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Quantum Mechanics of Chemical Reactions: Recent Developments in Reactive Scattering and in Reaction Path Hamiltonians

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QUANTUM MECHANICS OF CHEMICAL REACTIONS: RECENT DEVELOPMENTS IN REACTIVE SCATTERING AND IN REACTION PATH HAMILTONIANS

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ABSTRACT. Two recent developments in the theory of chemical reaction dynamics are reviewed. First, it has recently been discovered that the S-matrix version of the Kohn variational principle is free of the "Kohn anomalies" that have plagued other versions and prevented its general use. This has considerably simplified quantum mechanical reactive scattering calculations, which provide the rigorous characterizations of bimolecular reactions. Second, a new kind of reaction path Hamiltonian has been developed, one based on the "least motion" path that interpolates linearly between the reactant and product geometry of the molecule (rather than the previously used minimum energy, or "intrinsic" reaction path). The form of Hamiltonian which results is much simpler than the original reaction path Hamiltonian, but more important is the fact that it provides a more physically correct description of hydrogen atom transfer reactions.

1. INTRODUCTION

In this paper I will review some of the recent developments in the theory of chemical reactions. The first topic, quantum reactive scattering, pertains to the most rigorous theoretical description (i.e., explicit solution of the Schrödinger equation with appropriate boundary conditions) of a chemical reaction. Not surprisingly, this methodology is currently applicable only to the simplest chemical processes (but in full 3-dimensional space), e.g., an atom-diatom reaction, $A+BC \rightarrow AB+C$. It is nevertheless exciting to see that it is now becoming possible to carry out the rigorous quantum calculations (i.e., a "simulation") that characterize these simplest reactions to the most complete level of detail allowed by the laws of nature.

The second topic deals with the theoretical description of more complex chemical systems. Specifically, a new class of reaction path models is described, namely the diabatic reaction path Hamiltonian. The difference between this new model and the earlier reaction path Hamiltonian is that the present one is based on a least motion reference path (i.e., a path that is linear interpolation between reactants and products) rather than on the minimum energy path the ("intrinsic" reaction path). This new version is more useful for treating hydrogen atom transfer reactions than is the earlier one (which is useful for many other kinds of reactions).

Before beginning the discussion of reactive scattering in Section 2, it is perhaps useful to take a few paragraphs here in the Introduction to summarize the background to these developments. In 1969 a general formulation of quantum scattering for chemical reactions was presented[1] which was a natural generalization of earlier work in electron scattering. The novel feature was that the wavefunction is expressed as a coupled channel expansion in standard Jacobi coordinates, but in all arrangements (i.e., A+BC, AB+C, AC+B). Coupling between states of different arrangements leads to a non-local, i.e., exchange-type of interaction, and this is what makes reactive scattering difficult in this formulation. (This reactive exchange interaction is analogous to electron exchange interactions that result when the electronic wavefunctions is antisymmetrized, i.e., expressed as linear combinations of different "arrangements" of the electrons.) Some other formulations[2] of chemically reactive scattering avoid these exchange interactions, which is of course an advantage, but they have other kinds of disadvantages of their own.

The only general way to deal with these exchange interactions seems to be[3] to expand the dependence of the wavefunction on the scattering coordinates in a basis set, using a variational principle to determine the expansion coefficients. Several such variational principles exist,[4] and they all work, but the simplest one to apply is the Kohn variational principle;[5] this is because it involves matrix elements only of the Hamiltonian operator itself and not those involving the Green's function for a reference problem. The Kohn principle has not been of general use, however, because of "Kohn anomalies",[6,7] i.e., spurious singularities that appear in the energy dependence of the scattering results.

The important recent discovery, however, is that there are no such "anomalies" if the Kohn principle is applied with S-matrix-type boundary conditions[8] (as opposed to K-matrix boundary conditions). With this rather subtle feature of the Kohn principle now understood, it provides a reliable and extremely straight-forward approach to quantum scattering, equally applicable to reactive or non-reactive processes. Section 2 describes this S-matrix version of the Kohn variational principle as it applies to chemically reactive scattering. This S-matrix version of the Kohn method has also been recently applied to electron-atom/molecule scattering,[9] with excellent results.

Mention should also be made of a number of recent reactive scattering calculations by Kouri, Truhlar, and coworkers.[10] These workers employ the coupled operator formalism of Baer and Kouri[11] (though the version of it they use makes it identical to the formulation of ref. 1), and then use the Newton variational method[12] for the amplitude density[13] to solve the equations. These authors have obtained excellent results for reaction probabilities of several atom-diatom reactions ($H+H_2$, $O+H_2$, $Br+H_2$) for zero total angular momentum ($J=0$), though we note the obvious disadvantage that this approach requires matrix elements of the operator ($G_0-G_0VG_0$).

The new diabatic reaction path Hamiltonian[14] is described in Section 3, and more background and the motivation for its development is given there. Its most notable feature is that there are no "curvature couplings" as in the original reaction path Hamiltonian[15] - because the reference path is straight - and the coriolis couplings between different modes are also eliminated. The kinetic energy is thus completely Cartesian-like. The price for this simplification of the kinetic energy is that the quadratic part of the potential energy now has off-diagonal terms. (There is also a term in the potential energy that is linear in the "bath" modes because the reference path is not the minimum energy path.) This elimination of kinetic energy coupling, at the expense of introducing coupling into the potential energy, is analogous to the diabatic electronic representation of a vibronic Hamiltonian and is the reason for our use of the term. As in the vibronic case, it is often easier to deal with the dynamics when the coupling appear in the potential rather than the kinetic energy.

2. S-MATRIX VERSION OF THE KOHN VARIATIONAL PRINCIPLE

2.1. General Methodology

All relevant features of the methodology are illustrated by simple s-wave potential scattering. It[8b] will thus first be described with regard to this problem, and the generalization to multichannel rearrangement scattering given at the end.

The Hamiltonian is of the standard form

$$H = \frac{-\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r), \qquad (2.1)$$

where $V(r) \to 0$ as $r \to \infty$. The S-matrix version of the Kohn variational approximation to the S-matrix (at energy E) can be stated as

$$S = \mathrm{ext}[\tilde{S} + \frac{i}{\hbar}\langle\tilde{\psi}|H-E|\tilde{\psi}\rangle], \qquad (2.2)$$

where $\tilde{\psi}(r)$ is a trial wavefunction that is regular at $r=0$ and has asymptotic form (as $r \to \infty$)

$$\tilde{\psi}(r) \sim -e^{-ikr}v^{-\frac{1}{2}} + e^{ikr}v^{-\frac{1}{2}}\tilde{S} \qquad (2.3)$$

where $v=\hbar k/\mu$ is the asymptotic velocity. (Note: The convention is used throughout this paper that the wavefunctions in the bra symbol

< | in bra-ket matrix element notation are not complex conjugated.) "ext" in Eq. (2.2) means that the quantity in square brackets is to be extremized by varying any parameters in $\psi(r)$. (Note that for a given trial function ψ, Eq. (2.2) may also be viewed as the distorted wave Born approximation, where ψ is the distorted wave.)

A linear variational form is taken for the trial function $\bar{\psi}(r)$,

$$\bar{\psi}(r) = -u_0(r) + \sum_{\ell=1}^{N} u_\ell(r) c_\ell , \tag{2.4}$$

where $u_0(r)$ is a function that is regular at $r=0$ and has the asymptotic form (as $r \to \infty$)

$$u_0(r) \sim e^{-ikr} v^{-1/2} . \tag{2.5}$$

A simple choice for $u_0(r)$ is

$$u_0(r) = f(r) e^{-ikr} v^{-1/2} , \tag{2.6}$$

where $f(r)$ is a smooth cut-off function,

$$\begin{aligned} f(r) &\to 0 \ , \ r \to 0 \\ f(r) &\to 1 \ , \ r \to \infty , \end{aligned} \tag{2.7}$$

such as $f(r)=1-e^{-\alpha r}$. (More generally, $u_0(r)$ may be the (irregular) solution of some (e.g., long range) distortion potential that has asymptotic form Eq. (2.5), multiplied by a cut-off function to regularize it at $r=0$). The function $u_1(r)$ is

$$u_1(r) = u_0(r)^* , \tag{2.8}$$

and the basis functions $\{u_\ell(r)\}$, $\ell=2,\ldots,N$ are real, square-integrable functions. The coefficients $\{c_\ell\}$, $\ell=1,\ldots,N$ in Eq. (2.4) are the variational parameters in ψ.

With ψ of Eq. (2.4) substituted into Eq. (2.2) and the coefficients $\{c_\ell\}$ varied to extremize it, one obtains the following expression for the S-matrix

$$S = \frac{i}{\hbar} \left(M_{0,0} - \underline{M}_0^T \cdot \underline{\underline{M}}^{-1} \cdot \underline{M}_0 \right) , \tag{2.9}$$

where $M_{0,0}$ is a 1x1 "matrix", $\underline{M}_0$ a 1xN matrix, and $\underline{\underline{M}}$ an NxN matrix,

$$M_{0,0} = \langle u_0|H-E|u_0\rangle \tag{2.10a}$$

$$(\underline{M}_0)_\ell = \langle u_\ell|H-E|u_0\rangle \tag{2.10b}$$

$$(\underline{\underline{M}})_{\ell,\ell'} = \langle u_\ell|H-E|u_{\ell'}\rangle \ , \tag{2.10c}$$

for $\ell,\ell'=1,\ldots,N$, and where "T" denotes matrix transpose. Note that all matrix elements involving the unbounded basis functions u_0 and u_1 exist because

$$\lim_{r\to\infty} (H-E) \left\{ \begin{matrix} u_0(r) \\ u_1(r) \end{matrix} \right. = 0. \tag{2.11}$$

Since the matrix $\underline{\underline{M}}$ of Eq. (2.10c) is complex-symmetric, there are no real values of E for which the matrix inverse in Eq. (2.9) is singular, and thus no "Kohn anomalies". In fact, the condition that Eq. (2.9) is singular, namely

$$\det(\underline{\underline{M}}) = \det\,[\langle u_\ell|H-E|u_{\ell'}\rangle] = 0, \tag{2.12a}$$

$\ell,\ell'=1,\ldots,N$, is the secular equation for eigenvalues of the Schrödinger equation

$$(H-E)\psi(r) = 0, \tag{2.12b}$$

with boundary condition (as $r\to\infty$)

$$\psi(r) \propto e^{ikr}. \tag{2.12c}$$

I.e., Eq. (2.12a) is the expression that has been used before[16] for determining Siegert eigenvalues,[17] the complex energies that are the (physically correct) complex poles of the S-matrix which characterize the positions and widths of scattering resonances. Eq. (2.9) is thus singular only where it is supposed to be singular.

For comparison, the Kohn principle for the K-matrix gives a similar expression,[7]

$$K = -\frac{2}{\hbar}\left(\tilde{M}_{0,0} - \underline{\tilde{M}}_0{}^T \cdot \underline{\underline{\tilde{M}}}^{-1} \cdot \underline{\tilde{M}}_0\right), \tag{2.13a}$$

where the matrix elements here have the same form as Eq. (2.10) except that the function $\tilde{u}_0$ and $\tilde{u}_1$ are different,

$$\tilde{u}_0(r) = -\text{Im}\ u_0(r) - \frac{\sin kr}{v^{1/2}} \qquad (2.13b)$$

$$\tilde{u}_1(r) = \text{Re}\ u_0(r) - \frac{\cos kr}{v^{1/2}}. \qquad (2.13c)$$

The fact the matrix $\tilde{\underline{M}}$ is real and symmetric leads to real values of E for which

$$\det(\tilde{\underline{M}}) = 0, \qquad (2.14)$$

and thus real values of E for which Eq. (2.13a) is singular, i.e., the Kohn anomalies.[18]

To emphasize again, use of the Kohn variational principle with standing wave boundary conditions to obtain (an approximation to) the K-matrix, as in Eq. (2.13), and then the S-matrix via the relation $S = (1+iK)(1-iK)^{-1}$, is not equivalent to using the Kohn principle with running wave boundary conditions to obtain (an approximation to) the S-matrix directly, i.e., Eqs. (2.2)-(2.10). And furthermore, as discussed above, the latter procedure is free of anomalous singularities and thus the preferred version of the Kohn method.

The S-matrix Kohn approach also allows one to identify a corresponding basis set approximation to matrix elements of the full outgoing wave Green's function $G^+(E) = (E+i\varepsilon-H)^{-1}$. This is[8a]

$$\langle a|G^+(E)|b\rangle = -\sum_{\ell,\ell'=1}^{N} \langle a|u_\ell\rangle\, (\underline{M}^{-1})_{\ell,\ell'} \langle u_{\ell'}|b\rangle, \qquad (2.15)$$

where $\underline{M}$ is as above, Eq. (2.10c), and $|a\rangle$ and $|b\rangle$ are any square-integrable functions. Note that the complex-symmetric structure of the matrix $\underline{M}$ is the same as that in complex scaling/coordinate rotation theory,[19-22] and for the same reasons. If the functions $|a\rangle$ and $|b\rangle$ are real, then Eq. (2.15) leads to a useful way for calculating matrix elements of the density of states operator,

$$\langle a|\delta(E-H)|b\rangle = -\pi^{-1}\,\text{Im}\langle a|G^+(E)|b\rangle. \qquad (2.16)$$

In actual calculations for the S-matrix, Eq. (2.9), one does not wish to carry out numerical calculations with the complex symmetric matrix $\underline{M}$. This can be avoided by the usual partitioning methods, so that Eq. (2.9) can be written in the equivalent form

$$S = \frac{i}{\hbar}\,(B - C\cdot B^{*-1}\cdot C), \qquad (2.17)$$

$$u_{0n}^{\gamma}(r_{\gamma}) = e^{-ik_{n\gamma}r_{\gamma}}/v_{n\gamma}^{1/2} .$$

$\underline{M}$ is a "large" by "large" real symmetric matrix in the composite space, internal plus translational,

$$(\underline{M})_{\ell n\gamma,\ell' n'\gamma'} = \langle u_{\ell n}^{\gamma}\phi_{n}^{\gamma}|H-E|u_{\ell' n'}^{\gamma'}\phi_{n'}^{\gamma'}\rangle, \qquad (2.20c)$$

where $\{u_{\ell n}^{\gamma}(r_{\gamma})\}$ is a square integrable basis (that need not depend on n - i.e., the same translational basis can be used for every channel). $\underline{M}_0$ is a "large" by "small" rectangular matrix

$$(\underline{M}_0)_{\ell n\gamma,n'\gamma'} = \langle u_{\ell n}^{\gamma}\phi_{n}^{\gamma}|H-E|u_{0n'}^{\gamma'}\phi_{n'}^{\gamma'}\rangle. \qquad (2.20d)$$

Only open channels $\{n\gamma\}$ are included in the matrices $\underline{M}_{00}$, $\underline{M}_{1,0}$, and the "small" dimension of $\underline{M}_0$, while open and closed channels are required in the matrix $\underline{M}$ and the "large" dimension of $\underline{M}_0$.

Eqs. (2.19) - (2.20) thus express the S-matrix for reactive scattering in an extremely straight-forward manner: one chooses basis functions, computes matrix elements of the Hamiltonian, and then does a standard linear algebra calculation.

2.2. Application to $F+H_2$

Initial application[8c] of the above methodology was made to the standard benchmark problem, the 3-d $H+H_2 \rightarrow H_2+H$ reaction for J (the total angular momentum quantum number) = 0. The results showed the S-matrix version of the Kohn method to be accurate, efficient, and stable.

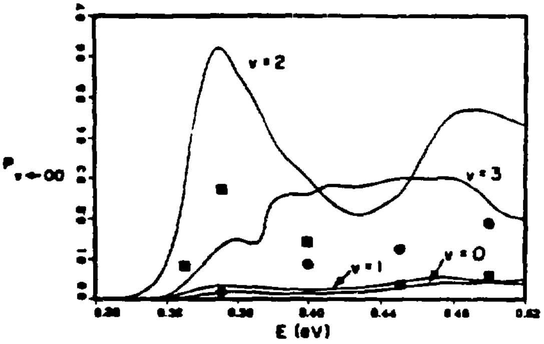

Figure 1. Reaction probabilities for $H_2(v=j=0)+F \rightarrow HF(v)+H$, summed

where B and C are the 1x1 "matrices"

$$B = M_{0,0} - \underline{M}_0^T \cdot \underline{\underline{M}}^{-1} \cdot \underline{M}_0 \qquad (2.18a)$$

$$C = M_{1,0} - \underline{M}_0^{*T} \cdot \underline{\underline{M}}^{-1} \cdot \underline{M}_0, \qquad (2.18b)$$

when $M_{0,0}$, $\underline{M}_0$, and $\underline{\underline{M}}$ are as before, Eq. (2.10), except that $\ell,\ell' = 2, \ldots, N$ (i.e., only the real basis functions), and

$$M_{1,0} = \langle u_0^* | H-E | u_0 \rangle. \qquad (2.18c)$$

Here the matrix $(M)_{\ell,\ell'}$, $\ell,\ell' = 2, \ldots, N$ is real and symmetric, and thus more easily dealt with. (One can readily verify that a value of E for which $\det(\underline{\underline{M}}) = 0$ does not lead to a singularity in Eq. (2.17.)

Finally, for general multichannel rearrangement scattering,[1] let (q_γ, r_γ) denote the internal coordinates and radial scattering (i.e., translational) coordinate for arrangement γ; $\{\phi_n^\gamma(q_\gamma)\}$ are the asymptotic channel eigenfunctions for the internal degrees of freedom. Eqs. (2.17) and (2.18) generalize as follows

$$\underline{\underline{S}} = \frac{i}{\hbar} (\underline{\underline{B}} - \underline{\underline{C}}^T \cdot \underline{\underline{B}}^{*-1} \cdot \underline{\underline{C}}), \qquad (2.19a)$$

where $\underline{\underline{S}}$, $\underline{\underline{B}}$, and $\underline{\underline{C}}$ are "small" square matrices, the dimension of the number of open channels, e.g., $\underline{\underline{S}} = [S_{n\gamma,n'\gamma'}]$, etc. $\underline{\underline{B}}$ and $\underline{\underline{C}}$ are given by

$$\underline{\underline{B}} = \underline{\underline{M}}_{0,0} - \underline{\underline{M}}_0^T \cdot \underline{\underline{M}}^{-1} \cdot \underline{\underline{M}}_0 \qquad (2.19b)$$

$$\underline{\underline{C}} = \underline{\underline{M}}_{1,0} - \underline{\underline{M}}_0^{*T} \cdot \underline{\underline{M}}^{-1} \cdot \underline{\underline{M}}_0, \qquad (2.19c)$$

where $\underline{\underline{M}}_{0,0}$ and $\underline{\underline{M}}_{1,0}$ are also "small" square matrices

$$(\underline{\underline{M}}_{0,0})_{n\gamma,n'\gamma'} = \langle u_{0n}^\gamma \phi_n^\gamma | H-E | u_{0n'}^{\gamma'} \phi_{n'}^{\gamma'} \rangle \qquad (2.20a)$$

$$(\underline{\underline{M}}_{1,0})_{n\gamma,n'\gamma'} = \langle u_{0n}^{\gamma*} \phi_n | H-E | u_{0n'}^{\gamma'} \phi_{n'}^{\gamma'} \rangle, \qquad (2.20b)$$

$u_{0n}^\gamma(r_\gamma)$ is a function regular at $r_\gamma = 0$ and with asymptotic form (as $r_\gamma \rightarrow \infty$),

$$u_{0n}^{\gamma}(r_\gamma) = e^{-ik_{n\gamma}r_\gamma}/v_{n\gamma}^{1/2} .$$

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where $\{u_{\ell n}^{\gamma}(r_\gamma)\}$ is a square integrable basis (that need not depend on n - i.e., the same translational basis can be used for every channel). $\underset{=}{M}_0$ is a "large" by "small" rectangular matrix

$$(\underset{=}{M}_0)_{\ell n\gamma,n'\gamma'} = \langle u_{\ell n}^{\gamma}\phi_n^{\gamma}|H-E|u_{0n'}^{\gamma'}\phi_{n'}^{\gamma'}\rangle . \qquad (2.20d)$$

Only open channels $\{n\gamma\}$ are included in the matrices $\underset{=}{M}_{00}$, $\underset{=}{M}_{1,0}$, and the "small" dimension of $\underset{=}{M}_0$, while open and closed channels are required in the matrix $\underset{=}{M}$ and the "large" dimension of $\underset{=}{M}_0$.

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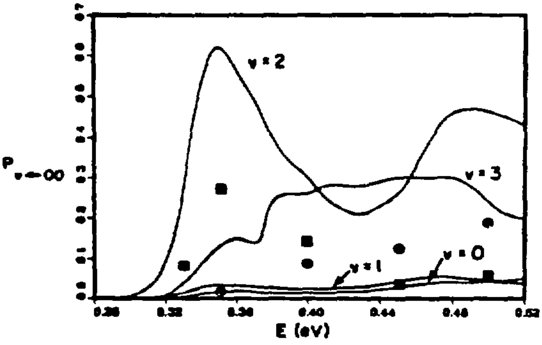


Figure 1. Reaction probabilities for $H_2(v=j=0)+F \rightarrow HF(v)+H$, summed

over final rotational states of HF, for total angular momentum J=0, as a function of total energy (relative to the minimum of the potential energy surface in the reactant valley). The squares (v=2) and circles (v=3) are results of earlier, less accurate calculations of other workers.

Much more impressive, though, is the calculation[8d] for the $F+H_2 \rightarrow HF+H$ reaction, also for J=0. Because the reaction is 32 kcal/mole exothermic, there are many HF vibrational and rotational states that must be included in the coupled channel expansion. Fig. 1 shows the reaction probabilities (the square of the S-matrix elements) for ground state (v=j=0) H_2 and various final vibrational states of HF (summed over final rotational states). These are the first quantitative calculations for the 3-d version of this reaction, and one sees the well-known population inversion that leads to the HF chemical laser.

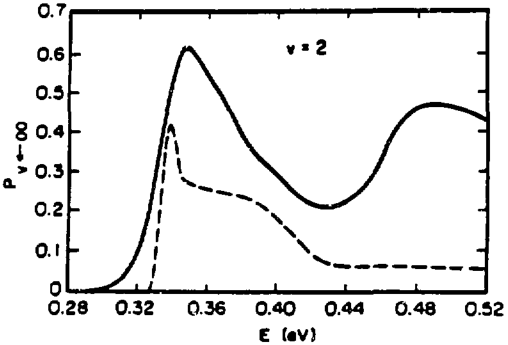


Figure 2. The HF(v=2) result of Fig. 1 (solid curve) compared to the collinear reaction probability (dashed curve) $H_2(v=0)+F \rightarrow HF(v=2)+H$ of ref. 23, using the same potential energy surface. The collinear result has been shifted in energy by $\hbar\omega_b^{\ddagger}$, $\omega_b^{\ddagger}$ being the bending frequency of H-H-F at the saddle point on the potential energy surface.

Fig. 2 shows the 0→2 reaction probability compared to the analogous collinear result,[23] the latter having been shifted in energy by $\hbar\omega_b^{\ddagger}$, $\omega_b^{\ddagger}$ being the bending frequency of the "activated complex". For reactions that have strongly collinear potential energy surfaces (i.e., large $\hbar\omega_b^{\ddagger}$) one often finds[24] that the energy-shifted collinear reaction probability is a good approximation to the corresponding 3-d vibrational reaction probabilities (summed over rotational states). This is seen not to be the case here, presumably because the bending frequency at the transition state is very small for $F-H_2$. Finally, Fig. 3 shows the distribution of final rotational states that results from the $F+H_2(v=0) \rightarrow HF(v=2)+H$ transition. One sees considerable rotational excitation in the products.

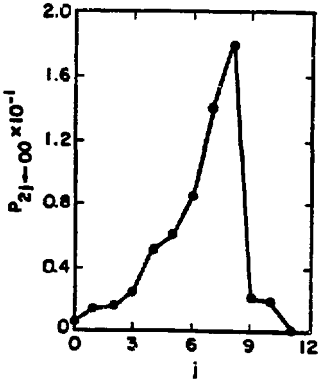


Figure 3. Reaction probability for $H_2(v=j=0)+F \rightarrow HF(v=2,j)+H$, as a function of j, the rotational quantum number of HF, also for total angular momentum J=0.

2.3. Enhancements

There are a number of further developments and enhancements that should make the S-matrix version of the Kohn variational principle even more useful for reactive (and electron-molecule) scattering. One of these is use of a discrete variable,[25] or pseudo-spectral representation[26] for the translational basis set. Though this might require the use of slightly larger translational bases, it has the very desirable feature that matrix elements of the potential energy are diagonal, i.e., simply the value of the potential function at the grid points. Thus rather than having to evaluate matrix elements by numerical integration for a 5000x5000 potential energy matrix, say, one has only to evaluate the potential energy function at 5000 points.

The idea of basis set contraction that is commonly used in computational quantum chemistry[27] should also prove useful for the present calculation. Thus to reduce the size of the transitional basis, one diagonalizes a zeroth matrix in the translational index alone and then chooses a sub-set of these eigenfunctions ("better" basis functions) as the translational basis for the full calculation.

Another extremely important simplification has been pointed out by Rescigno and Schneider,[28] namely that it is essentially no approximation to neglect exchange (i.e., $\gamma \neq \gamma'$) matrix elements in the "free-free" matrices $\underline{M}_{00}$ and $\underline{M}_{1,0}$, Eqs. (2.20a and b), and in the "bound-free" matrix $\underline{M}_0$, Eq. (2.20d). It is clear that this will be possible for the present application[29] because the "free" translational functions $u_{0n}^{\gamma}(r_\gamma)$ include a cut-off function that cause them to vanish in the close-in interaction region where exchange is significant. Thus the exchange interaction is mediated entirely by the "bound-bound" matrix $\underline{M}$, Eq. (2.20c). The practical significance of this is that "direct" matrix elements (the ones diagonal in the arrangement index γ) are much easier to compute than exchange ones, and furthermore it is the matrices $\underline{M}_{00}$, $\underline{M}_{1,0}$, and $\underline{M}_0$ that must be recalculated anew at each scattering energy (because $u_{0n}^{\gamma}(r_\gamma)$ is energy-dependent). This observation thus considerably simplifies the energy-dependent part of the calculation.

Another strategy that may be useful is that suggested parenthetically after Eq. (2.7), i.e., to incorporate distorted wave-like information into the function $u_0(r)$ (and $u_1 = u_0^*$). The most complete version of this idea would be to use a multichannel distorted wave[30] for u_0. More specifically, consider Eqs. (2.19)-(2.20) for the general multichannel rearrangement case. One modifies the function $u_{0n}(r)$ in the following way

$$u_{0n}(r)\phi_n(q) \to \sum_{n''} \phi_{n''}(q) u^{(0)}_{n''\leftarrow n}(r) f(r), \qquad (2.21)$$

where $f(r)$ is a cut-off function as before, and $u^{(0)}_{n''\leftarrow n}(r)$ satisfies the open channel inelastic coupled-channel Schrödinger equation with asymptotic boundary condition

$$u^{(0)}_{n''\leftarrow n}(r) \sim \delta_{n'',n}\, e^{-ik_n r}\, v_n^{-1/2}. \qquad (2.22)$$

(The arrangement index γ has been dropped here because, as noted in the above paragraph, we do not need to consider matrix elements with these functions between different arrangements.) In practice one determines the functions $\{u^{(0)}_{n''\leftarrow n}(r)\}$ by beginning at large r with the initial condition of Eq. (2.22) and integrating the inelastic (non-reactive) coupled channel equations inward as far as is needed; the cut-off function $f(r)$ determines how far in this is. The matrices $\underline{M}_{0,0}$ and $\underline{M}_{1,0}$ of Eqs. (2.20a) and (2.20b) (now diagonal in γ) can be shown then to take the very simple form

$$(\underline{M}_{0,0})_{n,n'} = \frac{\hbar^2}{2\mu} \sum_{n''} \langle u^{(0)}_{n''\leftarrow n} | f'^2 | u^{(0)}_{n''\leftarrow n'} \rangle \qquad (2.23a)$$

$$(\underline{M}_{1,0})_{n,n'} = \frac{i\hbar}{2} \delta_{n,n'} + \sum_{n''} \langle u^{(0)*}_{n''\leftarrow n} | f'^2 | u^{(0)}_{n''\leftarrow n'} \rangle \qquad (2.23b)$$

for each arrangement γ. The rectangular matrix takes a correspondingly simple form. The virtue of using this more sophisticated function for u_0 is that the short-range basis functions $\{u_{\gamma n}\}$ now need to span a much smaller region of space so that fewer of them will be required. Applications using this approach are in progress.[31]

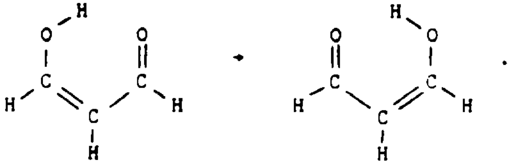
Finally, since it is the S-matrix that is being calculated, one has the option of computing the full matrix or only one row of it. If a general purpose (e.g., LU decomposition) algorithm is used to evaluate $\underset{=}{M}^{-1}\cdot\underset{=}{M}_{0}$ in Eq. (2.19), then there is little economy in evaluating only one row of the S-matrix. If iterative methods (e.g., Lanczos recursion[32]) are used, however, the effort is proportional to the number of rows of the S-matrix that one evaluates. If one is interested in only one, or a few initial states, then such a procedure will be considerably more efficient, meaning that substantially larger calculations will be feasible.

3. A DIABATIC REACTION PATH HAMILTONIAN

3.1. Background

The idea of a reaction path is a venerable one in the theory of chemical reactions.[33,34] The minimum energy reaction path on the Born-Oppenheimer potential energy surface, also called the intrinsic reaction path,[34d] is uniquely defined as the steepest descent path (in mass-weighted Cartesian coordinates) from the transition state (the saddle point on the potential surface) down to the local minima that are the equilibrium geometries of reactants and products. More recently[15] it was shown how to express the (classical or quantum) Hamiltonian of an N atom molecular system in terms of the reaction coordinate, the distance along this reaction path, and 3N-7 local normal mode coordinates for vibrations orthogonal to it (and three Euler angles for overall rotation of the N atom system), plus momentum variables (or operators) conjugate to these coordinates. This reaction path Hamiltonian has been used successfully to describe a variety of processes in polyatomic reaction dynamics.[35,36]

Though the reaction path Hamiltonian based on the minimum energy path has proved useful for many reactions, and will surely do so for many others, there are situations for which it is not appropriate. One of the most important of these is H-atom transfer reactions, a prototype of which is the symmetric H-atom transfer in malonaldehyde,[37]



(3.1)

This is a polyatomic version of a heavy + light-heavy mass combination reaction, for which the proto-type is a simple atom-diatom reaction such as

$$\mathrm{Cl} + \mathrm{HCl} \rightarrow \mathrm{ClH} + \mathrm{Cl}. \tag{3.2}$$

For this atom-diatom system it is well-known[38] that the minimum energy path is very sharply curved, so that the relevant dynamical motion deviates far from it. It is also well-known that the reaction path Hamiltonian (which reduces to Marcus' natural collision coordinates[33b] for an A+BC system) is not useful in this case.

The situation is actually much worse for H-atom transfer in a *polyatomic* system, e.g., (3.1), than for the atom-diatom case (3.2), because the minimum energy path undergoes *many* sharp turns (in 3N-6 dimensional space) on its way from the transition state down to reactants and products. In fact one knows in general that the steepest descent path approaches a local minimum on the potential surface (i.e., reactants or products) along the normal mode of lowest frequency.[39] For reaction (3.1), for example, the steepest descent path begins at the saddle point being mostly motion of the H-atom that is transferred, but in moving downhill it switches successively to other motions, finally approaching the potential minimum along some in-plane skeletal vibration, the in-plane mode of lowest frequency. This "kinky" path is clearly not appropriate for defining a reaction coordinate.

To deal with H-atom transfer reactions in polyatomic systems, such as (3.1), we have previously suggested[39] using a *straight-line Cartesian path*[40] on which to base the dynamical model. The purpose of this paper is to develop this idea in a more rigorous fashion than before, correctly incorporating conservation of total angular (and, trivially, linear) momentum. We also show rigorously how all coupling in the *kinetic* energy part of the Hamiltonian can be eliminated, it then appearing in the *potential* energy. For this reason we have termed this model a *diabatic* reaction path Hamiltonian in analogy with the adiabatic/diabatic language used for describing systems with electronic and nuclear (i.e., vibration, rotation, translation) degrees of freedom.[41] Following this analogy, the original reaction path Hamiltonian[15] would be called the *adiabatic* reaction path Hamiltonian since the local vibrational modes orthogonal to the reaction path are the exact normal modes for a fixed value of the reaction coordinate (i.e., a fixed position on the reaction path); coupling between these modes and the reaction coordinate appears in the kinetic energy, just as does the coupling between nuclear degrees of freedom and adiabatic electronic states. In the model developed in this paper, coupling between the reaction coordinate and perpendicular modes has been transformed from the kinetic to the potential energy, the same as for a diabatic electronic representation.

It is useful to discuss qualitatively why we think a linear reference, or reaction path, will be useful for H-atom transfer reactions. Fig. 4a shows the sketch of (contours of) a potential energy surface typical of a collinear heavy + light-heavy system, e.g., reaction (3.2) It is well known[39,42] in such cases that the tunneling dynamics does not follow the minimum energy path (the full line) but rather "cuts-the-corner"; the linear path from reactants to products is the extreme version of this. Fig. 4a also pertains to certain modes in a polyatomic system that have a predominantly symmetric type of coupling; for example, the 2-d potential surface for reaction (3.1) that includes the reaction coordinate (s-coordinate) and the O-O stretch (Q-coordinate) looks qualitatively like Fig. 4a.

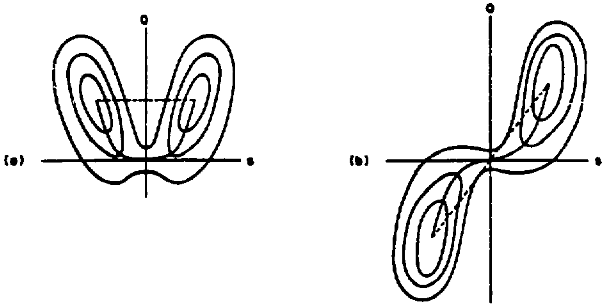
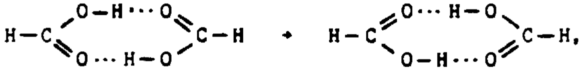


Figure 4. Sketch of contour plots for two characteristic potential energy surfaces. The solid lines indicate the minimum energy path from the transition state down to reactants and to products, and the broken line is the straight line path from reactants to products.

Fig. 4b, on the other hand, is for a mode with predominantly asymmetric coupling to the reaction coordinate, one for which the potential well in the reaction coordinate is asymmetric for a fixed (non-zero) value of the other coordinate. The minimum energy path in this case will also be sharply curved and not useful for defining a reaction coordinate. The straight-line path in this case "cuts" both corners, passing through the transition state. An example of this situation is the double H-atom transfer in formic acid dimer,


(3.3)

where the coordinate s of Fig. 4b is the concerted motion of the two H atoms and Q the asymmetric O-C-O stretch that is coupled strongly to it.

3.2. The Linear, or Least Motion, Reaction Path

First some comments on notation. Three-dimensional Cartesian vectors are indicated as bold-face quantities with an over arrow. Thus $\vec{\mathbf{R}}_i$, $i=1,\ldots,N$, are the Cartesian coordinates of the N atoms; $\vec{\mathbf{x}}_i$ are the corresponding mass-weighted coordinates

$$\vec{\mathbf{x}}_i = \sqrt{m_i}\;\vec{\mathbf{R}}_i . \tag{3.4a}$$

Bold-face $\mathbf{x}$ with no index i is the 3N dimensional vector $\{x_{i\gamma}\}$, $\gamma=x,y,z$, $i=1,\ldots,N$. We will switch on occasion between vector notation and component notation; thus in component notation Eq. (3.4a) is

$$x_{i\gamma} = \sqrt{m_i}\, R_{i\gamma}. \tag{3.4b}$$

The *linear reaction path* is defined by linear interpolation between reactant and product geometry, i.e.,

$$\underset{\sim}{x}_0(s) = \tfrac{1}{2}(\underset{\sim}{x}_r + \underset{\sim}{x}_p) + (\underset{\sim}{x}_p - \underset{\sim}{x}_r)(s/\Delta s) \tag{3.5a}$$

$$\Delta s = |\underset{\sim}{x}_p - \underset{\sim}{x}_r|, \tag{3.5b}$$

where $\underset{\sim}{x}_r$, $\underset{\sim}{x}_p$ $(=\{x_{i\gamma}^{(r)}\}, \{x_{i\gamma}^{(p)}\})$ are the 3N mass-weighted Cartesian coordinates of the atoms for the equilibrium geometry of the reactants and products, respectively. In terms of the coordinates $\underset{\sim}{\vec{R}}_i$, Eq. (3.5) is

$$\underset{\sim}{\vec{R}}_i^{(0)}(s) = \tfrac{1}{2}(\underset{\sim}{\vec{R}}_i^{(r)} + \underset{\sim}{\vec{R}}_i^{(p)}) + (\underset{\sim}{\vec{R}}_i^{(p)} - \underset{\sim}{\vec{R}}_i^{(r)})(s/\Delta s). \tag{3.5c}$$

s, the reaction coordinate, is the distance along this path, and as s varies from $-\Delta s/2$ to $+\Delta s/2$ the reference geometry varies from that of reactants to products. We note that

$$\underset{\sim}{x}_0'(s) = (\underset{\sim}{x}_p - \underset{\sim}{x}_r)/\Delta s, \tag{3.6a}$$

so that

$$|\underset{\sim}{x}_0'(s)| = 1, \tag{3.6b}$$

where prime denotes (d/ds).

To make the above definitions concrete we must specify how the axis system which defines product coordinates $\underset{\sim}{\vec{R}}_i^{(p)}$ is related to the axis that is used to define the reactant coordinates $\underset{\sim}{\vec{R}}_i^{(r)}$. This is intimately connected with the requirement[43] that the reference path $\underset{\sim}{x}_0(s)$ be one for which *no linear or angular momentum be generated* for displacements along it. I.e., to use the Hougen-Bunker-Johns[43] methodology the path $\underset{\sim}{x}_0(s)$ must satisfy the conditions

$$0 = \sum_i m_i\, \underset{\sim}{\vec{R}}_i^{(0)\prime}(s) \tag{3.7a}$$

where $\underline{T}$ is the 3x3 Cartesian rotation matrix[44] parameterized by three Euler angles that specify the rotation. These three Euler angles are chosen so that the three equations in Eq. (3.11) are satisfied.

It is useful to see explicitly how this works for the case that reactant and product molecule are <u>planar</u>, e.g., as for reactions (3.1) and (3.3). The reactant and product coordinate vectors thus have the form

$$\underline{\vec{R}}_i^{(r)} = \begin{pmatrix} X_i^{(r)} \\ Y_i^{(r)} \\ 0 \end{pmatrix}, \quad \underline{\vec{R}}_i^{(p)} = \begin{pmatrix} X_i^{(p)} \\ Y_i^{(p)} \\ 0 \end{pmatrix}, \tag{3.13}$$

and it is then easy to show that Eq. (3.11) reduces to the single equation

$$0 = \sum_i m_i \left(X_i^{(r)}Y_i^{(p)} - Y_i^{(r)}X_i^{(p)}\right] = \sum_i m_i \left(\underline{\vec{R}}_i^{(r)} \times \underline{\vec{R}}_i^{(p)}\right)_z . \tag{3.14}$$

If Eq. (3.14) is not true, then the product axis system is rotated by an angle ϕ about the z-axis, whereby $\underline{\vec{R}}_i^{(p)}$ of Eq. (3.13) is replaced by

$$\begin{pmatrix} X_i^{(p)} \\ Y_i^{(p)} \\ 0 \end{pmatrix} \to \begin{pmatrix} \cos\phi \; X_i^{(p)} + \sin\phi \; Y_i^{(p)} \\ -\sin\phi \; X_i^{(p)} + \cos\phi \; Y_i^{(p)} \\ 0 \end{pmatrix}. \tag{3.15}$$

With this replacement it is a simple calculation to show that (3.14) becomes

$$0 = -\sin\phi \sum_i m_i \left(X_i^{(r)}X_i^{(p)} + Y_i^{(r)}Y_i^{(p)}\right)$$
$$+ \cos\phi \sum_i m_i \left(X_i^{(r)}Y_i^{(p)} - Y_i^{(r)}X_i^{(p)}\right),$$

which is satisfied by the choice

$$\phi = \tan^{-1}\left[\frac{\sum_i m_i \left(\underline{\vec{R}}_i^{(r)} \times \underline{\vec{R}}_i^{(p)}\right)_z}{\sum_i m_i \; \underline{\vec{R}}_i^{(r)} \cdot \underline{\vec{R}}_i^{(p)}}\right] . \tag{3.16}$$

Thus if the original product coordinates $\underline{\vec{R}}_i^{(p)}$ do not satisfy Eq. (3.14), they are rotated according to Eq. (3.15), with the angle ϕ given by Eq. (3.16).

The requirement of no linear and angular momentum along the reaction path, Eq. (3.7), thus uniquely defines the axis system for the product coordinates with respect to that for the reactant.

3.3. Reaction Path Hamiltonian for a Linear Reaction Path

With the linear reaction path defined as in the previous section, one can proceed to construct the Hamiltonian in precisely the same manner as for the original reaction path Hamiltonian.[15] Thus the reaction path Hamiltonian for J=0 is given by

$$H(P_s, s, \{P_k, Q_k\}) = \tfrac{1}{2}[P_s - \sum_{k,k'=1}^{3N-7} Q_k P_{k'} B_{k,k'}(s)]^2$$

$$+ \sum_{k=1}^{3N-7} \tfrac{1}{2} P_k{}^2 + V_0(s) - \sum_{k=1}^{3N-7} Q_k f_k(s) + \sum_{k=1}^{3N-7} \tfrac{1}{2}\omega_k(s)^2 Q_k{}^2, \qquad (3.17)$$

where

$$f_k(s) = -\sum_{i\gamma} D_{i\gamma}(s) L_{i\gamma,k}(s) \qquad (3.18a)$$

$$D_{i\gamma}(s) = \left(\frac{\partial V}{\partial x_{i\gamma}}\right)_{\underline{x}=\underline{x}_0(s)} \qquad (3.18b)$$

and

$$B_{k,k'}(s) = \sum_{i\gamma} L_{i\gamma,k}{}'(s) L_{i\gamma,k'}(s). \qquad (3.19)$$

In the above equations $\{L_{i\gamma,k}(s)\}$, $k=1, \ldots, 3N-7$ are, as before,[15] the eigenvectors of the projected force constant matrix along the reaction path, and $\{\omega_k(s)^2\}$ are the eigenvalues.

Eq. (3.17) is the same as the original reaction path Hamiltonian[15] with two exceptions. First, because the reaction path is straight, the curvature coupling elements $B_{k,3N-6}(s) = 0$, so the first term in the Hamiltonian does not have the factor

$$[1 + \sum_{k=1}^{3N-7} Q_k B_{k,3N-6}(s)]^2 \qquad (3.20)$$

that appears in the denominator of the previous result.[15] Second, since the present linear reaction path is not the minimum energy path, the potential energy has a term that is linear in the coordinates $\{Q_k\}$. We note also that cubic and quartic terms in coordinates $\{Q_k\}$ can readily be added to Eq. (3.17) if the third and fourth Cartesian derivatives of the potential are evaluated along the reaction path. The cubic term, for example, is

$$\frac{1}{6} \sum_{k,k',k''=1}^{3N-7} Q_k Q_{k'} Q_{k''} \, C_{kk'k''}(s), \qquad (3.21a)$$

where

$$C_{kk'k''}(s) = \sum_{i\gamma} \sum_{i'\gamma'} \sum_{i''\gamma''} \left(\frac{\partial^3 V}{\partial x_{i\gamma} \partial x_{i'\gamma'} \partial x_{i''\gamma''}}\right)_{\underset{\sim}{x} = \underset{\sim}{x}_0(s)}$$

$$\cdot L_{i\gamma,k}(s) L_{i'\gamma',k'}(s) L_{i''\gamma'',k''}(s), \qquad (3.21b)$$

and the quartic term is similar. It is, of course, possible to include such higher order terms in only some modes k and not in others. Finally, we note that the Hamiltonian for J>0 is also constructed in the present case in the same manner as before.[15]

3.4. Elimination of Kinetic Energy Coupling

The final step in obtaining the diabatic reaction path Hamiltonian is to eliminate the "coriolis" coupling terms in Eq. (3.17) which involve the coupling elements $B_{k,k'}(s)$. Since this procedure has been carried out before,[35a] the result is given here without derivation. The diabatic reaction path Hamiltonian is thus given by (using matrix notation)

$$H(P_s, s, \underset{\sim}{P}, \underset{\sim}{Q}) = \tfrac{1}{2} P_s^2 + \tfrac{1}{2} \underset{\sim}{P}^T \cdot \underset{\sim}{P} + V_0(s) - \underset{\sim}{f}(s)^T \cdot \underset{\sim}{Q} + \tfrac{1}{2} \underset{\sim}{Q}^T \cdot \underline{\Lambda}(s) \cdot \underset{\sim}{Q}, \qquad (3.22a)$$

with

$$\underset{\sim}{f}^T(s) = - \underset{\sim}{D}^T(s) \cdot \underline{M}(s) \qquad (3.22b)$$

$$\underline{\Lambda}(s) = \underline{M}^T(s) \cdot \underline{K}(s) \cdot \underline{M}(s), \qquad (3.22c)$$

where the 3Nx(3N-7) transformation matrix $\underline{M}(s)$ is

$$\underline{M}(s) = \underline{L}(s) \cdot \underline{U}(s). \qquad (3.23)$$

and where the matrix $\{U_{k,k'}(s)\}$, k, k'=1, ..., 3N-7, is defined by the equation

$$\underline{U}'(s) = \underline{B}(s) \cdot U(s). \qquad (3.24)$$

$\underline{D}(s)$ and $\underline{K}(s)$ are the Cartesian gradient and force constant matrix, and we have emphasized that it is only the combination $\underline{L}(s)\cdot\underline{U}(s) = \underline{M}(s) = \{M_{i\gamma,k}(s)\}$ that is required to construct the quantities that go in the Hamiltonian. We will discuss below how this transformation matrix $\underline{M}(s)$ is determined.

The procedure for constructing the Hamiltonian is thus as follows: First the linear reaction path is properly determined as in Section 3.2 from the reactant and product equilibrium geometries. One then computes the energy $V_0(s)$, Cartesian gradient $\underline{D}(s)$, and Cartesian force constant matrix $\underline{K}(s)$ along this path (and also higher derivatives of the potential, eq. Eq. (3.21), if these are desired). The transformation matrix $\underline{M}(s)$ is then determined as below and the quantities $\underline{f}(s)$ and $\underline{A}(s)$ are computed via Eq. (3.22b) and (3.22c). If cubic, quartic, etc., terms in the potential are required, then the Cartesian terms, e.g., Eq. (3.21), are transformed from Cartesian space to Q_k-space via the matrix $\underline{M}(s)$.

To conclude this section we show a simple procedure for determining the transformation matrix $\underline{M}(s)$ of Eq. (3.23). (To make the notation below less cluttered we do not always denote the explicit s-dependence of the quantities $\underline{L}$, $\underline{M}$, and $\underline{U}$.) By using the definition of the coupling matrix $\underline{B}(s) = \{B_{k,k'}(s)\}$,

$$\underline{B}(s) = \underline{L}^{T'}(s)\cdot\underline{L}(s), \tag{3.25}$$

and the orthogonality and completeness relations of the matrix of eigenvectors $\underline{L}(s) = \{L_{i\gamma,k}(s)\}$,

$$\underline{L}^{T}(s)\cdot\underline{L}(s) = \underline{1} \tag{3.26a}$$

$$\underline{L}(s)\cdot\underline{L}^{T}(s) = \underline{1} - \underline{P}(s), \tag{3.26b}$$

where $\underline{P}(s) = \{P_{i\gamma,i'\gamma'}(s)\}$ is the projector[15] onto the six directions that are overall translation and rotation of the N-atom system, one can derive the following first order differential equation for $\underline{M}(s)$,

$$\underline{M}'(s) = -\underline{P}'(s)\cdot\underline{M}(s) \tag{3.27}$$

which can now take as the fundamental defining equation for $\underline{M}(s)$. One needs only to supplement it with a boundary (i.e., initial condition), e.g.,

$$\underline{M}(0) = \underline{L}(0)\cdot\underline{U}(0);$$

if we choose $\mathbf{U}(0) = \mathbf{1}$, then the initial condition is

$$\mathbf{M}(0) = \mathbf{L}(0), \tag{3.28}$$

where $\mathbf{L}(0)$ is obtained by diagonalizing the force constant matrix at the single position $s = 0$. With Eq. (3.28) as the initial condition for $\mathbf{M}(s)$, the differential equation Eq. (3.27) determines it at all other values of s.

Integrating Eq. (3.27) over a short increment (s_{k-1}, s_k) gives

$$\mathbf{M}_k - \mathbf{M}_{k-1} = -(\mathbf{P}_k - \mathbf{P}_{k-1})\cdot\mathbf{M}_{k-1}, \tag{3.29}$$

where

$$\mathbf{M}_k = \mathbf{M}(s_k)$$

$$\mathbf{P}_k = \mathbf{P}(s_k),$$

etc. Since

$$\mathbf{P}(s)\cdot\mathbf{M}(s) = 0$$

for all s (because $\mathbf{P}(s)\cdot\mathbf{L}(s) = 0$), Eq. (3.29) becomes

$$\mathbf{M}_k = (\mathbf{1} - \mathbf{P}_k)\cdot\mathbf{M}_{k-1}. \tag{3.30}$$

Iterating this relation gives

$$\mathbf{M}_k = (\mathbf{1} - \mathbf{P}_k)\cdot(\mathbf{1} - \mathbf{P}_{k-1})\cdots(\mathbf{1} - \mathbf{P}_1)\cdot\mathbf{M}_0 \tag{3.31}$$

as a simple way to compute $\mathbf{M}$ over a grid of $\{s_k\}$ values, given the initial condition $\mathbf{M}(0)$, i.e., Eq. (3.28).

In summary then, the matrix $\mathbf{M}(s)$ that transforms from the Cartesian space $(i\gamma)$ to the diabatic space (k) is given by Eq. (3.31), where the initial value $\mathbf{M}(0) = \mathbf{L}(0)$, Eq. (3.28), is determined by diagonalizing the projected force constant matrix at the one position $s = 0$. It is not necessary to diagonalize the projected force constant matrix at any other values; only the projectors $\mathbf{P}(s_k)$ are needed at the various values of the reaction coordinate in Eq. (3.31).

Finally, throughout Section 3 the use of classical mechanics has been implicitly assumed. Because the resulting Hamiltonian, Eq. (3.22), has a Cartesian kinetic energy, though, it is trivial to transform the result to a quantum mechanical Hamiltonian operator; i.e., in Eq. (3.22) one makes the standard replacements

$$\tfrac{1}{2} P_s^{\,2} \rightarrow -\frac{\hbar^2}{2}\frac{\partial^2}{\partial s^2}$$

$$\tfrac{1}{2} P_k^{\,2} \rightarrow -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_k^{\,2}}.$$

4. CONCLUDING REMARKS

It has been a pleasure to present this work to a group consisting largely of quantum chemists, for I believe that both topics are quite timely for this audience. First, the approach to reactive scattering is seen to reduce to quite standard quantum mechanics: choosing basis functions, computing matrix elements of the Hamiltonian, and then performing a large linear algebra calculation. Because quantum chemists have so much experience and have developed sophisticated methodologies for carrying out these tasks in electronic structure calculations, I believe that much of their expertise can now be fruitfully applied to reactive scattering.

Second, the new diabatic reaction path Hamiltonian gives one a framework for using ab initio quantum chemistry calculations to treat a new class of dynamical processes in polyatomic molecules. It is actually much simpler to apply than the original version, based on the minimum energy path, because for the new diabatic version one does not need to generate the minimum energy path. I.e., one needs to determine only the reactant and product geometries and then compute the energy, gradient, and force constant matrix (and higher derivatives if desired) along a pre-determined (i.e., the linear interpolation) path. The form of the diabatic reaction path Hamiltonian, having a Cartesian kinetic energy, is also much simpler for purposes of carrying out dynamics calculations. It should be especially useful for describing H-atom transfer reactions in polyatomic systems.

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