

Reactant–product decoupling approach to state-to-state dynamics calculation for bimolecular reaction and unimolecular fragmentation

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The main purpose of the study is to explore a number of computational methods to be used in the RPD approach to state-to-state quantum dynamics calculation of polyatomic reactions. Specifically, a mixed time-dependent (TD) and energy-dependent (ED) approach to solve the RPD equations is investigated. In the mixed TD and ED approach, the reactant wavefunction is computed by the method of wavepacket propagation while the product wavefunction is calculated by energy-dependent methods. As a result, the reactant–product coordinate transformation only needs to be carried out for the number of energies at which the state-to-state *S*-matrix elements are needed, which is advantageous if state-to-state information at only a few energies are needed. Similar implementation of the mixed RPD approach is given for calculation of product state distribution in molecular photofragmentation dynamics.

1 Introduction

The TD wavepacket approach currently provides a practical means for studying polyatomic reaction dynamics beyond triatomic reactions.¹ The TD method is especially suited for computing total reaction probabilities (*i.e.* probabilities summed over final states of the product arrangement). In the simplest approach to computing total reaction probabilities, one can employ the Jacobi coordinates, corresponding to the reactant arrangement, to carry out the time propagation for the scattering wavefunction and employ an absorbing boundary condition just beyond the transition-state region. Thus, one can obtain total reaction probabilities by using a single set of (reactant) Jacobi coordinates to propagate the wavepacket in a relatively small region of coordinate space, excluding asymptotic regions of the product arrangements. Such an approach has proven to be very robust in computational studies of tetraatomic reactions such as $\text{H}_2 + \text{OH}$, $\text{HO} + \text{CO}$ *etc.* as discussed in ref. 1.

However, if state-to-state dynamics information is needed, the use of a single set of Jacobi coordinates is numerically inefficient, because one has to extend the grid all the way from the reactant asymptotic region to the product asymptotic region. For example, if the product arrangement involves long-range inelastic interactions, using the reactant Jacobi coordinates for the entire configuration space is very inefficient. Although the use of the product Jacobi coordinates could help ease the problem of long-range inelastic interaction in the product arrangement, it will be inefficient if the reactant arrangement also has long-range inelastic scattering. In any event, the use of a single set of Jacobi coordinates (corresponding to either reactant or product) to calculate state-to-state quantum dynamics throughout the entire configuration space is numerically inefficient. This is an inherent difficulty associated with reactive scattering, because the reactant and product arrangements are properly described by different sets of Jacobi coordinates.

Thus, efficient calculation of state-to-state reaction dynamics entails the use of more than one set of Jacobi coordinates. A simple alternative approach is to use the reactant Jacobi coordinates to propagate the wavefunction initially and then transform the TD wavefunction to the product Jacobi coordinates in the interaction region. This is only applicable, however, if the wavepacket remains very compact in the interaction region, which is, in general, difficult to achieve in practical applications.

In previous papers,^{2–4} we proposed a general RPD approach for state-to-state quantum reactive scattering calculation for polyatomic reactions. In the RPD approach, the state-to-state dynamics calculation is divided into two separate calculations. The first part of the calculation is essentially identical to that for total reaction probability, which includes the interaction region but excludes the product asymptotic region by using the reactant Jacobi coordinates to carry out the wavepacket propagation. The calculated wavefunction in the first part of the calculation, denoted Ψ_r , in a narrow strip where absorbing potential is non-zero, is saved as a source term for the second part of the calculation for Ψ_p in the product arrangement. The latter yields state-to-state S -matrix elements. The main advantage of the RPD approach is that it splits the state-to-state reactive scattering calculation into two separate and smaller calculations. One does, however, need to perform an extra step to transform the quantity $V_p \Psi_r$, where V_p is the absorbing potential and is localized in a small strip, to product Jacobi coordinates. The RPD method is quite general and can be implemented in both time-dependent and time-independent applications.² In previous applications of the RPD approach, it was found that the coordinate transformation of the term $V_p \Psi_r(t)$ from the reactant Jacobi coordinates to that of the product is a major source of computational cost, since the transformation has to be performed at every time step.

In the present paper, we explore the mixed method, in which the first part of the calculation for Ψ_r is carried out by the standard TD method while the second part of the calculation for Ψ_p is done by ED methods. The main advantage of this mixed approach is that one only needs to perform coordinate transformation for the number of energies at which the state-to-state information is needed, regardless of the total propagation time required to propagate the wavepacket across the absorbing region. Thus, the entire RPD calculation can be very efficient if state-to-state information at only a few collision energies is needed. The same approach is equally applicable to molecular photofragmentation dynamics without much modification.

2 RPD approach to state-to-state reactive scattering

2.1 TD formalism

In the TD version, the RPD scheme partitions the full TD wavefunction into a sum of reactant component (Ψ_r) and all product components [$\Psi_p(p = 1, 2, 3, \dots)$] that satisfy the following decoupled equations²

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

where H is the full Hamiltonian and $-iV_p$ is the negative imaginary potential (absorbing potential) used to absorb the wavefunction $\Psi_r(t)$ completely in a narrow strip separating the reactant from the product, to prevent it from entering the p th product arrangement. Eqn. (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 eqn. (1), we recover the original Schrödinger equation

for the full wavefunction. It is noted that solving for $\Psi_r(t)$ is completely independent of solving 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,² provided that the absorbing potential is sufficiently smooth. The second equation in eqn. (1) is an inhomogeneous equation with a TD 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 non-zero only in the corresponding p th product space starting from where V_p becomes non-zero, its calculation involves only an inelastic propagation in that particular arrangement, completely independent of the component wavefunctions of other product arrangements.

In previous approaches, we directly calculated the TD wavefunction $\Psi_p(t)$ in eqn. (1) by using a short-time propagator such as the split-operator method as described in ref. 2–4

$$|\tilde{\Psi}_p(t + \Delta)\rangle = \exp\left(-\frac{i}{\hbar} H\Delta\right)|\tilde{\Psi}_p(t)\rangle + \frac{\Delta}{\hbar}|\xi_p(t + \Delta)\rangle \quad (2)$$

where $\tilde{\Psi}_p(t) = \Psi_p(t) + (\Delta/2\hbar)\xi_p(t)$. Since $\tilde{\Psi}_p(t)$ is everywhere the same as $\Psi_p(t)$, except in the absorbing region, we could use $\tilde{\Psi}_p(t)$ directly to extract the final state dynamics such as state-to-state S matrix elements or reaction probabilities. In this TD approach, we need to save the calculated source term $\xi_p(t) = V_p\Psi_r(t)$ at every time step, which requires one to represent the $\xi_p(t)$ in Jacobi coordinates of the product arrangement.

2.2 ED calculation of Ψ_p

Since $\Psi_r(t)$ is computed directly in the reactant Jacobi coordinates, it needs to be transformed to the Jacobi coordinate of the product arrangement at every time step for which $\Psi_r(t)$ is non-zero. Although this coordinate transformation is localized in a small region in the configuration space and is made very efficient by introducing the collocation quadrature scheme, it can still be computationally demanding when the transformation needs to be done many times. This is the case if the propagation of the wavefunction across the absorbing region requires many time steps. An alternative approach is to use the ED version of the RPD equation for the product component Ψ_p

$$\begin{aligned} (E - H)|\Psi_p(E)\rangle &= iV_p|\Psi_r(E)\rangle \\ &= i|\xi_p(E)\rangle \end{aligned} \quad (3)$$

where $\Psi_p(E)$ is the ED scattering wavefunction. In this equation, the source term $\xi_p(E)$ is ED but time independent. Therefore, one only needs to perform the coordinate transformation for the number of energies desired.

Eqn. (3) can be solved by a variety of methods. Using the integral equation approach, one obtains the solution for $\Psi_p(E)$

$$|\Psi_p(E)\rangle = iG^+(E)|\xi_p(E)\rangle \quad (4)$$

This equation can be solved by utilizing the Fourier transform of the Green's function $G^+(E)$ to propagate the ED wavepacket $\xi_p(E)$ directly

$$|\Psi_p(E)\rangle = \frac{1}{2\pi\hbar} \int_0^\infty \exp\left(\frac{i}{\hbar} Et\right) |\xi_p(t, E)\rangle \quad (5)$$

where the TD and ED wavepacket is given by

$$|\xi_p(t, E)\rangle = \exp\left(-\frac{i}{\hbar} Ht\right) |\xi_p(E)\rangle \quad (6)$$

In this approach, one needs to carry out the wavepacket propagation in the product arrangement for each energy, which is a straightforward inelastic propagation.

One could also solve the inhomogeneous Schrödinger eqn. (3) directly in differential form by propagating the wavefunction $\Psi_p(E)$ in coordinate space from the beginning of the absorbing boundary R_0 out to the asymptotic region of the product. For example, if R_p denotes the translational coordinate and Ψ_p the vector wavefunction, one can solve the differential equation in eqn. (3) in matrix form

$$\frac{d^2}{dR_p^2} \Psi_p + \frac{2\mu_p}{\hbar^2} (EI - V) \Psi_p = i \frac{2\mu_p}{\hbar^2} \Xi_p(E) \quad (7)$$

where μ_p is the translational mass of the product arrangement. The above differential equation can be solved outward from the beginning of the absorbing region $R_p = R_0$ where Ψ_p and its derivative Ψ'_p are zero. By propagating the wavefunction in the translational coordinate R_p to the asymptotic space of the product arrangement, one can easily extract a whole column of S -matrix elements by matching the wavefunction to the asymptotic boundary condition. This approach is worth future exploration.

A simpler alternative to eqn. (7) is to solve the homogeneous differential equation for the full vector wavefunction $\Psi = \Psi_r + \Psi_p$, viz

$$\frac{d^2}{dR_p^2} \Psi + \frac{2\mu_p}{\hbar^2} (EI - V) \Psi = 0 \quad (8)$$

with the initial condition $\Psi(R_0) = \Psi_r(R_0)$ and $\Psi'(R_0) = \Psi'_r(R_0)$. Eqn. (8) has the advantage that the coordinate transformation from the reactant Jacobi coordinates to that of the product is carried out only at a surface $R_p = R_0$ instead of the absorbing strip. Both eqn. (7) and (8) need to be further explored in the future.

The RPD equations can also be solved by the time-independent wavepacket method, as shown recently by Althorpe *et al.*⁵ using the extended Chebychev polynomials to expand the Green's function. In this approach, the absorbing potential is embedded in the Chebychev polynomial expansion as proposed by Mandelshtam and Taylor.⁶

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_p large) to obtain the ED S matrix elements or reaction probabilities by Fourier transforming the TD wavefunction $\Psi_p(t)$ to $\Psi_p(E)$ at large asymptotic distance

$$\Psi_p^i(E) \xrightarrow{R_p \rightarrow \infty} \sqrt{\frac{\mu_p}{2\pi\hbar^2}} \left[\sum_m S_{pm,ri}^R \frac{\exp(ik_m R_p)}{\sqrt{k_m}} \eta_{pm} \right] \quad (9)$$

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 $\exp(ik_m R_p)$ 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 and, instead, evaluate the flux, to obtain converged reaction probability at a relatively shorter radial distance.⁷

2.3 Calculation of $\Psi_r(E)$

In general, the calculation of $\Psi_r(E)$ can be efficiently carried out by TD wavepacket propagation using the Jacobi coordinates of the reactant arrangement. Using the split-operator propagation scheme, we propagate the TD wavefunction,⁸

$$\Psi_r(\mathbf{R}, \mathbf{r}, t + \Delta) = \exp(-iH_0 \Delta/2) \exp(-iV \Delta) \exp(-iH_0 \Delta/2) \Psi_r(\mathbf{R}, \mathbf{r}, t) \quad (10)$$

where the total Hamiltonian is defined as,

$$H = H_0 + V \quad (11)$$

The ED wavefunction $\Psi_r(E)$ is obtained by performing standard Fourier transformation of the TD wavefunction

$$\Psi_r^i(E) = \frac{1}{a_i(E)} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \exp\left(\frac{i}{\hbar} Et\right) \Psi_r(t) \quad (12)$$

where $\Psi_r^i(t) = \exp[-(i/\hbar)Ht]\chi_i^+$ and χ_i^+ is an initial incoming wavepacket localized in the asymptotic region of the reactant. The normalization coefficient is calculated by the standard method

$$a_i(E) = \langle \Psi^i | \chi_i^+ \rangle = \langle \phi_i | \chi_i^+ \rangle \quad (13)$$

where ϕ_i is an asymptotic function. In reality, only positive t are needed in the integration in eqn. (12) because the initial wavepacket χ_i^+ is an incoming wavepacket and travels toward the interaction region for $t > 0$.

2.4 Transformation of Jacobi coordinates

Since the reactant wavefunction $\Psi_r(E)$ is expressed in terms of basis functions defined in the reactant Jacobi coordinates while $\Psi_p(E)$ is defined in terms of the product basis function, we need to perform coordinate transformation between reactant and product arrangements. For atom-diatom reaction, the transformation of Jacobi coordinates from the reactant arrangement $A + BC$ (R, r) to the product arrangement $B + AC$ (R', r') is given by (cf. Fig. 1)

$$\begin{bmatrix} R' \\ r' \end{bmatrix} = \begin{bmatrix} a_2 & a_3 \\ 1 & a_1 \end{bmatrix} \begin{bmatrix} R \\ r \end{bmatrix} \quad (14)$$

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

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

$$\begin{aligned} r' &= \sqrt{R^2 + (a_1 r)^2 + 2a_1 Rr \cos \theta} \\ R' &= \sqrt{(a_2 R)^2 + (a_3 r)^2 + 2a_2 a_3 Rr \cos \theta} \\ \cos \theta' &= \frac{1}{R'r'} [a_2 R^2 + a_1 a_3 r^2 + (a_1 a_2 + a_3) Rr \cos \theta] \end{aligned} \quad (15)$$

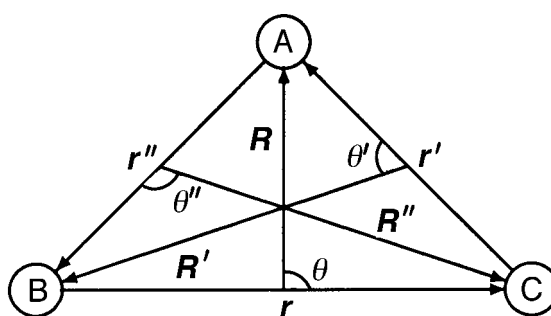


Fig. 1 Jacobi coordinates for a triatomic system ABC

2.5 A collocation-quadrature scheme

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

$$a_n(E) = \langle \phi_n | \xi_p(E) \rangle; \quad (n = 1, 2, \dots, N) \quad (16)$$

where ϕ_n are basis functions of the product arrangement. Because $\xi_p(E)$ and ϕ_n are defined with respect to basis functions of different arrangement, the numerical evaluation of eqn. (16) 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. In order to minimize the number of grid points at which the coordinate transformation is needed, a collocation-quadrature scheme is employed, such that the integral in eqn. (16) can be evaluated by an N -term summation

$$a_n = \sum_i W_{ni} \xi(q_i) \quad (17)$$

where q_i are N fixed multidimensional points in the Jacobi coordinates defined in the product arrangement and W_{ni} is obtained by a simple matrix inversion

$$W = \Phi^{-1} \quad (18)$$

where the matrix element Φ_{ni} is just the value of ϕ_n at given grid points (q_i). This collocation choice of the weighting matrix guarantees that the orthogonality of the overlap integral is strictly preserved

$$\langle \phi_n | \phi_m \rangle = \sum_i W_{ni} \Phi_{im} = \delta_{nm} \quad (19)$$

and the summation in eqn. (17) will be exact if the function ξ_p spans the N -dimensional vector space of ϕ_n . If the basis functions are not orthogonal, eqn. (18) is easily generalized to

$$W = O\Phi^{-1} \quad (20)$$

where O is the basis overlap matrix $O_{nm} = \langle \phi_n | \phi_m \rangle$.

For an atom-diatom system, Φ is the direct product of translation $T_n(R)$, vibration $V_v(r)$, and rotation $R_j(\theta)$ functions

$$\Phi = T \times V \times R \quad (21)$$

where $T_{nn'} = T_n(R_{n'})$, $V_{vv'} = V_v(r_{v'})$, and $R_{jj'} = R_j(\theta_{j'})$. Thus, eqn. (18) becomes

$$W = T^{-1} \times V^{-1} \times P^{-1} \quad (22)$$

3 RPD approach to molecular photofragmentation

The RPD approach can be easily generalized to molecular photodissociation dynamics^{9,10} as has been shown recently in TD calculation for photodissociation of water.¹⁰ Here, we discuss application of the ED version of the RPD equation to photofragmentation dynamics. In photofragmentation dynamics, one often wishes to calculate the final state distribution of the products (fragments) which is proportional to the generalized Franck-Condon (FC) factor

$$s_n = |\langle \Psi_n^{(-)} | \chi \rangle|^2 \quad (23)$$

where χ is the generalized initial bound wavefunction, and $\Psi_n^{(-)}$ is an incoming scattering wavefunction with the incoming boundary condition. The F-C factor in eqn. (23) can be calculated by evaluating the flux at a fixed asymptotic radial distance R_L ^{11,12} in a

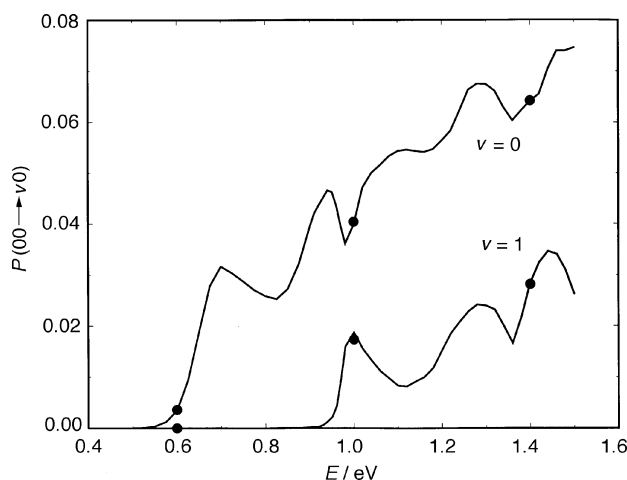


Fig. 2 Comparison of state-to-state reaction probabilities $P(v=j=00 \rightarrow v'j'=0)$ for $\text{H} + \text{H}_2$ reaction with total angular momentum $J=0$. Solid circles are the results of the present ED RPD calculation and the curves are the TD RPD results.

given arrangement

$$s_n = \frac{\hbar^2}{2\pi\mu} \text{Im} \left[A_n^{+*}(R) \frac{d}{dR} A_n^+(R) \right] \Big|_{R=R_L} \quad (24)$$

where μ is the reduced mass for the translational motion. The radial function $A_n^+(R)$ is obtained by projecting out the internal state $|\varphi_n\rangle$ from an ED outgoing wavefunction Ψ^+ at a large radial distance R^{12}

$$|A_n^+(R)\rangle = \langle R | \varphi_n | \Psi^+ \rangle \quad (25)$$

where Ψ^+ is defined as¹²

$$\Psi^+ = G^+ |\chi\rangle \quad (26)$$

which can be obtained by solving the inhomogeneous Schrödinger equation

$$(E - H) |\Psi^+\rangle = |\chi\rangle \quad (27)$$

We can now partition $|\Psi^+\rangle$ as

$$|\Psi^+\rangle = |\Psi_{\text{int}}\rangle + \sum_{\lambda} |\Psi_{\lambda}\rangle \quad (28)$$

and design the ED RPD equations

$$\begin{cases} (E - H) |\Psi_{\text{int}}\rangle = |\chi\rangle - i \sum_{\lambda} V_{\lambda} |\Psi_{\text{int}}\rangle \\ (E - H) |\Psi_{\lambda}\rangle = i V_{\lambda} |\Psi_{\text{int}}\rangle; \quad (\lambda = 1, 2, \dots) \end{cases} \quad (29)$$

The wavefunction Ψ_{int} is simply the replacement for Ψ_r in the reactive scattering of the previous section. However, since the initial state χ is localized in the interaction region, Ψ_{int} is bounded in the interaction region. One can calculate Ψ_{int} by the standard TD

method

$$\begin{aligned} |\Psi_{\text{int}}\rangle &= G^+(E)|\chi\rangle \\ &= \frac{1}{2\pi\hbar} \int_0^\infty \exp\left(-\frac{i}{\hbar} Et\right) \exp\left(\frac{i}{\hbar} Ht\right) |\chi\rangle \end{aligned} \quad (30)$$

where the absorbing potentials have been incorporated in the Hamiltonian of the propagator. The asymptotic wavefunction Ψ_λ can also be calculated by propagating the ED wavepacket, as in reactive scattering, discussed in the previous section

$$\begin{aligned} |\Psi_\lambda\rangle &= iG^+(E)V_\lambda|\Psi_{\text{int}}\rangle \\ &= \frac{1}{2\pi\hbar} \int_0^\infty \exp\left(-\frac{i}{\hbar} Et\right) \exp\left(\frac{i}{\hbar} Ht\right) |\xi_\lambda\rangle \end{aligned} \quad (31)$$

where the ED source term is $|\xi_\lambda\rangle = V_\lambda|\Psi_{\text{int}}\rangle$.

Thus, the RPD approach to photofragmentation is essentially identical to bimolecular reactive scattering. The main difference is that, in photofragmentation, the initial wavepacket χ is localized in the 'strong' interaction region while, in bimolecular collision, the initial wavepacket χ_i^+ is localized in the asymptotic region of the initial arrangement space. As a result, the calculation of Ψ_{int} (which replaces Ψ_r in bimolecular reactive scattering) is restricted to a relatively small interaction region and is much easier than that for Ψ_r in bimolecular reaction. Other than that, the calculations of the product components Ψ_λ are identical to that in bimolecular reactive scattering.

3.1 Numerical test for H + H₂ reaction

The current ED version of the RPD eqn. (5) has been tested on the 3D H + H₂ reaction for total $J = 0$, and the result is shown in Fig. 2 and 3 for a number of energies. The ED RPD calculation uses the same absorbing parameters as those used in the TD RPD calculation of ref. 3 and thus gives essentially the same result as in ref. 3. Comparing the computational cost of the present ED RPD calculation with the previous TD RPD calculation of ref. 3, the current version is much more efficient for a single energy, since the coordinate transformation is performed only once for one energy. This may be very useful if results at only a few energies are needed for reactions that may require long propagation time.

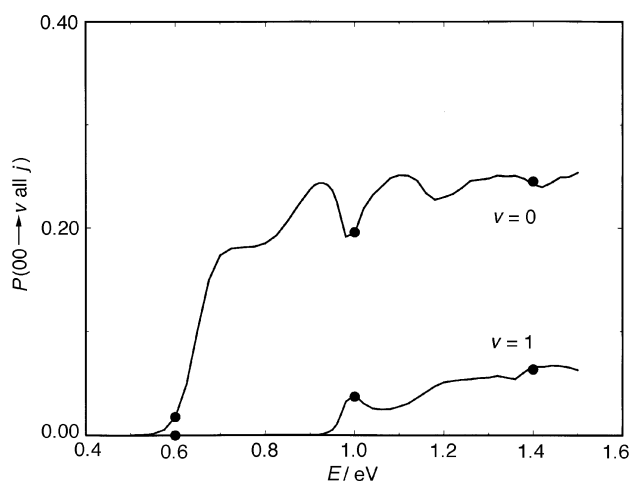


Fig. 3 Same as Fig. 2 except for $P(v = j = 00 \rightarrow v' \text{ all } j')$

3.2 A note on absorbing potential

In the RPD approach to state-to-state reactive scattering, the absorbing potential plays a crucial role.¹³ As a result, the calculated state-to-state reaction probabilities are generally more sensitive to the parameters of the absorbing potentials than that of the total reaction probabilities. It is thus important to use well behaved absorbing potentials. This is, in general, difficult to achieve, since the optimal absorbing potential will generally depend on the scattering energy. This problem can be overcome by using different parameters of absorbing potentials for different scattering energies in order to improve the numerical accuracy.

The problem is especially severe at very low scattering energy, such that the De Broglie wavelength is much larger than the width of the absorbing potential. A recent study¹⁴ showed that, by using a complex absorbing potential, *i.e.* by replacing the negative imaginary potential (NIP) $-iV_1$ by a negative complex potential (NCP) $V_c = -V_1 - iV_1$, it is possible to achieve an excellent result, even for a De Broglie wavelength much larger than the absorbing width. This works well for the single-channel case. For multichannels, however, one perhaps needs to use a channel-dependent NCP in order to achieve an accurate result for different outgoing channel states. This remains to be explored in the future.

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