

Reversible electron transfer dynamics in non-Debye solvents

Jianjun Zhu^{a)} and Jayendran C. Rasaiah
Department of Chemistry, University of Maine, Orono, Maine 04469

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The general solutions obtained earlier [J. Chem. Phys. **95**, 3325 (1991)] for the coupled diffusion-reaction equations describing reversible electron transfer reactions in Debye solvents, governed by Sumi–Marcus free energy surfaces, are extended to non-Debye solvents. These solutions, which depend on the time correlation function of the reaction coordinate $\Delta(t)$, are exact in the narrow and wide window limits for Debye and non-Debye solvents and also in the slow reaction and non-diffusion limits for Debye solvents. The general solution also predicts the behavior between these limits and can be obtained as the solution to an integral equation. An iterative method of solving this equation using an effective relaxation time is discussed. The relationship between $\Delta(t)$ and the time correlation function $S(t)$ of Born solvation energy of the reacting intermediates is elucidated.

I. INTRODUCTION

In a previous study,¹ an approximate general solution was obtained for two coupled diffusion-reaction equations governing reversible electron transfer (ET) reactions in a Debye solvent which are characterized by a single dielectric relaxation time. The solutions for reversible and nonreversible electron transfer reactions in Debye solvents have four limits;^{1,2} the *narrow* and *wide reaction window limits*, as well as the *slow reaction* and *nondiffusion limits*. Solvent dynamics play an important role in these reactions except in the slow reaction and wide window limits, when it can be neglected. In this paper we extend our theoretical analysis of reversible ET reactions to non-Debye solvents which are characterized by multiple dielectric relaxation times.

The free energy surface used in our earlier work was suggested by Sumi and Marcus² and includes contributions from solvent reorganization and ligand vibrations of the reacting species. The model is similar to the one introduced earlier by Kestner, Logan, and Jortner³ who treated the problem quantum mechanically without reference to the solvent dynamics. Sumi and Marcus' original discussion² of ET reactions in Debye solvents ignored the reverse reaction which simplified the mathematical analysis. However, the presence of a finite barrier for the reverse reaction¹ and the existence of multiple relaxation times for the solvent in which the reactions often take place⁴ can have a significant effect on the rates of these reactions. In an earlier paper we addressed the problem of including reversibility in the analysis of ET reactions in Debye solvents; here we consider the analysis the same reactions in non-Debye solvents which exhibit multiple relaxation times. The task of linking solvent relaxation in non-Debye solvents with the kinetics of reversible electron transfer reactions in these solvents is greatly simplified by the existence of a close relationship between the time correlation function $S(t)$ for the free energy of solvation of the reacting intermediates and the time correlation function $\Delta(t)$ of the reaction coordinate for the ET reaction. This is also discussed at length in this paper.

The dynamics of electron transfer reactions have been studied by many workers^{5–12} who considered primarily the contribution of solvent reorganization to the free energy of activation. It is well known that electron transfer dynamics in Debye solvents are governed by the longitudinal relaxation time τ_L .^{4(d)} Quite typically in non-Debye solvents however, the time correlation function $\Delta(t)$ of the reaction coordinate appears instead of e^{-t/τ_L} (where t is the elapsed time) in the expressions for the survival probabilities of the reacting species in ET reactions. This was shown by Hynes^{8(a)} who studied single outer-sphere electron transfer reactions and by Fonseca^{8(b)} who investigated the corresponding reversible reactions. Our analysis however deals with reversible ET reactions described by the Sumi–Marcus free energy surface. This considers ligand vibrational contributions as well as contributions from fluctuations in the solvent polarization to the activation energy of the reacting species. We find that the time correlation function along the reaction coordinate $\Delta(t)$ continues to play a key role in the dynamics of these model reactions and that an approximate solution for the survival probabilities of reactants and products is obtained by the substitution of $\Delta(t)$ for e^{-t/τ_L} in the expressions we have derived previously for the survival probabilities in Debye solvents.¹ We also show that in this model this substitution is exact for non-Debye solvents in the *narrow* and *wide reaction window limits*.

By applying linear response theory to the dynamics of ET reactions in continuum solvents, we find that $\Delta(t)$ is identical to the time correlation function $S(t)$ of the free energy of solvation of the reacting intermediates. This is so even when the solvent displays multiple relaxation times which are typical of non-Debye solvents⁴ and are readily observed and measured in time-dependent fluorescence Stokes (TDFS) shift experiments.^{13–15} This identity provides a useful link between TDFS experiments and the measured rates of electron transfer reactions in the same solvent.

Our paper is organized as follows. The Sumi–Marcus free energy surface, the general reaction diffusion equations and a summary of pertinent results for reversible electron transfer reactions in Debye solvents are given in Sec. II. In Sec. III we discuss the dynamics of the polarization coordinate and in Sec. IV we present our results for reversible ET

^{a)} Present address: Department of Chemistry, Michigan State University, East Lansing, Michigan 48824.

reactions in non-Debye solvents as the solution to an integral equation for the survival probabilities. Methods of solving these integral equations are treated in Sec. V followed by a short discussion in Sec. VI. An Appendix examines the time correlation function $S(t)$ of the Born solvation free energy for the reacting intermediates and its relationship to $\Delta(t)$.

II. FREE ENERGY SURFACES AND SOLUTIONS OF THE DIFFUSION-REACTION EQUATIONS FOR ELECTRON TRANSFER IN DEBYE SOLVENTS

A. Potential surfaces and diffusion-reaction equations

The Sumi-Marcus^{2(a)} free energy surfaces for reactants and products are

$$V_1(q,x) = aq^2/2 + x^2/2, \quad (2.1a)$$

$$V_2(q,x) = a(q - q_0)^2/2 + (x - x_0)^2/2 + \Delta G^0, \quad (2.1b)$$

where q and x are the vibrational and polarization coordinates, respectively, $a = \mu\omega^2$ is assumed to be the same for reactants and products (μ is the reduced mass and ω is the vibrational frequency of the ligand), ΔG^0 is the reaction free energy and the coordinate x is related to the outer solvent polarization $\mathbf{P}^{ex}(\mathbf{r})$ by¹

$$x^2 = (4\pi/c) \int |\mathbf{P}^{ex}(\mathbf{r}) - \mathbf{P}_1^{0,ex}(\mathbf{r})|^2 d\mathbf{r}, \quad (2.2a)$$

where

$$\mathbf{P}^{ex}(\mathbf{r}) = \mathbf{P}(\mathbf{r}) - \mathbf{P}^\infty(\mathbf{r}). \quad (2.2b)$$

$\mathbf{P}(\mathbf{r})$ and $\mathbf{P}^\infty(\mathbf{r})$ are the total polarization and electronic polarization respectively of the solvent, while $\mathbf{P}_1^{0,ex}(\mathbf{r})$ is the equilibrium value of this polarization at \mathbf{r} due to the charge distribution of the reactants. Both $\mathbf{P}^{ex}(\mathbf{r})$ and $\mathbf{P}_1^{0,ex}(\mathbf{r})$ can have contributions from the translation and rotation of the solvent molecules. In Eq. (2.2a),

$$c = 1/\epsilon_\infty - 1/\epsilon_0 \quad (2.3)$$

and $aq_0^2/2$ and $x_0^2/2$ in Eq. (2.1b) are contributions from intramolecular ligand vibration and outer solvent polarization, respectively, to the reorganization energy. The total reorganization energy is the sum of these

$$\lambda = \lambda_0 + \lambda_q, \quad (2.4)$$

with

$$\lambda_0 = x_0^2/2 = (2\pi/c) \int |\mathbf{P}_2^{0,ex}(\mathbf{r}) - \mathbf{P}_1^{0,ex}(\mathbf{r})|^2 d\mathbf{r} \quad (2.5a)$$

$$= (c/8\pi) \int |\mathbf{D}_2^0(\mathbf{r}) - \mathbf{D}_1^0(\mathbf{r})|^2 d\mathbf{r}, \quad (2.5b)$$

$$\lambda_q = aq_0^2/2, \quad (2.6)$$

where $\mathbf{P}_2^{0,ex}(\mathbf{r})$ is the equilibrium polarization at \mathbf{r} due to the charge distribution of the products and the relation

$$\mathbf{P}^{0,ex}(\mathbf{r}) = (c/4\pi)\mathbf{D}^0(\mathbf{r}) \quad (2.7)$$

between the equilibrium polarization $\mathbf{P}^{0,ex}(\mathbf{r})$ and the electric displacement $\mathbf{D}^0(\mathbf{r})$ has been used.

The ligand vibrational motion is much faster than the relaxation of the solvent polarization and electron transfer can take place at each value of x , leading to coordinate dependent rate coefficients¹⁻³

$$k_i(x) = \nu_q \exp[-\beta\Delta G_i^*(x)] \quad (i = 1,2), \quad (2.8)$$

in which

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

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

are the free energies of activation, and

$$x_{1c} = (\lambda + \Delta G^0)/(2\lambda_0)^{1/2}, \quad (2.9c)$$

$$x_{2c} = (\lambda + \Delta G^0 - 2\lambda_q)/(2\lambda_0)^{1/2}. \quad (2.9d)$$

The normalization constant in Eq. (2.8)

$$\nu_q = k_0 [2\pi\lambda_q/(\beta\lambda_0)]^{-1/2}, \quad (2.10)$$

where k_0 is determined by whether the reaction is adiabatic or nonadiabatic.¹ In the *narrow reaction window limit* when $\lambda_q \rightarrow 0$ the vibrational contribution to the reorganization energy is neglected and the rate coefficients are approximated by delta functions¹

$$k(x) = k_1(x) = k_2(x) = k_0\delta(x - x_c), \quad (2.11a)$$

where

$$x_c = (\lambda_0 + \Delta G^0)/(2\lambda_0)^{1/2} \quad (2.11b)$$

is identical to x_{1c} and x_{2c} in this limit.

The time dependence of reversible ET reactions is described by the following coupled diffusion reaction equations:

$$\partial P_1/\partial t = [L_1(t) - k_1(x)]P_1 + k_2(x)P_2, \quad (2.12a)$$

$$\partial P_2/\partial t = [L_2(t) - k_2(x)]P_2 + k_1(x)P_1, \quad (2.12b)$$

where $P_1 = P_1(x,t)$ and $P_2 = P_2(x,t)$ are the probabilities of reactants and products, respectively, $L_1(t)$ and $L_2(t)$ are generalized Fokker-Planck operators defined by

$$L_i = D(t) \frac{\partial^2}{\partial x^2} + \beta D(t) \frac{\partial}{\partial x} \left[\frac{dV_i(x)}{dx} \right] \quad (i = 1,2), \quad (2.13)$$

in which $D(t)$ is a time dependent diffusion coefficient, $\beta = (k_B T)^{-1}$ where k_B is Boltzman constant, T is temperature and $V_i(x)$ is given by the second term of Eq. (2.1), i.e.,

$$V_1(x) = x^2/2, \quad (2.14a)$$

$$V_2(x) = (x - x_0)^2/2 + \Delta G^0. \quad (2.14b)$$

The structure of the diffusion reaction Eqs. (2.12) is striking: the diffusion terms describe the diffusion of the polarization coordinate x , while the reaction terms $k_i(x)$ are rate coefficients averaged over the vibrational coordinate q at a particular x . The reactants are initially considered to be at thermal equilibrium, so that

$$P_1(x,0) = \exp[-\beta V_1(x)] / \int \exp[-\beta V_1(x)] dx, \quad (2.15a)$$

$$P_2(x,0) = 0. \quad (2.15b)$$

The survival probabilities $Q_i(t)$ for the reactants and products are obtained from the solutions of Eq. (2.12) by

$$Q_i(t) = \int_{-\infty}^{\infty} P_i(x,t) dx \quad (i = 1,2). \quad (2.16)$$

B. The solutions in a Debye solvent

In a *Debye solvent*, the diffusion constant is time independent and $D(t) = D$ is related to the longitudinal dielectric relaxation time τ_L by¹⁻³

$$\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D = (\beta D)^{-1}, \quad (2.17)$$

where τ_D is Debye relaxation time, and ϵ_∞ and ϵ_0 are the high frequency and static dielectric constants, respectively. In our previous paper we showed that an approximate but general solution of Eq. (2.12) for a Debye solvent leads to the Laplace transforms of the survival probabilities given by¹

$$Q_1(s) = 1/s - Q_2(s), \quad (2.18a)$$

$$Q_2(s) = k_{1e}/\{s^2[1 + a_{s1}(s) + a_{s2}(s)]\}. \quad (2.18b)$$

Here the Laplace transform $a_{si}(s)$ is defined by

$$a_{si}(s) = k_{ie}^{-1}\langle g_i | k_i(s + H_i)^{-1} k_i | g_i \rangle \quad (i = 1, 2) \quad (2.19a)$$

with

$$k_{ie} = \langle g_i(x) | k_i(x) | g_i(x) \rangle. \quad (2.19b)$$

The operator

$$H_i = -D \frac{\partial^2}{\partial x^2} + \frac{\beta D}{2} \left[\frac{\beta}{2} \left(\frac{dV_i}{dx} \right)^2 - \frac{d^2 V_i}{dx^2} \right] \quad (i = 1, 2) \quad (2.20)$$

is similar to the Hamiltonian operator for a harmonic oscillator with potentials given in Eq. (2.14). The eigenvalues are

$$\epsilon_n = n\tau_L^{-1} \quad (n = 0, 1, 2, \dots) \quad (2.21)$$

and $|u_{n,i}\rangle$ are the eigenkets of H_i with eigenfunctions ϵ_n which implies that $H_i|u_{n,i}\rangle = \epsilon_n|u_{n,i}\rangle$. There is no zero point energy and the lowest order eigenfunction

$$|u_{0,i}\rangle = g_i(x)$$

$$= \exp(-\beta V_i(x)/2) / \int \exp(-\beta V_i(x)/2) dx \quad (2.22)$$

so that $H_i g_i(x) = 0$. Inserting Eq. (2.22) into Eq. (2.19) and making use of Eqs. (2.8)–(2.10) one finds

$$k_{1e} = \nu \exp[-\beta(\lambda + \Delta G^0)^2/4\lambda], \quad (2.23a)$$

$$k_{2e} = k_{1e} \exp[\beta \Delta G^0], \quad (2.23b)$$

where $\nu = \nu_q [\lambda_q/\lambda]^{1/2}$. For a Debye solvent we have shown that¹

$$a_{si}(s) = k_{ie}^{-1} \sum_{n=0}^{\infty} c_{n,i} (s + \epsilon_n)^{-1} \quad (i = 1, 2), \quad (2.24a)$$

where $c_{n,i} = \langle u_{n,i} | k_i | g_i \rangle^2$. The inverse Laplace transform of Eq. (2.24a) is

$$a_i(t) = k_{ie} + k_{ie}^{-1} \sum_{n=1}^{\infty} c_{n,i} \exp(-\epsilon_n t) \quad (i = 1, 2), \quad (2.24b)$$

which can be written in closed form by making use of the density matrix of the Harmonic oscillator,^{1,2}

$$a_1(t) = k_{1e} (1 - A^2 e^{-2t/\tau_L})^{-1/2} \times \exp \left[\beta x_{1c}^2 \frac{A^2 e^{-t/\tau_L}}{1 + A e^{-t/\tau_L}} \right], \quad (2.25a)$$

$$a_2(t) = k_{2e} (1 - A^2 e^{-2t/\tau_L})^{-1/2} \times \exp \left[\beta (x_{2c} - x_0)^2 \frac{A^2 e^{-t/\tau_L}}{1 + A e^{-t/\tau_L}} \right]. \quad (2.25b)$$

Here

$$A = \lambda_0/\lambda \quad (2.26)$$

reflects the size of the reaction window. For example, in the *narrow window limit*, $\lambda_q \ll \lambda_0$ and $A \approx 1$ while in the *wide window limit*, $\lambda_q \gg \lambda_0$, $A \approx 0$. The generalization to non-Debye solvents is discussed in Sec. IV but before that we will review certain limiting cases of importance to our analysis.

Equation (2.18), with $a_i(t)$ displayed in Eq. (2.25) or (2.24), become exact in different limits. In the *slow reaction limit* ($k_i(x) \ll \tau_L$), thermal equilibrium of the polarization coordinate x is always maintained and the time scale in which the reaction takes place is much larger than τ_L . It follows from Eq. (2.2) that $a_i(t) = k_{ie}$ which is equivalent to $a_{si}(s) = k_{ie}/s$. Substituting in Eq. (2.18) and taking the inverse Laplace transform we have

$$Q_1(t) = 1 - Q_2(t), \quad (2.27a)$$

$$Q_2(t) = [k_{1e}/(k_{1e} + k_{2e})] \{1 - \exp[-(k_{1e} + k_{2e})t]\}. \quad (2.27b)$$

In the *wide reaction window limit* ($\lambda_q \gg \lambda_0$), $A = 0$ and $a_{si}(s) = k_i/s$ where k_i has the same form as Eq. (2.23) with $\nu = \nu_q$ and $\lambda = \lambda_q$. The survival probabilities are the same as Eqs. (2.27) with k_i replacing k_{ie} . In the *narrow reaction window limit* ($\lambda_q \ll \lambda_0$), $A = 1$, and Eqs. (2.12) reduce to¹

$$\partial P_1/\partial t = L_1 P_1 - k_0 \delta(x - x_c) (P_1 - P_2), \quad (2.28a)$$

$$\partial P_2/\partial t = L_2 P_2 + k_0 \delta(x - x_c) (P_1 - P_2), \quad (2.28b)$$

where $x_c = (\lambda_0 + \Delta G^0)/(2\lambda_0)^{1/2}$. The Laplace transforms of the survival probabilities are¹

$$Q_1(s) = s^{-1} - Q_2(s), \quad (2.29a)$$

$$Q_2(s) = k_0 P_1(x_c, 0) / \{s^2 [1 + k_0 G_{s1}(x_c | x_c, s) + k_0 G_{s2}(x_c - x_0 | x_c - x_0, s)]\}, \quad (2.29b)$$

where $k_0 G_{s1}(x_c | x_c, s)$ and $k_0 G_{s2}(x_c - x_0 | x_c - x_0, s)$ are precisely the Laplace transforms of $a_1(t)$ and $a_2(t)$, respectively, with $A = 1$. Equations (2.29) are exact but have been solved¹ only in certain approximations or limits. Examples are the long and short time approximations and barrierless reactions.¹ In the *nondiffusion limit* $k_i(x) \gg \tau_L^{-1}$ and the survival probabilities show a multiexponential time dependence which is discussed in detail in Ref. 1.

Away from these limits an interpolation formula between the long and short time limits of $a_i(t)$ leads to an expression which reproduces different types of single exponential time dependences found for the survival probabilities. This expression has the same form as Eq. (2.27) except that k_{ie} is replaced by $k'_i = k_{ie}/\alpha$, where

$$\alpha = 1 + \alpha_1 \tau_L / |x_{1c}| + \alpha_2 \tau_L / |x_{2c} - x_0| \quad (2.30)$$

and α_1 and α_2 are constants.¹ It is seen that $\alpha_1 = \alpha_2 = 0$ in the *slow reaction limit* and $\alpha_1 = \alpha_2 = 1$ in the *narrow reaction window limit*.¹ Multiexponential time dependence of the survival probabilities is found when terms beyond the leading term in the expansion of $a_{si}(s)$ are taken into ac-

count. Explicit expressions for the time dependence of the survival probabilities are given in Ref. 1. Numerical solutions of the reaction-diffusion equations were found to agree satisfactorily with the analytic results.¹

For a non-Debye solvent, the diffusion operators are generally time dependent, and the solution of Eq. (2.12) becomes more involved. We show in Sec. IV that Eq. (2.29) is exact in the narrow reaction window limit ($A = 1$) with $k_0 G_i(x_c | x_c, t) = a_i(t)$ of Eq. (2.25) except that e^{-t/τ_L} is replaced by $\Delta(t)$, the time correlation function of the reaction coordinate. More generally, when $A \neq 1$, we find that Eqs. (2.18) is a useful solution to Eq. (2.12) for non-Debye solvents provided $a_i(t)$ is similarly redefined with $\Delta(t)$ replacing e^{-t/τ_L} in the expressions for $a_i(t)$ given in Eq. (2.25). However, the interpolation formula and other approximations discussed in the previous paragraph can be carried over to non-Debye solvents only if we use an effective relaxation time τ_L^{eff} to characterize $\Delta(t)$. This is discussed in the next section where we investigate the dynamics of the polarization coordinate x .

III. DYNAMICS OF THE POLARIZATION COORDINATE x

Before we consider the solution of Eq. (2.12) for ET in non-Debye solvents, we will first describe the dynamics of the polarization coordinate x when the vibrational coordinate q is neglected. This should help to clarify our argument without the added complication of ligand or inner solvation shell vibration.

During electron transfer of the reacting intermediates, the polarization coordinate x at time t takes on a value

$$x^2(t) = (4\pi/c) \int |\mathbf{P}^{\text{ex}}(\mathbf{r}, t) - \mathbf{P}_1^{0,\text{ex}}(\mathbf{r})|^2 d\mathbf{r}, \quad (3.1)$$

which is an obvious extension of Eq. (2.2). The time dependent polarization $\mathbf{P}^{\text{ex}}(\mathbf{r}, t)$ is linearly related to the "effective" charges $e_i^{\text{eff}}(t)$ on the ions with which it would be in equilibrium and

$$e_i^{\text{eff}}(t) = e_i^* + z(t)(e_i - e_i^*) \quad (i = 1, 2), \quad (3.2)$$

where e_i^* and e_i are the charges on the reactant and products, respectively, and $z(t)$ changes from 0 to 1 as reactants are completely transformed into products. It follows that at any time t ,

$$\mathbf{P}^{\text{ex}}(\mathbf{r}, t) - \mathbf{P}_1^{0,\text{ex}}(\mathbf{r}) = z(t) [\mathbf{P}_2^{0,\text{ex}}(\mathbf{r}) - \mathbf{P}_1^{0,\text{ex}}(\mathbf{r})]. \quad (3.3)$$

Equation (3.3) simply mirrors (Eq. 3.2). Inserting this in Eq. (3.1) and using Eqs. (2.3), (2.5), (2.7), and (2.14a), we see that the potential energy for the reactants is given by

$$V_1 = x^2(t)/2 = \lambda_0 z^2(t), \quad (3.4a)$$

where λ_0 is defined in Eq. (2.5). Likewise for the product potential energy, given in Eq. (2.14b), we have

$$\begin{aligned} V_2 &= (1/2) [x(t) - x_0]^2 + \Delta G^0 \\ &= \lambda_0 [1 - z(t)]^2 + \Delta G^0. \end{aligned} \quad (3.4b)$$

The second of these relations in each of these equations has also been derived by Hynes.^{8(a)}

Linear response theory predicts that the nonequilibrium dielectric polarization $\mathbf{P}^{\text{ex}}(\mathbf{r}, t)$ is related to the displacement field $\mathbf{D}(\mathbf{r}, t)$ by¹⁶

$$\begin{aligned} \mathbf{P}^{\text{ex}}(\mathbf{r}, t) &= (4\pi)^{-1} \int_{-\infty}^t c(t - \tau) \mathbf{D}(\mathbf{r}, t) d\tau \\ &= (4\pi)^{-1} \int_{-\infty}^t c(\tau) \mathbf{D}(\mathbf{r}, t - \tau) d\tau. \end{aligned} \quad (3.5)$$

The response function $c(t)$ has the Laplace transform

$$c(s) = 1/\epsilon_\infty - 1/\epsilon(s), \quad (3.6a)$$

where ϵ_∞ is the high frequency dielectric constant and $\epsilon(s)$ is the frequency dependent dielectric function. If $\mathbf{D}(\mathbf{r}, t - \tau) = \mathbf{D}^0(\mathbf{r})$ for $t > 0$ and is zero for $t < 0$, $\mathbf{P}^{\text{ex}}(\mathbf{r}, t) \rightarrow \mathbf{P}^{\text{ex}}(\mathbf{r})$ as $t \rightarrow \infty$, and Eq. (3.5) reduces to Eq. (2.7). It follows from this that

$$c \equiv 1/\epsilon_\infty - 1/\epsilon = \int_0^\infty c(\tau) d\tau. \quad (3.6b)$$

In a Debye solvent

$$\epsilon(s) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + s\tau_D). \quad (3.7)$$

Inserting this in Eq. (10.1.6a), taking the inverse Laplace transform and recalling the definition of the longitudinal relaxation time $\tau_L = \epsilon_\infty \tau_D / \epsilon_0$ one finds

$$c(t) = (c/\tau_L) \exp(-t/\tau_L), \quad (3.8)$$

which is the response function for a Debye solvent.¹⁶

We now consider a thought experiment, similar to one suggested by Hynes,^{8(a)} in which we start with the reactant charge distribution and let it be transformed instantaneously at $t = 0$ to the product charge distribution. The medium then rearranges by translation and rotation to a new charge distribution. The change in the solvent polarization with time is

$$\begin{aligned} \mathbf{P}^{\text{ex}}(\mathbf{r}, t) - \mathbf{P}_1^{0,\text{ex}}(\mathbf{r}) &= (4\pi)^{-1} \int_0^t c(\tau) d\tau \\ &\quad \times [\mathbf{D}_2^0(\mathbf{r}) - \mathbf{D}_1^0(\mathbf{r})], \end{aligned} \quad (3.9)$$

which on combining with Eq. (3.1) gives

$$x(t) = x_0 c^{-1} \left[\int_0^t c(\tau) d\tau \right], \quad (3.10)$$

where $x_0 = x(\infty) = (2\lambda_0)^{1/2}$. This equation is equivalent to Hynes' Eq. (2.12) for $z(t)$.^{8(a)} The Laplace transform of Eq. (3.10) gives

$$x(s) = x_0 (cs)^{-1} c(s) = x_0 (cs)^{-1} [1/\epsilon_\infty - 1/\epsilon(s)]. \quad (3.11)$$

Defining the deviation $\delta x(t) = x(t) - x_0$, it follows that the normalized time correlation function

$$\Delta(t) = \langle \delta x(t) \delta x(0) \rangle / \langle \delta x^2(0) \rangle \quad (3.12a)$$

$$= - \langle \delta x(t) \rangle / x_0 \quad (3.12b)$$

$$= -c^{-1} \left[\int_0^t c(\tau) d\tau \right] + 1, \quad (3.12c)$$

where we have made use of the fact that $\delta x(0) = -x_0$ and $\delta x^2(0) = x_0^2$.

On taking the Laplace transforms one finds that

$$\delta x(s) = (x_0/s)[c(s)/c - 1] \quad (3.13)$$

and

$$\Delta(s) = (1/s)[1 - c(s)/c] \quad (3.14a)$$

$$= \epsilon_\infty [(\epsilon_0 - \epsilon(s))/(\epsilon_0 - \epsilon_\infty)]/(s\epsilon(s)) \quad (3.14b)$$

$$= \epsilon_\infty [1 - E(s)]/\{s[\epsilon_\infty + E(s)(\epsilon_0 - \epsilon_\infty)]\}, \quad (3.14c)$$

where

$$E(s) = [\epsilon(s) - \epsilon_\infty]/(\epsilon_0 - \epsilon_\infty). \quad (3.15)$$

Equation (3.14c) for the forward reaction which has been derived earlier by Hynes.^{8(a)} If we define the reaction coordinate $x'(t) = x_0 - x(t)$ for the backward reaction, a similar equation can be written for $\delta x'(t)$. For a Debye solvent, it follows from Eqs. (3.7), (3.14), and (3.15) that

$$E(s) = 1/(1 + s\tau_D), \quad (3.16)$$

$$\Delta(s) = [s + \tau_L^{-1}]^{-1} \quad (3.17)$$

or the inverse Laplace transform

$$\Delta(t) = \exp(-t/\tau_L). \quad (3.18)$$

Non-Debye solvents are characterized by a frequency dependent longitudinal dielectric relaxation time, when τ_L^{-1} in Eq. (3.17) is replaced by a "frequency dependent" $\tau_L(s)^{-1}$.

In the Appendix we show that in a continuum solvent, $\Delta(t)$ is identical to the time correlation function $S(t)$ of the Born solvation energy for the reacting species. This provides another source of information on $\Delta(t)$ since there are experimental probes which determine $S(t)$; for example, time-dependent fluorescence Stokes shift measurements (TDFS).¹³⁻¹⁵

The dynamics of the reaction coordinate can be studied using either a Langevin-type equation or a probability diffusion equation. In Sec. II the Fokker-Planck diffusion equation was used to describe the dynamics of the polarization coordinate x in Debye solvents. This is, as discussed below, consistent with the use of the Langevin equation in the overdamped limit. For non-Debye solvents one uses either a generalized Fokker-Planck equation or a generalized Langevin equation. The two approaches are equivalent, but the former provides a natural extension of our previous discussion¹ of reversible electron transfer reactions to non-Debye solvents. Since the polarization coordinate $x(t)$ is related to Hynes' reaction coordinate $z(t)$ through Eq. (3.4), the discussion which follows in this section is similar to his.^{8(a)}

A. Generalized Langevin equation approach

For non-Debye solvents the generalized Langevin equation for $\delta x(t)$ is

$$d^2[\delta x(t)]/dt^2 = -\omega_L^2 \delta x(t) - \int_0^t \zeta(t-\tau) \delta x(\tau) d\tau, \quad (3.19)$$

where $\delta x(t) = d[\delta x(t)]/dt$, $\zeta(t)$ is the frequency dependent friction and ω_L is given by $\omega_L^2 = 1/m_L$, which follows from the harmonic potential given in Eq. (3.4), and m_L is

the reduced mass. On taking the Laplace transform of Eq. (3.19) and using Eq. (3.12a) we have

$$\Delta(s) = \frac{s + \zeta(s)}{s^2 + \omega_L^2 + s\zeta(s)}. \quad (3.20)$$

In the overdamped limit $d^2[\delta x(t)]/dt^2 = 0$ we have, instead of Eqs. (3.20), the relation

$$\Delta(s) = [s + \tau_L^{-1}(s)]^{-1}, \quad (3.21)$$

where the frequency dependent longitudinal dielectric relaxation time $\tau_L(s)$ is defined by⁸ $\tau_L(s) = \zeta(s)/\omega_L^2$. By comparing Eq. (3.21) with Eq. (3.14) one finds that⁸

$$\tau_L(s) = \epsilon_\infty [1 - E(s)]/[s\epsilon_0 E(s)], \quad (3.22)$$

which provides a relation, in the overdamped limit, between the $\tau_L(s)$ and the measured dielectric response function $E(s)$. The relationship between $\Delta(s)$ and $E(s)$ follows from Eq. (3.23). For Debye solvents $E(s)$ is given by Eq. (3.16) and we see that $\tau_L(s) = \epsilon_\infty \tau_D/\epsilon_0 = \tau_L$, which is independent of the frequency. For non-Debye solvents with multiple dielectric relaxation times

$$E(s) = \sum_i f_i (1 + s\tau_i)^{-1}, \quad (3.23)$$

where f_i is a constant, the inverse of Eq. (3.23) becomes more complicated than that of Eq. (3.16). For instance, a double exponential form has been used by Hynes^{8(a)} for $\Delta(t)$ in *n*-propyl alcohol to reproduce the dielectric relaxation data.

B. The Fokker-Planck equation approach

For a non-Debye solvent, the generalized diffusion equations with no reaction are

$$\partial P_i(x,t)/\partial t = L_i(t)P_i(x,t) \quad (i=1,2), \quad (3.24)$$

where the generalized Fokker-Planck operator $L_i(t)$ is given in Eq. (2.9). The solutions of Eq. (3.24) for parabolic potential wells are well known⁸ and are

$$P_1(x,t) = [2\pi k_B T(1 - \Delta^2)]^{-1/2} \times \exp\left[-\frac{\beta(x - x(0)\Delta)^2}{2(1 - \Delta^2)}\right], \quad (3.25a)$$

$$P_2(x,t) = [2\pi k_B T(1 - \Delta^2)]^{-1/2} \times \exp\left\{-\frac{\beta[(x - x_0) - (x(0) - x_0)\Delta]^2}{2(1 - \Delta^2)}\right\}, \quad (3.25b)$$

where $x(0)$ is the initial value of x , and $\Delta = \Delta(t)$ is related to the diffusion constant by

$$D(t) = -\beta^{-1}d[\ln \Delta(t)]/dt. \quad (3.26)$$

This solution is easily verified by direct substitution.^{8(a)} For a Debye solvent $\Delta(t)$ is given, in the overdamped limit, by Eq. (3.18) and we have

$$D(t) = D = (\beta\tau_L)^{-1}, \quad (3.27)$$

which is independent of time and is just the result given in Eq. (2.17). This implies that the solutions given in reference 1 for ET reactions in Debye solvents using Fokker-Planck operators with a constant diffusion coefficient D are consis-

tent with the simple Langevin equation in the overdamped limit.

IV. SOLUTIONS OF THE GENERALIZED DIFFUSION-REACTION EQUATIONS FOR REVERSIBLE ET REACTIONS IN NON-DEBYE SOLVENTS

For non-Debye solvents, we need to solve Eq. (2.12) together with the initial conditions Eqs. (2.15). Since the diffusion coefficient D and the longitudinal relaxation time τ_L are now frequency dependent, the slow diffusion and slow reaction limits are not clearly defined unless we can identify an effective D and τ_L , but the narrow and wide reaction window limits still hold. We will first discuss the exact solutions in these two limits before considering the solutions for the general case.

A. Solutions in the wide and narrow window limits

In the wide window limit, one can still use the same argument given in Ref. 1 for Debye solvents and the solutions, for the survival probabilities, are single exponentials

$$Q_1(t) = 1 - Q_2(t), \quad (4.1a)$$

$$Q_2(t) = [k_1/(k_1 + k_2)] \{1 - \exp[-(k_1 + k_2)t]\}, \quad (4.1b)$$

with

$$k_1 = \nu_q \exp[-\beta(\lambda_q + \Delta G^0)^2/4\lambda_q], \quad (4.2a)$$

$$k_2 = k_1 \exp[\beta\Delta G^0]. \quad (4.2b)$$

In the *narrow reaction window limit*, Eqs. (2.12) reduce to¹

$$\partial P_1/\partial t = L_1(t)P_1 - k_0\delta(x - x_c)(P_1 - P_2), \quad (4.3a)$$

$$\partial P_2/\partial t = L_2(t)P_2 + k_0\delta(x - x_c)(P_1 - P_2), \quad (4.3b)$$

where x_c is given by Eq. (2.11b). The Laplace transforms of the survival probabilities are given by Eq. (2.29) where the Green's functions $G_1(x_c|x_c, s)$ and $G_2(x_c - x_0|x_c - x_0, s)$ are now the Laplace transforms of the solutions to the *generalized* diffusion equations

$$\partial G_1(x|x_c, t)/\partial t = L_1(t)G_1(x|x_c, t), \quad (4.4)$$

$$\partial G_2(x - x_0|x_c - x_0, t) = L_1(t)G_2(x - x_0|x_c - x_0, t), \quad (4.5)$$

with initial conditions $G_1(x|x_c, 0) = \delta(x - x_c)$ and $G_2(x - x_0|x_c - x_0, 0) = \delta[(x - x_0) - (x_c - x_0)]$. The operator $L_1(t)$, which has a time dependent diffusion coefficient $D(t)$, is defined in Eq. (2.13) and the solutions of Eqs. (4.4) and (4.5) are the same as Eq. (3.25) except that $x(0)$ has to be replaced by x_c ,

$$G_1(x_c|x_c, t) = [2\pi k_B T(1 - \Delta^2)]^{-1/2} \times \exp\left[-\frac{\beta x_c^2(1 - \Delta)^2}{2(1 - \Delta^2)}\right], \quad (4.6a)$$

$$G_2(x_c - x_0|x_c - x_0, t) = [2\pi k_B T(1 - \Delta^2)]^{-1/2} \times \exp\left[-\frac{\beta(x_c - x_0)^2(1 - \Delta)^2}{2(1 - \Delta^2)}\right]. \quad (4.6b)$$

Note that $\Delta = \Delta(t)$. These results together with Eqs. (2.29)

are exact for non-Debye solvents. They have been given earlier by Fonseca^{8(b)} but the argument used in its derivation here is exact since we do not replace $L_i(t)$ by an effective time independent operator L_i^{eff} to prove this result, see Ref. 8(b). It is seen that the generalized Green's functions depend on the time correlation function $\Delta(t)$ of the reaction coordinate which was discussed extensively in the preceding section. For Debye solvents the Green's functions reduce to $a_i(t)$, defined in Eq. (2.25), divided by k_0 as discussed in Sec. II.

B. Approximate solutions to the generalized diffusion reaction equations

We now come to our discussion of approximate general solutions of the reaction diffusion equations (2.12) in non-Debye solvents. Because the generalized Fokker-Planck operators are time dependent, the Laplace transform technique used in Ref. 1 becomes too complicated to use. This difficulty can be formally avoided by replacing the generalized Fokker-Planck operators by effective operators L_i^{eff} in which the effective diffusion constant D^{eff} is time independent. This argument was used by Fonseca^{8(b)} in deriving Eqs. (4.6) which we have shown to be exact. The use of operators L_i^{eff} instead of L_i implies that H_i defined in Eq. (2.20) can then be replaced by H_i^{eff} with eigenvalues $\epsilon_n^{\text{eff}} = n/\tau_L^{\text{eff}}$, where the effective relaxation time may be defined by

$$\tau_L^{\text{eff}} = \int_0^\infty \Delta(t) dt \quad (4.7)$$

$\tau_L^{\text{eff}} = \tau_L$ for Debye solvents. In this way, the final solutions have the same form as Eqs. (2.18) except that the generalized $a_i(t)$, which include the vibrational contribution to activation as well, are given by

$$a_1(t) = k_{1e}(1 - A^2\Delta^2)^{-1/2} \exp\left[\beta x_{1c}^2 \frac{A^2\Delta}{1 + A\Delta}\right], \quad (4.8a)$$

$$a_2(t) = k_{2e}(1 - A^2\Delta^2)^{-1/2} \exp\left[\beta(x_{2c} - x_0)^2 \frac{A^2\Delta}{1 + A\Delta}\right], \quad (4.8b)$$

where $\Delta = \Delta(t)$ and $A = \lambda_0/\lambda$. This should be compared with the corresponding relations given in Eq. (2.25) for Debye solvents to which it is similar.

In deriving Eq. (4.8), we began from the effective operators L_i^{eff} and used the approximation $\Delta(t) \approx \exp(-t/\tau_L^{\text{eff}})$, which is consistent with L_i^{eff} . But we also expect Eq. (4.8) to be an excellent approximation for any $\Delta(t)$ not limited to $\exp(-t/\tau_L^{\text{eff}})$. Indeed it gives the exact results in the limiting cases! For example, in the *narrow reaction window limit* $k_1(x) = k_2(x) = k_0\delta(x - x_c)$, $A = \lambda_0/\lambda = 1$, Eq. (2.19b) leads to

$$k_{1e} = k_0(2\pi k_B T)^{-1/2} \exp(-\beta x_0^2/2), \quad (4.9a)$$

$$k_{2e} = k_0(2\pi k_B T)^{-1/2} \exp(-\beta(x_c - x_0)^2/2), \quad (4.9b)$$

and $a_{s1}(t)$ and $a_{s2}(t)$ reduce to $k_0 G_1(x|x_c, t)$ and $k_0 G_2(x - x_0|x_c - x_0, t)$, respectively, as seen from the Green functions given in Eqs. (4.6). This result is exact. In the *wide reaction window limit*, $A \approx 0$, $\lambda_q \approx \lambda$, $a_{si}(s) \approx k_i/s$,

the inverse of Eq. (2.18) is identical to Eq. (4.1). Also for Debye solvents, as shown in Eq. (3.18), $\Delta(t) = \exp(-t/\tau_L)$, and Eqs. (4.8) is again exact and consistent with Eqs. (2.25).

The Laplace transforms of Eq. (4.8) are quite complicated functions even when $\Delta(t)$ for non-Debye solvents has the simple form of the sum of exponentials.⁸ This has led us to try to solve Eq. (2.18) in real space. Multiplying Eq. (2.18b) by $\{s^2[1 + a_{s1}(s) + a_{s2}(s)]\}$ and taking the inverse Laplace transform, we see that the survival probabilities can also be written as

$$Q_1(t) = 1 - Q_2(t), \quad (4.10a)$$

$$Q_2(t) = k_{1e}t - \int_0^t a(t-\tau)Q_2(\tau)d\tau, \quad (4.10b)$$

where $a(t) = a_1(t) + a_2(t)$ in which $a_1(t)$ and $a_2(t)$ are given in Eqs. (4.8). Equation (4.10b) is an integral equation for $Q_2(t)$. Any solution, numerical or analytical, for a non-Debye solvent would necessarily require detailed information about $\Delta(t)$. This is discussed in Sec. III [see Eqs. (3.14), (3.20), and (3.21)] and the Appendix.

Once an explicit analytic form of $\Delta(t)$, [or equivalently $D(t)$], is known, Eq. (4.10) can be solved analytically (see Sec. V) or numerically using Eq. (4.8). The accuracy of these solutions can be checked by comparison with direct numerical solutions of the reaction-diffusion equations given in Eq. (2.12) from which Eq. (4.10) is derived. Ref. 1 discusses the numerical solution of Eq. (2.12) for Debye solvents and compares it with the limiting solutions and other results (e.g. the interpolation formula and the double exponential approximation) to Eq. (4.8).

V. SOLUTION OF THE INTEGRAL EQUATION FOR THE SURVIVAL PROBABILITIES

Here we present a method of solving the integral equation (4.10b) for non-Debye solvents in the context of an

effective relaxation time τ_L^{eff} defined in Eq. (4.7). For Debye solvents the method of solution presented here is, in principle, exact since there is only one relaxation time τ_L . The kernel in Eq. (4.8b) for Debye and non-Debye solvents can then be expressed as

$$a(t) = a_1(t) + a_2(t) = \sum_{n=0}^{\infty} c_n \exp(-t\epsilon_n^{\text{eff}}) \quad (i = 1, 2), \quad (5.1)$$

where $\epsilon_n^{\text{eff}} = n/\tau_L^{\text{eff}}$ and

$$c_n = c_{n,1}k_{1e}^{-1} + c_{n,2}k_{2e}^{-1}. \quad (5.2)$$

Substituting Eq. (5.1) in Eq. (4.10b) we find

$$Q_2(t) = k_{1e}t - \sum_{n=0}^{\infty} c_n F_n(t), \quad (5.3)$$

where

$$F_n(t) = \int_0^t \exp\{-\epsilon_n^{\text{eff}}(t-\tau)\}Q_2(\tau)d\tau. \quad (5.4)$$

Differentiating Eq. (5.4) and making use of Eq. (5.3), we have

$$dF_n(t)/dt + \epsilon_n F_n(t) = Q_2(t), \quad (5.5)$$

which on combining with (5.3) leads to a set of linear ordinary differential equations for $n = 0, 1, 2, \dots$,

$$dF_n(t)/dt = k_{1e}t - \epsilon_n F_n(t) - \sum_{n=0}^{\infty} c_n F_n(t), \quad (5.6)$$

with constant coefficients. The initial condition $F_n(0) = 0$. The general solution of Eq. (5.6) is¹⁷

$$\mathbf{F}(t) = e^{t\mathbf{C}} \left(\int_0^t e^{-\tau\mathbf{C}} \mathbf{G}(\tau) d\tau + \mathbf{K}_0 \right), \quad (5.7)$$

where $\mathbf{F}(t)$ and $\mathbf{G}(t)$ are vectors whose components are $F_n(t)$ and $k_{1e}t$, respectively, and $e^{t\mathbf{C}}$ is the fundamental matrix¹⁷ in which the matrix \mathbf{C} , with $m \rightarrow \infty$, is given by

$$\mathbf{C} = \begin{bmatrix} -(c_0 + \epsilon_0) & -c_1 & -c_2 & \cdots & -c_m \\ -c_0 & -(c_1 + \epsilon_1) & -c_2 & \cdots & -c_m \\ -c_0 & -c_1 & -(c_2 + \epsilon_2) & \cdots & -c_m \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -c_0 & -c_1 & -c_2 & \cdots & -(c_m + \epsilon_m) \end{bmatrix}. \quad (5.8)$$

In Eq. (5.7), \mathbf{K}_0 is a constant vector to be determined from the initial conditions $\mathbf{F}(0) = 0$. It is apparent that the solution of Eq. (4.10), which up to this point is exact for a Debye solvent, can become quite complicated even though we know, in principle, how to solve it.

An approximate solution could be obtained by an iterative procedure. Starting from a first order approximation by taking only the first term $n = 0$ in the sum of Eq. (5.6), we have

$$dF_0(t)/dt = k_{1e}t - c_0 F_0(t), \quad (5.9)$$

which has the solution

$$F_0(t) = k_{1e}c_0^{-2}[-1 + c_0t + \exp(-c_0t)]. \quad (5.10)$$

Substitution in Eq. (5.3) yields

$$Q_2(t) \approx k_{1e}k^{-1}[1 - \exp(-kt)], \quad (5.11)$$

where $c_0 = k = k_{1e} + k_{2e}$. Equation (5.11) is just the *slow reaction limit* discussed in Sec. II.^{1,2} Using this approximate result for $Q_2(t)$ in Eq. (5.5) and solving the differential equation, we obtain

$$F_n(t) = k_{1e}k^{-1} \{ [1 - \exp(-\epsilon_n^{\text{eff}}t)]/\epsilon_n^{\text{eff}} - [\exp(-kt) - \exp(-\epsilon_n^{\text{eff}}t)]/(\epsilon_n^{\text{eff}} - k) \} \quad (n = 0, 1, 2, \dots). \quad (5.12)$$

This is in accord with $F_0(t)$ given in Eq. (5.10). Substitution in Eq. (5.3) leads to

$$Q_2(t) \approx k_{1e} k^{-1} [1 - \exp(-kt)] - \sum_{n=1} c_n F_n(t), \quad (5.13)$$

where $F_n(t)$ is given in Eq. (5.12). The terms beyond the first provide systematic corrections to the slow reaction limit outside this region. One can iterate again by substituting Eq. (5.13) into Eq. (5.5) to find an improved solution for $F_n(t)$, and so on.

VI. DISCUSSION

Electron transfer reactions are usually characterized in the literature by their rate constants. This assumes that the reaction dynamics is sufficiently well known to identify a unique rate constant which is the case when the reactants show a simple exponential time decay. One can then distinguish between adiabatic and nonadiabatic reactions as discussed in the text and in Ref. 1. When this decay is multiexponential, however, the rate constant becomes ambiguous except when the dynamics can be described in terms of an effective relaxation time τ_L^{eff} or when attention is focused on the decay at very long times when a residual single exponential time dependence remains. In this case the solvent dynamics affects electron transfer in complicated ways which have been elucidated by us in several limiting cases for Debye solvents.¹ For instance in the *narrow reaction window limit* the rate constant $k = 0.833\tau_L^{-1}$ for *barrierless reactions* while if the barrier $\beta\Delta G_2^*$ for the reverse reaction is large and the forward reaction is barrierless $k = [0.6 + (\pi/\beta\Delta G_2^*)^{1/2}]^{-1}\tau_L^{-1}$. Many electron transfer experiments in Debye solvents confirm the proportionality between k and the inverse longitudinal relaxation time⁴ which has also been discussed theoretically.^{5,7,9} A distribution of relaxation times for the solvent however would not generally produce such simple behavior or permit a full description of the kinetics by a simple rate constant.⁴ It requires instead a more complete analysis of the survival probabilities of the reacting species which we have attempted.

Equations (2.18) or (4.10), with $a_i(t)$ given by Eqs. (4.8), are our main results for ET reactions in non-Debye solvents when the free energy surfaces are described by the Sumi-Marcus model, see Eq. (2.1). The equations also apply to Debye solvents in which case $\Delta(t) = \exp(-t/\tau_L)$. The solutions are exact in the *narrow* and *wide reaction window limits* for Debye and non-Debye solvents and also in the *slow reaction and nondiffusion limits* for Debye solvents. The behavior between these limits, is predicted by the general solutions. An iterative method of solving these equations is discussed, which requires the identification of an effective relaxation time τ_L^{eff} . The interpolation formula and other approximations derived for barrierless reactions in Debye solvents can be carried over to non-Debye solvents with the use τ_L^{eff} .

This paper provides an explicit method of calculation of the survival probabilities in ET reactions when the solvent reorganization energy $\beta\lambda_0$, the ratio $\mathbf{A} = \lambda_0/\lambda$ of this to the total reorganization energy, the constant k_0 which depends on the reaction adiabaticity, the reaction free energy $\beta\Delta G^0$

and the time correlation function along the reaction coordinate $\Delta(t)$, are known. In certain limiting cases however one or more of these quantities is no longer an independent variable. For example, in the narrow and wide window limits $\mathbf{A} = 0$ and 1, respectively. Linear response theory shows that $\Delta(t)$ is identical to the time correlation function $S(t)$ of the solvation free energy of the reacting intermediates. While our derivation applies strictly for a continuum solvent we expect the result to hold accurately even in a discrete molecular solvent. This provides a useful link between time delayed fluorescence measurements of $S(t)$ for a solvent and the rates of electron transfer reactions in the same solvent.¹⁸

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APPENDIX: THE TIME CORRELATION FUNCTION OF THE BORN SOLVATION ENERGY

In recent years solvation dynamics, which plays an important role in the kinetics of ET reactions, has been studied extensively both experimentally¹³⁻¹⁵ and theoretically.¹⁹⁻²² The dynamics of solvation is measured by time dependent fluorescence Stokes shifts (TDFS) of chromophores forming suitable charge transfer complexes and is related to the time correlation function $S(t)$ of the Born solvation energy.¹⁸ In this appendix we will discuss the relationship between $S(t)$ and the time correlation function $\Delta(t)$ of the ET reaction along the reaction coordinate.

The Born solvation energy is defined by^{22(a)}

$$E_B(t) = -(1/2) \int \mathbf{D}(\mathbf{r}) \cdot \mathbf{P}(\mathbf{r}, t) d\mathbf{r}, \quad (\text{A1})$$

where $\mathbf{D}(\mathbf{r})$ is the bare field of the reacting ions and $\mathbf{P}(\mathbf{r}, t)$ is the total polarization of the medium, which is related, by linear response theory, to the field $\mathbf{D}(\mathbf{r})$ by

$$\mathbf{P}(\mathbf{r}, t) = \mathbf{P}^\infty(\mathbf{r}) + (4\pi)^{-1} \int_0^t c(\mathbf{r}, \tau) \mathbf{D}(\mathbf{r}, t - \tau) d\tau. \quad (\text{A2})$$

Here $\mathbf{P}^\infty(\mathbf{r})$ is the electronic polarizability, which follows the field instantaneously and is given by

$$\mathbf{P}^\infty(\mathbf{r}) = (4\pi)^{-1} (1 - 1/\epsilon_\infty) \mathbf{D}(\mathbf{r}) \quad (\text{A3})$$

$c(\mathbf{r}, \tau)$ is a response function, which is determined by the microscopic structure of the medium surrounding the ions. Substituting Eqs. (A3) and (A2) into Eq. (A1), we have

$$\begin{aligned} \Delta E_B(t) &= E_B(t) - E_B^{\text{el}} \\ &= -(8\pi)^{-1} \int d\mathbf{r} \int_0^t \mathbf{D}(\mathbf{r}) \cdot c(\mathbf{r}, \tau) \mathbf{D}(\mathbf{r}, t - \tau) d\tau, \end{aligned} \quad (\text{A4})$$

where

$$E_B^{\text{el}} = -(8\pi)^{-1} (1 - 1/\epsilon_\infty) \int \mathbf{D}(\mathbf{r}) \cdot \mathbf{D}(\mathbf{r}) d\mathbf{r}, \quad (\text{A5})$$

The Laplace transform of Eq. (A4) is

$$\Delta E_B(s) = -(8\pi)^{-1} \int d\mathbf{r} \mathbf{D}(\mathbf{r}) \cdot c(\mathbf{r}, s) \mathbf{D}(\mathbf{r}, s). \quad (\text{A6})$$

To pursue this further we need information about the response function $c(r,s)$ from a detailed molecular theory such as the dynamic mean spherical approximation (MSA).¹⁹⁻²³ For a continuum solvent, however, the response function $c(r,s)$ is

$$c(s) = 1/\epsilon_\infty - 1/\epsilon(s), \quad (\text{A7})$$

which is independent of r and was given earlier in Eq. (3.6a). If the charges on the ions are suddenly switched on, $\mathbf{D}(\mathbf{r}, t - \tau) = \mathbf{D}(\mathbf{r})$ for $t > 0$ and is zero otherwise. Equation (A4) then reduces to

$$\begin{aligned} \Delta E_B(t) &= - (8\pi)^{-1} \int d\mathbf{r} \mathbf{D}(\mathbf{r}) \cdot \mathbf{D}(\mathbf{r}) \int_0^t c(\tau) d\tau \\ &= E_B^0 c^{-1} \int_0^t c(\tau) d\tau, \end{aligned} \quad (\text{A8})$$

where c is defined in Eq. (3.6b) and the Born solvation energy at equilibrium²⁴

$$E_B^0 = \Delta E_B(\infty) = - (8\pi)^{-1} c \int d\mathbf{r} \mathbf{D}(\mathbf{r}) \cdot \mathbf{D}(\mathbf{r}). \quad (\text{A9})$$

The time correlation function of the Born solvation energy $E_B(t)$ is defined as

$$S(t) = [E_B(t) - E_B(\infty)] / [E_B(0) - E_B(\infty)] \quad (\text{A10a})$$

$$= [\Delta E_B(t) - \Delta E_B(\infty)] / [\Delta E_B(0) - \Delta E_B(\infty)] \quad (\text{A10b})$$

$$= - \Delta E_B(t) / \Delta E_B(\infty) + 1, \quad (\text{A10c})$$

where we have used $\Delta E_B(0) = 0$. Substituting (A9) and (A8) in (A10c) we have

$$S(t) = - c^{-1} \int_0^t c(\tau) d\tau + 1. \quad (\text{A11})$$

On comparing with Eq. (3.12c), we see that

$$\Delta(t) = S(t). \quad (\text{A12})$$

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