PHYSICAL REVIEW E, VOLUME 64, 061103

Dynamics of the spin-boson Hamiltonian by the projection operator technique: Applications to electron transfer reactions

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(Received 9 March 2001; revised 24 May 2001; published 20 November 2001)

A perturbative treatment developed by using the projection operator technique is provided to find dynamics of the spin-boson Hamiltonian in the second order approximation of the subsystem-bath interaction. In the framework of the generalized master equations and in the Markovian approximation it leads to the Redfield/Bloch-type equations. The treatment can be applied to both fast and slow bath cases; in this paper we consider the fast bath case. The relaxation times, energy splitting, and bath-induced renormalization effect of the coherence frequency are discussed and applied to a Lorentzian-Ohmic fast bath. A good agreement between our results and those obtained by the path-integral formalism is obtained. The treatment is applied to electron transfer reactions to test the possibility of apparition of the electronic coherence in certain photosynthetic reaction centers.

DOI: 10.1103/PhysRevE.64.061103 PACS number(s): 82.20.Rp, 31.70.Hq

I. INTRODUCTION

The description of the quantum dissipative dynamics of an open low-dimensional subsystem coupled to its environment (seen as a reservoir) by a Markovian theory has a wide variety of physical applications. Magnetic resonance, quantum optics and laser physics, condensed matter and condensed phase, and astrophysics are representative research areas where this treatment has been successfully used. The subsystem's dynamics has been described by several methods by using, for example, the time-dependent perturbation theory [1,2], susceptibility method [3], statistical operator method [4–8], or the path-integral formalism (PIF) [9–11].

Often the spin-boson Hamiltonian is chosen as a dissipative model to consider interaction between a subsystem, which is mapped onto a two-state system (TSS) and reservoir (thermal bath). Leggett *et al.* [11] and Weiss [10] exhaustively review the spin-boson problem in the PIF framework. The discrete path used by PIF to describe the two states of TSS often induces mathematical difficulties. Several different approaches have been reported on the dynamics of the spin-boson Hamiltonian. Earlier works, as those of Dekker [12] or Meyer and Ernst [13] focus on the weak subsystem-bath-coupling (weak-coupling) approaches. For example, by using the Heisenberg picture Dekker gives an implicit solution for the dynamics of the symmetric dissipative TSS and provides a solution concerning the influence of the bath on the coherence frequency (renormalized tunneling frequency) for the Ohmic dissipation case. Laird, Budimir and Skiner, [14] anticipating a secular Redfield-type equation for the spin-boson Hamiltonian dynamics, find a damped harmonic oscillator equation for the polarization vector. This anticipation as well as use of approximate relaxation times restrain the applicability of the treatment. In the same Redfield theory framework, Morillo, Denk, and Cukier [15] investigate the possibility of controlling tunneling with an external field in a four-level system and Jean, Friesner, and Fleming [16] consider a quantum-mechanical theory of photoinduced electron transfer. Neu and Rau [17] use the Robertson projection operator formalism and furnish a solution in the weak-coupling limit for a driven dissipative TSS. The transient regime is characterized by two relaxation times. The effect of the bath on the coherence frequency for the transient dynamics has not been taken into consideration. More recently, focusing on dissipation caused by the voltage source, Governale, Grifoni, and Schön [18] provide analytical and numerical results for the relaxation and dephasing rates in coupled qubits. The weak-coupling limit of the spin-boson Hamiltonian has been treated by PIF by the so-called noninteracting-blip approximation (NIBA) in Ref. [19] or beyond this approximation in Refs. [20], [21]. The projection operator technique is another successful formalism used to describe the spin-boson Hamiltonian dynamics; the NIBA equations have been obtained within this technique [22].

The aim of this paper is twofold. On the one hand, we provide a method to concretely describe the dynamics of the spin-boson Hamiltonian in the weak-coupling limit. On the other hand, the coherence decay in electron transfer reactions (ETR) is a well-known phenomenon, which appears in the case of electron transfer reactions when the bath is slow. The possibility of apparition of the electronic coherence for fast bath and weak-coupling limit is an interesting problem and it constitutes the second goal of this work. Technically, the dissipative TSS dynamics is found by using the generalized master equations (GME). They are obtained by projecting the statistical operator of the system onto the reduced TSS space [23–27]. The GME that we applied to the spin-boson Hamiltonian lead to certain Redfield/Bloch-type equations. A good agreement between our results and those obtained by PIF is obtained (the agreement between the Bloch/Redfield formalism and PIF is also reported in Ref. [28]).

The paper is structured as follows. In Sec. II, the perturbative treatment is introduced. Its capacity to recover some known results in the literature is examined. For the weak-coupling regime, we characterize the TSS decay and calculate the longitudinal and transversal relaxation times, T_1 and T_2, respectively, and the energy splitting, coherence frequency, and rate constant. Then, the treatment is considered in limits of the rotating wave approximation (RWA) and secular approximation (SA). The possibility of applying the perturbative treatment to the slow bath and apparition of dissipationless regime are the other two problems addressed in this part. In Sec. III, the results obtained in the precedent section are applied to a Lorentzian-Ohmic (LO) fast bath. The influence of the bath and of the temperature on the dynamics is discussed. In Sec. IV, the theoretical results obtained in the precedent sections are applied to test the presence of the electronic coherence in certain reaction centers (RC). Finally, conclusions are formulated.

II. DYNAMICS OF THE SPIN-BOSON HAMILTONIAN IN GME FORMALISM

We consider the usual hypothesis of the spin-boson Hamiltonian dynamics [11], that is, the interaction is switched on at the initial time $t=0$. At this moment the statistical operator of the system $\hat{\rho}(0)$, is written as a product between the statistical operator of the bath, $\hat{\rho}^b(0)$, and of subsystem, $\hat{\rho}^s(0)$. One assumes that the bath is all the time at equilibrium.

Let $\hat{H}$, $\hat{H}^s$, $\hat{H}^b$, and $\hat{H}^{\mathrm{sb}}$ be the Hamiltonian of the system, subsystem, bath, and of subsystem-bath interaction. Then $\hat{H}=\hat{H}^s+\hat{H}^b+\hat{H}^{\mathrm{sb}}$ and as an associated super operator Liouville form, $\mathbf{L}=\mathbf{L}^s+\mathbf{L}^b+\mathbf{L}^{\mathrm{sb}}$ with $\mathbf{L}=[\hat{H},]/\hbar$. (the brackets mean a commutator). In the second order approximation the Markovian GME, which constitutes the starting point of our derivation, reads (see details in Refs. [29,30])

$$\begin{aligned}\frac{d\hat{\rho}(t)}{dt}&=-i\mathbf{L}^s\hat{\rho}^s(t)\\&\quad-\int_0^\infty d\tau\langle\langle\mathbf{L}^{\mathrm{sb}}e^{-i\tau(L^s+L^b)}\mathbf{L}^{\mathrm{sb}}\rangle\rangle\exp(i\tau\mathbf{L}^s)\hat{\rho}^s(t)\\&=-i\mathbf{L}^s\hat{\rho}^s(t)-\Gamma\hat{\rho}^s(t),\end{aligned}\tag{1}$$

where $\langle\langle\mathbf{A}\rangle\rangle=\mathrm{Tr}_b[\mathbf{A}\hat{\rho}^b]$ represents a trace over the bath modes applied to superoperator $\mathbf{A}$ acting on $\hat{\rho}^b$ and Γ represents the damping superoperator. The spin-boson model is defined by the total Hamiltonian

$$\begin{aligned}\hat{H}=\frac{\varepsilon}{2}\hat{\sigma}_z-\frac{\hbar\Delta}{2}\hat{\sigma}_x+\sum_\alpha\left(\frac{\hat{p}_\alpha^2}{2m_\alpha}+\frac{m_\alpha\omega_\alpha^2\hat{x}_\alpha^2}{2}\right)\\+\frac{q_0}{2}\hat{\sigma}_z\sum_\alpha c_\alpha\hat{x}_\alpha.\end{aligned}\tag{2}$$

Mathematically, the system is constituted by TSS in interacting with a bath of harmonic oscillators representing the environment. The first two terms represent the TSS Hamiltonian, the third term represents the oscillators bath, and the fourth term represents their interaction. Responsible for the tunneling is the matrix element $\hbar\Delta$, which in many applications of the spin-boson model is of electronic type. In Eq. (2) we used the usual notation [11]. The bath's effect on dynamics is represented by the spectral density function $J(\omega)=\pi 2^{-1}\Sigma_\alpha c_\alpha^2(m_\alpha\omega_\alpha)^{-1}\delta(\omega-\omega_\alpha)$ for $\omega\geqslant 0$ and $J(\omega)=0$ for $\omega<0$. It has a superior cutoff frequency ω_c. For frequencies lower than ω_c and the Ohmic dissipation regime, $J(\omega)\propto\omega$. The strength of TSS-bath coupling is characterized by the dimensionless parameter $\alpha=\mu q_0^2/2\pi\hbar$. and μ is the classical measurable friction coefficient.

Many physical and chemical systems can be described by a reaction coordinate related to an effective potential energy function with two separated minima; in certain conditions they can be formulated in terms of the spin-boson Hamiltonian. For example, the ETR problem can be mapped on such a model (see, e.g., Refs. [31,32]). As we wish to apply the perturbative treatment in the fast bath limit to ETR, we shall consider a fast relaxation of the environment, i.e., a non-adiabatic reaction. This means a reaction where the electronic tunneling time is slow to respect to the bath relaxation or roughly $\Delta/\omega_c\ll 1$ [32,33].

By using the matrix Pauli algebra we denote by $|L\rangle$ and $|R\rangle$ the two-state vectors associated with the two states of TSS (obtained in absence of any coupling) as forming the localized basis set, so that $\hat{\sigma}_z=|L\rangle\langle L|-|R\rangle\langle R|$, $\hat{\sigma}_x=|L\rangle\langle R|+|R\rangle\langle L|$, with $\hat{\sigma}_z|L\rangle=|L\rangle$ and $\hat{\sigma}_z|R\rangle=-|R\rangle$. As we already mentioned, the two states are coupled by the tunneling Hamiltonian $(-\hbar\Delta/2)\hat{\sigma}_x$, which has real matrix elements in the $\{|L\rangle,|R\rangle\}$ basis set. We consider the "experimentalist representation," that is, the resonance framework, which introduces the stationary states of the system. Such a frame is involved when the relaxation times are to be experimentally determined. Thus, we transform Hamiltonian (2) by writing it in the basis set $\{|1\rangle,|2\rangle\}$, the so-called delocalized basis set, which diagonalizes the TSS Hamiltonian. In the language of the annihilation and creation operators, the transformed Hamiltonian reads

$$\begin{aligned}\hat{H}'=\sum_{i=1,2}\varepsilon_i'\hat{c}_i^\dagger\hat{c}_i+\sum_\alpha\hbar\omega_\alpha(\hat{b}_\alpha^\dagger\hat{b}_\alpha+\tfrac{1}{2})\\+\sum_{i,j=1,2}\sum_\alpha\hat{c}_i^\dagger\hat{c}_jV_{ij\alpha}(\hat{b}_\alpha+\hat{b}_\alpha^\dagger),\end{aligned}\tag{3}$$

where $\hat{\sigma}_{z'}\rightarrow\hat{c}_2^\dagger\hat{c}_2-\hat{c}_1^\dagger\hat{c}_1$, $\hat{\sigma}_{x'}\rightarrow\hat{c}_2^\dagger\hat{c}_1+\hat{c}_1^\dagger\hat{c}_2$, and $\hat{c}_1$ and $\hat{c}_2$ (the annihilation operators) obey the fermionic commutation rules (see, e.g., Ref. [34]) and the usual bosonic operators associated with the αth harmonic oscillator are introduced by

$$\hat{x}_\alpha=\sqrt{\hbar/(2m_\alpha\omega_\alpha)}(\hat{b}_\alpha^\dagger+\hat{b}_\alpha),\quad\hat{p}_\alpha=i\sqrt{\hbar m_\alpha\omega_\alpha/2}(\hat{b}_\alpha^\dagger-\hat{b}_\alpha).$$

Also,

$$\varepsilon_i'=(-1)^{i+1}(\hbar\Delta/2)\sqrt{1+r^2},$$

$$V_{11\alpha}=-V_{22\alpha}=q_0c_\alpha\sqrt{\hbar/(8m_\alpha\omega_\alpha)}\cos 2\theta,$$

$$V_{12\alpha}=V_{21\alpha}=-q_0c_\alpha\sqrt{\hbar/(8m_\alpha\omega_\alpha)}\sin 2\theta,$$

$$\cos 2\theta=r/\sqrt{1+r^2},\quad\sin 2\theta=-1/\sqrt{1+r^2},$$

$$\text{and} \quad r=\varepsilon/\hbar\Delta.$$

The energies are

$$E_1^{s'}=\hbar\Delta\sqrt{1+r^2}/2 \quad \text{for } |1\rangle,$$

$$E_2^{s'}=-\hbar\Delta\sqrt{1+r^2}/2 \quad \text{for } |2\rangle,$$

and

$$\omega_0=(E_1^{s'}-E_2^{s'})/\hbar=\Delta\sqrt{1+r^2}$$

is the natural frequency of the TSS coherence. This form (3) shows both phononic-intermediate interaction (for $i=j$) and direct interaction (phononic emission-absorption processes for $i\neq j$) between the levels of TSS [35(a)]. The first type of interaction causes fluctuations of the TSS's levels and the second changes the population of TSS.

Applied to $\hat{H}'$, Eq. (1) generates a certain Redfield GME [see Eq. (A1)]. The analytical solution of this equation is obtained by introducing the polarization vector $\mathbf{S}'(t)=\mathrm{Tr}[\hat{\rho}^{s'}(t)\hat{\sigma}']$ in the reference frame $ox'y'z'$ corresponding to the delocalized basis set

$$\begin{aligned}
\dot{S}_{x'}&=A_{11}S_{x'}+A_{12}S_{y'}+A_{13}S_{z'}+A_{10},\\
\dot{S}_{y'}&=A_{21}S_{x'}+A_{22}S_{y'}+A_{23}S_{z'}+A_{20},\\
\dot{S}_{z'}&=A_{31}S_{x'}+A_{33}S_{z'}+A_{30},
\end{aligned} \tag{4}$$

where the values of the A factors are given in the Appendix. The relation between the polarization's components in the two frames can be established, e.g., by using $\hat{\rho}^{s}(t)=\hat{U}\hat{\rho}^{s'}(t)\hat{U}^{\dagger}$, where $\hat{U}$ is the unitary operator used to diagonalize the TSS Hamiltonian [see Eq. (A4)]. Considering that at the initial moment TSS is in state $|L\rangle$, then $S_z(0)=1$, $S_x(0)=S_y(0)=0$ and with Eq. (A4) one obtains $S_{x'}(0)=1/\sqrt{1+r^2}$, $S_{y'}(0)=0$, and $S_{z'}(0)=r/\sqrt{1+r^2}$.

At this point the following remarks are necessary. At equilibrium, in the dissipative regime case TSS is found in a mixed state and the statistical operator is given by

$$\hat{\rho}^{s'(\mathrm{eq})}\to\frac{1}{2}\begin{pmatrix} 1+S_{z'}^{(\mathrm{eq})} & S_{x}^{(\mathrm{eq})}-iS_{y'}^{(\mathrm{eq})}\\ S_{x'}^{(\mathrm{eq})}+iS_{y'}^{(\mathrm{eq})} & 1-S_{z'}^{(\mathrm{eq})}\end{pmatrix},$$

where the superscript (eq) denotes the equilibrium state. One can observe that the asymptotic condition ($S_{x'}^{(\mathrm{eq})}=S_{y'}^{(\mathrm{eq})}=0$) requires that $A_{10},A_{20},A_{13},A_{23}$ must be disregarded in Eq. (4). Otherwise the equilibrium state would be a coherent one or in other words, TSS would situate in a dissipationless regime. Hence, for a right asymptotic behavior in the case of fast bath and dissipative regime, we have to impose that

$$A_{10}=A_{20}=A_{13}=A_{23}=0. \tag{5}$$

In case the bath relaxation is faster than $2\pi/\omega_0$ (that is, the fast bath case), then $a_{31}\approx -a_{32}$ and consequently, $A_{10}=A_{20}=0$ [see Eqs. (A5) and (A6)]. Thus, we conclude that, generally, A_{13} and A_{23} must be disregarded in Eq. (4). This requirement is imposed by the use of the approximate GME (1) as a starting point of the present treatment (a comprehensive discussion about the requirements of a right statistical operator can be found in Ref. [36]). As a prediction, the present second order treatment in non-Markovian limit suggests that in case of a slow bath, a dissipationless regime can be detected in the equilibrium state; mathematically, it is due to the presence of A_{10} and A_{20} in Eqs. (4). A confident answer concerning the dissipationless behavior (see a discussion of this regime in Ref. [37]) of a slow bath involves consideration of higher order approximations of GME, and we shall address this problem in a future work.

In the delocalized representation, the dynamics for the dissipative regime and fast bath predicted by Eq. (4) is found by the Laplace transform method. It is worth noting that an analytical solution can be obtained for the general case (we used MATHEMATICA3.0). From interesting features derived from its form (not presented here because of its length) we infer the following: (i) It predicts a biexponential decay; (ii) T_2^{-1} characterizes the coherence decay and it is present in $S_{x'}(t)$, $S_{y'}(t)$, and $S_{z'}(t)$ as well, it is associated with the diagonal transitions, where the number of phonon is not changed in the system; (iii) T_1^{-1} characterizes the population decay and it appears only in $S_{z'}(t)$, it is associated with the nondiagonal transitions, transitions between the TSS's levels occur by emission and absorption of phonons; (iv) Decay of $S_{z'}(t)$ has both coherent and incoherent components, which are damped by T_1^{-1} and T_2^{-1}, respectively. The features (ii) and (iii) reflect the resemblance of the Hamiltonian (3) with the small-polaron Hamiltonian [35(b)]. The same analysis allows calculation of the relaxation times and coherence frequency (see below). Thus, the two relaxation times calculated by us have the well-known form (see, e.g., Eq. (21.169) from Ref. [10])

$$\frac{1}{T_1}\equiv -A_{33}=-(W_{12}+W_{21})=\frac{\pi\alpha}{\mu(1+r^2)}\coth\left(\frac{\beta\hbar\omega_0}{2}\right)J(\omega_0), \tag{6a}$$

$$\frac{1}{T_2}\equiv -\frac{A_{11}+A_{22}}{2}=a_{33}=\frac{1}{2T_1}+\frac{1}{T_2'}, \tag{6b}$$

where

$$\frac{1}{T_2'}=\frac{2\alpha r^2}{\mu(1+r^2)}\coth\left(\frac{\beta\hbar\omega}{2}\right)J(\omega)\bigg|_{\omega\to 0}>0 \tag{6c}$$

is the so-called "pure dephasing rate constant." Thus, we recover the "spectroscopy law" [Eq. (6b)]. Additionally, Eq. (6c) predicts a positive pure dephasing rate constant as reported in experiments [38].

In the dissipative regime case, from Eq. (4) one obtains $S_z^{(\mathrm{eq})}=-A_{30}/A_{33}=A_{30}T_1$ and from Eq. (A4), $S_z^{(\mathrm{eq})}=-r\tanh(\beta\hbar\omega_0/2)/\sqrt{1+r^2}$, similar to the result obtained in the PIF literature for the weak-coupling limit [the NIBA prediction, $S_z^{(\mathrm{eq})}=-\tanh(\beta\varepsilon/2)$, is in contradiction with the result of a quantum-mechanical analysis [10]]. The energy splitting calculated with the detailed balance condition, $\rho_{11}^{s'(\mathrm{eq})}/\rho_{22}^{s'(\mathrm{eq})}=(1-S_z^{(\mathrm{eq})})/(1+S_z^{(\mathrm{eq})})$, is given by $E_1^{s'(\mathrm{eq})}-E_2^{s'(\mathrm{eq})}=\hbar\omega_0$. A similar result is reported by Ref. [14].

Next, we consider the effect of the bath on the natural frequency of TSS, ω_0. By using the expressions of the autocorrelation functions $a(\tau)$ and $b(\tau)$ from Eq. (A3) and the definition $\tilde{\omega}_0\equiv\omega_0+\mathrm{Im}(\Gamma_{1212})$, we obtain

$$\tilde{\omega}_0=\omega_0\left[1-\frac{q_0^2}{2\pi\hbar(1+r^2)}\mathrm{P}\int_0^\infty d\omega\,\frac{\coth(\beta\hbar\omega/2)}{\omega^2-\omega_0^2}J(\omega)\right], \tag{7}$$

where $\mathrm{P}\int\ldots$ means the Cauchy principal value of the integral.

For the dissipative regime, the coherence frequency obtained by us, Ω, is

$$\begin{aligned}\Omega^2&=-\frac{4A_{12}A_{21}+(A_{11}-A_{22})^2}{4}\\&=\omega_0^2\left[1-\frac{2\alpha}{\mu(1+r^2)}\mathrm{P}\int_0^\infty d\omega\,\frac{\coth(\beta\hbar\omega/2)}{\omega^2-\omega_0^2}J(\omega)\right]^2\\&\quad-\left[\frac{\pi\alpha}{4\mu(1+r^2)}J(\omega_0)\coth\left(\frac{\beta\hbar\omega_0}{2}\right)\right]^2\end{aligned} \tag{8}$$

and Ω equals $\tilde{\omega}_0$ in the RWA limit (see below). Thus, Eqs. (7) and (8) give the temperature corrections of the coherence frequency. These results are similar to those obtained by Görlich, Sassetti, and Weiss [39] in the PIF formalism [see also Eq. (21.169) from Ref. [10]].

To characterize the time evolution of TSS to the equilibrium state, following Ref. [40], we evaluate the rate constant by the "mean first passage time" expression of the type

$$k=\left(\int_0^\infty\frac{S_z(t)-S_z^{(\mathrm{eq})}}{1-S_z^{\mathrm{eq}}}dt\right)^{-1}. \tag{9}$$

This expression will be used to evaluate the rate constants for ETR in Sec. IV.

Rotating wave and secular approximations for dynamics of the spin-boson Hamiltonian

In this section, we consider the spin-boson Hamiltonian dynamics in the rotating wave and the secular approximation limits. We shall use the results obtained here in the following sections.

First, to find an analytical expression of the reduced statistical operator let us consider RWA by canceling a_{34} in Eq. (A1) (see justification of using RWA in Ref. [14]). It is worth noting that RWA limits the dynamics validity to values of $\tilde{\omega}_0$ close of ω_0. In RWA, $A_{11}=A_{22}=-T_2^{-1}$, $A_{12}=-A_{21}=-\tilde{\omega}_0$, and the dynamics is given by

$$S_{x'}(t)|_{\mathrm{RWA}}=S_{x'}(0)\cos\tilde{\omega}_0te^{-t/T_2}\equiv\Theta_{2x'}(\tilde{\omega}_0,t)e^{-t/T_2}. \tag{10a}$$

$$S_{y'}(t)|_{\mathrm{RWA}}=S_{x'}(0)\sin\tilde{\omega}_0te^{-t/T_2}\equiv\Theta_{2y'}(\tilde{\omega}_0,t)e^{-t/T_2}, \tag{10b}$$

$$\begin{aligned}S_{z'}(t)|_{\mathrm{RWA}}\\&=\left[S_{z'}(0)-S_z^{(\mathrm{eq})}+\frac{A_{31}S_{x'}(0)(T_1^{-1}-T_2^{-1})}{\tilde{\omega}_0^2+(T_1^{-1}-T_2^{-1})^2}\right]e^{-t/T_1}\\&\quad-\frac{A_{31}S_{x'}(0)[(T_1^{-1}-T_2^{-1})\cos\tilde{\omega}_0t+\tilde{\omega}_0\sin\tilde{\omega}_0t]}{\tilde{\omega}_0^2+(T_1^{-1}-T_2^{-1})^2}\\&\quad\times e^{-t/T_2}+S_{z'}^{(\mathrm{eq})}\equiv\Theta_{1z'}(r,A_{31},T_1,T_2,\tilde{\omega}_0)e^{-t/T_1}\\&\quad+\Theta_{2z'}(r,A_{31},T_1,T_2,\tilde{\omega}_0,t)e^{-t/T_2}+S_{z'}^{(\mathrm{eq})}.\end{aligned} \tag{10c}$$

The component of the polarization vector, $S_z(t)$, that is the probability to find TSS in its initial state $|L\rangle$ reads

$$\begin{aligned}S_z(t)|_{\mathrm{RWA}}&=\frac{1}{\sqrt{1+r^2}}[r\Theta_{1z'}e^{-t/T_1}+(\Theta_{2x'}+r\Theta_{2z'})e^{-t/T_2}]\\&\quad+\frac{r}{\sqrt{1+r^2}}S_{z'}^{(\mathrm{eq})}.\end{aligned} \tag{11}$$

As one can see, Eq. (11) reproduces both coherent and incoherent decays. In the RWA this equation has the simplest form if the factor A_{31} is disregarded. This happens if in Eq. (A1), a_{13},a_{31},a_{32} are canceled; thus SA is introduced. The time scale considerations mean that SA is acceptable if

$$S_A\equiv T_1^{-1}/\omega_0\ll1. \tag{12}$$

Using both the RWA and SA the dynamics equations in the delocalized basis have a simple form and Eqs. (10) give $\tilde{\omega}_0=\omega_0+\mathrm{Im}\,\Gamma_{1212}$ as the coherence frequency for either RWA or both RWA and SA. In the limit of RWA and SA, the *oz* component of **S** is very close to the PIF result (see, e.g., [10] and a discussion in Ref. [28]), namely,

$$\begin{aligned}S_z(t)|_{\mathrm{RWA+SA}}&=\frac{r}{\sqrt{1+r^2}}\left(\frac{r}{\sqrt{1+r^2}}-S_z^{(\mathrm{eq})}\right)e^{-t/T_1}\\&\quad+\frac{r}{\sqrt{1+r^2}}S_{z'}^{(\mathrm{eq})}+\frac{\cos\tilde{\omega}_0t}{1+r^2}e^{-t/T_2}.\end{aligned} \tag{13}$$

A geometrical description of the precession of $\mathbf{S}(t)$ given by Eq. (13) can be seen in Ref. [29]. In RWA and SA,

$$S_{z'}(t)|_{\mathrm{RWA+SA}}=\lfloor(S_{x'}(0)-S_{z'}^{(\mathrm{eq})})\rfloor\exp(-t/T_1)+S_{z'}^{(\mathrm{eq})}.$$

Thus, the coherence is absent in $S_{z'}(t)$ and utilization of both RWA and SA decreases the description accuracy.

III. APPLICATION TO A LORENTZIAN-OHMIC BATH

For a complete description of the dynamics, the right spectral distribution function of a particular system must be considered. Obviously, for ETR a LO form is chosen [31,41],

$$J(\omega)=\frac{\mu\omega}{1+\omega^2/\omega_L^2}\quad\text{with}\quad\omega_L=2\pi/\tau_L$$

and τ_L being the characteristic relaxation time of the bath. In this section, we shall consider the dynamics in the RWA limit. The two relaxation times T_1 and T_2 given by Eqs. (6a)–(6c) for this LO bath are

$$\frac{1}{T_1}=\frac{\pi\alpha}{(1+r^2)}\frac{\omega_0}{1+\omega_0^2/\omega_L^2}\coth\frac{\beta\hbar\omega_0}{2}\tag{14a}$$

and

$$\frac{1}{T_2}=\frac{\pi\alpha}{2(1+r^2)}\frac{\omega_0}{1+\omega_0^2/\omega_L^2}\coth\frac{\beta\hbar\omega_0}{2}+\frac{4\pi r^2\alpha}{\beta\hbar(1+r^2)}.\tag{14b}$$

Similar forms of the relaxation times obtained by different methods have been reported by Refs. [17,20]. Thus, in the second order approximation, T_1/T_2 is independent of the coupling α. The dependence of temperature is as follows. When temperature increases, T_1 becomes larger than T_2 and consequently Eq. (13) predicts that larger temperatures lead to incoherent dynamics.

On the other hand, from Eq. (7), by using $\coth cx/2=1+2\sum_{n=1}^{\infty}\exp(-ncx)$ for the modified natural frequency of TSS, we find

$$\tilde{\omega}_0|_{\mathrm{LO}}=\omega_0\left\{1+\frac{\alpha}{(1+r^2)(1+\omega_0^2/\omega_L^2)}\left[\ln\frac{\omega_0}{\omega_L}+\sum_{n=1}^{\infty}\{e^{n\beta\hbar\omega_0}\mathrm{Ei}(-ncx_0)+e^{-n\beta\hbar\omega_0}\mathrm{Ei}(ncx_0)-2[\mathrm{ci}(nc)\cos(nc)+\mathrm{si}(nc)\sin(nc)]\}\right]\right\},\tag{15}$$

where the functions $\mathrm{Ei}(x)$, $\mathrm{ci}(x)$, and $\mathrm{si}(x)$ are defined in accordance with Ref. [42], $c=\beta\hbar\omega_L$ and $x_0=\omega_0/\omega_L$. Equation (15) predicts that stronger TSS-bath coupling and smaller values of ω_0/ω_L result in decreasing the coherence frequency of the dissipative TSS.

From Eq. (15) one observes that the validity of RWA, $\tilde{\omega}_0\approx\omega_0$, is accomplished if

$$R_{\mathrm{WA}}\equiv\frac{\alpha}{(1+r^2)(1+\omega_0^2/\omega_L^2)}\ll 1.\tag{16}$$

If the last inequality is satisfied then (i) for large supraunitary r, the RWA condition can be accomplished for supraunitary α; (ii) for subunitary r, the RWA condition can be accomplished only for subunitary α. By connecting Eqs. (12) and (14), the SA validity conditions for LO fast bath read

$$S'_A\equiv\alpha/(1+r^2)\quad(\text{small subunitary})\tag{17a}$$

and

$$S''_A\equiv\beta\hbar\omega_0/2>1.\tag{17b}$$

From Eqs. (16) and (17a) one can observe that both RWA and SA conditions require a small subunitary value of $\alpha/(1+r^2)$ and they are simultaneously accomplished if $\alpha/(1+r^2)\ll 1$; a similar result concerning the equivalence of SA and RWA is reported by Kohen, Marston, and Tannor [36] in the case of Redfield equations. If in Eq. (15) one uses the equality [42]

$$e^{ncx_0}\mathrm{Ei}(-ncx_0)+e^{-ncx_0}\mathrm{Ei}(ncx_0)=-2\int_0^{\infty}dt\,\frac{t\cos t}{t^2+n^2c^2x_0^2},$$

then one can see that in limit of low temperatures, $cx_0\gg 1$, $c\gg 1$ (condition implicitly fulfilled in the fast bath case), and relevant in the sum appearing in Eq. (15) is the term $n=1$. Canceling $\mathrm{ci}(nc)$ and $\mathrm{si}(nc)$ as well, one obtains

$$\tilde{\omega}_0|_{\mathrm{LO}}\ \ (\text{low}\ \ T)=\omega_0\left\{1+\frac{\alpha}{(1+r^2)(1+\omega_0^2/\omega_L^2)}\times\left[\ln\frac{\omega_0}{\omega_L}-2\int_0^{\infty}dt\,\frac{t\cos t}{t^2+c^2x_0^2}\right]\right\}.\tag{18}$$

In the limit of the unbiased case, that is, $r=0$, Eq. (15) reads

$$\tilde{\omega}_0|_{\mathrm{LO}}(r=0)=\Delta\left\{1+\frac{2\alpha}{(1+\Delta^2/\omega_L^2)}\left[\ln\frac{\Delta}{\omega_L}+\sum_{n=1}^{\infty}\{e^{n\beta\hbar\omega_0}\mathrm{Ei}(-ncy_0)+e^{-n\beta\hbar\omega_0}\mathrm{Ei}(ncy_0)-2[\mathrm{ci}(nc)\cos(nc)+\mathrm{si}(nc)\sin(nc)]\}\right]\right\},\tag{19a}$$

where $y_0=\Delta/\omega_L$. In conformity with Ref. [43], $\tilde{\omega}_0(r=0,T=0)=0$; this cancellation of the tunneling frequency expresses the localization phenomenon of TSS in its initial state. Writing Eq. (19a) for $T=0$ one obtains

$$\tilde{\omega}_0|_{\mathrm{LO}}(r=0,T=0)=\Delta\left[1+\frac{2\alpha}{(1+\Delta^2/\omega_L^2)}\ln\frac{\Delta}{\omega_L}\right].\tag{19b}$$

This form provides a criterion in appreciating the extreme values of α for which the treatment in the limit of subunitary small r is still satisfactory,

$$-1<2\alpha\ln(\Delta/\omega_L)/[1+(\Delta/\omega_L)^2]<0.\tag{19c}$$

In Fig. 1 the renormalization factor of the coherence frequency of TSS, $\tilde{\omega}_0/\omega_0$, as function of temperature is represented for $r=0$ and $y_0=0.01$ in conformity with Eq. (19a); the chosen value of $\alpha=0.1$ respects condition (19c). We obtain that the temperature increases the coherence frequency; for high enough temperature the coherence frequency becomes larger then the natural frequency of TSS.

Figure 2 shows the dynamics predicted by the perturbative treatment in second order approximation for LO fast bath and unbiased case. It is obtained with the Laplace transform method applied to Eq. (4) with conditions (5) and use

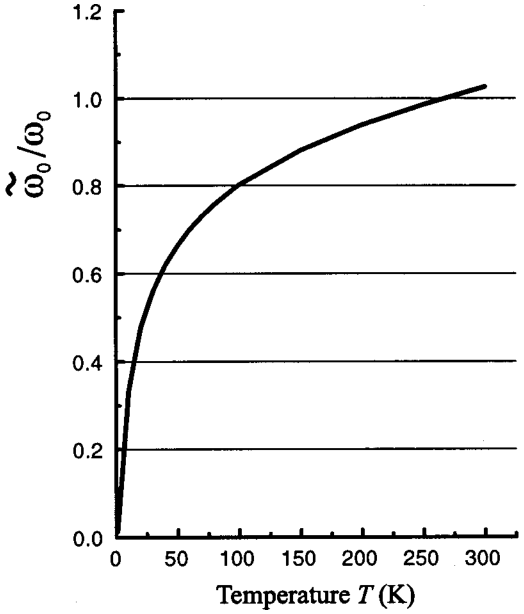

FIG. 1. The renormalization factor of the coherence frequency of TSS, $\tilde{\omega}_0/\omega_0$, for the unbiased case ($r=0$) as a function of temperature. The temperature increases the coherence frequency. The plot is obtained from Eq. (19a) with $y_0=0.01$, $\omega_L=10^{14}\,\mathrm{s}^{-1}$, and $\alpha=0.1$.

of Eqs. (A4) and (14). One observes (see the inset) that the use of RWA, Eq. (11), leads to an overestimation of the coherence frequency of TSS.

In the RWA limit an incoherent dynamics is obtained if the exponential $\exp(-t/T_2)$ decays fast enough to damp the sine and cosine oscillations [see Eq. (10c)]. Thus the inequality $I_D \equiv 2\pi T_2^{-1}/\tilde{\omega}_0 \gg 1$ characterizes an incoherent decay. A more restrictive condition, namely, $T_1^{-1}/2 \gg 2\tilde{\omega}_0/\pi$ imposes that the incoherent decay manifests if

$$\pi^2 \alpha \coth\frac{\beta\hbar\omega_0}{2} \Big/ 4(1+r^2) \gg 1.$$

This last inequality involves, as one expected, that the bath (coupling α) and temperature lead to an incoherent decay.

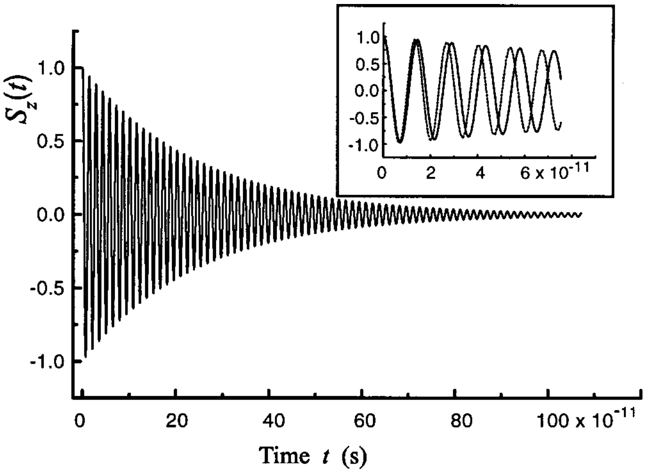

FIG. 2. Coherence predicted by the perturbative treatment in second order approximation for the fast bath and unbiased case. Figure shows the nonapproximate result. The inset compares the nonapproximate result (solid line) with the approximate result (dotted line) given by using RWA [Eqs. (11)]. The data used are $\omega_L=5\times10^{14}\,\mathrm{s}^{-1}$, $\alpha=0.005$, $x_0=0.001$, and $T=1$ K.

IV. APPLICATION TO ETR

As we have already mentioned, the treatment can be applied to the case of certain nonadiabatic electron transfer reactions in the fast bath limit. The obvious picture is to associate the vibration of the protein atoms surrounding the prosthetic groups involved in electron transfer with the bosonic bath modes [31,33,44]. The two states of TSS are electronic ones. The parameter α can be expressed in terms of the solvent reorganization energy E_r for the LO bath as (see, e.g., Ref. [41(a)] or [45])

$$\alpha = E_r \tau_L / \pi\hbar. \tag{20}$$

For the slow (adiabatic) bath, that is, for the case $\Delta/\omega_c \gg 1$, a coherence decay is reported both experimentally and theoretically by Chandler and co-workers [46], Coalson [47], Vos *et al.* [48], Evans, Nitzan, and Ratner [49], and Hornbach and Dakhnovskii [33]. There are two mechanisms that can generate nonexponential relaxation: (i) the slowly damped vibrational coherence of the low frequency modes of the bath and (ii) the electronic coherence. The problem of the electronic coherence in ETR has been addressed theoretically in Refs. [50–52] and these works shows the importance of the initial conditions in obtaining the electronic coherence. On the other hand, the attempt of Reid *et al.* [53] to observe an electronic coherence in biruthenium mixed-valence compounds has failed to yield any direct evidence. It seems that a better time resolution of the experimental observation is necessary to evidence this phenomenon. We shall use our treatment to predict if the presence of electronic coherent decay is possible in RCs for the fast bath model. Since the weak-coupling regime is the most favorable in manifesting the electronic coherence, prediction of the present treatment can be helpful for the experimentalists focused on detecting this phenomenon. In order to approximate the rate constant, we shall consider Eq. (A7) for ETR when the validity limits of RWA and SA are fulfilled. Additionally, we shall test the presence of coherence by using the I_D parameter. For a more accurate appreciation of the relaxation type of the bath, we infer from Refs. [32,33] the criterion of the fast bath, that is, $g=2\pi\sqrt{\beta E_r}/\Delta\tau_L \gg 1$. Applying this criterion to the LO bath via Eq. (20) the condition of fast bath reads $g=2\pi\sqrt{\pi\alpha\hbar\beta}/\sqrt{\tau_L^3} \gg 1$.

Next, the possibility of the electronic coherence manifestation is analyzed for the mutant strain of *Rhodobacter Spheroides* (Wilde type), in which tyrosine (M)210 is replaced by tryptophan (M)Y210, assuming a weak-coupling regime for ETR observed in this RC. In this case the electron transfer is seen as a unistep process from the excited bacteriochlorophyll dimer to bacteriopheophytin. The data we used are $\varepsilon=0.09$ eV and $k^{-1}=41$ ps from Ref. [54] and $\tau_L=0.095$ ps for $T=300$ K from Ref. [31]. As fitting data for k^{-1}, we consider $\hbar\Delta = 0.0005\,\mathrm{eV}$ and $E_r = 0.2\,\mathrm{eV}$, which are in normal limits for photosynthetic RCs [55]. These data establish for the rough parameter that characterizes the type of the bath, Δ/ω_L, a small subunitary value of 0.012. Thus the main requirement concerning the validity of application of the perturbative treatment in second order approximation to this case is fulfilled. The other confidence parameters characterizing the electron transfer are $T_1/T_2 = 1.9\times 10^5$, $g = 241$, $R_{\mathrm{WA}} = 5.4\times 10^{-3}$, $S_A = 1.1\times 10^{-3}$, and $I_D = 209$; they predict an incoherent decay and absence of any coherence. More interesting is the case of the low temperatures where an electronic coherence by quantum tunneling between the two potential energy surfaces characterizing the reactant and product states could manifest. Thus for the same data as above, but with $T = 1\,\mathrm{K}$ we obtain $T_1/T_2 = 658$, $g = 4182$, $R_{\mathrm{WA}} = 5.4\times 10^{-5}$, $S_A = 10^{-3}$, and $I_D = 0.698$. The value of the I_D parameter indicates a possible coherence manifestation and the value of the R_{WA} parameter allows the use of RWA. Consequently, for this situation we consider dynamics predicted by Eq. (11) including the renormalization effect of the coherence frequency as well. Figure 3(a) shows an incoherent relaxation even for short times of order ω_0^{-1}. The rate constant at this low temperature is obtained considering that the value of τ_L is temperature independent, in accordance with Ref. [31]. Its value, obtained with Eqs. (9), (10), and (A4) is $k^{-1} = 43.2\,\mathrm{ps}$. The nonsignificant dependence of temperature of the rate constant can be the result of low activation energy and in this case, as a consequence, the transfer is preeminently a thermal one, even at low temperatures. On the other hand, Fig. 3(b) shows a coherent decay for the same data as those used to obtain Fig. 3(a) except the unrealistic small chosen reorganization energy for ETR ($E_r = 0.002\,\mathrm{eV}$) and the very low temperature ($T = 0.001\,\mathrm{K}$). The parameters characterizing this dynamics are $T_1/T_2 = 1.16$, $g = 1.3\times 10^4$, $R_{\mathrm{WA}} = 5.4\times 10^{-7}$, $S_A = 10^{-5}$, and $I_D = 1.2\times 10^{-5}$. The small subunitary value of the I_D parameter indicates the presence of a coherent regime. In conformity with the small value of R_{WA}, we considered $\tilde{\omega}_0 \approx \omega_0$ for this figure. The coherence manifests for short times, for long time the relaxation becomes incoherent. This last case supports the general conclusion that the coherence manifests for low temperatures and weak TSS-bath coupling (or equivalently, small value of the reorganization energy).

V. CONCLUSIONS

The spin-boson dynamics has been obtained in the second order approximation of the TSS bath coupling (weak-coupling limit). A concrete solution has been furnished for a fast bath, which allows to recover the results obtained by other methods (e.g., the spectroscopy law and expression of the relaxation times, energy splitting and population decay). The results are in good agreement with those obtained by PIF. Our treatment supports the statement that stronger coupling and higher temperature results in increasing the coherence decay rate. For the fast bath case we obtained that the coupling decreases and the temperature increases the coherence frequency. We proved that generally, the second order approximation yields a biexponential decay for any spectral distribution of the bath. Based on physical considerations, we established validity criteria of the treatment applied to the LO bath for small subunitary values of r by Eq. (19c), and by Eq. (16) in the RWA limit for large values of r. More refined equations of dynamics show that utilization of the RWA gives an overestimation of the coherence frequency. Applied to ETR, the present perturbative treatment is a useful tool to evaluate the rate constant and to detect presence of the electronic coherence in the weak-coupling regime for the fast bath case. It is able to provide fine details concerning the relaxation type and its mechanism.

Thus, our treatment constitutes an alternative advantageous method to PIF for solving the dynamics of a dissipative TSS. Its extension to the slow bath case and consideration of higher order approximations of the GME kernel [29] can provide more refined information concerning the quantum dissipative phenomenon.

ACKNOWLEDGMENTS

This work was supported by Academia Sinica and National Science Council of the Republic of China. We would like to thank M. Grifoni for helpful comments and suggestions.

APPENDIX

GME generated by Eq. (1) applied to $\hat{H}'$ is

$$\begin{pmatrix} \dot{\rho}_{11}^{s'} \\ \dot{\rho}_{22}^{s'} \\ \dot{\rho}_{12}^{s'} \\ \dot{\rho}_{21}^{s'} \end{pmatrix} = \begin{pmatrix} -W_{21} & W_{12} & -a_{13} & -a_{13} \\ W_{21} & -W_{12} & a_{13} & a_{13} \\ -a_{31} & -a_{32} & -i\tilde{\omega}_0 - a_{33} & -a_{34} \\ -a_{31}^{*} & -a_{32}^{*} & -a_{34}^{*} & i\tilde{\omega}_0 - a_{33} \end{pmatrix} \times \begin{pmatrix} \rho_{11}^{s'} \\ \rho_{22}^{s'} \\ \rho_{12}^{s'} \\ \rho_{21}^{s'} \end{pmatrix}, \tag{A1}$$

with $\rho_{12}^{s'} = \rho_{21}^{s'*}$, $W_{12} \equiv \Gamma_{2222}$, $W_{21} \equiv \Gamma_{1111}$, $a_{13} \equiv \Gamma_{1112}$, $a_{31} \equiv \Gamma_{1211}$, $a_{32} \equiv \Gamma_{1222}$, $\tilde{\omega}_0 \equiv \omega_0 + \mathrm{Im}\,\Gamma_{1212}$, $a_{33} \equiv \mathrm{Re}\,\Gamma_{1212}$, and $a_{34} \equiv \Gamma_{1221}$. The specificity of Eq. (A1) is given by the form of the interaction term in Hamiltonian (2), $q_0 \hat{\sigma}_z \Sigma_\alpha c_\alpha \hat{x}_\alpha/2$. Calculus with Eq. (1) for the transformed Hamiltonian shows that the general form of tetradics is not changed compared to their usual form in the Redfield theory. It is

$$\Gamma_{m'mn'n} = \sum_k G^{+}_{m'kkn'} \delta_{nm} - G^{+}_{nmm'n'} - G^{-}_{nmm'n'} + \sum_k G^{-}_{nkkm} \delta_{n'm'} \,. \tag{A2}$$

As components of Eq. (A2) we find $G^{+}_{mm'nn'} = \int_0^\infty d\tau\, a(\tau) g^{+}_{mnn'nn'}(\tau)$ and $G^{-}_{mm'nn'} = \int_0^\infty d\tau\, b(\tau) g^{-}_{mm'nn'}(\tau)$; $a(\tau)$, $b(\tau)$ are the bath autocorrelation functions of the spin-boson Hamiltonian (see, e.g., Ref. [10]), namely,

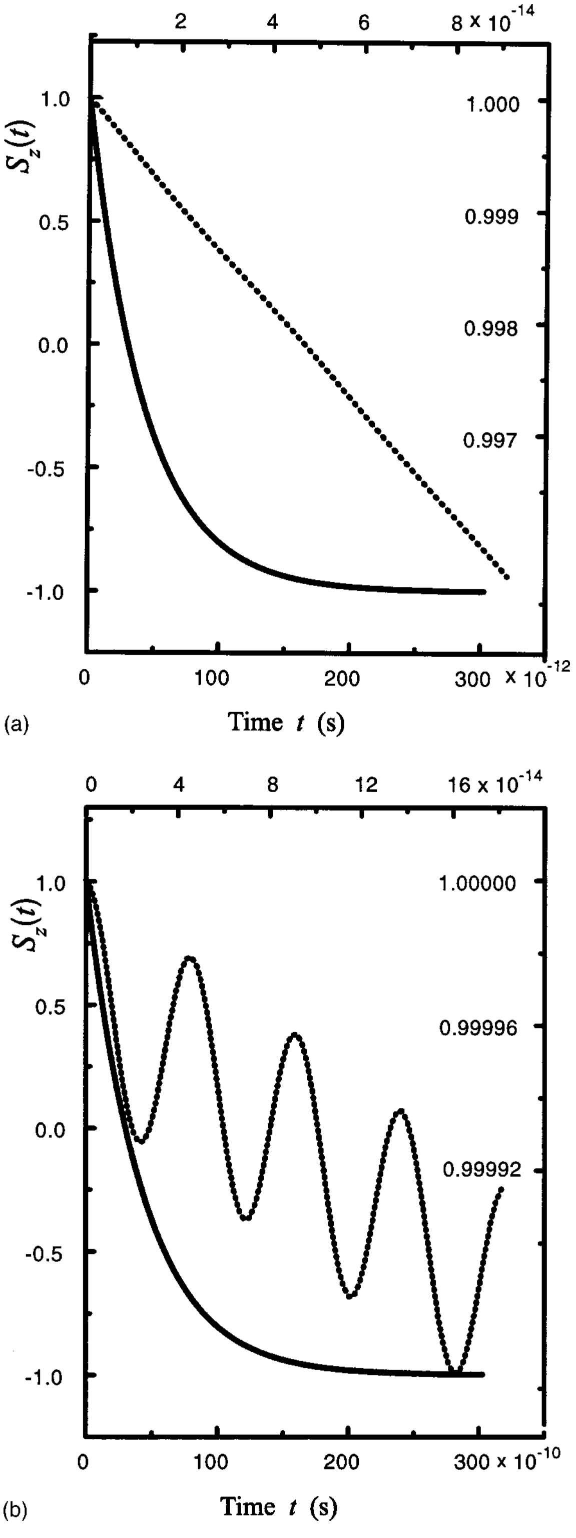

FIG. 3. Time-dependent incoherent and coherent dynamics. (a) The decay is incoherent even for short times $S_z(t)$ is obtained from Eq. (11); (b) coherent decay for unrealistic small chosen reorganization energy for ETR and low temperature $S_z(t)$ is obtained from Eq. (13). For both (a) and (b) the relaxation times T_1 and T_2 are calculated with Eqs. (14) and (20). The dotted curves (with top and right axes) show the behavior for the short times of the coherence order, $2\pi/\omega_0=4.6\times10^{-14}$ (s). See the data in the text.

$$a(\tau)=b(\tau)^*=\left\langle \sum_{\alpha} c_\alpha^2\hat{x}_\alpha(\tau)\hat{x}_\alpha(0)\hat{\rho}^b\right\rangle$$
$$=\frac{\hbar}{\pi}\int_0^\infty d\omega\, J(\omega)\left[\coth\frac{\hbar\omega\beta}{2}\cos\omega t-i\sin\omega t\right] \tag{A3}$$

and

$$g^{+}_{mm'nn'}(\tau)=\sum_{i,j}(s_i)_{mm'}(s_j)_{nn'}\exp(-i\tau\omega_{nn'}),$$

$$g^{-}_{mm'nn'}(\tau)=\sum_{i,j}(s_i)_{mm'}(s_j)_{nn'}\exp(-i\tau\omega_{mm'}),$$

with

$$\hat{x}_\alpha(\tau)=\exp(i\tau\mathbf{L}^b)\hat{x}_\alpha,\quad \hat{s}_i=-\frac{q_0}{2\hbar}\hat{\sigma}_i\sin 2\theta,$$

$$(s_i)_{mm'}=\langle m|\hat{s}_i|m'\rangle,\quad \omega_{n'n}=(E^{s'}_{n'}-E^{s'}_{n})/\hbar,$$

and $i, j=x', z'$ and $m, m', n, n'=1,2$.

The form of the A factors appearing in Eqs. (4) is as follows:

$$A_{10}=-i\frac{q_0^2r}{2\hbar^2(1+r^2)}\mathcal{I}_1,$$

$$A_{11}=-\left[T_2^{-1}-\frac{\pi\alpha}{2\hbar\mu}\frac{r}{(1+r^2)}\mathcal{I}_2\right],$$

$$A_{12}=-\tilde{\omega}_0-\frac{\pi\alpha}{2\hbar\mu}\frac{1}{(1+r^2)}\mathcal{I}_3,\quad A_{13}=\frac{\pi\alpha}{2\hbar\mu}\frac{r}{(1+r^2)}\mathcal{I}_2,$$

$$A_{20}=i\frac{2\pi\alpha}{\hbar\mu}\frac{r}{(1+r^2)}\mathcal{I}_4,\quad A_{21}=\tilde{\omega}_0+\frac{\pi\alpha}{2\hbar\mu}\frac{1}{(1+r^2)}\mathcal{I}_3,$$

$$A_{22}=-\left[T_2^{-1}+\frac{\pi\alpha}{2\hbar\mu}\frac{r}{(1+r^2)}\mathcal{I}_2\right],\quad A_{23}=\frac{\pi\alpha}{2\hbar\mu}\frac{r}{(1+r^2)}\mathcal{I}_3,$$

$$A_{30}=-\frac{\pi\alpha}{\mu}\frac{1}{(1+r^2)}J(\omega_0),$$

$$A_{31}=-2a_{13}=\frac{\pi\alpha}{\mu}\frac{r}{(1+r^2)}\left[J(\omega)\coth\frac{\beta\hbar\omega}{2}\right]_{\omega\to0},$$

$$A_{33}=-T_1^{-1}$$

and

$$\mathcal{I}_1=i\hbar J(\omega_0),\quad \mathcal{I}_2=\hbar J(\omega_0)\coth\frac{\beta\hbar\omega_0}{2},$$

$$\mathcal{I}_3=-\frac{2\hbar\omega_0}{\pi}\mathrm{P}\int_0^{\infty}d\omega\,\frac{J(\omega)\coth\frac{\beta\hbar\omega}{2}}{\omega^2-\omega_0^2},$$

$$\mathcal{I}_4=\frac{i\hbar}{\pi}\left[\mathrm{P}\int_0^{\infty}d\omega\,\frac{J(\omega)}{\omega}-\omega_0\mathrm{P}\int_0^{\infty}d\omega\,\frac{J(\omega)}{\omega^2-\omega_0^2}\right].$$

The relation between the polarization vectors in the two reference frames is (see Refs. [29,56])

$$\begin{pmatrix}S_x(t)\\S_y(t)\\S_z(t)\end{pmatrix}=\begin{pmatrix}\cos 2\theta & 0 & \sin 2\theta\\ 0 & 1 & 0\\ -\sin 2\theta & 0 & \cos 2\theta\end{pmatrix}\begin{pmatrix}S_{x'}(t)\\S_{y'}(t)\\S_{z'}(t)\end{pmatrix}. \tag{A4}$$

For the fast bath case we have

$$\begin{aligned}a_{31}&=\frac{\pi\alpha r}{2\hbar\mu(1+r^2)}\int_0^{\infty}d\tau[b(\tau)-a(\tau)-2b(\tau)\exp(-i\omega_0\tau)]\\&=\frac{\pi\alpha r}{2\hbar\mu(1+r^2)}\left(\int_0^{t_{\mathrm{short}}}+\int_{t_{\mathrm{short}}}^{\infty}\right)\approx\\&\quad-\frac{\pi\alpha r}{2\hbar\mu(1+r^2)}\int_0^{t_{\mathrm{short}}}d\tau[b(\tau)+a(\tau)],\end{aligned} \tag{A5}$$

$$\begin{aligned}a_{32}&=\frac{\pi\alpha r}{2\hbar\mu(1+r^2)}\int_0^{\infty}d\tau[b(\tau)-a(\tau)+2a(\tau)\exp(-i\omega_0\tau)]\\&=\frac{\pi\alpha r}{2\hbar\mu(1+r^2)}\left(\int_0^{t_{\mathrm{short}}}+\int_{t_{\mathrm{short}}}^{\infty}\right)\\&\approx\frac{\pi\alpha r}{2\hbar\mu(1+r^2)}\int_0^{t_{\mathrm{short}}}d\tau[b(\tau)+a(\tau)],\end{aligned} \tag{A6}$$

where t_{short} is of the correlation time order of the bath. Thus for the fast bath case $a_{31}\approx -a_{32}$ and $A_{10}=A_{20}=0$.

When both RWA and SA are used the analytical expression of the rate constant, as given by Eqs. (9) and (13), reads

$$k_{\mathrm{RWA+SA}}^{-1}=\frac{\frac{r}{\sqrt{1+r^2}}\left(\frac{r}{\sqrt{1+r^2}}-S_z^{(\mathrm{eq})}\right)T_1+[(1+r^2)(1+\tilde{\omega}_0^2T_2^2)]^{-1}T_2}{1-S_z^{(\mathrm{eq})}\frac{r}{\sqrt{1+r^2}}}. \tag{A7}$$

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