QUANTUM MECHANICAL REACTIVE SCATTERING THEORY FOR SIMPLE CHEMICAL REACTIONS: RECENT DEVELOPMENTS IN METHODOLOGY AND APPLICATIONS

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It has recently been discovered that the S-matrix version of the Kohn variational principle is free of the "Kohn anomalies" that have plagued other versions and prevented its general use. This has made a major contribution to heavy particle reactive (and also to electron-atom/molecule) scattering which involve non-local (i.e., exchange) interactions that prevent solution of the coupled channel equations by propagation methods. This paper reviews the methodology briefly and presents a sample of integral and differential cross sections that have been obtained for the $H+H_2 \rightarrow H_2+H$ and $D+H_2 \rightarrow HD+H$ reactions in the high energy region (up to 1.2 eV translational energy) relevant to resonance structures reported in recent experiments.

I. Introduction

The description of chemical reactions at the most fundamental, state-to-state level has been a vision of physical chemists ever since molecular beam methodology¹ ushered in the modern reaction dynamics era over 30 years ago. From a theoretical perspective, the rigorous description of a bimolecular reaction is, of course, a problem in quantum mechanical scattering theory. Unfortunately, however, it is the most complicated kind of scattering process, namely a "rearrangement"² of the particles (here atoms), and this has made progress quite slow. In the 1970's there were many treatments of the collinear model of atom-diatom ($A+BC \rightarrow AB+C$) reactions but only a few attempts at rigorous calculations for the three-dimensional version of such reactions.³ Almost all of the latter were for the prototype $H+H_2 \rightarrow H_2+H$ reaction,^{3d} and here one singles out the work of Schatz and Kuppermann^{3c} as the most successful for these early (1970's) calculations. The theoretical methodology employed for this, however, was sufficiently specialized to the $H+H_2$ system that it has not proved useful for extension to more general applications.

The 1980's have seen renewed activity in quantum reactive scattering calculations, spurred to some extent by the greater access academic researchers have had to supercomputer facilities and also by a new generation of state-to-state scattering experiments. At present there are several different categories of theoretical approaches that are being

pursued for carrying out such calculations: the R-matrix propagation method developed by Light and co-workers,⁴ methods based on the use of hyperspherical coordinates to describe the system of atoms,⁵ methods based on the Faddeev equations, and the formulation of the problem given some years ago⁶ by the author whereby the wavefunction is expressed as a coupled-channel expansion simultaneously in all arrangements, using the standard Jacobi coordinates of each arrangement. In addition to work at Berkeley using this latter approach, Truhlar, Kouri and co-workers⁷ employ a methodology based on this formulation (which they emphasize also results from use of a particular "coupling scheme" in the coupled T-operator formalism developed in the 1970's by Kouri, Baer, et al.⁸) It is also useful to note that the formulation given in ref. 6, which was developed as a generalization of Burke and Taylor's⁹ treatment of electron-atom scattering, is similar in spirit to the "resonating group method"¹⁰ that was developed earlier to treat nuclear reactions.

The central difficulty with the formulation developed in ref. 6 is that the coupled-channel Schrödinger equation contains non-local exchange interactions which characterize the reaction. The only general way for dealing with exchange is to expand the coupled-channel radial functions in a basis set (of known functions) and determine the expansion coefficients via a variational principle. There are several different variational principles for scattering²: the

Kohn¹¹ (essentially the Rayleigh-Ritz) principle is the simplest - because it involves matrix elements only of the Hamiltonian operator - but it has in the past¹² suffered from "Kohn anomalies" (i.e., spurious, unphysical singularities) that have rendered it unsatisfactory. The Schwinger variational principle² has previously been shown¹³ to yield reliable results for reactive scattering (and it has been widely used for electron-atom/molecule scattering¹⁴), and more recently the Newton variational principle⁷ has also been successfully applied to the formulation of ref. 6. The latter two variational principles, however, require matrix elements involving the Green's function for a reference scattering problem, and this makes their application considerably more difficult than the Kohn principle.

It has thus been a major breakthrough to realize that the S-matrix version¹⁵ of the Kohn variational principle is completely free of the "anomalies" that plague the K-matrix version that has traditionally been used. I.e., the results given by the Kohn variational principle are not invariant to how the scattering boundary conditions are applied (even with same basis set): applying it with standing wave boundary conditions to obtain the K-matrix, and then S via the Heitler damping equation, $(1+iK)(1-iK)^{-1}$, does not give the same S-matrix as applying it with incoming/outgoing wave boundary conditions to obtain the S-matrix directly. The latter (S-matrix) version is completely anomaly-free in a general and natural way, and though it may at first seem more difficult to apply because of the presence of complex basis functions (the incoming and outgoing waves), in practice this causes no additional effort.

The overall methodology¹⁶ that results from applying the S-matrix version of the Kohn principle to the formulation of ref. 6 is extremely straight-forward quantum mechanics: one chooses basis functions, computes matrix elements of the Hamiltonian, and then performs a standard linear algebra calculation. Most of the intellectual input comes about, as is usually the case in quantum mechanics, in the first step, i.e., in choosing basis functions in the most efficient and useful manner. We note also that McCurdy, Rescigno, and Schneider¹⁷ have made very significant advances in electron-molecule scattering by using this S-matrix version of the Kohn variational principle.

Section II briefly summarizes the basic working formulae for the S-matrix version of the Kohn variational principle. I have recently reviewed^{16b,c} the basic ideas and methodology of this approach and discussed in detail why "Kohn anomalies" do not arise in

this version. In this regard, another recent paper¹⁸ has shown that the S-matrix Kohn method is free of anomalous (i.e., spurious, unphysical) singularities even in cases for which the Schwinger variational principle - which has been previously thought to be anomaly-free - actually does show anomalous singularities.

Integral and differential cross sections for the $H+H_2(v=j=0) \rightarrow H_2(v', \text{odd } j') + H$ and $D+H_2(v=j=0) \rightarrow HD(v', j') + H$ reactions are presented in Sections III and IV. These involve J (total angular momentum) values up to 24 and 31, respectively, in the partial wave sums to obtain converged results for the cross sections.

II. S-Matrix Version of the Kohn Variational Principle

All of the relevant features are illustrated by simple s-wave potential scattering. The methodology¹⁶ will thus 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

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

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 as

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

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

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

where $v = \hbar k / \mu$ is the asymptotic velocity. (Note: The convention is used throughout this paper that the wavefunctions in the bra symbol $\langle \tilde{\psi} |$ in bra-ket matrix element notation are not complex conjugated.) "ext" in Eq. (2.2) means that the quantity in square brackets is to be extremized by varying any parameters in $\tilde{\psi}(r)$. (Note that for a given trial function $\tilde{\psi}$, Eq. (2.2) may also be viewed as the distorted wave Born approximation, where $\tilde{\psi}$ is the distorted wave.)

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

$$\bar{\psi}(r) = -u_0(r) + \sum_{l=1}^N u_l(r) c_l, \quad (2.4)$$

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

$$u_0(r) \sim e^{-ikr} r^{-1/2}. \quad (2.5)$$

A simple choice for $u_0(r)$ is

$$u_0(r) = f(r) e^{-ikr} r^{-1/2}, \quad (2.6)$$

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

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

$$f(r) \rightarrow 1, \quad r \rightarrow \infty, \quad (2.7)$$

such as $f(r) = 1 - e^{-ar}$. (More generally, $u_0(r)$ may be the (irregular) solution of some (e.g., long range) distortion potential that has asymptotic form Eq. (2.8), multiplied by a cut-off function to regularize it at $r=0$). The function $u_1(r)$ is

$$u_1(r) = u_0(r)^*, \quad (2.8)$$

and the basis functions $\{u_l(r)\}$, $l=2, \dots, N$ are real, square-integrable functions. The coefficients $\{c_l\}$, $l=1, \dots, N$ in Eq. (2.4) are the variational parameters in ψ .

With ψ of Eq. (2.4) substituted into Eq. (2.2) and the coefficients $\{c_l\}$ varied to extremize it, one obtains the following expression for the S-matrix

$$S = \frac{1}{N} (M_{0,0} - M_0^T M_N^{-1} M_0), \quad (2.9)$$

where $M_{0,0}$ is a 1x1 "matrix", M_0 a 1xN matrix, and M_N an NxN matrix,

$$M_{0,0} = \langle u_0 | H-E | u_0 \rangle \quad (2.10a)$$

$$(M_0)_l = \langle u_l | H-E | u_0 \rangle \quad (2.10b)$$

$$(M_N)_{l,l'} = \langle u_l | H-E | u_{l'} \rangle, \quad (2.10c)$$

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

$$\lim_{r \rightarrow \infty} (H-E) \begin{Bmatrix} u_0(r) \\ u_1(r) \end{Bmatrix} = 0. \quad (2.11)$$

Since the matrix M of Eq. (2.10c) is complex-symmetric, there are no real values of E for which the matrix inverse in Eq. (2.9) is singular, and thus no "Kohn anomalies". In fact, the condition that Eq. (2.9) is singular, namely

$$\det(M) = \det [\langle u_l | H-E | u_{l'} \rangle] = 0, \quad (2.12a)$$

$l, l'=1, \dots, N$, is the secular equation for eigenvalues of the Schrödinger equation

$$(H-E)\psi(r) = 0, \quad (2.12b)$$

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

$$\psi(r) \sim e^{ikr}; \quad (2.12c)$$

i.e., Eq. (2.12a) is the expression that has been used before¹⁹ for determining Siegert eigenvalues,²⁰ the complex energies that are the (physically correct) complex poles of the S-matrix which characterize the positions and widths of scattering resonances. Eq. (2.9) 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^{15a} to matrix elements of the full outgoing wave Green's function $G^+(E) = (E + i\epsilon - H)^{-1}$. This is

$$\langle a | G^+(E) | b \rangle = - \sum_{l, l'=1}^N \langle a | u_l \rangle (M_N^{-1})_{l, l'} \langle u_{l'} | b \rangle, \quad (2.15)$$

where M is as above, Eq. (2.10c), 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 scaling⁷ coordinate rotation theory,²¹⁻²⁴ and for the same reasons. If the functions $|a\rangle$ and $|b\rangle$ are real, then Eq. (2.15) leads to a useful way for calculating matrix elements of the density of states operator,

$$\langle a | \delta(E-H) | b \rangle = -\pi^{-1} \text{Im} \langle a | G^+(E) | b \rangle. \quad (2.16)$$

In actual calculations for the S-matrix, Eq. (2.9), 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. (2.9) can be written in the equivalent form

$$S = \frac{1}{N} (B - C \cdot B^{*-1} \cdot C), \quad (2.17)$$

where B and C are the 1×1 "matrices"

$$B = M_{0,0} - M_0^T \cdot M^{-1} \cdot M_0 \quad (2.18a)$$

$$C = M_{1,0} - M_0^{*T} \cdot M^{-1} \cdot M_0, \quad (2.18b)$$

when $M_{0,0}$, M_0 , and M are as before, Eq. (2.10), except that $l, l' = 2, \dots, N$ (i.e., only the real basis functions), and

$$M_{1,0} = \langle u_0^* | H-E | u_0 \rangle. \quad (2.18c)$$

Here the matrix $(M)_{l,l',l,l' = 2, \dots, N}$ 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. (2.17).)

Finally, for general multichannel rearrangement scattering,^{6,25} let (q_Y, r_Y) denote the internal coordinates and radial scattering (i.e., translational) coordinate for arrangement Y ; $\{\phi_n^Y(q_Y)\}$ are the asymptotic channel eigenfunctions for the internal degrees of freedom. Eqs. (2.17) and (2.18) generalize as follows

$$S = \frac{1}{N} (B - C^T \cdot B^{*-1} \cdot C), \quad (2.19a)$$

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

$$B = M_{0,0} - M_0^T \cdot M^{-1} \cdot M_0 \quad (2.19b)$$

$$C = M_{1,0} - M_0^{*T} \cdot M^{-1} \cdot M_0, \quad (2.19c)$$

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

$$(M_{0,0})_{nY,n'Y'} = \langle u_{0n}^Y \phi_n^Y | H-E | u_{0n'}^{Y'} \phi_{n'}^{Y'} \rangle \quad (2.20a)$$

$$(M_{1,0})_{nY,n'Y'} = \langle u_{0n}^{Y*} \phi_n^Y | H-E | u_{0n'}^{Y'} \phi_{n'}^{Y'} \rangle, \quad (2.20b)$$

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

$$u_{0n}^Y(r_Y) \sim e^{-ik_{nY} r_Y / v_{nY}}.$$

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

$$(M)_{lnY,l'n'Y'} = \langle u_{ln}^Y \phi_n^Y | H-E | u_{l'n'}^{Y'} \phi_{n'}^{Y'} \rangle, \quad (2.20c)$$

where $\{u_{ln}^Y(r_Y)\}$ 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

$$(M_0)_{lnY,n'Y'} = \langle u_{ln}^Y \phi_n^Y | H-E | u_{0n'}^{Y'} \phi_{n'}^{Y'} \rangle. \quad (2.20d)$$

Only open channels $\{nY\}$ are included in the matrices $M_{0,0}$, $M_{1,0}$, 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. (2.19) - (2.20) 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.

III. $H+H_2(v=j=0) \rightarrow H_2(v', \text{odd } j') + H$

In this section and the next I survey some selected results obtained by Zhang and Miller²⁶⁻²⁸ using this S-matrix Kohn approach. (The most complete summary of the methodology and its application to atom-diatom reactive in 3-d is given in ref. 28.) Integral cross sections are given by the standard formulae

$$\sigma_{v',j'+v_j}(E) = \pi[k_{v_j}^2(2j+1)]^{-1} \sum_{J=0} (2J+1) \times \sum_{l',l} |S_{v',j',l',vjl}^J(E)|^2, \quad (3.1)$$

and differential cross sections (= angular distributions) by

$$\sigma_{v',j',K'+v_jK}(\theta) = |(2ik_{v_j})^{-1} \sum_J (2J+1) d_{K',K}^J(\theta) \times \sum_{l',l} C(j'Jl';K',-K') i^{l-l'} S_{v',j',l',vjl}^J C(jJl;K,-K)|^2, \quad (3.2)$$

where J is the total angular momentum quantum number, $K=m_j$ is the helicity, i.e., the projection quantum number for the diatom rotation with the relative translational velocity vector as the quantization axis. All other quantities in Eq. (3.1) and (3.2) are their usual selves (i.e., Clebsch-Gordan coefficients, Wigner rotation functions, etc.)

The calculations have been carried out for total energies ($E_{\text{tot}} = E_{\text{trans}} + -0.27$ eV) up to 1.45 eV, and for the $\text{H}+\text{H}_2$ reaction this requires J values up to -20 to obtain convergence in the partial wave sums in Eqs. (3.1) and (3.2).

Figure 1. Reaction probability for the distinguishable atom reaction $\text{H}+\text{H}_2(v_1=j_1=0) \rightarrow \text{H}_2(v, \text{all } j) + \text{H}$ for total angular momentum $J=1$ as a function of total energy. The results for $v'=1$ and $v'=2$ have been multiplied by a factor of 2 and 10, respectively, for convenience in displaying them.

Fig. 1 first shows the energy dependence of the reaction probability for a single value of J ,

$$P_{v'+v_j}^J = \sum_{j'} \sum_{l',l} |S_{v',j',l',vjl}^J|^2, \quad (3.3)$$

for the initial ground state $v=j=0$ of H_2 . The most prominent feature is a resonance at $E = 0.95$ eV due to a short-lived (~ 10 -15 femtosec) collision complex.

Figure 2. Integral cross sections for the properly symmetrized reaction $\text{H}+\text{H}_2(vj) \rightarrow \text{H}_2(v'j') + \text{H}$ for $v=j=0$, $v'=j'=1$, as a function of total energy. The various curves connecting the (calculated) points are for various values of J_{max} , the upper limit in the sum over J . The lowest curve is for $J_{\text{max}}=0$, the next one above it for $J_{\text{max}}=1$, and so forth, with the uppermost curve for $J_{\text{max}}=18$.

Next, Fig. 2 shows the integral cross section for the $v=j=0 \rightarrow v'=j'=1$ reactive transition; the various curves correspond to various upper limits in the sum over J in Fig. (3.1). The uppermost curve is thus the converged result for the cross section. (Calculations with J_{max} up to 24 have subsequently been carried out to verify convergence.) The cross section is quite a smooth function of energy, showing no hint of the resonance at $E = 0.95$ eV seen in the reaction probability for a single small value of J (Fig. 1). This is what one would have expected²⁹ because of the large number of J values that contribute (incoherently) to the integral cross section.

Figure 3. The points are the experimental integral cross sections of ref. 30 for the reaction $\text{H}+\text{H}_2(vj) \rightarrow \text{H}_2(v'j') + \text{H}$ for $v=j=0$, j averaged over 0 and 2, $v'=1$, $j'=1$ (open circles) and 3 (solid circles). The curves are the present theoretical cross sections for $v=j=0$, $v'=1$, $j'=1$ (solid curve) and 3 (dashed curve).

This result for the integral cross

section is in significant disagreement with the recent experimental report by Nieh and Valentini;³⁰ this is shown in Fig. 3, along with the present theoretical result. The magnitudes of the reactive cross sections are in excellent agreement, but the resonance-like structure reported experimentally is absent in the theoretical cross section. Recent independent calculations by Manolopoulos and Wyatt³¹ have obtained results essentially identical to ours,²⁶ lending strong support to the belief that these theoretical calculations are the correct results for this potential energy surface,³² which is thought to be extremely accurate. (Unpublished calculations³³ with another surface gives only modest differences.)

Figure 4. Differential cross section, at several fixed center-of-mass scattering angles θ for the reaction $\text{H} + \text{H}_2(v=j=0) \rightarrow \text{H}_2(v',j') + \text{H}$, as a function of total energy E , for the final state $(v',j') = (1,3)$.

We have suggested²⁶ that a partial resolution of this experimental-theoretical disagreement could be that the experiments are actually observing primarily back-scattered products rather than a true integral cross section. (The differential cross section at $\theta=180^\circ$ should have its dominant contribution from a few small values of j .) Thus both we²⁷ and Wyatt and Manolopoulos³¹ have looked at the energy-dependence of the differential cross section at $\theta=180^\circ$ (and also other fixed angles). Fig. 4 shows this for the particular final state $v'=1, j'=3$. For $\theta=180^\circ$ there is indeed a structure in the energy dependence that seems roughly similar to the experimental structures in Fig. 3, but the similarity is at best only suggestive that this may be what the experiments have actually measured. Other suggestions³⁴ are that there may be non-linear optical effects in either the laser that photodissociates HI (to obtain fast H atoms) or in the CARS laser system used to observe the product $\text{H}_2(v',j')$.

Figure 5. Differential cross section for $\text{H} + \text{H}_2(v=j=0) \rightarrow \text{H}_2(v',j') + \text{H}$, summed over all odd values of j' , for several values of the total energy E . (a) and (b) are for $v'=0$ and 1, respectively.

For completeness, Fig. 5a and b show the complete center-of-mass angular distributions for the reaction $v=j=0 \rightarrow v'=0$, all odd j' and $v'=1$, all odd j' , respectively. As the energy increases, one sees the angular distribution in the backward direction flatten out (hard sphere-like behavior) and a small peak appear in the forward direction (stripping behavior).

Figure 6. Differential cross section for

$H+H_2(v=j=0) \rightarrow H_2(v',j')+H$ for various values of j' . (a) is for $v'=0$ and $E=1.0$ eV, and (b) is for $v'=1$ and $E=1.3$ eV.

Finally, Fig. 6a and b show the angular distribution for specific final rotational states. The most significant feature here is strong coupling between the angular and internal state (here rotational state) distributions, i.e., the angular distribution is quite different for different final rotational states. The most probable scattering angle moves progressively away from the backward direction with increasing rotational excitation of the products.

IV. $D+H_2(v=j=0) \rightarrow HD(v',j')+H$

Similar calculations have been carried out for the $D+H_2$ reaction; here J values up to 34 were necessary in the partial wave sums to obtain convergence at the highest energies. The paper²⁸ reporting these results includes a comprehensive summary of the S-matrix Kohn methodology as it applies to atom-diatom reactions in full 3-d space. Here we give a selection of some of the results that were obtained.

Figure 7. Reaction probability for $D+H_2(v=j=0) \rightarrow HD(v',\text{all } j')+H$ for $J=0$, as a function of total energy.

Fig. 7 shows the $J=0$ reaction probability from the ground state $v=j=0$ of H_2 to $v'=0$ and 1 (summed over final j' states) of HD , as a function of energy. One again sees a very broad resonance feature, here at $E=0.95$ eV.

Figure 8. (Converged) integral cross sections for $D+H_2(v=j=0) \rightarrow HD(v',\text{all } j')$, as a function of energy.

In the integral cross section shown in Fig. 8, however, one sees that it has been almost totally washed out by the partial wave sum; there is only a slight inflection seen in the $v'=1$ cross section at $E=0.95-1.0$ eV.

Figure 9. Integral cross sections for $D+H_2(v=j=0) \rightarrow HD(v'=0,j')+H$ as a function of j' , for several values of E (eV).

Fig. 9 shows the integral cross section to specific final rotational states, i.e., for the transition $v=j=0 \rightarrow v'=0,j'$, at several values of energy. They all have a quasi-Boltzmann form,³⁵ $P(j) \propto (2j+1) \exp[-Bj(j+1)/kT_{\text{eff}}]$, where T_{eff} increases with E .

Figure 10. Differential cross sections for $D+H_2(v=j=0) \rightarrow HD(v'=0,\text{all } j')+H$, for several values of E (eV).

Fig. 10 shows the angular distribution (summed over final rotational states) for several values of E . As in Section III for $H+H_2$, one here sees the angular distribution flatten out in the backward direction as the energy increases and also the appearance of a stripping peak in the forward direction.

Figure 11. Differential cross section for $D+H_2(v=j=0) \rightarrow HD(v'=0,j')+H$, for various values of j' , at $E = 1.25$ eV.

Finally, Fig. 11 shows the doubly differential cross section (i.e., differential in final scattering angle and final rotational state), and as in Section III one also sees here that the angular distribution depends very strongly on the final rotational state; $j'=0$ is strongly peaked in the backward direction ($\theta=180^\circ$), and the most probable scattering direction moves forward with increasing j' , to $\theta=90^\circ$ for $j'=10$.

V. Concluding Remarks

The S-matrix version of the Kohn variational principle thus leads to a very straight-forward methodology for carrying out rigorous quantum mechanical calculations. The results described in Section III and IV, which are the first rigorous cross section calculations for these reactions in this high energy region (Schatz and Kuppermann^{3c} earlier carried out rigorous calculations at lower energy), have employed the most simple minded version of the methodology. I.e., the basis set has been chosen to be of the simple direction product form, so that the same L^2 translational basis $\{u_\ell(r)\}$, $\ell=2, \dots, N$ is used for each channel. The calculations could be made much more efficient - i.e., the basis set reduced in size - by fine tuning; e.g., it is clear that highly excited channels, which have low translational energy, need fewer translational functions than low energy channels (which have high translational energy). This, and many other tricks from the quantum chemistry of bound state eigenvalue calculational methodology, are available to enhance the applicability of this S-matrix Kohn approach to reactive scattering. I believe that the next few years will see a number of these developments and their application to more complex (though still relatively simple) chemical reactions.

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