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# Theory of reversible electron transfer reactions in a condensed phase

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We have derived an exact analytical expression for the average forward rate of a reversible electron transfer reaction, modeled through a reaction coordinate undergoing diffusive motion in arbitrary potential wells of the reactant and the product in presence of a localized sink of arbitrary location and strength. The dynamics of diffusive motion is described by employing two coupled generalized diffusion reaction (Smoluchowski) equations with coordinate dependent diffusivity and delta sink. The average forward electron transfer rate constant obtained here for the system, with equilibrium or nonequilibrium distributions as initial condition, is determined by the forward and backward rate constants calculated based on the transition state theory and the weighted average rate for the well dynamics. We also discuss various limiting cases for the rate of electron transfer reactions corresponding to the different experimental situations. As an illustrative example, we have considered back electron transfer (ET) reaction and shown that the present theory can explain the non-Marcus free energy gap dependence of the rate of ET reactions. More importantly, the approach presented here can easily be extended to systems describing the dynamics of diffusive motion in coupled multipotential surfaces associated with electron transfer reactions.

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## I. INTRODUCTION

The study of electron transfer (ET) processes in condensed phase has attracted considerable attention [1–22] of the experimentalists as well as theoreticians over the last decades. In recent years, there has been a growing interest in this field because of phenomenal upsurge of experimental investigations on ET processes due to wide availability of spectroscopic techniques for dynamical measurements and the synthesis of tailor made artificial electron donor-acceptor systems which have led to a wealth of new experimental results. A great deal of effort has been directed to investigate the diverse behavior of the ET reactions exhibited by donor-acceptor pairs in solution and in organized media, much of which can be rationalized within the traditional well-known ET theory of Marcus [1], which includes only the energetic (viz., solvent reorganization energy and free energy of the reaction) aspect but is independent of the solvent dynamics. However, when the reaction coordinate is strongly coupled with the solvent coordinate, the ET reactions are found to be sensitive to the solvent dynamics. Since the pioneering work of Zusman [2], there have been a large number of theoretical studies devoted to the solvent effects on outer sphere ET reactions. For simplicity, in most of the cases, the backward processes have been neglected. A complete picture for the ET reaction between two states, however, should include the effect of diffusion and reaction in both directions as pointed out by Nadler and Marcus [23]. If equilibrium is to prevail between the initial and the final states, the consideration of the presence of a reverse reaction is essential and the survival probabilities obtained by taking into account for the reversible ET differs from those for a reaction in a single direction.

The rate of ET reaction and how fast the system reaches the state of dynamical equilibrium depends on the initial state of the system. The initial conditions for the system can be quite different depending on different experimental situations, i.e., the system can undergo reversible ET reaction starting with either equilibrium or nonequilibrium initial configuration. In Fig. 1, the potentials of the reactant and the product are drawn in one-dimensional space spanned by the reaction coordinates $x$. In the case of reversible ET processes with equilibrium initial configuration, the system moving initially on reactant potential well, crosses to the product well at the intersection point $x^*$ which is described in Fig. 1. Once the product is formed, it then starts recrossing to the reactant well through the same intersection point. This process con-

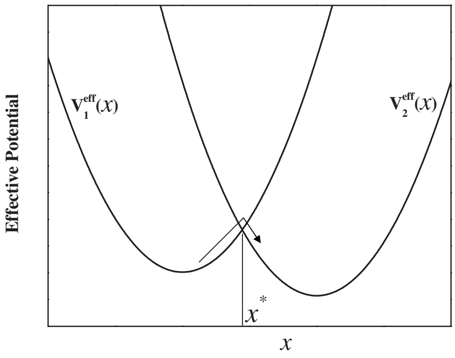

FIG. 1. Potential energy curves for the reactant and product in an ET reaction. The abscissa stands for the reaction coordinates $x$ and the ordinate stands for the effective potential. The system moving initially on reactant potential well, crosses to the product well at the intersection point and then the product starts crossing to the reactant well through the same intersection point.

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tinues and the system finally reaches dynamical equilibrium. On the other hand, in the case of reversible ET processes with nonequilibrium initial configuration (say with delta function distribution), the system is assumed to be in the ground state and is brought to the nonequilibrium excited state by laser excitation. Subsequently, the system at the higher level of excitation relaxes downward to the potential minimum of the excited-state surface due to relaxation of the polar solvent until its energy coincides with that of the ground state. Depending on the magnitude of the intrinsic ET rate $k_0$, there is an interplay between the relaxation and ET at the crossing point. If $k_0$ is small, the system relaxes to the potential minimum of the excited-state surface and ET hardly occurs during relaxation to the equilibrium state, although the system passes through the intersection point in the course of relaxation as shown in Fig. 2(a). Only after reaching the minimum of the excited-state surface, thermal fluctuation starts operating to bring the system back to the crossing point again and ET reaction then takes place with intrinsic rate $k_0$. Once the product is formed, it starts crossing to the reactant surface through the same intersection point till the dynamical equilibrium is reached. This process is then similar to the case of reversible ET reaction with initial equilibrium configuration as described in Fig. 1. However, when $k_0$ is large, the back ET reaction occurs almost exclusively at the intersection point in contrast to the relaxation of the system to the minimum of the excited-state surface as shown in Fig. 2(b). The nonequilibrium solvent configuration of charge transfer state created at the intersection point then starts relaxing slowly to attain the configuration of the minimum of the initial ground state. Finally, the system reaches the dynamical equilibrium. In the case of intermediate $k_0$, however, both the above processes start operating at the crossing point, viz., relaxation of the excited state to the potential minimum of the same state surface and back electron transfer as shown in Fig. 2(c). Finally, the system also reaches the dynamical equilibrium. It is important to note here that the analytical expressions for the rate of ET reactions corresponding to the various cases discussed above can be obtained if one can solve the relevant kinetic equation exactly for arbitrary sink strength $k_0$ and potential. In most of the conventional approaches, ET system of interest has been modeled through harmonic potentials with same curvature for the reactant and product surfaces and a diffusivity independent of reaction coordinate. However, there are many situations where ET in a system cannot be modeled through harmonic potentials and the curvature of the potential surfaces for the reactant and product may not be the same and also the diffusivity may be dependent on the reaction coordinate. Therefore, it will be useful to illustrate how the analytical expression for the rate constant of the reversible ET reactions can be evaluated in terms of arbitrary potential and position dependent diffusivity corresponding to the different initial states of preparation.

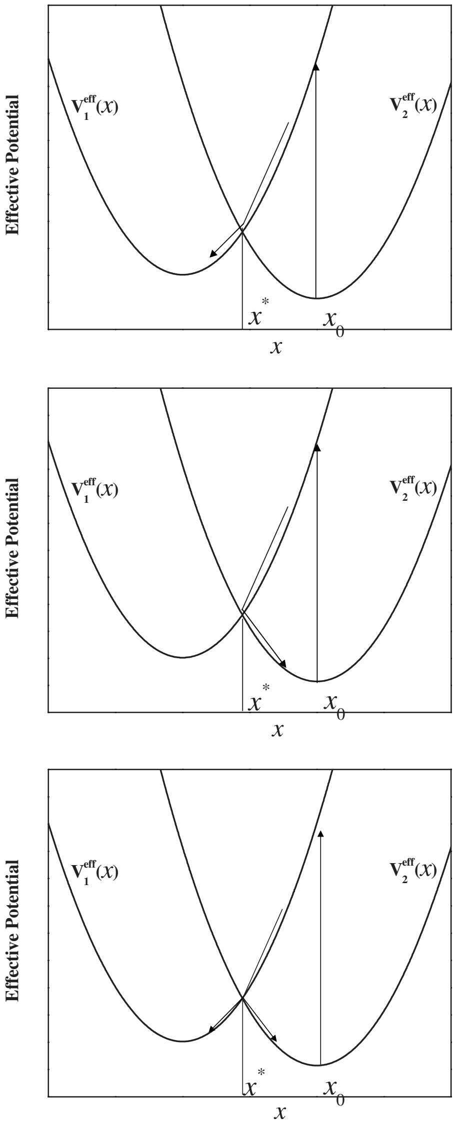

FIG. 2. (a) Potential energy curves for the reactant and product in an ET reaction. The abscissa and the ordinate are the same as in Fig. 1. It represents the relaxation of the system to the potential minimum of the excited-state surface when $k_0$ is small. (b) Potential energy curves for the reactant and product in an ET reaction. The abscissa and the ordinate are the same as in Fig. 1. It represents the back ET reaction almost exclusively at the intersection point when $k_0$ is large. (c) Potential energy curves for the reactant and product in an ET reaction. The abscissa and the ordinate are the same as in Fig. 1. It represents both the processes i.e., relaxation of the excited state to its potential minimum and the back ET in the case of intermediate $k_0$.

The organization of the rest of the paper is as follows. In the following Sec. II, we identify the reaction coordinate and transition point for ET reaction. In Sec. III we provide general kinetic equations for reversible ET reactions, consisting of two one-dimensional coupled Smoluchowski equations governing the probability distributions corresponding to the diffusive motions of the reaction coordinate in arbitrary potential wells of the reactant and the product in presence of localized sink of arbitrary strength at the transition point. This is followed by Sec. IV presenting details of the theoretical formulation for exact analytical expressions for the average forward rate constant of reversible ET reactions in terms of general effective potential and reaction coordinate dependent diffusivity considering different initial conditions. In Sec. V, we do discuss various limiting cases for the rate of electron transfer reactions corresponding to the different experimental situations in order to understand the relative contribution of the rate calculated based on transition state theory and also by solvent dynamics to the overall rate of ET.

In order to understand the free energy gap dependence of the rate of ET reactions, in Sec. VI, we have considered results for back ET reactions for charge recombination reactions. Section VII concludes with a brief summary.

## II. ELECTRON TRANSFER REACTION COORDINATE

There have been considerable efforts to construct a correct reaction coordinate for the ET reaction. As originally pointed out by Marcus [1], the following two conditions must be satisfied at the time of the electron transfer (in the transition state); (1) the positions and orientations of all the solvent molecules should be the same and (2) the total energy must be the same between the initial and final states. The first requirement is due to the character of heavy solvent motions as compared with a light electron motion. The second condition is just the energy conservation. A reaction coordinate with the dimension of energy proposed by Calef and Wolynes [3] and redefined by Yoshimori *et al.*[24], has often been used. While defining the reaction coordinate in the present formalism, we first write down the Hamiltonian for the reactant/product state of an ET reaction in a polar solvent in the general form

$$H^i(\Gamma) = H^i_{sol}(\Gamma) + H^i_{el} \quad (i = r,p), \tag{1}$$

where $\Gamma$ denotes all the accessible coordinates of the solvent molecules and the superscripts $r$ and $p$ correspond to the reactant and the product, respectively. Here $H^i_{el}$ is the electronic term, independent of solvent motions, corresponding to the energy of the isolated reactant or product pair, and consists of two parts, viz., the Coulomb interaction between the net charges of the donor ($z^i_d$) and the acceptor ($z^i_a$) sites separated by a distance $R$, and their electronic energies under vacuum. The other term, viz., solvent-dependent contribution $H^i_{sol}(\Gamma)$ can be expressed in the general form

$$H^i_{sol}(\Gamma) = \sum_m \left\{ z^i_a e \frac{(\vec{\mu}_m \,.\, \vec{r}_{ma})}{r^3_{ma}} + z^i_d e \frac{(\vec{\mu}_m \,.\, \vec{r}_{md})}{r^3_{md}} \right\} + \sum_{m>n} \sum \vec{\mu}_m \,.\, \vec{T}_{mn} \,.\, \vec{\mu}_n + H^i_{ind} + H_{c-c}, \tag{2}$$

where the first two terms represent the charge-dipole interaction with $e$ as the electronic charge, and $z^i_a(z^i_d)$ and $r_{ma}(r_{md})$ denoting, respectively, the valence of the acceptor (donor) and its distance from the *m-th* solvent molecule with a permanent dipole moment $\vec{\mu}_m$. $\vec{T}_{mn}$ represents the dipole-dipole interaction tensor. $H^i_{ind}$ accounts for the residual charge-dipole as well as the dipole-dipole interactions due to the electronic polarization of the solute and solvent molecules, and $H_{c-c}$ is the core-core interaction between solute and solvent molecules and between solvent molecules.

The electron, which is originally localized at the donor site in the reactant, will be delocalized when the following condition is satisfied, i.e.:

$$H^r_{sol}(\Gamma^*) - H^p_{sol}(\Gamma^*) = H^p_{el} - H^r_{el} = -\Delta G, \tag{3}$$

where $\Gamma^*$ corresponds to the transition point in multidimensional space. Due to thermal fluctuation, the only quantity that changes with the solvent configuration $\Gamma$ and determines the ET is $[H^r_{sol}(\Gamma) - H^p_{sol}(\Gamma)]$ suggesting an obvious choice of the microscopic reaction coordinate to be given by

$$A(\Gamma) = [H^r_{sol}(\Gamma) - H^p_{sol}(\Gamma)]. \tag{4}$$

Now we consider the probability distribution for the reaction coordinate. The probability of the microscopic reaction coordinate $A(\Gamma)$ to have the value $x$, when the system is in the reactant/product state, is defined as

$$\exp[-\beta V^{eff}_i(x)] = \beta^{-1} \int d\Gamma\, \delta(A(\Gamma) - x) \exp[-\beta H^i_{sol}(\Gamma)], \tag{5}$$

where $\exp[-\beta V^{eff}_i(x)]$ ($i=1,2$ for $r,p$ corresponds to the projection of the respective distribution function for the reactant/product in full phase space on subspace described by the function $\delta[A(\Gamma)-x]$ directed along the one-dimensional coordinate $x$. An important advantage of defining such effective potential energy curves $V^{eff}_i(x)$ is that the solvent configurations [corresponding to those phase space points that lie on the surface $A(\Gamma)=x$] along the reaction coordinate $x$ are the same between the initial (electron is on the donor site) and final state (electron is on the acceptor site) owing to the delta function. This property is very important because the condition (1) is always satisfied for all of the values of $x$, although the condition (2) is not satisfied always. However, at the transition point $x^*$, the condition (1) and the energy conservation [condition (2)] are guaranteed when the following relation holds, viz.,

$$\begin{aligned} \exp[-\beta V^{eff}_1(x^*)] &= \beta^{-1} \int d\Gamma\, \delta[A(\Gamma) - x^*] \exp\{-\beta H^p_{sol}(\Gamma) \\ &\quad + \beta[H^p_{sol}(\Gamma) - H^r_{sol}(\Gamma)]\} \\ &= \exp[\beta\Delta G]\beta^{-1} \int d\Gamma\, \delta[A(\Gamma) - x^*] \\ &\quad \times \exp[-\beta H^p_{sol}(\Gamma)] \\ &= \exp[-\beta V^{eff}_2(x^*) + \beta\Delta G]. \end{aligned}$$

The above derivation provides a relation between the effective potentials of the reactant and the product at the transition point $x^*$, viz.,

$$V^{eff}_1(x^*) = V^{eff}_2(x^*) - \beta\Delta G. \tag{6}$$

where $\Delta G$ denotes the free energy of ET reaction. The above Eq. (6) actually provides a root for obtaining the transition point $x^*$ for occurrence of the ET reaction provided the explicit expression for $V^{eff}_i(x^*)$ is known. An alternative approach can also be used to derive a relation similar to the above, valid for all values of $x$, viz.,

$$\begin{aligned} V_1^{eff}(x) &= -\beta^{-1}\ln\Bigg[\beta^{-1}\int d\Gamma\,\delta[A(\Gamma)-x]\exp\{-\beta H_{sol}^{p}(\Gamma) \\ &\qquad + \beta[H_{sol}^{p}(\Gamma)-H_{sol}^{r}(\Gamma)]\}\Bigg] \\ &= -\beta^{-1}\ln\Bigg\{\exp[-\beta x]\beta^{-1}\int d\Gamma\,\delta[A(\Gamma)-x] \\ &\qquad \times\exp[-\beta H_{sol}^{p}(\Gamma)]\Bigg\} \\ &= -\beta^{-1}\ln\{\exp[-\beta V_2^{eff}(x)-\beta x]\}, \end{aligned}$$

which can be rewritten as

$$V_1^{eff}(x) = V_2^{eff}(x) + x. \tag{7}$$

Combining Eq. (7) with Eq. (6), we obtain

$$x^{*} = -\Delta G. \tag{8}$$

The above relation is very important in the sense that the transition point is independent of the form of the effective potential $V_i^{eff}(x)$ but depends only on the free energy of reaction. Now in order to evaluate the rate of ET reactions, what is needed, is the kinetic equation for the reaction coordinate $x$ which describes the diffusive motion of the reaction coordinate along with ET reaction. In the following section we discuss it in details.

## III. THEORETICAL FORMALISM

In the reversible ET process, the system moving initially on a multidimensional reactant potential well, is brought by thermal fluctuation to the intersection point $\Gamma^{*}$ (transition point in multidimensional space) and ET does take place at this point. At the transition point, product is in nonequilibrium state, and solvent relaxation brings it down to the stable product state. Once the product is formed, it starts recrossing to the reactant well through the same intersection point until the dynamical equilibrium is reached. The ET reaction does occur with an intrinsic rate [12] $k_0$ (corresponding to $\Gamma^{*}$) i.e., when the reactant and product potential energies are equal. It is, therefore, possible to formulate the kinetic equation for ET reactions in terms of a nonlinear Smoluchowski-Vlasov equation, which would explicitly include the multidimensional nature of the diffusive motion but only at the cost of additional complexity. The theoretical description, that we propose here is based on a kinetic equation for the probability distribution $P_i(x,t|x_0,0)$ of a microscopic reaction coordinate $A$ constrained to have a value $x$ at time $t$ with its initial value $x_0$ at $t=0$, which was originally obtained by Zwanzig [25] and subsequently modified by others, and can be written [3] in the Markovian limit as

$$\frac{\partial P_i(x,t|x_0,0)}{\partial t} = \frac{\partial}{\partial x}\left\{D_i(x)\left[\frac{\partial P_i(x,t|x_0,0)}{\partial x} + P_i(x,t|x_0,0)\frac{\partial}{\partial x}\{\beta V_i^{eff}(x)\}\right]\right\}. \tag{9}$$

Here, $x$-dependent diffusivity $D_i(x)$ is defined as

$$D_i(x) = \int_0^{\infty} dt\,\frac{\int d\Gamma\,\dot{A}(\Gamma,t)\dot{A}(\Gamma)\delta(A(\Gamma)-x)\exp[-\beta H_{sol}^{i}(\Gamma)]}{\int d\Gamma\,\delta(A(\Gamma)-x)\exp[-\beta H_{sol}^{i}(\Gamma)]}, \tag{10}$$

where the dot corresponds to time derivative. Derivation of Eq. (9) is based on the assumption that the reaction coordinate varying slowly is not coupled to any other slowly relaxing quantity in the fluid and that the momentum and angular momentum correlations decay much more rapidly than the positions or orientations. We now consider here the descriptions of the kinetic equations for the forward as well as backward processes based on Smoluchowski equations governing the probability distributions $P_1(x,t|x_0,0)$ and $P_2(x,t|x_0,0)$ corresponding to the diffusive motions of one-dimensional reaction coordinate $x$ in the respective potential wells of the reactant and product state in presence of a delta sink of strength $k_0$ located at the transition point $x^{*}$, and can be given by,

$$\begin{aligned} \frac{\partial P_1(x,t|x_0,0)}{\partial t} &= \frac{\partial}{\partial x}\left\{D_1(x)\left[\frac{\partial P_1(x,t|x_0,0)}{\partial x} + P_1(x,t|x_0,0)\frac{\partial}{\partial x}\{\beta V_1^{eff}(x)\}\right]\right\} - k_0\delta(x-x^{*}) \\ &\quad \times[P_1(x,t|x_0,0)-P_2(x,t|x_0,0)], \end{aligned} \tag{11}$$

$$\begin{aligned} \frac{\partial P_2(x,t|x_0,0)}{\partial t} &= \frac{\partial}{\partial x}\left\{D_2(x)\left[\frac{\partial P_2(x,t|x_0,0)}{\partial x} + P_2(x,t|x_0,0)\frac{\partial}{\partial x}\{\beta V_2^{eff}(x)\}\right]\right\} - k_0\delta(x-x^{*}) \\ &\quad \times[P_2(x,t|x_0,0)-P_1(x,t|x_0,0)]. \end{aligned} \tag{12}$$

This one-dimensional motion actually involves the collective reorientation of a large number of solvent molecules. Here $D_1(x)$ and $D_2(x)$ denotes, respectively, the reaction coordinate $x$-dependent diffusivity in the reactant and product states and $V_1^{eff}(x)$ and $V_2^{eff}(x)$ are the corresponding effective potentials. In order to derive the average forward rate constant $k_{12}$, we start with the macroscopic kinetic equations for a reversible reaction defined as

$$\frac{dN_1(t)}{dt} = -k_{12}N_1(t) + k_{21}N_2(t), \tag{13a}$$

$$\frac{dN_2(t)}{dt} = -k_{21}N_2(t) + k_{12}N_1(t), \tag{13b}$$

where $k_{12}$ and $k_{21}$ denote, respectively, the rate constants for forward and backward reactions and $N_1(t) = \int_{-\infty}^{\infty}dxP_1(x,t|x_0,0)$ and $N_2(t)=\int_{-\infty}^{\infty}dxP_2(x,t|x_0,0)$. Now using Eqs. (13a) and (13b), one can easily obtain an expression for $N_1(t)$ in Laplace plane as

$$\tilde{N}_1(s) = \frac{s+k_{21}}{s^2+s(k_{12}+k_{21})}, \tag{14}$$

where $\tilde{N}_1(s)$ denotes the Laplace transform $[\tilde{N}_1(s) = \int_0^\infty dt\, \exp(-st)N_1(t)]$. Equation (14), on inverse Laplace transformation, leads to the expression

$$\frac{[N_1(t)-(1-\alpha)]}{\alpha} = \exp[-(k_{12}+k_{21})t], \tag{15}$$

where the parameter $\alpha$ can be expressed in terms of respective forward and backward rate constants $k_{12}$ and $k_{21}$ as

$$\alpha = \frac{k_{12}}{(k_{12}+k_{21})}. \tag{16}$$

The average forward rate constant $k_{12}$ can now be obtained by using the equilibrium constant relation $k_{eq}=k_{12}/k_{21}$ and Eq. (16), and after some algebra takes the form

$$k_{12}^{-1} = \lim_{s\to 0}\frac{(1+\exp[\beta\Delta G])}{\alpha}\left[\tilde{N}_1(s) - \frac{(1-\alpha)}{s}\right], \tag{17}$$

where $\beta(=1/k_BT)$ denotes the inverse temperature and $\Delta G$ represents the free energy of ET reaction. In order to obtain an analytical expression for $k_{12}$, what we need, is an exact expression for the function $P_1(x,t|x_0,0)$, which can be obtained from the Green's function solutions [26] of Eqs. (11) and (12). The space and time evolution of the quantity $P_1(x,t|x_0,0)$ and hence the rate constant $k_{12}$ depend on the initial conditions for the probability distributions of the reaction coordinate in the reactant and product wells. This can be quite different depending on different experimental situations, which are described in details in the following sections.

## IV. RATE OF REACTION FOR REVERSIBLE ELECTRON TRANSFER

### A. Rate constant for equilibrium initial distribution

One choice that we have considered here is the thermal equilibrium distribution as the initial condition for the reactant, i.e.,

$$P_1(x,t=0|x_0,0) = P_1^{eq}(x) = \frac{\exp[-\beta V_1^{eff}(x)]}{\int_{-\infty}^{\infty} dx'\, \exp[-\beta V_1^{eff}(x')]} \tag{18}$$

and

$$P_2(x,t=0|x_0,0) = 0 \tag{19}$$

for the product. It is obvious from Fig. 1 that the barrier height for ET along the reaction coordinate $x$ attains the lowest value only at the transition point $x^*$, therefore, the most probable path for ET is through the transition point. In this case, thermal fluctuation brings the system at the transition point $x^*$ and then the transfer of electron does take place from donor to acceptor. As the system is in thermal equilibrium at initial time $(t=0)$, in order to obtain the rate of ET reaction we first write the Green function solutions [26] of Eqs. (11) and (12) given by

$$P_1(x,t|x_0,0) = P_1^{eq}(x) - k_0\int_0^t dt'\, P_1^0(x,t-t'|x^*,0) \times[P_1(x^*,t'|x_0,0) - P_2(x^*,t'|x_0,0)], \tag{20}$$

$$P_2(x,t|x_0,0) = -k_0\int_0^t dt'\, P_2^0(x,t-t'|x^*,0)[P_2(x^*,t'|x_0,0) - P_1(x^*,t'|x_0,0)], \tag{21}$$

where the functions $P_1^0(x,t|x_0,0)$ and $P_2^0(x,t|x_0,0)$ are the respective solutions of Eqs. (11) and (12) in absence of sink terms. Equations (20) and (21) are the respective exact solutions of two one-dimensional coupled Smoluchowski equations corresponding to the diffusive motion of the reaction coordinate in the potential wells of the reactant and the product with a localized sink of arbitrary location and strength. Taking the Laplace transforms of Eqs. (20) and (21) and after some rearrangement, we obtain

$$\tilde{P}_1(x^*,s|x_0,0) = \frac{(P_1^{eq}(x^*)/s)[1+k_0\tilde{P}_2^0(x^*,s|x^*,0)]}{1+k_0[\tilde{P}_1^0(x^*,s|x^*,0)+\tilde{P}_2^0(x^*,s|x^*,0)]}, \tag{22}$$

$$\tilde{P}_2(x^*,s|x_0,0) = \frac{k_0\tilde{P}_2^0(x^*,s|x^*,0)\tilde{P}_1(x^*,s|x_0,0)}{1+k_0\tilde{P}_2^0(x^*,s|x^*,0)}. \tag{23}$$

Now integrating Eqs. (20) and (21) over $x$, taking the Laplace transforms of the resulting equations and finally combining with Eqs. (22) and (23), we obtain

$$\tilde{N}_1(s) = \frac{1}{s}\left[1 - \frac{k_0\{P_1^{eq}(x^*)/s\}}{1+k_0\{\tilde{P}_1^0(x^*,s|x^*,0)+\tilde{P}_2^0(x^*,s|x^*,0)\}}\right]. \tag{24}$$

Now combining Eqs. (17) and (24), one can express the rate constant $k_{12}$ in terms of $\tilde{P}_i^0(x^*,s|x^*,0)$ (i=1,2) as

$$k_{12}^{-1} = \lim_{s\to 0}\frac{(1+\exp[\beta\Delta G])}{\alpha}\left[\frac{\alpha+\alpha k_0\{\tilde{P}_1^0(x^*,s|x^*,0)+\tilde{P}_2^0(x^*,s|x^*,0)\} - k_0\{P_1^{eq}(x^*)/s\}}{s[1+k_0\{\tilde{P}_1^0(x^*,s|x^*,0)+\tilde{P}_2^0(x^*,s|x^*,0)\}]}\right]. \tag{25}$$

In the limit $s \to 0$, the Laplace transformed distribution functions $\tilde{P}_i^0(x^*,s|x^*,0)$ and $P_i^{eq}(x^*)/s$ diverge as the distribution functions $P_i^0(x^*,t|x^*,0)$ attain nonzero stationary values at $t \to \infty$. Therefore, it is difficult to evaluate the numerator in the limit $s \to 0$. However, this divergence problem can be avoided if we split $\tilde{P}_i^0(x^*,s|x^*,0)$ into two parts, viz.,

$$\tilde{P}_i^0(x^*,s|x^*,0) = [\tilde{P}_i^0(x^*,s|x^*,0) - \{P_i^{eq}(x^*)/s\}] + \{P_i^{eq}(x^*)/s\}, \tag{26}$$

where the first and second part of the right hand side of Eq. (26) represent the nondiverging and diverging terms, respectively, in the limit $s \to 0$. Now substituting Eq. (26) in the numerator of the Eq. (25) and after performing some algebra, one obtains an expression which is completely free from diverging terms. Therefore, in this limit, the numerator can be expressed as

$$\begin{aligned}&\lim_{s\to 0}\{\alpha + \alpha k_0[\tilde{P}_1^0(x^*,s|x^*,0) + \tilde{P}_2^0(x^*,s|x^*,0)] - k_0[P_1^{eq}(x^*)/s]\}\\ &\quad = \lim_{s\to 0}\alpha(1 + k_0[\{\tilde{P}_1^0(x^*,s|x^*,0) - [P_1^{eq}(x^*)/s]\}\\ &\qquad + \{\tilde{P}_2^0(x^*,s|x^*,0) - [P_2^{eq}(x^*)/s]\}])\end{aligned} \tag{27}$$

However, the denominator of Eq. (25) does not contain any diverging term and it can be expressed in terms of stationary distribution as

$$\begin{aligned}&\lim_{s\to 0}[s\{1 + k_0[\tilde{P}_1^0(x^*,s|x^*,0) + \tilde{P}_2^0(x^*,s|x^*,0)]\}]\\ &\quad = k_0[P_1^{eq}(x^*) + P_2^{eq}(x^*)].\end{aligned} \tag{28}$$

Now substituting Eqs. (27) and (28) into Eq. (25), one obtains a simple expression for the rate constant given by

$$k_{12}^{-1} = (1 + \exp[\beta\Delta G])\left[\frac{1}{k_0[P_1^{eq}(x^*) + P_2^{eq}(x^*)]} + \frac{\int_0^\infty dt[P_1^0(x^*,t|x^*,0) - P_1^{eq}(x^*)] + \int_0^\infty dt[P_2^0(x^*,t|x^*,0) - P_2^{eq}(x^*)]}{[P_1^{eq}(x^*) + P_2^{eq}(x^*)]}\right], \tag{29}$$

which can also be written as

$$\begin{aligned}k_{12}^{-1} = (1 + \exp[\beta\Delta G])\Bigg[&\frac{1}{k_0[P_1^{eq}(x^*) + P_2^{eq}(x^*)]}\\ &+ \frac{\tau_1(x^*)P_1^{eq}(x^*) + \tau_2(x^*)P_2^{eq}(x^*)}{[P_1^{eq}(x^*) + P_2^{eq}(x^*)]}\Bigg],\end{aligned} \tag{30}$$

where $\tau_i(x^*)$ represents the average time [26] for absorption for the reactant/product starting from the equilibrium distribution at time $t > 0$, defined as

$$\tau_i(x^*) = \frac{\int_0^\infty dt[P_i^0(x^*,t|x^*,0) - P_i^{eq}(x^*)]}{P_i^{eq}(x^*)}. \tag{31}$$

Equation (30) can also be expressed as

$$k_{12} = \frac{k_1^{TST}(x^*)}{\left[1 + \frac{k_1^{TST}(x^*)}{k_1^d(x^*)} + \frac{k_2^{TST}(x^*)}{k_2^d(x^*)}\right]}, \tag{32}$$

where $k_i^{TST}(x^*)[=k_0 P_i^{eq}(x^*)]$ represents the ET rate corresponding to passage from $i$th well to $j$th well calculated based on transition state theory (TST) and $k_i^d(x^*)[=1/\tau_i(x^*)]$ is the rate for well dynamics in $i$th well. This is an important result for the average forward rate constant for the system undergoing reversible ET reaction starting with equilibrium initial configuration.

### B. Rate constant for initial nonequilibrium distribution

The other initial condition, that we have considered here, is the nonequilibrium configuration i.e., $P_1(x,t=0|x_0,0) = \delta(x-x_0)$ as the initial condition for the reactant and $P_2(x,t=0|x_0,0)=0$ for the product. Such a nonequilibrium situation is associated with a large energy gap for ET reaction, and solvent configurations are the same between the initial and final state corresponding to before and after photoexcitation but electronic configurations are different. Such state cannot be brought by thermal fluctuation but can be achieved by photoexcitation. In the case of back ET reaction, the initial nonequilibrium configuration $x_0$ is produced during photoexcitation as shown in Figs. 2(a)–2(c). Here $x_0$ corresponds to the value of $x$ at which $V_2^{eff}(x)$ is minimum. In such situations, solvent configuration in both the ground and excited states is the same but $x_0$ is different from $x^*$. Therefore, the system at the higher level of excitation relaxes downward to the potential minimum of the excited-state surface due to relaxation of the polar solvent until its energy coincides with that of the ground state, i.e., ET takes place at the point $x=x^*$. For this situation, in order to obtain an expression for the rate of ET reaction, we first write exact

Green's function solutions [25] of Eqs. (11) and (12) as

$$P_1(x,t|x_0,0) = P_1^0(x,t|x_0,0) - k_0\int_0^t dt' P_1^0(x,t-t'|x^*,0) \times[P_1(x^*,t'|x_0,0) - P_2(x^*,t'|x_0,0)], \qquad (33)$$

$$P_2(x,t|x_0,0) = -k_0\int_0^t dt' P_2^0(x,t-t'|x^*,0)[P_2(x^*,t'|x_0,0) - P_1(x^*,t'|x_0,0)]. \qquad (34)$$

Now applying the same procedure discussed above, one can obtain the ET rate constant $k_{12}'$ defined as

$$k_{12}'^{-1} = (1+\exp[\beta\Delta G])\left[\frac{1}{k_0\{P_1^{eq}(x^*)+P_2^{eq}(x^*)\}} + \frac{(1+\exp[\beta\Delta G])\tau_1(x^*,x_0)P_1^{eq}(x^*) + \tau_2(x^*)P_2^{eq}(x^*) - \exp[\beta\Delta G]\tau_1(x^*)P_1^{eq}(x^*)}{\{P_1^{eq}(x^*)+P_2^{eq}(x^*)\}}\right], \qquad (35)$$

where $\tau_i(x^*,x_0)$ represents the first passage time for absorption of the particle starting from the position $x=x_0$ [the nonequilibrium distribution $P_i(x,t|x_0,0)=\delta(x-x_0)$] at time $t=0$, defined as

$$\tau_i(x^*,x_0) = \frac{\int_0^\infty dt[P_i^0(x^*,t|x^*,0) - P_i^0(x^*,t|x_0,0)]}{P_i^{eq}(x^*)} \qquad (36)$$

Equation (35) can be expressed in terms of the nonequilibrium relaxation dynamics rate $k_1^d(x^*,x_0)[=1/\tau_1(x^*,x_0)]$ in the reactant well, well dynamics rate $k_i^d(x^*)$ and intrinsic transition rate $k_i^{TST}(x^*)$ as

$$k_{12}' = \frac{k_1^{TST}(x^*)}{1+\frac{k_1^{TST}(x^*)}{k_1^d(x^*,x_0)}\left[1+\exp(\beta\Delta G)\left\{1+\frac{k_1^d(x^*,x_0)}{k_2^d(x^*)} - \frac{k_1^d(x^*,x_0)}{k_1^d(x^*)}\right\}\right]}. \qquad (37)$$

This is also another important result for the rate of reversible ET reaction for the system starting with nonequilibrium initial configuration. Here, the relation for the rate constant given by Eq. (37), which corresponds to nonequilibrium initial configuration of the system, shows that the ratio of TST rate and well dynamics rate in their respective wells does not appear in the expression symmetrically in contrast to the symmetric appearance of the same for the system initially in equilibrium configuration as is evident from Eq. (32).

Now, in order to have explicit analytical expression for the rate of ET reactions what is needed is analytical expressions for the quantities $\tau_1(x^*,x_0)$ and $\tau_i(x^*)$, which can be evaluated from the distribution function $P_i^0(x,t|x_0,0)$. For the special case when $V_i^{eff}(x)$ is harmonic and $D_i(x)$ is independent of the reaction coordinate, the exact expression for $P_i^0(x,t|x_0,0)$ can be obtained easily. However, there are many situations, where $V_i^{eff}(x)$ cannot be considered as harmonic potential and $D_i(x)$ is a function of the reaction coordinate, and it is difficult to obtain the exact distribution $P_i^0(x,t|x_0,0)$. In the following section, we derive analytical expression for the quantity $\tau_i(x^*,x_0)$ for an arbitrary potential $V_i^{eff}(x)$ and position dependent diffusivity $D_i(x)$ without the knowledge of the distribution function $P_i^0(x,t|x_0,0)$.

### C. Evaluation of first passage time $\tau_i(x^*,x_0)$

We first define the mean passage time [27] $\tau_i'(x^*,x_0)$ $(i=1,2)$ in terms of $p_i(t,x^*,x_0)$ as

$$\tau_i'(x^*,x_0) = \int_0^\infty dt p_i(t,x^*,x_0), \qquad (38)$$

where $p_i(t,x^*,x_0)$ represents the probability of finding the system at $i$th state (reactant or product) with its initial value $x_0$ at $t=0$, and is defined in terms of the conditional probability $P_i'(x,t|x_0,0)$ as

$$p_i(t,x^*,x_0) = \int_{-\infty}^{\infty} dx P_i'(x,t|x_0,0), \qquad (39)$$

where $P_i'(x,t|x_0,0)$ is the solution of the relevant kinetic equation for ET reaction from the reactant/product surface defined as

$$\frac{\partial P_i'(x,t|x_0,0)}{\partial t} = \frac{\partial}{\partial x}\left\{D_i(x)\left[\frac{\partial P_i'(x,t|x_0,0)}{\partial x} + P_i'(x,t|x_0,0)\frac{\partial}{\partial x}\{\beta V_i^{eff}(x)\}\right]\right\} - k_0\delta(x-x^*)P_i'(x,t|x_0,0). \qquad (40)$$

It can be shown that in the limit of $k_0\to\infty$, $\tau_i'(x^*,x_0)$ becomes $\tau_i(x^*,x_0)$. In order to prove that this relation holds good, we first write an exact Green's function solution of Eq. (40) as

$$P_i'(x,t|x_0,0) = P_i^0(x,t|x_0,0) - k_0\int_0^t dt' \times P_i^0(x,t-t'|x^*,0)P_i'(x^*,t'|x_0,0), \quad (41)$$

where the function $P_i^0(x,t|x_0,0)$ is the solution of Eq. (40) in absence of the sink term. Both $P_i'(x,t|x_0,0)$ and $P_i^0(x,t|x_0,0)$ correspond to the same initial condition, which we consider here to be $P_i'(x,t|x_0,0)=P_i^0(x,t|x_0,0)=\delta(x-x_0)$ at $t=0$. Taking the Laplace-transform of Eq. (41) and after rearrangement we obtain,

$$\tilde{P}_i'(x^*,s|x_{0,}0) = \frac{\tilde{P}_i^0(x^*,s|x_0,0)}{1+k_0\tilde{P}_i^0(x^*,s|x^*,0)}. \quad (42)$$

Now integrating Eq. (41) over $x$, taking the Laplace transform of the resulting equation and finally combining with Eq. (42), we obtain

$$\tilde{p}_i(s,x^*,x_0) = \frac{1+k_0[\tilde{P}_i^0(x^*,s|x^*,0)-\tilde{P}_i^0(x^*,s|x_0,0)]}{s[1+k_0\tilde{P}_i^0(x^*,s|x^*,0)]}. \quad (43)$$

Since $\tau_i'(x^*,x_0)=\lim_{s\to 0}\tilde{p}_i(s,x^*,x_0)$, we obtain from Eq. (43) the expression

$$\tau_i'(x^*,x_0) = \frac{1}{k_0P_i^{eq}(x^*)} + \frac{\int_0^\infty dt[P_i^0(x^*,t|x^*,0)-P_i^0(x^*,t|x_0,0)]}{P_i^{eq}(x^*)}, \quad (44)$$

where $P_i^{eq}(x^*)=P_i^0(x^*,\infty|x^*,0)$. Now employing the absorbing boundary condition i.e., $k_0\to\infty$, the above equation reduces to

$$\tau_i(x^*,x_0) = \frac{\int_0^\infty dt[P_i^0(x^*,t|x^*,0)-P_i^0(x^*,t|x_0,0)]}{P_i^{eq}(x^*)}. \quad (45)$$

It is clear from Eq. (44) that once the analytical expression for $\tau_i'(x^*,x_0)$ is known, one can obtain the analytical expression for $\tau_i(x^*,x_0)$ by employing the limiting condition $k_0\to\infty$. Although the expression for $\tau_i'(x^*,x_0)$ can be obtained from the knowledge of $p_i(t,x^*,x_0)$, but it is not possible to obtain an equation for $p_i(t,x^*,x_0)$ by merely integrating both sides of Eq. (41) over $x$. Therefore, it will be advantageous if one can write a differential equation equivalent of Eq. (40) in the variable $x_0$. This is indeed possible by using the substitution

$$P_i'(x,t|x_0,0) = \exp[-\beta V_i^{eff}(x)]U_i(x,t|x_0,0) \quad (46)$$

in Eq. (40) along with the reciprocity relation [28–30]

$$U_i(x,t|x_0,0) = U_i(x_0,t|x,0), \quad (47)$$

which leads, after some algebra, to the differential equation

$$\frac{\partial P_i'(x,t|x_0,0)}{\partial t} = \exp[\beta V_i^{eff}(x_0)]\frac{\partial}{\partial x_0}\left[D_i(x_0)\exp[-\beta V_i^{eff}(x_0)] \times \frac{\partial P_i'(x,t|x_0,0)}{\partial x_0}\right] - k_0\delta(x_0-x^*)P_i'(x,t|x_0,0). \quad (48)$$

Now integrating both sides over $x$, one obtains

$$\frac{\partial p_i(t,x^*,x_0)}{\partial t} = \exp[\beta V_i^{eff}(x_0)]\frac{\partial}{\partial x_0}\left[D_i(x_0)\exp[-\beta V_i^{eff}(x_0)] \times \frac{\partial p_i(t,x^*,x_0)}{\partial x_0}\right] - k_0\delta(x_0-x^*)p_i(t,x^*,x_0), \quad (49)$$

which on further integration over time, and using the boundary condition $p_i(0,x^*,x_0)=1$, leads to the differential equation

$$\exp[\beta V_i^{eff}(x_0)]\frac{\partial}{\partial x_0}\left[D_i(x_0)\exp[-\beta V_i^{eff}(x_0)]\frac{\partial \tau_i'(x^*,x_0)}{\partial x_0}\right] - k_0\delta(x_0-x^*)\tau_i'(x^*,x_0) = -1. \quad (50)$$

Integrating both sides over $x_0$ for $x_0 > x^*$ as well as $x_0 < x^*$, one obtains

$$\frac{\partial \tau_i'(x^*,x_0)}{\partial x_0} = \frac{\exp[\beta V_i^{eff}(x_0)]}{D_i(x_0)}\{C_i - \int^{x_0} dx \exp[-\beta V_i^{eff}(x)]\}, \quad (51)$$

where $C_i$ is an arbitrary constant of integration. Interestingly, the evaluation of the value of $C_i$ depends on, for example, employment of boundary conditions defined as

$$\left[\left(\frac{\partial \tau_i'(x^*,x_0)}{\partial x_0}\right)_{(x^*+\varepsilon)} - \left(\frac{\partial \tau_i'(x^*,x_0)}{\partial x_0}\right)_{x^*}\right] = \frac{k_0}{2D_i(x^*)}\tau_i'(x^*,x^*) \quad \text{for} \quad x_0 > x^*, \quad (52)$$

and

$$\left[\left(\frac{\partial \tau_i'(x^*,x_0)}{\partial x_0}\right)_{(x^*-\varepsilon)} - \left(\frac{\partial \tau_i'(x^*,x_0)}{\partial x_0}\right)_{x^*}\right] = -\frac{k_0}{2D_i(x^*)}\tau_i'(x^*,x^*) \quad \text{for} \quad x_0 < x^*, \quad (53)$$

where $\varepsilon$ is a very small positive number. Now substituting $x_0=x^*$ in Eq. (44), we obtain the simple expression for $\tau_i'(x^*,x^*)$ appearing in the above equations given by

$$\tau_i'(x^*,x^*) = \frac{1}{k_0P_i^{eq}(x^*)}. \quad (54)$$

By combining Eqs. (51)–(54) we obtain the expressions for $C_i$, given by

$$C_i = \frac{1}{2}\int_{-\infty}^{\infty} dx \exp[-\beta V_i^{eff}(x)] \quad \text{for} \quad x_0 > x^*, \tag{55}$$

and

$$C_i = -\frac{1}{2}\int_{-\infty}^{\infty} dx \exp[-\beta V_i^{eff}(x)] \quad \text{for} \quad x_0 < x^*, \tag{56}$$

Integrating both sides of Eq. (51) from $x^* \pm \varepsilon$ to $x_0$ and taking the limit $\varepsilon \to 0$, one obtains

$$\tau_i'(x^*,x_0) = \tau_i'(x^*,x^*) + \int_{x^*}^{x_0} dx \frac{\exp[\beta V_i^{eff}(x)]}{D_i(x)} \times \left\{ C_i - \int^{x} dx' \exp[-\beta V_i^{eff}(x')] \right\}. \tag{57}$$

Now employing the absorbing boundary condition, i.e., $k_0 \to \infty$, we obtain

$$\tau_i(x^*,x_0) = \int_{x^*}^{x_0} dx \frac{\exp[\beta V_i^{eff}(x)]}{D_i(x)} \times \left\{ C_i - \int^{x} dx' \exp[-\beta V_i^{eff}(x')] \right\}. \tag{58}$$

This is an important new result for the first passage time $\tau_i(x^*,x_0)$.

Now in order to obtain $\tau_i(x^*)$ from the knowledge of $\tau_i(x^*,x_0)$, what one needs is an averaging of $\tau_i(x^*,x_0)$ with equilibrium distribution function $P_i^{eq}(x_0)$, viz.,

$$\tau_i(x^*) = \int_{-\infty}^{+\infty} dx_0 P_i^{eq}(x_0)\tau_i(x^*,x_0), \tag{59}$$

where the relation for $\tau_i(x^*)$ expressed by Eq. (31) can be obtained by multiplying both sides of Eq. (45) by $P_i^{eq}(x_0)$, integrating over $x_0$ and using the identity [31]

$$P_i^{eq}(x_0)P_i^0(x,t|x_0,0) = P_i^{eq}(x)P_i^0(x_0,t|x,0). \tag{60}$$

The average time $\tau_i(x^*)$ can then be obtained by combining Eqs. (55), (56), (58), and (59) and can be written as

$$\tau_i(x^*) = \frac{1}{2A_i}\left[ g_i(-\infty)\int_{x^*}^{-\infty} dx \frac{\exp[\beta V_i^{eff}(x)]}{D_i(x)}F_i(x) + g_i(\infty)\int_{x^*}^{\infty} dx \frac{\exp[\beta V_i^{eff}(x)]}{D_i(x)}G_i(x) + \int_{-\infty}^{x^*} dx g_i(x)\frac{\exp[\beta V_i^{eff}(x)]}{D_i(x)}F_i(x) - \int_{x^*}^{\infty} dx g_i(x)\frac{\exp[\beta V_i^{eff}(x)]}{D_i(x)}G_i(x)\right], \tag{61}$$

where $A_i$, $g_i(x)$, $F_i(x)$ and $G_i(x)$ are, respectively, given by

$$A_i = [g_i(\infty) - g_i(-\infty)], \tag{62}$$

$$g_i(x) = \int^{x} dx' \exp[-\beta V_i^{eff}(x')], \tag{63}$$

$$F_i(x) = A_i + 2g_i(x), \tag{64}$$

$$G_i(x) = A_i - 2g_i(x). \tag{65}$$

Here Eqs. (32), (37), (58), and (61) are the new results and are valid for any arbitrary potential and position dependent diffusivity in contrast to the earlier analytical results obtained for the harmonic potential and position independent diffusivity. In the following section, we consider the analytical expressions for the ET rate for various limiting situations.

## V. RESULTS FOR LIMITING CASES

### A. Equilibrium distribution as initial condition

The relation expressed by Eq. (32) is related to the relaxation of the distribution at $x^*$, initially localized at $x^*$, to its equilibrium value. The more rapid this process is, the larger is the value of $k_i^d(x^*)$. Here $k_i^d(x^*)$ refers solely to the well relaxation and has nothing to do with the intrinsic transition process $k_i^{TST}(x^*)$ at $x^*$. In the case of exothermic reaction, (i.e., $\beta\Delta G \ll 0$), on using the relation $k_1^{TST}(x^*)/k_2^{TST}(x^*) = \exp[-\beta\Delta G]$, one can easily show the forward rate constant $k_{12}$ to be dependent only on the ET reaction in a single direction corresponding to transition from the well 1 into well 2, i.e.,

$$k_{12}^{-1} = \frac{1}{k_1^{TST}(x^*)} + \frac{1}{k_1^d(x^*)}. \tag{66}$$

For the self exchange reaction, (i.e., $\Delta G = 0$), the rate of ET reactions becomes

$$k_{12}^{-1} = \frac{1}{k^{TST}(x^*)} + \frac{1}{k_1^d(x^*)} + \frac{1}{k_2^d(x^*)}, \tag{67}$$

where $k_1^{TST}(x^*) = k^{TST}(x^*)$.

In general, the ET rate depends both on $k_i^{TST}(x^*)$ and $k_i^d(x^*)$. However if the latter process is faster $[k_i^{TST}(x^*) \ll k_i^d(x^*)]$, the nonadiabatic TST rate $[k_i^{TST}(x^*)]$ is the limiting one, i.e.,

$$k_{12}^{-1} = \frac{1}{k_1^{TST}(x^*)}, \tag{68}$$

which indicates the forward rate $k_{12}$ to be independent on the dynamics of diffusive motion in the potential wells of the reactant and the product. However, if the diffusion dynamics becomes slow $[k_i^{TST}(x^*) \gg k_i^d(x^*)]$, $k_{12}$ depends on the free energy of reaction as well as the diffusion dynamics in the respective potential wells, as given by

$$k_{12}^{-1} = \frac{1}{k_1^d(x^*)} + \exp[\beta\Delta G]\frac{1}{k_2^d(x^*)}. \tag{69}$$

It is clear from the above relation that for the exothermic ET reaction, (i.e., $\beta\Delta G \ll 0$), the forward ET rate solely depends on the diffusion dynamics in the potential well of the reactant.

### B. Nonequilibrium distribution as initial condition

In the relation expressed by Eq. (37), $k_1^d(x^*,x_0)$ is related to the difference of the relaxation of distribution functions initially at $x^*$(sink position) and $x_0$(other than sink position), to that, respectively, equilibrium distribution function at $x^*$. As the initial configuration, $x_0$ is more and more away from the sink position $x^*$ and the relative relaxation processes becoming slower and slower making the nonequilibrium relaxation dynamics rate $k_1^d(x^*,x_0)$ smaller and smaller. So in the case of exothermic reaction, i.e., $\beta\Delta G \ll 0$, large intrinsic ET rate $k_0$, and if $x_0$ is far away from $x^*$ one can expect $k_1^d(x^*,x_0) \ll k_i^d(x^*)$. In this case, the rate of ET reaction is controlled by the relaxation dynamics, i.e.,

$$k'_{12} = k_1^d(x^*,x_0), \tag{70}$$

which has been demonstrated in Fig. 2(b). However, when $k_0$ is small, the forward rate constant $k'_{12}$ of ET reaction becomes equal to $k_1^{TST}$, the relaxation process for this case is shown in Fig. 2(a). In the case of intermediate values of $k_0$, all the quantities, viz., nonequilibrium relaxation dynamics $k_1^d(x^*,x_0)$ in the reactant well, well dynamics $k_i^d(x^*)$ and intrinsic transition rate $k_i^{TST}(x^*)$ contribute to the overall rate $k'_{12}$ of ET reaction. In this case the interplay between the relaxation dynamics and ET reaction is shown in Fig. 2(c). If $x_0$ is close to the value of $x^*$ and $\beta\Delta G \ll 0$ then the Eq. (37) becomes

$$k'_{12} = \frac{k_1^{TST}}{1 + \dfrac{k_1^{TST}}{k_1^d(x^*,x_0)}}. \tag{71}$$

## VI. RESULTS AND DISCUSSION

As an illustrative example, we now consider a typical ET process corresponding to the situation depicted in Figs. 2(a)–2(c), where a molecule DA is excited from the ground state with an ultrashort laser pulse, leading to the formation of the ion-pair $D^+A^-$. Thus, the ion-pair is initially produced in a completely nonequilibrium configuration and then relaxes downward along its potential energy surface (corresponding to $D^+A^-$) through relaxation of the surrounding polar solvent till it meets the potential energy surface of the molecule DA, where the back ET reaction takes place. We consider here a simple theoretical model for the ET system of interest modeled through harmonic potential [24] for $D^+A^-$ and DA defined, respectively, as

$$V_1^{eff}(x) = \frac{1}{4\lambda}x^2, \tag{72}$$

$$V_2^{eff}(x) = \frac{1}{4\lambda}x^2 - x, \tag{73}$$

where λ represents the solvent reorganization energy. The expression for $V_2^{eff}(x)$ is obtained using the relation defined in Eqs. (6) and (72). In the case of back ET reaction, the initial nonequilibrium configuration $x_0 = 2\lambda$, produced during photo excitation, corresponds to the value of the reaction coordinate $x$ at which $V_2^{eff}(x)$ is minimum. We now calculate the average forward ET rate constant $k'_{12}$ using Eqs. (37), (72), and (73) as a function of the free energy change $\Delta G$ of the reaction. We assume here the microscopic reaction coordinate $A(t)$ to decay exponentially with relaxation time $\tau_s$. The solvent relaxation time, temperature and solvent reorganization energy are taken, respectively, as $\tau_s = 0.3$ ps, $T = 300$ K, and $\lambda = 1.0$ eV. In order to understand the effect of back ET on the free energy gap (FEG) dependence of the rate, we have calculated the ET rates for different values of electronic coupling $J$ [$k_0 = (4\pi^2/h)J^2$] and plotted $k'_{12}$ in Fig. 3. It is clear from the figure that with increase in $J$, there is a transition from the symmetric free energy gap (FEG) dependence rate, which was predicted by Marcus, to asymmetric FEG dependent rate. When the value of $J$ is small, one obtains the Marcus result i.e., $k'_{12} \approx k_{TST}$ [Eq. (68)]. In this situation, FEG dependence of the rate of ET becomes symmetric as predicted by Marcus. However, when the value of $J$ for ET system of interest is reasonably significant, the average rate constant $k'_{12} \approx k_1^d(x^*,x_0)$ is given by Eq. (70). In this case, the ET rate is controlled by the solvation dynamics leading to the non-Marcus FEG dependence. In many nonequilibrium situations, experimentally the asymmetric FEG dependence [32] of ET rate is observed, and therefore, the present theory is able to explain the non-Marcus FEG dependence of the rate of ET reactions.

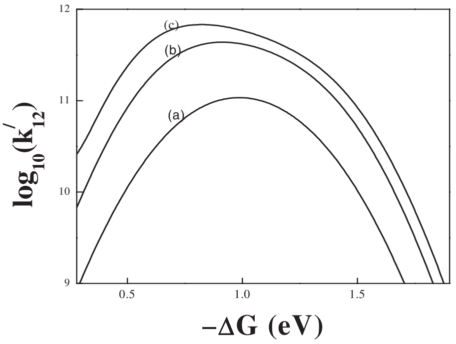

FIG. 3. Dependence of the average forward rate constant $k'_{12}$ of the reversible ET reaction on the free energy change $\Delta G$ for various values of the electronic coupling $J$: (a) 0.003 eV, (b) 0.01 eV, (c) 0.3 eV. The parameters used are $\lambda = 1.0$ eV, $\tau = 0.3$ ps, and $T = 300$ K.

## VII. CONCLUDING REMARKS

We have derived for the first time an analytical expression for the average forward rate constant $k_{12}$ of a reversible electron transfer reaction, modeled through a reaction coordinate undergoing diffusive motion in arbitrary potential wells of the reactant and the product in presence of a localized sink of arbitrary location and strength. The dynamics of diffusive motion is described by two coupled generalized diffusion-reaction (Smoluchowski) equations with reaction coordinate dependent diffusivity and delta sink at the transition point. The average rate constant $k_{12}$ obtained here for the system, with two initial conditions corresponding to the equilibrium and nonequilibrium (delta function) distributions, consists of contributions from the forward and backward rate constants [$k_1^{TST}(x^*)$ and $k_2^{TST}(x^*)$] calculated based on the transition state theory and diffusion dynamics with rate constants [$k_1^d(x^*)$ and $k_2^d(x^*)$] in the reactant and product potential wells and relaxation dynamics with rate constant $k_1^d(x^*,x_0)$. We also consider here various limiting cases to understand the relative contribution of the rate calculated based on TST, the well dynamics in their respective wells and the relaxation dynamics in the excited state to the overall rate of ET. As an illustrative example, we have considered back ET reaction and shown that the present theory can explain the non-Marcus FEG dependence [32] of the rate of ET reactions. More importantly, the approach presented here can easily be extended to the system describing the dynamics of diffusive motion in coupled multipotential surfaces associated with electron transfer reactions.

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