Quantum-mechanical derivation of the Bloch equations: Beyond the weak-coupling limit

Brian B. Laird
Institut für Festkörperforschung des Forschungszentrums, Jülich GmbH, Postfach 1913, D-5170 Jülich 1, Germany

Jane Budimir
Department of Chemistry, Columbia University, New York, New York 10027

James L. Skinner[a)]
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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Two nondegenerate quantum levels coupled off-diagonally and linearly to a bath of quantum-mechanical harmonic oscillators are considered. In the weak-coupling limit one finds that the equations of motion for the reduced density-matrix elements separate naturally into two uncoupled pairs of linear equations for the diagonal and off-diagonal elements, which are known as the Bloch equations. The equations for the populations form the simplest two-component master equation, and the rate constant for the relaxation of nonequilibrium population distributions is $1/T_1$, defined as the sum of the "up" and "down" rate constants in the master equation. Detailed balance is satisfied for this master equation in that the ratio of these rate constants is equal to the ratio of the equilibrium populations. The relaxation rate constant for the off-diagonal density-matrix elements is known as $1/T_2$. One finds that this satisfies the well-known relation $1/T_2 = 1/2T_1$. In this paper the weak-coupling limit is transcended by deriving the Bloch equations to fourth order in the coupling. The equations have the same form as in the weak-coupling limit, but the rate constants are calculated to fourth order. For the population-relaxation rate constants this results in an extension to fourth order of Fermi's golden rule. We find that these higher-order rate constants do indeed satisfy detailed balance. Comparing the dephasing and population-relaxation rate constants, we find that in fourth order $1/T_2 \neq 1/2T_1$.

I. INTRODUCTION

The coupling of a quantum-mechanical system to a thermal bath provides a mechanism for the relaxation of the system from its initial state to a state of thermal equilibrium. The understanding of this relaxation is of course very important in many different kinds of time- and frequency-domain spectroscopy. To a good approximation, in many spectroscopic situations one can consider the system to consist of only two relevant quantum states; therefore, it comes as no surprise that the study of the relaxation of such a two-level system (TLS) coupled to an appropriately described bath environment has received much attention over the years.

Consider a generic two-level system in which the ground (excited) state is labeled $|0\rangle$ ($|1\rangle$), and the energy difference between the states is $\hbar\omega_0$. The state of the system at a given time t is completely described by its density matrix,

$$\sigma(t) = \begin{bmatrix} \sigma_{00}(t) & \sigma_{01}(t) \\ \sigma_{10}(t) & \sigma_{11}(t) \end{bmatrix}, \tag{1}$$

where $\sigma_{00}(t)$ and $\sigma_{11}(t)$ are the populations of the ground and excited states, respectively, and the off-diagonal terms are a measure of the phase coherence between the states, and have the relationship $\sigma_{10}(t) = \sigma_{01}(t)^*$.

In the absence of any coupling of the TLS to its environment, the states $|0\rangle$ and $|1\rangle$ are eigenstates of the total Hamiltonian; therefore, the evolution of the density matrix is such that the diagonal terms remain constant and the off-diagonal elements oscillate with a frequency ω_0. When the TLS is energetically coupled to a bath that is in thermal equilibrium, the TLS states will no longer be eigenstates of the total Hamiltonian and the system will evolve toward thermal equilibrium; that is, the diagonal terms of the TLS density matrix will decay to the values dictated by the Boltzmann equilibrium criterion, and the off-diagonal elements will relax to zero (complete incoherence).

Phenomenologically, the simplest reasonable description of the relaxation of a TLS coupled to a bath is one in which the decay of the density-matrix elements to their equilibrium values is exponential. Such a description is provided by the Bloch equations—a coupled set of first-order differential equations for the density-matrix elements:

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

$$\dot{\sigma}_{11}(t) = k_{10}\sigma_{00}(t) - k_{01}\sigma_{11}(t), \tag{3}$$

$$\dot{\sigma}_{10}(t) = -[i(\omega_0 + \Delta\omega) + 1/T_2]\sigma_{10}(t), \tag{4}$$

$$\dot{\sigma}_{01}(t) = [i(\omega_0 + \Delta\omega) - 1/T_2]\sigma_{01}(t), \tag{5}$$

where k_{10} and k_{01} are the "up" and "down" rate constants, respectively, $\Delta\omega$ is the bath-induced shift in the natural frequency of the TLS, and $1/T_2$ is the decay rate constant of the off-diagonal terms. Equivalent equations were introduced by Bloch in his study of the relaxation of nuclear spins.[1] For many TLS/bath systems, the Bloch equations are an excellent phenomenological description of the relaxation to equilibrium, as long as one only considers times large enough so that any initial non-exponential transient behavior in the dy-

[a)] Author to whom correspondence should be addressed.

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namics has subsided.

The first two equations, for the TLS populations, are gain-loss type rate equations, and are the simplest example of the so-called master equation.[2] Observing that the populations of the ground and excited states must relax to their Boltzmann equilibrium values in the limit of infinite time leads to the detailed balance condition:

$$k_{10}/k_{01} = \sigma_{11}^{\mathrm{eq}}/\sigma_{00}^{\mathrm{eq}} \equiv K, \tag{6}$$

where K is the equilibrium constant. If we define $1/T_1$ as the rate of decay to zero of the population deviations from equilibrium, it can be easily seen from the Bloch equations that

$$1/T_1 = k_{01} + k_{10}. \tag{7}$$

Theories of bath-induced TLS relaxation, leading to Eqs. (2)–(5), can be more or less divided into two types. Theories of the first type involve the treatment of the bath degrees of freedom in a purely stochastic way. The Hamiltonian consists of a TLS coupled to one or more stochastic fields that represent the bath, whose nature is defined entirely by the statistical properties (correlation functions) of the stochastic fields. Such a treatment has proven useful in the study of NMR relaxation in liquids.[3–5] A drawback of this approach is that since the bath is not represented by dynamical variables (and the dynamics of the combined system is therefore not treated consistently), the rate constants k_{01} and k_{10} are equal, which from the detailed-balance condition can only be strictly true in the infinite-temperature limit.

In the second type of TLS/bath relaxation theory, the bath degrees of freedom are treated in a fully quantum-mechanical manner.[3–6] The TLS is coupled to a collection of quantum degrees of freedom and the dynamics of the combined system is calculated. The irreversible nature of the relaxation process is obtained by averaging over the initial, assumed thermally equilibrated, bath distribution. This type of approach is appropriate, for example, for describing the relaxation of optical or vibrational excitations in crystals.[7–9] Since in this type of theory the system and bath variables are treated on the same footing, and the temperature is now an explicit parameter, this approach can be used to describe relaxation at finite temperatures, where the up and down transition rates will not be equal.

The great majority of studies of TLS relaxation properties have focused on perturbation calculations that are second order in the TLS/bath coupling. Such calculations show that, to second order, the diagonal and off-diagonal coupling terms (in the basis of the TLS eigenstates) have well-defined and separate roles in the relaxation process. The population relaxation rate, $1/T_1$, is determined completely by the off-diagonal coupling terms. In addition, the off-diagonal coupling makes a contribution to the phase relaxation rate, $1/T_2$, which, in second-order perturbation theory is equal to half the population relaxation rate. The diagonal terms induce fluctuations in the TLS energy-level spacing that lead to a contribution to the phase relaxation rate. As the diagonal terms do not energetically couple the excited and ground states, these terms cannot cause additional population decay.

In light of these second-order results, theorists and spectroscopists have found it convenient to separate the contributions to the total phase relaxation (dephasing) rate in the following manner:[4,8–12]

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2'}. \tag{8}$$

The first term of the right-hand side is, in second order, the contribution from the off-diagonal coupling and is a concomitant to population relaxation. The second term represents the additional dephasing due to the diagonal coupling, and $1/T_2'$ is frequently referred to as the "pure dephasing" rate constant. Interpreted in this way, this additional contribution to the dephasing should necessarily be non-negative, as the fluctuations in the TLS energy-level splitting can only lead to disruption of the phase relationship between the excited and ground states and could not act to enhance it. This leads to an important inequality that is a major result of the second-order theory:

$$1/T_2 \geqslant 1/2T_1. \tag{9}$$

This inequality is used frequently in the analysis and interpretation of spectroscopic experiments and, despite its status as a result correct rigorously only to second order, seems to be accepted as a universally valid physical law.

The first calculations to go beyond second-order perturbation theory involved systems with only diagonal coupling. Kubo showed that, for a TLS linearly coupled to a Gaussian stochastic bath, the second-order results for the dephasing rate are exact.[13] Hsu and Skinner[6] obtained a similar result for a TLS linearly coupled to a bath of quantum harmonic oscillators. For the case of quadratic coupling to a quantum bath, Hsu and Skinner[6,14] showed that the second-order result was not exact and were able to obtain an exact nonperturbative result for the dephasing rate. The same result had also been previously obtained by another method by Osad'ko.[15] Quadratic coupling to a stochastic bath has been studied,[6,16] again yielding an exact non-perturbative solution. However, since diagonal coupling alone cannot alter the population levels of the two states, the population relaxation rate for such models is necessarily zero; therefore, the inequality of Eq. (9) holds trivially to all orders in the coupling.

Recently, Budimir and Skinner[17] performed a fourth-order perturbation-theory calculation to determine the relaxation rate constants of a TLS linearly coupled, both diagonally *and* off-diagonally, to a Gaussian stochastic bath. They showed that in this case, unlike in the case of diagonal coupling alone, the second-order result is not exact. Moreover they showed that in fourth order, the off-diagonal and diagonal fluctuations do not lead to independent contributions to the total dephasing rate as in Eq. (8). In particular, if one uses Eq. (8) as the definition of T_2', they showed that the off-diagonal terms can make a substantial contribution to $1/T_2'$. In fact, it is demonstrated that, due to this off-diagonal contribution, T_2' can actually be negative for certain reasonable values of the parameters that describe the stochastic fields, or in other words, that $T_2 > 2T_1$!

In order to check the validity of the perturbation expansion, and to determine at what point the relaxation to equilibrium is actually exponential, Sevian and Skinner[18] performed a series of computer simulations of this stochastic model. These simulations confirmed the results of Budimir and Skinner, demonstrating that the initial non-Markovian decay was short compared to the total decay time, even for systems that exhibit significant deviations from the inequality of Eq. (9). Sevian and Skinner also discuss some of the implications of this result. Aihara *et al.*[19] have very recently extended the analytic results of Budimir and Skinner to sixth order, and have also shown the equivalence of their results to the frequency-domain continued fraction results of Shibata and Sato,[20] which have recently been rederived with a novel method by Risken *et al.*[21] For a slightly different dichotomic (two-state jump) model of the fluctuations, Reineker *et al.*[22] have also shown that T_2 can be larger than $2T_1$.

As was previously mentioned, one of the major drawbacks of the stochastic-bath model is that it is strictly applicable only at infinite temperature. Therefore it is important to understand if the result that T_2 can be greater than $2T_1$, which has now been demonstrated convincingly for the stochastic model, is an artifact of this implied infinite-temperature limit, or is, in fact, more generally valid. To this end, one would like to generalize this result to finite temperature, which entails a fully quantum-mechanical derivation of the Bloch equations to fourth order in TLS/bath coupling.

There is also a more fundamental reason for providing a derivation of the Bloch equations to higher order in the perturbation: to the best of our knowledge there have been no explicit derivations of the master equation[2,23–26] that lead to tractable expressions for the rate constants to higher than second order in perturbation theory. In fact, at least one statement in the literature suggests that the convolutionless master equation is obtained only in the weak-coupling limit.[23] If one could show that Eqs. (2) and (3) were valid in higher-order perturbation theory, this would provide an example of a master equation valid outside the weak-coupling limit. Moreover, the higher-order expressions for the rate constants would produce an extension of Fermi's Golden Rule.

In this paper we derive generalized Bloch equations (Redfield equations[5]) to fourth order in the system/bath interaction, for a completely quantum-mechanical Hamiltonian involving a TLS coupled linearly and off-diagonally to a bath of harmonic oscillators. We consider only the case of off-diagonal coupling since it is for this case that the stochastic model produces the most interesting results. While this model is by no means the most general model of its type because of the specific form of both the bath and the TLS/bath coupling, its solution nonetheless involves a nontrivial calculation. The derivation of the Bloch equations closely follows the general approach discussed by Budimir and Skinner[17] for the stochastic model. We show that the rate equations for the populations do indeed form a master equation, and that the fourth-order expressions for the rate constants obey the property of detailed balance. As in the stochastic model, we also show that, in general, $T_2 \neq 2T_1$, which is in contrast to the expectation from second-order perturbation theory if there is only off-diagonal coupling. In the penultimate section we discuss the correspondence of our model and results with the "spin-boson" problem.[27,28]

In a companion paper,[29] which follows immediately, we introduce a model for the quantum-mechanical bath and its coupling to the TLS that reduces to the stochastic model in the limit $T \to \infty$. We show that, for some parameters of this model, $T_2 > 2T_1$, even at finite temperature.

II. FORMULATION OF THE PROBLEM

We consider a TLS that is off-diagonally coupled to a harmonic bath. The Hamiltonian for such a system is written as the sum of a TLS Hamiltonian, $H_{\rm TLS}$, a bath Hamiltonian, H_b, and a term, H_1, describing the TLS-bath coupling:

$$H = H_{\rm TLS} + H_b + H_1, \tag{10}$$

where

$$H_{\rm TLS} = \hbar\omega_0 |1\rangle\langle 1|, \tag{11}$$

$$H_b = \sum_k \hbar\omega_k (b_k^\dagger b_k + 1/2), \tag{12}$$

$$H_1 = \delta[\hbar\Lambda|1\rangle\langle 0| + \hbar\Lambda^\dagger|0\rangle\langle 1|], \tag{13}$$

$$\Lambda = \sum_k h_k (b_k^\dagger + b_k). \tag{14}$$

In the above, $\hbar\omega_0$ is the TLS excited-state energy (without loss of generality the ground-state energy has been set to zero), the Hamiltonian for the harmonic bath is a sum over normal modes of frequency ω_k, and $b_k^\dagger$ and b_k are boson creation and annihilation operators, respectively. As shown, Λ is linear in the normal-mode coordinates. The expansion coefficients, h_k, have units of frequency, and can, in general, be complex, although, for reasons of mathematical simplicity that will be clear later, we require that h_k^2 is real, i.e., each h_k is either purely real or purely imaginary. δ is a dimensionless expansion parameter enabling one to keep track of the perturbation order, and can be set equal to one at the end of the calculation if desired.

The dynamics of the total (TLS + bath) density operator, $\rho(t)$, is governed by the Liouville equation

$$\frac{\partial\rho(t)}{\partial t} = -\frac{i}{\hbar}[H,\rho(t)]. \tag{15}$$

Transforming to the interaction representation

$$\tilde{\rho}(t) \equiv e^{iH_0 t/\hbar}\rho(t)e^{-iH_0 t/\hbar}, \tag{16}$$

where H_0 is the unperturbed part of the total Hamiltonian

$$H_0 = H_{\rm TLS} + H_b, \tag{17}$$

leads to the interaction Liouville equation

$$\frac{\partial\tilde{\rho}(t)}{\partial t} = -i\tilde{L}(t)\tilde{\rho}(t), \tag{18}$$

where $\tilde{L}(t)$ is defined by

$$\tilde{L}(t)... \equiv (1/\hbar)[\tilde{H}_1(t),...], \tag{19}$$

$$\tilde{H}_1(t) \equiv e^{iH_0 t/\hbar}H_1 e^{-iH_0 t/\hbar}. \tag{20}$$

From Eqs. (13) and (14) this gives

$$\tilde{H}_1(t) = \delta[\hbar\tilde{\Lambda}(t)|1\rangle\langle 0| + \hbar\tilde{\Lambda}(t)^\dagger|0\rangle\langle 1|], \tag{21}$$

where

$$\tilde{\Lambda}(t) \equiv e^{i\omega_0 t}\Lambda(t), \tag{22}$$

$$\Lambda(t) = e^{iH_bt/\hbar}\Lambda e^{-iH_bt/\hbar}, \quad (23)$$

$$= \sum_k h_k (b_k^\dagger e^{i\omega_k t} + b_k e^{-i\omega_k t}). \quad (24)$$

The formal solution to Eq. (18) is

$$\tilde{\rho}(t) = \tilde{\rho}(0) - i\int_0^t dt_1\, \tilde{L}(t_1)\tilde{\rho}(t_1), \quad (25)$$

which can be iterated to give a perturbation series in $\tilde{L}(t)$ (and thus H_1)

$$\tilde{\rho}(t) = \tilde{\rho}(0) - i\int_0^t dt_1\, \tilde{L}(t_1)\tilde{\rho}(0) - \int_0^t dt_1 \int_0^{t_1} dt_2\, \tilde{L}(t_1)\tilde{L}(t_2)\tilde{\rho}(0) + \dots . \quad (26)$$

Defining a reduced TLS density matrix

$$\tilde{\sigma}(t) \equiv \mathrm{Tr}_b[\tilde{\rho}(t)], \quad (27)$$

where $\mathrm{Tr}_b[\cdots]$ denotes a trace over the bath states, and assuming an initial density matrix that is a product of the unperturbed equilibrium bath density, $\rho_b = e^{-\beta H_b}/\mathrm{Tr}_b[e^{-\beta H_b}]$ ($\beta = 1/kT$), and an arbitrary initial reduced TLS density matrix, $\tilde{\sigma}(0)$:

$$\tilde{\rho}(0) = \rho_b \tilde{\sigma}(0), \quad (28)$$

gives

$$\tilde{\sigma}(t) = \tilde{\sigma}(0) - i\int_0^t dt_1\, \mathrm{Tr}_b[\tilde{L}(t_1)\rho_b]\tilde{\sigma}(0) - \int_0^t dt_1 \int_0^{t_1} dt_2\, \mathrm{Tr}_b[\tilde{L}(t_1)\tilde{L}(t_2)\rho_b]\tilde{\sigma}(0) \times + \cdots . \quad (29)$$

Defining

$$\delta^n M^{(n)}(t) \equiv (-i)^n n! \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \times \mathrm{Tr}_b[\tilde{L}(t_1)\tilde{L}(t_2)\cdots\tilde{L}(t_n)\rho_b], \quad (30)$$

with

$$M^{(0)} \equiv 1, \quad (31)$$

Eq. (29) can now be written

$$\tilde{\sigma}(t) = \Phi(t)\tilde{\sigma}(0), \quad (32)$$

with

$$\Phi(t) \equiv \sum_{n=0}^{\infty} \frac{\delta^{2n}}{(2n)!} M^{(2n)}(t). \quad (33)$$

The sum in the above equation for $\Phi(t)$ is only over the even moments, because only even powers of H_1 are nonzero after the bath trace, since H_1 is linear in the bath coordinates. Taking the time derivative of Eq. (32)

$$\dot{\tilde{\sigma}}(t) = \dot{\Phi}(t)\tilde{\sigma}(0) = \dot{\Phi}(t)\Phi(t)^{-1}\tilde{\sigma}(t), \quad (34)$$

and defining

$$R(t) \equiv \dot{\Phi}(t)\Phi(t)^{-1}, \quad (35)$$

gives the following rate equation for $\tilde{\sigma}(t)$:

$$\dot{\tilde{\sigma}}(t) = R(t)\tilde{\sigma}(t). \quad (36)$$

Note that, since $\tilde{\sigma}(t)$ is a matrix, $R(t)$ is a fourth-rank tensor.

We define

$$R(t) \equiv \sum_{n=1}^{\infty} \delta^{2n} R^{(2n)}(t), \quad (37)$$

where $R^{(2n)}(t)$ is of perturbation order $2n$ in the interaction Hamiltonian H_1. The $R^{(2n)}(t)$ are obtained by explicitly expanding $\dot{\Phi}(t)$ and $\Phi(t)^{-1}$ in Eq. (34), and then collecting terms of like order in δ. This yields

$$R^{(2)}(t) = \tfrac{1}{2}\dot{M}^{(2)}(t), \quad (38)$$

and

$$R^{(4)}(t) = \tfrac{1}{4!}\dot{M}^{(4)}(t) - \tfrac{1}{4}\dot{M}^{(2)}(t)M^{(2)}(t), \quad (39)$$

and we will be content to stop at fourth order. These equations, together with the definition of $M^{(n)}(t)$ [Eq. (30)], give

$$\delta^2 R^{(2)}(t) = -\int_0^t dt_1\, \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_1)\rho_b], \quad (40)$$

and, after rearranging time integrals,

$$\delta^4 R^{(4)}t = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \{\mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_1)\tilde{L}(t_2)\tilde{L}(t_3)\rho_b] - \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_1)\rho_b]\mathrm{Tr}_b[\tilde{L}(t_2)\tilde{L}(t_3)\rho_b] - \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_2)\rho_b]\mathrm{Tr}_b[\tilde{L}(t_1)\tilde{L}(t_3)\rho_b] - \mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_3)\rho_b]\mathrm{Tr}_b[\tilde{L}(t_1)\tilde{L}(t_2)\rho_b]\}. \quad (41)$$

From Eqs. (40) and (41) we see that the integrands in the $R^{(n)}(t)$ have the form of ordered cumulants,[30,31] which obey the cluster property such that whenever the difference between any two time arguments becomes much greater than the correlation time, τ_c, of the double-time correlation function, to be defined below, the cumulant approaches zero. This property ensures that the integrands of the $R^{(n)}(t)$ are only non-zero inside a finite region of the integration volume of order τ_c^{n-1}. Thus, the limit $t \to \infty$ is well defined, and in this limit each $R^{(n)}(t)$ approaches a constant tetradic, except for possible oscillatory factors due to the interaction representation. From a second-order calculation we anticipate a structure of the Redfield form:[5]

$$\dot{\tilde{\sigma}}_{\alpha\alpha'}(t) = \sum_{\beta\beta'} e^{i(\alpha-\alpha'-\beta+\beta')\omega_0 t} R_{\alpha\alpha'\beta\beta'}\tilde{\sigma}_{\beta\beta'}(t), \quad (42)$$

where α, α', β and $\beta' \in \{0,1\}$, and $R_{\alpha\alpha'\beta\beta'}$ are constants. Therefore, these constants, if they exist, are given by

$$R_{\alpha\alpha'\beta\beta'} \equiv \lim_{t\to\infty} e^{-i(\alpha-\alpha'-\beta+\beta')\omega_0 t} \times \langle\alpha|\{R(t)|\beta\rangle\langle\beta'|\}|\alpha'\rangle. \tag{43}$$

Because H_1 is both off-diagonal in the TLS states and linear in the bath coordinates, a similar argument to that presented for the stochastic model[17] shows that $R_{\alpha\alpha'\beta\beta'} = 0$ if $\alpha + \alpha' + \beta + \beta'$ is odd, and thus, upon transformation back to the non-rotating frame, Eq. (42) yields two pairs of coupled equations

$$\dot{\sigma}_{00}(t) = R_{0000}\sigma_{00}(t) + R_{0011}\sigma_{11}(t), \tag{44}$$

$$\dot{\sigma}_{11}(t) = R_{1100}\sigma_{00}(t) + R_{1111}\sigma_{11}(t), \tag{45}$$

and

$$\dot{\sigma}_{10}(t) = (-i\omega_0 + R_{1010})\sigma_{10}(t) + R_{1001}\sigma_{01}(t), \tag{46}$$

$$\dot{\sigma}_{01}(t) = (i\omega_0 + R_{0101})\sigma_{01}(t) + R_{0110}\sigma_{10}(t). \tag{47}$$

The first pair of equations, for the state probabilities, can be simplified by using the probability conservation requirement that

$$\dot{\sigma}_{00}(t) + \dot{\sigma}_{11}(t) = 0, \tag{48}$$

leading to the relations $R_{0000} = -R_{1100}$ and $R_{1111} = -R_{0011}$, which can also be verified explicitly, at least to fourth order in δ. Defining

$$k_{10} = -R_{0000}, \tag{49}$$

$$k_{01} = -R_{1111}, \tag{50}$$

one then obtains the coupled rate Eqs. (2) and (3). Furthermore, defining

$$k_{10} = \sum_{n=1}^{\infty} \delta^{2n} k_{10}^{(2n)} \tag{51}$$

(and a similar equation for k_{01}) one can then calculate the second- and fourth-order contributions to the rate constants from Eqs. (37), (40), (41), and (43).

For the off-diagonal density matrix element pair, Eqs. (46) and (47), using $\sigma_{01}(t) = \sigma_{10}(t)^*$, it must be true that $R_{0101} = R^*_{1010}$, and $R_{0110} = R^*_{1001}$. (This can also be verified explicitly, at least to fourth order.) The term involving R_{1001} in Eq. (46) is a coupling between the two off-diagonal elements of the reduced density matrix, and is usually ignored. The traditional rationale for this neglect (known as the rotating wave approximation) is that, to zeroth-order, $\sigma_{10}(t)$ and $\dot{\sigma}_{10}(t)$ both oscillate like $e^{-i\omega_0 t}$, whereas $\sigma_{01}(t)$ oscillates like $e^{+i\omega_0 t}$. If ω_0 is sufficiently large, the fact that $\sigma_{10}(t)$ oscillates in concert with $\dot{\sigma}_{10}(t)$ makes it a much more efficient driving force in Eq. (46) than $\sigma_{01}(t)$. If these coupling terms are ignored, then one recovers the Bloch Eqs. (4) and (5), if one identifies

$$1/T_2 = -\mathrm{Re}\{R_{1010}\}, \tag{52}$$

$$\Delta\omega = -\mathrm{Im}\{R_{1010}\}. \tag{53}$$

Perhaps a better estimate of the effect of this coupling term is obtained by diagonalizing the coupled system of linear differential equations formed by Eqs. (46) and (47). This is performed in Appendix A. Associating the real and imaginary parts of the eigenvalues with $1/T_2$ and $\omega_0 + \Delta\omega$, respectively, we obtain

$$1/T_2 = -\mathrm{Re}\{R_{1010}\}, \tag{54}$$

$$\Delta\omega = (\omega_0 - \mathrm{Im}\{R_{1010}\}) \times \sqrt{1 - \frac{|R_{1001}|^2}{(\omega_0 - \mathrm{Im}\{R_{1010}\})^2}} - \omega_0. \tag{55}$$

Comparing Eqs. (53) and (55), we conclude that in general the coupling terms in Eqs. (46) and (47) cannot be neglected. [When $|R_{1001}| \ll (\omega_0 - \mathrm{Im}\{R_{1010}\})$, which is the case in the weak-coupling limit, then one indeed recovers $\Delta\omega = -\mathrm{Im}\{R_{1010}\}$, showing that in this limit one can neglect the coupling.] Nevertheless, we see that even if the coupling term is retained, $1/T_2$ is still simply $-\mathrm{Re}\{R_{1010}\}$. Finally, by defining

$$\frac{1}{T_2} = \sum_{n=1}^{\infty} \delta^{2n} \left(\frac{1}{T_2}\right)^{(2n)}, \tag{56}$$

$$\Delta\omega = \sum_{n=1}^{\infty} \delta^{2n} \Delta\omega^{(2n)}, \tag{57}$$

one can obtain expressions up to fourth order for $1/T_2$ and $\Delta\omega$.

III. POPULATION RELAXATION—THE MASTER EQUATION

The preceding section shows how, in principle, the asymptotic form of the equations of motion for the reduced density matrix elements is given by two uncoupled pairs of coupled equations, to arbitrarily high order in the interaction Hamiltonian H_1. In this section we focus on the two coupled equations for the level populations, which, as mentioned in the introduction, form the simplest possible two-component master equation. In subsection A we begin by calculating the "up" and "down" rate constants to second order in δ, which is equivalent to Fermi's Golden Rule. In subsection B we calculate k_{01} and k_{10} to fourth order in δ, yielding new expressions for these rate constants. In subsection C we show that the principle of detailed balance is satisfied by the master equation with these fourth-order rate constants, as long as the equilibrium constant is calculated to second order in δ.

A. Second-order calculation of the rate constants

From Eqs. (37), (40), (43), (49), and (51) we have

$$k_{10}^{(2)} = -\lim_{t\to\infty} R_{0000}^{(2)}(t), \tag{58}$$

$$= \lim_{t\to\infty} \delta^{-2} \int_0^t dt_1 \langle 0|\{\mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_1)\rho_b]|0\rangle\langle 0|\}|0\rangle. \tag{59}$$

Using the definition of $\tilde{L}(t)$ and $\tilde{H}_1(t)$ [Eqs. (19) and (21)] gives

$$k_{10}^{(2)} = \lim_{t\to\infty} \int_0^t dt_1 \,\mathrm{Tr}_b[\tilde{\Lambda}(t)^\dagger\tilde{\Lambda}(t_1)\rho_b + \rho_b\tilde{\Lambda}(t_1)^\dagger\tilde{\Lambda}(t)]. \tag{60}$$

Using the fact that a trace is invariant to cyclic permutations of its operator arguments, and defining a (non-time-ordered) bath correlation function by

$$C_1(t-t') = \mathrm{Tr}_b[\rho_b\Lambda^\dagger(t)\Lambda(t')] \tag{61}$$

(below we show explicitly that C_1 is a function only of the difference of the time arguments) gives

$$k_{10}^{(2)} = \lim_{t\to\infty} 2\,\mathrm{Re}\left\{\int_0^t dt_1\, e^{-i\omega_0(t-t_1)} C_1(t-t_1)\right\}. \quad (62)$$

Making the variable change, $\tau = t - t_1$ and taking the $t\to\infty$ limit gives

$$k_{10}^{(2)} = 2\mathrm{Re}\left\{\int_0^\infty d\tau\, e^{-i\omega_0\tau} C_1(\tau)\right\}. \quad (63)$$

We will find it useful to work with the spectral representation of the correlation function. To this end, defining

$$\hat{C}_1(\omega_0) = \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} C_1(\tau), \quad (64)$$

so that

$$C_1(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega\tau}\hat{C}_1(\omega), \quad (65)$$

allows us to write

$$k_{10}^{(2)} = \lim_{\epsilon\to 0}\frac{1}{\pi}\mathrm{Re}\left\{\int_{-\infty}^{\infty} d\omega\, \hat{C}_1(\omega)\int_0^\infty d\tau\, e^{-i(\omega+\omega_0)\tau} e^{-\epsilon\tau}\right\}, \quad (66)$$

where we have added a convergence factor. In Appendix B we discuss at some length how to deal with the time integral in the above, since in what follows several subtleties arise. For the present purposes, however, the situation is quite straightforward and we simply use the relation that

$$\int_0^\infty dt\, e^{-i(x-x_0)t} e^{-\epsilon t} = \pi\mathscr{D}(x-x_0) - i\mathscr{P}(x-x_0), \quad (67)$$

where $\mathscr{D}(x-x_0)$ is a generalized function such that $\lim_{\epsilon\to 0}\mathscr{D}(x-x_0) = \delta(x-x_0)$, the Dirac delta function, and $\mathscr{P}(x-x_0)$ is a generalized function defined by its action under an integral sign:

$$\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\, f(x)\mathscr{P}(x-x_0) = P\int_{-\infty}^{\infty} dx \frac{f(x)}{x-x_0}, \quad (68)$$

where $f(x)$ is integrable on $(-\infty,\infty)$ and P denotes the usual Cauchy principal value. Since, as we will see below, $\hat{C}_1(\omega)$ is real, this gives

$$k_{10}^{(2)} = \hat{C}_1(-\omega_0). \quad (69)$$

From Eqs. (24) and (61), we can explicitly write

$$C_1(t-t') = \sum_k |h_k|^2\{[n(\omega_k)+1]e^{-i\omega_k(t-t')} + n(\omega_k)e^{i\omega_k(t-t')}\}, \quad (70)$$

where $n(\omega)$ is the thermal occupation number for bosons of frequency ω

$$n(\omega) = (e^{\beta\hbar\omega}-1)^{-1}. \quad (71)$$

Using Eq. (64) and the integral representation of the delta function, yields

$$\hat{C}_1(\omega) = 2\pi\sum_k |h_k|^2\{[n(\omega_k)+1]\delta(\omega-\omega_k) + n(\omega_k)\delta(\omega+\omega_k)\}, \quad (72)$$

$$= 2\{\Gamma_1(\omega)[n(\omega)+1] + \Gamma_1(-\omega)n(-\omega)\}, \quad (73)$$

where $\Gamma_1(\omega)$ is a weighted density of states, having dimensions of frequency, and is defined as follows:

$$\Gamma_1(\omega) \equiv \pi\sum_k |h_k|^2\delta(\omega-\omega_k). \quad (74)$$

Since all the ω_k are non-negative, $\Gamma_1(\omega)$ is zero for $\omega<0$. Therefore Eq. (69) becomes

$$k_{10}^{(2)} = 2\Gamma_1(\omega_0)n(\omega_0). \quad (75)$$

This is the standard second-order perturbation theory result for the transition rate, which can be obtained easily from Fermi's Golden Rule.[7] Since the rate is proportional to the thermal occupation number of the vibrational modes with frequency ω_0, the "up" rate constant $k_{10}^{(2)}$ is interpreted as the absorption (destruction) of one vibrational quantum of frequency ω_0. Note that the $\lim_{T\to 0} k_{10}^{(2)} = 0$.

Once an expression for $k_{10}^{(2n)}$ is obtained for a given order in terms of the correlation function, the corresponding expression for $k_{01}^{(2n)}$ can be written down by inspection by noting that the roles of the ground and excited states are reversed upon $\omega_0\to -\omega_0$ and $\Lambda\to\Lambda^+$. However, it is easy to see that

$$\mathrm{Tr}_b[\rho_b\Lambda^+(t)\Lambda(t')] = \mathrm{Tr}_b[\rho_b\Lambda(t)\Lambda^+(t')], \quad (76)$$

and so this latter change has no consequence. Therefore we have simply

$$k_{01}^{(2)} = \hat{C}_1(\omega_0), \quad (77)$$

$$= 2\Gamma_1(\omega_0)[n(\omega_0)+1]. \quad (78)$$

The factor $n(\omega_0)+1$ signifies that the transition occurs by the emission (creation) of one vibrational quantum. Note that $\lim_{T\to 0} k_{01}^{(2)} \neq 0$, corresponding to "spontaneous emission."

The total population-decay rate constant, $1/T_1 = k_{01} + k_{10}$, can be expanded as

$$\frac{1}{T_1} = \sum_{n=1}^{\infty}\delta^{2n}\left(\frac{1}{T_1}\right)^{(2n)}. \quad (79)$$

From the above we have simply

$$\begin{aligned}(1/T_1)^{(2)} &= \hat{C}_1(\omega_0) + \hat{C}_1(-\omega_0),\\ &= 2\Gamma_1(\omega_0)[2n(\omega_0)+1],\\ &= 2\Gamma_1(\omega_0)\coth(\beta\hbar\omega_0/2).\end{aligned} \quad (80)$$

B. Fourth-order calculation of the rate constants

As one would expect, calculation of the fourth-order rate constants is much more involved than that of the second-order terms. We start with $k_{10}^{(4)}$. From Eqs. (37), (43), (49), and (51), we have

$$k_{10}^{(4)} = -\lim_{t\to\infty} R_{0000}^{(4)}(t). \quad (81)$$

Equation (41) gives an expression for the fourth-order term of the tetradic operator $R(t)$ in terms of integrals over traces of various products of the interaction Liouville operator. By taking the (0000) tensor element of $R^{(4)}(t)$ [see Eq. (43)]

and performing all the necessary commutations as indicated by the definition of the operator $\tilde{L}(t)$, Eqs. (19) and (21) (and paying strict attention to the operator orders since the Λ's do not commute), an expression is obtained that involves integrals over two types of terms. The first type of term consists of a product of two-time correlation functions, for example,

$$\mathrm{Tr}_b[\rho_b \Lambda^\dagger(t)\Lambda(t_2)]\mathrm{Tr}_b[\rho_b \Lambda^\dagger(t_3)\Lambda(t_4)]. \tag{82}$$

The second type of term is a single four-time correlation function and a typical such term is

$$\mathrm{Tr}_b[\rho_b \Lambda^\dagger(t)\Lambda(t_2)\Lambda^\dagger(t_3)\Lambda(t_4)]. \tag{83}$$

This type of term can be broken down into products of two-point functions by the use of Wick's theorem.[32] Simply stated for the present application, if $A(t_1)$, $B(t_2)$, $C(t_3)$, and $D(t_4)$ are linear combinations of boson creation and annihilation operators in the interaction representation, then

$$\begin{aligned}\mathrm{Tr}_b[\rho_b A(t_1)B(t_2)C(t_3)D(t_4)] &= \mathrm{Tr}_b[\rho_b A(t_1)B(t_2)]\mathrm{Tr}_b[\rho_b C(t_3)D(t_4)] \\ &\quad + \mathrm{Tr}_b[\rho_b A(t_1)C(t_3)]\mathrm{Tr}_b[\rho_b B(t_2)D(t_4)] \\ &\quad + \mathrm{Tr}_b[\rho_b A(t_1)D(t_4)]\mathrm{Tr}_b[\rho_b B(t_2)C(t_3)].\end{aligned} \tag{84}$$

After this factorization, a number of terms in $R^{(4)}_{0000}(t)$ cancel, leaving ten terms involving $C_1(t)$ [see Eq. (61)] and a new correlation function

$$C_2(t-t')\equiv\mathrm{Tr}_b[\rho_b\Lambda(t)\Lambda(t')], \tag{85}$$

with Fourier transform

$$\hat{C}_2(\omega)=2\{\Gamma_2(\omega)[n(\omega)+1]+\Gamma_2(-\omega)n(-\omega)\}, \tag{86}$$

where $\Gamma_2(\omega)$ is another weighted density of states, defined as:

$$\Gamma_2(\omega)\equiv\pi\sum_k h_k^2\delta(\omega-\omega_k). \tag{87}$$

Note that since by assumption h_k^2 is real, this implies that

$$\mathrm{Tr}_b[\rho_b\Lambda(t)\Lambda(t')]=\mathrm{Tr}_b[\rho_b\Lambda^\dagger(t)\Lambda^\dagger(t')], \tag{88}$$

and also that $\hat{C}_2(\omega)$ is real. Since $\hat{C}_1(\omega)$ is also real, we have [from Eq. (65)]

$$C_i(t)=C_i^*(-t), \tag{89}$$

for $i=1$ or 2. Upon changing variables to "relative" times, $\tau_1=t-t_1$, $\tau_2=t_1-t_2$, $\tau_3=t_2-t_3$, and taking the limit $t\to\infty$, one obtains

$$\begin{aligned}k^{(4)}_{10} = -2\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3\,\mathrm{Re}\{&C_2^*(\tau_1+\tau_2+\tau_3)C_2(\tau_2)e^{-i\omega_0(\tau_1-\tau_3)}+C_2^*(\tau_1+\tau_2+\tau_3)C_2^*(\tau_2)e^{-i\omega_0(\tau_1-\tau_3)}\\ &+C_2(\tau_1+\tau_2)C_2(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+\tau_3)}+C_2^*(\tau_1+\tau_2)C_2(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+\tau_3)}\\ &+C_1(\tau_1+\tau_2+\tau_3)C_1(\tau_2)e^{-i\omega_0(\tau_1+\tau_3)}-C_1^*(\tau_1+\tau_2+\tau_3)C_1^*(\tau_2)e^{-i\omega_0(\tau_1+\tau_3)}\\ &-C_1(\tau_1+\tau_2)C_1(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}-C_1^*(\tau_1+\tau_2)C_1(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}\\ &-C_1(\tau_1+\tau_2+\tau_3)C_1(\tau_2)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}-C_1^*(\tau_1+\tau_2+\tau_3)C_1(\tau_2)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}\}.\end{aligned} \tag{90}$$

The preceding expression for the "up" rate constant is very cumbersome. As mentioned in the course of the second-order rate-constant calculations, the spectral representations of the correlation functions are more convenient than the real-time functions in Eq. (90). Obtaining a tractable expression in terms of $\hat{C}_1(\omega)$ and $\hat{C}_2(\omega)$ is tricky, but possible. Each of the time integrals becomes the sum of two generalized functions, and products of these generalized functions are quite delicate. In Appendix B we derive several useful identities for these products. Therefore, with some care, the above expression can be evaluated on a term-by-term basis. As an illustration, the evaluation of one term of Eq. (90) is shown in detail in Appendix C. Once each term is evaluated and these results are combined and simplified, a surprisingly simple relation emerges:

$$\begin{aligned}k^{(4)}_{10}=(1/2\pi)\{&\omega_0^{-1}\hat{C}_2(-\omega_0)[P_2(\omega_0)-P_2(-\omega_0)]\\ &+\hat{C}_1'(-\omega_0)[P_1(\omega_0)-P_1(-\omega_0)]+P_1'(-\omega_0)\\ &\times[\hat{C}_1(\omega_0)-\hat{C}_1(-\omega_0)]-2\hat{C}_1(-\omega_0)P_1'(\omega_0)\},\end{aligned} \tag{91}$$

where

$$P_i(\omega)=P\int_{-\infty}^{\infty}d\omega'\frac{\hat{C}_i(\omega')}{\omega'-\omega}, \tag{92}$$

$$\hat{C}_i'(\omega)=\frac{\partial\hat{C}_i(\omega)}{\partial\omega}, \tag{93}$$

$$P_i'(\omega)=\frac{\partial P_i(\omega)}{\partial\omega}, \tag{94}$$

$$=P\int_{-\infty}^{\infty}d\omega'\frac{\hat{C}_i'(\omega')}{\omega'-\omega}, \tag{95}$$

and where the last line comes from integrating by parts (see Appendix B).

An explicit expression for $k^{(4)}_{10}$ in terms of $\Gamma_i(\omega)$ and T is obtained by substituting Eqs. (73) and (86) into the above. One feature that becomes immediately clear is that, unlike the second-order rate constants, one cannot interpret $k^{(4)}_{10}$ in terms of the absorption and/or emission of vibrational quanta. In particular, it is interesting to examine the low-temperature limit of $k^{(4)}_{10}$—one finds that

$$\lim_{T\to0}k^{(4)}_{10}=\frac{2\Gamma_1(\omega_0)}{\pi}\int_0^\infty d\omega\frac{\Gamma_1'(\omega)}{\omega+\omega_0}. \tag{96}$$

Thus the zero-temperature up rate constant is nonzero! This strange result must be due to the strong coupling of the TLS and bath degrees of freedom and the concomitant mixing of the nature of these states.

The above expression for $k_{10}^{(4)}$ can be converted by inspection to an expression for $k_{01}^{(4)}$ by letting $\omega_0 \to -\omega_0$:

$$k_{01}^{(4)} = (1/2\pi)\{\omega_0^{-1}\hat{C}_2(\omega_0)[P_2(\omega_0) - P_2(-\omega_0)] + \hat{C}_1'(\omega_0)[P_1(-\omega_0) - P_1(\omega_0)] + P_1'(\omega_0) \times [\hat{C}_1(-\omega_0) - \hat{C}_1(\omega_0)] - 2\hat{C}_1(\omega_0)P_1'(-\omega_0)\}. \quad (97)$$

The fourth-order population decay rate, $(1/T_1)^{(4)} = k_{10}^{(4)} + k_{01}^{(4)}$, is

$$(1/T_1)^{(4)} = (1/2\pi)\{\omega_0^{-1}[\hat{C}_2(\omega_0) + \hat{C}_2(-\omega_0)][P_2(\omega_0) - P_2(-\omega_0)] - [\hat{C}_1'(\omega_0) - \hat{C}_1'(-\omega_0)] \times [P_1(\omega_0) - P_1(-\omega_0)] - [\hat{C}_1(\omega_0) + \hat{C}_1(-\omega_0)][P_1'(\omega_0) + P_1'(-\omega_0)]\}. \quad (98)$$

C. Confirmation of detailed balance for fourth-order rate constants

Any master equation of the form of Eqs. (2) and (3) must obey the property of detailed balance of Eq. (6). In the usual derivation of the master equation, each of the rate constants is second order in the perturbation, and so their quotient is zeroth order, implying that this quotient is simply the zeroth-order equilibrium constant. When the rate constants are calculated to fourth order, their quotient has a term second order in δ. To verify detailed balance, then, the equilibrium constant must be calculated to second order in δ as well.

To begin, we write

$$K = \frac{\sigma_{11}^{\text{eq}}}{\sigma_{00}^{\text{eq}}} = \frac{\text{Tr}_b[\langle 1|e^{-\beta H}|1\rangle]}{\text{Tr}_b[\langle 0|e^{-\beta H}|0\rangle]} = \frac{K_{11}}{K_{00}}, \quad (99)$$

where

$$K_{ii} \equiv \frac{\text{Tr}_b[\langle i|e^{-\beta H}|i\rangle]}{\text{Tr}_b[e^{-\beta H_b}]}, \quad (100)$$

which can be expanded in δ as

$$K_{ii} = K_{ii}^{(0)} + \delta^2 K_{ii}^{(2)} + \cdots. \quad (101)$$

Note that only even powers of δ occur because H_1 is off-diagonal in the TLS states. Writing

$$K = K^{(0)} + \delta^2 K^{(2)} + \cdots, \quad (102)$$

we see that

$$K^{(0)} = \frac{K_{11}^{(0)}}{K_{00}^{(0)}}, \quad K^{(2)} = \frac{K_{11}^{(2)}}{K_{00}^{(0)}} - \frac{K_{00}^{(2)}K_{11}^{(0)}}{K_{00}^{(0)2}}. \quad (103)$$

To calculate $K_{ii}^{(2n)}$, a perturbation expansion of the operator $e^{-\beta H}$ is needed. To this end we write

$$e^{-\beta H} = e^{-\beta(H_0 + H_1)} = e^{-\beta H_0}\left(1 - \int_0^\beta d\lambda\, e^{\lambda H_0} H_1 e^{-\lambda(H_0 + H_1)}\right), \quad (104)$$

which is a standard operator identity that is easily proven by multiplying both sides by $e^{\beta H_0}$ and differentiating with respect to β. Iteration of this identity gives the perturbation series:

$$e^{-\beta H} = e^{-\beta H_0}\left(1 - \int_0^\beta d\lambda\, e^{\lambda H_0} H_1 e^{-\lambda H_0} + \int_0^\beta d\lambda \int_0^\lambda d\gamma\, e^{\lambda H_0} H_1 e^{-\lambda H_0} e^{\gamma H_0} H_1 e^{-\gamma H_0} + \cdots\right). \quad (105)$$

The first term of this series trivially gives

$$K_{00}^{(0)} = 1, \quad K_{11}^{(0)} = e^{-\beta\hbar\omega_0}, \quad (106)$$

and so that therefore

$$K^{(0)} = e^{-\beta\hbar\omega_0}. \quad (107)$$

From the third term, a change of integration variables gives

$$K_{00}^{(2)} = \hbar^2 \int_0^\beta d\lambda \int_0^\lambda d\tau\, e^{-\hbar\omega_0\tau} C_1(-i\hbar\tau), \quad (108)$$

$$K_{11}^{(2)} = \hbar^2 e^{-\beta\hbar\omega_0} \int_0^\beta d\lambda \int_0^\lambda d\tau\, e^{\hbar\omega_0\tau} C_1(-i\hbar\tau). \quad (109)$$

These expressions for $K_{00}^{(0)}$, $K_{11}^{(0)}$, $K_{00}^{(2)}$ and $K_{11}^{(2)}$, together with Eq. (103), yield

$$K^{(2)} = 2\hbar^2 e^{-\beta\hbar\omega_0} \int_0^\beta d\lambda \int_0^\lambda d\tau \sinh(\hbar\omega_0\tau) C_1(-i\hbar\tau). \quad (110)$$

Using Eq. (65) and performing the λ and τ integrations, gives

$$K^{(2)} = \frac{e^{-\beta\hbar\omega_0}}{2\pi} \int_{-\infty}^{\infty} d\omega\, \hat{C}_1(\omega) \times \left(\frac{e^{-\beta\hbar(\omega - \omega_0)} - 1 + \beta\hbar(\omega - \omega_0)}{(\omega - \omega_0)^2} - \frac{e^{-\beta\hbar(\omega + \omega_0)} - 1 + \beta\hbar(\omega + \omega_0)}{(\omega + \omega_0)^2}\right). \quad (111)$$

In order to verify detailed balance, we now need to compare the expansion for K term-by-term with the expansion for k_{10}/k_{01}:

$$\frac{k_{10}}{k_{01}} = \left(\frac{k_{10}}{k_{01}}\right)^{(0)} + \delta^2\left(\frac{k_{10}}{k_{01}}\right)^{(2)} + \cdots, \quad (112)$$

$$\left(\frac{k_{10}}{k_{01}}\right)^{(0)} = \frac{k_{10}^{(2)}}{k_{01}^{(2)}},$$

$$\left(\frac{k_{10}}{k_{01}}\right)^{(2)} = \frac{1}{k_{01}^{(2)}}\left(k_{10}^{(4)} - k_{01}^{(4)}\frac{k_{10}^{(2)}}{k_{01}^{(2)}}\right). \quad (113)$$

First, we look at the zeroth-order term: from Eqs. 69 and 77 we have

$$\left(\frac{k_{10}}{k_{01}}\right)^{(0)} = \frac{\hat{C}_1(-\omega_0)}{\hat{C}_1(\omega_0)} = \frac{n(\omega_0)}{n(\omega_0) + 1} = e^{-\beta\hbar\omega_0}. \quad (114)$$

Since from above, $K^{(0)} = e^{-\beta\hbar\omega_0}$, detailed balance is correctly satisfied by the second-order rate constants. Next, after explicitly substituting in the second-order rate constants, Eq. (113) for the second-order term gives

$$\left(\frac{k_{10}}{k_{01}}\right)^{(2)} = \frac{1}{\hat{C}_1(\omega_0)}(k_{10}^{(4)} - e^{-\beta\hbar\omega_0}k_{01}^{(4)}). \quad (115)$$

This expression is evaluated in Appendix D, where we show that it is exactly equal to Eq. (111) for $K^{(2)}$. This verifies that for the master equation with rate constants calculated to order δ^4, detailed balance is satisfied.

For later use we note that with Appendix D, we can write $K^{(2)}$ in a more convenient form as

$$K^{(2)} = (e^{-\beta\hbar\omega_0}/2\pi)\{\beta\hbar P_1(\omega_0) - \beta\hbar P_1(-\omega_0) + P_1'(-\omega_0) \times (e^{\beta\hbar\omega_0}+1) - P_1'(\omega_0)(e^{-\beta\hbar\omega_0}+1)\}. \quad (116)$$

From the above, we can easily take the limit $T\to 0$, yielding

$$\lim_{T\to 0} K = \frac{\delta^2}{\pi}\int_0^\infty d\omega \frac{\Gamma_1'(\omega)}{\omega+\omega_0} + O(\delta^4), \quad (117)$$

which is nonzero. This is of course intimately related to the fact that (as seen in Sec. III B) to fourth order the zero-temperature "up" and "down" rate constants are both nonzero.

We also note that for the model discussed in this paper it is straightforward to show that for arbitrarily strong TLS-bath coupling $\sigma^{eq} = \mathrm{Tr}_b[e^{-\beta H}]/\mathrm{Tr}[e^{-\beta H}]$ is diagonal in the 0-1 representation, which means that this basis is always the most appropriate one for describing the relaxation to equilibrium.

IV. DEPHASING

In subsection A of this section we calculate the dephasing rate constant, $1/T_2$, to second order in δ, and show that $(1/T_2)^{(2)} = (1/2)(1/T_1)^{(2)}$, which is the usual situation. In subsection B we calculate the frequency shift to second order, $\Delta\omega^{(2)}$, and we show that, somewhat surprisingly, it is different from the frequency shift inferred from the renormalized energy splitting. In subsection C we calculate the dephasing rate constant to fourth order in δ, and we see that $(1/T_2)^{(4)} \neq (1/2)(1/T_1)^{(4)}$.

A. Dephasing rate constant to second order

From Eq. (54) we see that

$$\left(\frac{1}{T_2}\right)^{(2)} = -\mathrm{Re}\{R^{(2)}_{1010}\} = \lim_{t\to\infty} \delta^{-2}\,\mathrm{Re}\left\{\int_0^t dt_1 \times \langle 1|\{\mathrm{Tr}_b[\tilde{L}(t)\tilde{L}(t_1)\rho_b]|1\rangle\langle 0|\}|0\rangle\right\}. \quad (118)$$

Using the definition of $\tilde{L}(t)$ and carrying out the commutations yields

$$\left(\frac{1}{T_2}\right)^{(2)} = \lim_{t\to\infty}\mathrm{Re}\left\{\int_0^t dt_1\, \mathrm{Tr}_b[\tilde{\Lambda}(t)\tilde{\Lambda}(t_1)^\dagger\rho_b + \rho_b\tilde{\Lambda}(t_1)^\dagger\tilde{\Lambda}(t)]\right\} \quad (119)$$

$$= \mathrm{Re}\left\{\int_0^\infty dt\, e^{i\omega_0\tau}[C_1(\tau)+C_1(-\tau)]\right\}. \quad (120)$$

Finally, transforming to the spectral representation for $C_1(t)$ [Eq. (65)] gives

$$(1/T_2)^{(2)} = \tfrac{1}{2}[\hat{C}_1(\omega_0) + \hat{C}_1(-\omega_0)]. \quad (121)$$

Comparing this to Eq. (80) shows that

$$\left(\frac{1}{T_2}\right)^{(2)} = \frac{1}{2}\left(\frac{1}{T_1}\right)^{(2)}, \quad (122)$$

which is the standard relationship between population and phase relaxation if there is only off-diagonal coupling to the TLS.

B. Second-order frequency shift

From Eq. (55) one sees that the second-order frequency shift is given by

$$\Delta\omega^{(2)} = -\mathrm{Im}\{R^{(2)}_{1010}\} \quad (123)$$

$$= \mathrm{Im}\left\{\int_0^\infty d\tau\, e^{i\omega_0\tau}[C_1(\tau)+C_1(-\tau)]\right\}. \quad (124)$$

Using Eqs. (67), (68), and (92) gives

$$\Delta\omega^{(2)} = (1/2\pi)[P_1(-\omega_0) - P_1(\omega_0)]. \quad (125)$$

It is interesting to compare this to the frequency shift inferred from the renormalized energy splitting. That is, for an isolated TLS, the off-diagonal density-matrix element oscillates with a frequency determined by the TLS energy splitting. For a TLS coupled to a bath, our intuition tells us that the reduced off-diagonal density-matrix element should oscillate with a frequency determined by the renormalized energy difference of the two levels, which can be defined by

$$K \equiv e^{-\beta\hbar\tilde{\omega}}. \quad (126)$$

Further defining

$$\Delta\tilde{\omega} = \tilde{\omega} - \omega_0 = \delta^2\Delta\tilde{\omega}^{(2)} + \delta^4\Delta\tilde{\omega}^{(4)} + \cdots, \quad (127)$$

then from Eqs. (102) and (126) we have

$$\Delta\tilde{\omega}^{(2)} = -e^{\beta\hbar\omega_0}K^{(2)}/\beta\hbar. \quad (128)$$

From Eqs. (116) and (125), we see that surprisingly, $\Delta\tilde{\omega}^{(2)} \neq \Delta\omega^{(2)}$ from above, and defining the difference $\Delta\omega'^{(2)} \equiv \Delta\tilde{\omega}^{(2)} - \Delta\omega^{(2)}$, we have

$$\Delta\omega'^{(2)} = (1/2\pi\beta\hbar)\{P_1'(\omega_0)(e^{-\beta\hbar\omega_0}+1) - P_1'(-\omega_0)(e^{\beta\hbar\omega_0}+1)\}. \quad (129)$$

C. Dephasing rate constant to fourth order

The fourth-order dephasing rate constant, $(1/T_2)^{(4)}$, is obtained from

$$(1/T_2)^{(4)} = -\mathrm{Re}\{R^{(4)}_{1010}\}. \quad (130)$$

Anticipating the result that $(1/T_2)^{(4)} \neq (1/2)(1/T_1)^{(4)}$, we define what has traditionally been called the pure-dephasing rate constant, $1/T_2'$, by

$$\frac{1}{T_2'} \equiv \frac{1}{T_2} - \frac{1}{2T_1}, \quad (131)$$

which can be expanded in powers of δ. As seen in part A of this section, $(1/T_2')^{(2)} = 0$. To fourth order we can write

$$\left(\frac{1}{T_2'}\right)^{(4)} = -\mathrm{Re}\{R_{1010}^{(4)}\} + \frac{R_{0000}^{(4)} + R_{1111}^{(4)}}{2}. \quad (132)$$

Following the laborious procedure outlined in Sec. III B, one can show that

$$\left(\frac{1}{T_2'}\right)^{(4)} = f(\omega_0) + f(-\omega_0), \quad (133)$$

where

$$f(\omega_0) = 2\int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \mathrm{Re}\{C_2^*(\tau_1+\tau_2+\tau_3)C_2(\tau_2)e^{-i\omega_0(\tau_1-\tau_3)} + C_2^*(\tau_1+\tau_2+\tau_3)C_2^*(\tau_2)e^{-i\omega_0(\tau_1-\tau_3)}$$
$$+ C_2^*(\tau_1+\tau_2)C_2(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+\tau_3)} - C_1^*(\tau_1+\tau_2+\tau_3)C_1^*(\tau_2)e^{-i\omega_0(\tau_1+\tau_3)}$$
$$- C_1^*(\tau_1+\tau_2)C_1(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)} - C_1^*(\tau_1+\tau_2+\tau_3)C_1(\tau_2)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}\}. \quad (134)$$

One sees, felicitously, that the above involves only terms that have already been calculated in Eq. (90). The resulting expression for $(1/T_2')^{(4)}$ is

$$\left(\frac{1}{T_2'}\right)^{(4)} = \frac{1}{\pi} P\int_{-\infty}^{\infty} \frac{d\omega}{\omega^2-\omega_0^2} \times\left(\omega\frac{\partial}{\partial\omega}[\hat{C}_1(\omega)\hat{C}_1(-\omega)] - \hat{C}_2(\omega)\hat{C}_2(-\omega)\right). \quad (135)$$

This expression will be evaluated for a specific model in the following paper.[29]

V. CONNECTION TO THE STOCHASTIC MODEL RESULTS OF BUDIMIR AND SKINNER

The above calculation is a generalization of the fourth-order derivation by Budimir and Skinner (BS) of the Bloch equations for a TLS under the influence of stochastic fluctuations.[17] The completely quantum mechanical model discussed in the present paper, when viewed in the interaction representation, is in fact very similar to the stochastic model. The Heisenberg operator $\Lambda(t)$ in the quantum-mechanical model becomes a random variable in the stochastic model. Similarly, the quantum-mechanical correlation functions $C_1(t)$ and $C_2(t)$ (both involving traces over the bath states) become statistical correlation functions. Furthermore, for the specific model of linear coupling to harmonic oscillators discussed above, Wick's theorem for the factorization of four-point functions is identical to the factorization of four-point statistical correlation functions of Gaussian random variables. The difference in the calculations involves the noncommutivity of quantum operators versus the commutivity of stochastic variables, which is intimately related to the existence or lack of detailed balance.

While this analogy between the two models will be developed at more length in the following paper,[29] here we simply want to point out some general connections between the two derivations. In particular, one can recover some results of the stochastic model by supposing that $C_1(t)$ and $C_2(t)$ are both real and even. [For example, from Eq. (70) we see that this occurs in the high-temperature limit, when $n(\omega_k) \gg 1$, meaning that $\mathrm{Tr}_b[\rho_b\Lambda^\dagger(t)\Lambda(t')] \approx \mathrm{Tr}_b[\rho_b\Lambda(t')\Lambda^\dagger(t)]$, or that $\Lambda^\dagger(t)$ and $\Lambda(t')$ commute.] From Eqs. (63) and (90) this gives

$$k_{10} = 2\delta^2\int_0^\infty d\tau\, \mathrm{Re}\{e^{-i\omega_0\tau}C_1(\tau)\} - 4\delta^4\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3 \mathrm{Re}\{C_2(\tau_1+\tau_2+\tau_3)C_2(\tau_2)e^{-i\omega_0(\tau_1-\tau_3)}$$
$$+ C_2(\tau_1+\tau_2)C_2(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+\tau_3)} - C_1(\tau_1+\tau_2)C_1(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}$$
$$- C_1(\tau_1+\tau_2+\tau_3)C_1(\tau_2)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}\} + O(\delta^6). \quad (136)$$

In the present derivation we assumed that $\Lambda(t)$ satisfies Eq. (88), which is equivalent to the assumption of the stochastic model[17] that

$$\langle\Lambda^*(t)\Lambda^*(0)\rangle = \langle\Lambda(t)\Lambda(0)\rangle. \quad (137)$$

Identifying

$$C_1(t) = \langle\Lambda^*(t)\Lambda(0)\rangle, \quad (138)$$

$$C_2(t) = \langle\Lambda(t)\Lambda(0)\rangle, \quad (139)$$

setting $\delta = 1$ in the above to be consistent with the usage in BS, and taking Δ in BS to be 0 (since in the present treatment we only consider off-diagonal perturbations), we obtain complete agreement between Eq. (136) above and Eqs. (39), (44), and (47) of BS.[17]

Therefore, some general stochastic-model results for $1/T_1$ and $1/T_2'$, not presented in BS, can be obtained from the present work simply by taking $\hat{C}_1(\omega)$ and $\hat{C}_2(\omega)$ to be even (which follows from the assumptions that $C_1(t)$ and $C_2(t)$ are real and even). From Eqs. (80), (98), and (135) this gives

$$1/T_1 = 2\delta^2\hat{C}_1(\omega_0) + (2\delta^4/\pi)\{\omega_0^{-1}\hat{C}_2(\omega_0)P_2(\omega_0) - \hat{C}_1'(\omega_0)P_1(\omega_0) - \hat{C}_1(\omega_0)P_1'(\omega_0)\} + O(\delta^6), \tag{140}$$

$$\frac{1}{T_2'} = \frac{\delta^4}{\pi} P\int_{-\infty}^{\infty} \frac{d\omega}{\omega^2 - \omega_0^2}\left(\omega\frac{\partial}{\partial\omega}[\hat{C}_1(\omega)^2] - \hat{C}_2(\omega)^2\right) + O(\delta^6). \tag{141}$$

In Appendix E, we evaluate these expressions for the two models considered in BS, finding complete agreement with the results therein.

VI. RELATION TO THE "SPIN-BOSON" PROBLEM

The coupling of two quantum levels to a collection of quantum-mechanical harmonic oscillators has been studied quite extensively in a somewhat different context. If one considers the tunneling of a particle through the barrier of a bistable symmetric potential, at low temperatures one can write the Hamiltonian for the isolated tunneling particle in terms of the zeroth-order states localized in the left and right wells as

$$H_0 = -(\hbar\Delta/2)(|l\rangle\langle r| + |r\rangle\langle l|), \tag{142}$$

where Δ is the tunneling frequency. To study dissipative tunneling, the system is then coupled to a bath of harmonic oscillators

$$H_b = \sum_k \left(\frac{p_k^2}{2m_k} + \frac{m_k\omega_k^2 q_k^2}{2}\right), \tag{143}$$

with an interaction Hamiltonian of the form

$$H_1 = \frac{q_0}{2}\sum_k C_k q_k(|r\rangle\langle r| - |l\rangle\langle l|), \tag{144}$$

where q_0 and the C_k are coupling parameters. The total Hamiltonian can then be written in terms of the Pauli matrices in the right–left basis as

$$H = -\frac{\hbar\Delta}{2}\sigma_x + \sum_k\left(\frac{p_k^2}{2m_k} + \frac{m_k\omega_k^2 q_k^2}{2}\right) + \frac{q_0}{2}\sum_k C_k q_k \sigma_z, \tag{145}$$

which is known as the "spin-boson" Hamiltonian. The static and dynamic properties of this Hamiltonian have been studied extensively, and two excellent and comprehensive reviews have recently appeared.[27,28]

The right and left localized states are in fact defined quite naturally as the "plus" and "minus" linear combinations of the two lowest eigenstates, $|0\rangle$ and $|1\rangle$, of the double well potential:

$$|r\rangle = (1/\sqrt{2})(|0\rangle + |1\rangle), \tag{146}$$

$$|l\rangle = (1/\sqrt{2})(|0\rangle - |1\rangle). \tag{147}$$

Inverting the above transformation we can then write our Hamiltonian in the right–left basis as (neglecting an additive constant)

$$H = -\frac{\hbar\omega_0}{2}\sigma_x + \sum_k \hbar\omega_k\left(b_k^\dagger b_k + \frac{1}{2}\right) + \frac{\delta\hbar(\Lambda + \Lambda^\dagger)}{2}\sigma_z + \frac{i\delta\hbar(\Lambda - \Lambda^\dagger)}{2}\sigma_y. \tag{148}$$

Thus we can see that if we take the coupling constants h_k in Eq. (14) to be real so that Λ is Hermitian, and if we identify $\omega_0 = \Delta$ and $\delta h_k(2m_k\hbar\omega_k)^{1/2} = q_0 C_k/2$, we recover Eq. (145) above.

Before we make a few specific comparisons with the spin-boson literature, several general remarks are in order. In the tunneling problem, one is particularly interested in the dynamics of tunneling between left and right wells, which involves the expectation value $P_z(t) \equiv \langle\sigma_z\rangle$, and one is less concerned with the quantities $P_x(t)$ and $P_y(t)$. Furthermore, one is interested in the full range of system-bath coupling strengths (which necessitates finding approximate solutions to the problem)—indeed, the most interesting results occur for strong coupling. On the other hand, in our problem we are equally interested (in the spin-boson language) in $P_x(t)$, $P_y(t)$, and $P_z(t)$, since (especially in the following paper[29]) we want to compare T_1 to T_2. In fact, we find that the most interesting result of $T_2 > 2T_1$ is obtained only when $\Lambda \neq \Lambda^\dagger$, which is not treated in the spin-boson literature. Finally, although the range of validity of our perturbative expressions is limited, the calculation to fourth order is exact.

To make a specific comparison between the two problems, let us consider the case where the h_k are real, so that $\Gamma_1(\omega) = \Gamma_2(\omega) \equiv \Gamma(\omega)$, and first discuss the weak-coupling limit. In this case we saw that the coupling terms in Eqs. (46) and (47) could be ignored, leading to the Bloch Eqs. (2)–(5), where the weak-coupling expressions for the rate constants have been obtained herein, and we will neglect $\Delta\omega$ in comparison with ω_0. These Bloch equations lead to the following expressions for $P_i(t) \equiv \langle\sigma_i\rangle = \mathrm{Tr}[\sigma(t)\sigma_i]$:

$$\dot{P}_x(t) = -(1/T_1)(P_x(t) - P_x^{\mathrm{eq}}), \tag{149}$$

$$\dot{P}_y(t) = \omega_0 P_z(t) - (1/T_2)P_y(t), \tag{150}$$

$$\dot{P}_z(t) = -\omega_0 P_y(t) - (1/T_2)P_z(t), \tag{151}$$

where $P_x^{\mathrm{eq}} = \tanh(\beta\hbar\omega_0/2)$ and $1/T_1 = 2/T_2 = 2\delta^2\Gamma(\omega_0)\coth(\beta\hbar\omega_0/2)$. Eliminating P_y from Eqs. (150) and (151) and neglecting $1/T_2$ compared to ω_0 (which is consistent with the weak-coupling limit), yields

$$\ddot{P}_z(t) + (2/T_2)\dot{P}_z(t) + \omega_0^2 P_z(t) = 0, \tag{152}$$

the equation for a damped harmonic oscillator, in agreement with Leggett *et al.*[27] and Silbey and Harris.[28] [Note that Leggett's definition of T_2 differs from ours by a factor of 2, and that his spectral density $J(\omega)$ is related to our $\Gamma(\omega)$ by $q_0^2 J(\omega) = 4\delta^2\hbar\Gamma(\omega)$.]

One of the interesting features of the spin-boson analysis is the renormalization of the tunneling frequency, especially at zero temperature. In our language this renormalized frequency is $\omega = \omega_0 + \Delta\omega$, where $\Delta\omega$ is given by Eq. (55). To lowest order we have

$$\omega = \omega_0 + \delta^2\Delta\omega^{(2)} + O(\delta^4), \tag{153}$$

where $\Delta\omega^{(2)}$ is defined in Eq. (125). Taking the limit $T\to 0$ we find that

$$\lim_{T\to 0}\omega=\omega_0\left(1-\frac{2\delta^2}{\pi}P\int_0^\infty d\omega\frac{\Gamma(\omega)}{\omega^2-\omega_0^2}\right)+O(\delta^4). \tag{154}$$

This is identical to the first term in the expansion of the Franck-Condon factor of Leggett *et al.*[27] [see their Eq. (3.23)] except for the presence of ω_0^2 in our denominator. It is also very similar to the first term in the expansion of the self-consistent Eq. (106b) of Silbey and Harris.[28] [In that work the spectral density $J(\omega)$ is related to our $\Gamma(\omega)$ by $J(\omega)=2\delta^2\Gamma(\omega)/\pi$, and their tunneling frequency 2δ is our ω_0.] Leggett *et al.* and Silbey and Harris are particularly interested in determining the coupling at which the renormalized tunneling frequency vanishes at zero temperature, which signifies the localization of the particle in one well or the other. With our perturbative treatment we cannot accurately address this issue. Nonetheless, since our expression is exact to second order (and without too much trouble one could find the fourth-order correction), this might suggest ways to improve the approximate treatments of Leggett *et al.* and Silbey and Harris.

VII. CONCLUSION

This work demonstrates, we believe for the first time, that from a completely quantum mechanical Hamiltonian it is possible to derive a master equation, or more generally, Bloch equations, where the relaxation-rate constants are calculated to fourth order in the system/bath coupling. The rate constants in the master equation provide, for this specific model, an extension of Fermi's Golden Rule to fourth order. We show explicitly that these fourth-order rate constants obey detailed balance.

Some surprises come out of this work, which, based on our familiarity with the usual weak coupling results, are quite unintuitive. First, unlike the weak-coupling results, the master equation rate constants in fourth order cannot be interpreted in terms of the emission and/or absorption of vibrational quanta. Furthermore, at $T=0$, the "up" rate constant and the equilibrium constant are both nonzero. Second, the frequency shift obtained from the equations of motion for the off-diagonal density-matrix element does not agree with that inferred from the renormalized energy splitting, as defined by the equilibrium constant. Finally, we find that in fourth order $1/T_2\neq 1/2T_1$, which is contrary to the expected result from both second-order calculations and our accumulated intuition.

In the following paper[29] we show, for a specific, physically reasonable model of the bath and its coupling to the system, that in fact sometimes $T_2>2T_1$, which demonstrates that this result, originally derived from a stochastic model,[17] holds at finite temperatures as well.

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APPENDIX A

In this appendix, the effect of the R_{1001} term on the dephasing rate and frequency shift is analyzed. Equations (46) and (47) give the following system of coupled linear differential equations:

$$\begin{bmatrix}\dot\sigma_{10}(t)\\ \dot\sigma_{01}(t)\end{bmatrix}=\begin{bmatrix}-i\omega_0+R_{1010} & R_{1001}\\ R^*_{1001} & i\omega_0+R^*_{1010}\end{bmatrix}\begin{bmatrix}\sigma_{10}(t)\\ \sigma_{01}(t)\end{bmatrix}. \tag{A1}$$

The damping constants and frequencies of this system are the eigenvalues of the above matrix. These are determined by solving the secular equation:

$$(-i\omega_0+R_{1010}-\lambda)(i\omega_0+R^*_{1010}-\lambda)-|R_{1001}|^2=0. \tag{A2}$$

The solution to this equation is

$$\lambda_\pm=\mathrm{Re}\{R_{1010}\}\pm i(\omega_0-\mathrm{Im}\{R_{1010}\})\times\sqrt{1-\frac{|R_{1001}|^2}{(\omega_0-\mathrm{Im}\{R_{1010}\})^2}}. \tag{A3}$$

For $|R_{1001}|\leqslant(\omega_0-\mathrm{Im}\{R_{1010}\})$, the argument of the square-root is positive; therefore, the real part of λ is the same for both eigenvalues, and its negative can be identified as the dephasing rate $1/T_2$:

$$1/T_2=-\mathrm{Re}\{R_{1010}\}. \tag{A4}$$

Thus, the dephasing rate is unaffected by the coupling parameter R_{1001}.

The natural frequency of the system is given by the imaginary part of $\lambda_\pm$:

$$\omega=(\omega_0-\mathrm{Im}\{R_{1010}\})\sqrt{1-\frac{|R_{1001}|^2}{(\omega_0-\mathrm{Im}\{R_{1010}\})^2}}. \tag{A5}$$

Expanding this in powers of δ, with $\Delta\omega\equiv\omega-\omega_0$, gives

$$\Delta\omega=-\delta^2\,\mathrm{Im}\{R^{(2)}_{1010}\}-\delta^4\left(\mathrm{Im}\{R^{(4)}_{1010}\}+\frac{|R^{(2)}_{1001}|^2}{2\omega_0}\right)+\cdots, \tag{A6}$$

which shows that the frequency is not affected by the coupling R_{1001} until fourth order in the perturbation.

APPENDIX B

An integral that appears many times in the course of this work is

$$S(x)=\int_0^\infty dt\,e^{-ixt}e^{-\epsilon t}=\frac{1}{\epsilon+ix}. \tag{B1}$$

Taking real and imaginary parts yields

$$S(x)=\pi\mathscr{D}(x)-i\mathscr{P}(x), \tag{B2}$$

where

$$\mathscr{D}(x)=\epsilon/\pi(\epsilon^2+x^2), \tag{B3}$$

$$\mathscr{P}(x)=x/(\epsilon^2+x^2). \tag{B4}$$

Of course

$$\lim_{\epsilon\to 0}\mathscr{D}(x)=\delta(x), \tag{B5}$$

$$\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\, f(x)\mathscr{P}(x) = P\int_{-\infty}^{\infty} dx\frac{f(x)}{x}, \tag{B6}$$

which are the Dirac delta function and Cauchy principal value, respectively. Indeed, the above is so well known it hardly seems worth belaboring.

The problem arises with products of these generalized functions, which must be treated with some care. For example,

$$S(x)^2 = \left(\frac{1}{\epsilon + ix}\right)^2 = i\frac{\partial}{\partial x}\left(\frac{1}{\epsilon + ix}\right) = iS'(x) \tag{B7}$$

$$= i\pi\mathscr{D}'(x) + \mathscr{P}'(x). \tag{B8}$$

Comparing this to the square of Eq. (B2) yields the identities

$$\pi^2\mathscr{D}(x)^2 - \mathscr{P}(x)^2 = \mathscr{P}'(x), \tag{B9}$$

$$\mathscr{D}(x)\mathscr{P}(x) = -\tfrac{1}{2}\mathscr{D}'(x). \tag{B10}$$

Next considering

$$S(x)S(-x) = 1/(\epsilon^2 + x^2) = \mathscr{P}(x)/x, \tag{B11}$$

and using Eq. (B2) immediately yields

$$\pi^2\mathscr{D}(x)^2 + \mathscr{P}(x)^2 = \mathscr{P}(x)/x. \tag{B12}$$

Eqs. (B9) and (B10) then lead to the further identities

$$2\mathscr{P}(x)^2 = \frac{\mathscr{P}(x)}{x} - \mathscr{P}'(x) = -x\frac{d}{dx}\left(\frac{\mathscr{P}(x)}{x}\right), \tag{B13}$$

$$2\pi^2\mathscr{D}(x)^2 = \mathscr{P}'(x) + \mathscr{P}(x)/x. \tag{B14}$$

Integration by parts makes quick work of the derivatives of these generalized functions:

$$\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\, f(x)\mathscr{D}'(x) = -\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\mathscr{D}(x)f'(x) = -f'(0), \tag{B15}$$

$$\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\, f(x)\mathscr{P}'(x) = -\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\mathscr{P}(x)f'(x) = -P\int_{-\infty}^{\infty} dx\frac{f'(x)}{x}. \tag{B16}$$

We will also make use of

$$\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\, \mathscr{D}(x)^2[f(x) - f(0)] = 0. \tag{B17}$$

APPENDIX C

Consider the seventh term of Eq. (90):

$$I_7 = 2\mathrm{Re}\left\{\int_0^{\infty} d\tau_1\int_0^{\infty} d\tau_2\int_0^{\infty} d\tau_3\, C_1(\tau_1+\tau_2) \times C_1(\tau_2+\tau_3)e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}\right\}. \tag{C1}$$

First we write $C_1(t)$ in terms of its Fourier transform using Eq. (65)

$$I_7 = \lim_{\epsilon\to 0}\frac{1}{2\pi^2}\mathrm{Re}\left\{\int_{-\infty}^{\infty} d\omega\,\hat{C}_1(\omega)\int_{-\infty}^{\infty} d\omega'\,\hat{C}_1(\omega')\int_0^{\infty} d\tau_1 \times\int_0^{\infty} d\tau_2\int_0^{\infty} d\tau_3 e^{-i\omega(\tau_1+\tau_2)}e^{-i\omega'(\tau_2+\tau_3)} \times e^{-i\omega_0(\tau_1+2\tau_2+\tau_3)}e^{-\epsilon\tau_1}e^{-\epsilon\tau_2}e^{-\epsilon\tau_3}\right\}. \tag{C2}$$

Using the definition of $S(x)$ in Appendix B this becomes

$$I_7 = \lim_{\epsilon\to 0}\frac{1}{2\pi^2}\mathrm{Re}\left\{\int_{-\infty}^{\infty} d\omega\,\hat{C}_1(\omega) \times\int_{-\infty}^{\infty} d\omega'\,\hat{C}_1(\omega')S(\omega+\omega_0) \times S(\omega'+\omega_0)S(\omega+\omega'+2\omega_0)\right\}. \tag{C3}$$

Substituting in Eq. (B2) from Appendix B for $S(\omega+\omega'+2\omega_0)$ yields

$$I_7 = \lim_{\epsilon\to 0}\frac{1}{2\pi}\mathrm{Re}\left\{\int_{-\infty}^{\infty} d\omega\,\hat{C}_1(\omega)\hat{C}_1(-\omega-2\omega_0) \times S(\omega+\omega_0)S(-\omega-\omega_0)\right\} - \lim_{\epsilon\to 0}\frac{1}{\pi}\int_{-\infty}^{\infty} d\omega\,\hat{C}_1(\omega)\int_{-\infty}^{\infty} d\omega'\,\hat{C}_1(\omega') \times\mathscr{D}(\omega+\omega_0)\mathscr{P}(\omega'+\omega_0)\mathscr{P}(\omega+\omega'+2\omega_0). \tag{C4}$$

With Eq. (B11) this gives

$$I_7 = \lim_{\epsilon\to 0}\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\,\hat{C}_1(\omega)\hat{C}_1(-\omega-2\omega_0)\frac{\mathscr{P}(\omega+\omega_0)}{\omega+\omega_0} - \lim_{\epsilon\to 0}\frac{1}{\pi}\hat{C}_1(-\omega_0)\int_{-\infty}^{\infty} d\omega\,\hat{C}_1(\omega)\mathscr{P}(\omega+\omega_0)^2. \tag{C5}$$

Finally, using Eqs. (B13) and (B16) gives

$$I_7 = \frac{1}{2\pi}P\int_{-\infty}^{\infty} d\omega\frac{\hat{C}_1(\omega)[\hat{C}_1(-\omega-2\omega_0) - \hat{C}_1(-\omega_0)]}{(\omega+\omega_0)^2} - \frac{1}{2\pi}\hat{C}_1(-\omega_0)P_1'(-\omega_0), \tag{C6}$$

where $P_1'(\omega)$ is defined in Eq. (95).

The other terms of Eq. (90) are evaluated in a similar, although not identical, fashion.

APPENDIX D

Using the fact that

$$n(\omega) + 1 = -n(-\omega) = e^{\beta\hbar\omega}n(\omega), \tag{D1}$$

one can easily show from Eqs. (73) and (86) that

$$\hat{C}_i(-\omega) = e^{-\beta\hbar\omega}\hat{C}_i(\omega), \tag{D2}$$

from which follows [see Eqs. (91), (97), and (115)]

$$(k_{10}/k_{01})^{(2)} = A + B, \tag{D3}$$

$$A = [1/2\pi\hat{C}_1(\omega_0)]\{\hat{C}_1'(-\omega_0) + e^{-\beta\hbar\omega_0}\hat{C}_1'(\omega_0)\} \times\{P_1(\omega_0) - P_1(-\omega_0)\}, \tag{D4}$$

$$B = (e^{-\beta\hbar\omega_0}/2\pi)\{P_1'(-\omega_0)(e^{\beta\hbar\omega_0}+1) - P_1'(\omega_0)(e^{-\beta\hbar\omega_0}+1)\}. \tag{D5}$$

From the definition of $\hat{C}_1(\omega)$ [Eq. (73)] and Eq. (D1) above, it is straightforward to show that

$$A = \frac{\beta\hbar e^{-\beta\hbar\omega_0}}{2\pi} P\int_{-\infty}^{\infty} d\omega\, \hat{C}_1(\omega)\left(\frac{1}{\omega-\omega_0} - \frac{1}{\omega+\omega_0}\right). \tag{D6}$$

Next, using the fact that [see Eq. (94) and Appendix B]

$$P_1'(\omega_0) = -\int_{-\infty}^{\infty} d\omega\, \hat{C}_1(\omega)\mathscr{P}'(\omega-\omega_0), \tag{D7}$$

and Eqs. (B14) and (B17), gives

$$B = \frac{e^{-\beta\hbar\omega_0}}{2\pi}\int_{-\infty}^{\infty} d\omega\, \hat{C}_1(\omega)\left((e^{\beta\hbar\omega_0}+1)\frac{\mathscr{P}(\omega+\omega_0)}{\omega+\omega_0} - (e^{-\beta\hbar\omega_0}+1)\frac{\mathscr{P}(\omega-\omega_0)}{\omega-\omega_0}\right). \tag{D8}$$

Finally, with Eq. (D2) above, this can be written

$$B = \frac{e^{-\beta\hbar\omega_0}}{2\pi} P\int_{-\infty}^{\infty} d\omega\, \hat{C}_1(\omega) \times\left(\frac{e^{-\beta\hbar(\omega-\omega_0)}-1}{(\omega-\omega_0)^2} - \frac{e^{-\beta\hbar(\omega+\omega_0)}-1}{(\omega+\omega_0)^2}\right). \tag{D9}$$

When A and B are added together, the principal value is no longer necessary, and one obtains Eq. (111).

APPENDIX E

Here we show how to reproduce the results of BS[17] from the general stochastic-model expressions of Eqs. (140) and (141). First considering the case discussed in Sec. 3.2 of BS, where $\Lambda(t)$ is real, and

$$\hat{C}_1(\omega) = \hat{C}_2(\omega) = 2\lambda\Lambda^2/(\lambda^2+\omega^2), \tag{E1}$$

the principal value in $P_1(\omega_0)$ (used in the calculation of $1/T_1$) is evaluated by considering the contour that proceeds along the real axis with an infinitesimal semicircle (above the real axis) around the pole at ω_0, and closed in the upper half plane. Since the contribution to the contour integral from the pole at ω_0 is imaginary, the principal value is simply the real part of the contour integral, yielding

$$P_1(\omega_0) = -2\pi\Lambda^2\omega_0/(\lambda^2+\omega_0^2). \tag{E2}$$

Setting $\delta = 1$ in Eq. (140) we then obtain complete agreement with Eq. (56) of BS. For $1/T_2'$, the principal value is evaluated with the same contour except now there are two infinitesimal semicircles above the real axis going around the poles at $\pm\omega_0$. A messy evaluation (because of the triple pole at $i\lambda$) of this contour integral leads to Eq. (60) of BS.

For the spin-1/2 particle in a fluctuating magnetic field considered in Sec. 3.3 of BS we take

$$\hat{C}_1(\omega) = \lambda\omega_x^2/(\lambda^2+\omega^2), \tag{E3}$$

and $\hat{C}_2(\omega) = 0$. A similar evaluation of the principal-value integrals leads to complete agreement with Eqs. (81) and (83) of BS.

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