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System-Bath Decomposition of the Reaction Path Hamiltonian. II.
Rotationally Inelastic Transitions in the 3-d H + H₂ Reaction.

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Abstract

Earlier work of the authors [J. Chem. Phys. 77, 2378 (1982)] has shown how the reaction path Hamiltonian of Miller, Handy, and Adams [J. Chem. Phys. 72, 99 (1980)] can be divided into a "system" of the reaction coordinate and modes strongly coupled to it, plus a "bath" of more weakly coupled modes. Quantum mechanical perturbation theory was used to show how one can combine an exact description of the "system" dynamics with an approximate (perturbative) treatment of the effect of the "bath". The present paper applies this approach to the 3-d H + H₂ reaction, where the two collinear degrees of freedom constitute the "system", and the two bending modes the "bath". Comparison with the accurate scattering calculations of Schatz and Kuppermann [J. Chem. Phys. 65, 4668 (1976)] shows it to provide a good description of the coupling between bending (i.e., rotational) and collinear modes.
I. Introduction.

The relative ease with which quantum mechanical reactive scattering calculations can be carried out for collinear \( A + BC \) systems, compared to the difficulty of such calculations for atom-diatom (or larger molecular) systems in three dimensions, has spurred the development of a variety of ways for using collinear calculations in approximate treatments of the more complex situation. Child\(^1\) and Wyatt\(^2\), for example, introduced a "rotating collinear" model some years ago, and Bernstein and Levine\(^3\) used their information-theoretic methodology to construct approximate 3-dimensional product state distributions from their collinear counterparts. More recently Bowman\(^4\) and co-workers have shown how collinear reactive scattering transition probability can be utilized to approximate 3-dimensional versions of transition state theory rate constants.

In this vein the present authors have shown\(^5\) (paper I) how the reaction path description\(^6,7\) of a general reactive system can be naturally divided into a small dynamical subsystem, the "system", plus the remaining (perhaps many) degrees of freedom, the "bath", whose dynamics need not be dealt with in as much detail. If the "system" consists of the reaction coordinate plus only one other vibrational mode, the one most strongly coupled to it, then this "system" of two degrees of freedom is equivalent to a collinear atom-diatom reaction. The overall model of the reaction is then that of a collinear reaction coupled to a (harmonic) "bath". (If the coupling to the bath is neglected, then this "system--bath" model becomes equivalent to Bowman's\(^4\) approach.) Paper I showed how the coupling can be taken into account perturbatively by using the distorted wave methodology of quantum scattering theory;
the novel feature here is that the perturbation is not defined as an interaction between states, as is usually done in quantum theory, but rather between degrees of freedom. It has also been shown that the classical mechanical version of the approach leads to a generalized Langevin equation for the reaction dynamics of the "system".

The purpose of the present paper is to describe the first application of the formulation developed in paper I, namely to the \( \text{H} + \text{H}_2 \) reaction in 3-dimensions. Here the "system" consists of the reaction coordinate and the symmetric stretch-like vibrational mode that is orthogonal to the reaction path, and the "bath" is then made up of the two bending modes. This is actually not an ideal test problem for the "system-bath" formalism, nor does it illustrate its full potential, but there are unfortunately few accurate quantum reactive scattering calculations for other than collinear systems which can serve as benchmarks to test approximate theories. Section II first summarizes the "system-bath" treatment of the reaction path Hamiltonian as it applies to the present application, and various specifics of the computation are discussed in Section III. The results are presented and discussed in Section IV. Even within this first order perturbative treatment, the "system-bath" methodology is seen to yield reasonable agreement with accurate coupled-channel scattering calculations for this system. The real interest in the approach, of course, is that it can be applied to the dynamics of truly polyatomic systems, and the results of the present test are thus encouraging with regard to pursuing this.
II. Summary of Basic Theory.

We first recall the classical form of the reaction path Hamiltonian for total angular momentum $J=0$,

$$
H(p_s, s, \{n_k, q_k\}) = \frac{1}{2} \left[ p_s - \sum_{k, k' = 2}^{F} Q_{k, k'} B_{k, k'}(s) \right]^2
\frac{1}{1 + \sum_{k=2}^{F} \sigma_k B_{k, 1}(s)}
+ V_0(s) + \sum_{k=2}^{F} \left( n_k + \frac{1}{2} \right) \omega_k(s),
\text{ (2.1)}
$$

with

$$
Q_k = \left[ \frac{2n_k + 1}{\omega_k(s)} \right]^{1/2} \cos q_k, \text{ (2.2a)}
$$

$$
P_k = - [(2n_k + 1)\omega_k(s)]^{1/2} \sin q_k, \text{ (2.2b)}
$$

where here the reaction coordinate degree of freedom has been labeled as mode $k=1$. The action-angle variables $\{n_k, q_k\}$ are the dynamical variables for the transverse vibrational modes, $\{\omega_k(s)\}$ their frequencies, with the coupling between them and between the reaction coordinate characterized by the coupling elements $\{B_{k, k'}(s)\}$. More discussion of this Hamiltonian, the physical interpretation of the various coupling elements, and various applications is found in earlier papers.\textsuperscript{5, 8, 9}

The "system-bath" idea\textsuperscript{5} is to identify the reaction coordinate, mode $k=1$, and the few modes $k=2, \ldots, f$ that are strongly coupled to it, as the "system", and the remaining weakly coupled modes $k=f+1, \ldots, F$, as the "bath". The uncoupled, zero\textsuperscript{th} order Hamiltonian is that of the
fully coupled "system" plus that of the "bath",

\[ H_0(p_s, s, \{n_k, q_k\}) = \frac{1}{2} \left[ p_s - \sum_{k,k'=2}^{f} Q_{k,k',1}(s) \right]^2 
- \frac{1}{2} \left[ 1 + \sum_{k=2}^{f} Q_{k,k',1}(s) \right]^2 
+ V_0(s) + \sum_{k=2}^{F} (n_k + \frac{1}{2}) \hbar \omega_k(s) \right] \tag{2.3a} \]

and the perturbation is the coupling between the "system" and the "bath", which is given to first order in the coupling elements by

\[ H_1 = - \frac{[p_s - \sum_{k,k'=2}^{f} Q_{k,k',1}(s)]}{[1 + \sum_{k=2}^{f} Q_{k,k',1}(s)]^2} \]

\[ \times \sum_{k=2}^{f} \sum_{k'=k+1}^{F} (Q_{k,k',1} B_{k,k',1}(s)) \]

\[ \frac{[p_s - \sum_{k,k'=2}^{f} Q_{k,k',1}(s)]^2}{[1 + \sum_{k=2}^{f} Q_{k,k',1}(s)]^3} \sum_{k=2}^{F} Q_{k,k',1}(s) \right] \tag{2.3b} \]

Specializing now to the H + H\textsubscript{2} system with J=0, one has F=4; the mode k=2 is the H\textsubscript{2} vibration asymptotically and the symmetric stretch vibration at the transition state (s=0); i.e., it and the reaction coordinate are the two collinear degrees of freedom. Modes k=3,4 are the two degenerate bending vibrations that become rotation asymptotically. Because of symmetry, the only non-zero coupling
elements are $B_{2,1}(s) = \kappa(s)$, the curvature of the collinear reaction
path, and the diagonal elements

$$B_{k,k}(s) = -\frac{\omega_k(s)}{2m_k(s)} . \quad (2.4)$$

The unperturbed, zeroth order Hamiltonian is the sum of that for
the "system", taken to be the two collinear modes $k=1,2$, and the
"bath", the two bending modes $k=3,4$, and is thus given by

$$H_0(p_s,s,n_2,q_2,n_3,n_4) = \frac{1}{2} \left[ \frac{p_s - Q_2 P_2 B_{2,2}(s)}{1 + Q_2 B_{2,1}(s)} \right]^2 + V_0(s)$$

$$+ (n_2 + \frac{1}{2})\omega_2(s) + (n_3 + n_4 + 1)\omega_3(s) , \quad (2.5a)$$

where the fact that $\omega_4 = \omega_3$ has been used. The perturbation is

$$H_1(p_s,s,n_2,q_2,n_3,q_3,n_4,q_4) = -\frac{[p_s - Q_2 P_2 B_{2,2}(s)]}{[1 + Q_2 B_{2,1}(s)]^2} \left( Q_3 P_3 + Q_4 P_4 \right) B_{3,3}(s) , \quad (2.5b)$$

where the fact that $B_{4,4}(s) = B_{3,3}(s)$ has been used.

Since for $H_0$ the "bath" quantum numbers $(n_3,n_4)$ are conserved,
one readily sees that it describes a collinear-like reaction, i.e.,
a dynamical system involving only the two degrees of freedom $(p_s,s,n_2,q_2)$, with the potential simply being modified by the inclusion
of the adiabatic energy of the "bath" (the last term in Eq. (2.5a)).
As has been noted before, this is essentially the approximation that has been used with a reasonable success by earlier workers.\textsuperscript{4}

Paper I went further and showed how the effect of the perturbation can be included via quantum perturbation theory. This requires the scattering wavefunctions from the zero\textsuperscript{th} order Hamiltonian, $H_0$, but since this is essentially a collinear scattering problem, these are readily obtainable. It is also necessary to convert the classical Hamiltonians above into their corresponding quantum operators, but this is carried out by standard methods.\textsuperscript{11}

The expression for the first order correction to the transmission (i.e., reactive) amplitude is given (in mass-weighted coordinates and $\hbar=1$) for the present $H + H_2$ case by\textsuperscript{5}

\[ t^{(1)}_{n_2n_3n_4',n_2',n_3',n_4} = -i \sum_{n_2''n_2'} \int_{-\infty}^{\infty} ds \ f_{n_2''+n_2'} \left( H_1 \right)_{n_2''n_3'n_4',n_2'n_3'n_4} n_3n_4(+) \times f_{n_2''+n_2}(s), \]  

(2.6)

where the translational functions \{\[ f_{n_2''+n_2}(s) \]\} are those obtained by solving the collinear reactive scattering problem with the zero\textsuperscript{th} order Hamiltonian $H_0$ and appropriate boundary conditions (see next section). The explicit quantum mechanical form of the matrix elements of the perturbation over the vibrational basis is discussed in the next section; even from the classical expression for $H_1$ [Eq. (2.5b)], however, one can readily see that the selection rule

\[ (\Delta n_3, \Delta n_4) = (\pm2,0), (0,\pm2) \]  

(2.7a)
maintains. Since we take the initial state to be the ground state, i.e.,

\[ (n_2, n_3, n_4) = (0, 0, 0) \quad , \quad (2.7b) \]

and since only the ground vibrational state is energetically open in the energy region considered, the only final states for which the first order correction, Eq. (2.6), is non-zero are

\[ (n_2', n_3', n_4') = (0, 0, 2) \text{ and } (0, 2, 0) \quad . \quad (2.7c) \]

Also, since the zero\(^{th}\) order transmission amplitude is diagonal in the bath quantum numbers \((n_3, n_4)\), the transitions specified by Eq. (2.7) have no zero\(^{th}\) order contribution, i.e., their lowest order contribution is given by the first order term, Eq. (2.6). To assess the usefulness of this perturbative treatment of the "system-bath" decomposition, therefore, it is particularly pertinent to consider these transitions.

The quantity of intent, therefore, is the transition (i.e., reaction) probability to the degenerate bending states \((n_3, n_4) = (0, 2)\) and \((2, 0)\),

\[ |t^{(1)}_{002,000}|^2 + |t^{(1)}_{020,000}|^2 \]

\[ = 2|t^{(1)}_{002,000}|^2 \quad , \quad (2.8) \]

where it is noted that the two terms are equal. There is a question, however, as to how this reaction probability labeled by the bending
vibrational quantum numbers \((n_3, n_4)\) relates to the more customary 3-d reaction probabilities labeled by initial and final rotational quantum numbers \((j, K)\), where \(j\) is the asymptotic rotational quantum number of \(H_2\) and \(K\) is the asymptotic helicity, the component of rotation along the relative velocity vector. Since the correlation \((n_3, n_4) \leftrightarrow (j, K)\) is not one-to-one, the only rigorous relation between the two reaction probabilities is between the total reaction probability for a given total energy \(E\) and total angular momentum \(J\); thus if
\[
S^J_{n'n'j'K',njK}
\]
denotes the reactive S-matrix between initial and final vibrational and rotational states, then one has
\[
\sum_{j',K'} |S^J_{0j'K',000}|^2 = 2 \sum_{n_3',n_4'} |t_{0n_3'n_4',000}|^2, \quad (2.9)
\]
where the initial state has been taken to be the ground state and the final vibrational quantum number is also the ground state; the factor of 2 on the right-hand side of Eq. (2.9) is present because the "system-bath" Hamiltonian describes the reaction on an H atom with one end of the \(H_2\) molecule, while the conventional 3-d reactive S-matrix corresponds to reaction at either end. (Other factors for nuclear symmetry are omitted.) Furthermore, for \(J=0\) one must have \(K=0\), so that to lowest order in the "system-bath" perturbation Eq. (2.9) becomes
\[ \sum_{j=0}^{\infty} |s_{0j0,000}^{J=0}|^2 = 2|t_{000,000}^{(0)}|^2 + |t_{002,000}^{(1)}|^2 + |t_{020,000}^{(2)}|^2, \]

and if we equate the ground state-to-ground state terms, then (utilizing Eq. (2.8)) we obtain the approximate identification

\[ 4|t_{002,000}^{(1)}|^2 \approx \sum_{j=1}^{\infty} |s_{0j0,000}^{J=0}|^2. \quad (2.10) \]

Equation (2.10) thus serves as the basis for comparing the results of our perturbative "system-bath" calculation of the reaction probability with the results of conventional 3-d coupled channel reactive scattering calculations.
III. Specifics of the Calculation.

To generate the explicit form of the quantum mechanical matrix elements in Eq. (2.6) it is simplest to write the distorted wave transmission amplitude as

\[ t^{(1)}_{n_2,n_3,n_4,n_2n_3n_4} = -i \langle \chi^{(-)}_{n_2n_3n_4} | H - E | \chi^{(+)}_{n_2n_3n_4} \rangle , \quad (3.1) \]

where \( H \) is the quantum mechanical reaction path Hamiltonian operator,

\[
H = -\frac{\hbar^2}{2} \left[ \left( \frac{1}{\eta} \right)^{1/2} p_s \left( \frac{1}{\eta} \right) p_s \left( \frac{1}{\eta} \right)^{1/2} + \left( \frac{1}{\eta} \right)^{1/2} p_s \left( \eta \right) p_s \left( \frac{1}{\eta} \right)^{1/2} + p_3^2 + p_4^2 \right]
\]

\[
+ \frac{1}{2} [\omega_2(s)^2 Q_2^2 + \omega_3(s)^2 Q_3^2 + \omega_4(s)^2 Q_4^2] + V_0(s) \quad , \quad (3.2)
\]

where

\[ \eta = 1 + B_{2,1}(s) Q_2 \quad , \]

\( E \) is the total energy, and the \( \chi \)'s are the distorted wave functions, which are given by

\[ \chi^{(\pm)}_{n_2n_3n_4}(s,Q_2,Q_3,Q_4) = \frac{n_3n_4(\pm)}{n_2} (s,Q_2) \phi_{n_3}(Q_3;s) \phi_{n_4}(Q_4;s) \quad . \quad (3.3) \]

The vibrational functions \( \phi_{n_k}(Q_k;s) \) are the adiabatic harmonic oscillator functions for mode \( k \); they depend on \( s \) because the frequencies \( \omega_k(s) \) are functions of \( s \). The functions \( \frac{n_3n_4(\pm)}{n_2}(s,Q_2) \)
are the solutions of the collinear-like Schrödinger equation, i.e., eigenfunctions of the quantum mechanical Hamiltonian that corresponds to $H_0$ of Eq. (2.5a),

$$H_0 = -\frac{\hbar^2}{2} \left[ \left( \frac{1}{\eta} \right)^{1/2} \frac{\partial}{\partial s} \frac{1}{\eta} \frac{\partial}{\partial s} \left( \frac{1}{\eta} \right)^{1/2} + \left( \frac{1}{\eta} \right)^{1/2} \frac{\partial}{\partial Q_2} \eta \frac{\partial}{\partial Q_2} \left( \frac{1}{\eta} \right)^{1/2} \right]$$

$$+ \frac{1}{2} \omega_2^2 \langle s, Q_2 \rangle_+^2 + V_0(s)$$

$$+ (n_3 + n_4 + 1)\omega_3(s) \quad , \quad (3.4)$$

with the appropriate scattering boundary conditions.

To solve this collinear-scattering problem in "natural collision coordinates" we have used the methodology of Wu and Levine. They eliminate trouble arising from the singularity in the Schrödinger equation caused by the factor $\eta^{-1}$ by including the factor $\eta^4$ in the expansion of the collinear wave function,

$$\phi_{n_2}^{n_3, n_4}(s, Q_2) = \eta^4 \sum_{n_2} \phi_{n_2}^{,}(Q_2; s) f_{n_2 + n_2}^{n_3, n_4}(s) \quad , \quad (3.5)$$

where $\phi_{n_2}^{,}(Q_2; s)$ is again an adiabatic harmonic oscillator function.

The coupled channel equations for the translational function $f(s)$, determined by substituting Eq. (3.5) in the Schrödinger equation with $H_0$ of Eq. (3.4), are then precisely those given by Wu and Levine. The boundary conditions for the translational functions with outgoing waves (i.e., "+"
where \( r(0) \) and \( t(0) \) are the zeroth order reflection and transmission amplitude. In the Appendix it is shown that for the present case of a symmetric reaction the translational functions with "+" and "-" boundary conditions are related by

\[
\begin{align*}
\lim_{n \to \infty} |k|^{-1/2} e^{ikn_2^s} & r(0) \\
\lim_{n' \to \infty} |k'|^{-1/2} e^{ik'n_2^s} \end{align*}
\]

so that it is not necessary to carry out a separate calculation to obtain the functions with "-" boundary conditions. For the numerical integration of these collinear coupled channel equations a variable step-size version of the Adams-Pece integrator was used, and five channels (i.e., four closed channels) were retained in the expansion Eq. (3.5). It should be noted, of course, that other methods of solving the collision reactive scattering problem can be used to generate the collinear scattering wavefunctions \( f_{n_3n_4}^{(\pm)}(s,Q_2) \), and some of these may actually be more convenient than the Wu-Levine method. The latter codes were most readily available to us, however, and since computational efficiency was not a major concern for this test case it was simplest to use them.
With the distorted wavefunctions given by Eqs. (3.3) and (3.5) and the Hamiltonian by Eq. (3.2), the first order correction to the transmission amplitude is evaluated by Eq. (3.1). Integration over the vibrational coordinates \((Q_2, Q_3, Q_4)\) can be carried out analytically, so only the integral over \(s\) need be performed numerically. It is interesting first, though, to note the quantum mechanical origin of the selection rule, Eq. (2.7), noted earlier on the basis of the classical perturbation Hamiltonian [Eq. (2.5b)]; in the present quantum mechanical expression it arises from derivatives of the adiabatic vibrational functions with respect to \(s\), which is given by, for mode \(k=3\) for example,

\[
\frac{\partial}{\partial s} \phi_{n_3}(Q_3; s) = \frac{\omega_3(s)}{2\omega_3(s)} \left[ \frac{1}{2} \sqrt{\frac{1}{n_3(n_3-1)}} \phi_{n_3-2}(Q_3; s) \right]
\]

\[
- \frac{1}{2(n_3+1)(n_3+2)} \phi_{n_3+2}(Q_3; s) \]

so that

\[
\langle \phi_n^i | \frac{\partial}{\partial s} \phi_{n_3} \rangle = \frac{\omega_3^i(s)}{4\omega_3(s)} \left[ \sqrt{\frac{1}{n_3(n_3-1)}} \delta_{n_3, n_3-2} \right]
\]

\[
- \sqrt{(n_3+1)(n_3+2)} \delta_{n_3, n_3+2} \]

this is the quantum mechanical analog to the classical term in \(H_1\) [Eq. (2.5)] involving mode \(k=3\),
The explicit expression for the first order transmission amplitude for the (000 $\rightarrow$ 020) transition is

\[
\frac{7}{2\sqrt{\mu}} < \sum_{n''_2} f^{02(+)}_{n''_2} (-s) \phi_{n''_2}(Q_2; s) \phi_{n_3=2}(Q_3; s) |\eta^6 B_{2,1}(s) Q_2|
\]

\[
\sum_{n''_2} f^{00(+)}_{n''_2} (s) \phi_{n''_2}(Q_2; s) \frac{\phi(Q_3; s)}{\partial s} n''_2 \eta^6 \frac{\partial \phi(Q_3; s)}{\partial n''_2} n_3=0
\]

\[
+ \frac{1}{\sqrt{\mu}} \sum_{n''_2} f^{02(+)}_{n''_2} (-s) \phi_{n''_2}(Q_2; s) \phi_{n_3=2}(Q_3; s) |\eta^7|
\]

\[
\sum_{n''_2} \frac{d}{ds} f^{00(+)}_{n''_2} (s) \phi_{n''_2}(Q_2; s) \frac{\partial \phi(Q_3; s)}{\partial s} n''_2 \eta^6 \frac{\partial \phi(Q_3; s)}{\partial n''_2} n_3=0
\]

\[
+ \frac{1}{\sqrt{\mu}} \sum_{n''_2} f^{02(+)}_{n''_2} (-s) \phi_{n''_2}(Q_2; s) \phi_{n_3=2}(Q_3; s) |\eta^7| \sum_{n''_2} f^{02(+)}_{n''_2} (s)
\]

\[
\phi_{n''_2}(Q_2; s) \frac{\partial \phi(Q_3; s)}{\partial s} n''_2 \eta^6 \frac{\partial \phi(Q_3; s)}{\partial n''_2} n_3=0
\]

\[
(3.9)
\]

where $\mu$ is the reduced mass of the H$_2$–H system.
IV. Results and Discussion.

The Porter-Karplus potential energy surface was used for the present calculations because it is the one for which Schatz and Kuppermann have calculated accurate 3-dimensional coupled channel results. Figure 1 shows the two coupling elements $B_{2,1}(s)$ and $B_{3,3}(s)$ as a function of the reaction coordinate. As noted above, $B_{2,1}(s) = \kappa(s)$ is the curvature of the collinear reaction path, and it is the "intra-system" coupling which is taken into account to infinite order in the present "system-bath" model. The coupling $B_{3,3}(s) = B_{4,4}(s)$ is that between the "system" and the "bath", and this is the coupling that is included perturbatively.

The results of our calculations are shown as the solid line in Figure 2, where the quantity plotted is the left-hand side of Eq. (2.10), i.e., four times the probability of the $(n_2, n_3, n_4) = (0, 0, 0)$ reaction probability. The most definite value for comparison is the result of Schatz and Kuppermann at 0.6 eV for the sum of reaction probabilities for the $j=0+1$, $0+2$, and $0+3$ transitions, and one sees that this (the solid point in Figure 2) is in excellent (perhaps fortuitously good) agreement with our results. ($j=0+4$ and higher transitions are negligible at this energy.) Unfortunately, this is the only energy for which the transitions to all final $j$'s are given, so that further detailed comparison is not possible.

The Schatz and Kuppermann values for the $j=0+1$ transition probability alone, however—which is the largest single transition at $E = 0.60$ eV—fall with decreasing energy more rapidly than our perturbative results in Figure 2; thus if one assumes that $j=0+1$ is still the largest transition at these lower energies, the
perturbative results would be too large in this region. One can perhaps understand that the perturbative results will become progressively too large at lower energy by noting Figure 1: with decreasing energy, larger values of the reaction coordinate $s$ are important to the tunneling process; i.e., larger values of $s$ contribute significantly to the integral in Eq. (3.9), and Figure 1 shows that for larger values of $s$, the coupling $B_{3,3}(s)$ which is treated perturbatively, becomes larger relative to the coupling $B_{2,1}(s)$ that is included exactly. Thus inclusion of the $B_{3,3}$ coupling only to first order, therefore, may not be sufficient at the lower energies.

In any event, however, one sees that even within the limitations of first order perturbation theory, the "system-bath" treatment of the reaction path Hamiltonian is able to describe the interaction between the bending ("bath") degrees of freedom and the collinear ("system") degrees of freedom reasonably well. The interest in this methodology, of course, is that it can be applied to fully polyatomic molecular systems, and future work will be directed toward these applications.
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Appendix.

Here we summarize some of the basic properties of scattering wavefunctions for transmission and reflection in one-dimension, \(-\infty < x < +\infty\). (The actual situation of interest in the present paper is multi-channel scattering, but the nature of the translational functions \(f_{n_3 \to n_4}(s), s = -\infty \to +\infty\), is revealed by considering the one-dimensional case.)

The scattering wavefunctions \(\psi_k^{(\pm)}(x)\) are defined as the solution of the Lipmann-Schwinger equation (i.e., a solution of the Schrödinger Equation with appropriate boundary conditions)

\[
\psi_k^{(\pm)}(x) = \phi_k(x) + \int_{-\infty}^{\infty} dx' G_0^{(\pm)}(x,x') V(x') \psi_k^{(\pm)}(x'), \quad (A.1)
\]

where \(V\) is the potential energy function \((V(x) \to 0, x \to \pm\infty)\), and

\[
\phi_k(x) = |k|^{-1/2} e^{ikx} \quad \text{(A.2)}
\]

\[
G_0^{(\pm)}(x,x') = \frac{2m}{2i\hbar^2 k} e^{i |x-x'|} \quad \text{(A.3)}
\]

In the asymptotic region one has

\[
\psi_k^{(+)}(x) \sim |k|^{-1/2} e^{ikx} \quad \text{as } x \to +\infty \quad \text{(A.4a)}
\]

\[
\sim |k|^{-1/2} [e^{-ikx} - e^{-ik|x-x'|}] \quad \text{as } x \to -\infty \quad \text{(A.4b)}
\]
and from the Lipmann-Schwinger equation one can readily take these limits and show that the transmission and reflection amplitudes are given by

\[ t = 1 + \frac{2m}{2i\hbar^2} \langle \phi_k | V | \psi_k^{(+)} \rangle \]  
(A.5a)

\[ r = -\frac{2m}{2i\hbar^2} \langle \phi_{-k} | V | \psi_k^{(+)} \rangle \]  
(A.5b)

If one divides the potential into two parts

\[ V(x) = V_0(x) + V_1(x) \]

and if \( \chi_k^{(\pm)}(x) \) are the solutions of the Lipmann-Schwinger equation with potential \( V_0 \), then one can show that \( t \) and \( r \) are also given by

\[ t = t_0 + \frac{2m}{2i\hbar^2} \langle \chi_k^{(-)} | V_1 | \psi_k^{(+)} \rangle \]  
(A.6a)

\[ r = r_0 - \frac{2m}{2i\hbar^2} \langle \chi_{-k}^{(-)} | V_1 | \psi_k^{(+)} \rangle \]  
(A.6b)

where \( t_0 \) and \( r_0 \) are the transmission and reflection amplitudes resulting from \( V_0 \) (i.e., those contained in the asymptotic form of the "distorted" wavefunction \( \chi_k^{(+)} \)). If \( V_1 \) is considered as a perturbation to \( V_0 \), then the first order of contribution to the transmission and reflection amplitudes is given by
By direct substitution into the Lipmann-Schwinger Eq. (A.1) one can readily verify the general microscopic reversibility relation

\[ \psi_k^(-)(x)^* = \psi_{-k}^+(x) \]  \hspace{1cm} (A.8)

Also by direct substitution into the Lipmann-Schwinger equation one can see that

\[ \psi_k^+(x) = \phi_k(-x) + \int_{-\infty}^{\infty} dx' \ G_0^{(+)}(-x,x') \ V(x') \ \psi_k^+(x') \]

and by changing integration variables \( x' \to -x' \) this becomes

\[ \psi_k^+(x) = \phi_k(-x) + \int_{-\infty}^{\infty} dx' \ G_0^{(+)}(-x,-x') \ V(-x') \ \psi_k^+(x') \] .

Then since

\[ \phi_k(-x) = \phi_{-k}(x) \]

\[ G_0^{(+)}(-x',-x') = G_0^{(+)}(x,x') \]

the relation becomes
If the potential function is symmetric, i.e., $V(-x) = V(x)$, then one recognizes Eq. (A.9) to be identical to the Lipmann-Schwinger equation for $\psi_k^{(+)}(x)$; i.e., for a symmetric potential one has the additional symmetry relation

$$\psi_k^{(+)}(-x) = \psi_k^{(+)}(x) \quad , \quad (A.10)$$

and if one also uses the microscopic reversibility relation, Eq. (A.8), one has

$$\psi_k^{(-)}(x) = \psi_k^{(+)}(-x) \quad , \quad (A.11)$$

for the case of a symmetric potential.

Equations (A.8)-(A.11) apply equally to the distorted wavefunctions $\chi$ with the potential $V_0(x)$. Thus by using Eq. (A.11), the first order contribution to the transition amplitude [Eq. (A.7a)]

$$t_1 = \frac{2m}{2i\hbar^2} \int_{-\infty}^{\infty} dx \; \chi_k^{(-)}(x)^* \; V_1(x) \; \chi_k^{(+)}(x) \quad ,$$

can be written as

$$t_1 = \frac{2m}{2i\hbar^2} \int_{-\infty}^{\infty} dx \; \chi_k^{(+)}(-x) \; V_1(x) \; \chi_k^{(+)}(x) \quad , \quad (A.12)$$
which was used in Section III. For completeness, we note also that use of Eq. (A.8) allows the first order contribution to the reflection amplitude to be written as

\[ r_1 = -\frac{2m}{2i\hbar^2} \int_{-\infty}^{\infty} dx \chi_k^{(+)}(x) V_1(x) \chi_k^{(+)}(x) \]  

(A.13)

and unlike Eq. (A.12), Eq. (A.13) does not require that \( V_0(x) \) be symmetric.
References

7. A number of workers have contributed to the development of the reaction path description of chemical reactions, for example:
   (a) G. L. Hofacker, Z. f. Naturforsch. 18a, 607 (1963);
   (b) S. F. Fischer, G. L. Hofacker, and R. Seiler, J. Chem. Phys. 51, 3951 (1969);
   (c) R. A. Marcus, J. Chem. Phys. 45, 4493, 4500 (1966); 49, 2610 (1968); 53, 4026 (1976);
   (d) S. F. Fischer and M. A. Ratner, J. Chem. Phys. 57, 2769 (1972);
   (e) P. Russegger and J. Brickmann, J. Chem. Phys. 62, 1086 (1976);
   (f) M. V. Basilevsky, Chem. Phys. 24, 81 (1977);


Figure Captions

1. The coupling elements $B_{2,1}(s)$ and $B_{3,3}(s)$ in the reaction path Hamiltonian of Section II [e.g., Eq. (2.5)], as a function of reaction coordinate.

2. Reaction probability (multiplied by 4) for the $(n_2,n_3,n_4) = (0,0,0) \rightarrow (0,0,2)$ transition of the bending modes, as a function of total energy. The point is the sum of the $j=0+1$, $0+2$, and $0+3$ reaction probabilities of Schatz and Kuppermann (reference 15).
Figure 1
Figure 2
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