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Progress of basis optimization techniques in variational calculation of quantum reactive scattering

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This paper describes several efficient basis optimization methods that we have developed in the application of S-matrix Kohn variational method to quantum reactive scattering. Specifically, we employ a minimum-K body-fixed representation combined with the use of quasiadiabatic basis functions for the expansion of the full reactive scattering wave function. This new basis function approach significantly reduces the size of the "larger" matrix of the final linear algebraic equation in the calculation of reaction cross sections. The accuracy of the calculation can be easily controlled by systematically increasing or decreasing the values of two parameters $K_{\text{max}}$ and $\alpha$, and convergence to the full basis set results can be reached. Numerical test calculations are carried out for the 3D $H + H_2$ reaction for the total angular momentum $J = 10$ and for the 3D $F + H_2$ reaction for $J = 0, 1, \text{and } 2$. These calculations demonstrate that our basis optimization approach is very efficient for computing reaction cross sections. Since variational scattering calculations are ultimately limited by the size of the basis set, our method is a stride forward in the applications of variational approach to quantum reactive scattering.

I. INTRODUCTION

Rapid progress has been made for the past few years in the theory of quantum reactive scattering. As a result of this progress one can now calculate exact state-to-state reaction cross sections for the simple reaction $H + H_2$, the isotopically related reaction $D + H_2$, and most recently, for the reaction $F + H_2$. The main thrust behind recent advancement is algebraic variational approach which is emerging as the most general and powerful approach to chemically reactive scattering. The hyperspherical coordinate methods as well as time-dependent quantum wave packet method are also making rapid progress. However, at present stage, it is still very difficult to carry out full cross section calculations for heavy systems. This is because the computation of cross sections requires scattering calculations for many high partial waves (large $J$ values). Since the number of basis function $\mathcal{N}$ increases linearly as $J$ and the computational time increases as $N^3$ it is easy to understand why complete cross section calculations quickly become prohibitive as $J$ increases.

Among various formulations of the variational approach, the S-matrix Kohn variational method, which we have been actively pursuing is extremely simple and efficient in numerical calculations. Other variational methods such as Newton variational method and log derivative (or inverse $R$-matrix) version of Kohn variational method have their own unique advantages as well. The common feature of various variational basis set methods is that they transform the complex reactive scattering problem to simple linear algebraic equations. The solution of these linear algebraic equations generally requires matrix inversion operation which scales as the cube of the size of the matrix (or the number of basis functions). Although recursive methods of various types have been proposed to iteratively solve linear equations without direct matrix inversion, no reliable iterative method has been found so far that could be applied to general reactive scattering problems efficiently.

On the other hand, whether we solve linear algebraic equations directly or iteratively, it is always important and often crucial that we should try to reduce the size of the matrix before any attempt is made to numerically solve the final algebraic equations. In order to reduce the size of the matrix we have to find "better" basis function representations in which to expand the scattering wave function. Two types of considerations are generally involved in "designing" "better" basis functions, viz. symmetry consideration and dynamical consideration. As a rule of thumb in variational scattering calculations, one should always try to construct basis functions with the proper symmetry and therefore to reduce the number of basis functions required in solving final linear algebraic equations. The result obtained from symmetrized calculation is exactly the same as that from nonsymmetrized one except that the calculation is carried out in reduced dimensions. This procedure can be called global block diagonalization because the Hamiltonian matrix of the system is block diagonal in the representation of symmetry adapted basis functions, and consequently, calculation is carried out for diagonal subblocks only which are generally much smaller in dimension than the full Hamiltonian matrix. An example is the scattering of an atom from a homonuclear diatomic molecule in which the selection rule forbids the transition between even and odd rotational states in the inelastic channel. The details of constructing symmetry adapted basis functions for atom–diatom reactive scattering is given in Ref. 4.

This paper concentrates on methods of reducing the number of basis functions based on dynamical consideration. This is generally more complicated and challenging because dynamics is very complex for molecular systems. However, conventional wisdom tells us that typical dynamical considerations for scattering problems are energetics, adiabaticity, and approximate conservations (such as $j_z$ conserving), etc.
The best known example is the electronic adiabatic approximation (or Bohn–Oppenheimer approximation) which separates the motion of electrons from that of nuclei based on different time scales on which electrons and nuclei move. These methods can be called local block diagonalization methods because they diagonalize sub-blocks of the Hamiltonian matrix and the new Hamiltonian matrix in the new basis representation is not strictly block diagonal but approximately. If off diagonal blocks can be neglected with little loss of dynamical information, then we in fact have achieved the reduction of basis functions successfully. The question is then how to find "better" basis functions that could approximately block diagonalize the Hamiltonian matrix and allows us to systematically converge the results within satisfactory accuracy. This takes some physical intuition and trial and error. Since primitive basis functions are primarily chosen on the properties of completeness and the ease of evaluation of the Hamiltonian matrix, they are generally not very efficient to expand the full scattering wave function. By transforming from primitive basis representation to new basis representation one can achieve numerical efficiency, and in the same time, gain some physical insight as to what is important to the dynamics. A well-known example is the normal mode analysis in vibrations in which the normal coordinate is interpreted as the coordinate of independent oscillation of that mode.

Recently, we adopted a quasiadiabatic basis function representation in the application of S-matrix Kohn variational method to reactive scattering problems. The method diagonalizes sub-blocks of the Hamiltonian matrix and discards eigenstates whose eigenenergies are much higher than the scattering energies we are considering. As a result, we were able to cut down the number of basis functions by an average factor of 2 with little loss of accuracy for any given total angular momentum J. The selection of the new basis functions in this method is purely based on the energetic criterion. On the other hand, when the total angular momentum J increases, the degeneracy of the basis functions also increases and using energetic criterion alone is not able to tell which basis function is more important than the other if they have comparable energies. It therefore requires other physical considerations to achieve further basis function reductions. The motivation here is clear, we hope to further reduce the number of basis functions in reactive scattering calculations for high total angular momentum J by utilizing some dynamical properties of the system.

In this paper we utilize the so called "J-conserving property" and construct basis functions in the body-fixed (BF) representation with an incomplete set of K states (K is the projection quantum number of the total angular momentum J on the axis of translational coordinate). This is possible because the coupling of different K states arises solely from a kinetic term (or Coriourious coupling) which is usually a weak term in the Hamiltonian as is well known in inelastic scattering calculations. Based on this argument we expect that relatively fewer K states would contribute significantly to the scattering process. It is interesting to note that so far all the variational calculations of reactive scattering have been carried out exclusively in the space-fixed representation. On the other hand, all the calculations using hyperspherical coordinate methods have been carried out exclusively in the body-fixed representation which makes it straightforward to utilize this property. It is our intention to demonstrate that the body-fixed representation can just easily be implemented in the variational approach to reactive scattering and the advantage of fast convergence with respect to the number of K states in the BF representation can be realized.

In Sec. II we briefly summarize the S-matrix Kohn variational method to scattering problem, describe in fair detail the implementation of minimum-K BF representation, review both the quasiadiabatic basis contraction scheme and the application of distorted incoming (outgoing) waves. Numerical test calculations for the 3D H + H₂ reaction and for the 3D F + H₂ reaction are presented in Sec. III, and Sec. IV concludes.

II. THEORY

A. Brief summary of the S-matrix Kohn variational method

The S-matrix version Kohn method gives the following expression for the scattering matrix:\(^{\text{a}, \text{b}}\)

\[
S = \frac{i}{\hbar} (B - C^T B^{-1} C),
\]

(2.1)

where S, B, and C are matrices whose dimension equals the number of open channels, and "T" denotes matrix transpose. B and C are given by

\[
B = M_{00} - M_{0}^T M^{-1} M_{0},
\]

(2.2a)

\[
C = M_{10} - M_{0}^T M^{-1} M_{0},
\]

(2.2b)

where \(M_{00}\) and \(M_{10}\) are given by

\[
(M_{00})_{\nu
u'} = \langle u_{\nu 0} | \phi_{\nu} \rangle \langle u_{\nu 0} | H - E | u_{\nu 0} \phi_{\nu'} \rangle,
\]

(2.3a)

\[
(M_{10})_{\nu
u'} = \langle u_{\nu 1} | \phi_{\nu} \rangle \langle u_{\nu 1} | H - E | u_{\nu 0} \phi_{\nu'} \rangle,
\]

(2.3b)

where \(n\) is a collective index for all the internal quantum numbers, for example, \(n = (\nu j l)\) for atom–diatom system. Our convention (as always) is that translational functions in the bra are not complex conjugated. \(M\) is a "large x large" matrix,

\[
(M)_{\nu t, \nu' t'} = \langle u_{\nu t} | \phi_{\nu} \rangle \langle u_{\nu t} | H - E | u_{\nu t} \phi_{\nu'} \rangle,
\]

(2.4)

t, t' = 2, ..., N; and \(M_{00}\) is a "large x small" rectangular matrix,

\[
(M_{0})_{\nu t} = \langle u_{\nu 0} | \phi_{\nu} \rangle \langle u_{\nu 0} | H - E | u_{\nu 0} \phi_{\nu} \rangle,
\]

(2.5)

t = 2, ..., N.

The square integrable translational basis functions \(u_t\) were chosen to be distributed gaussian functions \(<u_t | R) = e^{-\frac{1}{2} (R - R')^2}\), \(u_0\) (\(u_1 = u_0^*\)) is "free" function satisfying incoming (outgoing) boundary condition, and \(\phi_n\) are eigenfunctions of the asymptotic arrangement Hamiltonian. Therefore our primitive basis function is the direct product of the internal basis function and the translational (radial) basis function.

B. Body-fixed (BF) representation

The Hamiltonian for atom–diatom reactive scattering is given by
\[ H = - \frac{\hbar^2}{2\mu} \frac{1}{R_\gamma} \frac{\partial^2}{\partial R_\gamma^2} R_\gamma + \frac{\mathbf{L}^2}{2\mu R_\gamma^2} - \frac{\hbar^2}{2\mu} \frac{1}{r_\gamma} \frac{\partial^2}{\partial r_\gamma^2} r_\gamma + \frac{j^2}{2\mu r_\gamma^2} + \nu^v(r_\gamma) + V_j(R_\gamma, r_\gamma), \]  

(2.6)

where \( \gamma \) is the arrangement labeling index, \( \mu \) is the reduced mass, and \( (R_\gamma,r_\gamma) \) are the mass-scaled Jacobi coordinates given by the following definition:

\[ r_\gamma = \frac{R_\gamma}{S_\gamma}, \]  

(2.7a)

\[ R_\gamma = \frac{R_\gamma}{S_\gamma}, \]  

(2.7b)

where \( (R_\gamma, r_\gamma) \) are the unmass-scaled Jacobi coordinates. The scaling factor \( S_\gamma \) and the reduced mass \( \mu \) are given by

\[ S_\gamma = \left( \frac{m_\gamma (m_\gamma + m_\gamma')^2}{m_\gamma' m_\gamma (m_\gamma + m_\gamma' + m_\gamma'')} \right)^{1/4}, \]  

(2.8)

\[ \mu = \sqrt{\frac{m_\gamma m_\gamma'}{m_\gamma + m_\gamma'}}, \]  

(2.9)

The \( \nu^v(r_\gamma) \) is the diatomic potential and \( V_j(R_\gamma, r_\gamma) \) is the interaction potential in the \( \gamma \) arrangement and vanishes as \( R_\gamma \to \infty \). The reader is referred to Ref. 21 for more detailed explanation. So far all the variational calculations of quantum reactive scattering have been carried out exclusively in the space-fixed representation in which the orbital angular momentum operator is diagonal and thus facilitates the evaluation of the Hamiltonian operator acting on the SF basis functions. However, it is well known in scattering calculations that use of the body-fixed representation makes it straightforward to apply the so-called “centrifugal sudden” or CS approximation. This is because the Hamiltonian matrix in the BF representation is generally more diagonal than in the SF representation due to relatively weak centrifugal couplings. Therefore, using the BF representation in algebraic variational approach opens the possibility for carrying out reactive scattering calculations at different levels of approximation in the spirit of CS or more accurate approximation.

Actually, the implementation of the body-fixed representation in the S-matrix Kohn variational method is rather straightforward as is shown below. Of course due to similarities among various variational methods, it should also be straightforward to use the BF representation in other variational methods as well. The total angular momentum eigenfunction in the space-fixed representation is defined as

\[ \langle \text{JM} | \text{LM} - m \rangle = \sum_m \langle \text{JM} | m \rangle \langle \text{LM} - m \rangle. \]  

(2.10)

where \( \langle \text{JM} | m \rangle \) and \( \langle \text{LM} - m \rangle \) are eigenfunctions of the angular momentum operators \( \mathbf{j} \) and \( \mathbf{l} \), respectively. The total angular momentum eigenfunction \( \langle \text{JM} | \text{K} \rangle \) in the body-fixed representation is related to that in the space-fixed representation \( \langle \text{JM} | \text{L} \rangle \) by an orthogonal transformation, 

\[ \langle \text{JM} | \text{L} \rangle = \sum_{\text{LM} - m} C_{\text{LM}} \langle \text{JM} | \text{L} \rangle \]  

(2.11)

where the transformation matrix elements are given by

\[ C_{\text{LM}} = \sqrt{\frac{2L + 1}{2J + 1}} (2 - \delta_{\text{LM}}) \frac{1}{2} \langle \text{JM} | \text{L} \rangle, \]  

(2.12)

where \( \langle \text{JM} | \text{L} \rangle \) is the Clebsch-Gordon coefficient. It should be mentioned here that since the space-fixed basis \( \langle \text{JM} | \text{L} \rangle \) is also eigenfunction of the parity, the body-fixed function \( \langle \text{JM} | \text{K} \rangle \) has been defined here to preserve the parity. Since equation (2.11) holds for a given parity, the coefficient \( C_{\text{LM}} \) forms an orthogonal transformation. We thus have the following orthogonality relations:

\[ \sum_{\text{LM} - m} C_{\text{LM}} C_{\text{LM}' \text{L}'} = \sum_{L' \gamma, \gamma'} \frac{2L + 1}{2J + 1} (2 - \delta_{\text{LM}}) \frac{1}{2} \delta_{\text{LM}, \text{L}'} \delta_{\text{L} \gamma, \text{L}'} \times \langle \text{JM} | \text{L} \rangle \langle \text{L} | \text{L} \rangle \langle \text{L} | \text{L} \rangle = \delta_{\text{KL}}, \]  

(2.13a)

where \( \gamma = j + L \) is the parity and the summation over \( L \) is for a given parity \( \rho \) only (even or odd). The explicit coordinate representation of \( \langle \text{JM} | \text{K} \rangle \) is

\[ \langle \text{JM} | \text{K} \rangle = \left( 2 + 2\delta_{\text{L} \gamma} \right) - \frac{1}{2} \frac{2L + 1}{2J + 1} \frac{1}{2} \delta_{\text{L} \gamma} \frac{1}{2} \delta_{\text{L} \gamma} \frac{1}{2} \delta_{\text{L} \gamma} \langle \text{JM} \rangle \langle \text{L} \rangle \langle \text{L} \rangle \langle \text{L} \rangle = \delta_{\text{KL}}, \]  

(2.13b)

where \( \gamma^v \) is the translational basis function. The potential matrix \( V_{\text{L} \gamma, \gamma} \) is given by

\[ V_{\text{L} \gamma, \gamma} = 2\pi \delta_{\gamma} \langle \text{JM} | \text{L} \rangle \langle \text{L} | \text{L} \rangle \begin{cases} \delta_{\gamma} \langle \text{JM} | \text{L} \rangle \langle \text{L} | \text{L} \rangle \langle \text{L} | \text{L} \rangle = \delta_{\text{KL}}, \end{cases} \]  

(2.15)

where \( \gamma^v \) is the rovibrational eigenfunctions of the diatomic and,
\[ V_n(R,r) = \frac{2l + 1}{2} \int d\cos \gamma V(R, r, \gamma) P_n(\gamma), \quad (2.17) \]

with \( P_n(\gamma) \) being the Legendre polynomial. The centrifugal term \( W^{2-}_{K,K'} \) is given by

\[
\begin{align*}
[W^{2-}]_{K,K'} &= [J(J+1) + j(j+1) - 2K^2] \delta_{K,K'} \\
&- \frac{\gamma}{\gamma^{2}} \lambda^{2}_{-K} \lambda^{2}_{K} (1 + \delta_{K+1,K'}) \\
&- \frac{\gamma}{\gamma^{2}} \lambda^{2}_{-K} \lambda^{2}_{K} (1 + \delta_{K-1,K'}). \\
\end{align*}
(2.18)
\]

where

\[
\begin{align*}
\lambda^{2}_{-K} &= \sqrt{J(J+1)} \pm K(K\pm 1), \\
\lambda^{2}_{K} &= \sqrt{J(J+1)} \pm K(K\pm 1). \\
\end{align*}
(2.19a, 2.19b)
\]

The exchange matrix elements of the Hamiltonian are given by

\[
[H]_{\delta t'v'j'K'}(R_i) = \epsilon_{\delta t'v'j',vjK} + [V^{JK}]_{t'v'j'}(R_i) \delta_{K,K'}. \\
+ \frac{\mu^2}{2} [W^{2-}]_{K,K'} \frac{1}{R^2} \delta_{\delta t'v'j'}. \\
(2.24)
\]

The new basis function \( |JMn\rangle \) is just the eigenstate of this quasiadiabatic Hamiltonian expressed as a superposition of “old” states \( |JMt\rangle \) and the transformation matrix between the “old” and the “new” basis functions are just the eigenvenergies given by the matrix diagonalization. The index \( n \) denotes the quantum number of all the internal degrees of freedom. Now the full basis should be written as \( |JMn\rangle \) because \( n \) depends on \( t \). Now the new basis functions are no longer simply the direct products of translational and internal basis functions due to the dependence of \( n \) on \( t \). One then “filters” out those new basis functions whose corresponding eigenergies are higher than \( E_{\text{max}} = \alpha E \), where \( E \) is the scattering energy and \( \alpha \) is a parameter that controls the contraction. The choice of \( \alpha = \infty \) corresponds to no contraction. Typical values of \( \alpha \) that can give satisfactory results are between 1.1 and 1.4. This means that normally only 10% to 40% of the “locally” closed channels are needed in the scattering calculations. As a result of this filtering the transformed new Hamiltonian matrix is much smaller in dimension. The matrices in Eqs. (2.4) and (2.5) are then transformed to new ones by a rectangular matrix transformation as is described in Ref. 17.

\[ O^d \] and \[ O^e \] are the overlap matrix elements, and they are equivalent in the sense of completeness and should produce the same results iif all components of \( L \) or \( K \) of the total angular momentum \( J \) are included in the basis expansion. However, the main motivation of using the BF representation in this work is that we hope to obtain accurate results with fewer \( K \) states (minimum-K scheme) than are necessary by the completeness requirement based on the notion of approximate “\( j_s \) conserving propensity.” In minimum-K scheme, we retain only those primitive basis functions whose \( K \) values are less or equal to a fixed value \( K_{\text{max}} \). We systematically increase \( K_{\text{max}} \) until results are satisfactory.

\[ U \] is the full BF interaction potential matrix (open
channels only) in a given arrangement (including centrifugal terms), i.e.,

\[ U_{ef'K'}_{\gamma'\gamma K} = [V^{JK}]_{ef'q'q} \delta_{K',K} + \frac{\hbar^2}{2\mu} [W^{ij}]_{\gamma'\gamma K} \frac{1}{R^2} \delta_{ef'q'q}, \]

(2.25)

where matrix elements of \( V^{JK} \) and \( W^{ij} \) are given by Eqs. (2.16) and (2.18), respectively. The distorted incoming wave function in matrix form, denoted by \( u_0 \), satisfies the radial Schrödinger equation,

\[ \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + (E \mathbf{I} - \epsilon - U) \right] u_0 = 0, \]

(2.26)

where \( \epsilon \) is a diagonal matrix whose elements are eigenvalues of the asymptotic Hamiltonian for the internal degrees of freedom and \( \mathbf{I} \) is a unity matrix. We choose the asymptotic boundary condition corresponding to that of the body-fixed representation such that the resultant \( S \) matrix from the scattering calculation is directly given in the body-fixed representation. The asymptotic boundary condition for \( u_0 \) is

\[ [u_0]_{ef'K'}_{\gamma'\gamma K} (R \to \infty) = -\sum L_m \mathbb{C}_{KK'} \mathbb{H}_L' (R) L^0_m = \frac{e^{-ik_{\eta,K} R}}{\sqrt{k_{\eta}}} L^0_m \delta_{ef'K'}_{\gamma'\gamma K}, \]

(2.27)

where \( L_m = \min(J_J) + 0(1) \) for \( P = \text{even} \) (odd), \( h_L^{1-} \) is the Ricatti–Hankel function of the first kind, and

\[ k_{\eta} = \sqrt{\frac{2\mu}{\hbar^2} (E - \epsilon_\eta)}. \]

Since \( L - L_m = 2n(n = 0, 1, ...) \) for a given parity, the factor \( L^0_m \) is real.

The propagation of Eq. (2.26) is carried out by a direct Numerov method which integrates Eq. (2.26) inward toward the origin starting from the asymptotic condition in Eq. (2.27) for \( u_0 \). The propagation stops after entering the exchange region and more details are given in Ref. 24(d).

The relationship of the resultant \( S \) matrix using the above matrix elements because cutoff function \( f \) is chosen to be vanish inside the exchange region so that matrix elements of \( M_{00} \), \( M_{10} \), and \( M_0 \) between different arrangements can be neglected.

### III. NUMERICAL CALCULATIONS

#### A. 3D H + H\(_2\) reaction

To illustrate the efficiency of the new scheme, we have carried out three-dimensional calculation for the \( H + H_2 \) reaction for the total angular momentum \( J = 10 \) using the LSTH potential energy surface. The primitive basis set is chosen to be \( (11, 9, 7, 5) \times 13 \), i.e., asymptotic rovibrational states \( (v = 0, j = 0, ..., 11) \), \( (v = 1, j = 0, ..., 1) \), \( (v = 2, j = 0, ..., 7) \), \( (v = 3, j = 0, ..., 5) \), each with 13 distributed Gaussians for the translational degree of freedom. This corresponds to a total of 2457 primitive basis functions for \( J = 10 \) with all the possible \( K \) states included. The first step in our basis contraction scheme is to limit the number of \( K \) states. This is done by eliminating those states whose \( K \) quantum number is larger than \( K_{\max} \), a parameter set externally. The normal \( K \) quantum number runs from \( K = 0 \) or 1, depending upon the parity, up to the minimum of \( (J_J) \). We systematically increase \( K_{\max} \) until the results are stable with respect to increasing \( K_{\max} \). Thus the convergence is guaranteed if enough \( K \) states are included. It turns out that not many \( K \) states are actually needed in the scattering calculation as is shown in the following tables. Next the Hamiltonian matrix in Eq. (2.24) in the primitive basis set with minimum \( K \) states is diagonalized for each distributed Gaussian basis function \( u \) and those new quasiadiabatic basis functions whose eigenvalues \( (\epsilon_\eta) \) are larger than \( aE \) are simply discarded. \( E \) is the scattering energy and \( a \) is a parameter that characterizes the contraction scheme. The physical meaning of \( a \) is clear, for example, if \( a = 1.0 \), then all the “locally” open quasiadiabatic functions are retained in the scattering calculation. The number of quasiadiabatic functions retained thus increases as the parameter \( a \) is increased. As is shown in Ref. 17, an \( a \) value of 1.2 normally gives satisfactory results.

The partial cross section \( \sigma_{a\nu \nu' \infty} (J) = (\pi/k_\infty^2)(2J + 1)P_{\nu \nu'-\infty} \), which is the contribution of cross section from a fixed \( J \), for the reaction \( H + H_2 (v = j = 0) \rightarrow H_2 (v'j') + H \) for \( J = 10 \) with different choices of the parameters \( K_{\max} \) and \( a \) is given in Tables I and II at two different scattering energies. Table I shows results for \( E = 0.6 \) eV. The first row is the result using the full primitive basis set in the scattering calculation. The size of the “large” matrix is given in the last column. It is evident that the choice of \( K_{\max} = 3 \) gives good results with a much smaller basis set. Similar results are also obtained for \( E = 1.0 \) eV as is shown in Table II. We notice here that for low scattering energy the energy cutoff is very efficient in terms of reducing the number of basis functions. On the other hand at very low energies when reaction probabilities are very small, closed channels become more important and therefore larger \( a \) values are generally required in order to obtain high accurate results for very small reaction probabilities. This is very likely due to tunneling effect which becomes more important in the pre threshold region and consequently more closed channels are required to describe this effect accurately.
TABLE I. Comparison of the partial cross section $\sigma_{\mu, \alpha}$ for $H + H_2$ reaction with different values of $K_{\text{max}}$ and $\alpha$ for $J = 10$ and for total energy $E = 0.6$ eV.

<table>
<thead>
<tr>
<th>$K_{\text{max}}$</th>
<th>$\alpha$</th>
<th>$\nu' = 0$, $J' = 1$</th>
<th>$\nu' = 0$, all odd $J'$</th>
<th>Size $^b$</th>
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<td>60</td>
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</tbody>
</table>

$^a$ $\sigma_{\mu, \alpha} = (\pi/k_{\text{in}}^2)(2J + 1)P_{\mu, \alpha}.$

$^b$ This is the size of the "large x large" matrix with the corresponding choice of $K_{\text{max}}$ and $\alpha$.

B. 3D $F + H_2$ reaction

Three-dimensional dynamics calculation for the reaction $F + H_2 \rightarrow HF + H$ is considerably more difficult than that of $H + H_2$ reaction and therefore provides a more stringent test of our method. This reaction is of particular interest due to the evidence for possible long lived resonances observed in molecular beam experiments by Lee and co-workers. Full 3D quantum scattering calculations for $J = 0$ on the $M5$ potential surface have been reported. Recently several new calculations on the new $TSA$ potential surface have been reported. Although the $TSA$ surface is thought to be more accurate than the $M5$ surface, dynamics calculations carried out on the $TSA$ surface yielded larger reaction probabilities to final vibrational state $\nu_j = 3$ than to $\nu_j = 2$ state in contrast to experiments of Polanyi and Lee and co-workers. This suggests that the $TSA$ surface needs to be modified or new potential surface has to be constructed. Nevertheless, for our numerical test calculations we employed $TSA$ surface because our results can be checked with those of other groups.

We used a primitive rovibrational basis set of $(12,10,8,6,4) \times 16$ for the $F + H_2$ arrangement and $(22,18,15,11,7,4,3) \times 20$ for the product $H + HF$ arrangement. The meaning of this basis set notation is explained above for the $H + H_2$ reaction and remains the same for the $F + H_2$ reaction. This corresponds to a total of 2140 basis functions for $J = 0$, 4060 for $J = 1$ and 5840 for $J = 2$. We first show how the number of basis functions can be drastically reduced by using the energy cutoff criterion employing quasadiabatic basis functions. This is shown in Table III for the $J = 0$ calculation at the scattering energy of 0.35 eV. The computed reaction probabilities from ground state of $H_2$ to final vibrational state of HF resulting from different choices of the energy cutoff parameter $\alpha$ are given in Table III. It shows that the choice of $\alpha = 1.2$ gives satisfactory results with only 1000 basis functions required in the calculation, less than half the number of primitive basis functions (2140) which we otherwise have to use in applying our early version of the $S$-matrix Kohn method. In order to see how well the minimum-$K$ scheme works for $J > 0$ calculations, we performed several calculations for $J = 1$ and 2 using a fixed energy cutoff parameter $\alpha = 1.4$ but with different $K_{\text{max}}$. The $J = 1$ calculation with $K_{\text{max}} = 1$ corresponds to the complete $K$ state calculation and has almost twice as many basis functions as for $J = 0$ calculation. On the other hand, the choice of $K_{\text{max}} = 0$ in the $J = 1$ calculation corresponds to $CS$ approximation and has about the same number of basis functions as for $J = 0$ calculation.

It is encouraging to see that the computed reaction probabilities using $K_{\text{max}} = 0$ agrees with those using $K_{\text{max}} = 1$ to within a few percent in the $J = 1$ calculations. There are only 1067 basis functions in $K_{\text{max}} = 0$ calculation compared to 2055 basis functions in $K_{\text{max}} = 1$ calculation while the total number of primitive basis functions is 4060 without using the energy cutoff. The reaction probabilities for the total angular momentum $J = 2$ using a fixed energy cutoff $\alpha = 1.4$ but with $K_{\text{max}} = 0.1$ and 2, respectively, are also computed and results are given in Table IV. The reaction probabilities resulting from the $K_{\text{max}} = 0$ calculation ($CS$ approximation with 1066 basis functions) deviate only a few percent (less than 10%) from that of the $K_{\text{max}} = 2$ calculation (with 2960 basis functions) for $J = 2$ except for small transition probability to $\nu' = 1$ state. The $K_{\text{max}} = 1$ calculation gives essentially the same results as those of $K_{\text{max}} = 2$ calculation for $J = 2$. However, it is generally expected that for large $J$ calculations more than one $K$ states are needed if high accurate results are desired. Fortunately, for cross section calculations the final integral cross sections may not be very sensitive to detailed results of each individual partial wave due to the summation of $J_j$; it is conceivable that even the lowest level variational calculation ($K_{\text{max}} = 0$ or $CS$ approximation) could give satisfactory results.

TABLE II. Same as Table I except for total energy $E = 1.0$ eV.

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<thead>
<tr>
<th>$K_{\text{max}}$</th>
<th>$\alpha$</th>
<th>$\nu' = 0$, $J' = 1$</th>
<th>$\nu' = 0$, all odd $J'$</th>
<th>Size</th>
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</tr>
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<td>2.47E-01</td>
<td>844</td>
</tr>
<tr>
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<td>818</td>
</tr>
<tr>
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</tr>
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</table>

of Chemistry, New York University. Part of the calculations for the \( F + H_2 \) reaction for \( J = 1 \) and 2 were carried out on the Cray Y-MP at NASA-Ames Research Center.

APPENDIX: ASYMPTOTIC BOUNDARY CONDITION FOR THE FREE WAVE FUNCTION \( u_0 \) IN THE BF REPRESENTATION

We start with the standard definition of BF \( S \) matrix expressed in terms of the SF \( S \) matrix,

\[
S_{K',K}^B \equiv \sum_{L',L} i^{\ell - L} \sqrt{\frac{2L' + 1}{2J + 1}} \langle jK' L' 0 | jK \rangle S_{L',L}^S \times \sqrt{\frac{2L + 1}{2J + 1}} \langle jKL 0 | jK' \rangle,
\]

(A1)

where \( S_{K',K}^B \) is the BF \( S \) matrix and \( S_{L',L}^S \) is the SF \( S \) matrix. To simplify the notation we suppressed \( \ell \) and indices for the \( S \) matrices. The \( S_L^S \) vanishes if \( L' \) and \( L \) states belong to different parities. The parity of the system is determined by the \( J \) and \( \ell \) indices \( (p = \ell + J) \). Since the total angular momentum \( J \) is conserved we can also define the total parity of the system as \( P = J + \ell + L \) (even or odd) which is also a conserved quantity. The BF \( S \) matrix defined in Eq. (A1) is thus a superposition of both even and odd parity components. For transition from initial ground state, only one parity is needed in the calculation (\( P = \text{even} \)). The quantum numbers \( K \) and \( K' \) in Eq. (A1) can take both positive and negative values.

Now we define a parity adapted BF \( S \) matrix by the following:

\[
\bar{S}_{K',K}^B = \sum_{L,L'} D_{L',L}^{K'K} S_{L',L}^S D_{L,K},
\]

(A2)

where

\[
\bar{S}_{K,K'}^B \equiv \sum_{L,L'} (2 - \delta_{K'0})^{-1/2} \left[ i^{\ell - L_{\min}} \bar{S}_{K',K}^B \right] \times (2 - \delta_{K0})^{-1/2},
\]

where \( \delta_{K0} \) is the total parity (\( P = \text{even/odd} \)). Next we need to derive the asymptotic boundary condition for the BF incoming wave \( \bar{u}_0 \). Let us denote \( \Psi \) as the column vector wave function and its transpose \( \Psi^T \) as the row vector wave function where different components of the vector correspond to different initial states. The asymptotic condition of the wave functions are

\[
\Psi^T (R \to \infty) \sim \phi^T \bar{u}_0 + \phi^T \bar{u}_0 \bar{S}_0,
\]

(A5a)

\[
\bar{\Psi}^T (R \to \infty) \sim \bar{\phi}^T \bar{u}_0 + \bar{\phi}^T \bar{u}_0 \bar{S}_0,
\]

(A5b)

where variables in bold face are matrices, those with bar are in the BF representation, those without are in the SF representation.

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IV. CONCLUSIONS

The \( S \) matrix method, like other variational methods, reduces the treatment of quantum reactive scattering to straightforward quantum mechanical basis set calculations. It now becomes clear that the quest for "better" basis functions is going to be the main research focus in this area. The new scheme of using the minimum-\( K \) body-fixed representation and the quasidiabatic functions described in Sec. II is very simple and easy to use. The extra computational effort involved is minimal and is independent of the scattering energy. Although the propagation of distorted wave is energy dependent, the saving from it can more than compensate the extra computational effort. The methods described in this paper are both flexible and systematic. If the absolute accuracy is not very crucial we can relax the parameters \( K_{\text{max}} \) and \( a \) and be able to perform calculations at different levels of approximation with much smaller basis set. The crudest approximation within this framework is the CS approximation in which only one \( K \) state is included in the scattering calculation. This could make the cross section calculations for heavy systems much easier because calculation for a high total angular momentum \( J \) with \( K_{\text{max}} = 0 \) requires only the same computational effort as for the \( J = 0 \) calculation. Recently, both Kouri-Truhlar group 37 and Wyatt group 33 have proposed somewhat similar efficient basis contraction schemes in which the translational basis functions, instead of the internal basis functions, are optimized but otherwise are in the same spirit as ours. We have recently obtained integral cross sections for the \( F + H_2 \) reaction using the method presented in this paper and is reported elsewhere. 38

It is just the beginning in the search for "better" basis functions in quantum reactive scattering. We anticipate more progress in the near future that could greatly widen the range of applications of quantum reactive scattering to more complex systems.
sentation and $\phi$ are the eigenfunctions of total angular momentum. The transformation between $\phi$ and $\tilde{\phi}$, $S$ and $\tilde{S}$ are (cf. Eqs. (2.11) and (A2)),

\[
\tilde{\phi} = \tilde{\phi}^T C^T, \quad S = D \tilde{S} D^T,
\]

where matrix elements of $C$ and $D$ are given in Eqs. (2.12) and (A3), respectively. Using the above transformation it is easy to arrive at the following relation:

\[
\tilde{u}_0 = C^T u_0 D.
\]

Since the SF free function $u_0$ has the following asymptotic expression:

\[
[u_0]_{L^{-L}} (R \to \infty) \to h_{L}^{-\frac{(L+1)}{2}} \delta_{L^{-L}} \frac{e^{-iKR}}{\sqrt{K}} \delta_{L^{-L}}.
\]

the asymptotic form of $\tilde{u}_0$ is

\[
[\tilde{u}_0]_{K^{-K}} (R \to \infty) \to \sum_{L} C_{L^{-K}} h_{L}^{-\frac{(L+1)}{2}} L^{-L_{min}} C_{L^{-K}}
\]

\[
\to L^{-L_{min}} \frac{e^{-iKR}}{\sqrt{K}} \delta_{K^{-K}},
\]

which is exactly Eq. (2.27) in Sec. II.