

Time-Dependent Wave Packet Approach to State-to-State Reactive Scattering and Application to H + O₂ Reaction

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The time-dependent (TD) wave packet approach which we have been pursuing recently is extended to the calculation of state-to-state **S** matrix elements for reactive scattering in three dimensions for the H + O₂ reaction. Three specific methods for extracting state-to-state **S** matrix elements and reaction probabilities from the time-dependent wave packet propagation are specifically discussed in this paper. These methods are based, respectively, on the time correlation function expression for **S** matrix elements, scattering amplitude expression for **S** matrix elements, and flux formula for reaction probabilities. The implementation of these methods to TD reactive scattering is discussed and application to the resonant H + O₂ reaction is carried out to obtain state-to-state reaction probabilities for thousands of scattering energies.

I. Introduction

Much progress has been made in theoretical and experimental studies of elementary chemical reactions for the past decade or so. Experimentally, complete state-to-state integral cross sections have been measured for some simple reactions, and the measurement of state-to-state differential cross section now appears on the horizon. These state-to-state experiments are aimed to provide the most detailed dynamical information for chemical reactions. Even more impressive, perhaps, is the development of computational methods to accurately calculate the dynamics of elementary chemical reactions. Rigorous quantum dynamical calculations for many atom–diatom reactions and recently for some four-atom reactions have been reported by many researchers. These accurate quantum dynamical calculations serve to help interpret mechanisms of reactions through detailed comparison with experimental results and to predict dynamical features when experimental results are unavailable. These rigorous quantum calculations also provide benchmark results against which various approximate dynamical methods can be tested. However, accurate theoretical calculation of complete *state-to-state* reaction dynamics is currently still limited to some simple atom–diatom reactions. Although rapid progress has recently been made in the accurate quantum calculation of initial state selected reaction probabilities^{1–9} and cumulative reaction probabilities^{10,11} for four-atom reactions, there is still no state-to-state calculation of reaction dynamics for systems beyond atom–diatom systems. Currently, the only available state-to-state quantum dynamics calculations for four-atom reactions are those based on reduced dimensionality methods.^{12,13}

Recently, the time-dependent (TD) wave packet approach is emerging as a promising general approach to studying large and complex reactive scattering problems. It is especially efficient for calculating initial state-selected dynamics information as shown in recent TD studies for H + O₂,^{14,30} H₂ + OH,^{1–3,9} HD + OH,^{4,5} D₂ + OH,⁶ and HO + CO.^{7,8} These TD calculations provided initial state-selected total reaction probabilities, cross sections, and rate constants, but without final

state resolution. More computational effort is required to extract final state information because one has to propagate the wave packet all the way into the asymptotic product arrangement space. In this paper, we further extend the previous TD approach to the calculation of complete state-to-state reactive scattering **S** matrix elements and reaction probabilities for the resonance dominated H + O₂ reaction. We note in passing here a previous TD state-to-state by Judson et al. for the prototypical H + H₂ reaction.¹⁶

There are different formulations that one can use to extract state-to-state dynamics information in the TD approach. In this paper, we discuss several specific formalisms for calculating state-to-state **S** matrix elements and reaction probabilities in the time domain. These are the time correlation function formalism for the **S** matrix, the scattering amplitude formalism for the **S** matrix, and the flux formalism for reaction probability. Each method has certain unique advantages over others in specific applications. One persistent difficulty in state-to-state quantum reactive scattering calculations is the problem associated with the choice of coordinates in the TD wave packet propagation. To simplify applications, we specifically discuss the use of the reactant or product Jacobi coordinates to carry out TD wave packet propagation in state-to-state calculations. Although the long-term goal of our TD project is to study reactions involving four or more atoms at the state-to-state level, we apply current approaches to the difficult H + O₂ reaction to extract state-to-state reaction probabilities at thousands of energies in order to map out the resonance structure in a wide range of scattering energies. We also discuss several computational techniques aimed at improving numerical efficiencies in state-to-state TD calculations.

This paper is organized as follows. Section II presents the general theory of the TD wave packet approach to state-to-state reactive scattering calculation and gives simple derivations of several formalisms to extract state-to-state **S** matrix elements and reaction probabilities. Several computational techniques are also discussed in this section with the aim of enhancing the efficiency of the TD approach in practical applications. In section III, the state-to-state TD calculation for the H + O₂ reaction is carried out and the complete final state distribution of reaction probabilities at numerous energies is given. Finally, section IV gives a brief summary of the present work.

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II. Theory

A. Time Correlation Function Formalism for the S Matrix. We first present a brief discussion of the time correlation function formalism for **S** matrix which has been proposed recently for reactive scattering calculations by Tannor and Weeks.¹⁷ This formalism can be derived straightforwardly from the standard definition of the on-shell **S** matrix element $S_{\bar{f}\bar{i}}$

$$\delta(E_f - E_i)S_{\bar{f}\bar{i}} = \langle \psi_{\beta\bar{f}}^-(E_f) | \psi_{\alpha\bar{i}}^+(E_i) \rangle \quad (2.1)$$

where $|\psi_{\alpha\bar{i}}^+(E_i)\rangle$ and $|\psi_{\beta\bar{f}}^-(E_f)\rangle$ are δ -function energy-normalized incoming and outgoing scattering wave functions and i (f) denotes the initial (final) state label. In this paper, we use α as the initial arrangement label, β the final arrangement label, and γ an intermediate arrangement index label. The scattering wave functions $|\psi_{\alpha\bar{i}}^+(E_i)\rangle$ and $|\psi_{\beta\bar{f}}^-(E_f)\rangle$ satisfy the asymptotic boundary conditions¹⁸

$$\psi_{\alpha\bar{i}}^+(E) \xrightarrow{R_\gamma \rightarrow \infty} \left[\frac{\mu_\gamma}{2\pi\hbar^2} \right]^{1/2} \left[-\frac{e^{-ik_i R_\alpha}}{k_i^{1/2}} \eta_{\alpha\bar{i}} \delta_{\alpha\gamma} + \sum_m S_{\gamma m, \alpha\bar{i}} \frac{e^{ik_m R_\gamma}}{k_m^{1/2}} \eta_{\gamma m} \right] \quad (2.2)$$

$$\psi_{\beta\bar{f}}^-(E) \xrightarrow{R_\gamma \rightarrow \infty} \left[\frac{\mu_\gamma}{2\pi\hbar^2} \right]^{1/2} \left[-\frac{e^{ik_f R_\beta}}{k_f^{1/2}} \eta_{\beta\bar{f}} \delta_{\gamma\beta} + \sum_m S_{\gamma m, \beta\bar{f}}^* \frac{e^{-ik_m R_\gamma}}{k_m^{1/2}} \eta_{\gamma m} \right] \quad (2.3)$$

where μ_γ is the reduced translational mass and $\eta_{\gamma m}$ the internal channel function in γ arrangement.

We can construct a wave packet $\chi_{\alpha\bar{i}}^+$ which consists solely of incoming wave functions as

$$|\chi_{\alpha\bar{i}}^+\rangle = \int a_{\alpha\bar{i}}(E) |\psi_{\alpha\bar{i}}^+(E)\rangle dE \quad (2.4)$$

and similarly for the outgoing wave packet $\chi_{\beta\bar{f}}^-$

$$|\chi_{\beta\bar{f}}^-\rangle = \int a_{\beta\bar{f}}(E) |\psi_{\beta\bar{f}}^-(E)\rangle dE \quad (2.5)$$

Thus, both $\chi_{\alpha\bar{i}}^+$ and $\chi_{\beta\bar{f}}^-$ contain a range of energies determined by the coefficients $a_{\alpha\bar{i}}(E)$ and $a_{\beta\bar{f}}(E)$. Equation 2.4 or 2.5 can be inverted to express $|\psi_{\alpha\bar{i}}^+(E)\rangle$ and $|\psi_{\beta\bar{f}}^-(E)\rangle$ in terms of the wave packets

$$|\psi_{\alpha\bar{i}}^+(E)\rangle = \frac{1}{a_{\alpha\bar{i}}(E)} \delta(E - \hat{H}) |\chi_{\alpha\bar{i}}^+\rangle \quad (2.6)$$

$$|\psi_{\beta\bar{f}}^-(E)\rangle = \frac{1}{a_{\beta\bar{f}}(E)} \delta(E - \hat{H}) |\chi_{\beta\bar{f}}^-\rangle \quad (2.7)$$

The coefficient $a_{\alpha\bar{i}}(E)$ is obtained from³

$$a_{\alpha\bar{i}}(E) = \langle \psi_{\alpha\bar{i}}^+(E) | \chi_{\alpha\bar{i}}^+ \rangle = \langle \phi_{\alpha\bar{i}}(E) | \chi_{\alpha\bar{i}}^+ \rangle \quad (2.8)$$

where $\phi_{\alpha\bar{i}}(E)$ is the asymptotic function. The coefficient $a_{\beta\bar{f}}(E)$ is similarly obtained. Replacing the right hand side of eq 2.1 by eqs 2.6 and 2.7 and integrating out the energy E_f , one obtains the time-independent expression for the **S** matrix element

$$S_{\bar{f}\bar{i}}(E) = \frac{1}{a_{\alpha\bar{i}}(E) a_{\beta\bar{f}}^*(E)} \langle \chi_{\beta\bar{f}}^- | (E - \hat{H}) | \chi_{\alpha\bar{i}}^+ \rangle \quad (2.9)$$

Also, since

$$\delta(E - \hat{H}) = \frac{i}{2\pi} (G^+ - G^-) \quad (2.10)$$

and the contribution from the Green's function G^- term in eq 2.9 is zero because $\chi_{\alpha\bar{i}}^+$ is composed of only incoming waves, the **S** matrix element can also be written as

$$S_{\bar{f}\bar{i}}(E) = \frac{i}{2\pi a_{\alpha\bar{i}}(E) a_{\beta\bar{f}}^*(E)} \langle \chi_{\beta\bar{f}}^- | G^+(E) | \chi_{\alpha\bar{i}}^+ \rangle \quad (2.11)$$

We note that eq 2.11 is identical to the time-independent wave packet expression for the **S** matrix proposed by Kouri and co-workers.¹⁹ If we perform a standard energy \rightarrow time Fourier transform in eq 2.9, we obtain the time-dependent expression for the **S** matrix element,

$$\begin{aligned} S_{\bar{f}\bar{i}}(E) &= \frac{1}{2\pi\hbar a_{\alpha\bar{i}}(E) a_{\beta\bar{f}}^*(E)} \int_{-\infty}^{+\infty} dt e^{(i/\hbar)Et} \langle \chi_{\beta\bar{f}}^- | e^{(i/\hbar)\hat{H}t} | \chi_{\alpha\bar{i}}^+ \rangle \\ &= \frac{1}{2\pi\hbar a_{\alpha\bar{i}}(E) a_{\beta\bar{f}}^*(E)} \int_{-\infty}^{+\infty} dt e^{(i/\hbar)Et} C_{\bar{f}\bar{i}}(t) \end{aligned} \quad (2.12)$$

where $C_{\bar{f}\bar{i}}(t)$ is the correlation function defined as $C_{\bar{f}\bar{i}}(t) = \langle \chi_{\beta\bar{f}}^- | e^{-i(\hbar)\hat{H}t} | \chi_{\alpha\bar{i}}^+ \rangle$. This TD expression has been derived by Tannor and Weeks using a slightly different approach.¹⁷ In the approach of Tannor and Weeks, each final state wave packet $\chi_{\beta\bar{f}}^-$ is generated by a forward propagation of the asymptotic propagator $\exp(-iH_0 t_\infty)$ followed by a backward propagation of the full propagator $\exp(iH t_\infty)$. Such a procedure could be computationally complicated and expensive since one has to do this for each desired final state. In the present approach, the final state wave packet $\chi_{\beta\bar{f}}^-$ is chosen to be in the asymptotic region, and thus, one avoids the need to propagate each final state wave packet. One attractive feature of this **S** matrix expression is that the time correlation function is independent of the scattering energy. Thus, one can save the correlation function at discrete time steps for any desired final state and retrieve it later to extract the corresponding **S** matrix element at any desired energies contained in the energy range of the wave packets. However, the calculation of the correlation function entails the calculation of overlap integrals which have to be handled efficiently in practical applications. At this point, it is worth pointing out that efficient methods have also been proposed to directly calculate the time-independent expression in eq 2.11 by Kouri et al.¹⁹ and Mandelshtam and Taylor.²⁰

A crucial question is again the choice of the coordinates to carry out the TD propagation of the wave function. One can choose either the reactant or product Jacobi coordinates or any other complete set of coordinates to carry out the TD propagation. There are advantages and disadvantages associated with any set of coordinates, depending on specific applications. If we use the reactant Jacobi coordinates to propagate the initial wave packet, the explicit calculation of the correlation function is given by

$$\begin{aligned} C_{\bar{f}\bar{i}}(t) &= \langle \chi_{\beta\bar{f}}^- | \chi_{\alpha\bar{i}}^+(t) \rangle \\ &= \sum_n W_{\alpha n} \langle \chi_{\beta\bar{f}}^- (X_{\alpha n}) | \chi_{\alpha\bar{i}}^+(X_{\alpha n}, t) \rangle \end{aligned} \quad (2.13)$$

where $X_{\alpha n}$ and $W_{\alpha n}$ denote respectively a set of quadrature points and weights defined in the initial (α) arrangement Jacobi coordinates. If computer memory is not a severe limitation in

the calculation, one can store final state wave packets on these quadrature points and save them in memory in order to speed up the calculation of correlation function in eq 2.13. This is not impractical because the final state wave packet $\chi_{\beta f}^-$ is localized in the coordinate space and requires relatively fewer quadrature points to store them in the memory. Otherwise one has to recalculate the numerical values of the final state wave packets at given quadrature points at each time step.

One could also use the final (β) arrangement Jacobi coordinates to carry out the wave packet propagation. In this case, eq 2.13 is rewritten as

$$C_{\beta f}(t) = \sum_n W_{\beta n} \langle \chi_{\beta f}^-(X_{\beta n}) | \chi_{\alpha i}^+(X_{\beta n}, t) \rangle \quad (2.14)$$

where the quadrature points $X_{\beta n}$ and weights $W_{\beta n}$ are defined in the final (β) arrangement Jacobi coordinates. The use of final (product) Jacobi coordinates in the wave packet propagation facilitates the extraction of final state information because the TD wave packet is represented in the same coordinate system as the final state wave packets. Thus, the overlap integral in eq 2.14 is straightforward to calculate without the need to perform coordinate transformation. However, one still needs to transform the initial wave packet, which is inherently defined in the reactant Jacobi coordinates, to the product Jacobi coordinates prior to the calculation of correlation function. This coordinate transformation can be done at any stage during the wave packet propagation.

B. Scattering Amplitude Formalism for the S Matrix. If we choose the radial part of $\chi_{\beta f}^-$ in eq 2.12 to be a δ function times the asymptotic radial function such as the plane wave solution,

$$\langle R_{\beta} | \chi_{\beta f}^- \rangle = \delta(R_{\beta} - R_{\infty}) \exp(ik_f R_{\beta}) | \eta_{\beta f} \rangle \quad (2.15)$$

where R_{∞} is a fixed radial coordinate in the product asymptotic region, eq 2.12 becomes

$$\begin{aligned} S_{\beta f}(E) &= \frac{1}{a_{\alpha i}(E)} \left[\frac{k_f}{2\pi\mu_{\beta}} \right]^{1/2} e^{-ik_f R_{\infty}} \int_{-\infty}^{+\infty} dt e^{(i/\hbar)Et} \langle R_{\infty} | \langle \eta_{\beta f} | \chi_{\alpha i}^+(t) \rangle \\ &= \frac{1}{a_{\alpha i}(E)} \left[\frac{k_f}{2\pi\mu_{\beta}} \right]^{1/2} e^{-ik_f R_{\infty}} \int_{-\infty}^{+\infty} dt e^{(i/\hbar)Et} A_{\beta f}^+(R_{\infty}, t) \end{aligned} \quad (2.16)$$

Equation 2.16 is an amplitude formalism for the **S** matrix because one calculates the **S** matrix by integrating over time the amplitude of the TD wave function at a fixed surface $R_{\beta} = R_{\infty}$ in the product asymptotic region. A different derivation was given by Balint-Kurti et al.²¹ and by Zhang et al.¹⁸ for calculating product state distributions in photofragmentation. In the current context, however, the derivation of eq 2.16 is straightforward by using simply the asymptotic condition in eq 2.2. More generally, the plane wave $e^{ik_f R_{\infty}}$ should be replaced by a more appropriate asymptotic radial function $\phi_f(R)$, such as the Hankel type function, which approaches the plane wave in the limit of $R \rightarrow \infty$, i.e.,

$$\lim_{R \rightarrow \infty} \phi_f(R) \rightarrow e^{ik_f R}$$

Equation 2.16 has an attractive numerical advantage in that one does not need to calculate any overlap integral to extract **S** matrix elements. One only needs to evaluate the radial

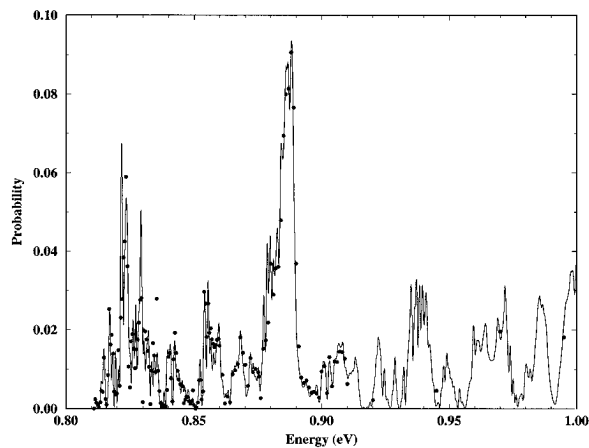


Figure 1. Reaction probability of $\text{H} + \text{O}_2(v=0, j=1) \rightarrow \text{H} + \text{HO}^- (v'=j'=0)$ as a function of energy defined as rovibrational energy of O_2 + translational energy of $\text{H} + \text{O}_2$. The black dots are the hyperspherical results of ref 24.

component of the TD wave function $A_{\beta f}^+(t)$ at a fixed radial coordinate R_{∞} in the product asymptotic region for any desired open channel of the product. The amplitude $A_{\beta f}^+(t)$ can be stored in disk at each time step and then retrieved later to obtain the corresponding **S** matrix element $S_{\beta f}$ at any desired energy according to eq 2.16. However, one has to use a relatively large value R_{∞} at which the radial wave function can be represented by the plane wave or other known asymptotic solution functions such as the Hankel function, e.g., when the centrifugal potential is present. The calculation of eq 2.16 in reactive scattering will be simplified if the TD wave function $\chi_{\alpha i}^+(t)$ is represented in the product Jacobi coordinates.

C. Flux Formalism for Reaction Probability. In both the correlation function and scattering amplitude formulations discussed above, one needs to know the asymptotic radial function in order to calculate the **S** matrix element $S_{\beta f}$. This will require one to propagate the wave packet into the proper asymptotic space where the radial function $\phi_{\beta f}(R)$ is known. However, if one only needs the absolute value of the **S** matrix element $|S_{\beta f}|$ or the probability $P_{\beta f} = |S_{\beta f}|^2$, one can use the flux formalism to calculate reaction probabilities,

$$\begin{aligned} |S_{\beta f}|^2 &= 2\pi\hbar \text{Re} [A_{\beta f}^{+*}(R_{\beta}, E) \hat{v}_{\beta} A_{\beta f}^+(R_{\beta}, E)] |_{R_{\beta}=R_L} \\ &= \frac{2\pi\hbar^2}{\mu_{\beta}} \text{Im} \left[A_{\beta f}^{+*}(R_{\beta}, E) \frac{d}{dR_{\beta}} A_{\beta f}^+(R_{\beta}, E) \right] |_{R_{\beta}=R_L} \end{aligned} \quad (2.17)$$

where $A_{\beta f}^+(R_{\beta})$ is the radial scattering amplitude obtained from

$$\begin{aligned} A_{\beta f}^+(R_{\beta}, E) &= \langle R_{\beta} | \langle \eta_{\beta f} | \psi_i^+(E_i) \rangle \\ &= \frac{1}{2\pi\hbar a_{\alpha i}(E)} \int_{-\infty}^{+\infty} dt e^{iEt} \langle R_{\beta} | \langle \eta_{\beta f} | \chi_{\alpha i}^+(t) \rangle \\ &= \frac{1}{2\pi\hbar a_{\alpha i}(E)} \int_{-\infty}^{+\infty} dt e^{iEt} A_{\beta f}^+(R_{\beta}, t) \end{aligned} \quad (2.18)$$

The flux is calculated at a surface defined by $R_{\beta} = R_L$ beyond which the final state interaction is over and the flux is invariant with respect to further increase of the distance. Thus, one does not need to know the exact form of the radial function at R_L if only square of the **S** matrix elements are desired. This flux formula has also been given by Manolopolous and Alexander in their time-independent approach to photodissociation²² and was put in a time-dependent context by Zhang et al.¹⁸ This

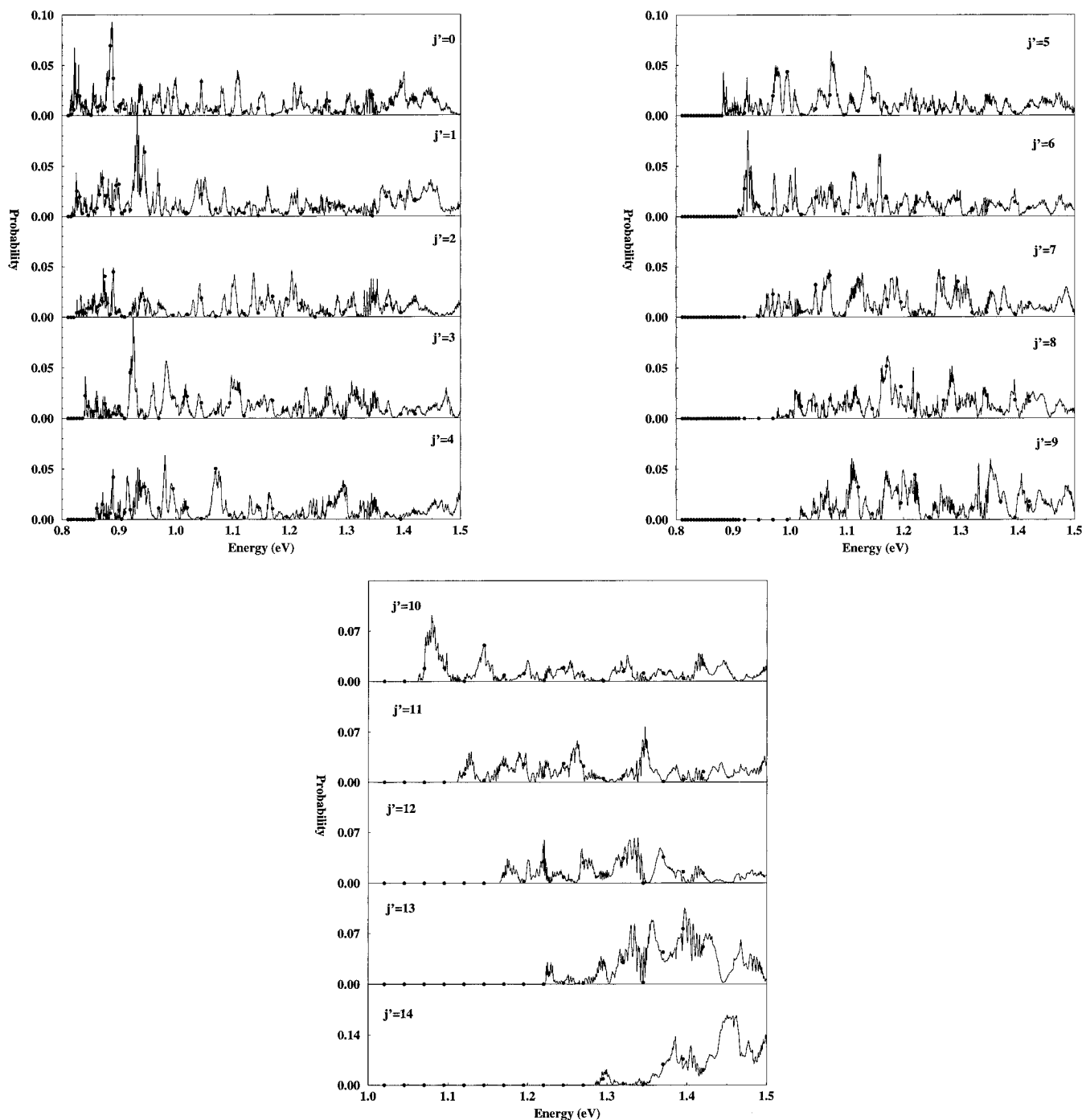


Figure 2. Similar to Figure 1 but for product HO($v'=0, j'$) with (a, top left) $j' = 0-4$, (b, top right) $j' = 5-9$, and (c, bottom) $j' = 10-14$. The black dots are the hyperspherical results of ref 24.

state-to-state approach is also simplified by using the product Jacobi coordinates to represent the TD wave function $\chi_{\alpha i}^+(t)$. As is discussed in ref 18, the flux formula (2.17) is valid in regions beyond which the inelastic scattering process is absent irrespective of elastic process. Therefore, one does not need to know the exact asymptotic radial wave functions to extract the product state distribution. This will generally enable one to obtain converged state-to-state reaction probability at a relatively short radial distance.

D. Prepropagation of the Initial Wave Packet. In order to reduce the number of grid points in the full scale state-to-state wave packet propagation, we should place the initial wave packet as close to the interaction region as possible. On the other hand, the initial wave packet $\chi_{\alpha i}^+$ of a given internal state

i is only known in the reactant asymptotic region. We could, however, prepropagate the initial wave packet $\chi_{\alpha i}^+$ toward the interaction region which involves just inelastic interactions. This is similar in spirit to the use of distorted wave approach in scattering calculations. The prepropagated wave packet

$$|\chi_{\alpha i}^{+'}\rangle = e^{-(i/\hbar)H_{t_0}}|\chi_{\alpha i}^+\rangle \quad (2.19)$$

is then used as the initial wave packet in the full scale TD propagation. The prepropagation involves just inelastic propagation to push the initial asymptotic wave packet into the interaction region and is therefore computationally insignificant compared to the full scale reactive wave packet propagation. We can actually use a shrinking wave packet as the initial radial

wave packet χ_{oi}^+ ²³

$$\chi_{\text{oi}}(R, t = 0) = \frac{(\pi\sigma)^{-1/4}}{1 - i(\hbar t_0/m\sigma^2)} \exp[-i(k_0 R - \hbar k_0^2 t_0/2m)] \times \exp\left[-\frac{[R - R_0 - (\hbar k_0 t_0/m)]^2}{2\sigma^2[1 - i(\hbar t_0/m\sigma^2)]}\right] \quad (2.20)$$

which shrinks to a minimal Gaussian function after a free propagation to $t = t_0$. By choosing an appropriate t_0 , one should be able to minimize the spatial range of χ_{oi}^+ which is used as the initial wave packet in the full scale reactive wave packet propagation.

III. Application to H + O₂ Reaction

In this section, we apply the TD state-to-state approach to the calculation of the H + O₂ reaction. Quantum dynamics calculation for H + O₂ reaction is much more difficult than the direct H + H₂ reaction due to the presence of a deep potential well which supports long-lived resonances in addition to heavier masses. Previous rigorous quantum mechanical calculations have been reported for this reaction by Pack et al.,²⁴ Leforestier and Miller,²⁵ and Zhang and Zhang.¹⁴ The time-independent calculation of Leforestier and Miller provided cumulative reaction probabilities for the H + O₂ reaction but without any state-resolved dynamics information.²⁵ The calculation of Pack et al. using the hyperspherical coordinate approach provided complete state-to-state reaction probabilities, but their results are available at only a limited number of energies due to computational cost for each energy.²⁴ On the other hand, the TD wave packet calculation of Zhang and Zhang provided reaction probabilities at numerous energies, but the calculated probabilities are only initially state-selected, while the final states are summed over.¹⁴ These rigorous quantum dynamics calculations show that the H + O₂ reaction probabilities are dominated by numerous resonances with lifetimes on the order of a picosecond. Several recent studies have also appeared that focus on the resonance studies of HO₂ including H + O₂ inelastic resonances^{27–30} and reactive resonances.³⁰ In the present application to the H + O₂ reaction, we further extend the previous TD work of ref 14 to calculate state-to-state reaction probabilities from the ground state of O₂ ($j=1$) for total angular momentum $J=0$ and for any desired scattering energies within a given range. As in previous scattering calculations for H + O₂,^{14,24,25,30} the DMBE IV potential energy surface (PES) of Varandas and co-workers²⁶ is used in the present calculation.

Since the current work is built on a previous TD study for the H + O₂ reaction, we use the reactant Jacobi coordinates to carry out the wave packet propagation and use the time correlation function formalism of eq 2.12 to extract the final state-to-state **S** matrix elements. The use of reactant Jacobi coordinates in the present calculation is mainly due to the consideration for simplification in the TD propagation, not for the sake of optimal computational efficiency. It would probably be more efficient to use the product Jacobi coordinates to carry out the wave packet propagation and use the methods in sections II.B and II.C to extract final state information. In the present correlation function approach, all final state wave packets are stored on reactant quadrature points to facilitate the computation of the time correlation function at each propagation time. The calculated time correlation function for each product state *f* at each time step is stored on hard disk which is later retrieved to calculate **S** matrix elements at any desired energies by a time → energy Fourier transform. The grid in the translational coordinate *R* of the H + O₂ arrangement extends from 0.5 to

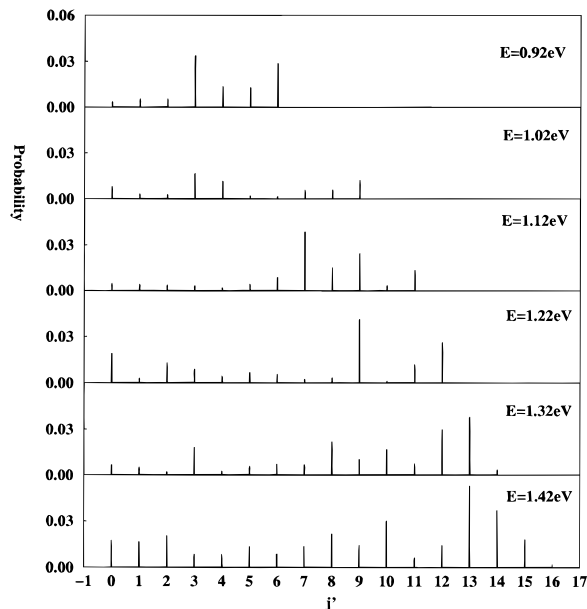


Figure 3. Rotational state distribution of the product HO($v'=0, j'$) at scattering energies of 0.92, 1.02, 1.12, 1.22, 1.32, and 1.42 eV.

14.0 au. In the O₂ stretching coordinate *r*, the grid extends from 0.8 to 16.0 au. A total of 45 odd rotational states of O₂ are included in the propagation. We found a time step of 4 au to be sufficient for the desired accuracy, and the wave packet is propagated to as long as about 5 ps to generate the time correlation function. Absorbing potentials are used to avoid boundary reflections in both reactant and product channels.

Figure 1 shows the state-to-state reaction probability for the reaction H + O₂ ($v=0, j=1$) → HO ($v'=0, j'=0$) + O in the energy range from 0.81 to 1.0 eV. The energy is defined as the internal energy of the diatom plus the translational energy. As is expected, the state-to-state reaction probability is dominated by narrow resonances and the present TD calculation is in good agreement with the hyperspherical coordinate calculation of Pack et al.,²⁴ which is represented by solid dots. Obviously, the complete determination of the resonance structure in Figure 1 requires calculations for numerous scattering energies, which is made easy by using the current TD approach. In fact, we could obtain reaction probabilities at any given energies in the range permitted by the initial and final state wave packets according to eq 2.12.

Reaction probabilities to various rotational states j' of HO ($v'=0$) are shown in Figure 2a–c for energies up to 1.5 eV. As is clear from these figures, the reaction probability to every product rotational state is dominated by narrow and mostly overlapping resonances. The resonance structure of the state-to-state reaction probability is similar to that of the final state-summed reaction probabilities calculated in ref 14. It is also assuring to see that the present TD results are in good agreement with the TI calculation of ref 24 at energies for which the TI results are available. It should be noted, however, that the TD curves in these figures are generated from the calculated reaction probabilities at more than 5000 scattering energies which are trivially obtained after the correlation function is computed.

Figure 3 is a plot of the rotational state distribution of the product OH at six evenly spaced scattering energies of 0.92, 1.02, 1.12, 1.22, 1.32, and 1.42 eV. A brief inspection of Figure 3 indicates that the reaction produces favorably rotationally excited OH product, but the detailed results are sensitive to the specific scattering energy.

In Figure 4a,b we also show rotation-specific probabilities for vibrationally excited product HO ($v'=1$), all of which are

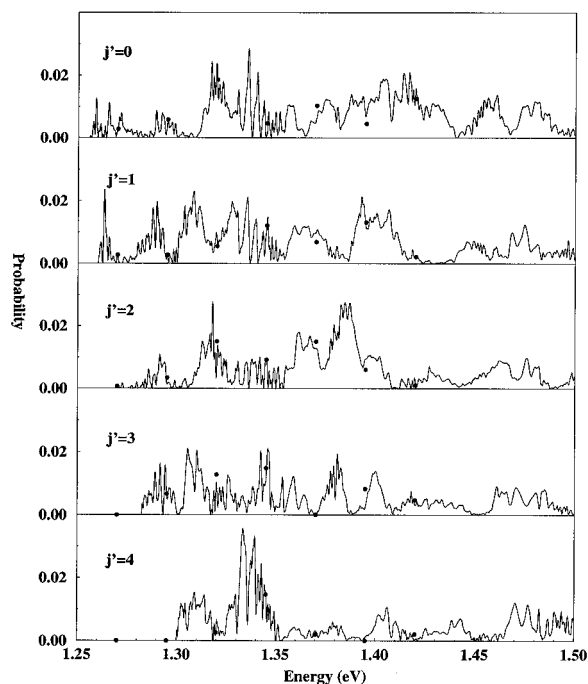


Figure 4. Similar to Figure 2 but for product HO($v'=1, j'$) with $j' = 0-4$.

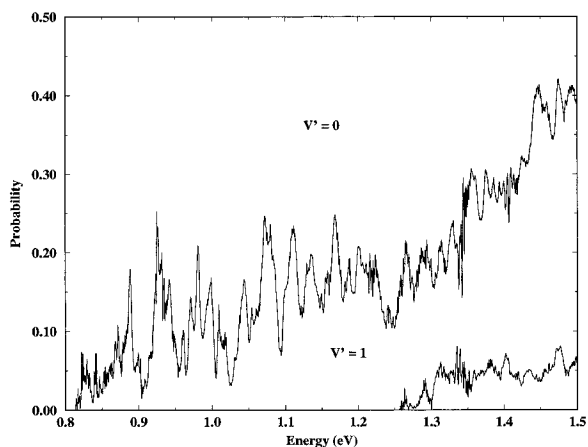


Figure 5. Reaction probability of $\text{H} + \text{O}_2(v=0, j=1) \rightarrow \text{H} + \text{HO}(v', \text{all } j')$ for $v' = 0$ and 1.

dominated by narrow resonances, similar to that for HO($v'=0$). Rotation-summed reaction probabilities for the product HO at $v' = 0$ and $v' = 1$ vibrational levels are also plotted in Figure 5, which shows that only a fraction of the reaction produces vibrationally excited OH product. Also, the probability curve of $v' = 1$ does not increase much as the scattering energy increases, while that of $v' = 0$ increases as the energy increases.

IV. Conclusions

The time-dependent state-to-state approach to reactive scattering is presented, and several methods for extracting the final state **S** matrix element and probability are discussed. State-to-state application using the time correlation function method to the resonant H + O₂ reaction for total angular momentum $J = 0$ is reported, and the computed final state distribution of reaction

probabilities are given. The state-to-state reaction probabilities from the present TD calculation are in good agreement with those from the time-independent calculation of Pack et al.²⁴ Current results show that the H + O₂ reaction on the DMBE IV surface²⁶ generally produces rotationally excited product and most OH molecules are produced in the ground vibrational state. The TD approach allows us to calculate **S** matrix elements or probabilities at numerous energies with ease as shown for the resonant H + O₂ reaction in this paper. The calculation was carried out on a four-processor SGI Power Challenge, and the final converged calculation took about 40 CPU hours. A major challenge is to extend the current approach to reactive scatterings involving four or more atoms in the future.

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