ARTICLE

Electron Transfer Dynamics in Solution Using Imaginary-time Split Operator Approach

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An imaginary-time split operator approach is proposed to study electron transfer (ET) dynamics using Sumi-Marcus theory. The approach is applied to evaluate the intermolecular ET rate between oxazine 1 and N,N-dimethlaniline. By measuring the two average survival times of the donor state probability and the rate constant in long time limit, the full kinetics of the ET is revealed with a variety of sink functions. Several new properties for the ET have been found in numerical simulations.

Key words: Electron transfer, Solvent dynamics, Imaginary time split operator

I. INTRODUCTION

Electron transfer (ET) dynamics processes constitute ubiquitous and fundamental phenomena in physics, chemistry, and biology [1]. Though it is very important in governing many dynamical processes in complex environments, theoretical studies of ET are difficult because the environment fluctuation has a great impact on it. In the early treatments, the environment fluctuation was commonly assumed to be faster than ET dynamics and the thermal equilibrium distribution was maintained in the donor state. Based on this point, Marcus developed the well-known Marcus theory [2,3] for the ET rate. The quantum formulas of the Marcus theory have also been proposed (e.g., Ref.[4] and references therein).

The fundamental assumption concerning the rapid thermalization in the donor state, however, is not always satisfying in many reactions. It has been known from Kramers' work [5] for adiabatic reactions. In Kramers theory, the reactive dynamics was regarded as a diffusive procedure over a potential barrier from the reactant to the product well. In order to take into account the diffusive dynamics of the environment in the ET, Zusman [6], and later Garg and coworkers [7], have extended Kramers theory and introduced the adiabatic parameter into the well-known Marcus classical formula [3]. The approaches were further developed to incorporate the inter- and intra-molecular vibrational modes. Jortner and Bixon (JB) reported a modification of the outer sphere ET starting from the quantum path integral representation [8]. Sumi and Marcus (SM) introduced a theory in which the solvent diffusive motion is described by the Smoluchowski equation and the vibrational contribution is involved through a sink function [9]; since the motions of the high frequency modes are assumed to be faster than the solvent one, the thermal-equilibrium population distribution of those modes is maintained. In order to explain their experimental data, Barbara *et al.* proposed a hybrid of the JB and SM theories [10]. In the SM theory or the hybrid approach, one has to solve a set of diffusion equations. In a variety of numerical approaches, the almost mature approach is the standard finite differentiation on numerical grids [11], where the numerical instability and the boundary conditions must be taken into account carefully. Other numerical approaches include the generalized moment expansion [12], the projection operator technique [13], the instanton approach [14], the Brownian trajectory method [15], and the path integral Monte Carlo approach [16].

In this work, the authors propose an imaginary-time split operator approach (ITSOA) to solve the reaction-diffusion equation. The approach is based on the real-time split operator [17] which has been widely used in the wave-packet simulations. Compared with finite differentiation, the split operator technique essentially overcomes the numerical instability and easily incorporates the boundary conditions by an absorbing potential. In addition, the ITSOA can predict long time dynamics very accurately. As a concrete example, the proposed approach is used to investigate the intermolecular electron transfer between oxazine 1 and N,N-dimethlaniline. Nagawa *et al.* has illustrated for this system that the time dependence of the survival probability in the donor state is non-exponential because of the complex interaction of solvation dynamics and the ET kinetics [18]. Therefore, the ET rates were reported with respect to two characteristic survival times τ_a and τ_b. The hybrid theory of the JB and SM models has been employed to explain the experimental data [18,19]. The results presented here demonstrate, however, that the SM model with a suitable sink function can reproduce the essential features of the experimental observations without using the hybrid approach.

Furthermore, the stationary ET rate constant is in-

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vestigated. This quantity is interesting in stationary measurement, such as electro-chemistry experiments. The stationary ET rate constant is only well defined if the probability exhibits an exponential decay. Therefore, a third quantity is used— a time-dependent decay rate, to investigate the behavior of population relaxation. For the tested system, it was found that the stationary rate constant does exist at a long time limit. For the reversible reaction, the backward reaction decreases the ET rate in the Marcus normal region although it gives a negligible contribution in the Marcus inverted region. However, the stationary rate constants are very different from the averaged rates τ_a and τ_b.

II. THE SUMI-MARCUS THEORY FOR ELECTRON TRANSFER

In the SM model [9], the free energy profiles of the donor ($i=1$) and acceptor ($i=2$) are modeled with harmonic oscillators of two degrees of freedom

$$V_1(q,x) = \frac{1}{2}(\omega^2 q^2 + x^2) \tag{1}$$

$$V_2(q,x) = \frac{1}{2}[\omega^2(q-q_0)^2 + (x-x_0)^2] + \Delta G_0 \tag{2}$$

here q represents the collective coordinate of the vibrational modes. x is the solvent coordinate. ΔG_0 is the exothermicity of the reaction. The total reorganization energy is given by the expression

$$\lambda = \lambda_q + \lambda_x, \quad \lambda_q = \omega^2 q_0{}^2/2, \quad \lambda_x = x_0{}^2/2 \tag{3}$$

where λ_q and λ_x represent the reorganization energies of the vibrational modes and outer sphere solvent polarization fluctuation, respectively.

In the ET process, both the intra-molecular vibrational motions and solvent fluctuation contribute to promote reactions. The solvent fluctuation, whose source is frequently the rotational motions of solvent molecules, is much slower than the vibration motions. Thus, one may use reaction-diffusion equations to treat motions in the solvent fluctuation and sink functions to incorporate the contribution from the vibrational motions. Denoting and $P_1(x,t)$ as $P_2(x,t)$ population distributions of finding the donor and acceptor states, respectively, at a given x and time t, one obtains the coupled diffusion-reaction equations [9]

$$\frac{\partial P_1(x,t)}{\partial t} = [L_1 - k_1(x)]P_1(x,t) + k_2(x)P_2(x,t) \tag{4}$$

$$\frac{\partial P_2(x,t)}{\partial t} = [L_2 - k_2(x)]P_2(x,t) + k_1(x)P_1(x,t) \tag{5}$$

where $k_i(x)$ is the sink function, and the generalized Smoluchowski operator L_i is given by

$$L_i = D(t)\left[\frac{\partial^2}{\partial x^2} + \beta\frac{\partial}{\partial x}\frac{dV_i(x)}{dx}\right] \tag{6}$$

with a time-dependent diffusion coefficient $D(t)$. $D(t)$ is related to the solvation time τ_s by an expression

$$D(t) = \frac{1}{\beta\tau_s} \tag{7}$$

When the backward ET from the acceptor to donor is ignored, i.e., for irreversible reactions, Eq.(4) becomes a simple reaction-diffusion equation

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2} + \frac{D}{k_B T}\frac{\partial}{\partial x}\left[P(x,t)\frac{dV_1}{dx}\right] - k_1(x)P(x,t) \tag{8}$$

In Eq.(4), Eq.(5), and Eq.(8), the sink function $k_i(x)$ is commonly calculated by transition state theory along the direction of the intra-molecular vibrational motion because of the much faster vibrational motion compared with solvent diffusion. In the original SM model, the vibrational mode was treated classically and the well-known Marcus formula in the high temperature limit was used as the sink function.

For many experimental systems, however, the inner-shell frequencies are sufficiently high so that the nuclear tunneling becomes significant. Furthermore, the electronic coupling strength may locate the regime out of the nonadiabatic and adiabatic transition to make the perturbation theory and adiabatic transition state theory invalid. Recently, Zhao *et al.* proposed a simple unified theory for the sink function which covers the nonadiabatic to adiabatic transition correctly [20-22]. The present work focuses on the nonadiabatic ET. This means that the perturbation theory is safely applied. In the following, only the sink function $k_1(x)$ is presented explicitly. Similar techniques can be used to obtain $k_2(x)$.

At a given solvent coordinate x, the Fermi Golden rule reads

$$k_1(x) = \frac{2\pi}{\hbar}\sum_n P_n \sum_{n'}|V_{n,n'}|^2\delta(E_{n'} - E_n) \tag{9}$$

here E_n is the n-th energy of the donor state. $V_{n,n'} = \langle n|V|n'\rangle$ represents the coupling matrix between the n-th and n'-th energy levels. P_n is the Boltzmann probability and it has an expression

$$P_n = \exp(-\beta E_n)Q^{-1} \tag{10}$$

where $\beta = 1/k_B T$, Q is the partition function. Eq.(9) can be cast into a form of the electronic coupling correlation function

$$k_1(x) = \frac{V^2}{\hbar^2}\int_{-\infty}^{\infty} dt \exp\left[\frac{i}{\hbar}\Delta G(x)t\right]\exp\{-S[(2n+1) - ne^{-i\omega t} - (n+1)e^{i\omega t}]\} \tag{11}$$

where $n = (e^{\hbar\omega/k_B T} - 1)^{-1}$, Huang-Rhys factor $S = m\omega q_0{}^2/2\hbar$, and the x-dependent $\Delta G(x)$ which is given by

$$\Delta G(x) = \Delta G_0 - xx_0 + \lambda_x \tag{12}$$

Eq.(11) predicts the rigorous sink function. Its numerical integration, however, is difficult because of a high oscillation integrand, especially in the Marcus inverted region. Fortunately, a variety of closed-form expressions can be obtained from Eq.(11) with different approximations. With use of the short-time approximation for $\exp(i\omega t)$, Eq.(11) leads to the following Marcus-Levich formula

$$
\begin{aligned}
k_1(x) &= \frac{V^2}{\hbar^2}\sqrt{\frac{2\pi}{S\omega^2(2n+1)}} \\
&\quad \cdot \exp\left\{-\frac{[\Delta G(x)/\hbar + S\omega]^2}{2S\omega^2(2n+1)}\right\} \quad (13)
\end{aligned}
$$

in which the nuclear tunneling effect is partially included. If one uses high temperature limitation of n in Eq.(13), the well-known Marcus formula is recovered

$$
k_1(x) = \frac{V^2}{\hbar^2}\sqrt{\frac{\pi}{\lambda_q k_B T}}\exp\left\{-\frac{[\Delta G(x)+\lambda_q]^2}{4\lambda_q k_B T}\right\} \quad (14)
$$

III. IMAGINARY-TIME SPLIT OPERATOR APPROACH

For the purpose of the numerical evaluation, it is convenient to transform the coupled equations Eq.(4) and Eq.(5) into Hermitian forms. To do so, one can use the substitution

$$
p_i(x,t) = \frac{P_i(x,t)}{g_i(x)} \quad (15)
$$

where $g_i(x)$ is the square root of equilibrium solution of the coupled equations in the absence of the reactions, and it has a form

$$
\begin{aligned}
g_i(x,t) &= [P_i^{eq}(x)]^{1/2} \\
&= \frac{\exp[-\beta V_i(x)/2]}{\int \mathrm{d}x\,\exp[-\beta V_i(x)/2]} \quad (16)
\end{aligned}
$$

Then, Eq.(4) and Eq.(5) can be transformed into the adjoint form

$$
\frac{\partial}{\partial t}\begin{bmatrix} p_1(x,t) \\ p_2(x,t) \end{bmatrix} = \begin{bmatrix} H_1(t) & k_2'(x) \\ k_1'(x) & H_2(t) \end{bmatrix}\begin{bmatrix} p_1(x,t) \\ p_2(x,t) \end{bmatrix} \quad (17)
$$

$$
k_1'(x) = k_1(x)\frac{g_1(x)}{g_2(x)} \quad (18)
$$

$$
k_2'(x) = k_2(x)\frac{g_2(x)}{g_1(x)} \quad (19)
$$

H_i is the Hermitian form of the Smoluchowski diffusion operator

$$
H_i(t) = T_i(t) + V_i(t) \quad (20)
$$

where T_i is the time-dependent kinetic operator

$$
T_i(t) = D(t)\frac{\partial^2}{\partial x^2} \quad (21)
$$

and $V_i(t)$ is the time-dependent potential

$$
V_i(t) = \frac{\beta D(t)}{2}\left\{\frac{\beta}{2}\left[\frac{\mathrm{d}V_i(x)}{\mathrm{d}x}\right]^2 - \frac{\mathrm{d}^2 V_i(x)}{\mathrm{d}x^2}\right\} - k_i(x) \quad (22)
$$

It is easy to show that Eq.(17) becomes standard coupled Schrödinger equations when one replaces t by it, i.e. replaces time by imaginary time. Therefore, the numerical approaches solving the Schrödinger equation can be used straightforwardly. The main difference between the imaginary time and real time is that the former replaces $\exp(i\hbar H)$ by $\exp(\hbar H)$. In this work, we choose an imaginary-time split operator approach. We chose this name to distinguish it from the approach used in solving Schrödinger equations. To apply the approach, the formal solution of Eq.(4) is written as

$$
\mathbf{p}(x,t) = \exp_+\left[\int_0^t \mathrm{d}\tau \mathbf{H}(\tau)\right]\mathbf{p}(x,0) \quad (23)
$$

where $\mathbf{p}(x,t)$ represents the array of p_1 and p_2. Consider the propagation in a short time step $\mathrm{d}t$. Under the Trotter approximation, the population at $t+\mathrm{d}t$ can be evaluated with an expression

$$
\begin{aligned}
\mathbf{p}(x,t+\mathrm{d}t) &= \exp\left[\mathbf{T}(t)\frac{\mathrm{d}t}{2}\right]\exp[\mathbf{V}(t)\mathrm{d}t] \\
&\quad \cdot \exp\left[\mathbf{T}(t)\frac{\mathrm{d}t}{2}\right]\mathbf{p}(x,t) \quad (24)
\end{aligned}
$$

where $\mathbf{T}(t)$ is the kinetic operator

$$
\mathbf{T}(t) = \begin{bmatrix} T_1(t) & 0 \\ 0 & T_2(t) \end{bmatrix} \quad (25)
$$

and $\mathbf{V}$ represents the potentials

$$
\mathbf{V}(t) = \begin{bmatrix} V_1(t) & k_2' \\ k_1' & V_2(t) \end{bmatrix} \quad (26)
$$

Thus, standard procedures for the real time split operator [17,23] can be employed to calculate Eq.(24). In this work, the fast Fourier transformation technique was used to evaluate the time-dependent kinetic operator.

IV. DEFINITION OF ELECTRON TRANSFER RATES

The ET rate constants are unambiguously defined only from a single exponential decay of the population at the donor state. However, the reaction-diffusion equation Eq.(4) does not always predict population decay with a single exponential term. For irreversible reactions, there are two kinds of the average survival time

$$
\tau_a = \int_0^\infty \mathrm{d}t\, S(t) \quad (27)
$$

$$
\tau_b = \int_0^\infty \mathrm{d}t\,\frac{t S(t)}{\tau_a} \quad (28)
$$

where $S(t) = \int P(x,t)\mathrm{d}x$. Two kinds of ET rate thus are defined with respect to the inverse of τ_a and τ_b, respectively. The quantity τ_a monitors the short-time dynamics of the population and is equivalent to the mean first passage time. τ_b detects information of a time region later than τ_a. Both become equal only if the population decays exponentially.

In order to investigate the single exponential decay, one can define a time-dependent rate

$$k_f(t) = -\frac{\mathrm{d}\ln S(t)}{\mathrm{d}t} \qquad (29)$$

If $k_f(t)$ reaches a plateau after long time the definition of a rate constant is meaningful. This ET rate constant is obtained by

$$k_f = \lim_{t\to\infty} k_f(t) \qquad (30)$$

For reversible reactions one has to involve the backward ET process. Under an assumption that the population decays exponentially for a sufficiently long time, the population dynamics can be described by simple kinetic equations [24,25]

$$\dot{S}_1(t) = -k_f S_1(t) + k_b S_2(t) \qquad (31)$$
$$\dot{S}_2(t) = -k_b S_2(t) + k_f S_1(t) \qquad (32)$$

where k_f and k_b denote the forward and backward electron transfer rates, respectively, which are related by the principle of detailed balance

$$k_f = k_b \mathrm{e}^{-\beta \Delta G_0} \qquad (33)$$

The corresponding kinetic equation for $S(t)(= S_1(t) - S_2(t))$ becomes

$$\dot{S}(t) = -(k_f - k_b) - (k_f + k_b)S(t) \qquad (34)$$

By using the initial condition $S(0)=S_0$, one may solve Eq.(34) and get

$$S(t) = (S_0 - S_\infty)\exp(-k_{th}t) + S_\infty \qquad (35)$$

where k_{th} is the total transfer rate, $k_{th} = k_f + k_b$, and $S_\infty = (\mathrm{e}^{\beta\Delta G_0} - 1)/(\mathrm{e}^{\beta\Delta G_0} + 1)$ denotes the population difference when the donor and accepter states reach thermal equilibrium distributions. The long-time total rate constant can be defined as follows:

$$k_{th} = \lim_{t\to\infty} -\frac{\mathrm{d}\ln | S(t) - S_\infty |}{\mathrm{d}t} \qquad (36)$$

The forward rate constants for reversible reactions is readily obtained from Eq.(33) and Eq.(36)

$$k_f{}^r = \frac{k_{th}}{1 + \exp(\beta\Delta G_0)} \qquad (37)$$

It is noted that although both Eq.(30) and Eq.(37) define the forward ET rate constants they are different because Eq.(37) essentially incorporates the effect from backward ET whereas Eq.(30) does not. This difference is demonstrated numerically below.

V. NUMERICAL SIMULATION

As a numerical example of the approach described in the previous sections, the ET between oxazine 1 (OX1) and solvent N,N-dimethyanline (DMA) was studied. This system has been investigated by both experiments and theoretical studies [18,19]. The experimental results have demonstrated that although OX1 is a strongly fluorescent molecule used as laser dye, the fluorescence is severely quenched with a life time of $\sim$280 fs when it is dissolved in DMA. The quenching is caused by the ET from DMA (donor state) to an excited state (acceptor state) of OX1. Nagasawa *et al.* have also investigated this system theoretically by using the hybrid approach of JB and SM models with parameters [18]: the solvent reorganization energy λ_x=124 meV, the exothermicity of the reaction ΔG_0=496 meV, and the coupling strength V=15 meV. They introduced the high- and low-frequency modes for inter-molecular vibrational motions. The corresponding reorganization energies are 124 and 372 meV, respectively. The effective frequency for the high-frequency mode was chosen to be 1430 cm^{-1}. The solvation time τ_s was deduced from the experimental data of the time correlation function of solvation fluctuation. This correlation function has been fitted to a double exponential function

$$C(t) = a_1\mathrm{e}^{-t/\tau_1} + a_2\mathrm{e}^{-t/\tau_2} \qquad (38)$$

The corresponding solvation time can be obtained by the equation

$$\tau_s \equiv \int_0^\infty C(t)\mathrm{d}t = a_1\tau_1 + a_2\tau_2 \qquad (39)$$

For DMA solvent, a_1=0.19, a_2=0.81, τ_1=7.9 ps, and τ_2=18.7 ps have been reported [18]. From those parameters we get τ_s to be 16.6 ps. Nagasawa *et al.* have defined a time dependent diffusion coefficient as

$$D(t) = -\frac{k_B T}{2\lambda_x}\frac{1}{C(t)}\frac{\mathrm{d}C(t)}{\mathrm{d}t} \qquad (40)$$

The present work has exactly repeated Nagasawa's results by using the same parameters with the new IT-SOA. Furthermore, it was found that there is almost no difference in the ET dynamics by using the time-dependent diffusive coefficient (Eq.(40)) and the time-independent one ($D = 1/\beta\tau_s$). In the following evaluation, the time-independent diffusive coefficient is used for the purpose of simplicity.

In the Nagasawa's. work, two vibrational modes are explicitly treated by quantum mechanics for the high-frequency mode and classical approximation for the low-frequency mode. In fact, Dogonadze has proposed an effective one-dimensional frequency by fitting the prefactor in the multi-dimensional system for the ET [26]. Our recent work indeed demonstrates that the ET rate for a multi-dimensional system can be nicely predicted

by the effective mode with a suitable frequency [22]. Therefore, the effective frequency is introduced as

$$\omega = \left(\frac{\lambda_{il}\omega_{il}^2 + \lambda_{ih}\omega_{ih}^2}{\lambda_{il} + \lambda_{ih}} \right)^{1/2} \qquad (41)$$

where subscript $ih(il)$ corresponds to the quantities of the high-(low-)frequency mode. The total vibrational reorganization energy is given by

$$\lambda_q = \lambda_{il} + \lambda_{ih} \qquad (42)$$

The low frequency ω_{il} was set to zero since it is not available experimentally and much lower than the high frequency. Figure 1 shows the time-dependence of the population obtained from the hybrid approach and SM model with the sink function from the effective mode. It explicitly shows that both approaches predict very similar results. The reduced error for τ_a is only 5%. Thus, we can conclude that the SM theory by using the effective vibrational mode can predict consistent results with the hybrid approach.
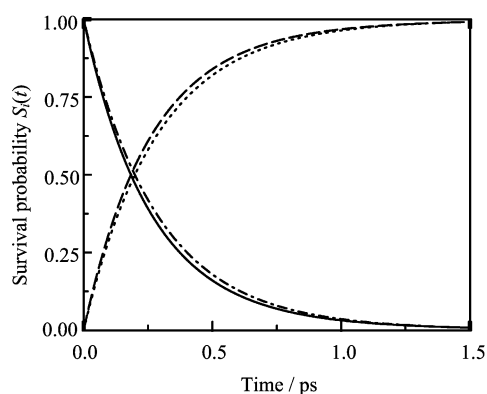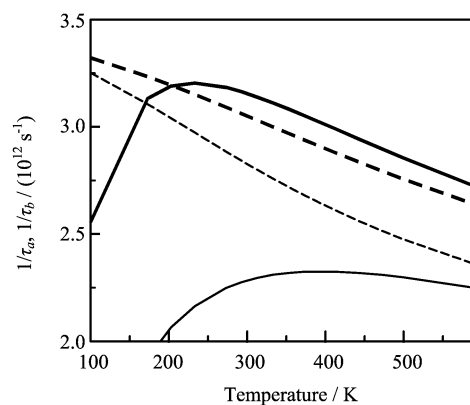

FIG. 2 Temperature dependence of the ET rates. Thick and thin solid lines represent $1/\tau_a$ and $1/\tau_b$, respectively, with use of the Marcus formula as the sink function. Thick and thin dashed lines are those with use of the Marcus-Levich equation as the sink function.
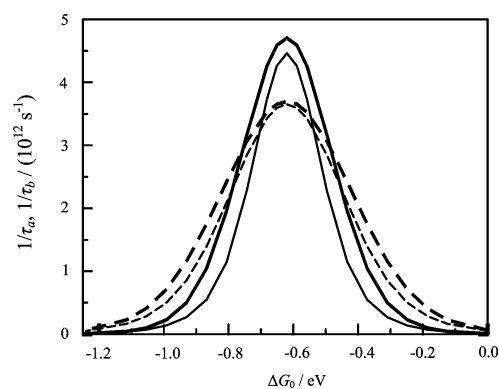

FIG. 3 ΔG_0 dependence of the ET rates at 293 K. The curves represent the same quantities as in Fig.2.

FIG. 1 The probabilities of the donor and acceptor *vs.* time at T=273 K. Solid line and dashed line are the results of the donor and acceptor states, from the hybrid approach respectively. Dot-dashed line and dotted line are those obtained from the SM model.

In order to investigate the nuclear tunneling contribution, the temperature dependence of τ_a and τ_b with different sink functions was evaluated for the irreversible reaction. The results are plotted in Fig.2. Here the Marcus-Levich equation (Eq.(13)) and the classical Marcus equation (Eq.(14)) are used for the sink functions. Both sink functions predict that the population dynamics does not follow exponential decay because the values for τ_a and τ_b are very different. At low temperature, the sink function from the Marcus equation predicts the opposite tendency with the decrease of temperature compared with the Marcus-Levich formula. This shows that the Marcus formula produces ambiguous average survival time in the low temperature and it cannot even predict the correct tendency with respect to temperature for the present system. Another interesting feature is that the values of τ_a and τ_b obtained from

the Marcus-Levich formula become closer with the decrease of temperature. This signals that population decay follows an almost exponential way. However, this conclusion contracts to the conventional idea that population dynamics will decay exponentially toward the equilibrium state at sufficiently high temperature.

With the use of the same parameters in Fig.1, the average survival times dependence of the driving force for the reaction (the free energy gap ΔG_0) at 293 K was calculated. The results are plotted in Fig.3. Both of the sink functions correctly predict the Marcus turnover theory, i.e. the rates follow the bell-shaped dependence of ΔG_0. As $\Delta G_0 = -(\lambda_i + \lambda_0) = -620$ meV, which corresponds to a barrierless reaction, the rate constant reaches the maximum. However, the nuclear tunneling effect makes the maximum rates smaller and the bell-shaped width wider.

As discussed in above, τ_a and τ_b predict the average rates, and the real rate constant can only be defined from the simple exponential decay. To find whether the rate constant definition is meaningful, the time de-
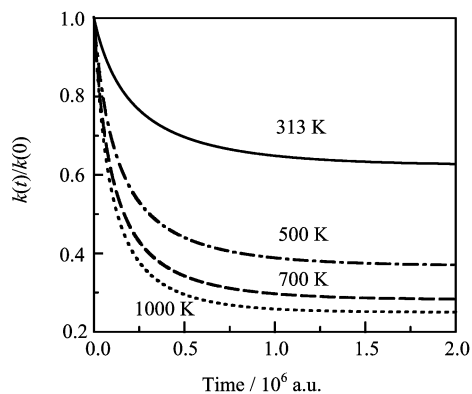

FIG. 4 Time dependent rates for four temperatures at $\Delta G_0 = 0$. The Marcus formula is used as the sink function.
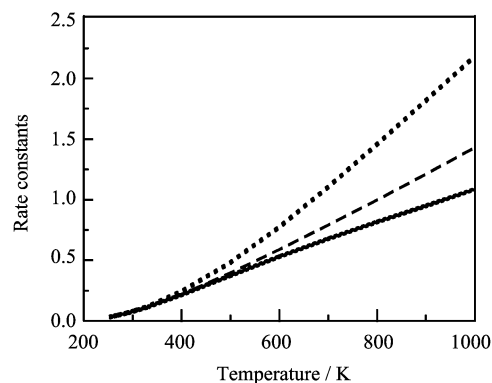

FIG. 5 ET rates as a function of temperature. The parameters are the same as those in Fig.4. Solid line: the long time rate constants. Dotted line: $1/\tau_a$; Dashed line: $1/\tau_b$.

pendent rate was plotted in Fig.4 by using Eq.(29) at several temperatures. The Marcus formula was used as the sink function in the calculation. The parameters used were the same as those in Fig.1. Figure 4 explicitly shows that the rate tends to plateau values after a long time, in a wide temperature regime. This indicates that the population indeed decays exponentially in the long time limit. From the plateau values, we can subtract the real rate constants. The results are shown in Fig.5. For the purpose of comparison, the values of τ_a and τ_b are also shown. As temperature is below 300 K, three rates are the same. However, the difference becomes obvious with the increase of temperature, and k_f is always smaller than $1/\tau_a$ and $1/\tau_b$. In the conventional transition state theory, the exponential decay is expected at high temperature even for short periods of time. However, Figure 2 and 5 show the opposite tendency. The mechanism of the ET in the SM model is very different from the conventional transition state theory. In the SM theory, the reaction can occur before population reaches the saddle point because of the sink function. With the increase of temperature, the electron may transfer in the avoid saddle point with large probability in this strong diffusive system. This creates a non-thermal equilibrium distribution after a short time and leads to the non-exponential decay.

The above simulation focused on the irreversible reaction, i.e. neglected the backward ET. In order to investigate the contribution of the backward ET, Eq.(29) and Eq.(36) can be used to evaluate the rate constant k_f with respect to ΔG_0. The results are shown in Fig.6 at 273 K. When ΔG_0 is located in the inverted regime, the backward ET has a negligible contribution while in the normal regime it slightly reduces the forward reaction rate constant. Thus we conclude that the backward ET may be negligible in the present system. However, one has to incorporate this effect for general systems in the normal regime.

VI. CONCLUSION

In this work, an imaginary time split operator approach is proposed to study ET dynamics using the Sumi-Marcus theory. Compared with finite differentiation, the split operator technique essentially overcomes the difficulties rising from the numerical instability and the boundary conditions by incorporating an
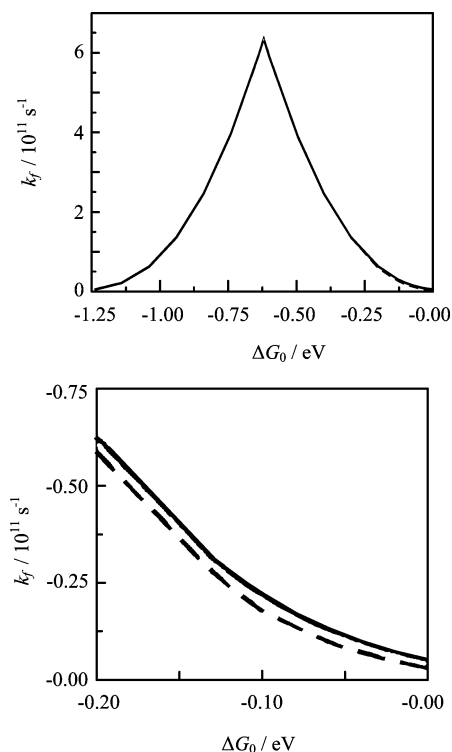

FIG. 6 ΔG_0 dependence of long-time rate constants at 273 K. Solid line represents ET rate constants obtained from the irreversible reaction. Dashed line represents those obtained from the reversible reaction. The below is the magnification of the values at the lower right corner.

absorbing potential. In addition, it can predict long time dynamics very accurately. Applying the technique to the intermolecular ET between oxazine 1 and N,N-dimethlaniline yields the following conclusions: (i) The Sumi-Marcus theory replacement of the hybrid of the Sumi-Marcus and Jortner-Bixon models can correctly predict experimental results by using a sink function from the effective vibrational mode. (ii) The nuclear tunneling has an important effect on the ET rate. Neglected, If it may even lead to a wrong rate tendency with respect to temperature. (iii) The population decays exponentially in the long time limit for the tested system. With the increase of temperature, the decay becomes more non-exponential in a short time. (iv) The backward ET has a negligible contribution to the rate constants. However, one has to take it into account in the Marcus normal regime for general systems.

In the present work, numerical tests are limited to the nonadiabatic ET in the thermal equilibrium state. However, this approach can be directly used from the nonadiabatic to adiabatic ET once the sink function is defined accordingly. Also, the approach is easily extended to study photo-induced ET where non-equilibrium distributions may dominate the ET procedures.

VII. ACKNOWLEDGMENTS

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