

Reactant-product decoupling method for state-to-state reactive scattering: A case study for 3D H+H₂ exchange reaction (*J*=0)

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In this paper, we present theoretical and computational details of implementing the recently developed reactant-product decoupling (RPD) method (J. Chem. Phys. **105**, 6072 (1996)) for state-to-state quantum reactive scattering calculations of the prototypical H + H₂ reaction in three dimensions. The main purpose of this paper is to explore important features of the RPD scheme for use as a general and efficient computational approach to study state-to-state quantum dynamics for polyatomic reactions by using 3D H + H₂ as an example. Specific computational techniques and numerical details are explicitly provided for efficient application of this method in the time-dependent (TD) implementation. Using the RPD method, the calculated state-to-state reaction probabilities for the 3D H + H₂ reaction are in excellent agreement with those from the time-independent variational calculations, and the computational cost of the RPD method is significantly lower than other existing TD methods for state-to-state dynamics calculations.

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I. INTRODUCTION

It is well known to the reactive scattering community that perhaps the most difficult problem in quantum reactive scattering theory is the choice of coordinates. If only total reaction probabilities (i.e., probabilities summed over final states of the product arrangement) are needed, it is quite reasonable (and often very efficient) to employ the Jacobi coordinates of the reactant arrangement to carry out the scattering calculation, as has been demonstrated successfully by recent time-dependent (TD) calculations for the reaction of H₂ + OH,¹⁻⁵ and more recently, its reverse reaction H + H₂O.⁶ However, the use of a single set of Jacobi coordinates (corresponding to either reactant or product) in complete state-to-state quantum dynamics calculation is very inefficient, if not computationally impossible. This is clearly evidenced by recent TD dynamics calculations of state-to-state reaction probabilities for the H₂ + OH reaction^{7,8} and its reverse reaction.⁹ These state-to-state calculations employed the reactant Jacobi coordinates in wavepacket propagation⁷⁻⁹ and required substantially more computational resources (memory and cpu time) than calculations of total reaction probabilities.^{1,2} These state-to-state calculations are now only possible on very large and fast workstations even for the H₂ + OH reaction.

In a preceding paper,¹⁰ we developed a general and efficient approach for state-to-state quantum reactive scattering calculation for polyatomic reactions. In that paper, we proposed a general reactant-product decoupling (RPD) scheme to separate the dynamics calculation of the reactant component of the wavefunction from those of product components. The main attraction of the RPD approach is that the overall computational effort is divided into that for each arrangement channel, and the scattering calculation for each arrangement component wavefunction can be carried out individually using the Jacobi coordinates of the corresponding arrangement channel. It is a divide and conquer strategy de-

vised to minimize the computational cost in state-to-state reactive scattering calculation to essentially the sum of separate dynamics calculations in each arrangement. The RPD scheme is quite general and can be implemented in both time-dependent and time-independent applications¹⁰ although the emphasis of our current research is in time-dependent implementation of the approach.

The basic strategy of the RPD scheme is to partition the full TD wavefunction into a sum of reactant component (Ψ_r) and all product components (Ψ_p ($p=1,2,3,\dots$)) that satisfy the following *decoupled* equations¹⁰

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\Psi_r(t)\rangle &= H |\Psi_r(t)\rangle - i \sum_p V_p |\Psi_r(t)\rangle \\ i\hbar \frac{\partial}{\partial t} |\Psi_p(t)\rangle &= H |\Psi_p(t)\rangle + i V_p |\Psi_r(t)\rangle \end{aligned} \quad (1)$$

where H is the full Hamiltonian and $-iV_p$ is the negative imaginary potential (absorbing potential) employed to completely absorb the wavefunction $\Psi_r(t)$ in a narrow strip separating the reactant from the product to prevent it from entering the p th product arrangement. Eq. (1) is *decoupled* in the sense that the solution for $\Psi_r(t)$ is independent of those for $\Psi_p(t)$ and the latter are independent of each other. If we sum over the equations for all the component wavefunctions in Eq. (1), we recover the original Schrödinger equation for the full wavefunction. It is noted that solving for $\Psi_r(t)$ is completely independent of that for $\Psi_p(t)$, and $\Psi_r(t)$ is the correct representation of the full scattering wavefunction in the reactant and strong interaction regions where V_p is zero,¹⁰ provided that the absorbing potential is sufficiently smooth as will be discussed later. The second equation in Eq. (1) is an inhomogeneous equation with a time-dependent source term $iV_p\Psi_r(t)$ that provides the driving force towards the asymptotic region in the p th product arrangement space. Since the product component wavefunction $\Psi_p(t)$

needs to be nonzero only in the corresponding p th product space starting from where V_p becomes nonzero, its calculation involves only an inelastic propagation in that particular arrangement, completely independent of component wavefunctions of other product arrangements. Thus the RPD method naturally allows us to use different Jacobi coordinates to calculate different arrangement component wavefunctions. Because the source term $V_p\Psi_p(t)$ is confined to the reactant-product transition region only which is defined by the absorbing potential V_p ,¹⁰ one does not need to calculate the full overlap matrix between basis functions of reactant and product arrangements for the source term.

This paper is organized as follows: Section II presents the methodologies for solving the RPD equations and gives specifics for applying the RPD method to the state-to-state calculation for the prototype H + H₂ reaction in three dimensions. Section III gives numerical details and comparisons of the state-to-state reaction probabilities from the present RPD calculation with those from a previous time-independent variational calculation. Section IV gives a summary of the present work and a prospective on future applications of the RPD method to polyatomic reactions.

II. THEORY

A. Solution of Ψ_r in the reactant Jacobi coordinates

The numerical methods for solving $\Psi_r(t)$ in Eq. (1) has been well developed for TD calculations of total reaction probabilities for atom-diatom reactions¹¹ and for diatom-diatom reactions^{1,2} in which the absorbing potentials V_p are placed just beyond the transition state region to completely absorb the wavefunction in order to prevent reflection.¹² Such TD calculation for Ψ_r in general can be efficiently carried out by using the Jacobi coordinates of the reactant arrangement, and the basic procedures of wavepacket propagation are identical to those described in Ref. 2. The main difference in the present calculation for Ψ_r , however, is that we do not discard the absorbed piece of wavefunction $V_p\Psi_p(t)$ but instead store them in a proper representation on computer disk for later calculation of the product component(s) $\Psi_p(t)$.¹⁰ For that purpose, we devised a collocation quadrature (CQ) scheme to make this procedure computationally efficient. We will discuss the CQ method for this application later in the paper. Since the source term $V_p\Psi_r$ has to be generated first, we will first describe the basic formalisms used in the TD propagation of wavefunction $\Psi_r(t)$ for an atom-diatom reaction.

For an atom-diatom reaction A + BC, there are two possible products (neglecting three body fragments): B + AC and C + AB as shown in Fig. 1. For a fixed total angular momentum J , the Hamiltonian of the system can be expressed in terms of the Jacobi coordinates of the reactant arrangement A + BC,

$$H = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + \frac{(\mathbf{J}-\mathbf{j})^2}{2\mu_R R^2} + \frac{\mathbf{j}^2}{2\mu_r r^2} + V(\mathbf{r}, \mathbf{R}) + h(r), \quad (2)$$

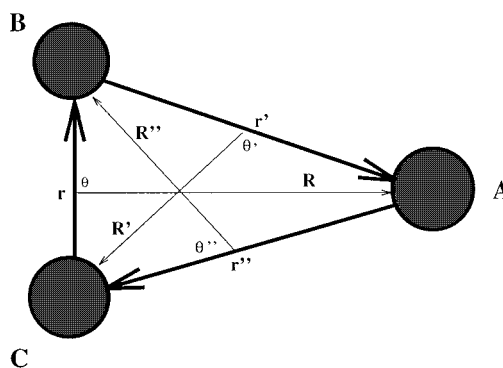


FIG. 1. Jacobi coordinates for a triatomic system ABC.

where μ_R is the reduced mass between the center-of-mass of A and BC, \mathbf{J} the total angular momentum operator of the system, \mathbf{j} the rotational angular momentum operator of BC, and μ_r the reduced mass of BC. The diatomic reference Hamiltonian $h(r)$ is defined as

$$h(r) = -\frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} + V_r(r), \quad (3)$$

where V_r is a diatomic reference potential (usually chosen as an asymptotic diatomic potential). The time-dependent wavefunction Ψ_r satisfying the absorbing boundary condition can be expanded in terms of the BF (body-fixed) translational-vibrational-rotational basis $\{u_n^v(R)\phi_v(r)Y_{jK}^{JM\epsilon}(\hat{R}, \hat{r})\}$ as

$$\Psi_{r, v_0 j_0 K_0}^{JM\epsilon}(\mathbf{R}, \mathbf{r}, t) = \sum_{n, v, j, K} F_{nvjK, v_0 j_0 K_0}^{JM\epsilon}(t) u_n^v(R) \times \phi_v(r) Y_{jK}^{JM\epsilon}(\hat{R}, \hat{r}), \quad (4)$$

where n is the translational basis label, M is the projection quantum number of J on the space fixed z axis, (v_0, j_0, K_0) denotes the initial rovibrational state, and ϵ is the parity of the system defined as $\epsilon = (-1)^{j+L}$ with L being the orbital angular momentum quantum number.

The functions $\phi_v(r)$ are eigenfunctions of the diatomic Hamiltonian of Eq. (3). The definition of the nondirect product basis functions $u_n^v(R)$ is given in Ref. 2. For the sake of clarity, we omit the labels $v_0 j_0 K_0$ and $JM\epsilon$ in the following discussion.

The split-operator propagation scheme for wavepacket propagation is given as,¹³

$$\Psi_r(\mathbf{R}, \mathbf{r}, t + \Delta) = e^{-iH_0\Delta/2} e^{-iU\Delta} e^{-iH_0\Delta/2} \Psi_r(\mathbf{R}, \mathbf{r}, t), \quad (5)$$

where the reference Hamiltonian H_0 is defined as,

$$H_0 = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + h(r), \quad (6)$$

and the effective potential operator U in Eq. (5) is defined as

$$U = \frac{(\mathbf{J}-\mathbf{j})^2}{2\mu_R R^2} + \frac{\mathbf{j}^2}{2\mu_r r^2} + V(R, r, \theta) = V_{\text{rot}} + V. \quad (7)$$

The matrix version of Eq. (5) for the expansion coefficient vector \mathbf{F} is then given by

$$\mathbf{F}(t + \Delta) = e^{-i\mathbf{H}_0\Delta/2} e^{-i\mathbf{U}\Delta} e^{-i\mathbf{H}_0\Delta/2} \mathbf{F}(t) \quad (8)$$

and the operator $e^{-i\mathbf{U}\Delta}$ is further split as

$$e^{-i\mathbf{U}\Delta} = e^{-iV_{\text{rot}}\Delta} e^{-iV\Delta} e^{-iV_{\text{rot}}\Delta}, \quad (9)$$

where V_{rot} is diagonal in angular momentum basis representation and V is diagonal in coordinate representation.²

The initial wavefunction is chosen as the product of a specific rovibrational eigenfunction and a localized translational wavepacket,

$$\Psi_i(0) = \varphi_{k_0}(R) \phi_{v_0j_0}(r) Y_{j_0k_0}^{JM\epsilon}(\hat{R}, \hat{r}), \quad (10)$$

where the wavepacket $\varphi_{k_0}(R)$ is chosen to be a standard Gaussian function

$$\varphi_{k_0}(R) = \left(\frac{1}{\pi\delta^2} \right)^{1/4} \exp[-(R-R_0)^2/2\delta^2] e^{-ik_0R}. \quad (11)$$

The exact rovibrational function $\phi_{v_0j_0}(r)$ of BC is expanded in terms of the reference vibrational functions $\phi_v(r)$ to generate the coefficient vector of the wavefunction at $t = 0$.

B. Propagation of Ψ_p in the product arrangement

In the RPD approach, one calculates the Ψ_p component wavefunction *independently* of other product components. The most straightforward approach is to directly calculate the TD wavefunction $\Psi_p(t)$ in Eq. (1) by using a short time propagator such as the split-operator method as described in Ref. 10

$$|\tilde{\Psi}_p(t + \Delta)\rangle = e^{-\frac{i}{\hbar}H\Delta} |\tilde{\Psi}_p(t)\rangle + \frac{\Delta}{\hbar} V_p |\Psi_r(t + \Delta)\rangle, \quad (12)$$

where $\tilde{\Psi}_p(t) = \Psi_p(t) + \Delta/2\hbar V_p \Psi_r(t)$. Since $\tilde{\Psi}_p(t)$ is everywhere the same as $\Psi_p(t)$ except in the absorbing region, we could directly use $\tilde{\Psi}_p(t)$ to extract the final state dynamics such as state-to-state S matrix elements or reaction probabilities. In this TD approach, we need to store the calculated source term $\xi_p(t) = V_p \Psi_r(t)$ from the previous section on computer disk at every time step which requires one to represent the $\xi_p(t)$ in Jacobi coordinates of the product arrangement. We will discuss an efficient collocation quadrature method to handle this coordinate transformation efficiently in order to minimize the computational cost.

An alternative approach is to use the time-independent version of Eq. (1)

$$E |\psi_r(E)\rangle = H |\psi_r(E)\rangle - i \sum_p V_p |\psi_r(E)\rangle \quad (13)$$

$$E |\psi_p(E)\rangle = H |\psi_p(E)\rangle + i V_p |\psi_r(E)\rangle$$

and solve the TI product wavefunction $\psi_p(E)$ by

$$|\psi_p(E)\rangle = iG^+(E) V_p |\psi_r(E)\rangle$$

$$= \frac{1}{\hbar} \int_0^\infty dt e^{\frac{i}{\hbar}Et} e^{-\frac{i}{\hbar}Ht} V_p |\psi_r(E)\rangle, \quad (14)$$

where the homogeneous term is zero. In Eq. (14), the wavefunction $\psi_p(E)$ is obtained by propagating the energy-dependent wavepacket $\xi_p(E) = V_p \psi_r(E)$ and performing the Fourier transform afterwards for each desired energy. The wavefunction $\psi_r(E)$ is obtained by Fourier transforming the time-dependent wavefunction $\psi_r(t)$ which is obtained by wavepacket propagation described above. This approach is attractive if dynamics at a limited number of energies are desired because in this case, we only need to store the source term $\xi_p(E) = V_p \psi_r(E)$ for the number of energies needed.

Essentially all the detailed formulas of basis functions described previously for propagating $\Psi_r(t)$ can be used for calculating $\Psi_p(t)$ in Eq. (12) or $\Psi_p(E)$ in Eq. (14), except that definitions of the basis functions are for the p th product arrangement instead of the reactant arrangement. For simplicity we use primes to denote all quantities defined in the product arrangement to distinguish them from those of reactant arrangement (unprimed ones). Since the product wavefunction $\Psi_p(t)$ is zero in the strong interaction region, the propagation of Ψ_p only involves an inelastic process and therefore the basis set used to represent $\Psi_p(t)$ is considerably smaller than that of $\Psi_r(t)$ described in the previous section. Consequently, the computational cost for calculating $\Psi_p(t)$ is generally insignificant compared to that for $\Psi_r(t)$.

After the wavepacket is fully developed in the inelastic region of the specific product arrangement with proper absorbing boundary conditions, one can straightforwardly perform the final state analysis in the asymptotic region (R' large) to obtain the energy-dependent S matrix elements or reaction probabilities by Fourier transforming the TD wavefunction $\Psi_p(t)$ to $\Psi_p(E)$ at large asymptotic distance

$$\psi_p(E) \xrightarrow{R' \rightarrow \infty} \sqrt{\frac{\mu_p}{2\pi\hbar^2}} \left[\sum_m S_{pm,ri} \frac{e^{ik_m R'}}{\sqrt{k_m}} |\eta_{pm}\rangle \right], \quad (15)$$

where μ_p is the reduced translational mass and η_{pm} the internal channel function in the p th product arrangement. If any long range elastic potential is present such as the centrifugal potential, one needs to replace the plane wavefunction $e^{ik_m R'}$ by the outgoing Hankel or other appropriate radial function. Alternatively, if only the square of the S matrix element or reaction probability is required, one can avoid specifying the specific form of the radial function by evaluating the flux to obtain converged reaction probabilities at a relatively shorter radial distance.¹⁴

C. Transformation of Jacobi coordinates between arrangements

Since the reactant wavefunction $\Psi_r(t)$ is expressed in terms of basis functions defined in the reactant Jacobi coordinates while $\Psi_p(t)$ is defined in terms of the product basis function, we need to perform coordinate transformation between reactant and product arrangements. The transformation of Jacobi coordinates from the reactant arrangement A + BC (\vec{R}, \vec{r}) to the product arrangement C + AB (\vec{R}', \vec{r}') is given by (cf. Fig. 1)

$$\begin{pmatrix} \vec{R}' \\ \vec{r}' \end{pmatrix} = \begin{pmatrix} a_2 & a_3 \\ 1 & a_1 \end{pmatrix} \begin{pmatrix} \vec{R} \\ \vec{r} \end{pmatrix}, \quad (16)$$

where $a_1 = -m_C/(m_C + m_B)$, $a_2 = -m_A/(m_A + m_B)$, and $a_3 = a_1 a_2 - 1$. By inverting the matrix relation, one can obtain the transformation formula from AB + C to A + BC as well.

In scalar form, the above transformation relation can be explicitly written as

$$\begin{aligned} r' &= \sqrt{R^2 + (a_1 r)^2 + 2a_1 R r \cos \theta}, \\ R' &= \sqrt{(a_2 R)^2 + (a_3 r)^2 + 2a_2 a_3 R r \cos \theta}, \end{aligned} \quad (17)$$

$$\cos \theta' = \frac{1}{R' r'} (a_2 R^2 + a_1 a_3 r^2 + (a_1 a_2 + a_3) R r \cos \theta).$$

Similarly, one can obtain the transformation relation from A + BC to B + AC,

$$\begin{aligned} r'' &= \sqrt{R^2 + (b_1 r)^2 + 2b_1 R r \cos \theta}, \\ R'' &= \sqrt{(b_2 R)^2 + (b_3 r)^2 + 2b_2 b_3 R r \cos \theta}, \end{aligned} \quad (18)$$

$$\cos \theta'' = \frac{1}{R'' r''} (b_2 R^2 + b_1 b_3 r^2 + (b_1 b_2 + b_3) R r \cos \theta),$$

with $b_1 = m_B/(m_C + m_B)$, $b_2 = m_A/(m_A + m_C)$, and $b_3 = b_1 b_2 - 1$.

D. A general collocation-quadrature scheme

In order to carry out the TD propagation for Ψ_p , we need to re-express the source term $\xi_p(t) = V_p \Psi_r(t)$ in terms of the product basis set. This involves the numerical calculation for the expansion coefficients

$$\xi_{pn}(t) = \langle \phi_n | \xi_p(t) \rangle, \quad (19)$$

where ϕ_n are N basis functions of the product arrangement. Because $\xi_p(t)$ and ϕ_n are defined with respect to basis functions of different arrangement, the numerical evaluation of Eq. (19) involves a coordinate transformation between reactant and product arrangements as described in the previous subsection. This can be computationally expensive since the numerical integrations are inherently multidimensional, and the transformation has to be done at each time step. Therefore efficient methods have to be used to minimize the computational cost for this step. For this purpose, we devised a collocation quadrature scheme to efficiently calculate the integral in Eq. (19). For clarity, we drop the subscript p and the variable t in the following discussion.

The integral in Eq. (19) can be evaluated by a N term summation

$$\xi_n = \sum_i W_{ni} \xi(\bar{q}_i), \quad (20)$$

where \bar{q}_i are N prefixed multidimensional points of the Jacobi coordinates defined in the product arrangement and W_{ni} is an undetermined weighting matrix. For an atom-diatom system, ϕ_n is the product of translation, vibration and

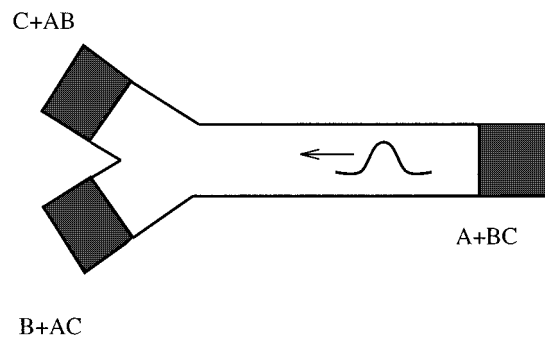


FIG. 2. The locations of various absorbing potentials.

rotation functions and \bar{q}_i denotes (R_i, r_i, θ_i) . The matrix W_{ni} is obtained by a simple matrix inversion

$$\mathbf{W} = \mathbf{\Phi}^{-1}, \quad (21)$$

where the matrix element Φ_{ni} is just the value of ϕ_n at the quadrature point (\bar{q}_i) . This collocation choice of the weighting matrix guarantees that the orthogonality of the overlap integral is strictly preserved

$$\langle \phi_n | \phi_m \rangle = \sum_i W_{ni} \Phi_{im} = \delta_{nm}, \quad (22)$$

and the summation in Eq. (20) will be exact if the function ξ span the N -dimensional vector space of ϕ_n . If the basis functions are not orthogonal, Eq. (21) is easily generalized to

$$\mathbf{W} = \mathbf{O} \mathbf{\Phi}^{-1}, \quad (23)$$

where \mathbf{O} is the basis overlap matrix $O_{nm} = \langle \phi_n | \phi_m \rangle$. Although the choice of N points can be rather arbitrary as long as the inverse $\mathbf{\Phi}^{-1}$ exists, it is best to use good quadrature points to minimize the numerical error. For direct product basis functions, a natural choice is DVR (discrete variable representation) points. For non-direct product basis functions, the choice of good points remains to be explored.

III. RESULTS

In this section, we present the first numerical implementation of the RPD method to the case study of 3D H + H₂ reaction for zero total angular momentum ($J=0$) on the LSTH potential energy surface.¹⁵ Through this numerical example, we hope to gain some experiences in choosing various numerical parameters in order to maximize the efficiency of the RPD method for practical applications. Although this is an atom-diatom application, the computational strategy discussed here is generally applicable to reactive scattering involving more than three atoms.

The most sensitive parameters are perhaps those of absorbing potentials defined in terms of the radial coordinate of the product B + AC.

$$V_{\text{abs}} = -i\alpha \left[\frac{R' - R'_1}{R'_2 - R'_1} \right]^\beta, \quad R'_1 < R < R'_2 \quad (24)$$

as schematically illustrated in Fig. 2. The R'_1 and $R'_2 - R'_1$ determine the starting position and the width of the absorb-

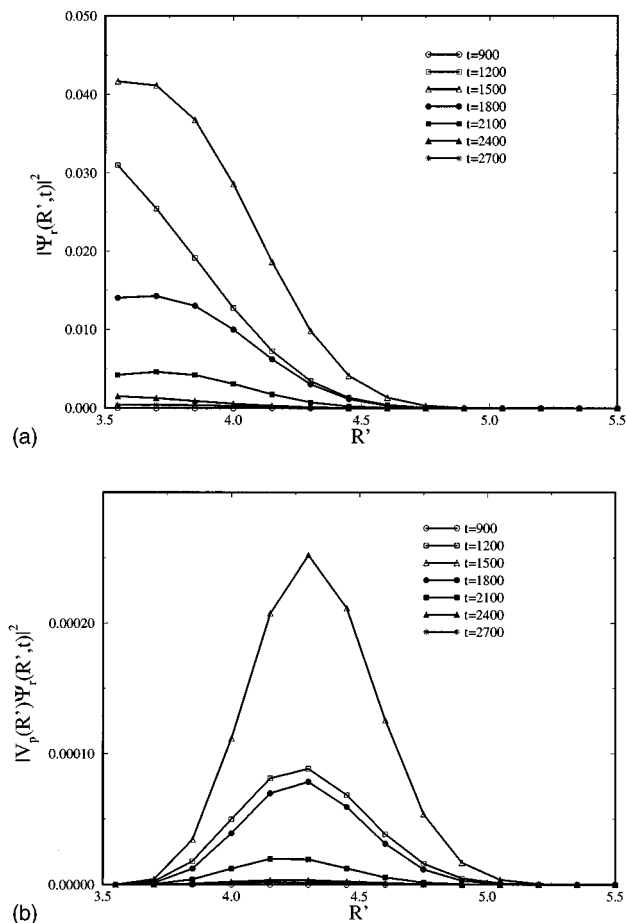


FIG. 3. (a) The absolute square of the component wavefunction $|\Psi_r(t)|^2$ plotted as a one-dimensional function of the radial coordinate of the product arrangement at various propagation times. The other two internal degrees of freedom have been integrated out. (b) The absolute square of the source term $|V_p \Psi_r(t)|^2$ plotted as a one-dimensional function of the radial coordinate of the product arrangement at various propagation times.

ing potential, respectively. The absorbing potentials used to block the product arrangements have been tested extensively for H + H₂. We found that excellent results can be obtained for $R'_1 \geq 3.25a_0$ and $R'_2 - R'_1 \geq 1.75a_0$. The value of α is generally in the range of [0.05, 0.15] a.u. and β between 1.0 and 3.0. Figure 3(a) shows one-dimensional plots of the wavefunction $\Psi_r(t)$ at various propagation times as a function of the radial coordinate R' of the product arrangement where the absorbing potential V_p is defined in the range of $3.5a_0$ to $5.5a_0$. No observable reflections are present in the plots of Fig. 3(a) and the wavefunctions are fully absorbed at $R' = 5.5a_0$. It turns out that state-to-state reaction probabilities are more sensitive to parameters of the absorbing potential than total reaction probabilities. This is expected because state-to-state dynamics is more sensitive to details of the potential energy surface. Therefore more care needs to be exercised in choosing the absorbing parameters in order to obtain accurate state-to-state S matrix elements or reaction probabilities. Similar plots are shown in Fig. 3(b) for the source term $\xi_p(t) = V_p \Psi_r(t)$. Here we see that the R' -dependence of $\xi_p(t)$ behaves exactly as expected: it has

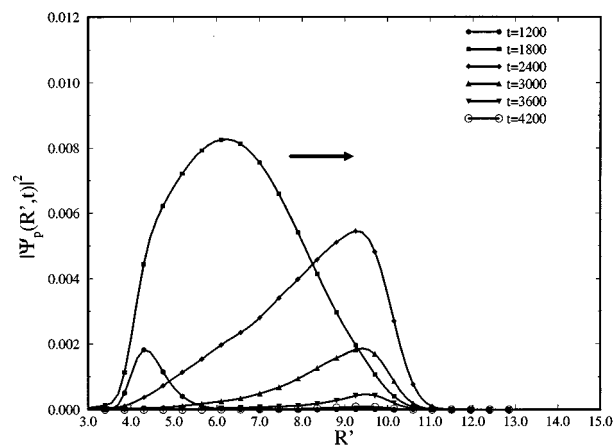


FIG. 4. Same as Fig. 2 except for the product component wavefunction $|\Psi_p(t)|^2$.

maxima in the middle of the absorbing region and decays to zero toward both ends of the absorbing region.

The propagation of $\Psi_p(t)$ in the product arrangement is quite straightforward and relatively trivial in comparison to that of $\Psi_r(t)$ since it only involves an inelastic propagation. For example, only four H₂ vibrational functions are used in the basis expansion of $\Psi_p(t)$ compared to about 30 H₂ vibrational functions used in the expansion of $\Psi_r(t)$. Thus only four collocation-quadrature points are used in the r' coordinate in Eq. (20). The number of rotational functions are also reduced by a factor of 2 in the calculation of $\Psi_p(t)$. Figure 4 shows one-dimensional plots of the wavefunction $\Psi_p(t)$ as a function of the radial coordinate R' in which vibrational and rotational degrees of freedom are integrated out. It is clear from Fig. 4 that $\Psi_p(t)$ is negligible in the strong interaction region and picks up amplitude when getting close to $R' = 3.5a_0$ where the absorbing potential is turned on. This is exactly what we expected $\Psi_p(t)$ to be because $\Psi_r(t)$ is a good representation of the full wavefunction already except near and in the absorbing region.

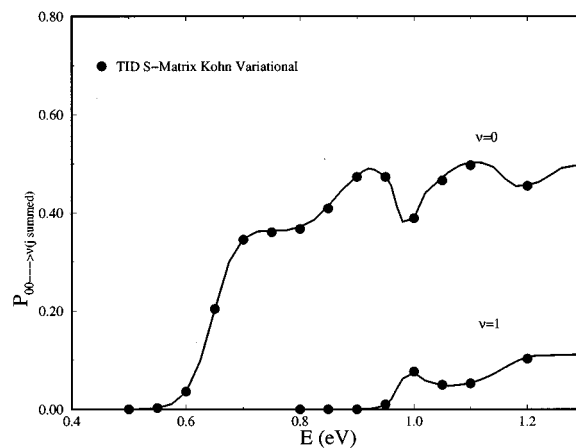
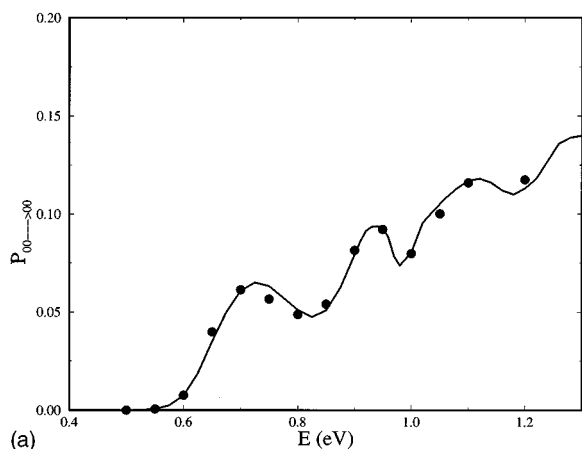
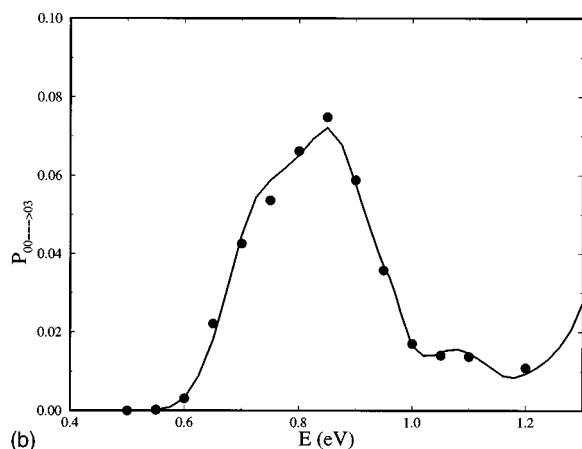


FIG. 5. Comparison of final vibration specific reaction probabilities obtained from the present TD RPD calculation and from the time-independent variational calculation of Ref. 16.



(a)



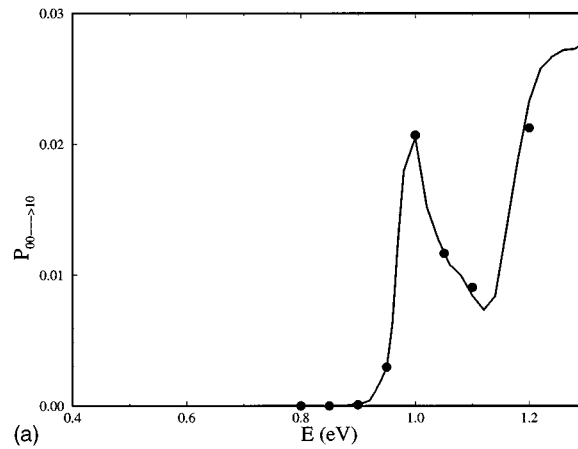
(b)

FIG. 6. Comparison of final rovibration specific reaction probabilities obtained from the present TD RPD calculation and from the time-independent variational calculation. Curves are different rotational states of the product H₂ at ground vibrational state ($v = 0$). Black dots denote the results from the time-independent variational calculation of Ref. 16.

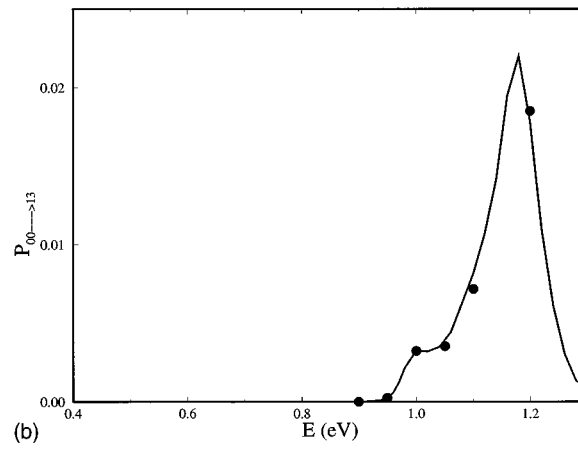
For convenience of easy plotting, the reaction probabilities from the present calculation are compared to those from a previous time-independent S matrix Kohn variational calculation.¹⁶ The results of Ref. 16 are in mutual good agreement with other time-independent calculations including those of Refs. 17 and 18. All results presented here are for reaction from the ground initial state. Figure 5 shows a plot of H + H₂ reaction probabilities to final vibrational states (summed over final rotational states). These results are in excellent agreement with the time-independent calculation at all energies shown in the figure. The complete state-to-state reaction probabilities are also compared to the time-independent calculation in Figs. 6 and 7. Figure 6 shows the energy-dependence of rotational state-selected reaction probabilities with the product at ground vibration ($v = 0$). These state-to-state probabilities are also in excellent agreement with the time-independent calculation. Similar results are shown in Fig. 7 for the diatomic product at the excited vibrational state ($v = 1$).

IV. DISCUSSIONS AND PROSPECTIVES

In this paper we presented a numerical application of the recently developed RPD method to the three-dimensional H



(a)



(b)

FIG. 7. Same as Fig. 6 except for the product H₂ at excited ($v = 1$) vibrational state.

+ H₂ reaction. Our calculation shows that the state-to-state reaction probabilities are generally more sensitive to parameters of the absorbing potentials than total reaction probabilities. Thus we need to exercise more care in choosing the absorbing parameters. The major computational cost of the RPD method is in the calculation of $\Psi_r(t)$ and the coordinate transformation performed on the source term $\xi_p(t) = V_p \Psi_r(t)$ while the inelastic calculation of Ψ_p is relatively insignificant. We introduced an efficient collocation-quadrature scheme to minimize the computational cost associated with transforming the source term between the reactant and product arrangement. The calculated state-to-state reaction probabilities for H + H₂ using the present RPD method are in excellent agreement with those from the time-independent variational calculation. Similarly good results have also been obtained for the D + H₂ reaction.¹⁹ The RPD scheme is a general and efficient computational approach to study state-to-state reaction dynamics for polyatomic systems. The collocation-quadrature (CQ) scheme is a general and efficient numerical approach for fast and accurate evaluation of integrals involving any basis set expansion. Its potential application to integrals involving multidimensional, non-direct product basis functions is very promising. For future application of the TD RPD method, we

need to develop more efficient basis function optimization techniques in order to drastically reduce the number of basis functions in the wavefunction expansion. Recently, extensions of the RPD method to more general applications have also been presented.²⁰

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