Effects of bath relaxation on dissipative two-state dynamics

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A formal solution to the two-state Liouville equations is used to derive quantum equations of motion for dissipative two-state systems without making the assumption of a harmonic bath. The first-order equation of motion thus obtained is equivalent to the noninteracting blip approximation and can be systematically improved by introducing high-order cumulants. The second-order equation of motion incorporates effects of bath relaxation on two-state dynamics and leads to an effective nonadiabatic rate expression, which in the classical limit reduces to the well-known electron transfer rate formula. Numerical results with an Ohmic bath show saturation at large coupling constants due to the rate-limiting effect of relatively slow bath relaxation, and a comparison with classical calculations demonstrates larger rate constants at low temperature when quantum coherence is taken into account. © *2000 American Institute of Physics.* [S0021-9606(00)50515-7]

I. INTRODUCTION

A typical quantum tunneling system exhibits transitions between well-defined quantum states that are coupled to a heat bath. Such a dissipative two-state model captures the basic physics of varieties of condensed phase quantum processes, most notably electron transfer, energy transfer, and quantum Brownian motion at low temperature, and electron tunneling in amorphous materials.[1–3] For an incoherent tunneling system, its transition rate is determined primarily by quantum and thermal fluctuations of the relative energy difference between the states, i.e., energy dephasing. Thus, to first order, dissipative two-state systems can be well described by master equations derived from the Redfield theory[4,5] or from the noninteraction blip approximation.[6,7] Often, these derivations are limited to effective harmonic baths and relatively small coupling constants. General expressions for the rate constant have been derived by means of the projection method or cumulant expansion, and higher order corrections of various forms have been obtained and compared.[8–11]

In this paper, we present a novel approach to derive first-order and second-order quantum master equations, which do not invoke the harmonic assumption and which can be systematically generalized to higher orders. The second-order equation of motion can be interpreted as the influence of bath relaxation on two-state tunneling dynamics. Because of the finite response time of the bath, transitions between the two states perturb the equilibrium distribution; hence, the effective transition rate is reduced by the relaxation time for the bath to restore equilibrium. For a classical bath, several authors have analyzed the effect of dynamic friction on outer-sphere electron transfer in polar solvents.[1,12,13] Zusman predicted the saturation for the electron transfer rate at large electronic coupling constants;[14] Sumi and Marcus extended the Agmon-Hopfield model to electron transfer;[15] Hynes applied the stable state picture to model solvent diffusion effects;[16] and Sparpaglione and Mukamel used the projection technique to derive rate expressions for quantum and classical solvents.[8] This paper focuses on master equations and rate expressions for a quantum bath and establishes a relation between classical and quantum rate constants.

Master equations for dissipative two-level systems have attracted the attention of theorists. Several derivations are particularly relevant in the current context. Formally, the projection operator technique can be used to formulate master equations accurate to all orders.[8,17–19] For a general electron transfer system, Hu and Mukamel derived the master equation formalism applicable to long-range transfer systems and studied the issue of coherent versus sequential transfer. Because of the generality of the projector operator technique, these formalisms are not limited to harmonic baths or the small coupling regime.[17] Cumulant expansion of the Liouville operator provides another general way to obtain master equations, which was employed by Skinner and coworkers in their study of non-Markovian effects in electronic dephasing.[9,20] Coalson and Evans also started from the Liouville equation and obtained first-order equations of motion.[21] The expressions derived from our approach are equivalent to those derived from the projection operator technique or from a general cumulant expansion method. Besides being a different way to derive master equations, the approach presented here explicitly expands the reduced Liouville equation term by term, thus clarifying the approximation involved in the master equation, and allowing for possible analysis of higher-order corrections. This study is also motivated by our efforts to describe electron transfer beyond the nonadiabatic limit.

Recently, we have developed a general approach to describe condensed phase dynamics: the spectral analysis method, which is based on eigen-structures of dissipative systems instead of dynamic trajectories.[22] When applied to electron transfer in Debye solvents, the analysis allows us to characterize multiple time scales in electron transfer processes, including solvent relaxation, electronic coherence,

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activated curve crossing or barrier crossing. In this approach, the first nonzero eigen value of the kinetic spectrum can be identified as the electron transfer rate. The rate constant thus obtained agrees with the diffusion-limited nonadiabatic rate expression in the weak electronic coupling limit, but demonstrates large deviations from the previous theory as the electronic coupling constant increases to the adiabatic regime. The discrepancy with theoretical predictions becomes particularly important in the inverted regime,[23] which has been extensively explored in recent experiments on long-range electron transfer in biological systems. Therefore, it is necessary to further examine relaxation effects on dissipative two-state dynamics when the solvent is treated fully quantum mechanically.

II. QUANTUM MASTER EQUATIONS

A two-state system coupled to its low-frequency bath is described by

$$H = H_1(q)|1\rangle\langle 1| + H_2(q)|2\rangle\langle 2| + V(|1\rangle\langle 2| + |1\rangle\langle 2|), \tag{1}$$

where H_1 and H_2 are the hamiltonians of the two states, respectively, and V is the coupling constant between the two states. The evolution of this system bath, Hamiltonian obeys the two-state Liouville equations,

$$\dot{\rho}_{12}(t) = -i\mathcal{L}_{12}\rho_{12} + iV(\rho_1 - \rho_2), \tag{2a}$$

$$\dot{\rho}_1(t) = -i\mathcal{L}_1\rho_1 + iV(\rho_{12} - \rho_{21}), \tag{2b}$$

$$\dot{\rho}_2(t) = -i\mathcal{L}_2\rho_2 - iV(\rho_{12} - \rho_{21}), \tag{2c}$$

where the Liouville operators are defined as $\mathcal{L}_1 A = [H_1, A]$, $\mathcal{L}_2 A = [H_2, A]$, $\mathcal{L}_{12} A = H_1 A - A H_2$, and the off-diagonal matrix elements satisfy $\rho_{12} = \rho_{21}^*$. The Planck constant $\hbar$ is omitted here and hereafter for simplicity of notation. The off-diagonal matrix element ρ_{12} in Eq. (2a) can be integrated to yield

$$\rho_{12}(t) = i\int_0^t e^{-i\mathcal{L}_{12}\tau} V[\rho_1(\tau) - \rho_2(\tau)]d\tau, \tag{3}$$

where $\rho_{12}(0) = 0$ is assumed. Substituting the solution for ρ_{12} into the Liouville equations for ρ_1 and ρ_2 leads to

$$\dot{\rho}_1(t) = -i\mathcal{L}_1\rho_1(t) - \int_0^t \mathcal{W}(t-t')[\rho_1(t') - \rho_2(t')]dt', \tag{4a}$$

$$\dot{\rho}_2(t) = -i\mathcal{L}_2\rho_2(t) - \int_0^t \mathcal{W}(t-t')[\rho_2(t') - \rho_1(t')]dt', \tag{4b}$$

with $\mathcal{W}(\tau) = V^2(e^{-i\mathcal{L}_{12}\tau} + e^{-i\mathcal{L}_{21}\tau})$ denoting the coherent propagator. Now we invoke the approximation that the density matrix elements $\rho_1(t)$ and $\rho_2(t)$ can be factorized as $\rho_1(t) = P_1(t)\rho_{b1}$ and $\rho_2(t) = P_2(t)\rho_{b2}$, respectively, where $P_1(t)$ and $P_2(t)$ are the populations in state 1 and 2, and where $\rho_{b1} \propto e^{-\beta H_1}$ and $\rho_{b2} \propto e^{-\beta H_2}$ are the equilibrium bath distributions associated with each state. Then, averaging over the equilibrium bath distribution, we arrive at the reduced equations of motion for the two-state system

$$\dot{P}_1(t) = -\int_0^t K_1(t-t')P_1(t')dt'$$

$$+ \int_0^t K_2(t-t')P_2(t')dt', \tag{5a}$$

$$\dot{P}_2(t) = -\int_0^t K_2(t-t')P_2(t')dt'$$

$$+ \int_0^t K_1(t-t')P_1(t')dt', \tag{5b}$$

which are accurate to linear order in V^2. The rate kernels are defined as

$$K_\mu(\tau) = \langle \mathcal{W} \rangle_\mu = 2V^2 \mathcal{R}\mathrm{Tr}(e^{-i\mathcal{L}_{21}\tau}\rho b_\mu)$$

$$= 2V^2 \mathcal{R}\mathrm{Tr}[e^{-i\int_0^\tau \delta H_\mu(t')dt'}\rho b_\mu], \tag{6}$$

where $\mu = 1$ and $\mu = 2$ denote the forward and backward transitions, respectively, and $\delta H(t)$ is the interaction representation of the hamiltonian difference between the two states, i.e., $\delta H_1(t) = e^{iH_1 t}(H_2 - H_1)e^{-iH_1 t}$ and $\delta H_2(t) = e^{iH_2 t}(H_1 - H_2)e^{-iH_2 t}$. Evidently, the forward and backward rate kernels are the same quantum operator evaluated with respect to different equilibrium bath distributions.

The approach developed above is simple and robust: In a similar fashion, substituting the solutions for ρ_1 and ρ_2 into Eq. (2a) results in master equations for describing dephasing. In addition, functional forms for the coupling can be introduced to better approximate many physical systems, and nonequilibrium bath configurations can be easily incorporated to reflect realistic conditions in ultrafast experiments. In particular, when time dependence is incorporated into electronic coupling, the formalism can be used to describe photoinduced electronic transition, thus leading to applications in condensed phase spectroscopy[24] and quantum coherence control.[25] Furthermore, our approach can be generalized to multiple states for studying electronic energy transfer[2] and long-range electron transfer.[26]

To examine the nature of the approximations involved in the derivation of Eqs. (5a) and (5b), we first rewrite the Liouville equation in Eqs. (4a) and (4b) as

$$\rho(t) = U(t)\rho(0) - \int_0^t \int_0^{t_1} U(t-t_1)W(t_1-t_1')\rho(t_1')dt_1 dt_1', \tag{7}$$

where the population vector is $\rho = [\rho_1, \rho_2]$, the population matrix operator is $U_{\mu\nu}(\tau) = \delta_{\mu\nu}e^{-i\mathcal{L}_\mu\tau}$ and the coherence matrix operator is $W_{\mu\nu}(\tau) = (2\delta_{\mu\nu} - 1)\mathcal{W}(\tau)$. Formally, Eq. (7) can be cast into a more compact form, $\rho = U\rho(0) - UW\rho$, so that the formal solution becomes

$$\rho(t) = (U - UWU + UWUWU - UWUWUWU$$

$$+ \cdots)\rho(0), \tag{8}$$

where each matrix multiplication is implicitly associated with a time integration, each W factor represents a coherence interval or a tunneling event, and each U factor represents a

bath relaxation interval which has no effect on an equilibrium bath. Taking the bath average of Eq. (8), we obtain a formally exact expression for the two-state population,

$$P(t) = (I - \langle W \rangle + \langle WUW \rangle - \langle WUWUW \rangle + \cdots)P(0),$$
(9)

where thermal equilibrium is assumed for the bath at the initial time. To first order in V^2, we can take the bath average of each factor in Eq. (9) independently, i.e., $\langle U \rangle = I$ and

$$\langle W \rangle = K = \begin{pmatrix} K_1 & -K_2 \\ -K_1 & K_2 \end{pmatrix},$$
(10)

such that

$$P(t) \approx (I - K + KK - KKK + \cdots)P(0)$$

$$= P(0) - \int_0^t dt_1 \int_0^{t_1} dt_1' K(t_1 - t_1')P(t_1'),$$
(11)

which is exactly the same as Eqs. (5a) and (5b). It is evident from the above analysis that the first-order equation of motion contains contributions from individual transition events but ignores correlations between different transition events. Therefore, the two-state dynamics described by Eq. (11) arises solely from dephasing and is accurate only if the coupling V^2 is small or the bath correlation time is short.[4,5,27–30,10,11]

To incorporate the next order correction (V^4), we define the second-order cumulant

$$F(\tau_1, \xi, \tau_2) = \overbrace{\langle W(\tau_1)W(\tau_2) \rangle}^{\xi} = \langle W(\tau_1)U(\xi)W(\tau_2) \rangle$$

$$- \langle W(\tau_1) \rangle \langle W(\tau_2) \rangle,$$
(12)

which describes the correlation between two neighboring coherence intervals τ_1 and τ_2 separated by a relaxation interval ξ. The contribution from the linear term is subtracted to isolate the correlation effect. With this definition, the third term in Eq. (9) becomes

$$\langle W(\tau_1)U(\xi)W(\tau_2) \rangle$$

$$= \langle W(\tau_1) \rangle \langle W(\tau_2) \rangle + \overbrace{\langle W(\tau_1)W(\tau_2) \rangle}^{\xi},$$
(13)

and the forth term in Eq. (9) becomes

$$\langle W(\tau_1)U(\xi_1)W(\tau_2)U(\xi_2)W(\tau_3) \rangle$$

$$= \langle W(\tau_1) \rangle \langle W(\tau_2) \rangle \langle W(\tau_3) \rangle + \overbrace{\langle W(\tau_1)W(\tau_2) \rangle}^{\xi_1}$$

$$\times \langle W(\tau_3) \rangle + \langle W(\tau_1) \rangle \overbrace{\langle W(\tau_2)W(\tau_3) \rangle}^{\xi_2} + \cdots,$$
(14)

where the terms represented by the dots include the correlation between the τ_1 and τ_3 coherence intervals and the cor-

relation of all three coherence intervals. We can, in principle, examine higher-order expansion terms in Eq. (9) in this fashion and evaluate only the terms corresponding to the dephasing of individual coherence intervals and the correlation between neighboring coherence intervals. All these terms can be resumed to give the second-order equation of motion for the two-state system

$$P(t) \approx P(0) - \langle W \rangle P + \overbrace{\langle WW \rangle}^{\xi} P$$

$$= P(0) - \int_0^t dt_1 \int_0^{t_1} dt_1' K(t_1 - t_1') \rho(t_1') P(t_1')$$

$$+ \int_0^t dt_1 \int_0^{t_1} dt_1' \int_0^{t_1'} dt_2 \int_0^{t_2} dt_2' F[(t_1 - t_1'), (t_1' - t_2),$$

$$(t_2 - t_2')]P(t_2'),$$
(15)

which reduces to Eq. (11) when $F = 0$. Equation (15) is the central result of this paper and can by systematically improved by incorporating higher-order cumulants.

The second-order forward rate kernel in Eq. (12) contains two terms,

$$F_1 = \sum_\mu \langle \mathcal{W}U_\mu \mathcal{W} \rangle_1 - \langle \mathcal{W} \rangle_\mu \langle \mathcal{W} \rangle_1 = \sum_\mu (F_{\mu,1}' - K_\mu K_1),$$
(16)

where the second-order moments are

$$F_{1,1}' = \langle \mathcal{W}(\tau_1)U_1(\xi)\mathcal{W}(\tau_2) \rangle_1$$

$$= 2\mathcal{R}f(\tau_1, \xi, \tau_2) + 2\mathcal{R}f(-\tau_1, \xi + \tau_1, \tau_2),$$
(17a)

$$F_{2,1}' = \langle \mathcal{W}(\tau_1)U_2(\xi)\mathcal{W}(\tau_2) \rangle_1$$

$$= 2\mathcal{R}f(-\xi, -\tau_1, \tau_1 + \xi + \tau_2)$$

$$+ 2\mathcal{R}f(-\xi - \tau_1, \tau_1, \xi + \tau_2),$$
(17b)

with the generic function f given explicitly by

$$f(\tau_1, \xi, \tau_2) = V^4 \mathrm{Tr} e^{-i\mathcal{L}_{21}\tau_1} e^{-i\mathcal{L}_1 \xi} e^{-i\mathcal{L}_{21}\tau_2} \rho_{b_1}$$

$$= V^4 \mathrm{Tr}[e^{-i\int_{\tau_2 + \xi}^{\tau_2 + \xi + \tau_1} \delta H_1(t')dt'} e^{-i\int_0^{\tau_2} \delta H_1(t')dt'} \rho_{b_1}].$$
(18)

In Eq. (16), $F_{1,1}'$ describes two consecutive forward transition events, and $F_{2,1}'$ describes a forward transition event followed by a backward transition event. If the bath relaxes instantaneously to the change in electronic population, the two transition events are independent with joint rare $K_\mu K_1$. Therefore, F in Eq. (16), which is the difference between $F_{\mu,1}'$ and $K_\mu K_1$, represents the correlation effect of the finite relaxation time on two-state dynamics.

In the asymptotic limit, Eq. (11) defines the first order rate constant $k_\mu^{(1)} = \int_0^\infty K_\mu(\tau)d\tau$, which is essentially the golden-rule nonadiabatic rate expression, and Eq. (15) defines the second-order rate constant $k_\mu^{(2)} = \int_0^\infty d\tau_1 \int_0^\infty d\xi \int_0^\infty d\tau_2 F_\mu(\tau_1, \xi, \tau_2) d\tau_1 d\xi d\tau_2$, which is the

leading order correction due to bath relaxation. Thus, the effective nonadiabatic rate constant can be expressed as

$$k_{\text{eff}} = k^{(1)} - k^{(2)} + \cdots \approx \frac{k^{(1)}}{1 + k^{(2)}/k^{(1)}}, \qquad (19)$$

where the second-order correlation is extended to a nonperturbative rate expression. The higher-order terms extrapolated from the second-order correction can be interpreted as correlations among three or more transition events. For large coupling constants, Eq. (19) predicts saturation due to the rate-limiting effect of bath relaxation on nonadiabatic transitions and therefore fails to describe the crossover from nonadiabatic transfer to adiabatic transfer.[31,32,22]

III. SPECIAL CASE: SPIN-BOSON MODEL

The above formulation is general and makes no assumptions about the functional form of H_1 and H_2. In order to evaluate the rate constant, we now specialize to the spin-boson Hamiltonian,

$$H = V\sigma_x - \frac{\epsilon}{2}\sigma_z + \sum_n \frac{1}{2} m_n \omega_n^2 \left(x - \frac{c_n}{m_n \omega_n^2} \sigma_z \right)^2, \qquad (20)$$

where σ_z and σ_x are the Pauli matrices and ϵ is the energy bias between the two states. The effect of the bath on the two-state system is contained in the spectral density $J(\omega) = \pi/2 \Sigma_n \delta(\omega - \omega_n) c_n^2 / m_n \omega_n$. Applying Eq. (6) to the spin-boson Hamiltonian yields

$$K_\mu(\tau) = \sum_{\pm\tau} V^2 \exp{-i[g(\tau) \pm \epsilon\tau]}, \qquad (21)$$

where the phase-correlation function is defined by

$$g(t) = \frac{4}{\pi} \int \frac{J}{\omega^2} \{ [1 - \cos(\omega t)] \coth(\beta\omega\hbar/2)$$
$$+ i \sin(\omega t) \} d\omega, \qquad (22)$$

which also appears in Mukamel's formulation of condensed phase spectroscopy.[24] In Eq. (21) and thereafter, the plus sign is for the forward transition process with $\mu = 1$ and the minus sign is for the backward transition process with $\mu = 2$. In the asymptotic limit, we recover the golden-rule rate,[33] which satisfies the detailed balance condition $k_1/k_2 = \exp(-\beta\epsilon)$. The first order equation of motion in Eq. (15) with $K(\tau)$ given above is exactly the same result as obtained from the noninteracting blip approximation (NIBA) using path integral analysis. The simple procedure employed in deriving Eqs. (5a) and (5b) takes the bath averaging on the level of the Liouville equations and thus avoids the double-path summation in the influence functional representation.[34,6,7]

Further, for the spin-boson model the complex function in Eq. (18) becomes

$$f(\tau_1, \xi, \tau_2) = V^4 \exp[-i(\tau_1 + \tau_2)\epsilon - g(\tau_1) - g(\tau_2)$$
$$- g(\tau_1 + \tau_2 + \xi) - g(\xi) + g(\tau_1 + \xi)$$
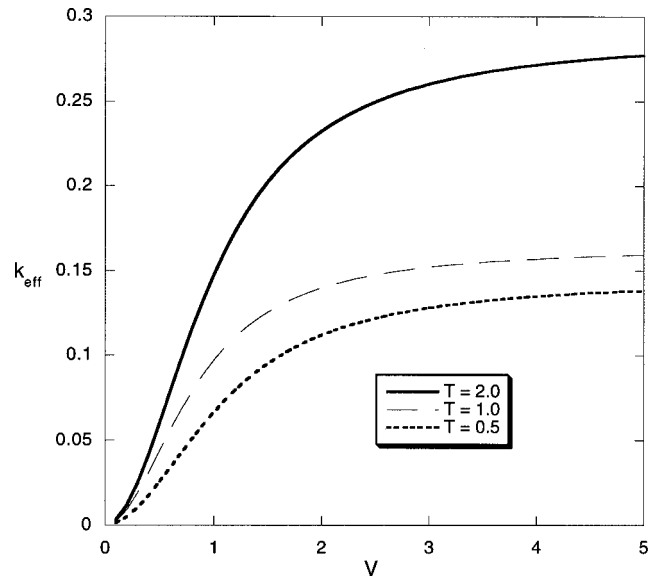$$+ g(\tau_2 + \xi)], \qquad (23)$$

FIG. 1. Plot of the effective quantum rate constant k_{eff} as a function of the coupling constant V for three different temperatures, $k_B T/\hbar\omega_c = 2$ (dotted curve), $k_B T/\hbar\omega_c = 1$ (dash curve), and $k_B T/\hbar\omega_c = 0.5$ (solid curve). An Ohmic bath, $J(\omega) = \eta\omega \exp(-\omega/\omega_c)$, is used in the spin-boson model with the friction strength η chosen to give $\lambda = 5\hbar\omega_c$. In the figure, all the physical quantities are scaled by the cutoff frequency $\omega_c : k_B T/\hbar\omega_c$, k_{eff}/ω_c, and $V/\hbar\omega_c$.

from which the second-order cumulant in Eq. (16) and thus the effective rate in Eq. (19) can be evaluated accordingly. The second-order equation of motion with f given in Eq. (23) can also be derived using path integral analysis.[35] It should be noted that the influence functional method is limited to harmonic baths and hence is not as general as Eq. (15).

To gain insights of the physical meaning of the second-order correction, we explicitly evaluate the rate constant in the classical limit. The leading term of the phase correlation function $g(t)$ is quadratic $g(t) = \lambda\tau^2/\beta + i\tau$ so that the golden-rule rate can be obtained from a Gaussian integral,
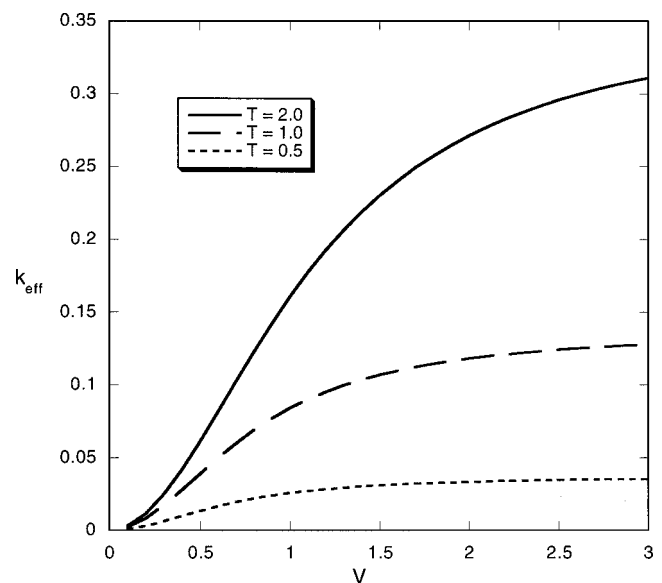

FIG. 2. Plot of the effective classical rate constant k_{eff} for the same set of parameters as in Fig. 1.

$$k_\mu^{(1)} = V^2 \int_{-\infty}^{\infty} \exp[-i(\lambda \pm \epsilon)\tau - \lambda \tau^2/\beta] d\tau$$

$$= 2\pi V^2 \sqrt{\frac{\beta}{4\pi\lambda}} \exp\left[-\beta \frac{(\lambda \pm \epsilon)^2}{4\lambda}\right], \tag{24}$$

which is the product of the transition coefficient $2\pi V^2$ and the equilibrium probability at the transition state. The Gaussian distribution of τ limits the length of the coherence interval to a short period of time so that τ in Eqs. (17a) and (17b) can be expanded to quadratic order, giving

$$F'_{1,1}(\tau_1, \xi, \tau_2) \approx \sum_{\pm\tau_1, \pm\tau_2} V^4 \exp\{-i(\tau_1 + \tau_2)(\epsilon + \lambda)$$
$$-(\lambda/\beta)[\tau_1^2 + \tau_2^2 + 2\tau_1\tau_2 C(\xi)]\} \tag{25a}$$

and

$$F'_{2,1}(\tau_1, \xi, \tau_2) \approx \sum_{\pm\tau_1, \pm\tau_2} V^4 \exp\{-i\tau_1(\epsilon + \lambda)$$
$$-i\tau_2[\epsilon - \lambda + 2\lambda C(\xi)] - (\lambda/\beta)$$
$$\times [\tau_1^2 + \tau_2^2 + 2\tau_1\tau_2 C(\xi)]\}. \tag{25b}$$

Here, $g''(t) \approx 2\lambda(t)/\beta$ and $g'(-t) + g'(t) = i2\lambda(t)$ are used, $\lambda = (4/\pi)\int J(\omega)/\omega d\omega$ is the reorganization energy in the context of electron transfer, $\lambda(t) = (4/\pi)\int J(\omega)/\omega \cos(\omega t) d\omega$ is the time-dependent reorganization energy with $\lambda(0) = \lambda$, and $C(t) = \lambda(t)/\lambda$ characterizes the bath relaxation of the bath. Completing the time integration, we have the second-order rate, $k^{(2)} = k^{(1)}(\kappa_1 + \kappa_2)$, and the correction factor due to bath relaxation

$$\kappa_\mu = 2\pi V^2 \int_0^{\infty} d\xi[G_\mu(\xi) - G_\mu(\infty)], \tag{26}$$

where $G(t)$ is the survival probability at the transition state

$$G_\mu(\xi) = \sqrt{\frac{\beta}{4\pi\lambda[1 - C^2(\xi)]}}$$
$$\times \exp\left[-\frac{\beta}{4\lambda} \frac{1 - C(\xi)}{1 + C(\xi)}(\lambda \pm \epsilon)^2\right]. \tag{27}$$

From Eq. (19), we have

$$k_{\text{eff}} = \frac{k^{(1)}}{1 + \kappa_1 + \kappa_2}, \tag{28}$$

which reduces to the diffusion-limited nonadiabatic electron transfer rate derived earlier.[14–16,7,8,36,22]

As an example, we calculate the effective rate constant for a two-state system coupled to an Ohmic bath with $J(\omega) = \eta\omega \exp(-\omega/\omega_c)$. The friction strength η is fixed by $\lambda/\hbar\omega_c = 4\eta/\pi$ with $\lambda = 5\hbar\omega_c$. Here, the cutoff frequency ω_c is used to scale all the physical quantities: $k_B T/\hbar\omega_c$, k_{eff}/ω_c, and $V/\hbar\omega_c$. In Fig. 1, the effective quantum rate constant defined in Eq. (19) is evaluated for three different temperatures, $k_B T/\hbar\omega_c = 2$, $k_B T/\hbar\omega_c = 1$, and $k_B T/\hbar\omega_c = 0.5$. Except for small values of the coupling constant, the rate curve deviates significantly from the quadratic dependence on V and exhibits saturation at large coupling. For

comparison, in Fig. 2, the classical rate computed from Eq. (28) is plotted for the same set of parameters as in Fig. 1. Comparing Fig. 1 and Fig. 2, the effective quantum rate is consistently larger than the effective classical rate at low temperature. This observation is the consequence of quantum coherence in the bath motion.

IV. SUMMARY

In summary, the approach presented in this paper is based on a formal solution to the two-state Liouville equations under the condition of thermal equilibrium for the initial bath. This derivation makes no assumption about the functional form of the bath Hamiltonian and recovers the same first-order equation of motion as obtained from the non-interacting blip approximation. To second-order, we incorporate the role of bath relaxation in an effective nonadiabatic rate, which in the classical limit reduces to the electron transfer rate in dynamic solvents. Our theory is valid for both classical and quantum baths and therefore can be employed to examine dynamic effects of intramolecular quantum modes or phonons as well as dynamic effects of classical solvents. This subject is most relevant for long-range electron transfer and other charge transfer processes and will be further studied.

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