T_2 can be greater than $2T_1$ even at finite temperature

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

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

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The relaxation of a nondegenerate two-level quantum system linearly and off-diagonally coupled to a thermal bath of quantum-mechanical harmonic oscillators is studied. The population and phase relaxation times, T_1 and T_2, are calculated to fourth order in the system/bath interaction. Focus is on a specific model of the bath spectral density that is both Ohmic (proportional to frequency at low frequency) and Lorentzian, and which has the property that, in the semiclassical or high-temperature limit, it reproduces the stochastic model studied previously by Budimir and Skinner [J. Stat. Phys. **49**, 1029 (1987)]. For this fully quantum-mechanical model, it is found that under certain conditions the standard inequality, $T_2 \leqslant 2T_1$, is violated, demonstrating that this unusual result, which was originally derived from the (infinite-temperature) stochastic model, is valid at finite temperature as well.

I. INTRODUCTION

The reduced dynamics of two quantum levels coupled to a thermal bath is of fundamental interest in many different fields of spectroscopy, and, as discussed in the introduction to the previous paper,[1] this dynamics is described under many circumstances by the Bloch equations for the reduced density-matrix elements. These equations involve the two times T_1 and T_2, for population and phase relaxation, respectively. Until recently, both experimental and theoretical indications were that $T_2 \leqslant 2T_1$.

Recently, for a particular stochastic model, Budimir and Skinner[2] showed that, if the relaxation rate constants were calculated to fourth order in the system/bath coupling, one found that for some parameters $T_2 > 2T_1$. In that calculation T_1 and T_2 are the relaxation times for the asymptotic exponential decay of the density-matrix elements. This analytic calculation does not address the issue of when in the time course of the relaxation the decay becomes exponential. This prompted Sevian and Skinner[3] to perform computer simulations of this stochastic model, which showed that, for a nontrivial range of parameters, (1) the relaxation was exponential after only a short transient time, (2) the relaxation rates were in good agreement with the fourth-order calculation of Budimir and Skinner,[2] and (3) $T_2 > 2T_1$, thus showing that at least for the stochastic model the Budimir–Skinner results are both correct and meaningful.

More problematic for the theoretical (not to mention experimental) relevance of this result is the role of temperature. In the stochastic model the two-level system (TLS) responds to external fluctuations, and one finds that the two rate constants for population transfer are equal, implying equal asymptotic populations of the two levels. For nondegenerate levels in thermal equilibrium, this would imply an infinite temperature. Thus one might be suspicious that our strange result of $T_2 > 2T_1$ is an artifact of this "infinite-temperature" model, and would not survive the transition to finite temperature.

As far as we are aware there is no way to correct this "infinite-temperature" defect within the stochastic model framework, and the only satisfactory theoretical approach to studying relaxation at finite temperature is to consider a fully quantum-mechanical TLS/bath system. In the previous paper[1] we consider a TLS coupled linearly and off-diagonally to a collection of harmonic oscillators. We show that, when the relaxation rate constants are calculated to fourth order in the system/bath interaction, $T_2 \neq 2T_1$, unlike the weak-coupling result. In that work we do not consider specific models for the oscillator density of states and the TLS coupling.

In this paper we study a model for the oscillator density of states and the TLS coupling that, in the high-temperature limit, is identical to the stochastic model studied by Budimir and Skinner.[2] In Sec. II, we show that this is achieved by assuming a weighted density of states (spectral density) that is both Ohmic (proportional to frequency for small frequency) and Lorentzian in form. This is done by exploiting the well-known connection between a Gaussian stochastic bath and a collection of classical harmonic oscillators in thermal equilibrium.[4,5,6] In Sec. III, the case of a TLS coupled to a single real bath field is studied, where we see that the conventional wisdom is correct and $T_2 < 2T_1$ for all temperatures. In Sec. IV, we consider the case where the TLS is coupled to two independent bath fields—one real and one imaginary—which models the relaxation of a spin-1/2 particle in the presence of fluctuating transverse magnetic fields. We show that, for certain temperatures and spectral density parameters, $T_2 > 2T_1$. In Sec. V, we discuss these results and conclude.

II. THE "OHMIC-LORENTZIAN" MODEL

Our strategy for devising a quantum-mechanical model that reduces to the stochastic model in the infinite-temperature limit involves two steps. First we consider a semiclassical model where the TLS is described quantum mechanical-

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

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ly, but is driven by a collection of classical harmonic oscillators. We show that this is identical to the stochastic model. Then to obtain the fully quantum-mechanical theory we simply quantize the oscillators, incorporate the oscillator Hamiltonian into the total Hamiltonian, and retain the spectral density from the semiclassical analysis.

To this end, we first consider a Hamiltonian of the form[2]

$$H = H_{\rm TLS} + H_1(t), \tag{1}$$

where

$$H_{\rm TLS} = \hbar\omega_0|1\rangle\langle 1|, \tag{2}$$

$$H_1(t) = \delta[\hbar\Lambda(t)|1\rangle\langle 0| + \hbar\Lambda^*(t)|0\rangle\langle 1|], \tag{3}$$

δ is a dimensionless expansion parameter (as in the previous paper[1]), and $\Lambda(t)$ is a complex function of time with units of frequency. In the stochastic case,[2] $\Lambda(t)$ describes a Gaussian process, and is therefore completely determined by the two-point statistical correlation functions. In the models studied by Budimir and Skinner[2] (BS) there are only two independent two-point correlation functions, which are

$$C_1(t_1 - t_2) = \langle \Lambda^*(t_1)\Lambda(t_2)\rangle, \tag{4}$$

$$C_2(t_2 - t_2) = \langle \Lambda(t_1)\Lambda(t_2)\rangle. \tag{5}$$

For the semiclassical model we instead take

$$\Lambda(t) = \sum_k h_k (2m_k\omega_k/\hbar)^{1/2} q_k(t), \tag{6}$$

where m_k and ω_k are the effective mass and frequency of the kth harmonic oscillator, h_k is a complex coupling constant (with units of frequency) for mode k, and $q_k(t)$ is the time-dependent coordinate for mode k, whose dynamics is determined by the bath Hamiltonian:

$$H_b = \sum_k \left(\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 q_k^2 \right). \tag{7}$$

Note that we are assuming that, although the evolution of the TLS is perturbed by the oscillators, the oscillators evolve only according to the unperturbed bath Hamiltonian. The time dependence of the coordinate q_k can be written in terms of its initial position and velocity as

$$q_k(t) = q_k(0)\cos(\omega_k t) + [\dot{q}_k(0)/\omega_k]\sin(\omega_k t). \tag{8}$$

We assume that the bath harmonic oscillators are in thermal equilibrium, that is, $q_k(0)$ and $\dot{q}_k(0)$ are Maxwell–Boltzmann distributed. For the harmonic-oscillator Hamiltonian above, this corresponds to Gaussian distributions for both:

$$P_q(q_k(0)) = \sqrt{\beta m_k \omega_k^2/2\pi}\, e^{-\beta m_k \omega_k^2 q_k(0)^2/2}, \tag{9}$$

$$P_{\dot{q}}(\dot{q}_k(0)) = \sqrt{\beta m_k/2\pi}\, e^{-\beta m_k \dot{q}_k(0)^2/2}, \tag{10}$$

where $\beta = 1/kT$. An average such as those in the correlation functions $C_i(t)$ is performed by integrating over the initial coordinates and velocities weighted by the above initial distributions:

$$\begin{aligned}\langle f(q_1(0), q_2(0)\cdots;\dot{q}_1(0),\dot{q}_2(0)\cdots)\rangle &= \int dq_1(0)dq_2(0)\cdots d\dot{q}_1(0)d\dot{q}_2(0)\cdots \\ &\quad\times P_q(q_1(0))P_q(q_2(0))\cdots P_{\dot{q}}(\dot{q}_1(0)) \\ &\quad\times P_q(\dot{q}_2(0))\cdots f(q_1(0),q_2(0)\cdots;\dot{q}_1(0),\dot{q}_2(0)\cdots).\end{aligned} \tag{11}$$

Therefore we have

$$\langle \Lambda(t)\rangle = \langle \Lambda^*(t)\rangle = 0, \tag{12}$$

$$C_1(t) = \frac{2}{\beta}\sum_k \frac{|h_k|^2}{\hbar\omega_k}\cos(\omega_k t), \tag{13}$$

$$C_2(t) = \frac{2}{\beta}\sum_k \frac{h_k^{\,2}}{\hbar\omega_k}\cos(\omega_k t), \tag{14}$$

Moreover, since the initial distributions are Gaussian, and the solution for $q_k(t)$ is linear in the initial conditions, $\Lambda(t)$ defines a Gaussian process, which means that, like the stochastic model, multipoint correlation functions factor into a sum of products of two-point functions.

In general, it is more convenient to work with the spectral representation of $C_i(t)$:

$$\hat{C}_i(\omega) = \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} C_i(\tau) = \frac{2\Gamma_i(|\omega|)}{\hbar\beta|\omega|}, \tag{15}$$

where $\Gamma_i(\omega)$ are weighted densities of states (spectral densities) with units of frequency and defined as follows:

$$\Gamma_1(\omega) = \pi\sum_k |h_k|^2 \delta(\omega - \omega_k), \tag{16}$$

$$\Gamma_2(\omega) = \pi\sum_k h_k^2 \delta(\omega - \omega_k). \tag{17}$$

Note that since $\omega_k > 0$ for all k, $\Gamma_i(\omega) = 0$ for $\omega < 0$.

In BS, the statistical correlation functions were taken to have the form[2]

$$C_i(t) = C_i e^{-\lambda|t|}, \tag{18}$$

which gives

$$\hat{C}_i(\omega) = 2\lambda C_i/(\omega^2 + \lambda^2). \tag{19}$$

Comparing Eqs. (15) and (19), we see that the classical weighted densities of states that would lead to these correlation functions are

$$\Gamma_i(\omega) = [A_i\lambda\omega/(\omega^2 + \lambda^2)]\theta(\omega), \tag{20}$$

where $A_i = C_i\beta\hbar$, which has units of frequency, and $\theta(\omega)$ is the step function. In order to make the correspondence with the semiclassical model, we note that although temperature was never mentioned explicitly in the stochastic model, it follows that $C_i = A_i/\beta\hbar$ is proportional to T, since $\Gamma_i(\omega)$ is a temperature-independent spectral density, and therefore A_i is also temperature independent. Because this model for $\Gamma_i(\omega)$ is Ohmic (proportional to ω at small ω) and is derived from a Lorentzian (frequency-domain) correlation function, we refer to it as the "Ohmic-Lorentzian" (OL) model. This semiclassical OL model as defined above, has the same time-dependent correlation functions as the stochastic model, and has the same Gaussian property, and is therefore identical to it.

To obtain the fully quantum-mechanical version of the

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OL model we simply replace q_k and p_k by their second-quantized equivalents, and include H_b in the total Hamiltonian. [Note that although in the semiclassical theory the perturbation $\Lambda(t)$ is time-dependent, in the quantum-mechanical theory with H_b included in the Hamiltonian the perturbation is time independent—it becomes time dependent upon transforming to the interaction representation.] This procedure yields

$$H = H_{\rm TLS} + H_b + H_1, \tag{21}$$

$$H_{\rm TLS} = \hbar\omega_0|1\rangle\langle 1|, \tag{22}$$

$$H_b = \sum_k \hbar\omega_k\left(b_k^\dagger b_k + \frac{1}{2}\right), \tag{23}$$

$$H_1 = \delta[\hbar\Lambda|1\rangle\langle 0| + \hbar\Lambda^\dagger|0\rangle\langle 1|], \tag{24}$$

$$\Lambda = \sum_k h_k(b_k^\dagger + b_k), \tag{25}$$

which is exactly the model considered in the previous paper.[1] Therefore the results of that work, together with the OL spectral density from above, should reduce to the stochastic model in the limit $T\to\infty$, but for finite temperatures will satisfy detailed balance.

For completeness, we summarize below the results from the previous paper[1] that we need for further analysis. For $1/T_1$, we have

$$1/T_1 = \delta^2[\hat{C}_1(\omega_0) + \hat{C}_1(-\omega_0)] + (\delta^4/2\pi)\{\omega_0^{-1}[\hat{C}_2(\omega_0) + \hat{C}_2(-\omega_0)][P_2(\omega_0) - P_2(-\omega_0)] - [\hat{C}_1'(\omega_0) - \hat{C}_1'(-\omega_0)][P_1(\omega_0) - P_1(-\omega_0)] - [\hat{C}_1(\omega_0) + \hat{C}_1(-\omega_0)][P_1'(\omega_0) + P_1'(-\omega_0)]\} + O(\delta^6), \tag{26}$$

where

$$\hat{C}_i(\omega) = 2\{\Gamma_i(\omega)[n(\omega)+1] + \Gamma_i(-\omega)n(-\omega)\}, \tag{27}$$

$$n(\omega) = 1/(e^{\hbar\beta\omega} - 1), \tag{28}$$

$$P_i(\omega) = P\int_{-\infty}^{\infty} d\omega' \frac{\hat{C}_i(\omega')}{\omega' - \omega}, \tag{29}$$

$$\hat{C}_i'(\omega) = \frac{\partial \hat{C}_i(\omega)}{\partial\omega}, \tag{30}$$

$$P_i'(\omega) = \frac{\partial P_i(\omega)}{\partial\omega} = P\int_{-\infty}^{\infty} d\omega' \frac{\hat{C}_i'(\omega')}{\omega' - \omega}. \tag{31}$$

Defining a "pure dephasing" rate by

$$\frac{1}{T_2'} = \frac{1}{T_2} - \frac{1}{2T_1}, \tag{32}$$

we have

$$\frac{1}{T_2'} = \frac{\delta^4}{\pi} P\int_{-\infty}^{\infty} \frac{d\omega}{\omega^2 - \omega_0^2}\left(\omega\frac{\partial}{\partial\omega}[\hat{C}_1(\omega)\hat{C}_1(-\omega)] - \hat{C}_2(\omega)\hat{C}_2(-\omega)\right) + O(\delta^6). \tag{33}$$

Finally, for the equilibrium constant, which is the ratio of the excited-state to ground-state equilibrium populations, we have

$$K = e^{-\beta\hbar\omega_0} + (\delta^2 e^{-\beta\hbar\omega_0}/2\pi)[\beta\hbar P_1(\omega_0) - \beta\hbar P_1(-\omega_0) + P_1'(-\omega_0)(e^{\beta\hbar\omega_0}+1) - P_1'(\omega_0)(e^{-\beta\hbar\omega_0}+1)] + O(\delta^4). \tag{34}$$

In the limit $T\to\infty$, we see from Eqs. (27) and (28) that the quantum-mechanical correlation functions, $\hat{C}_i(\omega)$, defined in the time domain by[1]

$$C_1(t_1 - t_2) = Tr_b[\rho_b\Lambda^\dagger(t_1)\Lambda(t_2)], \tag{35}$$

$$C_2(t_1 - t_2) = Tr_b[\rho_b\Lambda(t_1)\Lambda(t_2)], \tag{36}$$

correctly reduce to the classical result of Eq. (15). We also note that since $\hat{C}_i(\omega)\sim T$ as $T\to\infty$, the perturbation expansion of the previous paper and Eqs. (26), (33) and (34) above is meaningful in this limit only if δ goes to zero such that $\lim_{\delta\to 0}\lim_{T\to\infty}\delta^2 T = \text{constant}$.

III. REAL OHMIC–LORENTZIAN FIELD

Consider a coupling bath field, Λ, where the h_k are all purely real. In this case, the correlation functions $\hat{C}_1(\omega)$ and $\hat{C}_2(\omega)$ are equal and are defined to be simply $\hat{C}(\omega)$, which is given by Eqs. (27) and (20). Equations (26) and (33) then yield expressions for $1/T_1$ and $1/T_2'$. We are particularly interested in the relative magnitude of $2T_1$ and T_2, and so therefore we would like to ascertain the sign of T_2'. Using

$$\hat{C}(\omega)\hat{C}(-\omega) = 4\Gamma(|\omega|)^2 n(|\omega|)[n(|\omega|)+1], \tag{37}$$

after some algebra we obtain (setting $\delta = 1$)

$$\frac{1}{T_2'} = \frac{8\omega_0\bar{A}^2\bar{\lambda}^2\bar{\beta}^3}{\pi} \times P\int_0^{\infty} dx \frac{x^2e^x}{(x^2-\bar{\beta}^2)(x^2+\bar{\beta}^2\bar{\lambda}^2)^2(e^x-1)^2} \times\left(\frac{\bar{\beta}^2\bar{\lambda}^2 - 3x^2}{\bar{\beta}^2\bar{\lambda}^2 + x^2} - \frac{x(e^x+1)}{e^x-1}\right), \tag{38}$$

where $\bar{\beta} = \beta\hbar\omega_0$, $\bar{\lambda} = \lambda/\omega_0$, and $\bar{A} = A_1/\omega_0 = A_2/\omega_0$. The low-temperature behavior of $1/T_2'$ can be easily obtained from the previous equation by letting $\bar{\beta}\to\infty$. One finds that

$$\frac{1}{T_2'} = \frac{8\alpha\omega_0\bar{A}^2}{\pi\bar{\lambda}^2\bar{\beta}^3}, \quad \frac{1}{\bar{\beta}} = \frac{kT}{\hbar\omega_0} \ll 1, \tag{39}$$

where

$$\alpha = \int_0^{\infty} dx \frac{x^2e^x(xe^x + x - e^x + 1)}{(e^x-1)^3} = 6.5797\cdots. \tag{40}$$

Notice that this "pure dephasing" rate is positive at low temperatures, and goes to zero like T^3.

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In the high-temperature limit we have seen that $\hat{C}(\omega)$ becomes an even function of ω and, indeed, reduces to the semiclassical or stochastic result of Eq. (19). Therefore, in this limit, the model discussed in this section is identical to the stochastic model discussed in Sec. 3.2 of BS. Furthermore, in Sec. V and Appendix E of the previous paper,[1] we showed explicitly that the results of BS are recovered from the quantum-mechanical framework. Thus, for the high-temperature limit we have, from Eq. (60) of BS,

$$\frac{1}{T_2'}=\frac{4\omega_0\bar{A}^2(5\bar{\lambda}^2+1)}{\bar{\beta}^2\bar{\lambda}(\bar{\lambda}^2+1)^3}, \tag{41}$$

where we have used the correspondence, as discussed in Sec. II, that $C_1=C_2=\Lambda^2$ in BS is equal to $A/\beta\hbar$. This expression for $1/T_2'$ is always positive, showing that, at least in the low- and high-temperature limits, $T_2<2T_1$.

In Fig. 1, we plot $T_2/2T_1=(1+2T_1/T_2')^{-1}$ vs T for $\bar{\lambda}=1$ and $\bar{A}=0.03$ (setting $\delta=1$), where T_2' and T_1 are obtained numerically from Eqs. (26) and (33) [or (36)]. We see that for these parameters $T_2\leqslant 2T_1$. We also see that at $T=0$, $T_2=2T_1$, which follows from the fact that while T_2' becomes infinite, T_1 remains finite.

For comparison in Fig. 1, we have also plotted the high-temperature limit or stochastic-model results from Eq. (41) for $1/T_2'$, and

$$\frac{1}{2T_1}=\frac{2\omega_0\bar{\lambda}\bar{A}}{\bar{\beta}(\bar{\lambda}^2+1)}-\frac{16\omega_0\bar{\lambda}\bar{A}^2}{\bar{\beta}^2(\bar{\lambda}^2+1)^3}, \tag{42}$$

from Eq. (56) of BS. We see that by $kT/\hbar\omega_0=2$, we have nearly obtained agreement between the quantum and stochastic models.

Finally, we note that for the parameters and temperatures studied, the fourth-order contributions to $1/T_2$ and $1/T_1$ make less than 20% corrections to the second-order results, and so we feel confident in truncating the perturbation expansion. For the stochastic model the perturbation expansion is well-behaved,[3,7] and for the magnitudes of fourth-order corrections here, leads to accurate results.

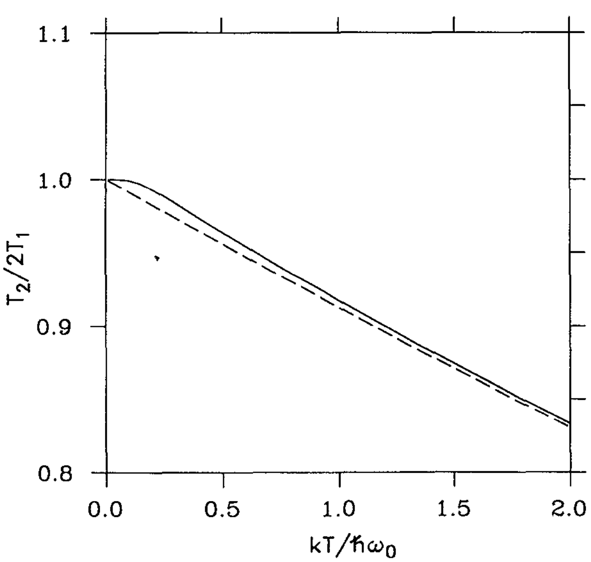

FIG. 1. $T_2/2T_1$ vs $kT/\hbar\omega_0$ for the real OL model discussed in Sec. III, with $\bar{\lambda}=1$ and $\bar{A}=0.03$. The dotted line is the semiclassical (stochastic) result.

IV. COMPLEX OHMIC–LORENTZIAN FIELD–SPIN-1/2 PARTICLE IN FLUCTUATING TRANSVERSE MAGNETIC FIELDS

Another interesting special case of the fluctuations occurs when some of the coupling constants h_k are purely real while others are purely imaginary, but in just such a way as to render $\Gamma_2(\omega)=\hat{C}_2(\omega)=0$. (We note that in this case Λ is neither Hermitian not anti-Hermitian, and thus the system does not possess time-reversal symmetry.[8]) A physical realization of precisely this situation is a spin-1/2 particle in a static longitudinal magnetic field with equal strength but uncorrelated fluctuating magnetic fields in the two transverse directions.[2] In this case we have (again setting $\delta=1$)

$$\frac{1}{T_2'}=\frac{8\omega_0\bar{\lambda}^2\bar{A}^2\bar{\beta}^3}{\pi}\times P\int_0^\infty dx\,\frac{x^2e^x}{(x^2-\bar{\beta}^2)(x^2+\bar{\beta}^2\bar{\lambda}^2)^2(e^x-1)^2}\times\left(\frac{2(\bar{\beta}^2\bar{\lambda}^2-x^2)}{\bar{\beta}^2\bar{\lambda}^2+x^2}-\frac{x(e^x+1)}{e^x-1}\right), \tag{43}$$

where $\bar{A}=A_1/\omega_0$. As before, the low-temperature behavior of $1/T_2'$ can be easily obtained from the previous equation by letting $\bar{\beta}\to\infty$, with the result

$$\frac{1}{T_2'}=\frac{8\bar{\alpha}\omega_0\bar{A}^2}{\pi\bar{\lambda}^2\bar{\beta}^3},\quad \frac{1}{\bar{\beta}}=\frac{kT}{\hbar\omega_0}\ll 1, \tag{44}$$

where

$$\bar{\alpha}=\int_0^\infty dx\,\frac{x^2e^x(xe^x+x-2e^x+2)}{(e^x-1)^3}=3.2899\cdots. \tag{45}$$

Again we see that $1/T_2'$ is positive at low temperatures, and goes to zero like T^3.

The high-temperature limit can be obtained directly from Eq. (83) of BS, with the definition $\omega_x^2/2=C_1=A/\beta\hbar$:

$$\frac{1}{T_2'}=\frac{2\omega_0\bar{A}^2(1+6\bar{\lambda}^2-3\bar{\lambda}^4)}{\bar{\beta}^2\bar{\lambda}(\bar{\lambda}^2+1)^3}. \tag{46}$$

The most interesting property of this high-temperature result is that whenever $\bar{\lambda}>\bar{\lambda}_c=\sqrt{1+2\sqrt{3}/3}=1.4679\cdots$ $1/T_2'$ is negative, implying that $T_2>2T_1$. Since we have shown that $1/T_2'$ is always positive at low temperatures, if $\bar{\lambda}>\bar{\lambda}_c$ this quantity must undergo a change in sign as the temperature increases.

In Fig. 2 $T_2/2T_1$ is plotted for $\bar{\lambda}=3$ and $\bar{A}=0.375$. One sees that for $kT/\hbar\omega_0>0.4$, this ratio is indeed larger than 1. Also shown in Fig. 2 is the stochastic-model result from Eq. (46), and

$$\frac{1}{2T_1}=\frac{2\omega_0\bar{A}\bar{\lambda}}{\bar{\beta}(\bar{\lambda}^2+1)}\left(1+\frac{2\bar{A}(\bar{\lambda}^2-3)}{\bar{\beta}(\bar{\lambda}^2+1)^2}\right), \tag{47}$$

from Eq. (81) of BS.

V. DISCUSSION AND CONCLUSION

For a given temperature or more precisely, equilibrium constant K, which is the ratio of the excited state to ground state equilibrium populations), not all possible values of the

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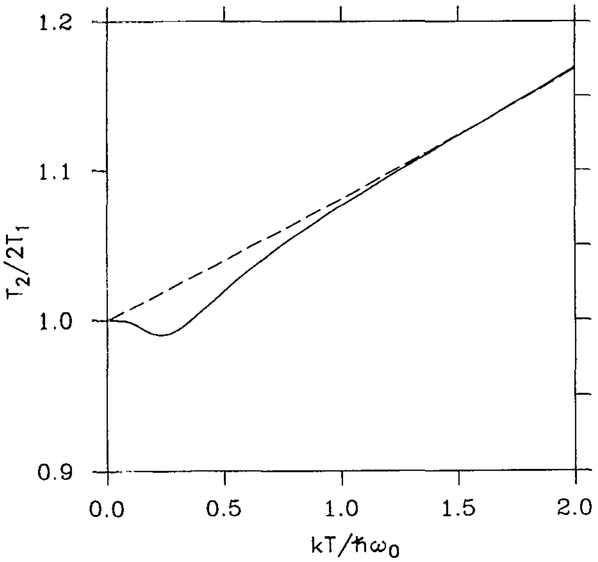

FIG. 2. $T_2/2T_1$ vs $kT/\hbar\omega_0$ for the complex OL model discussed in Sec. IV, with $\bar{\lambda} = 3$ and $\bar{A} = 0.375$. The dotted line is the semiclassical (stochastic) result.

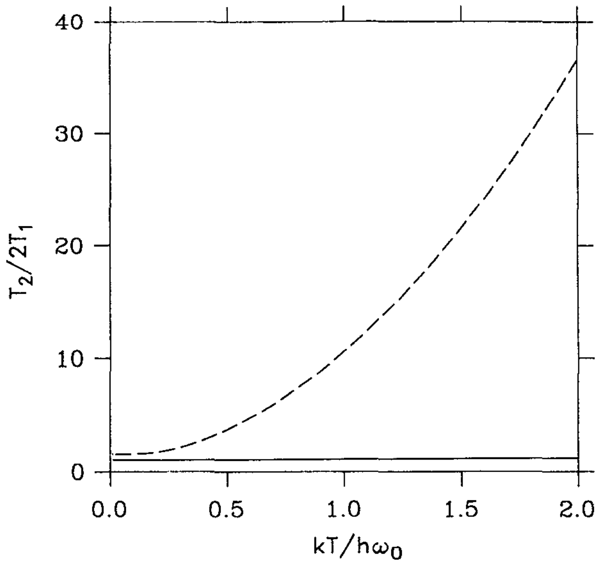

FIG. 3. Same as Fig. 2, except the dotted line is the upper bound for $T_2/2T_1$.

ratio $T_2/2T_1$ are acceptable, due to the positivity requirement of the density matrix. In the appendix we show that if we assume the Bloch equations are valid for all times, this positivity requirement leads to the inequality

$$T_2/2T_1 \leqslant g(K), \tag{48}$$

with

$$g(K) = (1+K)/(1-\sqrt{K})^2. \tag{49}$$

Note that when $K = 0$, and only the ground state is populated, we recover the usual inequality $T_2 \leqslant 2T_1$, while for $K = 1$ (both states equally populated) the value of T_1 puts no restriction whatsoever on T_2, as shown by Sevian and Skinner.[3]

To illustrate this upper bound, in Fig. 3 we show our quantum result for $T_2/2T_1$ for the magnetic model discussed in Sec. IV, and with the same parameters in Fig. 2, along with the bound from Eq. (48), which is calculated from Eq. (34) for K. We see that the quantum result is well below the bound, and therefore does not violate the density-matrix positivity condition.

From Fig. 3, we see that the bound does not go to 1 as $T \to 0$, because, as discussed in the previous paper,[1] the equilibrium constant remains nonzero at $T = 0$. Setting $\delta = 1$, we have from Eq. (117) of Ref. 1

$$\lim_{T\to 0} K = \frac{1}{\pi}\int_0^\infty d\omega\, \frac{\Gamma_1'(\omega)}{\omega + \omega_0}, \tag{50}$$

which for the OL model is

$$\lim_{T\to 0} K = \frac{\bar{A}\bar{\lambda}}{\pi}\int_0^\infty dx\, \frac{\bar{\lambda}^2 - x^2}{(\bar{\lambda}^2 + x^2)^2 (x+1)} = \frac{\bar{A}\bar{\lambda}}{\pi(\bar{\lambda}^2+1)}\left(\frac{\bar{\lambda}\pi + (\bar{\lambda}^2 - 1)\ln(\bar{\lambda})}{\bar{\lambda}^2+1} - 1\right). \tag{51}$$

For $\bar{\lambda} = 3$ and $\bar{A} = 0.375$ (as in Figs. 2 and 3), this gives $\lim_{T\to 0} K = 0.02941\ldots$.

In conclusion, we have shown that, under certain conditions, it is possible for the inequality $T_2 \leqslant 2T_1$ to be violated for the relaxation of a nondegenerate two-level system linearly and off-diagonally coupled to a bath of quantum-mechanical harmonic oscillators. The model that we have developed progresses smoothly from zero temperature up to infinite temperature, where it is equivalent to the semiclassical or stochastic models. The results for the ratio $T_2/2T_1$ also show a smooth dependence on temperature. Therefore this work shows that the inequality $T_2 > 2T_1$, which was originally derived from the stochastic model, is not an artifact of the infinite-temperature limit inherent in that model, but can occur at finite temperature as well. This work, coupled with the exact numerical results for the stochastic model[3] (which showed that, even away from the weak-coupling limit, T_1 and T_2 were meaningful quantities), makes us hopeful that this violation of the usual inequality will eventually be seen experimentally.

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APPENDIX

We assume that the dynamics of the density matrix is governed by the Bloch equations [see Eqs. (2)–(5) of Ref. 1], with population and phase relaxation times T_1 and T_2, respectively, and that detailed balance is satisfied in that $K = \sigma_{11}^{eq}/\sigma_{00}^{eq} = k_{10}/k_{01}$. The solution of these equations is

$$\sigma_{00}(t) = \frac{1}{1+K} + \left(\sigma_{00}(0) - \frac{1}{1+K}\right)e^{-t/T_1}, \tag{A1}$$

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$$\sigma_{11}(t)=\frac{K}{1+K}+\left(\sigma_{11}(0)-\frac{K}{1+K}\right)e^{-t/T_1}, \quad (A2)$$

$$\sigma_{10}(t)=\sigma_{10}(0)e^{-i\omega t}e^{-t/T_2}, \quad (A3)$$

$$\sigma_{01}(t)=\sigma_{01}(0)e^{i\omega t}e^{-t/T_2}, \quad (A4)$$

where $\omega=\omega_0+\Delta\omega$.

A physical density matrix must be positive semidefinite at all times, that is, its eigenvalues must remain non-negative as the matrix evolves in time. For a given value of K, this positivity condition puts a restruction on the values of T_1 and T_2 that a physical TLS can possess. The two eigenvalues of the density matrix are

$$\lambda_{\pm}=[1\pm\sqrt{1-4c(t)}]/2, \quad (A5)$$

where

$$c(t)\equiv x(t)-s(t), \quad (A6)$$

$$x(t)\equiv\sigma_{00}(t)\sigma_{11}(t), \quad (A7)$$

and

$$s(t)\equiv\sigma_{01}(t)\sigma_{10}(t). \quad (A8)$$

Therefore the positivity condition is equivalent to the requirement that $0\leqslant c(t)\leqslant 1/4$.

It is easy to see that the requirement that $c(t)\leqslant 1/4$ is satisfied by the Bloch equations since $x(t)\leqslant 1/4$ [because $\sigma_{00}(t)+\sigma_{11}(t)=1$] and $s(t)\geqslant 0$ [because $\sigma_{10}(t)$ and $\sigma_{01}(t)$ form a complex conjugate pair]. So only the requirement that $c(t)\geqslant 0$ remains to be analyzed. If the initial density matrix is assumed to be positive semidefinite, then $c(t)$ is initially non-negative. For $c(t)$ to take on a negative value at some later value of time, it must first take on the value zero, since the equations governing the dynamics are continuous. Since the Bloch equations are Markovian and, therefore, any time can be used as the initial time without altering the equations, the positivity requirement is equivalent to the statement that if $c(0)=0$, then $c'(0)\geqslant 0$.

One finds that if $c(0)=0$ $[x(0)=s(0)]$, then $c(t)$ is

$$c(t)=\frac{K}{(1+K)^2}+\left(\frac{K+\sigma_{11}(0)(1-K)}{1+K}-\frac{2K}{(1+K)^2}\right)\times e^{-t/T_1}+\left(\sigma_{11}(0)[1-\sigma_{11}(0)]-\frac{K+\sigma_{11}(0)(1-K)}{1+K}+\frac{K}{(1+K)^2}\right)e^{-2t/T_1}-\sigma_{11}(0)[1-\sigma_{11}(0)]e^{-2t/T_2}. \quad (A9)$$

The time derivative of $c(t)$ at $t=0$ is

$$c'(0)=-\frac{1}{T_1}[1-2\sigma_{11}(0)]\left(\sigma_{11}(0)-\frac{K}{1+K}\right)+\frac{2}{T_2}\sigma_{11}(0)[1-\sigma_{11}(0)]. \quad (A10)$$

The positivity condition that $c'(0)\geqslant 0$ then yields

$$\frac{1}{T_2}\geqslant\frac{[1-2\sigma_{11}(0)][\sigma_{11}(0)-K/(1+K)]}{\sigma_{11}(0)[1-\sigma_{11}(0)]}\frac{1}{2T_1}. \quad (A11)$$

Since $\sigma_{11}(0)$ is an arbitrary constant between zero and one, the most general inequality relating T_1 and T_2 is

$$1/T_2\geqslant f(K)(1/2T_1), \quad (A12)$$

where

$$f(K)=\max\left(\frac{[1-2\sigma_{11}(0)][\sigma_{11}(0)-K/(1+K)]}{\sigma_{11}(0)[1-\sigma_{11}(0)]}\right), \quad \text{for } 0\leqslant\sigma_{11}(0)\leqslant 1. \quad (A13)$$

This maximum value can easily be found, yielding

$$f(K)=(1-\sqrt{K})^2/(1+K). \quad (A14)$$

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