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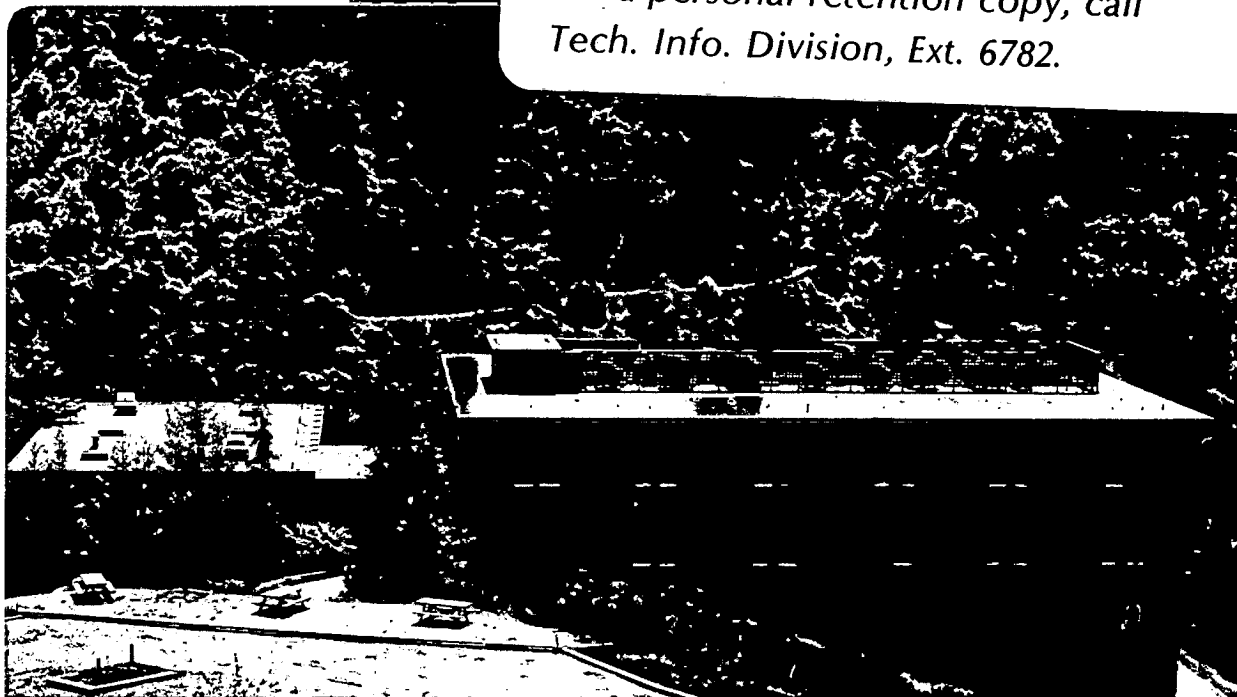
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FOR REACTIVE SCATTERING

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Multichannel Distorted Wave Born Approximation for Reactive Scattering

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Abstract

Previous applications of the distorted wave Born approximation (DWBA) to reactive scattering have often given reasonably good relative cross sections--i.e., angular distributions, product state distributions, etc.--but absolute reactive cross sections have been poor. It is argued in this paper, however, that the DWBA for reactive scattering should be accurate if (1) the reaction probability is sufficiently small (as it is, for example, in the threshold region of a reaction), and (2) the non-reactive scattering is described sufficiently accurately. To describe the non-reactive scattering "sufficiently accurately" this paper utilizes a non-reactive coupled-channel scattering wavefunction for distorted waves in the DWBA. Application to a standard test problem (collinear $H + H_2$) shows this multichannel DWBA indeed to be extremely accurate if the reaction probability is no larger than 0.1 and if ~ 3 to 4 vibrational states are included in the non-reactive coupled-channel expansion. This approach thus provides an excellent description of the threshold region of a reaction which has an activation barrier.

I. Introduction.

Although classical trajectory simulations adequately describe many aspects of chemical reaction dynamics, there are situations for which a quantum mechanical treatment is necessary. One such case where quantum effects are important is the threshold region of a chemical reaction with an activation barrier, where tunneling can significantly modify the reaction rate (particularly so for light atom transfer reactions). Also, it is the threshold region of the cross section that is most important for determining the thermal rate constant.

The goal of describing the tunneling behavior of the threshold region has, in fact, been one of the motivations for recent work seeking a rigorous quantum mechanical version of transition state theory.¹ The reasoning is that since classical transition state theory is known to describe the classical threshold of reactions correctly, a correct quantum extension of classical transition state theory ought to describe the quantum threshold correctly. Although considerable progress has been made within this framework of "tunneling corrections to transition state theory,"² the ultimate triumph has been illusive because, as emphasized by Pechukas,³ there is no absolutely rigorous quantum version of transition state theory other than the complete solution of the reactive scattering problem.

In this paper we consider another approach to describing the threshold region of chemical reactions, namely the distorted wave Born approximation (DWBA).⁴ This is basically first order quantum mechanical perturbation theory, and our reasoning is as follows: in the threshold region the reactive cross section is small compared

to non-reactive (inelastic/elastic) cross sections, so in some sense reaction is a small perturbation to non-reactive scattering; therefore if one describes the non-reactive scattering sufficiently accurately, one should be able to describe the reactive scattering perturbatively.

The key to achieving this goal lies in describing the non-reactive scattering "sufficiently accurately". Thus there have been over the years many applications of DWBA's to reactive scattering,⁵⁻¹² and although the results often seem to describe relative cross sections (product state distributions, angular distributions, etc.) quite well, they have given poor results¹³ for the absolute reactive cross sections (or probabilities). In our view this shortcoming is due to the fact that the distorted wavefunctions in these applications have essentially described only elastic scattering in each arrangement channel, and this is certainly not an accurate description of the non-reactive scattering which includes inelastic as well as elastic scattering.

The purpose of this paper, therefore, is to explore use of the DWBA for reactive scattering but where the distorted wavefunctions describe the elastic and inelastic scattering (in each arrangement channel separately) as accurately as possible; i.e., the distorted wavefunctions are those which result from non-reactive coupled-channel scattering calculations in each arrangement. Section II summarizes the essential theoretical methodology, and application to a standard test problem (the collinear $H + H_2$ reaction on the Porter-Karplus potential energy surface) is presented in Section III. The important observation here is that in the threshold region the DWBA reaction probability does indeed converge to the correct quantum mechanical values as the number of channels in the non-reactive coupled channel

wavefunctions is increased, i.e., as the description of the non-reactive scattering is made more exact. Section IV concludes with a discussion of some additional features of the DWBA for reactive scattering.

II. Summary of Relevant Features of the DWBA.

All expressions in this section pertain explicitly to a collinear $A + CB \rightarrow AC + B$ reaction, although they can be taken over in a straight-forward manner to general reactions. The notation and methodology follows that of earlier work⁷ by one of us, and the relevant aspects of the DWBA are only summarized (not derived).

If $\chi_{n_a}^{(+)}$ is the distorted wavefunction for arrangement a ($A + CB$) with outgoing wave boundary conditions and normalization as given below, and $\chi_{n_b}^{(-)}$ the similar distorted wavefunction (with incoming wave boundary conditions) for arrangement b ($AC + B$), then the S-matrix element for the reaction from vibrational state n_a of CB to vibrational state n_b of AC, is given within the DWBA by

$$S_{n_b, n_a} = (i/\hbar) \langle \chi_{n_b}^{(-)} | H - E | \chi_{n_a}^{(+)} \rangle, \quad (2.1)$$

where H is the total Hamiltonian and E the total energy. Often in DWBA expressions the Hamiltonian H is divided into a distorting Hamiltonian for arrangement a, H_a , and a residual interaction W_a ,

$$H = H_a + W_a, \quad (2.2)$$

with the operator (H-E) in Eq. (2.1) replaced by W_a . Since the distorted wavefunction $\chi_{n_a}^{(+)}$ satisfies the Schrödinger equation with H_a ,

$$(H_a - E) \chi_{n_a}^{(+)} = 0, \quad (2.3)$$

one easily sees that

$$(H-E)\chi_{n_a}^{(+)} = W_a \chi_{n_a}^{(+)} \quad , \quad (2.4)$$

so that Eq. (2.1) is equivalent to the more common expression. An advantage of Eq. (2.1) is that the residual interaction need not be explicitly constructed; one simply utilizes the best possible distorted wavefunction $\chi_{n_a}^{(+)}$ (and $\chi_{n_b}^{(-)}$ for arrangement b), and the operator (H-E) generates the effective residual interaction automatically. (There are errors in the literature, in fact, because a residual interaction W_a has been used that was inconsistent with the distorted wavefunction that was used; this can never happen if one starts with Eq. (2.1).) The only restriction on the distorted wavefunctions for the validity of Eq. (2.1) is that neither contain any reactive amplitude in it;⁴ i.e., $\chi_{n_a}^{(+)}$ must decay exponentially in the asymptotic region of arrangement b, and vice versa for $\chi_{n_b}^{(-)}$.

The distorted wavefunctions utilized in this paper are coupled channel expansions,

$$\chi_{n_a}^{(+)}(r_a, R_a) = \sum_{n'_a} \phi_{n'_a}(r_a) u_{n'_a \leftarrow n_a}^{(+)}(R_a) \quad , \quad (2.5a)$$

$$\chi_{n_b}^{(-)}(r_b, R_b) = \sum_{n'_b} \phi_{n'_b}(r_b) u_{n'_b \leftarrow n_b}^{(-)}(R_b) \quad , \quad (2.5b)$$

where $\{\phi_{n_a}\}$ and $\{\phi_{n_b}\}$ are the eigenfunctions of the vibrational Hamiltonian for the free diatomic molecules CB and AC, respectively. Coordinates r_a and R_a are the usual Jacobi coordinates, i.e., the

vibrational coordinate of the diatom CB and the translation coordinate of A relative to the center of mass of CB, respectively, and coordinates r_b and R_b are the corresponding coordinates for arrangement b. (Only two coordinates are independent; e.g., if (r_a, R_a) are considered as the independent coordinates, r_b and R_b can be expressed as linear combinations of them.) The sums over vibrational states $\{n_a\}$ and $\{n_b\}$ in Eqs. (2.5a) and (2.5b) include all the open channels in each arrangement, and possibly a finite number of closed channels as well.

The translational functions $\{u_{n'_a, n''_a}^{(+)}(R_a)\}$ satisfies the standard non-reactive coupled channel Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu_a} \frac{d^2}{dR_a^2} - E_{n'_a}\right) u_{n'_a, n''_a}^{(+)}(R_a) + \sum_{n''_a} V_{n'_a, n''_a}(R_a) u_{n''_a, n''_a}^{(+)}(R_a) = 0 \quad (2.6)$$

where μ_a is the translational reduced mass for arrangement a, and the coupling potential is

$$V_{n'_a, n''_a}(R_a) = \int dr_a \phi_{n'_a}(r_a)^* V_a(r_a, R_a) \phi_{n''_a}(r_a) \quad (2.7)$$

where

$$V_a = V - v_a(r_a) \quad (2.8)$$

where V is the total potential energy function and $v_a(r_a)$ the vibrational potential function for diatom CB. The translational functions for

arrangement b satisfies similar nonreactive coupled-channel Schrödinger equations for arrangement b. The boundary conditions which define the translational functions uniquely are

$$\lim_{R_a \rightarrow \infty} u_{n_a' \leftarrow n_a}^{(+)}(R_a) \sim v_{n_a'}^{-1/2} \left[-e^{-ik_{n_a'} R_a} \delta_{n_a', n_a} + e^{ik_{n_a'} R_a} S_{n_a', n_a} \right], \quad (2.9)$$

if n_a' is an open channel; if n_a' is a closed channel then $k_{n_a'} \rightarrow i|k_{n_a}'|$. (Note that here n_a is always an open channel.) $v_{n_a'}$ is the asymptotic velocity for channel n_a' ,

$$v_{n_a'} = \sqrt{2E_{n_a'} / \mu_a},$$

where $E_{n_a'}$ is the asymptotic translational energy for channel n_a' ,

$$E_{n_a'} = E - \epsilon_{n_a'},$$

where $\epsilon_{n_a'}$ is the vibrational energy for state n_a' of diatom CB.

Similar boundary conditions apply to the translational functions of arrangement b.

Taking the total Hamiltonian H in the form

$$H = -\frac{\hbar^2}{2\mu_a} \frac{d^2}{dR_a^2} + h_a + V_a$$

where

$$h_a = -\frac{\hbar^2}{2m_a} \frac{d^2}{dr_a^2} + v_a(r_a)$$

is the vibrational Hamiltonian for diatom CB, and utilizing Eq. (2.6), one can easily show that

$$\begin{aligned} (H-E)\chi_{n_a}^{(+)} &= \sum_{n_a'} [V_a(r_a, R_a)\phi_{n_a'}(r_a) \\ &\quad - \sum_{n_a''} \phi_{n_a''}(r_a) V_{n_a'', n_a'}(R_a)] u_{n_a' \leftarrow n_a}^{(+)}(R_a) \end{aligned} \quad (2.10)$$

Also, in the integral in Eq. (2.1),

$$\int dr_a \int dR_a \chi_{n_b}^{(-)}(r_b, R_b)^* (H-E)\chi_{n_a}^{(+)}(r_a, R_a) \quad ,$$

it is useful to change from integration variables r_a and R_a to R_a and R_b ; with Eq. (2.10), Eq. (2.1) then takes the form

$$S_{n_b, n_a} = (i/\hbar) \sum_{n_b', n_a'} \int dR_b \int dR_a u_{n_b' \leftarrow n_b}^{(-)}(R_b)^* W_{n_b', n_a'}(R_b, R_a) u_{n_a' \leftarrow n_a}^{(+)}(R_a) \quad , \quad (2.11)$$

where the exchange kernel W is defined by

$$W_{n_b', n_a', (R_b, R_a)} = \frac{(m_B + m_C)(m_A + m_C)}{m_C(m_A + m_B + m_C)} \phi_{n_b'}(r_b) \\ \times [V_a(r_a, R_a) \phi_{n_a'}(r_a) - \sum_{n_a''} \phi_{n_a''}(r_a) V_{n_a'', n_a'}(R_a)] \quad (2.12)$$

where m_A, m_B, m_C are the masses of atoms A, B, C, and where r_a and r_b in Eq. (2.12) are expressed as linear combinations of R_a and R_b . Equation (2.11) is conveniently expressed in matrix notation

$$S_{\approx b, a} = (i/\hbar) \langle u_{\approx b}^{(-)} | W_{\approx b, a} | u_{\approx a}^{(+)} \rangle \quad (2.13)$$

where $\langle u_{\approx b}^{(-)} |$ is the adjoint (complex conjugate and matrix transpose) of $u_{\approx b}^{(-)}$. It is of practical importance to note that the exchange kernel W , defined by Eq. (2.12), is energy-independent.

For numerical calculations one wishes always to integrate the coupled channel equations, Eq. (2.6), with real boundary conditions, and then to construct the formally proper wavefunction by multiplying the matrix function from the right by the appropriate constant matrix. For our applications the real translational functions $\tilde{u}_{n_a', n_a}(R_a)$ are defined by the boundary conditions

$$\lim_{R_a \rightarrow \infty} \tilde{u}_{n_a', n_a}(R_a) \sim v_{n_a'}^{-1/2} [\sin(k_{n_a'} R_a) \delta_{n_a', n_a} \\ + \cos(k_{n_a'} R_a) K_{n_a', n_a}] \quad (2.14a)$$

for $n_a' =$ open channels, and

$$\sim |v_{n_a}|^{-1/2} [\sinh(k_{n_a, R_a}) \delta_{n_a', n_a} + \cosh(k_{n_a, R_a}) K_{n_a', n_a}] \quad , \quad (2.14b)$$

for $n_a' =$ closed channels, where $n_a =$ open and closed channels.

Defining the matrix $E_{\tilde{z}_a}$ by

$$E_{\tilde{z}_a} = 2i \left(\begin{array}{c|c} 1-iK_{\tilde{z}_a oo} & -K_{\tilde{z}_a oc} \\ \hline K_{\tilde{z}_a co} & 1+K_{\tilde{z}_a cc} \end{array} \right)^{-1} \quad , \quad (2.15)$$

where the indicated partitioning of the K-matrix is between open (subscript "o") and closed (subscript "c") channels, the proper translational functions for arrangement a, $u_{\tilde{z}_a}^{(+)}(R_a) \equiv \{u_{n_a', n_a}^{(+)}(R_a)\}$, are given by

$$u_{\tilde{z}_a}^{(+)}(R_a) = \tilde{u}_{\tilde{z}_a}(R_a) \cdot E_{\tilde{z}_a} \quad . \quad (2.16a)$$

(Eq. (2.16a) defines $u_{\tilde{z}_a}^{(+)}$ as a full (i.e., square) matrix between open and closed channels, but the only physically meaningful part is for the right matrix index an open channel.) The real translational functions for arrangement b $\{\tilde{u}_{n_b', n_b}(R_b)\}$ and the matrix $E_{\tilde{z}_b}$ are defined by equations precisely analogous to Eqs. (2.14) and (2.15), and $u_{\tilde{z}_b}^{(-)}(R_b)$ is given by

$$u_{\tilde{z}_b}^{(-)}(R_b) = \tilde{u}_{\tilde{z}_b}(R_b) \cdot E_{\tilde{z}_b}^* \quad , \quad (2.16b)$$

where * denotes complex conjugation. The final expression for the DWBA reactive S-matrix is then

$$S_{\approx b, a} = E_{\approx b}^{\text{tr}} \cdot \langle \tilde{u}_{\approx b} | W_{\approx b, a} | \tilde{u}_{\approx a} \rangle \cdot E_{\approx a} \quad , \quad (2.17)$$

where $\tilde{u}_{\approx a}(R_a)$ and $\tilde{u}_{\approx b}(R_b)$ are the real translational wavefunctions ($\langle \tilde{u}_{\approx b} |$ is the matrix transpose of $\tilde{u}_{\approx b}(R_b)$.) Equation (2.17) gives $S_{\approx b, a}$ as a matrix between open and closed channels of arrangement a and b, but only the corner of the matrix between open channels of each arrangement is physically meaningful.

Additional specifics of the calculations are described in the Appendix.

III. Results and Discussion.

The collinear $H + H_2 \rightarrow H_2 + H$ reaction on the Porter-Karplus¹⁵ potential energy surface provides an excellent test problem for describing quantum threshold behavior for a reaction with an activation barrier. Exact quantum results¹⁶ for this now standard model problem are available for comparison.

Table I gives our results for the distorted wave reaction probability for various numbers of channels (i.e., vibrational states) in the non-reactive coupled channel expansion for the distorted wavefunctions; only one channel is energetically open at these energies, so that all channels except the ground vibrational state are closed channels. For reference, the exact quantum reaction probabilities are also listed in Table I.

The most important feature seen in Table I is that the energy region for which the reaction probability is small, $P \leq 0.1$, the distorted wave value converges quickly (with three to four or fewer channels) and is quite stable with respect to the addition of more closed channels; up to 14 channels were included in some calculations. Furthermore, the converged distorted wave reaction probability is in excellent agreement (within a few %) with the exact quantum values in this region. In contrast, the one-channel distorted wave result--which is what is usually meant by "distorted wave"--is seen to be much too small (by a factor of ~ 2 to 5) over the entire region. These results thus confirm our supposition that the failure of the ordinary (i.e., one-channel) DWBA is due to its poor description of the non-reactive scattering within a given arrangement.

As the reactive probability becomes large, $P \gtrsim 0.1$, the DWBA begins to fail, as one knows it must. This shows up in the present calculations by a lack of convergence in the reaction probability as the number of channels in the non-reactive distorted wavefunctions is increased. This behavior is depicted graphically in Figure 1: shown is the ratio of the distorted wave reaction probability to the exact quantum value, as a function of the number of channels in the non-reactive distorted wavefunctions. The solid line connects the values corresponding to energy $E = 0.4276$ eV, for which the reaction probability is small (1.7×10^{-2}) and which thus does show convergence; as noted above, this is typical of all cases for which $P \leq 0.1$, and the values are essentially unchanged even up to 14 channels. The dashed and dash-dot lines, on the other hand, connect values corresponding to energies $E = 0.4826$ eV and 0.50 eV, respectively, with reaction probabilities of 0.37 and 0.60 , which do not converge. This behavior is typical of all cases here for which $P \gtrsim 0.1$: the reaction probability goes through a maximum as the number of channels is increased, and then becomes quite unstable if the number of channels is increased beyond this. In this higher energy region, $P \gtrsim 0.1$, we make a "best estimate" of the distorted wave reaction probability by choosing the probabilities to be the "most nearly stable" value, i.e., the value at the relative maximum with respect to channel number. Thus for $E = 0.4826$ eV (the dashed curve in Figure 1) we choose the probability to be the value given by the 5 channel calculation, and for $E = 0.50$ eV (the dash-dot curve) we choose the value given by the 4 channel calculation.

Figure 2 shows how the resulting multichannel DWBA reaction probability (DW) diverges from the exact quantum (EQ) values as the probability increases from below 0.1, in which region it is essentially exact, to above 0.1, where it becomes progressively too large. The dotted curve shows that the distorted wave values can be improved by resorting to an exponential unitarization¹⁷ of the "primitive" DWBA: If P_{DW} is the primitive DWBA, then in the present case of one open channel, the exponentially unitarized reaction probability is given by

$$P_{EU} = \sin^2(P_{DW}^{1/2}) \quad (3.1)$$

Finally, the dashed curve in Figure 2 shows the one-channel DWBA values which, as noted above, are considerably too small.

In summarizing the results, therefore, one sees that a first order perturbative treatment of the reaction is quantitatively accurate if (1) the reaction probability is sufficiently small ($P \lesssim 0.1$ in the present application), and (2) the non-reactive scattering is determined sufficiently accurately (a 3 to 5 non-reactive coupled channel calculation for the present example). This multichannel DWBA is thus an accurate description of the threshold region of the reaction that is important for the thermal rate constant.

IV. Concluding Remarks.

It is clear that the formulae developed in Section II can be applied in a straight-forward manner to the three-dimensional version of an $A + CB \rightarrow AC + B$ reaction. This would, however, require non-reactive coupled-channel wavefunctions for rotationally/vibrationally inelastic scattering of $A + CB$ and $AC + B$, not a trivial matter in itself. In many cases, though, it has been found that rotational inelasticity can be treated reasonably accurately within the sudden approximation;¹⁸ it is then necessary only to carry out vibrationally inelastic coupled channel calculations at several different fixed relative orientation angles. Thus one relatively practical avenue for extending the present approach to three-dimensional systems is to employ this "sudden rotation-coupled channel vibration" model to generate the non-reactive distorted wavefunctions, and then to proceed as in Section II.

Finally, it is interesting to show how the reactive DWBA can be written in a much more compact, and perhaps more useful form if one is interested only in the net thermal rate constant for the reaction and not initial and/or final state information. The quantity needed is the cumulative reaction probability¹⁹ $N(E)$, in terms of which the rate constant is given by

$$k_{b \leftarrow a}(T) = (2\pi h Q_a)^{-1} \int_0^{\infty} dE N(E) e^{-E/kT} \quad , \quad (4.1)$$

where Q_a is the partition function of reactants. $N(E)$ can be expressed in several equivalent ways, and for present purposes its most useful form is

$$N(E) = \sum_{\substack{\vec{n}_a, \vec{n}_b \\ \sim a, \sim b}} \int d_2 \hat{k}_b \sigma_{\vec{k}_b \vec{n}_b \rightarrow \vec{k}_a \vec{n}_a}^{\rightarrow} \cdot (k_a^2 / \pi) \quad , \quad (4.2)$$

where σ is the reactive cross section for an incident relative wave vector \vec{k}_a and initial diatom state \vec{n}_a ($\vec{n} = v_a, j_a, m_a$) and final relative wave vector \vec{k}_b and final diatom state \vec{n}_b . The reactive cross section is given within the DWBA by⁴

$$\sigma_{\vec{k}_b \vec{n}_b \rightarrow \vec{k}_a \vec{n}_a}^{\rightarrow} = \frac{\mu_a k_b}{\mu_b k_a} \left| - \frac{2\mu_b}{4\pi\hbar^2} \langle \chi_{\vec{k}_b \vec{n}_b}^{\rightarrow(-)} | H-E | \chi_{\vec{k}_a \vec{n}_a}^{\rightarrow(+)} \rangle \right|^2 \quad , \quad (4.3)$$

where the translational part of the distorted wavefunctions are normalized here like plane waves. Since after integrating the cross section over the angles \hat{k}_b the result is independent of the angles \hat{k}_a , one can also integrate over \hat{k}_a and divide by 4π , so that with Eq. (4.3), Eq. (4.2) takes on the following more symmetrical form

$$N(E) = (4\pi^2)^{-1} \sum_{\substack{\vec{n}_a, \vec{n}_b \\ \sim a, \sim b}} \int d_2 \hat{k}_b \int d_2 \hat{k}_a \left(\frac{2\mu_a k_a}{4\pi\hbar^2} \right) \left(\frac{2\mu_b k_b}{4\pi\hbar^2} \right) \left| \langle \chi_{\vec{k}_b \vec{n}_b}^{\rightarrow(-)} | H-E | \chi_{\vec{k}_a \vec{n}_a}^{\rightarrow(+)} \rangle \right|^2 \quad . \quad (4.4)$$

This can be written as

$$N(E) = 4\pi^2 \sum_{\substack{\vec{n}_a, \vec{n}_b \\ \sim a, \sim b}} \int d_2 \hat{k}_a \int dE_a \rho_a \int d_2 \hat{k}_b \int dE_b \rho_b \delta(E-E_a) \delta(E-E_b) \left| \langle \chi_{\vec{k}_b \vec{n}_b}^{\rightarrow(-)} | H-E | \chi_{\vec{k}_a \vec{n}_a}^{\rightarrow(+)} \rangle \right|^2 \quad , \quad (4.5)$$

where ρ_a and ρ_b are the "densities of translational states"²⁰

$$\rho_a = \frac{1}{4\pi^2} \frac{2\mu_a k_a}{4\pi\hbar^2} ,$$

$$\rho_b = \frac{1}{4\pi^2} \frac{2\mu_b k_b}{4\pi\hbar^2} .$$

Then since one has the identities

$$\begin{aligned} \sum_{\substack{\vec{n}_a \\ \vec{a}}} \int d_2 \hat{k}_a \int dE_a \rho_a \delta(E-E_a) | \chi_{\vec{k}_{a\vec{a}} \vec{n}_a}^{(+)} \rangle \langle \chi_{\vec{k}_{a\vec{a}} \vec{n}_a}^{(+)} | \\ = \delta(E-H_a) \end{aligned} \quad (4.6a)$$

$$\begin{aligned} \sum_{\substack{\vec{n}_b \\ \vec{b}}} \int d_2 \hat{k}_b \int dE_b \rho_b \delta(E-E_b) | \chi_{\vec{k}_{b\vec{b}} \vec{n}_b}^{(-)} \rangle \langle \chi_{\vec{k}_{b\vec{b}} \vec{n}_b}^{(-)} | \\ = \delta(E-H_b) \end{aligned} \quad (4.6b)$$

where H_a and H_b are the non-reactive Hamiltonians for reactants and products, respectively, Eq. (4.5) can be written in its final simplified form as

$$N(E) = 4\pi^2 \text{trace} [\delta(E-H_a)(H-E)\delta(E-H_b)(H-E)] \quad (4.7)$$

Equation (4.7) shows that in order to construct $N(E)$ one does not need the individual wavefunctions $\chi_{\vec{k}_{a\vec{a}} \vec{n}_a}^{(+)}$ and $\chi_{\vec{k}_{b\vec{b}} \vec{n}_b}^{(-)}$, which contain information on initial and final states, but rather only the projection operators $\delta(E-H_a)$ and $\delta(E-H_b)$ onto any complete set of states of H_b

and H_a , respectively, at energy E . Equation (4.7) is in principal easier to evaluate directly than the individual DWBA reactive cross sections, for it involves only the net reactive flux and contains no information on how this flux comes from and goes into individual reactant and product states, respectively. In this regard, Eq. (4.7) is similar to transition state theory, which is also an approximation to $N(E)$. Also similar to transition state theory, one can show that the trace in Eq. (4.7) depends mainly on the transition state theory region of the potential energy surface and not on the asymptotic regions. Equation (4.7) may, in fact, be a useful expression by which to define a quantum transition state theory in the tunneling region near and below the classical threshold for reaction.

Appendix

Here we give more specifics about the methodology used to generate the non-reactive coupled channel wavefunctions. In matrix form the coupled-channel equations are

$$\left[1 \frac{d^2}{dR^2} - \frac{2\mu}{\hbar^2} (V(R) - E) \right] \cdot u(R) = 0 \quad , \quad (A.1)$$

where the arrangement indices, a or b, have been dropped, and

$$E_{n,n'} = \delta_{n,n'} (E_{\text{tot}} - \epsilon_n) \quad ,$$

$\{\epsilon_n\}$ being the vibrational eigenvalues for the free diatom.

The renormalized Numerov method²¹ was used to integrate Eq. (A.1).

Its matrix version is based on the three-term recursion relation

$$\begin{aligned} \left(1 - \frac{h^2}{12} T_{\approx m} \right) \cdot u_{\approx m} - 2 \left(1 + \frac{5h^2}{12} T_{\approx m-1} \right) \cdot u_{\approx m-1} \\ + \left(1 - \frac{h^2}{12} T_{\approx m-2} \right) \cdot u_{\approx m-2} = 0 \quad , \end{aligned} \quad (A.2)$$

where the index m corresponds to a particular translational coordinate R_m , i.e., $u_{\approx m} = u(R_m)$, h is the (constant) spacing between grid points, and

$$T_{\approx m} = \frac{2\mu}{\hbar^2} (V(R_m) - E) \quad . \quad (A.3)$$

Defining

$$F_{\approx m} = 1 - \frac{h^2}{12} T_{\approx m} \quad (\text{A.4})$$

and introducing the matrix ratio of the function matrix at two adjacent grid points,

$$Q_{\approx m} = u_{\approx m-1} \cdot u_{\approx m}^{-1}, \quad (\text{A.5})$$

Eq. (A.2) gives the following two-point recursion formulae for

$Q_{\approx m}$:

$$Q_{\approx m} = [12 I_{\approx m} - 10 F_{\approx m-1} - F_{\approx m-2} \cdot Q_{\approx m-1}]^{-1} \cdot F_{\approx m} \quad (\text{A.6})$$

Since the initial conditions for the function matrix are $u_{\approx 1} = 0$ and $u_{\approx 2} \neq 0$, the initial condition for $Q_{\approx 1}$ is $Q_{\approx 1}$. From Eq. (A.6) one can then generate $Q_{\approx 2}, Q_{\approx 3}, \dots, Q_{\approx M}$.

Having obtained the quotient matrix $Q_{\approx m}$ at the grid points $m=1, \dots, M$, it is a straight-forward matter to generate the function matrix $u_{\approx m}$ at these grid points; the integrals over R_a and R_b in Eq. (2.17) are then carried out by Simpson's rule using these grid points. It is also straight-forward to match the function matrix to the boundary conditions specified by Eq. (2.14); the K matrix, for example, is given explicitly by

$$K_{\approx m} = -[Q_{\approx m} \cdot N_{\approx m} - N_{\approx m-1}]^{-1} \cdot [Q_{\approx m} \cdot J_{\approx m} - J_{\approx m-1}] \quad (\text{A.7})$$

for m any grid point in the asymptotic region, and where the matrices

$N_{\approx m}$ and $J_{\approx m}$ are

$$J_{n,n'}(R) = \delta_{n,n'} |v_n|^{-1/2} \sin(k_n R)$$

$$N_{n,n'}(R) = \delta_{n,n'} |v_n|^{-1/2} \cos(k_n R)$$

for n an open channel, and

$$J_{n,n'}(R) = \delta_{n,n'} |v_n|^{-1/2} \sinh(k_n R)$$

$$N_{n,n'}(R) = \delta_{n,n'} |v_n|^{-1/2} \cosh(k_n R)$$

for n a closed channel.

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Table I. DWBA Reaction Probabilities for Collinear H + H₂ on the Porter-Karplus Potential Surface

Total Energy (eV) ^a	No. of Channels ^b						Exact Quantum ^c	
	1	2	3	4	6	8		14
0.3028	2.91-10		7.61-10	7.74-10	7.75-10	7.75-10		7.76-10
0.3128	4.07-9		1.08-8	1.10-8	1.10-8	1.10-8		1.07-8
0.3228	3.43-8		9.28-8	9.44-8	9.45-8	9.45-8		9.33-8
0.3428	1.03-6		2.89-6	2.94-6	2.95-6	2.95-6		2.88-6
0.3628	1.43-5		4.24-5	4.32-5	4.33-5	4.33-5		4.37-5
0.3828	1.19-4		3.78-4	3.87-4	3.90-4	3.90-4		3.89-4
0.4028	6.90-4		2.39-3	2.47-3	2.50-3	2.51-3		2.46-3
0.4228	3.03-3		1.16-2	1.22-2	1.25-3	1.25-3		
0.4276	4.20-3	1.21-2	1.64-2	1.73-2	1.77-2	1.77-2	1.74-2	1.74-2
0.4324	6.00-3	1.79-2	2.46-2	2.61-2	2.68-2	2.68-2	2.66-2	2.65-2
0.4428	1.06-2		4.57-2	4.90-2	5.07-2	4.97-2		4.90-2
0.4405	1.31-2	4.11-2	5.77-2	6.21-2	6.45-2	6.42-2	6.45-2	6.17-2
0.4546	2.01-2	6.56-2	9.34-2	1.02-1	1.06-1	9.32-2	1.06-1	1.00-1
0.4628	3.04-2	1.03-1	1.48-1	1.63-1	1.71-1	8.94-2		1.56-1
0.4768	5.79-2	2.06-1	3.06-1	3.41-1	3.43-1	3.76+1	4.09-2	2.97-1
0.4820	7.40-2	2.69-1	3.99-1	4.49-1	4.28-1	5.40	1.12+1	3.70-1
0.4898	9.44-2	3.66-1	5.45-1	6.15-1	5.07-1	1.20-1	8.90-1	4.65-1
0.50	1.43-1	5.47-1	8.14-1	9.08-1	4.09-1	1.31-1		6.01-1
0.60	1.46+1	3.77+1	9.95-1	8.41-1	8.74-2	2.87-1		1.00

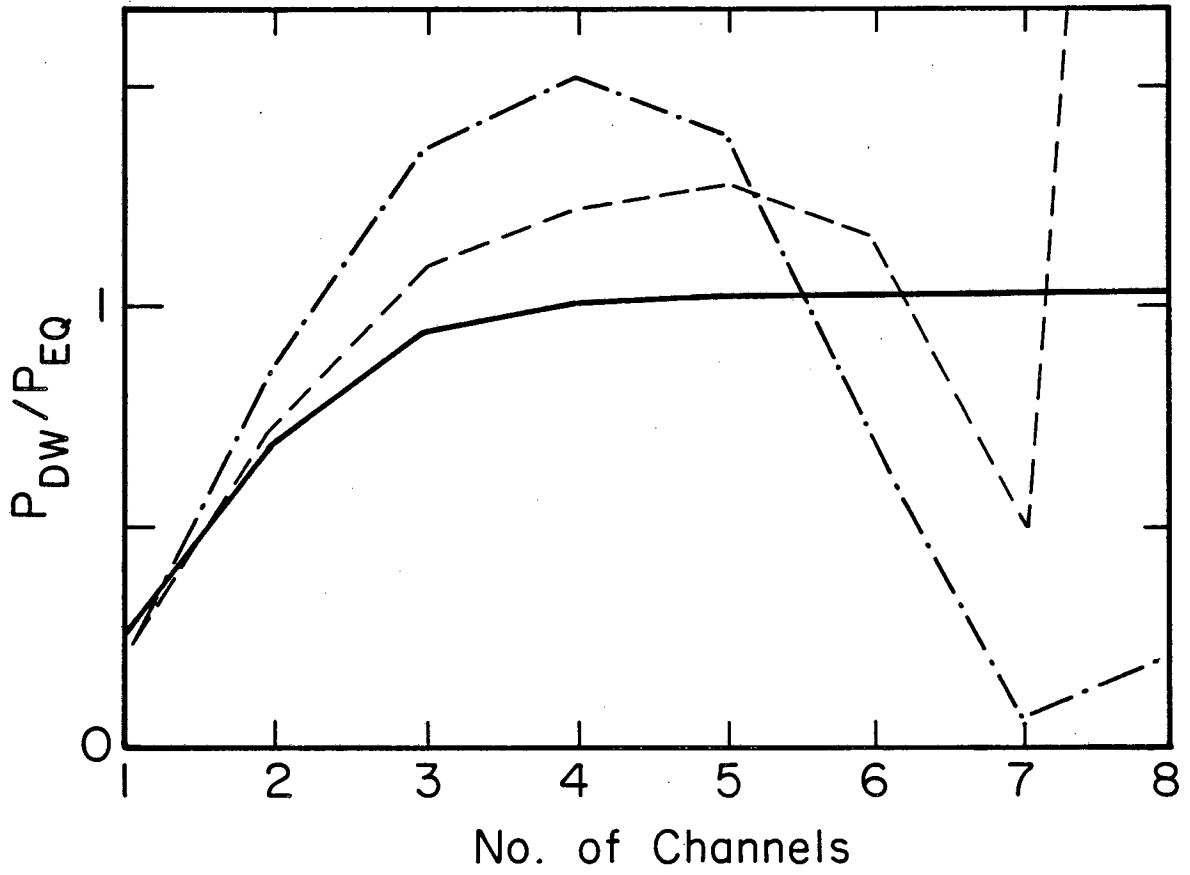
^aThe zero of energy is the bottom of the reactant diatom potential well.

^bThis is the numbers of channels in the non-reactive coupled-channel expansion for the distorted waves; see Section II.

^cRef. 16.

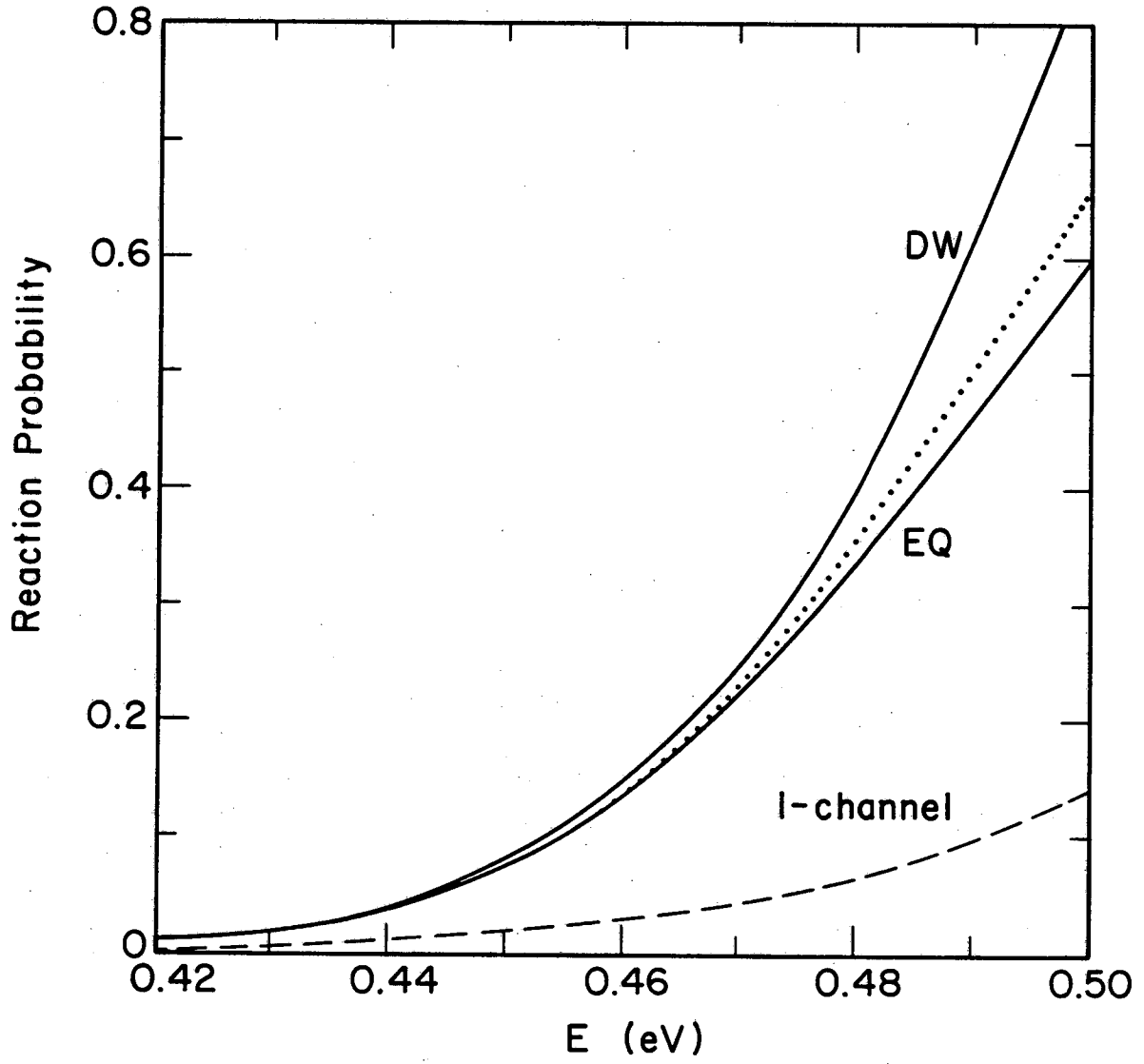
Figure Captions

1. Ratio of the distorted wave (DW) reaction probability to the exact quantum (EQ) value, as a function of the number of channels used in the non-reactive coupled channel expansion of the distorted waves. The reaction probabilities are those from Table I.
2. Reaction probability as a function of energy E . The distorted wave (DW), exact quantum (EQ), and one-channel (dashed curve) are the values given in Table I. The dotted curve is the exponentially unitarized result as defined by Eq. (3.1).



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Figure 1



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Figure 2

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