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On the relaxation of a two-level system: Beyond the weak-coupling approximation

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The model of two nondegenerate quantum levels coupled linearly and off-diagonally to a bath of quantum mechanical harmonic oscillators studied previously by Laird, Budimir, and Skinner is re-examined. Interpretations are made for both the fourth order population relaxation and dephasing processes. Some of the methods used are applied to the standard spin-boson problem. The question of experimental detection of predicted phenomena is discussed. An approximate method, based on a canonical transformation of the original Hamiltonian is proposed to study the problem. © *1996 American Institute of Physics.* [S0021-9606(96)50402-7]

I. INTRODUCTION

The study of two quantum mechanical levels coupled to a heat bath of harmonic oscillators has surfaced in numerous areas of chemistry and physics for over 30 years.[1–4] Much of condensed phase spectroscopy can be reduced to the study of two nondegenerate levels interacting with a bath of independent modes.[1,2] When second order perturbation theory in the system–bath coupling is used, equations of motions for the reduced density matrix elements (Bloch equations) may be obtained,[1,3,5]

$$\dot{\sigma}_{00}(t) = -k_{10}\sigma_{00}(t) + k_{01}\sigma_{11}(t), \tag{1}$$

$$\dot{\sigma}_{11}(t) = k_{10}\sigma_{00}(t) - k_{01}\sigma_{11}(t), \tag{2}$$

$$\dot{\sigma}_{10}(t) = -[i(\omega_0 + \Delta\omega) + 1/T_2]\sigma_{10}(t), \tag{3}$$

$$\dot{\sigma}_{01}(t) = [i(\omega_0 + \Delta\omega) - 1/T_2]\sigma_{01}(t), \tag{4}$$

where $\sigma_{ij}(t)$ are the matrix elements of the reduced density matrix[3] (the density matrix of the ''system''), k_{10} and k_{01} are the ''up'' and ''down'' rate constants, respectively, ω_0 is the natural frequency of the two level system, $\Delta\omega$ is the frequency shift of the system induced by the bath, and $1/T_2$ is the decay rate of the off-diagonal element of the reduced density matrix element. The diagonal elements of the reduced density matrix are referred to as populations, as they measure the probability for the system to be measured in the system states, which are labeled ($|0\rangle$ and $|1\rangle$). The off-diagonal terms are often called coherences, as they are a measure of the phase coherence between system states. This set of equations is valid for times such that the initial, non-exponential behavior has decayed, and the remaining approach to equilibrium is exponential.

For a wide range of problems, the Bloch equations provide an exceptionally good description of the dynamics of two levels coupled to a dissipative bath. This is especially true in the field of nuclear magnetic resonance, where the equations were introduced.[1,5] When the standard second order approach is adopted, Eqs. (1)–(4) and the parameters involved have simple, physical interpretations.[6,8] For example, the equations that govern the time evolution of the populations have the ''gain–loss'' form typical of the Pauli Master equation.[7] The ''up'' and ''down'' rate constants are given by standard, second order golden rule expressions. When the coupling is linear in the coordinate of the bath modes, these expressions can be understood in terms of the absorption and emission of phonons of frequency ω_0, i.e., modes of the bath in resonance with the two-level system (TLS). Coupling diagonal in the system states leads to phase relaxation via the modulation of the energy levels of the system by the bath.[8] Coupling that is off-diagonal in the system states lead to both changes in population, and to loss of phase coherence, since the relative phase between system states must change (in an averaged sense) when the populations relax. A simple derivation shows the relation, at second order,[1,3,6,8]

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2'}, \tag{5}$$

where $1/T_2$ is the rate of total dephasing of the system, $1/T_1$ is the rate of population relaxation, and $1/T_2'$ is the ''pure'' dephasing rate, caused by adiabatic fluctuations that modulate the system frequency. Such fluctuations tend to destroy the phase coherence, thus rendering a positive pure dephasing rate. this leads to the standard relation,

$$1/T_2 \geqslant 1/2T_1. \tag{6}$$

This relation has been of great use in the analysis of spectroscopic experiments, although it is rigorously valid only to second order in perturbation theory.

Recently, there have been studies that transcend second order perturbation theory. Budimir and Skinner performed a fourth order perturbation theory calculation to determine the relaxation properties of a TLS linearly coupled, both diagonally and off-diagonally, to a Gaussian stochastic bath.[9] They showed that at fourth order, the relation (5) is not valid, and for some parameters, $1/T_2 \leqslant 1/2T_1$. Simulations on the same model were performed by Sevian and Skinner.[10] They showed that even for systems that violate the inequality (6), the initial non-Markovian behavior is often short compared to the asymptotic, exponential relaxation. Reineker *et al.*, for a different model of bath fluctuations, also showed that the breakdown of the inequality (6) is possible.[11] Laird, Budimir,

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and Skinner (hereafter denoted LBS), performed calculations on a TLS linearly and off-diagonally coupled to a quantum heat bath of harmonic oscillators.[12] Unlike the stochastic studies, their model is valid at finite temperature. They also find that the relaxation properties at fourth order are different than at second order, although the form of the Bloch equations (1)–(4) still hold. By using the results of the study of LBS, Laird and Skinner showed that for the particular model that reproduces the interesting stochastic results in the limit of infinite temperature (the ''complex Ohmic–Lorentzian'' model), that the inequality (6) breaks down at finite temperature as well.[13] Chang and Skinner refined these calculations by discarding the assumption that the density matrix is initially factorized, and included the short time, non-Markovian relaxation behavior in their study.[14] They found once again that the inequality (6) can be violated. Laird, Chang, and Skinner have recently shown that such a breakdown is possible for a ''super-Ohmic'' model of the heat bath.[15]

While much work has been done on the calculational aspects of this problem, little has been done to put the results on a physical foundation. The second order results are useful and meaningful in part because physical interpretation can be found for the processes involved. In the case of a TLS coupled linearly and off-diagonally to a bath of harmonic oscillators, we expect the population relaxation rates to depend on the number of phonons in the bath at a given temperature that have a frequency ω_0. We expect the absence of pure dephasing since the system–bath coupling lacks the ability to cause fluctuations in the system's natural frequency. No such understanding exists at fourth order. In fact, based on our knowledge of second order perturbation theory, many of the fourth order results are surprising. What is the physical meaning of $1/T_2'$ at fourth order? Why can it become negative in some instances (when system–bath coupling constants are complex) and not in others (real system–bath coupling parameters)? Why does the frequency shift of the TLS not agree with the shift inferred from the renormalized energy splitting? How are the fourth-order population shifts to be interpreted? We will attempt in this note to interpret the fourth order expressions, and thus answer some of these questions. Along the way, we will touch upon more familiar problems in the theory of quantum relaxation, such as the celebrated spin-boson problem.[16–24]

We will also address the question of experimental measurability of the results obtained in the fourth order calculations of Laird, Budimir, and Skinner. In doing so, we will propose an alternate method of study for the ''complex Ohmic–Lorentzian'' model of Laird and Skinner. Our methods and results will provide a first step in producing a unified view of the dissipative dynamics of a TLS beyond the weak-coupling limit.

II. REVIEW OF THE PROBLEM

LBS considered the Hamiltonian,[12]

$$H = H_{\mathrm{TLS}} + H_b + H', \tag{7}$$

where ($\hbar = 1$)

$$H_{\mathrm{TLS}} = \omega_0 |1\rangle\langle 1|, \tag{8}$$

$$H_b = \sum_k \ (b_k^\dagger b_k + 1/2), \tag{9}$$

$$H' = \Lambda |1\rangle\langle 0| + \Lambda^+ |0\rangle\langle 1|, \tag{10}$$

$$\Lambda = \sum_k \ h_k (b_k^\dagger + b_k). \tag{11}$$

The Hamiltonian consists of the TLS with excited state energy ω_0, a free, harmonic bath, and a coupling that is off-diagonal in the system states, and linear in the bath normal mode coordinates. The model is confined to coupling constants that are either purely real or purely imaginary.

The dynamics for the total density matrix (system +Bath) is contained in the Liouville equation,

$$\frac{\partial \rho(t)}{\partial t} = -i[H, \rho(t)]. \tag{12}$$

A Redfield-type formalism[4] is then use to calculate equations of motion for the bare reduced density matrix, defined by $\sigma(t) = Tr_b \rho(t)$. By bare we mean that the states used as a basis in the perturbation theory are pure system states, as opposed to ''dressed states'' that mix system and bath. The initial conditions are taken to be factorized,

$$\rho(0) = \sigma(0) \otimes \rho_{\mathrm{eq}}^b,$$

where ρ_{eq}^b is the equilibrium density matrix of the bath. After transformation to the interaction picture, the equation of motion,

$$\dot{\tilde{\sigma}}(t) = R(t) \tilde{\sigma}(t), \tag{13}$$

where

$$R(t) = \sum_n \ R^{(2n)}(t), \tag{14}$$

with

$$R^{(2)}(t) = -\int_0^t dt_1 \ \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_1)\rho_b], \tag{15}$$

and

$$\begin{aligned} R^{(4)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \{ & \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_1)\tilde{L}(t_2)\tilde{L}(t_3)\rho_b] \\ & - \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_1)\rho_b]\mathrm{Tr}_b[\tilde{L}(t_2)\tilde{L}(t_3)\rho_b] \\ & - \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_2)\rho_b][\tilde{L}(t_1)\tilde{L}(t_3)\rho_b] \\ & - \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_3)\rho_b]\mathrm{Tr}_b[\tilde{L}(t_1)\tilde{L}(t_2)\rho_b] \}, \end{aligned} \tag{16}$$

is found, and then is projected onto the system states. An equation of the Redfield form results,

$$\dot{\tilde{\sigma}}_{\alpha\alpha'}(t) = \sum_{\beta\beta'} \ e^{i(\alpha - \alpha' - \beta + \beta')\omega_0 t} R_{\alpha\alpha'\beta\beta'} \tilde{\sigma}_{\beta\beta'}(t), \tag{17}$$

where

$$R_{\alpha\alpha'\beta\beta'} \equiv \lim_{t\to\infty}[e^{-i(\alpha-ga'-\beta+\beta')\omega_0 t}\langle\alpha|\{R(t)|\beta\rangle \times\langle\beta'|\}|\alpha'\rangle]. \tag{18}$$

Due to the fact that H' is off-diagonal in the system states, and has zero thermal average, the equations, after transformation back to the Schrödinger picture,

$$\dot{\sigma}_{00}(t) = R_{0000}\sigma_{00}(t) + R_{0011}\sigma_{11}(t), \tag{19}$$

$$\dot{\sigma}_{11}(t) = R_{1100}\sigma_{00}(t) + R_{0110}\sigma_{11}(t), \tag{20}$$

$$\dot{\sigma}_{10}(t) = (-i\omega_0 + R_{1010})\sigma_{10}(t) + R_{1001}\sigma_{01}(t), \tag{21}$$

$$\dot{\sigma}_{01}(t) = (i\omega_0 + R_{0101})\sigma_{01}(t) + R_{0110}\sigma_{10}(t), \tag{22}$$

are found to hold to all orders in the coupling constant. LBS immediately identify the "up" and "down" rate constants as

$$k_{10} = -R_{0000}, \tag{23}$$

and

$$k_{10} = R_{1111}, \tag{24}$$

respectively. A rotating wave approximation is made to decouple the coherences in Eqs. (21) and (22). The identifications

$$1/T_2 = -\mathrm{Re}\{R_{1010}\}, \tag{25}$$

and

$$\Delta\omega = -\mathrm{Im}\{R_{1010}\}, \tag{26}$$

can then be made, relating the dephasing rate and the frequency shift to the relaxation parameters in Eq. (18). The effect of the decoupling of the coherences is detailed in LBS. There it is shown that the definition of $1/T_2$ is not effected by such an approximation, while the expression for $\Delta\omega$ is modified at fourth order. Once the definitions (23)–(26) are in place, a perturbative calculation of the rates may be made.

At second order in the coupling strength, the calculation of the "up" rate constant is quite simple. By using Eq. (15) and (23), the expression for the "up" rate constant

$$k_{10}^{(2)} = \lim_{t\to\infty} 2\ \mathrm{Re}\left[\int_0^t dt_1 e^{-i\omega_0(t-t_1)}C_1(t-t_1)\right], \tag{27}$$

is found. $C(t-t')$ is the standard harmonic oscillator correlation function,

$$C_1(t-t') = \mathrm{Tr}_b[\rho_b\Lambda(t)\Lambda(t')] = \sum_k |h_k|^2\{[n(\omega_k)+1]e^{-i\omega_k(t-t')} + n(\omega_k)e^{i\omega_k(t-t')}\}, \tag{28}$$

and $n(\omega_k)$ is the Bose factor, giving the thermal occupation of phonons at frequency ω_k. It is convenient to express the rates in the frequency domain. We define

$$\hat{C}_1(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau}C_1(\tau)d\tau. \tag{29}$$

$\hat{C}_1(\omega)$ can be expressed as,

$$\hat{C}_1(\omega) = 2\{\Gamma_1(\omega)[n(\omega)+1] + \Gamma_1(-\omega)n(-\omega)\}, \tag{30}$$

where the weighted density of states, $\Gamma_1(\omega)$, is defined as,

$$\Gamma_1(\omega) \equiv \pi\sum_k |h_k|^2\delta(\omega-\omega_k). \tag{31}$$

The rate, Eq. (27), may thus be expressed,

$$\hat{C}_1(-\omega_0) = 2\Gamma_1(\omega_0)n(\omega_0), \tag{32}$$

which, due to the proportionality to the thermal occupation of phonons at ω_0, may be interpreted as the absorption of one vibrational quantum of frequency ω_0. The rate k_{01} and thus $1/T_1$, which is defined as $1/T_1 = k_{01}+k_{10}$ may be calculated in a similar manner. It is a simple exercise to show that, at second order, $(1/T_2)^{(2)} = (1/2T_1)^{(2)}$, demonstrating that for the model under consideration, the second order dephasing rate has no contribution from pure dephasing.

The fourth order terms may be calculated by applying Eqs. (16), (18), and (23)–(25). The tedious details are outlined in LBS. At fourth order, a new weighted density of states, $\Gamma_2(\omega)$ comes into play. This density of states, which arises from terms containing correlation functions $C_2(t-t') = \mathrm{Tr}_b[\rho_b\Lambda(t)\Lambda(t')]$, has the form,

$$\Gamma_2(\omega) \equiv \pi\sum_k h_k^2\delta(\omega-\omega_k). \tag{33}$$

This density of states gives rise to a correlation function $\hat{C}_2(\omega)$ with the same form as Eq. (30), with $|h_k|^2$ replaced with h_k^2. Since the coupling constants are purely real or purely imaginary by assumption, the density of states $\Gamma_2(\omega)$ is real. Note that $\Gamma_2(\omega)$ may vanish for arbitrarily strong coupling if the coupling constants are chosen to come in pairs in which one coupling constant is real and the other is imaginary, but have equal modulus. This model will be discussed later in the paper.

The fourth order population excitation rate may be expressed in frequency space as,

$$k_{10}^{(4)} = \left(\frac{1}{2\pi}\right)\{\omega_0^{-1}\hat{C}_2(-\omega_0)[P_2(\omega_0)-P_2(-\omega_0)] + \hat{C}_1'(-\omega_0)[P_1(\omega_0)-P_1(-\omega_0)] + P_1'(-\omega_0) \times[\hat{C}_1(\omega_0)-\hat{C}_1(-\omega_0)] - 2\hat{C}_1(-\omega_0)P_1'(\omega_0)\}, \tag{34}$$

where

$$P_i(\omega) = \wp\int_{-\infty}^{\infty} d\omega'\ \frac{\hat{C}_i(\omega')}{\omega'-\omega}, \tag{35}$$

$$\hat{C}_i'(\omega) = \frac{\partial\hat{C}_i(\omega)}{\partial\omega}, \tag{36}$$

$$P_i'(\omega) = \wp\int_{-\infty}^{\infty} d\omega'\ \frac{\hat{C}_i'(\omega')}{\omega'-\omega}, \tag{37}$$

where $\wp$ denotes Cauchy principle part. The coupling and temperature dependence of this rate expression may be obtained by substituting Eqs. (30), (31), and (33) into Eq. (34).

Note that the zero temperature thermal excitation rate does not vanish in the limit of zero temperature. In fact,

$$\lim_{T\to 0} k_{10}^{(4)} = \frac{2\Gamma_1(\omega_0)}{\pi} \int_0^\infty d\omega \, \frac{\Gamma_1'(\omega)}{\omega+\omega_0}. \tag{38}$$

We will return to this result in Sec. III. The total population relaxation rate $(1/T_1)^{(4)}$ may be computed simply from the sum of the fourth order ''up'' and ''down'' rate constants.

The second order frequency shift may be calculated perturbatively from Eq. (26). The result found by LBS is,

$$\Delta\omega^{(2)} = \left(\frac{1}{2\pi}\right)[P_1(-\omega_0) - P_1(\omega_0)]. \tag{39}$$

When compared to the ''frequency'' defined through,

$$K \equiv e^{-\beta\tilde{\omega}}, \tag{40}$$

where K is the equilibrium constant, defined as,[3,12]

$$K = \frac{\sigma_{11}(\infty)}{\sigma_{00}(\infty)} \tag{41}$$

and $\sigma_{ii}(\infty)$ is the equilibrium system population in state $|i\rangle$, LBS found that $[\tilde{\omega}-\omega_0]^{(2)}$ differs from $\Delta\omega^{(2)}$. That is, the second order frequency shift is not equal to the frequency shift obtained from the equilibrium constant. This result will be discussed in Sec. VI.

Finally, LBS calculate the fourth order contribution to $(1/T_2)^{(4)}$. As a *mathematical means* to test the inequality (6), LBS define, in analogy to second order perturbation theory,

$$\frac{1}{T_2'} \equiv \frac{1}{T_2} - \frac{1}{2T_1}. \tag{42}$$

The fourth order contribution to $(1/T_2)$ is found to be,

$$\left(\frac{1}{T_2'}\right)^{(4)} = \frac{1}{\pi} \wp \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2-\omega_0^2} \left\{ \omega \, \frac{\partial}{\partial\omega} [\hat{C}_1(\omega)\hat{C}_1(-\omega)] - \hat{C}_2(\omega)\hat{C}_2(-\omega) \right\}. \tag{43}$$

It is to be emphasized that within the context of the calculations performed by LBS, the fourth order definition of ''pure dephasing'' is a mathematical tool to study the inequality (6), and does not have the physical meaning of its second order counterpart. Laird and Skinner study two models for the spectral densities (31) and (33). In both models, they choose spectral densities that are Ohmic–Lorentzian in form, i.e.,

$$\Gamma_i(\omega) \sim \frac{\omega\alpha}{\omega^2+\alpha^2}. \tag{44}$$

This type of spectral density reproduces the exponentially damped decay of correlation functions (in the time domain) that are produced by Gaussian stochastic theories. The first model used by Laird and Skinner takes the coupling constants of Eq. (33) to be real. In this case, $\hat{C}_1(\omega) = \hat{C}_2(\omega)$. Here, it is found that Eq. (43) is always positive, so that the inequality (6) is never violated. For a model with coupling constants take so that $\Gamma_2(\omega)$ vanishes (called ''complex Ohmic–Lorentzian''), Laird and Skinner found that Eq. (43) can become negative, indicating a violation of Eq. (6). This model for the coupling is important because it is the physical realization of a spin-1/2 particle in a static longitudinal magnetic field with equal strength but uncorrelated fluctuating magnetic fields in the two transverse directions.[1,9] With the same ''complex'' coupling model, Laird, Chang, and Skinner have shown that Eq. (43) may be negative even if the spectral densities are super-Ohmic. These results will be discussed in Secs. V and VI.

III. POPULATION RELAXATION

We begin by examining closely the fourth order population relaxation terms. Perhaps the most surprising result uncovered by LBS is the fact that the population excitation rate (the ''up'' rate constant) is nonzero at zero temperature. This result was in fact anticipated by Lindenberg and West[25] in their study of the harmonic oscillator linearly coupled to a quantum heat bath, and by Kassner[26] in his study of correlated initial conditions in the spin-boson problem. All of these studies have shown that there is residual excited state population at $T=0$. The origin of this population is easy to trace in our case. We note that at zero temperature, the equilibrium density matrix of the entire system+bath complex is a projection operator for the ground state, assuming that the ground state may be found. Then,[26]

$$\rho_{\rm eq} = |\psi_g\rangle\langle\psi_g|. \tag{45}$$

By computing the ground state of Hamiltonian (7) to first order in the coupling strength, we find

$$|\psi_g\rangle = N_0 \left[1 - \sum_k \frac{h_k \sigma + a_k^\dagger}{(\omega_0+\omega_k)}\right] |\Phi_g^0\rangle, \tag{46}$$

where N_0 is a normalization factor, and $|\Phi_g^0\rangle$ is the ground state of H_0, consisting of the direct product of the system ground state, and the vacuum state of the bath. The following consequences of the mixing of the system and bath states may be noted:

(1) The density matrix, for calculations extending beyond the strict weak coupling limit, has an expansion in powers of the coupling strength,[27]

$$\rho(t) = \rho^{(0)}(t) + \delta\rho^{(1)}(t) + \delta^{(2)}\rho^{(2)} + \cdots . \tag{47}$$

In a precise treatment, attention must be paid to the various time scales in the problem,[28] so that the ''time'' appearing in Eq. (47) is really a hierarchy of time scales. We will not be concerned with such a treatment here. In our problem, $\rho^{(2)}(\infty)$ will contain states mixed by H' at first order in the perturbation. Thus, $\sigma^{(2)}(\infty)$, obtained by tracing out the bath degrees of freedom, will only contain population in the excited state of the system,

$$\sigma^{(2)}(\infty) = \left[\frac{1}{\pi} \int_0^\infty \frac{\Gamma'(\omega) d\omega}{(\omega+\omega_0)}\right] |1\rangle\langle 1|. \tag{48}$$

Note that $\sigma^{(1)}(\infty)$ is identically zero. By appealing to the properties of the system–bath coupling in the thermody-

namic limit, we find that the residual population is $\mathcal{O}(N^0)$ in magnitude, and thus cannot be neglected.[29,30]

(2) Equation (46) shows that, due to the mixing of states, bath excitations exist at zero temperature. If we define the total occupancy of phonons, $N(\omega_0)$, as

$$N(\omega_0)=\sum_k \langle a_k^\dagger a_k\rangle, \tag{49}$$

then a simple calculation gives,

$$N(\omega_0)=\frac{1}{\pi}\int_0^\infty \frac{\Gamma'(\omega)d\omega}{(\omega+\omega_0)}, \tag{50}$$

which is, at this temperature, equal to the equilibrium system population.

We now turn to a discussion of the population excitation rate constant. To see if the rate expression (34) is really a fourth order extension of Fermi's golden rule, we compute the Fermi golden rule rate expression directly[31]

$$W_{0\to 1}=\mathrm{Re}\int_0^\infty d\tau\langle T_{01}(\tau)T_{10}^\dagger\rangle e^{-i\omega_0\tau}, \tag{51}$$

where the transition operator is defined $T\equiv H'+H'GT$, and G is the zeroth order Green's function. This calculation is confined in the Appendix. Some subtleties arise in the calculation. When properly interpreted, $W_{0\to 1}$ is identical to the expression (34) for k_{10}. This confirms that these rates are indeed higher order Fermi golden rule expressions.

We may note that cross terms between second order rates and second order populations are contained within the fourth order rate expression. For example, the Bloch equation describing the evolution of the population difference $P_z(t)$ has the form

$$\dot{P}_z(t)=-\frac{1}{T_1}[P_z(t)-P_z(\infty)]. \tag{52}$$

For times $(1/T_1)^{-1}\gg t\gg \tau_b$, where τ_b is the correlation time of the bath, a cross term

$$(1/T_1)^{(2)}P_z^{(2)}(\infty) \tag{53}$$

contributes to the fourth order expression of $1/T_1$. The same argument holds for the individual population transfer rates. This accounts for the appearance of several terms in Eq. (34). For example, at zero temperature, the ''up'' rate constant has the same form as the second order expression at finite temperature, with the population of modes $n(\omega_0)$ replaced by the total number of excited modes $N(\omega_0)$ [see Eqs. (38) and (49)–(50)]. Thus the rate may be interpreted as the product of the weighted density of states at the resonance frequency times the total number of phonons created with the system excitation.

IV. APPLICATION TO THE SPIN-BOSON PROBLEM

In this section, we apply the methods used in Eqs. (45) and (48) to compute some equilibrium properties of the standard spin-boson Hamiltonian.[16–24] We wish to show that a direct calculation of the zero temperature localization diagram (as well as relaxation rate and line shift expressions) is possible by a simple, static application of Rayleigh–Schrödinger perturbation theory. Our method will reproduce the localization behavior given by the noninteracting blip approximation (NIBA),[19] which, for the case of Ohmic dissipation, is quantitatively in error as $t\to\infty$.[21] A more rigorous analysis, based on mapping the spin-boson model with Ohmic dissipation onto the Ising model with long range interactions, has been carried out by Spohn and Dümcke.[22] We will be content to show that Eqs. (45) and (48) are deceptively simple, and may be used to extract information that has been obtained previously by more complicated, dynamical means.

We begin with the spin-boson Hamiltonian (in the notation of Aslangul *et al.*[19])

$$H=-\omega_0\sigma_x+\sigma_z\sum_k G_k(b_k^\dagger+b_k)+\sum_k \omega_k b_k^\dagger b_k, \tag{54}$$

where, again, $\hbar$ has been set to one, and σ_x,σ_z are standard Pauli matrices defined in the basis $|L\rangle,|R\rangle$ of ''left'' and ''right'' states. This Hamiltonian describes a tunneling system linearly coupled to a bath of harmonic oscillators. The tunneling system can be envisioned as the lowest two levels of a symmetric double well potential. In this picture, the coupling term causes fluctuations in the well depths of the potential. The case of Ohmic dissipation, which is our focus here, is defined by a spectral density[16]

$$J(\omega)\equiv\sum_k G_k^2\delta(\omega-\omega_k)=\frac{\alpha}{2}\omega e^{-\omega/\omega_c}. \tag{55}$$

Our goal is to compute the degree of localization at $T=0$, defined by,[19]

$$\Sigma(\infty)=\frac{\langle\sigma_z(\infty)\rangle}{\langle\sigma_z(0)\rangle}. \tag{56}$$

Instead of computing the dynamics of the system, and letting $t\to\infty$, we use Eq. (45) directly, tracing out the bath degrees of freedom, and projecting onto the eigenstates of σ_z to compute Eq. (56). It is simple to show that $\Sigma(\infty)$ is zero until a critical value of the coupling constant α. We will simply borrow the result $\alpha_{\mathrm{critical}}=1$ from previous studies.[16] To find the form of $\Sigma(\infty)$ for coupling constants equal to or greater than $\alpha_{\mathrm{critical}}$, we perform a small polaron transformation on Eq. (54), defined by[19,20]

$$\begin{aligned}&\tilde{H}=UHU^\dagger,\\ &U=\exp\left[\sigma_z\sum_k \frac{G_k}{\omega_k}(b_k^\dagger-b_k)\right].\end{aligned} \tag{57}$$

The transformed Hamiltonian is given by

$$\begin{aligned}&\tilde{H}=\tilde{H}_0+\tilde{H}_{\mathrm{int}},\\ &\tilde{H}_0=\sum_k \omega_k b_k^\dagger b_k,\\ &\tilde{H}_{\mathrm{int}}=-\omega_0(B_+\sigma_+ +B_-\sigma_-),\end{aligned} \tag{58}$$

$$B_{\pm}=\exp\left[\pm 2\sum_k \frac{G_k}{\omega_k}(b_k^{\dagger}-b_k)\right].$$

For Ohmic dissipation, $\langle B_{\pm}\rangle=0$. The (left, right) system states are now degenerate, and the interaction term cannot break the degeneracy. A ground state is found by the choice of the initially prepared state, which now mixes with the higher energy states through $\tilde{H}_{\rm int}$. Choosing the particle to be initially localized in the left well, the (unnormalized) ground state is given by

$$|\psi_g\rangle=|L\rangle|\mathbf{0}\rangle-\omega_0|R\rangle\sum_{\{\mathbf{n}\}\neq\mathbf{0}}\frac{\langle\{\mathbf{n}\}|B_-|\mathbf{0}\rangle}{\Sigma_i n_i\omega_i}|\{\mathbf{n}\}\rangle, \tag{59}$$

where $|\mathbf{0}\rangle$ is the vacuum state of the bath, and $\{\mathbf{n}\}$ denotes a set of phonon occupations of the bath. Applying Eq. (45) and tracing out the bath degrees of freedom, we find,

$$\langle R|\sigma(\infty)|R\rangle=\omega_0^2\sum_{\mathbf{n}\neq\mathbf{0}}\frac{|\langle\{\mathbf{n}\}|B_-|\mathbf{0}\rangle|^2}{(\Sigma_i n_i\omega_i)^2}. \tag{60}$$

An explicit calculation of this term is possible, which gives,

$$\langle R|\sigma(\infty)|R\rangle=\omega_0^2\int_0^{\infty}dz_1\int_0^{\infty}dz_2 e^{-2S}\times\left\{\exp\left[\sum_k\frac{4G_k^2}{\omega_k^2}e^{-\omega_k(z_1+z_2)}-1\right]\right\}, \tag{61}$$

where

$$S=\sum_k\frac{2G_k^2}{\omega_k^2}. \tag{62}$$

Note that the energy denominators have been rewritten in a Laplace transformed form, which introduces the integrals over z_1 and z_2. Using the spectral density for the Ohmic bath, and explicitly calculating the integral, the result, valid to second order in ω_0,

$$\Sigma(\infty)=\frac{1}{1+\left(\frac{\omega_0}{\omega_c}\right)^2\{[(2\alpha-1)(2\alpha-2)]\}^{-1}};\quad \alpha>1, \tag{63}$$

is obtained. This result is identical to the result found in earlier dynamical studies.[16,19] The zero temperature relaxation rate and line shift could be calculated in a similar manner, without recourse to standard dynamical techniques. We also note that the method of Spohn and Dümcke is also ''nondynamical,'' in that it does not proceed through the Liouville equation. This method, although much more complicated, is necessary for obtaining the true long time behavior of the Ohmic spin-boson model.

V. DEPHASING

In the usual second order Redfield approach,[3,4] the relation (5) holds. The interpretation of Eq. (5) is simple. The decay of the coherence variable is caused by both energy relaxation (expressed through T_1) and the (stochastic) modulation of the system energy levels by the bath (expressed through T_2'). The pure dephasing rate is positive, since the bath can only increase the rate of phase randomization in the system states. Generally, at second order, the pure dephasing rate is expressed,[6]

$$\Gamma_{\rm pd}=\int_{-\infty}^{\infty}d\tau\langle\{H_{11}'(\tau)-H_{00}'(\tau)\}\{H_{11}'-H_{00}'\}\rangle, \tag{64}$$

where H_{ii}' is an operator in the bath Hilbert space, obtained by taking the matrix element of the coupling term diagonal in the system state $|i\rangle$ (here $i=0,1$). Notice that the correlation function is composed of operators that determine the instantaneous energy fluctuation induced by the bath on the system, in agreement with the discussion above. The Hamiltonian (7) contains no diagonal terms in the system–bath coupling. Thus, at second order, the dephasing rate can be expressed solely in terms of T_1, i.e., there is no pure dephasing. As discussed in Sec. II, the fourth order dephasing rate deviates from the second order result. If we continue to view pure dephasing processes as those arising from diagonal fluctuations (this is the view expressed by Sevian and Skinner[10]), then Eq. (5) is violated at fourth order. An alternative view is expressed by LBS. They define

$$\frac{1}{T_2'}\equiv\frac{1}{T_2}-\frac{1}{2T_1}$$

as a mathematical means to test the inequality (6). The quantity $(1/T_2')^{(4)}$, expressed in Eq. (43) can become negative for certain parameters in a specific model, signaling the breakdown of the inequality (6).

In order to probe the physical meaning of this result, we rely on the observations made in Secs. II and VI, which dictate that much of the bare rate expressions can be expressed and understood in terms of states that mix system and bath character. We perform a unitary transformation

$$\tilde{H}=U^{\dagger}HU, \tag{65}$$

where

$$U=\exp(S).$$

S is chosen to diagonalize tha Hamiltonian (7) to first order by the condition

$$[H_{\rm TLS}+H_b,S]=-H'. \tag{66}$$

In the context of the Hamiltonian (7), this is referred to as Fröhlich diagonalization.[32] The transformation is given by

$$S=\sum_k\frac{1}{(\omega_k^2-\omega_0^2)}\{\omega_k(b_k-b_k^{\dagger})[h_k\sigma_+ +h_k^*\sigma_-]+\omega_0(b_k+b_k^{\dagger})[h_k\sigma_+ -h_k^*\sigma_-]\}. \tag{67}$$

We will assume for now that the density of states of the phonon bath does not overlap significantly with the energy splitting of the (TLS), so that no divergence problems occur in Eq. (67).[33] We will return to this point later in this section. With the transformation (65), the effective Hamiltonian, $\tilde{H}$, may be written

$$\tilde{H}=H_{\mathrm{TLS}}+H_b+\tilde{H}',$$
$$\tilde{H}'=\sum_{k,k'}\frac{1}{\omega_{k'}^2-\omega_0^2}[A_{k,k'}\omega_{k'}(b_k+b_k^\dagger)(b_{k'}-b_{k'}^\dagger) - B_{k,k'}\omega_0(b_k+b_k^\dagger)(b_{k'}+b_{k'}^\dagger)]|1\rangle\langle 1|, \tag{68}$$

where

$$A_{k,k'}=2i\ \mathrm{Im}(h_k h_{k'}^*),$$
$$B_{k,k'}=2\ \mathrm{Re}(h_k h_{k'}^*).$$

We are now in position to consider the lowest order dynamics of the states

$$|\tilde{\phi}\rangle=U^\dagger|\phi_0\rangle. \tag{69}$$

For instance, the first order ground state may be calculated by expanding $U^\dagger$ and applying the expansion to the ground state of $H_0+H_{\mathrm{TLS}}+H_b$. The state (46) is then recovered.

Before rate expressions can be considered, we must remove the secular terms from the potential $\tilde{V}$. To do this, we place the thermal average of $\tilde{V}$ into H_{TLS}.[18] This will leave an interaction with zero thermal average, thereby eliminating spurious divergences that might occur in the calculation of rate expressions. We find

$$\langle\tilde{V}\rangle=\left\{-2\omega_0\sum_k\frac{|h_k|^2}{(\omega_k^2-\omega_0^2)}\coth\frac{\beta\omega_k}{2}\right\}|1\rangle\langle 1|. \tag{70}$$

If we use the identity

$$\frac{1}{\omega_k^2-\omega_0^2}=\lim_{\eta\to 0}\frac{1}{[\omega_k^2-(\omega_0-i\eta)^2]} =\wp\frac{1}{\omega_k^2-\omega_0^2}-i\frac{\pi}{\omega_0}\delta(\omega_k-\omega_0)$$

to express the diagonal matrix element of $\langle\tilde{V}\rangle$ as

$$\langle\tilde{V}\rangle_{11}=-\frac{\omega_0}{\pi}\wp\int_0^\infty\frac{2\Gamma_1(\omega)}{(\omega^2-\omega_0^2)}\coth\frac{\beta\omega}{2} +2i\Gamma(\omega_0)\coth\frac{\beta\omega_0}{2}. \tag{71}$$

The real part is the second order frequency shift, and the imaginary part is the second order dephasing rate (which is equal to the second order population relaxation rate). Using the notation in Eqs. (30)–(33) and (35), these results are seen to be identical to Eq. (39) and the discussion following Eq. (32), respectively.

We note from the transformed Hamiltonian (68) that the basis of states (69) undergoes only pure dephasing. This is not quite correct, however, since the factorized initial conditions in the basis of H_0 are correlated initial conditions for the states (69). This will also lead to population relaxation at fourth order, although we will not pursue this avenue. We now compute the pure dephasing rate of the states (69) to lowest (fourth) order. We use the Redfield formula (64), with the effective potential

$$\tilde{V}-\langle\tilde{V}\rangle.$$

The result is

$$\Gamma_{\mathrm{pd}}^{(4)}=\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega\left[\frac{(\omega^2+\omega_0^2)}{(\omega^2-\omega_0^2)^2}\hat{C}_1(\omega)\hat{C}_1(-\omega) -\frac{1}{(\omega^2-\omega_0^2)}\hat{C}_2(\omega)\hat{C}_2(-\omega)\right] =\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{d\omega}{(\omega^2-\omega_0^2)}\left\{\omega\frac{\partial}{\partial\omega}[\hat{C}_1(\omega)\hat{C}_1(-\omega)] -\hat{C}_2(\omega)\hat{C}_2(-\omega)\right\}, \tag{72}$$

where we have use the fact that, by assumption, ω_0 does not overlap $\Gamma_1(\omega)$ significantly, so that the integration by parts above is valid. The amazing feature of Eq. (72) is that it is identical in form to the fourth order result (43) for the "pure" dephasing $(1/T_2')^{(4)}$ that was introduced solely as a mathematical means to test the validity of the inequality (6). We can make the following observations:

(1) The fact that Eqs. (72) and (43) agree when ω_0 does not significantly overlap $\Gamma_1(\omega)$ [or more precisely $\hat{C}_1(\omega)\hat{C}_1(-\omega)$] shows that, in these instances, the inequality (6) holds, and $(1/T_2')^{(4)}$ may be interpreted as the pure dephasing of the states (69). This means that, in cases where ω_0 does not significantly overlap with $\Gamma_1(\omega)$, the expression (43) is derivable from the second order formula (64). In these cases, the inequality (6) must hold, *regardless of the form of* $\hat{C}_1(\omega)$ and $\hat{C}_2(\omega)$.

(2) The strange result [the negativity of Eq. (43)] is thus a consequence of a resonance phenomena, wherein the result (72) is not valid. Heuristically, we may view this behavior as a consequence of the lack of stability of the potential (68), which, as a significant number of phonons reach resonance with the TLS, gives rise to "imaginary" modes.

(3) The numerical results of Laird and Skinner, and Laird, Chang, and Skinner support the conclusion of point (1). If we plot the high temperature behavior of $\hat{C}_1(\omega)\hat{C}_1(-\omega)$ (essentially $[\Gamma_1(\omega)^2/\omega^2]$), we see that the negative dephasing occurs *only* when there is significant overlap between ω_0 and $\Gamma_1(\omega)^2/\omega^2$. In Fig. 1 $\Gamma_1^2(\omega)/\omega^2$ is plotted for the "Ohmic–Lorentzian" density of states $(\Gamma_1(\omega)\propto[\lambda\omega/(\lambda^2+\omega^2)])$ for various values of λ and a value of ω_0 equal to one. In Figs. 2 and 3 the same function is plotted for the super-Ohmic density of states $(\Gamma_1(\omega)\propto[\omega^3 e^{-\omega/\omega_c}/\omega_c^3])$ that corresponds to a Debye bath in the deformation potential approximation. A fundamental difference in $\Gamma_1^2(\omega)/\omega^2$ between the two types of spectral functions can be noted. For the Ohmic bath, the overlap of ω_0 and a significant concentration of phonons increases in the large bandwidth limit $(\lambda\to\infty)$, whereas this overlap is reduced in the super-Ohmic cases. This is due to the fact that Ohmic baths have

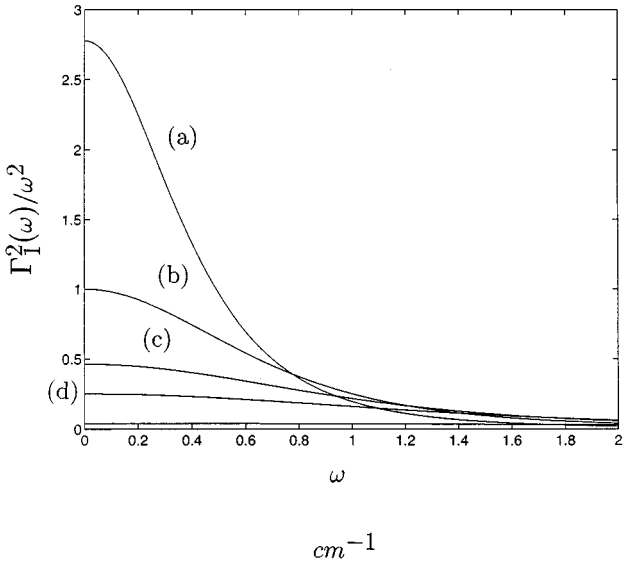

FIG. 1. $\Gamma_1^2(\omega)/\omega^2$ for "Ohmic–Lorentzian" density of states $\Gamma_1(\omega)=[A\lambda\omega/(\omega^2+\lambda^2)]$. The value of A, which has units of frequency, is taken to be 1 cm^{-1}. ω_0 is taken to be 1 cm^{-1}. The values of λ (in units of cm^{-1}) are (a) 0.6, (b) 1, (c) 1.47, (d) 2. For $(\lambda/\omega_0)>1.4679$, $(1/T_2')^{(4)}$ becomes negative.

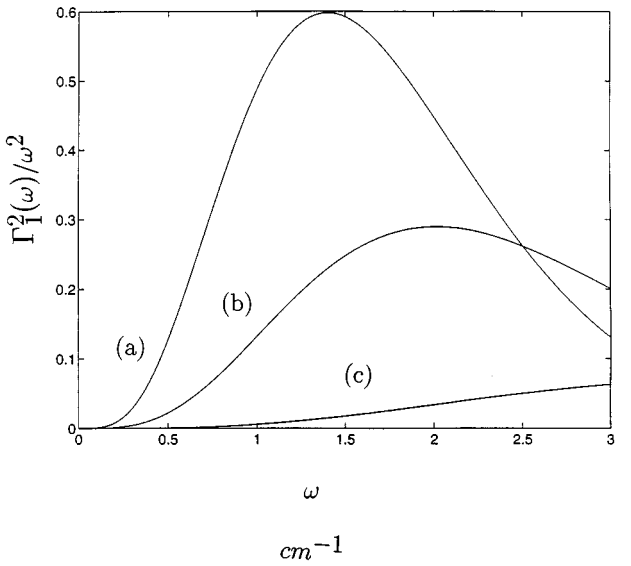

FIG. 3. Same plot as Fig. 2 with the values of ω_c (in units of cm^{-1}) (a) 0.7, (b) 1.006, (c) 2. The function $(1/T_2')^{(4)}$ is negative for $0.218>\omega_c/\omega_0>1.006$.

extensive density of modes at low frequencies, unlike their super-Ohmic counterparts.[16] It is in the large bandwidth limit of the bath that most theories become tractable.[20,34] Furthermore, in most condensed phase (crystal) systems, the TLS energy is ten to one hundred times smaller than the cutoff frequency of the bath. For these reasons, most previous studies have taken $\omega_c \gg \omega_0$.

We may also expect that, for the resonance case in super-Ohmic systems, the method outlined in Sec. II may not be adequate to describe the experimental situation. This is because the Redfield approach neglects the reaction force of the system on the bath.[23,35] To make such a thermodynamically consistent calculation tractable, it is often necessary to assume the bandwidth of the bath is larger than *any time scale of the system*.[35,36] Otherwise, the dynamics become extremely complicated and the interesting dephasing behavior may be hopelessly buried. When the timescale separation exists, we expect that the methods described in Sec. II to be adequate. As we have discussed, for super-Ohmic systems this is precisely the regime where Eq. (6) holds. The question of the effects of the resonance is still open, however we believe that in super-Ohmic systems (which are often the most realistic for condensed phase physical chemistry), the violation of Eq. (6) may be very difficult to detect.

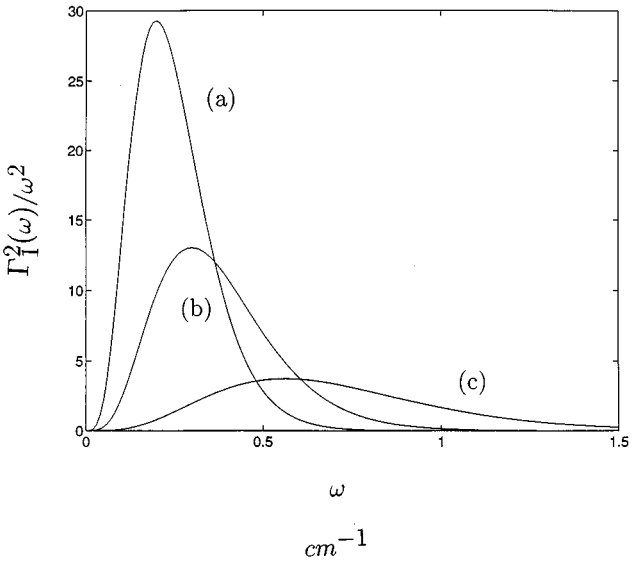

FIG. 2. Same plot for the super-Ohmic density of states $\Gamma_1(\omega) = (B\omega^3/\omega_0^3)e^{-\omega/\omega_0}$. B is taken to be 1 cm^{-1}, ω_0 has the value 1 cm^{-1}, and the values of ω_c (in units of cm^{-1}) are (a) 0.1, (b) 0.15, (c) 0.281.

VI. VARIATIONAL PROCEDURE

We now turn to a different approach to the problem considered by LBS. Our shift in focus is necessitated by the following observations:

(1) The approach of LBS is valid only for a small range of coupling strengths (coupling strengths for which second order perturbation theory is not sufficient to explain TLS dynamics, and sixth order perturbation theory is unnecessary). We would like to have an analytic method that covers a larger range of coupling strengths, and is flexible enough to handle both the "real" and "complex" coupling models.

(2) The interpretation of the physical processes contained in the fourth order theory of LBS is difficult. The interpretation of population relaxation terms is relatively straightforward and is expounded in Sec. III, the Appendix, and further in this section. We have already shown how, for the particular Hamiltonian (7), the "pure dephasing" rate, $1/T_2'$, can be related to the pure dephasing of states that are mixed at first order in perturbation theory. This correspondence, we believe, is strictly valid only for potentials of the

type (10), which allow no pure dephasing at second order. Can higher order dephasing processes be given interpretations akin to the interpretation of their second order counterparts in the case of more general coupling?

Consider the Hamiltonian (7) with a (perhaps more realistic) modified system–bath coupling,[6]

$$H' = |1\rangle H'_{10}\langle 0| + |0\rangle H'_{01}\langle 1| + |1\rangle H'_{11}\langle 1|, \tag{73}$$

where the terms H'_{ij} are bath operators. This type of coupling appears in the stochastic study of Budimir and Skinner. At finite temperature, the Bloch equations will not be valid at fourth order for such a potential. In fact, at equilibrium, it is simple to show

$$\sigma_{10}(\infty) = \mathrm{Tr}_b\langle 1|\exp\{-\beta H\}|0\rangle = \int_0^\beta d\lambda \int_0^\lambda d\gamma e^{\gamma\omega_0}\langle H'_{11}(-i\lambda)H'_{10}(-i\gamma)\rangle, \tag{74}$$

where

$$H'_{ij}(-i\epsilon) = e^{\epsilon H_b}H'_{ij}e^{-\epsilon H_b}. \tag{75}$$

Thus, in the basis of states defined by H_0, the equilibrium reduced density matrix of the system is not diagonal. We could choose a basis of states that makes $\sigma_{10}(\infty)$ vanish, however this seems artificial in light of the fact that even the fourth order calculation is, strictly speaking, a weak coupling calculation, and should be rendered in the eigenstates of H_0.[27] The previous point highlights a difficulty of using the ''bare'' representation even at fourth order. We would like to have a method that incorporates a ''dressed'' basis that allows for clear physical interpretation of the rate processes.

(3) Based on the points (1) and (2), we note that the experimental line shape may, in fact, be given by

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty dt e^{-i\omega t}\langle\tilde{\mu}\tilde{\mu}(t)\rangle, \tag{76}$$

where $\tilde{\mu}$ is the dressed dipole operator. Clearly, as shown in connection with the discussion of dephasing and population relaxation much of the bare relaxation rates at fourth order may be expressed in terms of lower order rate expressions involving states that mix system and bath character. The true test of the correct calculation of the line shape must, in the end, come from experiments.

(4) Lastly, the fourth order theory of LBS provides a testing ground for the ability of variational methods to reproduce the exact, perturbative behavior of a small quantum mechanical system coupled to quantum reservoir.[20,37]

The models studied by LBS consist of a real coupling model [$\Gamma_1(\omega)=\Gamma_2(\omega)$, see Eqs. (31) and (33)], and a complex coupling model [$\Gamma_1(\omega)\equiv\Gamma(\omega)$, $\Gamma_2(\omega)=0$]. The real coupling model is identical to the standard spin-boson model [see Eq. (54)] in a basis of states,

$$|0\rangle = \frac{1}{\sqrt{2}}[|L\rangle + |R\rangle], \quad |1\rangle = \frac{1}{\sqrt{2}}[|L\rangle - |R\rangle]. \tag{77}$$

We employ the variational polaron transformation, utilized earlier in the study of the spin-boson problem,[20]

$$U = \exp\left[-(|1\rangle\langle 0| + |0\rangle\langle 1|)\sum_k \frac{f_k}{\omega_k}(b_k - b_k^+)\right], \tag{78}$$

where $\{f_k\}$ is a set of variational parameters. In the $|0\rangle,|1\rangle$ basis, the transformed Hamiltonian is found to be

$$\tilde{H} = U^+ H U = \tilde{H}_0 + \tilde{V},$$

$$\tilde{H}_0 = \tilde{\omega}_0[|1\rangle\langle 1| - |0\rangle\langle 0|] + H_b,$$

$$\tilde{V} = \tfrac{1}{2}(V_+ + V_-)[|1\rangle\langle 1| - |0\rangle\langle 0|] + (V_z + V_- - V_+)|1\rangle\langle 0| + (V_z + V_+ - V_-)|0\rangle\langle 1|, \tag{79}$$

where

$$\tilde{\omega}_0 = \omega_0 e^{-2\Sigma_k (f_k^2/\omega_k^2)\coth \beta\omega_k/2}, \tag{80}$$

$$V_+ = V_-^* = \frac{\omega_0}{2}\left\{e^{-2\Sigma_k (f_k/\omega_k)(b_k - b_k^+)} - \frac{\tilde{\omega}_0}{\omega_0}\right\}, \tag{81}$$

$$V_z = \sum_k (h_k - f_k)(b_k + b_k^+). \tag{82}$$

We have again identified the renormalized frequency of the system by the removal of the secular term from $\tilde{V}$. As an illustration of the utility of the dressed picture, we note that

$$\tilde{b}_k = b_k + \frac{f_k}{\omega_k}\sigma_x,$$

where σ_x is expressed in the $|0\rangle,|1\rangle$ basis. If we chose f_k to minimize the free energy of the system, then we find the implicit equation for the variational constants,

$$f_k = h_k\left(1 + \frac{\tilde{\omega}_0}{\omega_k}\coth\frac{\beta\omega_k}{2}\tanh\frac{\beta\tilde{\omega}_0}{2}\right)^{-1}. \tag{83}$$

Thus, at zero temperature we find the second order result

$$\langle\tilde{b}_k^\dagger\tilde{b}_k\rangle = \frac{1}{\pi}\int_0^\infty \frac{\Gamma'_1(\omega)}{(\omega+\omega_0)}d\omega, \tag{84}$$

in exact agreement with Eq. (50). Thus the dressed representation is able to account for the number of ''bath'' excitations present at zero temperature.

Next we show that, for the purpose of calculating relaxation rates, a minimization of the energy of the system is more accurate than a minimization of the free energy, *even at finite temperature*. Consider the ''up'' rate constant, calculated from Eq. (79) by the use of the second order Fermi golden rule expression,[3]

$$\Gamma_{0\to 1}=\int_{-\infty}^{\infty}dt e^{i\tilde{\omega}_0 t}\left\langle\left\{V_z(t)+\frac{1}{2}\left[V_+(t)-V_-(t)\right]\right\}\times\left\{V_z+\frac{1}{2}\left[V_--V_+\right]\right\}\right\rangle$$
$$=\int_{-\infty}^{\infty}dt e^{-i\tilde{\omega}_0 t}\left\langle\left\{V_z(t)-\frac{\omega_0}{2}\sinh\Phi(t)\right\}\times\left\{V_z+\frac{\omega_0}{2}\sinh\Phi\right\}\right\rangle, \tag{85}$$

where

$$\Phi=e^{2\Sigma_k(f_k/\omega_k)(b_k-b_k^\dagger)}.$$

We chose the variational constants to minimize the energy of the system, which is the zero temperature limit of Eq. (83),

$$f_k=h_k\left(1+\frac{\tilde{\omega}_0}{\omega_k}\right)^{-1}. \tag{86}$$

Note that in this approximation the frequency shift at second order is given by

$$\Delta\omega_{\rm var}^{(2)}=\omega_0\int_0^\infty d\omega\,\frac{\Gamma_1(\omega)\coth\dfrac{\beta\omega}{2}}{(\omega+\omega_0)^2}, \tag{87}$$

which differs from the exact result Eq. (39) by the form of the energy denominator. This error can be viewed as the failure to incorporate a minimization of the energy in *both* the ground and excited states of the system. An energy minimization of the excited state of the system yields Eq. (86) with a minus sign in the denominator. In fact, if we heuristically replace f_k^2 with $f_k^g f_k^e$, where f_k^g represents a variational constant [equivalent to Eq. (86)] for energy minimization in the ground state, and f_k^e represents a variational constant for energy minimization in the system's excited state, then Eq. (39) would be reproduced exactly at second order, as long as it is understood that the principle part of the sum is to be taken (see Sec. V for a discussion).

Using Eq. (86) in Eq. (85), we calculate terms arising from the lowest order expansion of $\sinh\Phi$, finding

$$\Gamma_{0\to 1}^{[\rm partial]}=\frac{\pi}{2}\left(1+2\frac{\omega_0}{\tilde{\omega}_0}+\frac{\omega_0^2}{\tilde{\omega}_0^2}\right)\times\sum_k|h_k|^2 n(\omega_k)\delta(\omega_k-\tilde{\omega}_0), \tag{88}$$

where "partial" is used to indicate that terms of fourth and higher order involving Φ^{2n+1}, $n\geqslant 1$ arising from the expansion of $\sinh\Phi$ have been omitted. At second order in the coupling we can make the replacement $\omega_0=\tilde{\omega}_0$, and we find

$$\Gamma_{0\to 1}^{(2)}=2\pi\sum_k|h_k|^2 n(\omega_k)\delta(\omega_k-\omega_0)\equiv\hat{C}_1(-\omega_0) \tag{89}$$

in exact agreement with Eq. (32). While we expect this agreement based on the fact that at second order we are essentially using bare states, the result is not obvious, in the sense that it depends on the choice of the variational constant. We conclude that *the minimization of the system's energy is more accurate in the calculation of weak coupling rates than a minimization of the system's free energy*, [which would not reproduce Eq. (32)].

Equation (88) may be expanded to fourth order as

$$\Gamma_{0\to 1}^{[\rm partial],(4)}=-\frac{1}{\omega_0}\hat{C}_1(-\omega_0)\Delta\omega_{\rm var}^{(2)}-\hat{C}_1'(-\omega_0)\Delta\omega_{\rm var}^{(2)}. \tag{90}$$

The label "partial" is now included because we have left out some fourth order terms. Note that this is identical to the first two terms of Eq. (34) where the definition (39) of $\Delta\omega^{(2)}$ has been used [since we are dealing here with the real coupling model, $P_2(\omega)=P_1(\omega)$]. Thus these terms may be viewed as second order type expressions oscillating about the shifted frequency. This gives explicit support to the claim that resumed, dressed expressions will appear in higher order calculations of bare relaxation rates. From Eq. (88) we can find sixth and higher order contributions to the rate constant by simple Taylor expansion of the delta function and the renormalized frequency. Other fourth order terms can be found simply by expanding the $\sinh\Phi$ term to third order and including all cross products in the correlation function. This will contribute terms akin to the mixing of first and third order amplitudes as outlined in the Appendix. Note, however, that these terms cannot be identical to the remaining terms in Eq. (39). This is due to the fact that second order rates calculated from Eq. (76) obey

$$K_{\rm eq}\equiv\frac{\Gamma_{0\to 1}}{\Gamma_{1\to 0}}=e^{-\beta\tilde{\omega}_0}, \tag{91}$$

that is, the equilibrium constant defined by the quotient of the dressed rate constants is given by a Boltzmann factor containing the renormalized frequency. This illustrates precisely why the equilibrium constant of Eq. (91) differs from the equilibrium rate constant defined as the ratio of rates given by Eq. (34) and its "down" rate counterpart at fourth order. The equilibrium constant given by Eq. (91) is a property of the dressed, not the bare, basis.

We now turn to a calculation of the dephasing properties in the dressed basis. In the transformed picture, the pure dephasing rate may be calculated with second order perturbation theory as

$$\Gamma_{\rm pd}=\frac{\omega_0^2}{2}\int_{-\infty}^{\infty}dt\left[\langle\cosh\Phi(t)\cosh\Phi\rangle-\frac{\tilde{\omega}_0^2}{\omega_0^2}\right]$$
$$=\frac{\tilde{\omega}_0^2}{2}\int_{-\infty}^{\infty}[\cosh\xi(t)-1], \tag{92}$$

where

$$\xi(t)=\frac{4}{\pi}\int_{-\infty}^{\infty}d\omega\Gamma_1(\omega)\frac{\left(\cos\omega t\coth\dfrac{\beta\omega}{2}-i\sin\omega t\right)}{(\omega+\tilde{\omega}_0)^2}. \tag{93}$$

Note that the pure dephasing rate is zero at second order, again due to the fact that the second order expansion of the transformed results are really bare results, and should agree with standard second order results in the basis of H_0. At fourth order, we find

$$\Gamma_{\rm pd}^{(4)}=\frac{4\omega_0^2}{\pi}\int_0^\infty d\omega\,\frac{\hat{C}_1(\omega)\hat{C}_1(-\omega)}{(\omega+\omega_0)^4}, \tag{94}$$

where the definition (30) has been used for $\hat{C}_1(\omega)$. For the real coupling model, this expression is identical to Eqs. (43) and (72) except for the denominator [if the integration by parts in Eq. (72) is valid, see Sec. V]. Again, as in the discussion of the renormalized frequency, the two expressions would be identical if, in Eq. (85), we replaced f_k^2 with $f_k^e f_k^g$.

We now discuss how the technique described earlier in this section may be applied to the complex coupling model of (LBS). This model is of importance because it provides a model of dipole with spin-1/2 precessing with Larmor frequency ω_0 around a fixed magnetic field along the z-axis while being perturbed by equal strength but uncorrelated magnetic fields in the two transverse directions.[1,9] In this model, the spectral density $\Gamma_2(\omega)$ is identically zero, that is

$$\Gamma_2(\omega)=\sum_k h_k^2\delta(\omega-\omega_k)=0. \tag{95}$$

In the spin-boson language, our Hamiltonian for this complex coupling model may be written

$$H=-\frac{\omega_0}{2}\sigma_x+\sum_k \omega_k(b_k^\dagger b_k+a_k^\dagger a_k)$$
$$+\sigma_z\sum_k |h_k|(a_k^\dagger+a_k)+\sigma_y\sum_k |h_k|(b_k^\dagger+b_k). \tag{96}$$

We have written the Hamiltonian in the $|L\rangle,|R\rangle$ basis of Eq. (77) to show the similarity with the standard spin-boson Hamiltonian of Eq. (54). We have separated the bath into two independent sets of modes that couple with equal strength to orthogonal system operators. This is precisely the physical situation that gives rise to the condition (95). Note that in this form, the Hamiltonian (96) is *nothing more than the pseudo-Jahn–Teller system*.[38,39] This insight allows us to chose a dressing transformation from an impressive set of methods that have been applied to this and similar problems. As discussed by Alper and Silbey,[39] a transformation of the form (78), coupled with second order perturbation theory (as was applied to the real coupling model) accurately accounts for the energy spectrum of the Hamiltonian (96). By applying the transformation (78) to the Hamiltonian (96), and by treating the two sets of modes as independent, i.e.,

$$[a,b^\dagger]=0$$

for any a and b, we can express the Hamiltonian (96) in the form (79), with the modification

$$V_+=V_-^*=\frac{\omega_0}{2}\left[e^{-2\Sigma_k(f_k/\omega_k)(a_k-a_k^\dagger)}\hat{B}-\frac{\tilde{\omega}_0}{\omega_0}\right],$$

$$\hat{B}=\left[\mathbf{1}_b-\frac{i}{\omega_0}\sum_k |h_k|(b_k^\dagger+b_k)\right]. \tag{97}$$

$\mathbf{1}_b$ is the unit operator for the bath. The expressions for V_z and f_k are unchanged. We find that the pure dephasing for this model

$$\Gamma_{\rm pd}=\frac{\tilde{\omega}_0^2}{2}\int_{-\infty}^\infty dt[\cosh\,\xi(t)-1]$$
$$+2\frac{\tilde{\omega}_0^2}{\omega_0^2}\int_{-\infty}^\infty \hat{C}_1(t)\sinh\,\xi(t)dt. \tag{98}$$

Note that the dephasing rate in the complex coupling model can be expressed as the pure dephasing rate of the real coupling model plus an additional term. When expanded to fourth order, an expression similar to Eqs. (43) and (72) (with $\hat{C}_2(\omega)=0$) is found. In both the real and complex coupling models, the dephasing rate at fourth order is greater than the population relaxation rate, in contrast to results found with the bare perturbation theory. However, when the energy splitting of the system, ω_0, does not overlap with the bath density of states, the results are essentially identical (with the few modifications discussed in this section). We note in passing that the method used to study the complex coupling model may be used to study other physical systems of interest that have the generalized spin-boson form (96).[40]

VII. CONCLUSION

We briefly recap what has been accomplished in this paper. We have used the study of a two level system linearly and off-diagonally coupled to a bath of harmonic oscillators conducted by Laird, Budimir, and Skinner to highlight several aspects of dynamical calculations that transcend the weak coupling limit. We have clarified the origin and meaning of the finite zero temperature population excitation rate, and have shown the relationship between the population transfer constants calculated by LBS and the standard, fourth-order Fermi golden rule expression. The fourth order ''pure'' dephasing expression, introduced by LBS as a purely mathematical entity, has been give a physical meaning. In certain instances, this rate has been shown to be derivable from the second order Redfield expression for pure dephasing, which means that, in these instances, the expression derived for ''pure'' dephasing by LBS must remain positive, rendering $1/T_2\geqslant 1/2T_1$. We have briefly discussed the detection of the violation of the inequality (6). Lastly, we have discussed the relationship between the dynamics of the density matrix calculated in a bare basis (as is done in LBS), and a dressed basis, defined by a suitable canonical transformation of the Hamiltonian. This allows for a better understanding of the frequency shift, and rate constant calculated in (LBS). Lastly, it is shown how a variational method may be use to handle the various models studied by Laird and Skinner. It is shown that, in some instances, the results are very similar to the results of (LBS). The approximate method is easier to implement and more flexible (in terms of extensions

beyond fourth order) than the method of (LBS), but is not able to show a breakdown of the inequality (6).

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APPENDIX

The purpose of this appendix is to calculate the population excitation (''up'') rate constant by standard means, and to show the relationship between this expression and the expression calculated in (LBS).

We begin with the standard definition of the transition rate [equivalent to Eq. (51)],[31]

$$W_{0\to 1}=\lim_{t\to\infty}\frac{d}{dt}\langle|\langle 1|\tilde{U}(t,0)|0\rangle|^2\rangle, \tag{A1}$$

where the tilde refers to the interaction picture. It can be seen immediately that for the particular form of H' given in Eq. (10), the fourth order contributions to Eq. (A1) consist of the mixing of first and third order amplitudes, while the contribution from the mixing of the second order amplitudes vanishes.

Computing $W_{0\to 1}$ to fourth order gives

$$\begin{aligned}W_{0\to 1}=&-\lim_{t\to\infty}\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\{e^{-i\omega_0 t}e^{i\omega_0 t_1}e^{i\omega_0 t_2}e^{-i\omega_0 t_3}\langle\Lambda^\dagger(t_3)\Lambda(t_2)\Lambda^\dagger(t)\Lambda(t_1)\rangle\\&+e^{-i\omega_0 t}e^{i\omega_0 t_1}e^{i\omega_0 t_2}e^{-i\omega_0 t_3}\langle\Lambda^\dagger(t_3)\Lambda(t_1)\Lambda^\dagger(t)\Lambda(t_2)\rangle+e^{-i\omega_0 t}e^{i\omega_0 t_1}e^{-i\omega_0 t_2}e^{i\omega_0 t_3}\langle\Lambda^\dagger(t_2)\Lambda(t_1)\Lambda^\dagger(t)\Lambda(t_3)\rangle\\&+e^{i\omega_0 t}e^{-i\omega_0 t_1}e^{i\omega_0 t_2}e^{-i\omega_0 t_3}\langle\Lambda^\dagger(t_3)\Lambda(t_2)\Lambda^\dagger(t_1)\Lambda(t)\rangle\}.\end{aligned} \tag{A2}$$

Using Wick's theorem[2] to break up the four point correlation functions into products of two point functions, and making the changing of variables $\tau_1=t-t_1,\tau_2=t_1-t_2,\tau_3=t_2-t_3$, we find, (letting $t\to\infty$)

$$\begin{aligned}W_{0\to 1}=&-2\,\mathrm{Re}\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3\{e^{-i\omega_0(\tau_1-\tau_3)}[C_1(\tau_1)C_1^*(\tau_3)+C_2(\tau_2)C_2^*(\tau_1+\tau_2+\tau_3)+C_1^*(\tau_1+\tau_2)C_1^*(\tau_2+\tau_3)\\&+C_1(\tau_1+\tau_2)C_1^*(\tau_2+\tau_3)+C_2^*(\tau_1+\tau_2+\tau_3)C_2(\tau_2)+C_1^*(\tau_1)C_1^*(\tau_3)]+e^{-i\omega_0(\tau_1+\tau_3)}[C_1^*(\tau_2)C_1(\tau_1+\tau_2+\tau_3)\\&+C_2^*(\tau_1+\tau_2)C_2(\tau_2+\tau_3)+C_1(\tau_3)C_1^*(\tau_1)C_1(\tau_1)C_1(\tau_3)+C_2(\tau_1+\tau_2)C_2(\tau_2+\tau_3)+C_1(\tau_1+\tau_2+\tau_3)C_1(\tau_2)]\},\end{aligned} \tag{A3}$$

where the notation of Eq. (28) has been used. The first notable feature of this expression is that part of it diverges as $t\to\infty$. The origin of these divergent terms has been discussed by Zwanzig.[30] In fact, one reason for introducing the ''Van-Hove limit'' ($\lambda^2 t$ constant, $\lambda\to 0$, $t\to\infty$) is to eliminate such terms. These terms arise when a virtual state in the third order amplitude coincides with the initial (real) state from which the transition is made. If we make the restriction that the virtual states are to be distinct from the states physically involved in the transition, then these terms may be neglected.[42] It is interesting to note that the divergent terms have the form

$$-\left(\frac{1}{T_1}\right)^{(2)}\langle|\langle 1|\tilde{U}(t,0)|0\rangle|^2\rangle^{(2)} \tag{A4}$$

as $t\to\infty$. Here, $1/T_1$ is the sum of ''up'' and ''down'' rate constants, and $\langle|\langle 1|\tilde{U}(t,0)|0\rangle|^2\rangle$ is the thermally averaged transition probability for a transition to occur between the ground and excited states of the system.

Even with the removal of the divergent terms, the expression (A3) appears different from the equivalent expression [Eq. (90)] in LBS. If we evaluate Eq. (A3) in frequency space by using the methods outlined in Appendix B of LBS, we find

$$\begin{aligned}W_{0\to 1}=&\frac{1}{2\pi}\{\omega_0^{-1}[P_2(\omega_0)-P_2(-\omega_0)]+\hat{C}_1'(-\omega_0)\\&\times[P_1(\omega_0)-P_1(-\omega_0)]+P_1'(-\omega_0)[\hat{C}_1(\omega_0)\\&-\hat{C}_1(-\omega_0)]-2\hat{C}_1(-\omega_0)P_1'(\omega_0)\end{aligned} \tag{A5}$$

in the notation of Eqs. (29), (30), and (35)–(37). This result is identical to Eq. (34).

We may ask why the rate calculated by the method outlined in Sec. II naturally avoids the divergence problems associated with Eq. (A3). To investigate this, we recast the problem by projecting the Liouville equation onto the system states.[41] We find,

$$\dot{\mathbf{P}}(t)=\mathbf{K}(t)\mathbf{P}(t), \tag{A6}$$

where

$$\mathbf{P}(t)=\begin{bmatrix}\sigma_{00}(t)\\ \sigma_{10}(t)\\ \sigma_{01}(t)\\ \sigma_{11}(t)\end{bmatrix},$$

$$\mathbf{K}(t)=\dot{\mathbf{A}}(t)\mathbf{A}^{-1}(t),$$

$$\mathbf{A}(t)=\begin{bmatrix}G_{0000}(t) & G_{0010}(t) & G_{1000}(t) & G_{1001}(t)\\ G_{0010}(t) & G_{0011}(t) & G_{1010}(t) & G_{1011}(t)\\ G_{0100}(t) & G_{0101}(t) & G_{1100}(t) & G_{1101}(t)\\ G_{0110}(t) & G_{0111}(t) & G_{1110}(t) & G_{1111}(t)\end{bmatrix},$$

and

$$G_{ijkl}(t)=\langle (U^{\dagger})_{ij}(t)U_{kl}(t)\rangle.$$

By noting the form $\mathbf{K}(t)$ must take for the Bloch equations to hold, we find, as $t\rightarrow\infty$

$$\dot{\mathbf{A}}(t)=\mathbf{B}\mathbf{A}(t), \tag{A7}$$

where

$$\mathbf{B}=\begin{pmatrix}-k_{10} & 0 & 0 & k_{01}\\ 0 & -\left\{\frac{1}{T_2}+i(\omega_0+\Delta\omega)\right\} & 0 & 0\\ 0 & 0 & -\left\{\frac{1}{T_2}-i(\omega_0+\Delta\omega)\right\} & 0\\ k_{10} & 0 & 0 & -k_{01}\end{pmatrix}.$$

Note that at orders higher than fourth, the matrix $\mathbf{B}$ must be modified to incorporate the coupling of coherences. From Eq. (A7), we find the implicit equation for the ''up'' rate,

$$k_{10}=\frac{1}{T_1}\langle|\langle 1|\tilde{U}(\infty,0)|0\rangle|^2\rangle+\frac{d}{dt}\langle|\langle 1|\tilde{U}(\infty,0)|0\rangle|^2\rangle. \tag{A8}$$

The noteworthy feature of Eq. (A8) is that the rate explicitly contains terms canceling the divergence associated with unrestricted summation over virtual states.[42] We also note that Eq. (A7) provides a much easier evaluation of the rate expression than the method of LBS since no commutators are involved. In fact, Eqs. (A3) and (A8) show that the standard definition [Eqs. (51) or (A1)] is all that is needed, since the remaining term merely serves to cancel the divergence due to the unrestricted summation over virtual states. We thus could (much more easily) compute $1/T_2$ as

$$\left(\frac{1}{T_2}\right)^{(4)}=\mathrm{Re}\left\{\frac{\dot{G}_{0011}}{G_{0011}}\right\}^{(4)}. \tag{A9}$$

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