# An integral equation approximation for the dynamics of reversible electron-transfer reactions

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The solution to an integral equation [J. Zhu and J. C. Rasaiah, J. Chem. Phys. **96**, 1435 (1992)] for the survival probabilities in the Sumi–Marcus model of reversible electron-transfer (ET) reactions, in which ligand vibrations and fluctuations in the solvent polarization play important roles, is obtained numerically using a simple computer program suitable for use on a PC. The solutions depend on the time correlation function $\Delta(t)$ of the reacting intermediates along the reaction coordinate which is shown to be equal to the time correlation function of the Born free energy of solvation of these intermediates even in discrete molecular solvents provided its response is linear. This enables $\Delta(t)$ to be determined accurately from time-delayed fluorescence Stokes shift experiments or from dynamical theories of ion solvation; it is usually an exponential (Debye solvent) function of time or a sum of such exponentials (non-Debye solvent). The solutions to the integral equation, which can be obtained numerically for any given $\Delta(t)$, are found to predict the electron-transfer dynamics successfully over a wide range of model parameters. They can also be approximated by single or multiexponential interpolation formulas in which the thermally equilibrated rate constants are modified by a factor which reflects the relative importance of ligand (or inner-sphere solvent) vibration and outer-sphere solvation dynamics. The use of an effective longitudinal relaxation time in calculations of ET rates in solution is shown to be a poor assumption in some solvents. The theory is compared with an experiment in the inversion region, and its extension to include high-frequency vibrational modes that lead to an increased ET rate in other experiments is discussed.

## I. INTRODUCTION

An approximate general solution of two coupled diffusion-reaction equations

$$\partial P_1/\partial t=[L_1(t)-k_1(x)]P_1+k_2(x)P_2\,, \qquad (1.1a)$$

$$\partial P_2/\partial t=[L_2(t)-k_2(x)]P_2+k_1(x)P_1\,, \qquad (1.1b)$$

describing the kinetics of reversible electron transfer (ET) reactions in solvents characterized by single (Debye) or multiple (non-Debye) dielectric relaxation times was derived recently.[1,2] Interest in these equations goes beyond their relevance for electron transfer since they also describe the rates of many other reactions which are controlled by diffusive motion along the reaction coordinate $x$. Examples are the kinetics of rebinding carbon monoxide to heme in myoglobin,[3] the rates of isomerization reactions,[4] and transitions between metastable states characterized by double (or multiple) potential-energy minima.[5] The reactant decay curves display simple exponential or multiexponential behavior in different circumstances determined, for example, by the solvent viscosity. Moreover, the kinetic rate constants can, in appropriate cases, be correlated with the solvent relaxation times, the ligand vibrational frequencies, or the electronic coupling between the donor and acceptor sites.[1–18] The solutions to these coupled differential equations, which show such diverse effects, and the methods of obtaining them, even in approximate form, are naturally of great interest to chemists and biochemists and forms the principal subject of this paper.

In our studies, the survival probabilities of the reactants and products in the ET reactions governed by Eq. (1.1) are obtained as the solutions to an integral equation[2] which is approximate except in certain limits when it is exact. However, the error in the integral equation outside these limits (see below) is small. Although the Laplace transforms of the survival probabilities are known, they can be inverted analytically only in special cases. A general method of solving the integral equation, which does not use an effective solvent relaxation time as an additional approximation,[2] is desirable. In this communication we address this problem and show how the integral equation can be solved numerically using a simple program of a few lines suitable for use on a personal computer.

On comparing our solutions to the integral equations with the numerical (finite-difference) solutions of the diffusion-reaction differential equations (1.1), we find that the former is generally quite accurate and useful except possibly in narrow regions of solvent relaxation times and reorganization energies. This is fortunate because it is much easier to solve the integral equation numerically than

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it is to solve the coupled differential equation from which it is derived. In addition, the numerical method used applies equally well to ET reactions in solvents with multiple or single relaxation times, thus providing a practical route to the kinetics of these reactions in a variety of solvents and different experimental conditions.

Apart from our numerical studies we also derive new and improved single and multiexponential interpolation formulae for the survival probabilities in these solvents. On comparing our numerical and analytic results we find that the survival probabilities are in many cases well approximated by these formulas in which the thermally equilibrated rate constants are modified by a factor that reflects the relative importance of inner sphere ligand vibration and outer sphere solvation dynamics for the ET rate.

The connection between the rate of electron transfer in a solvent and its solvation dynamics is further clarified in this paper by relating the time correlation function of the Born free energy of the reacting intermediates to the time correlation function along the reaction coordinate. The equality of the two was shown earlier,[2] within the context of linear response theory, for ET reactions in continuum solvents; its extension to discrete molecular solvents, which we discuss here, is an important generalization that is exploited in our calculations of ET rates. These studies reveal that the use of an effective longitudinal relaxation time to describe the solvation dynamics of the reacting intermediates in these ET calculations is a poor approximation in some solvents.

In the model electron-transfer reactions considered in this study, $P_1=P_1(x,t)$ and $P_2=P_2(x,t)$ of Eq. (1.1) are the probabilities that reactants and products, respectively, at time $t$ are in states characterized by a fluctuation $x$ of the excess solvent polarization $\mathbf{P}^{\text{ex}}(\mathbf{r})$ from its equilibrium average $\mathbf{P}_1^{0,\text{ex}}(\mathbf{r})$ due to the charge distribution on the reactants, and $k_1(x)$ and $k_2(x)$ are the rates of the forward and backward reactions in these states. Here $\mathbf{P}^{\text{ex}}(\mathbf{r})=\mathbf{P}(\mathbf{r})-\mathbf{P}^{\infty}(\mathbf{r})$, where $\mathbf{P}(\mathbf{r})$ and $\mathbf{P}^{\infty}(\mathbf{r})$ are the total and electronic polarization of the solvent, respectively. The fluctuation $x$ in the solvent polarization is defined by[1,2]

$$x^2=(4\pi/c)\int\left|\mathbf{P}^{\text{ex}}(\mathbf{r})-\mathbf{P}_1^{0,\text{ex}}(\mathbf{r})\right|^2 d\mathbf{r}, \tag{1.2}$$

where

$$c=1/\epsilon_\infty-1/\epsilon_0 \tag{1.3}$$

in which $\epsilon_\infty$ and $\epsilon_0$ are the high-frequency and static dielectric constants, respectively. Both $\mathbf{P}^{\text{ex}}(\mathbf{r})$ and $\mathbf{P}_1^{0,\text{ex}}(\mathbf{r})$ have contributions from the translation and rotation of the solvent molecules. It is assumed that the time dependence of the probability functions $P_1(x,t)$ and $P_2(x,t)$ on the polarization fluctuations is determined by the generalized Smoluchowski operators[6]

$$L_i=D(t)\frac{\partial^2}{\partial x^2}+\beta D(t)\frac{\partial}{\partial x}\left(\frac{dV_i(x)}{dx}\right)\quad(i=1,2) \tag{1.4}$$

in which $\beta=(k_BT)^{-1}$, where $k_B$ is the Boltzmann constant, $T$ is the temperature,

$$\beta D(t)=-d\ln\Delta(t)/dt \tag{1.5}$$

is a time-dependent diffusion coefficient, and

$$\Delta(t)=\langle\delta x(t)\delta x(0)\rangle/\langle\delta x^2(0)\rangle \tag{1.6}$$

is the time correlation function along the reaction coordinate. In Eq. (1.6), $\delta x(t)=x(t)-x_0$, where $x(t)$ is defined by an equation analogous to Eq. (1.2) except that $\mathbf{P}^{\text{ex}}(\mathbf{r})$ is replaced by $\mathbf{P}^{\text{ex}}(r,t)$ and $x_0$ is defined by

$$x_0^2=(4\pi/c)\int|\mathbf{P}_2^{0,\text{ex}}(\mathbf{r})-\mathbf{P}_1^{0,\text{ex}}(\mathbf{r})|^2 d\mathbf{r} \tag{1.7}$$

in which $\mathbf{P}_2^{0,\text{ex}}(\mathbf{r})$ is the equilibrium excess solvent polarization at $\mathbf{r}$ due to the product charge distribution.

Marcus[7] and Hush[8] in their pioneering studies showed that

$$V_1(x)=x^2/2, \tag{1.8a}$$

$$V_2(x)=(x-x_0)^2/2+\Delta G^0, \tag{1.8b}$$

are harmonic free-energy functions. In subsequent developments (Sumi and Marcus[6] and Kestner, Logan, and Jortner[9]), the vibrational contributions of the ligands were also included in the total free energies of the reactants ($i=1$) and products ($i=2$) which are then given by[6]

$$V_1(q,x)=aq^2/2+V_1(x), \tag{1.9a}$$

$$V_2(q,x)=a(q-q_0)^2/2+V_2(x), \tag{1.9b}$$

where $q$ is the vibrational coordinate of the ligands and $a=\mu\omega^2$ is taken to be the same for reactants and products ($\mu$ is the reduced mass and $\omega$ is the vibrational frequency of the ligand). In Eq. (1.8b) $\Delta G^0$ is the standard free energy for the forward reaction ($1\rightarrow2$).

The ligand vibrational motions, which are treated classically in this model,[6] are assumed to be much faster than the relaxation of the solvent polarization, and electron transfer can then take place at each value of $x$. This leads to the coordinate dependent rate coefficients[6]

$$k_i(x)=\nu_q\exp[-\beta\Delta G_i^*(x)]\quad(i=1,2) \tag{1.10}$$

which appear in Eqs. (1.1). Here

$$\Delta G_1^*(x)=(1/2)(\lambda_0/\lambda_q)(x-x_{1c})^2, \tag{1.11a}$$

$$\Delta G_2^*(x)=(1/2)(\lambda_0/\lambda_q)(x-x_{2c})^2, \tag{1.11b}$$

are the free energies of activation of reactants and products, respectively, and

$$x_{1c}=(\lambda+\Delta G^0)/(2\lambda_0)^{1/2}, \tag{1.12a}$$

$$x_{2c}=(\lambda+\Delta G^0-2\lambda_q)/(2\lambda_0)^{1/2}. \tag{1.12b}$$

In these expressions $\lambda$ is the total reorganization energy which has contributions[6,1] from ligand vibration $\lambda_q$ and outer solvent polarization $\lambda_0$ so that $\lambda=\lambda_0+\lambda_q$ and

$$\lambda_0=x_0^2/2, \tag{1.13a}$$

$$\lambda_q=aq_0^2/2. \tag{1.13b}$$

The preexponential factor

$$\nu_q=k_0[(\beta\lambda_0/2\pi\lambda_q)]^{1/2} \tag{1.14}$$

in Eq. (1.10) contains the factor $k_0$ which is determined by electronic coupling between the donor and acceptor sites and other details of the electron reaction; e.g., by whether the reaction is adiabatic or not.[1] The determination of $k_0$ is a quantum-mechanical problem, but it is treated as a parameter in our calculations.

Our main interest is in the rate constants and survival probabilities $Q_i(t)$ for the reactants and products which are related to the solutions of Eq. (1.1) by integration:

$$Q_i(t)=\int_{-\infty}^{\infty} P_i(x,t)dx \quad (i=1,2) \tag{1.15}$$

Assuming that the reactants are initially at equilibrium, our solution for the survival probabilities is[1,2]

$$Q_1(s)=1/s-Q_2(s), \tag{1.16a}$$

$$Q_2(s)=k_{1e}/\{s^2[1+a_{s1}(s)+a_{s2}(s)]\}, \tag{1.16b}$$

where $Q_i(s)$ are Laplace transforms of the survival probabilities and $a_{s1}(s)$ and $a_{s2}(s)$ are the Laplace transforms of[2]

$$a_1(t)=k_{1e}(1-A^2\Delta(t)^2)^{-1/2}\exp\left(\beta x_{1c}^2\frac{A^2\Delta(t)}{1+A\Delta(t)}\right), \tag{1.17a}$$

$$a_2(t)=k_{2e}(1-A^2\Delta(t)^2)^{-1/2}\exp\left(\beta(x_{2c}-x_0)^2\frac{A^2\Delta(t)}{1+A\Delta(t)}\right), \tag{1.17b}$$

respectively. The time correlation function $\Delta(t)$ appears in these equations together with the size of the reaction window

$$A=\lambda_0/\lambda \tag{1.18}$$

which reflects the relative contributions of the ligand vibration (or inner sphere) and outer sphere solvation to the dynamics of electron transfer and

$$k_{ie}=\int k_i(x)\exp[-\beta V_i(x)]dx \bigg/ \int \exp[-\beta V_i(x)]dx \quad (i=1,2) \tag{1.19}$$

are average rate constants in the forward and reverse directions. Substitution of Eqs. (1.8) and (1.10) in Eq. (1.19) and integration leads to

$$k_{1e}=\nu\exp[-\beta(\lambda+\Delta G^0)^2/4\lambda], \tag{1.20a}$$

$$k_{2e}=k_{1e}\exp(\beta\Delta G^0), \tag{1.20b}$$

where

$$\nu=\nu_q[\lambda_q/\lambda]^{1/2}=(\beta A/2\pi)^{1/2}k_0. \tag{1.21}$$

Taking the inverse Laplace transform of Eq. (1.16), one finds[2]

$$Q_1(t)=1-Q_2(t), \tag{1.22a}$$

$$Q_2(t)=k_{1e}t-\int_0^t a(t-u)Q_2(u)du, \tag{1.22b}$$

where $a(t)=a_1(t)+a_2(t)$ in which $a_1(t)$ and $a_2(t)$ are given in Eqs. (1.16).

Equation (1.22b) is our integral equation[2] for the survival probability $Q_2(t)$ in which the kernel $a(t-u)$ depends on the time correlation function $\Delta(t)$ along the reaction coordinate. For a Debye solvent, $\Delta(t)$ is just $\exp(-t/\tau_L)$, where $\tau_L$ is the longitudinal relaxation time, the diffusion coefficient $D=1/(\beta\tau_L)$, and Eq. (1.17) can also be written as

$$a_i(t)=k_{ie}+k_{ie}^{-1}\sum_{n=1}^{\infty}c_{n,i}\exp(-nt/\tau_L) \quad (i=1,2), \tag{1.23}$$

where $c_{n,i}=|\langle u_{n,i}|k_i(x)|g_i\rangle|^2$, $|u_{n,i}\rangle$ are the eigenkets of a harmonic oscillator with energy eigenvalues $\epsilon_n=n/\tau_L$ (no zero-point energy) and $|g_i\rangle$ is the lowest eigenket ($n=0$). Equation (1.17), with $\Delta(t)=\exp(-t/\tau_L)$, is equivalent to Eq. (1.23). It is obtained by observing that the adjoint of Eqs. (1.1) involves the Hamiltonian for a harmonic oscillator whose density matrix leads directly to Eq. (1.17). The details are discussed in Refs. 6 and 1 and the extension of the argument to non-Debye solvents is given in Ref. 2. The Laplace transform of Eq. (1.23) is

$$a_{si}(s)=k_{ie}+k_{ie}^{-1}\sum_{n=1}^{\infty}c_{n,i}(s+\epsilon_n)^{-1} \quad (i=1,2). \tag{1.24}$$

Long- and short-time approximations are readily derived from Eq. (1.23) or Eq. (1.24)—see the Appendix. The limiting solutions (Sec. II), a double-exponential approximation and an interpolation formula (Sec. III) for $Q_i(t)$ also follow from the limiting forms or approximations to these equations.[1,2]

For a perfectly symmetrical ET reaction (e.g., $Fe^{+2}+Fe^{+3}\rightarrow Fe^{+3}+Fe^{+2}$) the inclusion of the reverse reaction only changes the rate constant by a factor of 2 in the regime where the survival probability shows a single exponential time dependence. The situation is not so simple when the time dependence is multiexponential or when the reaction is unsymmetrical and the standard free energy change for the reaction $\Delta G^0$ is not zero. Theoretical calculations of the ET rates for the forward and reverse reactions must also be consistent with the equilibrium constant for the reaction which is determined by $\Delta G^0$. This serves as an important check on the theoretical approximations used. The theory and numerical methods described in this paper satisfy these expectations and also apply to electron-transfer reactions in solvents characterized by single as well as multiple relaxation times.[10] We note that the numerical and analytic solutions for the survival probabilities in reversible ET reactions described here also furnish the answers to a similar class of problems dealing with the kinetics of escape over a barrier between two harmonic potential wells.

This paper is organized as follows: In Sec. II we discuss the time correlation functions $\Delta(t)$ along the reaction coordinate and in Sec. III we summarize the exact limiting solutions to the coupled differential equations (1.1) and the integral equations. This is followed by a discussion in

Sec. IV of approximate solutions to these integral equations for ET in Debye and non-Debye solvents. These single and double exponential interpolation formulas are applicable in the regions between the limiting cases. The single exponential interpolation formula is also compared with the results of a recent experiment on ET in the inverted region. The numerical solution to the integral equation is described in Sec. V and our calculations are presented in Sec. VI where they are compared with the solutions to the coupled differential equations which describe this model. Extensions of the theory which lead to increased electron transfer rates when the model is modified to include high-frequency vibrational modes of the acceptor are also briefly described in Sec. V. The Appendix contains a comprehensive mathematical discussion of the long- and short-time approximations used in formulating the approximate solutions discussed in Sec. IV.

## II. THE TIME CORRELATION FUNCTION $\Delta(t)$

A major accomplishment of this paper is to show how the rates of ET reactions can be calculated for any known $\Delta(t)$ regardless of its detailed functional form. The time dependence of $\Delta(t)$ in many solvents is usually more complicated than a simple exponential function and is often represented as the sum of two or more exponentials. Before discussing the details we wish to comment on the relationship of $\Delta(t)$ to the solvation dynamics of the reacting intermediates. We have shown earlier[2] that $\Delta(t)$ for electron transfer in a continuum solvent is identical to the time correlation function $S(t)$ for the Born free energy of solvation of the reacting intermediates when a linear response of the environment to the charge is assumed. The extension of this proof to ET in discrete molecular solvents, which follows, also depends on the same assumption which is implicit in the theory of Marcus.

As suggested by Marcus,[7] the excess solvent polarization $\mathbf{P}^{\text{ex}}(\mathbf{r},t)$ may be considered to arise from effective charges

$$e_i^{\text{eff}}(t) = e_i^* + z(t)(e_i - e_i^*) \tag{2.1}$$

on the ions, where $e_i^*$ and $e_i$ in Eq. (2.1) are the charges on ion $i$ in the reactant and product states, respectively, and the switching function $z(t)$ changes from 0 to 1 during the course of ET as reactants are transformed into products. The time variable in Eq. (2.1) was introduced by Hynes.[10] The ensemble average of this switching function is related to the time correlation function $\Delta(t)$. Assuming a linear response of the polarization to the charges, we have

$$\mathbf{P}^{\text{ex}}(\mathbf{r},t) - \mathbf{P}_1^{0,\text{ex}}(\mathbf{r}) = z(t)\,[\mathbf{P}_2^{0,\text{ex}}(\mathbf{r}) - \mathbf{P}_1^{0,\text{ex}}(\mathbf{r})]. \tag{2.2}$$

Since $z(t)$ is proportional to $\mathbf{P}^{\text{ex}}(\mathbf{r},t)$ it also follows from the definition of $x(t)$, which is the analog of Eq. (1.2) with $\mathbf{P}^{\text{ex}}(\mathbf{r},t)$ replacing $\mathbf{P}^{\text{ex}}(\mathbf{r})$, that

$$z(t) = x(t)/x_0. \tag{2.3}$$

Substituting this in Eq. (1.6) and recalling $z(0)=0$, we have

$$\Delta(t) = 1 - \langle z(t) \rangle. \tag{2.4}$$

TABLE I. Dielectric properties and relaxation times of a few solvents [from Ref. 17(a)].

| Solvent | $\epsilon_\infty$ | $\epsilon_0$ | $\tau_L$ (ps) | $\tau_D$ (ps) |
|---|---|---|---|---|
| Acetone | 1.9 | 21.20 | 0.30 | 3.3 |
| Acetonitrile | 1.8 | 37.3 | 0.2 | 4.0 |
| Dimethylsulfoxide | 4.8 | 46.5 | 2.1 | 20.6 |
| *N*-methylpropionamide | 6.0 | 163.0 | 5.0 | 125.0 |
| Propylenecarbonate | 11.0 | 63.9 | 8.0 | 43.5 |
| methanol | 5.6 | 33.7 | 9.2 | 55.6 |
| *n*-propanol | 3.65 | 20.6 | 77.0 | 435.0 |
| Water | 5.16 | 8.36 | 0.54 | 8.27 |

The time correlation function of the Born solvation energy $E_B(t)$ is[2]

$$S(t) = \langle [E_B(t) - E_B(\infty)] \rangle / \langle [E_B(0) - E_B(\infty)] \rangle, \tag{2.5}$$

where

$$E_B(t) = -(1/2) \int \mathbf{D}(r) \cdot \mathbf{P}(\mathbf{r},t)\, d\mathbf{r}. \tag{2.6}$$

Inserting this into Eq. (2.5), one finds, after subtracting and adding the electronic polarization $\mathbf{P}^\infty(\mathbf{r})$ to the polarization factors in the numerator and denominator, that

$$S(t) = \frac{\left\langle \int \mathbf{D}(r)\,[\mathbf{P}^{\text{ex}}(\mathbf{r},t) - \mathbf{P}^{\text{ex}}(\mathbf{r},\infty)]\, d\mathbf{r} \right\rangle}{\left\langle \int \mathbf{D}(r)\,[\mathbf{P}^{\text{ex}}(r,0) - \mathbf{P}^{\text{ex}}(\mathbf{r},\infty)]\, d\mathbf{r} \right\rangle}. \tag{2.7}$$

Subtracting and adding $\mathbf{P}_1^{0,\text{ex}}(\mathbf{r})$ to the polarization factors in the numerator and denominator and making use of Eq. (2.2), we see that

$$S(t) = \langle z(t) - z(\infty) \rangle / \langle z(0) - z(\infty) \rangle. \tag{2.8}$$

Since $z(\infty)=1$ and $z(0)=0$ in an ET reaction, it follows that

$$S(t) = 1 - \langle z(t) \rangle = \Delta(t). \tag{2.9}$$

This proves the equality of the time correlations functions for both continuum and discrete molecular solvents when the solvent response is linear. Its importance lies in the realization that $\Delta(t)$ can now be determined from theoretical calculations of the solvation dynamics of the reacting ion intermediates[11–15] and also from measurements of $S(t)$ in time-dependent fluorescence Stokes (TDFS) shift experiments on solute chromophores[16–18] dissolved in the solvent. The latter provides an important link between TDFS experiments and the measured rates of electron transfer reactions in the same solvent. Computer simulations of the solvent dynamics also furnish an additional source of information and serve as an excellent testing ground for model theories.[19–24]

Measurements of the solvation dynamics from picosecond and subpicosecond time-dependent Stokes shift studies have shown that a simple exponential form for the time correlation function $S(t)$ is the exception rather than the rule; the exceptions include acetone and surprisingly, according to some sources, the alcohols which are expected

TABLE II. Experimental solvation parameters [entries from Ref. 18(c)].

| Solvent | $\tau_1$ (ps) | $\tau_2$ (ps) | $A_1$ | $A_2$ | $\tau^{\mathrm{eff}}$ (ps) |
|---|---|---|---|---|---|
| Acetone[a] | 0.31 | 0.99 | 0.47 | 0.53 | 0.67 |
| Acetonitrile | 0.27 | 1.05 | 0.73 | 0.27 | 0.48 |
| Dimethylsulfoxide | 0.33 | 2.3 | 0.57 | 0.43 | 1.2 |
| Propylenecarbonate | 0.43 | 4.1 | 0.46 | 0.54 | 2.4 |
| Methanol | 1.16 | 9.57 | 0.40 | 0.60 | 6.2 |
| *n*-propanol | 14.0 | 40.0 | 0.30 | 0.70 | 32.2 |
| Water | 0.16 | 1.2 | 0.33 | 0.67 | 0.86 |

[a] Acetone is also well represented by a single exponential time decay of $S(t)$ with a relaxation time of 0.70 ps.

to show the effects of hydrogen bonding.[17(a),18(c)] The continuum model with the phenomenological Debye form (see Table I)

$$\epsilon(\omega)=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1+i\omega\tau_D) \tag{2.10}$$

for the frequency-dependent dielectric constant leads to

$$S(t)=\exp(-t/\tau_L), \tag{2.11}$$

where $\tau_L=(\epsilon_0/\epsilon_\infty)\tau_D$. However the same dispersion relation yields a multiexponential form for $S(t)$, with relaxation times ranging from $\tau_L$ to $\tau_D$, in the dynamical mean spherical approximation introduced by Wolynes[11–15] for a dipolar hard-sphere solvent. Other dielectric response functions such as the Davidson and Cole–Cole functions also predict nonexponential behavior of $S(t)$ in the dielectric continuum model.

Careful measurements by Jarzeba *et al.*[18(c)] have shown that the solvation dynamics in many solvents can be fitted to

$$S(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2), \tag{2.12}$$

where $A_1+A_2=1$. The relaxation times $\tau_1$ and $\tau_2$ differ by almost an order of magnitude in some cases (e.g., propylene carbonate and methanol) but only by a factor of about 3 or so in other solvents when a single exponential fit is reasonably accurate. The parameters for several solvents taken from their work and used in our calculations are collected together in Table II. In the case of acetone (see also Table II), a single exponential decay also provides an accurate fit. An effective relaxation time, defined by

$$\tau^{\mathrm{eff}}=\int_0^\infty S(t)dt, \tag{2.13}$$

is also displayed in Table II and is equal to $A_1\tau_1+A_2\tau_2$; it lies within a factor of 2 of the longitudinal relaxation times for the same solvents quoted by Maroncelli *et al.*[17(a)] which are reproduced in Table I. A simple calculation shows that the initial relaxation time $\tau_{\mathrm{init}}$ is related to $\tau_1$ and $\tau_2$ by $\tau_{\mathrm{init}}=\tau_1\tau_2/(A_1\tau_2+A_2\tau_1)$. The diffusion coefficient $D(t)$ is time dependent; at short times $D(t)=1/(\beta\tau_{\mathrm{init}})$ and at long times $D(t)=1/(\beta\tau_1)$ assuming $\tau_1>\tau_2$.

## III. LIMITING SOLUTIONS

The integral equation (1.22b) for the survival probabilities and the coupled differential equations (1.1), from which it is derived, lead to the same exact solutions in limiting cases.[1,2,6] They provide an important check on our numerical computations and are briefly recapitulated in this section.

There are four limiting cases for ET in solvents which are characterized by a single relaxation time $\tau_L$ and a constant diffusion coefficient $D=kT/\tau_L$ (i.e., Debye solvents).[6,1,2] They are the *narrow* and *wide reaction window limits*, as well as the *slow reaction* and *nondiffusion limits.* For ET in non-Debye solvents, which are distinguished by the existence of multiple dielectric relaxation times, there are just two well-defined limiting solutions; namely the *narrow* and *wide reaction window limits.*

In the slow reaction limit for ET in Debye solvents $(k_i(x)\ll\tau_L^{-1})$, thermal equilibrium of the polarization coordinate $x$ is always maintained and the time scale in which the reaction takes place is much larger than $\tau_L$. It follows from Eq. (1.23) that $a_i(t)=k_{ie}$ which is equivalent to $a_{si}(s)=k_{ie}/s$. This leads to a simple exponential time dependence for the survival probabilities:

$$Q_1(t)=1-Q_2(t), \tag{3.1a}$$

$$Q_2(t)=[k_{1e}/(k_{1e}+k_{2e})]\{1-\exp[-(k_{1e}+k_{2e})t]\}. \tag{3.1b}$$

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. (1.20) with $\nu=\nu_q$ and $\lambda=\lambda_q$:

$$k_1=\nu_q\exp[-\beta(\lambda_q+\Delta G^0)^2/4\lambda_q], \tag{3.2a}$$

$$k_2=k_1\exp[\beta\Delta G^0]. \tag{3.2b}$$

The survival probabilities are the same as in Eqs. (3.1) with $k_i$ replacing $k_{ie}$.

In the nondiffusion limit $[k_i(x)\gg\tau_L^{-1}]$ and $a_{si}(s)\approx k_i(x)/s$. Substituting this in Eq. (1.16) and taking the inverse Laplace transform one finds $Q_1(t)=1-Q_2(t)$ and

$$Q_2(t)=\int P_1(x,0)\left\{\frac{k_1(x)}{k_1(x)+k_2(x)}\times[1-e^{-[k_1(x)+k_2(x)]t}]\right\}dx. \tag{3.3}$$

This leads to multiexponential decay of the reactants.

In the narrow reaction window limit $\lambda_q \ll \lambda_0$, $A \approx 1$, and the vibrational contribution of the ligands to the reorganization energy is negligible. The rate coefficients are delta functions[1,2,6]

$$k(x)=k_1(x)=k_2(x)=k_0\delta(x-x_c), \tag{3.4a}$$

where

$$x_c=(\lambda_0+\Delta G^0)/(2\lambda_0)^{1/2} \tag{3.4b}$$

is, for this case, identical to $x_{1c}$ and $x_{2c}$ defined in Eqs. (1.12). Note that $x_c=0$ when $\lambda_0=-\Delta G^0$. At this point the rate is maximum (zero activation energy for the forward reaction) in the Marcus inversion region of this narrow window limit. It follows from Eq. (3.4a) that $k_{ie}=k_0P_i(x_c,0)$ $(i=1,2)$ and the diffusion reaction Eqs. (1.1) reduce to[1]

$$\partial P_1/\partial t=L_1P_1-k_0\delta(x-x_c)(P_1-P_2), \tag{3.5a}$$

$$\partial P_2/\partial t=L_2P_2+k_0\delta(x-x_c)(P_1-P_2). \tag{3.5b}$$

The Laplace transforms of the survival probabilities are given by Eq. (1.16), with $A=1$ in the expressions for $a_{s1}(s)$ and $a_{s2}(s)$.[1] Equations (1.16) and (1.22b) are now *exact* but they do not lead to a general analytic solution for $Q_i(t)$ in the time domain. However, approximate solutions to these have been obtained for electron transfer in Debye solvents.[1] Examples are barrierless ET reactions[1] which lead to multiexponential decay and the single exponential interpolation formula discussed in Ref. 1.

For barrierless reactions ($\beta\Delta G_1^*(x) \ll 1$, $\beta\Delta G_2^*(x) \ll 1$) in the narrow window limit $(A=1)$, which occur when the reorganization energy $\lambda_0$ and the reaction free energy $\Delta G^0$ are both small, $k_{ie}\approx(\beta/2\pi)^{1/2}\,k_0$ if the initial state is in equilibrium and [see Eq. (A3) of the Appendix]

$$a_{si}(s)=(\beta/2\pi)^{1/2}k_0f(s), \tag{3.6}$$

where

$$f(s)=\sum_{n=0}^{\infty}\frac{(2n)!}{[(2n)!!]^2}\frac{1}{s+2n/\tau_L}. \tag{3.7}$$

Assuming $(\beta/2\pi)^{1/2}k_0\tau_L\gg 1$ one obtains[1] from (1.16),

$$Q_1(t)=1-(1/\pi)\arccos[\exp(-t/\tau_L)]. \tag{3.8}$$

However, if the reverse reaction is neglected, which corresponds to $\beta\Delta G_1^*\ll 1, \beta\Delta G_2^*\gg 1$, one has instead

$$Q_1(t)=(2/\pi)\arcsin[\exp(-t/\tau_L)] \tag{3.9}$$

and $Q_2(t)=0$ which is Sumi and Marcus result.[6] Equations (3.8) and (3.9) predict the values of $\frac{1}{2}$ and zero, respectively, for $Q_1(t)$ as $t\to\infty$. The extraction of an overall single exponential rate constants $k_1$ and $k_2$ in both directions from the long-time behavior of the multiexponential survival probabilities is discussed in Ref. 1. It is found that at long times,

$$Q_1(t)=1-Q_2(t), \tag{3.10a}$$

$$Q_2(t)=[1-\exp(-2kt)]/2, \tag{3.10b}$$

where

$$k=(\beta/2\pi)^{1/2}k_0/[1+2(\beta/2\pi)^{1/2}k_0\tau_Lf_n]. \tag{3.11}$$

This demonstrates single-exponential behavior in this long-time approximation and identifies $k$ as a first-order rate constant. If $(\beta/2\pi)^{1/2}\,k_0\tau_L\gg 1$, we have

$$k=k_1=k_2=(2\tau_Lf_n)^{-1} \tag{3.12}$$

which is independent of the strength of the delta function $k_0$ and is inversely proportional to the solvent relaxation time $\tau_L$. It follows from Eq. (3.12) that $k\approx 0.833\tau_L^{-1}$ which is close to many experimentally observed values of $k\approx\tau_L^{-1}$.

## IV. APPROXIMATE SOLUTIONS TO THE INTEGRAL EQUATIONS

Analytic approximations[2] to our integral equations for electron transfer which are not confined to the limiting regions are discussed in this section. These results extend our previous work to solvents with multiple relaxation times. We also discuss some new results in the inversion region and an improved interpolation formula which is applicable also to non-Debye solvents.

### A. Single exponential interpolation formula

An approximate solution to the integral equation can be obtained by interpolation between the long- and short-time limits of the kernels $a_i(t)$. The mathematical details are given in the Appendix from which we find that when $A\neq 0$, the sum of Eqs. (A8) and (A17) provides the required interpolation in transform space. When $C_i'\neq 0$ (i.e., $x_{1c}$ and $x_{2c}-x_0$ are not zero) a simpler form is obtained by using Eq. (A19) instead of Eq. (A17) when we have

$$a_{s1}(s)\approx k_{1e}[F_A(\tau)+1/s]+\alpha_1\tau_{\text{init}}/|x_{1c}|, \tag{4.1a}$$

$$a_{s2}(s)\approx k_{2e}[F_A(\tau)+1/s]+\alpha_2\tau_{\text{init}}/|x_{2c}-x_0|, \tag{4.1b}$$

where $\tau_{\text{init}}$ is the initial relaxation time (see Sec. II) and $F_A(\tau)$, defined in Eq. (A9) of the Appendix, is determined by the solvation dynamics $(\tau)$ of the reacting intermediates which include relative contributions from the ligand (inner sphere solvent) vibrations and outer sphere solvent reorientation and translation as measured by $A$. This equation extends our previous interpolation formula[1] to non-Debye solvents and differs from it by the presence of the new term $F_A(\tau)$. In Debye solvents $\tau_{\text{init}}=\tau_L$, and $F_A(\tau)=\tau_Lf_A$, where $f_A$ is defined in Eq. (A5). Substitution in Eq. (1.16) leads to

$$Q_1(s)=1/s-Q_2(s), \tag{4.2a}$$

$$Q_2(s)=k_{1e}\alpha^{-1}/[s^2+s\alpha^{-1}(k_{1e}+k_{2e})], \tag{4.2b}$$

where the correction factor

$$\alpha=[1+(k_{1e}+k_{2e})F_A(\tau)+\tau_{\text{init}}(\alpha_1/|x_{1c}|+\alpha_2/|x_{2c}-x_0|)] \tag{4.3a}$$

and (see the Appendix for derivation)

$$\alpha_i=k_0[(1+A)/(2A^{3/2})]\exp[y_i(1-A)]$$
$$\times[1-\mathrm{erf}(\sqrt{y_i}/A)] \quad (i=1,2) \qquad (4.3b)$$

in which

$$y_1=\beta x_{1c}^2(1-A)/[2(1+A)], \qquad (4.4a)$$

$$y_2=\beta(x_{2c}-x_0)^2(1-A)/[2(1+A)], \qquad (4.4b)$$

and

$$\mathrm{erf}(x)=(2/\pi^{1/2})\int_0^x \exp(-t^2)dt. \qquad (4.5)$$

On taking the inverse Laplace transform of (4.2b)

$$Q_2(t)=[k_{1e}/(k_{1e}+k_{2e})]\{1-\exp[-(k_{1\alpha}+k_{2\alpha})t]\}, \qquad (4.6a)$$

with the rate constants given by $k_{i\alpha}=k_{ie}/\alpha$. In the narrow window limit $A=1$, $\alpha_i=k_0$, and $x_{1c}=x_{2c}=x_c$ so that

$$\alpha=[1+(k_{1e}+k_{2e})F_A(\tau)$$
$$+k_0\tau_{\mathrm{init}}(1/|x_c|+1/|x_c-x_0|)]. \qquad (4.7)$$

For Debye solvents $\tau_{\mathrm{init}}=\tau_L$, $F_A(\tau)=\tau_L f_A$, and the rate constants are seen to be related to $\tau_L^{-1}$.

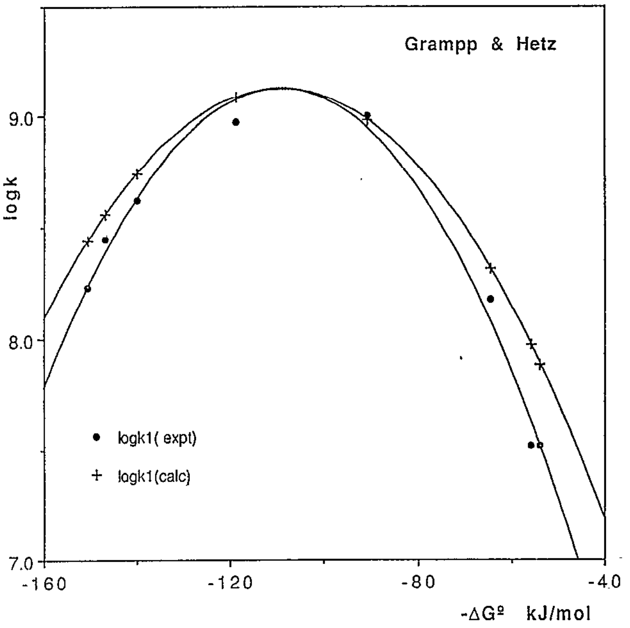

FIG. 1. Log of the rate constants vs the standard free energy for ET in the inversion region for triplet thionine and several donors (data of Ref. 25). Lower curve: least squares fit [Eq. (4.11)] through experimental points (*o*). Upper curve: theory [see Eq. (4.12)].

### B. The inversion region

In Sec. III we discussed barrierless reactions[1] ($\beta\Delta G_1^{*} \ll 1$, $\beta\Delta G_2^{*} \ll 1$) in the narrow window limit when multiexponential time dependence is found for the survival probabilities. The reaction could also be barrierless in one direction only ($\beta\Delta G_1^{*} \ll 1$, $\beta\Delta G_2^{*} \gg 1$): this interesting case occurs in the vicinity of the inversion limit where the reorganization energy $\lambda$ is approximately the negative of the reaction free energy $\Delta G^0$ which is assumed to be neither zero (as in certain isotopic exchange reactions) nor small.

The ET rate of barrierless reactions in Debye solvents in the narrow window limit at the inversion point when $\lambda=-\Delta G^0$ has been discussed earlier.[1] We extend that discussion here by considering the whole region around the inversion point. Also unlike the previous study, our discussion considers the reverse reaction also at and near this point and the influence of ligand vibrations ($A\neq 1$) as well as the contributions from solvent polarization fluctuations to the kinetics of these reactions.

We cannot use Eq. (A19a) or the interpolation formula (4.1a) for $a_{s1}(s)$ in the inversion region for the forward reaction since it diverges at $x_{1c}=0$ which occurs when the activation energy is zero or the rate is maximum in the narrow window limit. A linear combination of Eqs. (A8) and (A17) would be the logical choice similar to Eq. (4.1) but it is not easily manipulated. Hence we use only the long-time approximation, Eq. (A8), for $a_{s1}(s)$:

$$a_{s1}(s)\approx k_{1e}[F_A(\tau)+1/s] \qquad (4.8)$$

which is equivalent to dropping the last term of Eq. (4.1a) in this region.

The interpolation formula Eq. (4.1b) is used for $a_{2s}(s)$. The argument given in the previous paragraphs then leads to the single-exponential form (4.6) for the survival probabilities with

$$\alpha=1+[(k_{1e}+k_{2e})F_A(\tau)+\alpha_2\tau_{\mathrm{init}}/|x_{2c}-x_0|]. \qquad (4.9)$$

Note that $|x_{2c}-x_0|=(\Delta G^0-\lambda)/(2\lambda_0)^{1/2}$ is related to the activation energy for the reverse reaction. If it is large, the term involving this in Eq. (4.9) can be neglected and

$$\alpha\approx 1+(k_{1e}+k_{2e})F_A(\tau). \qquad (4.10)$$

In Debye solvents $\tau_{\mathrm{init}}=\tau_L$, and $F_A(\tau)=\tau_L f_A$. When the last term in Eq. (4.10) is larger than unity, the rate constant in the inversion region is inversely proportional to the longitudinal relaxation time. If this term is negligible (i.e., $\alpha\approx 1$) the rate constant is independent of $\tau_L$ and is given by the simple Marcus form, Eq. (1.20a), which is the maximum possible rate for this simple mechanism.

As an example of a simple ET reaction in the inverted region, consider the recent experiments of Grampp and Hetz[25] on the back electron transfer in geminate radical pairs of triplet thionine and several aromatic donors in methanol (buffered at a pH of 8.6). A least-squares fit of the first-order rate constants vs the standard free energy of reaction $\Delta G^0$ (Fig. 1) has the quadratic form

$$\log_{10}k_{1\alpha}=2.8218-0.115\,26\Delta G^0-5.268\times 10^{-4}\Delta G^{02} \qquad (4.11)$$

from which we find the free energy and rate at the maximum by setting the derivative equal to zero. From the discussion in this section and Eq. (1.20a), it follows that the the maximum rate occurs when the reorganization energy $\lambda=-\Delta G_{\max}^0=109.4$ kJ mol$^{-1}$ which leads to $k_{\max}=(\beta A/2\pi)^{1/2}k_0/\alpha=1.336\times 10^9$ s$^{-1}$. To get an approximate measure of $\alpha$ we neglect the reverse reaction and assume that the solvent (methanol) has a single relaxation time (see Tables I and II). A simple calculation shows that in this case $\alpha \approx 1$ and $k_{1\alpha} \approx k_{1e}$. Assuming that the total reorganization energy $\lambda$ is not significantly changed for the triplet thionine-donor pairs as $\Delta G^0$ changes one can predict the variation of $k_{1\alpha}$ with $\Delta G^0$ using only the data at the maximum of the inversion region. It follows from Eq. (1.20a) that at 295 K,

$$\log_{10} k_{1\alpha} = 4.283 - 0.088\,512 \Delta G^0 - 4.046 \times 10^{-4} \Delta G^{02}. \tag{4.12}$$

The agreement is reasonable (see Fig. 1) in view of the assumptions that have been made. Many ET reactions in the inversion region, however, show much higher rates due to smaller activation energies associated with different channels. This is discussed in Sec. V.

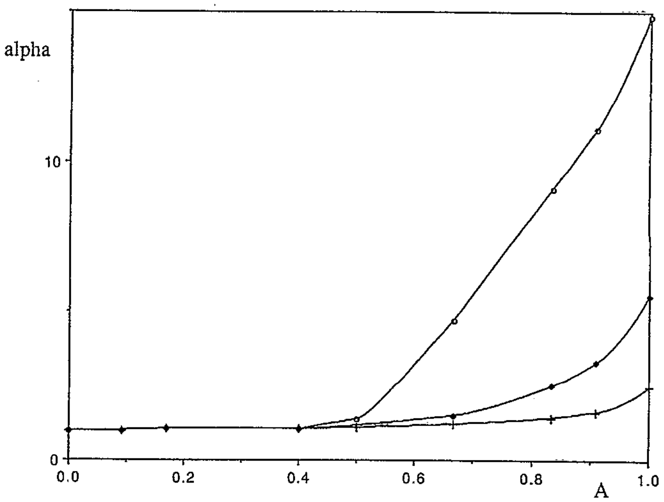

FIG. 2. Plot of $\alpha$ or $\alpha_D$ vs $A = \lambda_0/\lambda$ for a symmetrical ET reaction in a Debye solvent with $\tau = 10$ ps, $\Delta G^0 = 0.0$, and $\sqrt{\beta} k_0 = 1\ \mathrm{ps}^{-1}$. The middle curve shows the empirically determined values $\alpha_D$ used in the improved double-exponential formula that provides a good fit to the integral equation solutions—see Fig 3. The upper curve for $\alpha$ is calculated from Eq. (4.3a) and the lower curve for $\alpha_D$ from Eq. (4.21).

### C. Multiexponential time dependence

This may be observed for the survival probabilities even when the solvent is characterized by a single relaxation time. It is also evident in the numerical solutions to the integral equations described in Sec. V. An analytic approximation to the integral equation shows this form[1] if one includes several terms in the series expansion of $a_{si}(s)$ given in Eq. (1.24) for ET in Debye solvents. If we use a two term approximation

$$a_{s1}(s) \approx k_{1e}[1/s + \beta A^2 x_{1c}^2/(s + \tau_L^{-1})], \tag{4.13a}$$

$$a_{s2}(s) \approx k_{2e}[1/s + \beta A^2 (x_{2c} - x_0)^2/(s + \tau_L^{-1})], \tag{4.13b}$$

for $a_{si}(s)$, substitute this in Eq. (1.16), and take the inverse Laplace transform, one finds the double-exponential form[1]

$$Q_2(t) \approx k_{1e}/(k_{1e} + k_{2e}) + C^+ \exp(-\kappa^+ t) + C^- \exp(-\kappa^- t). \tag{4.14}$$

The rate constants $-\kappa^+$ and $-\kappa^-$ are the roots of

$$f(s) = s^2 + Bs + \tau_L^{-1}(k_{1e} + k_{2e}) \tag{4.15}$$

and (correcting a sign error in Ref. 1) the coefficients

$$C^{\pm} = \pm k_{1e}[1 - (\tau_L \kappa^{\pm})^{-1}]/(\kappa^- - \kappa^+) \tag{4.16a}$$

$$= \pm k_{1e}[1 - (\tau_L \kappa^{\pm})^{-1}]/[B^2 - 4\tau_L^{-1}(k_{1e} + k_{2e})]^{1/2}, \tag{4.16b}$$

where

$$B = \tau_L^{-1} + k_{1e} + k_{2e} + \beta A^2 [k_{1e} x_{1c} + k_{2e}(x_{2c} - x_0)^2]. \tag{4.17}$$

From the solution to Eq. (4.16) one finds

$$-2\kappa^{\pm} = -B \pm [B^2 - 4\tau_L^{-1}(k_{1e} + k_{2e})]^{1/2}. \tag{4.18}$$

It is easily 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. In the limit $A \to 0$, Eq. (4.13) becomes identical to the single-exponential formula characteristic of the wide reaction window limit (Sec. II) when one finds $\kappa^+ = k_{1e} = k_1$ and $C^- = 0$. A similar limit ($\kappa^+ = k_{1e}$) is reached in the inversion region ($x_{1c} \approx 0$) when the barrier for the reverse reaction is large, i.e., $k_{2e} \approx 0$.

We can improve on this by taking the union of Eq. (4.13) and the long-time approximation Eq. (A8) of the Appendix when we have

$$a_{s1}(s) \approx k_{1e}[F_A(\tau) + 1/s + \beta A^2 x_{1c}^2/(s + \tau_L^{-1})], \tag{4.19a}$$

$$a_{s2}(s) \approx k_{2e}[F_A(\tau) + 1/s + \beta A^2 (x_{2c} - x_0)^2/(s + \tau_L^{-1})], \tag{4.19b}$$

where Eq. (4.19) differs from Eq. (4.13) by the presence of a term which is independent of $s$. Note that $F_A(\tau) \to 0$ as $A \to 0$. Repeating the argument used previously[1] we find that the rate constants ($-\kappa^+$ and $-\kappa^-$) are the roots of

$$f(s) = \alpha_D s^2 + B_\alpha s + \tau_L^{-1}(k_{1e} + k_{2e}), \tag{4.20}$$

where $\alpha_D$ defined by

$$\alpha_D = 1 + (k_{1e} + k_{2e}) F_A(\tau) \tag{4.21}$$

is identical to Eq. (4.10) and

$$B_\alpha = \alpha_D \{\tau_L^{-1} + k'_{1\alpha} + k'_{2\alpha} + \beta A^2 [k'_{1\alpha} x_{1c} + k'_{2\alpha}(x_{2c} - x_0)^2]\} \tag{4.22}$$

and $k'_{i\alpha} = k_{ie}/\alpha_D$. Solving for the roots of $f(s)$ we find that the coefficients $C_\alpha^{\pm}$ and rate constants $\kappa_\alpha^{\pm}$ are given by the same equations as the corresponding unsubscripted quantities except that $k_{ie}$ is replaced by $k'_{i\alpha}$ and $B$ by $B_\alpha/\alpha_D$. Explicitly,

$$-2\kappa_\alpha^{\pm} = -B' \pm [B'^2 - 4\tau_L^{-1}(k'_{1\alpha} + k'_{2\alpha})]^{1/2} \tag{4.23}$$

and

$$C_\alpha^{\pm} = \pm k'_{1\alpha}[1 - (\tau_L \kappa_\alpha^{\pm})^{-1}]/(\kappa_\alpha^- - \kappa_\alpha^+), \tag{4.24}$$

where $B' = B_\alpha/\alpha_D$. One easily verifies again that $Q_2(t) = 0$ when $t = 0$, and that $Q_2(t) \to k_{1e}/(k_{1e} + k_{2e})$ as $t \to \infty$.

$F_A(\tau)$ already reflects the complex solvation dynamics of non-Debye solvents. The double-exponential form may

TABLE III. The empirically determined correction factor $\alpha_D$ and rate constants for the double-exponential interpolation formulas describing electron transfer in Debye solvents when $\tau_L=10$ ps, $\Delta G^0=0$ and $\sqrt{\beta}k_0 = 1\ \mathrm{ps}^{-1}$ as a function of $A=\lambda_0/\lambda$.

| $A$ | $\alpha_D$ | $C_\alpha^+$ | $C_\alpha^-$ | $\tau_L\kappa_\alpha^+$ | $\tau_L\kappa_\alpha^-$ | $\tau_L k'_{1\alpha}$ |
|---|---|---|---|---|---|---|
| 0.999 | 5.5 | −0.4443 | −0.0557 | 0.1829 | 2.271 | 0.2077 |
| 0.909 | 3.30 | −0.419 | −0.0803 | 0.2249 | 2.936 | 0.3302 |
| 0.833 | 2.50 | −0.4050 | −0.0949 | 0.2512 | 3.322 | 0.417 |
| 0.667 | 1.5 | −0.3737 | −0.1263 | 0.3104 | 4.007 | 0.622 |
| 0.500 | 1.28 | −0.355 | −0.1442 | 0.3629 | 3.472 | 0.630 |
| 0.200 | 1.06 | −0.335 | −0.1648 | 0.4114 | 3.322 | 0.683 |

thus be extended to non-Debye solvents by replacing $\tau_L$ by $\tau_{\mathrm{init}}$ or by assuming an effective relaxation time [Eq. (2.13)]. The general accuracy of the last assumption (see Sec. VI) may not be good. Another method of solving the integral equation for ET in non-Debye solvents assuming an effective relaxation time $\tau_L^{\mathrm{eff}}$ has been presented elsewhere[2] to which the reader is referred.

The correction factors $\alpha$ and $\alpha_D$ which modify the thermal equilibrium rate constants $k_{ie}$ in the single-exponential interpolation formula and improved double-exponential formulas enable the survival probabilities to be predicted not only in the different limits, but also in the regions between them. When $\alpha$ or $\alpha_D$ is significantly greater than unity, the electron-transfer rate is controlled by the solvation dynamics. Figure 2 shows that this occurs as $A$ approaches the narrow window limit when the dynamics of the outer solvation sphere plays an increasingly significant role in the kinetics of electron transfer.

Although Eq. (4.3a) for $\alpha$ is qualitatively correct, its accuracy is limited by the approximations used in deriving it (see the Appendix). In Fig. 2 we plot $\alpha$ and $\alpha_D$ vs $A$ for a symmetrical electron-transfer reaction ($\Delta G^0=0$) in a Debye solvent assuming $\tau_L=10$ ps and $\sqrt{\beta}k_0 = 1.0\ \mathrm{ps}^{-1}$. Note that $\alpha_D<\alpha$ and both $\alpha$ and $\alpha_D\to 1$ when $\tau_L\to 0$. On comparing the improved double-exponential form with the solutions to the integral equations that are discussed in Sec. V, we find that $\alpha_D$ calculated from Eq. (4.21) is a little too small above $A=0.5$. Values that give a better fit to the integral equation solutions at longer times can be determined empirically; they are also shown in Fig. 2. Table III contains the corresponding rate constants and coefficients obtained in this way and Fig. 3 displays results that are quite typical. It is seen that the agreement with the integral equation solutions is excellent at long times but less so at very short times. Since $\alpha_D$ is strongly correlated with the reaction parameters ($\Delta G^0$, etc.), the values displayed in Table III are accurate only for the particular reaction considered. In the discussions that follow in Sec. V, the survival probabilities in the improved double-exponential approximation are calculated using Eq. (4.22) for $\alpha_D$. The analytic expressions discussed here (double- and single-exponential time dependencies) are also useful in deducing the approximate functional forms of the numerical solutions to the integral equations described in the next section.

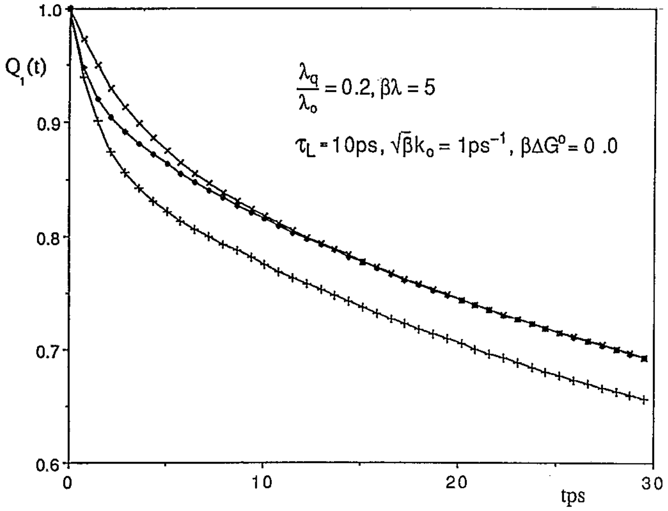

FIG. 3. Comparison of the survival probabilities after ET calculated from the integral equation and the double exponential approximations. The system parameters are $\lambda_q/\lambda_0=0.2$, $\tau_L=10$ ps, $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \mathrm{ps}^{-1}$, and $\beta\Delta G^0=0.0$. The curves are identified as follows: (-----) integral equation; (—+—) double-exponential approximation; (----×----) improved double-exponential approximation ($\alpha_D=2.5$).

## V. NUMERICAL SOLUTION TO THE INTEGRAL EQUATIONS

The solutions discussed in Secs. III and IV are limiting cases or approximations to the integral equations. No general analytic solution in the time domain is possible except in special cases and the solution, especially for systems with multiple relaxation times, has to be obtained numerically. This can be done in small time increments starting from the initial condition at zero time as follows. Let $t=mt'$ and $u=nt'$, where $t'$ is the time step and $m$ and $n$ are integers with $m\geqslant n$. Using the trapezoid rule and the initial condition $Q_2(t)=0$, we have, at the first time step ($m=1$),

$$Q_2(t')=k_{1e}t'/[1+a(0)t'/2] \tag{5.1}$$

and in the following time steps ($m\geqslant 2$)

$$Q_2(mt')=k_{1e}t'-(t'/2)\left(a(0)Q_2(mt') +2\sum_{n=1}^{m-1} a[(m-n)t']Q_2(nt')\right). \tag{5.2}$$

Solving for $Q_2(mt')$, and making use of Eq. (5.1), we get

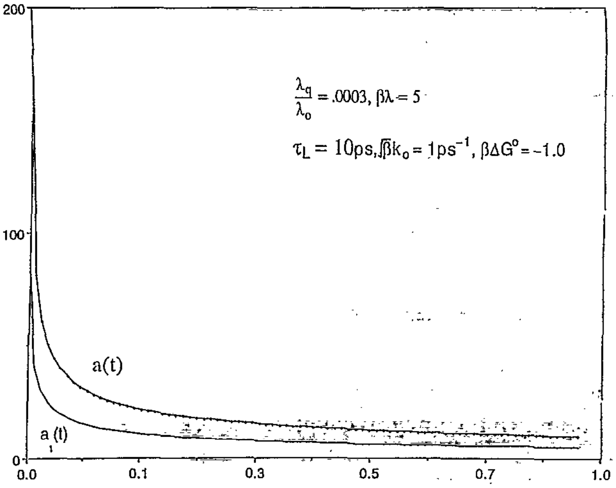

FIG. 4. Plots of the kernel $a'(t) = a_1'(t) + a_2'(t)$ of the integral equation and $a_1'(t)$ near the narrow window limit ($\lambda_q/\lambda_0=0.0003$) for ET in a Debye solvent ($\tau_L=10$ ps) with $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \mathrm{ps}^{-1}$, and $\beta\Delta G^0 = -1.0$. [Note: $a_2'(t) = a_1'(t)$ at the narrow window limit.]

$$Q_2(mt')=Q_2(t')\left(m-\sum_{n=1}^{m-1} a'[(m-n)t']Q_2(nt')\right)$$

$$(m\geqslant 2,n<m), \tag{5.3}$$

where

$$a'[(m-n)t']=a[(m-n)t']/k_{1e}. \tag{5.4}$$

The recurrence formula (5.3) connects the survival probability at time $t=mt'$ ($m\geqslant 2$) with the probabilities at previous time steps $t=nt'$ ($n<m$). It is easily calculated even on a personal computer with a few lines of programming. The solutions to the integral equation can be obtained on a MacIntosh personal computer with 4 MB memory.

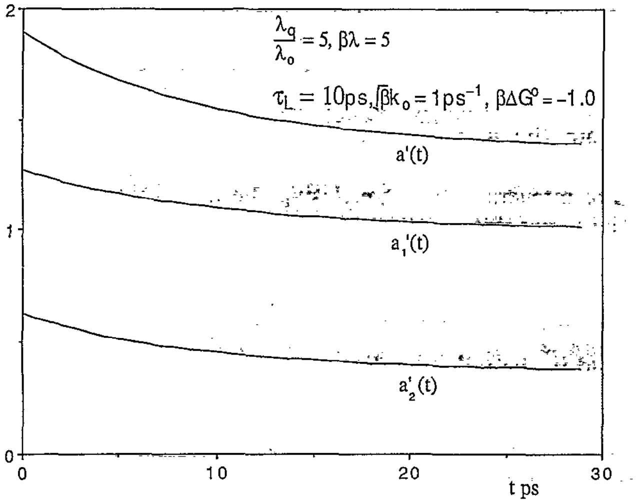

FIG. 5. Plots of the the kernel $a'(t) = a_1'(t) + a_2'(t)$ of the integral equation, $a_1'(t)$ and $a_2'(t)$ when $\lambda_q/\lambda_0=5$ for ET in a Debye solvent ($\tau_L=10$ ps) with $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \mathrm{ps}^{-1}$, and $\beta\Delta G^0=-1.0$.

The numerical solution of the integral equation using Eqs. (5.1) and (5.3) could become inaccurate in the narrow window limit (where the integral equation is exact) unless care is excercised. This is because of the singularity in $a_i(t)$ at $t=0$ when $A=1$—see Eq. (1.18). The problem is illustrated by Figs. 4 and 5 which show plots of $a'(t)$ close to the narrow window limit and away from it. In spite of this singularity at $t=0$ for $A=1$, the integral in Eq. (1.22) is finite which suggests that special precautions have to be taken in getting a numerical solution. The singularity appears explicitly only in Eq. (5.1) in the expression for $Q_2(t')$ but not in Eq. (5.3). The difficulty with the singularity can then be circumvented if $Q_2(t')$, which is the survival probability at the first time step, is calculated analytically. Equation (5.3) can then be used to calculate the survival probabilities at subsequent time steps since $a(t)$ is finite when $t>0$.

Since $a'(t)$ is very steep (Fig. 3), the first time step should be small. It follows from Eq. (1.17) that $a_i(t) \approx (\mathrm{const.})_i t^{-1/2}$ for ET in Debye solvents where the constant depends on the longitudinal relaxation time $\tau_L$. The same expression applies also for non-Debye solvents except that the constant is determined by the relaxation at short times—see Sec. IV. It follows that $ta_i(t)$ is well behaved in the limit $t\to 0$. Using this in Eq. (5.1), enables the survival probability $Q_2(t')$ after the first time step to be calculated accurately.

The method described here is similar to the procedure introduced by Perram in the theory of fluids to compute the correlation functions from Baxter's integral equation which follows from the Wiener–Hopf factorization of the direct correlation function.[26] It provides a convenient and general method to determine the survival probabilities for electron transfer in all solvents, even those with multiple relaxation times, without the introduction of additional approximations, e.g., an effective relaxation time. An alternative is the numerical solution of the coupled differential equations which is much more computationally demanding.[27]

## VI. RESULTS AND DISCUSSION

The standard free energy of the reaction $\beta\Delta G^0$, the contributions of ligand vibration $\lambda_q$ and solvent polarization $\lambda_0$ to the reorganization energy, the time correlation function $\Delta(t)$ along the reaction coordinate, and the constant $k_0$, which is determined by the reaction adiabaticity, are input parameters or functions in our calculations of the survival probabilities in ET reactions. Of these, the standard free-energy change $\Delta G^0$ and the time correlation function $\Delta(t)$, as we have seen in Sec. II, can be determined experimentally. Although we treat $\sqrt{\beta}k_0$ as a parameter in our calculations, its determination is, strictly speaking, a quantum-mechanical problem. The contributions of the reorganization energies are conveniently characterized by their sum $\lambda$ and the ratio $\lambda_q/\lambda_0$ or $A=\lambda_0/\lambda$ which is equal to 0 and 1, respectively, in the wide and narrow window limits. A simple exponential time decay of the reactants is predicted in the wide window limit and additionally, for Debye solvents, in the slow reaction limit

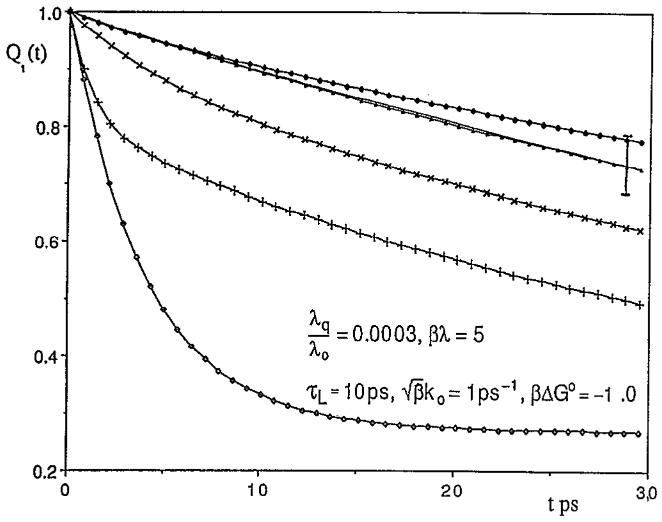

FIG. 6. Plot of the survival probabilities of the reactants on ET near the narrow window limit ($\lambda_q/\lambda_0=0.0003$) in a Debye solvent ($\tau_L=10$ ps). $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \text{ps}^{-1}$, and $\beta\Delta G^0=-1.0$. (—) Numerical solution of the coupled differential equation; (—◆—) integral equation; (—+—) double exponential; (—◇—) single exponential; (—▲—) single-exponential interpolation formula; (—×—) double-exponential interpolation formula. The difference between the solutions to the differential and integral equations is of the same order as the error in the numerical solution to the differential equation.

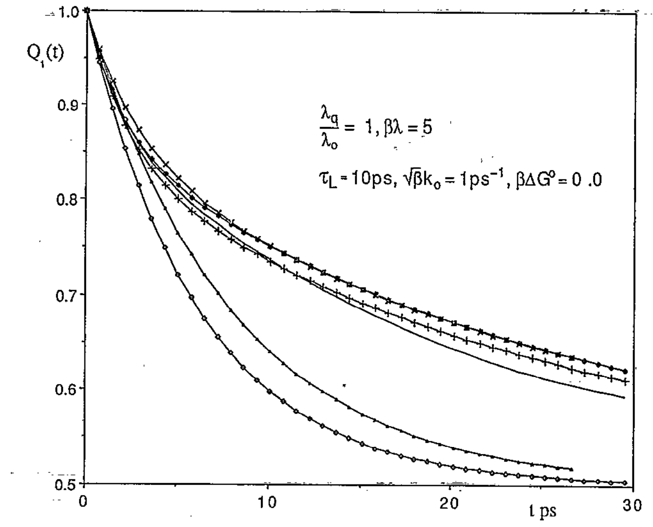

FIG. 8. Plot of the survival probabilities of the reactants after ET when when $\lambda_q/\lambda_0=1$ in a Debye solvent ($\tau_L=10$ ps) assuming $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \text{ps}^{-1}$, and $\beta\Delta G^0=0.0$. Legend as in Fig. 6.

while multiexponential behavior is expected, even for ET in Debye solvents, in the narrow window and nondiffusion limits. As discussed in Sec. III, multiexponential time dependence of the survival probabilities becomes a single exponential at long times which allows a rate constant to be determined.

The accurate determination of the parameters $\sqrt{\beta}k_0$, $\beta\lambda$, and $\lambda_q/\lambda_0$ for a particular ET reaction is beyond the scope of this investigation and we do not attach any special relevance to the particular values chosen for our calculations except that they fall within the expected range. The detailed functional form (e.g., exponential or biexponential) assumed for the time correlation function $\Delta(t)$, however, has a firmer theoretical foundation based on its identity with the experimentally determined time correlation function $S(t)$ for the free energy of solvation of the reacting intermediates. As discussed in Sec. II, this assumes that the solvent response to the polarization field is linear.

In Figs. 6–9 we present our calculations of the survival probabilities for ET in solvents whose solvation dynamics is determined by a single relaxation time—see Eq. (2.11) and Table II. The practical difficulty in solving the integral equation at the narrow window limit, where it is exact, was discussed in Sec. V. We used the approximate but accurate solution given there or the solution to the differential equation itself to determine the survival probability in the first

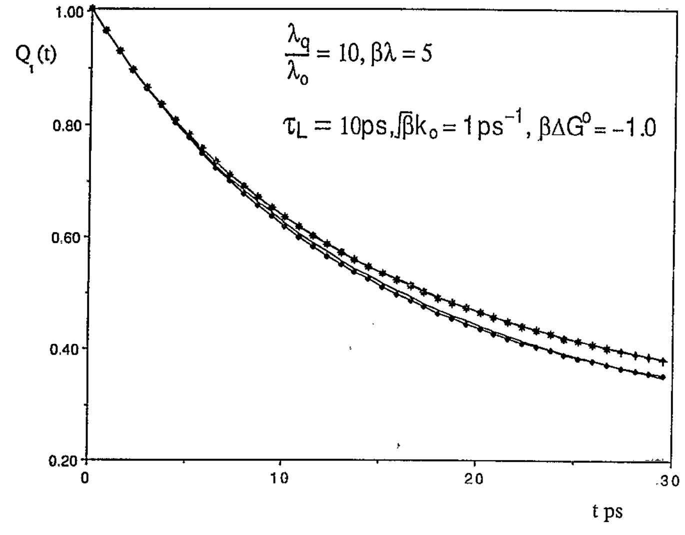

FIG. 7. Plot of the survival probabilities of the reactants after ET near the wide window limit ($\lambda_q/\lambda_0=10$) in a Debye solvent ($\tau_L=10$ ps) when $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \text{ps}^{-1}$, and $\beta\Delta G^0=-1.0$. Legend as in Fig. 6.

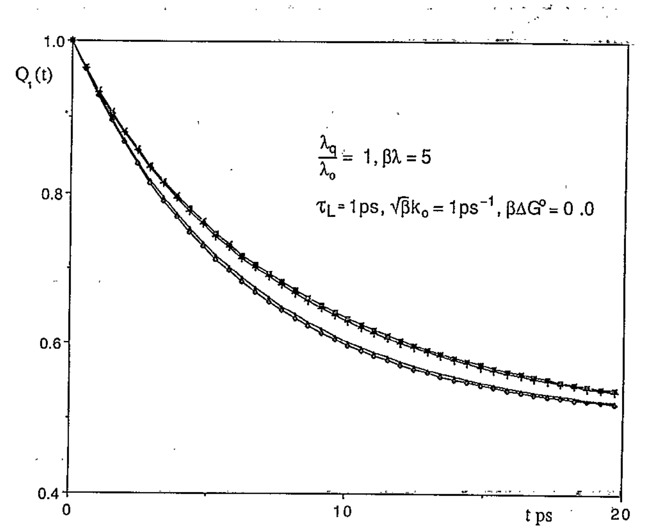

FIG. 9. Plot of the survival probabilities of the reactants after ET in a Debye solvent ($\tau_L=1$ ps) when $\lambda_q/\lambda_0=1$, $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \text{ps}^{-1}$, and $\beta\Delta G^0=0.0$.

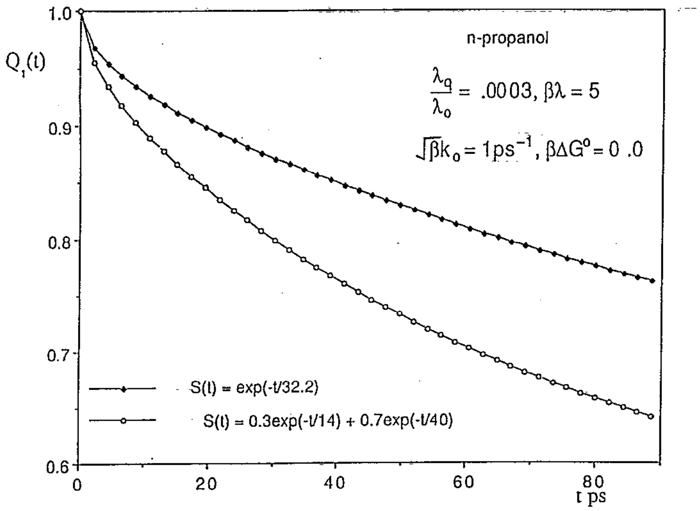

FIG. 10. Plots of the survival probabilities of the reactants for ET in $n$-propanol calculated from the integral equation assuming $\lambda_q/\lambda_0=0.0003, \beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \mathrm{ps}^{-1}$, and $\beta\Delta G^0=0.0$ and two different expressions for $S(t)=\Delta(t)$—see Table II and text for details.

time step ($\approx 5$ fs). Equation (5.3) was used in subsequent time steps to solve the integral equation near this narrow window limit ($\lambda_q/\lambda_0=0.0003$). Figures 6 and 7 show that the agreement with the solution to the coupled differential equation[27] is good. No special precautions are neccesary to obtain the solutions to the integral equation away from the narrow window limit; examples are shown in Figs. 7–9.

As discussed in Sec. III the integral equation is exact, not only in the narrow window limit, but also in the wide window, slow diffusion, and fast reaction limits. Figure 7 illustrates the behavior near the wide window limit and Figs. 8 and 9 confirm that the solutions to the integral equation are close to those of the coupled differential equations even away from these limits. It is seen that the double-exponential formulas [Eq. (4.14)] provide an excellent approximate solution for the parameters used in Figs 7–9. By inference a simple exponential time dependence would be a poor approximation in these examples.

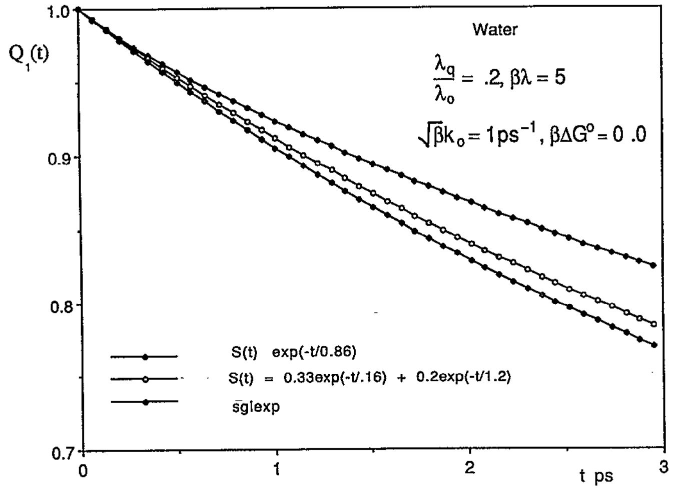

FIG. 11. Plots of the survival probabilities of the reactants for ET in water calculated from the integral equation assuming $\lambda_q/\lambda_0=0.2$, $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \mathrm{ps}^{-1}$, and $\beta\Delta G^0=0.0$ and two different expressions for $S(t)=\Delta t$—see Table II and text for details. The single-exponential solution is also shown—see Eqs. (3.1).

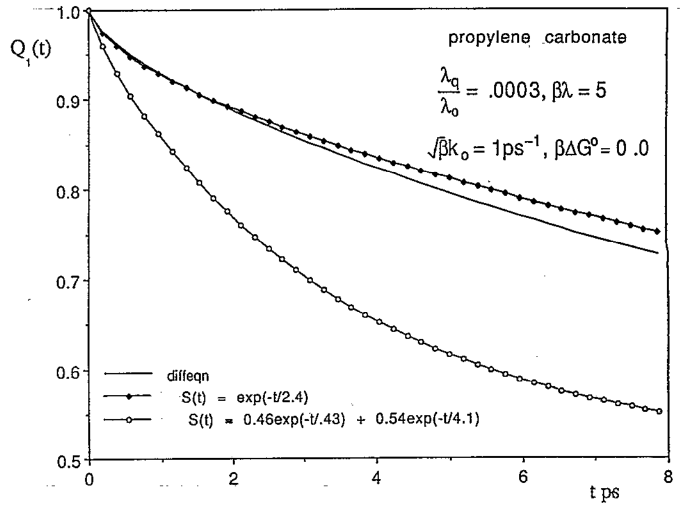

FIG. 12. Plots of the survival probabilities of the reactants for ET in propylene carbonate calculated from the integral equation assuming $\lambda_q/\lambda_0=0.0003$, $\beta\lambda=5$, $\sqrt{\beta}k_0 = 1\ \mathrm{ps}^{-1}$, and $\beta\Delta G^0=0.0$ and two different expressions for $S(t)=\Delta(t)$—see Table II and text for details. The solution to the coupled differential equations when $S(t)$ is determined by a single effective relaxation time is also shown.

An advantage to the integral equation formulation is that it is just as easy to solve for ET reactions in non-Debye solvents as it is for ET in Debye solvents. Additional difficulties do not arise in obtaining the numerical solution when the time correlation function $\Delta(t)$ along the reaction coordinate [or, equivalently, $S(t)$] is more complicated than a simple exponential. The coupled differential equations, on the other hand, are more difficult to solve when $S(t)$ is other than a simple exponential, since the diffusion coefficient becomes time dependent. The relative effects of ligand vibration and solvent relaxation on ET rates are easily studied in our approximation by simply changing the parameter $A$ in the kernel of the integral equations. The demonstration that $\Delta(t)=S(t)$, albeit in the linear regime, enables ET rates in a wide variety of solvents to be compared and investigated systematically.

Our calculations for "model" ET reactions in $n$-propanol, water, and propylene carbonate using the coefficients and relaxation times given in Table II for $S(t)$ are displayed in Figs. 10–12. In all cases, the standard free-energy change was assumed to be zero as it is for simple isotopic exchange reactions (e.g., the $\mathrm{Fe}^{+2}/\mathrm{Fe}^{+3}$ couple). $\sqrt{\beta}k_0$ and $\beta\lambda$ were assumed to be 1.0 ps$^{-1}$ and 5, respectively, which is the assumption made in the other cases that were investigated (Figs. 6–9). A significant vibrational contribution to the reorganization energy ($\lambda_q/\lambda_0=0.2$) was considered for electron transfer in water while the others were studied near the narrow window limit.

From these figures it is clear that the survival probabilities for ET in $n$-propanol and propylene carbonate depend significantly on whether a biexponential or an effective single-exponential time dependence is assumed for

$\Delta(t)$. This difference is much less important for ET reactions in water where the use of the biexponential form for $\Delta(t)$ gives results that are close to the single-exponential decay predicted by [Eq. (4.1)]. It is also clear from these figures that the assumption of an effective longitudinal relaxation time in the calculation of electron-transfer rates is a poor approximation when the solvation dynamics is controlled by widely different relaxation times in different time domains.

We close with a brief comment on some of the main limitations of the present approach to electron transfer and how they may be rectified. First of all it is based on a model (Sumi and Marcus[6]) which treats the vibrational contribution to the reorganization energy in the classical limit. This gives rate constants, in the single-exponential regime, that are in some cases too small by several orders of magnitude,[28] while in others they appear to be correct as seen in Sec. IV.[25] Low values of the calculated ET rates in many cases are attributed to the neglect of high-frequency vibrational modes of the acceptor which increase the rates by decreasing the activation energy and the standard free energy in the inverted region. This problem has been treated theoretically by Jortner and Bixon.[29] To extend the present approach to include this modification of the model we treat each vibrational mode in the multichannel system independently and replace Eq. (1.1) by a pair of equations

$$\partial P_1^i/\partial t = [L_1^i(t) - k_1^i(x)]P_1^i + k_2^i(x)P_2^i, \tag{6.4a}$$

$$\partial P_2^i/\partial t = [L_2^i(t) - k_2^i(x)]P_2^i + k_1^i(x)P_1^i, \tag{6.4b}$$

for each channel $i$. Here $k_1^i(x)$ and $k_2^i(x)$ are defined by equations similar to Eq. (1.20) in which $\nu_q$, $\beta\Delta G_1^*$, and $\beta\Delta G_2^*$ are replaced by the corresponding functions for each channel identified by the superscript $i$. Each channel has the same solvent reorganization energy $\lambda_0$ but different vibrational reorganization energies $\lambda_q^i$ and standard reaction free energies defined by

$$\Delta G^{0,i} = \Delta G^0 - ih\omega. \tag{6.5}$$

The dependence of $\Delta G^{0,i}$ on $i$ produces a corresponding change in the characteristic rate for each channel. Since each channel is dealt with separately, the total rate coefficients in each direction are the corresponding sums over all vibronic channels as suggested in the theory of Jortner and Bixon.[29] This means that the numerical solutions and analytical approximations to the integral equations for ET discussed in Secs. III–V can be carried over to this case by taking the appropriate sums over the different vibronic channels. Recently, Akesson, Walker, and Barbara[28(a)] have used such a model to explain the ET rates of betain-30 in slowly relaxing solvents (the nondiffusion limit) in the inversion region assuming a single solvent relaxation time by summing over just two channels. Our work shows how the multichannel theory can be applied to solvents characterized even by multiple relaxation times.

A second limitation to our solutions is that an equilibrium distribution is assumed initially for the reactants. This can be rectified by going back to Eq. (4.25a) of Ref. 1 which gives the general operator solution for an arbitrary initial state $|f\rangle$ from which the corresponding integral equation approximation for the general case can be derived. Another limitation is the assumption of linear response of the solvent which leads to parabolic potential-energy wells. Deviations from this and the roles of nuclear and electron tunneling which are not explicitly considered in this study remain areas for future investigation.[30,31]

## ACKNOWLEDGMENTS

One of us (J.C.R.) thanks Joseph Hubbard for helpful conversations on solvation dynamics, Professor Robert Dunlap for his interest, and Professor Andrew McCammon for his hospitality at Houston where this work was done.

## APPENDIX: LONG- AND SHORT-TIME APPROXIMATIONS FOR $a_i(t)$ AND ITS LAPLACE TRANSFORM $a_{si}(s)$

When $A=0$, $a_i(t)=k_{ie}$ and the Laplace transform $a_{si}(s)=k_{ie}/s$. We need not discuss this case further in detail and assume in what follows that $A\neq 0$.

### 1. Long-time approximation

The correlation function $\Delta(t)$ is small at long times and it follows from Eqs. (1.17) that

$$a_i(t) \approx k_{ie}[1 - A^2\Delta(t)^2]^{-1/2}. \tag{A1}$$

This equation is indeed exact at all times for $i=1$ when $x_{1c}=0$ ($\lambda=-\Delta G^0$) and for $i=2$ when $x_{2c}-x_0=0$ ($\lambda=\Delta G^0$). These special cases characterize "barrierless" reactions in the forward and reverse directions, respectively, in the narrow window limit. Expansion of Eq. (A1) in powers of $\Delta(t)$ leads to

$$a_i(t) = k_{ie}\sum_{n=0}^{\infty}\frac{2n!}{[2n!!]^2}A^{2n}\Delta(t)^{2n}. \tag{A2}$$

For Debye solvents, $\Delta(t)=\exp(-t/\tau_L)$ and the Laplace transform of Eq. (A2) is

$$a_{si}(s) = k_{ie}\sum_{n=0}^{\infty}\frac{2n!A^{2n}}{[2n!!]^2}\frac{1}{(s+2n/\tau_L)}. \tag{A3}$$

When $\tau_L$ is of the order of picoseconds and $n$ is not zero, we may assume that $n > s\tau_L/2$ for small enough $s$. It follows that in the long-time limit,

$$a_{si}(s) \approx k_{ie}(\tau_L f_A + 1/s), \tag{A4}$$

where

$$f_A = \sum_{n=1}^{\infty}\frac{A^{2n}2n!}{[2n!!]^2 2n}. \tag{A5}$$

When $A=1$ (narrow window limit), explicit summation shows[1] that $f_A \approx 0.6$. Since $0 \leqslant A \leqslant 1$ it follows that $0 \leqslant f_A \leqslant f_1$. To extend this discussion to non-Debye solvents we assume the biexponential form

$$\Delta(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2). \tag{A6}$$

Then $\Delta(t)^{2n}$ can be expanded as

$$\Delta(t)^{2n}=\sum_{i=0}^{2n} C_{2n,i}A_1^{2n-i}A_2^{i}\exp[-t[(2n-i)/\tau_1+i/\tau_2]], \tag{A7}$$

where $C_{2n,i}$ are the binomial coefficients. Substituting this in Eq. (A2), taking Laplace transforms, and using the same argument as for Debye solvents we find

$$a_{si}(s)\approx k_{ie}[F_A(\tau)+1/s], \tag{A8}$$

where

$$F_A(\tau)=\sum_{n=0}^{\infty}\frac{A^{2n}2n!}{[2n!!]^2}\sum_{i=0}^{2n} C_{2n,i}A_1^{2n-i}A_2^{i}\frac{\tau_1\tau_2}{(2n-i)\tau_1+i\tau_2}. \tag{A9}$$

As $A\rightarrow 0$, $F_A(\tau)\rightarrow 0$. For Debye solvents $F_A(\tau)=\tau_L f_A$.

### 2. Short-time approximation

We first discuss the short-time behavior in Debye solvents before discussing the same limit in non-Debye solvents. At short times $t\ll\tau_L$ and $\exp(-t/\tau_L)\approx 1-t/\tau_L$. Using this in Eq. (1.17) we find

$$a_i(t)\approx k_{ie}B_i\exp(-C_i't/\tau_L)/(1+A^2+2A^2t/\tau_L)^{1/2}, \tag{A10}$$

where $C_1' = \beta x_{1c}^2A^2/(1+A)^2$ and $B_1=\exp[\beta x_{1c}^2A^2/(1+A)]$ while $C_2'$ and $B_2$ have the same form as $C_1'$ and $B_1$, respectively, except that $x_{1c}$ is replaced by $x_{2c}-x_0$. Since $A\neq 0$, we can also write this as

$$a_i(t)\approx k_{ie}B_iA^{-1}2^{-1/2}\exp(-C_i't/\tau_L)/[(C+t/\tau_L)^{1/2}], \tag{A11}$$

where $C=(1-A)/2A^2$. The Laplace transform of Eq. (A11) is

$$a_{is}(s)=k_{ie}(B_i\tau_L/A\sqrt{2})\left(\frac{\pi}{C_i'+s\tau_L}\right)^{1/2}\times\exp(X_i)[1-\mathrm{erf}(\sqrt{X_i})], \tag{A12}$$

where $X_i=C(C_i'+s\tau_L)$ and $\mathrm{erf}(\sqrt{X_i})$ is the error function. Equations (A11) and (A12) are our primary results for short times. In the narrow window limit ($A=1$) both $C$ and $X_i\rightarrow 0$ and

$$a_i(t)\approx k_{ie}B_iA^{-1}(\tau_L/2t)^{1/2}\exp(-C_i't/\tau_L). \tag{A13}$$

The coefficient of $\exp(X_i)[1-\mathrm{erf}(\sqrt{X_i})]$ in Eq. (A12) is the Laplace transform of Eq. (A13).

Equation (A12) can be simplified further by assuming $X_i\approx CC_i'=y_i$ in $\exp(X_i)[1-\mathrm{erf}(\sqrt{X_i})]$ which is equivalent to the assumption $\exp(s\tau_L)\approx 1$, which applies when $s\tau_L$ is small. We then find

$$a_{is}(s)=k_{ie}(B_i\tau_L/A\sqrt{2})\left(\frac{\pi}{C_i'+s\tau_L}\right)^{1/2}\exp(y_i)[1-\mathrm{erf}(\sqrt{y_i})], \tag{A14}$$

where

$$y_1=\beta x_{1c}^2(1-A)/[2(1+A)], \tag{A15a}$$

$$y_2=\beta(x_{2c}-x_0)^2(1-A)/[2(1+A)]. \tag{A15b}$$

When $x_{1c}=0$, $C_1'=0$ which occurs in the inversion region for the forward reaction and

$$a_{si}(s)\approx k_{ie}\frac{B_i}{A}\left(\frac{\pi\tau_L}{2s}\right)^{1/2}. \tag{A16}$$

A similar expression for $a_{s2}(s)$ is obtained when $x_{2c}-x_0$ (i.e., $\lambda=\Delta G^0$). Using the definitions of $B_i$, $k_{ie}$, and $C_i'$, and recalling that $A\neq 0$, Eq. (A14) can be written as

$$a_{s1}(s)\approx\alpha_1\tau_L/(x_{1c}^2+s\tau_L\gamma)^{1/2}, \tag{A17a}$$

$$a_{s2}(s)\approx\alpha_2\tau_L/[(x_{2c}-x_0)^2+s\tau_L\gamma]^{1/2}, \tag{A17b}$$

where[32]

$$\alpha_i=k_0[(1+A)/(2A^{3/2})]\exp[y_i(A-1)][1-\mathrm{erf}(\sqrt{y_i})], \tag{A18a}$$

$$\beta\gamma=(1+A)^2/A^2. \tag{A18b}$$

In the narrow window limit ($A\rightarrow 1$), $\alpha_i=k_0$. Equation (A18) can be extended to the wide window limit by using a switching function which lets $\alpha_i\rightarrow 0$ as $A\rightarrow 0$. A simple change which achieves this is to replace $\mathrm{erf}(\sqrt{y_i})$ by $\mathrm{erf}(A^{-1}\sqrt{y_i})$ in Eq. (A18a).

When $x_{1c}\neq 0$ and $x_{2c}-x_0\neq 0$, and for small enough $s$, we recover the simpler approximation:[1,32]

$$a_{s1}(s)\approx\alpha_1\tau_L/|x_{1c}|, \tag{A19a}$$

$$a_{s2}(s)\approx\alpha_2\tau_L/|x_{2c}-x_0|. \tag{A19b}$$

It follows from Eq. (A16) or Eq. (A17) that when $C_i'=0$ (i.e., $x_{1c}=0$ for $i=1$ and $x_{2c}-x_0=0$ for $i=2$) that

$$a_{si}(s)\approx(k_0/2)(\tau_L/A\beta)^{1/2}(1/s)^{1/2}. \tag{A20}$$

This applies at the rate maximum in the inversion region. Elsewhere one could use Eq. (A19).

To extend our discussion of the short-time approximation to non-Debye solvents we need only to replace $\tau_L$ by the initial relaxation time $\tau_{\mathrm{init}}$. For example, if $\Delta(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$, $\tau_{\mathrm{init}}=\tau_1\tau_2/(A_1\tau_2+A_2\tau_1)$.

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