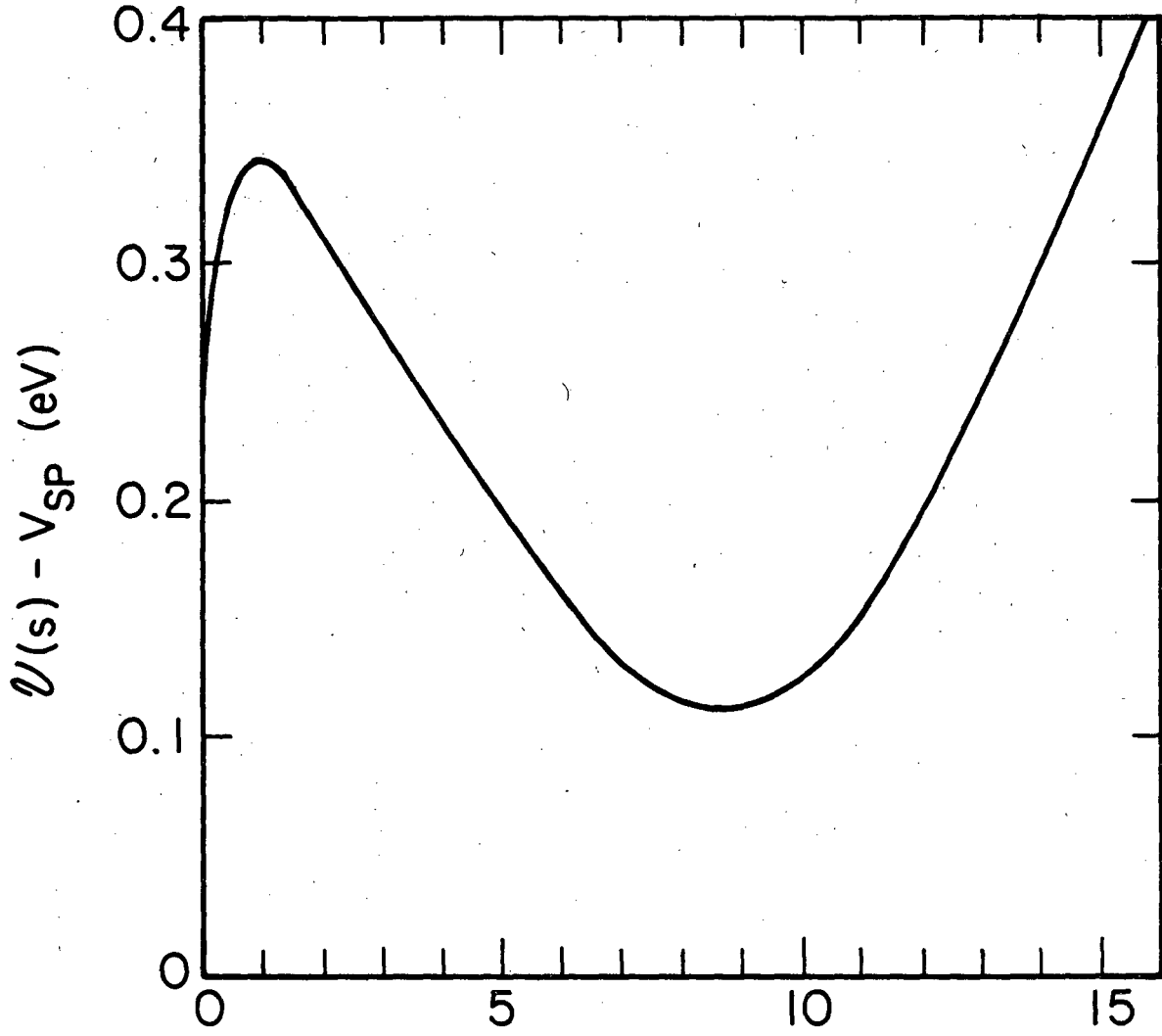


Fig. 1

s

XBL 8011-7398

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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