System-bath decomposition of the reaction path
Hamiltonian. II. Rotationally inelastic reactive scattering of
H+H₂ in three dimensions

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(Received 7 March 1983; accepted 17 July 1983)

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 3d 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
Kuperman [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 re-
active 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 develop-
ment of a variety of ways for using collinear calcula-
tions in approximate treatments of the more complex
situation. Connor and Child¹ and Wyatt,² e.g., intro-
duced a "rotating collinear" model some years ago,
and Bernstein and Levine³ used their information-theo-
retic methodology to construct approximate three-di-
imensional product state distributions from their collin-
er counterparts. More recently, Bowman⁴ and co-
workers have shown how collinear reactive scattering
transition probabilities can be utilized to approximate
two-dimensional reactive scattering.

In this vein the present authors have shown⁵ (paper I)
how the reaction path description⁶,⁷ of a general reactive
system can be naturally divided into a small dy-
namical 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's⁴ approach. In an anal-
ogous zeroth order approximation, Walker and Hayes⁸
have shown how the bending degree of freedom can be
included in the rotating collinear model of Connor and
Child¹ and Wyatt.²) Paper I showed how the coupling can be
taken into account perturbatively by using the dis-
torted wave methodology of quantum scattering theory;
the novel feature here is that the perturbation is not de-
finid as an interaction between states, as is usually done
in quantum theory, but rather between degrees of free-
dom. It has also been shown⁹,¹⁰ that the classical me-
chanical version of the approach leads to a generalized
Langevin equation for the reaction dynamics of the sys-
tem.

The purpose of the present paper is to describe
the first application of the formulation developed in paper I,
namely to the H + H₂ reaction in three dimensions. Here
the system consists of the reaction coordinate and the
symmetric stretchlike vibrational mode that is orthogo-
nal 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 il-
lustrate 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 re-
action path Hamiltonian as it applies to the present ap-
lication and various specifics of the computation are
discussed in Sec. III. The results are presented and
discussed in Sec. IV. Even within this first order per-
turbative treatment, the system–bath methodology is
seen to yield reasonable agreement with accurate cou-
pied-channel scattering calculations for this system.
The real interest in the approach, of course, is that it
may be applied to the dynamics of truly polyatomic sys-
tems and the results of the present test are thus encou-
grating 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,

\[
H(\rho, s, \{q_a, p_a\}) = \frac{1}{2} (\rho - \rho_0)^2 + \sum_{a \neq s} \frac{q_a \cdot B_{2a}(s)}{1 + \sum_b Q_{ab}B_{2b}(s)}
\]

+ \nu_0(s) + \sum_{a \neq s} (q_a + \frac{1}{2}) \omega_a(s) \quad (2.1)

with


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More discussion of this Hamiltonian, the physical interpretation of the various coupling elements, and various applications is found in earlier papers.  

The system–bath idea 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 zeroth order Hamiltonian is that of the fully coupled system plus that of the bath.

\[
H_0(p, q, \{ n_k \}) = \frac{1}{2} \left( p - \sum_{k=1}^{F} n_k \frac{Q_k P_k B_{k,1}(s)}{1 + \sum_{k=2}^{F} Q_k B_{k,1}(s)} \right)^2 + V_0(s) + \sum_{k=1}^{F} \left( n_k + \frac{1}{2} \right) \omega_k(s) \tag{2.3a}
\]

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

\[
H_1 = \left( p - \sum_{k=1}^{F} n_k \frac{Q_k P_k B_{k,1}(s)}{1 + \sum_{k=2}^{F} Q_k B_{k,1}(s)} \right) \sum_{k=1}^{F} \left( Q_k P_k - Q_k P_k \right) B_{k,1}(s) = \left( p - \sum_{k=1}^{F} n_k \frac{Q_k P_k B_{k,1}(s)}{1 + \sum_{k=2}^{F} Q_k B_{k,1}(s)} \right) \sum_{k=1}^{F} Q_k B_{k,1}(s) \tag{2.3b}
\]

Specializing now to the H + H₂ system with \( J = 0 \), one has \( F = 4 \); the mode \( k = 2 \) is the H₂ vibration asymptotically and the symmetric stretch vibration at the transition state \( \{ 0, 0 \} \); 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, only the non-zero coupling elements are \( B_{3,1}(s) = \kappa(s) \), the curvature of the collinear reaction path and the diagonal elements

\[
B_{k,1}(s) = -\frac{\omega_k(s)}{2\omega_0(s)} \tag{2.4}
\]

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

\[
H_0(p, q, n_1, n_2, n_3, n_4) = \left[ p - \sum_{k=1}^{F} n_k \frac{Q_k P_k B_{k,1}(s)}{1 + \sum_{k=2}^{F} Q_k B_{k,1}(s)} \right]^2 + V_0(s) + (n_3 + \frac{1}{2}) \omega_3(s) + (n_4 + n_4 + 1) \omega_4(s) \tag{2.5a}
\]

where the fact that \( \omega_3 = \omega_4 = \omega_0 \) has been used. The perturbation is

\[
H_1(p, q, n_1, n_2, n_3, n_4) = -\frac{p - \sum_{k=1}^{F} n_k \frac{Q_k P_k B_{k,1}(s)}{1 + \sum_{k=2}^{F} Q_k B_{k,1}(s)}}{Q_3 P_3 + Q_4 P_4} \tag{2.5b}
\]

where the fact that \( B_{3,1}(s) = B_{4,1}(s) \) has been used.

Since for \( H_0 \) the bath quantum numbers \( (n_1, n_4) \) are conserved, one readily sees that it describes a collinear-like reaction, i.e., a dynamical system involving only the two degrees of freedom \( (p, q, n_1, n_2) \), 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.

Paper I went further and showed how the effect of the perturbation can be included via quantum perturbation theory. This requires the scattering wave functions from the zeroth 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.

The expression for the first order correction to the transmission (i.e., reactive) amplitude is given (in mass-weighted coordinates and \( \kappa = 1 \)) for the present H + H₂ case by

\[
\langle \phi^{(+)}_{n_1, n_2, n_3, n_4} | \phi^{(+)}_{n_1, n_2, n_3, n_4} \rangle = -i \sum_{n_1'} \int ds f_{n_2}^{(+)}\left( s \right) \times \langle \mathcal{H}_1 \rangle_{n_1' = n_1, n_2 = n_2, n_3 = n_3, n_4 = n_4} \tag{2.6}
\]

where the translational functions \( \{ f_{n_2}^{(+)} \} \) are those obtained by solving the collinear reactive scattering problem with the zeroth order Hamiltonian \( H_0 \) and appropriate boundary conditions (see the 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

\[
(\Delta n_1, \Delta n_4) = (\pm 2, 0), \quad (0, \pm 2) \tag{2.7a}
\]

maintains. Since we take the initial state to be the ground state, i.e.,

\[
(n_1, n_2, n_3, n_4) = (0, 0, 0), \tag{2.7b}
\]

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 nonzero are

\[
(n_1', n_2', n_3, n_4') = (0, 2, 0) \quad \text{and} \quad (0, 0, 2) \quad . \tag{2.7c}
\]
Also, since the zeroth order transmission amplitude is diagonal in the bath quantum numbers \((n_3, n_4)\), the transitions specified by Eqs. (2.7) have no zeroth 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 interest, therefore, is the transition (i.e., reaction) probability to the degenerate bending states \((n_3, n_4) = (0, 2)\) and \((2, 0)\),

\[
\left| t_{20}^{(0)} \right|^2 + \left| t_{02}^{(0)} \right|^2 = 2 \left| t_{00}^{(0)} \right|^2, \tag{2.8}
\]

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 3d 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 \((n_3, n_4) \rightarrow (j, K)\) 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 \(J\), if \(S_{j', j''}^{(K', K'')}\) denotes the reactive \(S\) matrix between initial and final vibrational and rotational states, then equating total reaction probabilities gives

\[
\sum_{j', j''} \left| S_{j', j''}^{(0, 0, 0, 0)} \right|^2 = 2 \sum_{n_3, n_4} \left| t_{n_3 n_4}^{(0, 0, 0, 0)} \right|^2, \tag{2.9a}
\]

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. (2.9a) 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 3d 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 through second order in the system–bath perturbation Eq. (2.9a) becomes

\[
\sum_{j', j''} \left| S_{j', j''}^{(0, 0, 0, 0)} \right|^2 = 2 \left| t_{00}^{(0, 0, 0, 0)} \right|^2 + 2 \text{Re}(t_{00}^{(0, 0, 0, 0)} t_{00}^{*(0, 0, 0, 0)}) + 4 \left| t_{00}^{(0, 0, 0, 0)} \right|^2, \tag{2.9b}
\]

where Eq. (2.8) has also been used. We wish in addition, however, to identify, at least approximately, the rotationally inelastic part of the reactive scattering, and to do so we assume that we may equate the ground state terms on each side of Eq. (2.9b), i.e., the \(j = 0\) term on the left-hand side and the \(K = 0\) term (the one in square brackets) on the right-hand side. It is difficult to provide direct numerical support for this ground state–to-ground state correlation, for to do so through second-order requires calculation of the second-order term \(t_{20}^{(0)}\), which is considerably more difficult than the first-order corrections we have calculated. (Approximating the \(K = 0\) term with just the zeroth order contribution, \(\left| t_{00}^{(0, 0, 0, 0)} \right|^2\), which would be equivalent to Bowman’s model, does not give good agreement with the \(j = 0\) term on the left-hand side, but this is understandable because the correction is large.) Nevertheless, one expects this correlation to be better for the ground states, than for any other states; this is clearly implied by the works of Harms and Wyatt.\(^{15}\) With this approximate identification we then obtain

\[
4 \left| t_{00}^{(0, 0, 0, 0)} \right|^2 \approx \sum_{j' \neq 0} \left| S_{j'0,00,00}^{(0)} \right|^2 \tag{2.10}
\]

as the relation we can use to compare the results of our perturbative system–bath calculation of the reaction probability with the results of conventional 3d 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

\[
(\chi_{n_3 n_4}^{(0)} \chi_{n_3 n_4}^{(0,0,0,0)}) = -i \langle \chi_{n_3 n_4}^{(0)} | H - E | \chi_{n_3 n_4}^{(0)} \rangle, \tag{3.1}
\]

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

\[
H = -\frac{1}{\hbar} \left[ \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \right] \beta_s \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \beta_s \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \beta_s \\
+ P_x^2 + P_y^2 \right] + \frac{1}{2} \left( \omega_1(s)^2 Q_1^2 + \omega_2(s)^2 Q_2^2 + \omega_3(s)^2 Q_3^2 \right) + V_0(s), \tag{3.2}
\]

where

\[
\eta = 1 + B_{13,1}(s) Q_2, \tag{3.3}
\]

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

\[
\chi_{n_3 n_4}^{(0)}(s, Q_2, Q_3, Q_4) = C_{n_3 n_4}^{(0)}(s, Q_2, Q_3, Q_4) \phi_{n_3}^{(s)}(Q_3, s) \phi_{n_4}^{(s)}(Q_4, s). \tag{3.4}
\]

The vibrational functions \(\phi_{n_3}^{(s)}(Q_3, s)\) are the adiabatic harmonic oscillator functions for mode \(k_i\) that depend on \(s\) because the frequencies \(\omega_i(s)\) are functions of \(s\). The functions \(C_{n_3 n_4}^{(0)}(s, Q_2, Q_3, Q_4)\) are the solutions of the colinearlike Schrödinger equation, i.e., eigenfunctions of the quantum mechanical Hamiltonian that corresponds to \(H_0\) of Eq. (2.5a),

\[
C_{n_3 n_4}^{(0)}(s, Q_2, Q_3, Q_4) = \frac{-1}{\sqrt{2} \pi} \left( \frac{1}{\sqrt{s}} \right) \frac{1}{\sqrt{\eta \pi \eta}} \left( \frac{1}{\sqrt{s}} \right) \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \beta_s \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \beta_s \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \beta_s \\
+ \left( \frac{1}{\sqrt{s}} \right) \frac{1}{\sqrt{\eta \pi \eta}} \left( \frac{1}{\sqrt{s}} \right) \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \beta_s \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \beta_s \left( \begin{array}{ccc} 1/2 & 1/2 \\ 1/2 & 1/2 \\ \end{array} \right) \beta_s \\
+ (n_3 + n_4 + 1) \omega_3(s), \tag{3.5}
\]

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.\(^{14}\) They eliminate trouble arising from the singularity in the Schrödinger equation caused by the factor \(\eta^{-1}\) by including the factor \(\eta^1\) in the expansion of the collinear wave function

\[
C_{n_3 n_4}^{(0)}(s, Q_2) = \eta^1 \sum_{n_2} \phi_{n_2}^{(s)}(Q_2, s) f_{n_3 n_4}^{(0)}(s), \tag{3.6}
\]

where \(\phi_{n_2}^{(s)}(Q_2, s)\) 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 outgong waves (i.e., "+"") are

\[
\begin{align*}
\phi_E^{(+)n}(s) & \rightarrow \left[ k_{n+1}^{-1/2} \exp(-ik_n s) r_{n+1,n} \right] \\
\phi_E^{-1/2} \exp(i k_n s) t_{n+1,n} & ,
\end{align*}
\]

(3.6a)

where \( r^{(+)n} \) and \( t^{(+)n} \) 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

\[
f^{(+)}(s) = f^{(-)}(-s),
\]

(3.7)

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–Peece 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 wave functions \( \psi_{n_1 n_2}^{(+n)}(s, Q_3) \), 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.

\[
\frac{7}{2 \mu} < \sum_{n_2} \left[ f_{n_2}^{(+n)}(s) \phi_{n_2}(Q_2, s) \phi_{n_2}(Q_3, s) \right] \frac{d}{ds} B_{n_1,1}(s) Q_2 \sum_{n_2} \left[ f_{n_2}^{(+)}(s) \phi_{n_2}(Q_2, s) \phi_{n_2}(Q_3, s) \right] \frac{d}{ds} B_{n_2,1}(s) Q_2
\]

\[
+ \frac{1}{\sqrt{\mu}} \left( \sum_{n_2} f_{n_2}^{(+n)}(s) \phi_{n_2}(Q_2, s) \phi_{n_2}(Q_3, s) \right) \left[ \sum_{n_2} \left[ \frac{d}{ds} f_{n_2}^{(+n)}(s) \right] \phi_{n_2}(Q_3, s) \left( \frac{d}{ds} B_{n_2,1}(s) Q_2 \right) \right]
\]

\[
+ \frac{1}{\sqrt{\mu}} \left( \sum_{n_2} f_{n_2}^{(+n)}(s) \phi_{n_2}(Q_2, s) \phi_{n_2}(Q_3, s) \right) \left[ \sum_{n_2} \left[ \frac{d}{ds} f_{n_2}^{(+n)}(s) \right] \phi_{n_2}(Q_2, s) \left( \frac{d}{ds} B_{n_2,1}(s) Q_2 \right) \right]
\]

(3.9)

where \( \mu \) is the reduced mass of the \( H_2-H \) system.

IV. RESULTS AND DISCUSSION

The Porter–Karpplus potential energy surface was used for the present calculations because it is the one for which Schatz and Kuppermann have calculated accurate three-dimensional coupled channel results. Figure 1 shows the two coupling elements \( B_{n_1,1}(s) \) and \( B_{n_2,1}(s) \) as a function of the reaction coordinate. As noted above, \( B_{n_1,1}(s) = \gamma(s) \) is the curvature of the collinear reaction path and it is the "intrasystem" coupling which is taken into account to infinite order in the present system–bath model. The coupling \( B_{n_2,1}(s) = B_{n_2,1}(s) \) 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 Fig. 2, where the quantity plotted is the left-hand side of Eq. (2.10), i.e., four times the probability of the \( (n_2, n_3, n_4) = (0, 0, 0) \rightarrow (0, 0, 2) \) 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 Fig. 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 \( E = 0.6 \) eV—fall with decreasing
energy more rapidly than our perturbative results in
Fig. 2; thus, if one assumes that \( j = 0 \to 1 \) is still the
largest transition at these lower energies, the perturbative
results would be too large in this region; e.g., at
0.5 eV Schatz and Kupperman report a reaction prob-
ability of \( \sim 10^{-3} \) for the \( 0 \to 1 \) transition, while our result
in Fig. 1 is \( \sim 3 \times 10^{-5} \). One can perhaps understand that
the perturbative results will become progressively too
large at lower energy by noting Fig. 1: with decreasing
ergy, 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 Fig. 1 shows that for larger values of \( s \), the
coupling \( B_{2,1}(s) \) which is treated perturbatively, becomes
ger rather relative to the coupling \( B_{1,1}(s) \) that is included
exactly. Thus, inclusion of the \( B_{2,1} \) coupling only to
first order, therefore, may not be sufficient at the low-
er energies.

In any event, however, one sees that even within the
limitations of first order perturbation theory, the sys-
tem–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.

**ACKNOWLEDGMENTS**

SDS would like to thank Dr. Charles Cerjan and Pro-
fessor Robert Wyatt for many helpful discussions on
quantum scattering calculations. This work was sup-
ported by the Director, Office of Energy Research, Of-
cife of Basic Energy Sciences, Chemical Sciences Di-
vision of the U. S. Department of Energy under Contra-
t Number DE-AC03-76SF00098. Calculations were car-
rried out on a Harris H800, funded by National Science
Foundation Grant CHE-79-20181.

**APPENDIX**

Here we summarize some of the basic properties of
scattering wave functions for transmission and reflection
in one-dimension \(- \infty < x < \infty \). The actual situation of interest in the present paper is multichannel scatter-
ing, but the nature of the translational functions \( f_{\pm}^{\pm}\psi^{\pm}(s) \),
\( s = -\infty \to \infty \) is revealed by considering the one-dimen-
sional case.

The scattering wave functions \( \psi^{\pm}(x) \) are defined as
the solution of the Lipmann–Schwinger equation (i.e., a
solution of the Schrödinger equation with appropriate
boundary conditions)

\[
\psi^{\pm}(x) = \phi_k(x) + \int dx' G^{\pm}(x, x') V(x') \psi^{\pm}(x'), \tag{A1}
\]

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

\[
\phi_k(x) = |k|^{-1/2} \exp(i k x), \tag{A2}
\]

\[
G^{\pm}(x, x') = \frac{2m}{2\pi n k} \exp(\pm i k |x - x'|), \quad k = \sqrt{2mE/\hbar^2}. \tag{A3}
\]

In the asymptotic region one has

\[
\psi^{\pm}(x) \sim |k|^{-1/2} \exp(ik|x|), \quad x \to \pm \infty, \tag{A4a}
\]

\[
-|k|^{-1/2} \exp(ikx) \psi^{\pm}(x), \quad x \to \infty, \tag{A4b}
\]

and from the Lipmann–Schwinger equation one can read-
y take these limits and show that the transmission and
reflection amplitudes are given by

\[
t = 1 + \frac{2m}{2\pi n k} \langle \phi_k | V | \phi_k \rangle, \tag{A5a}
\]

\[
v = -\frac{2m}{2\pi n k} \langle \phi_k | V | \phi_k \rangle. \tag{A5b}
\]

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–Schwin-
er equation with potential \( V_0 \), then one can show that \( t \)
and \( r \) are also given by

\[
t = t_0 + \frac{2m}{2\pi n k} \langle \chi_k^{\pm} | V_1 | \chi_k^{\pm} \rangle, \tag{A6a}
\]

\[
v = -\frac{2m}{2\pi n k} \langle \chi_k^{\pm} | V_1 | \chi_k^{\pm} \rangle. \tag{A6b}
\]

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where $l_0$ and $r_0$ are the transmission and reflection amplitudes resulting from $V_0$ (i.e., those contained in the asymptotic form of the "distorted" wave function $\chi_0^*\). 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

$$l_1 = \frac{2m}{2i\hbar^2} \left\langle \chi_0^* \right| V_1 \left| \chi_0^* \right\rangle,$$

(A7a)

$$r_1 = -\frac{2m}{2i\hbar^2} \left\langle \chi_0^* \right| V_1 \left| \chi_0^* \right\rangle.$$

(A7b)

By direct substitution into the Lipmann–Schwinger equation (A1) one can readily verify the general microscopic reversibility relation

$$\psi_0^\ast(x)^* = \psi_0(x).$$

(A8)

Also be direct substitution into the Lipmann–Schwinger equation, one can see that

$$\psi_1^*(-x) = \phi_0(x) + \int_{-\infty}^{x} dx' G_0^*(x' - x') V(x') \psi_1(x')$$

and by changing integration variables $x' = -x'$ this becomes

$$= \phi_0(-x) + \int_{-\infty}^{x} dx' G_0^*(x' - x') V(-x') \psi_1(x').$$

Then since

$$\phi_0(-x) = \phi_0(x), \quad G_0^*(-x', -x') = G_0(x', x'),$$

the relation becomes

$$\psi_1^*(-x) = \phi_0(-x) + \int_{-\infty}^{x} dx' G_0^*(x' - x') V(-x') \psi_1(x').$$

(A9)

If the potential function is symmetric, i.e., $V(-x) = V(x)$, then one recognizes Eq. (A9) to be identical to the Lipmann–Schwinger equation for $\psi_0(x)$; i.e., for a symmetric potential one has the additional symmetry relation

$$\psi_2^*(-x) = \psi_2(x),$$

(A10)

and if one also uses the microscopic reversibility relation [Eq. (A8)], one has

$$\psi_3^*(-x) = \psi_3(x),$$

(A11)

for the case of a symmetric potential.

Equations (A8)−(A11) apply equally to the distorted wave functions $\chi$ with the potential $V(x)$. Thus, by using Eq. (A11), the first order contribution to the transition amplitude [Eq. (A7a)]

$$l_1 = \frac{2m}{2i\hbar^2} \int_{-\infty}^{\infty} dx \chi_0^*(x)^* V(x) \chi_0^*(x),$$

can be written as

$$l_1 = \frac{2m}{2i\hbar^2} \int_{-\infty}^{\infty} dx \chi_0^*(-x) V(x) \chi_0^*(x),$$

(A12)

which was used in Sec. III. For completeness, we note also that use of Eq. (A8) allows the first order contribution to the reflection amplitude to be written as

$$r_1 = -\frac{2m}{2i\hbar^2} \int_{-\infty}^{\infty} dx \chi_0^*(x)^* V(x) \chi_0^*(x),$$

(A13)

and unlike Eq. (A12), Eq. (A13) does not require that $V(x)$ be symmetric.