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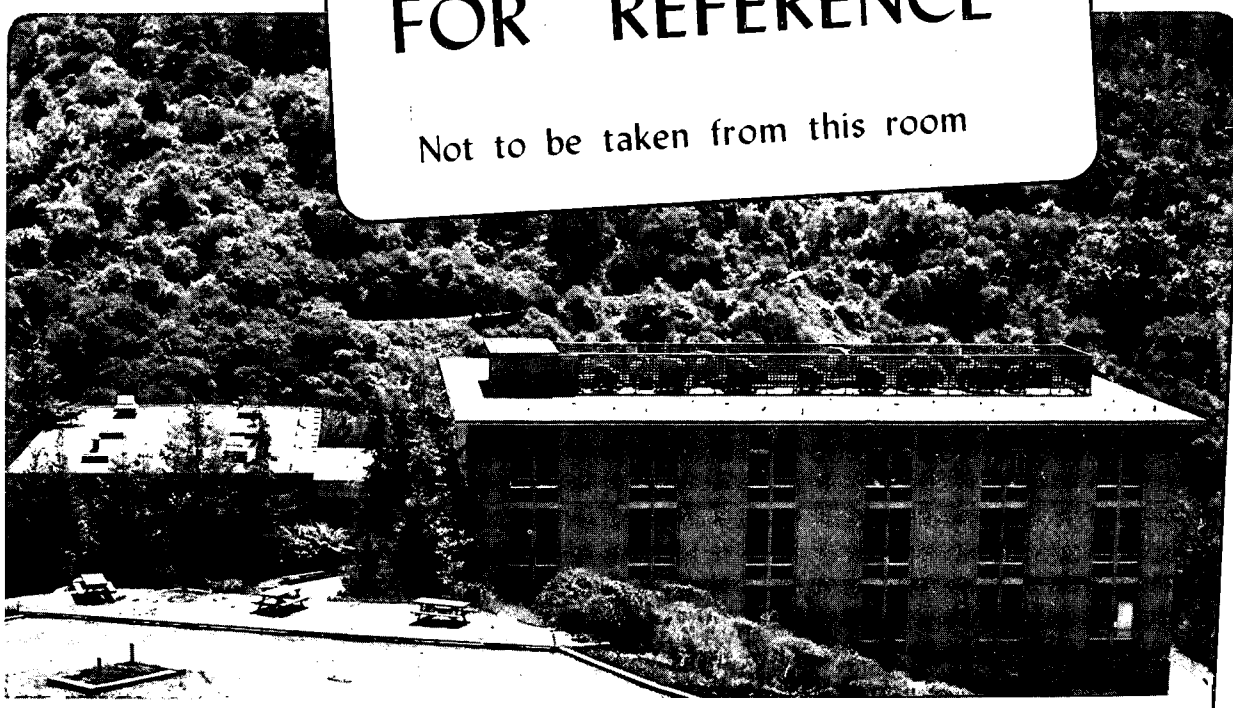

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S-Matrix Version of the Kohn Variational Principle for Quantum Scattering Theory of Chemical Reactions

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ABSTRACT

The S-matrix version of the Kohn variational principle reduces quantum scattering (e.g., for describing a bimolecular chemical reaction) to a straightforward quantum mechanical calculation: one chooses basis functions (as cleverly and efficiently as possible), computes matrix elements of the Hamiltonian operator with respect to this basis, and then performs a standard linear algebra calculation (i.e., solves a set of simultaneous linear equations $\mathbf{M} \cdot \mathbf{x} = \mathbf{a}$ for $\mathbf{x} = \mathbf{M}^{-1}\mathbf{a}$). This paper reviews the basic S-matrix Kohn methodology and describes recent developments. The latter are essentially all variations on the theme of searching for "better basis functions". "Better" may mean more accurate basis functions, so that fewer of them are required; examples of this are a contracted basis of L^2 functions and distorted "free" functions. "Better" may also mean simpler basis functions, that make the Hamiltonian matrix easier to construct and the subsequent linear algebra problem easier to solve; the discrete variable representation (DVR), or basis of grid points for the L^2 basis is an example of this. A different way of reducing the size of the basis set is to use a semiclassical correction to the Kohn S-matrix. All of these developments are discussed.

I. INTRODUCTION

It is well recognized that quantum mechanical reactive scattering theory provides the most complete description of an elementary bimolecular chemical reaction allowed by the basic laws of nature. Thus ever since the 1960s, when crossed molecular beam experiments[1] opened the door to studying reactions at this most rigorous state-to-state level, there has been intense interest and effort devoted to developing the theory to the practical stage that reliable calculations can be carried out for real chemical reactions. The last few years have seen major progress[2,3] toward achieving this goal, to which this entire volume is witness.

The recent work here at Berkeley (ref. 4 gives an up-to-date bibliography) has been based primarily on the S-matrix version of the Kohn variational principle,[4a,d,5] for once it was realized that this version of the Kohn method is free of the anomalous singularities that have plagued other versions of it in the past,[6] scattering calculations (even *reactive* scattering) are reduced to very standard quantum mechanical procedures, i.e., choosing appropriate basis functions, computing matrix elements of the Hamiltonian, and performing a linear algebra calculation. The S-matrix Kohn approach has also been very fruitfully applied to electron-molecule scattering,[7] producing the most impressive such calculations to date in that field.

In an earlier review[2b] I focused primarily on recent *applications* of the S-matrix Kohn approach to the $H+H_2$ family of reactions and comparison of the theoretical results with recent experiments, while the present one concentrates on the theoretical concepts and methodology. Sections II and III present the S-matrix

Kohn method as we have formulated and used it to date, and Sections IV and V describe new developments and directions. The discrete variable representation (DVR) approach as discussed in Section IVc appears in particular to offer the simplest, and thus most powerful avenue for extending these S-matrix Kohn methods to more complex chemical reactions.

INSERT FIGURE 1 ABOUT HERE

To keep the presentation as clear and simple as possible, to focus on the essentials, most discussion will refer explicitly to the collinear atom-diatom reaction,

$$A+BC(n_1) \rightarrow AB(n_2)+C\ , \tag{1.1}$$

where $n_1(n_2)$ denote initial (final) vibrational states. It is extremely important, of course, that the methodology can be applied to such reactions (and even more complex reactions) in full three-dimensional space, and for all values of total angular momentum J; the significance of the recent applications is that this was actually done, so that the physically observable integral and differential cross sections could be calculated.[4i,k,ℓ,u] All of the extra subscripts involved in the three-dimensional formulae, however, tend to obscure the fundamental theoretical considerations, and in fact all of these technical details — angular momentum coupling, integration over Euler angles, etc. — were worked out with regard to reactive scattering many years ago[8] and have been employed essentially unchanged by us and others.

To conclude this Introduction it is perhaps useful to discuss why variational (i.e., basis set expansion) methods have emerged as so useful for *reactive* scattering

problems. The theory of *reactive* scattering is more complicated than that for elastic and inelastic scattering[9] 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 → AB + C reaction. If one were treating only an inelastic scattering process (i.e. vibrational excitation),

$$A + BC(n) \rightarrow A + BC(n'), \tag{1.2}$$

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

$$\psi_{n_1} = \sum_n \phi_n(r_a) f_{n\leftarrow n_1}(R_a), \tag{1.3}$$

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

$$0 = \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR_a^2} - E_n\right) f_{n\leftarrow n_1}(R_a) + \sum_{n'} V_{n,n'}(R_a) f_{n'\leftarrow n_1}(R_a), \tag{1.4a}$$

$$V_{n,n'}(R_a) = \int dr_a \phi_n(r_a)(V-v)\phi_{n'}(r_a); \tag{1.4b}$$

$E_n = E-\varepsilon_n$ 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 formulation[8] 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

$$\Psi_{\gamma_1 n_1} = \sum_n \phi_n^a(r_a) f_{an\leftarrow\gamma_1 n_1}(R_a) + \sum_n \phi_n^c(r_c) f_{cn\leftarrow\gamma_1 n_1}(R_c) \tag{1.5}$$

where γ = 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. (1.5) 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,

$$\chi(r) = \sum_i a_i \phi_i^a(\mathbf{r}_a) + \sum_i b_i \phi_i^b(\mathbf{r}_b), \tag{1.6}$$

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. I.e., when the electron coordinate $\mathbf{r}$ is close to nucleus a

(located at position $\mathbf{R}_a$), then $\mathbf{r}_a \equiv \mathbf{r} - \mathbf{R}_a$ are the natural coordinates in which to choose basis functions to expand the orbital (the first terms in Eq. (1.6)), and when $\mathbf{r}$ is near nucleus b (located at $\mathbf{R}_b$) then the natural coordinates to use are $\mathbf{r}_b \equiv \mathbf{r}-\mathbf{R}_b$ (the second set of functions in Eq. (1.6)). To cover both possibilities, one uses *both* sets of coordinates, but note that there are only three independent coordinates in Eq. (1.6), i.e., $\mathbf{r}_a$ is a function of $\mathbf{r}_b$, or vice-versa, (specifically $\mathbf{r}_a = \mathbf{r}_b+\mathbf{R}_b-\mathbf{R}_a$).

The expansion of the wavefunction in Eq. (1.5) is also essentially the same basic idea as the "resonating group model" (RGM) used in nuclear physics.[10] 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 (1.5) 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. (1.4a) are thus generalized as follows:[8]

$$0 = \left(-\frac{\hbar^2}{2\mu_a}\frac{d^2}{dR_a^2} - E_n^a\right) f_{an\leftarrow\gamma_1 n_1}(R_a) + \sum_{n'} V^a_{n,n'}(R_a) f_{an'\leftarrow\gamma_1 n_1}(R_a)$$

$$\sum_{\substack{\gamma \\ \gamma\neq a}} \sum_{n'} \int dR_\gamma V_{an,\gamma n'}(R_a,R_\gamma) f_{\gamma n'\leftarrow\gamma_1 n_1}(R_\gamma). \tag{1.7}$$

The exchange interactions (the last terms in the above equation), which couple

states of different arrangements, are 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. (1.7), 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 Karplus[11] 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.

II. THE S-MATRIX VERSION OF THE KOHN VARIATIONAL PRINCIPLE — POTENTIAL SCATTERING

The Kohn variational principle[5a] 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 employ S-matrix type boundary conditions[4a,d] for the scattering wavefunctions and comment below on other possibilities. Most of the general and relevant features of the S-matrix Kohn method are revealed by simple s-wave potential scattering, so we first describe how the methodology

works in this elementary case, and the generalization to multichannel reactive scattering is given in the next Section.

The Hamiltonian is thus of the simple form

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

where $V(r) \to 0$ as $r \to \infty$. The S-matrix version of the Kohn variational approximation to the S-matrix (at energy E) can be stated as[4d]

$$S = \text{ext}[\tilde{S} + \frac{i}{\hbar} \langle\tilde{\psi}|H\text{-}E|\tilde{\psi}\rangle], \tag{2.2}$$

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

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

where $v = \hbar k/\mu$ is the asymptotic velocity. (Note: The convention is used throughout this paper that wavefunctions in the bra symbol $\langle|$ in bra-ket matrix element notation are <u>not</u> complex conjugated.) "ext" in Eq. (2.2) means that the quantity in square brackets is to be extremized by varying any parameters in $\tilde{\Psi}(r)$.

To prove that Eq. (2.2) is indeed a variational functional for the S-matrix (a 1x1 "matrix" in this case of potential scattering), suppose that the trial function $\tilde{\Psi}(r)$ is of the form

$$\tilde{\psi}(r) = \psi_{ex}(r) + \delta\psi(r)\,, \tag{2.4}$$

where $\psi_{ex}(r)$ is the exact solution of the Schrödinger equation, which is regular at $r = 0$ and has asymptotic form

$$\psi_{ex}(r) \sim -e^{-ikr}v^{-1/2} + e^{ikr}v^{-1/2}\,S_{ex}\,, \tag{2.5}$$

and $\delta\psi(r)$ is arbitrary infinitesimal function (the "error" in $\tilde{\psi}$ is usual calculus of

variation parlance). Because of Eqs. (2.3) and (2.5), one sees that $\delta\psi(r) \equiv \tilde{\psi}(r)-\psi_{ex}(r)$ is also regular at $r = 0$ and has asymptotic form

$$\delta\psi(r) \sim e^{ikr}v^{-1/2}\,\delta S\,, \tag{2.6a}$$

where

$$\delta S \equiv \tilde{S}-S_{ex}\,. \tag{2.6b}$$

Since $\tilde{S} = S_{ex} + \delta S$ [Eq. (2.6b)], the variational functional, Eq. (2.2), reads

$$S[\psi_{ex}+\delta\psi] = S_{ex}+\delta S + \frac{i}{\hbar}\langle\psi_{ex}+\delta\psi|H-E|\psi_{ex}+\delta\psi\rangle\,, \tag{2.7}$$

and since $(H-E)\psi_{ex} = 0$ this becomes

$$S[\psi_{ex}+\delta\psi] = S_{ex}+\delta S + \frac{i}{\hbar}\langle\psi_{ex}|H-E|\delta\psi\rangle\,, \tag{2.8}$$

where, as usual, terms of order $\delta\psi^2$ have been discarded. If one integrates by parts twice, then

$$\begin{aligned}\langle\psi_{ex}|H-E|\delta\psi\rangle &= \langle\delta\psi|H-E|\psi_{ex}\rangle \\ &+ \left(\frac{-\hbar^2}{2\mu}\right)[\psi_{ex}(r)\delta\psi'(r) - \psi'_{ex}(r)\delta\psi(r)]_0^\infty\,,\end{aligned} \tag{2.9}$$

and using the asymptotic forms in Eqs. (2.5) and (2.6a) (and that $(H-E)\psi_{ex} = 0$), this becomes

$$\langle\psi_{ex}|H-E|\delta\psi\rangle = 0 + \left(\frac{-\hbar^2}{2\mu}\right)\left(\frac{-2ik}{v}\right)\delta S = i\hbar\delta S\,. \tag{2.10}$$

Substituting this result into Eq. (2.8) then gives

$$S[\psi_{ex}+\delta\psi] = S_{ex}+\delta S + \left(\frac{i}{\hbar}\right)(i\hbar\delta S) = S_{ex} + O(\delta\psi^2)\,; \tag{2.11}$$

i.e., error in the trial wavefunction enters only as second order error in the S-matrix, which is the statement that Eq. (2.2) is indeed a variational functional for the S-matrix.

It is interesting (and useful for later reference in Section V) to note that Eq. (2.2) can also be viewed as a statement of the *distorted wave Born approximation.*[12] In this picture, $\tilde{\Psi}(r)$ is the zeroth order wavefunction (for *some* zeroth order Hamiltonian); the first term in Eq. (2.2) is then the zeroth order term in the perturbative expansion of the S-matrix, the second term is the first order perturbation correction, and the second and higher order terms are omitted.

In practice the variational procedure implied by Eq. (2.2) is implemented[4d] by choosing the trial function $\tilde{\Psi}(r)$ as a linear variational function,

$$\tilde{\Psi}(r) = -u_0(r) + \sum_{t=1}^{N} u_t(r)c_t, \tag{2.12}$$

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

$$u_0(r) \sim e^{-ikr}v^{-1/2}. \tag{2.13}$$

A simple choice for $u_0(r)$ is

$$u_0(r) = f(r)e^{-ikr}v^{-1/2}, \tag{2.14}$$

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

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

$$f(r) \to 1,\ r \to \infty, \tag{2.15}$$

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

$$u_1(r) = u_0(r)^* \sim e^{ikr}\, v^{-1/2}, \tag{2.16}$$

and the basis functions $\{u_t(r)\}$, $t = 2, ..., N$ are real, square-integrable functions. The coefficients $\{c_t\}$, $t = 1, ..., N$ in Eq. (2.12) are the variational parameters in $\widetilde{\Psi}$.

With $\widetilde{\Psi}(r)$ of Eq. (2.12) substituted into Eq. (2.2), the functional $S[\widetilde{\Psi}]$ becomes a function of the N coefficients $\{c_t\}$, $t = 1, ..., N$. (Note that $\widetilde{S} \equiv c_1$.) After an integration by parts (analogous to that in Eqs. (2.9)-(2.10)), this function takes the form

$$S(c_1, ..., c_n) = \frac{i}{\hbar}\left(M_{0,0} - 2\sum_{t=1}^{N} c_t M_{t,0} + \sum_{t,t'=1}^{N} c_t c_{t'} M_{t,t'}\right) \tag{2.17a}$$

$$= \frac{i}{\hbar}\left(M_{0,0} - 2\mathbf{c}^T\bullet\mathbf{M}_0 + \mathbf{c}^T\bullet\mathbf{M}\bullet\mathbf{c}\right), \tag{2.17b}$$

where $M_{0,0}$ is a 1x1 "matrix", $\mathbf{M}_0$ an Nx1 matrix and $\mathbf{M}$ an NxN matrix,

$$M_{00} = \langle u_0|H-E|u_0\rangle \tag{2.18a}$$

$$(\mathbf{M}_0)_t = \langle u_t|H-E|u_0\rangle \tag{2.18b}$$

$$(\mathbf{M})_{t,t'} = \langle u_t|H-E|u_{t'}\rangle, \tag{2.18c}$$

for $t,t' = 1, ..., N$, and where "T" denotes matrix transpose. Applying the variational criterion

$$\frac{\partial}{\partial c_t} S(c_1,...,c_n) = 0 , \tag{2.19}$$

for all $t = 1, ..., N$, leads to linear equations for the coefficients

$$\mathbf{M}\bullet\mathbf{c} = \mathbf{M}_0 , \tag{2.20a}$$

with solution

$$\mathbf{c} = \mathbf{M}^{-1}\bullet\mathbf{M}_0 . \tag{2.20b}$$

Substitution of this solution back into Eq. (2.17) then gives the variational result for

the S-matrix

$$S = \frac{i}{\hbar}\left(M_{0,0} - M_0^T \bullet M^{-1} \bullet M_0\right). \tag{2.21}$$

Note that all matrix elements involving the unbounded basis functions u_0 and u_1 exist because

$$\lim_{r\to\infty} (H-E)\begin{Bmatrix} u_0(r) \\ u_1(r) \end{Bmatrix} = 0. \tag{2.22}$$

This follows because

$$(H-E)u_0(r) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - E\right)u_0(r) + V(r)u_0(r)\ ; \tag{2.23}$$

the first term above vanishes as $r \to \infty$ because of the asymptotic boundary condition of $u_0(r)$, Eq. (2.13), and the second term vanishes as $r \to \infty$ because $V(r)$ does.

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.[6] The Kohn functional for K is

$$K[\tilde{\psi}] = \tilde{K} - \frac{2}{\hbar}\langle\tilde{\psi}|H-E|\tilde{\psi}\rangle, \tag{2.24a}$$

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

$$\tilde{\psi}(r) \sim \sin(kr)v^{-1/2} + \cos(kr)v^{-1/2}\tilde{K}. \tag{2.24b}$$

One then proceeds precisely as above, the difference being that now the "free" functions $u_0(r)$ and $u_1(r)$ are

$$u_0(r) = f(r)\sin(kr)v^{-1/2} \tag{2.25a}$$

$$u_1(r) = f(r)\cos(kr)v^{-1/2} \tag{2.25b}$$

(The cut-off function f(r) is actually not required in Eq. (2.25a) for u_0.) The arithmetic is also essentially the same as before, and the variational result obtained for the K-matrix is similar to Eq. (2.21)

$$K = \frac{-2}{\hbar}(M_{0,0} - \mathbf{M}_0^T \bullet \mathbf{M}^{-1} \bullet \mathbf{M}_0), \tag{2.26}$$

where the M-matrix elements are the same as those in Eq. (2.18) but here with the real functions u_0 and u_1 of Eq. (2.25). And now the problem appears: in the matrix $\mathbf{M} \equiv M_{t,t'} = \langle u_t|H-E|u_{t'}\rangle$ of Eq. (2.26) the matrix $H_{t,t'}$ is real-symmetric, so that its eigenvalues are real. Every time that the energy E is equal to one of these eigenvalues, the matrix inverse $\mathbf{M}^{-1}$ in Eq. (2.26) 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.[6a] In the limit of an infinite basis they become infinitely narrow, and thus unobservable, but they are a serious problem in practical calculations (which necessarily use <u>finite</u> basis sets).

In contrast, the S-matrix version[4a,d,5b] of the Kohn variational method does not have anomalous singularities[4m] because the matrix of H in Eq. (2.18c) is complex-symmetric (because the function u_1 of Eq. (2.16) is complex and functions inside the bra symbol <| are not complex-conjugated). In fact, the condition that Eq. (2.21) is singular, namely

$$\det(\mathbf{M}) = \det[u_t|H-E|u_{t'}>] = 0, \tag{2.27a}$$

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

$$(H-E)\psi(r) = 0, \tag{2.27b}$$

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

$$\psi(r) \propto e^{ikr}; \tag{2.27c}$$

i.e., Eq. (2.27) is the expression that has been used before[13] for determining Siegert[14] 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. (2.21) 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 $G^+(E) \equiv (E+i\varepsilon-H)^{-1}$. This is[4a]

$$<a|G^+(E)|b> = -\sum_{t,t'=1}^{N} <a|u_t>(\mathbf{M}^{-1})_{t,t'}<u_{t'}|b>, \tag{2.28}$$

where $\mathbf{M}$ is as above, Eq. (2.18c), and $|a>$ and $|b>$ are any square-integrable functions. Note that the complex-symmetric structure of the matrix $\mathbf{M}$ is the same as that in complex scaling/coordinate rotation theory,[15-18] and for the same reasons. If the functions $|a>$ and $|b>$ are real, then Eq. (2.28) leads to a useful way for calculating matrix elements of the microcanonical density operator,

$$<a|\delta(E-H)|b> = -\pi^{-1}\mathrm{Im}<a|G^+(E)|b>. \tag{2.29}$$

In actual calculations for the S-matrix, Eq. (2.21), one does not wish to carry out numerical calculations with the complex symmetric matrix $\mathbf{M}$. This can be

avoided by the usual partitioning methods, so that Eq. (2.21) can be written in the equivalent form[4d]

$$S = \frac{i}{\hbar}(B - C \cdot B^{*-1} \cdot C), \tag{2.30}$$

where B and C are the 1x1 "matrices"

$$B = M_{0,0} - M_0^T \cdot M^{-1} \cdot M_0 \tag{2.31a}$$

$$C = M_{1,0} - M_0^{*T} \cdot M^{-1} \cdot M_0, \tag{2.31b}$$

where $M_{0,0}$, M_0, and M are as before, Eq. (2.18), except that t,t' = 2, ..., N (i.e., only the real basis functions), and

$$M_{1,0} = \langle u_0^* | H - E | u_0 \rangle. \tag{2.31c}$$

Here the matrix $(M)_{t,t'}$,t,t' = 2, ..., 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 <u>not</u> lead to a singularity in Eq. (2.30)).

III. GENERALIZATION TO MULTICHANNEL REACTIVE SCATTERING

The methodology described in Section II generalizes in a transparent fashion to multichannel reactive scattering[4d] and that is of course why we are interested in it. The derivations are patterned after those above so only the results are given.

Thus let (q_γ, r_γ) denote the internal coordinates and radial scattering (i.e., translational) coordinate for arrangement γ; i.e., r_γ is the generalization of the translational coordinates R_γ of the Introduction, Eqs. (1.5) and (1.7). $\{\phi_n^\gamma(q_\gamma)\}$ are the asymptotic channel eigenfunctions for the internal degrees of freedom. The partitioned form of the multichannel generalization of Eqs. (2.30) and (2.31) then

read as follows:

$$\mathbf{S} = \frac{i}{\hbar}(\mathbf{B}-\mathbf{C}^{T}\bullet\mathbf{B}^{*-1}\bullet\mathbf{C}), \tag{3.1a}$$

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

$$\mathbf{B} = \mathbf{M}_{0,0} - \mathbf{M}_0^{T}\bullet\mathbf{M}^{-1}\bullet\mathbf{M}_0 \tag{3.1b}$$

$$\mathbf{C} = \mathbf{M}_{1,0} - \mathbf{M}_0^{*T}\bullet\mathbf{M}^{-1}\bullet\mathbf{M}_0, \tag{3.1c}$$

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

$$(\mathbf{M}_{0,0})_{n\gamma,n'\gamma'} = \langle u_{0n}^{\gamma}\phi_n^{\gamma}|H-E|u_{0n'}^{\gamma'}\phi_{n'}^{\gamma'}\rangle \tag{3.2a}$$

$$(\mathbf{M}_{1,0})_{n\gamma,n'\gamma'} = \langle u_{0n}^{\gamma *}\phi_n^{\gamma}|H-E|u_{0n'}^{\gamma'}\phi_{n'}^{\gamma'}\rangle; \tag{3.2b}$$

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

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

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

$$(\mathbf{M})_{tn\gamma,t'n'\gamma'} = \langle u_{tn}^{\gamma}\phi_n^{\gamma}|H-E|u_{t'n'}^{\gamma'}\phi_{n'}^{\gamma'}\rangle, \tag{3.2c}$$

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). $\mathbf{M}_0$ is a "large" by "small" rectangular matrix

$$(\mathbf{M}_0)_{tn\gamma,n'\gamma'} = \langle u_{tn}^{\gamma}\phi_n^{\gamma}|H-E|u_{0n'}^{\gamma'}\phi_{n'}^{\gamma'}\rangle. \tag{3.2d}$$

Only open channels $\{n\gamma\}$ are included in the matrices $\mathbf{M}_{00}$, $\mathbf{M}_{1,0}$, and the "small"

dimension of $\mathbf{M}_0$, while open and closed channels are required in the matrix $\mathbf{M}$ and the "large" dimension of $\mathbf{M}_0$.

The essential aspect of the multichannel generalization of the Kohn variational S-matrix is that the translational wavefunctions $f_{\gamma n \leftarrow \gamma_1 n_1}(r_\gamma)$ in the coupled-channel Schrödinger equation, Eq. (1.7), are expanded in a variational basis for *each channel* (γ,n), i.e.,

$$f_{\gamma n \leftarrow \gamma_1 n_1}(r_\gamma) = - u^{\gamma}_{0n}(r_\gamma) + \sum_{t=1}^{N} u^{\gamma}_{tn}(r_\gamma)\, c_{n\gamma t \leftarrow \gamma_1 n_1}\,, \tag{3.3}$$

and the expansion coefficients (the c's in Eq. (3.3)) are the variational parameters, as before. The multichannel variational calculation thus proceeds in a completely parallel fashion to the one channel case of Section II (one has only to keep up with the additional indices!).

The exchange interaction in the coupled channel Schrödinger equation, Eq. (1.7), is thus reduced in the Kohn variational result, Eqs. (3.1)-(3.2), to *exchange integrals*, namely the matrix elements of (H-E) in Eq. (3.2) between different arrangements, $\gamma \neq \gamma'$. I.e., in Eq. (3.2c), the direct product basis function

$$u^{\gamma}_{tn}\phi^{\gamma}_{n} \equiv u^{\gamma}_{tn}(r_\gamma)\phi^{\gamma}_{n}(q_\gamma) \tag{3.4a}$$

is a function of the coordinates for arrangement γ, whereas

$$u^{\gamma'}_{t'n'}\phi^{\gamma'}_{n'} \equiv u^{\gamma'}_{t'n'}(r_\gamma)\phi^{\gamma'}_{n'}(q_\gamma) \tag{3.4b}$$

is a function of the coordinate for arrangement γ'. The matrix elements diagonal in the arrangement index, $\gamma = \gamma'$, on the other hand, are "direct" integrals that describe elastic and inelastic scattering within a given arrangement.

It was realized quite early[4f] that one could simplify matters considerably by

eliminating exchange ($\gamma \neq \gamma'$) matrix elements in the "free-free" and "bound-free" matrix elements $\mathbf{M}_{0,0}$, $\mathbf{M}_{1,0}$ and $\mathbf{M}_0$, respectively, in Eq. (3.2). By proper choice of the cut-off function f(r) in the "free" functions u_0 and u_1 (for each channel) one can insure that these matrix elements vanish when $\gamma \neq \gamma'$, i.e.,

$$(\mathbf{M}_{0,0})_{n\gamma,n'\gamma'} = \delta_{\gamma,\gamma'}(\mathbf{M}^{\gamma}_{0,0})_{n,n'}, \tag{3.5}$$

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 that the direct matrix elements (those with $\gamma = \gamma'$). With this simplification, the only non-zero exchange matrix elements are the bound-bound ones, Eq. (3.2c), 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.

Eqs. (3.1) - (3.2) 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 all given in refs. 8 and 4k.

As noted in the Introduction, the methodology summarized above has been used to calculate integral and differential cross sections for several A+BC $\rightarrow$ AB+C reactions.[4i,k,l] It is a very robust and straight-forward quantum mechanical

calculation. The next Section describes some enhancements and generalizations of the basic methodology summarized above, the goal being to take advantage as much as possible of standard quantum mechanical methodology so as to be able to extend reactive scattering to deal with an even wider class of chemical reactions.

IV. GENERALIZATIONS AND ENHANCEMENTS OF THE METHODOLOGY

Essentially all the generalizations and enhancements of the basic S-matrix Kohn approach, Eqs. (3.1)-(3.2), have to do with "better basis functions". Here "better" may mean more accurate basis functions, so that fewer are required to represent the wavefunction, or it may mean more convenient basis functions so that the matrix elements of the Hamiltonian in Eq. (3.2) are more easily evaluated.

It is first useful to re-write the S-matrix Kohn equations, Eqs. (3.1)-(3.2) in a more general fashion. Combining the generic coupled channel expansion of the wavefunction [Eq. (1.5)] with a basis set expansion of the translational functions, cf. Eq. (3.3), shows that the general form of the Kohn trial function is

$$\Psi_{\gamma_1 n_1} = - \Phi_{\gamma_1 n_1} + \sum_{\gamma,n} \Phi^*_{\gamma n}\, C_{\gamma n,\gamma_1 n_1} + \sum_{\lambda} \chi_\lambda\, C_{\lambda,\gamma_1 n_1}, \tag{4.1}$$

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

$$\lim_{r_\gamma \to \infty} \Phi_{\gamma n}(q_\gamma, r_\gamma) \sim \phi^\gamma_n(q_\gamma)\, e^{-ik_{\gamma n} r_\gamma}/v_{\gamma n}^{1/2}, \tag{4.2}$$

$\Phi_{\gamma n}^*$ is the corresponding asymptotically outgoing wave, and $\{\chi_\lambda\}$ is an L^2 (square integrable) basis that spans the interaction region. The bound-bound and bound-free matrix elements in Eq. (3.2c) and (3.2d) are then designated as

$$(\mathbf{M})_{\lambda,\lambda'} = \langle\chi_\lambda|H-E|\chi_{\lambda'}\rangle \tag{4.3a}$$

$$(\mathbf{M}_0)_{\lambda,n'\gamma'} = \langle\chi_\lambda|H-E|u^{\gamma'}_{0n'}\phi^{\gamma'}_{n'}\rangle\ . \tag{4.3b}$$

In Eqs. (3.1) - (3.2) above — and in all applications to date — the L^2 basis $\{\chi_\lambda\}$ has been chosen to be the direct product of the various channel eigenfunctions and a translational basis,

$$\chi_\lambda = \phi^\gamma_n(q_\gamma)\ u_t(r_\gamma), \tag{4.4}$$

so that $\lambda \equiv \gamma nt$, but this is not necessary. The $\{\chi_\lambda\}$ 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. Distorted Free Functions

One way to keep the L^2 basis as small as possible is to use better *free* functions, 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 functions $\Phi_{\gamma n}$ in Eq. (4.1) and (4.2) can be chosen as

$$\Phi_{\gamma n}(q_\gamma,r_\gamma) = \sum_{n'} \phi^\gamma_{n'}(q_\gamma)\, f(r_\gamma)\, u^\gamma_{n'\leftarrow n}(r_\gamma)\ , \tag{4.5a}$$

where the translational function matrix $u^\gamma_{n'\leftarrow n}$ is the solution of the <u>inelastic</u> coupled channel Schrödinger equation for channel γ,

$$0 = \left(-\frac{\hbar^2}{2\mu_\gamma}\frac{d^2}{dr^2_\gamma} - E_{\gamma n'}\right) u^\gamma_{n'\leftarrow n}(r_\gamma) + \sum_{n''} V^\gamma_{n',n''}(r_\gamma) u^\gamma_{n''\leftarrow n}(r_\gamma)\ , \tag{4.5b}$$

with asymptotic boundary condition

$$\lim_{r_\gamma \to \infty} u^{\gamma}_{n' \leftarrow n}(r_\gamma) = \delta_{n',n}\, e^{-ik_{\gamma n} r_\gamma}\, v_{\gamma n}^{-1/2}\,; \tag{4.5c}$$

this radial function is irregular as $r_\gamma \to 0$, but the cut-off function f(r) regularizes it. These "distorted" free functions[4t] 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:[4k]

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

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

$$(\mathbf{M}_0)_{\tau\gamma n,\gamma n'} = -\delta_{\gamma,\gamma} \frac{\hbar^2}{2\mu_\gamma} \left\langle u_{\tau\gamma n} | f'' + 2f' \frac{d}{dr_\gamma} | u^{\gamma}_{n \leftarrow n'} \right\rangle \tag{4.6c}$$

b. Contraction of the L^2 Basis

Another way to reduce the size of the L^2 basis is to borrow the idea of *basis set contraction* from *ab initio* electronic structure theory. I.e., one begins with a set of "primitive", easy-to-use functions, and then transforms to a better basis, e.g., by diagonalizing the Hamiltonian for some reference problem. The new basis functions are linear combinations of the original ones, but one actually uses fewer of these good basis functions than the original number of the primitive ones (cf. the transformation from many atomic orbitals to a fewer number of molecular orbitals).

A *quasi-adiabatic contraction*[4q] 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 L^2 basis functions necessary to achieve convergence. Since the computational time is proportioned to the cube of the size of the matrix **M** that is inverted in Eq. (3.1), this reduces the computational time by almost an order of magnitude.

The quasi-adiabatic contraction procedure[4q] starts with the primitive direct product basis of Eq. (4.4), i.e.,

$$\chi_\lambda(q,r) = \phi_n(q)\, u_t(r)\ , \tag{4.7}$$

where for the moment the arrangement index γ has been dropped since the quasi-adiabatic contraction is carried out separately in each arrangement. The channel index n includes open and closed channels, and the translational basis is a set of distributed Gaussians[19]

$$u_t(r) = \left(\frac{2A_t}{\pi}\right)^{1/4} e^{-A_t(r-r_t)^2} \tag{4.8}$$

$t = 2, \ldots, N_t$. *Adiabatic* internal functions $\{\phi_n(q;r\}$ are the eigenfunctions of the Hamiltonian

$$h(q;r) \equiv h(q) + V(q,r)\ , \tag{4.9a}$$

the full Hamiltonian with the translational kinetic energy operator omitted. The adiabatic eigenvalue equation thus reads

$$h(q;r)\, \phi_n(q;r) = \varepsilon_n(r)\, \phi_n(q;r)\ . \tag{4.9b}$$

Use of adiabatic internal eigenfunctions, however, is complicated by derivative couplings that result from such a basis; a *quasi*-adiabatic basis accomplishes

essentially the same goal and is much simpler to implement. Quasi-adiabatic basis functions have been widely used in solving coupled channel scattering equations using propagation methods,[20-24] in which different internal basis functions are used in different sectors of the reaction coordinate. This is especially convenient here because the translational basis $\{u_t(r)\}$ of distributed Gaussians, Eq. (4.8), is a *localized* basis. We thus utilize the adiabatic internal functions not at all values of r, but only those values $\{r_t\}$ at which the distributed Gaussians are located. Defining

$$\phi_n^t(q) \equiv \phi_n(q;r_t) \ , \tag{4.10a}$$

the L^2 basis $\{\chi_\lambda(q,r\}$ that we use is thus

$$\chi_\lambda(q,r) = \phi_n^t(q)\ u_t(r) \tag{4.10b}$$

with $\lambda \equiv (n,t)$. Each translational function $u_t(r)$ thus has the internal function that is the adiabatic eigenfunction at the position r_t about which $u_t(r)$ is localized. (Note that this is essentially the same idea as the "shifted oscillator basis" used in another context by Makri and Miller.[25])

In practice the adiabatic internal eigenfunctions are determined by expanding them in terms of the asymptotic channel eigenfunctions

$$\phi_n^t(q) = \sum_{n'} \phi_{n'}(q) W^t_{n',n} \ ; \tag{4.11a}$$

i.e., $W^t_{n',n}$ is the transformation matrix in the internal space, whose column vectors are the eigenvectors of the matrix representation of $h(q;r_t)$ in the asymptotic basis

$$(h^t)_{n'n} \equiv \langle\phi_{n'}|h(q;r_t)|\phi_n\rangle = \delta_{n'n}\varepsilon_n + V_{n',n}(r_t) \tag{4.11b}$$

where

$$V_{n',n}(r) = \int dq\ \phi_{n'}(q)^*\ V(q,r)\phi_n(q)\ . \tag{4.11c}$$

The matrix eigenvalue equation thus reads

$$\mathbf{h}^t \bullet \mathbf{W}^t = \mathbf{W}^t \bullet \boldsymbol{\varepsilon}^t \tag{4.11d}$$

where

$$\varepsilon_n^t \equiv \varepsilon_n(r_t) \; .$$

With the index λ now identified as $\lambda \equiv (n,t)$, the bound-free and bound-bound matrices of Eq. (3.2) are given by

$$(\mathbf{M}_0)_{n't',n} = \langle \phi_{n'}^{t'} u_{t'} | H-E | \phi_n u_{0n} \rangle \tag{4.12a}$$

$$(\mathbf{M})_{n't',nt} = \langle \phi_{n'}^{t'} u_{t'} | H-E | \phi_n^t u_t \rangle \tag{4.12b}$$

The transformation matrix $\mathbf{U}$ in the composite space of all degrees of freedom is then defined by

$$(\mathbf{U})_{n't',nt} = \delta_{t't} \mathbf{W}^t_{n'n} \tag{4.13}$$

and the $\mathbf{M}_0$ and $\mathbf{M}$ matrices of Eq. (4.12) can then be conveniently expressed in terms of the matrices $\mathbf{M}_0'$ and $\mathbf{M}'$ in the asymptotic basis:

$$\mathbf{M}_0 = \mathbf{U}^T \bullet \mathbf{M}_0' \tag{4.14a}$$

$$\mathbf{M} = \mathbf{U}^T \bullet \mathbf{M}' \bullet \mathbf{U} \tag{4.14b}$$

where $\mathbf{M}_0'$ and $\mathbf{M}'$ are the matrices in the asymptotic internal ("primitive") basis

$$(\mathbf{M}_0')_{n't',n} = \langle \phi_{n'} u_{t'} | H-E | \phi_n u_{0n} \rangle \tag{4.15a}$$

$$(\mathbf{M}')_{n't',nt} = \langle \phi_{n'} u_{t'} | H-E | \phi_n u_t \rangle \tag{4.15b}$$

In applications one typically first computes the bound-free and bound-bound matrices in the asymptotic (or *diabatic*) basis, $\mathbf{M}_0'$ and $\mathbf{M}'$ of Eq. (4.15), and then transforms them to the quasi-adiabatic representation Eq. (4.14). If the same number of quasi-adiabatic eigenfunctions is retained in the L^2 basis as the number

of asymptotic functions used to represent them — i.e., if the matrix $\mathbf{W}^t$ of Eq. (4.11) is *square* — then the same results will be obtained by using the asymptotic (i.e., *diabatic*) internal eigenfunctions as the quasi-adiabatic internal eigenfunctions. This is obvious since the relevant quantities in the expression for the S-matrix are invariant to this orthogonal transformation of basis; e.g.,

$$\mathbf{B} \equiv \mathbf{M}_{00} - \mathbf{M}_0^{\mathrm{T}} \bullet \mathbf{M}^{-1} \bullet \mathbf{M}_0 \tag{4.16a}$$

$$= \mathbf{M}_{00} - (\mathbf{U}^{\mathrm{T}} \bullet \mathbf{M}_0')^{\mathrm{T}} \bullet (\mathbf{U}^{\mathrm{T}} \bullet \mathbf{M}'\mathbf{U})^{-1} \mathbf{U}^{\mathrm{T}} \bullet \mathbf{M}_0' \tag{4.16b}$$

$$= \mathbf{M}_{00} - \mathbf{M}_0'^{\mathrm{T}} \bullet \mathbf{U} \bullet \mathbf{U}^{-1} \bullet \mathbf{M}'^{-1} \bullet (\mathbf{U}^{\mathrm{T}})^{-1} \bullet \mathbf{U}^{\mathrm{T}} \bullet \mathbf{M}_0' \tag{4.16c}$$

$$= \mathbf{M}_{00} - \mathbf{M}_0'^{\mathrm{T}} \bullet \mathbf{M}'^{-1} \bullet \mathbf{M}_0' \,. \tag{4.16d}$$

As noted, however, many *fewer* quasi-adiabatic internal eigenfunctions are needed than the "primitive" asymptotic (diabatic) internal eigenfunctions that are used to represent them. Thus the matrix $\mathbf{W}$, and the transformation matrix $\mathbf{U}$, are *rectangular* matrices, so that Eq. (4.16d) is no longer equivalent to Eqs. (4.16a) and (4.16b). The matrices $\mathbf{M}_0$ and $\mathbf{M}$ in the quasi-adiabatic representation will thus be much smaller than the matrices $\mathbf{M}_0'$ and $\mathbf{M}'$ in the diabatic (asymptotic) representation; i.e., Eqs. (4.16a,b) describe a *contraction* of the internal basis set.

The quasi-adiabatic contraction of the basis is applied separately in each arrangement γ to obtain a contracted set of functions for that arrangement. The complete basis set is then the union of the contracted sets from each arrangement. The transformation matrix $\mathbf{U}$ of Eq. (4.13) is thus diagonal in the arrangement index

$$(\mathbf{U})_{\gamma' n' t', \gamma n t} = \delta_{\gamma'\gamma} \delta_{t't} \, \mathbf{W}^{\gamma t}_{n',n} \tag{4.13'}$$

where $\mathbf{W}^{\gamma t}$ is the quasi-adiabatic transformation for the internal degrees of freedom

at r_t^γ of arrangement γ. All further aspects of the calculation are then precisely as above; i.e., the contracted matrices **M** and $\mathbf{M}_0$ are given in terms of the primitive ones by Eq. (4.14) and the S-matrix by Eqs. (3.1) and (3.2)

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,[26] and the *space-fixed, or ℓ-representation* for the free functions. Thus the channel index n in Eq. (3.1) - (3.2) 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 $\vec{r}_\gamma$ (the atom to diatom center of mass coordinate vector) as quantization axis; this is the body-fixed, or helicity representation. For the free functions in Eq. (3.1) - (3.2), the channel index is $n \equiv (v,j,\ell)$, where v and j are the same as above, 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 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.[8] Application to the $F+H_2 \rightarrow HF+H$ reaction has shown the enormous utility of this approach.[26]

c. Discrete Variable Representation for the L^2 Basis

A more radical choice for the L^2 basis $\{\chi_\lambda\}$ is a *discrete variable representation* (DVR), i.e., a set of grid points that span the interaction region. The particularly advantageous aspects of this L^2 basis is that *no integrals* are required in order to construct the Hamiltonian matrix involved in the bound-bound and bound-free matrices $\mathbf{M}$ and $\mathbf{M}_0$ of Eq. (4.3) and also that the matrix $\mathbf{M}$ (the one that must be inverted, cf. Eq. (3.1)) is extremely sparse. Both of these features of the DVR make it extremely attractive for extending the S-matrix Kohn methodology to chemical reactions involving more than three atoms.

DVR methods have been pioneered in recent years by Light and co-workers[27] (through the origins go back much farther[28]) for use in vibrational eigenvalue calculations, Peet and Yang[29] have made similar applications of the related collocation method, and Friesner and colleagues[30] have utilized similar methods for the electronic Schrödinger equation. Peet *et al.*[31] have shown previously that DVR and collocation methods can in principle be efficiently used in S-matrix Kohn variational calculations, but this previous work was not readily generalizable to *reactive* scattering. More recently, though, Colbert and Miller[32] have presented a DVR methodology that does deal with reactive scattering, and efficiently so. The specific DVR they have devised also has a particularly simple and generic or universal character; it involves only the grid points themselves, with no explicit reference to an underlying basis set, both for the bound-bound and bound-free matrix elements in Eq. (4.3).

For a collinear A+BC $\rightarrow$ AB+C reaction, for example, one first lays down a

two-dimensional direct product grid in some convenient coordinate system that covers the interaction region. Colbert and Miller[32] have used the normal mode coordinates associated with the transition state, but other choices are possible (e.g., hyperspherical coordinates should also work well). Figure 2 shows such an x-y grid superimposed on a contour plot of the $H+H_2 \rightarrow H_2+H$ potential energy surface. If $\{x_i\}$ and $\{y_j\}$ are the grid points, then the grid is truncated by introducing an energy cutoff V_c, and only grid points (i,j) are retained for which

$$V_{ij} \equiv V(x_i,y_j) < V_c \,. \tag{4.17}$$

The grid is also truncated in the asymptotic regions at a value R_{max}, the translational coordinate in the reactant and product regions. Therefore even though one begins with a direct product grid, the energy cutoff criterion, Eq. (4.17), adapts it to the shape of the potential energy surface for the specific problem in a very simple and controllable way. Convergence can be tested simply by increasing the value of V_c.

INSERT FIGURE 2 ABOUT HERE

The L^2 basis $\{|\chi_\gamma\rangle\}$ of Eq. (4.1) and (4.3) is thus the set of grid points $|i,j\rangle$. The bound-bound matrix **M** of Eq. (4.3a) is

$$(\mathbf{M})_{ij,i'j'} = H_{ij,i'j'} - E\delta_{ii'}\,\delta_{jj'} = T_{ii'}\,\delta_{jj'} + T_{jj'}\,\delta_{ii'} + \delta_{ii'}\,\delta_{jj'}(V(x_i,y_j)-E) \;; \tag{4.18}$$

the potential matrix is diagonal, as always in a DVR, and the kinetic energy is the sum of two one-dimensional kinetic energy matrices. The latter has the form[32]

$$T_{ii'} = \frac{\hbar^2(-1)^{i-i'}}{2m\Delta x^2}\begin{cases} \pi^2/3, & i=i' \\ \dfrac{2}{(i-i')^2}, & i\neq i' \end{cases}, \tag{4.19}$$

the only parameter involved being the grid spacing Δx, or the "energy quantum of the grid", $\hbar^2/(2m\Delta x^2)$; $T_{jj'}$ for the y-degree of freedom is similar, and the grid spacings are chosen in a mass-weighted fashion, $m_x\Delta x^2 = m_y\Delta y^2$. The bound-free matrix of Eq. (4.3b) is given by

$$(\mathbf{M}_0)_{ij,\gamma n} = \sqrt{\Delta x \Delta y}\ \langle x_i y_j | H-E | \Phi_{\gamma n}\rangle; \tag{4.20}$$

i.e., (H-E) operate on the free function $\Phi_{\gamma n}(r_\gamma, R_\gamma)$ and then one evaluates this at the coordinates (x_i, y_j). Thus no integrals are required to obtain $\mathbf{M}$ and $\mathbf{M}_0$ in Eqs. (4.3).

The most novel feature of Colbert *et al.*'s[32] DVR is the kinetic energy matrix Eq. (4.19). It is not only extremely simple, but independent of any specific underlying basis set; i.e., it is a property only of the grid itself. It can be derived[32] as the infinite limit of a Fourier expansion and also as an infinite order finite difference expansion.

Test calculations by Colbert *et al.*[32] for the collinear $H+H_2 \rightarrow H_2+H$ and $C\ell+HC\ell \rightarrow C\ell H+C\ell$ reactions obtained converged reaction probabilities with only ~20% more grid points than conventional basis functions (i.e., Eq. (4.4) for the L^2 basis. This is extremely encouraging with regard to the possibility of carrying out such calculations for more complex systems because the DVR, or grid basis avoids integral evaluation in order to obtain the Hamiltonian matrix and also because the Hamiltonian matrix is extremely sparse (which facilitates evaluation of the matrix inverse $\mathbf{M}^{-1}$ in Eq. (3.1)). Quasi-adiabatic, or other contraction schemes used with conventional basis functions can also be employed in an identical fashion with a DVR.[33]

V. A SEMICLASSICAL CORRECTION TO THE KOHN S-MATRIX

Recall the (formally exact) distorted wave representation[34] for a generic S-matrix element

$$S_{f,i} = S^0_{f,i} + \frac{i}{\hbar} \{<\Psi_f|\Delta V|\Psi_i> + <\Psi_f|\Delta V G^+(E)\Delta V|\Psi_i>\} , \tag{5.1}$$

where Ψ_i and Ψ_f are distorted waves for the initial and final states, i.e., scattering solutions of some zeroth order Hamiltonian H_0, normalized with the unit incoming flux that we have been using throughout this paper,

$$\Psi_i(q,r) \sim \sum_j \phi_j(q)\, v_j^{-1/2}\, [-e^{-ik_j r}\, \delta_{ji} + e^{ik_j r}\, S^0_{ji}] , \tag{5.2}$$

where $\{\phi_j(q)\}$ are the channel eigenfunctions. S^0_{ji} is the zeroth order S-matrix that which results from H_0. ΔV in Eq. (5.1) is the residual interaction, the part of the total Hamiltonian H not included in H_0, i.e.,

$$\Delta V = H - H_0 , \tag{5.3}$$

and $G^+(E)$ is the Green's function (operator) for H,

$$G^+(E) = \lim_{\varepsilon \to 0} (E + i\varepsilon - H)^{-1} . \tag{5.4}$$

Since

$$(H_0 - E)\, \Psi_i = 0 , \tag{5.5a}$$

Eq. (5.3) shows that

$$(H - E)\, \Psi_i = \Delta V \Psi_i , \tag{5.5b}$$

and similarly for Ψ_f, so that Eq. (5.1) can also be written as

$$S_{f,i} = S^0_{f,i} + \frac{i}{\hbar} \{<\Psi_f|H-E|\Psi_i> + <(H-E)\Psi_f|G^+(E)|(H-E)\Psi_i>\} . \tag{5.6}$$

Eq. (5.6) is formally exact for *any* distorted waves Ψ_i and Ψ_f that satisfy the boundary conditions Eq. (5.2), from free waves

$$\Psi_i(q,r) = \phi_i(q)v_i^{-1/2}\,[-e^{-ik_ir} + e^{ik_ir}] = \phi_i(q)2i\,\sin(k_ir)/v_i^{1/2} \qquad (5.7a)$$

with

$$S^0_{ji} = \delta_{ji}\,, \qquad (5.7b)$$

to Ψ_i and Ψ_f being the exact solutions of the total Hamiltonian (in which case $S^0_{ji} = S_{ji}$ and $(H-E)\Psi_i=(H-E)\Psi_f=0$). Eq. (5.6) is a more useful form than Eq. (5.1) because there is no explicit reference to the zeroth Hamiltonian (or the residual interaction) which define the distorted waves Ψ_i and Ψ_f; one only needs to specify the two distorted wavefunctions themselves. This is most convenient for the case of *reactive* scattering for which the two zeroth order Hamiltonians are in fact different.

If one discards the term in Eq. (5.6) (or (5.1)) involving the Green's function, then the distorted wave Born approximation (DWBA) is obtained,

$$S^{DWBA}_{f,i} = S^0_{f,i} + \frac{i}{\hbar}\langle\Psi_f|H-E|\Psi_i\rangle\,. \qquad (5.8)$$

One also recognizes Eq. (5.8) as the Kohn variational functional (Eq. (2.2) for the case of potential scattering), as was noted before. The S-matrix Kohn variational method can thus be thought of as the distorted wave Born approximation with "very good distorted waves", i.e., the best ones that can be obtained (in a variational sense) within the basis set that is used. If the basis set is sufficiently large, then the distorted waves can be made arbitrarily good and the DWBA then approaches the

exact S-matrix.

Here we consider the possibility of *correcting* an S-matrix Kohn variational calculation by approximating the last term in Eq. (5.6), the one involving the Green's function. If the variational basis is sufficiently large then this is of course unnecessary, but there may be situations for which this limit is unattainable. Eq. (5.6) thus has the form

$$S_{f,i} = S_{f,i}^{KVP} + \frac{i}{\hbar} <\chi_f|G^+(E)|\chi_i> , \tag{5.9}$$

where the first term here is the result of an S-matrix Kohn variational (KVP) calculation, and the functions χ_i and χ_f are

$$\chi_i = (H-E)\psi_i \tag{5.10a}$$

$$\chi_f = (H-E)\psi_f , \tag{5.10b}$$

where Ψ_i and Ψ_f are the variational wavefunctions resulting from the variational calculation. Note that χ_i and χ_f are L^2 functions. One thus needs a useful way to approximate matrix elements of $G^+(E)$ between L^2 functions. (If one uses a *basis set* approximation[4a] to this matrix element, with the same basis used for the Kohn variational calculation, then this correction term varnishes identically. I.e., one needs to approximate this matrix element of $G^+(E)$ *beyond* the basis that has already been used.)

The approach considered here is a semiclassical approximation. Using the standard relation between $G^+(E)$ and the time evolution operator $\exp(-iHt/\hbar)$, one has

$$<\chi_f|G^+(E)|\chi_i> = (i\hbar)^{-1} \int_0^\infty dt\, e^{iEt/\hbar} <\chi_f|e^{-iHt/\hbar}|\chi_i>, \tag{5.11}$$

and with the standard semiclassical approximation[35] for the propagator this becomes

$$K_{f,i}(t) \equiv <\chi_f|e^{iHt/\hbar}|\chi_i> = \sum \int d\mathbf{x}_2 \int d\mathbf{x}_1\, \chi_f(\mathbf{x}_2)$$

$$\left[(2\pi i\hbar)^F \left|\frac{\partial \mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1)}{\partial \mathbf{p}_1}\right|\right]^{-1/2} \exp[iS(\mathbf{x}_2,\mathbf{x}_1;t)\hbar - \nu\tfrac{\pi}{2}]\, \chi_i(\mathbf{x}_1)\,. \tag{5.12}$$

Here $\mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1)$ is the final position that results from a classical trajectory with initial position and momentum $(\mathbf{x}_1,\mathbf{p}_1)$ (and final time t), with $\mathbf{p}_1 \equiv \mathbf{p}_1(\mathbf{x}_2,\mathbf{x}_1)$ determined by the (non-linear) boundary condition

$$\mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1) = \mathbf{x}_2\ ; \tag{5.13}$$

i.e., for $\mathbf{x}_1$ fixed, one must find the value of $\mathbf{p}_1$ such that the final position at time t, $\mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1)$, is equal to the specified value $\mathbf{x}_2$. The sum in Eq. (5.12) is over all roots of Eq. (5.13), and S is the classical action integral along the classical trajectory (or trajectories) determined by boundary conditions $(\mathbf{x}_1,\mathbf{x}_2)$,

$$S(\mathbf{x}_2,\mathbf{x}_1) = \int_0^t dt'\,[\mathbf{p}(t')\cdot\dot{\mathbf{x}}(t') - H(\mathbf{p}(t'),\mathbf{x}(t'))]\ , \tag{5.14}$$

where H is the classical Hamiltonian. ν in Eq. (5.12) is the Maslov index, the

number of zeros experienced by the determinant of the Jacobian $\partial \mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1)/\partial \mathbf{p}_1$ in the time interval (0,t).

One can avoid dealing with the non-linear boundary problem, Eq. (5.13), however, by using the "initial value representation";[36-39] i.e., by changing integration variables in Eq. (5.12): inside the integral over $\mathbf{x}_1$, one changes from $\mathbf{x}_2$ to $\mathbf{p}_1$ as the integration variable, and since $\mathbf{x}_1$ is constant inside the $\mathbf{x}_1$ integral, one has

$$d\mathbf{x}_2 = d\mathbf{p}_1 \left| \frac{\partial \mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1)}{\partial \mathbf{p}_1} \right| \tag{5.15}$$

so that Eq. (5.12) becomes

$$K_{f,i}(t) = \int d\mathbf{x}_1 \int d\mathbf{p}_1\, \chi_f(\mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1)) \left[\left| \frac{\partial \mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1)}{\partial \mathbf{p}_1} \right| / (2\pi i\hbar)^F \right]^{1/2}$$

$$\exp[iS(\mathbf{x}_1,\mathbf{p}_1)/\hbar - i\nu\pi/2]\, \chi_i(\mathbf{x}_1)\,. \tag{5.16}$$

Eq. (5.16) entails no approximation beyond the basic semiclassical approximation itself, and its obvious advantage over Eq. (5.12) is that the integration variables are *initial conditions*, so that double ended boundary are avoided. It is also advantageous that the classical Jacobian factor $|\partial \mathbf{x}_2(\mathbf{x}_1,\mathbf{p}_1)/\partial \mathbf{p}_1|$ appears in the *numerator* in the integrand of Eq. (5.16); therefore even though the semiclassical propagator is most in error near the zeros of this Jacobian, these enter as *zeros* in the integrand, and not as singularities (as they do in the propagator itself). Also, since it is when the Jacobian passes through zero that the Maslov index ν increases (discontinuously) by unity, the fact the integrand is zero at such points means that

the integrand is continuous throughout.

The practical task in utilizing Eq. (5.16) is thus to evaluate the integral over the phase space of initial conditions, a problem complicated by the fact that the integrand is oscillatory. Heller[37] describes one way of doing this, which appears to work well. For systems with more than one or two degrees of freedom it may prove necessary to resort to Monte Carlo methods for dealing with such integrals.[40]

The semiclassical correction to an S-matrix Kohn calculation is thus given by utilizing Eq. (5.16) in Eqs. (5.9)-(5.11). Specifically, this correction term (the second term on the right hand side of Eq. (5.9)) is approximated semiclassically as

$$\Delta S^{sc}_{f,i} \equiv (\frac{i}{\hbar}) <\chi_f|G^+(E|\chi_i> \cong \hbar^{-2} \int dx_1 \int dp_1 \int_0^\infty dt \left[\left| \frac{\partial x_2(x_1,p_1)}{\partial p_1} \right| / (2\pi i\hbar)^F \right]^{1/2}$$

$$\times \chi_f(x_2((x_1,p_1;t))\, \chi_i(x_1) \exp[iS(x_1,p_1;t)/\hbar + iEt/\hbar - \nu\frac{\pi}{2}] \,, \qquad (5.17)$$

with χ_i and χ_f given by Eq. (5.10). Since χ_i and χ_f vanish as L^2 functions in the asymptotic regions — the more rapidly the better Ψ_i and Ψ_f approach the solution of the Schrödinger equation — one will need to integrate the classical trajectories for only short times to evaluate the integral over time in Eq. (5.17) (because $x_2 \rightarrow \infty$ as $t \rightarrow \infty$, and thus $\chi_f \rightarrow 0$).

One may think of Eq. (5.17) as being a correction for the error in the Kohn variational calculation due to lack of completeness of the variational basis set. Therefore if the semiclassical approximation is accurate, one can obtain accurate S-matrix elements from Eq. (5.9) and (5.17) with much smaller basis sets than would

be required for convergence of the variational calculation alone. (E.g., if the semiclassical approximation were *exact*, one would obtain the correct S-matrix with *no* L^2 basis functions in the variational calculation.) This may thus be a very important procedure if one can evaluate the oscillatory integrals in Eq. (5.17) in a generally practical way. It is also interesting and ironic to realize that one is using *classical mechanics* (semiclassically) to correct *quantum mechanics*!

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 be usefully 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. For this reason I believe that the DVR methodology described in

Section IVc, and developments therefrom, are extremely important for further progress.

The semiclassical correction procedure described in Section V is another approach for reducing the size of the L^2 basis that is required. One obviously needs to test this scheme to see how *poor* an S-matrix Kohn variational calculation can be (i.e., how small an L^2 basis can be used) for the semiclassical correction to be able to provide an accurate *net* S-matrix, $S_{f,i} = \Delta S_{f,i}^{KVP} + \Delta S_{f,i}^{sc}$. Since classical trajectories can be computed for extremely complex systems, this could open the door to applications for much more complex chemical reactions. Much thus remains to be done!

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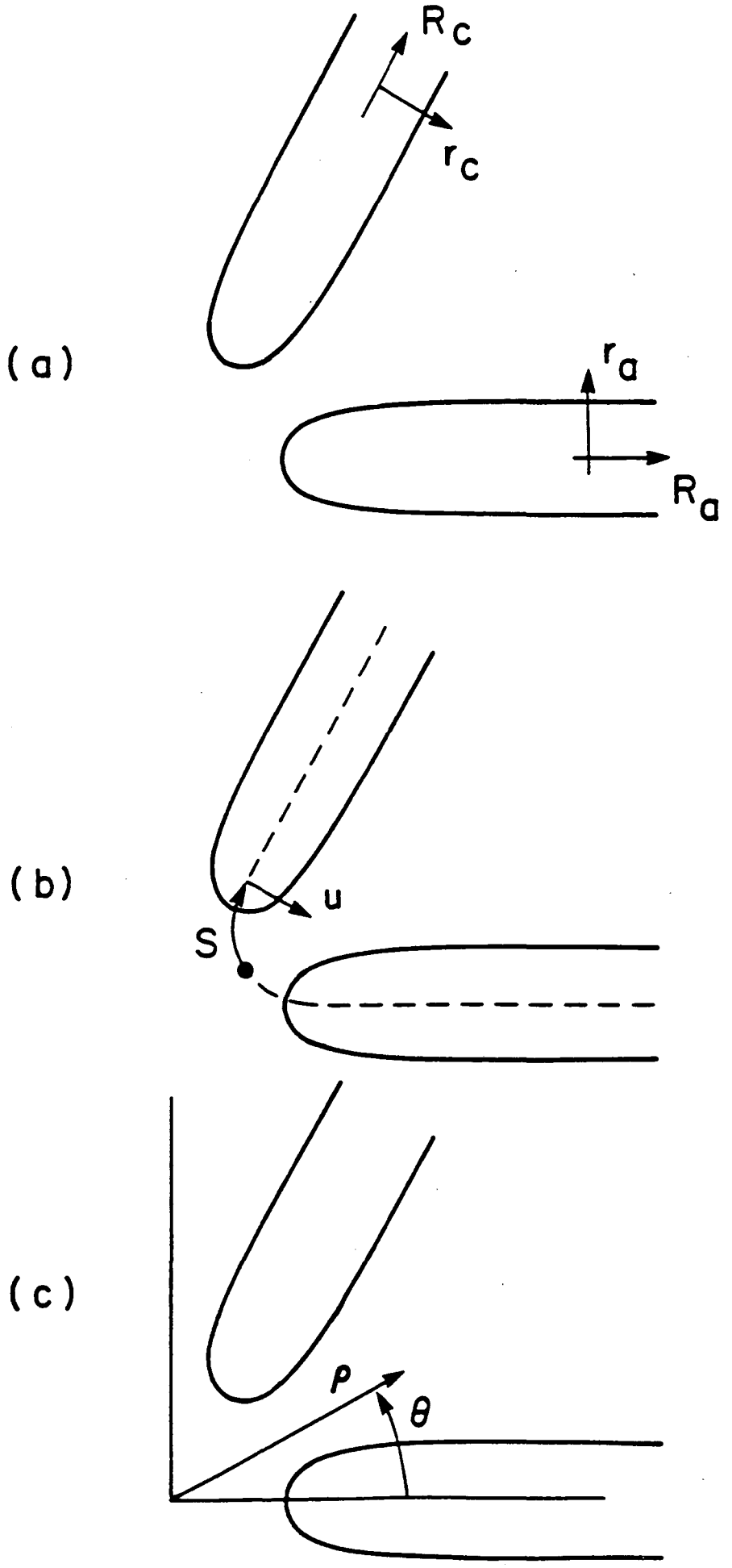
Figure 1 Schematic depiction of a collinear A + BC → AB + C potential energy surface and different ways of choosing coordinates. (a) Jacobi coordinates for arrangement a(A + BC) and c(AB + C); (b) reaction path ("natural collision") coordinates; (c) hyperspherical (here simply polar) coordinates.

Figure 2 Contour plot of the LSTH potential energy surface for the $H+H_2 \rightarrow H_2+H$ reaction in mass-weighted Jacobi coordinates. The points indicate the DVR grid in mass-weighted normal coordinates (x,y) of the transition state. The larger grid (the smaller points, which also lie underneath the larger points) results from cutoff parameters V_c=4 eV and R_{max}=8 a_0, and the smaller grid (the larger points) is the one obtained with V_c=2 eV and R_{max}=6 a_0.


(a)
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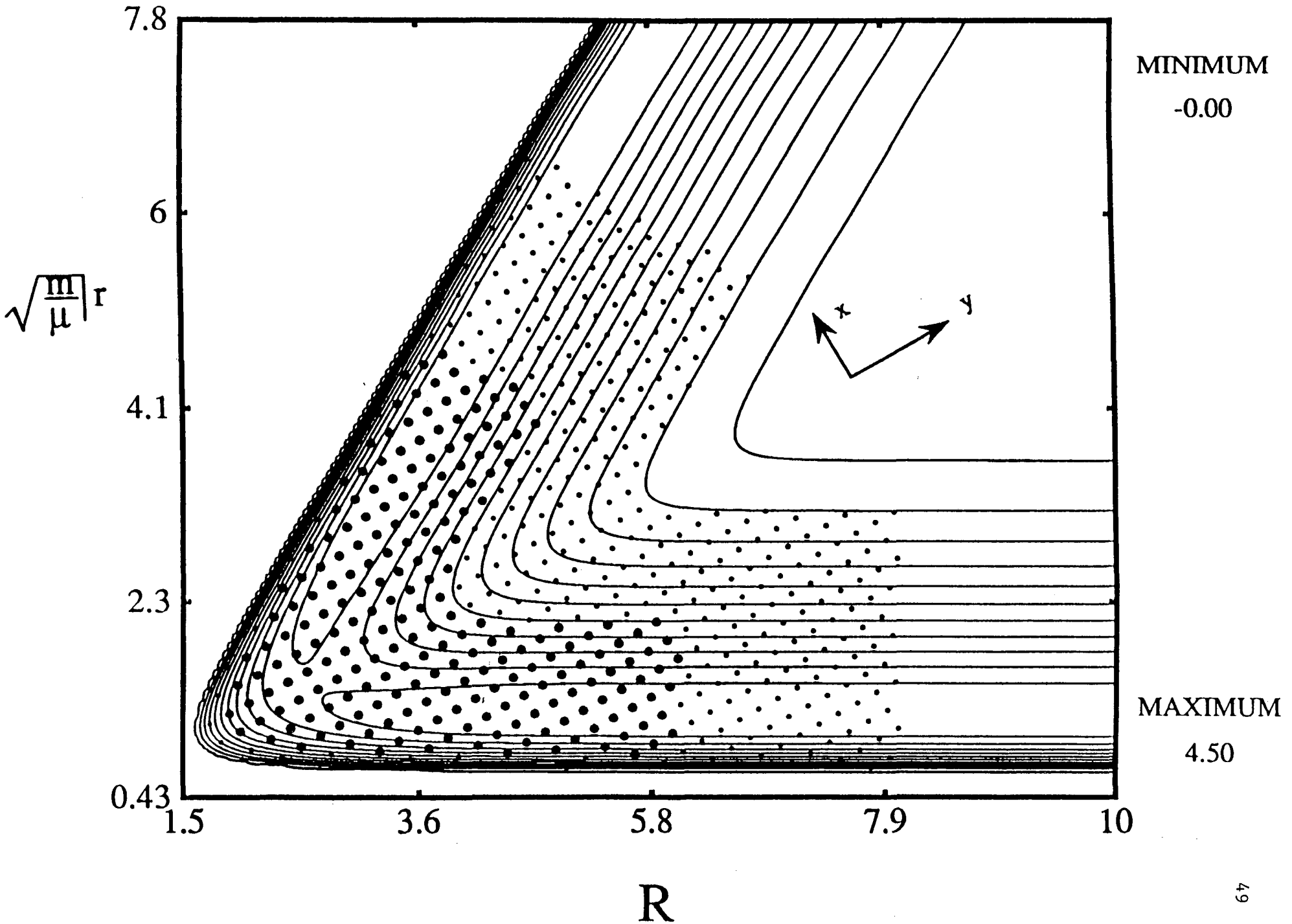
7.8
6
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