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Wavepacket correlation function for electronically nonadiabatic reactions

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Abstract

A time-dependent formulation of quantum mechanical scattering theory for electronically nonadiabatic reactions is developed based on wavepacket correlation function theory. The total wavefunction of the system is expanded in terms of electronic basis functions in diabatic representation. Multi-state diabatic wavepackets, which correlate with particular adiabatic states in the asymptotic region, are propagated by the direct exponentiation method for the Hamiltonian matrix in the split operator formalism. The theory is applied to two model reactions of the one-dimensional reactive curve-crossing problem and a simple two-dimensional quasi-Jahn–Teller reaction model with conical intersection.
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1. Introduction

The study of the dynamics of molecular systems has traditionally been done by following nuclear motions on a potential energy surface (PES) obtained a priori using the Born–Oppenheimer approximation. Reactive scattering studies based on a single electronically adiabatic PES have been very successful for 3 and 4-atom bimolecular reactions [1,2]. Concerning the possible extension of scattering studies to reactions involving polyatomic molecules, time-dependent methods possess some attractive features for large-scale numerical calculations [2,3]. The time-dependent wavepacket approach can also provide direct information on the underlying reaction dynamics. Another useful aspect of the time-dependent studies is that they can be used to develop approximate theories such as semiclassical, mixed quantum/classical, or time-dependent self-consistent-field (TDSCF) methods.

Theoretical studies of reaction dynamics on multiple PESs including the effects of electronically nonadiabatic

processes have been quite limited. Only a handful of quantum mechanical scattering studies have been attempted so far [4–6]. On the other hand, even for conditions where the BO approximation is valid, i.e., for low enough energies such that upper electronic states cannot be populated, the presence of electronic degeneracy has been found to affect molecular dynamics including scattering processes [7–10]. Time-dependent studies on general reactive scattering processes involving multiple electronic states will undoubtedly reveal much richer dynamical phenomena.

Tannor and coworkers [11–16] have developed a time-dependent reactive scattering formulation in which the individual S-matrix elements or the cumulative reaction probabilities are obtained from time-correlation functions between reactant and product wavepackets with appropriate boundary conditions. Similar formulations based on time-dependent wavepackets have also been introduced by others [17,18]. In this paper, we present a simple extension of the wavepacket correlation function formulation to electronically nonadiabatic reactions. The total wavefunction of a system is expanded in terms of appropriate electronic basis and nuclear wavepackets, as represented by N-dimensional vectors for the N-state problem,

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and are propagated on multiple PESs. It is found that a diabatic representation provides a convenient formalism for such purposes. The purpose of the present study is to illustrate the application of a time-dependent approach to electronically nonadiabatic reactions.

2. Theory

We consider the extension of a simplified form of the correlation function formalism of the S-matrix element proposed by Tannor and Weeks [11,12]

$$S_{\gamma\alpha}(E) = \frac{(2\pi)^{-1}}{\eta_\gamma^*(E)\eta_\alpha(E)} \int_{-\infty}^{\infty} C_{\gamma\alpha}(t) \mathrm{e}^{\mathrm{i}Et} \, \mathrm{d}t, \tag{1}$$

where the time-correlation function and the energy expansion coefficients are given by:

$$C_{\gamma\alpha}(t) = \langle \Phi_\gamma^- | \mathrm{e}^{-\mathrm{i}Ht} | \Phi_\alpha^+ \rangle, \tag{2}$$

$$\eta_\alpha(E) = \sqrt{\frac{m}{2\pi p}} \int \Phi_\alpha^+(q) \mathrm{e}^{-\mathrm{i}pq} \, \mathrm{d}q, \tag{3}$$

where Φ_α^+ represents the in-coming wavepacket of reactant channel α, while Φ_γ^- is for the out-going wavepacket of product channel γ. $\eta_\alpha(E)$ is the $p \equiv \sqrt{2m(E - E_\alpha)}$ Fourier component of Φ_α^+ and similarly for $\eta_\gamma(E)$ with Φ_γ^-. Here we note that there is no need to apply the Møller scattering operator to the reactant and product wavepackets if they are located far enough in the asymptotic regions [17]. Atomic units with $\hbar \equiv 1$ will be used throughout the paper.

In the case of reactions on multiple electronic states, the total (nuclear + electronic) wavefunction of the system is expanded in terms of appropriate basis functions for the electronic degrees of freedom. Now the state descriptions (α, γ) for the nuclear wavepackets also include the specification of the electronic states. For simplicity, we will consider the model 1D reaction (no internal states) with two electronic states. We can choose the asymptotic wavepackets to be on a specific electronic state. For example, in the two-state problem, one may write

$$|\mathbf{\Phi}_1^+\rangle = (\phi_1^+, 0)^{\mathrm{T}}; \quad \langle \mathbf{\Phi}_2^- | = (0, \phi_2^-). \tag{4}$$

Then the time-correlation function for such a case is given by

$$C_{21}(t) = \langle \mathbf{\Phi}_2^- | \exp(-\mathrm{i}\mathbf{H}t) | \Phi_1^+ \rangle, \tag{5}$$

where

$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}. \tag{6}$$

The propagation of the initial wavepacket originating from a specific electronic state will result in mixing of other electronic states as it passes through the nonadiabatic interaction region. The time-correlation function is obtained by the overlap between the mixed time-dependent wavepacket with the product asymptotic wavepacket representing another electronic state. The S-matrix element calculated from such time-correlation function describes the transition between the two electronic states specified by the asymptotic wavepackets.

We need to choose the type of electronic basis functions to be used. Usually, diabatic and adiabatic states coincide asymptotically. Therefore, either type of basis can be used in the formalism. Diabatic representation provides a convenient theoretical framework for studying nonadiabatic processes [19]. We have adopted a diabatic representation in this study, which is also closely related to the wavepacket propagation method to be described next.

In order to propagate nuclear wavefunctions on multiple PESs, we will use the approach proposed by Broeckhove et al. [20] and independently by Fernandez and Micha [21]. In the two-state problem, the general forms for the total Hamiltonian matrix in different representations (adiabatic and diabatic) are well known:

$$\mathbf{H}^{\mathrm{a}} = \mathbf{K}^{\mathrm{a}} + \mathbf{U}^{\mathrm{a}} \quad \text{(adiabatic)}, \tag{7a}$$

$$\mathbf{H}^{\mathrm{d}} = \mathbf{K}^{\mathrm{d}} + \mathbf{V}^{\mathrm{d}} \quad \text{(diabatic)}. \tag{7b}$$

In the adiabatic representation, the potential energy matrix, $\mathbf{U}^{\mathrm{a}}$, is diagonal, while the kinetic energy matrix, $\mathbf{K}^{\mathrm{a}}$, is complicated by nonadiabatic coupling terms in both the diagonal and off-diagonal elements. On the contrary, a diabatic representation can be defined such that $\mathbf{K}^{\mathrm{d}}$ is diagonal with the full 2×2 matrix for $\mathbf{V}^{\mathrm{d}}$. The short-time propagator for the diabatic representation in the split-operator (SPO) algorithm can be written as

$$\exp(-\mathrm{i}\mathbf{H}^{\mathrm{d}}\delta t) \approx \exp\left(-\frac{1}{2}\mathrm{i}\mathbf{V}^{\mathrm{d}}\delta t\right) \exp(-\mathrm{i}\mathbf{K}^{\mathrm{d}}\delta t) \exp\left(-\frac{1}{2}\mathrm{i}\mathbf{V}^{\mathrm{d}}\delta t\right). \tag{8}$$

Since $\mathbf{K}^{\mathrm{d}}$ is diagonal, the kinetic energy part can be evaluated straightforwardly by using an efficient FFT method [22,23]. For the application of the potential energy propagator, we take advantage of a simple analytical expression available for the exponential of a Hermitian 2×2 matrix. It is found that the following expression is convenient for actual computation [21]:

$$\exp(-\mathrm{i}\mathbf{V}^{\mathrm{d}}\delta t) = \exp(-\mathrm{i}U_1^{\mathrm{a}}\delta t)\mathbf{I} + (U_2^{\mathrm{a}} - U_1^{\mathrm{a}})^{-1}[\exp(-\mathrm{i}U_2^{\mathrm{a}}\delta t) \\ - \exp(-\mathrm{i}U_1^{\mathrm{a}}\delta t)](\mathbf{V}^{\mathrm{d}} - U_1^{\mathrm{a}}\mathbf{I}), \tag{9}$$

where $\mathbf{I}$ represents the unit matrix and the relation between the adiabatic and the diabatic potential energy matrix elements is given by

$$U_{1,2}^{\mathrm{a}} = \frac{1}{2}\left[(V_1^{\mathrm{d}} + V_2^{\mathrm{d}}) \pm \sqrt{(V_1^{\mathrm{d}} - V_2^{\mathrm{d}})^2 + 4(V_{12}^{\mathrm{d}})^2}\right]. \tag{10}$$

During the time-evolution of the diabatic wavefunctions, corresponding adiabatic ones can be obtained by the following transformation:

$$\begin{pmatrix} \xi_1^{\mathrm{a}} \\ \xi_2^{\mathrm{a}} \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \chi_1^{\mathrm{d}} \\ \chi_2^{\mathrm{d}} \end{pmatrix} \tag{11}$$

with

$$\tan 2\theta = \frac{2V_{12}^{\mathrm{d}}}{(V_2^{\mathrm{d}} - V_1^{\mathrm{d}})}. \tag{12}$$

In the two-state problem, the transformation matrix is completely determined by the mixing angle or ADT (adiabatic–diabatic transformation) angle, θ.

3. Application to model nonadiabatic reactions

As a first example of an electronically nonadiabatic reaction, we considered the one-dimensional model of Shin and Light [24]. It is based on a symmetric Eckart potential as a lower adiabatic potential:

$$U_1^a(x) = V_0[\cosh(ax)]^{-2}. \tag{13}$$

The upper adiabatic potential is defined to satisfy the relation $U_1^a + U_2^a = 2E_D$. It is noted that the minimum energy gap between the two adiabatic potentials at the barrier top is given by $\Delta = 2(E_D - V_0)$. The diabatic potentials are obtained from the adiabatic potentials by using the same transformation matrix as in Eq. (11). The diabatic coupling potential is determined by relating the mixing angle to a switching function. We are considering the situation where the two diabatic curves cross in the barrier region ($x = 0$) of lower adiabatic potential. Far from the crossing point, each diabatic curve coincides with either the lower or upper adiabatic potential. As we pass through the crossing point, the diabatic curve switches from one adiabatic potential to another. This change of character for diabatic potentials due to diabatic coupling can be represented by a switching function going smoothly from 0 for one side of the crossing point to 1 for the other side. Shin and Light introduced the following form for the switching function [24]:

$$\sin^2 \theta(x) \equiv h(x) = \frac{1}{2}[1 - \tanh(\alpha x)]. \tag{14}$$

The above model nonadiabatic reaction is characterized by the position of the upper adiabatic potential (E_D) or the energy gap (Δ) and the range of electronic coupling as represented by the parameter α. The parameters for the Eckart potential are chosen to represent a 1D model of the $H_2 + H$ reaction. We set $V_0 = 0.425$ eV, $m = 1060$ au, and $a = 1.3624$ au.

We use Gaussian wavepackets for the asymptotic wavepackets on the diabatic curves (see Eq. (4))

$$\phi_n^{+,-}(x) = (2\gamma_n/\pi)^{1/4} \exp[-\gamma_n(x - x_n^0)^2 + ip_n(x - x_n^0)]$$
$$(n = 1, 2). \tag{15}$$

It is noted that both ϕ_1^+ (on the diabatic state 1) and ϕ_2^- (on the diabatic state 2) correspond to the lower adiabatic state asymptotically on each side of the crossing point, respectively. Therefore, we are considering the barrier crossing of the lower adiabatic potential in the presence of nonadiabatic coupling to the upper adiabatic surface. We set the parameter values as: $q_1 = -5$, $\gamma_1 = 5$, $p_1 = 7.5$ for ϕ_1^+; $q_2 = +5$, $\gamma_2 = 5$, $p_2 = 7.5$ for ϕ_2^- (all in atomic units).

As a model nonadiabatic reaction, we considered the parameters $E_D = 1.05V_0$ ($\Delta = 0.1V_0$) and $\alpha = 5.0$ au. Fig. 1(a) shows the correlation function (Eq. (5)) and
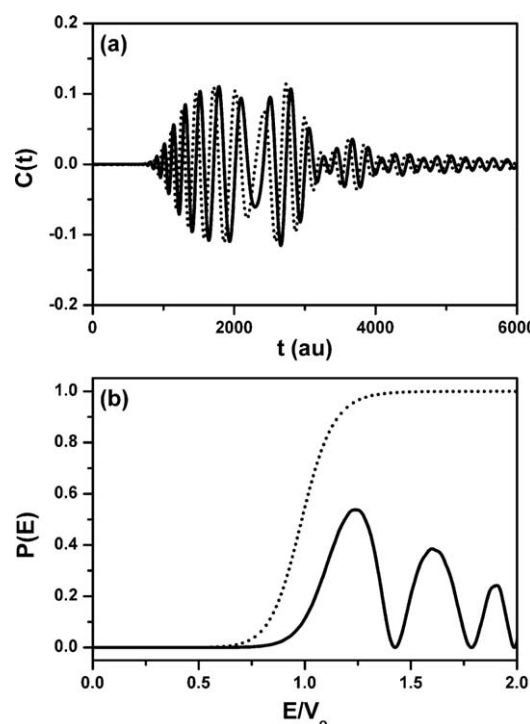

Fig. 1. (a) Correlation function as a function of time for a nonadiabatic reaction on the potentials with the parameters of $E_D = 1.05V_0$ ($\Delta = 0.1V_0$) and $\alpha = 5.0$ au. The solid line is the real part and the dotted line is the imaginary part. (b) Reaction probability (transmission coefficient) $P(E) = |S(E)|^2$ as a function of energy. The solid line is for the two-state reaction and the dotted line is for the reaction on the lower adiabatic surface (Eckart potential) alone.

Fig. 1(b) the reaction probability (transmission coefficient) $P(E) = |S(E)|^2$. The results are compared with those for the lower adiabatic potential alone. First, we note that the amplitude of $C(t)$ for the nonadiabatic reaction is reduced and shows persistent (small) oscillations for longer times, compared with the adiabatic case. These long-time oscillations arise because some of the initial wavepacket is transferred to and trapped in the upper adiabatic surface before leaking out to the product side of the lower surface at later times. The reaction probability clearly shows the signature of resonance structure [25,26], reflecting such trapping on the upper surface. The time-dependence of diabatic wavefunctions also exhibits interesting behavior (Fig. 2). The separation between χ_1^d and χ_2^d for longer times is not complete and the two diabatic wavefunctions are mixed on the product side. This behavior can also be examined by calculating the occupation probabilities of adiabatic states. Fig. 3 shows the time dependence of a fraction of the lower and the upper adiabatic states contained in the total wavefunction. It is clearly seen that the upper surface is appreciably populated when the wavepacket is traversing the nonadiabatic coupling region.

The second example of an electronically nonadiabatic reaction is a reactive two-state curve-crossing model studied by Baer and Child [27]. The model was introduced to mimic $Ar^+ + H_2(v = 0) \rightarrow ArH^+ + H$ reaction. It is based on exponential-type diabatic potentials:
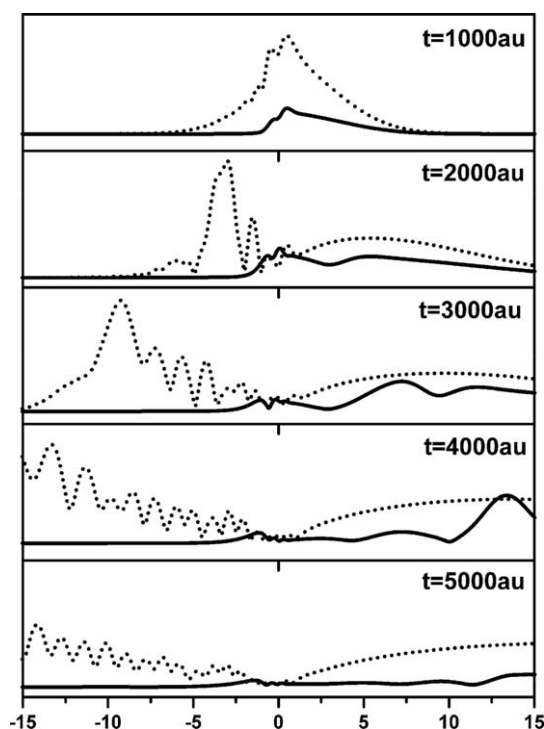
Fig. 2. Snapshots of the wavepacket motions for the diabatic states as a function of time for a nonadiabatic reaction as described in Fig. 1. The dotted line is for χ_1^d and the solid line is for χ_2^d.
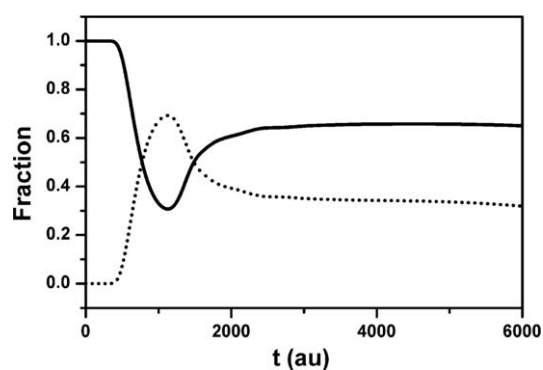

Fig. 3. The fraction of the lower (dotted line) and the upper (solid line) adiabatic states as a function of time for nonadiabatic reaction as described in Fig. 1.

$$V_1 = A\exp(-\alpha x); \quad V_2 = A\exp(\alpha x) \tag{16}$$

with constant coupling potential V_{12}. We used the same parameter set as in Baer and Child: $m = 1.905$ amu; $A = 0.1$ eV; $\alpha = 8$ Å^{-1}; $V_{12} = 0.08$ eV. We set the parameter values for the asymptotic wavepackets to be: $q_1 = -2$, $\gamma_1 = 5$, $p_1 = 7.5$ for ϕ_1^+; $q_2 = +2$, $\gamma_2 = 5$, $p_2 = 7.5$ for ϕ_2^- (all in atomic units).

Fig. 4 shows the correlation function and Fig. 5 the reaction probability (transmission coefficient) $P(E) = |S(E)|^2$. The results show the same resonance features, i.e., oscillations of $P(E)$ with complete reflections at certain energies, as in the first model reaction. In Fig. 5, we also plotted the results obtained from the semiclassical theory by Zhu and Nakamura [28–31], and the time-inde-
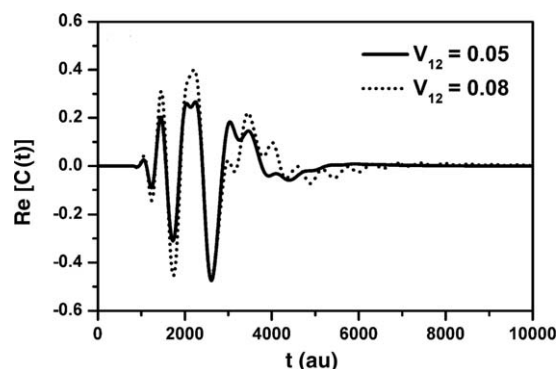

Fig. 4. Correlation function as a function of time for the reaction on the potentials of model two-state curve-crossing problem of Baer and Child (Ref. [27]), with the parameters of $A = 0.1$ eV; $\alpha = 8$ Å^{-1}; $V_{12} = 0.05$ eV. The solid line is for $V_{12} = 0.05$ eV and the dotted line is for $V_{12} = 0.08$ eV.
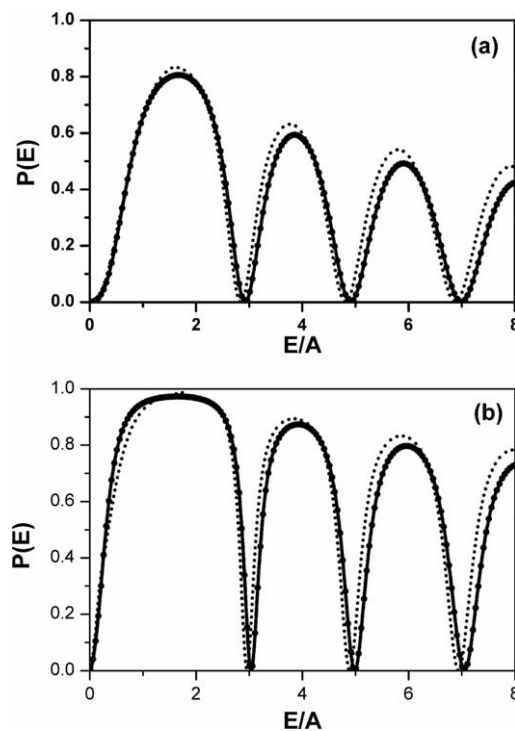

Fig. 5. Reaction probability (transmission coefficient) $P(E) = |S(E)|^2$ as a function of energy for the reaction on the potentials as given in Fig. 4. (a) $V_{12} = 0.05$ eV; (b) $V_{12} = 0.08$ eV. The solid line is for the present calculations; the dotted line is for the semiclassical calculations of Zhu and Nakamura (Ref. [28]); and the solid symbol is for the time-independent nonadiabatic scattering calculations (Ref. [24]).

pendent scattering theory for nonadiabatic reactions [24]. Both time-independent and time-dependent scattering calculations give identical results and they show fairly good agreement with the semiclassical calculations. It is found that the complete reflection occurs at the energies somewhat larger than the bound states of the upper adiabatic surface.

The third example of nonadiabatic reactions is a simple two-dimensional quasi-JT (Jahn–Teller) model proposed by Baer et al. [32] and Adhikari and Billing [33]. This model was introduced in order to examine the effect on the

symmetry of the nuclear wavefunctions due to conical intersection (CI) in reactive scattering problems. In the reactive double slit model (RDSM), the two adiabatic potential energy surfaces are given by:

$$U_1(R,r) = \frac{1}{2}m(\omega_0 - \tilde{\omega}_1(R))^2 r^2 + A f(R,r),$$

$$U_2(R,r) = \frac{1}{2}m\omega_0^2 r^2 + (D-A)f(R,r) + D, \qquad (17)$$

where $\tilde{\omega}_1(R) = \omega_1 \exp\left(-\left(\frac{R}{\sigma_1}\right)^2\right)$ and $f(R,r) = \exp\left(-\frac{R^2+r^2}{\sigma^2}\right)$ with R and r representing translational and vibrational coordinates, respectively. We used the same parameter set as in Baer et al. [32]: $m = 0.58$ amu; $A = 3.0$ eV; $D = 5.0$ eV; $\sigma = 0.30$ Å; $\sigma_1 = 0.75$ Å; $\omega_0 = 39.14 \times 10^{13}$ s^{-1}; $\omega_1 = 7.83 \times 10^{13}$ s^{-1}. We select initial wavepacket to be Gaussian form in R and vibration eigenfunction in r with initial momentum corresponding to kinetic energy of 2.0 eV.

Fig. 6 shows the correlation function and Fig. 7 the reaction probability of $0 \rightarrow 1$ transition. The results show the similar resonance features as in the one-dimensional model reactions. It is noted that the conical intersection between
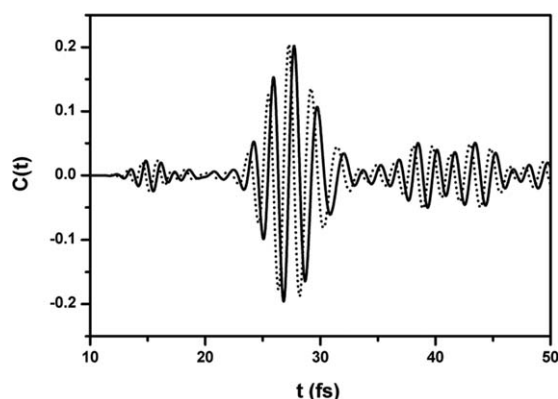

Fig. 6. Correlation function as a function of time for the reaction on the potentials of two-dimensional quasi-Jahn–Teller model proposed by Baer et al. (Ref. [32]), with the parameters as described in the text. The solid line is the real part and the dotted line is the imaginary part.
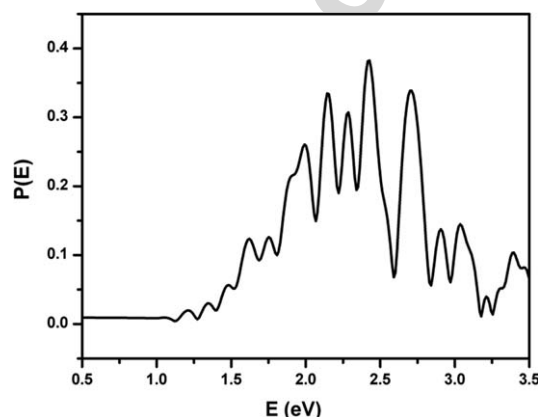

Fig. 7. Reaction probability of $0 \rightarrow 1$ transition as a function of energy for the reaction on the potentials of two-dimensional quasi-Jahn–Teller model as given in Fig. 6.

two surfaces occurs at 3.0 eV for the present model. The calculated reaction probabilities are consistent with the results of the previous works [32,33]. The detailed analysis of theoretical calculations on the quasi-JT model will be reported elsewhere.

4. Concluding remarks

A time-dependent formulation of quantum mechanical scattering theory for reactions on multiple electronic states has been presented. We extended the wavepacket correlation function theory of Tannor and coworkers to electronically nonadiabatic processes. The total wavefunction of the system is expanded in terms of electronic basis functions in diabatic representation. The asymptotic nuclear wavepacket can be defined on a diabatic state, which correlates with a particular adiabatic state in the asymptotic region. The propagation of the N-state diabatic wavefunction is carried out by the direct exponentiation method for the Hamiltonian matrix in the split operator formalism.

We have applied the theory to a one-dimensional, two-electronic-state model of Shin and Light, and a reactive curve-crossing model of Baer and Child. It was shown that one can obtain insight into the detailed mechanism of nonadiabatic processes by examining the time-dependent behavior of both diabatic and corresponding adiabatic wavepackets. In both model reactions, the correlation function persists over an extended period of time, leading to clear resonance structure in the reaction probability $P(E)$, when the two electronic states are strongly coupled nonadiabatically. Most interestingly, $P(E)$ goes to zero at certain energies of the system. The phenomenon of complete reflection has been noted in previous studies [26,29–31]. In particular, the semiclassical theory of Zhu and Nakamura provides a relation for the occurrence of such complete reflection, which is similar to a simple quantization condition with an extra correction due to nonadiabatic correction [30,31]. This phenomena is due to the interference between the wave which transmits the barrier and the wave which is trapped by the upper state. Based on the intriguing phenomenon of complete reflection, a new mechanism of molecular switching was proposed by using a finite periodic array of nonadiabatic tunneling type potential units [31]. We also applied the present method to a simple two-dimensional quasi-JT (Jahn–Teller) model. It was found that the results of calculations show the resonance features in the reaction probability due to the conical intersection.

It is known that the split operator propagator may have error in phase, which can cause problems in calculating reaction probabilities. In our implementation of the present numerical scheme to the one-dimensional model reactions, there are no noticeable difficulties in the convergence of the calculations. The preliminary calculations on the two-dimensional model reaction with CI also showed consistent results with other theoretical methods. More detailed analysis on the two-dimensional model or examination of a multiple curve crossing problem will be useful.

The present study illustrates a simple and straightforward extension of the wavepacket correlation function method to electronically nonadiabatic reactions. It has been shown that time-dependent formulation of reactive scattering theory can be cast into various forms in order to provide an improved route to the evaluation of S-matrix or cumulative reaction probabilities. It should be possible to apply similar modifications to our time-dependent formulation for handling reactions on multiple electronic states. The use of semiclassical wavepacket propagation and implementations based on the ideas of quantum transition state theory will be the subject of future studies.

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