

Cumulative reaction probability via transition state wave packets

Dong H. Zhang and John C. Light

*Department of Chemistry and The James Franck Institute, The University of Chicago,
Chicago, Illinois 60637*

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A new time-dependent approach to the cumulative reaction probability, $N(E)$, has been developed based on the famous formulation given by Miller and co-workers [J. Chem. Phys. **79**, 4889 (1983)], $N(E) = [(2\pi)^2/2] \text{tr}[\delta(E-H)F\delta(E-H)F]$. Taking advantage of the fact that the flux operator has only two nonzero eigenvalues, we evaluate the trace efficiently in a direct product basis of the first flux operator eigenstates and the Hamiltonian eigenstates on the dividing surface (internal states). Because the microcanonical density operator, $\delta(E-H)$, will eliminate contributions to $N(E)$ from an internal state with the energy much higher than the total energy E , we can minimize the number of internal states required by choosing a dividing surface with the lowest density of internal states. If the dividing surface is located in an asymptotic region, one just needs to include all the open channels, i.e., with internal energy lower than the total energy. Utilizing the Fourier transform for $\delta(E-H)$, we can obtain the information for all the energies desired by propagating these wave packets once. Thus the present approach will be much more efficient than the initial state selected wave packet (ISSWP) approach to $N(E)$ for systems with many rotation degrees of freedom because the density of states in asymptotic region for such systems is much higher than that in the transition state region. With the present method one can also calculate the cumulative reaction probability from an initial state (or to a final state) by locating the second flux operator in the corresponding asymptotic region. This provides an alternative to the ISSWP approach which may be more efficient if the reaction probabilities from a large number of initial states are desired. The method is applied to the 3D H + H₂ (even rotation) reaction for $J=0$ by locating the first dividing surface in the transition state region. The demonstration also shows an aspect less than ideal; the contribution to $N(E)$ from a wave packet may be slightly larger than 1 or slightly smaller than 0, making it improper to interpret the contribution as a probability. © 1996 American Institute of Physics. [S0021-9606(96)01216-2]

I. INTRODUCTION

Transition state theory (TST) has been a staple of reaction rate theory since its introduction some 60 years ago by Wigner¹ and Eyring.² It provided an excellent conceptual framework within which reaction rate constants could be understood at a significantly more reliable level than Arrhenius theory alone. In the absence of accurate potential energy surfaces (PES), however, it provided limited predictive power since the parameters required were chosen to fit the rate data.

More recently classical TST was shown to provide upper bounds to the reaction rate constants for classical systems for a given potential energy surfaces.^{1,3-6} This was based on a concept, valid in both classical and quantum mechanics, that the *net* flux through a surface dividing reactants and products is invariant to the position of the surface for a microcanonical ensemble of reactants. By choosing the surface which minimized the flux toward products (but does not subtract flux returning to reactants), a variational upper bound on the rate constant can be obtained classically. This is the basis for variational transition state theory (VTST).^{4,6-9} Quantum corrections to TST and VTST have been used for many years to give correct partition functions at the transition state, tunneling corrections, etc. It is only recently, however, that reformulations of exact quantum rate expressions have opened the possibility of exact TST-like quantum approaches to reactive scattering.

Some time ago Miller¹⁰⁻¹³ and co-workers gave convenient quantum mechanical operator representations of quantities related to reactive scattering. The formulation of compact operators for such "averaged" quantities as the thermal rate constant, $k(T)$, the cumulative reaction probability, $N(E)$, and more recently the "transition state reaction probability operator," has stimulated a number of applications as well as a number of reformulations. The basic objective of many of these studies has been to determine the most efficient methods to obtain reactive scattering information at a given level of detail.¹⁰⁻³⁶ In particular if $N(E)$ only is desired, the range of the quantum calculation may be limited to the transition state and environs by absorbing potentials.³⁷⁻⁴⁰ If information on reactivity from specified initial states is required, then the range of the calculation must extend into the reactant asymptotic region. An approximate "Detailed Quantum Transition State Theory" of this type was first proposed by Light and Altenberger-Siczek.^{41,42}

The "transition state probability operator" approach of Manthe and Miller^{13,20,21} is elegant for determining $N(E)$. Working with operators largely localized in the transition state region, $N(E)$ can be approached essentially variationally by extracting, in order of decreasing magnitude, the eigenvalues of the positive semidefinite TS probability operator. However, these must be extracted at each energy separately by evaluating operators including the Green op-

erator, $(H - E - i\epsilon)^{-1}$ which includes optical potentials for both reactants and products, ϵ_r and ϵ_p which sum to ϵ . This may be time consuming if the Hamiltonian operator is represented by a large matrix and $N(E)$ is desired at many energies in order to evaluate $k(T)$ for example. At each energy the number of eigenvalues of the TS probability operator required is roughly proportional to the number of "transition states" contributing to the reaction probability at E .

Recently, significant progress has been made in the quantum mechanical study of four-atom reactions by using time-dependent wave packet (TDWP) techniques.⁴³⁻⁵⁰ With scaling slower than N^2 (N is the number of basis functions) and providing information for all the desired energies for an initial state from one propagation, the TDWP approach is extremely efficient in calculating the cumulative reaction probabilities from a few initial states. Benchmark results have been reported for the simplest diatom-diatom reaction $H_2 + OH \rightarrow H_2O + H$ (Refs. 45, 48) and atom-triatom reaction $H_2O + H \rightarrow H_2 + OH$ (Ref. 50) in full six dimensions. However this initial state selected wave packet approach is essentially not applicable to calculating the cumulative reaction probability $N(E)$ because of the enormous number of open rotational channels in four-atom systems even for quite modest translational energy. Thus a TDWP based approach to $N(E)$, which can take full advantage of the TDWP techniques and at the same time can avoid propagation of the huge number of wave packets for all the asymptotic open channels, is of great practical importance.

In this article we explore a wave packet approach to the determination of $N(E)$ and/or the reaction probabilities from (or to) specific reactant (or product) internal states. We note that in the formulation of a variety of reaction operators the two flux operators may be placed at arbitrary (and different) surfaces dividing reactants and products. In our formulation wave packets starting at one surface are propagated in time until the flux across both the surfaces disappears. The coordinate range is limited by absorbing potentials placed beyond the flux surfaces toward reactants and products. The energy dependence of the desired quantities is obtained by Fourier transform of the time evolution of the flux.

This formulation is very flexible and offers several advantages. First the "starting" flux surface may be located to minimize the number of wave packet propagations required to converge the results in a desired energy range. This will often be the TS surface for reactions with a barrier, but may be toward the reactant channel for exothermic reactions with "loose" transition states, etc. Second, the location of the second flux surface will depend on the information desired. If only $N(E)$ is required, the two surface will normally be chosen to be the same. If a "state" cumulative reaction probability is required, for reaction from a given state or for reaction to a give state, then one flux surface must be located toward the appropriate asymptotic region where a projection of the flux on to the internal states is possible. In all cases only one propagation per initial (internal state) wave packet is required for information at all energies.

One feature of the approach which is less than ideal concerns the contributions of individual wave packets to the

positive definite quantities desired, $N(E)$ or $N_i(E)$. The contribution of a given wave packet may be negative at some energies, leading to some uncertainty about convergence. Although negative contributions are observed, they are usually quite small and cause no real problem. This does mean, however, that one cannot speak of probabilities of reaction from a given TS within this formulation. However, convergence to zero contribution from very high energy transition states is observed.

In the following section we present the basic theory which is simply derived from Miller's contributions¹¹ to the formulation of $N(E)$ in terms of flux operators and delta functions. In the following sections we discuss first the theory and then the implementation for the 3D $H + H_2$ reaction. Finally we discuss the results and conclusions about the general applicability of the approach and its advantages and drawbacks.

II. THEORY

Miller *et al.* showed that the cumulative reaction probability can be expressed [in atomic units ($\hbar = 1$)] as,¹¹

$$N(E) = \frac{(2\pi)^2}{2} \text{tr}[\delta(E-H)F\delta(E-H)F], \quad (1)$$

where H is the total Hamiltonian of the molecular system, and F is a flux operator which is defined as,

$$F = \frac{1}{2\mu} [\delta(q-q_0)\hat{p}_q + \hat{p}_q\delta(q-q_0)], \quad (2)$$

where μ is the reduced mass of the system, q is the coordinate perpendicular to a dividing surface located at $q=q_0$ which separates products from reactants, and \hat{p}_q is the momentum operator conjugate to the coordinate q . Because the flux through any dividing surface which separates products from reactants is equal, the dividing surfaces for the two F operators in Eq. (1) can be chosen at different positions.

It is well known^{23,24,18} that there only exist *two nonzero eigenvalues* for any finite real basis for a flux operator in *one dimension*, with all other eigenvalues being degenerate with value zero. The two nonzero eigenvalues are a \pm pair and the corresponding eigenstates are also complex conjugates because a matrix representation of F is *imaginary antisymmetric* (thus Hermitian).²³ If the eigenvectors corresponding to the nonzero eigenvalues $\pm\lambda$ are $|+\rangle$ and $|-\rangle$, and ϕ_i ($i=1, N_0$) forms a complete basis set for the coordinates other than the coordinate q , we can evaluate the trace in Eq. (1) simply as

$$N(E) = \frac{(2\pi)^2}{2} \lambda \sum_i [\langle \phi_i^+ | \delta(E-H)F\delta(E-H) | \phi_i^+ \rangle - \langle \phi_i^- | \delta(E-H)F\delta(E-H) | \phi_i^- \rangle], \quad (3)$$

where ϕ_i^\pm denotes the direct product of ϕ_i with $|+\rangle$ or $|-\rangle$, respectively. Because $\delta(E-H)F\delta(E-H)$ is a Hermitian operator, each term on the right-hand side of Eq. (3) is real. Utilizing the equalities, $F^* = -F$ and $|-\rangle = |+\rangle^*$, we easily find

$$\begin{aligned}
& \langle \phi_i^- | \delta(E-H)F \delta(E-H) | \phi_i^- \rangle \\
&= \langle \phi_i^- | \delta(E-H)F \delta(E-H) | \phi_i^- \rangle^* \\
&= -\langle \phi_i^+ | \delta(E-H)F \delta(E-H) | \phi_i^+ \rangle. \quad (4)
\end{aligned}$$

Thus $N(E)$ in Eq. (3) can be written

$$N(E) = (2\pi)^2 \lambda \sum_i \langle \phi_i^+ | \delta(E-H)F \delta(E-H) | \phi_i^+ \rangle. \quad (5)$$

Writing $\delta(E-H)$ in the widely used Fourier transform fashion and splitting λ equally, we define

$$\begin{aligned}
\psi_i(E) &= \sqrt{\lambda} 2\pi \delta(E-H) | \phi_i^+ \rangle \\
&= \sqrt{\lambda} \int_{-\infty}^{+\infty} e^{i(E-H)t} dt | \phi_i^+ \rangle. \quad (6)
\end{aligned}$$

The cumulative reaction probability $N(E)$ then can be written as,

$$N(E) = \sum_i \langle \psi_i | F | \psi_i \rangle = \sum_i N_i(E), \quad (7)$$

where $N_i(E) = \langle \psi_i | F | \psi_i \rangle$ is the contribution to $N(E)$ from the i th “transition state” wave packet. Equation (7) says that $N(E)$ can be calculated as follows: (1) prepare initial wave packets on any dividing surface \mathbf{S}_1 by taking the direct product of the one dimensional eigenstate of the flux operator $|+\rangle$ and basis functions for the other coordinates; (2) propagate each of these wave packets once to generate wave functions ψ_i at all energies desired; (3) using these, calculate the flux for each ψ_i on any dividing surface \mathbf{S}_2 and add them together to obtain $N(E)$. Note that since the flux operator is localized near \mathbf{S}_2 , the energy dependent wave functions, ψ_i , are required on this surface only, although the time dependent wave functions spread throughout the coordinate space. Because the flux operator F is a singular operator,^{10,51} (i.e., its nonzero eigenvalues and the corresponding eigenstates depend on the basis set. As the representation becomes exact the largest eigenvalue will go to infinity), the “transition state” wave packets, hence the $N_i(E)$ s, will depend somewhat on the basis set for coordinate q in Eq. (2). [However the sum converges to $N(E)$.] The traditional transition state can be regarded as the limit when the basis set for coordinate q is exact; then the largest eigenvalue of F goes to infinity, and the corresponding eigenstate localizes to a point at $q=q_0$.

Now let us see what Eq. (7) actually means if \mathbf{S}_1 is chosen at the translational coordinate S in the asymptotic region. Then the total Hamiltonian H reduces to

$$H = H_0 = T_S + H_{\bar{S}}, \quad (8)$$

where \bar{S} represents the coordinates other than S , and $H_{\bar{S}}$ is the Hamiltonian for these coordinates. Because the kinetic energy for S is positive in the asymptotic region, the energy in \bar{S} should be smaller than total scattering energy E . Thus if we choose the asymptotic internal channel bases of the system, i.e., $H_{\bar{S}}\phi_i = E_i\phi_i$, as the basis functions for the other

internal coordinates, the sum in Eq. (7) only needs to include all the open channels for a scattering energy. In this case, Eq. (7) can be written as

$$N(E) = \sum_i P_i(E), \quad (9)$$

where P_i defined as

$$P_i(E) = \langle \psi_i | F | \psi_i \rangle, \quad (10)$$

is just the cumulative reaction probability for an initial state i . The sum of P_i gives the cumulative reaction probability $N(E)$ which of course can also be achieved by calculating the initial state selected cumulative reaction probability using the regular wave packet approach.^{45,48,49,52}

If \mathbf{S}_1 is chosen at S equal to a large value, the only difference between Eq. (7) and the regular wave packet approach is that in Eq. (7) one propagates a wave packet which is the eigenstate of flux operator for S , while one usually propagates a Gaussian wave packet in the regular wave packet approach. However, the important difference between these two approaches actually is that one can *only* propagate Gaussian wave packets for initial states at large S in the regular wave packet approach, but one can choose *any* dividing surface as \mathbf{S}_1 and thus propagate wave packets from any dividing surface with Eq. (6). This means we can choose a \mathbf{S}_1 on which the density-of-states for other coordinates is minimized. This will reduce the number of wave packets we need to propagate, since the density-of-states for other coordinates on a dividing surface usually strongly dependent on the location of the surface. In particular, for a reaction involving multiple rotational degrees of freedom with a barrier on the PES, the density-of-states on a dividing surface passing through the saddle point of the potential surface is usually significantly lower than that in the asymptotic region. In this case even though some “close transition states” (with energy higher than the total energy) can also contribute to the $N(E)$ due to the quantum tunneling effects, the number of wave packets we need to propagate will be significantly smaller than that required in the regular wave packet approach in which the initial wave packet can only be located in asymptotic region.

Finally we choose \mathbf{S}_2 to evaluate the flux in Eq. (7) at $x=x_0$, here x can be any coordinate as long as the surface $x=x_0$ divides the product from the reactant. We find the final equation to calculate the cumulative reaction probability,

$$N(E) = \sum_i \left\{ \frac{1}{\mu} \sum_n \operatorname{Im} \left[(C_n^i)^* \frac{\partial C_n^i}{\partial x} \right] \Bigg|_{x=x_0} \right\}, \quad (11)$$

where C_n^i is the expansion coefficient for ψ_i on φ_n , the basis set for q (the coordinates other than x), i.e.,

$$\psi_i(x, q) = \sum_n C_n^i(x) \varphi_n(q). \quad (12)$$

If \mathbf{S}_2 is chosen at a large value of S , and φ_n is the internal basis with n representing the collection of rovibrational quantum numbers for the system in the asymptotic region, then Eq. (11) can be rewritten as

$$N(E) = \sum_n P_n, \quad (13)$$

where P_n is just the cumulative reaction probability for the initial state n . P_n is given from Eq. (11) as,

$$P_n = \frac{1}{\mu} \sum_i \text{Im} \left[(C_n^i)^* \frac{\partial C_n^i}{\partial x} \right] \Bigg|_{S=S_0}. \quad (14)$$

While Eqs. (10) and (14) both give the cumulative reaction probability for an initial state, they are totally different in their origins. For Eq. (10), S_1 is located at a large value of S where the initial wave packets are constructed. These are propagated and measurements of the flux on surface S_2 (which can be located on any position) give the initial state selected cumulative reaction probability as in the regular wave packet approach. For Eq. (14), the surface S_1 can be located at any position which means the initial flux wave packets can be started from any position, but the projection of the flux into internal states at a large value of S will also give you the initial state selected cumulative reaction probability.

Equation (14) not only provides an alternative to the time-dependent wave packet approach to the initial state selected total reaction probability, but it can be more efficient. It should be used for systems with several rotation degrees of freedom when one is interested in total reaction probabilities from a substantial number of initial rotation excited states. Of course Eq. (14) is not a good choice if only the reaction probabilities from a few initial states are desired because one needs to propagate a number of “transition state” wave packets which all will contribute to P_n in Eq. (14).

As can be seen from Eq. (6), the present method has one very attractive feature; one is only required to propagate these “transition state” wave packets once to obtain the $N(E)$ at all energies. This is in contrast to the “reaction probability operator” approach to $N(E)$ by Manthe *et al.*,^{13,20,21} in which one needs to perform the full calculations for each energy desired. The number of wave packets we need to propagate may be slightly larger than the number of states required in the “reaction probability operator” approach at the highest total energy of interest. However because the propagation is done only once for each transition state, the computational saving offered by the present method is quite substantial. Also as can be seen the present method is capable of obtaining the initial state selected reaction probability by adding minor extra efforts. Of course, we realize that the eigenvalues of the “reaction probability operator” all lie between 0 and 1, and thus can be interpreted as eigenreaction probabilities for the activated complex, while at some energies the contributions from present transition state wave packets may be negative (although they are quite small and cause no real problem), or may be slightly larger than one. Thus we are not calculating probabilities.

Although the present method does not give the thermal rate constants directly, when the energy dependence of $N(E)$ is known, the thermal rate constant is just a matter of Boltzmann averaging,

$$k(T) = \frac{1}{2\pi Q_r(T)} \int_0^\infty dE e^{-\beta E} N(E), \quad (15)$$

where $Q_r(T)$ is the reactant partition function per unit volume and $\beta = 1/k_b T$. Thus the present method is a “direct” way to calculate thermal rate constants. One should note that the “transition state” wave packet idea can also apply directly to the flux–flux correlation function approach to the thermal rate constant by propagating the flux operator eigenstates. The thermal rate constant can be expressed in terms of flux–flux autocorrelation function as,

$$k(T) = \frac{1}{Q_r} \int_0^\infty C_{ff}(T, t) dt, \quad (16)$$

where the flux–flux autocorrelation function $C_{ff}(T, t)$ is given by,

$$C_{ff}(T, t) = \text{tr}(e^{iHt_c} F e^{-iHt_c} F), \quad (17)$$

where $t_c = t - i\beta/2$. Evaluating the trace in Eq. (17) as in Eq. (3), we can obtain,

$$\begin{aligned} k(T) &= \frac{\lambda}{Q_r} \sum_i \int_0^\infty \{ \langle \phi_i^+ | e^{iHt_c} F e^{-iHt_c} | \phi_i^+ \rangle \\ &\quad - \langle \phi_i^- | e^{iHt_c} F e^{-iHt_c} | \phi_i^- \rangle \} dt \\ &= \frac{\lambda}{Q_r} \sum_i \int_{-\infty}^\infty \langle \phi_i^+ | e^{iHt_c} F e^{-iHt_c} | \phi_i^+ \rangle dt \\ &= \frac{\lambda}{Q_r} \sum_i \int_{-\infty}^\infty dt \langle \psi_i^+(t) | \Gamma(T) | \psi_i^+(t) \rangle, \end{aligned} \quad (18)$$

where $|\psi_i^+(t)\rangle = e^{-iHt} |\phi_i^+\rangle$, $\Gamma(T) = e^{-\beta/2} F e^{-\beta/2}$ is the thermal flux operator²⁴ with eigenstates $|\Phi_j^\pm\rangle$, i.e.,

$$\Gamma(T) |\Phi_j^\pm\rangle = \pm \gamma_j(T) |\Phi_j^\pm\rangle. \quad (19)$$

Writing the thermal flux operator in term of its eigenstates as,

$$\Gamma(T) = \sum_j [|\Phi_j^+\rangle \gamma_j(T) \langle \Phi_j^+| - |\Phi_j^-\rangle \gamma_j(T) \langle \Phi_j^-|], \quad (20)$$

we can get the thermal rate constant as,

$$\begin{aligned} k(T) &= \frac{\lambda}{Q_r} \sum_{i,j} \gamma_j \int_{-\infty}^\infty dt [| \langle \Phi_j^+ | \psi_i^+(t) \rangle |^2 \\ &\quad - | \langle \Phi_j^- | \psi_i^+(t) \rangle |^2]. \end{aligned} \quad (21)$$

This approach is essentially what Park and Light did in their first paper²⁴ except two aspects. First, in the present approach the absorption potentials are utilized beyond the transition state region to get rid of the boundary reflection which caused problem at high temperature previously; and second, the treatment of the second flux operator in the present approach avoids the calculation of the autocorrelation functions between all the thermal flux operator eigenstates, thus avoids storing all the thermal flux operator eigenstates in the computer memory which can be quite a serious problem for a large system. As one can see that Eq. (21) does provide a

direct way to evaluate the thermal rate constant, $k(T)$. However one cannot see any advantage than the approach via $N(E)$ calculation by using Eq. (7). In order to use Eq. (21), one has to solve the eigenstates of the thermal flux operator which is not a very hard problem as shown by Park and Light,²⁴ nevertheless it makes Eq. (21) less straightforward than that by using Eqs. (7) and (16) for the calculation of the thermal rate constants.

The recent flux-position correlation function approach proposed by Thompson and Miller,²² and the reaction rate operator approach by Manthe^{35,36} both used a Lanczos iterative procedure to calculate the eigenvalues of corresponding low rank operator. The backward propagation required in these approaches makes it very difficult to use an absorbing potential. Thus these approaches demand a much larger grid space, especially for high temperatures, than the present approach. It would also be very hard to apply these two approaches to reactions with resonances.

III. IMPLEMENTATION FOR THE 3D H + H₂ REACTION

In this section, we apply the present theory to the 3D H+H₂ reaction to illustrate the implementation of the approach. The Hamiltonian for the reaction in mass-scaled Jacobi coordinates for total angular momentum $J=0$ can be written as⁵³

$$H = -\frac{1}{2\mu} \left(\frac{\partial}{\partial S^2} + \frac{\partial}{\partial s^2} \right) + \frac{\mathbf{j}^2}{2\mu} \left(\frac{1}{S^2} + \frac{1}{s^2} \right) + V(S, s, \theta), \quad (22)$$

where μ is the three-body reduced mass,

$$\mu = \sqrt{m_{\text{H}} m_{\text{H}} m_{\text{H}} / (m_{\text{H}} + m_{\text{H}} + m_{\text{H}})}, \quad (23)$$

S and s are mass-scaled coordinates for R and r ,

$$S = dR, \quad s = r/d, \quad (24)$$

with d given by

$$d = \sqrt{\frac{m_{\text{H}}}{\mu} \left(1 - \frac{m_{\text{H}}}{m_{\text{H}} + m_{\text{H}} + m_{\text{H}}} \right)}. \quad (25)$$

We will define the dividing surface in rotated ‘‘transition state’’ coordinates. Thus we define two new variables Q and q by rotating the S and s axes by the angle χ .⁵⁴

$$\begin{pmatrix} Q \\ q \end{pmatrix} = \begin{pmatrix} \cos \chi & \sin \chi \\ -\sin \chi & \cos \chi \end{pmatrix} \begin{pmatrix} S \\ s \end{pmatrix}. \quad (26)$$

The Hamiltonian in Eq. (22) can be written in Q and q as

$$H = -\frac{1}{2\mu} \left(\frac{\partial}{\partial Q^2} + \frac{\partial}{\partial q^2} \right) + \frac{\mathbf{j}^2}{2\mu} \left[\frac{1}{S(Q, q)^2} + \frac{1}{s(Q, q)^2} \right] + V(Q, q, \theta). \quad (27)$$

By choosing \mathbf{S}_1 at $q=0$, i.e., $q_0=0$ in Eq. (2), we can obtain the ‘‘internal’’ transition states for Q and θ , simply by solving the eigenstates of the 2D Hamiltonian,

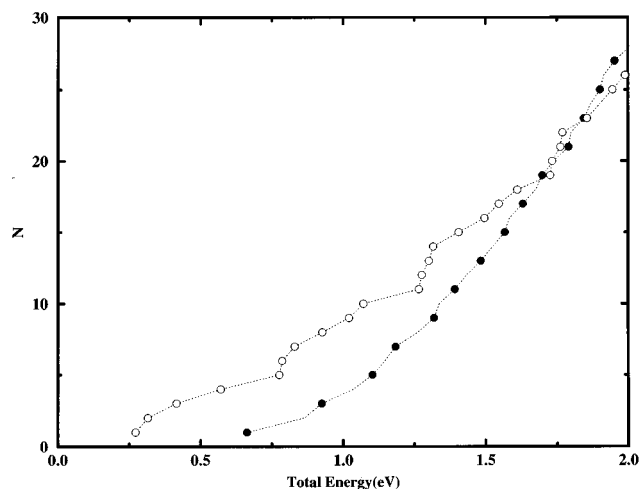


FIG. 1. Number of open states as a function of total energy in asymptotic region (open circles) and on the $s = S/\sqrt{3}$ surface (solid circles) for the H + H₂ (even rotation) reaction.

$$H_{2D} \phi_i = \left\{ -\frac{1}{2\mu} \frac{\partial}{\partial Q^2} + \frac{\mathbf{j}^2}{2\mu} \left[\frac{1}{S(Q, q=0)^2} + \frac{1}{s(Q, q=0)^2} \right] + V(Q, q=0, \theta) \right\} \phi_i = E_i \phi_i. \quad (28)$$

The initial wave packets to propagate, ϕ_i^+ , are just the direct product of ϕ_i and the eigenstate of the F operator in Eq. (2) with $q_0=0$ with positive eigenvalue. After constructing the initial wave packets, one can propagate them as in the regular wave packet approach either in (Q, q, θ) coordinate, or in (S, s, θ) coordinate by transferring the initial wave packets in (Q, q, θ) coordinates to the (S, s, θ) coordinates.

Optical (absorbing) potentials are located toward the asymptotic regions to prevent spurious reflections of the wave packets.

IV. NUMERICAL RESULTS AND DISCUSSIONS

Because the density of states is important in this approach we show it first in Fig. 1 for the H + H₂ (even rotation) reaction. The open circles in Fig. 1 represents the number of open states in the asymptotic region as a function of total energy, the solid circles represents the number of open states on the $s = S/\sqrt{3}$ surface (transition state region). The $s = S/\sqrt{3}$ surface in the 3D H + H₂ reaction actually is not a conventional surface with one normal-mode coordinate equal to constant which is used in TST calculation, and in quantum cumulative reaction probability calculation by Miller’s group.^{12,13} We used it because it is as simple as the Jacobi coordinates, and the ‘‘transition state’’ wave packets initially constructed on that coordinate can be very easily transferred to the Jacobi coordinate on which the asymptotic projection can be easily carried out when the initial state selected cumulative reaction probabilities are desired.

Because of the barrier, at low total energy the number of open internal states in the transition state region is substantially lower than that in the asymptotic region. But the vibra-

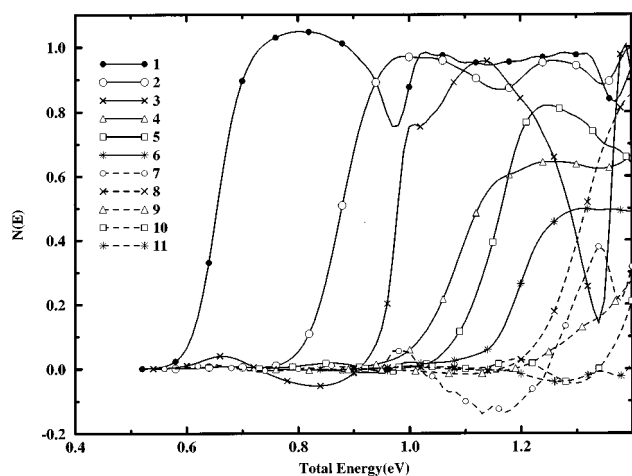


FIG. 2. Contributions to the cumulative reaction probability from the first 11 "transition states" as a function of total energy.

tional frequency is lowered in the TS, and these two curves get close very quickly. For energy larger than 1.8 eV, the number of open states in the transition state region is even larger than that in the asymptotic region. Thus it is clear that the present approach to the cumulative reaction probability can only be more efficient than the regular wave packet approach for low total energy (at least in terms of the number of wave packets to be propagated). Figure 1 also indicates that it is not always true that one can save computation by limiting the calculation to the transition region. Of course, we realize that the $\text{H} + \text{H}_2$ system is not a good system to illustrate the advantage of the TS approach because the rotation constant for the H_2 molecule in the asymptotic region is already very large, and at the same time the potential in the transition region is anharmonic and not too anisotropic. This means the reduction in the density of states from the hindered rotational degree of freedom will not very significant.

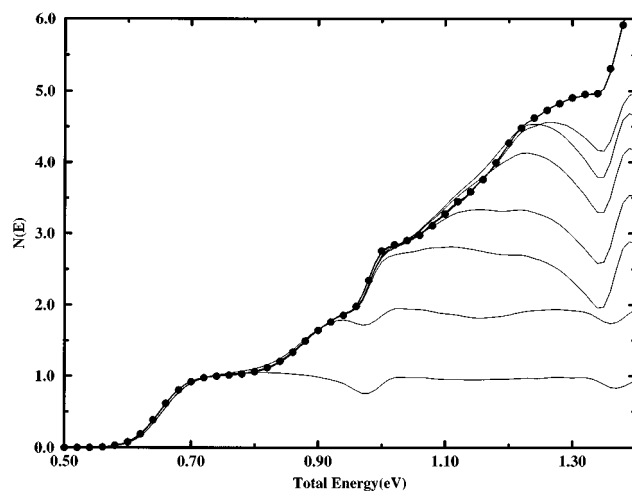


FIG. 3. The convergence of the cumulative reaction probability, $N(E)$, with respect to the number of "transition states." The solid circles are the cumulative reaction probabilities from ISSWP calculations. The heavy line is obtained by adding the contributions from the first 13 "transition states."

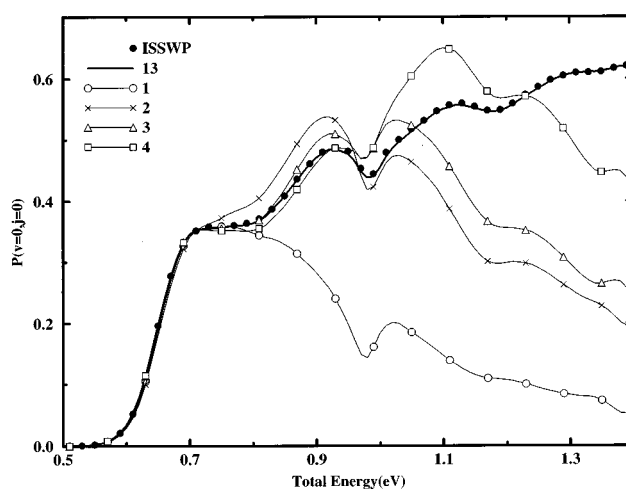


FIG. 4. The convergence of the cumulative reaction probability for initial ($v=0, j=0$) state with respect to the number of "transition states." The solid circles are the reaction probabilities from ISSWP calculation.

However, it is well known that the density of states in the transition region will be much lower than that in the asymptotic region for systems with many rotational degrees of freedom and with very restricted transition state geometry, as in many four-atom reaction systems.

Figure 2 shows the contributions to the cumulative reaction probability from the first 11 transition states as a function of total energy, $N_i(E)$. As can be seen from the figure that the cumulative reaction probabilities in the very low energy region comes essentially from the first transition state, and the first two states contribute most significantly to $N(E)$ in the entire energy range we consider. Except for the first two states, the other states only contribute significantly to the cumulative reaction probability when the total energy is higher than their internal energies. However for the first two states, especially for the first state, the tunneling contributions are very important. The overall behavior of $N_i(E)$ has some similarities with TST. Here we see that the

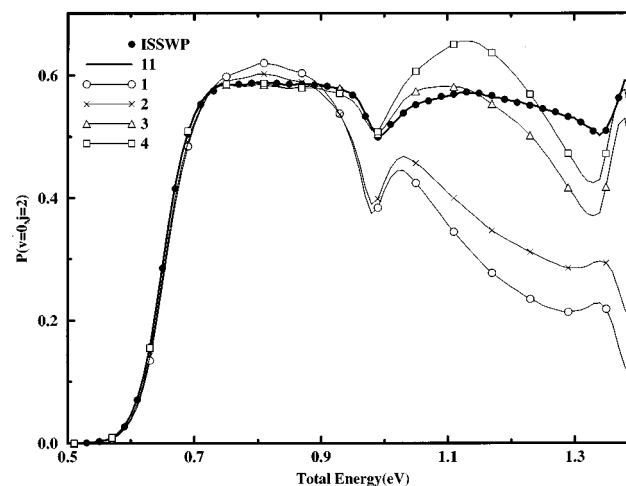


FIG. 5. Same as Fig. 4 except for initial ($v=0, j=2$) state.

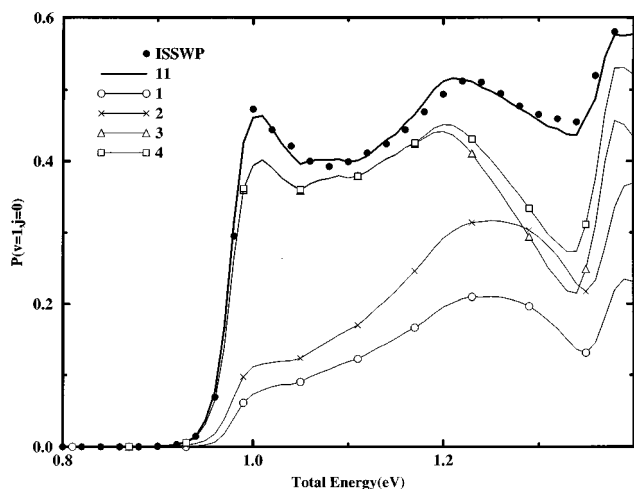


FIG. 6. Same as Fig. 4 except for initial ($v=1, j=0$) state.

$N_i(E)$ do not increase monotonically from 0 to 1, in contrast, they can saturate far before reaching 1, or can have oscillating behaviors, or even can have negative values. The $N_i(E)$ has some values slightly larger than 1 for the total energy around 0.8 eV. Thus these individual transition state quantities are not probabilities although their sum is the cumulative reaction probability $N(E)$.

In Fig. 3, we show the convergence of the cumulative reaction probability $N(E)$ with respect to the number of transition states. For energy lower than 0.95 eV, the first three states have already given very accurate results. As also can be seen from Fig. 2 the contribution from other states is negligible in that energy region. The convergence with the number of transition states get slower and slower as the energy increases because of the fairly rapid increase in the density of states as shown in Fig. 1. Adding the $N_i(E)$ up to $i=13$, produces very well converged $N(E)$ up to $E=1.4$ eV which is in perfect agreement with the cumulative reaction probabilities (shown in solid circles) obtained by ISSWP method in which one also needs to propagate wave packets for 13 initial states. Thus for energy up to $E=1.4$ eV the present approach gets essentially the same convergence speed as the ISSWP method. The overall convergence property of the present approach is quite close to that shown by Miller's group who calculated the eigenvalues of the reaction probability operator \hat{p} in Ref. 13. This may be expected because they both reflect the contributions from open channels in the reactive complex for a given energy.

The initial state selected cumulative reaction probabilities for $(v, j)=(0,0)$, $(0,2)$, and $(1,0)$, obtained as the byproduct in calculating $N(E)$ are shown in Figs. 4, 5, and 6 together with the accurate results from the regular wave packet approach. As can be seen from the figures, for every initial state the convergence becomes quite slow after the probability get saturated. In the low energy region, the first two "transition state" wave packets contribute almost all the reaction probabilities for $(0,0)$ and $(0,2)$ states, while the reaction probabilities for $(1,0)$ state essentially come from the

third "transition state," the first stretch excited "transition state."

V. CONCLUSION

We have introduced a new method to calculate the cumulative reaction probabilities $N(E)$ via the time-dependent "transition state" wave packets. The method takes advantage of the facts that the flux operator F has only two non-zero eigenvalues and the microcanonical density operator, $\delta(E-H)$, makes the contribution to $N(E)$ from a transition state with internal energy much higher than E negligible. For systems with the density of states in transition state region much lower than that in asymptotic region (as in systems with many rotation degrees of freedom), the reduction in the number of wave packets required to be propagated compared to the regular wave packet approach will be very substantial. By representing the $\delta(E-H)$ as the Fourier transform, we can obtain the $N(E)$ at all the desired energies by propagating each wave packet once. With very transparent physics, the new approach, we believe, essentially achieves the highest efficiency which Miller's operator formulations can offer.

Another important feature of the present approach is that one can locate the position for the second flux operator depending on the information desired. If a "state" cumulative reaction probability is desired, one just needs to put the second flux operator in the corresponding asymptotic region. Thus the present method also provides a new time-dependent approach to the initial (or final) state selected reactive scattering calculation. For systems with many rotation degrees of freedom, the present method will be more efficient than the regular wave packet approach if the reaction probabilities from many initial rotation excited states are desired. The demonstration on the 3D $H + H_2$ (even rotation) reaction for $J=0$ has clearly revealed all important features of the present method mentioned above.

However, the demonstration also showed that the contribution to $N(E)$ from a "transition state" wave packet can be negative or slightly larger than 1 at some energies. This makes it improper to interpret the contribution as the transmission probabilities, also makes the convergence property less than ideal.

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