Dynamics of reversible electron transfer reactions

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The dynamics of reversible electron transfer reactions in Debye solvents are studied by employing two coupled diffusion–reaction equations with the rate constants depending on the reaction coordinate. The equations are solved analytically in four limiting cases: fast and slow reactions as well as wide and narrow reaction windows. A general solution for the survival probabilities is obtained by employing a decoupling approximation similar to the one used by Sumi and Marcus [J. Chem. Phys. **84**, 4896 (1986)] for nonreversible reactions; our solution verifies the existence of four limiting cases and also predicts the behavior between these limits. Interpolation between long and short time approximations to the general solution, leads to survival probabilities with a single exponential time dependence and rate constants k_i satisfying the relation $k_1/k_2 = \exp(-\beta\Delta G^0)$, where ΔG^0 is the standard free energy change for the reaction. Multiexponential behavior of the survival probabilities is exhibited when higher order terms are included in the evaluation of the general solution, but this deteriorates to a single exponential, governed by a first order rate constant, at long times. In the narrow reaction window limit the multiexponential solution is exact when both the forward and reverse reactions are barrierless, and the behavior at long times is determined by a rate constant $k = 0.83\,\tau_L^{-1}$ where τ_L is the longitudinal relaxation time. Similar behavior is found when the forward reaction alone is barrierless and the barrier for the reverse reaction is large $(\beta\Delta G_1^\ddagger = 0, \beta\Delta G_2^\ddagger \gg 1)$, except that the forward rate constant $k_1 \approx \tau_L^{-1}[0.6 + (\pi/\beta\Delta G_2^\ddagger)^{1/2}]^{-1}$ depends on the barrier height for the reverse reaction which has a small rate constant. Our solutions reduce to those of Sumi and Marcus when the reverse reaction is ignored. They are also compared with numerical solutions to the diffusion reaction equations. The extension to non-Debye solvents is briefly discussed.

I. INTRODUCTION

Since the pioneering research of Marcus[1] and Hush,[2] the study of electron transfer reactions has been of continuing interest.[3-5] Two limiting cases are usually discussed for these reactions: the adiabatic limit, in which the electronic coupling is very strong at the intersection of the product and reactant potential energy surfaces, leading to a crossover from the initial to the final state along a smooth curve, and the nonadiabatic limit, for which this coupling is very weak leading instead to a crossover shaped like a cusp. The details of this classification can be found elsewhere.[3,5(a)]

The current theory[1] of adiabatic electron transfer is based on the Born–Oppenheimer approximation which supposes that the motion of the electron can be separated from that of the nuclei and that a radiationless electronic transition takes place between states of equal energy. The rate constant is derived either from the transition state theory[1] or from Kramers' theory[6,7] or from the theory of mean first passage times.[8,9] For nonadiabatic electron transfer reactions, the transition probability is calculated from the Fermi Golden Rule,[3(a),10(a),10(b)] which leads to a rate constant proportional to the electronic coupling matrix element. Unified theories which try to cover both adiabatic and nonadiabatic limits, have also been proposed.[11,12]

It is generally accepted, since the work of Marcus and Hush,[1,2] that fluctuations of the solvent polarization play an essential role in electron transfer reactions. A diffusion equation can be used to describe the motion of the solvent polarization along the reaction coordinate. If the fluctuations of the solvent polarization are very fast, the thermal equilibrium population of reactants in the transition state is maintained during the reaction, and transition state theory can be used to determine the rate, otherwise Kramers[6] theory of barrier crossing is more reasonable. If the barrier height in Kramers' theory is chosen to correspond to the activation energy, the rate constant obtained differs from that predicted by the transition state theory only in the preexponential factor.

The dynamic effect of the solvent polarization on electron transfer reactions has been discussed by many workers over the years.[5(a),7,11-14] A number of experimental results have also been reported,[15-17] which show that the rate constant for intermolecular electron transfer is inversely proportional to the longitudinal dielectric relaxation time τ_L of the polar solvent and also depends on the energetics of the reaction, while in many intramolecular electron transfer reactions, which are essentially barrierless,[12(c)] the rate constant is approximately equal to τ_L^{-1}. The longitudinal relaxation time is defined by $\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D$ where τ_D is the dielectric relaxation time and $\epsilon_\infty/\epsilon_0$ is the ratio of the high frequency dielectric constant to the static dielectric constant. The dependence of electron transfer rates on a single relaxation time is usually characteristic of Debye solvents. For this case the general dependency on τ_L was first shown theoretically by Zusman,[13] and found later by Calef and Wolynes[7] who obtained a rate constant approximately equal to

$0.1\ \tau_L^{-1}$ which is qualitatively in agreement with experiments for barrierless reactions but falls short of the observed values.

Prompted by this, Sumi and Marcus[18] used a diffusion-reaction equation to study the dynamic effects of electron transfer reactions in which intramolecular vibration of the reactants also plays a role in bringing them to the activated state. The physical picture given by them is that the reactants diffuse through a potential well along a polarization coordinate x, which connects the reactant and the products, and the reaction, which may be activated by vibrational motion, takes place anywhere along this coordinate with a rate constant $k(x)$ dependent on x. For simplicity, the reverse reaction was neglected. The differential equation for diffusion and reaction is similar to the one studied by Agmon and Hopfield[19] in their investigation of the kinetics of CO binding to heme in myoglobin and by Bagchi, Fleming, and Oxtoby[20] in their analysis of barrierless reactions. A complete picture, however, for the electron transfer reaction between two states should contain diffusion and reaction in both directions as pointed out by Nadler and Marcus.[21] If equilibrium is to prevail between the initial and final states, the presence of a reverse reaction is essential and the time dependence of the survival probabilities will be different from those for a reaction in a single direction. Moreover, the relation between the equilibrium constant and the rate constants $K = k_1/k_2$ can be employed to check whether the analysis is correct.

In this paper, we carry out a detailed analysis of reversible electron transfer reactions which are characterized by a single relaxation time and show how the overall survival probabilities satisfy the general equations for a two state problem. Our work necessarily covers some of the same ground as Zusman[13(a)] and Sumi and Marcus[18] which is also limited to Debye solvents but extends their work to general reversible reactions and provides, at the same time, a link between the two approaches. We derive an approximate general solution for these reversible reactions and show how it can be used to obtain not only the exact solutions in certain limiting cases but also approximate solutions which lie between these extremes. An interpolation formula for the survival probabilities between long and short times which leads to a single exponential decay is discussed and we elucidate the nature of multiexponential decays. The dynamical control of these reactions and their well-known dependence on the longitudinal relaxation time of the solvent is clarified: explicit relations are obtained for barrierless reactions in which there is essentially no barrier in either direction and also for the more realistic example of a large but finite barrier in one and almost no barrier in the other direction.

Reversible electron transfer reactions are well known; a classic example is the Fe^{+2}/Fe^{+3} electron exchange in water,[9] another is the intramolecular charge transfer in *p*-dimethylaminobenzonitrile (DMAB).[22,23] The relative importance of the "in" vibrational motion of water ligands and the reorganization of "outer" solvent in electron transfer reactions in Fe^{+2}/Fe^{+3} has already been investigated by Tembe, Friedman, and Newton.[9(b)] However, their investigation is different from the one considered here which uses a diffusion–reaction picture rather than the chemical kinetic representation employed by them. Other aspects of electron transfer reactions which have been studied are the solvent nuclear tunneling effect on the aqueous ferrous–ferric electron transfer reaction. This was also investigated earlier by Friedman and Newton,[9] and has been studied more recently by Bader, Kuharski, and Chandler[14] through computer simulation. The importance of tunneling corrections have also been considered recently by Warshel and Chu.[4]

Experimental work on solvent controlled electron transfer reactions which exhibit a more complex relaxation behavior than what is expected of simple Debye solvents is well known. Theoretical studies of these systems have been carried out independently by Hynes,[5(a)] Sparpaglione and Mukamel,[5(c)] and Fonseca;[24(a)] intramolecular vibrations play no part in the activation step of these model electron transfer reactions which are assumed to be governed by the dynamics of solvent dielectric fluctuations. In the discussion section of our paper we indicate very briefly how our results for the Sumi–Marcus model can be extended to non-Debye solvents.

The outline of the present paper is as follows: In Sec. II the two-dimensional potential surface, the forward and reverse activation energies and the coordinate dependent rate constants are discussed. The diffusion reaction equations and their solutions in four limiting cases are presented in Sec. III and the general solutions to the adjoint equations, which allow interpolation among and extrapolation beyond these four limiting cases, are discussed in Sec. IV. In Sec. V we present numerical solutions to the differential equations. These are compared with theoretical and experimental results in Sec. VI which ends with a brief analysis of the extension of our work to non-Debye solvents. Some technical aspects are presented in the Appendix.

II. POTENTIAL SURFACES AND THE RATE CONSTANTS

Our system contains an electron and a macromolecule S- - - -S' or two molecules with sites S and S' in a polarizable environment where one of the sites (S or S') is a donor and the other is an acceptor. The electron can jump between S and S'. For this system, parabolic potential wells with two reaction coordinates (one a vibrational coordinate and the other a polarization coordinate) have been adopted by Sumi and Marcus.[18] We will first provide a quantum mechanical discussion of this.

If r and n represent the electronic and the nuclear coordinates, the Born–Oppenheimer approximation leads to the following Schrödinger equations for the electronic and nuclear eigenstates of the reactant and the product

$$H_{\alpha,\mathrm{el}}\phi_\alpha(r,n) = \epsilon_\alpha(q)\phi_\alpha(r,n), \tag{2.1a}$$

$$H_\alpha\psi_\alpha(n) = E_\alpha\psi_\alpha(n), \tag{2.1b}$$

where $H_{\alpha,\mathrm{el}}$ and H_α are the electronic and nuclear Hamiltonians, respectively, of $\alpha = 1,2$ (reactant or product), while ϵ_α and E_α are the corresponding electronic and total energies for state α. Let $n = (q_{v,\alpha}, q_{s,\alpha})$ where $q_{v,\alpha}$ are the ligand vibrational coordinates of α and $q_{s,\alpha}$ are the coordinates of the surrounding solvent molecules. If we consider the vibrational motion of α to be harmonic, the Hamiltonian H_α can be written as

$$H_\alpha = \hbar^2(2\mu_\alpha)^{-1}\partial^2/\partial q_{v,\alpha}^2 + \mu_\alpha\omega_\alpha^2 q_{v,\alpha}^2/2 + \epsilon_\alpha(q) + H_s, \tag{2.2}$$

where μ_α and ω_α are the reduced mass and vibrational frequency, respectively, H_s is the contribution to the Hamiltonian from the surrounding medium, and $\hbar$ is Planck's constant divided by 2π. Unfortunately, the Schrödinger equation for the many particle system cannot be solved. If we expand $\epsilon_\alpha(q)$ about the equilibrium position[3(a),24(b)] the leading terms in the potential energy operator V_α corresponding to H_α are given by

$$V_\alpha = (\mu_\alpha\omega_\alpha^2/2)(q_v - q_{v,\alpha}^0)^2 + (2\pi/c)\int |\mathbf{P}_{or}(\mathbf{r}) - \mathbf{P}_{\alpha,or}^0(\mathbf{r})|^2 d\mathbf{r} + J_\alpha, \tag{2.3}$$

where $q_{v,\alpha}^0$ and $\mathbf{P}_{\alpha,or}^0$ are the equilibrium values of the vibrational coordinate and the orientation polarization of the solvent medium around α, respectively, and

$$c = \epsilon_\infty^{-1} - \epsilon_0^{-1}, \tag{2.4a}$$

$$J_\alpha = \epsilon_\alpha(q_{v,\alpha}^0) + (\mu_\alpha\omega_\alpha^2/2)(q_{v,\alpha}^0)^2 + (2\pi/c)\int |\mathbf{P}_{\alpha,or}^0(\mathbf{r})|^2 d\mathbf{r}. \tag{2.4b}$$

The potential given in Eq. (2.3) is clearly parabolic. By shifting the origin and defining $q = q_v - q_{v,1}^0$ we have

$$V_1(q,x) = aq^2/2 + x^2/2, \tag{2.5a}$$

$$V_2(q,x) = a(q-q_0)^2/2 + (x-x_0)^2/2 + \Delta G^0, \tag{2.5b}$$

where $q_0 = q_{v,2}^0 - q_{v,1}^0$, the reaction coordinate x is defined by

$$x^2/2 = (2\pi/c)\int |\mathbf{P}_{or}(\mathbf{r}) - \mathbf{P}_{1,or}^0(\mathbf{r})|^2 d\mathbf{r} \tag{2.6a}$$

and

$$x_0^2/2 = (2\pi/c)\int |\mathbf{P}_{2,or}^0(\mathbf{r}) - \mathbf{P}_{1,or}^0(\mathbf{r})|^2 d\mathbf{r}. \tag{2.6b}$$

$\Delta G^0 = J_2 - J_1$ represents the reaction energy and $a = \mu_\alpha\omega_\alpha^2$ is assumed to be the same for $\alpha = 1$ or 2. The quantities $x_0^2/2$ and $aq_0^2/2$ are the solvent reorganization energy λ_0 and intramolecular reorganization energy λ_q, respectively.

Equations (2.5a) and (2.5b) are the potentials used by Sumi and Marcus.[18] It is seen from Eq. (2.6) that the reaction coordinate x, which is a scalar, is proportional to a certain integral of the orientation polarization of the solvent. Since the dielectric relaxation of the solvent has a diffusive nature, the relaxation of the polarization coordinate x is much slower than that of the vibrational coordinate q. During the time an electron transfers between donor and acceptor, the polarization coordinate x may not be at equilibrium, but the vibrational coordinate q may be assumed to be so. In this case, as argued by Sumi and Marcus, the reaction can be described by reaction–diffusion equations, in which the polarization coordinate x diffuses in potential wells given by the second terms of Eqs. (2.5), while at each x, the reaction occurs with rate constants $k_1(x)$ and $k_2(x)$, which are the rates *averaged* over the vibrational coordinate q.

In the transition state $V_1(q,x) = V_2(q,x)$ and one finds from Eq. (2.5) that in this state (or states)

$$xx_0 + aqq_0 = \lambda + \Delta G^0, \tag{2.7}$$

where

$$\lambda = \lambda_0 + \lambda_q. \tag{2.8}$$

The forward and reverse activation energies at each x are then given by

$$\Delta G_1^*(x) = (1/2)(\lambda_0/\lambda_q)(x - x_{1c})^2, \tag{2.9a}$$

$$\Delta G_2^*(x) = (1/2)(\lambda_0/\lambda_q)(x - x_{2c})^2, \tag{2.9b}$$

with

$$x_{1c} = (\lambda + \Delta G^0)/(2\lambda_0)^{1/2}, \tag{2.10a}$$

$$x_{2c} = (\lambda + \Delta G^0 - 2\lambda_q)/(2\lambda_0)^{1/2}. \tag{2.10b}$$

The forward and reverse rate constants at each x are defined by[18]

$$k_i(x) = \nu_q \exp[-\beta\Delta G_i^*(x)] \quad i = 1,2, \tag{2.11}$$

where $\beta = 1/k_B T$ and

$$\nu_q = k_0[2\pi\lambda_q/(\beta\lambda_0)]^{-1/2} \tag{2.12}$$

in which k_0 is an independent constant.

III. DIFFUSION–REACTION EQUATIONS AND THEIR LIMITING SOLUTIONS

If we use $P_1(x,t)$ and $P_2(x,t)$ to express the probabilities for the reactants and the products to have a particular value of x at time t, the diffusion reaction equations can be written as[13,21]

$$\partial P_1/\partial t = [L_1 - k_1(x)]P_1 + k_2(x)P_2, \tag{3.1a}$$

$$\partial P_2/\partial t = [L_2 - k_2(x)]P_2 + k_1(x)P_1, \tag{3.1b}$$

where L_1 and L_2 are operators defined by

$$L_i = D\frac{\partial^2}{\partial x^2} + \frac{D}{k_B T}\frac{\partial}{\partial x}\left[\frac{dV_i(x)}{dx}\right] \quad i = 1,2, \tag{3.2a}$$

in which D is the diffusion constant, and $V_1(x)$ and $V_2(x)$ are given by the second terms in Eqs. (2.5),

$$V_1(x) = x^2/2, \tag{3.2b}$$

$$V_2(x) = (x - x_0)^2/2 + \Delta G^0. \tag{3.2c}$$

The operator L_i has the form of a Fokker–Planck operator when the potential V_i is parabolic. The initial conditions for the probability distribution of the reactants and the products can be quite different in different experimental situations. One choice is the thermal equilibrium distribution as the initial condition for the reactant,

$$P_1(x,0) = \exp[-\beta V_1(x)] \Big/ \int \exp[-\beta V_1(x)]dx, \tag{3.3a}$$

$$P_2(x,0) = 0. \tag{3.3b}$$

The survival probabilities, which are the quantities directly relevant to experiments, are defined by

$$Q_i(t) = \int_{-\infty}^{\infty} P_i(x,t)dx, \tag{3.4a}$$

$$Q_2(t) = \int_{-\infty}^{\infty} P_2(x,t)dx, \tag{3.4b}$$

with the initial conditions $Q_1(0) = 1$, $Q_2(0) = 0$, and $Q_1(t) + Q_2(t) = 1$ which should be satisfied by the solutions of Eq. (3.1). If the reaction terms are neglected in Eq. (3.1) and the motion of $P_1(x,t)$ and $P_2(x,t)$ are still governed by $V_1(x)$ and $V_2(x)$, it is easily shown[18] that the average value of x decays exponentially,

$$\begin{aligned}\langle x\rangle_i &= \int_{-\infty}^{\infty} xP_i(x,t)dx \\ &= \langle x\rangle_{in,i} \exp(-t/\tau_L) \quad i=1,2,\end{aligned} \tag{3.5}$$

where $\langle x\rangle_{in,i}$ is the initial value and τ_L is the longitudinal dielectric relaxation time of the Debye solvent which is related to the diffusion coefficient by[5(a),18]

$$\tau_L^{-1} = \beta D. \tag{3.6}$$

Therefore, when the reaction does not occur, τ_L serves as the time scale in which $P_i(x,t)$ approaches its equilibrium distribution in the potential well $V_i(x)$.

The coupled equations (3.1) have different limiting solutions. For example, when the diffusion terms are extremely small, we have the *nondiffusion limit* and when the reaction is very slow, we have the *slow reaction limit*. In addition there are the *wide* and *narrow reaction window limits*. We will now discuss these limits as analytic solutions to Eqs. (3.1); the corresponding limits for a single reaction have already been treated by Sumi and Marcus.[18]

A. The slow reaction limit: $[k_i(x) \ll \tau_L^{-1}]$

When the reactions, which disturb the thermal equilibrium distribution of x take place very slowly compared to the rate of the polarization fluctuations of the solvent, we can assume that the thermal equilibrium distribution of x is always maintained. The solution to the diffusion–reaction equations (3.1a) and (3.1b) can then be written as

$$P_i(x,t) = f_i(t)p_i^{\text{eq}}(x,t). \tag{3.7}$$

Substitution in Eq. (3.1) leads to

$$\partial p_i^{\text{eq}}(x,t)/\partial t = L_i p_i^{\text{eq}}(x,t) = 0 \quad i=1,2, \tag{3.8}$$

$$\begin{aligned}p_i^{\text{eq}}(x,t)\partial f_1(t)/\partial t &= -k_1(x)p_1^{\text{eq}}(x,t)f_1(t) \\ &\quad + k_2(x)p_2^{\text{eq}}(x,t)f_2(t),\end{aligned} \tag{3.9a}$$

$$\begin{aligned}p_2^{\text{eq}}(x,t)\partial f_2(t)/\partial t &= -k_2(x)p_2^{\text{eq}}(x,t)f_2(t) \\ &\quad + k_1(x)p_1^{\text{eq}}(x,t)f_1(t).\end{aligned} \tag{3.9b}$$

The solution of Eq. (3.8) is

$$p_i^{\text{eq}}(x) = \exp[-\beta V_i(x)] \Big/ \int \exp[-\beta V_i(x)]dx \quad i=1,2. \tag{3.10}$$

Integrating Eqs. (3.9) and (3.7) over x, and noting that $f_i(t) = Q_i(t)$ we have

$$dQ_1(t)/dt = -k_{1e}Q_1(t) + k_{2e}Q_2(t), \tag{3.11a}$$

$$dQ_2(t)/dt = -k_{2e}Q_2(t) + k_{1e}Q_1(t), \tag{3.11b}$$

where k_{ie} is the thermal equilibrium rate constant defined by

$$\begin{aligned}k_{ie} &= \int k_i(x)p_i^{\text{eq}}(x)dx \\ &= \int k_i(x)\exp[-\beta V_i(x)]dx \Big/ \int \exp[-\beta V_i(x)]dx \quad i=1,2.\end{aligned} \tag{3.12}$$

In this way, the problem is reduced to finding the solution of the detailed balance equations (3.11) for just two states. Taking Laplace transforms and solving

$$Q_1(s) = 1/s - Q_2(s), \tag{3.13a}$$

$$Q_2(s) = k_{1e}/[s(s + k_{1e} + k_{2e})], \tag{3.13b}$$

which can be inverted to give

$$Q_1(t) = 1 - Q_2(t), \tag{3.14a}$$

$$Q_2(t) = \frac{k_{1e}}{k_{1e} + k_{2e}}[1 - e^{-(k_{1e}+k_{2e})t}]. \tag{3.14b}$$

This shows that the time dependencies of the survival probabilities are single exponentials and equilibrium is reached eventually at infinite time. Making use of Eqs. (2.11) and (2.5) and carrying out the integration in Eq. (3.12), we have

$$k_{1e} = \nu \exp[-\beta(\lambda + \Delta G^0)^2/4\lambda], \tag{3.15a}$$

$$k_{2e} = \nu \exp[-\beta(\lambda + \Delta G^0)^2/4\lambda + \beta\Delta G^0], \tag{3.15b}$$

with the preexponential factor

$$\nu = \nu_q(\lambda_q/\lambda)^{1/2}. \tag{3.16}$$

It is seen that the rate constants do not depend on τ_L because the thermal equilibrium distribution is maintained during the reaction. They also satisfy the relation $k_{1e}/k_{2e} = K = \exp(-\beta\Delta G^0)$, as required by the principle of chemical equilibrium. The preexponential factor[18]

$$\nu = (\Sigma \nu_{j,q}^2 \lambda_{j,q}/\lambda)^{1/2} \tag{3.17a}$$

for adiabatic reactions, and

$$\nu = (J^2/h)(\pi\beta/\lambda)^{1/2} \tag{3.17b}$$

for a nonadiabatic reaction, where $\nu_{j,q}$ and $\lambda_{j,q}$ are the jth vibrational frequency and the jth vibrational contribution to λ_i, respectively, and J is the electronic coupling matrix element.

B. The nondiffusion limit: $[k_i(x) \gg \tau_L^{-1}]$

In this limit, the reactions are so fast that the thermal equilibrium distribution of the x is not restored by diffusion during the reaction. The diffusive process can now be neglected and Eqs. (3.1) and (3.2) reduce to

$$\partial P_1/\partial t = -k_1(x)P_1 + k_2(x)P_2, \tag{3.18a}$$

$$\partial P_2/\partial t = -k_2(x)P_2 + k_1(x)P_1, \tag{3.18b}$$

which have the solutions

$$P_1(x,t) = P_1(x,0) - P_2(x,t), \tag{3.19a}$$

$$P_2(x,t) = P_1(x,0)\left\{\frac{k_1(x)}{k_1(x) + k_2(x)} \times [1 - e^{-[k_1(x)+k_2(x)]t}]\right\}, \tag{3.19b}$$

where $P_1(x,0)$ is the initial distribution. The survival probabilities $Q_1(t)$ and $Q_2(t)$, found by integrating Eqs. (3.19), will show multiexponential decay.

C. Narrow reaction window limit: ($\lambda_q \ll \lambda_0$)

In contrast to the preceding case, if the width of $k_i(x)$ is very narrow, the Gaussian distribution can be approximated by a delta function

$$k(x) = k_1(x) = k_2(x) = k_0\delta(x - x_c), \tag{3.20}$$

where k_0 is a constant [see Eq. (2.12)]. Equations (2.10) then reduce to

$$x_c = x_{1c} = x_{2c} = (\lambda_0 + \Delta G^0)/(2\lambda_0)^{1/2} \tag{3.21}$$

at which point the vibrational coordinate $q = 0$. In this case, Eq. (2.9) is meaningless and the activation energies for the forward and reverse reactions have to be reformulated as

$$\Delta G_1^* = x_c^2/2 = (\lambda_0 + \Delta G^0)^2/(4\lambda_0), \tag{3.22a}$$

$$\Delta G_2^* = (x_c - x_0)^2/2 = (\lambda_0 - \Delta G^0)^2/(4\lambda_0). \tag{3.22b}$$

The reaction–diffusion equations (3.1) reduce to

$$\partial P_1/\partial t = -k_0\delta(x - x_c)(P_1 - P_2) + L_1 P_1, \tag{3.23a}$$

$$\partial P_2/\partial t = k_0\delta(x - x_c)(P_1 - P_2) + L_2 P_1, \tag{3.23b}$$

which are similar to the equations derived by Zusman[13(a)] for describing the electron transfer reactions from Burschtein's theory of sudden modulation; our analysis, which follows, is similar to his. Taking Laplace transforms, the solutions of Eq. (3.23) can be written as

$$P_1(x,s) = P_1(x,0)/s - k_0 G_1(x|x_c,s) \times [P_1(x_c,s) - P_2(x_c,s)], \tag{3.24a}$$

$$P_2(x,s) = k_0 G_2(x - x_0|x_c - x_0,s) \times [P_1(x_c,s) - P_2(x_c,s)], \tag{3.24b}$$

where $P_1(x,0)$ is the initial condition and the Green's functions $G_1(x|x_c,s)$ and $G_2(x - x_0|x_c - x_0,s)$ are the Laplace transforms of the solutions to the Fokker–Planck equations

$$\partial G_1(x|x_c,t)/\partial t = L_1 G_1(x|x_c,t), \tag{3.25a}$$

$$\partial G_2(x - x_0|x_c - x_0,t)/\partial t = L_2 G_2(x - x_0|x_c - x_0,t), \tag{3.25b}$$

with the initial conditions $G_1(x|x_c,0) = \delta(x - x_c)$ and $G_2(x - x_0|x_c - x_0,0) = \delta(x - x_c)$. Solving these equations it follows that

$$G_1(x|x_c,s) = \int_0^\infty e^{-st}[2\pi k_B T(1 - e^{-2t/\tau_L}]^{-1/2} \times \exp\left[-\frac{\beta(x - x_c e^{-t/\tau_L})^2}{2(1 - e^{-2t/\tau_L})}\right] dt \tag{3.26}$$

and $G_2(x - x_0|x_c - x_0,s)$ has the same form as $G_1(x|x_c,s)$ with $x - x_0$ and $x_c - x_0$ replacing x and x_c in Eq. (3.26). Integrating Eq. (3.24) with respect to x, we have for the Laplace transforms of the survival probabilities $Q_i(t)$,

$$Q_1(s) = s^{-1} - Q_2(s), \tag{3.27a}$$

$$Q_2(s) = s^{-1}k_0[P_1(x_c,s) - P_2(x_c,s)]. \tag{3.27b}$$

In deriving this we have used the normalization conditions for $P_1(x,0)$, $G_1(x|x_c,t)$ and $G_2(x - x_0|x_c - x_0,t)$. Letting $x = x_c$ in Eqs. (3.24) one has

$$[P_1(x_c,s) - P_2(x_c,s)] = [P_1(x_c,0)/s]/\{1 + k_0[G_1(x_c|x_c,s) + G_2(x_c - x_0|x_c - x_0,s)]\}, \tag{3.27c}$$

which gives

$$Q_2(s) = k_0 P_1(x_c,0)/\{s^2[1 + k_0 G_1(x_c|x_c,s) + k_0 G_2(x_c - x_0|x_c - x_0,s)]\}. \tag{3.27d}$$

Equation (3.27) is exact for this limit but we recall that it applies only to systems with a single relaxation time, i.e., a Debye solvent.

If one could carry out the integral in Eqs. (3.26) analytically, the problem, in this limit for a Debye solvent would be solved completely. This is done in Sec. IV; here instead we discuss three simpler approximations for the Green's functions given in Eq. (3.26).

1. Long and short time approximations

Analytical results can be obtained at long and short times. When $t \gg \tau_L$, $\exp(-t/\tau_L) \approx 0$, and Eq. (3.26) gives

$$G_1(x_c|x_c,s) \approx P_1(x_c,0)/s;$$

$$G_2(x_c - x_0|x_c - x_0,s) \approx P_1(x_c - x_0,0)/s. \tag{3.28a}$$

When $t \ll \tau_L$, $\exp(-t/\tau_L) \approx 1 - t/\tau_L$, then Eq. (3.26) gives

$$G_1(x_c/x_c,s) \approx \tau_L/|x_c|;$$

$$G_2(x_c - x_0|x_c - x_0,s) \approx \tau_L/|x_c - x_0|. \tag{3.28b}$$

Interpolating between these limits, $G_1(x|x_c,s)$ and $G_2(x_c - x_0|x_c - x_0,s)$ can be approximated as[13]

$$G_1(x_c|x_c,s) \approx P_1(x_c,0)/s + \tau_L/|x_c|, \tag{3.28c}$$

$$G_2(x_c - x_0|x_c - x_0,s) \approx P_2(x_c - x_0,0)/s + \tau_L/|x_c - x_0|. \tag{3.28d}$$

Substituting these into Eq. (3.27) and using Eq. (3.3a) we have

$$Q_1(s) = 1/s - Q_2(s), \tag{3.29a}$$

$$Q_2(s) = k_1/[s(s + k_1 + k_2)], \tag{3.29b}$$

where

$$k_1 = A_1 \exp[-\beta(\lambda_0 + \Delta G^0)^2/4\lambda_0], \tag{3.30a}$$

$$k_2 = A_1 \exp[-\beta(\lambda_0 + \Delta G^0)^2/4\lambda_0 + \beta\Delta G^0], \tag{3.30b}$$

and A_1 is defined by

$$A_1 = k_0(2\pi k_B T)^{-1/2} \times [1 + k_0\tau_L(1/|x_c| + 1/|x_c - x_0|)]^{-1}. \tag{3.31}$$

Equation (3.29) has the same form as Eq. (3.13). It follows that the time dependence of the survival probabilities is again the simple exponential given in Eq. (3.14) with k_{1e}

and k_{2e} replaced by k_1 and k_2. It is seen that $k_1/k_2 = K = \exp(-\beta\Delta G^0)$ is satisfied in the present approximation. When the second term in the denominator is much bigger than unity, Eq. (3.31b) can be approximated as

$$A_1 \approx \tau_L^{-1}(2\pi k_B T)^{-1/2}(|x_c||x_c - x_0|)/(|x_c| + |x_c - x_0|) \tag{3.32a}$$

and for $\Delta G^0 = 0$, $x_c = (\lambda_0/2)^{1/2}$

$$A_1 \approx (2\tau_L)^{-1}(\beta\lambda_0/4\pi)^{1/2}. \tag{3.32b}$$

Here A_1 is independent of the strength of the delta function k_0 and is inversely proportional to the solvent dielectric relaxation time τ_L. If $\beta\lambda_0$ is in the range π to 4π, Eqs. (3.32b) and (3.30) gives $k_1 = k_2 \approx 0.11\tau_L^{-1}$ to $0.02\tau_L^{-1}$, which shows the rate constants cannot reach the value τ_L^{-1} if there is a barrier present between the reactant and product potential surfaces.

2. Barrierless reaction ($\beta\Delta G_1^\ddagger \ll 1$, $\beta\Delta G_2^\ddagger \ll 1$)

This occurs when the reaction energy ΔG^0 and solvent reorganization energy λ_0 are both small. For this case, analytical results can be obtained for the survival probabilities.

Since $\beta\Delta G_1^\ddagger \ll 1$, $\beta\Delta G_2^\ddagger \ll 1$, $G_1(x_c|x_c,s)$ and $G_2(x_c - x_0|x_c - x_0,s)$ in Eq. (3.26) can be approximated as

$$\begin{aligned} G_1(x_c|x_c,s) &= G_2(x_c - x_o|x_c - x_o,s) \\ &\approx (\beta/2\pi)^{-1/2}\int_0^\infty [1 - \exp(-2t/\tau_L)]^{-1/2} \\ &\quad \times \exp(-st)dt = (\beta/2\pi)^{1/2}f(s), \end{aligned} \tag{3.33}$$

with

$$f(s) = \sum_{n=0}^{\infty} \frac{(2n)!}{[(2n)!!]^2}\frac{1}{s + 2n/\tau_L}, \tag{3.34}$$

where we have expanded $[1 - \exp(-2t/\tau_L)]^{-1/2}$ in an infinite series. Combining Eqs. (3.33) and (3.27) we have

$$Q_1(s) = 1/s - Q_2(s), \tag{3.35a}$$

$$Q_2(s) = \frac{k_0(\beta/2\pi)^{1/2}}{s^2\{1 + 2k_0(\beta/2\pi)^{1/2}f(s)\}} \tag{3.35b}$$

$$\approx \frac{1}{2}\frac{1}{s^2 f(s)}. \tag{3.35c}$$

Here we have used $P_1(x_c,0) = (\beta/2\pi)^{1/2}$ for the barrierless reaction. In going from Eq. (3.35b) to (3.35c) the approximation has been made that the second term in the denominator[18] is much bigger than one, which is true if $k_0\tau_L(\beta/2\pi)^{1/2} \gg 1$. It is seen that the poles of $Q_2(s)$ are at $s = 0$ and $s = -(2n+1)/\tau_L$ for $n = 0,1,2...$ which are also the poles of $f(s)$.[18] From the general partial fraction expansion of the inverse Laplace transform about these poles, $Q_2(s)$ can be written as

$$\hat{Q}_2(s) = \frac{1}{2s} + \frac{1}{2}\sum_{n=0}^{\infty}\left(\frac{\tau_L}{2n+1}\right)^2 \times \frac{1}{f'\left(-\dfrac{2n+1}{\tau_L}\right)}\frac{1}{s + (2n+1)/\tau_L}, \tag{3.36}$$

where the first term comes from expansion about $s = 0$, and the second term is from the expansion about $s = -(2n+1)/\tau_L$ for $n = 0,1,2...$. The derivative of $f(s)$ at $s = -(2n+1)/\tau_L$ has the general form[18]

$$f'[-(2n+1)/\tau_L] = -(\pi\tau_L^2/2)[(2n)!!]^2/(2n+1)!. \tag{3.37}$$

Substitution of this in Eq. (3.37) leads to

$$Q_2(s) = \frac{1}{2s} - \frac{1}{\pi} \times \sum_{n=0}^{\infty}\frac{(2n)!}{(2n+1)[(2n)!!]^2}\frac{1}{s + (2n+1)/\tau_L}, \tag{3.38}$$

which gives the inverse Laplace transform

$$\begin{aligned} Q_2(t) &= \frac{1}{2} - \frac{1}{\pi}\sum_{n=0}^{\infty}\frac{(2n)!}{(2n+1)[(2n)!!]^2}e^{-(2n+1)t/\tau_L} \\ &= \frac{1}{\pi}\arccos(e^{-t/\tau_L}). \end{aligned} \tag{3.39}$$

The inverse Laplace transform of Eq. (3.35a) is then

$$Q_1(t) = 1 - (1/\pi)\arccos[\exp(-t/\tau_L)]. \tag{3.40}$$

However, if one neglects the reverse reaction, which corresponds to $\beta\Delta G_1^\ddagger \ll 1$, $\beta\Delta G_2^\ddagger \gg 1$ and is discussed later in detail, a factor (1/2) will be removed from Eqs. (3.35) and (3.38) and instead of Eq. (3.40), the inverse Laplace transform of Eq. (3.35a) produces

$$Q_1(t) = (2/\pi)\arcsin[\exp(-t/\tau_L)] \tag{3.41}$$

and $Q_2(t) = 0$ which is Sumi and Marcus' result.[18] The difference between the two is determined by whether the reverse reaction is neglected or not. When $t \to \infty$, Eqs. (3.40) and (3.41) predict the values of 1/2 and zero, respectively, for $Q_1(t)$.

From the above equations it is clear that the time dependence of the survival probabilities are multiexponential which makes it difficult to identify overall rate constants k_1 and k_2 in either direction. But if the time is fairly long compared to τ_L, which corresponds to small values of s, Eq. (3.34) can be approximated as

$$f(s) \approx \frac{1}{s} + \tau_L f_n, \tag{3.42}$$

with

$$f_n = \sum_{n=1}^{\infty}\frac{(2n)!}{[(2n)!!]^2}\frac{1}{2n}. \tag{3.43}$$

Combining Eq. (3.42) with Eq. (3.33) leads to

$$\begin{aligned} G_1(x_c|x_c,s) &= G_2(x_c - x_0|x_c - x_0,s) \\ &= (\beta/2\pi)^{1/2}[1/s + \tau_L f_n], \end{aligned} \tag{3.44}$$

which with Eq. (3.27) gives

$$[P_1(x_c,s) - P_2(x_c,s)] = (\beta/2\pi)^{1/2}[s + k_0(\beta/2\pi)^{1/2}(1 + s\tau_L f_n)]. \quad (3.45)$$

The solution of Eq. (3.27) then reduces to $Q_1(s) = s^{-1} - Q_2(s)$, where

$$Q_2(s) = \frac{k}{s(s+2k)}, \quad (3.46)$$

with

$$k = \frac{k_0(\beta/2\pi)^{1/2}}{1 + 2k_0\tau_L f_n(\beta/2\pi)^{1/2}}. \quad (3.47)$$

Now the inverse Laplace transforms are

$$Q_1(t) = 1 - Q_2(t), \quad (3.48a)$$

$$Q_2(t) = [1 - \exp(-2kt)]/2, \quad (3.48b)$$

which show single exponential behavior in this long time approximation and identifies $k = k_1 = k_2$ in Eq. (3.47) as a first order rate constant. If $k_0\tau_L(\beta/2\pi)^{1/2} \gg 1$, we have

$$k = k_1 = k_2 = (2\tau_L f_n)^{-1}, \quad (3.49)$$

which is independent of the strength of the delta function k_0 and is inversely proportional to the solvent relaxation time τ_L. The series in Eq. (3.43) converges slowly but, carrying out the summation to as many terms as necessary (about forty), we find $f_n \approx 0.6$, which leads to $k \approx 0.833\tau_L^{-1}$. This is close to many experimentally observed values of $k \approx \tau_L^{-1}$.

3. Barrierless reaction ($\beta\Delta G_1^\ddagger \ll 1$, $\beta\Delta G_2^\ddagger \gg 1$)

If the reaction free energy ΔG^0 and the solvent reorganization energy λ_0 are not small, but the intersection of the two potential wells is near the minimum for the reactant, then the activation energy for the forward reaction ($\beta\Delta G_1^\ddagger = \beta x_c^2/2 \approx 0$) is small but it is large for the reverse reaction. One limiting approximation is, of course, to neglect the reverse reaction when $G_2(x_c - x_0|x_c - x_0,s) \approx 0$. As discussed above, the survival probability $Q_1(t)$ will then be given by Eq. (3.41) showing a multiexponential decay. However, if the reverse reaction cannot be neglected, one can use Eq. (3.33) which is exact for $G_1(x_c|x_c,s)$ and the interpolation formula given in Eq. (3.28d) for $G_2(x_c - x_0|x_c - x_0,s)$, which would lead to Eq. (3.27). However, a simpler expression is found if instead we use the approximation Eq. (3.44) for $G_1(x_c|x_c,s)$ but retain Eq. (3.28d) for $G_2(x_c - x_0|x_c - x_0,s)$, when Eq. (3.27) reduces to

$$Q_1(s) = 1/s - Q_2(s), \quad (3.50a)$$

$$Q_2(s) = k_0\gamma^{-1}P_1(x_c)/\{s^2 + sk_0\gamma^{-1}[(\beta/2\pi)^{1/2} + P_1(x_c - x_0)]\}, \quad (3.50b)$$

where

$$\gamma = 1 + \tau_L k_o(\beta/2\pi)^{1/2}[f_n + (\pi/\beta\Delta G_2^\ddagger)^{1/2}]. \quad (3.51)$$

f_n is given by Eq. (3.43) and $\Delta G_2^\ddagger \approx x_0^2/2$, while $P_1(x_c)$ and $P_1(x_c - x_0)$ depend on the initial conditions. Choosing these to be the thermal equilibrium distribution of Eq. (3.3a), we have $P_1(x_c) = (\beta/2\pi)^{1/2}$ and $P_1(x_c - x_0) = (\beta/2\pi)^{1/2}\exp(-\beta x_0^2/2)$. Taking the inverse Laplace transforms, the survival probabilities are those displayed in Eq. (3.14) with the rate constants k_{1e} and k_{2e} replaced by

$$k_1 = k_0(\beta/2\pi)^{1/2}/\gamma, \quad (3.52a)$$

$$k_2 = k_0(\beta/2\pi)^{1/2}\exp(-\beta x_0^2/2)/\gamma, \quad (3.52b)$$

respectively. If $\tau_L k_0(\beta/2\pi)^{1/2} \gg 1$ the first term of Eq. (3.51) can be neglected and we have

$$k_1 \approx \tau_L^{-1}[f_n + (\pi/\beta\Delta G_2^\ddagger)^{1/2}]^{-1}, \quad (3.53)$$

where we have found earlier that $f_n \approx 0.6$. This shows how the rate constant for a barrierless forward reaction changes with the height of the activation barrier for the reverse reaction. We will compare this with the experimental results in the Sec. V.

D. The wide reaction window limit: ($\lambda_q \gg \lambda_0$)

Here the distribution of $k_i(x)$ [see Eqs. (2.11) and (2.9)] is Gaussian, with a width $(k_B T\lambda_q/\lambda_0)^{1/2}$. When $\lambda_q \gg \lambda_0$, the width of this distribution, which is the reaction window, is much wider than the width $(k_B T)^{1/2}$ of the thermal equilibrium distribution of x. In this case, as suggested by Sumi and Marcus,[18] one can approximate $k_i(x)$ as a constant which may be taken as k_{ie} by letting $\lambda = \lambda_q$ and $\nu = \nu_q$.

$$k_1 = \nu_q \exp[-\beta(\lambda_q + \Delta G^0)^2/4\lambda_q], \quad (3.54a)$$

$$k_2 = \nu_q \exp[-\beta(\lambda_q + \Delta G^0)^2/4\lambda_q + \beta\Delta G^0]. \quad (3.54b)$$

Since the reactions span the x coordinate so widely, the shift $x_0 = \sqrt{2\lambda_0}$ in the product potential well becomes relatively unimportant and can be neglected. Therefore the diffusion operators are essentially equal to each other $L_1 \approx L_2$, and the solutions to the reaction diffusion equation can then be written as the product of the probabilities for reaction and diffusion,

$$P_i(x,t) = f_i(t)p_1^{\text{dif}}(x,t). \quad (3.55)$$

Substitution in Eq. (3.1) leads to

$$\partial p_1^{\text{dif}}(x,t)/\partial t = L_1 p_1^{\text{dif}}(x,t) \quad (3.56)$$

and

$$\partial f_1(t)/\partial t = -k_1 f_1(t) + k_2 f_2(t), \quad (3.57a)$$

$$\partial f_2(t)/\partial t = -k_2 f_2(t) + k_1 f_1(t), \quad (3.57b)$$

with the initial conditions $f_1(0) = 1$, $f_2(0) = 0$ and $p_1^{\text{dif}}(x,0) = \delta(x)$. Since $\int p_1^{\text{dif}}(x,t)\,dx = 1$, the survival probability $Q_i(t)$ is just $f_i(t)$ and is given by Eq. (3.14) with k_{ie} replaced by k_i.

So far we have solved the coupled reaction–diffusion equations (3.1) separately in different limiting conditions. As pointed by Sumi and Marcus,[18] for the case of a single reaction, a theory which encompasses the four limiting cases, can be set up by considering the adjoint equation.[18,11] In the following section, we discuss this for reversible electron transfer reactions.

IV. THE ADJOINT DIFFUSION–REACTION EQUATIONS AND APPROXIMATE GENERAL SOLUTIONS

To find a general solution we first transform the diffusion reaction equation (3.1) into an adjoint form. Following Zusman[13] and Sumi and Marcus,[18] we define

$$P_i(x,t) = g_i(x) q_i(x,t) \quad i = 1,2, \tag{4.1}$$

with $g_i(x)$ related to the thermal equilibrium distribution

$$\begin{aligned} g_i(x) &= [P_i^{\text{eq}}(x)]^{1/2} \\ &= \exp[-\beta V_i(x)/2] / \\ &\quad \int \exp[-\beta V_i(x)/2] dx \quad i = 1,2. \end{aligned} \tag{4.2}$$

Substituting Eqs. (4.1) and (4.2) into Eq. (3.1) leads to the adjoint equations

$$\begin{aligned} \partial q_1(x,t)/\partial t = & -[H_1 + k_1(x)] q_1(x,t) \\ & + k_2'(x) q_2(x,t), \end{aligned} \tag{4.3a}$$

$$\begin{aligned} \partial q_2(x,t)/\partial t = & -[H_2 + k_2(x)] q_1(x,t) \\ & + k_1'(x) q_1(x,t), \end{aligned} \tag{4.3b}$$

where

$$H_i = -D\frac{\partial^2}{\partial x^2} + \frac{\beta D}{2}\left[\frac{\beta}{2}\left(\frac{dV_i}{dx}\right)^2 - \frac{d^2 V_i}{dx^2}\right] \quad i = 1,2 \tag{4.4}$$

is similar to the Hamiltonian operator for a harmonic oscillator with the potential energy given in Eq. (3.2). The eigenvalues are

$$\epsilon_n = n\tau_L^{-1} \quad n = 0,1,2,\ldots, \tag{4.5}$$

and the eigenfunctions are given in the Appendix [Eq. (A1)]. The lowest order eigenfunction $g_i(x)$ satisfies

$$H_i g_i(x) = 0 \quad i = 1,2 \tag{4.6}$$

$k_1'(x)$ and $k_2'(x)$, which appear in Eq. (4.3), are defined by

$$k_1'(x) = k_1(x) g_1(x)/g_2(x), \tag{4.7a}$$

$$k_2'(x) = k_2(x) g_2(x)/g_1(x), \tag{4.7b}$$

with $k_1(x)$ and $k_2(x)$ given in Eq. (2.11). The survival probabilities, defined in Eq. (3.4), turn out to be

$$Q_i(t) = \int g_i(x) q_i(x,t) dx = \langle g_i | q_i(t) \rangle \quad i = 1,2 \tag{4.8}$$

and the initial conditions can be written as

$$q_1(x,0) = f_1(x), \tag{4.9a}$$

$$q_2(x,0) = 0, \tag{4.9b}$$

or

$$Q_1(0) = \int P_1(x,0) dx = \langle g_1 | f_1 \rangle = 1, \tag{4.9c}$$

$$Q_2(0) = 0. \tag{4.9d}$$

Defining

$$A_i = s + H_i + k_i(x) \quad i = 1,2 \tag{4.10}$$

the Laplace transform solution of Eq. (4.3), with the initial condition (4.9), can be written as

$$q_1(x,s) = \frac{1}{A_1 - k_2' A_2^{-1} k_1'} q_1(x,0), \tag{4.11a}$$

$$q_2(x,s) = A_2^{-1} k_1' \frac{1}{A_1 - k_2' A_2^{-1} k_1'} q_1(x,0). \tag{4.11b}$$

Then from Eq. (4.8) we have for the Laplace transforms of the survival probabilities

$$\begin{aligned} Q_1(s) &= \langle g_1(x) | \frac{1}{A_1 - k_2' A_2^{-1} k_1'} | f_1(x) \rangle \\ &= \langle g_1(x) | A_1^{-1} \\ &\quad \times \frac{1}{1 - A_1^{-1} k_2' A_2^{-1} k_1'} | f_1(x) \rangle, \end{aligned} \tag{4.12a}$$

$$\begin{aligned} Q_2(s) &= \langle g_2(x) | A_2^{-1} k_1' \frac{1}{A_1 - k_2' A_2^{-1} k_1'} | f_1(x) \rangle \\ &= \langle g_2(x) | A_2^{-1} k_1' A_1^{-1} \\ &\quad \times \frac{1}{1 - A_1^{-1} k_2' A_2^{-1} k_1'} | f_1(x) \rangle. \end{aligned} \tag{4.12b}$$

The analytic solutions to these equations cannot be obtained without the introduction of approximations. We discuss these approximations for a single reaction before considering reversible reactions.

When the reverse reaction is ignored [i.e., $k_2(x) = 0$], which is the case studied by Sumi and Marcus, Eqs. (4.11a) and (4.12a) reduce to

$$q_1(x,s) = A_1^{-1} q_1(x,0), \tag{4.13a}$$

$$Q_1(x,s) = \langle g_1 | A_1^{-1} | f_1 \rangle. \tag{4.13b}$$

This also cannot be solved exactly. Sumi and Marcus[18] introduced a decoupling approximation which is equivalent to representing the unit operator by

$$1 \approx k_{1e}^{-1} | g_1 \rangle \langle g_1 | k_1, \tag{4.14}$$

where

$$k_{1e} = \langle g_1(x) | k_1(x) | g_1(x) \rangle \tag{4.15}$$

is the thermal equilibrium rate constant given in Eqs. (3.15). It follows from Eq. (4.15) that Eq. (4.14) is exact when the expectation value of operator $k_{1e}^{-1} | g_1 \rangle \langle g_1 | k_1$ is computed in the state $| g_1 \rangle$. In general, however, it is an approximation. Introducing Eq. (4.14) after $k_1 = k_1(x)$ in the operator identity

$$A_1^{-1} = (s + H_1)^{-1} [1 - k_1 A_1^{-1}], \tag{4.16}$$

we have

$$A_1^{-1} \approx (s + H_1)^{-1} [1 - k_{1e}^{-1} k_1 | g_1 \rangle \langle g_1 | k_1 A_1^{-1}]. \tag{4.17}$$

Operating with this on $\langle g_1 | k_1$ we find that

$$\langle g_1 | k_1 A_1^{-1} \approx [1 + a_{s1}(s)]^{-1} \langle g_1 | k_1 (s + H_1)^{-1}, \tag{4.18}$$

where the scalar

$$a_{s1}(s) = k_{1e}^{-1} \langle g_1 | k_1 (s + H_1)^{-1} k_1 | g_1 \rangle. \tag{4.19}$$

Substitution of Eq. (4.18) in Eq. (4.17) leads to an approximate representation of the operator A_1^{-1},

$$A_1^{-1} \approx (s + H_1)^{-1} \{1 - [1 + a_{s1}(s)]^{-1} k_1 (s + H_1)^{-1}\}. \tag{4.20}$$

The advantage of this is that it contains the operator $(s + H_1)^{-1}$ instead of $[s + H_1 + k_1(x)]^{-1}$ which defines A_1^{-1}. This makes it possible to use the properties of the Hermitian operator H_1 in determining the inverse operators. For example, if $(s + H_1)^{-1}$ operates on an eigenfunction $u_{n,1}(x)$ of H_1, we have

$$(s + H_1)^{-1} | u_{n,1}(x) \rangle = (s + \epsilon_n)^{-1} | u_{n,1}(x) \rangle, \tag{4.21}$$

where the ϵ_n is given in Eq. (4.5). Since $g_1(x) = |u_{0,1}(x)\rangle$ is the lowest order eigenfunction, $(s+H_1)^{-1}|g_1(x)\rangle = s^{-1}|g_1(x)\rangle$ while if $|u_{n,1}(x)\rangle$ is replaced by an arbitrary function $f_1 = f_1(x)$, which can be expanded in the set of eigenfunctions $|u_{n,1}(x)\rangle$, we see that

$$(s+H_1)^{-1}|f_1(x)\rangle = \sum_{n=0} (s+\epsilon_n)^{-1}\langle u_{n,1}|f_1\rangle|u_{n,1}\rangle. \tag{4.22a}$$

It follows immediately that

$$\langle g_1|(s+H_1)^{-1}k_1|g_1\rangle = \sum_{n=0} (s+\epsilon_n)^{-1}\langle u_{n,1}|k_1|g_1\rangle \times \langle g_1|u_{n,1}\rangle = k_{1e}s^{-1}. \tag{4.22b}$$

Likewise $a_{s1}(s)$, defined in Eq. (4.19), can be written as

$$a_{s1}(s) = k_{1e}^{-1} \sum_{n=0} (s+\epsilon_n)^{-1}\langle u_{n,1}|k_1|g_1\rangle\langle g_1|k_1|u_{n,1}\rangle \tag{4.23a}$$

$$= k_{1e}s^{-1} + k_{1e}^{-1} \sum_{n=1} (s+\epsilon_n)^{-1}|\langle u_{n,1}|k_1|g_1\rangle|^2, \tag{4.23b}$$

where $\epsilon_n = n/\tau_L$. Taking the inverse Laplace transform

$$a_1(t) = k_{1e} + k_{1e}^{-1} \sum_{n=1} c_{n,1} \exp(-\epsilon_n t), \tag{4.24}$$

where $c_{n,1} = |\langle u_{n,1}|k_1|g_1\rangle|^2$. Further discussion of this is given in Appendix A.

Equation (4.20) is simpler than the approximations derived by Sumi and Marcus although they also used Eq. (4.14). All of their results can also be derived from Eq. (4.20). Using this in the expression for the survival probability we find that

$$Q_1(s) = s^{-1} - [s(1+a_{s1})]^{-1}\langle g_1|k_1(s+H_1)^{-1}|f_1\rangle \tag{4.25a}$$

which is our main result when the initial state is $|f_1\rangle$. If this is taken as the thermal equilibrium condition $f_1 = g_1$

$$Q_1(s) = \langle g_1|A_1^{-1}|g_1\rangle = 1/s - k_{1e}/[s^2(1+a_{s1})]. \tag{4.25b}$$

This is our approximate general solution for a single reaction with these initial conditions which was also obtained by Sumi and Marcus in the special case of a narrow reaction window limit; the general solution given by them in Eq. (5.24) of Ref. 18 contains an additional operator h which makes the subsequent discussion more involved. It is easy to show that Eq. (4.25b) generates the four limiting cases discussed by Sumi and Marcus. For example, in the slow reaction limit, $a_{s1} \approx s^{-1}k_{1e}$, and Eq. (4.25b) leads to

$$Q_1(s) \approx (s+k_{1e})^{-1}. \tag{4.26}$$

This leads to a single exponential decay $Q_1(t) \approx \exp(-k_{1e}t)$. In the narrow reaction window limit, Eq. (4.25b) is (E3) of Sumi and Marcus' paper. We omit the derivations of the other two limiting cases which lead to the same form since they are quite simple but we consider them all in our discussion of reversible electron transfer reactions which follows.

In the reversible reaction case, the decoupling approximation Eq. (4.14) and (4.20a) are generalized and extended to

$$1 \simeq \langle g_i|g_j\rangle k_{je}^{-1}|g_i\rangle\langle g_j|k_j \quad i,j = 1,2 \tag{4.27}$$

and

$$A_i^{-1} \approx (s+H_i)^{-1}\{1 - [1+a_{si}(s)]^{-1} \times k_i(s+H_i)^{-1}\} \quad i = 1,2, \tag{4.28}$$

respectively, where

$$a_{si}(s) = k_{ie}^{-1}\langle g_i|k_i(s+H_i)^{-1}k_i|g_i\rangle \quad i = 1,2 \tag{4.29}$$

and

$$k_{ie} = \langle g_i|k_i|g_i\rangle \quad i = 1,2. \tag{4.30}$$

Equation (4.27) is exact if we evaluate $\langle g_i|1|g_j\rangle$ although generally it is an approximation. We will discuss the simple case of letting $f_1 = g_1$ when the use of the decoupling approximation in Eq. (4.12) leads to

$$Q_1(s) \approx \langle g_1|A_1^{-1}|g_1\rangle k_{1e}^{-1}\langle g_1k_1|\frac{1}{1-A_1^{-1}k_2'A_2^{-1}k_1'}|g_1\rangle = \langle g_1|A_1^{-1}|g_1\rangle \times \frac{1}{1-k_{1e}^{-1}\langle g_1k_1|A_1^{-1}k_2'A_2^{-1}k_1'|g_1\rangle}, \tag{4.31a}$$

$$Q_2(s) \approx \langle g_2|A_2^{-1}k_1'A_1^{-1}|g_1\rangle k_{1e}^{-1} \times \langle g_1k_1|\frac{1}{1-A_1^{-1}k_2'A_2^{-1}k_1'}|g_1\rangle = \langle g_2|A_2^{-1}k_1'A_1^{-1}|g_1\rangle \times \frac{1}{1-k_{1e}^{-1}\langle g_1k_1|A_1^{-1}k_2'A_2^{-1}k_1'|g_1\rangle}, \tag{4.31b}$$

where, in the second step of each of these equations, we have used the expansion $(1-A)^{-1} = 1 + A + A^2 + \cdots$ in which $A = A_1^{-1}k_2'A_2^{-1}k_1'$. The scalar $\langle g_1|A_1^{-1}|g_1\rangle$ appearing in Eq. (4.13a) has already been given in Eq. (4.25b) and $\langle g_1k_1|A_1^{-1}k_2'A_2^{-1}k_1'|g_1\rangle$ and $\langle g_2|A_2^{-1}k_1'A_1^{-1}|g_1\rangle$ are calculated, using the decoupling approximation and Eq. (4.28), as follows:

$$k_{1e}^{-1}\langle g_1k_1|A_1^{-1}k_2'A_2^{-1}k_1'|g_1\rangle \approx k_{1e}^{-1}\langle g_1k_1|A_1^{-1}|g_1\rangle k_{1e}^{-1}\langle g_2|k_1k_2|g_2\rangle k_{2e}^{-1}\langle g_2k_2|A_2^{-1}|g_2\rangle k_{2e}^{-1}\langle g_1|k_2k_1|g_1\rangle$$
$$= [s^2(1+a_{s1})(1+a_{s2})]^{-1}k_{1e}^{-1}\langle g_1|k_2k_1|g_1\rangle k_{2e}^{-1}\langle g_2|k_1k_2|g_2\rangle, \tag{4.32a}$$

$$\langle g_2|A_2^{-1}k_1'A_1^{-1}|g_1\rangle \approx \langle g_2|A_2^{-1}|g_2\rangle k_{2e}^{-1}\langle g_1|k_1k_2|g_2\rangle\langle g_1|g_2\rangle k_{1e}^{-1}\langle g_1k_1|A_1^{-1}|g_1\rangle$$
$$= \langle g_2|A_2^{-1}|g_2\rangle\langle g_1k_1|A_1^{-1}|g_1\rangle = k_{1e}\{s^{-1} - k_{2e}[s^2(1+a_{s2})]^{-1}\}[s(1+a_{s1})]^{-1}. \tag{4.32b}$$

Combining Eqs. (4.32), (4.31), and (4.25), we have

$$Q_1(s) = \frac{s(1+a_{s1}+a_{s2}) - k_{1e} + a_{s2}(sa_{s1} - k_{1e})}{s^2(1+a_{s1}+a_{s2}) + \left(s^2 a_{s1} a_{s2} - \dfrac{\langle g_1|k_1k_2|g_1\rangle\langle g_2|k_1k_2|g_2\rangle}{k_{1e}k_{2e}}\right)}, \tag{4.33a}$$

$$Q_2(s) = \frac{k_{1e} - (k_{1e}/s)(sa_{s2} - k_{2e})}{s^2(1+a_{s1}+a_{s2}) + \left(s^2 a_{s1} a_{s2} - \dfrac{\langle g_1|k_1k_2|g_1\rangle\langle g_2|k_1k_2|g_2\rangle}{k_{1e}k_{2e}}\right)}. \tag{4.33b}$$

Since the dominant term in a_{si} is k_{ie}/s, as shown below in Eq. (4.45), and $\langle g_i|k_ik_j|g_i\rangle \approx \langle g_i|k_ik_j|g_j\rangle\langle g_j|g_i\rangle k_{ie}^{-1} \times \langle g_i|k_i|g_i\rangle \approx k_{ie}k_{je}$, we expect the quantity $(s^2 a_{s1}a_{s2} - \langle g_1|k_1k_2|g_1\rangle\langle g_2|k_1k_2|g_2\rangle/k_{1e}k_{2e})$ in the denominator of Eq. (4.33) to be small and negligible compared with $s^2(1+a_{s1}+a_{s2})$. Therefore, Eq. (4.33) can be approximated as

$$Q_1(s) \approx 1/s - [k_{1e} - a_{s2}(sa_{s1} - k_{1e})]/ [s^2(1+a_{s1}+a_{s2})], \tag{4.34a}$$

$$Q_2(s) \approx [k_{1e} - (k_{1e}s^{-1})(sa_{s2} - k_{2e})]/ [s^2(1+a_{s1}+a_{s2})], \tag{4.34b}$$

When the reverse reaction is neglected, $Q_1(s)$ in Eq. (4.34a) is identical to Eq. (4.25b). These equations obey the self-consistency condition $Q_1(s) + Q_2(s) = 1/s$ when the factors of the form $(sa_{si} - k_{ie})$ appearing in these equations are neglected, i.e., set equal to zero. They are indeed zero to leading order in the expansions of a_{si} in $(s+\epsilon_n)^{-1}$ and in the four limiting cases discussed below. Hence we arrive at the self-consistent approximations

$$Q_1(s) = 1/s - Q_2(s), \tag{4.35a}$$

$$Q_2(s) = k_{1e}/[s^2(1-a_{s1}+a_{s2})]. \tag{4.35b}$$

This is our approximate general solution for the reversible case and is the main result of this section. The problem now reduces to the calculation of a_{s1} and a_{s2} from the properties of the operators $\hat{H}_i$ and $\hat{k}_i$ and the inversion of the Laplace transforms $\hat{Q}_1(s)$ and $\hat{Q}_2(s)$. From the argument leading to a_{s1} it follows, mutatis mutandis, that

$$a_{si}(s) = k_{ie}^{-1} \sum_{n=0} (s+\epsilon_n)^{-1} \langle u_{n,i}|k_i|g_i\rangle^2 \quad i = 1,2. \tag{4.36}$$

This spectral decomposition of $a_{si}(s)$ is related to the Green's functions introduced in Sec. III. The inverse Laplace transform can be evaluated in closed form and is given by the integrand in Eq. (A10) of the Appendix.

The resemblance of Eq. (4.35) to Eqs. (3.13) and (3.27) of the previous section is very striking. In the *slow reaction limit* the thermal equilibrium distribution of the polarization coordinate is maintained. For the diffusion process alone, this corresponds to "large" $t \gg \tau_L$, or small s. In this case, Eqs. (4.36) and (A10) give $a_{si} \approx k_{ie}/s$ and Eq. (4.35) then leads to Eq. (3.13). In the *nondiffusion limit* $k_i(x) \gg \tau_L^{-1}$, which is proportional to the eigenvalues of H_i [see Eq. (4.5)]. Diffusion along the reaction coordinate may then be neglected and the operator $(s+H_i)^{-1} \approx s^{-1}$. From Eq. (4.29), $a_{si} \approx k_{ie}^{-1}\langle g_i|k_i^2|g_i\rangle/s. \approx k_i(x)/s$ since $k_i(x)$ is independent of the diffusion in this limit. This can also be derived from Eq. (4.28) by letting $H_i = 0$. Substituting these into Eq. (4.35) and taking the inverse Laplace transform we have $Q_1(t) = 1 - Q_2(t)$ and

$$Q_2(t) = \int P_1(x,0)\left\{\frac{k_1(x)}{k_1(x)+k_2(x)} \times [1 - e^{-[k_1(x)+k_2(x)]t}]\right\}dx, \tag{4.37}$$

which is essentially identical to Eq. (3.19). In the *wide reaction window limit* $\lambda_q \gg \lambda_0$, $A \approx 0$ [see Eq. (A11)], $k_i(x)$ can be approximated as a constant k_i, and Eq. (4.29) or Eq. (A10) gives $a_{si} \approx k_i/s$. Equation (4.35) then leads to Eq. (3.13) with the rate constants k_i shown in Eq. (3.54). In the *narrow reaction window limit*, $k_1(x) = k_2(x) = k_0\delta(x - x_c)$, $A = \lambda_0/\lambda = 1$ and Eq. (3.20) applies. It follows that

$$k_{1e} = k_0\langle g_1(x_c)|g_1(x_c)\rangle = k_0(2\pi k_B T)^{-1/2}\exp(-\beta x_c^2/2), \tag{4.38a}$$

$$k_{2e} = k_0\langle g_2(x_c - x_0)|g_2(x_c - x_0)\rangle = k_0(2\pi k_B T)^{-1/2}\exp[-\beta(x_c - x_0)^2/2]. \tag{4.38b}$$

From Eq. (4.36) we have

$$a_{si}(s) = k_{ie}^{-1}k_o \sum_{n=0} (s+\epsilon_n)^{-1} \times \langle u_{n,i}(x_c)|g_i(x_c)\rangle^2 \quad i = 1,2, \tag{4.39}$$

which, following the discussion in the Appendix, can also be written in the form

$$a_{s1}(s) = \frac{k_0}{\sqrt{2\pi k_B T}} \int_0^\infty e^{-st}(1 - e^{-2t/\tau_L})^{-1/2} \times \exp\left[-\frac{\beta x_c^2}{2}\left(\frac{1 - e^{-t/\tau_L}}{1 + e^{-t/\tau_L}}\right)\right]dt, \tag{4.40a}$$

$$a_{s2}(s) = \frac{k_0}{\sqrt{2\pi k_B T}} \int_0^\infty e^{-st}(1 - e^{-2t/\tau_L})^{-1/2} \times \exp\left[-\frac{\beta(x_c - x_0)^2}{2}\left(\frac{1 - e^{-t/\tau_L}}{1 + e^{-t/\tau_L}}\right)\right]dt, \tag{4.40b}$$

which are exactly the Green functions $k_0G_1(x_c|x_c,s)$ and $k_0G_2(x_c - x_0|x_c - x_0,s)$ appearing in Eq. (3.27). In this case Eq. (4.35) is identical to Eq. (3.27).

Our general solutions also allow us to go beyond these limiting cases. For instance, in the same spirit as our analysis in Sec. III we can consider an interpolation between the long and short time limits.

A. Single exponential time dependence

When $t \gg \tau_L, a_{si}(s) \approx k_{ie}/s (i = 1,2)$ but when $t \ll \tau_L$, $\exp(-t/\tau_L) \approx 1 - t/\tau_L$, and it follows from Eq. (A10) that

$$a_{s1}(s) \approx \alpha_1 \tau_L / |x_{1c}|, \tag{4.41a}$$

$$a_{s2}(s) \approx \alpha_2 \tau_L / |x_{2c} - x_0|, \tag{4.41b}$$

where

$$\alpha_i = \nu_q [\pi \lambda_q (1+A)/(\beta \lambda A^4)]^{1/2} \times \exp[y_i (1-A)/(1+A)][1 - \Phi(y_i)] \quad i = 1,2 \tag{4.42}$$

in which $A = \lambda_0 / \lambda$,

$$y_1 = \beta(1-A) x_{1c}^2 / 4, \tag{4.43a}$$

$$y_2 = \beta(1-A)(x_{2c} - x_0)^2 / 4, \tag{4.43b}$$

and $\Phi(y_i)$ is the error function defined by

$$\Phi(y) = \mathrm{erf}(y) = (2/\pi^{1/2}) \int_0^y \exp(-t^2) dt. \tag{4.44}$$

Interpolating between these limits we write

$$a_{s1}(s) \approx k_{1e}/s + \alpha_1 \tau_L / |x_{1c}|, \tag{4.45a}$$

$$a_{s2}(s) \approx k_{2e}/s + \alpha_2 \tau_L / |x_{2c} - x_0|, \tag{4.45b}$$

and on substitution in Eq. (4.35) we find $Q_1(s) = 1/s - Q_2(s)$ and

$$Q_2(s) \approx (k_{1e}/\alpha)/[s(s + k_{1e}/\alpha + k_{2e}/\alpha)], \tag{4.46}$$

where

$$\alpha = 1 + \alpha_1 \tau_L / |x_{1c}| + \alpha_2 \tau_L / |x_{2c} - x_0|. \tag{4.47}$$

Taking the inverse Laplace transform of Eq. (4.47), $Q_1(t) = 1 - Q_2(t)$ with

$$Q_2(t) = [k_{1e}/(k_{1e} + k_{2e})]\{1 - \exp[-(k_1 + k_2)t]\} \tag{4.48}$$

which show a single exponential time dependence with the overall rate constants given by

$$k_i = k_{ie}/\alpha = k_{ie}/[1 + \alpha_1 \tau_L / |x_{1c}| + \alpha_2 \tau_L / |x_{2c} - x_0|] \quad i = 1,2. \tag{4.49}$$

This expression covers the different limiting cases and conforms to the principle of chemical equilibrium which requires that $k_1/k_2 = K = \exp(-\beta \Delta G^0)$. We expect that this interpolation will have wider applications.

B. Multiexponential time dependence

This is found when one includes higher terms in the series expansion of Eq. (4.36). If we take a two term approximation of $a_{si}(s)$, $Q_1(t)$ displays a double exponential decay with time from which the general pattern is clear. Taking into the first two terms of Eq. (4.36) we have

$$a_{s1}(s) \approx k_{1e} s^{-1} + (s + \tau_L^{-1})^{-1} k_{1e} \beta A^2 x_{1c}^2, \tag{4.50a}$$

$$a_{s2}(s) \approx k_{2e} s^{-1} + (s + \tau_L^{-1})^{-1} k_{2e} \beta A^2 (x_{2c} - x_0)^2 ..., \tag{4.50b}$$

where we have made use of the fact that $\langle u_{1,1} | k_1 | g_1 \rangle^2 = k_{1e}^2 \beta A^2 x_{1c}^2$ and $\langle u_{1,2} | k_2 | g_2 \rangle^2 = k_{2e}^2 \beta A^2 (x_{2c} - x_0)^2$. Substituting in Eq. (4.35), $Q_1(s) = 1/s - Q_2(s)$

$$Q_2(s) \approx k_{1e}(s + \tau_L^{-1}) / \{s[s^2 + sB + (k_{1e} + k_{2e})\tau_L^{-1}]\}, \tag{4.51}$$

where

$$B = \tau_L^{-1} + k_{1e} + k_{2e} + \beta A^2 [k_{1e} x_{1c}^2 + k_{2e}(x_{2c} - x_0)^2]. \tag{4.52}$$

The denominator of Eq. (4.51b) is a polynomial of order three; using the familiar partial fraction decomposition and taking the inverse Laplace transform we find $Q_1(t) = 1 - Q_2(t)$ and

$$Q_2(t) \approx k_{1e}/(k_{1e} + k_{2e}) + C^+ \exp(-\kappa^+ t) + C^- \exp(-\kappa^- t), \tag{4.53}$$

where

$$C^{\pm} = \pm k_{1e}[1 + (\tau_L \kappa^{\pm})^{-1}] / [B^2 - 4\tau_L^{-1}(k_{1e} + k_{2e})]^{1/2} \tag{4.54}$$

and $-\kappa^{\pm}$ are the roots of the second order polynomial in the denominator of Eq. (4.51) given by

$$-2\kappa^{\pm} = -B \pm [B^2 - 4\tau_L^{-1}(k_{1e} + k_{2e})]^{1/2}. \tag{4.55}$$

It can be verified that when $t = 0$, $Q_2(t) = 0$, and that as $t \to \infty$, $Q_2(t) \to k_{1e}/(k_{1e} + k_{2e})$ which is its equilibrium value. If instead of two, we used the first n terms the expansion of $a_{si}(s)$, the form of $Q_2(t)$ will be

$$Q_2(t) \approx k_{1e}/(k_{1e} + k_{2e}) + \Sigma_i C_i \exp(-\kappa_i t), \tag{4.56}$$

where $-\kappa_i$ are the roots of an nth order polynomial. The addition of more terms thus leads to multiexponential decays which are attentuated by the eigenvalues $\epsilon_n = n/\tau_L$ of the operator H_i. This type of multiexponential behavior has also been discussed earlier.[19]

V. NUMERICAL SOLUTION OF THE DIFFUSION–REACTION EQUATIONS

In the last section we have discussed the analytic solution for several approximations to the reaction–diffusion equations and various limiting cases were derived in Sec. III. Here we compare these with the numerical solutions to the same equations. To do so Eqs. (3.1) and (3.2) are written as

$$\partial P_1/\partial t' = \partial^2 P_1/\partial z^2 + z \partial P_1/\partial z + P_1 - k_1 \tau_L P_1 + k_2 \tau_L P_2, \tag{5.1a}$$

$$\partial P_2/\partial t' = \partial^2 P_2/\partial z^2 + (z - z_0) \partial P_1/\partial z + P_2 - k_2 \tau_L P_2 + k_1 \tau_L P_1, \tag{5.1b}$$

where $P_1 = P_1(z,t)$, $P_2 = P_2(z,t)$, $t' = t/\tau_L$, $z = x\beta^{1/2}$ and $z_0 = (2\beta\lambda_0)^{1/2}$. The rate constants are now rewritten as

$$k_1(z) = \nu_q' \exp[-(z - z_{1c})^2], \tag{5.2}$$

$$k_2(z) = \nu_q' \exp[-(z - z_{2c})^2], \tag{5.3}$$

with $v_q' = v_q/\beta^{1/2}$ and $z_{ic} = x_{ic}\beta^{1/2}$ for $i = 1,2$ where x_{ic} is defined in Eq. (2.10). The differential equations (5.1) are then transformed into the following difference equations:

$$\begin{aligned} P_1(m,n+1) &= b_1 P_1(m,n) + r[P_1(m+1,n) \\ &\quad + P_1(m-1,n)] + hrz_m[P_1(m+1,n) \\ &\quad - P_1(m,n)] + \tau\tau_L k_2 P_2(m,n), \qquad (5.4\text{a}) \\ P_2(m,n+1) &= b_2 P_2(m,n) + r[P_2(m+1,n) \\ &\quad + P_2(m-1,n)] + hr(z_m - z_o) \\ &\quad \times [P_2(m+1,n) - P_2(m,n)] \\ &\quad + \tau\tau_L k_1 P_1(m,n), \qquad (5.4\text{b}) \end{aligned}$$

where the discrete quantities m and n represent the continuous variables z and t', respectively, $\tau = t'_{n+1} - t'_n$ is the time step, $h = z_{m+1} - z_m$ is the spacing of the grid, $r = \tau/h^2, b_1 = 1 - 2r + \tau(1 - \tau_L k_1)$ and $b_2 = 1 - 2r + \tau(1 - \tau_L k_2)$.

The solution of Eqs. (5.4) requires the initial distributions which are assumed to be the thermal equilibrium distribution for $P_1(z,0)$ and zero for $P_2(z,0)$. The boundary conditions are $P_1(-\infty,t) = P_1(\infty,t) = 0$ and $P_2(-\infty,t) = P_2(\infty,t) = 0$. Physically this means the probability of observing the system at infinitely large values of x is zero both for reactants and products. For a given initial distribution of $P_1(z,0)$ and $P_2(z,0)$, the probabilities $P_i(z,t)$ at different time steps are calculated from Eq. (5.4) and then averaged over z to get the survival probabilities $Q_i(t)$. The results are presented in Figs. 1–4, where the full lines represent the numerical results. The curves with crosses are calculated from the double exponential approximation Eq. (4.53) and those with black circles and squares are determined from the interpolation formula Eq. (4.49) and the nondiffusion limit given in Eq. (4.37).

In Figs. 1 and 2, the parameters are chosen as $\beta\Delta G^0 = -1$, $k_0 = 1/ps$, $\lambda_0 = 2.5$, $\lambda_q/\lambda_0 = 1$ but the longitudinal relaxation time τ_L is allowed to vary between small values characteristic of the slow reaction limit and large values typical of the nondiffusion limit. It is seen that the interpolation formula Eq. (4.48) gives a good agreement with the numerical results near the slow reaction limit where it merges with double exponential approximation. As τ_L is increased the multiexponential character of the decay emerges and the double exponential approximation gives better agreement. For higher values of τ_L more terms need to be considered in the multiexponential decay expression to obtain better agreement with experiment. At the largest value of $\tau_L = 1000$ ps the numerical results essentially coincide with the nondiffusion limit given in Eq. (4.37).

In Figs. 3 and 4, $\tau_L = 10$ ps and the other parameters are the same except for λ_q/λ_0 which is changed between values typical of the narrow window limit and the wide window limit. In the wide window limit, the interpolation formula Eq. (4.49) agrees with the numerical results and merges with the double exponential approximation. As λ_q becomes smaller, the double exponential approximation gives a better description than the interpolation formula. Further decrease in λ_q leads to progressive deterioration of the double exponential approximation. Finally when the narrow window limit is reached the double exponential approximation fails completely and the interpolation formula leads again to a good agreement at short times.

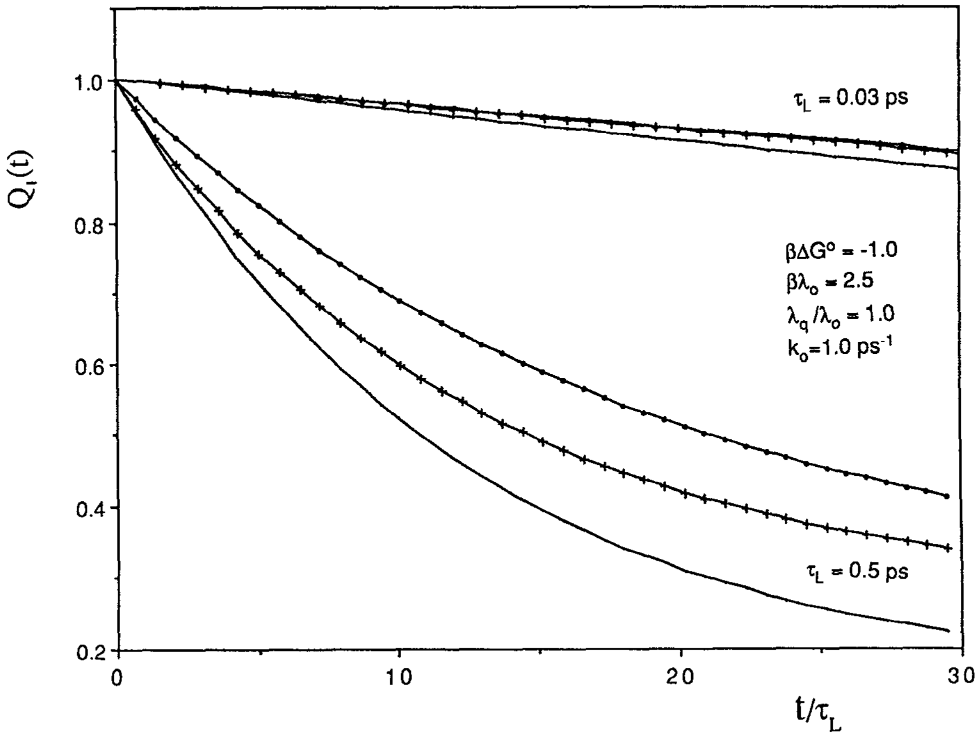

FIG. 1. Plot of the survival probability $Q_1(t)$ vs time t with $\tau_L = 0.03$ ps and 0.5 ps. The other parameters are $\beta\Delta G^0 = -1.0$, $\beta\lambda_0 = 2.5$, $\lambda_q/\lambda_0 = 1.0$, and $k_0 = 1.0\ \text{ps}^{-1}$. The full lines (—) represent the numerical results and the lines with dots (-●-) and crosses (-+-) represent the results calculated from interpolation formula Eq. (4.48) and double exponential approximation Eq. (4.53), respectively, using $Q_1(t) = 1 - Q_2(t)$.

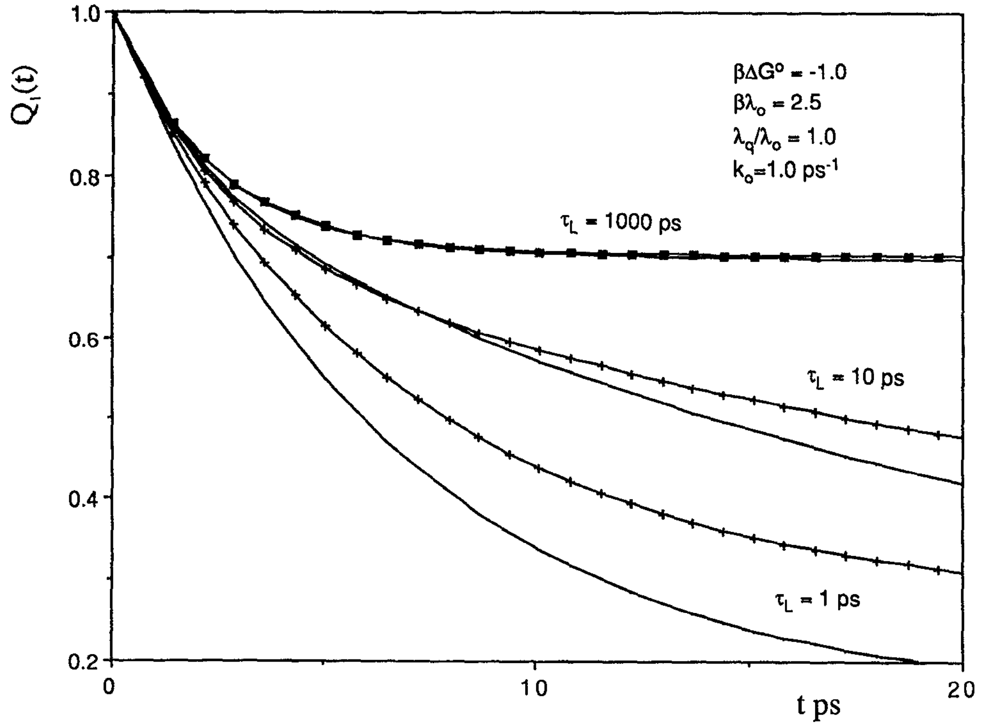

FIG. 2. Plot of the survival probability $Q_1(t)$ vs time t with $\tau_L = 1$, 10, and 1000 ps. The line with squares (-■-) represents the results calculated from the nondiffusion limit Eq. (4.37) and $Q_1(t) = 1 - Q_2(t)$. The other parameters are the same as for Fig. 1.

VI. DISCUSSION

We have discussed in considerable detail the dynamics of reversible electron transfer reactions in a Debye solvent in which the intramolecular and solvent reorganization energies play a role in bringing the reactants to the activated state. The motion of the reactants and products along the reaction coordinate is described by a pair of coupled diffusion–reaction equations which can be solved in four limiting cases as discussed in Sec. III. An approximate general solution to these equations, derived in Sec. IV, also describes the four limiting cases and predicts the behavior between these limits. These predictions are compared in Sec. V to numerical solutions of the coupled differential equations and are found to be useful and often quite accurate. When the time dependence of the survival probabilities are single exponen-

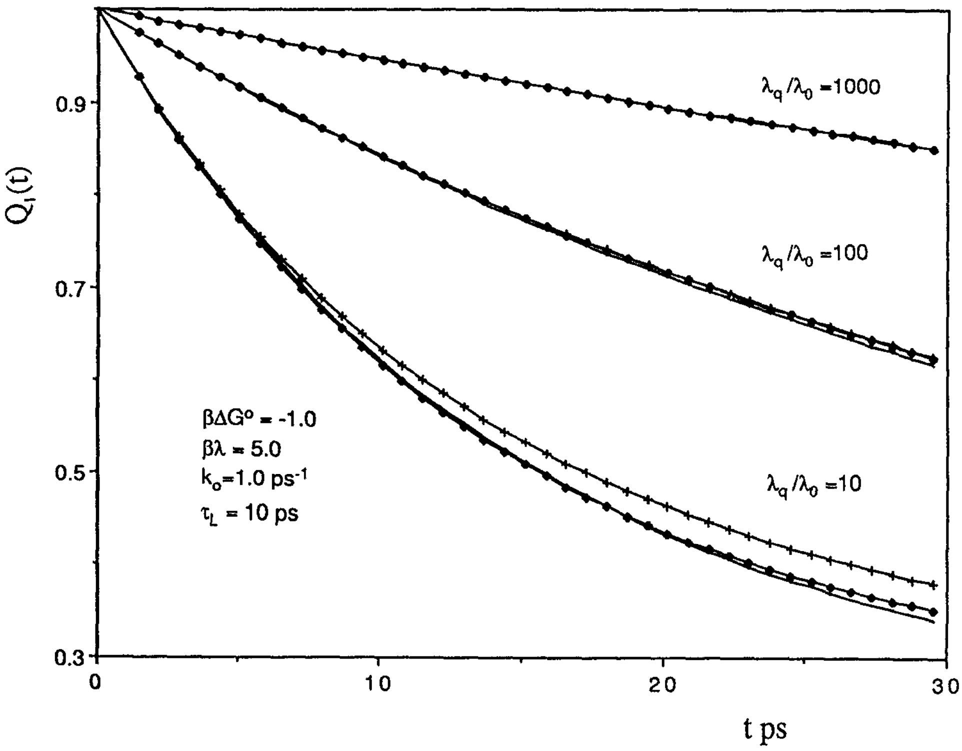

FIG. 3. Plot of the survival probability $Q_1(t)$ vs time t with $\lambda_q/\lambda_0 = 10$, 100, and 1000. The other parameters are $\beta\Delta G^0 = -1.0$, $\beta\lambda = 5.0$, $\tau_L = 10$ ps and $k_0 = 1.0$ ps^{-1}. See the caption of Fig. 1 for other details.

tials, the corresponding rate constants satisfy the equilibrium requirement that $k_1/k_2 = \exp(-\beta\Delta G_0)$; this also serves as a check on our analysis. The Green's functions arising in the narrow window limit (Sec. III) are precisely the $a_{si}(s)$ functions which appear in our general solutions.

Our general solution Eqs. (4.35) predicts that the time dependence of the survival probabilities is usually multiexponential [see Eq. (4.56)] but the lowest order approximation for the Laplace transform functions a_{si} $(i = 1,2)$ appearing in this equation leads to a single exponential dynamics at sufficiently long times. In the Sumi–Marcus model discussed here, the potential energy surface for the diffusion process is parabolic, and the eigenvalues of the diffusion operator are $\epsilon_n = n\tau_L^{-1}$ [see Eq. (4.5)] where τ_L is the longitudinal relaxation time of the solvent. When diffusion along the reaction coordinate is relatively fast, the interval between the eigenvalues is large, and one or two terms in the expansion of a_{si} may be adequate. This will lead to single or double exponential time dependence of the survival probabilities. In the long time limit, which corresponds to small s, the first term in a_{si} becomes dominant, in which case single exponential dynamics is expected (see Figs. 1 and 3). If the diffusion process is not so fast, the eigenvalues ϵ_n are packed closer to each other and the higher order terms in the expansion of a_{si} have to be taken into account; in this case multiexponential dynamics would prevail as illustrated in Figs. 1–4. The higher eigenvalues correspond to regions near the top of the barrier and are more important in determining the transient dynamics at short times. In these regions we expect tunneling, which has not been explicitly considered in this study, to play a more important role. The lower eigenvalues regulate the behavior of the survival probabilities at long times when single exponential behavior eventually prevails.

In both the slow and wide reaction window limits, the single exponential time dependence is determined by a combined rate constant $k_1 + k_2$, which is independent of the solvent longitudinal relaxation time τ_L. Between these two limits there are regions in which the relaxation of the solvent plays an important role.[26] The interpolation formula given in Eq. (4.49) shows that the rate constants depend on τ_L and the intramolecular and solvent reorganization energies λ_q and λ_o, respectively, as well as the free energy for the reaction ΔG^0. It follows from Eq. (4.49) that when τ_L is small, i.e., in the slow reaction limit, $k_i \rightarrow k_{ie}$ which is independent of τ_L. When λ_q is very large $(\lambda_q \gg \lambda_0)$ and τ_L is finite, α_i defined in Eq. (4.42) tends to zero and the interpolation formula leads to the wide reaction window limit. At and near both these limits, the single exponential interpolation formula gives good agreement with the numerical results (see Figs. 1 and 3). If λ_q is very small $(\lambda_q \ll \lambda_0)$ and τ_L is finite, $A = 1$, $\alpha_i \rightarrow \nu_q [2\pi\lambda_q/(\beta\lambda)]^{1/2} \rightarrow k_0$, and Eq. (4.49) for the rate constants reduces to Eq. (3.30) which characterizes the narrow window limit. If the strength of the delta function k_o is set equal to $2\pi J^2$, we regain Zusman's[13(a)] single exponential interpolation formula from Eqs. (3.30). In spite of the fact that multiexponential decay is expected in this limit, Fig. 4 shows that the interpolation approximation also gives fair agreement. Thus, although the reaction dynamics generally depends on the solvent dynamics and the height of the reaction barrier, one or the other factor is dominant in different cases.

In the narrow reaction window limit, it follows from

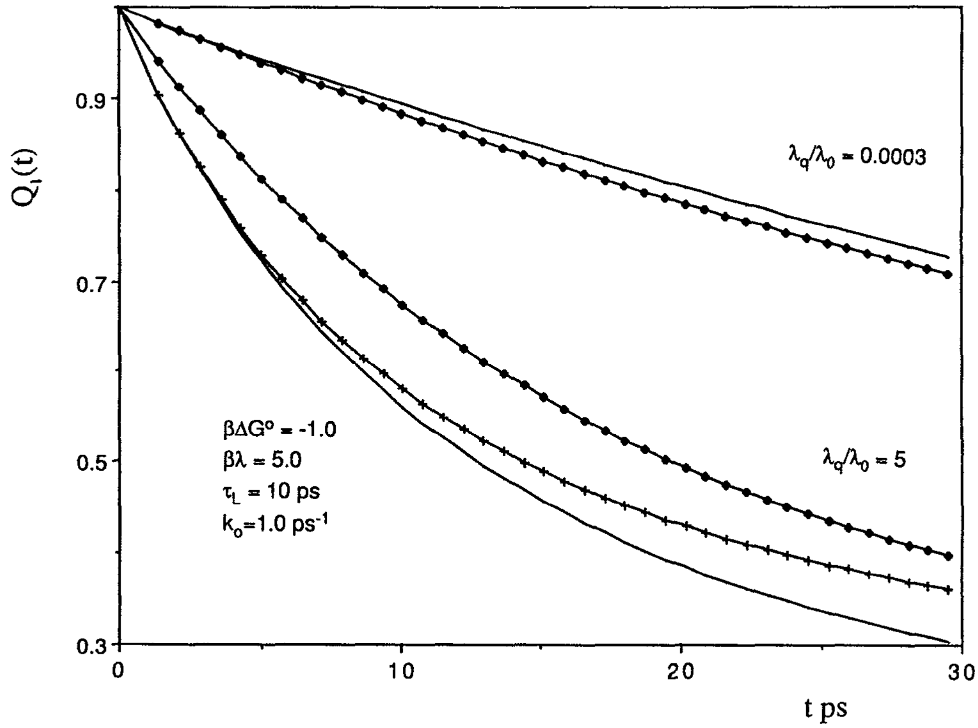

FIG. 4. Plot of the survival probability $Q_1(t)$ vs time t with $\lambda_q/\lambda_0 = 5$ and 0.0003. The other parameters are the same as Fig. 3. See the caption of Fig. 1 for other details.

Eqs. (3.39) and (3.40) that multiexponential time dependence of the survival probabilities is expected when the activation energies for both the forward and reverse reaction are negligible, i.e., the reactions are barrierless. At times fairly long compared with τ_L, a single exponential can be extracted; assuming $k_0\tau_L \gg 1$ in Eq. (3.47), a symmetrical rate constant ($k_1 = k_2$) of $0.833\tau_L^{-1}$ is obtained. At short times, the decay would be faster and we expect the rate constant to be larger ($\approx\tau_L^{-1}$). Therefore the rate is totally controlled by the solvent dynamics in this situation. Even though this case is expected to be rare, we anticipate that this could occur in charge transfer reactions in nonpolar solvents.

With the introduction of the reverse reaction in this paper, we have also been able to consider the case where the forward reaction is barrierless but the reverse reaction has a large barrier. The time dependence of the survival probabilities is again generally multiexponential but a single exponential decay can be derived at long times with the rate constants given by Eqs. (3.52) and (3.53). When the barrier for the reverse reaction is infinitely high (i.e., $\Delta G_2^* = \infty$), $k_2 = 0$ and $k_1 \approx (0.6\tau_L)^{-1}$, which is close to the mean first passage time calculation of Sumi and Marcus[18] for a nonreversible reaction. But with a finite barrier for the reverse reaction, $\beta\Delta G_2^*$ is estimated[1(c),12(c)] in intramolecular electron transfer reactions to lie in the range 5π to 16π, and Eqs. (3.52) and (3.53) predict that k_2 is small but k_1 lies between $0.96\tau_L^{-1}$ and $1.176\tau_L^{-1}$. This explains the experimental facts fairly well. Although there are three dielectric relaxation times in alkanol solvents, the longest one, which is ascribed to the breaking of hydrogen bonds followed by reorientation of the molecules, is used in Refs. 15 and 16 to calculate τ_L which is roughly equal to the fluorescence life time in the excited state for charge transfer reactions (DMAB) in alkanol ($k \approx \tau_L^{-1}$). Another group has reported $(k_1 + k_2) \approx 2\tau_L^{-1}$ in propanol.[22] These intramolecular charge transfer process are usually considered to be a barrierless reactions.[1,12,20]

Finally we make a few comments on how to extend the present results to non-Debye solvents. The Fokker–Planck equation corresponds to the Langevin equation with a frequency independent friction which models electron transfer in a Debye solvent for which the Laplace transform of τ_L is frequency independent. For a non-Debye solvent the dynamics of the reaction coordinate will obey the generalized Langevin equation and the Fokker–Planck operator appearing in the present paper has to be replaced by a generalized one.[5(a)] If the potential well is still parabolic, the probability distribution corresponding to the generalized Fokker–Planck operator is still Gaussian[5(a)] as given in Eq. (3.26) except that the time dependent factor $\exp(-t/\tau_L)$ has to be replaced by the time correlation function of the reaction coordinate $\Delta(t) = \langle x(t)x(0)\rangle/\langle x(0)^2\rangle$.[5(a),24(a)] In the overdamped limit the Laplace transform[5(a)] of this time correlation function is

$$\Delta(s) = [s + \tau_L^{-1}(s)]^{-1}. \tag{6.1}$$

For the Debye solvent, $\tau_L(s) = \tau_L$ is a constant, and Eq. (6.1) leads to $\Delta(t) = \exp(-t/\tau_L)$. For a non-Debye solvent, Hynes[5(a)] and Fonseca[24(a)] have considered the case where $\Delta(t)$ is the sum of the exponentials each with its own relaxation time. Using this argument to extend our general results for electron transfer reactions characterized by two reaction coordinates (vibration and solvent polarization) to non-Debye solvents, we need to replace the factor $\exp(-t/\tau_L)$ in the $a_{si}(t)$ of Eq. (4.35) by the time correlation function $\Delta(t)$ of the reaction coordinate. The details will be discussed elsewhere.[27]

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APPENDIX A: CALCULATION OF $a_{si}(s)$

The general solutions for the Laplace transforms of the survival probabilities given in Eqs. (4.35) depend on $a_{si}(s)$, which are defined in Eqs. (4.29), and we discuss its calculation in this Appendix. An expansion of $a_{si}(s)$ in terms of the eigenvalues ϵ_n and eigenfunctions $|u_{ni}\rangle$ of the operator H_i is given in Eq. (4.36). The operator H_i, defined by Eq. (4.4), has no zero point energy but is similar to the Hamiltonian operator for a harmonic oscillator. The eigenfunctions are

$$|u_{ni}\rangle = (2^n n!)^{-1/2}(2\pi)^{-1/4}\exp(-z_i^2/4) \times H_n(z_i/2^{1/2}) \quad i = 1,2, \tag{A1}$$

where $z_1 = \beta^{1/2}x$, and $z_2 = \beta^{1/2}(x - x_0)$, H_n is the Hermite polynomial. Note that the eigenfunctions depend on the temperature T through $\beta = 1/k_B T$. The k_i which appears in the expansion of a_{si} is given in Eq. (2.21) and the scalar products appearing in the same expansion can be calculated term by term. Generally $a_{s1} \neq a_{s2}$, but for the special case of activationless reactions, $\Delta G_1^* = x_{1c}^2/2 = 0$ and $\Delta G_2^* = (x_{2c} - x_0)^2/2 = 0$, a complete form can be obtained for $i = 1$ or 2. We have

$$\langle u_{ni}|k_i|g_i\rangle = 0, \quad n \text{ odd} \tag{A2}$$

$$\begin{aligned}\langle u_{ni}|k_i|g_i\rangle &= \nu_q(2\pi 2^n n!)^{-1/2}\int \exp[-(1/2+\gamma)z_1^2] \times H_n(z_i/2^{1/2})dz_i \\ &= \nu_q(2\pi 2^n n!)^{-1/2} \times \sum_{k=0}^{n/2}\frac{(-1)^k n!(\sqrt{2})^{n-2k}}{k!(n-2k)!}I_{(n-2k)/2},\end{aligned} \tag{A3}$$

where we have used Eqs. (A1), (2.21) with $k_e = \nu_q(\lambda_i/\lambda)^{1/2}$ and $\gamma_o = \lambda_o/2\lambda_i$. In Eq. (A3), the integral I_n is given by

$$\begin{aligned}I_n &= \int z^{2n}\exp[-(1/2+\gamma_0)z^2]dz \\ &= (\lambda_i/\lambda)^n(2\pi\lambda_i/\lambda)^{1/2}(2n-1)!! \quad n = 0,1,2,3\ldots.\end{aligned} \tag{A4}$$

Substitution of Eq. (A4) into Eq. (A3) leads to

$$\langle u_{ni}|k_i|g_i\rangle = k_e(-1)^{n/2}(\lambda_0/\lambda)^{n/2}(n!)^{-1/2} \times (n-1)!! \quad (n \text{ even}). \tag{A5}$$

It follows from this that, for a barrierless reaction,

$$\begin{aligned} a_{si}(s) &= k_e \sum_{n=0}^{\infty} \frac{(2n)!}{[(2n)!!]^2}\left(\frac{\lambda_o}{\lambda}\right)^{2n}\frac{1}{s+2n/\tau_L} \\ &= k_e f(s). \end{aligned} \tag{A6}$$

This is identical to the expression derived by Sumi and Marcus[18] from the density matrix for the harmonic oscillator when $\lambda_o/\lambda = 1$. Our expression is thus slightly more general than theirs. Note that $f(s)$ in Eq. (A6) is the same $f(s)$ defined in Eq. (3.34) when $\lambda_0/\lambda = 1$ (i.e., $\lambda_i = 0$).

Equations (A5) and (A6) do not apply to reactions in which the barrier is nonzero but, following Sumi and Marcus,[18] a_{si} $(i = 1,2)$ can be calculated from the density matrix for a harmonic oscillator. Taking the inverse Laplace transform of Eq. (4.29) we have

$$\begin{aligned} a_i(t) &= k_{ie}^{-1}\langle g_i k_i|\exp(-H_i(t)|k_i g_i\rangle \\ &= k_{ie}^{-1}\Sigma_n\Sigma_m\langle g_i|k_i|u_{ni}\rangle\langle u_{ni}| \\ &\quad \times \exp(-\epsilon_m t)|u_{mi}\rangle\langle u_{mi}|k_i g_i\rangle \\ &= k_{ie}^{-1}\langle g_i k_i|[\Sigma_n u_{ni}\rangle\exp(-\epsilon_n t)\langle u_{ni}]|k_i g_i\rangle \\ &= k_{ie}^{-1}\int\int g_i(x)k_i(x)\rho_i(x,y,t)k_i(y)g_i(y)dxdy, \end{aligned} \tag{A7}$$

where the density matrix $\rho_i(x,y,t)$ defined by

$$\rho_i(x,y,t) = \Sigma_n u_{ni}(x)u_{ni}(y)\exp(-\epsilon_n t) \tag{A8}$$

corresponds to that of a harmonic oscillator and is well known.[25,18] Since $\epsilon_n = n/\tau_L$ it follows that

$$\begin{aligned} \rho_1(x,y,t) &= [2\pi k_B T](1-e^{-2t/\tau_L})^{-1/2} \\ &\quad \times \exp\left\{-\frac{\beta}{8}[(x+y)^2\tanh(t/2\tau_L) \right. \\ &\quad \left. + (x-y)^2\coth(t/2\tau_L)]\right\} \end{aligned} \tag{A9}$$

and $\rho_2(x,y,t)$ has the same form as $\rho_1(x,y,t)$ except that $(x+y)^2$ has to be replaced by $(x+y-2x_o)^2$ in the argument of the exponential term. Substituting in Eq. (A7), doing the integral and taking Laplace transforms

$$\begin{aligned} a_{s1}(s) &= k_{1e}\int_o^\infty e^{-st}(1-A^2e^{-2t/\tau_L})^{-1/2} \\ &\quad \times \exp\left(\beta x_{1c}^2 \frac{A^2e^{-t/\tau_L}}{1+Ae^{-t/\tau_L}}\right)dt, \end{aligned} \tag{A10a}$$

$$\begin{aligned} a_{s2}(s) &= k_{2e}\int_o^\infty e^{-st}(1-A^2e^{-2t/\tau_L})^{-1/2} \\ &\quad \times \exp\left(\beta(x_{2c}-x_o)^2 \frac{A^2e^{-t/\tau_L}}{1+Ae^{-t/\tau_L}}\right)dt, \end{aligned} \tag{A10b}$$

where k_{ie} and x_{ic} are given in Eqs. (4.30) and (2.20), respectively, and

$$A = \lambda_0/\lambda. \tag{A11}$$

For the barrierless reaction, $x_{1c} = 0$, and $x_{2c} - x_0 = 0$, and Eq. (A6) can be derived from Eqs. (A10). Equation (A10a) has been given earlier by Sumi and Marcus,[18] where in our opinion, A^2 in the numerator of the exponential is misprinted as A. When $A = 1$, $a_{s1}(s)$ and $a_{s2}(s)$ are identical to the Green's functions discussed in Sec. III in connection with the narrow window limit.

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