

NEW METHOD FOR QUANTUM REACTIVE SCATTERING, WITH APPLICATIONS TO THE 3-D H+H₂ REACTION

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A method for carrying out quantum-mechanical scattering calculations (J. Chem. Phys. 86 (1987) 6213) is successfully applied to 3-D H+H₂ reactive scattering. This new method (essentially the Kohn variational method, but applied directly to the *S*-matrix rather than to the *K*-matrix) is general, straightforward, variationally stable, and applies equally well to reactive (i.e., rearrangement) and non-reactive scattering process. Its most important practical feature, compared to other similar basis-set approaches, is that it requires matrix elements only of the Hamiltonian operator itself and not those involving the scattering Green's function of some reference problem. Our calculations show that the method is numerically stable within a broad range of energies and converges fast with respect to basis set and numerical parameters. The method allows the use of a flexible distortion potential and contracted basis functions. Due to its generality and straightforwardness, the method is potentially powerful for studying more complex reactive systems beyond atom/diatom reactive scattering.

1. Introduction

A new method for carrying out quantum-mechanical scattering calculations was recently presented by Miller and Jansen op de Haar [1]. The purpose of this paper is to report the successful application of this approach to reactive scattering of H+H₂→H₂+H in three dimensions (for total angular momentum *J*=0).

The method [1] we use relies on a variational expansion of the full scattering Green's function $G^+(E) \equiv (E + i\epsilon - H)^{-1}$ in a discrete set of basis functions,

$$G^+(E) = \sum_{t,t'=0}^N |u_t\rangle \langle u_{t'}^* | E - H | u_{t'} \rangle^{-1} \langle u_t^* |, \quad (1)$$

where $\langle u_t^* | E - H | u_{t'} \rangle^{-1}$ denotes the (*t*, *t'*) elements of the inverse matrix of the matrix $\langle u_t^* | E - H | u_{t'} \rangle$. Eq. (1) has a similar structure to that of the complex scaling/coordinate rotation method of Nuttall and co-workers [2], Reinhardt and co-workers [3], and McCurdy and Rescigno [4], in that the matrix of *E*−*H* is complex symmetric (not Hermitian). Our use of eq. (1) differs from the complex scaling approach in that the basis functions are chosen to impose the correct outgoing wave boundary conditions of $G^+(E)$ exactly, rather than approximately.

The important practical feature of the method is that it applies equivalently to non-local (i.e. exchange), as well as local interaction potentials. It is thus applicable to electron-atom/molecule and also to Miller's formulation [5] of chemically reactive scattering, both of which involve exchange interactions. The final "working formulae" of the method are similar in structure to the Schwinger variational method, as well as to the L^2 method of Kouri, Truhlar and co-workers [6,7] (which also utilizes Miller's formulation [5]). The primary advantage of the present method over these others is that it requires that one computes matrix elements only of the Hamiltonian operator between the various basis functions; no matrix elements involving the Green's function G_0 of a reference Hamiltonian are required. (For example, matrix elements of VG_0V are required in

the Schwinger method, and even more complicated ones in the approaches used in refs. [6,7].)

Section 2 briefly summarizes the methodology, while specializations for the present application to A+BC 3-D reactive scattering is given in section 3. Results of the calculations are presented and discussed in section 4.

2. Review of method

2.1. Elastic scattering

To see the essence of the method it is useful first to consider the case of s-wave potential scattering, for which the Hamiltonian is

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R). \quad (2)$$

The resulting expression is essentially a direct utilization of eq. (1) in the formally exact expression for the scattering operator, $T = V + VG^+(E)V$. Specifically, the S-matrix is given in the present method as

$$S = 1 - \frac{4i}{\hbar} \left(\langle \Phi | V | \Phi \rangle + \sum_{t,t'=0}^N \langle \Phi | V | u_t \rangle (\langle u_t^* | E - H | u_{t'} \rangle)^{-1} \langle u_{t'}^* | V | \Phi \rangle \right), \quad (3)$$

where the plane wave Φ is normalized as

$$\Phi(R) = \sqrt{v^{-1}} \sin(kR), \quad (4)$$

$v = \hbar k / \mu$, and $\{u_t(R)\}$, $t = 1, \dots, N$ is some (real) square integrable basis set. The function $u_0(R)$ enforces the outgoing wave boundary conditions of the problem; it is regular at the origin, and its asymptotic form is

$$\lim_{R \rightarrow \infty} u_0(R) \approx \exp(ikR). \quad (5a)$$

Our choice for $u_0(R)$ is

$$u_0(R) = [1 - \exp(-\lambda R)] \exp(ikR), \quad (5b)$$

though this is not unique. The reader should see ref. [1] for the derivation of this variational result and a more complete discussion of its characteristics and relation to other approaches.

In most applications it is more satisfactory to use a distorted-wave representation rather than the plane-wave representation in eq. (3). If $V_0(R)$ is the zeroth-order (distorting) potential and $V' = V - V_0$, then eq. (3) is modified as follows

$$S = S^{(0)} - \frac{4i}{\hbar} \left(\langle \chi^{(-)} | V' | \chi^{(+)} \rangle + \sum_{t,t'=0}^N \langle \chi^{(-)} | V' | u_t \rangle (\langle u_t^* | E - H | u_{t'} \rangle)^{-1} \langle u_{t'}^* | V' | \chi^{(+)} \rangle \right), \quad (6a)$$

where here $\chi^{(\pm)}$ is the regular scattering solution for the potential $V_0(R)$ with asymptotic form

$$\chi^{(\pm)} \underset{R \rightarrow \infty}{\approx} \exp(\pm i\eta) \sqrt{v^{-1}} \sin(kR + \eta), \quad (6b)$$

η being the phase shift for potential V_0 ; $S^{(0)} = \exp(2i\eta)$. We note also that since

$$V' | \chi^{(\pm)} \rangle = (H - E) | \chi^{(\pm)} \rangle, \quad (7)$$

the matrix element of V' in eq. (6a) may be equivalently expressed also as matrix elements of $H - E$. In general, the better the distorted wave representation, i.e. the closer V_0 is to V and thus the smaller V' , the smaller is the basis set $\{u_t\}$ that is required to obtain converged result.

2.2. Inelastic and reactive scattering

The above expressions are generalized in a straightforward manner to treat inelastic and reactive scattering. Since the reactive case was dealt with only cursorily before [1], we consider it in more detail here. Specifically, we consider a general reactive system with N possible asymptotic arrangements of particles, with γ being the arrangement channel label; non-reactive scattering is the special case of only one asymptotic arrangement. The total Hamiltonian is naturally partitioned in N different ways,

$$H = H_\gamma + V_\gamma, \quad (8a)$$

where H_γ is the Hamiltonian which describes arrangement γ asymptotically, and V_γ is the interaction potential in arrangement γ . If R_γ denotes the radial translational coordinate for arrangement γ , and q_γ the internal coordinates (including the two angles \hat{R}_γ), so that

$$\lim_{R_\gamma \rightarrow \infty} V_\gamma = 0 \quad (8b)$$

or

$$\lim_{R_\gamma \rightarrow \infty} H = H_\gamma, \quad (8c)$$

then H_γ has the generic form

$$H_\gamma = -\frac{\hbar^2}{2\mu_\gamma} \left(\frac{1}{R_\gamma} \frac{\partial^2}{\partial R_\gamma^2} R_\gamma - \frac{\hat{l}_\gamma^2}{R_\gamma^2} \right) + h_\gamma(q_\gamma) + V_\gamma^{(0)}(R_\gamma), \quad (9)$$

where an elastic distortion potential $V_\gamma^{(0)}$ has been included. \hat{l}_γ is the orbital angular momentum operator, and h_γ is the Hamiltonian for the internal degrees of freedom, with eigenfunctions $\{\phi_{n_\gamma}(q_\gamma)\}$ and eigenvalues $\{\epsilon_{n_\gamma}\}$, n_γ being the collective quantum number for all the internal degrees of freedom.

The scattering matrix for a transition from arrangement α to arrangement β , i.e. a chemical reaction, is proportional to matrix elements of the operator $V_\alpha + V_\beta G^+(E) V_\alpha$, where in the present method a variational expression of the $G^+(E)$ has the form of eq. (1). The boundary conditions for the variational approximation require that the basis set used to represent G^+ have outgoing waves in all open channels of all arrangements. We thus chose the following basis

$$u_{t_\gamma}^{n_\gamma}(R_\gamma) \phi_{n_\gamma}(q_\gamma), \quad (10)$$

which is characterized by the composite index $(\gamma, n_\gamma, t_\gamma)$. The translational functions $\{u_{t_\gamma}^{n_\gamma}(R_\gamma)\}$, $t_\gamma \geq 1$, are real, square-integrable functions (distributed Gaussians [8,9] in our calculations), and $u_0^{n_\gamma}(R_\gamma)$ is the special translational function (cf. eq. (5b)) which enforces the correct boundary conditions; we choose it as

$$u_0^{n_\gamma}(R_\gamma) = [1 - \exp(-\lambda R_\gamma)] \exp(ik_{n_\gamma} R_\gamma) R_\gamma^{-1}. \quad (11)$$

The S -matrix element for a typical transition is then the matrix generalization of eq. (6a),

$$S_{\beta n_\beta, \alpha n_\alpha} = S_{\beta n_\beta, \alpha n_\alpha}^{(0)} - \frac{4i}{\hbar} \left(\langle \chi_{\beta n_\beta}^{(-)} | V_\alpha | \chi_{\alpha n_\alpha}^{(+)} \rangle + \sum_{\gamma n_\gamma; t_\gamma} \sum_{\gamma' n_{\gamma'}; t_{\gamma'}} \langle \chi_{\beta n_\beta}^{(-)} | V_\beta | u_{t_\gamma}^{n_\gamma} \phi_{n_\gamma} \rangle (\langle u_{t_{\gamma'}}^{n_{\gamma'}} \phi_{n_{\gamma'}} | E - H | u_{t_\gamma}^{n_\gamma} \phi_{n_\gamma} \rangle)^{-1} \langle u_{t_{\gamma'}}^{n_{\gamma'}} | V_\alpha | \chi_{\alpha n_\alpha}^{(+)} \rangle \right), \quad (12)$$

where the distorted wavefunctions $\chi_{\gamma n_\gamma}^{(\pm)}$ are given by

$$\chi_{\gamma n_\gamma}^{(\pm)}(R_\gamma, q_\gamma) = \phi_{n_\gamma}(q_\gamma) f_{n_\gamma}^{(\pm)}(R_\gamma); \quad (13)$$

the translational function $f_{n_\gamma}^{(\pm)}$ is the (regular) elastic scattering solution satisfying the radial Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu_\gamma} \left(\frac{1}{R_\gamma} \frac{\partial^2}{\partial R_\gamma^2} R_\gamma - \frac{l_\gamma(l_\gamma+1)}{R_\gamma^2} \right) + \epsilon_{\gamma\nu_j l_\gamma} - E + V_\gamma^{(0)}(R_\gamma) \right] f_{n_\gamma}^{(\pm)}(R_\gamma) = 0 \quad (14)$$

with asymptotic normalization similar to eq. (6b), generalized to include orbital angular momentum. It is useful to define the real translational functions f_{n_γ} by

$$f_{n_\gamma}^{(\pm)} = \exp(\pm i\eta_{n_\gamma}) f_{n_\gamma} \quad (15)$$

and then f_{n_γ} has the asymptotic boundary condition

$$f_{n_\gamma} \underset{R_\gamma \rightarrow \infty}{\simeq} \sqrt{v_{n_\gamma}^{-1}} R_\gamma^{-1} [\cos \eta_{n_\gamma} J_{l_\gamma}(k_{\gamma\nu_j l_\gamma} R_\gamma) + \sin \eta_{n_\gamma} N_{l_\gamma}(k_{\gamma\nu_j l_\gamma} R_\gamma)], \quad (16)$$

where J_{l_γ} and N_{l_γ} are spherical Riccati-Bessel functions with the asymptotic forms

$$J_{l_\gamma}(k_{\gamma\nu_j l_\gamma} R_\gamma) \underset{R \rightarrow \infty}{\simeq} \sin(k_{\gamma\nu_j l_\gamma} R_\gamma - \frac{1}{2} l_\gamma \pi) \quad (17a)$$

and

$$N_{l_\gamma}(k_{\gamma\nu_j l_\gamma} R_\gamma) \underset{R \rightarrow \infty}{\simeq} \cos(k_{\gamma\nu_j l_\gamma} R_\gamma - \frac{1}{2} l_\gamma \pi). \quad (17b)$$

Note that only open channel distorted wavefunctions are needed. A full elastic potential matrix is used as the distortion potential.

$$V_\alpha^{(0)}(R_\gamma) = \sum_{n_\gamma} |\phi_{n_\gamma}\rangle \langle \phi_{n_\gamma}| V_\gamma(R_\gamma) |\phi_{n_\gamma}\rangle \langle \phi_{n_\gamma}|. \quad (18)$$

To evaluate the reactive S -matrix elements via eq. (12) there are basically three matrices one needs to calculate; these are defined as

$$A_{n_\beta, n_\alpha} = \langle f_{n_\beta} \phi_{n_\beta} | V_\alpha - V_\alpha^{(0)} | \phi_{n_\alpha} f_{n_\alpha} \rangle, \quad (19a)$$

$$B_{i_\beta n_\beta, n_\alpha} = \langle u_{i_\beta}^{n_\beta} \phi_{n_\beta} | V_\alpha - V_\alpha^{(0)} | \phi_{n_\alpha} f_{n_\alpha} \rangle \quad (19b)$$

and

$$C_{i_\beta n_\beta, i_\alpha n_\alpha} = \langle u_{i_\beta}^{n_\beta} \phi_{n_\beta} | E - H | \phi_{n_\alpha} u_{i_\alpha}^{n_\alpha} \rangle. \quad (19c)$$

We partition the $C_{i_\beta n_\beta, i_\alpha n_\alpha}$ matrix into four matrix blocks as follows:

$$C_{i_\beta n_\beta, i_\alpha n_\alpha} = \begin{pmatrix} C_{i_\beta n_\beta, i_\alpha n_\alpha}^{oo} & C_{i_\beta n_\beta, i_\alpha n_\alpha}^{oc} \\ C_{i_\beta n_\beta, i_\alpha n_\alpha}^{co} & C_{i_\beta n_\beta, i_\alpha n_\alpha}^{cc} \end{pmatrix}, \quad (20)$$

where the superscript o denotes the one translational basis function u_o , which is energy dependent, and c denotes the translational basis functions $u_i(t>0)$, which are energy independent. The zeroth-order S -matrix is

$$S_{\beta n_\beta, \alpha n_\alpha}^{(0)} = \delta_{\beta\alpha} \delta_{n_\beta n_\alpha} \exp(2i\eta_{n_\alpha}). \quad (21)$$

In terms of these partitioned matrices A , B and C , therefore, the final "working formula" for the S -matrix is

$$S = \exp(i\eta) S' \exp(i\eta), \quad (22a)$$

where

$$S' = I - (4i/\hbar)[A + B^T C^{-1} B], \quad (22b)$$

and matrix notation is assumed.

Finally, we note again the identity

$$V_\gamma |\chi_{\gamma n_\gamma}^{(\pm)}\rangle = (H - E) |\chi_{\gamma n_\gamma}^{(\pm)}\rangle \quad (23)$$

for $\gamma = \alpha$ or β , and this shows the obvious way that one can generalize eq. (12) to use a multichannel (non-reactive) distorted-wave representation to lessen further the demands put on the translational basis $\{u_i\}$.

3. Specifics for atom/diatom reactive scattering

We consider now a specific system composed of three atoms, A, B, C, with possible reaction channels $A + BC(\gamma = a)$, $B + CA(\gamma = b)$, $C + AB(\gamma = c)$, where γ is the arrangement label. The Jacobi coordinates for arrangement γ are denoted (r_γ, R_γ) , where r_γ is the interatomic vector of the diatom directed from B to C, C to A, or A to B depending on the channel γ , and R_γ is the vector from the diatom mass center to the remaining atom in the arrangement channel γ . It is convenient to use mass-scaled vectors defined by

$$R_\gamma = \lambda_\gamma R'_\gamma, \quad (24a)$$

$$r_\gamma = \lambda_\gamma^{-1} r'_\gamma, \quad (24b)$$

where R'_γ and r'_γ are the unscaled coordinate vectors. Using α, β , and γ as distinct, cyclic channel indices and denoting the mass of the projector atom in channel γ by m_γ , the scale factors λ_γ are defined as

$$\lambda_\gamma = [m_\gamma(m_\alpha + m_\beta)^2 / m_\alpha m_\beta (m_\alpha + m_\beta + m_\gamma)]^{1/4}. \quad (25)$$

The transformation among the scaled Jacobi coordinates (r_γ, R_γ) for the various channels is an orthogonal transformation,

$$\begin{pmatrix} R_\beta \\ r_\beta \end{pmatrix} = \begin{pmatrix} \cos A_{\beta\alpha} & -\sin A_{\beta\alpha} \\ \sin A_{\beta\alpha} & \cos A_{\beta\alpha} \end{pmatrix} \begin{pmatrix} R_\alpha \\ r_\alpha \end{pmatrix}, \quad (26)$$

where

$$\cos A_{\beta\alpha} = -[m_\beta m_\alpha / (M - m_\beta)(M - m_\alpha)]^{1/2} \quad (27a)$$

and

$$\sin A_{\beta\alpha} = (1 - \cos^2 A_{\beta\alpha})^{1/2}, \quad (27b)$$

where M is the total mass of the system ($M = m_\alpha + m_\beta + m_\gamma$). In terms of the scaled Jacobi coordinates the kinetic energy operator T_γ contains only one reduced mass,

$$\mu = (m_\alpha m_\beta m_\gamma / M)^{1/2}. \quad (28)$$

The following discussion will specifically refer to a case of elastic distortion potential.

The distorted wavefunction of eq. (13) then takes the specific form

$$\chi^{(\pm)} = \phi_{n_\gamma}(r_\gamma, \hat{R}_\gamma) f_{n_\gamma}^{(\pm)}(R_\gamma) \quad (29)$$

where ϕ_{n_γ} is a channel basis function, which is a product of vibrational- and rotational-orbital functions in space-fixed coordinates,

$$\phi_{n_\gamma} = \chi_{\gamma v_\gamma j_\gamma}(r_\gamma) y_{j_\gamma l_\gamma}^{j_\gamma M}(\hat{r}_\gamma, \hat{R}_\gamma). \quad (30)$$

The vibrational functions, $\chi_{\gamma v_\gamma j_\gamma}$, satisfy the usual vibrational eigenvalue equation,

$$\left(-\frac{\hbar^2}{2\mu} \frac{1}{r_\gamma} \frac{\partial^2}{\partial r_\gamma^2} r_\gamma + \frac{\hbar^2}{2\mu} \frac{j_\gamma(j_\gamma+1)}{r_\gamma^2} + V_\gamma^{\text{vib}}(r_\gamma) - \epsilon_{\gamma v_\gamma} \right) \chi_{\gamma v_\gamma}(r_\gamma) = 0, \quad (31)$$

where $\epsilon_{\gamma v_\gamma}$ is a diatomic eigenvalue, and the rotational-orbital functions, $y_{j_\gamma l_\gamma}^{JM}$, are defined in terms of spherical harmonics by [10]

$$y_{j_\gamma l_\gamma}^{JM} = \sum_{m_l, m_j} \langle j_\gamma l_\gamma m_j, m_l | j_\gamma l_\gamma JM \rangle Y_{j_\gamma m_j}(\hat{r}_\gamma) Y_{l_\gamma m_l}(\hat{R}_\gamma), \quad (32)$$

where $\langle j_\gamma l_\gamma m_j, m_l | j_\gamma l_\gamma JM \rangle$ is a Clebsch-Gordan coefficient. To evaluate these matrix elements it is useful to note that the coupled total angular momentum eigenfunctions in space-fixed coordinates can be written as [5]

$$y_{j_\gamma l_\gamma}^{JM}(\hat{R}_\gamma, \hat{r}_\gamma) = \left(\frac{2l_\gamma + 1}{4\pi} \right)^{1/2} \sum_{\Omega_\gamma} \langle j_\gamma l_\gamma \Omega_\gamma 0 | j_\gamma l_\gamma J \Omega_\gamma \rangle Y_{j_\gamma \Omega_\gamma}(\gamma_\gamma, 0) D_{\Omega_\gamma, M}^J(\Phi_\gamma, \Theta_\gamma, \Xi_\gamma), \quad (33)$$

where γ_γ is the angle between vectors \mathbf{R}_γ and \mathbf{r}_γ , $\Phi_\gamma, \Theta_\gamma, \Xi_\gamma$ are three rotational Euler angles, and $D_{\Omega_\gamma, M}^J$ is the Wigner rotation matrix [11]. For translational basis set we used floating Gaussians [8,9], defined as

$$u_{t>0}(R) = R^{-1} \exp[-\alpha_t(R-R_t)^2], \quad (34)$$

where R_t is the center of the t basis function; α_t is chosen for simplicity to be constant for all basis functions, i.e. the Gaussians are equally spaced.

The $B_{l_\beta n_\beta, l_\alpha n_\alpha}$ matrix defined in eq. (19b) is explicitly integrated as

$$\begin{aligned} B_{l_\beta n_\beta, l_\alpha n_\alpha} &= \frac{2\pi [(2l_\beta + 1)(2l_\alpha + 1)]^{1/2}}{2J + 1} \sum_{\Omega_\beta, \Omega_\alpha} \langle j_\beta l_\beta \Omega_\beta 0 | j_\beta l_\beta J \Omega_\beta \rangle \langle j_\alpha l_\alpha \Omega_\alpha 0 | j_\alpha l_\alpha J \Omega_\alpha \rangle \\ &\times \int d \cos \gamma_\alpha \int r_\alpha^2 dr_\alpha \int R_\alpha^2 dR_\alpha u_{l_\beta n_\beta}^{n_\beta}(R_\beta) \chi_{\beta v_\beta}(r_\beta) Y_{l_\beta \Omega_\beta}(\gamma_\beta, 0) (V_\alpha - V_\alpha^{(0)}) d_{\Omega_\alpha, \Omega_\beta}^J(\Delta_{\beta\alpha}) \\ &\times Y_{l_\alpha \Omega_\alpha}(\gamma_\alpha, 0) \chi_{\alpha v_\alpha}(r_\alpha) f_{\alpha v_\alpha}(R_\alpha), \end{aligned} \quad (35)$$

where Ω_β and Ω_α are projection quantum numbers of total angular momentum on body-fixed coordinate Z axes around direction \hat{R}_β and \hat{R}_α , $\Delta_{\beta\alpha}$ is the angle between \hat{R}_β and \hat{R}_α , and $d_{\Omega_\alpha, \Omega_\beta}^J$ is the reduced rotation matrix. We use the standard Jacobi coordinates $r_\alpha^2 dr_\alpha R_\alpha^2 dR_\alpha d \cos \gamma_\alpha$ to evaluate $B_{l_\beta n_\beta, l_\alpha n_\alpha}$ to avoid interpolation because the distorted wavefunction is generated numerically on an evenly spaced grid. For the same reason, we use coordinates [5] $\sin^{-3} \Delta_{\beta\alpha} R_\beta^2 dR_\beta R_\alpha^2 dR_\alpha d \Delta_{\beta\alpha}$, to evaluate the integrals in eq. (19a), where $\Delta_{\beta\alpha}$ is the angle between vectors \mathbf{R}_β and \mathbf{R}_α . The expression for this integral is similar to that for $B_{l_\beta n_\beta, l_\alpha n_\alpha}$ matrix except that the distorted wavefunction replaces the translational basis function. In evaluating the $C_{l_\beta n_\beta, l_\alpha n_\alpha}$ matrix of eq. (19c), we used a new set of integration coordinates, $r_\beta, r_\alpha, \omega_{\beta\alpha}$, where $\omega_{\beta\alpha}$ is the angle between two diatomic vectors \mathbf{r}_β and \mathbf{r}_α . It is not difficult to show that the Jacobian for these coordinates is

$$\sin^{-3} \Delta_{\beta\alpha} r_\beta^2 dr_\beta r_\alpha^2 dr_\alpha d \cos \omega_{\beta\alpha} = r_\alpha^2 dr_\alpha R_\alpha^2 dR_\alpha d \cos \gamma_\alpha. \quad (36)$$

The reason we use these coordinates rather than the standard Jacobi coordinates is because the integrand of the exchange integrals is weighted by two vibrational eigenfunctions, one of each arrangement, which are much more limited in space than the translational functions. For example, the range in r for H_2 vibration eigenfunction $v=5$ is between 0.6 and 3.2 bohr; as a result, many fewer integral points are needed.

4. Results of calculation

We carried out numerical calculations for 3-D $\text{H} + \text{H}_2$ reaction for a broad range of energies on both Porter-Karplus potential surface and LSTH potential surface. The results are very stable with respect to numer-

Table 1

Convergence of 3-D H + H₂ reactive probability $P^R(00 \rightarrow \text{all})$ on LSTH potential surface for $J=0$ with respect to basis functions

E_{tot} (eV)	Number of translational basis functions ^{a)}		
	22	25	28
0.50	1.9(-4)	1.8(-4)	1.8(-4)
0.90	0.46	0.47	0.47
1.30	0.60	0.61	0.61
	number of vibration-rotation basis functions ^{b)}		
	30 ^{c)}	36 ^{d)}	45 ^{e)}
0.50	1.8(-4)	1.8(-4)	1.8(-4)
0.90	0.47	0.47	0.48
1.30	0.60	0.61	0.60

^{a)} Thirty-six vibration-rotation basis functions (12, 10, 8, 6). (This notation means rotational states $j=0, 1, \dots, 11$ for vibrational state $v=0$, rotational states $j=0, \dots, 9$ for $v=1$, and so forth.)

^{b)} Twenty-five translational basis functions.

^{c)} (12, 10, 8). ^{d)} (12, 10, 8, 6). ^{e)} (13, 11, 9, 7, 5).

ical parameters and basis functions. Table 1 shows the cumulative reaction probability from the ground state of H₂ for three typical energies, 0.5, 0.9, and 1.3 eV, representing low, medium, and high energy. The results are given for different sizes of the two types of basis functions, vibration-rotation functions and translational functions, to show the stability and degree of convergence. One sees that a total of 36 vibration-rotation functions and 25 primitive Gaussians are sufficient to converge the calculation for a broad range of energies with up to three vibration states open. It is suggested that the variational character of the method is largely responsible for the numerical stability and fast convergence achieved in the calculation.

Finally, tables 2 and 3 compare our results with those obtained by several other groups on both Porter-Karplus and LSTH potential surfaces. In table 2, for the LSTH potential surface, we note excellent agreement of our results with those of the L^2 method of ref. [7], and table 3, for the Porter-Karplus potential, shows good agreement with results obtained using the hyperspherical coordinate method [16,17].

5. Concluding remarks

This work demonstrates that the S -matrix Kohn method, developed in ref. [1], provides a stable and efficient way for carrying out chemical reactive scattering calculations in 3-D. Furthermore, the methodology is sufficiently general that it is directly applicable to reactions other than "standard" atom-diatom systems.

Our approach is similar in many aspects to other basis set methods, in that the scattering calculation reduces essentially to linear algebra. Its principle advantage compared to others is that it requires calculation only of matrix elements of the Hamiltonian operator itself, there being no appearance of a Green's function for some reference problem. (We note in passing that it is Miller's formulation [5] of reactive scattering, i.e. a coupled channel expansion simultaneously in all arrangements, that necessitates the use of a basis set method, for that formulation produces non-local exchange interactions which couple the various arrangements. Use of hyperspherical coordinates [16,17] or matching methods [15] are alternate formulations that do not lead to non-local interactions and thus can be treated with local propagation algorithms.)

At this stage in the methodological development it would be useful to incorporate various technologies developed in quantum chemistry for handling the large linear algebra part of the calculations. In particular, one needs

Table 2

Distinguishable H+H₂ reactive probability (P_{00-0}^R), summed over final rotational states for total angular momentum $J=0$, and on LSTH potential surface

E_{tot} (eV)	WL ^{a)}	WSL ^{b)}	CS ^{c)}	L^2 ^{d)}	Present
0.50			2.4(-4)	1.8(-4)	1.8(-4)
0.55				3.0(-3)	3.06(-3)
0.60	0.050	0.036	0.025	0.036	0.036
0.65	0.247	0.195		0.20	0.20
0.70	0.358	0.333		0.34	0.34
0.80	0.364	0.349	0.27	0.36	0.36
0.85	0.432	0.397	0.30	0.41	0.41
0.90	0.506	0.464	0.37	0.47	0.47
0.95	0.433	0.450	0.38	0.47	0.47
1.00	0.347	0.386	0.32	0.39	0.39
1.05	0.395	0.417	0.36	0.44	0.47
1.10	0.469			0.50	0.50
1.15					0.48
1.20	0.287			0.45	0.45
1.25					0.48
1.30				0.50	0.51
1.35					0.51
1.40				0.49	0.49
1.45					0.49
1.50				0.51	0.52

^{a)} Ref. [12]. ^{b)} Ref. [13]. ^{c)} Ref. [14]. ^{d)} Ref. [7].

Table 3

Distinguishable H+H₂ reactive probability from initial ground state to several final states for total angular momentum $J=0$ on Porter-Karplus potential surface

E_{tot} (eV)	$P(0, 0 \rightarrow 0, j)$	SK ^{a)}	PP ^{b)}	Present
0.65	0	0.085		0.087
	1	0.160		0.162
	2	0.097		0.098
0.70	0	0.095	0.086	0.087
	1	0.180	0.173	0.176
	2	0.120	0.122	0.122
0.75	0	0.072		0.076
	1	0.157		0.162
	2	0.127		0.132
0.80	0	0.071		0.071
	1	0.161	0.152	0.154
	2	0.135	0.136	0.136
1.00	0	0.130	0.128	0.127
	1	0.230	0.200	0.205
	2	0.068	0.082	0.083

^{a)} Ref. [15]. ^{b)} Ref. [16].

to explore the possibility of basis set contractions to reduce the number of basis functions. It would also be useful to see if the use of a multi-channel distorted-wave representation [18] would significantly reduce the size of the basis set required.

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