Quantum Effects in Electron Transfer Reactions and Solvation Dynamics

Thesis by

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Abstract

This thesis focuses on the quantum effects of electron transfer reactions in solutions and solvation dynamics of pure solvent. A prototypical model system, the $Fe^{+2} + Fe^{+3} \rightleftharpoons Fe^{+3} + Fe^{+2}$ reaction in water, is treated using the spin-boson Hamiltonian model. The spectral density is related to the experimentally accessible data on the dielectric dispersion of the solvent, using a dielectric continuum approximation. On this basis the quantum correction for the ferrous-ferric electron transfer rate is found to be a factor of 9.6, which is significantly smaller than the corresponding values calculated from molecular models which neglect the electronic and vibrational polarization of the solvent. Using an imaginary free energy method, a general formula for the rate valid in all orders of perturbation in electronic coupling is derived for a renormalized classical bath. It is found that the quantum degrees of freedom can be effectively eliminated from the model by renormalizing the electronic coupling matrix element to the first order approximation for the quantum modes. Furthermore, a similar result is obtained for the quantum bath with a better approximation scheme. In application it has been shown that the rate has a nonmonotonic behavior as a function of the coupling matrix element in the inverted region. In the solvent dynamics controlled regime a one-particle Green function method is used to calculate the electron transfer reaction rate with a spin-boson Hamiltonian. A quantum version of Zusman's result on solvent dynamical effect in electron transfer reactions is obtained for the symmetric case. It is shown that the quantum effect for most of the realistic systems is not significant at room temperature and it would become important for some fast dielectric relaxation solvents like water. In solvation dynamics studies a Gaussian field model is used to obtain the charge density correlation function of the solution in terms of charge density correlation function of the solvent. It then becomes possible to calculate the time-dependent solvation free energy without using the "uniform dielectric approximation." It is found that the nonuniformity in the

vicinity of the solute indeed retards the solvation relaxation.

Table of Contents

Summary

This thesis consists of several independent chapters based on my research at Caltech. It is tentatively divided into two parts. The first part(Chapters 1-5) reflects our effort to try to understand the quantum effects on electron transfer reactions in solutions, which is one of the most fundamental reactions in chemistry and biology. The second part(Chapter 6) deals with the solvation dynamics of pure solvent, which is an important step to understand the role of solvent in the chemical reactions in solutions.

In chapter 1 a prototypical model system, the $Fe^{+2} + Fe^{+3} \rightleftharpoons Fe^{+3} + Fe^{+2}$ reaction in water, is treated using the spin-boson Hamiltonian model. The spectral density is related to the experimentally accessible data on the dielectric dispersion of the solvent, using a dielectric continuum approximation. On this basis the quantum correction for the ferrous-ferric electron transfer rate is found to be a factor of 9.6. This value is significantly smaller than the corresponding values calculated from molecular models which neglect the electronic and vibrational polarization of the solvent.

In chapters 2-3 using an imaginary free energy method a general formula for the rate valid in all orders of perturbation in electronic coupling is derived for a renormalized classical bath. It is found that the quantum degrees of freedom can be effectively eliminated from the model by renormalizing the electronic coupling matrix element to the first order approximation for the quantum modes. Furthermore a similar result is obtained for the quantum bath with a better approximation scheme. One application has shown the rate has a nonmonotonic behavior as a function of the coupling matrix element in the inverted region.

In chapter 4 in order to address the quantum effect in the solvent dynamics

controlled regime, a one particle Green function method is used to calculate the electron transfer reaction rate with spin-boson Hamiltonian. A quantum version of Zusman's result on solvent dynamical effect in electron transfer reactions is obtained for the symmetric case. The quantum correction due to the new rate expression is discussed. It is shown that the quantum effect for most of the realistic systems is not significant at room temperature, although it would become important for some fast dielectric relaxation solvents like water. In chapter 5 the effect of solvent dynamics on electron transfer reactions is discussed from a different perspective. An equation of motion for the reduced density matrix(master equation) is derived from the modified spin-boson Hamiltonian for Debye relaxation and under classical approximation this equation reduces to Zusman's original equation. The approximations involved in the Zusman's model are clarified. A numerical scheme to solve the master equation to obtain the quantum reaction rate is discussed so that a comparison with the quantum rate obtained from chapter 4 can be made. A more important aspect of this study is that the solvent dynamical effect on asymmetric electron transfer reactions can be studied within this model.

In chapter 6 a Gaussian field model is used to obtain the charge density correlation function of the solution in terms of charge density correlation function of the solvent. It then becomes possible to calculate the time-dependent solvation free energy without using the "uniform dielectric approximation." It is found that the nonuniformity in the vicinity of the solute indeed retards the solvation relaxation for our model, thereby is in agreement with Onsager's "inverted snowball" picture.

Chapter 1

Quantum Correction for Electron Transfer Rates. Comparison of Polarizable versus Nonpolarizavle Descriptions of Solvent

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Quantum correction for electron transfer rates. Comparison of polarizable versus nonpolarizable descriptions of solvent

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The electron transfer rate constant is treated using the spin-boson Hamiltonian model. The spectral density is related to the experimentally accessible data on the dielectric dispersion of the solvent, using a dielectric continuum approximation. On this basis the quantum correction for the ferrous–ferric electron transfer rate is found to be a factor 9.6. This value is smaller than the corresponding result (36) of Chandler and co-workers in their pioneering quantum simulation using a molecular model of the system [J. S. Bader, R. A. Kuharski, and D. Chandler, J. Chem. Phys. **93**, 230 (1990)]. The likely reason for the difference lies in use of a rigid water molecular model in the simulation, since we find that other models for water in the literature which neglect the electronic and vibrational polarizability also give a large quantum effect. Such models are shown to overestimate the dielectric dispersion in one part of the quantum mechanically important region and to underestimate it in another part. It will be useful to explore a polarizable molecular model which reproduces the experimental dielectric response over the relevant part of the frequency spectrum.

I. INTRODUCTION

Electron transfer reactions are among the most fundamental chemical processes.[1-3] As a prototypical model system, the $Fe^{+2} \rightleftharpoons Fe^{+3}$ electron exchange in water has been actively studied.[4,5] Recently, Chandler and co-workers[6,7] used a molecular model to study this process by quantum and classical simulation methods. Their results have shed an illuminating light on this system.

By classical and quantum simulation methods they observed the parabolic behavior of the free energy surface with respect to the solvent polarization coordinate, a behavior which plays the important role in the theory developed by one of us.[1] They also studied the quantum correction for the electron transfer rate constant. The full quantum Monte Carlo simulation gave a quantum correction factor for the rate of about 65 for water.[6] Under a harmonic approximation their quantum correction was about 36, which is still substantially larger than the traditional estimate[5] of a factor of about 7.

In the present paper an expression for the nonadiabatic rate constant (the Golden Rule rate expression) is used in which the rate is expressed in terms of the spectral density (the dielectric response) of the system. The spectral density is then obtained from experimental data, for fixed position of the reactants, using the dielectric continuum approximation and the harmonic approximation for the inner shell of ion–water complex breathing modes. For the electron transfer rate constant for the aqueous ferrous–ferric system it is found that under the above approximation our estimation of the quantum correction factor is a factor of 9.6, which is smaller than the above result of 36 for the harmonic case. Other computer simulation models of water which also neglect the vibrational and the electronic polarization are also considered. We again find a large quantum effect for the rate constant of the model water solvent and find that these models overestimate the dielectric response in one region important for the quantum correction and underestimate it in another.

This paper is organized as follows: In Sec. II the theoretical basis of this paper is discussed. The nonadiabatic rate constant is expressed there in terms of the spectral density of the system. The relations between the spectral density and the experimental data are given. In Sec. III the calculation details are presented and the role of the electronic polarizability in electron transfer is discussed. The paper concludes with some remarks.

II. THEORY

A. Introduction

In this section a brief discussion of the nonadiabatic rate constant expression is given. Then, the relation between the spectral density and the experimentally accessible data, which forms the basis of the calculations, is presented.

In electron transfer reactions the reactant and product electronic states can usually be approximated as a two electronic-state system. If the solvent and the nuclear motion of the reactants and products are described as a harmonic bath, the electron transfer can be viewed as an electron jump between the two states modulated by a harmonic bath. This kind of system has been described by the spin-boson Hamiltonian[6,8,9]

$$H=\frac{H_{AB}}{2}\sigma_x+\frac{\epsilon}{2}\sigma_z+\frac{\sigma_z}{2}\sum_{i=1}^{N}2c_iy_i+\sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i}+\frac{m_i\omega_i^2y_i^2}{2}\right), \tag{2.1}$$

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[a] Contribution No. 8833.

where $H_{AB}/2$ is the electronic matrix element which couples the reactants' state $|-\rangle$ and the products' state $|+\rangle$. The y_l is a polarization coordinate, p_l is the canonically conjugate momentum, and ϵ is the driving force of the reaction (i.e., $-\Delta G^0$). σ_z and σ_x are Pauli matrices in the two-state ($|+\rangle$ and $|-\rangle$) representation. A harmonic bath having the same frequencies for the reactants' and the products' electronic states is assumed in this Hamiltonian. In such an approximation any changes in metal-ligand frequencies accompanying the electron transfer are replaced by a particular symmetric combination.[5]

For the nonadiabatic case, the electron transfer rate constant is given by the following Golden Rule formula:[2,3]

$$k=\frac{2\pi}{\hbar Z_b}\left|\frac{H_{AB}}{2}\right|^2\sum_i\sum_f\exp(-\beta E_i^0)|\langle\chi_i^0|\chi_f^0\rangle|^2$$
$$\times\delta(E_f^0-E_i^0+\epsilon), \tag{2.2}$$

where i and f specify the quantum numbers of the reactant and the product system, E_i^0 and E_f^0 are the energy levels of their systems, χ_i^0 and χ_f^0 are the corresponding wave functions, and Z_b is the partition function of the reactant system.

Upon using the usual δ-function expression

$$\delta(E_f^0-E_i^0+\epsilon)$$
$$=\frac{\beta}{2\pi}\int_{-\infty}^{\infty}\exp[-i(E_f^0-E_i^0+\epsilon)\beta R]\,dR \tag{2.3}$$

and the overlap integral of the wave functions assumed to be harmonic, the following formula has been obtained:[2,3]

$$k=\frac{\beta}{\hbar}\left|\frac{H_{AB}}{2}\right|^2\int_{-\infty}^{+\infty}dR\exp\left[-\left(\frac{\beta}{2}+i\beta R\right)\epsilon\right.$$
$$\left.-\frac{2}{\pi\hbar}\int_0^{\infty}d\omega\frac{J(\omega)}{\omega^2}\frac{\cosh(\beta\hbar\omega/2)-\cosh(iR\beta\hbar\omega)}{\sinh(\beta\hbar\omega/2)}\right], \tag{2.4}$$

where $J(\omega)$ is spectral density of the system

$$J(\omega)=\sum_{l=1}^{N}\pi\delta(\omega-\omega_l)\frac{c_l^2}{m_l\omega_l}. \tag{2.5}$$

This well-known quantum rate constant expression of electron transfer in the nonadiabatic case was first derived by Soviet scientists.[2,3] Later Chandler and co-workers[6] rederived this result within a spin-boson Hamiltonian description by the Golden Rule. Recently,[8] Song and Stuchebrukhov gave a general description of electron transfer reactions using the spin-boson Hamiltonian, in which the above formula appears as a special case of a more general one. A key assumption in the above formula is the use of a harmonic approximation for the bath modes.[2] Equation (2.4) is the fundamental result of nonadiabatic quantum electron transfer theory within the harmonic approximation. Another approach, in which only a linear response approximation is used for the solvent bath,[2(c)] leads to the same result, where the $J(\omega)$ is expressed, as given later, in terms of the dielectric response function.

TABLE I. The quantum correction of aqueous ferrous–ferric system ($T=298$ K).

	Saddle-point approximation[a]			
	Inner part	Outer part	Total	Ratio
Quantum exponential	-12.97	-10.84	-23.81	8.4
Classical exponential	-14.11	-11.86	-25.97	
Quantum prefactor			1.65×10^{11}	1.1
Classical prefactor			1.48×10^{11}	
Quantum rate (s^{-1})			7.53	9.6(36[c])
Classical rate (s^{-1})			0.78	
	Full calculation[b]			
Quantum rate (s^{-1})			7.78	10.0
Classical rate (s^{-1})			0.78	

[a] From Eq. (2.13).
[b] From Eq. (2.4) with $\epsilon=0$.
[c] From Ref. 6.

For the ferrous–ferric system ϵ is zero. The saddlepoint of R is zero in this case. The rate constant can be expressed in the following simple form using the saddlepoint approximation,[5]

$$k\simeq\frac{2\pi}{\hbar}\left|\frac{H_{AB}}{2}\right|^2\left[4\hbar\int_0^{\infty}d\omega J(\omega)\cosh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-1/2}$$
$$\times\exp\left[-\frac{2}{\pi\hbar}\int_0^{\infty}d\omega\frac{J(\omega)}{\omega^2}\tanh\left(\frac{\beta\hbar\omega}{4}\right)\right]. \tag{2.6}$$

In the classical approximation for bath ($\beta\hbar\omega\ll1$) Eq. (2.6) reduces to the usual classical nonadiabatic expression for the rate of electron transfer in symmetric reactions. A test of the saddlepoint approximation, by a comparison of Eqs. (2.6) and (2.4), is given later in Table I.

In order to calculate the electron transfer rate constant for the actual system the explicit form of spectral density $J(\omega)$ is needed. There are several ways of obtaining this quantity. For example, Bader *et al.*[6,7] calculate it by a quantum Monte Carlo simulation using a microscopic model of aqueous ferrous–ferric system. Another way is to relate this quantity to some phenomenological experimentally measurable variable.[3] In the present paper the latter approach is used; the bath is divided into an inner part [the first coordination shell, consisting of $Fe(H_2O)_6^{+2}$–$Fe(H_2O)_6^{+3}$ subsystem] contributing an amount $J_i(\omega)$ to the spectral density, and an outer part, namely the rest of the water solvent interacting with the hexacoordinated aqueous Fe^{+2} and Fe^{+3} ions, treated as spheres. The outer contribution $J_0(\omega)$ to the spectral density is then related to experimental data on the dielectric response of the solvent. Thus we have

$$J(\omega)=J_0(\omega)+J_i(\omega). \tag{2.7}$$

The electron transfer rate constant is then calculated.

B. The spectral density of the outer contribution

Phenomenologically, the outer contribution can be treated using a dielectric continuum interacting with the ionic charge distribution.[3] The response of the dielectric to the electric field is defined by the dielectric permittivity function $\epsilon(\omega)$, which is experimentally available. If the polar medium is treated as a collection of harmonic oscillators characterizing the dielectric polarization, the changes in electric field of the ions, where the products are compared with the reactants, shift the equilibrium positions of oscillators describing the polarization. According to Eq. (3.87) in Ref. 3, the shift of the dielectric polarization oscillator of the medium q_{i0} is related to the dielectric constant in the following way, neglecting spatial dispersion:

$$\frac{1}{2}\sum_i \hbar\omega_i q_{i0}^2=\frac{\int d\mathbf{r}\,|D^f-D^i|^2}{4\pi^2}\int_0^\infty \frac{d\omega}{\omega}\frac{\mathrm{Im}\,\epsilon(\omega)}{|\epsilon(\omega)|^2}, \tag{2.8}$$

where $\epsilon(\omega)$ is the dielectric constant as a function of frequency, the imaginary part of it being related to the absorption of the medium, D^f and D^i are the dielectric displacement vectors of the products' and the reactants' forms of the ions. For two ionic spheres with radii a_1 and a_2 and separated by a center-to-center distance R (Δe is the charge difference) we have,[1,17] neglecting dielectric image effects,

$$\frac{1}{8\pi}\int d\mathbf{r}\,|D^f-D^i|^2=\left(\frac{1}{2a_1}+\frac{1}{2a_2}-\frac{1}{R}\right)(\Delta e)^2. \tag{2.9}$$

The left-hand side of Eq. (2.8), λ_0, represents the classical form of the outer part of the reorganization energy of the system. For the spin-boson model this reorganization energy can be written as[8]

$$\lambda_0=\sum_i \frac{2c_i^2}{m_i\omega_i^2}=\int_0^\infty \frac{2}{\pi}\frac{d\omega}{\omega}J_0(\omega). \tag{2.10}$$

The same formula relating λ_i to $J_i(\omega)$ also applies. Comparing Eqs. (2.8) and (2.10), the outer contribution $J_0(\omega)$ to the spectral density can be written as

$$J_0(\omega)=\frac{\int d\mathbf{r}\,|D^f-D^i|^2}{8\pi}\frac{\mathrm{Im}\,\epsilon(\omega)}{|\epsilon(\omega)|^2}. \tag{2.11}$$

Equation (2.4), with J given by Eq. (2.11), was first obtained by a different method by Ovchinnikov and Ovchinnikova.[2(c)] They showed that above result is valid under linear response theory. A more elaborate description, based on $\epsilon(\mathbf{k},\omega)$ could be deduced from the results given in Ref. 3, $\mathbf{k}$ being the wave vector. However, the relevant experimental data for $\epsilon(\mathbf{k},\omega)$ do not appear to be available.

C. The spectral density of the inner-shell contribution

The inner part of the spectral density $J_i(\omega)$, i.e., the contribution from the inner-shell, is relatively simple. The main contribution for electron transfer comes from the two shifted symmetric breathing modes (they are normal modes) of the reactant pair, $Fe(H_2O)_6^{+2}$–$Fe(H_2O)_6^{+3}$, and the product pair, $Fe(H_2O)_6^{+3}$–$Fe(H_2O)_6^{+2}$.[10,11] The equilibrium shift of harmonic coordinates is the equilibrium bond length change d_0 from $Fe(H_2O)_6^{+2}$ to $Fe(H_2O)_6^{+3}$, the breathing mode frequency is ω_1 for $Fe(H_2O)_6^{+2}$ and ω_2 for $Fe(H_2O)_6^{+3}$, and the constant frequency ω_0 used in the Hamiltonian can be expressed approximately[1,5] by $\omega_0^2=2\omega_1^2\omega_2^2/(\omega_1^2+\omega_2^2)$; m in Eq. (2.5) for J_i is the mass for a ligand molecule in a symmetric breathing mode. Thus, the spectral density of the inner contribution can be written as

$$J_i(\omega)=(\pi/2)\omega\delta(\omega-\omega_0)\lambda_i, \tag{2.12a}$$

where

$$\lambda_i=6m\omega_0^2d_0^2, \tag{2.12b}$$

using the fact that there are six ligands for the symmetric breathing mode in $Fe(H_2O)_6^{+2}$ and in $Fe(H_2O)_6^{+3}$.

D. Rate constant result

The calculation of the electron transfer rate constant can be made by direct numerical integration of Eq. (2.4), using Eqs. (2.7), (2.11), (2.12), and the spectral density obtained from the experimental data. Or the saddle-point approximation can be used, so that a somewhat more transparent picture can be obtained. In this case Eq. (2.6) can be written in the following form:

$$\begin{aligned}k\approx\frac{2\pi}{\hbar}\left|\frac{H_{AB}}{2}\right|^2&\left[4\int_0^\infty d(\ln\omega)J_0(\omega)\hbar\omega\cosh\left(\frac{\beta\hbar\omega}{2}\right)\right.\\&\left.+2\pi\hbar\omega_0\lambda_i\cosh\left(\frac{\beta\hbar\omega_0}{2}\right)\right]^{-1/2}\\&\times\exp\left[-\int_0^\infty d(\ln\omega)\frac{2J_0(\omega)}{\pi\hbar\omega}\tanh\left(\frac{\beta\hbar\omega}{4}\right)\right.\\&\left.-\frac{\lambda_i}{\hbar\omega_0}\tanh\left(\frac{\beta\hbar\omega_0}{4}\right)\right],\end{aligned} \tag{2.13}$$

where $J_0(\omega)$ is given by Eq. (2.11) and λ_i is given by Eq. (2.12b). Because of the wide range of ω's which contribute to the integrand from the outer part it was convenient to introduce $\ln\omega$ as the integration variable in Eq. (2.13). Equations (2.4) [with Eqs. (2.7), (2.11), and (2.12)] and Eq. (2.13) represent the starting point for the present calculation.

III. CALCULATIONS AND DISCUSSION

In this section the quantum and classical rate constants are calculated from the experimental data for the present model. From the above formulas, a key step is to use the experimentally observed complex-valued dielectric constant of solvent as a function of frequency. In general, there exist two broad regions of absorption in water, the Debye region (or orientational region) and the resonance region. In the Debye region, the Debye formula can be used to

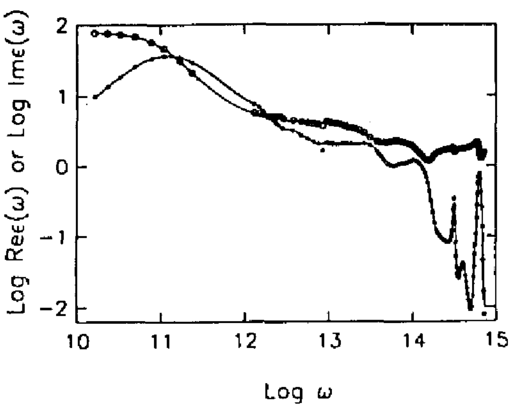

FIG. 1. The experimental data (Refs. 12–15) and the empirical fit. ○ denotes the real part of the experimental dielectric constant; ● the imaginary part. The solid line is a cubic spline interpolation and the dotted line is Debye fit.

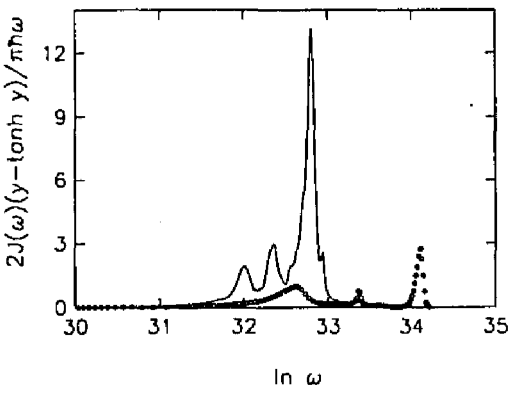

FIG. 2. The experimental data (Refs. 12–15) and the simulation result of the SPC model (Ref. 6). ○ denotes the integrand of experimental quantum correction factor from the outer part of the spectral density J_0, with $y=\beta\hbar\omega/4$. The solid line is the integrand of SPC model quantum correction from the spectral density of Ref. 7, noting that the two small peaks around ln $\omega=32$ arise from the inner part contribution.

provide an excellent description of the experimental data, using the following parameters:[13] $\epsilon_\infty=4.21$, $\epsilon_s=78.3$, $\tau=8.2\times10^{-12}$ s in the expressions

$$\mathrm{Re}\,\epsilon=\epsilon_\infty+\frac{\epsilon_s-\epsilon_\infty}{1+\omega^2\tau^2}, \tag{3.1a}$$

$$\mathrm{Im}\,\epsilon=\frac{(\epsilon_s-\epsilon_\infty)\omega\tau}{1+\omega^2\tau^2}. \tag{3.1b}$$

In the resonance region there is no general formula to fit the experimental data. Here, a cubic spline interpolation[16] is used to fit the experimental data and the integral is evaluated using this spline to interpolate the experimental results. For a thermal electron transfer only, frequencies below the electronic excitation region are relevant to our calculation. Thereby, the angular frequency (ω) region we consider is from 0 to 7.2×10^{14} rad/s, abbreviated in the following as s^{-1} (3844 cm^{-1}), since from 7.2×10^{14} s^{-1} to the optical frequency the imaginary part of dielectric constant is extremely small[15] (cf. Fig. 1). From 0 to 1.0×10^{11} s^{-1} the Debye formula is used and from 1.0×10^{11} to 7.2×10^{14} s^{-1} the spline interpolation is employed. The experimental data and the fitted results are collected in Fig. 1.

The inner contribution data is well-known from the literature,[10,11] $\omega_1=390$ cm^{-1}, $\omega_2=490$ cm^{-1}, $d_0=0.14$ Å, $m=3.0\times10^{-26}$ kg/molecule.

The results of these calculations are given in Table I. Comparing the values for the quantum rate constant it is clear that the saddlepoint approximation is very good, and the following discussion is based on that approximation. This quantum effect is seen in Table I to be substantially smaller than the simulation result from Chandler and coworkers[6,7] who used the SPC model for water. This difference is due to the different spectral density employed. In their calculations the spectral density is obtained from the cosine transformation of the classical real time bath autocorrelation function which is calculated from the computer simulation. To illustrate this point we plot in Fig. 2 the integrand difference between the exact expression and the classical expression in the exponential part of Eq. (2.13) which gives most of the quantum correction factor (cf. Table I). In Fig. 2 the result is given for both the experimental outer spectral density and for the SPC water model, using in the latter case the results of Ref. 7. It should be remembered that the two small peaks around $\omega=1.0\times10^{14}$ s^{-1} are contributed by the inner part of the spectral density $J_i(\omega)$ since the curve is the total spectral density calculated from their simulation. From Fig. 2 we see that in one region (around 1.6×10^{14} s^{-1}) important for the quantum correction the SPC model considerably overestimates the dielectric response. In another region (around 6.5×10^{14} s^{-1}) important for quantum correction it has no contribution at all. Thus, we believe that the spectral density used in the SPC model is not accurate due to the rigid model of the solvent molecules employed—it contains neither the electronic nor the vibrational polarizability of the individual solvent molecules.

In order to test this supposition we have used two computer simulations available in the literature[18] for the water, namely the TIP4P and the MCY models, both of which also omit the two molecular polarizabilities just mentioned. Although there exist some polarizable water models in the literature[19] no detailed dielectric dispersion curve appears to be available from them. We have used the spectral density for the TIP4P and MCY models, with Eqs. (2.12) and (2.13), to calculate the quantum correction factor under the saddlepoint approximation. For the TIP4P model the outer spectral density $J_0(\omega)$ is calculated from a phenomenological formula, given in Ref. 18, which fits the simulation result well (Fig. 9 in Ref. 18), and the inner part, $J_i(\omega)$, is kept the same as above. The resulting quantum correction factor is 26 when the upper limit is 2.1×10^{14} s^{-1}, which is the valid limit of the phenomenological formula. For the MCY model the quantum correction factor is 21 when the upper limit is 2.2×10^{14} s^{-1}.

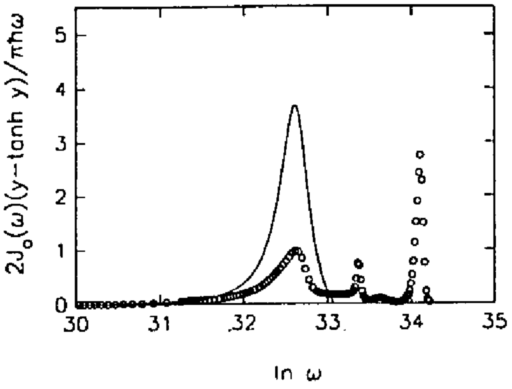

FIG. 3. The experimental data (Refs. 12–15) and the simulation result of the MCY and TIP4P models (Ref. 18). ○ denotes the integrand of experimental quantum correction from the outer part spectral density J_0, with $y=\beta\hbar\omega/4$. The solid line is the integrand of MCY model quantum correction from the outer part of the spectral density of Ref. 18. The dotted line is the integrand of the TIP4P model quantum correction from the outer part of the spectral density of Ref. 18.

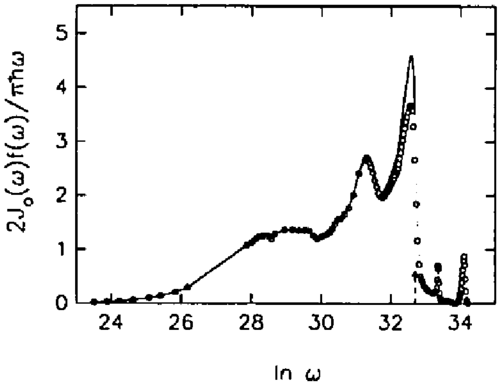

FIG. 5. The separation of classical modes and quantum modes approximation. ○ denotes the integrand of experimental data from the outer part of the spectral density [$f(\omega)=\tanh(\beta\hbar\omega/4)$]; the solid curve is the classical integrand [$f(\omega)=\beta\hbar\omega/4$] from the experimental data; and the dotted curve the quantum integrand [$f(\omega)=1.0$] from the experimental data. The arrow mark gives the separation frequency with $\beta\hbar\omega/4=1.0$.

These results can be understood from Fig. 3. Like the SPC model both the TIP4P and the MCY models overestimate the dielectric response in a region ($32<\ln\omega<33$) and underestimate in another ($33<\ln\omega<34.3$), regions which are critical for the quantum effect calculation. For the TIP4P and the MCY models the large spectral density is due to the small Re ϵ of the model simulations in a critical region (Fig. 4).

For comparison with previous work, we give next an approximation to the outer contribution in Eq. (2.13) by dividing the complete frequency range of the dielectric response into two parts, a "classical" part and a "quantum" part, where a separation frequency $\omega_{\rm cl}$ is defined by relation $\beta\hbar\omega_{\rm cl}/4=1.0$. From 0 to $\omega_{\rm cl}$ the classical approximation ($\beta\hbar\omega/4<1.0$) is used for the first part of the exponential factor in Eq. (2.13), written as $\exp[-\beta\lambda_0^{(1)}/4]$, where

$$\lambda_0^{(1)}=-\frac{\int|D^f-D^i|^2dr}{4\pi^2}\int_0^{\omega_{\rm cl}}d\omega\frac{\operatorname{Im}\epsilon(\omega)}{\omega|\epsilon(\omega)|^2}. \quad (3.2)$$

By a sum rule,[3] we have

$$\int_0^{\omega_{\rm cl}}d\omega\frac{2}{\pi}\frac{\operatorname{Im}\epsilon(\omega)}{\omega|\epsilon(\omega)|^2}=\frac{1}{\epsilon(\omega_{\rm cl})}-\frac{1}{\epsilon_s}. \quad (3.3)$$

Equations (3.2) and (3.3) give the well-known classical type of expression for reorganization energy arising from this portion of the outer contribution. From $\omega_{\rm cl}$ to $\omega_{\rm op}$ the quantum limit gives $\tanh(\beta\hbar\omega/4)\simeq1$, and that contribution to the exponential factor in Eq. (2.13) can then be written as

$$\sigma=\exp\left[-\frac{2}{\pi\hbar}\frac{\int|D^f-D^i|^2dr}{8\pi}\int_{\omega_{\rm cl}}^{\omega_{\rm op}}d\omega\frac{\operatorname{Im}\epsilon(\omega)}{\omega^2|\epsilon(\omega)|^2}\right]. \quad (3.4)$$

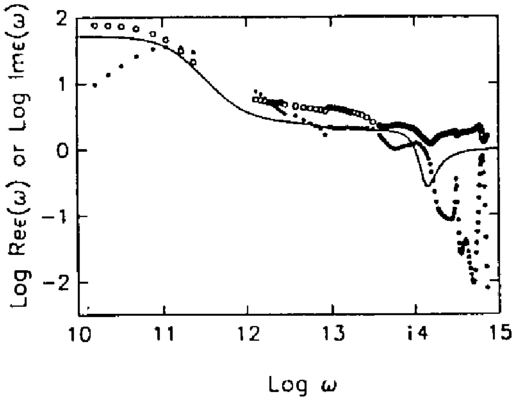

FIG. 4. The experimental data (Refs. 12–15) and the simulation result of the TIP4P model (Ref. 18). ○ denotes the real part of dielectric constant; ● the imaginary part. The solid line is the real part of the model simulation, and the dotted line is the imaginary part of the model simulation.

This latter factor is temperature independent and produces the tunneling factor arising from the quantum modes. A similar discussion can be found in Ref. 20. In general, the quantum modes renormalize the coupling matrix.[8] This limiting situation of dividing the modes into quantum and classical modes yields a fairly good approximation as seen in Fig. 5, the rate calculated from this approximation is smaller by a factor of 2. These two types of modes tend to play different roles in the electron transfer, the former giving a nuclear tunneling effect and the latter generating an activation barrier, an effect which has been often discussed in the literature.[1,2,3] From the tunneling factor expression (3.4), it is clear the really high frequency modes (say, higher than $7.2\times10^{14}\ {\rm s}^{-1}$) do not make a significant contribution to the tunneling effect due to the negligible imaginary part of the dielectric constant. In this sense the electronic polarization does not make large contribution to the electron transfer rate. However, the electronic polarization, by creating a shielding effect, does influence the other aspect of the $\epsilon(\omega)$ behavior. Furthermore, the atomic polarization (in the vibrational resonance region) does contribute to the electron transfer, both directly and via shielding, indirectly.

IV. CONCLUDING REMARKS

One of the particular features of the present work is to illustrate the calculation of nonadiabatic electron transfer rate from the experimentally available data using the linear response approximation and to test certain solvent molecular models (SPC, TIP4P, and MCY) in the literature. For aqueous ferrous–ferric system, the calculated rate from the experimental data is near the traditional estimate,[4,5] but different from a recent pioneering molecular simulation result of Chandler and co-workers. Even where the latter is approximated by introducing a harmonic bath approximation a significant difference remains. It will be interesting to repeat the molecular simulation using a molecular model of liquid water which includes both the atomic and electronic polarization and gives the correct dielectric dispersion behavior of water, rather than mainly the static dielectric constant.

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Chapter 2

Outer-sphere Electron Transfer in Polar Solvent: Quantum Scaling of Strongly Interacting Systems

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Outer-sphere electron transfer in polar solvents: Quantum scaling of strongly interacting systems

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The spin–boson Hamiltonian model is used to study electron transfer (ET) reactions of strongly interacting systems in polar solvents in the limit of fast dielectric relaxation of the solvent. The spectrum of polarization modes consists of low frequency modes which are treated classically, and high frequency modes which are treated quantum mechanically. A general explicit formula for the rate valid in all orders of perturbation theory in electronic coupling is derived. The rate formula is applicable in a wide range of parameters, including the inverted region of the reaction where the quantum tunneling corrections give the main contribution to the rate. It is found that the quantum degrees of freedom can be effectively eliminated from the model by renormalizing the electronic coupling matrix element. This renormalization results in the following scaling property of the electron transfer systems: a system containing both classical and quantum degrees of freedom is equivalent to a system of lower dimensionality, containing only classical degrees of freedom, with renormalized electronic coupling matrix element. An explicit formula for the renormalization is obtained.

I. INTRODUCTION

In the present paper outer-sphere electron transfer (ET) reactions in polar media in the limit of fast dielectric relaxation are discussed. In this limit the reaction rate is independent of the relaxation properties of the solvent and can be studied within the traditional statistical equilibrium formulation of the problem.[1,2] In recent years the opposite case of reactions controlled by the solvent dynamics has attracted the most attention.[3,4] In particular, a clear understanding of all possible limiting cases has been achieved.[5–7]

The case of fast dielectric relaxation is commonly believed to be well understood[5,6]—for weakly interacting systems a well developed nonadiabatic theory is applicable, and for strongly interacting systems a reaction taking place on an adiabatic potential surface is described by transition state theory.[1,2] The latter case, however, is much less studied than the former one. Moreover, neither the rate expression has actually been rigorously derived from the electron transfer Hamiltonian of a strongly interacting system, nor has a general rigorous theory unifying two extreme cases been ever formulated, although numerous attempts to do so have been undertaken from the early stages of the development of the electron transfer theory.[1,8] The unsatisfactory situation with the strongly interacting systems has renewed interest in such systems[9–12] recently. In particular, the role of the fast electronic component of the solvent polarization in the reaction rate has been extensively discussed although the picture is far from clear.

The spin–boson Hamiltonian model of ET provides an excellent tool for studying the strong coupling limit and discussing a unified approach to adiabatic and nonadiabatic regimes.[7,10,12,13] In particular, the free energy of strongly interacting electron transfer systems has been calculated[10,12] and the role of the electronic polarization has been studied within this model. In Refs. 10 and 12 an exponential part of the rate for symmetric ET systems is obtained and it is shown that the activation energy depends on the electronic coupling matrix element. This result has never been rigorously derived before, although it has been commonly accepted. As far as the electronic polarization is concerned the authors reached a conclusion that it does not affect the free energy of ET reaction.

In this paper we continue development of the spin–boson Hamiltonian model of ET. In comparison with Refs. 10 and 12 we discuss not only the exponential factor of the rate, the free energy, but also a pre-exponential factor. The spectrum of the system is assumed to contain low (classical) as well as high (quantum) frequencies, the latter ones describe the high frequency part of the solvent polarization, including the electronic part. We derive an explicit expression for the rate, Eq. (4.13), which is a sum of all perturbation orders in electronic coupling, and show how the general formula reduces to a traditional golden rule formula and to the transition state theory for electron transfer in two extremes of a small and a strong coupling. The general formula is applicable in a wide range of parameters, including the inverted region of the reaction,[1] where the quantum tunneling corrections give the main contribution to the rate.

To study the quantum corrections we develop a quantum-classical approximation for the correlation function of the solvent. Our quantum correlation function is exponential, and is essentially the next order approximation to the δ-function approximation proposed in Ref. 10. The latter approximation formally corresponds to infinitely large (∞) quantum frequencies of the solvent polarization. For this reason the δ-function approximation does not describe the quantum effects in the system. In a recent paper Gehlen and Chandler[12] have developed an approximate

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[a] Contribution No. 8799.

method to account for the effect of high (but finite) frequency polarization modes in the free energy of the reaction. According to their approximation the quantum corrections can be described as an additional quantum part of the activation energy of the reaction, which vanishes as frequency of the polarization becomes infinitely high. In the present paper we have developed a different approximation and found that the quantum modes modify the classical ET system in a different way. It turns out that all quantum tunneling effects can be incorporated into a renormalized (reduced) electronic coupling matrix element of the system, Eq. (4.10). This result reveals an interesting scaling property of the ET systems. We find that a system with both classical and quantum degrees of freedom is equivalent to a system of lower dimensionality, containing only classical degrees of freedom, with a renormalized electronic coupling matrix element.

The method of our calculation is based on a correlation function expression for the rate constant,[14–17]

$$k(\tau)\,\frac{Z_R^0}{Z^0}=\mathrm{Im}\langle\dot{\bar{n}}(\tau)\bar{n}(0)\rangle, \tag{1.1a}$$

$$k=\lim_{t>\tau_p} k(\tau+it), \tag{1.1b}$$

where $\bar{n}(\tau)$ is the occupation operator of the reactant state in Matsubara representation. The dot above $\bar{n}(\tau)$ is a derivative with respect to τ, τ_p is the plateau time, Z^0 is the partition function of the whole system (reactants plus products), and Z_R^0 is the partition function of the reactants. Using the path integral representation of the correlation function and introducing a quantum centroid reaction coordinate of the system[18–20] the rate can be expressed as $(k_B=1)$[20]

$$k=A\,\frac{2\,\mathrm{Im}\int Z(R)dR}{Z_R^0}=A\,\frac{2\,\mathrm{Im}\,Z}{Z_R^0}, \tag{1.2}$$

where

$$A=\begin{cases}T, & \text{if } T<T_c=\omega_b/2\pi\\ T_c, & \text{if } T>T_c\end{cases} \tag{1.3}$$

and $Z(R)$ is the partition function of the system with a fixed centroid R. In Ref. 20 a simplified *ad hoc* derivation of Eq. (1.2) is discussed. In the temperature dependence of the prefactor A there is a crossover between two different regimes[7,18,20,21] at $T_c=\omega_b/2\pi$, where ω_b is the activation barrier frequency. Below T_c the reaction takes place primarily from the metastable quantum states lying below the activation barrier, i.e., due to tunneling, while for temperatures above T_c the states lying above the activation barrier mainly contribute to the reaction, which is a classical activation process.

An imaginary part of the partition function of the reaction appears in an analytical continuation of the partition function into a complex plane R. The final formula for the rate constant has the form[20]

$$k=A\,\frac{\mathrm{Re}\int_{-\infty}^{+\infty}Z(iR)dR}{Z_R^0}. \tag{1.4}$$

The structure of the paper is as follows. In Sec. II a general expression for the partition function $Z(R)$ of the spin–boson Hamiltonian is derived. In Sec. III it is shown how the method of the present paper exactly reproduces the conventional nonadiabatic quantum rate expression in the lowest perturbation order. In Sec. IV results of the previous section are generalized to strongly interacting systems which require summation of all perturbative terms. A general formula for the rate constant is obtained. The quantum renormalization of the electronic coupling constant and scaling in the ET reactions are discussed. In Sec. V nonadiabatic and adiabatic asymptotics are discussed along with a saddle point approximations of the general formula for the rate constant. Section VI concludes this paper with some remarks on the limitations of the method and discussion of an experiment to check the scaling prediction of the present paper.

II. PARTITION FUNCTION OF THE SPIN–BOSON HAMILTONIAN

The Hamiltonian of ET system is written in a conventional form[1,2,13]

$$H=\frac{\Delta}{2}\sigma_x+\frac{\epsilon}{2}\sigma_z+\frac{\sigma_z}{2}\sum_{i=1}^{N}2c_iy_i+\sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i}+\frac{m_i\omega_i^2y_i^2}{2}\right), \tag{2.1}$$

where $\Delta/2$ is the electronic matrix element coupling the reactant state, $|-\rangle$, and the product state, $|+\rangle$, y_i and p_i are the nuclear motion coordinates and conjugated momenta, respectively, ϵ is the exothermicity of the reaction, σ_z and σ_x are the Pauli matrices in a two-state ($|+\rangle$ and $|-\rangle$) representation. The Hamiltonian (2.1) represents a two-state system coupled linearly to a harmonic bath which describes the nuclear motion of the environment (e.g., polarization of the solvent) as well as the nuclear motion of the reactant and product molecules. The harmonic bath for the reactant and product states is assumed to have the same frequencies. This assumption is a good approximation for most of the electron transfer systems.[1,2]

The key role in the present theory is played by the partition function of the whole system, which is written as

$$Z=\langle+|\mathrm{Tr}\,e^{-\beta H}|+\rangle+\langle-|\mathrm{Tr}\,e^{-\beta H}|-\rangle=Z_++Z_-, \tag{2.2}$$

where the trace is taken over all of the bath coordinates. Following the standard procedure of calculations[22–25] the harmonic nuclear coordinates can be integrated out and the trace over the spin coordinate can be conveniently written as a path integral. The result of such calculation is given by Eq. (2.10). For the convenience of those who are not familiar with this technique, and in order to introduce some useful notations, the sketch of the derivation is shown below.

The electronic coupling in Eq. (2.1) is treated as a perturbation and the Hamiltonian is written as $H=H_0+H'$, where $H'=(\Delta/2)\sigma_x$ and H_0 is the rest of the Hamiltonian. The density operator can be written as (hereafter $\hbar=1$)

$$e^{-\beta H}=e^{-\beta H_0}\times\sum_{n=0}^{\infty}(-1)^n\int_0^{\beta}d\tau_n\cdots\int_0^{\tau_2}d\tau_1\,H'(\tau_n)\cdots H'(\tau_1),\tag{2.3}$$

where $H'(\tau)=e^{\tau H_0}H'e^{-\tau H_0}$. After that, the partition function of the $|+\rangle$ state reads

$$Z_+=\langle+|\mathrm{Tr}\,e^{-\beta H}|+\rangle=\mathrm{Tr}\sum_{n=0}^{\infty}\left(\frac{\Delta}{2}\right)^{2n}\int_0^{\beta}d\tau_{2n}\cdots\int_0^{\tau_2}d\tau_1e^{-(\beta-\tau_{2n})H_{0+}}\times e^{-(\tau_{2n}-\tau_{2n-1})H_{0-}}\cdots e^{-(\tau_2-\tau_1)H_{0-}}e^{-H_{0+}\tau_1},\tag{2.4}$$

where

$$H_{0\pm}=H_b\pm\frac{1}{2}\left(\sum_{i=1}^{N}2c_iy_i+\epsilon\right),\tag{2.5}$$

$$H_b=\sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i}+\frac{m_i\omega_i^2y_i^2}{2}\right).\tag{2.6}$$

H_b in Eqs. (2.5) and (2.6) is the harmonic bath Hamiltonian.

Now a τ-dependent Hamiltonian, $H_{0n}(\tau)$, is defined by

$$H_{0n}(\tau)=H_b+\frac{\sigma_n(\tau)}{2}\left(\sum_{i=1}^{N}2c_iy_i+\epsilon\right),\tag{2.7}$$

$$\sigma_n(\tau)=\begin{cases}1 & \text{if } \tau\in[\tau_{2i-1},\tau_{2i-2}),\ 1<i<n+1;\\ -1 & \text{if } \tau\in[\tau_{2i},\tau_{2i-1}),\ 1<i<n;\end{cases}\tag{2.8}$$

where $0<\tau<\beta$, $\tau_0=0$, and $\tau_{2n+1}=\beta$. Thus $\sigma_n(\tau)$ takes values ±1 in the interval $0<\tau<\beta$ and changes sign sequentially n times at the points $\tau_1,\tau_2,\ldots,\tau_{2n}$. This variable explicitly describes the quantum paths of the two-state electronic coordinate.

In terms of the τ-dependent Hamiltonian, $H_{0n}(\tau)$, the partition function of the $|+\rangle$ state, Eq. (2.4), can be written in a compact form[23]

$$Z_+=\sum_{n=0}^{\infty}\left(\frac{\Delta}{2}\right)^{2n}\int_0^{\beta}d\tau_{2n}\cdots\int_0^{\tau_2}d\tau_1\,\mathrm{Tr}[\hat{T}e^{-\int_0^{\beta}H_{0n}(\tau)d\tau}],\tag{2.9}$$

where $\hat{T}$ is the τ-ordering operator. A similar procedure can be done for the $|-\rangle$ state and, finally, making use the cumulant expansion for the harmonic variables $\{y_i's\}$, $Z_\pm$ takes the form:

$$Z_\pm=Z_b\sum_{n=0}^{\infty}\left(\frac{\Delta}{2}\right)^{2n}\int_0^{\beta}d\tau_{2n}\cdots\int_0^{\tau_2}d\tau_1\times\exp\left[\frac{1}{2}\int_0^{\beta}\int_0^{\beta}d\tau\,d\tau'\,\frac{\sigma_n(\tau)\sigma_n(\tau')}{4}\times\sum_{i=1}^{N}4c_i^2\langle\hat{T}y_i(\tau)y_i(\tau')\rangle_b\mp\epsilon\int_0^{\beta}\frac{\sigma_n(\tau)}{2}d\tau\right],\tag{2.10}$$

where

$$Z_b=\mathrm{Tr}\,e^{-\beta H_b}\tag{2.11}$$

and $\langle\cdots\rangle_b$ stands for the ensemble averaging over the harmonic bath coordinates with Hamiltonian (2.6).

$\langle\hat{T}y_i(\tau)y_i(\tau')\rangle_b$ in Eq. (2.10) is the time-ordered correlation function of the harmonic variables,[13,22]

$$\langle\hat{T}y_i(\tau)y_i(\tau')\rangle_b=\frac{1}{2m\omega_i}\frac{\cosh\left(\frac{\beta\omega_i}{2}-\omega_i|\tau-\tau'|\right)}{\sinh\frac{\beta\omega_i}{2}}.$$

The sum over all nuclear coordinates in Eq. (2.10) is conventionally written with a spectral density, $J(\omega)$, defined by the following equation:

$$J(\omega)=\sum_{i=1}^{N}\pi\delta(\omega-\omega_i)\frac{c_i^2}{m_i\omega_i}.\tag{2.12}$$

Up to this point the transformations of the initial Hamiltonian have been known for a very long time. Recently Chandler and co-workers[13,19] suggested a new idea to use the centroid R of the spin coordinate $\sigma(\tau)$ as a reaction coordinate of the electron transfer. In a different situation the centroid approach has been discussed before in Refs. 18–20. In our notation the centroid reaction coordinate, R, is written as

$$R=\frac{1}{\beta}\int_0^{\beta}\frac{\sigma_n(\tau)}{2}d\tau=\frac{1}{2}-\frac{x_2+x_4+\cdots+x_{2n}}{\beta}\tag{2.13}$$

with

$$x_n=\tau_n-\tau_{n-1}.\tag{2.14}$$

In order to calculate the imaginary part of the partition function we first calculate it as a function of the real parameter R and then analytically continue it into complex plane of R, as required by Eq. (1.4).

With the introduced notations and with the definition of the reaction coordinate (2.13), the partition function at a fixed real R can be written as

$$Z(R)=Z_+(R)+Z_-(R),\tag{2.15}$$

$$Z_\pm(R)=Z_b\sum_{n=1}^{\infty}\left(\frac{\Delta}{2}\right)^{2n}\int_0^{\beta}dx_{2n}\cdots\int_0^{\beta}dx_1\exp\left[-\beta R\epsilon+\frac{1}{\pi}\int_0^{\infty}d\omega\,J(\omega)\int_0^{\beta}\int_0^{\beta}d\tau\,d\tau'\times\frac{\sigma_n(\tau)\sigma_n(\tau')}{4}\frac{\cosh((\beta\omega/2)-\omega|\tau-\tau'|)}{\sinh(\beta\omega/2)}\right]\theta[\beta-(x_1+x_2+\cdots+x_{2n})]\delta\left(R\mp\frac{1}{2}\pm\frac{x_2+x_4+\cdots+x_{2n}}{\beta}\right).\tag{2.16}$$

In the above formula the θ function is introduced in order to change variables from τ_n to x_n and the δ function fixes the centroid at R. Notice that summation in the above formula begins with $n=1$. The zero-order term was omitted since it only gives the partition function of the unperturbed system ($\Delta=0$) and does not contribute to the rate.

The above formula is the central point of our calculation of rate constant of electron transfer. The sum over n represents summation of all orders of perturbation theory. One needs first to evaluate Eqs. (2.15) and (2.16) for a real reaction coordinate R, then make an analytical continuation into the complex plane of R, and use Eqs. (1.4) and (1.3) to find the rate constant.

A critical step for further transformation of Eq. (2.16) is to analytically evaluate the double integral in the exponent involving spin variable,

$$I_n=\frac{1}{\pi}\int_0^\infty d\omega\, J(\omega)\int_0^\beta\int_0^\beta d\tau\, d\tau' \times\frac{\sigma_n(\tau)\sigma_n(\tau')}{4}\,\frac{\cosh[(\beta\omega/2)-\omega|\tau-\tau'|]}{\sinh(\beta\omega/2)} \tag{2.17}$$

for an arbitrary value of n. We recall that, according to Eq. (2.8), $\sigma_n(\tau)$ is a function which takes values of ± 1 in the interval $0<\tau<\beta$ and changes sign n times. It turns out that this integral can be taken exactly only in $n=1$ case. This is the lowest order of perturbational theory which corresponds to a nonadiabatic case. This case is considered in the next section. For a general case of arbitrary matrix element Δ, Eq. (2.17) can be evaluated approximately for most realistic systems. This approximation will be developed in Sec. IV.

III. NONADIABATIC CASE

In order to show how the method of the present paper works, in this section the golden rule formula for a nonadiabatic electron transfer rate is reproduced. This case will also help to clarify some subtle points of the analytical continuation required for the rate calculations.

The nonadiabatic case corresponds to a small Δ, hence, only the first term, $n=1$, of the perturbation expansion in Eq. (2.15) can be taken into account. This term is proportional to Δ^2 and obviously corresponds to the golden rule. For $n=1$ the double integral involving the spin variable, Eq. (2.17), can be taken exactly,

$$I_1=E_a\beta-\frac{2}{\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega^2}\,\frac{\cosh(\beta\omega/2)-\cosh(R\beta\omega)}{\sinh(\beta\omega/2)}, \tag{3.1}$$

where

$$E_a=\sum_{i=1}^{N}\frac{c_i^2}{2m_i\omega_i^2}=\frac{1}{2\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega}. \tag{3.2}$$

The remaining two integrals in Eq. (2.16) over x_1, x_2 are easy to take directly returning to τ_1, τ_2 variables. The result is

$$Z_\pm^{(1)}(R)=Z_b\left(\frac{\Delta\beta}{2}\right)^2\left(\frac{1}{2}\pm R\right)\exp\left[-\beta R\epsilon+E_a\beta-\frac{2}{\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega^2}\,\frac{\cosh(\beta\omega/2)-\cosh(R\beta\omega)}{\sinh(\beta\omega/2)}\right]. \tag{3.3}$$

Now it is recalled that the reactant partition function, Z_R^0, is the partition function of the unperturbed $|-\rangle$ state and, according to (2.5) can be conveniently expressed as

$$Z_R^0=\mathrm{Tr}\, e^{-\beta H_{0^-}}=e^{(\beta\epsilon/2)+E_a\beta}Z_b. \tag{3.4}$$

Thus

$$Z^{(1)}(R)=Z_R^0\left(\frac{\Delta\beta}{2}\right)^2\exp\left[-\left(\frac{\beta}{2}+R\beta\right)\epsilon-\frac{2}{\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega^2}\,\frac{\cosh(\beta\omega/2)-\cosh(R\beta\omega)}{\sinh(\beta\omega/2)}\right]. \tag{3.5}$$

Finally, using Eq. (1.4) with a prefactor $A=1/\beta$, the nonadiabatic rate can be written as

$$k=\beta\left(\frac{\Delta}{2}\right)^2\mathrm{Re}\int_{-\infty}^{+\infty}dR\,\exp\left[-\left(\frac{\beta}{2}+i\beta R\right)\epsilon-\frac{2}{\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega^2}\,\frac{\cosh(\beta\omega/2)-\cosh(iR\beta\omega)}{\sinh(\beta\omega/2)}\right]. \tag{3.6}$$

This is a well-known quantum rate expression of the electron transfer in nonadiabatic case. In the classical approximation, $\beta\omega\ll 1$, Eq. (3.6) reduces to Marcus' nonadiabatic rate expression.[1,2] Eq. (3.6) was first derived from the golden rule by the Soviet researchers[26,27] and after that was rederived by many authors, e.g., Refs. 2 and 28.

In the original derivation a variable corresponding to our R (in Refs. 2 and 26 it is $\alpha-\frac{1}{2}$) was introduced as a formal integration parameter to represent a δ function from the golden rule. As it is seen from the above derivation, R is a centroid of the electron coordinate. It has a clear physical meaning of the reaction coordinate of the system.

Notice that for the nonadiabatic case the prefactor A is always $1/\beta$. As it was discussed in Sec. I, in the normal region there are two regimes, quantum and classical, with a crossover temperature T_c. However, in a nonadiabatic case, $\Delta\to 0$, the crossover temperature, $T_c=\omega_b/2\pi$, is indefinitely high and for this reason any finite temperature of the system is always below T_c, i.e., in the quantum regime where prefactor $A=1/\beta$. As it is shown in Appendix B, the barrier frequency ω_b, given by Eq. (B14), becomes indefinitely large when $\Delta\to 0$, so $T_c\to\infty$. In the inverted region, on the other hand, there is no classical barrier crossing at all, and the electron transfer always takes place from the quantum metastable states. In this case the prefactor is again $1/\beta$.

In many practical cases Eq. (3.6) can be further simplified by making use of the fact that the low and high frequency modes in the system are well separated. The low frequency modes can be treated classically, and the high frequency modes, quantum mechanically. To make use of this approximation two cutoff frequencies, classical, $\omega_{\rm cl}$, and quantum, ω_q, are introduced. In the integral expression of the exponent of Eq. (3.6), for all $\omega<\omega_{\rm cl}$ the classical limit ($\beta\omega\ll 1$) is used and for $\omega>\omega_q$ the quantum limit ($\beta\omega\gg 1$) is used. In a general case only one separation frequency is usually employed,[2] $\omega_c=\omega_{\rm cl}=\omega_q\sim T$. Two corresponding asymptotics of the hyperbolic functions give

$$k=\beta\left(\frac{\Delta}{2}\right)^2 \mathrm{Re}\int_{-\infty}^{+\infty} dR \exp\left[-\left(\frac{\beta}{2}+i\beta R\right)\epsilon-\frac{2\beta}{\pi}\right.$$
$$\left.\times\int_0^{\omega_{\rm cl}} d\omega\,\frac{J(\omega)}{\omega}\left(\frac{1}{4}+R^2\right)-\frac{2}{\pi}\int_{\omega_q}^{\infty} d\omega\,\frac{J(\omega)}{\omega^2}\right]. \tag{3.7}$$

In this approximation the integral over R can be taken exactly. It should be recalled at this point that R in Eqs. (3.6) and (3.7) is in fact a pure imaginary reaction coordinate which becomes complex in the transformation $R\rightarrow iR$ in Eq. (3.6), according to the prescription of Eq. (1.4). The integrand is exponentially decaying for large R in the complex plane, and for this reason the integral converges. This became possible only after the analytical continuation of the partition function, $Z(R)$, into the complex plane was done.

Integration in Eq. (3.7) gives

$$k=\left(\frac{\Delta}{2}\right)^2\sqrt{\frac{\beta\pi}{E_{\rm rc}}}\exp\left[-\frac{\beta E_{\rm rc}}{4}\left(1+\frac{\epsilon}{E_{\rm rc}}\right)^2-\frac{2}{\pi}\int_{\omega_q}^{\infty} d\omega\,\frac{J(\omega)}{\omega^2}\right], \tag{3.8}$$

where $E_{\rm rc}=4E_{\rm ac}$ is the classical reorganization energy. The classical activation energy is

$$E_{\rm ac}=\frac{1}{2\pi}\int_0^{\omega_{\rm cl}} d\omega\,\frac{J(\omega)}{\omega}. \tag{3.9}$$

As it is seen from Eq. (3.8), the classical modes contribute to the activation energy of the reaction and quantum modes give a temperature independent tunneling factor.[1,2]

Thus for $n=1$, our approach reproduces exactly all known results for the nonadiabatic case of the electron transfer theory. In the next section generalization of the theory to the case of arbitrary n, which corresponds to a strongly interacting system, is developed.

IV. ELECTRON TRANSFER RATE FOR STRONGLY INTERACTING SYSTEMS

In the case of strongly interacting systems, large Δ, all perturbation orders of the expansion in Eq. (2.16) must be taken into account. First, the integral involving spin variable, I_n of Eq. (2.17), has to be evaluated for an arbitrary value of n. This can be done as follows.

We notice that the integral is a sum of contributions of all frequencies in the system. The spectrum of the system is assumed to be divided into a low frequency region, $\omega<\omega_{\rm cl}$, and a high frequency region, $\omega>\omega_q$. In the approximation of this section the low frequency modes are treated classically, $\beta\omega_{\rm cl}\ll 1$, and the high frequency modes are treaded quantum mechanically, $\beta\omega_q\gg 1$. In many realistic systems the low and high frequencies are indeed well separated. For a system where this is not the case the separation can be made by a single frequency $\omega_c=T$. Such an approximation has been previously discussed in the literature.[2]

The correlation function of the classical modes is constant,

$$\langle \hat{T}y_i(\tau)y_i(\tau')\rangle_b=\frac{1}{m\omega_i^2\beta} \tag{4.1}$$

and their contribution is easy to evaluate. For an arbitrary n, the classical contribution to I_n is

$$I_{n\rm cl}=\beta E_{\rm ac}-\frac{2\beta}{\pi}\int_0^{\omega_{\rm cl}} d\omega\,\frac{J(\omega)}{\omega}\left(\frac{1}{4}-R^2\right). \tag{4.2}$$

The quantum contribution is more difficult to evaluate. To understand the general case of arbitrary n, it is convenient to start from the analysis of the case $n=1$, which can be treated exactly and, hence, our approximation can be verified. When $n=1$, the integration area in the τ, τ' plane is divided into nine regions, as shown in Fig. 1(a). In each of the nine regions the product of two spin variables is ± 1. The quantum correlation function has a sharp maximum along the diagonal of the square integration area and exponentially decays in the regions away from the diagonal. The quantum approximation for the correlation function (2.11) is

$$\langle \hat{T}y_i(\tau)y_i(\tau')\rangle_b=\frac{1}{2m\omega_i}e^{-\omega_i|\tau-\tau'|}. \tag{4.3}$$

The integral is calculated in the following way. First it is assumed that the product of the spin variables is +1 everywhere and the integral is taken with the exact correlation function (2.11). The result of the integration is $E_{aq}\beta$, where

$$E_{aq}=\sum_{i=N_q}^{N}\frac{c_i^2}{2m_i\omega_i^2}=\frac{1}{2\pi}\int_{\omega_q}^{\infty}\frac{J(\omega)}{\omega}\,d\omega. \tag{4.4}$$

Then, a double contribution of the negative regions of the spin variables (those regions are shaded in Fig. 1) is subtracted from $E_{aq}\beta$. An additional factor of two comes from the fact that one should first compensate a positive contribution which was overcounted in $E_{aq}\beta$, and then add a negative contribution, as is required by Eq. (2.17). There are four such equal contributions for $n=1$ case. Because of the sharp exponential decay of the correlation function, each of the negative contributions can be calculated independently of the others. This can be done for most of the points τ_1, τ_2 inside of the interval $(0,\beta)$ which are separated from each other farther than $1/\omega_q$. The negative contribution is calculated with the quantum approximation (4.2). Each of the four shaded regions in Fig. 1(a) gives a negative contribution

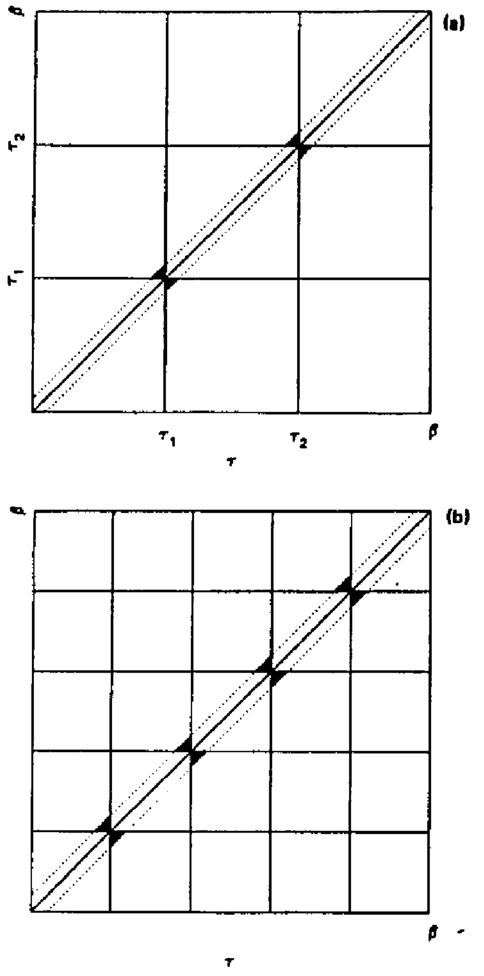

FIG. 1. The integration area for I_n, Eq. (2.17), in the $n=1$(a) and $n=2$(b) cases. The integration function is exponentially decaying in the regions away from the diagonal. In shaded regions the integration function is negative. Contribution of such negative regions is proportional to n for $\beta \gg 1/\omega_q$, Eq. (4.5).

$$\frac{1}{4\pi}\int_{\omega_q}^{\infty}\frac{J(\omega)}{\omega^2}\,d\omega. \qquad (4.5)$$

The final result of such calculations is $E_{aq}\beta$ minus the eight contributions of Eq. (4.5). It can be verified that the same result is obtained in the quantum limit of the exact formula, Eq. (3.1).

In a general case of arbitrary n, as it clearly follows from Fig. 1(a) and Fig. 1(b), instead of eight contributions (4.5), there will be eight times n such negative contributions. So, the quantum contribution into Eq. (2.17) is

$$I_{nq}=E_{aq}\beta-\frac{2n}{\pi}\int_{\omega_q}^{\infty}\frac{J(\omega)}{\omega^2}\,d\omega. \qquad (4.6)$$

The first temperature dependent term, $E_{aq}\beta$, can be also obtained from the δ-function approximation of the correlation function. Indeed, the correlation function is very sharp and one would think that it is possible to approximate it by a δ function. Such an approximation was used by Gehlen *et al.*[10] It turns out, however, as shown below, that this temperature dependent term does not correspond to any physical effects. The same term is present in the denominator of the rate expression, and two terms cancel each other. The true quantum effects are incorporated in the second temperature independent term which can not be reproduced with the δ-function approximation. The way in which the integral in the general n case has been taken is essentially equivalent to a so-called independent blip approximation of Garg, Onuchic, and Ambegaokar,[29] see also Ref. 25. This approximation is correct for all $n<n_q=\omega_q\beta\gg 1$.

Thus the contribution of classical and quantum modes to the integral I_n, Eq. (2.17), for an arbitrary n is

$$I_n=\beta E_{ac}-\frac{2\beta}{\pi}\int_0^{\omega_{cl}}d\omega\,\frac{J(\omega)}{\omega}\left(\frac{1}{4}-R^2\right)+E_{aq}\beta$$
$$-\frac{2n}{\pi}\int_{\omega_q}^{\infty}\frac{J(\omega)}{\omega^2}\,d\omega. \qquad (4.7)$$

From the above expression it is seen that the exponential factor in the partition function (2.16) depends only on R and can be taken out of the integral. The remaining multidimensional integral of θ and δ functions represents a purely geometrical factor. It is easy to recognize in it a cross section area of the n-dimensional cube. The calculation is rather straightforward although a bit tedious. Details for the purpose of references are given in Appendix A. The result of the calculation is

$$Z_\pm(R)=Z_b\sum_{n=1}^{\infty}\left(\frac{\beta\Delta}{2}\right)^{2n}\frac{1}{n!(n-1)!}\,[(\tfrac{1}{2})^2-R^2]^{n-1}$$
$$\times(\tfrac{1}{2}\pm R)\exp\Bigg[4\beta E_{ac}R^2-\beta R\epsilon+\beta E_{aq}$$
$$-\frac{2n}{\pi}\int_{\omega_q}^{\infty}d\omega\,\frac{J(\omega)}{\omega^2}\Bigg]. \qquad (4.8)$$

In the sum of the above expression the Bessel function can be recognized. Thus

$$Z(R)=Z_+(R)+Z_-(R)$$
$$=Z_bI_1\left(\beta\Delta'\sqrt{\tfrac{1}{4}-R^2}\right)\left(\frac{\beta\Delta'}{2}\right)\left(\sqrt{\tfrac{1}{4}-R^2}\right)^{-1}$$
$$\times\exp\,[4\beta E_{ac}R^2-\beta R\epsilon+\beta E_{aq}], \qquad (4.9)$$

where $I_1(x)$ is the modified Bessel function.[30]

Δ' in the partition function of the system (4.9) is an effective matrix element modified by quantum modes in the system,

$$\Delta'=\Delta\,\exp\left(-\frac{1}{\pi}\int_{\omega_q}^{\infty}d\omega\,\frac{J(\omega)}{\omega^2}\right). \qquad (4.10)$$

This modification (renormalization) of the electronic coupling matrix element is one of the central results of the present paper. The expression for the partition function, Eq. (4.9), shows that there are no other effects due to the quantum degrees of freedom except for the renormalization of the electronic coupling. This fact results in a very interesting scaling property of the electron transfer systems. Namely, a system with classical and "frozen" quantum degrees of freedom is equivalent to a system of lower dimensionality, containing only classical degrees of freedom, with renormalized electronic coupling (4.10).

As it will be made clear below, the decrease of the matrix element due to renormalization by quantum modes results in an increase of the reaction rate compared with the case when all modes, including quantum ones, are treated classically.

Gehlen *et al.*[10] calculated the partition function of the spin–boson Hamiltonian and they also obtained the modified Bessel function. Their result, however, contains an unchanged electronic matrix element, because a δ-function approximation for the correlation function of nuclear coordinates was used in the calculations. In a later publication Gehlen and Chandler[12] developed an approximation which extends their previous result with an additional quantum exponential factor. In our case the quantum corrections, as it is seen from Eq. (4.9), are incorporated into argument of the Bessel function.

In Eq. (4.9), Z_b should be substituted in the form [cf. Eq. (3.5)]

$$Z_b=e^{-\beta\epsilon/2-E_{ac}\beta-E_{aq}\beta}Z_R^0. \tag{4.11}$$

It is seen that the quantum part of the activation energy, E_{aq}, cancels out of the final expression of the partition function and, hence, from the corresponding rate expression, see Eq. (4.13) below.

A general expression for the rate constant is written as

$$k=A\,\mathrm{Im}\int I_1\left(\beta\Delta'\sqrt{\tfrac{1}{4}-R^2}\right)\left(\frac{\beta\Delta'}{2}\right)\times\left(\sqrt{\tfrac{1}{4}-R^2}\right)^{-1}\exp\left[4\beta E_{ac}R^2-\beta E_{ac}-\left(\frac{\beta}{2}+\beta R\right)\epsilon\right]dR. \tag{4.12}$$

After transformation of the integration contour into the complex plane according to Eq. (1.4) it takes the final form

$$k=A\int_{-\infty}^{+\infty} I_1\left(\beta\Delta'\sqrt{\tfrac{1}{4}+R^2}\right)\left(\frac{\beta\Delta'}{2}\right)\left(\sqrt{\tfrac{1}{4}+R^2}\right)^{-1}\times\exp\left(-4\beta E_{ac}R^2-\beta E_{ac}-\frac{\beta\epsilon}{2}\right)\cos(\beta R\epsilon)\,dR. \tag{4.13}$$

This is the main result of the present paper. The electron transfer rate constant is given for an arbitrary electronic matrix element where both quantum and classical modes are taken into account. All known results for the electron transfer theory can be reproduced as different asymptotics of this formula. In addition, it predicts several new results for strongly interacting electron transfer systems.

V. NONADIABATIC AND ADIABATIC ASYMPTOTICS OF THE GENERAL FORMULA (4.13)

As Gehlen *et al.*[10] pointed out, the nonadiabatic and adiabatic limits can be obtained from two asymptotics of *the Bessel function*[30]

$$I_1(x)\sim\begin{cases}\dfrac{x}{2}, & \text{if}\quad x\to 0;\\ e^x/\sqrt{2\pi x} & \text{if}\quad x\to\infty;\end{cases} \tag{5.1}$$

For the nonadiabatic rate [small x in Eq. (5.1)], as discussed in the previous section, $A=1/\beta$. In a saddle point approximation Eq. (4.13) reduces to

$$k=\left(\frac{\Delta'}{2}\right)^2\sqrt{\frac{\beta\pi}{E_{rc}}}\exp\left[-\frac{\beta E_{rc}}{4}\left(1+\frac{\epsilon}{E_{rc}}\right)^2\right] \tag{5.2}$$

which is the Marcus nonadiabatic electron transfer formula with quantum corrections.[1,2] In the above expression $E_{rc}=4E_{ac}$ is the classical part of the reorganization energy. This result also coincides with Eq. (3.8) which was derived in a different way as an approximation for the exact result (3.7). The nonadiabatic quantum correction in Eq. (3.8) has been known for a long time, although it was not recognized that this correction, in fact, is connected with modification of the electronic matrix element, as seen from Eqs. (5.2) and (4.10).

The exact condition for the nonadiabatic asymptotics ($x\ll 1$) is written as

$$\frac{\beta\Delta'}{2}\sqrt{1+\frac{1}{\beta E_{ac}}}\ll 1. \tag{5.3}$$

Usually $\beta E_{ac}\gg 1$ and, thus, condition (5.3) is defined solely by the coupling matrix element and temperature. It should be noticed it is the modified electronic matrix element, Δ', and not the initial one, that enters the nonadiabatic condition (5.3). An important consequence is that the applicability of the classical formula, Eqs. (3.8) and (5.2), can be extended to some cases of the conventional strong coupling,[5] $\Delta\beta\gg 1$. In this situation, due to the quantum modes in the system, the effective interaction can still be small, $\Delta'\beta\ll 1$, and the nonadiabatic asymptotics, Eqs. (3.8) and (5.3), valid. In this case, the nonadiabaticity of the reaction is induced by the quantum modes in the system.

The adiabatic asymptotics, large arguments of the Bessel function, is more difficult to study. There are two cases of large and small $|R|$ contributing to the integral (4.13) which are important in dealing with square roots in expression (4.13). In both cases the saddle point approximation is used in the evaluation of the integral in Eq. (4.13).

A large value of ϵ corresponds to the inverted region[1,2] of the reaction. In this case the prefactor $A=1/\beta$, as was explained in the previous section. If

$$\epsilon\gg 8E_{ac}\gg\Delta' \tag{5.4}$$

and

$$\Delta'\beta\gg 1 \tag{5.5}$$

then the adiabatic asymptotics of the Bessel function [second line in Eq. (5.1)] can be used, and at the same time the saddle point $|R^*| = \epsilon/8E_{ac} \gg 1$. The rate of reaction (4.13) in this approximation is

$$k = \frac{E_{ac}}{\epsilon\beta}\sqrt{\frac{8\Delta'}{\epsilon}}\, e^{-\beta\epsilon^2/16E_{ac}}. \tag{5.6}$$

Unfortunately, the saddle point approximation (and this estimate) in this case is very inaccurate because of the presence of the branch cuts on the complex plane of the integrand in Eq. (4.13).

In case of small ϵ,

$$\frac{\epsilon}{4E_{ac} - \Delta'} \ll 1 \tag{5.7}$$

and large Δ', Eq. (5.5), the saddle point $|R^*| = \epsilon/2(4E_{ac} - \Delta') \ll 1$. In this case the square roots in the integral of Eq. (4.13) can be expanded in small R, and the saddle point approximation can be simply obtained. This case corresponds to a normal region, where there is an activation barrier for the reaction. Let the frequency of the barrier be ω_b (this frequency will be found below). There are two regimes in the temperature dependence of the prefactor A with the crossover temperature $T_c = \omega_b/2\pi$.

For the low temperature regime, $T < T_c$, the prefactor $A = 1/\beta$ and the adiabatic rate is

$$k = \frac{1}{\beta}\sqrt{\frac{\Delta'}{4E_{ac} - \Delta'}}\exp\left[-\frac{4E_{ac} - \Delta'}{4}\beta\left(1 + \frac{\epsilon}{4E_{ac} - \Delta'}\right)^2 + \frac{\beta\Delta'}{4}\right]. \tag{5.8}$$

Because of condition (5.7) the rate is essentially proportional to

$$k \sim e^{-\beta(E_{ac} - \Delta'/2)}. \tag{5.9}$$

Modification of the activation energy of the reaction in a classical system by the electronic interaction (due to splitting of two potential surfaces by $\pm\Delta/2$ at the intersection points) is a well known result.[1,2] However, the exponential factor obtained in Eq. (5.9) is not at all trivial. First, because E_{ac} is not a total activation energy but only the classical part of it, second, and more surprisingly, because Δ' above is not the original matrix element of the Hamiltonian (2.1) but is the one renormalized by quantum modes in the system. This result is a direct consequence of the scaling nature of the quantum interactions.

In the regime corresponding to Eq. (5.8), many vibrational states of the classical modes are thermally excited, $\omega_{cl}/T \ll 1$, however, because of the condition $T < T_c$ the reaction mainly takes place from the metastable quantum states below the barrier top, i.e., due to tunneling. Thermal excitation of those states is described by the Arrhenius factor in Eq. (5.8). The high frequency quantum modes are not excited and the reaction takes place from the ground state of those modes. The contribution of the quantum modes to the reaction rate is described by the modification of the electronic matrix element, Eq. (4.9). Thus, in this regime the reaction takes place due to tunneling of both low and high frequency modes. The difference between them is that in the former case the tunneling takes place from the ground state, and in the latter case from the highly excited states, just under the classical barrier top.

In the high temperature regime, $T > T_c$, the prefactor A is $\omega_b/2\pi$. The frequency of the classical barrier found in Appendix B is

$$\omega_b = \sqrt{\frac{4E_{ac}}{\Delta'} - 1}\,\prod_{i=1}^{N_c}\omega_i \Big/ \prod_{i=2}^{N_c}\omega_i', \tag{5.10}$$

where ω_i and ω_i' are the classical frequencies of the reactant well and of the transition state respectively.

Thus, for the same condition as above, but for $T > T_c$, the reaction rate takes the following form

$$k = \frac{1}{2\pi}\prod_{i=1}^{N_c}\omega_i \Big/ \prod_{i=2}^{N_c}\omega_i' \exp\left[-\frac{4E_{ac} - \Delta'}{4}\beta\left(1 + \frac{\epsilon}{4E_{ac} - \Delta'}\right)^2 + \frac{\beta\Delta'}{4}\right]. \tag{5.11}$$

Again, due to condition (5.7) the exponential factor in the above expression is in fact simplified to Eq. (5.9). This formula exactly reproduces the well known result of the multidimensional transition state theory for the electron transfer when all modes in the system are classical,[1,2,31,32] in which case $\Delta' = \Delta$ and $E_{ac} = E_c$. Eq. (5.11) shows how the strong electronic interaction and the quantum modes modify the classical transition state theory expression. Surprisingly, all changes are incorporated in the modified electronic matrix element Δ'.

VI. CONCLUSION

In this paper a theory for strongly interacting electron transfer systems is proposed. The theory is based on the spin–boson Hamiltonian model of the electron transfer. A general formula for the rate is derived such that all of the electron transfer rate cases (weakly and strongly interacting systems, nonadiabatic and adiabatic cases) can be derived as different asymptotics of the general formula.

There are several limitations for this treatment. First of all, in the strong coupling case the electronic coupling matrix element should be still small enough so that the coupling would not affect the reactant and the product wells dramatically. Second, our treatment is not applicable to infinitely low temperature. Even for the low temperature regime, $T < T_c$, the temperature must be higher than the typical classical bath frequency. Otherwise the bath will be frozen in the ground state and the dynamics of the system will consist of coherent oscillations between reactants and products instead of exponential decay.[18,25]

It is shown that the quantum degrees of freedom can be effectively eliminated from the model by renormalizing the electronic coupling matrix element according to Eq. (4.10). This renormalization results in the following scaling property of the electron transfer systems: a system containing both classical and quantum degrees of freedom is equivalent (the same reaction rate) to a system of lower dimensionality containing only classical degrees of freedom, with renormalized electronic coupling matrix element. It would be interesting to check this theoretical prediction experimentally.

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APPENDIX A: EVALUATION OF THE GEOMETRICAL FACTOR IN EQ. (2.16)

In Sec. IV the calculation of the partition function (2.16) is reduced to evaluation of the following geometrical factor (for Z_+):

$$G=\sum_{n=1}^{\infty}\left(\frac{\Delta}{2}\right)^{2n}\int_0^{\beta}dx_{2n}\cdots\int_0^{\beta}dx_1$$
$$\times\theta[\beta-(x_1+x_2+\cdots+x_{2n})]$$
$$\times\delta\left(R-\frac{1}{2}+\frac{x_2+x_4+\cdots+x_{2n}}{\beta}\right). \tag{A1}$$

Using the integral representations of δ and θ functions,

$$\delta(x)=\int_{-\infty}^{+\infty}\frac{dk}{2\pi}e^{ikx},\quad \theta(x)=\int_{-\infty}^{+\infty}\frac{dk}{2\pi i}\frac{e^{ikx}}{k-i0} \tag{A2}$$

and defining dimensionless variables $z_i=x_i/\beta$, G is written in the following form:

$$G=\sum_{n=1}^{\infty}\left(\frac{\beta\Delta}{2}\right)^{2n}\int_0^1 dz_{2n}\cdots\int_0^1 dz_1\int_{-\infty}^{+\infty}\frac{dk}{2\pi i}$$
$$\times\frac{e^{ik-ik(z_1+z_2+\cdots+z_{2n})}}{k-i0}\int_{-\infty}^{+\infty}\frac{dt}{2\pi}$$
$$\times e^{itR-it/2+it(z_2+z_4+\cdots+z_{2n})}. \tag{A3}$$

Integration over $\{z_1,z_2,\cdots z_{2n}\}$ gives

$$G=\sum_{n=1}^{\infty}\left(\frac{\beta\Delta}{2}\right)^{2n}\int_{-\infty}^{+\infty}\frac{dk}{2\pi i}\frac{e^{ik}}{k-i0}\int_{-\infty}^{+\infty}\frac{dt}{2\pi}$$
$$\times e^{itR-it/2}\left\{\frac{1-e^{-ik}}{ik}\right]^n\left[\frac{1-e^{-i(k-t)}}{i(k-t)}\right]^n. \tag{A4}$$

Expanding Eq. (A4) in t and then integrating over t in the complex plane results in

$$G=\sum_{n=1}^{\infty}\left(\frac{\beta\Delta}{2}\right)^{2n}\int_{-\infty}^{+\infty}\frac{dk}{2\pi i}\frac{e^{ik}}{k-i0}\left[\frac{1-e^{-ik}}{ik}\right]\sum_{m=1}^{n}$$
$$\times\frac{1}{(n-1)!}C_n^m(-1)^{m+n}(R+m-1/2)^{n-1}e^{ik(R-1/2)}. \tag{A5}$$

Integration in k-space gives:

$$G=\sum_{n=1}^{\infty}\left(\frac{\beta\Delta}{2}\right)^{2n}\frac{(-1)^n}{n!(n-1)!}(R+1/2)^n$$
$$\times\sum_{m=1}^{n}C_n^m(-1)^m(R+m-1/2)^{n-1}. \tag{A6}$$

Expanding the second sum and using the following summation relation:[30]

$$\sum_{m=1}^{n}C_n^m(-1)^m m^{m'}=-\delta_{m'0} \tag{A7}$$

we finally obtain

$$G=\sum_{n=1}^{\infty}\left(\frac{\beta\Delta}{2}\right)^{2n}\frac{1}{n!(n-1)!}(1/4-R^2)^{n-1}(1/2+R). \tag{A8}$$

To find the similar factor for Z_-, R should be taken with the minus sign. The sum of both factors $Z_\pm$ results in Eq. (4.8).

APPENDIX B: EVALUATION OF THE BARRIER FREQUENCY

The barrier frequency is evaluated for only classical degrees of freedom and for the renormalized coupling matrix element Δ'. Here we follow the method of Dakhnovskii and Ovchinnikov.[31,32]

The uncoupled reactant and product harmonic potentials in the mass-weighted coordinates are written as

$$U_+=\frac{\epsilon}{2}+\sum_{i=1}^{N_c}\left(\frac{\omega_i^2y_i^2}{2}+c_iy_i\right), \tag{B1a}$$

$$U_-=-\frac{\epsilon}{2}+\sum_{i=1}^{N_c}\left(\frac{\omega_i^2y_i^2}{2}-c_iy_i\right). \tag{B1b}$$

Electronic coupling with matrix element $\Delta'/2$ results in two adiabatic surfaces, the lower one is

$$U_l=\frac{U_++U_-}{2}-\sqrt{\left(\frac{U_+-U_-}{2}\right)^2+\left(\frac{\Delta'}{2}\right)^2}$$
$$=\sum_{i=1}^{N_c}\frac{\omega_i^2y_i^2}{2}-\sqrt{\left[\frac{\epsilon}{2}+\sum_{i=1}^{N_c}c_iy_i\right]^2+\left(\frac{\Delta'}{2}\right)^2}. \tag{B2}$$

In order to find a saddle point we set

$$\frac{\partial U_l}{\partial y_i}=0. \tag{B3}$$

Thus we find

$$y_i^*=\frac{2Bc_i}{\omega_i^2}, \tag{B4}$$

where y_i^* is the saddle point coordinate, and B satisfies the following equation

$$B=\frac{\epsilon}{4}+\frac{BE_r}{2}\Bigg/\sqrt{\left(\frac{\epsilon+2BE_r}{2}\right)^2+\left(\frac{\Delta'}{2}\right)^2}. \tag{B5}$$

If $\Delta'/E_r \ll 1$ one can solve the equation for B approximately. We find $B=\epsilon/2E_r$, which gives the saddle point coordinates by Eq. (B4).

To calculate the frequencies of the barrier one needs to calculate the second derivative of U_I,

$$\frac{\partial^2 U_I}{\partial y_i \partial y_j}=\omega_i^2\delta_{ij}-c_i c_j C, \tag{B6}$$

where

$$C=\left(\frac{\Delta'}{2}\right)^2 \Big/ \left[\left(\frac{\epsilon+2BE_r}{2}\right)^2+\left(\frac{\Delta'}{2}\right)^2\right]^{3/2}. \tag{B7}$$

The eigenvalue equation for frequencies can be written as follows:

$$\sum_{i=1}^{N_c}(\omega_i^2\delta_{ij}\psi_i-c_i c_j C\psi_i)=\lambda\psi_j, \tag{B8}$$

where ψ_j's is an eigenvector corresponding to λ. Thus

$$\psi_j=\frac{Cc_j\Sigma_{i=1}^{N}c_i\psi_i}{\omega_j^2-\lambda}. \tag{B9}$$

Summation over j on both sides of this equation results in

$$\sum_{j=1}^{N_c}c_j\psi_j=\sum_{j=1}^{N_c}\frac{Cc_j^2}{\omega_j^2-\lambda}\sum_{i=1}^{N_c}c_i\psi_i. \tag{B10}$$

Thus

$$1=\sum_{j=1}^{N_c}\frac{Cc_j^2}{\omega_j^2-\lambda}. \tag{B11}$$

The product of the roots of this equation equals to the constant term (the Vieta's theorem), hence

$$\prod_j\frac{\lambda_j}{\omega_j^2}=1-\frac{E_rC}{2}, \tag{B12}$$

when $\Delta'/2E_{rc}\ll 1$ and $\epsilon \ll \Delta'/2$ we have

$$\prod_j\frac{\lambda_j}{\omega_j^2}\simeq 1-\frac{E_{rc}}{\Delta'}. \tag{B13}$$

Defining the barrier frequency by $\lambda_1=-\omega_b^2$ and the stable frequencies of the transition state by $\lambda_j=\omega_j'^2$ we finally obtain the equation for the barrier frequency

$$\omega_b\prod_{j=2}^{N_c}\omega_j' \Big/ \prod_{j=1}^{N_c}\omega_j=\sqrt{\frac{E_r}{\Delta'}-1}. \tag{B14}$$

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Chapter 3

Quantum Effects in Electron Transfer Reactions with Strong Electronic Coupling

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Quantum effects in electron transfer reactions with strong electronic coupling

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A new complex centroid reaction coordinate method is used to study electron transfer systems with strong electronic coupling. Formal analogy between current problem and the Ising model of one-dimensional spin system is used to develop a useful approximation for the partition function of electron transfer system in all orders of perturbation theory and when quantum effects are present. The reactions in the inverted region are discussed. The range of applicability of the usual nonadiabatic theory is re-examined. It is concluded that quantum solvent modes can effectively reduce electronic coupling in such a way that a nonadiabatic behavior can sometimes be induced in conventionally strongly coupled systems. Such an induced quantum nonadiabaticity is demonstrated in a numerical calculation. © *1994 American Institute of Physics.*

I. INTRODUCTION

The present paper is an extension of our earlier discussion[1] of quantum effects in electron transfer (ET) reactions with strong electronic coupling. In the previous paper a new approach was introduced which combines the ideas of the quantum centroid reaction coordinate method[2–4] and path integral technique developed over the past decade for treatment of quantum effects in condensed media.[5]

The problem of strong electronic coupling has a long history. Essentially from the very beginning of the development of the electron transfer theory,[6–9] it has been recognized that there are two limits—nonadiabatic and adiabatic, depending on the strength of the coupling of electronic states. Since then numerous attempts have been undertaken to develop a unified theory which would include these two limits on equal footing. The quantitative theory of nonadiabatic reactions is well developed because in this case the reaction can be described in the lowest order of electronic coupling. When the coupling is not small, however, the higher order of interactions are needed to be accounted for, and the situation becomes much more complicated. Usually the adiabatic limit is treated essentially phenomenologically with employment of ideas of classical[6] or quantum[10] transition state theory or, using the Landau–Zener formula for transition probability.[9,11]

Related to the problem of strong electron coupling is the problem of solvent dynamic effects.[12–22] The slow relaxation of the solvent makes the electronic time scale relatively faster which in some sense is equivalent to strong electronic coupling. As a result, in both cases the summation of infinite number of perturbation terms in electronic coupling is required.[20–22] Yet, the true adiabatic reaction is different from the nonadiabatic reaction with slow solvent polarization modes. The difference was clarified in Refs. 14, 15, and 21. In the present paper we will study the ET system in a traditional statistical equilibrium formulation, leaving discussion of the dynamic effects outside the scope of the present paper.

Recently there has been a renewed interest in the literature to the problem of rigorous treatment of systems with strong coupling, and several new ideas have been introduced.[23–26]

The analytical method of the present paper is based on combination of two ideas: for the reaction rate we use Langer's formula[27,28] which gives the rate in terms of complex valued partition function of the system, and for the reaction coordinate we use Chandler's idea of expressing it in terms of the centroid of electronic quantum paths.[3,24,26,29] The solvent modes are treated in standard harmonic approximation with path integrals which allow us to integrate out these coordinates and introduce an effective two- (electronic) state system with nonlocal interactions.

The centroid coordinate method, introduced by Gillan[2] has been a subject of a recent discussion in the literature.[3,4] The main physical idea underlying the method is in separation of statistical and pure dynamical contributions to the reaction rate. Chandler and co-workers applied this idea to electron transfer reactions.[24,26] The central quantity in their calculation was the centroid density, the statistical part of the rate expression, at the transition state. The centroid approach provided encouraging results with a hope that a method was found for treating effectively the high orders of electronic coupling and quantum effects. Recently, however, Mak and co-workers[30,31] studied the dynamic prefactor in the rate expression with exact treatment of real time correlation functions and found that the main assumption of the very existence of the transition state in centroid coordinate space breaks down for electron transfer systems. Such an assumption is one of the central points in the centroid theory for semiclassical adiabatic reactions (such as proton transfer), as originally proposed by Voth, Chandler, and Miller.[3] Thus, the finding of Mak and co-workers posed a question of applicability of the method to essentially quantum systems such as electron transfer.

The method of the present paper, which is based on recent contribution of one of the authors,[4] seems to provide a solution to the problem encountered by Mak and co-workers. In our formulation we find it necessary to treat the centroid reaction coordinate as a complex variable. The reaction rate

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is still proportional to the centroid density, however, the transition state of the reaction now has to be found in general in complex plane by analytic continuation, in some cases (as in the inverted region) outside the region of the original definition of the centroid coordinate. The partition function of the system for complex values of the reaction coordinate also becomes complex and the whole formulation of the theory becomes very similar to Langer's method for decay rates of metastable systems. In this paper we discuss electron transfer reactions in the inverted region, the region where the problem found by Mak and co-workers is most acute.

The structure of the paper is as follows. In Sec. II the Hamiltonian and the method of calculation of the rate of electron transfer reaction is discussed. Different approaches mentioned above are discussed in greater detail.

In Sec. III we calculate the partition function of the ET system mapping it on the equivalent Ising model. The analogy between electron transfer systems and the Ising model has been discussed earlier in the literature.[24,26,29] The picture of interacting spins provides an exceptional insight into the nature of the quantum interactions in electron transfer systems and helps to develop a nontrivial approximation for treatment of quantum effects.

In Sec. IV the rate constant of strongly interacting ET systems in the inverted region is discussed. A numerical result will be provided which demonstrates a nontrivial behavior of the rate in the inverted region as electronic coupling increases. The applicability of the nonadiabatic formula will be re-examined. In Sec. V we comment on the difference of our approach from the recent work of other authors on the same subject, discuss the limitations of the model, and discuss some possible future work.

II. ET HAMILTONIAN AND RATE CONSTANT

Thermal electron transfer reaction can be formally described as relaxation in a two-level system coupled to a harmonic bath.[29,32] The Hamiltonian of ET system in this model is written in the form

$$H=\frac{\Delta}{2}\,\sigma_x+\frac{\epsilon}{2}\,\sigma_z+\frac{\sigma_z}{2}\sum_{i=1}^{N}2c_iy_i+\sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i}+\frac{m_i\omega_i^2y_i^2}{2}\right), \tag{2.1}$$

where $\Delta/2$ is the electronic matrix element coupling the reactant state, $|+\rangle$, and the product state, $|-\rangle$, y_i and p_i are the coordinates and conjugated momenta, respectively, referring to nuclear motions of the solvent, ϵ is the driving force of the reaction $(-\Delta G_0)$, σ_z and σ_x are the Pauli matrices in a two-state ($|+\rangle$ and $|-\rangle$) representation. In a more familiar and explicit representation the spin operators are written as

$$\sigma_x=(|+\rangle\langle-|+|-\rangle\langle+|), \tag{2.2}$$

$$\sigma_z=(|+\rangle\langle+|-|-\rangle\langle-|). \tag{2.3}$$

Hamiltonian (2.1) describes the relevant to ET nuclear motions of the solvent molecules in a harmonic approximation. Coordinates y_i describe "normal modes" of the solvent and also vibrational modes of the first coordination shell, or inner part of the reaction complex. The total number of such modes is macroscopic. Fortunately, it is not the coordinates itself, y_i, but rather their frequencies, ω_i, are of significance for the dynamics of electron transfer.

To make a connection of the model Hamiltonian (2.1) to a real reacting system it is sufficient to describe the spectral density of the harmonic bath, even without specifying the coordinates y_i. The spectral density is defined by

$$J(\omega)=\sum_{i=1}^{N}\pi\delta(\omega-\omega_i)\,\frac{c_i^2}{m_i\omega_i}. \tag{2.4}$$

The contribution of each frequency ω_i is weighted with a "coupling constant" c_i^2. The final result for the rate can always be expressed in terms of $J(\omega)$ which, in turn, can be expressed in terms of longitudinal dielectric function of the solvent and parameters of the inner part of the reaction complex by well-established formulas.[32,33]

The method of our calculation is based on Langer's formula[27] for the decay rate of a metastable system, often used in the literature[28] $(k_B=1)$

$$k=A\,\frac{2\,\mathrm{Im}\,Z}{Z_R^0}, \tag{2.5}$$

where Z_R^0 is the partition function of the reactants, Z is formally exact partition function for the whole system, calculated in a certain special way (discussed below) as to assume complex values, and A is a so-called dynamic prefactor.

The prefactor A, for low temperatures or for a system with essentially quantum character of the reaction, coincides with the temperature in the system[2–4,27,28]

$$A=T. \tag{2.6}$$

In our previous paper[1] we have shown that for nonadiabatic electron transfer systems the prefactor always equals T, although for adiabatic systems in the normal region (i.e., for reactions with well-defined barrier in the electronically adiabatic potential surfaces), the prefactor is different from Eq. (2.6).[1] In the present paper we focus only on the systems in the inverted region. Electron transfer in the inverted region in both adiabatic and nonadiabatic cases is an essentially quantum process, because quantum tunneling of the nuclear coordinates dominates in the reaction rate.[32] For this reason for the prefactor we take $A=T$. For nonadiabatic reaction this choice of A is exact,[1] for strong coupling systems we assume Eq. (2.6) is still valid as an approximation.

The statistical part of the rate formula in Eq. (2.5) requires special comments. A detailed discussion of the unusual form of the rate expression in terms of complex valued partition function is given in the original paper of Langer.[27] In his discussion of the decay rates of metastable systems (one of the simplest examples of a metastable system is a localized state in a cubic parabola), he showed that the partition function of a metastable system can be rigorously defined only as an analytic continuation in the parameter space from the region where the system is stable and well defined to the region where the system is metastable. The partition function of a reacting system is usually written as a multidimensional integral over all generalized coordinates from which one coordinate, or mode, is unstable. This unstable coordinate for classical systems coincides with the usual reaction coordinate. The accurate continuation of the expression for the partition function results in transformation of the integration contour for the unstable mode of the system into the complex plane. As a result of such transformation the formal expression for the partition function assumes a small imaginary part which is proportional to the decay rate.[27] (Without such a transformation the integration over the unstable mode would give a diverging result. Usually the integrand is a Gaussian with a "wrong" plus sign.)[4,27]

For certain systems with relaxation such as electron transfer described by the Hamiltonian (2.1), or double well system in a harmonic bath[2] and others, the total partition function is well defined and does not formally require analytic continuation. Nevertheless, the relaxation rate in such systems can be found in a formally similar way as proposed by Langer, namely, by transforming the integration contour over a properly defined reaction coordinate of the system into the complex plane and using Eq. (2.5) for the rate. (Usually the saddle point approximation is used for the reaction coordinate and in this case integrals do diverge in real space in the same way as for real metastable systems). This procedure has been actively used in the literature in the past in the discussion of relaxation in quantum systems with dissipation,[5] and is especially useful for low temperature semiclassical instanton technique.[28]

Recently Gillan proposed a new formula[2] which gives the rate constant in terms of the centroid density of quantum thermal paths of the reaction coordinate at the transition state. The relation of Gillan's formula to the usual Green–Kubo–Yamamoto correlation formalism has been discussed by Voth, Chandler, and Miller in Ref. 3 and the relation to Eq. (2.5) has been discussed by one of the present authors in Ref. 4.

As shown in Ref. 4, the centroid coordinate plays the same role in the centroid theory as the unstable coordinate in Langer's theory. The analytic continuation of the centroid coordinate integral in the expression of the partition function into the complex plane, results in the following expression for the rate:[4]

$$k=A\,\frac{\operatorname{Im}\int_{-i\infty}^{+i\infty}Z(R)dR}{Z_R^0}, \tag{2.7}$$

where $Z(R)$ is a partition function of the system with fixed centroid of the reaction coordinate, analytically continued into the complex plane. The prefactor A can in principle be expressed in terms of the Green's function of the reaction coordinate.

Equation (2.7) essentially coincides with Langer's formula (2.5). The total partition function now assumes complex values as a result of analytic continuation of the centroid coordinate integral into the complex plane. On the other hand, the complex centroid formula (2.7) also coincides with Gillan's formula. To show this one assumes that the centroid density, which is proportional to $Z(R)$, at the transition state has a minimum and is written as $\sim\exp(aR^2)$ with some positive coefficient a. For real R the integral over R would diverge. Our formalism, however, requires R to assume pure imaginary values, iR, hence, the integral in Eq. (2.7) is perfectly defined. The result of integration of the Gaussian form of the centroid density in Eq. (2.7) reproduces Gillan's formulas for high and low temperatures.[2,4]

The strategy of calculation based on Eq. (2.7) is the following. Calculate first the partition function for a fixed real centroid coordinate, then make analytic continuation, treating centroid coordinate as complex variable, and evaluate integral (2.7) over a contour running from $-i\infty$ to $+i\infty$. The contour can be transformed in a convenient way as to pass the saddle point of the integrand. The saddle point gives the largest contribution to the integral and represents the transition state of the reaction.

III. PARTITION FUNCTION OF ET SYSTEM AND EQUIVALENT ISING MODEL

The partition function of the ET system is given by

$$Z=Z_{+}+Z_{-}=\langle +|\mathrm{Tr}\,e^{-H\beta}|+\rangle+\langle -|\mathrm{Tr}\,e^{-H\beta}|-\rangle. \tag{3.1}$$

Here Tr is taken over all nuclear coordinates of the system, H is the total Hamiltonian given by Eq. (2.1), β is an inverse temperature, $1/T$, and $|\pm\rangle$ are two electronic states. The formal expression for Z is given by Eq. (2.10) of our previous paper.[1] That formal expression can be conveniently interpreted in terms of a path integral which allows one to draw a useful analogy between the ET system and the Ising model of a one-dimensional ferromagnet.[29] In order to introduce some useful notations, below we repeat some standard steps in developing Eq. (3.1) in terms of path integrals.

The Tr operation in Eq. (3.1) can be easily performed, because of the harmonic nature of the nuclear coordinates in Hamiltonian (2.1). The remaining Tr over two electronic states can be conveniently written in the form of a path integral over the electronic "coordinate" $\sigma(\tau)$,[29]

$$Z=Z_b\int\mathscr{D}\sigma(\tau)e^{-S[\sigma(\tau)]}. \tag{3.2}$$

Here τ is a thermodynamic time, $0\leqslant\tau\leqslant\beta$, $\sigma(\tau)$ is a trajectory of the electronic coordinate, and $S[\sigma]$ is the action defined below. Z_b is the partition function of harmonic nuclear coordinates. In this form of the partition function, the coupling of the nuclear coordinates and electronic coordinates is hidden in the expression for S, see Eqs. (3.5)–(3.7) below.

There are only two electronic states in the system, accordingly, the electronic coordinate $\sigma(\tau)$ assumes only two values which are chosen to be ± 1. When the electron is in the reactant state $|+\rangle$ the variable $\sigma=+1$, in the opposite case, when the electron is in the product state $|-\rangle$, the variable $\sigma=-1$. The time evolution of the variable $\sigma(\tau)$ describes sequential jumps of the electron between the reactant and product states, $|\pm\rangle$. Due to the nature of the Tr operation $\sigma(\tau)$ is subject to the periodic boundary condition

$$\sigma(0)=\sigma(\beta). \tag{3.3}$$

When a trajectory starts in the $|+\rangle$ state, i.e., when $\sigma(0)=1$, it gives contribution to the partition function of the reactant, Z_+, otherwise the trajectory contributes to Z_-, the partition function of the products.

The symbol for the path integral in Eq. (3.2) has the following precise meaning:

$$\int \mathcal{D}\sigma(\tau)=\sum_{\sigma(0)=\pm 1}\sum_{n=0}^{\infty}\left(\frac{\Delta\beta}{2}\right)^{2n}\int_0^{\beta}\frac{d\tau_{2n}}{\beta}\times\int_0^{\tau_{2n}}\frac{d\tau_{2n-1}}{\beta}\cdots\int_0^{\tau_2}\frac{d\tau_1}{\beta}. \tag{3.4}$$

The function $\sigma(\tau)=\pm 1$ sequentially changes sign $2n$ times at the moments τ_i, $0\leq\tau_1\leq\tau_2\cdots\leq\tau_{2n}\leq\beta$. The integral over all possible trajectories $\sigma(\tau)$ is given by the integration over all possible values of τ_i, the summation over all possible number of jumps between two electronic states, $2n$, and by the summation over two possibilities to start a trajectory in the reactant electronic state, $\sigma(0)=+1$, or in the product state, $\sigma(0)=-1$.

The action S in Eq. (3.2) is a functional of the electron trajectory $\sigma(\tau)$. It has the form,

$$S[\sigma(\tau)]=-\frac{1}{2}\int_0^{\beta}\int_0^{\beta}\frac{d\tau_1}{\beta}\frac{d\tau_2}{\beta}\,\sigma(\tau_1)\sigma(\tau_2)K(\tau_2-\tau_1)+HM\beta, \tag{3.5}$$

where

$$K(\tau_2-\tau_1)=\frac{\beta^2}{2}\int_0^{\infty}\frac{d\omega}{\pi}J(\omega)\,\frac{ch\left(\frac{\omega\beta}{2}-\omega|\tau_2-\tau_1|\right)}{sh\left(\frac{\omega\beta}{2}\right)} \tag{3.6}$$

is a correlation function of nuclear coordinates, weighted with the spectral density $J(\omega)$ defined in Eq. (2.4).

The last two variables H and M in Eq. (3.5) are defined as

$$H=\epsilon/2, \tag{3.7}$$

where ϵ is the driving force of the reaction, and M is defined as

$$M=2R=\int_0^{\beta}\frac{d\tau}{\beta}\sigma(\tau). \tag{3.8}$$

In Ref. 1, the centroid coordinate of the reaction R was defined as one-half of M.

Thus the partition function of the electron transfer system can be written as a path integral Eq. (3.2) where the sum over all paths is defined by Eq. (3.4) and the action for each path is given by Eqs. (3.5)–(3.8).

Written in this way the expression for the partition function, except for the unimportant factor Z_b, coincides with the partition function of a one-dimensional Ising model of continuously distributed spins $s=1/2$ along the "coordinate" τ with the spin density $\sigma(\tau)$. The spins are said to be 1/2 in a sense that they can be oriented only in two ways, up, $\sigma=+1$, and down, $\sigma=-1$. Due to the periodic boundary condition (3.3) the beginning and the end points of the coordinate τ coincide, hence the corresponding magnetic system has a geometry of a circle of length β. The function $K(\tau_2-\tau_1)$ describes the interaction of two spins located at τ_1 and τ_2, as is follows from Eq. (3.5). Because $K\geq 0$ the type of interactions is ferromagnetic—the neighboring spins prefer to be oriented the same way. The variable M describes the magnetization of the spin system, H is an external field, and the last term in Eq. (3.5) corresponds to energy of the system in an external magnetic field H. Sum over all possible trajectories is obviously the sum over all configurations of the spin system. Finally, the thermal electron transfer rate, which is the goal of our calculations, coincides with the relaxation rate of the corresponding magnetic system from the initial state when all spins are oriented upward, $\sigma(\tau)=+1$, to the state of statistical thermal equilibrium.

Having this analogy in mind it is convenient to write the partition function of our system in a more conventional form

$$Z=Z_b\sum_{\{\sigma(\tau)\}}e^{-E[\sigma(\tau)]\beta}, \tag{3.9}$$

where the sum is taken over all states (or, configurations) of the magnetic system and $E[\sigma(\tau)]$ is the energy of the state.

According to our method of calculation of the rate one needs to calculate the partition function of ET system with a fixed reaction coordinate R, or, in terms of the equivalent Ising model, the partition function of the spin system as a function of magnetization $M=2R$ in an external field H.

A magnetic configuration is a sequence of domains of up, $\sigma=+1$, and down, $\sigma=-1$, oriented spins. A configuration is also characterized by a magnetization M, Eq. (3.8). For a given magnetization there are many ways to change the size of domains leaving magnetization the same. Hence, there is a pure geometrical degeneracy factor, $g_n(M)$, for each configuration with $2n$ domains and a given magnetization M.

We will write the partition function of the system in the form,

$$Z(M)=Z_b\sum_{n=0}^{\infty}g_n(M)e^{-E_n(M)\beta}, \tag{3.10}$$

where $g_n(M)$ is a degeneracy factor discussed above, and $E_n(M)$ is an averaged energy of a configuration with $2n$ domains and magnetization M. Rigorously speaking, the energy of a configuration is a function of $\tau_1\leq\tau_2\cdots\leq\tau_{2n}$, and implicit function of the magnetization M. Thus Eq. (3.10) is a kind of mean field approximation. Below we calculate exactly $g_n(M)$ and propose an approximation for $E_n(M)$ which will allow one to calculate the partition function (3.10) and ultimately the reaction rate (2.7).

A. Degeneracy factor $g_n(M)$

For a given number of domains and magnetization M, one can change the position of boundaries of domains $\tau_1\leq\tau_2\cdots\leq\tau_{2n}$ leaving the magnetization unchanged. Thus, the statistical weight of a configuration can be calculated by taking a $2n$ dimensional integral (3.4) over all possible values of τ_i restricted by an appropriate δ function which fixes the value of M. The calculation of the integral described in Appendix A gives

$$g_n(M)=\frac{1}{2}\,\frac{1}{n!(n-1)!}\left(\frac{1-M^2}{4}\right)^{n-1}. \tag{3.11}$$

The degeneracy factor has a characteristic combinatorial part, which is connected with the possibility of exchanging the domains, and a part which describes the dependence on magnetization M. For small M (the total size of domains of up and down spins are about the same) there are more possibilities to move boundaries of domains while keeping M unchanged. Accordingly, the degeneracy factor has a maximum at $M=0$.

B. Configuration energy $E_n(M)$

The total configuration energy $E_n(M)$ in Eq. (3.10) can be written in the form

$$E_n(M)=-\frac{2n}{\beta}\ln\left(\frac{\Delta\beta}{2}\right)+HM+I_n(M). \tag{3.12}$$

The first term in this expression is a contribution of the weighting factors in Eq. (3.4). It can be interpreted as an energy of the boundaries between domains of spins with opposite orientation. This contribution arises when the two spins of the opposite sign are in immediate contact. The second term, HM, is the energy of the system due to an external magnetic field H, and the last term, $I_n(M)$ is the energy of interactions of spins. The interaction energy is due to the coupling of the electronic and nuclear coordinates in the system. The expression for I_n, except for the factor $1/\beta$, is given by the double integral in Eq. (3.5) (see also Appendix B). The calculation of the interaction energy $I_n(M)$ is a crucial step in the present method. The rest of this section is devoted to find a good approximations for $I_n(M)$.

One possible approximation for the interaction energy $I_n(M)$ was discussed in Ref. 1. It is assumed that there are well separated low and high frequency nuclear (and polarization) modes in the system, such that for the low frequency modes the classical approximation is valid, $\omega_{\rm cl}\beta\ll 1$, and for the high frequency modes the quantum approximation, $\omega_q\beta\gg 1$, can be used. The interaction energy of two spins $K(\tau_2-\tau_1)$, Eq. (3.6), is given by the sum over all frequencies in the system. Hence, the interaction $K(\tau)$ can be divided into two parts—classical and quantum,

$$K(\tau)=K_{\rm cl}(\tau)+K_q(\tau). \tag{3.13}$$

The correlation function of the classical modes is independent of time τ, because of $\omega_{\rm cl}\beta\ll 1$, and hence, in the language of magnetic interactions, the classical interaction is independent of distance $\tau=\tau_2-\tau_1$ between two spins. In other words, the classical modes produce a long-range interaction in the equivalent Ising model. The contribution of long-range interactions to the total energy of a configuration is easy to evaluate directly by taking the integral in Eq. (3.5) with $K=$const.

For quantum modes, the correlation function decays very fast with time τ, due to $\omega_q\beta\gg 1$, hence the quantum modes produce short-range interactions in the equivalent Ising model. The contribution of short-range interactions can be found by a method described in Ref. 1 assuming that the boundaries between domains on average are located far from each other and can be treated independently. This approximation holds whenever the total number of domains is not very large, $n<n_q=(\omega_q\beta)\gg 1$, and the total magnetization is far from its extreme values ± 1. In the physical literature this approximation corresponds to a so-called dilute instanton gas approximation[5] (instantons are simply the boundaries between domains).

In both cases, when the number of domains is sufficiently large $n>n_q$ or when M is close to ± 1 the approximation of our previous paper breaks down. It is recalled that n is the perturbation order of our calculation and the restriction $n<n_q$ means that only a finite number of perturbation terms (although this number can be very large, $n_q=\omega_q\beta\gg 1$) can be calculated with this approximation.

A restriction on M in this approximation has the following consequences. According to our method of calculation, we calculate first the partition function on a real axes $M=2R$ and then we analytically continue this function into the complex plane of the reaction coordinate. The expression for the partition function with the approximation described above is valid only in the vicinity $M=0$. When the analytical continuation is required to the regions in the complex plane which are far from $M=0$, then the approximation described above is not sufficient. Such a situation occurs when the reaction is in the inverted region. In this case the saddle point of $Z(M)$ is located in the complex plane a large distance away from the point $M=0$, and an accurate knowledge of $Z(M)$ in all points of the real initial interval $-1\leqslant M\leqslant +1$ is necessary for accurate analytical continuation to the regions outside of this interval. Thus, for the inverted region the dilute instanton model breaks down and one must go beyond this simple approximation.

As a next level of approximation we calculate I_n in Eq. (3.12) for a configuration where all domains of spins up and spins down are of equal size. Thus for a given magnetization M, the average size of domains with spins up is

$$x=\beta\,\frac{(1+M)}{2n} \tag{3.14}$$

and the average size of the domains of spins down is

$$y=\beta\,\frac{(1-M)}{2n}. \tag{3.15}$$

The calculation of I_n requires an evaluation of the double integral in Eq. (3.5). Calculation of this integral is described in Appendix B. The result for the energy $I_n(M)$ is

$$I_n(M)=-E_a+\frac{2n}{\pi\beta}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega^2}\times\frac{\cosh\left(\frac{\beta\omega}{2n}\right)-\cosh\left(\frac{M\beta\omega}{2n}\right)}{\sinh\left(\frac{\beta\omega}{2n}\right)}, \tag{3.16}$$

where

$$E_a=\sum_{i=1}^{N}\frac{c_i^2}{2m_i\omega_i^2}=\frac{1}{2\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega} \tag{3.17}$$

is the total (quantum and classical) activation energy. This formula essentially is the key result of the present paper. It gives an accurate approximation for the configuration energy valid for *all* values of n and *all* values of M. Both quantum and classical modes are taken into account in the same way.

For $n=1$ the above expression coincides with the exact result derived in Ref. 1. This case corresponds to nonadiabatic reactions, which has been studied thoroughly by the golden rule approach by many authors in the past.

For a system with quantum modes, such that $n<n_q=(\omega_q\beta)$ and when M is far from the extreme values ± 1, Eq. (3.16) reproduces results of our quantum approximation of the previous paper Ref. 1. In this case one can neglect the second cosh in the integrand of Eq. (3.16), and the remaining temperature-dependent hyperbolic function cot $(\omega\beta/2)$ is very close to 1, due to $(\omega_q\beta)\gg 1$.

Whenever $|M|\to 1$ or $n\to\infty$ the second term in the Eq. (3.16), which describe the interaction of boundaries, reduces to zero. In this case the boundaries between domains are located on average so close to each other that any approximation (like rare instanton gas approximation and similar) breaks down, and the energy associated with individual boundaries looses its physical meaning.

Thus the quantum expression for a configuration energy Eq. (3.16) provides an accurate and uniform description of all possible cases of the magnetic interactions of the Ising model and, hence, of the equivalent electron transfer system. Next we make use of the above expression, Eq. (3.16), and of other terms of the configuration energy, Eq. (3.12), together with the expression for the statistical degeneracy factor, Eq. (3.11) for the calculation of the reaction rate using the prescription of the analytical continuation, Eq. (2.7).

IV. THE REACTION RATE FORMULA

Using Eq. (3.10) for the partition function $Z(M)$, Eq. (3.11) for the degeneracy factor $g_n(M)$, the expression for the energy of a configuration $E_n(M)$, Eq. (3.12), and finally the expression for the interaction term I_n, Eq. (3.16) the partition function can now be written in the final form

$$Z(M)=\frac{Z_b}{2}\sum_{n=1}\left(\frac{\Delta\beta}{2}\right)^{2n}\frac{1}{n!(n-1)!}\left(\frac{1-M^2}{4}\right)^{n-1}\times\exp\left\{E_a\beta-HM-2n\int_0^\infty\frac{d\omega}{\pi}\frac{J(\omega)}{\omega^2}\times\left[\coth\left(\frac{\beta\omega}{2n}\right)-\frac{ch\left(\frac{M\beta\omega}{2n}\right)}{sh\left(\frac{\beta\omega}{2n}\right)}\right]\right\}. \tag{4.1}$$

According to Eq. (2.7), in order to obtain the rate constant from the above expression for the partition function, one should analytically continue it into the complex plane M and integrate over the contour running from $-i\infty$ to $+i\infty$. [Reaction coordinate in Eq. (2.7) $R=M/2$ and factor of 2 from changing dR to dM has already been taken into account automatically in the degeneracy factors.] On a pure imaginary axes one substitute iM for M. The partition function of the reactants Z_R^0 from Eq. (2.7) is related to the partition function of the bath Z_b in Eq. (4.1) by

$$Z_b=e^{-E_a\beta-\beta\epsilon/2}Z_R^0. \tag{4.2}$$

It is recalled also that the "external field" $H=\epsilon/2$, according to Eq. (3.7).

Our final formula for the reaction rate in the inverted region takes the form

$$k=\frac{1}{\beta}\sum_{n=1}^{\infty}\left(\frac{\Delta\beta}{2}\right)^{2n}\frac{1}{n!(n-1)!}\int_{-\infty}^{+\infty}\frac{dM}{2}\left(\frac{1+M^2}{4}\right)^{n-1}\times\exp\left\{-\frac{\epsilon\beta}{2}(1+iM)-2n\int_0^\infty\frac{d\omega}{\pi}\frac{J(\omega)}{\omega^2}\times\left[\coth\left(\frac{\beta\omega}{2n}\right)-\frac{\cos\left(\frac{M\beta\omega}{2n}\right)}{sh\left(\frac{\beta\omega}{2n}\right)}\right]\right\}. \tag{4.3}$$

Expression (4.3) is the main result of the present paper. Below in this section we discuss it for several limiting cases.

A. Nonadiabatic quantum case

The sum over n in Eq. (4.3) is a sum over all perturbation orders in the electronic coupling Δ. When Δ is small only the first term of the above expansion (4.3) can be taken into account. The term with $n=1$ coincides exactly with the well-known exact quantum mechanical expression for the nonadiabatic rate[32,34]

$$k=\beta\left(\frac{\Delta}{2}\right)^2\int_{-\infty}^{+\infty}\frac{dM}{2}\exp\left\{-\frac{\epsilon\beta}{2}(1+iM)\right.$$
$$\left.-2\int_0^{\infty}\frac{d\omega}{\pi}\frac{J(\omega)}{\omega^2}\left[\coth\left(\frac{\beta\omega}{2}\right)-\frac{\cos\left(\frac{M\beta\omega}{2}\right)}{sh\left(\frac{\beta\omega}{2}\right)}\right]\right\}. \tag{4.4}$$

A more standard expression is recovered from Eq. (4.4) assuming that there is a single quantum oscillator with a frequency ω_q, all other modes being classical. In this case the above formula reads,

$$k=\left(\frac{\Delta}{2}\right)^2\sqrt{\frac{\pi\beta}{\lambda}}\exp\left(-\frac{E_{rq}}{\omega_q}\coth\left(\frac{\omega_q\beta}{2}\right)\right)$$
$$\times\sum_{\nu=-\infty}^{+\infty}\exp\left(\frac{\omega_q\beta}{2}\nu\right)I_{|\nu|}(\kappa)\exp\left(-\beta\frac{(\epsilon+\lambda+\omega_q\nu)^2}{4\lambda}\right), \tag{4.5}$$

where the classical reorganization energy $\lambda=4E_{ac}$ is defined by a low frequency part of the spectrum, and the quantum counterpart E_{rq} is written as

$$E_{rq}=\frac{\omega_q d_q^2}{2}, \tag{4.6}$$

d_q being the dimensionless shift of the equilibrium of the quantum mode. The coefficients I_ν are the modified Bessel functions,[35] which appear as a result of the Fourier expansion

$$e^{-\kappa\cos(\theta)}=\sum_{\nu=-\infty}^{+\infty}I_{|\nu|}(\kappa)e^{-i\nu\theta} \tag{4.7}$$

and

$$\kappa=\left(\frac{E_{rq}}{\omega_q}\right)\frac{1}{sh\,\frac{\omega_q\beta}{2}}. \tag{4.8}$$

For a low temperature such that $\omega_q\beta\gg1$ and $\kappa\ll1$ the above formula takes the following most popular form in the literature:[32,36]

$$k=\left(\frac{\Delta}{2}\right)^2\sqrt{\frac{\pi}{\lambda T}}e^{-S}\sum_{\nu=0}^{+\infty}\frac{1}{\nu!}S^\nu$$
$$\times\exp\left(-\frac{(\epsilon+\lambda+\omega_q\nu)^2}{4\lambda T}\right), \tag{4.9}$$

where $S=E_{rq}/\omega_q=d_q^2/2$. [The terms with negative ν's contain an additional factor $\exp(-|\nu|\omega_q\beta)$ and for this reason were omitted in Eq. (4.9).]

When the reaction is in the inverted region, $\epsilon<-\lambda$, the terms with $\nu>0$ give the main contribution. In this case the reaction occurs from the excited states of the quantum oscillator. Especially important can be the term with $\omega_q\nu\sim-(\lambda+\epsilon)$. When this term gives the main contribution, the reaction is almost activationless, and hence the temperature dependence of the reaction is very weak.[36]

Thus, the first term reproduces exactly the well-known results for quantum nonadiabatic reactions. Equation (4.3) provides, obviously, a generalization of the nonadiabatic result (4.4) to the case of strong electronic coupling. In this case many terms with $n>1$ contribute to the rate.

B. Crude quantum approximation

Suppose that in Eq. (4.3) the sum over perturbation orders n can be limited by a large, but finite number $n_q=\beta\omega_q$. The exact result can be simplified in this case, approximately, in the following way. In this case the first term in square brackets in the exponential of Eq. (4.3) only weakly depends on the temperature T, and can be safely approximated by $\coth(\omega\beta/2)$. In the second term, $\cos(\omega\beta M/2n)/\sin(\omega\beta/2n)$, at least qualitatively correctly, one can also neglect the n dependence. To convince oneself that it is indeed qualitatively correct one can again recall the analogy with the Ising model and our analysis of the magnetic interactions in it for a real reaction coordinate M. In this case the formula for the rate takes the form of our previous paper,[1]

$$k=T\int_{-\infty}^{+\infty}I_1\left(\beta\Delta'\sqrt{\frac{1}{4}+R^2}\right)\left(\frac{\beta\Delta'}{2}\right)$$
$$\times\left(\sqrt{\frac{1}{4}+R^2}\right)^{-1}\exp\left(-4\beta E_{ac}R^2-\beta E_{ac}-\frac{\beta\epsilon}{2}\right)$$
$$\times\cos(\beta R\epsilon)dR, \tag{4.10}$$

where the electronic coupling is now a function of the reaction coordinate and temperature

$$\Delta'=\Delta'(M,T)=\Delta\exp(-\textstyle\int_{\omega_q}^{\infty}d\omega/\pi J(\omega)/\omega^2[\coth(\beta\omega/2)$$
$$-\cos(M\beta\omega/2)/sh(\beta\omega/2)]). \tag{4.11}$$

The temperature dependence of the effective electronic coupling is weak because for quantum modes $\omega_q\beta\gg1$. The reaction coordinate dependence, on the other hand, is the key to describe the contribution of the excited quantum states in the inverted region.

If there is only one quantum mode in the system, as in the example from the previous section, Eq. (4.10) can be further simplified as follows:

$$k=\sum_{\nu=0}^{+\infty}\frac{1}{\nu!}S^\nu k_{cq}(\epsilon+\nu\omega_q), \tag{4.12}$$

where the partial rates k_{cq} are calculated according to Eq. (4.10) with the driving force ϵ modified by the excited states of the quantum mode, and with renormalized electronic coupling

$$\Delta'=\Delta\exp\left(-\int_{\omega_q}^{\infty}\frac{d\omega}{\pi}\frac{J(\omega)}{\omega^2}\right). \tag{4.13}$$

Expression (4.12) is obviously is a generalization of Eq. (4.9).

C. Accurate quantum approximation

The approximation of the previous subsection is valid only for a finite number of terms $n \sim n_q = \omega_q \beta \gg 1$ in the sum of the general formula Eq. (4.3). If the system is such that all terms in the sum have to be retained then only general formula (4.3), which is an accurate quantum approximation, can be applied.

It turns out that further simplifications of Eq. (4.3) are difficult to make for a very fundamental reason related to the presence of different time scales in the system. Below we discuss this point.

In general case the effective electronic coupling, as one can see from the last exponential terms in Eq. (4.3), is not only the function of the reaction coordinate and temperature but also a function of the order of coupling n. The number n in the sum of Eq. (4.3) for the rate is the number of jumps the electron makes between the two electronic states on the time scale of $\beta = 1/T$. Hence, the electronic time scale in the reaction dynamics,

$$\tau_n = \beta / n, \tag{4.14}$$

and the corresponding frequency,

$$\Omega_n = \tau_n^{-1}, \tag{4.15}$$

are functions of the order of electronic coupling n. The principal difference between the quantum and classical modes of the solvent is revealed in comparison of the solvent dynamics time scale and the electronic time scale. For the classical modes, in all orders of the coupling n, the electronic time scale is much shorter than that of the solvent dynamics,

$$\omega_{\rm cl} \ll \Omega_n = n / \beta. \tag{4.16}$$

The classical solvent coordinates are always "static" as the electron sees them during the reaction. The averaging over thermal distribution of classical solvent coordinates occurs when the Gaussian integral over the reaction coordinate is taken in the expression for the rate.

The quantum modes are much more difficult to treat in general because their dynamical nature is different in low and high orders of the electronic coupling. For low orders of coupling n the quantum modes are very fast on the time scale of electron dynamics,

$$\omega_q \gg \Omega_n = n / \beta \tag{4.17}$$

and their contribution can be described within the crude quantum approximation discussed above. However, when n becomes sufficiently large, $n > n_q = \omega_q \beta$, the situation changes, as is seen from the above equation, and the quantum modes become slow on the electronic time scale. Thus, in the very high orders of the coupling the quantum modes behave as if they were classical. It is because of this quantum-classical "crossover" the general expression (4.3) is difficult to simplify in a uniform way for all orders of coupling n.

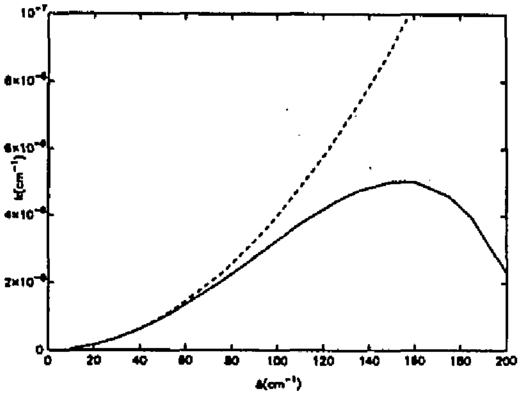

FIG. 1. Rate constant for the reaction in the inverted region calculated with Eq. (4.3). $\Delta G_0 = \epsilon = -2.1$ eV, $E_{rs} = 0.75$ eV, room temperature. The solid line is exact result given by Eq. (4.3) in the text. Broken line is nonadiabatic theory, i.e., the first term in the sum of Eq. (4.3).

D. Numerical results

As an application of our formalism we next present results of numerical calculation of Eq. (4.3). For model calculations we use a system studied recently by Liang, Miller, and Closs in their experiments, Ref. 36. For a benzoquinonyl/biphenylyl system bridged by a steroid group they observed a very weak temperature dependence of the reaction and argued that quantum effects play a major role. For a driving force of -2.1 eV the reaction falls in deep inverted region. For this system we have made a series of calculations with different model coupling electronic matrix element. Although for the real system the electronic coupling is such that the reaction is nonadiabatic, we used that system as prototype of a general quantum system in the inverted region and studied the behavior of such a system as electronic coupling varied from weak to strong.

The main purpose of this calculations is to demonstrate a possible contribution of the high order terms in Eq. (4.3) with $n > 1$. We recall that $n = 1$ term in Eq. (4.3), proportional to Δ^2, corresponds to nonadiabatic theory and higher order terms are presumably important for strongly coupled systems. In Figs. 1 and 2 both the nonadiabatic contribution, the first term, as well as the whole sum of all terms in Eq. (4.3) are shown for comparison. In Fig. 1 a system with only classical modes is shown. The classical modes create an activation barrier for the reaction of 0.75 eV. In Fig. 2 one quantum mode was added with frequency $\omega_q = 1500$ cm^{-1} and quantum reorganization energy $E_{rq} = 0.45$ eV. The phenomenological parameters were deduced from the experimental results in Ref. 36.

Several interesting features are observed in Figs. 1 and 2. First, is that in both purely classical and quantum systems the reaction initially increases quadratically for small couplings, as predicted by nonadiabatic formula, but then, when the coupling becomes sufficiently large, the reaction rate reaches maximum and then decreases with further increase

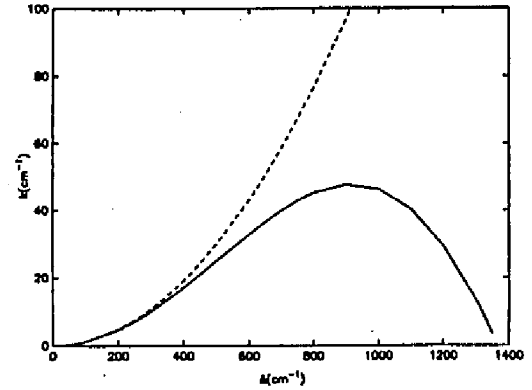

FIG. 2. The same as in Fig. 1 but with one quantum mode added. $\omega_q = 1500$ cm^{-1}, $E_{rq} = 0.45$ eV.

of the coupling. This behavior is a reflection of the fact that large electronic coupling causes separation of the adiabatic surfaces and the reaction dramatically slows down as a result. We note that this type of behavior is only characteristic for the inverted region. For the normal region the rate is always a monotonically increasing function of the coupling.

Second interesting feature to notice is that the quantum mode dramatically increases rate by almost eight orders of magnitude. This is in correspondence with a well-established fact that in the inverted region quantum modes can provide an effective tunneling path for the reaction when the classical activation contribution is extremely small. This becomes even more evident for a large electronic coupling, when adiabatic surfaces are well separated and the classical rate is practically negligible.

Finally, an interesting and practically important question is to what extent the nonadiabatic formula can be used when the electronic coupling becomes large. We recall that nonadiabatic formula is derived as a first perturbation order in coupling constant. With our general formula Eq. (4.3) we can easily address this question because all perturbation orders are present in it. A surprising result from our calculation is that for the quantum system, the nonadiabatic formula turns out to be applicable for an unexpectedly large range of parameter $\Delta\beta = \Delta/T$. (This parameter is usually used to discuss the adiabatic–nonadiabatic transition, as, e.g., in Ref. 19.) This phenomenon was in fact predicted in our previous paper.[1] It was found that quantum modes in the system renormalize (decrease) the electronic coupling in all orders of perturbation theory by exponential factor as in Eq. (4.13) and as a result the effective coupling Δ' can become much smaller than the "bare" initial coupling in the Hamiltonian. Thus, even for a conventionally strongly coupled system the quantum modes can "induce" nonadiabaticity. It is such an induced nonadiabatic behavior that is observed in Fig. 2 of our calculation.

V. DISCUSSION

The results that we have obtained in this and in the previous paper[1] provides some new insight into quantum dynamics of an electron transfer system with strong coupling. For weakly coupled systems, i.e., in the nonadiabatic case, our results revealed some new aspects of the role that quantum modes of the solvent play in the reaction. The renormalization of the electronic coupling by quantum modes can be of potential importance in a long-range electron transfer reactions, which have been a focus of very intensive investigation recently as, e.g., in Refs. 37–42 and references therein.

The rate in the present theory (2.7) is written in a form of a product of two terms which have different nature. The partition function term describes the statistical aspect of the reaction, while the prefactor A describes the dynamics of the reaction in the region corresponding to the quantum transition state. The latter can be defined as a most important region in the reaction coordinate space. In the present theory the reaction coordinate $R = M/2$ was first defined as a real variable and then we argued that the analytical continuation of the partition function into the complex plane R is, actually, what one needs in order to find the rate constant. The most important regions of the complex plane R (or M) are those which give the largest contribution to the integral in the expression for the rate, Eq. (4.3). Those regions are saddle points of the integrand of the rate expression and they in principle can be located at any point on the complex plane R.

For the normal region and for classical solvent modes the saddle point, (i.e., the transition state) is in the real interval of originally defined reaction coordinate $1/2 < R < 1/2$. However, when quantum modes are present, or in the inverted region, the saddle points are outside the interval $1/2 < R < 1/2$.

The present paper discussed the statistical part of the rate expression. An accurate quantum approximation for the solvent polarization modes was developed which is applicable in all orders of electronic coupling. However, the nature of the dynamical factor A is unfortunately too complicated to be treated rigorously. For this reason the results of this paper are only an approximation which is valid as long as valid Eqs. (2.5)–(2.7). Between the nonadiabatic and strong adiabatic regimes treated in the present paper, there is another transition (or crossover) corresponding to Zusman's regime of the reaction (a so-called weak adiabatic regime).[14,15] How this crossover can be described within the present formulation of the theory is not clear at present. We hope to address this problem in the future.

Recently Mak and co-workers[30,31] applied the formalism of Voth, Chandler, and Miller (VCM) to electron transfer systems and found that the main assumption of VCM formalism breaks down for electron transfer systems. Namely, the product of density of electron centroid and the dynamic factor introduced by VCM was found to be independent of the centroid coordinate in the second order of electronic coupling, thus showing that there is no transition state in the centroid space for electron transfer systems. In high orders of coupling the situation did not improve.[31]

In our method, which is based on Ref. 4, the centroid idea is used in a slightly different way compared with the VCM approach. The main difference is that the centroid of the reaction coordinate was defined in Ref. 4 for cyclic thermal paths (in the same way as originally proposed by Gillan) while in VCM theory the centroid was defined for thermal paths which run from the reactant state to product state. The difference is due to the fact that in the VCM formalism the correlation function was defined from the very beginning for real time, while in Ref. 4 the correlation function first was calculated for pure imaginary time and only then analytic continuation to real time was performed. As was shown, the required analytic continuation of the correlation function to real time forces the integration contour of the centroid coordinate to be transformed into the complex plane. This mathematical mechanism is essentially the same as in Langer's theory: the continuation to real plateau time corresponds to Langer's continuation from a stable to a metastable state in parameter space.

As a result of the analytic continuation to real time, the dynamic factor defined in Ref. 4 becomes constant A in Eq. (2.7) (the dynamic factor of VCM theory is different from ours and is sharply peaked at the transition state).[3] The rest of the integrand in the expression for the rate coincides with the centroid density, and the contour of integration over centroid coordinate is transformed into the complex plane. Thus one arrives at the complex centroid formulation of the rate Eq. (2.7).

The subtle difference between the real centroid coordinate of VCM[3] and a complex version of the theory[4] can most clearly be seen in the expression for nonadiabatic electron transfer rate from paper of Mak and Gehlen.[30] In their expression the integration over a formal variable running from minus to plus infinity in imaginary direction corresponds to our complex centroid coordinate, while the VCM centroid corresponds to a point where the integration contour intersects the real axis. Due to analytical properties of the integrand the result is independent of the real centroid coordinate[31] but have a sharp maximum in complex coordinate space.

In the inverted region the real centroid density does not reach its minimum value (transition state) in the interval of originally defined real values of the centroid coordinate. Our method provides a solution to this problem. According to our strategy of calculation, we calculate first the partition function for a fixed real centroid coordinate, then make analytic continuation, treating the centroid coordinate a as complex variable, and evaluate integral (2.7) over a contour running from $-i\infty$ to $+i\infty$. The contour can be transformed in a convenient way as to pass the saddle point of the integrand. The saddle point gives largest contribution to the integral and represents the transition state of the reaction. For the inverted region this transition point is located outside the interval of the real centroid coordinate and can only be reached by analytic continuation. Thus, in contrast to real centroid coordinate formulation, the complex version of the theory does not suffer the deficiency when applied to electron transfer reactions.

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APPENDIX A. DEGENERACY FACTOR $g_n(M)$

The degeneracy factor $g_n(M)$ in Eq. (3.10) was in fact calculated in the previous paper,[1] where it was called a G factor. The derivation given there is unnecessary overcomplicated. Recently we have found a much more simplified way of calculation, which is as follows.

The degeneracy factor is given by

$$g_n(M)=g_n^+(M)+g_n^-(M), \tag{A1}$$

where $g_n^\pm(M)$ are degeneracies of ($\pm$) configurations, $\sigma(0)=\pm 1$.

$$\begin{aligned} g_n^\pm(M)=&\int_0^\beta \frac{d\tau_{2n}}{\beta}\int_0^{\tau_{2n}}\frac{d\tau_{2n-1}}{\beta}\cdots\int_0^{\tau_2}\frac{d\tau_1}{\beta}\\ &\times\delta\left(M-\int_0^\beta\frac{d\tau}{\beta}\sigma(\tau)\right)\\ =&\int_0^\infty\frac{dx_{2n}}{\beta}\int_0^\infty\frac{dx_{2n-1}}{\beta}\cdots\int_0^\infty\frac{dx_1}{\beta}\\ &\times\theta(\beta-(x_1+x_2+\cdots+x_{2n}))\\ &\times\delta\left(M\mp\left(1-\frac{2(x_2+x_4+\cdots x_{2n})}{\beta}\right)\right), \end{aligned}\tag{A2}$$

where the new variables x_i describing the size of domains are introduced. Compared with the equivalent expression from Ref. 1, the upper limits of integration over x_i are extended to infinity, although by their meaning x_i are limited by the total length of the system β. This extension, however, is valid because the θ function restricts the total length of the system and each of the domains by β, no matter what the formal limits for variations of x_i are, as long as they are larger than β. This trivial modification results in a significant simplification of the calculation. Using the integral representations of δ and θ functions, as in Ref. 1, and integrating over all x_i one gets

$$\begin{aligned} g_n^\pm(M)=&\frac{1}{2}\int_{-\infty}^{+\infty}\frac{dk_1}{2\pi i}\frac{e^{ik_1}}{k_1-i0}\int_{-\infty}^{+\infty}\frac{dk_2}{2\pi}\\ &\times e^{ik_2(1\mp M)/2}\left(\frac{1}{ik_1}\right)^n\left(\frac{1}{ik_1+ik_2}\right)^n, \end{aligned}\tag{A3}$$

where it is assumed that $\text{Re}(ik_j)>0$. Introducing then the Laplace variables $\lambda_j=ik_j$ and integrating first over λ_2 and then over λ_1 one gets

$$g_n^\pm(M)=\frac{1}{2}\frac{1}{n!(n-1)!}\left(\frac{1-M^2}{4}\right)^{n-1}\left(\frac{1\pm M}{2}\right). \tag{A4}$$

The sum of $g_n^{\pm}(M)$ according to Eq. (A1) gives the final result Eq. (3.11).

APPENDIX B. CONFIGURATION ENERGY $I_n(M)$

The interaction energy has the form

$$I_n(M)=-\frac{1}{2\beta}\int_0^{\beta}\int_0^{\beta}\sigma(\tau_1)\sigma(\tau_2)K(\tau_2-\tau_1)\,\frac{d\tau_1}{\beta}\,\frac{d\tau_2}{\beta}. \tag{B1}$$

The integral will be calculated here for a configuration with n domains $\sigma=+1$, and n domains $\sigma=-1$, where all domains of the same sign have equal size, as discussed in the text, before Eqs. (3.14) and (3.15).

For a single frequency ω the interaction kernel is proportional to the correlation function of a harmonic oscillator with frequency ω,

$$K(\tau_2-\tau_1)=\beta^2\tfrac{1}{2}\,\frac{ch\left(\frac{\omega\beta}{2}-\omega\left|\tau_2-\tau_1\right|\right)}{sh\left(\frac{\omega\beta}{2}\right)}. \tag{B2}$$

The sum over all frequencies in the system involves an additional integration with the spectral density $J(\omega)$:

$$\int_0^{\infty}\frac{d\omega}{\pi}\,J(\omega)\cdots \tag{B3}$$

Due to the periodic nature of the system, $K(\tau)$ is expanded in the Fourier harmonics,

$$K(\tau_2-\tau_1)=\beta^2\sum_{\nu=-\infty}^{+\infty}g(\nu)e^{-iz\nu(\tau_2-\tau_1)}, \tag{B4}$$

where

$$z=2\pi/\beta \tag{B5}$$

and

$$g(\nu)=\frac{1}{\beta}\,\frac{\omega}{\omega^2+(z\nu)^2}. \tag{B6}$$

Substitution of the Fourier series for K in Eq. (B1) results in the expression for $I_n(M)$ which involves the following terms:

$$\left(\int_0^{\beta}\sigma(\tau)e^{-iz\nu\tau}\frac{d\tau}{\beta}\right)(\mathrm{cc})=\delta_{\nu,kn}\left[\delta_{0k}M^2+(1-\delta_{0k})\times\left(\frac{2}{\pi k}\right)^2\sin^2\pi k\theta\right] \tag{B7}$$

where cc is a complex conjugation, and θ is defined as

$$\theta=\frac{1-M}{2}. \tag{B8}$$

Expression (B7) is nonzero for only

$$\nu=kn,\quad k=0,\pm 1,\pm 2,\ldots \tag{B9}$$

Collecting all Fourier harmonics we find

$$I_n(M)=-\frac{1}{2}\left(\frac{M^2}{\omega}+4\sum_{k\neq 0}\frac{\omega}{\omega^2+(znk)^2}\,\frac{\sin^2\pi k\theta}{(\pi k)^2}\right). \tag{B10}$$

Summation in the above expression is accomplished by differentiating Eq. (B10) twice over θ. After the differentiation the expression coincides with the correlation function in τ—representation of a harmonic oscillator with frequency ω and temperature $T'=Tn$. Subsequent integration of that expression over θ two times with appropriate boundary conditions gives for a single mode

$$I_n(M)=-\frac{1}{2\omega}+\frac{2n}{\beta}\,\frac{1}{\omega^2}\left(\coth\left(\frac{\omega\beta}{2n}\right)-\frac{ch\left(\frac{\omega\beta}{2n}M\right)}{sh\left(\frac{\omega\beta}{2n}\right)}\right). \tag{B11}$$

Integration over all frequencies with Eq. (B3) results in Eq. (3.16) in the text.

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Chapter 4

Quantum Effects in Electron Transfer Reactions: Solvent Dynamics Controlled Regime I

The Quantum Effect of Electron Transfer Reactions: Solvent Dynamics Controlled Regime

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Abstract

In this work the one-particle Green function method is used to calculate the electron transfer reaction rate constant with a spin-boson Hamiltonian. A quantum version of Zusman's result on the solvent dynamical effect in electron transfer reactions is obtained for the symmetric case. The quantum correction due to the new rate expression is discussed. It is shown that, as expected, the quantum effect is significant at room temperature only when the dielectric relaxation of the solvents has substantial high frequency components, as in water.

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I. INTRODUCTION

In recent years there have been many studies on the role of solvent dynamics in the electron transfer reactions and an example of the great interaction between the theoretical prediction and the experimental confrontation is given in Ref.1. Since Zusman's initial formulation of solvent dynamical effects on the electron transfer reactions fifteen years ago[2] there have been numerous attempts to understand this result from different perspectives[3]. A major conclusion of his work is that the rate of electron transfer reactions can be controlled by the dynamics of the solvent dielectric relaxation and is inversely proportional to the longitudinal relaxation time of the Debye solvent. There remain some questions still to be answered. One of the issues we are concerned with here is a microscopic derivation of the rate constant from the Hamiltonian of the system and a possible quantum correction. Garg *et al*[4] used a path integral method to derive a stochastic Liouville equation, which is the original equation Zusman used, from the Hamiltonian of the system. Their result sheds light on our understanding of the assumptions involved in the Zusman's result. Mukamel *et al*[5]'s Green function method in Liouville space gave an insightful derivation but did not obtain the quantum correction. One motivation in the present paper is to try to obtain a robust derivation for Zusman's result and to obtain a possible quantum correction for the rate constant.

A second motivation for this work comes from a more general perspective for the calculation of rate constant from the Hamiltonian of the system or from first principles. Currently a standard way to formulate such a treatment is by the population correlation function method which was originally introduced by Yamamoto[6] and developed by many others[7]. The direct calculation of the correlation function for nontrivial systems is difficult, so that most of the theories are based on some type of transition state theory approximation—-the separation of the dynamical factor and the statistical factor[8,9]. It is well known now that this kind of separation is inherently impossible for a quantum system. A possible scheme to calculate the rate exactly, though not by correlation function of population would be desirable. The present method to calculate rate constant through the one-particle Green function is an attempt in this direction.

In this paper the electron transfer reaction is taken as an example to illustrate the basic strategy. The model we will use for the electron transfer reaction is the conventional spin-boson Hamiltonian, *i.e.*, two electronic states (electron in donor and electron in acceptor) coupled bilinear to a harmonic bath which describes the nuclear motion of the solvent and the intramolecular vibrations of the donor and of the acceptor. Then the one-electron Green function is calculated and the rate constant of the electron transfer is derived from this Green function. A similar version of the one-electron Green function method was used in the polaron hoping problem[10]. In the present case a quantum version of Zusman's rate constant is obtained and the rate constant is inversely proportional to the longitudinal relaxation time for Debye solvent.

The paper is organized as follows. The general formulation of the problem is discussed in Section II and a general perturbative expansion for the rate constant is given. In Section III the Golden Rule formula for the electron transfer is recovered from our general expression, which serves as the first check for the method. In Section IV a quantum rate expression Eq.(4.10) is derived for the symmetric electron transfer reactions. For the Debye solvent the usual classical Zusman formula follows, as a special case of the present result. The new features of this expression are discussed. In Section V several conclusions are drawn from the present study and possibilities of further extensions are discussed.

II. BASIC FORMULATION OF THE METHOD

A thermal electron transfer reaction can be formally described as a relaxation in a two-level system coupled to a harmonic bath [4,5,9]. The Hamiltonian of the ET system in this model is written in the form(usually referred as the spin-boson Hamiltonian)

$$H = \frac{\Delta}{2}\sigma_x + \frac{\epsilon}{2}\sigma_z + \frac{\sigma_z}{2}\sum_i 2c_i y_i + \sum_i \left(\frac{p_i^2}{2m_i} + \frac{m_i\omega_i^2 y_i^2}{2}\right) \tag{2.1}$$

where $\Delta/2$ is the electronic matrix element coupling the reactant state $|1\rangle$ and the product state $|2\rangle$, y_i and p_i are the coordinates and conjugate momenta, respectively, for the nuclear motion of the solvent and the intramolecular vibrational modes of the donor and the acceptor. ϵ is the driving force of the reaction $(-\Delta G_0)$. σ_z and σ_x are the Pauli matrices in a two-state ($|1\rangle$ and $|2\rangle$) representation. To relate the model Hamiltonian (2.1) to the properties of the real reacting system it is sufficient to describe the spectral density of the harmonic bath, thereby not specifying in the final equation all of the coordinates and the momenta. The spectral density is defined as[4,5,9]

$$J(\omega) = \sum_i \pi\delta(\omega - \omega_i)\frac{c_i^2}{m_i\omega_i}. \tag{2.2}$$

The contribution of each frequency ω_i is weighted with a "coupling constant" c_i^2. The final result for the rate constant can always be expressed in terms of $J(\omega)$ which, in turn, can be expressed in terms of dielectric function of the solvent and parameters of the vibrational modes of the reaction complex by standard formulas[9,13].

In order to facilitate the subsequent derivation it is useful to recast the Hamiltonian in term of creation and annihilation operators of the two electronic states. The Pauli matrices can be written in the following form

$$\sigma_z = a_1^+ a_1 - a_2^+ a_2 \tag{2.3a}$$

$$\sigma_x = a_1^+ a_2 + a_2^+ a_1 \tag{2.3b}$$

$$\sigma_y = i(a_1^+ a_2 - a_2^+ a_1). \tag{2.3c}$$

Thus the Hamiltonian in terms of the creation and annihilation operators will be

$$H = \frac{\Delta}{2}(a_1^+ a_2 + a_2^+ a_1) + \varepsilon_1 a_1^+ a_1 + \varepsilon_2 a_2^+ a_2 + \sum_i c_i y_i (a_1^+ a_1 - a_2^+ a_2) + H_b \tag{2.4}$$

where ε_1 and ε_2 are the energies of the electronic states $|1>$ and $|2>$. H_b is the last term of the Eq.(2.1) ,which is the harmonic bath Hamiltonian of the system.

Because of the linear nature of the coupling between the bath and the electronic states, the linear coupling term can be removed through the following unitary transformation[8]

$$U = exp\Big\{ i \sum_i c_i' (a_1^+ a_1 - a_2^+ a_2) p_i \Big\} \tag{2.5}$$

where p_i is the momentum operator associated with the mode i and

$$c_i' = \frac{c_i}{m_i \omega_i^2}. \tag{2.6}$$

Thus, the Hamiltonian can be written as a sum of a zeroth-order term H_0 and a perturbation V:

$$H = H_0 + V = \varepsilon_1 a_1^+ a_1 + \varepsilon_2 a_2^+ a_2 + H_b + V \tag{2.7}$$

where

$$V = \frac{\Delta}{2}(a_2^+ a_1 e^{2i\sum_i c_i' p_i} + a_1^+ a_2 e^{-2i\sum_i c_i' p_i}). \tag{2.8}$$

We next calculate the one-electron Green function of the above Hamiltonian[10,11]

$$G(t>0) = -i\mathrm{Tr_b} < 0|a_1(t) a_1^+(0)|0> \tag{2.9a}$$

$$= -i\mathrm{Tr}_b < 0|e^{iHt}a_1 e^{-iHt}a_1^+|0> \qquad (2.9b)$$

$$= -i\mathrm{Tr}_b < 0|a_1 e^{-iHt}a_1^+|0> \qquad (2.9c)$$

where $|0>$ is the electronic vacuum state and Tr_b is the trace over bath Hamiltonian H_b. From Eq.(2.9a) to Eq.(2.9b) the relation $a_1(t) = e^{iHt}a_1 e^{-iHt}$ is used and from Eq.(2.9b) to Eq.(2.9c) $H|0>=|0>$ is used.

Physically this one-electron Green function gives the amplitude of the following event: at t=0 an eigenstate $|1>$ is created by a_1^+ and this state evolves to time t under the influence of the whole Hamiltonian H and then the overlap with the initial state $|1>$ is calculated. In general, the state at time t is no longer an eigenstate of H_0 due to the interaction with the bath and with another electronic state. Thus, we expect the amplitude will take the following form

$$G(t) \approx -i \quad e^{-i\varepsilon_1' t - \frac{\Gamma}{2}t} \qquad (2.10a)$$

$$\approx -i \quad e^{-i\varepsilon_1' t}(1 - \frac{\Gamma}{2}t + \cdots\cdots) \qquad (2.10b)$$

where ε_1' is the modified energy of electronic state $|1>$ and $1/\Gamma$ represents the lifetime of the initial state or, in other words, yields the rate constant of the electron transfer. The expansion in Eq.(2.10b) shows that the term linear in t yields the rate constant. This result provides the basic strategy of the present calculation of the rate constant. This procedure is equivalent to calculating the imaginary part of the self energy for the Green function. One of the possible advantages of the method is that the one-particle Green function is used in contrast to the usual population correlation method, which is a two-particle Green function method.

Taking V as a perturbation to H_0, the evolution operator of H can be written in terms of the T-ordered form

$$e^{-iHt} = e^{-iH_0 t}\hat{T}e^{-i\int_0^t d\tau V(\tau)}. \qquad (2.11)$$

The Green function can be expanded as

$$G(t) = -i\mathrm{Tr}_{\mathrm{b}} < 0|a_1 e^{-iH_0 t}\hat{T}e^{-i\int_0^t d\tau V(\tau)} a_1^{+}|0 > \tag{2.12a}$$

$$= -i\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_0^t dt_1 \cdots \int_0^t dt_n \mathrm{Tr}_{\mathrm{b}} < 0|\hat{T}[a_1(t)V(t_1)\cdots V(t_n)a_1^{+}]|0 > \tag{2.12b}$$

$$= -i\sum_{n=0}^{\infty}(-1)^n(\frac{\Delta}{2})^{2n} A_{2n} e^{-i\varepsilon_1 t + i\varepsilon\sum_{k=1}^{n}(t_{2k-1}-t_{2k})} \tag{2.12c}$$

where

$$A_{2n} = \frac{1}{(2n)!}\int_0^t dt_1 \cdots \int_0^t dt_{2n}\mathrm{Tr}_{\mathrm{b}} < \hat{T}e^{-2i\sum_i c_i' p_i(t_1)} \dots e^{2i\sum_i c_i' p_i(t_{2n})} >$$

$$= \int_0^t dt_1 \cdots \int_0^{t_{2n-1}} dt_{2n}\mathrm{Tr}_{\mathrm{b}} < e^{-2i\sum_i c_i' p_i(t_1)} \dots e^{2i\sum_i c_i' p_i(t_{2n})} > \tag{2.13}$$

where the $n = 0$ term is 1. From Eq.(2.12b)to Eq.(2.12c) the following equations have been used

$$a_1(t) = e^{-i\varepsilon_1 t} a_1 \tag{2.14a}$$

$$a_1^{+}(t) = e^{i\varepsilon_1 t} a_1^{+}. \tag{2.14b}$$

There are only even terms in Eq.(2.12c) due to the fact that the creation and annihilation operators for the electronic states appear in pairs in the perturbation term V.

Using Feymann's operator disentangling formula[11,15] the thermal average in Eq.(2.13) can be evaluated and the result can be written as

$$A_{2n} = \int_0^t dt_1 \cdots \int_0^{t_{2n-1}} dt_{2n} e^{\sum_{j>i}^{2n}(-1)^{i+j}\Phi(t_i - t_j)} \tag{2.15}$$

where

$$\Phi(t) = \frac{2}{\pi}\int_0^{\infty} d\omega \frac{J(\omega)}{\omega^2}\Big\{ \coth(\frac{\beta\omega}{2}) - \frac{\cosh[\frac{\beta\omega}{2} - i\omega t]}{\sinh(\frac{\beta\omega}{2})} \Big\}. \tag{2.16}$$

Finally, the one-electron Green function can be written as

$$G(t) = -i\sum_{n=0}^{\infty}(-1)^n(\frac{\Delta}{2})^{2n}\int_0^t dt_1 \cdots \int_0^{t_{2n-1}} dt_{2n}$$

$$e^{-i\varepsilon_1 t+i\varepsilon\sum_{k=1}^{n}(t_{2k-1}-t_{2k})+\sum_{j>i}^{2n}(-1)^{i+j}\Phi(t_i-t_j)}. \tag{2.17}$$

Suppose the rate constant can be expressed in terms of a perturbation series of Δ a comparison between the real term linear in t in Eq.(2.10) and the real part of the term linear in t in Eq.(2.17) should yield the rate constant expansion in Δ for a large t(so that the rate can be defined) ,*i.e.*, the rate can be written as

$$k = \sum_{n=1}^{\infty} k_n \tag{2.18}$$

and

$$k_n = \lim_{t\to\infty} 2(-1)^{n+1}(\frac{\Delta}{2})^{2n}\text{term linear in } t \text{ of}$$
$$\Big\{\int_0^t dt_1\cdots\int_0^{t_{2n-1}} dt_{2n} e^{i\varepsilon\sum_{k=1}^{n}(t_{2k-1}-t_{2k})+\sum_{j>i}^{2n}(-1)^{i+j}\Phi(t_i-t_j)}\Big\}. \tag{2.19}$$

Let

$$x_1 = t-t_1, x_2 = t_1-t_2, \cdots, x_{2n-1} = t_{2n-2}-t_{2n-1}, x_{2n} = t_{2n-1}-t_{2n} \tag{2.20}$$

it can be shown that the Jacobian of the transformation from the t_i's to the x_i's is unity, thus, k_n can be rewritten as

$$k_n = \lim_{t\to\infty} 2(-1)^{n+1}(\frac{\Delta}{2})^{2n}\text{term linear in } t \text{ of}$$
$$\Big\{\int_0^{\infty} dx_1\cdots\int_0^{\infty} dx_{2n}\theta(t-x_1-x_2-\cdots-x_{2n})$$
$$e^{i\varepsilon\sum_{k=1}^{n}x_{2n}+\sum_{j>i}^{2n}(-1)^{i+j}\Phi(x_j+x_{j-1}+\cdots+x_{i+1}+x_i)}\Big\}. \tag{2.21}$$

Using the integral expression of the $\theta-$function and noticing that the exponential part is independent of x_1 so that an integration over x_1 can be performed we have

$$k_n = \lim_{t\to\infty} 2(-1)^{n+1}(\frac{\Delta}{2})^{2n}\text{term linear in } t \text{ of}\Big\{\int_0^{\infty} dx_2\cdots\int_0^{\infty} dx_{2n}$$

$$\int_{-\infty}^{\infty} \frac{ds}{2\pi i} \frac{e^{is(t-x_2-\cdots-x_{2n})}}{(s-i0)^2} e^{i\varepsilon \sum_{k=1}^{n} x_{2n} + \sum_{j>i}^{2n} (-1)^{i+j} \Phi(x_j + x_{j-1} + \cdots + x_{i+1} + x_i)} \Big\}. \quad (2.22)$$

Integrating over odd x_j's and taking the term linear in t and letting $t \to \infty$ the n-th order rate contribution becomes

$$k_n = 2(-1)^{n+1}(\frac{\Delta}{2})^{2n} \int_0^{\infty} dx_2 \cdots \int_0^{\infty} dx_{2n}$$

$$e^{i\varepsilon \sum_{k=1}^{n} x_{2n} + \sum_{j>i}^{2n} (-1)^{i+j} \Phi(x_j + x_{j-1} + \cdots + x_{i+1} + x_i)}. \quad (2.23)$$

This expression is our general formula to calculate the n-th order perturbation rate constant based on the one-electron Green function method. Another way to get the n-th order rate is by the linked cluster theorem in Green function theory[11].

In the next sections the Golden Rule result will be derived as a simple example of the present method and other examples will be given to show how this method can be used.

III. THE GOLDEN RULE FORMULA

The Golden Rule formula of the electron transfer reactions has been derived in various ways[9,11,16]. Here, the one-electron Green function method can be used as a trivial example to derive the Golden Rule case and can be used as an example of how the method can be applied.

In this case the rate is just the second order rate contribution in the general formula Eq.(2.19)

$$k_2 = 2\mathrm{Re}(\frac{\Delta}{2})^2 \int_0^{\infty} dx e^{i\varepsilon x - \Phi(x)} \quad (3.1)$$

and noticing $\Phi(-x) = \Phi^*(x)$ the Golden Rule rate constant can be written as

$$k_2 = \mathrm{Re}(\frac{\Delta}{2})^2 \int_{-\infty}^{\infty} e^{i\varepsilon x - \Phi(x)}. \quad (3.2)$$

This is the exact formula which had been derived by different methods and it is one of the most fundamental results in electron transfer theory.

For the symmetric electron transfer reactions ε is zero and the saddle-point can be easily found to be $-i\beta/2$. Thus under the saddle-point approximation the rate constant can be expressed in the following simple form

$$k_2 = (\frac{\Delta}{2})^2 \Big[\frac{\pi^2}{\int_0^\infty d\omega J(\omega)\csc(\frac{\beta\omega}{2})}\Big]^{1/2} exp\Big[-\frac{2}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega^2}\tanh(\frac{\beta\omega}{4})\Big]. \tag{3.3}$$

In the classical approximation for the bath($\beta\omega \ll 1$) Eq.(3.3) reduces to the usual classical nonadiabatic expression[13] for the rate constant of electron transfer reactions in symmetric case. As shown in Ref.13 the saddle-point approximation is exact in the classical case and is a very good approximation for the general case. In the next section a multidimensional version of the saddle-point approximation is used to derive Zusman's result for the dynamical solvent effect in electron transfer reactions.

IV. THE FOURTH ORDER CORRECTION AND A QUANTUM VERSION OF ZUSMAN'S RESULT

In this section a fourth-order contribution to the rate constant is given and as an example of the present formula a quantum version of the Zusman's result is derived for the symmetric electron transfer reactions. Therefore, the present method can give not only known results but also generate a new formula which can help in the understanding of the solvent dynamical effect on the electron transfer reactions.

From the general formula Eq.(2.19) the fourth-order correction can be written as

$$k_4 = -2(\frac{\Delta}{2})^4 \mathrm{Re}\int\!\!\int\!\!\int_0^\infty dx_2 dx_3 dx_4 e^{i\varepsilon(x_2+x_4)-F(x_2,x_3,x_4)} \tag{4.1}$$

where

$$F(x_2, x_3, x_4) = \Phi(x_2) + \Phi(x_3) + \Phi(x_4) + \Phi(x_2 + x_3 + x_4) -$$

$$\Phi(x_2 + x_3) - \Phi(x_3 + x_4). \tag{4.2}$$

For the symmetric case it can be shown that the fourth-order correction to the rate constant can be approximately written as[10]

$$k_4 \approx -\frac{1}{4}(\frac{\Delta}{2})^4 \mathrm{Re} \iiint_{-\infty}^{\infty} dx_2 dx_3 dx_4 e^{-F(x_2, x_3, x_4)}. \tag{4.3}$$

This expression for the rate constant is not exact because of the asymmetry with respect to the x's. Nevertheless it is a reasonable approximation, as we will show later that after an orthogonal transformation of x's the new integral variables will become symmetric for F-function in the neighborhood of the saddle-point which gives the main contribution to the whole integral. The detailed justification can be found in Ref.10. The saddle-point in this case can be easily shown to occur at $x_2^s = x_3^s = x_4^s = -i\beta/4$. Therefore, the fourth-order contribution to the rate constant can be rewritten as

$$k_4 \approx -\frac{1}{4}(\frac{\Delta}{2})^4 e^{-F(x_2^s, x_3^s, x_4^s)} \iiint_{-\infty}^{\infty} dx_2 dx_3 dx_4 e^{-\frac{1}{2}\sum_{i,j} x_i M_{ij} x_j} \tag{4.4}$$

where

$$F(x_2^s, x_3^s, x_4^s) = \frac{4}{\pi} \int_0^{\infty} d\omega \frac{J(\omega)}{\omega^2} \tanh(\frac{\beta\omega}{8}) \tag{4.5}$$

and M is the second derivative matrix of $F(x_2, x_3, x_4)$ with respect to x's at the saddle-points.

$$M = \begin{pmatrix} a & b & a-b \\ b & 2b & b \\ a-b & b & a \end{pmatrix} \tag{4.6}$$

where

$$a = \frac{2}{\pi} \int_0^{\infty} d\omega \frac{J(\omega)}{\sinh(\frac{\beta\omega}{2})} (2\cosh(\frac{\beta\omega}{4}) - 1) \tag{4.7a}$$

$$b = \frac{2}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\sinh(\frac{\beta\omega}{2})}(\cosh(\frac{\beta\omega}{4}) - 1). \tag{4.7b}$$

The above matrix can be diagonalized by an orthogonal transformation(which has unit Jacobian) and hence the coupled integrals in Eq.(4.4) become a product of three one-dimensional Gaussian integrals. That is,

$$k_4 \approx -\frac{1}{4}(\frac{\Delta}{2})^4 e^{-F(x_2^*, x_3^*, x_4^*)} \prod_{i=1}^{3} \int_{-\infty}^{\infty} dx_i e^{-\frac{1}{2}\lambda_i x_i^2} \tag{4.8}$$

where λ_i's are the eigenvalues of the matrix M. Finally, the contribution k_4 to the rate constant can be written as

$$k_4 \approx -(\frac{\Delta}{2})^4 \sqrt{\frac{\pi^3}{8b^2(a-b)}} e^{-\frac{4}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \tanh(\frac{\beta\omega}{8})}. \tag{4.9}$$

This is the general fourth-order formula for symmetric electron transfer reactions.

There are several new features in this result. First, for really high frequency modes ($\beta\omega \gg 1$) the prefactor part correction is exponentially small because the contribution to a or b is the order of $\int_{\omega_c}^\infty d\omega J(\omega) exp(-\beta\omega/4)$, where ω_c is the cutoff of high frequency modes. On the other hand, the correction due to the exponential part is to renormalize the coupling matrix

$$\Delta' = \Delta e^{-\frac{1}{\pi}\int_{\omega_c}^\infty d\omega \frac{J(\omega)}{\omega^2}},$$

which has been extensively discussed elsewhere [8,9].

Second interesting result that can be obtained is a quantum version of Zusman's result on solvent dynamical effect on electron transfer reactions. From a Padè approximation with the second and fourth-order rates and a partial summation, the total rate constant is given by

$$k_z = \frac{k_2}{1 - k_4/k_2}. \tag{4.10}$$

In order to show how the above formula reduces to the symmetric Zusman's classical rate constant the Debye spectral density and classical approximation will be used. The Debye spectral density can be written as

$$J_D(\omega) = \frac{E_r \omega \gamma}{\omega^2 + \gamma^2} \tag{4.11}$$

where E_r is the reorganization energy which makes the spectral density appropriately normalized, $\gamma = 1/\tau_L$, and τ_L is the usual longitudinal relaxation time. In this case the prefactor constant a and b in Eq.(4.9) can be evaluated

$$a - b = \frac{2E_r}{\beta} \tag{4.12a}$$

$$b = -2E_r\gamma \sum_{k=1}^{\infty} \frac{(-1)^k}{k\pi + \beta\gamma/2}. \tag{4.12b}$$

Under the classical approximation the exponential part of the rate gives $\beta E_r/4$ and $b \approx 2E_r\gamma \ln 2/\pi$ ($\beta\gamma \ll 1$ which is true for almost all of the solvent at room temperature), thus the Zusman rate can be written as

$$k_z = \frac{(\frac{\Delta}{2})^2 \sqrt{\frac{\pi\beta}{E_r}} e^{-\frac{\beta E_r}{4}}}{1 + (\frac{\Delta}{2})^2 \tau_L \frac{\pi^2}{8E_r \ln 2}}. \tag{4.13}$$

This result is precisely Zusman's rate constant for Debye relaxation case, except for a factor of order unity in the factor with $(\Delta/2)^2$ in the denominator.

In order to estimate the importance of the quantum effect for the solvent dynamical controlled electron transfer reactions a simple model calculation is given here. The comparison is made for the exact adiabatic rate constant $-k_2^2/k_4$(within Padè approximation of course) and the adiabatic rate constant from Eq.(4.13) as a function of $\beta\gamma$. The ratio of these two rates is calculated and the result is shown in figure 1. The parameters used in the calculation are $E_r = 9373\text{cm}^{-1}$(reorganization energy of ferrous-ferric self-exchange in water), $1/\beta = 200\text{cm}^{-1}$(room temperature) and τ_L varies from 300ps to 0.2ps(the longitudinal relaxation time for water which is the fastest among almost all solvents)[1,4b]. The result clearly shows quantum effect is not significant for most of the solvents at room temperature, which concentrates in the $\beta\gamma < 1$ region. But for water the quantum effect will become more important since $\beta\gamma \approx 0.8$. As the temperature becomes lower $\beta\gamma$ would increase and the quantum correction will become significant. Therefore, the quantum effect may be observable in the real systems.

VI. Concluding Remarks

One of the major goals of this work is to show that it is possible to calculate the reaction rate constant with dynamical factor and statistical factor without using the population correlation function method. In this case two examples were used to show that the one-particle Green function will be sufficient to provide the rate constant of the reaction. More examples would be needed to solidify the usage of this kind of method.

Another conclusion can be drawn from this study is the quantum effect in solvent dynamical effect on electron transfer reactions. Our result shows that in some cases the quantum correction may become important. In this work Padè approximation is used to derive Zusman's result. The sixth-order rate contribution can be evaluated with similar method, and it can be shown that the sixth-order term is different from $-k_4^2/k_2$ which is the sixth-order correction under Padè approximation. An interesting improvement to Zusman's result may be obtained if the higher order terms are calculated and the higher order Padè approximation is used to calculate the rate constant.

In the present paper the Debye solvent is used to show our more general rate constant expression indeed gives the usual behavior of the solvent dynamical effects on electron transfer reactions. But the general rate constant can be applied to arbitrary dielectric relaxation functions and even the inner sphere vibration modes. One of the interesting questions is how the present formula can be used to study how the intramolecular vibration modes would modify the solvent dynamical effect.

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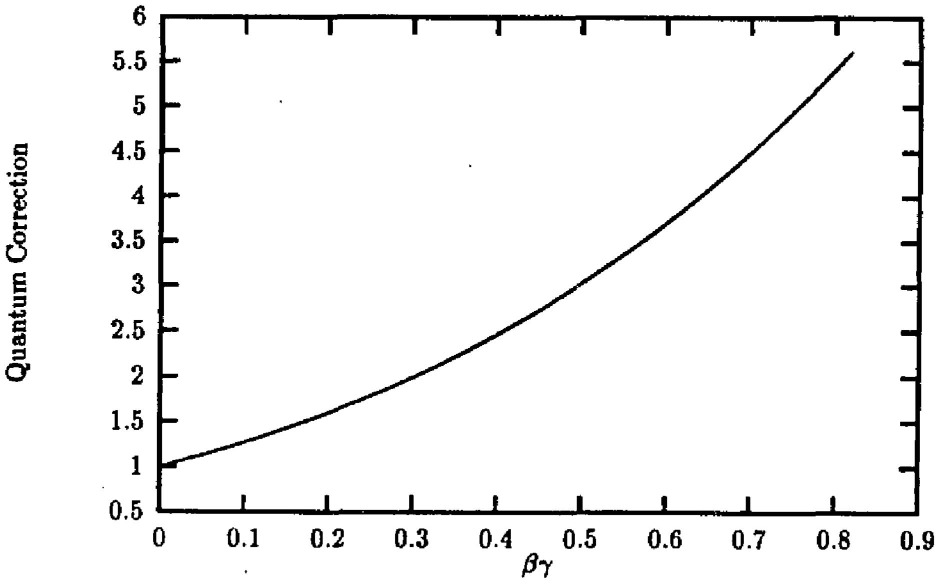

Caption

The ratio between the exact adiabatic rate and the approximate adiabatic rate from Eq.(4.13).

Chapter 5

Quantum Effects in Electron Transfer Reactions:
Solvent Dynamics Controlled Regime II

The Derivation of the Zusman's Equation from Projection Operator Method

Abstract

In this chapter the effect of solvent dynamics on electron transfer reactions is discussed from a different perspective. An equation of motion for the reduced density matrix(master equation) is derived from the modified spin-boson Hamiltonian for the Debye relaxation. Under a classical approximation this equation reduces to the Zusman's original equation and the approximations involved in the Zusman's model are clarified. A numerical scheme is discussed for solving the master equation to obtain the quantum reaction rate, so that a comparison with the quantum rate obtained from chapter four can be made. A second important aspect of this study is that the solvent dynamical effect on asymmetric electron transfer reactions can be studied within this model.

I. INTRODUCTION

In recent years there have been many studies on the role of solvent dynamics in electron transfer reactions and an example of the great interaction between theoretical predictions and the experimental confrontation is given in Ref. 1. According to the well-known electron transfer theory due to Marcus the reaction occurs as follows. The energies of the two electronic states(reactant and product)depend on the polarization of the solvent. The thermal fluctuations in the polarization of the dielectric medium lead to the modulation of the energies of the electronic states and when the energies are in resonance the electron can jump from donor to acceptor and then the solvent relaxes to a new set of equilibrium configurations which are in equilibrium with the product. When the response of the solvent to the electron jump is not fast enough, it may become the rate-determining step for electron transfer reactions. This effect is the solvent dynamic effect on electron transfer reactions first formulated by Zusman[2].

Since Zusman's initial formulation fifteen years ago there have been numerous attempts to understand this result from different perspectives[3]. The major conclusion in his work was that when the solvent motion is sluggish the rate of the reaction is controlled by the dynamics of the solvent dielectric relaxation and is inversely proportional to the longitudinal relaxation time for the Debye solvent. There still remain some questions to be answered. Two of the issues are the microscopic derivation of the Zusman's equation from the Hamiltonian of the system and a possible quantum correction. Garg *et al.* used a path integral method to derive from the Hamiltonian of the system the stochastic Liouville equation, which is the original equation used by Zusman [4]. Their results shed light on our understanding of the assumptions involved in the Zusman's result. Mukamel and coworkers applied a Green function method in Liouville space to derive their results but did not obtain a quantum correction[5]. Our recent work based on a one-electron Green function method provides a sound derivation for Zusman's rate and a quantum correction of the rate for symmetric reactions,but a quantum correction for asymmetric reactions is hard to obtain due to the difficulty in evaluating the saddle-point[6].

The derivation of Zusman's equation by the path integral method by Garg, Onuchic and Ambegaokar began with a modified spin-boson Hamiltonian but as the authors noted there remain some subtle points to be clarified,such as the conservation of probability [4]. In this chapter the equation of motion for reduced density matrix is derived and it is examined how the the Zusman's equation can be obtained from the equation of motion by a more elementary method. In this way the approximations involved can be clarified and problems from the path integral method can be avoided. Furthermore, if the equation of motion for the reduced density matrix can be solved it is possible to obtain a quantum rate which can be compared with the quantum rate which has been derived from a completely different method. In this case we are not restricted to symmetric reactions.

In the next section Zusman's equation is derived by a projection operator method from the modified spin-boson Hamiltonian. The purpose of this study is to clarify the approximations involved in the Zusman's equation and will be discussed along the way. In section III the equation of motion for the reduced density matrix is transformed into a form which can be solved by numerical methods. A potential consequence is calculating quantum rate constant, which can be compared with the rate obtained from another method for symmetric reactions and which can be used to generalize the the quantum rate calculation to asymmetric cases.

II. THE DERIVATION OF ZUSMAN'S EQUATION

The model Hamiltonian we shall begin with is the modified spin-boson Hamiltonian which can be transformed into the the conventional spin-boson Hamiltonian through a diagonalization of the harmonic degrees of freedom[4],

$$H = H_s + H_b + H_1 = H_0 + H_1 \tag{2.1a}$$

$$H_s = \frac{\Delta}{2}\sigma_x + \frac{p^2}{2m} + \frac{1}{2}m\Omega^2(y + y_0\sigma_z)^2 + \frac{1}{2}\varepsilon\sigma_z + \sum_i \frac{c_i^2 y^2}{2m_i\omega_i^2} \tag{2.1b}$$

$$H_b = \sum_i \left\{ \frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2 x_i^2 \right\} \tag{2.1c}$$

$$H_1 = \sum_i c_i x_i y \tag{2.1c}$$

where $\sigma_z = |1 >< 1| - |2 >< 2|, \sigma_x = |1 >< 2| + |2 >< 1|$ in the usual two states($|1 >$ and$|2 >$) representation and H_s is the system Hamiltonian which describes two shifted harmonic parabola for the reaction coordinate y coupled by electronic interaction matrix Δ. The collective coordinate y is crucial and has been explicitly singled out for the derivation of Zusman's equation. It represents the diffusive dielectric relaxation coordinate in Zusman's equation. H_b is the harmonic bath Hamiltonian and H_1 accounts for the bilinear coupling between the reaction coordinate and the bath.

The density matrix of the entire system $\rho(t)$ satisfies the following Liouville equation[7,8]

$$\frac{\partial\rho}{\partial t} = -i[H,\rho] = -iL_0\rho - iL_1\rho \tag{2.2}$$

where the Liouville operator L is defined as the following commutator

$$L = [H, \ ]. \tag{2.3}$$

If the $iL_1\rho$ term is treated as an inhomogeneous term then it can be shown that $\rho(t)$ satisfies the following integral equation

$$\rho(t) = e^{-iL_0t}\rho(0) - i\int_0^t ds e^{-iL_0s}L_1\rho(t-s). \tag{2.4}$$

Substituting eq(2.4) into eq(2.2) we have the equation of motion for the density matrix

$$\frac{\partial \rho}{\partial t} = -iL_0\rho - \int_0^t ds L_1 e^{-iL_0 s} L_1 \rho(t-s) - iL_1 e^{-iL_0 t}\rho(0). \tag{2.5}$$

Introducing the interaction picture

$$\tilde{\rho}(t) = e^{iL_0 t}\rho(t) = e^{iH_0 t}\rho(t)e^{-iH_0 t} \tag{2.6}$$

$$\tilde{L}_1(t) = e^{iL_0 t} L_1 e^{-iL_0 t} \tag{2.7}$$

Eq.(2.5)can be written as

$$\frac{\partial \tilde{\rho}}{\partial t} = -\int_0^t \tilde{L}_1(t)\tilde{L}_1(t-s)\tilde{\rho}(t-s) - i\tilde{L}_1(t)\rho(0). \tag{2.8}$$

Since the present goal is to derive an equation of motion for the density matrix involving only the reaction coordinate and the two-state variables $\sigma_x$andσ_z, regardless of the detailed states of the bath variables, a reduced density matrix defined as the thermal average over the bath is useful

$$\tilde{\sigma}(t) = \mathrm{Tr_b}\tilde{\rho}(t) \tag{2.9}$$

where $\mathrm{Tr_b}\cdots$ is the trace over the bath states. If it is assumed that initially the bath is in equilibrium and the system can be described by a density matrix $\sigma(0)$ and there is no interaction between them then the density matrix at time zero can be written as

$$\rho(0) = \rho_b\sigma(0) \tag{2.10}$$

where

$$\rho_b = \frac{e^{-\beta H_b}}{Z_b}, Z_b = \mathrm{Tr_b} e^{-\beta H_b}$$

gives the equilibrium density matrix for the bath. With this separation at t=0, the trace over the bath variables for the second term in Eq.(2.8) vanishes. The reduced density matrix equation of motion in interaction picture will be

$$\frac{\partial\tilde{\sigma}}{\partial t} = -\int_0^t ds \mathrm{Tr_b}[\tilde{L}_1(t)\tilde{L}_1(t-s)\tilde{\rho}(t-s)]. \tag{2.11}$$

The above equation is not useful in practice because it involves the reduced density matrix implicitly under the trace over the bath variables. In order to obtain a closed equation for $\tilde{\sigma}(t)$ the customary way is to introduce the Born approximation $\tilde{\rho}(t-s) \approx \rho_b\tilde{\sigma}(t-s)$. Physically, this step means the interaction between the system and the bath is weak and the bath is maintained at thermal equilibrium for all time. The weak coupling case is nevertheless interesting because even though the interaction between the reaction coordinate and each bath mode is weak the presence of many bath modes can make the total coupling substantial. In the particular case of Debye solvent the resultant Zusman solvent dynamical effect on electron transfer reaction rates has been confirmed by experiments[1]. It can be shown[8] that the Born approximation is equivalent to performing a second order perturbation to the bath and system interaction H_1. Thus we have

$$\frac{\partial\tilde{\sigma}}{\partial t} = -\int_0^t ds \mathrm{Tr_b}[\tilde{L}_1(t)\tilde{L}_1(t-s)\rho_b]\tilde{\sigma}(t-s) \tag{2.12a}$$

or equivalently

$$\frac{\partial\tilde{\sigma}}{\partial t} = -\int_0^t ds \mathrm{Tr_b}[\tilde{H}_1(t), [\tilde{H}_1(t-s), \rho_b\tilde{\sigma}(t-s)]] \tag{2.12b}$$

where

$$\tilde{H}_1(t) = e^{iH_0t}H_1e^{-iH_0t}$$

denotes H_1 in the interaction picture.

Introducing the spectral density for the bath and the correlation function for the harmonic variables[9]

$$J(\omega) = \sum_i \pi\delta(\omega - \omega_i)\frac{c_i^2}{m_i\omega_i} \tag{2.13}$$

$$\begin{aligned} \mathrm{Tr_b} x_i(t)x_i(0) &= \frac{\phi(t)}{2m_i\omega_i} \\ &= \frac{1}{2m_i\omega_i}\frac{\cosh[\frac{\beta\omega_i}{2} - i\omega_i t]}{\sinh\frac{\beta\omega_i}{2}} \end{aligned} \tag{2.14}$$

and using the expression for H_1 we have

$$\begin{aligned} \frac{\partial\tilde{\sigma}}{\partial t} = &-\int_0^t ds \int_0^\infty \frac{J(\omega)}{2\pi}[\phi(s)(y(t)y(t-s)\tilde{\sigma}(t-s) - y(t-s)\tilde{\sigma}(t-s)y(t)) \\ &+\phi(-s)(\tilde{\sigma}(t-s)y(t-s)y(t) - y(t)\tilde{\sigma}(t-s)y(t-s))]. \end{aligned} \tag{2.15}$$

Using

$$\tilde{\sigma}(t) = e^{iH_s t}\sigma(t)e^{-iH_s t}$$

and

$$y(t) = e^{iH_s t}ye^{-iH_s t}$$

the above equation can be transformed back into the Schödinger picture(from now on the dummy variable s has been changed into τ for later notational convenience)

$$\begin{aligned} \frac{\partial\sigma}{\partial t} = &-i[H_s,\sigma(t)] - \int_0^t d\tau \int_0^\infty d\omega\frac{J(\omega)}{2\pi}[\phi(\tau)(ye^{-iH_s\tau}y\sigma(t-\tau)e^{iH_s\tau} \\ &-e^{-iH_s\tau}y\sigma(t-\tau)e^{iH_s\tau}y) \\ &+\phi(-\tau)(e^{-iH_s\tau}\sigma(t-\tau)ye^{iH_s\tau}y - ye^{-iH_s\tau}\sigma(t-\tau)ye^{iH_s\tau})]. \end{aligned} \tag{2.16}$$

Under a Markovian approximation[10], the history-dependent reduced density matrix $\sigma(t-\tau)$ becomes history-independent $\sigma(t)$, so yielding

$$\frac{\partial\sigma}{\partial t} = -i[H_s,\sigma(t)] - \int_0^t d\tau \int_0^\infty d\omega\frac{J(\omega)}{2\pi}[\phi(\tau)(yy(-\tau)\sigma(t) - y(-\tau)\sigma(t)y)$$

$$+\phi(-\tau)(\sigma(t)y(-\tau)y - y\sigma(t)y(-\tau))]. \tag{2.17}$$

Untill now the above equation of motion for reduced density matrix contains only the Born and Markovian approximations.

For the convenience of later development another form of the above equation will be useful. Inserting Eq.(2.14) into Eq.(2.17) and collecting terms we have

$$\frac{\partial\sigma}{\partial t} = -i[H_s, \sigma(t)] - \int_0^t d\tau \int_0^\infty d\omega \frac{J(\omega)}{2\pi}\Big\{\coth\frac{\beta\omega}{2}\cos(\omega\tau)[y,[y(-\tau),\sigma(t)]]$$

$$-i\sin(\omega\tau)[y,[y(-\tau),\sigma(t)]_+]\Big\} \tag{2.18}$$

where [, $]_+$ is the usual anticommutator.

Since the original equation of Zusman is formulated for Debye relaxation solvent it will be sufficient for its derivation to choose the spectral density, which describes the dynamical relaxation property of the bath, to be of the Debye form. The Debye spectral density can be written as[6]

$$J(\omega) = \frac{E_r\omega\gamma}{\gamma^2+\omega^2}, \tag{2.19}$$

where $1/\gamma = \tau_L$ is the longitudinal relaxation time and E_r is the reorganization energy in electron transfer theory. Substituting Eq.(2.19) into Eq.(2.18) we have

$$\frac{\partial\sigma}{\partial t} = -i[H_s, \sigma(t)] - \int_0^t d\tau \int_0^\infty d\omega \frac{E_r\omega\gamma}{2\pi(\gamma^2+\omega^2)}\Big\{\coth\frac{\beta\omega}{2}\cos(\omega\tau)$$

$$[y,[y(-\tau),\sigma(t)]] - i\sin(\omega\tau)[y,[y(-\tau),\sigma(t)]_+]\Big\}. \tag{2.20}$$

In the above equation the integral over ω part can be evaluated exactly

$$\int_0^\infty d\omega \frac{\omega\sin(\omega\tau)}{\gamma^2+\omega^2} = \frac{\pi}{2}e^{-\gamma\tau} \tag{2.21a}$$

and

$$\int_0^\infty d\omega \frac{\omega\coth\frac{\beta\omega}{2}\cos(\omega\tau)}{\gamma^2+\omega^2} =$$

$$\frac{\pi}{2}\Big\{\cot\frac{\beta\gamma}{2}e^{-\gamma\tau}-\sum_{k=1}^{\infty}\frac{4k\pi}{(\beta\gamma)^2-(2k\pi)^2}e^{-\frac{2k\pi\tau}{\beta}}\Big\}. \tag{2.21b}$$

The partial integration for the anticommutator term can be performed with the upper limit extended to infinity for the case that the reaction rate time scale is much longer than the dynamical relaxation of the solvent. Thus, the equation of motion now reads

$$\frac{\partial\sigma}{\partial t}=-i[H'_s,\sigma(t)]-\int_0^{\infty}d\tau\frac{E_r\gamma}{4}\Big\{(\cot\frac{\beta\gamma}{2}e^{-\gamma\tau}-\sum_{k=1}^{\infty}\frac{4k\pi}{(\beta\gamma)^2-(2k\pi)^2}e^{-\frac{2k\pi\tau}{\beta}}$$

$$[y,[y(-\tau),\sigma(t)]]-\frac{i}{\gamma}e^{-\gamma\tau}[y,[\dot{y}(-\tau),\sigma(t)]_+]\Big\} \tag{2.22}$$

where H'_s is the system Hamiltonian without the last term in Eq.(2.1b), which has been canceled with the first part of the partial integration. $\dot{y}(-\tau)$ is the derivative of $y(-\tau)$ with respect to τ. When the dielectric relaxation is slow compared with the time scale of the reaction coordinate it will be a good approximation to take $y(\tau)\approx y$ then the τ integration can be performed. Finally, the equation of motion for reduced density matrix can be written as

$$\frac{\partial\sigma}{\partial t}=-i[H'_s,\sigma(t)]-\frac{E_r}{4}\Big\{(\cot\frac{\beta\gamma}{2}-\sum_{k=1}^{\infty}\frac{2\beta\gamma}{(\beta\gamma)^2-(2k\pi)^2})[y,[y,\sigma(t)]]+$$

$$\frac{i}{\gamma}[y,[\frac{p}{m},\sigma(t)]_+]\Big\}. \tag{2.23}$$

This equation is the one which would be used for numerical calculation of the electron transfer rate and is discussed in next section.

If the dielectric relaxation time scale τ_L is large compared with the thermal time or $\beta\gamma \ll 1$(this often referred as classical approximation for the bath) the equation of motion for density matrix Eq.(2.23) takes the following simple form

$$\frac{\partial\sigma}{\partial t}=-i[H'_s,\sigma(t)]-\frac{E_r}{2\beta\gamma}[y,[y,\sigma(t)]]-i\frac{E_r}{4\gamma m}[y,p,\sigma(t)]. \tag{2.24}$$

This equation is the equation of motion for reduced density matrix for Debye relaxation[4] and can be transformed into Zusman's equation by a Wigner transformation, the latter converts the density matrix into the classical distribution function, and then by integration over fast momentum variable. The details can be found elsewhere[4,12].

Our derivation here clearly avoids the problem faced by Garg *et al.*[4] for the conservation of probability by the path integral method and the approximations involved in the derivation can be stated unambiguously. A numerical calculation of the reduced density matrix as a function of time based on Eq.(2.22) provides an opportunity to obtain the quantum rate constant, which can be compared with our recent quantum Zusman rate for symmetric case obtained in an independent method in chapter 4. This will be discussed in the next section.

III. THE NUMERICAL CALCULATIONS

The strategy to calculate rate from master equation is to convert the general operator form of the equation Eq.(2.23) to the form in the coordinate representation and then solve the resultant differential equation to obtain the population as a function of time[13]. Under certain conditions the population *vs* time is a simple exponential form and a rate constant can be obtained in this case. For our master equation (2.21) using Eq.(2.1b) and the operator form of p in coordinate representation we have

$$
\begin{aligned}
\frac{\partial\sigma(y,y',t)}{\partial t} = -i\Big\{ & \frac{\Delta}{2}[\sigma_x\sigma(y,y',t) - \sigma(y,y',t)\sigma_x] + \\
& \frac{\varepsilon}{2}[\sigma_z\sigma(y,y',t) - \sigma(y,y',t)\sigma_z] \\
-\frac{1}{2m}[\frac{\partial^2\sigma(y,y',t)}{\partial y^2} - \frac{\partial^2\sigma(y,y',t)}{\partial y'^2}] & + m\Omega^2 y_0[y\sigma_z\sigma(y,y',t) - y'\sigma(y,y',t)\sigma_z] \\
& + \frac{1}{2}m\Omega^2(y^2 - y'^2)\sigma(y,y',t)\Big\}
\end{aligned}
$$

$$-\frac{E_r}{4}[\cot\frac{\beta\gamma}{2}-\sum_{k=1}^{\infty}\frac{2\beta\gamma}{(\beta\gamma)^2-(2k\pi)^2}](y-y')^2\sigma(y,y',t)$$

$$-i\frac{E_r}{4m\gamma}[y\frac{\partial\sigma(y,y',t)}{\partial y}+y\frac{\partial\sigma(y,y',t)}{\partial y'}-y'\frac{\partial\sigma(y,y',t)}{\partial y}-\frac{\partial y'\sigma(y,y',t)}{\partial y')}]. \qquad (3.1)$$

Next the reduced density matrix in two electronic states representation can be introduced

$$\sigma_{11}(y,y',t) =< 1|\sigma(y,y',t)|1 >$$

$$\sigma_{22}(y,y',t) =< 2|\sigma(y,y',t)|2 >$$

$$\sigma_{12}(y,y',t) =< 1|\sigma(y,y',t)|2 >$$

$$\sigma_{21}(y,y',t) =< 2|\sigma(y,y',t)|1 > .$$

Eq.(3.1) can then be transformed into the following coupled reduced density matrices in coordinate space(the arguments of the σ's are omitted for brevity)

$$\frac{\partial\sigma_{11}}{\partial t} = -i\Big\{\frac{\Delta}{2}[\sigma_{21}-\sigma_{12}]-\frac{1}{2m}[\frac{\partial^2\sigma_{11}}{\partial y^2}-\frac{\partial^2\sigma_{11}}{\partial y'^2}]+m\Omega^2y_0(y-y')\sigma_{11}$$

$$+\frac{1}{2}m\Omega^2(y^2-y'^2)\sigma_{11}\Big\}-\frac{E_r}{4}\Big]\cot\frac{\beta\gamma}{2}-\sum_{k=1}^{\infty}\frac{2\beta\gamma}{(\beta\gamma)^2-(2k\pi)^2}\Big](y-y')^2\sigma_{11}$$

$$-i\frac{E_r}{4m\gamma}\Big[y\frac{\partial\sigma_{11}}{\partial y}+y\frac{\partial\sigma_{11}}{\partial y'}-y'\frac{\partial\sigma_{11}}{\partial y}-\frac{\partial y'\sigma_{11}}{\partial y')}\Big] \qquad (3.2a)$$

$$\frac{\partial\sigma_{12}}{\partial t} = -i\Big\{\frac{\Delta}{2}[\sigma_{22}-\sigma_{11}]+\varepsilon\sigma_{12}-\frac{1}{2m}[\frac{\partial^2\sigma_{12}}{\partial y^2}-\frac{\partial^2\sigma_{12}}{\partial y'^2}]+m\Omega^2y_0(y+y')\sigma_{12}$$

$$+\frac{1}{2}m\Omega^2(y^2-y'^2)\sigma_{12}\Big\}-\frac{E_r}{4}\Big[\cot\frac{\beta\gamma}{2}-\sum_{k=1}^{\infty}\frac{2\beta\gamma}{(\beta\gamma)^2-(2k\pi)^2}\Big](y-y')^2\sigma_{12}$$

$$-i\frac{E_r}{4m\gamma}\Big[y\frac{\partial\sigma_{12}}{\partial y}+y\frac{\partial\sigma_{12}}{\partial y'}-y'\frac{\partial\sigma_{12}}{\partial y}-\frac{\partial y'\sigma_{12}}{\partial y')}\Big] \qquad (3.2b)$$

$$\begin{aligned}\frac{\partial\sigma_{21}}{\partial t} &= -i\Big\{\frac{\Delta}{2}[\sigma_{11}-\sigma_{22}]-\epsilon\sigma_{21}-\frac{1}{2m}[\frac{\partial^2\sigma_{21}}{\partial y^2}-\frac{\partial^2\sigma_{21}}{\partial y'^2}]+m\Omega^2 y_0(-y-y')\sigma_{21}\\ &+\frac{1}{2}m\Omega^2(y^2-y'^2)\sigma_{21}\Big\}-\frac{E_r}{4}\left[\cot\frac{\beta\gamma}{2}-\sum_{k=1}^{\infty}\frac{2\beta\gamma}{(\beta\gamma)^2-(2k\pi)^2}\right](y-y')^2\sigma_{21}\\ &-i\frac{E_r}{4m\gamma}\left[y\frac{\partial\sigma_{21}}{\partial y}+y\frac{\partial\sigma_{21}}{\partial y'}-y'\frac{\partial\sigma_{21}}{\partial y}-\frac{\partial y'\sigma_{21}}{\partial y')}\right]\end{aligned} \tag{3.2c}$$

$$\begin{aligned}\frac{\partial\sigma_{22}}{\partial t} &= -i\Big\{\frac{\Delta}{2}[\sigma_{12}-\sigma_{21}]-\frac{1}{2m}[\frac{\partial^2\sigma_{22}}{\partial y^2}-\frac{\partial^2\sigma_{22}}{\partial y'^2}]+m\Omega^2 y_0(-y+y')\sigma_{22}\\ &+\frac{1}{2}m\Omega^2(y^2-y'^2)\sigma_{22}\Big\}-\frac{E_r}{4}\left[\cot\frac{\beta\gamma}{2}-\sum_{k=1}^{\infty}\frac{2\beta\gamma}{(\beta\gamma)^2-(2k\pi)^2}\right](y-y')^2\sigma_{22}\\ &-i\frac{E_r}{4m\gamma}\left[y\frac{\partial\sigma_{22}}{\partial y}+y\frac{\partial\sigma_{22}}{\partial y'}-y'\frac{\partial\sigma_{22}}{\partial y}-\frac{\partial y'\sigma_{22}}{\partial y')}\right].\end{aligned} \tag{3.2d}$$

If we use a one-dimensional coordinate y with N grid points, the above equations become coupled N×N equations of motion for the density matrices and can be solved numerically with the following initial condition[14]

$$\sigma_{11}(y,y',0)=\sqrt{\frac{m\Omega}{2\sinh\beta\Omega}}\,e^{-\frac{m\Omega}{2\sinh\beta\Omega}[((y+y_0)^2+(y'+y_0)^2)\cosh\beta\Omega-2(y+y_0)(y'+y_0)}]. \tag{3.3}$$

This condition is the equilibrium density matrix for a harmonic potential centered at y_0 with frequency Ω for equilibrium point at $y = y_0$. The real part of diagonal element $\sigma_{11}(y, y, t)$ gives the population density at y and the integration over y gives the population in electronic state 1 as a function of time. The rate constant calculated this way should give a quantum rate constant of Zusman's problem and can be compared with the quantum rate constant we derived from the Green function method[6] for symmetric reactions. However for the asymmetric reactions the numerical solution of the master equation can also be used to obtain a generalized quantum rate constant in contrast to the Green function method by which the asymmetric quantum rate constant is difficult to obtain.

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Chapter 6

A Gaussian Field Model in Solvation Dynamics

A Gaussian Field Model in Solvation Dynamics

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Abstract

A Gaussian field model is used to obtain the charge density correlation function of the solution in terms of the charge density correlation function of the solvent. It then becomes possible to calculate the time-dependent solvation free energy without using the "uniform dielectric approximation." It is found that the nonuniformity in the vicinity of the solute indeed retards the solvation relaxation for a particular model, and thereby is in agreement with Onsager's "inverted snowball" picture.

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I. INTRODUCTION

Many chemical reactions in solution involve a rearrangement of the charge in the reactants and the time-response of the solvent molecules to this change influences reaction dynamics. The measurement of the solvent response in the absence of a chemical reaction can provide a reasonable first step towards the understanding of this influence. The charge distribution of a solute in its ground electronic state is initially in thermal equilibrium with the solvent. When that solute charge distribution is suddenly changed by light absorption to an excited electronic state of the solute, the latter is, in general, not in equilibrium with the solvent. This sudden change of solute charge distribution forces the solvent to rearrange to a state in equilibrium with the new solute charge distribution. The question that arises is how this relaxation process can be described microscopically in terms of the solvent-solute molecular interactions.

With the advent of ultrafast laser techniques it is now possible to probe the detailed solvent relaxation dynamics. The results, combined with the developments of theoretical models and computer simulations, have enhanced the physical understanding of these processes [1]. Unlike the initial theories, which were typically based upon a dielectric continuum model of the solvent, various current theories have been introduced to incorporate the molecular aspect of solvent-solute interaction. A now commonly used microscopic theory of solvation dynamics, the dynamical mean spherical approximation(MSA), was first proposed by Wolynes and extended by others[2]. Here, the time-autocorrelation function of the solvation(tcf), which is frequently used to describe the relaxation process, is expressed in terms of the macroscopic dielectric response function $\epsilon(\omega)$ of the pure solvent and the spatial dependence of the solvation is accounted for through the use of the static MSA solvation free energy of the solution. Other theories differ in the methods used to relate the $\epsilon(\omega, k)$ to $\epsilon(\omega)$, the dielectric response function of the pure solvent at k=0, where k accounts for the space dependence of ϵ, and some factor is used to describe the k-dependence of $\epsilon(\omega, k)$. Bagchi and Chandra[3], for example, used a linearized Smoluchowski-Vlasov equation for polarization density fluctuations. Fried and Mukamel[4] employed a generalized Langevin equation for the equilibrium density-density correlation functions. In all of the theories, other than the dynamical MSA, the dielectric response function $\epsilon(\omega, k)$ of the pure solvent is used up to the boundary between the solvent and the solute. The latter assumption is sometimes called the "dielectric approximation"[5] and we call it here the "uniform dielectric approximation" to state more explicitly the nature of its assumption.

In this paper the uniform dielectric approximation is avoided for the calculation of solvation correlation function. Instead, a Gaussian field model of liquids[6] is used to derive an equation relating the solute-influenced dielectric response function of the solvent to the pure solvent dielectric response function. Further, the dynamical k-dependence is introduced rigorously, representing a step forward from the dynamical MSA, in which the k-dependence is introduced through the static MSA solvation free energy of the hard sphere solution. A model calculation based on a particular charge density correlation function of the pure solvent is introduced. According to the results obtained from it the uniform dielectric approximation overestimates the rate of solvation relaxation. The nonuniform nature of the solvent around the solute makes the solvation relaxation process slower near the solute, assuming a k-dependent charge density correlation function. The latter effect is consistent with the "inverted snowball" picture introduced by Onsager two decades ago[7].

The relation derived between the charge density correlation function of the solution and the one of pure solvent is not restricted to charge densities and could be applied to the usual density correlation function. In the latter case both the k- and $\omega-$dependence of the pure solvent density correlation is known from experimental measurements, such as neutron scattering studies of liquids[8].

The paper is organized as follows. In Section II some results of the conventional solvation dynamics are derived to provide a starting point for the present work. This section is a reformulation of known literature results. In Section III an exact relation of the correlation function between the pure solvent and the solution is derived within a Gaussian field model and a hard-sphere solute-solvent interaction framework, which forms the foundation for the present calculation of the solvation relaxation function without the uniform dielectric approximation. Eq.(3.10) is the main result of this work. In Section IV a simple example is used to illustrate the application of the present model and discuss the implications of the results.

II THEORETICAL FORMULATION

In this section useful results from the dielectric theory of liquids are discussed for the subsequent development[5,8]. We consider a space- and time-dependent external charge distribution $n^o(\mathbf{r},t)$ for a liquid. This $n^o(\mathbf{r},t)$ could be created by the solute molecule, for example. From Poisson's equation the electrostatic potential $\varphi^o(\mathbf{r},t)$ associated with $n^o(\mathbf{r},t)$ satisfies

$$\nabla^2\varphi^o(\mathbf{r},t) = -4\pi n^o(\mathbf{r},t). \tag{2.1}$$

As it changes in time $\varphi^o(\mathbf{r},t)$ induces a macroscopic charge distribution $\rho(\mathbf{r},t)$ in the liquid due to the electronic motion of the liquid molecules and to the nuclear motion of the liquid molecules.

By Maxwell's equations, the dielectric displacement and the electric field for the system satisfy

$$\nabla \cdot \mathbf{D}(\mathbf{r},t) = 4\pi n^o(\mathbf{r},t) \tag{2.2}$$

$$\nabla \cdot \mathbf{E}(\mathbf{r},t) = 4\pi(n^o(\mathbf{r},t) + \rho(\mathbf{r},t)). \tag{2.3}$$

The Fourier transform in space and time of the above equations yields

$$k^2\varphi^0(\mathbf{k},\omega) = -i\mathbf{k} \cdot \mathbf{D}(\mathbf{k},\omega) = 4\pi n^o(\mathbf{k},\omega) \tag{2.4}$$

$$-i\mathbf{k} \cdot \mathbf{E}(\mathbf{k},\omega) = 4\pi(n^o(\mathbf{k},\omega) + \rho(\mathbf{k},\omega)). \tag{2.5}$$

For the isotropic liquids the longitudinal dielectric function $\varepsilon_L(k,\omega)$ of the liquid is defined as

$$D_L(\mathbf{k},\omega) = \varepsilon_L(k,\omega)E_L(\mathbf{k},\omega). \tag{2.6}$$

Thus from Eqs.(2.4) to (2.6) we have

$$\frac{1}{\varepsilon_L(k,\omega)} = 1 + \frac{\rho(\mathbf{k},\omega)}{n^o(\mathbf{k},\omega)} = 1 + \frac{4\pi}{k^2}\frac{\rho(\mathbf{k},\omega)}{\varphi^0(\mathbf{k},\omega)}. \tag{2.7}$$

Here, the reason that we are interested in the longitudinal dielectric function is because the usual optical excitation of the solute changes the charge distribution, which in turn produces a change of the longitudinal electric field .

For the solvation time scale of concern here the electronic part can be considered as being instantaneous and its contribution to the dielectric function can be accounted by ε_∞ if the spatial dispersion is neglected

$$\frac{1}{\varepsilon_L(k,\omega)} - \frac{1}{\varepsilon_\infty} = \frac{4\pi}{k^2}\frac{\rho_\nu(\mathbf{k},\omega)}{\varphi^o(\mathbf{k},\omega)} \tag{2.8}$$

where $\rho_\nu(\mathbf{k},\omega)$ is an induced charge density due to the nuclear motion of the solvent molecules.

In linear response theory an induced charge density is related to the external potential by a nuclear susceptibility, χ^8:

$$\rho_\nu(\mathbf{k},\omega) = \chi(k,\omega)\varphi^o(\mathbf{k},\omega) \tag{2.9}$$

with

$$\chi(k,\omega) = \beta(i\omega C_{\nu\nu}(k,\omega) - S_{\nu\nu}(k)) \tag{2.10}$$

$$C_{\nu\nu}(k,\omega) = \int_0^\infty dte^{-i\omega t}C_{\nu\nu}(k,t) \tag{2.11}$$

$$C_{\nu\nu}(k,t) =< \hat{\rho}_\nu(\mathbf{k},t)\hat{\rho}_\nu(-\mathbf{k}) > \tag{2.12}$$

and

$$S_{\nu\nu}(k) = C_{\nu\nu}(k,t=0) \tag{2.13}$$

where $< \cdots >$ is the average over the equilibrium distribution function of the pure liquid and $\hat{\rho}_\nu(\mathbf{r},t)$ is the microscopic charge density corresponding to the macroscopic quantity $\rho_\nu(\mathbf{r},t)$. Thus, an expression to calculate the dielectric response function from the correlation function of charge density can be written as

$$\frac{1}{\varepsilon_L(k,\omega)} - \frac{1}{\varepsilon_\infty} = \frac{4\pi}{k^2}\chi(k,\omega). \tag{2.14}$$

Next a time-dependent solvation free energy expression is derived as a step towards the calculation of the solvation response correlation function $S(t)$. The latter is defined as

$$S(t) = \frac{F(t) - F(\infty)}{F(0) - F(\infty)}$$

where $F(t)$ is the solvation free energy change at time t due to the change in the charge distribution of solute at t=0, namely that in the excited state minus that in the ground state. For a solute acquiring a new charge distribution instantaneously at t=0 the time-dependent solvation free energy change can be written as

$$F(t) = \frac{1}{2}\int d^3\mathbf{r}\Delta\rho_\nu(\mathbf{r},t)\Delta\varphi^o(\mathbf{r},t) \tag{2.15}$$

where $\Delta\rho_\nu(\mathbf{r},t)$ is the change in the function $\rho_\nu(\mathbf{r},t)$ of the nuclear charge density of the solvent molecules in response to the time-dependent perturbation $\Delta\varphi^o(\mathbf{r},t) = \theta(t)\Delta\varphi^o(\mathbf{r})$. Here, $\theta(t)$ is a step function and $\Delta\varphi^o(\mathbf{r})$ is the electrostatic potential change arising from the difference in the two charge distributions of the solute. By linear response theory the change in charge density is related to the perturbation $\Delta\varphi^o(\mathbf{r},t)$ by[8]

$$\Delta\rho_\nu(\mathbf{r},t) = \beta\int d^3\mathbf{r}(C^m_{\nu\nu}(\mathbf{r},\mathbf{r}',t) - C^m_{\nu\nu}(\mathbf{r},\mathbf{r}',t=0))\Delta\varphi^o(\mathbf{r}) \tag{2.16}$$

where $C^m_{\nu\nu}(\mathbf{r},\mathbf{r}',t)$ is the charge density correlation function for the solution at time t, the superscript m distinguishing it from the function for the pure solvent.

The time-dependent solvation free energy change is obtained from Eqs.(2.15) and (2.16)

$$F(t) = \frac{1}{2}\beta\int\int d^3\mathbf{r}d^3\mathbf{r}'(C^m_{\nu\nu}(\mathbf{r},\mathbf{r}',t) - C^m_{\nu\nu}(\mathbf{r},\mathbf{r}',t=0))\Delta\varphi^o(\mathbf{r},t)\Delta\varphi^o(\mathbf{r}'). \tag{2.17}$$

Its Laplace transform, given here for later convenience, is

$$\tilde{F}(s) = \frac{1}{2s}\int\int d^3\mathbf{r}d^3\mathbf{r}'\chi^m(\mathbf{r},\mathbf{r}',s)\Delta\varphi^o(\mathbf{r})\Delta\varphi^o(\mathbf{r}') \tag{2.18}$$

where Eq.(2.10) with an m superscript has been used.

In general, the relationship between the charge density correlation function $\chi^m(\mathbf{r},\mathbf{r}',s)$ of the solution and the $\chi(\mathbf{r},\mathbf{r}',s)$ of the solvent is difficult to obtain due to the solute-solvent interaction. The conventional way to estimate the solution value $\chi^m(\mathbf{r},\mathbf{r}',s)$ is to assume that the solvent outside the volume occupied by the solute remains the same as the bulk solvent, namely behaves like an unperturbed pure isotropic solvent. Thus, the only effect of the solute is an excluded volume effect on the correlation function and, in turn, on the calculation of the solvation relaxation function. This assumption is the "uniform dielectric approximation" used, as already noted, in most of the solvation dynamics theories[1].

We derive next a relation between the charge density correlation functions of the pure solvent and the solution for the hard-sphere solute, which is exact within the linear response approximation. As a consequence, the nonuniformity effect of the solvent around the solute can be accounted for exactly in this case for the solvation dynamics, provided that the pure solvent dielectric response function is known.

III THE GAUSSIAN FIELD MODEL OF THE SOLUTION

The Gaussian field model(GFM) of fluids is often used in the development of theories for fluctuations over large length scale[13,14]. Chandler showed that this model could be applicable even at a very small length scale by showing that some static molecular theories of fluids can be derived from the Gaussian field model[6]. In the present work we extend this application of the GFM to a time-dependent problem. For a GFM of the liquid, the Hamiltonian of the pure solvent can be written as[6]

$$H = \frac{k_B T}{2} \int d\mathbf{r} \int d\mathbf{r}' \delta\rho(\mathbf{r}) C^{-1}(\mathbf{r}, \mathbf{r}') \delta\rho(\mathbf{r}') \tag{3.1}$$

where

$$C(\mathbf{r}, \mathbf{r}') =< \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') > \tag{3.2}$$

$\delta\rho(\mathbf{r})$ is the deviation of microscopic charge density from its mean value ρ in the solvent, $k_B T = \beta^{-1}$, and $< \cdots >$ denotes the usual statistical average.

In the presence of a hard-sphere-like solute the charge density inside the region occupied by the solute will be zero. The partition function of the system is then[13]

$$Z[\phi(\mathbf{r}, \tau)] = \int \mathcal{D}\rho(\mathbf{r}, \tau) \{ \prod_{\mathbf{r}\ \mathbf{inside}} \delta[\rho(\mathbf{r}, \tau)] \} e^{S_0[\rho(\mathbf{r}, t]} \tag{3.3}$$

where the symbol $\mathcal{D}$ indicates that the integration is a functional integration, and the action S_0 is given by

$$S_0[\rho(\mathbf{r},\tau)] = -\frac{1}{2}\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar)}\int_0^{\beta\hbar}\frac{d\tau'}{\beta\hbar}\int d\mathbf{r}\int d\mathbf{r}'\delta\rho(\mathbf{r},\tau)C^{-1}(\mathbf{r},\mathbf{r}',\tau-\tau')\delta\rho(\mathbf{r}',\tau')$$

$$+\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int d\mathbf{r}\rho(\mathbf{r},\tau)[u(\mathbf{r})+\phi(\mathbf{r},\tau)] \qquad (3.4)$$

where the standard auxiliary field $\phi(\mathbf{r},\tau)$ has been introduced to facilitate the subsequent calculation[10]. The δ function part of Eq.(3.3), $\delta[\rho(\mathbf{r},\tau)]$, accounts for the excluded volume effect due to the solute and the term "**r** inside" indicates the space spanned by the solute hard-sphere potential. The $u(\mathbf{r})$ denotes the interaction potential between solute and solvent outside that domain.

By using the δ-function integral expression in functional space

$$\delta[\rho(\mathbf{r},\tau)] = \int \mathcal{D}\psi(\mathbf{r},\tau)e^{i\rho(\mathbf{r},\tau)\psi(\mathbf{r},\tau)} \qquad (3.5)$$

the partition function of the system can be rewritten as

$$Z[\phi(\mathbf{r},\tau)] = \int \mathcal{D}\rho(\mathbf{r},\tau)\int \mathcal{D}\psi(\mathbf{r},\tau)e^{S[\rho(\mathbf{r},\tau),\psi(\mathbf{r},\tau)]} \qquad (3.6)$$

with the action

$$S[\rho(\mathbf{r},\tau),\psi(\mathbf{r},\tau)] = S_0[\rho(\mathbf{r},\tau)] + i\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int_{\mathrm{in}} d\mathbf{r}\rho(\mathbf{r},\tau)\psi(\mathbf{r},\tau) \qquad (3.7)$$

where "in" indicates the integration is over the domain occupied by the solute. Since the action is still of Gaussian form in the functional space the integration can be performed in the standard way[6,10] and the result is

$$Z[\phi(\mathbf{r},\tau)] = N[detC_{\mathrm{in}}]^{-1/2}exp\Bigg\{\rho\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int_{\mathrm{in}} d\mathbf{r}[u(\mathbf{r})+\phi(\mathbf{r},\tau)]$$

$$+\frac{1}{2}\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int_0^{\beta\hbar}\frac{d\tau'}{\beta\hbar}\int d\mathbf{r}\int d\mathbf{r}'[u(\mathbf{r})+\phi(\mathbf{r},\tau)]C(\mathbf{r},\mathbf{r}',\tau-\tau')[u(\mathbf{r}')+\phi(\mathbf{r}',\tau')]$$

$$-\frac{1}{2}\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int_0^{\beta\hbar}\frac{d\tau'}{\beta\hbar}\iint_{\text{in}} d\mathbf{r}d\mathbf{r}'$$

$$\Big[\rho+\int_0^{\beta\hbar}\frac{d\tau''}{\beta\hbar}\int d\mathbf{r}''C(\mathbf{r},\mathbf{r}'',\tau-\tau'')([u(\mathbf{r}'')+\phi(\mathbf{r}'',\tau'')\Big]C_{in}^{-1}(\mathbf{r},\mathbf{r}',\tau-\tau')$$

$$\Big[\rho+\int_0^{\beta\hbar}\frac{d\tau'''}{\beta\hbar}\int d\mathbf{r}'''C(\mathbf{r}',\mathbf{r}''',\tau'''-\tau')([u(\mathbf{r}''')+\phi(\mathbf{r}''',\tau''')\Big]\Big\}. \tag{3.8}$$

This is a time-dependent generalization of Chandler's result, Eq.(2.7), in Ref.6.

Using the partition function as a generating function, the correlation function of the charge density for the solution can be obtained by differentiating the partition function twice with respect to the auxiliary field $\phi(\mathbf{r},\tau)^{6,10}$. We then have

$$C^m(\mathbf{r},\mathbf{r}',\tau-\tau')=C(\mathbf{r},\mathbf{r}',\tau-\tau')-$$

$$\int_0^{\beta\hbar}\frac{d\tau''}{\beta\hbar}\int_0^{\beta\hbar}\frac{d\tau'''}{\beta\hbar}\iint_{\text{in}} d\mathbf{r}''d\mathbf{r}'''$$

$$C(\mathbf{r},\mathbf{r}'',\tau-\tau'')C_{\text{in}}^{-1}(\mathbf{r}'',\mathbf{r}''',\tau''-\tau''')C(\mathbf{r}''',\mathbf{r}',\tau'''-\tau'). \tag{3.9}$$

The corresponding relation in real-time is found through the following procedure. First transforming the imaginary time form to Fourier space

$$C^m(\mathbf{r},\mathbf{r}',\omega_n)=C(\mathbf{r},\mathbf{r}',\omega_n)-$$

$$\iint_{\text{in}} d\mathbf{r}''d\mathbf{r}'''C(\mathbf{r},\mathbf{r}'',\omega_n)C_{\text{in}}^{-1}(\mathbf{r}'',\mathbf{r}''',\omega_n)C(\mathbf{r}''',\mathbf{r}',\omega_n), \tag{3.10a}$$

where $\omega_n = \frac{2\pi n}{\beta\hbar}$ is the usual Matsubara frequency. Then this function at discrete frequency points is analytically continued to the entire complex plane of the frequency

$$C^m(\mathbf{r},\mathbf{r}',s)=C(\mathbf{r},\mathbf{r}',s)-$$

$$\iint_{\text{in}} d\mathbf{r}''d\mathbf{r}'''C(\mathbf{r},\mathbf{r}'',s)C_{\text{in}}^{-1}(\mathbf{r}'',\mathbf{r}''',s)C(\mathbf{r}''',\mathbf{r}',s) \tag{3.10b}$$

where s is the complex variable. Finally the correlation function in the complex plane is inverted by using the Laplace transformation to yield the real-time correlation function[10,11].

Equation (3.10b) is our fundamental result relating the correlation function in the solution to the correlation function of the pure solvent. Thus, if the dielectric response function is known for the pure solvent then the dielectric response function for the solution, which in general will not be uniform and isotropic, can be calculated from the above equation. One noteworthy point about this relation is that it is not dependent upon the non-hard-sphere interaction part $u(\mathbf{r})$. This consequence is due to the Gaussian assumption of the present model. An improvement could be made by treating the $u(\mathbf{r})$ part as a perturbation of the hard-sphere solution, the latter treated as the zeroth-order solution. In the next section a simple model calculation is used to illustrate how the nonuniformity around the solute can affect the solvation dynamics.

IV CALCULATIONS AND RESULTS

In this section a simple model correlation function for the pure solvent is used to illustrate the application of the Gaussian field model in solvation dynamics. For the pure solvent the charge density susceptibility can be approximated as[5]

$$\chi(\mathbf{r}, s) = -\beta S_{\nu\nu}(r) \frac{1}{1 + s\tau(r)} \tag{4.1}$$

where $S_{\nu\nu}(r)$ is the charge density correlation function at $t = 0$ and $\tau(r)$ is the r-dependent longitudinal relaxation time of the pure solvent. This type of separation in k-space is a standard approximation to obtain the charge density susceptibility[5,15], but here the approximation used is a separation in r-space. The charge density correlation function corresponding to the above charge density susceptibility is

$$C(\mathbf{r},s) = S_{\nu\nu}(r)\frac{\tau(r)}{1+s\tau(r)}. \tag{4.2}$$

The time-dependent solvation free energy with the "uniform dielectric approximation" in this case is

$$F(t) = -\frac{1}{2}\beta \iint d\mathbf{r}d\mathbf{r}' S_{\nu\nu}(|\mathbf{r}-\mathbf{r}'|)\{1 - e^{-\frac{t}{\tau(|\mathbf{r}-\mathbf{r}'|)}}\}\Delta\varphi(\mathbf{r})\Delta\varphi(\mathbf{r}') \tag{4.3}$$

where Eqs.(4.1) and (2.18) have been used. This equation is the one that would be used for the calculation of the time-dependent solvation free energy under the "uniform dielectric approximation."

Let $\Delta F^m(t)$ denote the difference between the uniform dielectric approximation solvation free energy and the modification due to the present theory. Then, the Laplace transform of the solvation free energy difference can be written as

$$\Delta\tilde{F}^m(s) = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}' \iint_{\text{in}} d\mathbf{r}''d\mathbf{r}''' \frac{S_{\nu\nu}(|\mathbf{r}-\mathbf{r}''|)S_{\nu\nu}(|\mathbf{r}'''-\mathbf{r}'|)}{S_{\nu\nu}(|\mathbf{r}''-\mathbf{r}'''|)}$$

$$\left\{\frac{\tau(|\mathbf{r}-\mathbf{r}''|)\tau(|\mathbf{r}'''-\mathbf{r}'|)(1+s\tau(|\mathbf{r}''-\mathbf{r}'''|)}{\tau(|\mathbf{r}''-\mathbf{r}'''|)(1+s\tau(|\mathbf{r}-\mathbf{r}''|))(1+s\tau(|\mathbf{r}'''-\mathbf{r}'|)} - \frac{1}{s}\right\}\Delta\varphi(\mathbf{r})\Delta\varphi(\mathbf{r}') \tag{4.4}$$

where the Eqs.(2.10),(2.18), (3.10) and (4.2) have been used. Inverting the Laplace transform, the time-dependent solvation free energy change is

$$\Delta F^m(t) = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}' \iint_{\text{in}} d\mathbf{r}''d\mathbf{r}''' \frac{S_{\nu\nu}(|\mathbf{r}-\mathbf{r}''|)S_{\nu\nu}(|\mathbf{r}'''-\mathbf{r}'|)}{S_{\nu\nu}(|\mathbf{r}''-\mathbf{r}'''|)}\Delta\varphi(\mathbf{r})\Delta\varphi(\mathbf{r}')$$

$$\left\{\frac{1/\tau(|\mathbf{r}-\mathbf{r}''|) - 1/\tau(|\mathbf{r}''-\mathbf{r}'''|)}{1/\tau(|\mathbf{r}-\mathbf{r}''|) - 1/\tau(|\mathbf{r}'''-\mathbf{r}'|)}e^{-\frac{t}{\tau(|\mathbf{r}-\mathbf{r}''|)}}\right.$$

$$\left. - \frac{1/\tau(|\mathbf{r}'''-\mathbf{r}'|) - 1/\tau(|\mathbf{r}''-\mathbf{r}'''|)}{1/\tau(|\mathbf{r}-\mathbf{r}''|) - 1/\tau(|\mathbf{r}'''-\mathbf{r}'|)}e^{-\frac{t}{\tau(|\mathbf{r}'''-\mathbf{r}'|)}} - 1\right\}. \tag{4.5}$$

This ormula is the one that we would use for the time-dependent solvation free energy correction due to the nonuniformity in the vicinity of the solute.

For a hard-dipolar model of pure solvent the charge correlation function at time zero $S_{\nu\nu}(r)$ can be crudely approximated as

$$S_{\nu\nu}(r) = e^{-a\left[\frac{r-\sigma}{\sigma}\right]^2}\theta(r-\sigma) \tag{4.6}$$

where σ is the diameter of the solvent molecules, $\theta(r-\sigma)$ ensures that there is no correlation when the distance between the solvent molecules is smaller than their diameter and a is a constant. The r-dependent relaxation time is more complicated. From the studies of collective orientational relaxation in dense dipolar liquids the relaxation time decreases as wavevector k increases[15]. Here a simple functional form for the r-dependent relaxation time is used to account for this trend, namely the relaxation time approaches the usual longitudinal relaxation time when $r \rightarrow \infty$ and the relaxation time becomes larger as $r \rightarrow 0$

$$\tau(r) = \frac{\tau_L}{(1 - be^{-(r/\sigma-1)^2})} \tag{4.7}$$

where τ_L is the longitudinal relaxation time and b is a constant. The region occupied by the solute is taken to be a sphere of radius R_c and the potential difference $\Delta\varphi^0(\mathbf{r})$ is taken as due to a dipole change in the solute from zero to unit dipole. Then, the electrostatic potential change is

$$\Delta\varphi^0(\mathbf{r}) = -\frac{\hat{z}\cdot\hat{\mathbf{r}}}{r^3}. \tag{4.8}$$

The ratio between the diameter of a solvent molecule and the solute radius R_c is taken as 0.2. The result of the calculation is shown in Figure 1 with a=0.04 and b=0.8. It is clear from the figure that the nonuniform dielectric medium retards the solvation relaxation considerably. It is in agreement with Onsager's "inverted snowball" picture, which states that the relaxation in the remote media from the solute is faster than the closer region. Other ratios between the solvent molecules diameter and the solute R_c give similar pronounced slow relaxation if the uniform dielectric approximation is not used. This result may be the first time that the effect of the nonuniform solvent around the solute on the solvation relaxation is accounted for dynamically in a somewhat quantitative manner. It will be interesting to see how large this effect will be for more realistic solvent dielectric response functions.

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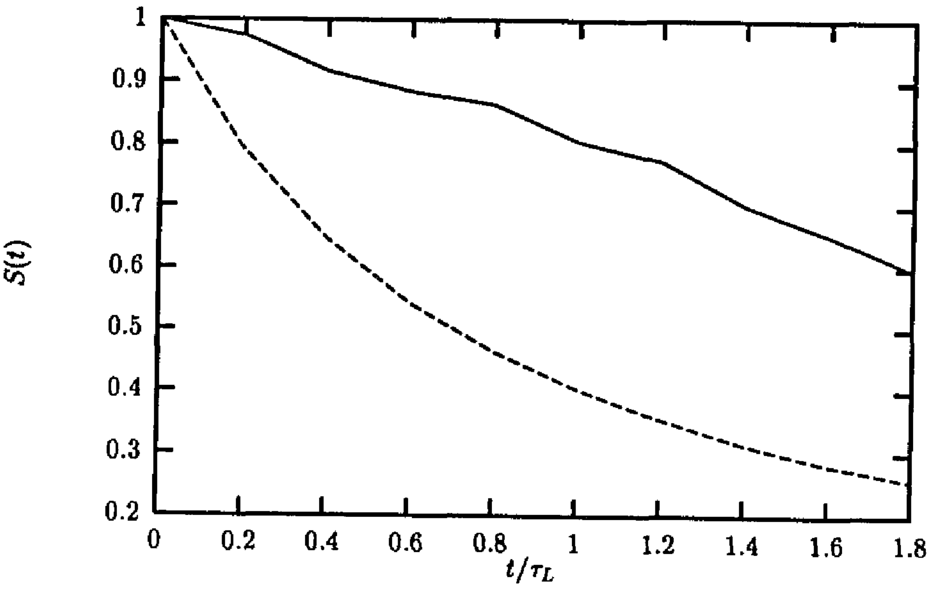

Caption for Figure

Solvation correlation function as a function of t/τ_L. Solid line: uniform dielectric approximation. Dashed line: present result.