The Journal of Chemical Physics

On the nonperturbative theory of pure dephasing in condensed phases at low temperatures

David Reichman, Robert J. Silbey, and Alberto Suárez

Citation: J. Chem. Phys. **105**, 10500 (1996); doi: 10.1063/1.472976
View online: http://dx.doi.org/10.1063/1.472976
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v105/i23
Published by the American Institute of Physics.

On the nonperturbative theory of pure dephasing in condensed phases at low temperatures

David Reichman and Robert J. Silbey
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Alberto Suárez
Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles-Campus Plaine-C.P. 231, 1050 Brussels, Belgium

(Received 21 June 1996; accepted 10 September 1996)

The nonperturbative treatment of the pure dephasing problem studied by Osad'ko and Skinner and Hsu is reexamined. It is found that these treatments are inadequate for very low temperatures in the case of Ohmic friction. New nonperturbative methods are used to expose interesting pure dephasing behavior at very low temperatures in this case. The methods are shown to coincide with the previous theories at higher temperatures. The experimental detection of such phenomena is discussed. © *1996 American Institute of Physics.* [S0021-9606(96)50647-1]

I. INTRODUCTION

The relaxation of a two level system coupled to a quantum mechanical heat bath has been a topic of great interest in the past decade. One aspect of this subject is the thermal broadening of the zero-phonon line (ZPL),[1,2] which is intimately connected to the ''pure'' dephasing of two quantum levels.[3] Such dephasing arises from a system-bath (electron-phonon) coupling that is diagonal in the system states, leading to the decay of the off-diagonal element $[\sigma_{10}(t)]$ of the reduced density matrix. The study of this problem was advanced by Osad'ko,[4] who provided a nonperturbative expression for the decay of the off-diagonal element of the reduced density matrix for two quantum levels coupled quadratically and diagonally to a bath of quantum mechanical harmonic oscillators. Using a different approach, Skinner and Hsu[3] were able to rederive the result of Osad'ko, and then used this result to interpret the experimentally obtained absorption zero-phonon line shapes for dilute impurities in crystals. Good agreement was found in various cases, including the dephasing induced by acoustic,[5] optical,[5] and pseudolocal phonons.[6] The derivations of Osad'ko and Skinner and Hsu are correct only in the asymptotic regime $t \gg \tau_b$, where τ_b is the relaxation time of the bath. As is well known, at low temperatures compared to the phonon frequencies, the bath takes on two distinct timescales.[7] The first is the ''mechanical'' scale $1/\omega_c$, where ω_c is the upper cutoff frequency for the bath modes. This is the same timescale that governs the decay of bath correlations at high temperatures, and is usually on the order of 10–100 ps. The second time scale is the quantum-thermal scale $\beta\hbar$, which may become significantly longer than the mechanical timescale at very low temperatures ($T \sim 10$ mK and lower). Since the theories of Osad'ko and Skinner and Hsu are exact only in the limit of times much greater than the larger of the two scales, interesting behavior may be missed at very low temperatures. At such temperatures, the quantum-thermal times scale is on the order of 10 ns or longer, and thus such behavior may be observable by modern spectroscopic techniques, e.g., photon echoes.

We thus wish to investigate the intermediate time effects at very low temperatures in the pure dephasing problem. In doing so, we will introduce a method distinct from that of Osad'ko and Skinner and Hsu that is valid for all times, while remaining formally exact (i.e., nonperturbative). This will allow us to probe the intermediate time regime for very low temperatures, and to assess the relevance of the results, if any, to experiments.

We focus on the case of the Ohmic bath.[8] This is done for several reasons. First, the results for the Ohmic bath are the most interesting. Second, while the Ohmic case is often unrealistic for condensed phase optical dephasing experiments at low temperatures, we will argue that the effects uncovered here may indeed manifest themselves in a variety of experimental settings. From a theoretical point of view, little is known about the behavior of quadratic system-bath coupling in the Ohmic case.[9] While the pure dephasing problem is certainly much simpler than other related problems (e.g., the spin–boson problem[8]), an exact solution could give insight into the nonlinear effect of an Ohmic bath in more demanding problems. Last, we wish to study the Ohmic case because it is a paradigm for the simulation of systems with an abundance of low frequency modes, such as liquids, proteins, and polymers.[10] The methods we employ are flexible enough to treat any spectral distribution of bath modes. In the next section, we will study the case of linear electron-phonon coupling in some detail. In Sec. III, we will discuss some possible settings where these results may be relevant. In Sec. IV, we treat the quadratic electron–phonon coupling. In Sec. V, we conclude.

II. LINEAR ELECTRON-PHONON COUPLING

We begin with the Hamiltonian for a two level system coupled linearly to a bath of harmonic oscillators ($\hbar=1$)

$$H=\omega_0|1\rangle\langle 1|+H_b+\Delta|1\rangle\langle 1|, \tag{1}$$

where

$$H_b=\sum_k \omega_k a_k^\dagger a_k,$$

$$\Delta=\sum_k h_k(a_k^\dagger+a_k),$$

and $|0\rangle$, $|1\rangle$ are the ground and excited states of the two level system, respectively. In general, such an interaction will not induce relaxation of the reduced density matrix elements, diagonal or off diagonal. However, if we choose the coupling constants to have an Ohmic distribution,[8] i.e.,

$$\lim_{\omega\to 0} J(\omega)\sim\omega, \tag{2}$$

where the spectral density $J(\omega)$ is defined

$$J(\omega)=\pi\sum_k h_k^2\delta(\omega-\omega_k).$$

Then Skinner and Hsu (see also Duke and Mahan[11]) found that the coherence variable of the two level system decays to zero exponentially with a pure dephasing rate proportional to temperature. We now proceed to solve this model exactly for all times. We assume that the initial value of the density operator takes the factorized form[12]

$$\rho(0)=\sigma(0)\rho_b, \tag{3}$$

where

$$\rho_b=\frac{\exp(-\beta H_b)}{Tr_b[\exp(-\beta H_b)]}. \tag{4}$$

It is simple to show that the off-diagonal element of the reduced density operator (defined as $\sigma(t)=Tr_b[\rho(t)]$) equals

$$\sigma_{10}(t)=e^{-i\omega_0 t}\sigma_{10}(0)Tr_b[\rho_b\ \exp\{-i(H_b+\Delta)t\}\times\exp(iH_b t)]. \tag{5}$$

Note that $H_b+\Delta$ is diagonalized by the unitary shift operator

$$U=\exp\left[\sum_k \frac{h_k}{\omega_k}(a_k^\dagger-a_k)\right].$$

Using the cyclic property of the trace, we find

$$\sigma_{10}(t)=\exp\left\{-i\left(\omega_0+\sum_k \frac{h_k^2}{\omega_k}\right)t\right\}Tr_b[U(t)U^\dagger\rho_b], \tag{6}$$

where

$$U(t)=\exp\left[\sum_k \frac{h_k}{\omega_k}(a_k^\dagger e^{i\omega_k t}-a_k e^{-i\omega_k t})\right]. \tag{7}$$

Combining the shift operators, and using the expression for the thermal average of the exponential of a linear combination of bosonic raising and lowering operators, we find

$$\sigma_{10}(t)=\exp\left[-i\left\{\tilde{\omega}_0 t+\frac{2}{\pi}\int_0^\infty d\omega J(\omega)\frac{\sin\omega t}{\omega^2}\right\}\right]\times\exp\left[-\frac{2}{\pi}\left\{\int_0^\infty d\omega\frac{J(\omega)}{\omega^2}\times(1-\cos(\omega t))\coth(\beta\omega/2)\right\}\right], \tag{8}$$

where we have combined the polaron shift $(1/\pi)\int_0^\infty d\omega J(\omega)/\omega$ and the bare frequency ω_0 into the renormalized frequency $\tilde{\omega}_0$. Using the spectral density $J(\omega)=\alpha\omega e^{-\omega/\omega_c}$ we find, for low temperatures compared to the bath[13] (i.e., $\beta\omega_c\gg 1$),

$$\sigma_{10}(t)=\left(\frac{1}{1+\omega_c^2t^2}\right)^{\alpha/\pi}\left[\frac{\left(\frac{\pi t}{\beta\hbar}\right)}{\sinh\left(\frac{\pi t}{\beta\hbar}\right)}\right]^{2\alpha/\pi}\times\exp\left(-i\left(\tilde{\omega}_0 t+\left(\frac{2\alpha}{\pi}\right)\tan^{-1}(\omega_c t)\right)\right), \tag{9}$$

where the $\hbar$ has been reinserted for dimensional convenience. For $t>\beta\hbar$ the dephasing is exponential with a rate constant

$$\frac{1}{T_2}=\frac{2\alpha\pi}{\beta\hbar},$$

as discussed by Skinner and Hsu.[3] However, for times $\beta\hbar/\pi>t\gg 1/\omega_c$, we find that the coherence variable decays with the power law

$$|\sigma_{10}(t)|\sim(\omega_c t)^{-2\alpha/\pi}.$$

At zero temperature, after an initial short lived Gaussian decay, the decay of the coherence variable is seen to be algebraic for all times. Thus, pure dephasing may indeed occur at zero temperature, and the low and zero temperature line shapes will show marked deviations from the usual Lorentzian behavior. For $\beta\omega_c\gg 1$ the line shape will not be Lorentzian in the wings due to the algebraic decay at short times. At zero temperature, (neglecting the line shift), the line shape function may be expressed

$$I(\omega)\sim\int_{-\infty}^{\infty} dt e^{i\omega t}\frac{1}{(1+\omega_c^2t^2)^{\bar{\alpha}}}=\frac{2\sqrt{\pi}}{\omega_c\Gamma(\bar{\alpha})}\left(\frac{|\omega|}{2\omega_c}\right)^{\bar{\alpha}-1/2}K_{\bar{\alpha}-1/2}\left(\frac{|\omega|}{\omega_c}\right),$$

where K_ν is a modified Bessel function. Note here that the line shape shows a singularity at $\omega=0$ for $\bar{\alpha}\leqslant 1/2$ and a singularity in its derivative at $\omega=0$ for $\bar{\alpha}>1/2$. We may conclude, perhaps somewhat imprecisely, that the anomalous dephasing results from an abundance of low frequency modes which are ''active'' at arbitrarily low temperatures.

We wish to emphasize that pure dephasing at zero temperature is not expected for super-Ohmic baths. Note, how-

ever, that algebraic decay may also occur for super-Ohmic spectral densities. Consider the spectral density

$$J(\omega)=\alpha\omega^2 e^{-\omega/\omega_c}.$$

For high temperatures compared to the bath, $\coth(\beta\omega/2)\approx 2/\beta\omega$, and thus

$$\int_0^\infty \frac{J(\omega)}{\omega^2}(1-\cos(\omega t))\coth(\beta\omega/2)\approx\frac{\alpha}{\beta}\ln(1+\omega_c^2 t^2).$$

This gives rise to a coherence decay at high temperatures

$$\sigma_{10}(t)\sim\frac{1}{(1+\omega_c^2 t^2)^{2\alpha/\pi\beta}},$$

which is similar to that of an Ohmic bath at zero temperature. This quadratic spectral density could represent, for example, a two dimensional system (surface) with deformation potential coupling.

These results are essentially the same as those found by Wu, Brown, and Lindenberg[14] for a similar model proposed to study quantum tunneling in excimeric molecular crystals. Our results, however, are analytically exact, and interpolate smoothly between the various decay regimes, while the work of Wu, Brown, and Lindenberg relies on numerical integration and interpolation. The result is also similar to that obtained by Duke and Mahan[11] in their study of the phonon induced broadening of line shapes in crystals. Similar results are also discussed by Mahan in his work on x-ray spectra in metals.[15] In light of these results, the above may not seem surprising, although within the chemical physics community, the fact that ''pure dephasing'' may occur at zero temperature in special circumstances seems to be somewhat unappreciated.

III. EXPERIMENTAL RELEVANCE

Before generalizing the above results to the case of quadratic electron–phonon coupling, we would like to discuss the experimental detection of the phenomena discussed above.

We have treated an idealized Hamiltonian with a system-bath coupling incapable of causing transitions between the two states of the system. We thus focus on only one aspect of the relaxation process (pure phase relaxation). In general, optical experiments can probe either population decay rates (''T_1'' processes probed, for instance, by a three pulse echo experiment) or phase relaxation (''T_2'' processes probed by a two pulse echo experiment). The T_2 process will have contributions from both population relaxation induced by perturbations off diagonal in the system states, and pure phase relaxation, induced by diagonal perturbations.[16] Only in the weak coupling limit are such processes independent,[16,17] giving rise to phase relaxation comprised of noninterfering contributions from population decay and pure dephasing. Thus, our results require that the strength of the diagonal coupling be much stronger than that of the off-diagonal coupling. In this way, we may hope to treat the T_1 processes to lowest order, while treating the pure dephasing nonperturbatively and thus ignore the interference between the two types of relaxation. Ideal experimental situations would choose systems with long excited state lifetimes and weak nonadiabatic coupling, etc., so that T_1 effects are kept as small as possible. Since the pure dephasing contribution does not extrapolate to zero at zero temperatures, the T_2 process will not reach a lifetime limited value. Such effects may indeed by noticeable at very low temperatures. Last, parameters such as ω_c and α must take on values appropriate for experimental detection. By this, we mean that these parameters must conspire to maintain a decay slow enough to be observable in the time window of $\sim$1 ps to $\sim$1 μs.

The interesting aspect of the pure dephasing behavior occurs in the time interval $1/\omega_c \ll t < \beta\hbar$. This time domain will be accessible experimentally for $T\leqslant 10$ mK. Such temperatures are indeed experimentally reachable, but factors such as inhomogeneous heating effects make these experiments somewhat difficult to perform.[18]

Last, we would like to briefly sketch some condensed phase systems for which the Ohmic constraint (2) is valid. The first is the case studied by Duke and Mahan,[11] namely dilute impurity spectra in a piezoelectric crystal. Certain semiconductors such as CdS have the property that an electric field is produced when the crystal is squeezed, and vice versa. This gives rise to an electron–phonon coupling that is proportional to the amplitude of the phonon field. This amplitude dependent coupling, combined with the density of states for Debye (long wavelength) phonons, gives rise to an Ohmic-type coupling.[1,19] Thus, an electronic transition at an impurity site in a piezoelectric crystal may be crudely described by the Hamiltonian (1) combined with the constraint (2). One difficulty in this description may be screening effects due to other electrons, which might wash out the algebraic behavior given in Eq. (9). However, it may be possible that a very low temperature echo experiment probing an optical transition at an impurity site in a piezoelectric crystal may indeed expose such interesting behavior.

Another situation that naturally gives rise to the Ohmic constraint (2) is the relaxation of tunneling systems in metallic glasses at low temperatures.[20] Here the Ohmic friction arises from the excitation of electron-hole pairs near the Fermi surface. Consider the standard spin–boson problem,

$$H_{\mathrm{SB}}=\left(\frac{\Delta_0}{2}\right)\sigma_x-\left(\frac{\epsilon_0}{2}\right)\sigma_z+\sum_k \omega_k a_k^\dagger a_k + \sum_k h_k(a_k^\dagger+a_k)\sigma_z, \tag{10}$$

which is thought to govern the dynamics of tunneling systems at low temperatures in glasses (metallic as well as insulating). For the case of a metallic glass, the bosonic bath excitations are electron-hole pairs, giving rise to an Ohmic spectral density.[20,21] We may diagonalize the spin portion of Eq. (10) simply, leaving

$$\widetilde{H}_{\mathrm{SB}}=(E/2)\sigma_z+[(\Delta_0/E)\sigma_x+(\epsilon_0/E)\sigma_z] \times\sum_k h_k(a_k^\dagger+a_k), \tag{11}$$

where

$$E=\sqrt{\Delta_0^2+\epsilon_0^2}.$$

In general, the parameters Δ_0 and ϵ_0 have a distribution of values. Tunneling is observed at very low temperatures only for the few tunneling systems for which the effects of the bias are weak. In such cases, due to the large density of states of the electron-hole pairs at the Fermi level in metallic glasses, the T_1 rate is often so large that all phase coherence is lost before an echo can be produced.[20] It may be possible, however, to ''tune'' the bias, so that the diagonal coupling is stronger than the nondiagonal coupling. Such a bias may be produced by a static external field. In fact, this possibility has been proposed as a way of initially preparing localized tunneling states.[22] If Δ_0/E is small enough, T_1 processes may be suppressed, and we may hope to see the effect of the algebraic loss of phase coherence. Even with the suppression of tunneling, however, the large cutoff energy of the bath, and the large diagonal coupling strength would make observation of this effect difficult.[20] In any event, the search for such behavior is worthwhile since it would reveal dramatic behavior induced by Ohmic coupling.

Ohmic-type dephasing may also occur in confined geometries, or in special cases where coupling to the strain field is much stronger in one direction than the others. Recently, Kikas *et al.*[23] have proposed a novel explanation of some anomalous impurity spectra in low temperature insulating glasses. They have noticed that the low temperature spectral holes for chlorin dopant photoproduct states in several different glasses show a peculiar, non-Lorentzian shape. They explain this by postulating that a local defect (''planar crack'') caused by dopant phototransformation, induces quasi-one dimensional electron–phonon coupling. This behavior is essentially given by the Ohmic model outlined in Sec. II. There are some problems with the explanation of Kikas *et al.* The first is their use of a zero temperature calculation to explain the product spectra at 5 K. There is also no direct evidence for the ''crack'' formation. Thus, while the work of Kikas *et al.* would provide an interesting example of Ohmic dephasing, the evidence is not convincing enough at this time to draw any firm conclusions.

IV. QUADRATIC ELECTRON-PHONON COUPLING

We now turn to a study of the effect of quadratic electron–phonon coupling on pure dephasing when an abundance of low frequency modes of the bath are present. Again, we use the Ohmic bath as a model. We will use the Hamiltonian studied by Skinner and Hsu[3] (again setting $\hbar=1$)

$$H=\omega_0|1\rangle\langle 1|+H_b+\Delta|1\rangle\langle 1|, \tag{12}$$

with

$$H_b=\sum_k \omega_k a_k^\dagger a_k,$$

$$\Delta=\frac{W}{2}\phi^2,$$

and

$$\phi=\sum_k h_k(a_k^\dagger+a_k).$$

We note that the linear electron–phonon term has been neglected, and a particular form of the quadratic term has been used. Neither of these assumptions are necessary. We neglect the linear term simply to focus on the nonlinear effect. As we will see, this term could easily be included in our study. The form of the coupling is chosen to make contact with the work of Skinner and Hsu. In fact, we will show that our method is somewhat better adapted than the method of Skinner and Hsu for treating more general quadratic electron–phonon coupling terms.[24]

There have been two previous nonperturbative theories of the pure dephasing of a two level system coupled quadratically to a bath of harmonic oscillators. Osad'ko[4] used an integral equation approach to find a nonperturbative expression for the off diagonal reduced density matrix element in the limit $t\to\infty$. Skinner and Hsu found the expression[3]

$$\sigma_{10}(t)=\sigma_{10}(0)\exp(-i\omega_0 t)\langle F(t)\rangle, \tag{13}$$

where

$$\langle F(t)\rangle=\left\langle \exp_T\left[-i\int_0^\infty d\tau\Delta(\tau)\right]\right\rangle.$$

$\Delta(t)$ is the Heisenberg expression for the operator Δ, T is the time ordering operator, and the brackets represent a thermal average over phonon states. Skinner and Hsu evaluate (13) by means of a cumulant expansion. Unlike the linear case, all cumulants contribute in general. In the limit $t\gg\tau_c$, where τ_c is the characteristic decay time of bath correlations, all cumulants are proportional to time, giving rise to exponential decay of the coherence variable. The resulting dephasing rate is obtained by exactly resuming all the cumulants in this limit. The methods of Osad'ko and of Skinner give identical results.

We recall that, in general, there are two correlation times for the bath at low temperatures. The methods of Osad'ko and Skinner and Hsu are valid only in the time regime $t\gg\max(1/\omega_c,\beta\hbar)$ and thus say nothing about the potentially interesting regime between the mechanical and thermal correlation times. In fact, in the case of linear electron–phonon coupling, these methods are incorrect in predicting that the pure dephasing vanishes as the temperature approaches zero for the Ohmic density of states. It would be interesting to see if similar effects exist when the system-bath coupling is quadratic in the bath coordinates. We thus would like to have a method that reproduces the Osad'ko and Skinner and Hsu results when they are valid, while properly describing the pure dephasing at very low temperatures.

Our method is based on a powerful but somewhat unappreciated many body technique introduced by Balian and Brezin as a means to generalize Wick's theorem.[25] This method is useful for evaluating the thermal average of exponential quadratic phonon operators. The method has been used, for example, by Friesner *et al.*[26] in their study of mul-

timode resonance Raman line shapes. The details of the procedure are outlined in Refs. 26 and 27. We begin with the expression for $\langle F(t)\rangle$ in the form

$$\langle F(t)\rangle = Tr_b[\rho_b \exp(iH_b t)\exp(-i(H_b+\Delta)t)], \tag{14}$$

where ρ_b is the equilibrium phonon density matrix given in Eq. (4). It is the function $\langle F(t)\rangle$ which governs the pure dephasing in Eq. (13). Instead of casting this thermal average as a time ordered integral, and calculating the resulting cumulant series, we recast the thermal average as a matrix determinant, thereby effectively summing all cumulants for all times. The basics of the method of Balian and Brezin are as follows. Any exponential quadratic operator of creation and annihilation operators is first put in the form $\mathscr{G} = \exp \frac{1}{2}\boldsymbol{\alpha}\mathbf{S}\boldsymbol{\alpha}$, where $\boldsymbol{\alpha}$ is a $2N$ dimensional vector of boson creation and annihilation operators $\boldsymbol{\alpha} = (a_1,\ldots a_N, a_1^\dagger,\ldots a_N^\dagger)$, and $\mathbf{S}$ is a symmetric matrix. Such an operator is represented by the matrix

$$[\mathscr{G}] = \exp \boldsymbol{\tau}\mathbf{S}, \tag{15}$$

with

$$\boldsymbol{\tau} = \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{pmatrix}. \tag{16}$$

Here $\mathbf{0}$ is the $N\times N$ null matrix, and $\mathbf{1}$ is the $N\times N$ unit matrix. Any product of exponential quadratic operators $\mathscr{G}_3 = \mathscr{G}_1\mathscr{G}_2$ is represented by the matrix $[\mathscr{G}_3]=[\mathscr{G}_1][\mathscr{G}_2]$. It is then possible to show (see Refs. 26 and 27 for details) that the trace of $\mathscr{G}$ can be written

$$Tr\ \mathscr{G} = [(-1)^N \det([\mathscr{G}]-\mathbf{1})]^{-1/2}. \tag{17}$$

With this technology, the dephasing function $\langle F(t)\rangle$ can be expressed

$$\langle F(t)\rangle = \left(\frac{\det([\rho][\theta_1][\theta_2]-\mathbf{1})}{\det([\rho]-\mathbf{1})}\right)^{-1/2}, \tag{18}$$

where $[\theta_1]$ is the matrix representation of the operator $\exp(iH_b t)$, $[\theta_2]$ is the matrix representation of the operator $\exp(-i(H_b+\Delta)t)$, and $[\rho]$ is matrix the representation of the density operator.

The method just described is an alternate nonperturbative approach to the quadratic pure dephasing problem. There are two advantages of this method. First, it is valid *for all times*, and not just in the asymptotic regime (as are the methods of Osad'ko and Skinner and Hsu). Second, the factorized initial conditions (3) need not be used. This second point is generally irrelevant in the time regime for which the method of Skinner and Hsu is valid. However, it may be of extreme importance at short times. The disadvantage of the method is that it requires the input of a finite number of bath modes, which means that the bath never reaches equilibrium, causing phase recurrences.[28] Thus, we must test the domain of validity by varying the number of modes in the bath, and comparing the results to the previous nonperturbative theory.

We choose an Ohmic bath by selecting frequencies from a flat distribution of values in the interval $(0,\omega_c)$, and choosing coupling constants[5]

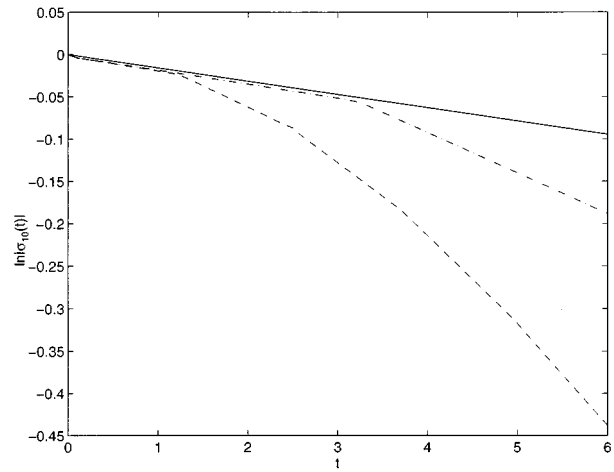

FIG. 1. Plot of $\ln|\sigma_{10}(t)|$ vs t in units where $\hbar=1$. $\beta=0.1$, and $W=0.3$. The cutoff frequency of the bath is taken to be $\omega_c=95$. Dashed line is from Eq. (18) with a 20 mode bath. Dashed-dot line is from Eq. (18) with 50 mode bath, solid line is the Skinner–Hsu result (19). The time domain for which Eqs. (18) and (19) agree depends on the number of bath modes employed. Eventually, the nonergodic nature of the finite mode simulations is manifested in deviations from the result (19). The fact that the dashed and dashed-dot lines do not directly overlap with the solid line at short times may be attributed to correct short time evolution described by Eq. (18) and not Eq. (19). In these cases, such differences are negligible.

$$h_k = \sqrt{\frac{\omega_k}{2N}}.$$

Note that the high frequency cutoff function is now taken to have a sharp step function form. This will only have consequences in the inaccessible time regime $t\sim 1/\omega_c$. Our choice of the normalization for the coupling constants requires that[5] $-1\leqslant W\leqslant\infty$. Negative values of W correspond to the case for which ''soft modes'' are present.

We first test the new method by comparing the results with the nonperturbative result of Skinner and Hsu. In their treatment, the asymptotic decay of the coherence variable is given by $|\sigma_{10}(t)|=\exp[-(1/T_2)t]$, where[2,3,5]

$$\frac{1}{T_2} = \int_0^\infty \frac{d\omega}{4\pi} \ln\left[1+\frac{4n(\omega)(n(\omega)+1)W^2J(\omega)^2}{(1-W\Omega(\omega))^2+W^2J(\omega)^2}\right], \tag{19}$$

$$\Omega(\omega) = \frac{2}{\pi}\int_0^\infty d\nu J(\nu) P\left(\frac{1}{\omega^2-\nu^2}\right). \tag{20}$$

$J(\omega)$ was defined in Eq. (2), and P stands for Cauchy principle part. For this calculation, $J(\omega)$ takes the form $J(\omega)=(\pi/2\omega_c)\omega$ for $0<\omega<\omega_c$ and is zero for all other values of ω.

Figure 1 shows the plot of $\ln|\sigma_{10}(t)|$ vs time for $W=0.3$, $\beta=0.1$, and $\omega_c=95$. Time is measured in units where $\hbar=1$. The new method is seen to be in excellent agreement with the result of Skinner and Hsu for time intervals that depend on the number of bath modes employed. After a certain time, recurrence of phase destroys the apparent thermodynamic behavior. Figure 2 shows one such large scale recurrence. For all temperatures $\beta\omega_c\leqslant 10$, the results of Skinner and Hsu were confirmed. In this temperature range, for any coupling

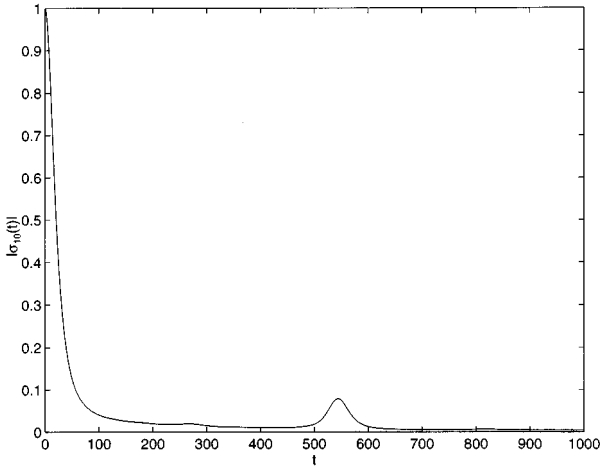

FIG. 2. Plot of the decay of $|\sigma_{10}(t)|$ vs t ($\hbar=1$) from Eq. (18). $\beta=0.1$ and $W=0.1$. The cutoff frequency of the bath is taken to be $\omega_c=95$. 20 bath modes were employed. A large scale phase recurrence can clearly be seen.

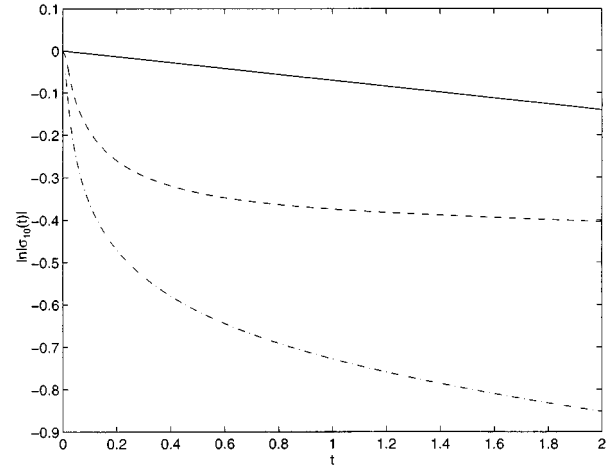

FIG. 4. Low temperature evolution of $\ln|\sigma_{10}(t)|$ vs $t(\hbar=1)$. The dashed line is a 50 mode simulation with $\beta=7$, $W=-1$, and the cutoff frequency of the bath taken to be $\omega_c=95$. The dashed-dot line is the linear electron–phonon expression (9) shown for reference with $\beta=7$ and $2\alpha/\pi=0.0785$. The solid line, also for reference, gives exponential decay that matches dashed-dot line asymptotically.

strength, the timescale for nonexponential behavior is very short $[t_{\text{nonexp}}\sim\mathscr{O}(1/\omega_c)]$. After such short transients, exponential decay of the coherence variable results with a rate described by Eq. (19). Thus in this temperature regime, the result of Skinner and Hsu is valid. Figure 3 shows the excellent agreement between the matrix technique and the method of Skinner and Hsu for a variety of temperatures and coupling strengths. It is interesting to note that the appearance of the logarithmic term in Eq. (19) is not accidental. Its origin can be traced to the matrix expression (17), written in the form

$$Tr\ \mathscr{G}=\exp\left[-\tfrac{1}{2}\sum_k \ln(1-\lambda_k)\right],$$

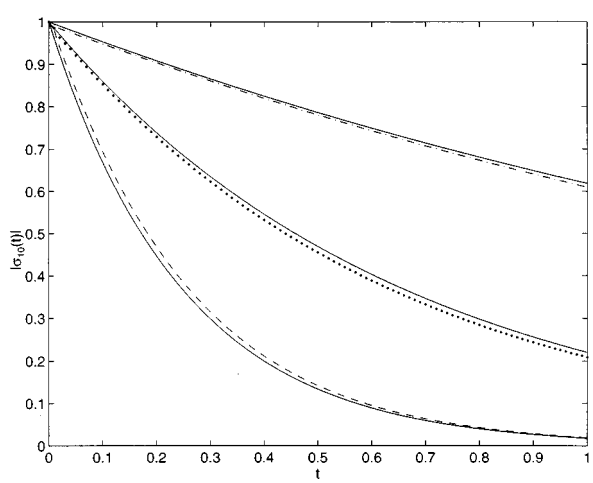

FIG. 3. Plot of $|\sigma_{10}(t)|$ vs t ($\hbar=1$) for several values of β and W. Solid lines correspond to the Skinner–Hsu result (19), while broken lines correspond to Eq. (18) with 20 bath modes employed. The set with the dashed-dot line corresponds to $\beta=0.04$, $W=0.5$, the set with the dotted line corresponds to $\beta=0.027$, $W=0.6$, and the set with the dashed line corresponds to $\beta=0.01$, and $W=0.3$. The cutoff frequency of the bath is taken to be $\omega_c=95$.

where $\{\lambda_k\}$ are the eigenvalues of the exponential quadratic operator. In the limit of a continuous bath spectrum and asymptotically long times the eigenvalues of the matrix product in Eq. (18) are related to the argument of the logarithmic term in Eq. (19).

For $\beta\omega_c\gg 1$ we may expect the methods of Osad'ko and Skinner and Hsu to break down, as they do in the linear coupling case. This is indeed the case. An example of this behavior is shown in Fig. 4. Here, 50 modes were used to simulate the bath, which is a sufficient number to produce accurate results in the time interval studied. The figure shows the results of a simulation with $W=-1$ and $\beta\omega_c=665$. For times $t\gg 1/\omega_c$ the decay of the coherence variable is nonexponential. The behavior is qualitatively similar to the algebraic behavior in the linear case [Eq. (9)]. This behavior becomes more pronounced as the temperature is lowered, and the interval $1/\omega_c\ll t<\beta\hbar$ becomes larger. Note that the deviation from exponential behavior is weaker for quadratic as opposed to linear electron–phonon coupling. This behavior is more pronounced for negative values of W. However, in many glassy and crystalline environments ''soft modes'' are prevalent, thus giving hope that the nonexponential decay of the coherence variable may be detectable at very low temperatures, perhaps in one of the settings described in Sec. III. The reason for the qualitative differences in the dephasing behavior between positive and negative values of the coupling W is unclear. It must be noted that the simulations are difficult to perform at low temperatures due to the fact that the timescale $\beta\hbar$ becomes long and more bath modes must be employed to achieve accurate results. However, as the (accurate) simulation results displayed in Fig. 4 show, the signature of the temperature independent nonexponential decay is clear. This leads one to expect such decay persists for arbitrarily low temperatures.

As briefly mentioned before, similarities exist between

the results of Sec. II, and Mahan's work on the x-ray spectra of metals.[14] It is also interesting to note the similarity between our method for treating the quadratic dephasing problem based on the field theoretic method of Balian and Brezin, and the matrix method of Combescot and Nozieres, which provides an exact solution to the Mahan, Nozieres, and De-Dominicis (MND) theory of the x-ray spectra of metals.[29] In this method, the ''corehole'' Green's function (analogous to $\langle F(t)\rangle$) is calculated by a matrix method that employs a finite number of conduction electrons to simulate thermodynamic behavior.

To conclude this section, we note that our method can easily handle any type of quadratic system-bath coupling [through the input of the matrix $[\theta_2]$ in Eq. (18)] and any quadratic initial condition. Last, the addition of an extra linear term in the bath portion of the system-bath coupling may be handled in a manner discussed by Friesner *et al.*[26]

V. CONCLUSION

We briefly recap what has been accomplished in this paper. We have shown that, in certain cases, the nonperturbative methods of Osad'ko and Skinner and Hsu fail to describe the behavior of the pure dephasing of a two level system. These anomalies occur at very low temperatures when the heat bath has an abundance of low frequency modes, as in the Ohmic case. We have developed exact methods capable of handling the low temperature dynamics for all times. Such dynamics may show marked deviations from the expected exponential behavior for experimentally accessible times. The detection of this behavior has also been discussed. It is hoped that some aspects of this behavior may be uncovered in future experiments.

ACKNOWLEDGMENTS

We would like to thank the National Science Foundation for partial support of this research. One of us (D.R.R.) would like to thank Dr. Peter Neu for useful discussions, and the Air Force Office of Scientific Research for Support through a Department of Defense fellowship.

[1] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1990).
[2] D. Hsu and J. L. Skinner, J. Chem. Phys. **81**, 1604 (1984).
[3] J. L. Skinner and D. Hsu, J. Phys. Chem. **90**, 4931 (1986).
[4] I. S. Osad'ko, Sov. Phys. Solid State **17**, 2098 (1976).
[5] D. Hsu and J. L. Skinner, J. Chem. Phys. **81**, 5471 (1984); **83**, 2107 (1985).
[6] D. Hsu and J. L. Skinner, J. Chem. Phys. **83**, 2097 (1985); **87**, 54 (1987).
[7] K. Lindenberg and B. West, Phys. Rev. A **30**, 568 (1984); E. Braun and P. A. Mello, Phys. Lett. A **115**, 54 (1987).
[8] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[9] For a discussion of quadratic, super-Ohmic effects in the Spin–Boson problem, see A. Heuer, J. Phys. A: Math. Gen. **26**, 7181 (1993); Yu. Kagan and N. V. Prokof'ev, Sov. Phys. JETP **69**, 1250 (1989).
[10] See, for example, D. E. Makarov and N. Makri, Chem Phys. Lett. **221**, 482 (1994).
[11] C. B. Duke and G. D. Mahan, Phys. Rev. **139**, A1965 (1965).
[12] For a discussion of the effect of initial conditions on Ohmic damping, see M. Sassetti and U. Weiss, Phys. Rev. A **41**, 5383 (1990).
[13] C. Aslangul, N. Pottier, and D. Saint-James, J. Phys. (Paris) **12**, 2031 (1985).
[14] T-M. Wu, D. W. Brown, and K. Lindenberg, Chem. Phys. **146**, 445 (1990).
[15] G. D. Mahan, in *Solid State Physics, Vol. 29*, edited by H. Eherenreich, F. Seitz, and D. Turnbull (Academic, New York, 1974).
[16] B. B. Laird, J. Budimir, and J. L. Skinner, J. Chem. Phys. **94**, 4391 (1991).
[17] D. R. Reichman and R. Silbey, J. Chem. Phys. **104**, 1506 (1996).
[18] Temperatures below 1 mK have been reached in experiments on glasses, see, for example, P. Esquinazi, R. König, and F. Pobell, Z. Phys. B-Condensed Matt. **87**, 305 (1992).
[19] G. D. Mahan, in *Polarons in Ionic Crystals and Polar Semiconductors*, edited by J. T. Devreese (North-Holland, Amsterdam, 1972).
[20] J. L. Black, in *Glassy Metals 1*, edited by H. J. Güntherodt and H. Beck (Springer-Verlag, Berlin, 1981).
[21] L-D. Chang and S. Chakravarty, Phys. Rev. B **29**, 154 (1985).
[22] U. Weiss, *Quantum Dissipative Dynamics* (World Scientific, Singapore, 1993).
[23] J. Kikas, A. Suisalu, V. Zazubovich, and P. Vois, J. Chem. Phys. **104**, 4434 (1996).
[24] D. Hsu and J. L. Skinner, J. Lumin. **37**, 331 (1987).
[25] R. Balian and E. Brézin, Nuovo Cim. **64B**, 37 (1969).
[26] R. Friesner, M. Pettitt, and J. Jean, J. Chem. Phys. **82**, 2918 (1985).
[27] R. W. Munn and R. Silbey, J. Phys. A: Math. Gen. **11**, 939 (1978).
[28] See also, D. G. Evans and R. Coalson, J. Chem. Phys. **97**, 5081 (1992); J. Cao, L. W. Ungar, and G. A. Voth, J. Chem. Phys. **104**, 4189 (1996).
[29] See G. D. Mahan, in *Fermi Surface Effects*, edited by J. Kondo and A. Yoshimori (Springer-Verlag, Berlin, 1988).