

# Solvent dynamical effects on electron transfer reactions

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An integral equation [Rasaiah and Zhu, *J. Chem. Phys.* **98**, 1213 (1993)] for the survival probabilities of electron transfer (ET) between thermally equilibrated reactants in solution is extended to include quantum effects on the ligand vibration and ET from a nonequilibrium initial state. We derive the kernel of the integral equation using a Green's function technique and demonstrate that it is determined by the solvent dynamics, the relative contributions of ligand and solvent reorganization energies, and the barrier heights for electron transfer. The extension of the theory to ET from a nonequilibrium initial state modifies the integral equation to provide the survival probabilities for the reactants that are not necessarily kinetically of first order, but can be directly compared with experiment. The long time rate, however, shows a simple exponential time dependence that is analyzed in terms of a rate constant with a diffusive solvent controlled component and a remainder. The effect of solvent dynamics on the diffusive part is governed by the same factors that determine the kernel. We find that the fast diffusive mode (small relaxation time) affects the rate of ET reactions with high barriers, while the slow diffusive part (large relaxation times) influences the rate when the barriers are low. Quantum corrections to these effects are calculated using the semiclassical approximation. The theory is used to analyze the ET kinetics of betaine-30 in glycerol triacetate (GTA) over a 100° temperature range and the influence of the details of solvent dynamics on the rates of electron transfer is elucidated. An appendix discusses improved saddle point approximations for the rates of electron transfer reactions calculated using the golden rule. © 1994 American Institute of Physics.

## I. INTRODUCTION

Electron transfer (ET) reactions are ubiquitous in chemistry and theories of their mechanisms and rates continue to develop as new experimental observations are made. The energetic control of the rates of these reactions in solution is well understood,<sup>1</sup> but many other aspects of ET reactions in chemical and biological systems remain to be investigated.<sup>2</sup> Quite recently, advances in ultrafast spectroscopy have led to renewed interest in the role that solvent dynamics play on electron transfer reactions in solution.<sup>3-8</sup> This paper concerns this problem.

Our main theoretical tool is an integral equation approximation for the coupled reaction diffusion differential equations governing reversible electron transfer rates in solution using a model proposed by Sumi and Marcus.<sup>3</sup> This equation is exact in several different limits and is quite accurate between them. It was discussed by us in a series of papers<sup>4-6</sup> and is easily solved on a personal computer<sup>6</sup> providing a simple way to calculate the rates given the details of the solvent dynamics, the total reorganization energy  $\lambda$ , its partitioning between liquid vibrations  $\lambda_q$  and solvent polarization fluctuations  $\lambda_0$ , the standard free energy change  $\Delta G^0$ , and a parameter  $k_0$  that represents the effects of tunneling and curve crossing. The concentrations of the reacting species can also, in many cases, be represented analytically by single or multiexponential functions of time that are, as

shown by a specific example in this paper, very useful in the analysis of experimental data.

A limitation to our integral equation is that it is restricted to ET from thermally equilibrated initial states that precludes its application to experiments in which the reactants are prepared, e.g., by laser excitation. Another unsatisfactory feature is that the kernel of the integral equation was obtained rigorously<sup>5,6</sup> only for ET reactions in non-Debye solvents when ligand vibrations do not contribute to the activation energy. However, ligand vibrations play a significant role in many reactions that require modification of the kernel to include this feature also if the results are to be generally useful. This was done earlier by introducing an effective time-independent operator in the adjoint differential equations without complete justification.<sup>5</sup> A third limitation is that the ligand vibrations were treated classically and transition state theory was used to calculate the rate coefficients.

In this paper, we extend our theoretical work to include ET reactions from a nonequilibrium initial state. This leads to a modified integral equation that is also easily solved on a personal computer with only trivial changes in the numerical methods used earlier.<sup>6</sup> We demonstrate how the kernel of the integral equation can be derived using a Green's function technique that is applicable even when the ligand vibrations contribute significantly to the activation energy of ET reactions in either Debye and non-Debye solvents. We extend these results further by treating the ligand vibrations and rate coefficients quantum mechanically using the golden rule. This leads to a modification of the kernel that presents no additional difficulties in the numerical or analytic solutions

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to the integral equation. We also discuss how the effect of solvent dynamics on the diffusive part of the ET rate constant is modulated by several factors such as the contribution of the outer-shell solvent fluctuations to the total reorganization energy, the barrier heights for the forward and reverse reactions, and quantum effects on the ligand vibrations and the rates of barrier crossing. The theory is used to analyze the ET kinetics of betaine-30 in glycerol triacetate (GTA) that has been studied experimentally<sup>9</sup> over a wide range of temperatures, and we elucidate the conditions under which the details of the solvent dynamics, determined by experiment, computer simulation or theory, can affect the rates of electron transfer. The mathematical treatment presented here extends and simplifies our earlier derivation of the integral equation for the survival probabilities,<sup>4-6</sup> making it broader in scope, and we hope, more readily accessible to others interested in this field.

This paper is subdivided as follows: Section II summarizes the theoretical background to the Sumi-Marcus model of ET and the coupled reaction-diffusion differential equations governing the time dependence of the solvent polarization fluctuations. A Green's function method is used, in Sec. III, to derive the integral equation for ET transfer from non-equilibrated initial states in any solvent. We follow this up in Sec. IV with a semiclassical treatment of the effect of ligand vibration on ET rate coefficients. Section V discusses how the solvent controlled rate constant is modulated by the slow and fast relaxation times, the barrier heights, and ligand vibrations, and we use the theory to discuss an ET experiment (betaine-30 in GTA) in Sec. VI. Section VII discusses the effect of the details of the solvent dynamics in acetonitrile on the rates of model ET reactions. Appendix A contains a brief discussion of the Green's function operator for ET in Debye solvents when the analysis becomes simpler. Appendix B discusses saddle point approximations to the golden rule rate constant for ET rates and improvements to the semiclassical rate coefficients.

## II. THEORETICAL PRELIMINARIES

In the Sumi-Marcus model<sup>3</sup> of electron transfer, both ligand vibration and solvent polarization fluctuations contribute to the total free energies of the reactants ( $i=1$ ) and products ( $i=2$ ) given by

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

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

where

$$V_1(x) = x^2/2, \quad (2.2a)$$

$$V_2(x) = (x-x_0)^2/2 + \Delta G^0. \quad (2.2b)$$

The vibrational motions of the ligands are represented collectively by the coordinate  $q$  and  $\Delta G^0$  is the standard free energy change for the reaction. It is assumed that ligand vibration is much faster than the outer-shell solvent reorganization energy  $x(t)$  that is proportional to the mean square fluctuations of the excess solvent polarization  $\mathbf{P}^{\text{ex}}(\mathbf{r},t)$  away

from its equilibrium value  $\mathbf{P}_1^{0,\text{ex}}(\mathbf{r})$  before ET when the charge distribution is that of the reactants. It is defined by

$$x(t)^2 = (4\pi/c) \int |\mathbf{P}^{\text{ex}}(\mathbf{r},t) - \mathbf{P}_1^{0,\text{ex}}(\mathbf{r})|^2 d\mathbf{r}, \quad (2.3)$$

in which  $c = 1/\epsilon_\infty - 1/\epsilon_0$  is the Pekar factor,  $\epsilon_\infty$  and  $\epsilon_0$  are the high and zero frequency dielectric constants, respectively, and  $\mathbf{P}^{\text{ex}}(\mathbf{r},t)$  is the difference between the total and electronic polarizations of the solvent. The reorganization energy  $\lambda = \lambda_q + \lambda_0$  has contributions from ligand vibrations  $\lambda_q = aq_0^2/2$ , and "outer sphere" solvent polarization fluctuations  $\lambda_0 = x_0^2/2$ , where

$$x_0^2 = (4\pi/c) \int |\mathbf{P}_2^{0,\text{ex}}(\mathbf{r}) - \mathbf{P}_1^{0,\text{ex}}(\mathbf{r})|^2 d\mathbf{r}. \quad (2.4)$$

Here  $\mathbf{P}_2^{0,\text{ex}}(\mathbf{r})$  is the equilibrium excess solvent polarization at  $\mathbf{r}$  due to the product charge distribution. Both  $\mathbf{P}^{\text{ex}}(\mathbf{r},t)$  and  $\mathbf{P}_i^{0,\text{ex}}(\mathbf{r})$  ( $i=1,2$ ) have contributions from the translation and rotation of the solvent molecules, but not from electronic polarization that is assumed to be instantaneous and has been subtracted out. The time correlation function of the excess polarization fluctuations is defined by

$$\Delta(t) = \langle \delta x(t) \delta x(0) \rangle / \langle \delta x^2(0) \rangle, \quad (2.5)$$

where  $\delta x(t) = x(t) - x_0$  and  $\delta x(0) = -x_0$ . It is this function that is related to the solvent dynamics.

Electron transfer, in the Sumi-Marcus model, occurs with rate coefficients  $k_i(x)$  over a range of polarization fluctuations. Generally, ligand vibrations also assist in the activation; the extent of the vibrational stretching  $q$  needed to reach the activated state for a given fluctuation  $x$  of the solvent polarization is obtained from the intersection of the two free energy surfaces along  $xx_0 + aqq_0 = \lambda + \Delta G^0$ . Transition state theory provides the rate coefficient

$$k_i(x) = \nu_q \exp[-\beta \Delta G_i^*(x)] \quad (i=1,2) \quad (2.6)$$

at each polarization fluctuation  $x$ ; it is a Gaussian since the corresponding vibrational free energy barriers  $\Delta G_i^*$  are quadratic. It is readily shown that<sup>3</sup>

$$\Delta G_1^*(x) = (1/2)(\lambda_0/\lambda_q)(x-x_{1c})^2 = [\Delta G^0(x) + \lambda_q]^2/4\lambda_q, \quad (2.7a)$$

$$\Delta G_2^*(x) = (1/2)(\lambda_0/\lambda_q)(x-x_{2c})^2 = [\Delta G^0(x) - \lambda_q]^2/4\lambda_q, \quad (2.7b)$$

where

$$x_{1c} = (\lambda + \Delta G^0)/(2\lambda_0)^{1/2}, \quad (2.8a)$$

$$x_{2c} = (\lambda + \Delta G^0 - 2\lambda_q)/(2\lambda_0)^{1/2}. \quad (2.8b)$$

and the free energy gap

$$\Delta G^0(x) = \Delta G^0 + \lambda_0 - x(2\lambda_0)^{1/2} \quad (2.8c)$$

which depends on the slow coordinate  $x$ . In Eq. (2.6),  $\beta = 1/k_B T$ , where  $k_B$  is Boltzmann's constant and the preexponential factor may be written as

$$\nu_q = k_0 [(\beta \lambda_0 / 2\pi \lambda_q)]^{1/2}, \quad (2.9)$$

where  $k_0$  is a constant. Its calculation is a quantum mechanical problem since it reflects the effects of tunneling through

the barrier, electronic coupling between the free energy surfaces where they intersect, and other characteristics of the electron transfer reaction, e.g., by whether the reaction is adiabatic or not. For nonadiabatic reactions  $\nu_q = (J^2/\hbar)(\beta\pi/\lambda_q)^{1/2}$ , where  $J$  is the electronic coupling matrix element of the reactant and product surfaces at their intersection and  $\hbar = h/(2\pi)$ , where  $h$  is Planck's constant.

Fluctuations in the solvent polarization are determined by the motions of many solvent molecules that are assumed to be similar to Brownian motion in the overdamped limit. The probabilities  $P_1(x,t)$  and  $P_2(x,t)$  of finding the reactant and products, respectively, with a fluctuation  $x$  in the solvent polarization at time  $t$  are then given by pair of coupled reaction-diffusion equations<sup>3-8</sup>

$$\begin{aligned} dP_1(x,t)/dt &= [L_1 - k_1(x)]P_1(x,t) + k_2(x)P_2(x,t), \\ dP_2(x,t)/dt &= [L_2 - k_2(x)]P_2(x,t) + k_1(x)P_1(x,t), \end{aligned} \quad (2.10)$$

where the generalized Smoluchowski operator

$$L_i = D(t)\{\partial^2/\partial x^2 + \beta\partial/\partial x[dV_i(x)/dx]\}, \quad (2.11)$$

in which the diffusion coefficient  $D(t)$  is related to  $\Delta(t)$  by<sup>10,11</sup> by

$$D(t) = -(1/\beta)d \ln \Delta(t)/dt. \quad (2.12)$$

It has been shown that  $\Delta(t)$  is identical to the time correlation function  $S(t)$  of the Born free energy of solvation of the reacting intermediates when the solvent response is linear.<sup>5,6</sup> Solvation dynamics in Debye solvents is characterized by a single relaxation time  $\tau_L$ , when  $S(t) = \exp(-t/\tau_L)$  and  $\beta D(t) = 1/\tau_L$  is a constant. However,  $S(t)$  in many solvents has a more complicated time dependence spanning several relaxation times. In this case,  $D(t)$  becomes time dependent.  $S(t)$  can be determined experimentally using a suitable probe in time delayed fluorescence spectroscopy (TDFS) experiments<sup>9,10</sup> assuming that the system studied (e.g., the probes in TDFS experiments or the Hamiltonian in computer simulations) mimics the reacting intermediates closely enough.

The solution to the coupled differential equations is obtained<sup>3,4</sup> by transforming to the adjoint form

$$\partial q_1(x,t)/\partial t = -[H_1 + k_1(x)]q_1(x,t) + k_2'(x)q_2(x,t), \quad (2.13a)$$

$$\partial q_2(x,t)/\partial t = -[H_2 + k_2(x)]q_2(x,t) + k_1'(x)q_1(x,t) \quad (2.13b)$$

using the substitution

$$q_i(x,t) = P_i(x,t)/g_i(x), \quad (2.14)$$

where

$$\begin{aligned} g_i(x) &= [P_i^{\text{eq}}(x,0)]^{1/2} \\ &= \exp[-\beta V_1(x)/2] \int \exp[-\beta V_i(x)/2] dx \\ &\quad (i=1,2). \end{aligned} \quad (2.15)$$

In Eqs. (2.13),

$$k_1'(x) = k_1(x)g_1(x)/g_2(x), \quad (2.16a)$$

$$k_2'(x) = k_2(x)g_2(x)/g_1(x), \quad (2.16b)$$

and

$$\begin{aligned} H_i(t) &= -D(t) \frac{\partial^2}{\partial x^2} + \frac{\beta D(t)}{2} \left[ \frac{\beta}{2} \left( \frac{dV_i}{dx} \right)^2 - \frac{d^2 V_i}{dx^2} \right] \\ &\quad (i=1,2). \end{aligned} \quad (2.17)$$

For the parabolic potentials considered in Eq. (2.1),

$$H_i(t) = -D(t)[\partial^2/\partial x^2 - (\beta x)^2/4 + \beta/2] \quad (2.18)$$

is similar to the Hamiltonian for a harmonic oscillator except that it has no zero-point energy. The eigenvalues are  $\epsilon_n(t) = n\beta D(t) = -nd \ln \Delta(t)/dt$  ( $n=0,1,2,\dots$ ), i.e.,

$$H_i(t)|u_{n,i}\rangle = \epsilon_n(t)|u_{n,i}\rangle, \quad (2.19)$$

where  $|u_{n,i}\rangle$ 's are the eigenkets and  $|u_{0,i}\rangle = |g_i\rangle$  is the ground state eigenfunction. Note that the time dependence of  $H_i(t)$  leads to time-dependent eigenvalues in non-Debye solvents. The eigenkets are, however, time independent and, after a simple change of variables, they are seen to be essentially those of a harmonic oscillator.<sup>3,4</sup> In Debye solvents,  $D(t)$  is time independent and the eigenvalues of  $H_i$  are  $\epsilon_n = n/\tau_L$ . The ground state eigenfunction  $g_i(x)$  satisfies the equation  $H_i g_i(x) = 0$  for ( $i=1,2$ ).

The survival probabilities and thermally averaged rate constants are<sup>3-8</sup>

$$Q_i(t) = \int g_i(x)q_i(x,t)dx = \langle g_i|q_i(t)\rangle \quad (i=1,2), \quad (2.20)$$

$$k_{ie} = \langle g_i(x)|k_i(x)|g_i(x)\rangle \quad (i=1,2), \quad (2.21)$$

respectively, and the initial conditions, written as  $q_1(x,0) = f_1(x)$  and  $q_2(x,0) = 0$ , imply

$$Q_1(0) = \int P_1(x,0)dx = \langle g_1|f_1\rangle = 1, \quad (2.22a)$$

$$Q_2(0) = 0. \quad (2.22b)$$

Carrying out the integration in Eq. (2.21) using Eq. (2.15), one finds that the averaged rate constants in the forward and backward directions are given by

$$k_{ie} = \nu \exp(-\beta E_i) \quad (i=1,2), \quad (2.23)$$

where

$$E_1 = \lambda(1 + \delta)^2/4, \quad (2.24a)$$

$$E_2 = \lambda(1 - \delta)^2/4 \quad (2.24b)$$

are the activation energies in the forward and reverse directions, respectively, and  $\delta = \Delta G^0/\lambda$ . As expected  $E_1 - E_2 = \Delta G^0$  and it follows that

$$k_{2e} = k_{1e} \exp(\beta \Delta G^0). \quad (2.25)$$

The preexponential factor in Eq. (2.23) is  $\nu = \nu_q(\lambda_q/\lambda)^{1/2}$ . For nonadiabatic reactions,  $\nu = (J^2/\hbar)(\beta\pi/\lambda)^{1/2}$ , where  $J$  is the electronic coupling matrix.

In the next section, we consider the derivation of our integral equation for the survival probabilities for ET transfer reactions from a nonequilibrated state in any solvent for

which the time correlation function  $\Delta(t)$  is known. As discussed earlier, this can be obtained from experiment, simulation, or theory when the solvent response is linear.

### III. GREEN'S FUNCTION SOLUTION FOR ET IN NON-DEBYE SOLVENTS

Our solution of Eq. (2.13), which leads to an integral equation for ET from an arbitrary state  $|f_1\rangle$ , starts with the Green's functions  $G_i(x,y;t)$  that are the solutions to

$$\frac{\partial G_i(x,y;t)}{\partial t} + H_i(t)G_i(x,y;t) = \delta(x-y)\delta(t) \quad (i=1,2). \quad (3.1)$$

To determine this, consider the (Schrödinger-like) equation

$$\frac{\partial \Psi_i}{\partial t} = -H_i(t)\Psi_i \quad (i=1,2). \quad (3.2)$$

The time dependence of the Hamiltonian is only in the factor  $D(t)$  and in this case

$$\Psi_i(x,t) = \sum_n \exp\left[-\int_0^t H_i(t')dt'\right] u_{n,i}(x), \quad (3.3)$$

where  $u_{n,i}(x)$ 's are the eigenfunctions of  $H_i(t)$ . The eigenvalues of  $H_i(t)$  are  $\epsilon_{n,i}(t) = -n \ln \Delta(t)/dt$ . Using this in Eq. (3.3), we have

$$\Psi_i(x,t) = \sum_n \exp[n \ln \Delta(t)] u_{n,i}(x). \quad (3.4)$$

The Green's functions  $G_i(x,y;t)$  are the density matrices defined by

$$G_i(x,y;t) = \sum_n u_{n,i}^*(x) \exp\left[-\int_0^t H_i(t')dt'\right] u_{n,i}(y) \quad (i=1,2), \quad (3.5)$$

where it follows, from the eigenvalues of  $H_i(t)$ , that the argument in the exponential is  $n \ln \Delta(t)$ . The corresponding Green's function operator is

$$G_i(t) = \sum_n |u_{n,i}\rangle \exp[n \ln \Delta(t)] \langle u_{n,i}| \quad (i=1,2). \quad (3.6)$$

When ET occurs in Debye solvents,  $H_i(t)$  is time independent and  $n \ln \Delta(t) = -n/\tau_L$ . The Green's functions are then essentially the density matrices of a Harmonic oscillator. It has been discussed elsewhere,<sup>3,4</sup> where it was shown that

$$G_1(x,y;t) = (2\pi k_B T C_1)^{-1/2} \exp\{-(\beta/8)[(x+y)^2 C_2 + (x-y)^2 C_3]\}, \quad (3.7a)$$

$$G_2(x,y;t) = (2\pi k_B T C_1)^{-1/2} \exp\{-(\beta/8)[(x+y-2x_0)^2 C_2 + (x-y)^2 C_3]\}, \quad (3.7b)$$

in which  $C_1 = [1 - \exp(-2t/\tau_L)]$ ,  $C_2 = \tanh[t/(2\tau_L)]$ , and  $C_3 = 1/C_2$ . This suggests that the general solution for non-Debye solvents has the same form except that

$$C_1 = 1 - \Delta(t)^2, \quad (3.8a)$$

$$C_2 = [1 - \Delta(t)]/[1 + \Delta(t)]. \quad (3.8b)$$

That this is indeed the case can be verified by direct substitution in Eq. (3.1) taking note of Eq. (2.12)! As  $t \rightarrow 0$ ,  $\Delta(t) \rightarrow 1$  and  $G_i(x,y;t) \rightarrow \delta(x-y)$ .

The solution to Eq. (2.13) with initial conditions  $q_1(x,0) = f_1(x)$  and  $q_2(x,0) = 0$  can now be written as

$$q_1(x,t) = \int dy G_1(x,y;t) f_1(y) - \int_0^t dt' \int dy G_1(x,y;t-t') [k_1(y)q_1(y,t') - k_2'(y)q_2(y,t')], \quad (3.9a)$$

$$q_2(x,t) = - \int_0^t dt' \int dy G_2(x,y;t-t') [k_2(y)q_2(y,t') - k_1'(y)q_1(y,t')]. \quad (3.9b)$$

Taking the Laplace transform with respect to time, we have

$$q_1(x,s) = \int dy G_1(x,y;s) f_1(y) - \int dy G_1(x,y;s) \times [k_1(y)q_1(y,s) - k_2'(y)q_2(y,s)], \quad (3.10a)$$

$$q_2(x,s) = - \int dy G_2(x,y;s) [k_2(y)q_2(y,s) - k_1'(y)q_1(y,s)], \quad (3.10b)$$

where, in our notation,  $G_i(x,y;s)$  is the Laplace transform of  $G_i(x,y;t)$ . It is convenient to define the operator

$$O_i(s) = \int dy G_i(x,y;s), \quad (3.11)$$

from which it follows that  $O_i(s)|g_i\rangle = |g_i\rangle/s$ . This enables Eq. (3.10) to be rewritten as

$$|q_1(x,s)\rangle = O_1(s)|f_1\rangle - O_1(s)[k_1|q_1(y,s)\rangle - k_2'|q_2(y,s)\rangle], \quad (3.12a)$$

$$|q_2(x,s)\rangle = -O_2(s)[k_2|q_2(y,s)\rangle - k_1'|q_1(y,s)\rangle]. \quad (3.12b)$$

It is shown in the Appendix that  $O_i(s) = (s + H_i)^{-1}$  when the Hamiltonian is time independent (Debye solvent). We also note that the inverse Laplace transform of  $\langle r(x)|O_i(s)|q(y)\rangle$  is  $\langle r(x)|G_i(t)|q(y)\rangle$ , where the bra-ket notation implies multiplication and integration over the variables  $x$  and  $y$ .

Equations (3.12) are a set of equations that are decoupled by inserting the approximation<sup>3,4</sup>

$$1 \approx k_{ie}^{-1}|g_i\rangle \langle g_i| = k_{ie}^{-1}|k_{ig}i\rangle \langle g_i| \quad (i=1,2) \quad (3.13)$$

after  $k_1$  and before  $k_2'$  in Eq. (3.12a) and similarly in Eq. (3.12b). Decoupling Eq. (3.12), we find

$$|q_1(x,s)\rangle = O_1(s)|f_1\rangle - C k_{1e}^{-1} O_1(s)|k_1 g_1\rangle, \quad (3.14a)$$

$$|q_2(x,s)\rangle = -C k_{2e}^{-1} O_2(s)|k_2 g_2\rangle, \quad (3.14b)$$

where

$$C = \langle g_1|k_1|q_1(s)\rangle - \langle g_2|k_2|q_2(s)\rangle. \quad (3.15)$$

Taking the scalar products of Eq. (3.14a) with  $|k_1 g_1\rangle$  and Eq. (3.14b) with  $|k_2 g_2\rangle$ , we find on subtraction that

$$C = \langle g_1 k_1 | O_1(s) | f_1 \rangle / [1 + a_{s1}(s) + a_{s2}(s)] \quad (3.16a)$$

$$= \int \int dx dy g_1(x) k_1(x) G_1(x, y; s) f_1(y) / \\ \times [1 + a_{s1}(s) + a_{s2}(s)], \quad (3.16b)$$

where

$$a_{si}(s) = k_{ie}^{-1} \langle g_i k_i | O_i(s) | k_i g_i \rangle \quad (3.17a)$$

$$= k_{ie}^{-1} \int \int dx dy g_i(x) k_i(x) G_i(x, y; s) k_i(y) g_i(y) \\ (i=1, 2). \quad (3.17b)$$

Inserting Eq. (3.7) for  $G_i(x, y; t)$  in the inverse transform of Eq. (3.17), we obtain after a tedious integration that

$$a_1(t) = k_{1e} [1 - A^2 \Delta(t)^2]^{-1/2} \exp \left[ \beta x_{1c}^2 \frac{A^2 \Delta(t)}{1 + A \Delta(t)} \right], \quad (3.18a)$$

$$a_2(t) = k_{2e} [1 - A^2 \Delta(t)^2]^{-1/2} \exp \left[ \beta (x_{2c} - x_0)^2 \frac{A^2 \Delta(t)}{1 + A \Delta(t)} \right], \quad (3.18b)$$

where  $A = \lambda_0 / \lambda$  measures the relative contribution of solvent polarization fluctuations to the total reorganization energy.

These expressions for  $a_i(t)$  were derived earlier by us<sup>5,6</sup> using a less rigorous argument; here they are obtained unambiguously for inner- and outer-sphere ET reactions in all (Debye and non-Debye) solvents when ligand vibrations also contribute to the reorganization energy, i.e., when  $A \neq 1$ . Making use of Eqs. (2.8) and (2.24), they can be written as

$$a_1(t) = k_{1e} [1 - A^2 \Delta(t)^2]^{-1/2} \exp \left[ \beta E_1 \frac{2A \Delta(t)}{1 + A \Delta(t)} \right], \quad (3.19a)$$

$$a_2(t) = k_{2e} [1 - A^2 \Delta(t)^2]^{-1/2} \exp \left[ \beta E_2 \frac{2A \Delta(t)}{1 + A \Delta(t)} \right], \quad (3.19b)$$

which displays their dependence on the activation energies  $E_1$  and  $E_2$  for the forward and back reactions. Since  $k_{2e}/k_{1e} = \exp(\beta \Delta G^0)$  and  $E_1 - E_2 = \Delta G^0$ , we see that

$$a_2(t) = a_1(t) \exp \{ \beta \Delta G^0 [1 - A \Delta(t)] / [1 + A \Delta(t)] \}. \quad (3.20)$$

The sum of  $a_2(t)$  and  $a_1(t)$  is the kernel  $a(t)$  in our integral equation solution for the survival probabilities that we will derive. Note that as  $t \rightarrow \infty$ ,  $a_i(t) \rightarrow k_{ie}$ . Also  $a_2(t) = a_1(t)$  when  $\Delta G^0 = 0$  (e.g., isotopic exchange reactions like  $\text{Fe}^{+2} + \text{Fe}^{*+3} = \text{Fe}^{*+2} + \text{Fe}^{+3}$ , where the asterisk denotes isotopic substitution) and  $a_2(t) = a_1(t) \exp(\beta \Delta G^0)$  in the wide window limit when  $A = 0$ . In this case, the reorganization energy is due entirely to inner-sphere ligand vibrations. However, when solvent polarization fluctuations play a significant role in electron transfer (i.e.,  $A \neq 0$ ), the ratio of  $a_2(t)$  to  $a_1(t)$  changes with time when  $\Delta G^0$  is finite.

The scalar products of Eqs. (3.14) with  $|g_i\rangle$  provide the transforms of the survival probabilities [see Eq. (2.20)]

$$Q_1(s) = 1/s - Q_2(s), \quad (3.21a)$$

$$Q_2(s) = C/s, \quad (3.21b)$$

where  $C$  is given by Eq. (3.16). Expanding  $f(y)$  in the set of eigenfunctions of  $H_1(t)$  and inserting this in Eq. (3.16), we have

$$C[1 + a_{s1}(s) + a_{s2}(s)] = \langle g_1 k_1 | O_1(s) | f_1 \rangle \quad (3.22)$$

$$= k_{1e} s^{-1} + \sum_{n=1}^{\infty} \langle g_1 k_1 | O_1(s) | u_{n,1} \rangle \\ \times \langle u_{n,1} | f_1 \rangle, \quad (3.23)$$

where we have used  $\langle g_1 k_1 | O_1(s) | g_1 \rangle = k_{1e} s^{-1}$ . Substituting Eq. (3.23) in Eq. (3.19), taking the inverse Laplace transform, and using the convolution theorem, we see that the survival probabilities are given by

$$Q_1(t) = 1 - Q_2(t), \quad (3.24a)$$

$$Q_2(t) = k_{1e} t + F(t) - \int_0^t a(t-u) Q_2(u) du, \quad (3.24b)$$

where the kernel  $a(t) = a_1(t) + a_2(t)$  and

$$F(t) = \sum_{n=1}^{\infty} \int_0^t \langle u_{n,1} | f_1 \rangle \langle g_1 k_1 | G_1(x, y; t-t') | u_{n,1} \rangle dt'. \quad (3.25)$$

$F(t)$  is identically zero when the initial state  $|f_1\rangle$  is the thermally equilibrated state  $|g_1\rangle$ . Using Eq. (3.6) it is found that

$$F(t) = \sum_{n=1}^{\infty} d_{n,1} \int_0^t \exp[n \ln \Delta(t')] dt', \quad (3.26)$$

where

$$d_{n,1} = \langle u_{n,1} | f_1 \rangle \langle g_1 k_1 | u_{n,1} \rangle. \quad (3.27)$$

In a Debye solvent,  $\ln \Delta(t') = -t'/\tau_L$  and it follows that

$$F(t) = \sum_{n=1}^{\infty} \frac{d_{n,1} \tau_L}{n} [1 - \exp(-nt/\tau_L)] \quad (3.28)$$

which vanishes for very large and very small values of  $\tau_L$ . This extends the integral equation derived previously<sup>6</sup> for ET in Debye and non-Debye solvents to reactions in which the initial state is not necessarily thermally equilibrated. It leads to an additional term  $F(t)$  that was absent from our earlier discussions of the integral equation for ET.<sup>4-7</sup>

The solution to the integral equation is determined by the kernel  $a(t)$  in which  $A$  and  $\Delta(t)$  always occur together as a pair. As  $A$  ranges from 0 to 1, the primary contribution to the reorganization energy changes from inner-sphere ligand vibration to outer-sphere solvent polarization effects. The parameter  $A$ , which is the fractional contribution of the solvent polarization fluctuations to the total reorganization energy, also acts as a switching function that turns on the effect of solvent dynamics characterized by the time correlation function  $\Delta(t)$ . The numerical method described previously<sup>6</sup> to solve the integral equation when  $F(t)$  is zero can be applied to Eq. (3.24) as well with trivial modification.

In the next section, we discuss the modification of the thermally equilibrated rate constant  $k_{ie}$  and the kernel due to quantum effects on ligand vibration.

#### IV. THE GOLDEN RULE RATE COEFFICIENTS AND THE MODIFIED KERNELS IN THE SEMICLASSICAL APPROXIMATION

The rate coefficients defined by Eqs. (2.6) and (2.7) follow from classical transition state theory and are correct at high temperatures. Here we discuss approximations that take into account some of the quantum effects that have been neglected, leading to a modification of the kernel for the rates of electron transfer.

In the transition state approximation for  $k_i(x)$ , the vibrational motion of the ligands is treated classically although, as noted in the Introduction, the preexponential factor allows for quantum mechanical tunneling through the barrier. A more satisfactory treatment is to use the golden rule assuming a finite number of vibrational modes for the ligands.<sup>11,12</sup> The vibrational contributions to the free energy surfaces are the sums over these modes and Eqs. (2.1) are replaced by

$$V_1(q, x) = \sum_i a_i q_i^2 / 2 + V_1(x), \quad (4.1a)$$

$$V_2(q, x) = \sum_i a_i (q_i - q_{i,0})^2 / 2 + V_2(x), \quad (4.1b)$$

where  $a_i = \mu_i \omega_i^2$ , in which  $\mu_i$  is the reduced mass and  $\omega_i$  is the ligand vibrational frequency. Identifying  $q_{i,0}$  with  $2\gamma_i / (\mu_i \omega_i^2)$ , where  $\gamma_i$  is the coupling constant of the  $i$ th mode between the initial and final states, one finds that Eqs. (4.1) correspond to the well-known spin-boson model with the vibrational reorganization energy given by

$$\lambda_q = \sum_i a_i q_{i,0}^2 / 2 = \sum_i 2\gamma_i^2 / (\mu_i \omega_i^2). \quad (4.1c)$$

As seen in Eqs. (2.7) and (2.8), the slow motion of the solvent polarization provides an effective free energy gap  $\Delta G^0(x)$  when  $x$  is out of equilibrium. The rate coefficients for the fast modes can be evaluated by using standard reaction rate theories, e.g., classical transition state theory, or one could include quantum effects by using the golden rule to evaluate the rate, treating  $\Delta G^0(x)$  as a constant. Although the rate constant for harmonic potential wells has been discussed by a number of authors,<sup>11,12</sup> the incorporation of solvent dynamics presents new difficulties.

In principle, one can easily write down a general golden rule expression with the effective nonequilibrium free energy gap given in Eq. (2.8c) [see Eqs. (B1)–(B3)], but it is a formidable task to solve the corresponding diffusion-reaction equations with several vibrational modes without introducing further approximations. Expressions of varying accuracy can be realized by using saddle point approximations<sup>14</sup> to calculate electron transfer rate coefficients.<sup>13,15–19</sup> The details are discussed in Appendix B and the important results are presented in this section.

A saddle point approximation obtained by expanding the phase integral to second order in  $t$  is Eq. (B18) of Appendix B which leads to a semiclassical rate coefficient<sup>15</sup>

$$k(x) = \frac{2\pi J^2}{\hbar} \sqrt{\frac{1}{4\pi k T^\dagger \lambda_q}} \exp\left\{-\frac{[\Delta G^0(x) + \lambda_q]^2}{4\pi k T^\dagger \lambda_q}\right\}. \quad (4.2)$$

Here the effective temperature  $T^\dagger$  is defined by<sup>11</sup>

$$k_B T^\dagger = \frac{\hbar}{4\lambda_q} \sum_j a_j \omega_j q_{j0}^2 \coth \frac{\beta \hbar \omega_j}{2}, \quad (4.3)$$

in which the sum is over all the vibrational modes. This incorporates many quantum modes in a compact but approximate form and leads to the classical limit, when  $T^\dagger = T$ , for all  $\Delta G^0(x)$ . Equation (4.2) can be rewritten as

$$k_i^\dagger(x) = \nu_q^\dagger \exp[-\beta^\dagger \Delta G_i^*(x)] \quad (i=1,2), \quad (4.4a)$$

where  $\Delta G_i^*(x)$  is defined by Eqs. (2.7) which contain the free energy gap  $\Delta G^0(x)$ . For a nonadiabatic reaction, the preexponential factor in Eq. (4.4a)

$$\nu_q^\dagger = (J^2/\hbar)(\beta^\dagger \pi/\lambda_q)^{1/2}. \quad (4.4b)$$

At high temperatures, Eq. (4.4a) reduces to the classical limit given in Eq. (2.6). On taking the thermal Boltzmann average of  $k_i^\dagger(x)$ , we find

$$k_{ie}^\dagger = \nu_q D^{-1/2} \exp(-\beta E_i^\dagger) \quad (i=1,2), \quad (4.5)$$

where  $\nu_q = \nu_q^\dagger (\beta/\beta^\dagger)^{1/2}$ ,  $E_1^\dagger = (\lambda + \Delta G^0)^2 / (4D\lambda_q)$ ,  $E_2^\dagger = (\lambda - \Delta G^0)^2 / (4D\lambda_q)$ , and  $D = \lambda_0/\lambda_q + T^\dagger/T$ . This can be simplified further by defining

$$A^\dagger = \lambda_0/D\lambda_q = A/[A + (1-A)(T^\dagger/T)] \quad (4.6a)$$

and

$$\nu^\dagger = \nu(A^\dagger/A)^{1/2}, \quad (4.6b)$$

where  $\nu = \nu_q(\lambda_q/\lambda)^{1/2}$ . It is then easily shown that

$$E_i^\dagger = E_i(A^\dagger/A) \quad (i=1,2), \quad (4.7)$$

and

$$k_{ie}^\dagger = \nu^\dagger \exp(-\beta E_i^\dagger) \quad (i=1,2), \quad (4.8)$$

which is similar in form to Eq. (2.23). We see that quantum effects of intramolecular ligand vibration influence both the exponential and preexponential factors of the thermally equilibrated rates. Since  $T^\dagger \geq T$ ,  $A^\dagger \geq A$ , one expects from Eq. (4.8) that  $k_{ie}^\dagger \geq k_{ie}$  unless the reaction is barrierless. At high temperature,  $T^\dagger \approx T$ , and Eq. (4.8) becomes identical to Eq. (2.23).

On repeating our derivation of the integral equation in Sec. III using Eq. (4.2) instead of Eq. (2.6) for  $k_i(x)$ , we find, after some lengthy analysis, that the kernels given in Eqs. (3.19) are now changed to

$$a_1^\dagger(t) = k_{1e}^\dagger (1 - A^{\dagger 2} \Delta(t)^2)^{-1/2} \exp\left[\beta E_1^\dagger \frac{2A^\dagger \Delta(t)}{1 + A^\dagger \Delta(t)}\right], \quad (4.9a)$$

$$a_2^\dagger(t) = k_{2e}^\dagger [1 - A^{\dagger 2} \Delta(t)^2]^{-1/2} \exp\left[\beta E_2^\dagger \frac{2A^\dagger \Delta(t)}{1 + A^\dagger \Delta(t)}\right]. \quad (4.9b)$$

The modified kernels [Eqs. (4.9)] should be used, instead of Eqs. (3.19), when quantum corrections to the thermal equi-

librium rate constant are significant but can be treated in the semiclassical approximation. The numerical method of solution of the integral equations<sup>6</sup> remains the same. At high temperatures  $T^\ddagger \rightarrow T$ ,  $A^\ddagger \rightarrow A$ ,  $E_i^\ddagger \rightarrow E_i$ , and the results in Sec. V are recovered. Note also that  $A^\ddagger \rightarrow A$  as  $A \rightarrow 1$  or 0 when the quantum effects of ligand vibration on the switching functions can be neglected. Their influence on the diffusion controlled rate  $k_{id}$  is discussed in the next section.

A criticism<sup>17,18</sup> of the semiclassical approximation equation (4.2) is that it overestimates the rate for symmetrical self-exchange reactions, e.g., the ferrous/ferric reaction and underestimates the rates in the extreme inverted region. Siders and Marcus<sup>13(b)</sup> studied quantum effects in several ET reactions, and it is evident from their comparisons in Table II of Ref. 13(b) that the semiclassical approximation is a good approximation for some reactions in the normal and weakly inverted regimes. In such cases, its transparent form and easy manipulation makes it useful in introducing quantum effects in the analytic development of a theory and we have used it in discussing quantum corrections to the kernels of our integral equation for electron transfer. Justification of its application to betaine-30 is discussed in Sec. VI.

van Duyne and Fischer and Fischer and van Duyne<sup>17</sup> also developed approximations for electron transfer reactions with large free energies (i.e., unsymmetrical reactions) by

expanding the rate coefficient to second order in  $t$  [see Eq. (13) of Ref. 17(b)] around the saddle point. This is similar to the semiclassical approximation derived in Appendix B and leads to a saddle point approximation for electron transfer rates that has been used to discuss ET rates in the inverted region.

To go beyond the semiclassical approximation, we note that a compact saddle-point expression for rate coefficient in symmetrical ET systems has been derived by Chandler and Bader.<sup>19</sup> It is accurate to within 20% by comparison with computer simulations of the self-exchange ferrous/ferric reaction. Saddle point approximations discussed earlier by Buhks *et al.*<sup>18</sup> and Siders and Marcus<sup>13</sup> are in less convenient form. We discuss the general problem in Appendix B and suggest the approximation

$$t_0 = i\beta\hbar[1 + a(T)\Delta G^0(x)/\lambda_q]/2 \quad (4.10)$$

for the stationary phase value of the time at the saddle point for symmetrical and unsymmetrical ET reactions. It reduces to the well-known  $t_0 = i\beta\hbar/2$  for symmetrical self-exchange reactions<sup>19</sup> and contains, for other cases, a parameter  $a(T)$  that approaches one at high temperatures. Elsewhere,  $a(T)$  must be determined numerically or empirically. e.g.,  $a(T) \approx T/T^\ddagger$ , where  $T^\ddagger$  is defined in Eq. (4.3). The rate coefficient which follows from Eq. (4.10) is

$$k^\ddagger(x) = \frac{\pi(J^2/\hbar^3)^{1/2} \{ \exp[-\beta\Delta G^0(x)[1 + a(T)\Delta G^0(x)/\lambda_q]/2 + f(t_0) \}}{\int_0^\infty d\omega \phi(\omega) \cosh(\eta\omega) \operatorname{cosech}(\beta\hbar\omega/2)}^{1/2}, \quad (4.11)$$

where

$$f(t_0) = -\frac{2}{\pi\hbar} \int_0^\infty d\omega \phi(\omega) \omega^{-2} \{ \tanh(\beta\hbar\omega/4) - [\cosh(\eta\omega) - 1] \operatorname{cosech}(\beta\hbar\omega/2) \}, \quad (4.12)$$

$\eta = a(T)\beta\hbar\Delta G^0(x)/(2\lambda_q)$ , and the density of states  $\phi(\omega)$  is defined in Eq. (B4) of Appendix B. Equation (4.11) reduces to the rate coefficient (B12) for symmetrical ET reactions discussed by Chandler and Bader<sup>19</sup> when  $\eta=0$ . It leads correctly to the classical limit at high temperature.

## V. THE DIFFUSION LIMITED RATE CONSTANT

Solvation dynamics affects ET reactions in solution when the intrinsic rate of barrier crossing is coupled to the translational and rotational motions of the solvent molecules. It is characterized by the explicit form of  $\Delta(t)$ , the magnitudes of the different relaxation times, and several other factors which will be discussed in this section.

One expects a strong dependence on  $A = \lambda_0/\lambda$  which represents the relative contribution of the solvent polarization fluctuations to the total reorganization energy. As noted earlier,  $A$  acts like a switching function in the kernel that turns on the influence of solvent dynamics on the rate of electron transfer. The barrier heights  $E_1$  and  $E_2$  that appear in the kernels also influence solvent dynamical effects on ET;

they could be high or low or in between these extremes with different consequences for the rates. Quantum effects on ligand vibration also modify the kernels, and we expect to see this reflected in the way that solvation dynamics control the kinetics of electron transfer.

To analyze these effects, we focus our attention on the survival probabilities  $Q_2(t)$  that are described by a first order rate constant at relatively large times even when the overall dynamics<sup>6</sup> is more complicated. To see this, consider the Laplace transform of the integral equation [with  $F(t)=0$ ] which is

$$Q_2(s) = k_{ie} / \{ s^2 [1 + a_{s1}(s) + a_{s2}(s)] \}. \quad (5.1)$$

The  $s=0$  limit of  $a_{s1}(s)$  in transform space corresponds to  $t \rightarrow \infty$  in real space when  $a_i(t) \rightarrow k_{ie}$ . It is helpful to split by writing

$$a_i(t) = k_{ie} + k_{ie} [a_i^0(t) - 1], \quad (5.2)$$

where  $a_i^0(t) = a_i(t)/k_{ie}$ . It follows from Eqs. (3.19) that

$$a_i^0(t) = [1 - A^2\Delta(t)^2]^{-1/2} \exp\{2\beta E_i A \Delta(t) / [1 + A\Delta(t)]\}. \quad (5.3)$$

Note that the barrier height  $E_i$  appears only in the exponential factor and its influence decreases when it is low or if  $A$  is small.

The Laplace transform of Eq. (5.2) is

$$a_{si}(s) = k_{ie}/s + \alpha_i(s), \quad (5.4)$$

where

$$\alpha_i(s) = k_{ie} \int_0^\infty e^{-st} [a_i^0(t) - 1] dt. \quad (5.5)$$

In the limit  $s \rightarrow 0$  limit (i.e., at long times),  $\alpha_i(s)$  becomes a constant  $\alpha_i$ , and substitution of Eq. (5.4) into Eq. (5.1) leads to

$$Q_2(s) = k_{1\alpha} / [s(s + k_{1\alpha} + k_{2\alpha})], \quad (5.6)$$

where

$$k_{1\alpha} = k_{ie} / (1 + \alpha), \quad (5.7)$$

$\alpha = \alpha_1 + \alpha_2$ , and

$$\alpha_i = k_{ie} \int_0^\infty [a_i^0(t) - 1] dt. \quad (5.8)$$

The inverse Laplace transform of Eq. (5.6) shows that the sum of  $k_{1\alpha}$  and  $k_{2\alpha}$  is a first order rate constant for the survival probabilities (at long times)

$$Q_1(t) = 1 - Q_2(t), \quad (5.9a)$$

$$Q_2(t) = k_{1e} / (k_{1e} + k_{2e}) \exp[1 - (k_{1\alpha} + k_{2\alpha})t]. \quad (5.9b)$$

The reciprocal

$$1/k_{i\alpha} = 1/k_{ie} + 1/k_{id}, \quad (5.10)$$

where  $k_{ie}$  is given in Eq. (2.23) and

$$k_{id} = k_{ie} / \alpha. \quad (5.11)$$

Either  $k_{ie}$  or  $k_{id}$  will dominate the rate if one is much smaller than the other.

Since  $k_{ie}$  is known, we focus our attention in what follows on  $k_{id}$ . The preexponential factor  $\nu$  in the definition of  $k_{ie}$  appears in the numerator and denominator of Eq. (5.11) and cancels to make  $k_{id}$  independent of  $\nu$  and the factors that determine it, e.g., the electronic coupling at the intersection of the reactant and product free energy surfaces and tunneling through the barrier. Thus

$$k_{id} = k'_{ie} / \alpha', \quad (5.12)$$

where

$$k'_{ie} = k_{ie} / \nu = \exp(-\beta E_i), \quad (5.13a)$$

and  $\alpha' = \alpha / \nu$  is the sum of two integrals determined by the kernels

$$\alpha' = k'_{1e} \int_0^\infty [a_1^0(t) - 1] dt + k'_{2e} \int_0^\infty [a_2^0(t) - 1] dt. \quad (5.13b)$$

The rate coefficient  $k_{id}$  depends on the solvent dynamics.<sup>7,8,19-22</sup> We discuss its modulation by changes in solvent contributions to the reorganization energy (i.e., by  $A = \lambda_0/\lambda$ ), by variations in the barrier heights  $E_1$  and  $E_2$ , and by the quantum effects discussed earlier in Sec. IV. Although  $\alpha$  and  $\alpha'$  can be calculated numerically, we will derive analytic expressions in two limits that reveal the factors controlling them. Our mathematical treatment of low and

high barrier limits is closely related to our previous discussion of the kernels at short and long times, respectively,<sup>5,6</sup> but the physical content and interpretation are different.

When the barriers are low ( $E_i \approx 0$ ) or  $A$  is small, it follows from Eq. (5.2) that  $a_i^0(t) \approx [1 - A^2 \Delta(t)^2]^{-1/2}$ . Inserting this in Eq. (5.8) and expanding in powers of  $\Delta(t)$ , we have<sup>6</sup>

$$\alpha_i = k_{ie} F_A(\tau) \quad (i=1,2), \quad (5.14)$$

where

$$F_A(\tau) = \sum_{n=1}^{\infty} \frac{A^{2n} 2n!}{(2n!)^2} \langle \tau^{2n} \rangle \quad (5.15)$$

and  $\langle \tau^{2n} \rangle = \int_0^\infty \Delta(t)^{2n} dt$ . Substituting Eq. (5.13) in Eq. (5.11), we see that

$$k_{id} = k_{ie} / [(k_{1e} + k_{2e}) F_A(\tau)] \quad (i=1,2), \quad (5.16)$$

where we recall that  $k_{1e}/k_{2e} = \exp(-\beta \Delta G^0)$ . This implies that the rate constants  $k_{ie}$  can be eliminated from the expression for  $k_{id}$  in the low barrier limit. In Debye solvents  $F_A(\tau) = \tau_L f_A$  and<sup>6</sup>

$$f_A = \sum_{n=1}^{\infty} \frac{A^{2n} 2n!}{(2n!)^2 2^n}, \quad (5.17)$$

while in non-Debye solvents, we use an approximation for  $F_A(\tau)$  by replacing  $\tau_L$  by the average relaxation time

$$\langle \tau \rangle = \int_0^\infty \Delta(t) dt, \quad (5.18)$$

so that  $F_A(\tau) \approx \langle \tau \rangle f_A$ . When  $\Delta(t)$  is the sum of two exponentials,  $\langle \tau \rangle = A_1 \tau_1 + A_2 \tau_2$ . In this case,  $F_A(\tau)$  can be calculated as an infinite sum.<sup>23</sup> It follows from our discussion that in the low barrier limit

$$\alpha' = (k'_{1e} + k'_{2e}) f_A \langle \tau \rangle. \quad (5.19)$$

When the barriers are high, the main contribution to the integral in Eq. (5.8) comes from the integrand at short times when  $\Delta(t) \approx 1 - t/\tau_{\text{init}}$ , where  $\tau_{\text{init}}$  is the initial relaxation time. For example,  $1/\tau_{\text{init}} = A_1/\tau_1 + A_2/\tau_2$  when  $\Delta(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ . Assuming that  $A \neq 0$ , we approximate  $\exp[2\beta A E_i \Delta(t)] - 1$  in the integrand of Eq. (5.8) by  $\exp(2\beta A E_i) \exp(-t/\tau_{\text{init}})$  and find after integration that

$$\alpha' = \tau_{\text{init}} (\gamma_1 / |1 + \delta| + \gamma_2 / |1 - \delta|), \quad (5.20)$$

in which  $\delta = \Delta G^0 / \lambda$  and

$$\gamma_i = (\pi / \beta \lambda)^{1/2} [(1 + A) / A^{3/2}] \exp[y_i(1 - A)] [1 - \text{erf}(\sqrt{y_i})], \quad (5.21)$$

where  $y_i = \beta E_i(1 - A) / [A(1 + A)]$  for  $i=1,2$ .

In nonadiabatic ET reactions,  $\nu = (2\pi J^2 / \hbar) (\beta / 4\pi\lambda)^{1/2}$  and one usually defines

$$k'_{ie}(\text{nonad}) = (\beta\lambda / 4\pi)^{1/2} \exp(-\beta E_i), \quad (5.22)$$

so that  $\alpha'(\text{nonad}) = (\beta\lambda / 4\pi)^{1/2} \alpha'_i$  and

$$\gamma_i(\text{nonad}) = [(1 + A) / (2A^{3/2})] \exp[y_i(1 - A)] [1 - \text{erf}(\sqrt{y_i})]. \quad (5.23)$$



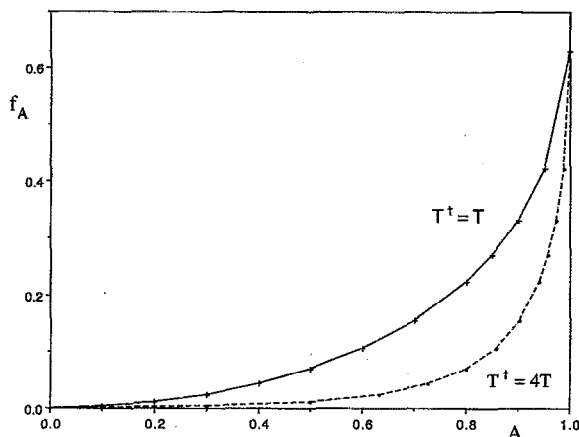


FIG. 1.  $f_A$  vs  $A$  in the low barrier approximation for  $T^\ddagger = T$  and  $T^\ddagger = 4T$ .

To take account of quantum effects on high frequency ligand vibrations, we need to substitute the modified kernels  $a_i^\ddagger(t)$ , discussed in Sec. IV, for  $a_i(t)$  in deriving the rate constants defined in Eqs. (5.10) and (5.11). Calling these  $k_{ie}^\ddagger$  and  $k_{id}^\ddagger$ , respectively, where  $k_{ie}^\ddagger$  is defined in Eq. (4.4), we have  $k_{id}^\ddagger = k_{ie}^\ddagger/\alpha^\ddagger$ , where  $\alpha^\ddagger = \alpha_1^\ddagger + \alpha_2^\ddagger$ ,

$$\alpha_i^\ddagger = k_{ie}^\ddagger \int_0^\infty [a_i^{\ddagger 0}(t) - 1] dt \quad (5.24)$$

and  $a_i^{\ddagger 0}(t) = a_i^\ddagger(t)/k_{ie}^\ddagger$ .

For low barriers,  $\alpha_i^\ddagger = k_{ie}^\ddagger F_A^\ddagger(\tau)$ , where  $F_A^\ddagger(\tau)$  is defined by an equation analogous to Eq. (5.14), with  $A$  replaced by  $A^\ddagger$ .  $A$  is related to  $A^\ddagger$  by Eq. (4.6). In Debye solvents  $F_A^\ddagger(\tau) = f_A^\ddagger \tau_L$ , where  $f_A^\ddagger$  is also given by Eq. (5.16) with  $A$  occurring instead of  $A^\ddagger$ . A similar relation holds for  $F_A^\ddagger(\tau)$  in non-Debye solvents except that the average  $\langle \tau \rangle$  should be substituted for  $\tau_L$ . Figure 1 shows a plot of  $f_A$  [or  $f_A^\ddagger$ ] as a function of  $A$  when  $T^\ddagger = T$  and  $T^\ddagger = 4T$ .

The quantum corrections to the rate constants for ET at high barriers are readily obtained. Defining  $k_{ie}^{\ddagger'} = k_{ie}^\ddagger/\nu^\ddagger = \exp(-\beta E_i^\ddagger)$ , we find that

$$k_{id}^{\ddagger'} = k_{ie}^{\ddagger'}/\alpha^{\ddagger'}, \quad (5.25)$$

with  $\alpha^{\ddagger'} = \alpha_1^{\ddagger'} + \alpha_2^{\ddagger'}$ ,

$$\alpha^{\ddagger'} = \tau_{\text{init}}(\gamma_1^{\ddagger'}/|1 + \delta| + \gamma_2^{\ddagger'}/|1 - \delta|), \quad (5.26)$$

in which

$$\gamma_i^{\ddagger'} = (A \pi / A^\ddagger \beta \lambda)^{1/2} [(1 + A^\ddagger) / A^{\ddagger 3/2}] \exp[y_i^{\ddagger'}(1 - A^\ddagger)] \times [1 - \text{erf}(\sqrt{y_i^{\ddagger'}})] \quad (5.27)$$

and  $y_i^{\ddagger'} = \beta E_i^\ddagger(1 - A^\ddagger) / [A^\ddagger(1 + A^\ddagger)]$ . These equations are analogous to Eqs. (5.20) and (5.21) except that  $A^\ddagger$  and  $y_i^{\ddagger'}$  occur instead of  $A$  and  $y_i$ , respectively, and an additional factor  $(A/A^\ddagger)^{1/2}$  appears in Eq. (5.27). Defining  $k_{ie}^{\ddagger'}(\text{nonadiab}) = (\beta \lambda / 4 \pi)^{1/2} \exp(-\beta E_i^\ddagger)$ , the corresponding expression for nonadiabatic ET reactions is

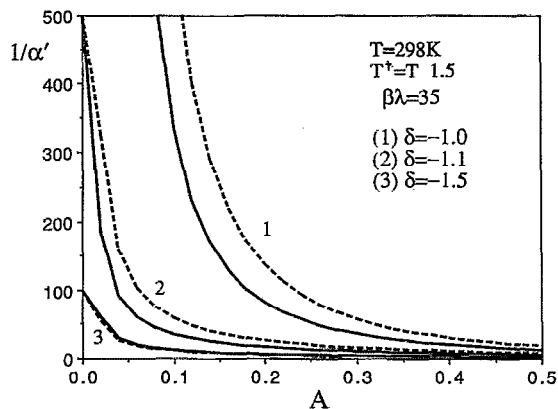


FIG. 2.  $1/\alpha'$  vs  $A$  at 298 K in the high barrier approximation when the reorganization energy  $\beta \lambda = 35$  and  $\delta = \Delta G^0/\lambda = -1.0, -1.1, \text{ and } -1.5$ , respectively. The dotted lines are  $1/\alpha^{\ddagger'}$  vs  $A$  in which quantum effects of ligand vibrations are taken into account in the calculations with  $T^\ddagger = 1.5T$ .

$$\gamma_i^{\ddagger'}(\text{nonad}) = (A/A^\ddagger)^{1/2} [(1 + A^\ddagger) / (2A^{\ddagger 3/2})] \times \exp[y_i^{\ddagger'}(1 - A^\ddagger)] [1 - \text{erf}(\sqrt{y_i^{\ddagger'}})]. \quad (5.28)$$

Clearly the influence of solvent dynamics on the diffusion controlled rate  $k_{id}$  is determined not only by the relaxation times, but also by the switching functions  $A$  or  $A^\ddagger$ . With few exceptions,<sup>5-8</sup> previous discussions have ignored this since they usually treated electron transfer reactions in the narrow window limit when  $A = 1$ .

Figure 2 illustrates how  $1/\alpha'$  changes with  $A$  for typical nonadiabatic reactions when  $\alpha'$  is calculated numerically from Eq. (5.13) or Eq. (5.24). As expected, quantum effects on  $1/\alpha'$  and  $k_{id}$  are more pronounced for low barriers. We have already seen that the barrier height modulates the influence of solvation dynamics on ET rates in solvents with multiple relaxation times. When these relaxation times are equally effective in controlling the solvent dynamics [e.g., the  $A_i$  coefficients in Eq. (6.1) are the same], we infer from Eqs. (5.20) and (5.26) that the faster solvent relaxation mode (smaller  $\tau_i$ ), which dominates  $\tau_{\text{init}}$ , has a greater effect on the rate of ET reactions with high barriers. Similarly, Eq. (5.13) shows that the slower relaxation (larger  $\tau_i$ ) component, which determines  $\langle \tau \rangle$ , has a more pronounced effect on the ET rate when the barrier height is low.

## VI. AN ILLUSTRATION—ELECTRON TRANSFER RATES OF BETAINE-30 IN GTA

We use the results derived in the previous section to analyze the ET kinetics of betaine-30 in glycerol triacetate (GTA). Walker *et al.*<sup>9(d)</sup> measured the rates of this reaction from 228 to 318 K and interpreted their data using a hybrid of the Sumi-Marcus and Bixon-Jortner models,<sup>24</sup> in which they invoked a high frequency vibrational mode and multiple reaction channels with different activation energies to vibrationally excited product states. We have also discussed such a model<sup>6</sup> though not directly in connection with these experiments. Section IV of this paper discusses corrections to our integral equation due to high frequency ligand vibrational

modes. We will show that the Sumi–Marcus model explains the ET kinetics of betaine-30 in GTA assuming that the diffusion limited rate is modulated by an appreciable reorganization energy contribution from intramolecular vibration modes. The parameter  $A = \lambda_0/\lambda$ , which is the relative contribution of the solvent fluctuations to the total reorganization energy, is thus less than one and is strongly temperature dependent.

The standard free energy change of this reaction  $\Delta G^0 \approx 10\,609\text{ cm}^{-1}$  at 303 K and an Arrhenius plot suggests a small activation energy  $E_1 \approx 472\text{ cm}^{-1}$  for the forward reaction. Inserting this in Eq. (2.24a), we calculate  $\lambda \approx 6979\text{ cm}^{-1}$  for the total reorganization energy, or  $\beta\lambda \approx 34$  at  $T = 303\text{ K}$  ( $kT \approx 210\text{ cm}^{-1}$ ) in the inverted regime where this reaction occurs. The free energy change is  $\approx -1.3\text{ eV}$ , and the reorganization energy  $\lambda \approx 0.8\text{ eV}$ .

Walker *et al.* estimate the matrix coupling element  $J \approx 2500\text{ cm}^{-1}$  in their hybrid model. Using this, we find  $k_{1e} \approx 0.2 \times 10^{15}\text{ s}^{-1}$  at 303 K in the nonadiabatic limit [see Eq. (2.23)]. It is much larger than their estimate of the first order rate constant from the Sumi–Marcus theory, and it is also larger than the observed rate constant  $k_{1\alpha} \approx 0.34 \times 10^{12}\text{ s}^{-1}$  at this temperature. This is consistent with an ET rate that is solvent controlled [see Eq. (5.10)]. Although we have calculated  $k_{1e}$  in the nonadiabatic limit, its exact value is unimportant as long as it is much greater than the observed rate when the reaction becomes solvent controlled. We next determine the diffusion controlled rate coefficient  $k_{id}$  using the data provided in the paper of Walker *et al.*<sup>9(d)</sup>

The solvent dynamics in GTA are characterized by an average relaxation time of 40 ps at 303 K. In our low barrier approximation ( $E_1 = 0$  and  $\delta = -1.0$ )

$$k_{id} = 1/(\langle\tau\rangle f_A), \quad (6.1)$$

and we find a lower limit of  $4.16 \times 10^{10}\text{ s}^{-1}$  for  $k_{id}$  assuming  $A \approx 1.0$  when  $f_A \approx 0.63$ .<sup>4,6</sup> This is smaller than the observed rate. However,  $f_A$  changes with  $A$ , as seen in Fig. 1, and  $k_{id}$  increases as  $A$  decreases below one. The accuracy of our low barrier approximation also improves as  $A$  decreases, since  $A$  appears with  $E_1$  in the argument of the exponential in the kernel. We find that the diffusion limited rate  $k_{id}$  is equal to the observed rate at 303 K, in this approximation, when  $f_A = 0.074$ . This corresponds to  $A \approx 0.5$ .

The same argument can be used to analyze the kinetic data<sup>9(d)</sup> for this reaction at all temperatures (318–228 K) at which ET rates were measured. The average relaxation time  $\langle\tau\rangle$  for the solvent GTA changes from a few picoseconds to several hundred or thousand times this number over this temperature range. Table I summarizes the experimental results and other parameters calculated from Eq. (2.23) and the activation energy. Since the ET reaction is solvent controlled, we expect  $k_{1\alpha} \approx k_{1d}$  and  $f_A$  is easily calculated at different temperatures  $T$  from Eq. (6.1) and the experimental values of  $\langle\tau\rangle$ . The corresponding values of  $A$  inferred from Eq. (5.6) and  $f_A$  are presented in columns two and three of Table II.

For this system, the calculations of ET rates remain essentially unaltered when quantum effects of ligand vibrations on the rates are taken into account using the semiclassical approximation.  $f_A$  and  $A$  now correspond to  $f_A^\ddagger$  and  $A^\ddagger$ , re-

TABLE I. Parameters for ET kinetics of betaine-30 in triacetin (GTA).

$T(\text{K})^a$	$\langle\tau\rangle(\text{ps})^a$	$k_{\text{et,obs}}(\text{ps}^{-1})$	$\Delta G^0(\text{cm}^{-1})^a$	$\lambda(\text{cm}^{-1})$	$\delta$	$k_{1e}^\ddagger$
228	$7 \times 10^6$	0.18	-10 993	7284	-1.509	0.186
263	410	0.22	-10 711	7060	-1.517	0.233
293	125	0.290	-10 660	7020	-1.518	0.270
303	40	0.34	-10 609	6979	-1.520	0.280
308	28	0.36	-10 583	6958	-1.520	0.285
313	18	0.40	-10 557	6938	-1.521	0.290
318	12	0.38	-10 532	6918	-1.522	0.295

<sup>a</sup>Data from Ref. 9(d).  $\lambda$  calculated from Eq. (2.25a) in the inverted region and  $k_{1e}^\ddagger = (\beta\lambda/4\pi)\exp(-\beta E_1)$  with  $E_1 = 472\text{ cm}^{-1}$ .

spectively, as they are listed in the second and third columns of Table II. Following Kjaer and Ulstrup's discussion of betaine-20,<sup>26</sup> we assume a single frequency of  $\approx 1600\text{ cm}^{-1}$  which corresponds to  $T^\ddagger \approx 1.1T$  at 293 K. This corresponds to a small quantum correction. Inverting Eq. (4.6), we have  $A$  as a function of  $A^\ddagger$  and  $T^\ddagger/T$ ,

$$A = A^\ddagger(T^\ddagger/T)/[1 + A^\ddagger(T^\ddagger/T - 1)], \quad (6.2)$$

in which the relationship between  $T^\ddagger$  and  $T$  [see Eq. (4.3)] is determined by the high frequency ligand vibrational modes. Our estimates of  $A$  and  $\lambda_0$ , using the exact  $T^\ddagger/T$  calculated from Eq. (4.3), are displayed in columns four and five of Table II.

The calculation is easily repeated for a finite barrier when

$$f_A^\ddagger(\tau) = \int_0^\infty [a_1^{\ddagger 0}(t) - 1] dt, \quad (6.3)$$

which follows from Eq. (5.24). Numerical integration of Eq. (6.3) with  $E_1^\ddagger = 472\text{ cm}^{-1}$  determines  $A^\ddagger$  and  $A$  recorded in columns six and seven of Table II. They are slightly smaller than the values obtained in the zero barrier limit confirming our assumption that an activation energy of  $472\text{ cm}^{-1}$  has a relatively small effect on  $A$ . The corresponding solvent reorganization energies  $\lambda_0$  are listed in column eight of Table III.

The accuracy of the semiclassical approximation for the rate coefficient for ET in the betaine-30 system can be determined by calculating the error in the saddle point  $t_0$  from the approximate and exact expressions Eqs. (B22) and (B8), respectively, the second by iteration. At 303 K, the error in  $t_0$  is 14% which corresponds to an error of 7% in the semiclassical

TABLE II. Quantum and barrier height corrections for ET kinetics of betaine-30 in triacetin (GTA).

$T(\text{K})^a$	$f_A^\ddagger$	$E_1^\ddagger = 0$			$E_1^\ddagger = 472\text{ cm}^{-1}$		
		$A^\ddagger$	$A$	$\lambda_0(\text{cm}^{-1})$	$A^\ddagger$	$A$	$\lambda_0(\text{cm}^{-1})$
228	$\approx 0.00$	0.018	0.022	160	0.002	0.002	15
263	0.011	0.208	0.232	1638	0.160	0.222	1567
293	0.028	0.325	0.350	2457	0.290	0.329	2310
303	0.074	0.514	0.542	3782	0.488	0.516	3601
308	0.099	0.585	0.612	4258	0.560	0.588	4091
313	0.139	0.672	0.695	4822	0.650	0.675	4683
318	0.219	0.795	0.813	5624	0.780	0.799	5527

<sup>a</sup> $f_A^\ddagger$  vs  $A^\ddagger$  is identical to  $f_A$  vs  $A$  at  $T^\ddagger = T$ .

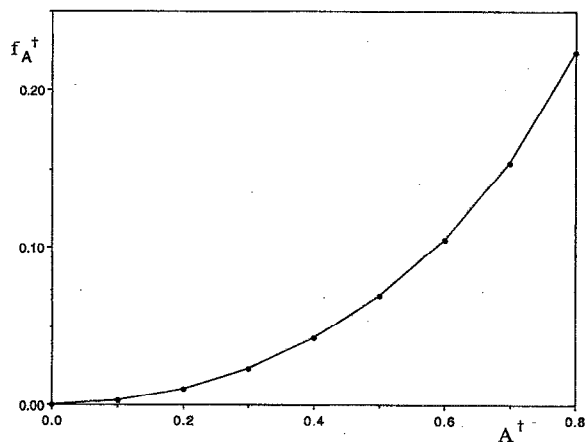


FIG. 3.  $f_{A^\ddagger}$  vs  $A^\ddagger$  inferred from the ET rates of betaine-30 in glycerol triacetate (GTA) between 228 and 318 K assuming that the reaction is controlled by the solvent and intramolecular ligand vibrations. The low barrier approximation is assumed.

sical approximation for the rate coefficient. This is small and justifies our use of this approximation for the rate coefficient.

The increase of  $f_{A^\ddagger}$  with temperature implies that  $A$  also does the same. The hybrid model of Walker *et al.*<sup>9(d)</sup> on the other hand predicts a nearly constant value of  $A \approx 0.4$  deduced from Table VI of their paper. The temperature dependence of  $A$  in our theory partly reflects the  $T$  dependence of the Pekar factor that appears in expressions for the solvent reorganization energy  $\lambda_0$ .<sup>1</sup> Figure 3 shows a plot of  $f_{A^\ddagger}$  vs  $A^\ddagger$  and Fig. 4 shows that  $\lambda_0$  (column eight of Table II) increases with temperature in this range. In contrast to this, Walker *et al.* report solvent reorganization energies ( $\lambda_{\text{cl,solv}}$  in their notation), decreasing with increasing temperature according to their model. This is the opposite of what we find and seems intuitively less obvious.

In summary, our theoretical explanation of ET of betaine-30 in the solvent GTA characterizes it as a low barrier reaction in which kinetic control by intramolecular vibration at low temperatures shifts to control by solvent dynamics as the temperature rises (see Fig. 4). Quantum corrections due to high frequency vibrational modes make a small contribution to the reaction rate and the dynamics of the solvent modulates the rate at all temperatures above freezing. These conclusions are qualitatively in accord with those of Walker *et al.*<sup>9(d)</sup> although our theoretical treatment is different.

## VII. DETAILED SOLVENT DYNAMICS AND THE SOLUTIONS TO THE INTEGRAL EQUATION

In this section, we present the numerical solutions to the integral equations for ET using information on solvent dynamics from different sources. Our objective is to determine how sensitive the survival probabilities in ET reactions are to details of the solvent dynamics such as the oscillations in the times correlation functions  $S(t)$  for the free energy of solvation.  $S(t)$  obtained from TDFS experiments, computer simu-

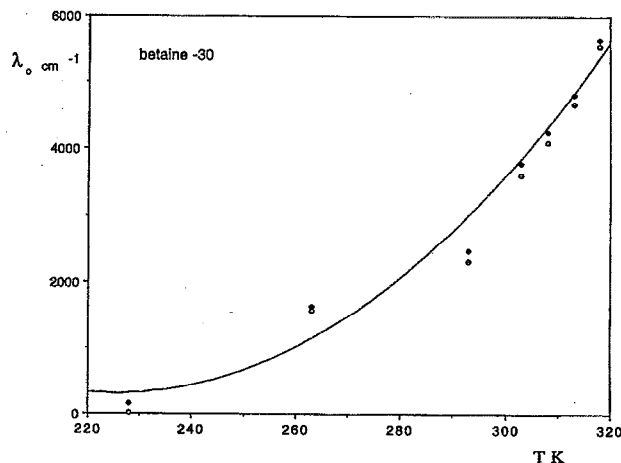


FIG. 4. The solvent contribution to the reorganization energy  $\lambda_0$  as a function of  $T$  calculated from the experimental data for ET of betaine-30 in GTA. Points correspond to  $E^\ddagger=0$  and  $472 \text{ cm}^{-1}$ , respectively (see Table II).

lation, and theoretical calculations for the same solvent differ in detail and it is useful to know what effect these differences have on the rates of ET reactions.

TDFS experiments in Barbara's laboratory<sup>9</sup> have shown that  $S(t)$  for many solvents can be represented as the sum of two exponentials

$$S(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (7.1)$$

where  $A_1 + A_2 = 1$  and the relaxation times  $\tau_1$  and  $\tau_2$  are usually of the order of 0.2–4 ps. Exceptions are methanol and *n*-propanol, where  $(\tau_1, \tau_2)$  is approximately (1.16, 9.57) and (14.0, 40.0) ps, respectively. The ratio of the relaxation times (larger to smaller) is usually not greater than 5, although there are notable exceptions, e.g., propylene carbonate and methanol. The solvation parameters derived from TDFS data that characterize Eq. (6.1) are reproduced from Ref. 6 in Table III.

Instrument limitations and probe insensitivity may have masked some of the fine structure of solvation dynamics measured in earlier TDFS experiments. Solvation dynamics should also be, to some extent, probe dependent; changing,

TABLE III. Experimental solvation parameters at 298 K<sup>a</sup>  $S(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ .

Solvent	$\tau_1$ (ps)	$\tau_2$ (ps)	$A_1$	$A_2$	$\tau^{\text{eff}}$ (ps)
Acetone <sup>b</sup>	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
<i>n</i> -propanol	14.0	40.0	0.30	0.70	32.2
Water <sup>c</sup>	0.16	1.2	0.33	0.67	0.86

<sup>a</sup>Entries from W. Jarzeba *et al.* Chem. Phys. **152**, 57 (1991).

<sup>b</sup>Acetone is also well represented by a single exponential time decay of  $S(t)$  with a relaxation time of 0.70 ps.

<sup>c</sup>For water, TDFS experiments on a femtosecond time scale [R. Jimenez *et al.*, Nature **369**, 471 (1994)] have been fitted to Eq. (7.2) with  $A_g = 0.45$ ,  $\omega_g = 38.5 \text{ ps}^{-1}$ ,  $A_1 = 0.20$ ,  $\tau_1 = 0.126 \text{ ps}$ ,  $A_2 = 0.35$ , and  $\tau_2 = 0.88 \text{ ps}$ .

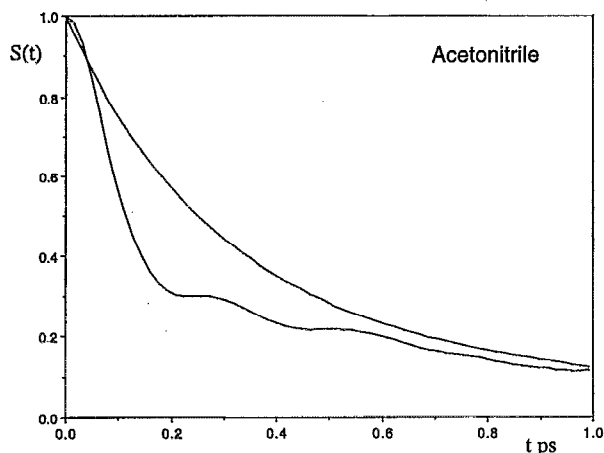


FIG. 5.  $S(t)$  vs  $t$  in picoseconds for acetonitrile (a) biexponential equation (7.1) fitted to TDFS experiment (Ref. 9) (upper curve) and (b) theoretical calculation of Ranieri and Friedman (Ref. 34) using two center Lennard-Jones model with charges for acetonitrile.

for instance, with the size, shape, and charge distribution of the probe. Computer simulations<sup>10,27-31</sup> and theoretical calculations<sup>32-36</sup> provide additional information, and it appears that in many instances,  $S(t)$  shows a fast Gaussian response, on a femtosecond time scale, followed by a slower decay for several picoseconds that is modulated by oscillatory behavior. These features are seen in the  $S(t)$  simulations of SPC water at 25 °C by Kumar and Tembe<sup>30</sup> and Bader and Chandler.<sup>31</sup> The fast inertial response of the solvent has been observed recently in TDFS experiments in water carried out in Fleming's laboratory<sup>10(c),10(g)</sup> and its main effect on the solvent dynamics is included by modifying Eq. (7.1) to read

$$S(t) = A_g \exp(-\omega_g^2 t^2 / 2) + A_1 \exp(-t/\tau_1) + A_2 \times \exp(-t/\tau_2), \quad (7.2)$$

where  $A_g$  and  $\omega_g$  are parameters representing the inertial response. The parameters for water are  $A_g = 0.45$ ,  $\omega_g = 38.5 \text{ ps}^{-1}$ ,  $A_1 = 0.20$ ,  $\tau_1 = 0.126 \text{ ps}$ ,  $A_2 = 0.35$ , and  $\tau_2 = 0.88 \text{ ps}$ .<sup>10(g)</sup> The extent to which the details of solvent dynamics affect ET rates depends on many factors, e.g., the barrier height, the intrinsic rate of barrier crossing, and the time scales of solvent dynamics. We will briefly explore some of them for a model ET reaction in acetonitrile.

Figure 5 compares the theoretical calculations of  $S(t)$  for acetonitrile by Ranieri and Friedman<sup>34</sup> using a two-center Lennard-Jones model for the solvent and the biexponential form of Eq. (7.1) which does not show any of the fine structure or the initial fast Gaussian response found in the calculated  $S(t)$ . The results of some of our integral equation calculations of the survival probabilities for model ET reactions in water, propylene carbonate, and *n*-propanol using Eq. (7.1) for  $S(t)$  have been discussed elsewhere.<sup>6</sup> The input parameters are  $\Delta(t) = S(t)$ , the total reorganization energy  $\beta\lambda$ , the fraction of this  $A = \lambda_0/\lambda$  due to solvent polarization fluctuations, and the intrinsic rate of barrier crossing given by  $\sqrt{\beta}k_0$ , where  $k_0$  is defined by  $\nu = (\beta A/2\pi)^{1/2} k_0$ , in which  $\nu$  is the preexponential factor of the rate constant. It

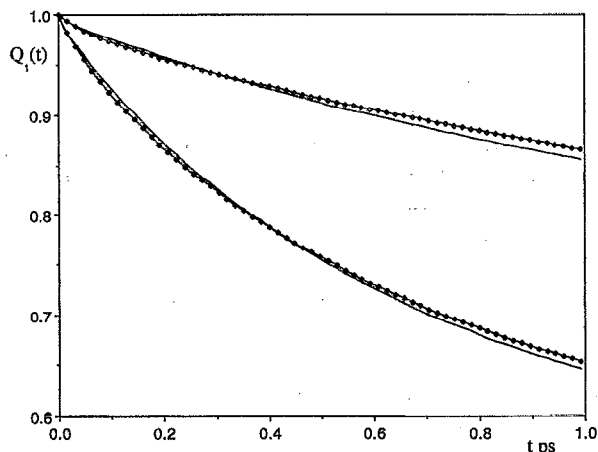


FIG. 6. Survival probabilities  $Q_1(t)$  of a reversible and symmetrical model electron transfer reaction in acetonitrile using  $S(t)$  from (a) Eq. (7.1) fitted to TDFS data [Ref. 9(a)] or (b) from theory (Ref. 34) as input in the integral equation (3.24b) for ET with  $F(t) = 0.0$ . The model parameters are  $\Delta G^0 = 0.0$ ,  $A = 0.997$  (near narrow window limit),  $\nu = 15 \times 10^{12} \text{ s}^{-1}$  (i.e.,  $\sqrt{\beta}k_0 = 4.0 \times 10^{13} \text{ s}^{-1}$ ), and  $\beta\lambda = 1$  or 7. The solid lines were calculated using  $S(t)$  from theory (Ref. 34) and the remainder using the biexponential form of Eq. (7.1) for  $S(t)$  (see Fig. 5).

was seen that in many cases, the survival probabilities of the reactants in an ET reaction are not simple first order decays. It was also found that the use of an average relaxation time with a single exponential time dependence for  $S(t)$  typical of Debye solvents leads to incorrect ET rates in sluggish solvents, like propylene carbonate, that have (see Table III) relaxation times differing by a factor of about 10.

The integral equation for ET is just as easily solved using the more detailed representations of  $S(t)$  that have been suggested by recent TDFS measurements, computer simulation, and theory. Figure 6 shows our calculations of the survival probabilities for symmetrical model ET reactions with ( $\Delta G^0 = 0.0$ ) in acetonitrile with  $A = 0.997$  and  $\nu = 15 \times 10^{12} \text{ s}^{-1}$  (i.e.,  $\sqrt{\beta}k_0 = 4.0 \times 10^{12} \text{ s}^{-1}$ ) using  $S(t)$  (i) from TDFS experiments and (ii) from the model calculations by Ranieri *et al.*<sup>34</sup> The solutions to the integral equation with the reorganization energies  $\beta\lambda = 1$  and 7, respectively, were obtained by the numerical method outlined in Ref. 7 assuming a thermally equilibrated initial state [i.e.,  $F(t) = 0$ ]. The two  $S(t)$ 's are also shown in Fig. 6. It appears that in this particular case, the details of the solvent dynamics have only a small effect on the survival probabilities.

However, our discussion in Sec. VI shows that the initial relaxation time  $\tau_{\text{init}}$  has a strong effect on the rates of ET in reactions with a moderate to high barriers when the rate of barrier crossing is comparable to this time. In aqueous systems,  $\tau_{\text{init}}$  should be identified with the characteristic time for the ultrafast Gaussian response of  $S(t)$ . The rate coefficients and survival probabilities of ET reactions in this and other solvents can be calculated using the theoretical and numerical methods discussed in this paper.

## VIII. DISCUSSION AND CONCLUSIONS

We have derived an integral equation for reversible electron transfer in Debye and non-Debye solvents using a

Green's function technique and a decoupling approximation for the reaction diffusion equations that describe the kinetics of these reactions. Although the decoupling of the differential equations is an approximation, it is exact in several limits<sup>3-8</sup> including the outer-sphere electron transfer (or narrow window) limit. Since the ligand vibrational contributions to the reorganization energy of ET reactions are not very large, it is also expected to be reasonably accurate in most cases of practical interest.

The discussion also extends our previous work in several ways (a) by considering ET from an initial state that is not in thermal, equilibrium with its surroundings as in many experiments initiated by laser excitation; (b) by incorporating quantum mechanical corrections to the classical high temperature transition state rate coefficients used in our previous study. The integral equation is easily solved on a personal computer, and is useful in the interpretation of ET experiments in which solvent dynamics and the relative contributions of ligand vibration and solvent polarization fluctuations to the rates of ET reactions play important roles. It is found that in solvents with more than one relaxation time, the faster component of solvent relaxation (smaller  $\tau$ ) controls the rate of ET reactions with a high barrier, while the slower relaxation component (larger  $\tau_i$ ) controls the ET rate when the barrier height is low and the reaction is solvent controlled. Quantum corrections to these effects are more pronounced when the ET barriers are low. We have derived a compact saddle point approximation for the rate coefficient of electron transfer reactions that reduces to the expression obtained by Chandler and Bader<sup>19,39</sup> for symmetrical self-exchange reactions when  $\Delta G^0(x) = 0$ .

The ET kinetics of betaine-30 in glycerol triacetate (GTA) over a 100° temperature range is analyzed by treating it as a low barrier solvent-controlled reaction in which molecular vibrations and quantum effects contributing the reorganization energy and the overall rate. Interestingly, a strong coupling between molecular vibrations and ET in photosynthesis has also been suggested recently.<sup>38</sup>

The detailed fine structure of the solvent dynamics in acetonitrile is only weakly reflected in the electron transfer rates of a model system that was studied. However, as discussed in this paper, the initial ultrafast inertial response of the solvation dynamics in solvents like water will modulate the kinetics of moderate to high barrier ET reactions and rates of these reactions can also be calculated by the methods presented in this paper. Related work on electron transfer reactions with bond breaking is discussed elsewhere.<sup>37</sup>

## ACKNOWLEDGMENTS

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## APPENDIX A: OPERATOR SOLUTION FOR ET IN DEBYE SOLVENTS

Consider the case where  $D(t)$  is time independent as in Debye solvents. The Laplace transform of Eq. (3.1) leads to

$$(s + H_i)G_i(x, y; s) = \delta(x - y). \quad (\text{A1})$$

Multiplication by  $(s + H_i)^{-1}$  followed by integration over  $y$  leads to

$$O_i(s) = \int dy G_i(x, y; s) = (s + H_i)^{-1}. \quad (\text{A2})$$

In the general case, when  $D(t)$  is time dependent, an effective operator  $H_i^{\text{eff}}$  can be defined by replacing  $H_i$  by  $H_i^{\text{eff}}$ , i.e.,

$$O_i(s) \approx (s + H_i^{\text{eff}})^{-1}. \quad (\text{A3})$$

Returning to ET in Debye solvents, it follows from Eq. (3.16) that

$$C = \langle g_1 k_1 | (s + H_1)^{-1} | f_1 \rangle / [1 + a_{s1}(s) + a_{s2}(s)] \quad (\text{A4})$$

and

$$a_{si}(s) = k_{ie}^{-1} \langle g_i k_i | (s + H_i)^{-1} | k_i g_i \rangle \quad (\text{A5})$$

$$= k_{ie}^{-1} \sum_{n=0}^{\infty} (s + \epsilon_n)^{-1} |\langle u_{n,i} | k_i g_i \rangle|^2. \quad (i=1,2) \quad (\text{A6})$$

and  $|u_{n,i}\rangle$  are the eigenfunctions of  $H_i$  with  $|u_{0,i}\rangle = |g_i\rangle$ , the ground state eigenfunction. Equation (A6) follows from Eq. (A5) on using the properties of the Hermitian operator  $H_i$ ; the details are in Ref. 4. The inverse transform of Eq. (A6) is an infinite sum of exponentials that, in closed form,<sup>4-6</sup> is Eq. (3.18) with  $\Delta(t) = \exp(-t/\tau_L)$ .

Expanding  $|f_i\rangle$  in the set of eigenfunctions of  $H_i$  (Refs. 5-7) and inserting this in the expression for  $C$ , we find

$$Q_2(s) = \left\{ [1 + a_{s1}(s) + a_{s2}(s)]^{-1} \left\{ k_{1e}/s^2 + \sum_{n=1}^{\infty} d_{n,1} \right. \right. \\ \left. \left. \times [s(s + \epsilon_n)]^{-1} \right\} \right\}, \quad (\text{A7})$$

where  $d_{n,1}$  is defined in Eq. (3.27). Multiplying by  $[1 + a_{s1}(s) + a_{s2}(s)]$ , using the convolution theorem, we find the solution given in Eq. (3.24), where  $F(t)$  is defined in Eq. (3.28). This confirms that our integral equation solution for ET in any solvent reduces to the correct result for ET in Debye solvents.

## APPENDIX B: SADDLE POINT APPROXIMATIONS OF THE GOLDEN RULE RATE CONSTANT

The golden rule rate coefficient for a harmonic oscillator bath is well known<sup>11,39,40</sup> and can be expressed as

$$k^\ddagger(x) = \frac{J^2}{\hbar^2} \int_{-\infty}^{\infty} dt e^{A(t)}, \quad (\text{B1})$$

where

$$A(t) = \frac{i\Delta G^0(x)t}{\hbar} + f(t) \quad (\text{B2})$$

and

$$f(t) = \sum_j \frac{2\gamma_j^2}{\hbar\mu_j\omega_j^3} \left[ \coth \frac{\beta\hbar\omega_j}{2} (\cos \omega_j t - 1) + i \sin \omega_j t \right]. \quad (\text{B3})$$

In Eq. (B2),  $\Delta G^0(x)$  is the free energy gap and  $\gamma_j$  is the coupling constant of mode  $j$  between the initial and final states. It is related to  $q_j^0$  and the vibrational reorganization energy by Eq. (4.1c).

Defining the density of states<sup>19</sup>

$$\phi(\omega) = \sum_j \frac{\pi\gamma_j^2}{\mu_j\omega_j} \delta(\omega - \omega_j), \quad (\text{B4})$$

we see that

$$f(t) = (2/\pi\hbar) \int_0^\infty d\omega \phi(\omega) \omega^{-2} \times \left[ \coth \frac{\beta\hbar\omega_j}{2} (\cos \omega_j t - 1) + i \sin \omega_j t \right] \quad (\text{B5})$$

and

$$\lambda_q = \sum 2\gamma_j^2 / (\mu_j\omega_j^2) = (2/\pi) \int_0^\infty \phi(\omega) \omega^{-1} d\omega. \quad (\text{B6})$$

The saddle point approximation<sup>14</sup> to Eq. (B1) is

$$k^\ddagger(x) = \frac{J^2}{\hbar^2} \sqrt{\frac{2\pi}{|A''(t_0)|}} e^{A(t_0)}, \quad (\text{B7})$$

where  $A''(t) = d^2A(t)/dt^2$  and  $t_0$  is the saddle point. At this point,  $A'(t_0) = 0$  and it follows from (B2) that

$$k^\ddagger(x) = \frac{\pi(J^2/\hbar^{3/2}) \exp[-(2/\pi\hbar) \int_0^\infty d\omega \phi(\omega) \omega^{-2} \tanh(\beta\hbar\omega/4)]}{[\int_0^\infty d\omega \phi(\omega) \text{cosech}(\beta\hbar\omega/2)]^{1/2}} \quad (\text{B12})$$

for the rate coefficient obtained earlier by Chandler<sup>19,38</sup> and Bader *et al.* [Eq. (4.4) of Ref. 19(a)]. It is known to be accurate for ferrous/ferric system by comparison with path integral simulations of the rate.<sup>19</sup>

To obtain the classical limit at high temperature ( $\beta\hbar\omega_j \ll 1$ ), expand the hyperbolic functions  $\cosh x \approx 1$ ,  $\sinh x \approx x$ , and  $\tanh x \approx x$ , when Eqs. (B10) and (B11) become

$$A(t_0) = -\frac{\beta}{4} \sum_j \frac{2\gamma_j^2}{\mu_j\omega_j^2} = -\frac{\beta\lambda_q}{4}, \quad (\text{B13})$$

$$|A''(t_0)| = \frac{2}{\beta\hbar^2} \sum_j \frac{2\gamma_j^2}{\mu_j\omega_j^2} = \frac{2\lambda_q}{\beta\hbar^2}, \quad (\text{B14})$$

respectively. Substitution in Eq. (B7) leads to

$$0 = \frac{i\Delta G^0(x)}{\hbar} + \sum_j \frac{2\gamma_j^2}{\hbar\mu_j\omega_j^2} \times \left( -\sin \omega_j t_0 \coth \frac{\beta\hbar\omega_j}{2} + i \cos \omega_j t_0 \right), \quad (\text{B8})$$

Generally, the saddle point cannot be determined analytically except in special situations discussed below.

(a)  $\Delta G^0(x) = 0$ . If only one mode is involved, the saddle point can be determined exactly. It follows from Eq. (B8)<sup>13,18,19</sup> that

$$t_0 = i\beta\hbar/2. \quad (\text{B9})$$

If two or more modes are involved, no analytic solution is possible unless we assume that each mode satisfies the condition (B8) independently when Eq. (B9) obtains, and one finds

$$A(t_0) = -\sum_j \frac{2\gamma_j^2}{\hbar\mu_j\omega_j^3} \tanh(\beta\hbar\omega_j/4) = -(2/\pi\hbar) \int_0^\infty d\omega \phi(\omega) \omega^{-2} \tanh(\beta\hbar\omega/4) \quad (\text{B10})$$

and

$$|A''(t_0)| = \sum_j \frac{2\gamma_j^2}{\hbar\mu_j\omega_j} \text{cosech}(\beta\hbar\omega_j/2) = (2/\pi\hbar) \int_0^\infty d\omega \phi(\omega) \text{cosech}(\beta\hbar\omega/2). \quad (\text{B11})$$

Substitution of Eqs. (B10) and (B11) in Eq. (B4) leads to

$$k(x) = \frac{2\pi J^2}{\hbar} \sqrt{\frac{1}{4\pi kT\lambda_q}} e^{-\beta\lambda_q/4}, \quad (\text{B15})$$

which can also be obtained directly from Eq. (B12) by retaining only the leading term in the expansions of each hyperbolic function. This is the correct classical limit of Eq. (B1) when  $\Delta G^0(x) = 0$ . However, use of (B9) in Eq. (B2) and (B4) when  $\Delta G^0(x) \neq 0$  leads instead to

$$k(x) = \frac{2\pi J^2}{\hbar} \sqrt{\frac{1}{4\pi kT\lambda_q}} \left\{ \exp\left[-\frac{[\Delta G^0(x) + \lambda_q/4]}{kT}\right] \right\} \quad (\text{B16})$$

at high temperatures. This is inconsistent with the classical result given below in Eq. (B20) with  $T^\ddagger = T$ . Therefore, although Eq. (B9) works well for the symmetric ferrous/ferric

system,<sup>19</sup> it is not useful when the free energy gap is not zero as pointed out earlier by several others.<sup>13,18,39</sup>

(b)  $\Delta G^0(x) \neq 0$ . The saddle point in this case cannot be determined exactly in simple algebraic form even for a single mode. To obtain a compact approximate expression, the methods provided in Refs. 15 and 16 are quite attractive. At not too low a temperature or when the curvature close to the saddle point is fairly steep, expansion of Eq. (B3) to second order in  $t$  (Refs. 15 and 16) leads to

$$A(t) = \frac{i\Delta G^0(x)t}{\hbar} + \sum_j \frac{2\gamma_j^2}{\hbar\mu_j\omega_j^3} \times \left( -\frac{\omega_j^2 t^2}{2} \coth \frac{\beta\hbar\omega_j}{2} + i\omega_j t \right). \quad (\text{B17})$$

The saddle point approximation, which now includes all the modes, is then easily obtained as

$$t_0 = i[\Delta G^0(x) + \lambda_q]/D_q, \quad (\text{B18})$$

where

$$D_q = \sum_j \frac{2\gamma_j^2}{\mu_j\omega_j} \coth(\beta\hbar\omega_j/2). \quad (\text{B19})$$

Setting  $t=t_0$  in Eq. (B17) and its second derivative, one obtains the rate coefficient

$$k^\ddagger(x) = \frac{2\pi J^2}{\hbar} \sqrt{\frac{1}{4\pi k T^\ddagger \lambda_q}} \exp\left\{-\frac{[\Delta G^0(x) + \lambda_q]^2}{4k T^\ddagger \lambda_q}\right\} \quad (\text{B20})$$

from Eq. (B7), in which the effective temperature  $T^\ddagger$  is defined by

$$k_B T^\ddagger = \frac{\hbar}{\lambda_q} \sum_j \frac{\gamma_j^2}{\mu_j\omega_j} \coth \frac{\beta\hbar\omega_j}{2}. \quad (\text{B21})$$

Equation (B20) is a semiclassical approximation<sup>2(a),15,16</sup> which contains quantum corrections to the rate coefficient. It leads to the correct classical limit when  $T^\ddagger = T$ . van Duyne and Fischer, and Fischer and Van Duyne<sup>17</sup> also expanded the rate coefficient to second order in  $t$  [see Eq. (13) of Ref. 17(b)] around the saddle point to obtain a compact saddle point approximation for electron transfer rate.

To go beyond the semiclassical expression and improve on Eq. (B18), we first note that it can be rewritten as

$$t_0 = i\beta^\ddagger \hbar [1 + \Delta G^0(x)/\lambda_q]/2, \quad (\text{B22})$$

where  $\beta^\ddagger = 1/(k_B T^\ddagger)$ . When  $\Delta G^0(x) = 0$ , Eq. (B22) agrees with Eq. (B9), only in the high temperature limit. This explains why the semiclassical approximation (B20) for the rate is less accurate for symmetric systems (e.g.,  $\text{Fe}^{+2}/\text{Fe}^{+3}$ ) than it is for some unsymmetric systems.<sup>13</sup> It also suggests an interpolation formula

$$t_0 = i\beta\hbar [1 + a(T)\Delta G^0(x)/\lambda_q]/2 \quad (\text{B23})$$

for the saddle points of symmetric and unsymmetric systems. In Eq. (B23), the temperature-dependent parameter  $a(T) \approx \beta^\ddagger/\beta$ , which  $\rightarrow 1$  as  $T \rightarrow \infty$  and reduces to Eq. (B9) when  $\Delta G^0(x) = 0$ . For unsymmetrical systems [ $\Delta G^0(x) \neq 0$ ],  $a(T)$  can be calculated more accurately by

iterative solution of Eq. (B8) for the saddle point condition. At high temperatures,  $a(T) \rightarrow 1$  when Eq. (B23) becomes identical to the initial guess suggested by Buks *et al.*<sup>17</sup> and Siders and Marcus<sup>18</sup> as the starting point for iteration.

Introducing the approximation (B23) in Eqs. (B2) and (B5), we find

$$A(t_0) = \frac{i\Delta G^0(x)t_0}{\hbar} + f(t_0), \quad (\text{B24})$$

where

$$f(t_0) = -(2/\pi\hbar) \int_0^\infty d\omega \phi(\omega) \omega^{-2} [\tanh(\beta\hbar\omega/4) - [\cosh(\eta\omega) - 1] \text{cosech}(\beta\hbar\omega/2)] \quad (\text{B25})$$

and

$$|A''(t_0)| = (2/\pi\hbar) \int_0^\infty d\omega \phi(\omega) \cosh(\eta\omega) \text{cosech}(\beta\hbar\omega/2), \quad (\text{B26})$$

where  $\eta = -(it_0 + \beta\hbar/2) = a(T)\beta\hbar\Delta G^0(x)/(2\lambda_q)$ . The saddle point approximation for the rate coefficient which follows from Eq. (B7) is Eq. (4.11). It reduces to the rate coefficient (B12) for symmetrical ET reactions discussed in Refs. 19 and 39 when  $\Delta G^0(x) = 0$ . The high temperature limit is attained by retaining just the leading term in the expansions of the hyperbolic functions in Eq. (4.11) when one gets Eq. (B20) with  $T^\ddagger = T$ .

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- <sup>24</sup>This is calculated in Ref. 7 for  $\Delta(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ . Correcting two minor typographical errors
- $$F_A(\tau) = \sum_{n=1}^{\infty} \frac{A^{2n} 2n!}{(2n!)^2} \sum_{i=0}^{2n} C_{2n,i} A_1^{2n-i} A_2^i \frac{\tau_1 \tau_2}{(2n-i)\tau_2 + i\tau_1},$$
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