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Miller, W.H.

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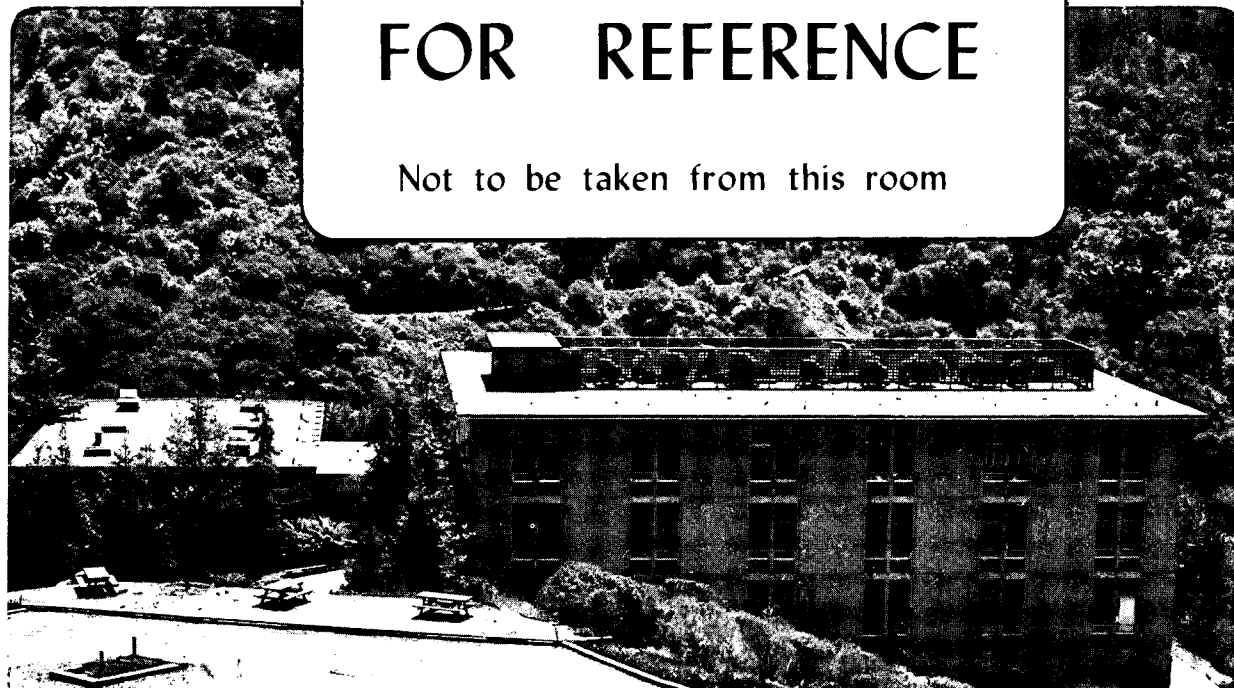
W.H. Miller

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**Quantum Mechanical Scattering Theory for
Chemical Reactions**

William H. Miller

Department of Chemistry
University of California

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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QUANTUM MECHANICAL SCATTERING THEORY FOR CHEMICAL REACTIONS

William H. Miller

Department of Chemistry, University of California, and
Chemical Sciences Division, Lawrence Berkeley Laboratory
Berkeley, California 94720

I. INTRODUCTION

Quantum mechanical reactive scattering theory provides the most complete description of a chemical reaction allowed by the basic laws of nature. Thus ever since the 1960's, when crossed molecular beam experiments opened the door to studying reactions at the most detailed state-to-state level, there has been intense interest and effort devoted to developing the theory to the practical stage that calculations can be carried out for real chemical reactions. These lectures review reactive scattering theory, in particular recent theoretical developments that have played a key role in the dramatic theoretical advances since ~1987. Two other recent reviews that I recommend are refs. 1 and 2.

II. WHY A BASIC SET VARIATIONAL APPROACH TO REACTIVE SCATTERING?

The theory of *reactive* scattering is more complicated than that for elastic and inelastic scattering^{3a-c} because of *coordinates*, and different formulations of reactive scattering turn on how one deals with this coordinate problem. Figure 1 depicts the situation for the collinear $A + BC \rightarrow AB + C$ reaction. If one were treating only an inelastic scattering process (i.e. vibrational excitation),



then the standard Jacobi's coordinates (r_a, R_a) are the natural choice, and the coupled-channel expansion of the wavefunction has the form

$$\Psi_{n_1} = \sum_n \phi_n(r_a) f_{n \leftarrow n_1}(R_a), \quad (2.2)$$

where $\{\phi_n\}$ are the (known) vibrational eigenfunctions for diatom BC and n_1 denotes the initial vibrational state. Substitution of this expansion into the Schrödinger equation leads to the standard coupled-channel equations for the unknown translational functions

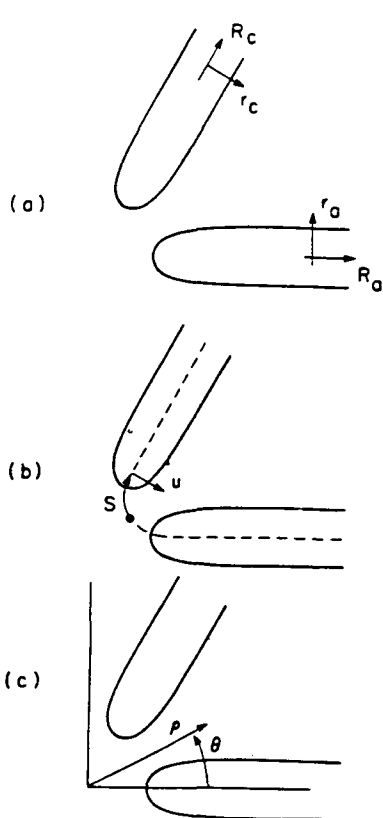


Figure 1 Schematic depiction of a collinear $A + BC \rightarrow AB + C$ potential energy surface and different ways of choosing coordinates.

(a) Jacobi coordinates for arrangement a ($A + BC$) and c ($AB + C$);

(b) reaction path ("natural collision") coordinates;

(c) hyperspherical (here simply polar) coordinates.

$$0 = \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR_a^2} - E_n \right) f_{n \leftarrow n_1}(R_a) + \sum_{n'} V_{n,n'}(R_a) f_{n' \leftarrow n_1}(R_a), \quad (2.3a)$$

$$V_{n,n'}(R_a) = \int dr_a \phi_n(r_a) (V - v) \phi_{n'}(r_a); \quad (2.3b)$$

$E_n = E - \epsilon_n$ is the translational energy for channel n , where E is the (fixed) total energy and ϵ_n the vibrational energy for state n , V is the total potential energy function, and v the potential for the isolated diatom BC.

The "coordinate problem" referred to above for reactive scattering is that the Jacobi coordinates (r_a, R_a) that are natural for describing the reactants $A+BC$ are not appropriate for describing the products, $AB+C$. There are several ways to deal with this situation, but most of the recent progress in reactive scattering has been based on the formulation⁴ in which the Jacobi coordinates for the various "arrangements" (i.e. $A+BC$, $AB+C$, $AC+B$) are all used simultaneously. For the collinear case of Figure 1, for example, the expansion for the wavefunction in this approach is

$$\Psi_{\gamma_1 n_1} = \sum_n \phi_n^a(r_a) f_{a n \leftarrow \gamma_1 n_1}(R_a) + \sum_n \phi_n^c(r_c) f_{c n \leftarrow \gamma_1 n_1}(R_c) \quad (2.4)$$

where $\gamma = a(A+BC)$, $b(B+AC)$, or $c(C+AB)$ labels the arrangement of the atoms, and $\{\phi_n^a\}$ and $\{\phi_n^c\}$ are the vibrational eigenstates of diatoms BC and AB, respectively. Note that there are only two independent coordinates (degrees of freedom) in Eq. (2.4) for the collinear case shown in Figure 1; i.e., r_a and R_a are functions of r_c and R_c , or vice-versa (specifically, they are linear combinations of each other).

The philosophy of this approach is similar to that in quantum chemistry of using *multicenter* (LCAO = linear combination of atomic orbitals) expansions for molecular orbitals. For a diatomic molecule, for example, the molecular orbital $\chi(\mathbf{r})$ for an electron is expanded in basis functions utilizing the coordinates of the electron with respect to *both* nuclear centers,

$$\chi(\mathbf{r}) = \sum_i a_i \phi_i^a(\mathbf{r}_a) + \sum_i b_i \phi_i^b(\mathbf{r}_b), \quad (2.5)$$

where \mathbf{r}_a are the coordinates of the electron with respect to nucleus a and \mathbf{r}_b those with respect to nucleus b. (Note that there are only three independent coordinates in Eq. (2.5), i.e., \mathbf{r}_a is a function of \mathbf{r}_b , or vice-versa, specifically, $\mathbf{r}_a = \mathbf{r}_b + \mathbf{R}_b - \mathbf{R}_a$, where \mathbf{R}_a and \mathbf{R}_b are the coordinates of the nuclei.)

One may also think of this approach to reactive scattering as a generalization of the standard description of electron scattering.⁵ Thus in Figure 1, consider the case that atom B = H⁺ (a proton), and A and C are electrons, i.e. the collinear version of electron-hydrogen atom scattering. In this case $m_B \gg m_A, m_C$, and it is clear that the two translational coordinates coincide with the two interparticle coordinates, i.e. $\mathbf{R}_C = \mathbf{r}_a$ and $\mathbf{R}_a = \mathbf{r}_C$, and that the two sets of terms in Eq. (2.4) are related to one another simply by *exchange* of the electrons. (By symmetry, the two sets of terms are the same, with a + or - combination corresponding to the singlet and triplet case, respectively.) Thus even if one did not know that the (spatial) two-electron wavefunction should be symmetric or antisymmetric upon exchange of the two electrons, the fact that the electrons can actually interchange by virtue of the collision (a "chemical reaction") requires that the wavefunction include both sets of terms in Eq. (2.4). (The chemical reaction H+IH \rightarrow HI+H is a molecular case very close to the e-H atom limit.) The general chemical reaction is more complicated than the electron scattering case because the finite mass of all atoms makes the relation between the various sets of Jacobi coordinates more complicated than simply exchanging them, but the basic idea is the same.

The expansion of the wavefunction in Eq. (2.4) is also essentially the same basic idea as the "resonating group model" (RGM) used in nuclear physics.⁶ The different sets of Jacobi coordinates define different "groups" (or groupings) of atoms, and the fact that the wavefunction is a linear combination of these different terms allows for "resonance" (i.e. coupling, interaction) between them if there are non-zero matrix elements of the Hamiltonian ("resonance integrals") connecting them.

Equation 2.4 is thus a natural and efficient way to represent a reactive scattering wavefunction, but it introduces the complexity that the coupling between terms corresponding to different arrangements are nonlocal, exchange type interactions. The coupled-channel equations Eq. (2.3a) are thus generalized as follows:⁴

$$0 = \left(-\frac{\hbar^2}{2\mu_a} \frac{d^2}{dR_a^2} - E_n^a \right) f_{an \leftarrow \gamma_1 n_1}(R_a) + \sum_{n'} V_{n,n'}^a(R_a) f_{an' \leftarrow \gamma_1 n_1}(R_a) \\ + \sum_{\substack{\gamma \\ \gamma \neq a}} \sum_{n'} \int dR_\gamma V_{an, \gamma n'}(R_a, R_\gamma) f_{\gamma n' \leftarrow \gamma_1 n_1}(R_\gamma). \quad (2.6)$$

The exchange interaction (the last term in the above equation), which couples states of different arrangements, is analogous to electron exchange interactions in quantum chemistry that arise from matrix elements in which the electron coordinates have been permuted (i.e.

exchanged). The coupled *integro*-differential equations for the translational functions, Eq. (2.6), are thus analogous to the Hartree-Fock equations of electronic structure theory, and as such they cannot be solved by finite difference algorithms.

Indeed, it is the presence of the exchange interaction in this formulation of reactive scattering that until recently has stymied this approach. Wolken and Karplus⁷ made some early attempts using it, but these were not completely successful. It has ultimately become clear that the most satisfactory way of dealing with exchange is analogous to what quantum chemists do in the Hartree-Fock problem, namely to expand the unknown wavefunctions in a basis set and determine the expansion coefficients via a variational principle.

III. THE S-MATRIX VERSION OF THE KOHN VARIATIONAL PRINCIPLE

The Kohn variational principle^{8,9} is essentially the Rayleigh-Ritz variational principle familiar from quantum eigenvalue problems, generalized to deal with scattering boundary conditions; i.e., the basic functional to be varied is $\langle \tilde{\Psi} | H - E | \tilde{\Psi} \rangle$, where $\tilde{\Psi}$ is a trial function. We will employ S-matrix type boundary conditions¹⁰ for the scattering wavefunctions and comment below on other possibilities. All of the relevant features are illustrated by simple s-wave potential scattering, so the methodology will 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

$$H = \frac{-\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r), \quad (3.1)$$

where $V(r) \rightarrow 0$ as $r \rightarrow \infty$. The S-matrix version of the Kohn variational approximation to the S-matrix (at energy E) can be stated as¹¹

$$S = \text{ext} \left[\tilde{S} + \frac{i}{\hbar} \langle \tilde{\Psi} | H - E | \tilde{\Psi} \rangle \right], \quad (3.2)$$

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

$$\tilde{\Psi}(r) \sim -e^{-ikr} v^{-1/2} + e^{ikr} v^{-1/2} \tilde{S}, \quad (3.3)$$

where $v = \hbar k / \mu$ is the asymptotic velocity. (Note: The convention is used throughout this paper that the wavefunctions in the bra symbol \langle in bra-ket matrix element notation are not complex conjugated.) "ext" in Eq. (3.2) means that the quantity in square brackets is to be extremized by varying any parameters in $\tilde{\Psi}(r)$. (Note that for a given trial function, Eq. (3.2) may also be viewed as the distorted wave Born approximation, where $\tilde{\Psi}$ is the distorted wave.)

A linear variational form¹¹ is taken for the trial function $\tilde{\Psi}(r)$,

$$\tilde{\Psi}(r) = -u_0(r) + \sum_{t=1}^N u_t(r) c_t, \quad (3.4)$$

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

$$u_0(r) \sim e^{-ikr} v^{-1/2}. \quad (3.5)$$

A simple choice for $u_0(r)$ is

$$u_0(r) = f(r)e^{-ikr}v^{-1/2}, \quad (3.6)$$

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

$$f(r) \rightarrow 0, r \rightarrow 0$$

$$f(r) \rightarrow 1, r \rightarrow \infty, \quad (3.7)$$

such as $f(r) = 1 - e^{-\alpha r}$. The function $u_1(r)$ is

$$u_1(r) = u_0(r)^* \sim e^{ikr} v^{-1/2}, \quad (3.8)$$

and the basis functions $\{u_t(r)\}$, $t = 2, \dots, N$ are real, square-integrable functions. The coefficients $\{c_t\}$, $t = 1, \dots, N$ in Eq. (3.4) are the variational parameters in $\tilde{\Psi}$.

With $\tilde{\Psi}$ of Eq. (3.4) substituted into Eq. (3.2) and the coefficients $\{c_t\}$ varied to extremize it, one obtains the following expression for the S-matrix

$$S = \frac{i}{\hbar} (M_{0,0} - M_0^T \cdot M^{-1} \cdot M_0), \quad (3.9)$$

where $M_{0,0}$ is a 1×1 "matrix", M_0 a $N \times 1$ matrix and M an $N \times N$ matrix,

$$M_{00} = \langle u_0 | H - E | u_0 \rangle \quad (3.10a)$$

$$(M_0)_t = \langle u_t | H - E | u_0 \rangle \quad (3.10b)$$

$$(M)_{t,t'} = \langle u_t | H - E | u_{t'} \rangle, \quad (3.10c)$$

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

$$\lim_{r \rightarrow \infty} (H - E) \begin{Bmatrix} u_0(r) \\ u_1(r) \end{Bmatrix} = 0. \quad (3.11)$$

At this point it is useful to compare the above procedure with the K-matrix version of the Kohn variational principle that has typically been used in the past.¹² The Kohn functional for K is

$$K[\tilde{\Psi}] = \tilde{K} - \frac{2}{\hbar} \langle \tilde{\Psi} | H - E | \tilde{\Psi} \rangle, \quad (3.12a)$$

where here the (real) trial function $\tilde{\Psi}$ has the asymptotic form

$$\tilde{\Psi}(r) \sim \sin(kr)v^{-1/2} + \cos(kr)v^{-1/2}\tilde{K}. \quad (3.12b)$$

One then proceeds precisely as above, the difference being that now the "free" functions $u_0(r)$ are

$$u_0(r) = f(r)\sin(kr)v^{-1/2} \quad (3.13a)$$

$$u_1(r) = f(r)\cos(kr)v^{-1/2} \quad (3.13b)$$

(The cut-off function $f(r)$ is actually not required in Eq. (3.13a) for u_0) The arithmetic is also similar, and the variational result obtain for the K-matrix is similar to Eq. (3.9)

$$K = \frac{2}{\hbar} (M_{0,0} - M_0^T \cdot M^{-1} \cdot M_0), \quad (3.14)$$

where the M-matrix elements are the same as those in Eq. (3.10) but here with the real functions u_0 and u_1 of Eq. (3.13). And now the problem appears: the matrix $H_{t,t'}$ in Eq. (3.10c) is real-symmetric in the present case, so that its eigenvalues are real. Every time that the energy E is equal to one of these eigenvalues, the matrix inverse M^{-1} in Eq. (3.14) is singular; this may happen as the energy E is varied, or at fixed E if non-linear parameters in the basis set $\{u_t\}$ are varied to cause one of the eigenvalues to pass through the value E . These "Kohn anomalies", or "false resonances", have been a plague of the Kohn variational principle ever since they were discovered by Schwartz in 1961.¹² In the limit of an infinitive basis they become infinitely narrow, and thus unobservable, but they have been a serious problem in practical calculations (which necessarily use finite basis sets).

In contrast, the S-matrix version^{10,11} of the Kohn variational method has no anomalous singularities because the matrix of H in Eq. (3.10c) is complex-symmetric (because the function u_1 of Eq. (3.8) is complex and functions inside the bra symbol $\langle |$ are not complex-conjugated). In fact, the condition that Eq. (3.9) is singular, namely

$$\det(M) = \det[u_t | H - E | u_{t'} \rangle] = 0, \quad (3.15a)$$

$t, t' = 1, \dots, N$, is the secular equation for eigenvalues of the Schrödinger equation

$$(H - E)\psi(r) = 0, \quad (3.15b)$$

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

$$\psi(r) \propto e^{ikr}; \quad (3.15c)$$

i.e., Eq. (3.15) is the expression that has been used before¹³ for determining Siegert¹⁴ eigenvalues, the complex energies that are the (physically correct) complex poles of the S-matrix which characterize the positions and widths of scattering resonances. Eq. (3.9) is thus singular only where it is supposed to be singular.

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 $G^+(E) \equiv (E + i\epsilon - H)^{-1}$. This is¹⁰

$$\langle a | G^+(E) | b \rangle = - \sum_{t, t'=1}^N \langle a | u_t \rangle (M^{-1})_{t, t'} \langle u_{t'} | b \rangle, \quad (3.16)$$

where M is as above, Eq. (3.10c), and $|a\rangle$ and $|b\rangle$ are any square-integrable functions. Note that the complex-symmetric structure of the matrix M is the same as that in complex scaling/coordinate rotation theory,¹⁵⁻¹⁸ and for the same reasons. If the functions $|a\rangle$ and $|b\rangle$ are real, then Eq. (3.16) leads to a useful way for calculating matrix elements of the microcanonical density operator,

$$\langle a | \delta(E-H) | b \rangle = -\pi^{-1} \text{Im} \langle a | G^+(E) | b \rangle. \quad (3.17)$$

In actual calculations for the S-matrix, Eq. (3.9), one does not wish to carry out numerical calculations with the complex symmetric matrix M . This can be avoided by the usual partitioning methods, so that Eq. (3.9) can be written in the equivalent form

$$S = \frac{i}{\hbar} (B-C \cdot B^{*-1} \cdot C), \quad (3.18)$$

where B and C are the 1×1 "matrices"

$$B = M_{0,0} - M_0^T \cdot M^{-1} \cdot M_0 \quad (3.19a)$$

$$C = M_{1,0} - M_0^{*T} \cdot M^{-1} \cdot M_0, \quad (3.19b)$$

where $M_{0,0}$, M_0 , and M are as before, Eq. (3.10), except that $t, t' = 2, \dots, N$ (i.e., only the real basis functions), and

$$M_{1,0} = \langle u_0^* | H-E | u_0 \rangle. \quad (3.19c)$$

Here the matrix $(M)_{t,t',t,t' = 2, \dots, N}$ is real and symmetric, and thus more easily dealt with. (One can readily verify that a value of E for which $\det(M) = 0$ does not lead to a singularity in Eq. (3.18).

Finally, for general multichannel rearrangement scattering,^{4,19} 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. (3.18) and (3.19) generalize as follows:

$$S = \frac{i}{\hbar} (B-C^T \cdot B^{*-1} \cdot C), \quad (3.20a)$$

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

$$B = M_{0,0} - M_0^T \cdot M^{-1} \cdot M_0 \quad (3.20b)$$

$$C = M_{1,0} - M_0^{*T} \cdot M^{-1} \cdot M_0, \quad (3.20c)$$

where $M_{0,0}$ and $M_{1,0}$ are also "small" square matrices

$$(M_{0,0})_{n\gamma, n'\gamma} = \langle u_{0n}^\gamma \phi_n^\gamma | H-E | u_{0n'}^\gamma \phi_{n'}^\gamma \rangle \quad (3.21a)$$

$$(M_{1,0})_{n\gamma, n'\gamma} = \langle u_{0n}^{\gamma*} \phi_n^\gamma | H-E | u_{0n'}^\gamma \phi_{n'}^\gamma \rangle; \quad (3.21b)$$

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

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

M is a "large" by "large" real symmetric matrix in the composite space, internal plus translational,

$$(M)_{\gamma\gamma',t'n'\gamma} = \langle u_{tn}^\gamma \phi_n^\gamma | H - E | u_{t'n'}^\gamma \phi_n^\gamma \rangle, \quad (3.21c)$$

where $\{u_{tn}^\gamma(r_\gamma)\}$ is a square integrable basis (that need not depend on n - i.e. the same translational basis can be used for every channel). M_0 is a "large" by "small" rectangular matrix

$$(M_0)_{\gamma\gamma',n'\gamma} = \langle u_{tn}^\gamma \phi_n^\gamma | H - E | u_{0n'}^\gamma \phi_n^\gamma \rangle. \quad (3.21d)$$

Only open channels $\{\gamma\}$ are included in the matrices M_{00} , $M_{1,0}$, and the "small" dimension of M_0 , while open and closed channels are required in the matrix M and the "large" dimension of M_0 .

Eqs. (3.20) - (3.21) 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. Specifics related to $A+BC \rightarrow AB+C$ reaction in three-dimensional space - i.e. angular momentum coupling, elimination of the three Euler angles for overall rotation, conservation of total angular momentum, identical atom symmetry, etc. - are given in refs. 4 and 19.

IV. ENHANCEMENTS OF THE METHODOLOGY

Note that the generic form of the S-matrix Kohn trial function in the general multichannel case above is

$$\Psi_{\gamma_1 n_1} = -\Phi_{\gamma_1 n_1} + \sum_{\gamma, n} \Phi_{\gamma n}^* C_{\gamma n, \gamma_1 n_1} + \sum_i \chi_i C_{i, \gamma_1 n_1}, \quad (4.1)$$

where $\Phi_{\gamma n}(q_\gamma, r_\gamma)$ is an asymptotically incoming wave in channel γn ,

$$\lim_{r_\gamma \rightarrow \infty} \Phi_{\gamma n}(q_\gamma, r_\gamma) = \phi_n^\gamma(q_\gamma) e^{-ik_\gamma r_\gamma / v_\gamma} 1/2, \quad (4.2)$$

$\Phi_{\gamma n}^*$ is the corresponding asymptotically outgoing wave, and $\{\chi_i\}$ is a L^2 (square integrable) basis that spans the interaction region. In Eqs. (3.20) - (3.21) above, the L^2 basis $\{\chi_i\}$ was chosen to be the direct product of the various channel eigenfunctions and a translational basis,

$$\chi_i = \phi_n^\gamma(q_\gamma) u_t(r_\gamma), \quad (4.3)$$

so that $i \equiv \gamma n t$, but this is not necessary. The $\{\chi_i\}$ basis can be chosen in a variety of ways, using a variety of coordinates. There is even some flexibility in the choice of the "free" wavefunctions $\{\Phi_{\gamma n}\}$, the only requirement being the asymptotic form in Eq. (4.2). Here we note several of these possibilities that have been tried so far.

a. Elimination of Exchange in the Free-Free and Bound-Free Matrix Elements

This was a simplification that was realized early on.²⁰ By proper choice of the cut-off function $f(r)$ in the "free" functions u_0 and u_1 [cf. Eqs. (3.6) - (3.7)], one can insure that the matrix elements involving the free functions - $M_{0,0}$, $M_{1,0}$, and M_0 in Eq. (3.21) - vanish between different arrangements; i.e.,

$$(\mathbf{M}_{0,0})_{n\gamma,n'\gamma'} = \delta_{\gamma,\gamma'} (\mathbf{M}_{0,0}^{\gamma})_{n,n'}, \quad (4.4)$$

and similarly for $\mathbf{M}_{1,0}$ and \mathbf{M}_0 . This is quite important practically because it is these matrix elements which must be re-computed at each scattering energy E (because the "free" functions u_0 and u_1 depend on E), and furthermore, the exchange integrals are more difficult to evaluate numerically than the direct matrix elements (those with $\gamma = \gamma'$). With this simplification, the only non-zero exchange matrix elements are the bound-bound ones, Eq. (3.21c), but these are independent of the energy E , so that they can be computed once and then used to compute the S-matrix at many values of E .

b. Basis Set Contraction of the L^2 Basis

This is an obvious procedure borrowed from *ab initio* electronic structure theory. One initially evaluates the Hamiltonian in an L^2 basis of "simple", easy-to-use functions, and then transforms to a better basis, e.g., by diagonalizing some simpler reference problem. For the L^2 basis actually used for the calculation, one then chooses fewer of these good basis functions than the original number of the simple functions (cf. the transformation from many atomic orbitals to a fewer number of molecular orbitals). A quasi-adiabatic contraction²¹ of the channel eigenfunctions has been especially easy to use, and in applications to the $H+H_2$ and $D+H_2$ reactions it approximately halves the number of basis functions necessary to achieve convergence. Since the computational time is proportioned to the cube of the size of the matrix \mathbf{M} that is inverted in Eq. (3.20), this reduces the computational time by almost an order of magnitude.

Another important example of a contraction - or actually just a clever choice of basis - is to use the body-fixed, or helicity representation for the L^2 basis functions,²² and the space-fixed, or ℓ -representation for the free functions. Thus the channel index n in Eq. (3.20) - (3.21) is $n \equiv (v,j,K)$ for the L^2 basis, where (v,j) are the vibrational and rotational quantum numbers for the diatom, and K is the projection quantum number for the diatom rotation with respect to \hat{r}_γ (the atom to diatom center of mass) as quantization axis; this is the body-fixed, or helicity representation. For the free functions in Eq. (3.20) - (3.21), the channel index is $n \equiv (v,j,\ell)$, where v and j are the same as before, and ℓ is the orbital angular momentum quantum number for the relative motion between the atom and the center of mass of the diatom; this is the space-fixed, or ℓ -representation. For the large separations between atom and diatom, the Hamiltonian tends to be more nearly diagonal in the ℓ -representation (because the centrifugal potential, $\ell^2/2\mu r^2$, is larger than the interaction potential for large r), but for small distances it is more nearly diagonal in the K -representation (because here the interaction is typically larger than the centrifugal potential). The transformation element $\langle k|\ell \rangle$ relating the ℓ - and k - representations is a Clebsch-Gordan coefficient.⁴ Application to the $F+H_2 \rightarrow HF+H$ reaction has shown the enormous utility of this approach.²²

Finally, an even more novel choice of L^2 basis is a point-wise basis, i.e., a pseudo-spectral, or discrete variable, or collocation representation.^{23,24} This has the advantage of great flexibility, i.e., one has only to choose points that span the interaction region (of all arrangements). The other great advantage is that no integrals are required to obtain the matrix of the Hamiltonian in the L^2 representation. Initial applications have shown the feasibility of these approaches, and they are currently the object of intense research.

c. Distorted Free Functions

Another strategy to keep the L^2 basis as small as possible is to use better free functions,

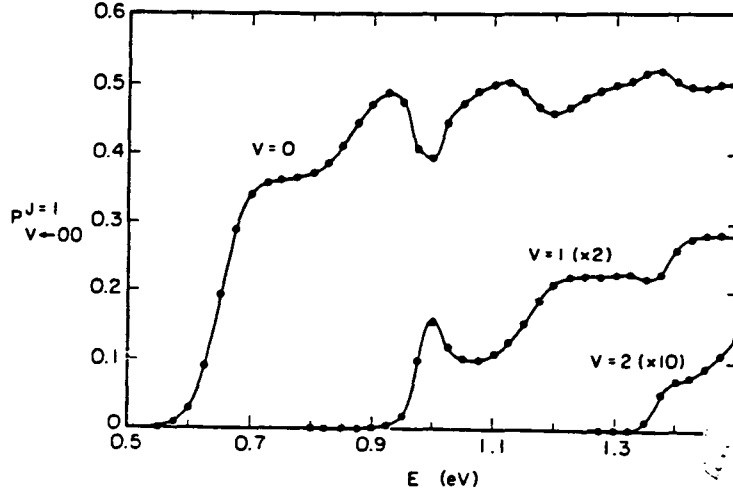


Figure 2 Reaction probability for $\text{H} + \text{H}_2(v = j = 0) \rightarrow \text{H}_2(v', \text{all } j') + \text{H}$, for total angular momentum $J = 1$, as a function of total energy E . The results for $v' = 1$ and $v' = 2$ have been multiplied by factors of 2 and 10, respectively, for convenience in displaying them.

i.e., functions u_0 and u_1 that describe the wavefunction accurately to smaller values of r_γ than the simple plane waves discussed above. For example, the function $\Phi_{\gamma n}$ of Eq. (4.1) and (4.2) can be chosen as

$$\Phi_{\gamma n}(\mathbf{q}_\gamma, r_\gamma) = \sum_{n'} \Phi_{n'}^\gamma(\mathbf{q}_\gamma) f(r_\gamma) u_{n' \leftarrow n}^\gamma(r_\gamma), \quad (4.5a)$$

where the translational function matrix $u_{n' \leftarrow n}^\gamma$ is the solution of the inelastic coupled channel Schrödinger equation for channel γ ,

$$0 = \left(-\frac{\hbar^2}{2\mu_\alpha} \frac{d^2}{dR_\alpha^2} - E_{\gamma n'} \right) u_{n' \leftarrow n}^\gamma(r_\gamma) + \sum_{n''} V_{n', n''}^\gamma(r_\gamma) u_{n'' \leftarrow n}^\gamma(r_\gamma), \quad (4.5b)$$

with asymptotic boundary condition

$$\lim_{r_\gamma \rightarrow \infty} u_{n' \leftarrow n}^\gamma(r_\gamma) = \delta_{n', n} e^{-ik_\gamma r_\gamma} v_{\gamma n}^{-1/2}; \quad (4.5c)$$

this radial function is irregular as $r_\gamma \rightarrow 0$, but the cut-off function $f(r)$ regularizes it. These "distorted" free functions²⁵ describe inelastic scattering separately in each arrangement, so that the L^2 basis can be restricted more specifically to the very short range exchange region (and thus be smaller). The free-free and bound-free matrix elements are also considerably simplified with these distorted free functions:¹⁹

$$(\mathbf{M}_{0,0})_{\gamma n, \gamma n'} = \delta_{\gamma, \gamma} \frac{\hbar^2}{2\mu_\gamma} \sum_{n''} \langle u_{n'' \leftarrow n}^\gamma | f^2 | u_{n'' \leftarrow n}^\gamma \rangle \quad (4.6a)$$

$$(\mathbf{M}_{1,0})_{\gamma n, \gamma n'} = \delta_{\gamma, \gamma} \left[\frac{i\hbar}{2} \delta_{n, n'} + \frac{\hbar^2}{2\mu_\gamma} \sum_{n''} \langle u_{n'' \leftarrow n}^{\gamma*} | f^2 | u_{n'' \leftarrow n}^\gamma \rangle \right] \quad (4.6b)$$

$$(M_0)_{\gamma m, \gamma' n'} = -\delta_{\gamma, \gamma'} \frac{\hbar^2}{2\mu_\gamma} \left\langle u_{\gamma m} | f' + 2f' \frac{d}{dr_\gamma} | u_{\gamma' n'} \right\rangle \quad (4.6c)$$

V. SOME APPLICATIONS

Accurate differential and integral cross sections have been calculated (in full three-dimensional space) with the methodology discussed above for the reactions $\text{H} + \text{H}_2(\text{para}) \rightarrow \text{H}_2(\text{ortho}) + \text{H}$,^{26,27} $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$,¹⁹ and $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$,²⁸ for a wide range of energies. Here I will review only the results for the $\text{H} + \text{H}_2$ reaction that has been of special interest because of experimental reports of resonance structure in the energy dependence of the integral cross section.

Figure 2 shows the reaction probability for $\text{H} + \text{H}_2(v = j = 0) \rightarrow \text{H}_2(v', \text{all odd } j') + \text{H}$ as a function of energy E , for various final vibrational states v' , for one value of total angular momentum J . The resonance feature at $E \cong 1.0$ eV, due to a short-lived collision complex, is readily apparent. The integral cross section, however, is a sum of reaction probabilities over all values of J (which requires values up to ~ 20 for convergence in the present case),

$$\sigma_{v'j' \leftarrow vj}(E) = \pi [k_{vj}^2 (2j+1)]^{-1} \sum_{J=0} (2J+1) \sum_{\ell, \ell'} |S_{v'j' \ell', vj \ell}^J(E)|^2, \quad (5.1)$$

and since the position of the resonance varies with J the resonance feature is averaged out (cf. inhomogeneous broadening) in the integral cross section.

Figure 3 shows the theoretical cross sections for final states $v' = 1, j' = 1$ and 3 , compared to the experimental results of Nieh and Valentini.²⁹ Through the absolute magnitudes of the theoretical and experimental cross sections are in good agreement, the theoretical results do not show the resonance-like structure seen experimentally. This

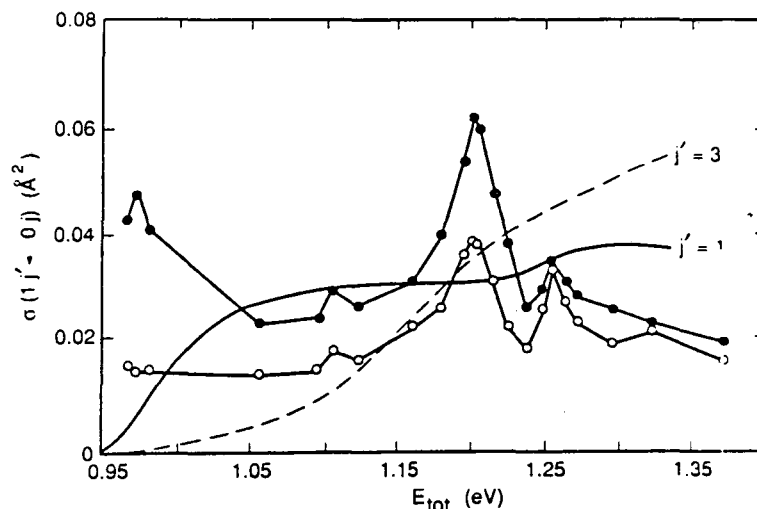


Figure 3 Integral cross section for the para \rightarrow ortho reaction $\text{H} + \text{H}_2(v = 0, j) \rightarrow \text{H}_2(v' = 1, j') + \text{H}$ as a function of total energy. The solid and dashed lines are the theoretical results of ref. 26 for $j' = 1$ and 3 , respectively; they both are the rotational ground state ($j = 0$). The solid and open circles are the corresponding experimental results of ref. 29 for which the initial rotational state is a Boltzmann distribution of para states (52% $j = 0$, 48% $j = 2$).

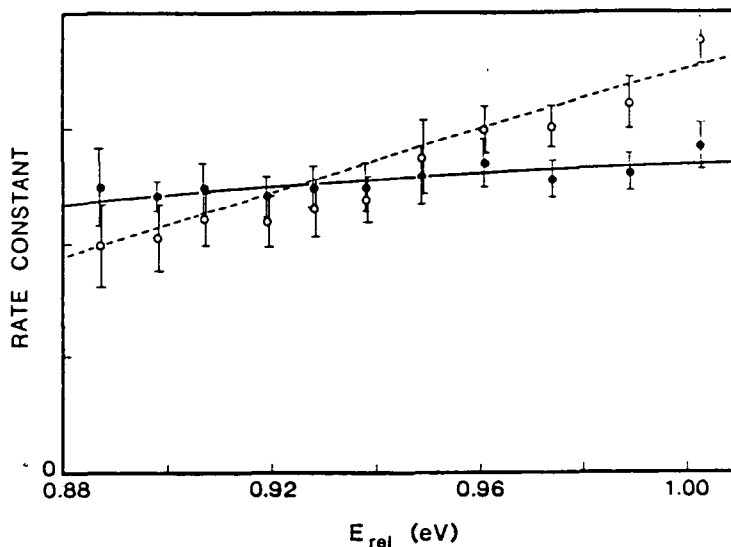


Figure 4 Same as Figure 3 except the points are the experimental results of ref. 30. (Precisely speaking, the experiments in both Figures 3 and 4 measure rate constants.) These experimental values have been normalized to the theoretical results (which have been appropriately averaged over the experimental energy resolution), though the $j' = 1$ and 3 values are absolute relative to one another; see ref. 30 for more details. Since E_{tot} of Figure 3 is related to E_{rel} here by (for $j = 0$) $E_{\text{tot}} \cong E_{\text{rel}} + 0.27$ eV, the energy scale here covers the range $E_{\text{tot}} \cong 1.15 - 1.28$ eV in Figure 3.

disagreement caused considerable concern until the very recent experiments³⁰ by Zare's group which agree well with the theoretical cross sections. These more recent experimental results are shown in Figure 4. Though over a narrower energy range, and only relative cross sections, they nevertheless cover the critical region where the structure was reported in the earlier experiments; they see no such structure and are in quantitative agreement with the theoretical results.

More recently, calculations have been carried out for the differential cross section over a range of energies,

$$\sigma_{v'j'K' \leftarrow vjK}(\theta, E) = \left| (2ik_{vj})^{-1} \sum_J (2J+1) d_{K'K}^J(\theta) S_{v'j'K', vjK}(J, E) \right|^2. \quad (5.2)$$

Figure 5 shows these results³¹ for the transitions $v = j = 0 \rightarrow v' = 0, 1, j' = 1, 3, 5$. At low energies the cross section is strongly peaked in the backward direction ($\theta = 180^\circ$), but at the highest energies shown a peak begins to emerge in the forward scattering direction ($\theta = 0^\circ$). This is very typical for reactions with an activation barrier.

Of particular interest is a "ridge" along a line in the E - θ plane (seen most distinctly for final state $v' = 0, j' = 1$ in Figure 5). This feature in the cross section is attributed to the resonance relation $E = E_r(J)$, where $E_r(J)$ is the resonance energy as a function of total angular momentum J . I.e., the position of the resonance in Figure 2 for $J = 1$, E_r is different for different values of J ; $E_r(J)$ is essentially the rotational energy of the collision complex, and in fact the J -dependence is well described as

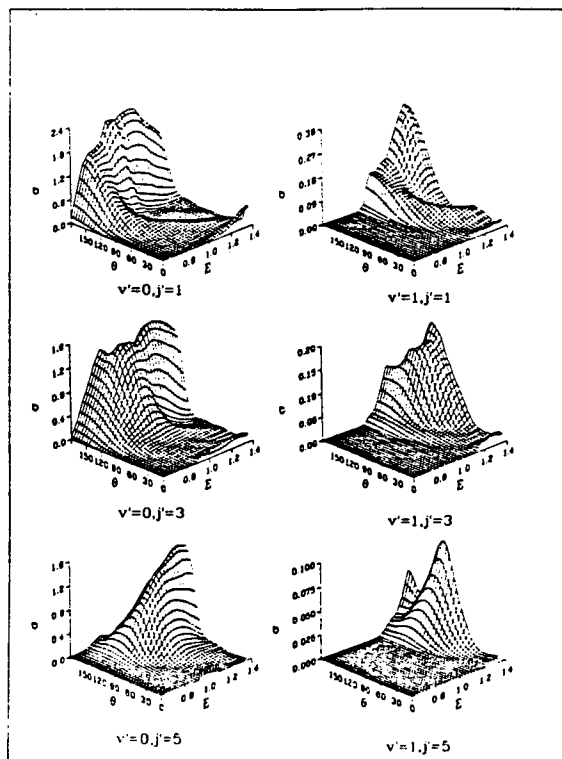


Figure 5 Three-dimensional plot of the differential cross sections $\sigma(\theta, E)$ as a function of θ and E , for the transitions $H + H_2(v = j = 0) \rightarrow H_2(v', j') + H$, for various final states (v', j') .

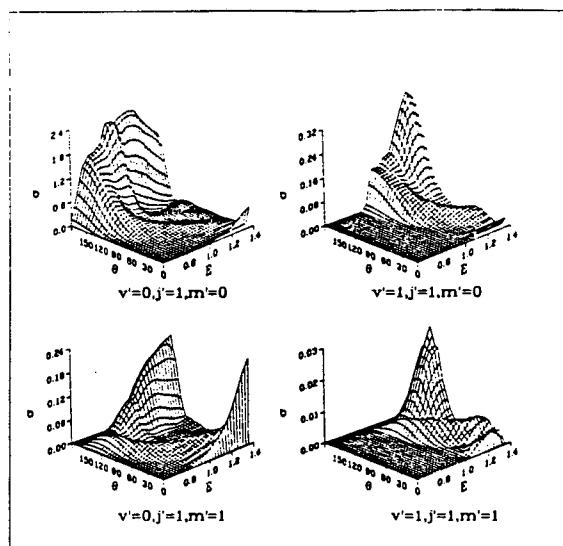


Figure 6 Three-dimensional plot of the completely state resolved differential cross section for $H + H_2(v = j = 0) \rightarrow H_2(v', j', m') + H$, as a function of θ and E . Note that the σ scale for $m' = 1$ is an order of magnitude smaller than that for $m' = 0$ final states.

$$E_r(J) = \text{constant} + BJ(J+1), \quad (5.3)$$

where the rotation constant $B \sim 10\text{-}12 \text{ cm}^{-1}$, normal for an $\text{H}\cdots\text{H}\cdots\text{H}$ geometry. Within a semiclassical analysis, furthermore, J is a function of θ by virtue of the stationary phase relation

$$\Theta(J) = \theta, \quad (5.4)$$

where $\Theta(J)$ is the classical deflection function; i.e., by observing the differential cross section as a function of θ one to some extent unfolds the sum over J that is inherent in the integral cross section (cf. Eq. 5.1). The ridge, or peak in the cross section along the line in the E - θ plane is thus identified as the resonance relation $E = E_r(J(\theta))$, with $J(\theta)$ determined by Eq. 5.4.

Finally, this feature is seen even more clearly in the energy-dependent differential cross sections that are not summed over final helicity quantum number K' , as shown in Figure 6 (here $m \equiv K$). These cross sections correspond to Eq. (5.2) with all possible initial and final quantum numbers specified and are thus the most complete description of the bimolecular reaction that is possible. The resonance ridge in the $K'(\equiv m') = 1$ cross section for $v' = 0, j' = 1$ is stronger than that in the $K'(\equiv m') = 0$ cross section, which is plausible because one expects most of the direct (i.e., non-resonant) scattering to appear in the $\Delta K = 0$ channel (i.e., $K' = 0$ since $K = 0$ by virtue of the fact that $j = 0$).

VI. CONCLUDING REMARKS

One may thus say that the general prescription for carrying out quantum mechanical reactive scattering calculations is now quite clear but that one has just begun down the road of practical developments that can be made. Section IV describes some of these methodological developments - all of which can be characterized as how to choose basis functions more efficiently - but one expects to see many additional contributions. It very much reminds one of the early days of quantum chemistry, and it is clear already that many ideas developed in that field can usefully be brought to bear on quantum reactive scattering.

One major difference with quantum chemistry is that matrix elements of the Hamiltonian (i.e., integrals) will never be able to be evaluated analytically in the present case as they can be in electronic structure theory. (This is because the potential energy surface is a very complicated function of the nuclear coordinates, different for every system, and not simply Coulomb's law.) For reactions more complex than an atom-diatom system, integral evaluation will likely be a major bottleneck. This is one reason for interest in developing the pointwise representations noted in Section IVb. Some of you at this Advanced Study Institute, however, may find other ways to solve these problems. I wish you luck!

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720