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Mean first-passage time and multiexponential relaxation of the activationless nonadiabatic electron transfer reaction

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We discuss the mean first-passage time of the activationless nonadiabatic electron transfer reaction by using the stochastic Liouville equation for the study of outer sphere electron transfer in polar solvents characterized by Debye dielectric relaxation. We obtain an approximate expression for the mean first-passage time which incorporates the width of the transition with an arbitrary initial condition far from equilibrium. We derive an analytical expression for the rate corresponding to harmonic potential surfaces in the overdamped regime. For Fokker-Planck operators of the Smoluchowski type, we introduce a method to solve all of the generalized moments by using the eigenfunction expansion method.

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I. INTRODUCTION

Since the pioneering work of Marcus and Hush [1], electron transfer (ET) reactions have attracted a lot of attention. Solvent dynamic effects on the rate of electron transfer reaction have been the focus of experimental [2] and theoretical investigations. When the microscopic electronic processes are faster than the medium dielectric relaxation, the observed ET rate is determined by the longitudinal dielectric relaxation time τ_L. This solvent-controlled ET has been demonstrated by Kosower, Huppert, and co-workers. The theory of solvent-controlled ET was first studied by Zusman [3] using the stochastic Liouville equation method. Subsequently the solvent-controlled ET has been developed by using the generalized Langevin equation [4], the mean first-passage time approach [5], and the path integral method [6]. Most of them are based on the assumption of a high barrier and thermal equilibrium initial condition. The ET rate assumes the Arrhenius form $k_{\mathrm{ET}} = A \exp(-E_a/kT)$ where E_a is the activation energy. The preexponential frequency factor A is determined by the electronic coupling constant, the reorganization energy, the driving force, and τ_L. This implies the ET rate has a different time scale from a medium dielectric relaxation and can be described in terms of single-exponential decay. However, some chemical processes have little or no intrinsic barrier, e.g., some isomerization reactions, ET, and the primary charge separation step in photosynthesis [7]. The dynamics of activationless transition reaction differ considerably from those of high barrier. Without the high barrier, the time scales of transition cannot be separated. The steady state flux across the transition region cannot be obtained. The general time-independent rate constant is not valid. This implies that multiexponential decay relaxation processes may occur. The lowest non-zero eigenvalue of the kinetic equation may not be sufficient to describe the reaction, because the eigenvalue spectrum may be dense. Since the activationless transition is fast, the relaxation processes may depend on the initial condition. To explore the activationless transition reaction, we need to use the mean first-passage time method.

II. THE METHOD

A. Zusman equation

We consider the transition between two shifted potential surfaces V_{11} and V_{22} which correspond to the donor and acceptor state, respectively. The transition between the diabatic potential surfaces is induced by the electronic coupling constant V_{12} (see Fig. 1). In condensed phases, these potential surfaces are coupled to a heat bath. The time evolution of this system obeys the Zusman equation (for a detailed derivation see Ref. [8]) for the coarse-grained density matrix ρ_{ij} $(i,j=1,2)$. The Zusman equation is a semiclassical equation which describes the solvent dielectric fluctuation as a low frequency fluctuation with energy smaller than $k_B T$. The diagonal elements ρ_{11} and ρ_{22} are the probabilities of finding the system in the initial and final potential well. The diffusion motion is slow since it is activated by thermal energy. The off-diagonal terms include not only the diffusion motion but also the high frequency quantum transition behavior. The Zusman equation can be reduced to two coupled equations by invoking the assumption that the off-diagonal element ρ_{12} varies with reaction coordinate much faster than the diagonal elements ρ_{11}

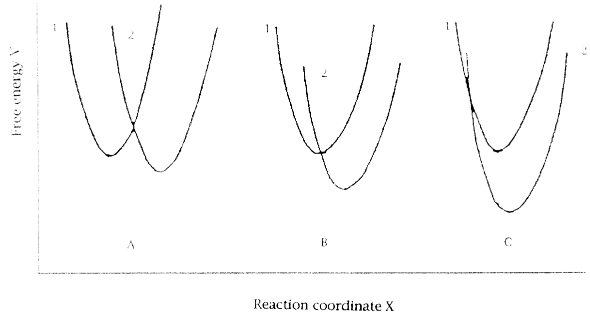

FIG. 1. Schematic illustration of the reactant (well 1) and product (well 2) potential energy surfaces for nonadiabatic electron transfer reaction in the text: (a) normal regime; (b) activationless regime; (c) invert regime.

and ρ_{22}. The reduced Zusman equation is

$$\frac{\partial}{\partial t}\rho=[L-K]\rho\ , \tag{1}$$

with

$$\rho=[\rho_{11},\rho_{22}]^T\ ,\quad L=\begin{bmatrix} L_{11} & 0 \\ 0 & L_{22}\end{bmatrix}\ ,$$

$$K(x)=2\,\mathrm{Re}K_{12}(x)\begin{bmatrix} 1 & -1 \\ -1 & 1\end{bmatrix}\ ,$$

and

$$K_{12}(x)=\left[\frac{V_{12}}{\hbar}\right]^2\int_{-\infty}^{\infty}dx_1\int_0^{\infty}d\tau\, G_{12}(x_1,\tau|x,0)\ ,$$

where $G_{12}(x_1,\tau|x,0)$ is the propagator $[\partial/\partial t-L_{12}+i(V_{22}-V_{11})/\hbar]^{-1}$. L_{ii} is the Fokker-Planck operator with potential V_{ii}. The G_{12} propagator describes motion in well $\frac{1}{2}(V_{11}+V_{22})$ and quantum transition between V_{11} and V_{22}. $K(x)$ depends on the reaction coordinate and includes the information of the delocalized transition. By using projection operator techniques on Eq. (1), we obtained an expression for the recrossing long time transition rates,

$$k^{12}=\frac{k_{\mathrm{NA}}^{12}}{1+k_{\mathrm{NA}}^{12}/k_{D1}+k_{\mathrm{NA}}^{21}/k_{D2}}\ , \tag{2a}$$

$$k^{21}=\frac{k_{\mathrm{NA}}^{21}}{1+k_{\mathrm{NA}}^{12}/k_{D1}+k_{\mathrm{NA}}^{21}/k_{D2}}\ , \tag{2b}$$

where k_{NA}^{ij} describes the motion along the surface as modulated by the surface splitting and a delocalized transition. The rate k_{Di} characterizes the stochastic motion on the ith well. It also accounts for the deviation from equilibrium in the well that may occur if the crossing motion, characterized by k_{NA}^{ij}, is sufficiently fast.

B. Mean first-passage time and averaged survival time

Define the populations as the integration of probability density over space:

$$Q(t)=\int_{-\infty}^{\infty}dx\begin{bmatrix}\rho_{11}(x,t)\\ \rho_{22}(x,t)\end{bmatrix}=\begin{bmatrix}Q_1(t)\\ Q_2(t)\end{bmatrix}\ , \tag{3}$$

with the probability conservation $Q_1(t)+Q_2(t)=1$. Since our system is a closed system, the equilibrium distribution (i.e., the background) has to be subtracted from the population $Q(t)$. Also, define the fluctuation of populations via

$$\delta Q=Q(t)-Q^e\ , \tag{4}$$

then $\lim_{t\to\infty}\delta Q(t)=0$ and Q^e is unknown here. In the following, t and x are in units of τ_L and $\sqrt{\beta m\omega^2}$ [see Eq. (17)]. Mean first-passage time and averaged survival time are defined as

$$\tau_0=\int_0^{\infty}dt\,\delta Q(t)=\left[\tilde{Q}(s)-\frac{1}{s}Q^e\right]_{s=0} \tag{5}$$

and

$$\tau_1=\int_0^{\infty}dt\,t\delta Q(t)=-\frac{\partial}{\partial s}\left[\tilde{Q}(s)-\frac{1}{s}Q^e\right]_{s=0}\ , \tag{6}$$

respectively. In the above equation, we define the Laplace transform as $\delta\tilde{Q}(s)=\int_0^{\infty}dt\,e^{-st}\delta Q(t)$.

Define the projection operator $P=g\int dx$ and its complement $Q=1-P$ where g is a 2×2 diagonal matrix of equilibrium distribution at each well, $g_i=e^{-\beta V_{ii}}/\int_{-\infty}^{\infty}dx\,e^{-\beta V_{ii}}$, $i=1,2$. Applying P and Q to the Laplace transform of Eq. (1), standard projection operator manipulation leads to

$$Q_1^e=\frac{k^{21}}{k^{12}+k^{21}}\ ,\quad Q_2^e=\frac{k^{12}}{k^{12}+k^{21}}\ . \tag{7}$$

Mean first-passage time and averaged survival time are

$$\tau_0=Q_2^e(k_{0,D1}^{\mathrm{ini}-1}-\tau)\ ,\quad \tau=(k^{12}+k^{21})^{-1}\ , \tag{8}$$

$$\tau_1=Q_2^e\left[-k_{1,D1}^{\mathrm{ini}-1}+Q_1^ek_{1,D2}^{-1}+Q_2^ek_{1,D1}^{-1}+\tau^2-\frac{\tau}{k_{0,D1}^{\mathrm{ini}}}\right]\ , \tag{9}$$

$k_{1,Di}^{-1}$ and $k_{i,D1}^{\mathrm{ini}-1}$ are given in Sec. II D.

C. Relaxation times

The first order kinetics that we used in Ref. [8] is based on the assumption that the reaction starts in a near equilibrium configuration and the equilibrium state is approximately maintained during the reaction. In the activationless regime, the rate is fast and the initial configuration is usually far from the equilibrium distribution. The reaction rate $(\partial/\partial t)Q_2(t)|_{t=0}$ should vanish initially, approach some maximum rate at later time, and finally decay to zero. This needs a multiple exponential decay time description. In this section we evaluate two relaxation times from the known information of the moments: (1) probability conservation, i.e., $Q_1(t)+Q_2(t)=1$; (2) $(\partial/\partial t)Q_2(t)|_{t=0}=0$ (in our harmonic oscillator potential surface model, the initial conditions $\rho_{12}=\rho_{21}=0$ imply this condition); (3) $\int_0^{\infty}dt\,\delta Q(t)=\tau_0$; (4) $\int_0^{\infty}dt\,t\delta Q(t)=\tau_1$.

Assume a two-relaxation-time description of the population in well 2,

$$Q_2(t)=Q_2^e+ae^{-\lambda_1 t}+be^{-\lambda_2 t}\ . \tag{10}$$

With the conditions (1)–(4), we obtain

$$a=-\frac{1/\lambda_1}{1/\lambda_1-1/\lambda_2}Q_2^e\ ,\quad b=\frac{1/\lambda_2}{1/\lambda_1-1/\lambda_2}Q_2^e\ ,$$

and

$$1/\lambda_{1,2}=\frac{1}{2}\frac{\tau_0}{Q_2^e}\pm\left[\frac{\tau_1}{Q_2^e}-\frac{3}{4}\frac{\tau_0^2}{(Q_2^e)^2}\right]^{1/2}\ . \tag{11}$$

D. Application to harmonic potential surfaces

In this section, we obtain an approximate rate constant expression given in Sec. II C with a special model of harmonic potential surfaces. With a given initial distribution (δ function and Gaussian distribution function), we evaluate τ_0 and τ_1. The harmonic potential surfaces are given in Eq. (17). The stochastic processes correspond to overdamped Brownian motion, i.e.,

$$L_{ii}=D\frac{\partial}{\partial x}\left[\frac{\partial}{\partial x}+\beta\frac{\partial}{\partial x}V_{ii}\right]\ , \quad i=1,2\ ;$$

and

$$L_{12}=L_{21}=\tfrac{1}{2}(L_{11}+L_{22})\ .$$

Here D is the diffusion coefficient and $\beta=1/k_BT$.

The exact solution of the propagator of the off-diagonal term is [10]

$$G_{21}(x,t|x_i,0)=\frac{1}{\sqrt{2\pi D\tau_L}}\frac{1}{\sqrt{1-e^{-2t}}}\exp\left\{\frac{1}{2}\frac{1}{D\tau_L}\frac{1}{1-e^{-2t}}\left[2D\frac{\gamma\tau_L^2}{\hbar}(1-e^{-t})-i\left[x-x_ie^{-t}-\frac{1}{2}x_0(1-e^{-t})\right]\right]^2 - D\left[\frac{\gamma\tau_L}{\hbar}\right]^2\tau_Lt+i\frac{\gamma\tau_L}{\hbar}\left[x-x_i-\frac{1}{2}x_0t+\sigma t\right]\right\}\ , \tag{12}$$

where σ is the crossing point and $\gamma=k_\omega x_0$ is the force difference at the crossing point. The use of Eq. (12) yields the nonadiabatic transition rate

$$k_{\rm NA}^{12}=2\left[\frac{a}{4}\right]^2\frac{1}{\tau_L}\,{\rm Re}\exp\left[\frac{\lambda}{\beta\hbar\omega_L}\left[\frac{2\lambda}{\beta\hbar\omega_L}-i\right]\times(2\sqrt{\beta\Delta G_1^{\neq}}-\sqrt{\beta E_r})^2\right]\times B^{-\mu}\gamma(\mu,B)\ , \tag{13a}$$

where

$$a=\frac{4\tau_LV_{12}}{\hbar}\ , \quad \lambda=\omega_L\tau_L\ ,$$

$$B=\left[\frac{\lambda}{\beta\hbar\omega_L}\right]^22(x+y)^2-i\frac{\lambda}{\beta\hbar\omega_L}(x+y)\ ,$$

$$\mu=\left[\frac{\lambda}{\beta\hbar\omega_L}\right]^22(x+y)^2+i\frac{\lambda}{\beta\hbar\omega_L}(y-x)\ ,$$

$$x=\beta\Delta G_1^{\neq}\ , \quad y=(\sqrt{\beta\Delta G_1^{\neq}}-\sqrt{\beta E_r})^2\ ,$$

$$\gamma(\mu,B)=\sum_{n=0}^{\infty}\frac{(-1)^nB^{n+\mu}}{n!(\mu+n)}\ ,$$

and

$$k_{\rm NA}^{21}=2\left[\frac{a}{4}\right]^2\frac{1}{\tau_L}\,{\rm Re}\left[\frac{\lambda}{\beta\hbar\omega_L}\left[\frac{2\lambda}{\beta\hbar\omega_L}+i\right]\times(2\sqrt{\beta\Delta G_2^{\neq}}+\sqrt{\beta E_r})^2\right]\times B^{-\mu}\gamma(\mu,B)\ , \tag{13b}$$

where

$$\mu=\left[\frac{\lambda}{\beta\hbar\omega_L}\right]^22(x+y)^2-i\frac{\lambda}{\beta\hbar\omega_L}(y-x)\ ,$$

$$x=(\sqrt{\beta\Delta G_2^{\neq}}+\sqrt{\beta E_r})^2\ , \quad y=\beta\Delta G_2^{\neq}\ .$$

The diffusion rate constants on each well are

$$k_{D1}^{-1}=\left[B\left[\frac{1}{2},s\right]\Phi_1\left[\frac{1}{2},s,s+\frac{1}{2},-1,-\beta\Delta G_1^{\neq}\right]\times\exp(\beta\Delta G_1^{\neq})-\frac{1}{s}\right]\tau_L\ , \tag{14a}$$

where $B(x,y)$ is the beta function, $\Phi_1(\alpha,\beta,\gamma,x,y)$ is the degenerate hypergeometric series [12], and

$$k_{D2}^{-1}=\tau_L\left[\exp(\beta\Delta G_2^{\neq})B\left[\frac{1}{2},s\right]\times\Phi_1\left[\frac{1}{2},s,s+\frac{1}{2},-1,-\beta\Delta G_2^{\neq}\right]-\frac{1}{s}\right]\ . \tag{14b}$$

Introducing a series expansion of Eq. (14a), the diffusion moments are

$$k_{0,D1}^{-1}=g_1^{-1}(x^*)\{-I(0)+S(\tfrac{1}{2}\beta\Delta G_1^{\neq})\}\ , \tag{15a}$$

$$k_{1,D1}^{-1}=g_1^{-1}(x^*)\sum_{n=0}^{\infty}\frac{1}{n!}(-\beta\Delta G_1^{\neq})^nJ_1(n)\ , \tag{15b}$$

where

$$I(n)=-\ln 2+\sum_{m=1}^{n}\frac{1}{m-\frac{1}{2}}\ , \quad S(x)=\sum_{n=1}^{\infty}(-1)^{n-1}I(n)\frac{x^n}{n!},$$

$$J_m(n)=m!\left[\sum_{k=1}^{\infty}\frac{1}{k!}[(n+\tfrac{1}{2})_{-k}+(n+\tfrac{1}{2})_{k-2}]\times(-1)^kk^{-m-1}+\sum_{i,m=1}^{\infty}\frac{(n+\frac{1}{2})_{-k}(n+\frac{1}{2})_{n-2}}{k!i!}(-1)^{k+i}\times(k+i)^{-m-1}\right]\ ,$$

$$(\alpha)_m=\alpha(\alpha+1)\cdots(\alpha+m-1)\ .$$

$k_{0,D2}^{-1}$ and $k_{1,D2}^{-1}$ can be obtained from Eq. (14b) by replacing $\beta\Delta G_1^{\neq}$ by $\beta\Delta G_2^{\neq}$.

When the initial distribution is a delta function, $\delta(y-y_0)$, the diffusion moments are

$$k^{\text{ini}-1}_{0,D1}=\tfrac{1}{2}[Ei(-x)-\ln x]\ ,\quad x=\tfrac{1}{2}y_0^2\ , \tag{16a}$$

where Ei is the exponential integral function, and

$$k^{\text{ini}-1}_{1,D1}=\tfrac{1}{4}\sum_{n=1}^{\infty}\frac{(-\tfrac{1}{2}y_0^2)^n}{n^2 n!}\ . \tag{16b}$$

Equations (13)–(16) give all of the factors in Eqs. (8) and (9).

III. NUMERICAL RESULT

In this section, we calculate the mean first-passage time and averaged survival time by solving the four coupled equations, i.e., the Zusman equation, given in Ref. [8]. We use the standard harmonic oscillator model as the potential surfaces

$$V_{11}=\tfrac{1}{2}m\omega^2x^2\ , \tag{17a}$$

$$V_{22}=\tfrac{1}{2}m\omega^2(x-x_0)^2+\Delta E\ , \tag{17b}$$

where ΔE is the driving force ($\Delta E<0$ for exothermic processes, and $\Delta E>0$ for endothermic processes) and x_0 is the horizontal displacement. It is useful to transform the Zusman equation to a set of first order differential equations [8] by using the right eigenfunction of L_{12}.

The mean first-passage time and averaged survival time can be obtained by

$$\tau_n=\tau_L(-1)^n\frac{\partial^n}{\partial s^n}\delta\tilde{Q}_2(s)\ . \tag{18}$$

For detailed numerical method, see Ref. [11].

Since the difference between δ initial distribution and Gaussian initial distribution is small, we only show the δ initial distribution. The probability distribution in well 2 is obtained by $Q_2(t)=[1-(2\pi)^{1/4}a_0^-(t)]$. The expansion coefficient $a_0^-(t)$ can be obtained by solving the Zusman equation with the Bulirsch-Stoer method [9] to integrate out $4n$ ($n=200$) first order differential equations. We compare the numerical calculation of $Q(t)$ and $\dot{Q}(t)$ from the approximate analytic formula Eq. (3).

A full account of the comparison between analytical result and exact numerical calculation is studied in Ref. [11]. In Fig. 2, the behavior of a two-relaxation-time description is very satisfactory for $Q(t)$ and $\dot{Q}(t)$ in an exothermic activationless regime. Other transition regimes need more than two relaxation times.

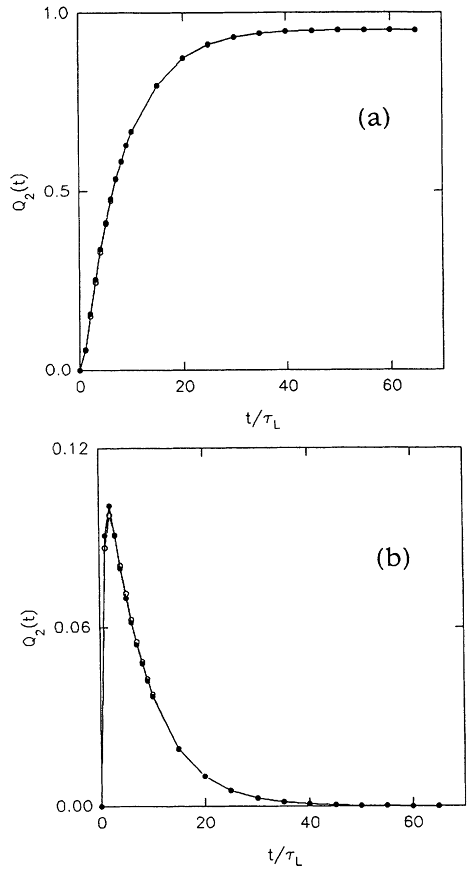

FIG. 2. Comparison between numerical (●) and analytical (○) calculation of population (a) and reaction rate (b) in well 2 with two relaxation times $\lambda_1^{-1}=1.97$ and $\lambda_2^{-1}=7.38$. Both of these two plots correspond to activationless regime with $h\omega_L=100\ \text{cm}^{-1}$, $\lambda=20$, $T=300$ K, $x_i=-2$, $a=10$, $S=6.256$, $P=-6.256$. Here we use the notation $S=\frac{1}{2}x_0^2/\hbar\omega_L$, and $P=-\Delta E/\hbar\omega_L$.

In conclusion, we have developed a systematic way to calculate the mean first-passage time and averaged survival time with consecutive approximation. A method is developed to simulate a numerical result. This method is much easier to solve than the differential equation by the grid point method.

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