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Comparative Study of Spontaneous Emission and Spin-Lattice Relaxation at $T = 0$

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In this paper we present a comparative study of spontaneous emission and spin-lattice relaxation at zero temperature. In particular, we study the time evolution of the density matrix for two simple models as determined from an analysis of the Prigogine-Résibois master equation. The first model treated is that of the Wigner-Weisskopf atom in a three-dimensional radiation field; the second model is that of a single, effective spin in interaction with the phonon modes of a three-dimensional lattice. The divergence which arises in the solution of the master equation for the first model is avoided using a frequency cutoff. A frequency cutoff in the second model is imposed by the upper bound of the spectrum of modes in the crystal, and this fact manifests itself when one integrates over the first Brillouin zone only. From a detailed numerical study of the analytic results obtained in solving the master equation, we find that for both models the relaxation to equilibrium is characterized, in part, by a sequence of slowly damped oscillations. This result seems to be in agreement with the observation made by Zwanzig, namely, that exponential decay in time seems not to be universal, and may, in fact, be hidden behind some other kind of time dependence. The numerical study also reveals, however, that the nonexponential modes of decay can be quantitatively different in magnitude and qualitatively different in structure for atomic versus spin systems. Finally, based on the solution obtained for the spin problem, an estimate is made of the relaxation time for cerium ethyl sulfate, and this estimate is found to be consistent with experiment.

I. INTRODUCTION

The possible importance of nonexponential decay in the evolution to equilibrium of systems interacting with many degrees of freedom was brought up in an article of Zwanzig in 1960.[1] From an analysis of an equation similar in structure to what is now usually referred to as the Prigogine-Résibois master equation,[2] he pointed out that exponential decay in time may not be universal and indeed may be hidden behind some other kind of time dependence. It was in the attempt to clarify certain aspects of this problem, that the authors undertook a rather detailed investigation of a simple model, that of a two-level atom in interaction with a radiation field.[3] Although a rich variety of new problems has sprung from our initial investigation of this simple model,[4,5] we have felt it worthwhile to return to the problem raised by Zwanzig, cited above, for at least two reasons. First of all, one might reasonably ask whether nonexponential behavior is a general property of the time evolution of all systems, or whether this behavior is an artifact of the particular models which have been studied to date. Second, one might question whether the nonexponential behavior exhibited by the solution of the master equation for the particular model studied in Ref. 3 was a necessary consequence of the assumptions used in solving this equation, and in particular, the assumption which was employed to avoid the ultraviolet divergence. It is our objective in this paper to address ourselves to these questions.

We begin our study by reconsidering the Wigner-Weisskopf atom in interaction with a radiation field. Various features of this model have been investigated by the authors, and the present paper represents a departure from this earlier work in at least two ways. First of all, the radiation field treated here is three dimensional, whereas the field considered in Ref. 3 was assumed one dimensional. Second, the divergences which arise in the solution of the master equation for this model were handled earlier using the resonant-k approximation, whereas the results reported in this study were obtained using a frequency cutoff. Apart from displaying the role of the approximation used to avoid the ultraviolet divergence, this latter approximation was

introduced because of the very natural way in which a frequency cutoff arises in treating the second model studied in this paper. Since it was our desire to compare, insofar as possible, the temporal behavior of both models within the same framework of approximations, a frequency cutoff was introduced in the solution of the master equations for both models. Finally, we note that the two-level atom is assumed to be in its excited state initially, with all modes of the radiation field de-excited, so that, in fact, the problem being considered here is that of spontaneous emission. This investigation differs from previous treatments on spontaneous emission[6–12] since it is our intention here to study explicitly the behavior of the quantum-statistical system in the thermodynamic limit.

The second model studied in this paper is that of two, closely separated energy levels, treated as an effective spin, in interaction with the phonon modes of a crystal. This effective spin is assumed to be in its excited state initially, and all the phonon modes of the crystal are assumed to be de-excited. The investigation of the temporal evolution of this system corresponds, then, to the study of spin-lattice relaxation at zero temperature, a problem which, to the best of our knowledge, has never been treated by the methods of nonequilibrium statistical mechanics starting from the master equation. The lattice is assumed to be three dimensional, and in solving the master equation, we use the cutoff characteristic of the Debye-sphere approximation to the first Brillouin zone.

In light of the essential role played by the Hamiltonian in investigations based on the Prigogine-Résibois master equation, rather detailed discussions accompany the derivation of the second-quantized Hamiltonians used to define each model. In Sec. II the Hamiltonian for the Wigner-Weisskopf atom in interaction with a three-dimensional radiation field is developed, and in Sec. III the solution of the master equation for this problem is obtained using a frequency cutoff. The relevance of these results to those obtained in earlier work is noted. In Sec. IV, Sears's development[13] of a second-quantized Hamiltonian describing spin-lattice interactions (in the sense used above) is reviewed, and the specialization of this Hamiltonian to the case of a single, effective spin is made. In Sec. V, the solution of the master equation is obtained, again using a frequency cutoff. Finally, in Sec. V, the results of several numerical calculations are presented, which allow both a qualitative and quantitative comparison of the two models. Differences and similarities between the atomic and spin systems are noted, and the importance of nonexponential modes of decay in each case is emphasized. Finally, the parameters which appear in the solution of the master equation for the spin problem are estimated for cerium ethyl sulfate from known experimental data, and an estimate of the relaxation time for this compound is given.

II. WIGNER-WEISSKOPF ATOM IN A THREE-DIMENSIONAL FIELD

The Wigner-Weisskopf model consists of a two-level fermion and a massless boson field in interaction. The term in the Hamiltonian for the bosons is chosen as for a set of harmonic oscillators in the second-quantization notation:

$$H_{\rm bos}=\sum_\lambda[\tfrac{1}{2}\hbar\omega_\lambda(a_\lambda^\dagger a_\lambda+1)]\,. \tag{1}$$

Here λ labels the possible modes of oscillation and ω_λ is the corresponding frequency. The creation and destruction operators $a_\lambda^\dagger$ and a_λ, respectively, are defined by their matrix elements in the occupation-number representation:

$$\langle n_\lambda|a_\lambda|m_\lambda\rangle=[2(n_\lambda+1)]^{1/2}\delta^{\rm Kr}(m_\lambda-n_\lambda-1)\,, \tag{2a}$$

$$\langle m_\lambda|a_\lambda^\dagger|n_\lambda\rangle=[2(n_\lambda+1)]^{1/2}\delta^{\rm Kr}(m_\lambda-n_\lambda-1)\,, \tag{2b}$$

where a state $|n_\lambda\rangle$ is the state with n_λ ($n=0$, 1, 2, ...) photons in the λth mode. The $\delta^{\rm Kr}(\cdots)$ is the Kronecker δ.

For the fermion, there are two quantum states which may be written $|1\rangle$ and $|2\rangle$. Then, if ϵ_1 is the energy of $|1\rangle$ and ϵ_2 that of $|2\rangle$, the fermion term in the Hamiltonian is

$$H_{\rm fer}=\epsilon_1\alpha\alpha^\dagger+\epsilon_2\alpha^\dagger\alpha\,, \tag{3}$$

where the operators α and $\alpha^\dagger$ are

$$\alpha=|1\rangle\langle 2|\,, \tag{4a}$$

$$\alpha^\dagger=|2\rangle\langle 1|\,. \tag{4b}$$

It is readily checked that

$$[\alpha,\alpha^\dagger]_+=1\,.$$

For the interaction between the fermion and the mode λ, we choose simply

$$V_\lambda=h_\lambda^\dagger\alpha^\dagger a_\lambda+h_\lambda\alpha a_\lambda^\dagger+g_\lambda^\dagger\alpha^\dagger a_\lambda^\dagger+g_\lambda\alpha a_\lambda\,, \tag{5}$$

where the coefficients $h_\lambda^\dagger$ and $g_\lambda^\dagger$ must be the complex conjugates of h_λ and g_λ, respectively, to ensure hermiticity. The full Hamiltonian is then

$$H=\epsilon_1\alpha\alpha^\dagger+\epsilon_2\alpha^\dagger\alpha+\sum_\lambda[\tfrac{1}{2}\hbar\omega_\lambda(a_\lambda^\dagger a_\lambda+1)]$$
$$+\sum_\lambda[h_\lambda^\dagger\alpha^\dagger a_\lambda+h_\lambda\alpha a_\lambda^\dagger+g_\lambda^\dagger\alpha^\dagger a_\lambda^\dagger+g_\lambda\alpha a_\lambda]\,. \tag{6}$$

For the particular choice of initial condition that is taken in this study and for weak coupling in the thermodynamic limit, it will be seen that terms proportional to $g_\lambda^\dagger$ and g_λ do not play a role in determining the time evolution of the system. The matrix elements of this Hamiltonian are to be taken between states of the system given by

$$|i;\{n_\lambda\}\rangle = |i\rangle \prod_{\lambda\in\Lambda} |n_\lambda\rangle ,$$

with $i=1, 2$ and with $n_\lambda = 0, 1, 2, \ldots$ for each mode λ.

It still remains to choose h_λ and g_λ so as to specify completely the problem. This we shall do by making the model resemble as closely as possible the situation of an electron in an atom interacting with a field of electromagnetic radiation, here three dimensional. A pure radiation field can be characterized by the vector potential satisfying the wave equation,

$$\vec{\nabla}^2\vec{A} - \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = 0 \qquad (7a)$$

in free space, and the gauge condition,

$$\mathrm{div}\vec{A} = 0 . \qquad (7b)$$

This has to be solved with periodic boundary conditions in a cuboid of sides L_1, L_2, L_3. Accordingly, we write

$$\vec{A} = \sum_\lambda [q_\lambda(t) e^{i\vec{k}_\lambda\cdot\vec{x}}\vec{e}_\lambda + q_\lambda^\dagger(t) e^{-i\vec{k}_\lambda\cdot\vec{x}}\vec{e}_\lambda] ,$$

with

$$\frac{\partial^2 q_\lambda}{\partial t^2} + c^2k_\lambda^2 q_\lambda = 0 ,$$

where $\vec{e}_\lambda$ is the polarization vector, orthogonal to $\vec{k}_\lambda$ by the gauge condition. For periodicity, we need

$$\vec{k}_\lambda = \left(\frac{2\pi}{L_1}n_{\lambda x}, \frac{2\pi}{L_2}n_{\lambda y}, \frac{2\pi}{L_3}n_{\lambda z}\right) ,$$

the n's being integers.

The energy of the radiation field inside the box is given by the general expression

$$(1/8\pi)\int_{\mathrm{box}} (\vec{E}^2 + \vec{H}^2)\, d\vec{\chi} ,$$

with

$$\vec{E} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t} , \quad \vec{H} = \mathrm{curl}\vec{A} .$$

A simple but lengthy calculation (see, for example, Ref. 14) yields the result

$$\text{energy} = E_{\text{electric}} + E_{\text{magnetic}}$$

$$= \frac{L_1L_2L_3}{8\pi}\sum_\lambda k_\lambda^2 (q_\lambda q_\lambda^\dagger + q_\lambda^\dagger q_\lambda)$$

$$+ \frac{L_1L_2L_3}{8\pi}\sum_\lambda k_\lambda^2 (q_\lambda q_\lambda^\dagger + q_\lambda^\dagger q_\lambda) .$$

Now we know that in the second-quantization representation

$$H = \tfrac{1}{4}\sum\hbar\omega_\lambda (a_\lambda a_\lambda^\dagger + a_\lambda^\dagger a_\lambda) ,$$

where this summation counts the two polarizations separately. Accordingly, we identify

$$q_\lambda = \frac{(\pi\hbar\omega_\lambda)^{1/2}}{k_\lambda(L_1L_2L_3)^{1/2}}\, a_\lambda ,$$

and this completes the expression of $\vec{A}$ in terms of the second-quantization operators a_λ.

As regards the interaction, since the Hamiltonian for a particle of charge e, mass m in a field with vector potential $\vec{A}$ is

$$H = (1/2m)(\vec{p} - e\vec{A}/c)^2 ,$$

where $\vec{p}$ is the momentum operator, we may, for weak fields, consider only the linear terms in $\vec{A}$ in this expression. Thus we take as the interaction

$$H_1 = -(e/mc)\vec{A}\cdot\vec{p}$$

$$= -(e/mc)\sum_\lambda (q_\lambda e^{i\vec{k}_\lambda\cdot\vec{x}} + q_\lambda^\dagger e^{-i\vec{k}_\lambda\cdot\vec{x}})\vec{e}_\lambda\cdot\vec{p} . \qquad (8)$$

When matrix elements of H_1^λ are taken, using the dipole approximation

$$e^{i\vec{k}_\lambda\cdot\vec{x}} = 1 ,$$

there results

$$\langle 1, n_\lambda | H_1^\lambda | 2, n_\lambda - 1\rangle = \frac{iex\omega}{c}\left(\frac{\pi\hbar c}{k_\lambda L_1L_2L_3}\right)^{1/2}(2n_\lambda)^{1/2} ,$$

where we have put

$$\langle 1|\vec{e}_\lambda\cdot\vec{p}|2\rangle = -im\omega x .$$

Here, ω is the resonant frequency between states $|1\rangle$ and $|2\rangle$ and x is some quantity with dimensions of length.

Comparison with the matrix element

$$\langle 1, n_\lambda | H_1^\lambda | 2, n_\lambda - 1\rangle = h_\lambda \langle n_\lambda | a_\lambda^\dagger | n_\lambda - 1\rangle = h_\lambda (2n_\lambda)^{1/2}$$

leads to the identification

$$h_\lambda = iex\omega\left(\frac{\pi\hbar}{ck_\lambda L_1L_2L_3}\right)^{1/2} ,$$

$$|h_\lambda|^2 = \frac{\pi\alpha'\hbar^2x^2\omega^2}{|k_\lambda| L_1L_2L_3} , \qquad (9)$$

where α' is the fine-structure constant of electrodynamics, $e^2/\hbar c$. Later expressions will be simplified if a redefinition of the coupling parameter is made at this point, namely,

$$\alpha = \alpha' x^2\omega^2/c^2 . \qquad (10)$$

We then have that

$$|h_\lambda|^2 = \frac{\alpha\pi\hbar^2c^2}{|k_\lambda| L_1L_2L_3} . \qquad (11)$$

In a similar fashion, evaluation of the matrix element

$$\langle 1, n_\lambda | H_1^\lambda | 2, n_\lambda + 1 \rangle$$

leads to

$$|g_\lambda|^2 = \frac{\beta \pi \hbar^2 c^2}{|k_\lambda| L_1 L_2 L_3} \ . \tag{12}$$

In this equation, β is a dimensionless coupling constant. In the particular case studied here, it can be shown that $\alpha = \beta$; however, this identification is not necessary in what follows, or, in fact, even true in the general case. Accordingly we shall retain the explicit use of β in Eq. (12). This completes the specification of the Hamiltonian for the Wigner-Weisskopf atom in a three-dimensional radiation field.

III. SOLUTION OF MASTER EQUATION FOR WIGNER-WEISSKOPF ATOM

Having specified the Hamiltonian for the model of the Wigner-Weisskopf atom in a three-dimensional radiation field, we now study the evolution of the system to quantum-statistical equilibrium. For the readers convenience, we begin by summarizing those aspects of the work presented in Ref. 3 (hereafter referred to as I) which will be used in the following development. For a system whose Hamiltonian can be separated into unperturbed and perturbed parts,

$$H = H_0 + H_1 \ ,$$

the Liouville–von Neumann equation has the iterative solution for the diagonal elements of the density matrix:

$$\begin{aligned} \partial_t \rho_0(N, t) = \sum_{m=0}^{\infty} \int_{T_m} \langle N | \, [e^{-iH_0(t-t_1)/\hbar} \\ \times [H_1, e^{-iH_0(t_1-t_2)/\hbar} [H_1, \ldots \\ \times [H_1, e^{-iH_0 t_m/\hbar} \rho(0) e^{+iH_0 t_m/\hbar}] \ldots] \\ \times e^{iH_0(t_1-t_2)/\hbar}] e^{iH_0(t-t_1)/\hbar}] | N \rangle \ , \end{aligned} \tag{13}$$

where

$$\int_{T_m} \equiv [1/(i\hbar)^m] \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \cdots \int_0^{t_{m-1}} dt_m \ .$$

It is convenient to introduce the (ν, N) notation

$$\langle n | A | m \rangle = A_\nu(N) \ ,$$

where $\nu = n - m$, $N = \frac{1}{2}(n+m)$, and make the following definitions:

$$\langle \nu | \mathcal{H}_1(N) | \nu' \rangle = \eta^\nu H_{1,\nu-\nu'}(N) \eta^{-\nu} - \eta^{-\nu'} H_{1,\nu-\nu'}(N) \eta^{\nu} \ ,$$

where

$$\eta^\nu f(N) = f(N + \tfrac{1}{2}\nu) \ ,$$

$$\langle \nu | G(t) | \nu \rangle = \langle N + \tfrac{1}{2}\nu | e^{-iH_0 t/\hbar} | N + \tfrac{1}{2}\nu \rangle \times \langle N - \tfrac{1}{2}\nu | e^{-iH_0 t/\hbar} | N - \tfrac{1}{2}\nu \rangle \ .$$

One may make, therefore, a separation of terms in Eq. (13) to obtain

$$\partial_t \rho_0(N, t) = \int_0^t d\tau \, \mathcal{C}(\tau) \rho_0(N, t-\tau) + \mathfrak{D}(t, \{\rho_\nu(N, 0)\}) \ , \tag{14}$$

where

$$\mathcal{C}(\tau) = (i\hbar)^{-1} \sum_{f=0}^{\infty} \int_{T_{f-1}} \langle 0 | \mathcal{H}_1(N) G(t-t_1) \cdots \times G(t_{f-1}) \mathcal{H}_1(N) | 0 \rangle_{\text{irr}} \tag{15}$$

and

$$\mathfrak{D}(t, \{\rho_\nu(N, 0)\}) = (i\hbar)^{-1} \sum_{m=0}^{\infty} \sum_{\nu \neq 0} \int_{T_m} \langle 0 | \mathcal{H}_1(N) G(t-t_1) \cdots \times \mathcal{H}_1(N) G(t_m) | \nu \rangle_{\text{irr}} \rho_\nu(N, 0) \ . \tag{16}$$

Here $\mathcal{C}(\tau)$ is referred to as the collision operator and $\mathfrak{D}(t, \{\rho_\nu(N, 0)\})$ the destruction operator. The suffix "irr" is short for "irreducible," and has the sense that the intermediate ν variables in the expansion of an operator product may not assume the value zero. Equation (14) is a convenient statement of the Prigogine-Résibois master equation. For the initial condition for spontaneous emission,

$$\rho_\nu(N, 0) = \delta^{\text{Kr}}(\nu) \, \delta^{\text{Kr}}(N_p - 2) \prod_\lambda \delta^{\text{Kr}}(N_\lambda) \ , \tag{17}$$

one finds that the destruction term can be set rigorously equal to zero. Laplace transformation of Eq. (14) gives

$$\rho_0(N, t) = (1/2\pi) \int_C dz \, e^{-izt} (\psi(z) + iz)^{-1} \rho_0(N, 0) \ ,$$

where C is a contour in the z plane parallel to the real axis and above all singularities of the integrand, and where

$$\psi(z) = \int_0^\infty dt \, e^{izt} \, \mathcal{C}(t) \ . \tag{18}$$

The calculation of $\psi(z)$ is straightforward but lengthy. We demonstrate explicitly in the Appendix that terms proportional to g_λ and $g_\lambda^\dagger$ in the Hamiltonian do not contribute to the time evolution of the system for the infinite-system limit with weak coupling. We therefore drop these terms in our three-dimensional Hamiltonian and recognize that the

fermion and boson terms now become structually the same as the corresponding terms of the one-dimensional Hamiltonian, Eq. (6) of I [hereafter we use the notation Eq. (I. 6), etc.]. The expression for $\psi(z)$ for the three-dimensional model is identical to Eq. (I. 34). Choosing $N_p = 2$ and $N_\mu = 0$ for all modes μ, and then considering the case of an inifinite system for which the summation over the modes λ can be replaced by integration over the wave number k,

$$(8\pi^3/L_1L_2L_3)\sum_\lambda \to 2\int d\vec{k}$$

(keeping in mind that there are two polarizations), one obtains in the limit $L \to \infty$ the result

$$\tilde{\rho}(\mathfrak{N}, z) = \frac{1}{iz}\left(1 - \frac{4\alpha c^2}{\pi}\int_0^\infty dk \frac{|k|}{z^2 - (c|k| - E)^2}\right)^{-1} . \tag{19}$$

Here, $\tilde{\rho}$ is the Laplace transform of the density operator

$$\tilde{\rho}(\mathfrak{N}, z) = \int_0^\infty dt\, e^{izt}\rho(\mathfrak{N}, t) .$$

We note that the three-dimensional coupling parameter α has been defined in such a way that the solution to the master equation has the same form in both one- and three-dimensional cases.

As it stands, the integral appearing in Eq. (19) is divergent. To avoid the (ultraviolet) divergence, the expedient was chosen in Ref. 3 of replacing the factor $|k|$ in the coupling constant $|h_\lambda|^2$ by its resonant value E/c. The expression for the diagonal element of the density matrix was then obtained by taking the inverse Laplace transform of $\tilde{\rho}(\mathfrak{N}, z)$. Since Eq. (19) above has the same form as Eq. (I. 41), the use of the resonant-k approximation in the three-dimensional case leads to the same result as obtained earlier in the one-dimensional case, namely, Eq. (I. 62). For convenience, this equation is reproduced below:

$$\rho(\tau) = \left(1 + \frac{4\alpha}{\pi}\right)e^{-4\tau - 16\alpha\tau/\pi} - \frac{1}{2\pi}\int_0^\alpha d\xi \left(\frac{12\cos(\tau/\xi) + 2[\xi^{-1} + (2/\pi)\ln|(\xi-\alpha)/(\xi+\alpha)|]\sin(\tau/\xi)}{36\xi^2 + [1 + (2\xi/\pi)\ln|(\xi-\alpha)/(\xi+\alpha)|]^2}\right.$$

$$\left. - \frac{4\cos(\tau/\xi) + 2[\xi^{-1} + (2/\pi)\ln|(\xi-\alpha)/(\xi+\alpha)|]\sin(\tau/\xi)}{4\xi^2 + [1 + (2\xi/\pi)\ln|(\xi-\alpha)/(\xi+\alpha)|]^2}\right) , \tag{20}$$

where we have introduced the independent dimensionless variables,

$$\tau = \alpha E t , \quad \xi = \alpha E/x , \tag{21}$$

where x is the real part of the complex variable z.

Having examined the resonant-k approximation, we wish to investigate in the remainder of this section the possibility of avoiding the ultraviolet divergence by establishing a finite upper bound on the integral appearing in Eq. (19). The use of such a bound amounts to imposing a cutoff (denoted by μ) on the possible values of k. If one integrates Eq. (19) directly and then replaces all divergent terms in the resultant expression by the appropriate factor involving μ, the result is

$$-\frac{1}{2c^2}\ln\left(\frac{z^2 - (c\mu - E)^2}{z^2 - E^2}\right) - \frac{E}{2c^2 z}\left[\ln\left(\frac{E-z}{E+z}\right) + 2\pi i\right] . \tag{22}$$

Hence, the expression for $\tilde{\rho}(\mathrm{N}, z)$ is

$$\tilde{\rho}(\mathrm{N}, z) = \left[iz + \frac{2\alpha i z}{\pi}\ln\left(\frac{z^2 - (c\mu - E)^2}{z^2 - E^2}\right) + \frac{2\alpha E i}{\pi}\ln\left(\frac{E-z}{E+z}\right) - 4\alpha E\right]^{-1} . \tag{23}$$

The diagonal element of the density matrix is found by taking the inverse Laplace transform of $\tilde{\rho}(\mathfrak{N}, z)$. Thus,

$$\rho_0(\mathfrak{N}, t) = -\frac{1}{2\pi}\int_{ai-\infty}^{ai+\infty} dz\, e^{-izt}\tilde{\rho}(\mathfrak{N}, z)$$

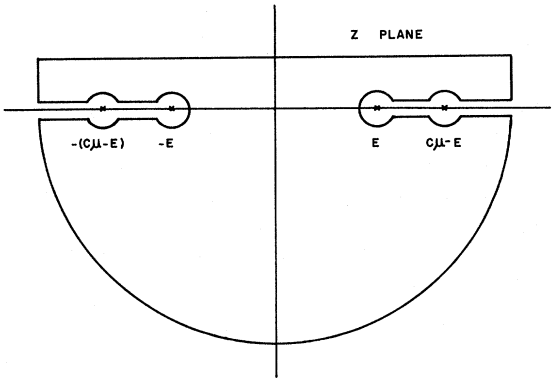

FIG. 1. Contour used in evaluating Eqs. (25) and (44).

$$= -\frac{1}{2\pi}\int_{ai-\infty}^{ai+\infty} dz\, e^{-izt}\left[iz+\frac{2\alpha iz}{\pi}\right.$$

$$\left.\times \ln\left(\frac{z^2-(c\mu-E)^2}{z^2-E^2}\right)+\frac{2\alpha Ei}{\pi}\ln\left(\frac{E-z}{E+z}\right)-4\alpha E\right]^{-1}, \tag{24}$$

where the integration is to be performed along a path slightly above and parallel to the real axis. It is seen that the integrand is not analytic over the entire z plane, but has branch points at

$$z=\pm E,\ \pm(c\mu-E)\ .$$

One can evaluate the integral using Cauchy's theorem by closing the contour in the lower half-plane, but in such a way that the above singularities are avoided. Our choice of contour is given in Fig. 1. We look for the poles of the integrand by separating the denominator into real and imaginary parts and then setting each part equal to zero. One finds that there is a pole in the z plane at

$$z=-4\alpha Ei-\frac{16E}{\pi}\alpha^2\left[1-\ln\left(\frac{c\mu-E}{E}\right)\right]i\ .$$

The residue of the integrand at this pole is

$$e^{-izt}\left\{i+\frac{4\alpha i}{\pi}\left[-1+\ln\left(\frac{c\mu-E}{E}\right)\right]\right\}^{-1}\ .$$

The large semicircle and the small indentations around the branch points contribute negligibly, so that the integral is equal to the sum of $2\pi i$ times the residue at the pole, plus the contributions from the eight line segments parallel to the branch cuts. These contributions due to the branch cuts are easily evaluated, and one obtains as the final expression for the diagonal element of the density matrix the following result:

$$\rho(\tau)=\exp\left\{\left[-4-\frac{16\alpha}{\pi}\left(1-\ln\frac{c\mu-E}{E}\right)\right]\tau\right\}\left\{1+\frac{4\alpha}{\pi}\left[\ln\left(\frac{c\mu-E}{E}\right)-1\right]\right\}^{-1}$$

$$-\frac{1}{2\pi}\int_0^{\alpha E/(c\mu-E)} d\xi\,\frac{12\cos(\tau/\xi)+2Q(\xi)\sin(\tau/\xi)}{\xi^2[36+Q(\xi)^2]}+\frac{1}{2\pi}\int_0^{\alpha E/(c\mu-E)} d\xi\,\frac{4\cos(\tau/\xi)+2Q(\xi)\sin(\tau/\xi)}{\xi^2[4+Q(\xi)^2]}$$

$$-\frac{1}{2\pi}\int_{\alpha E/(c\mu-E)}^{\alpha} d\xi\,\frac{(12-4\alpha/\xi)\cos(\tau/\xi)+2Q(\xi)\sin(\tau/\xi)}{(2\alpha-6\xi)^2+\xi^2Q(\xi)^2}+\frac{1}{2\pi}\int_{\alpha E/(c\mu-E)}^{\alpha} d\xi\,\frac{(4+4\alpha/\xi)\cos(\tau/\xi)+2Q(\xi)\sin(\tau/\xi)}{(2\alpha+2\xi)^2+\xi^2Q(\xi)^2}, \tag{25}$$

where we have introduced the dimensionless variables τ and ξ defined earlier, and where

$$Q(\xi)=\frac{1}{\xi}+\frac{2\alpha}{\pi\xi}\ln\left|\frac{\alpha^2-\xi^2[(c\mu-E)/E]^2}{\alpha^2-\xi^2}\right|+\frac{2}{\pi}\ln\left|\frac{\alpha-\xi}{\alpha+\xi}\right|\ . \tag{26}$$

It is to be noted that when the ratio $(c\mu-E)/E$ is set equal to unity, Eq. (25) collapses into Eq. (20). That is, if one replaces the factor μ by twice the resonant value of $|k|$, namely $2E/c$, the results obtained using the resonant-k approximation and those obtained using the frequency-cutoff approximation are identical. In view of this relationship, the calculations presented in I can be compared with those derived from a numerical study of Eq. (25), and hence some estimate can be obtained as to the sensitivity of the results to the particular choice of approximation used to avoid the ultraviolet divergence in Eq. (19). The presentation of the numerical results and the discussion will be deferred until Sec. VI.

IV. A MODEL HAMILTONIAN FOR SPIN-LATTICE INTERACTIONS

The model of the Wigner-Weisskopf atom is, in essence, that of a two-level system in interaction with a (radiation) field. It is interesting to see if the methods developed in Sec. III are useful in studying another well-known two-level model, that of a single spin in interaction with the phonon modes of a harmonic lattice. Such a system is describable by a Hamiltonian having the following form:

$$H=H_L+H_S+H_{SL}\ .$$

There is a considerable similarity between the spin-lattice Hamiltonian and the Wigner-Weisskopf Hamiltonian. The structure of the "field" term in both representations is formally the same, since a lattice may be characterized in the harmonic approximation as a collection of harmonic oscillators. Thus,

$$H_L=\textstyle\sum_\lambda \frac{1}{2}\hbar\omega_\lambda(a_\lambda^\dagger a_\lambda+1)\ , \tag{27}$$

where $a_\lambda^\dagger$ and a_λ are the phonon creation and destruc-

tion operators and λ designates the phonon modes. For a single spin-$\frac{1}{2}$ there are two spin states accessible to the system, $|1\rangle$ and $|2\rangle$ having energies ϵ_1 and ϵ_2, respectively. We write the spin Hamiltonian in second-quantized form as

$$H_S = \epsilon_1 \alpha\alpha^\dagger + \epsilon_2 \alpha^\dagger\alpha \,, \tag{28}$$

where

$$\alpha = |1\rangle\langle 2| \,, \quad \alpha^\dagger = |2\rangle\langle 1| \,. \tag{29}$$

It is evident that α and $\alpha^\dagger$ obey the usual fermion commutation relation.

Spin-lattice relaxation in ionic solids has been studied for several decades, the earliest contributions in this field being due to Waller, Kronig, and Van Vleck.[15] In ionic solids, spin-lattice transitions are caused predominantly by phonon modulation of the crystalline electric field, and involve both spin-orbit and orbit-lattice couplings. Taking all of these effects into account in a rigorous way in the interaction term of the Hamiltonian leads, as one might expect, to a rather complicated expression. Recently, however, several workers have shown that many of the general features of spin-lattice systems can be understood by using the less detailed dynamical spin-lattice formalism.[16–18] Sears,[13] in particular, has suggested a spin-lattice interaction term which was used in a study of the heat capacity of cerium ethyl sulfate. Other properties of spin-lattice systems which have been studied using the Sears type of interaction term include Schottky anomalies and excitation lifetimes.[19,20]

Sears assumes that for low enough temperatures only the two lowest electronic energy levels are appreciably populated, and hence one can treat the electronic degrees of freedom of each ion as an *effective* spin. The energy of interaction between an effective spin and the lattice is assumed to be directly proportional to the displacements of the ion from its equilibrium position. Thus,

$$H_{SL} = \sum_{i,j=1}^{N} \sum_{\alpha,\beta} S_{i\alpha} A_{\alpha\beta} (\vec{R}_j - \vec{R}_i) u_{j\beta} \,. \tag{30}$$

In this equation, N is the number of effective spins in the system, α and β refer to the Cartesian indices x, y, and z, and the $S_{i\alpha}$ are operators, given below, which Sears defines in terms of the spin creation and destruction operators. The $S_{i\alpha}$ satisfy the commutation relations for angular momentum. Finally, $\vec{R}_j - \vec{R}_i$ is the relative displacement vector, $u_{j\beta}$ is the displacement from its equilibrium position of the jth ion in the β direction, and $A_{\alpha\beta}$ is an unspecified constant. It is also assumed that the spins are sufficiently far apart that spin-spin interactions are negligible.

In his development, the requirement of time-reversal invariance is used by Sears to eliminate various terms in the interaction expression. More precisely, since time reversal inverts a spin and since by definition, using Sears's notation,

$$a = |1\rangle\langle 2| \,, \tag{31a}$$

$$a^+ = |2\rangle\langle 1| \,, \tag{31b}$$

and

$$S_{ix} = \tfrac{1}{2}(a_i + a_i^+) \,, \tag{32a}$$

$$S_{iy} = \tfrac{1}{2}(a_i - a_i^+) \,, \tag{32b}$$

$$S_{iz} = \tfrac{1}{2} - a_i^+ a_i \,, \tag{32c}$$

it is evident that S_{ix} and S_{iz}, but not S_{iy}, are time-reversal invariant. Since H_{SL} must be invariant, Sears sets $A_{y\beta} = 0$. Note also that S_{iz} does not represent a coupling between the spin and lattice, in that it cannot bring about transitions from one spin state to the other. Therefore, Sears also sets $A_{z\beta}$ equal to zero. The interaction term thus assumes the form

$$H_{SL} = \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\beta} (a_i + a_i^+) A_{x\beta} (\vec{R}_j - \vec{R}_i) u_{j\beta} \,. \tag{33}$$

The standard transformation to normal coordinates is performed to yield

$$H_{SL} = N^{-1/2} \sum_{i=1}^{N} \sum_{k,p} (a_i + a_i^+) \times \{A_{kp} e^{i\vec{k}\cdot\vec{R}_i} C_{kp} + A_{kp}^\dagger e^{-i\vec{k}\cdot\vec{R}_i} C_{kp}^+\}, \tag{34}$$

where

$$A_{kp} = A_{-kp}^\dagger = \left(\frac{\hbar}{2m\omega_{kp}}\right)^{1/2} \sum_{j=1}^{N} \sum_{\beta} e^{i\vec{k}\cdot(\vec{R}_j - \vec{R}_i)} \times \tfrac{1}{2} A_{x\beta} (\vec{R}_j - \vec{R}_i) e_{kp\beta} \,. \tag{35}$$

Here m denotes the mass of the atom, and $e_{kp\beta}$ denotes the unit polarization vector for phonons of type (k, p). Upon considering the matrix elements of H_{SL}, where in the long-wavelength limit

$$\omega_{kp} = vk \,,$$

we find that the A_{kp} can be written

$$A_{kp} = \epsilon(\hbar^2 \omega_0 v k / 12)^{1/2} \,. \tag{36}$$

In this expression, v is the velocity of sound, ϵ refers to a dimensionless spin-lattice coupling parameter, and ω_0 is the frequency separation of the two lowest electronic energy levels of the ion.

Having reviewed the assumptions inherent in the Sears formulation, it is a simple matter to rewrite

the interaction term using the notation of the Wigner-Weisskopf model studied earlier. We set

$$\epsilon_1 = -\tfrac{1}{2}\hbar\omega_0 , \quad \epsilon_2 = +\tfrac{1}{2}\hbar\omega_0 . \tag{37}$$

For simplicity, we limit the number of spins in the system to one; for certain choices of the initial condition, no generality is lost in this restriction. If only energy-conserving terms are retained in the interaction Hamiltonian, it is found that the full spin-lattice Hamiltonian can be written in the form,

$$H = \sum_\lambda \tfrac{1}{2}\hbar\omega_\lambda (a_\lambda^\dagger a_\lambda + 1) + \epsilon_1 \alpha\alpha^\dagger + \epsilon_2 \alpha^\dagger\alpha + \sum_\lambda \epsilon (\hbar^2\omega_0\omega_\lambda/12N)^{1/2} (e^{i\vec{k}\cdot\vec{R}}\alpha^\dagger a_\lambda + e^{-i\vec{k}\cdot\vec{R}}\alpha a_\lambda^\dagger) . \tag{38}$$

In order to simplify later expressions, it is convenient to define at this point a new coupling parameter σ, where

$$\sigma = \epsilon^2 E^3/24\pi d v^3 . \tag{39}$$

Here, $E = \omega_0$ is the frequency difference of the energy levels, and d is the density of lattice sites, that is, $N/L_1L_2L_3$. In order to demonstrate further the relationship between the Wigner-Weisskopf Hamiltonian and the one presently under study, one can identify constants h_λ and $h_\lambda^\dagger$, where

$$|h_\lambda|^2 = \frac{\sigma\hbar^2 2\pi v^4 |k|}{E^2 L_1 L_2 L_3} . \tag{40}$$

This completes the specification of the Hamiltonian for a spin in interaction with the phonon modes of a lattice.

V. SOLUTION OF MASTER EQUATION FOR SPIN-LATTICE PROBLEM

The analysis of the Wigner-Weisskopf atom can be used as a guide in solving the master equation for systems characterized by spin-lattice interactions. The calculation of $\psi(z)$, the Laplace transform of the creation operator, is straightforward and yields the same result as that given in Eq. (I. 34). As initial conditions, we specify that the spin is in the excited state, and that all phonon modes are de-excited; that is, the lattice is at the absolute zero of temperature. These requirements correspond to the same initial conditions as those used in the treatment of the Wigner-Weisskopf atom. We choose

$$N_p = 2 , \quad N_\mu = 0 ,$$

for all modes μ. In the spin-lattice Hamiltonian, the summation over λ refers to a sum over all modes of vibration accessible to the system, namely, those modes characterized by wave vectors which lie in the first Brillouin zone. We approximate the first Brillouin zone by the Debye sphere. In this approximation, one replaces summations over the modes λ by integrals over the wave vector k; that is, we replace

$$(8\pi^3/L_1L_2L_3)\sum_\lambda \to 4\pi \int_0^\mu k^2\, dk ,$$

where μ refers to the Debye cutoff for the wave vector k. Using Eq. (40) for $|h_\lambda|^2$, and recognizing that in the limit of an infinite system,

$$\tilde{\rho}_1(\lambda, z) = 0 ,$$

we find that

$$\tilde{\rho}(N, z) = \frac{1}{iz}\left(1 - \frac{4\sigma v^4}{\pi E^2}\int_0^\mu \frac{k^3\, dk}{z^2 - (vk - E)^2}\right)^{-1} . \tag{41}$$

In order to provide a basis for comparison with the results obtained earlier, the integral appearing in Eq. (41) was evaluated using the technique suggested in the study of the Wigner-Weisskopf atom. That is, we assume that the cutoff is large enough so that terms proportional to reciprocal powers of μ vanish, but small enough so that terms proportional to μ or powers of μ do not diverge. With this prescription, we find Eq. (41) becomes

$$\int_0^\mu \frac{k^3\, dk}{z^2 - (vk - E)^2} = -\frac{\mu^2}{2v^2} - \frac{2E\mu}{v^3} - \frac{3E^2 + z^2}{2v^4}\ln\frac{z^2 - (v\mu - E)^2}{z^2 - E^2} - \frac{3Ez^2 + E^3}{2v^4 z}\left[\ln\left(\frac{E - z}{E + z}\right) + 2\pi i\right] . \tag{42}$$

Hence, we have that

$$\rho_0(N, t) = -\frac{1}{2\pi}\int_{ai-\infty}^{ai+\infty} dz\, e^{-izt}\left\{iz + \frac{2\sigma v^2 iz\mu}{E^2\pi} + \frac{8\sigma v\mu iz}{E\pi} + \frac{6\sigma izE^2 + 2\sigma iz^3}{E^2\pi}\ln\left(\frac{z^2 - (v\mu - E)^2}{z^2 - E^2}\right) + \frac{6\sigma iz^2 + 2\sigma iE^2}{E\pi}\left[\ln\left(\frac{E - z}{E + z}\right) + 2\pi i\right]\right\}^{-1} . \tag{43}$$

Cauchy's theorem can be used to evaluate this integral, and, in fact, one can choose the same contour as

the one given in Fig. 1. The integrand of Eq. (43) has a pole at

$$z=-4E\sigma i+\left[\frac{8v^2\mu^2}{E}+\frac{32v\mu}{\pi}+48\ln\left(\frac{v\mu-E}{E}\right)\right]\frac{\sigma^2}{\pi}\,i+\cdots\ .$$

The residue of the integrand at this pole is

$$e^{-izt}\left[i+\frac{2\sigma v^2\mu^2 i}{\pi E^2}+\frac{8\sigma v\mu i}{\pi E}+12\frac{\sigma i}{\pi}\ln\left(\frac{v\mu-E}{E}\right)-\frac{4\sigma i}{\pi}\right]^{-1}.$$

Adding together the contribution from the cuts and this pole, we have the result

$$\rho(\tau)=\frac{\exp[-4+(8R^2+32R+48\ln\mathfrak{R})\sigma/\pi+\cdots]\tau}{1+(2\sigma R^2+8\sigma R-4\sigma+12\sigma\ln\mathfrak{R})/\pi}-\frac{1}{2\pi}\int_0^{\sigma/\mathfrak{R}}d\xi\,\frac{6a(\xi)\cos(\tau/\xi)+2q(\xi)\sin(\tau/\xi)}{\xi^2[9a(\xi)^2+q(\xi)^2]}$$

$$-\frac{1}{2\pi}\int_0^{\sigma/\mathfrak{R}}d\xi\,\frac{2a(\xi)\cos(\tau/\xi)-2q(\xi)\sin(\tau/\xi)}{\xi^2[a(\xi)^2+q(\xi)^2]}-\frac{1}{2\pi}\int_\sigma^{\sigma/\mathfrak{R}}d\xi\,\frac{2[b(\xi)-3a(\xi)]\cos(\tau/\xi)-2q(\xi)\sin(\tau/\xi)}{\xi^2\{[6(\xi)-3a(\xi)]^2+q(\xi)^2\}}$$

$$-\frac{1}{2\pi}\int_\sigma^{\sigma/\mathfrak{R}}d\xi\,\frac{2[b(\xi)+a(\xi)]\cos(\tau/\xi)+2q(\xi)\sin(\tau/\xi)}{\xi^2\{[b(\xi)+a(\xi)]^2+q(\xi)^2\}}\ . \quad (44)$$

In this expression, we have used the definitions,

$$\xi=\sigma E/\hbar x\ , \quad (45a)$$

$$\tau=\sigma Et\ , \quad (45b)$$

$$R=v\mu/E\ , \quad (45c)$$

$$\mathfrak{R}=(v\mu-E)/E\ . \quad (45d)$$

Also, we have introduced

$$a(\xi)=6\sigma^2/\xi^2+2\ , \quad (46a)$$

$$b(\xi)=6\sigma/\xi-2(\sigma/\xi)^3\ , \quad (46b)$$

$$q(\xi)=\frac{1}{\xi}\left(1+\frac{2\sigma R^2}{\pi}+\frac{8\sigma R}{\pi}\right)+\frac{b(\xi)}{\pi}\ln\left|\frac{\sigma^2-\xi^2\mathfrak{R}^2}{\sigma^2-\xi^2}\right|$$

$$+\frac{a(\xi)}{\pi}\ln\left|\frac{\sigma-\xi}{\sigma+\xi}\right|\ . \quad (46c)$$

Calculations based on Eq. (44) will be presented in Sec. VI.

VI. DISCUSSION

In this section, we present the results of numerical calculations based on Eqs. (25) and (44), and then attempt to analyze these results. In Figs. 2–6 we study the effect of changing the coupling constant α and the ratio $(c\mu-E)/E$ in the expression for the time evolution of the diagonal element of the density matrix for the Wigner-Weisskopf atom. In these figures, the solid line refers to the purely exponential term in Eq. (25), while the dashed line refers to the nonexponential contributions in this equation. Then, in Figs. 7–9 we study the effects of changing the coupling constant σ and the ratio $(v\mu-E)/E$ in the spin problem. Here again, in these figures, the solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions in the solution, Eq. (44).

For the two-level atom in interaction with a three-dimensional radiation field, we find that for fixed ratio, as the coupling constant α increases, the number of peaks per unit interval of time τ, or what might be characterized as a frequency of peaks, decreases while the amplitude of corresponding peaks increases. On the other hand, for fixed coupling constant, as the ratio $(c\mu-E)/E$ increases, the frequency of peaks increases while the amplitude of corresponding peaks decreases.

For the case of a single spin in interaction with

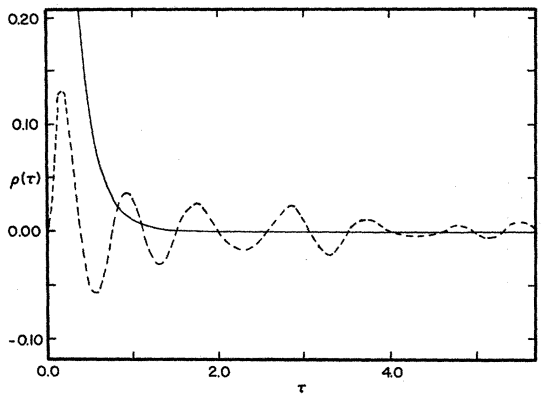

FIG. 2. A study of Eq. (25) with $\alpha=0.1$ and $(c\mu-E)/E=\frac{1}{2}$. The solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions.

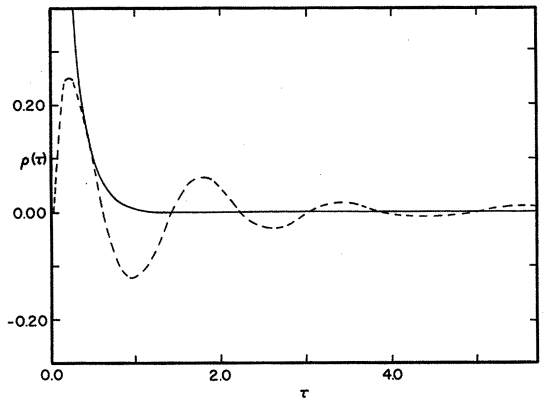

FIG. 3. A study of Eq. (25) with $\alpha = 0.2$ and $(c\mu - E)/E = \frac{1}{2}$. The solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions.

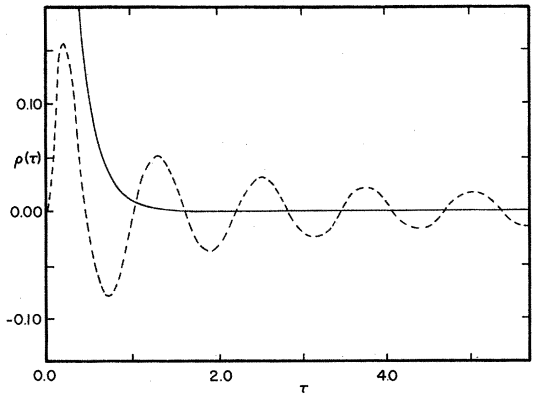

FIG. 5. A study of Eq. (25) with $\alpha = 0.2$ and $(c\mu - E)/E = 1$. The solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions.

the phonon modes of a three-dimensional lattice, the results obtained are slightly different. For fixed ratio $(v\mu - E)/E$, as the coupling constant σ increases, the frequency of peaks decreases. This is in agreement with the behavior observed in the case of the two-level atom. However, in the spin problem, it is found that for fixed ratio, the amplitude of corresponding peaks decreases as the coupling constant increases, a behavior which is in marked contrast to that observed in the case of the two-level atom. Second, we notice that for fixed coupling constant σ, as the ratio increases, the frequency of peaks increases, in accord with the results for the two-level atom. On the other hand, the amplitude does not appear to be very sensitive to increasing values of the ratio $(v\mu - E)/E$ for fixed σ. The sensitivity of the amplitude under the same variation has been noted in the preceding paragraph for the two-level atom.

Apart from the differences and similarities observed in the frequency and amplitude of peaks, it is worth noting that whereas the curves generated from Eq. (25) are continuous and smooth for the most part, the curves generated from Eq. (44) are rather "jagged" for certain values of the coupling constant σ and ratio $(v\mu - E)/E$. In particular, compare the behavior exhibited in Figs. 2 and 8, and Figs. 3 and 9. It is important to determine whether this apparent difference is real, or whether the jagged profiles observed in Figs. 7 and 8 are an artifact of the numerical calculation. To study this question, we performed the numerical integrations for a variety of grid spacings, in double precision, and finally using an entirely independent integration procedure (the BEEFM, INTEG 1 package). The results of these various tests revealed

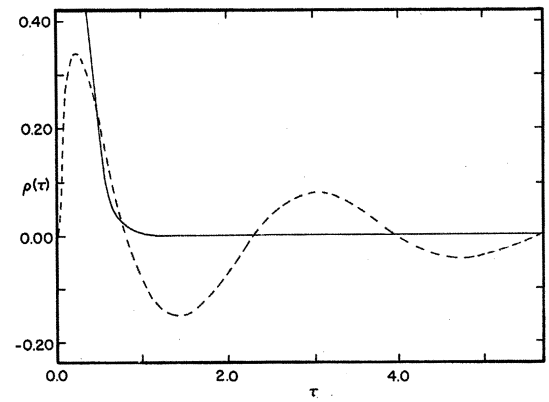

FIG. 4. A study of Eq. (25) with $\alpha = 0.4$ and $(c\mu - E)/E = \frac{1}{2}$. The solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions.

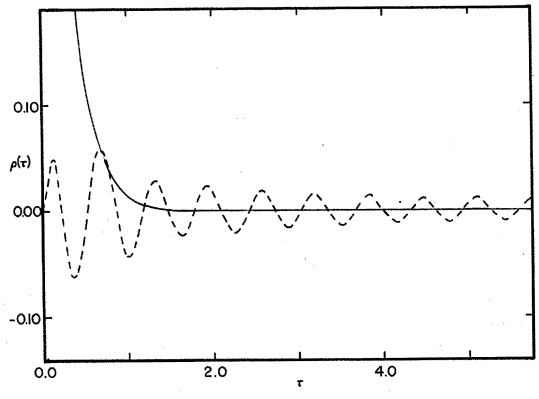

FIG. 6. A study of Eq. (25) with $\alpha = 0.2$ and $(c\mu - E)/E = 2$. The solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions.

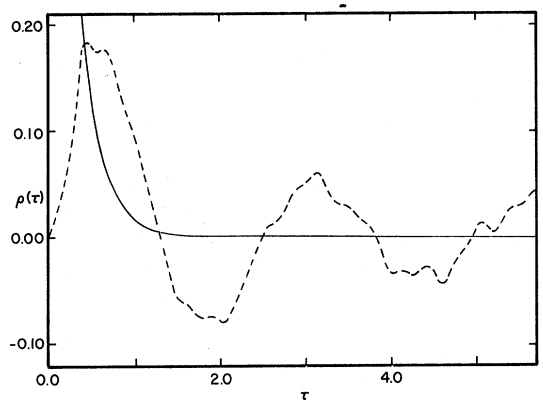

FIG. 7. A study of Eq. (44) with $\sigma = 0.1$ and $(v\mu - E)/E = \frac{1}{4}$. The solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions.

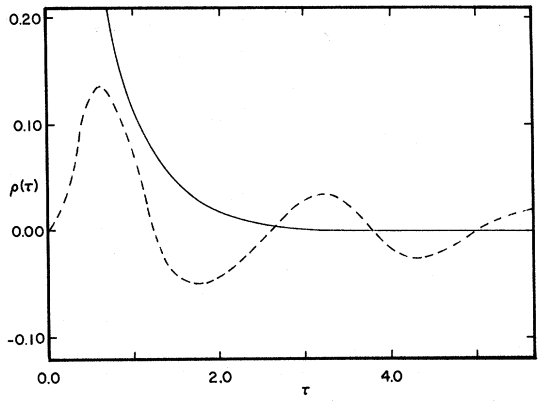

FIG. 9. A study of Eq. (44) with $\sigma = 0.2$ and $(v\mu - E)/E = \frac{1}{2}$. The solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions.

that the behavior exhibited in Figs. 7 and 8 is not an artifact of the integration routine used in our calculations.

With the numerical results at hand, we now turn to a discussion of the two models studied in this paper. As indicated in the Introduction, one of our objectives here was to determine whether the nonexponential behavior predicted by Zwanzig and demonstrated in the earlier work on the Wigner-Weisskopf atom was a consequence of the particular approximation used to avoid the ultraviolet divergence. We have investigated this possibility by using a different approximation scheme to avoid this divergence, namely, that of imposing a frequency cutoff. We have found that nonexponential behavior is still manifest in the solution of the master equation for the two-level atom when finite values of the cutoff are chosen. We observe, however, that for large values of the cutoff the amplitude of the nonexponential relaxation is smaller and the rate of oscillation faster, and, in fact, for extremely large values of the cutoff, the nonexponential behavior is negligibly small. It must be emphasized, however, that for the two-level atomic system the frequency cutoff cannot be regarded as a physical parameter, in the sense that a value of the cutoff parameter can be determined by considering some real system. The frequency cutoff for the two-level spin system, on the other hand, arises quite naturally, and to each particular system there corresponds a definite Debye cutoff.

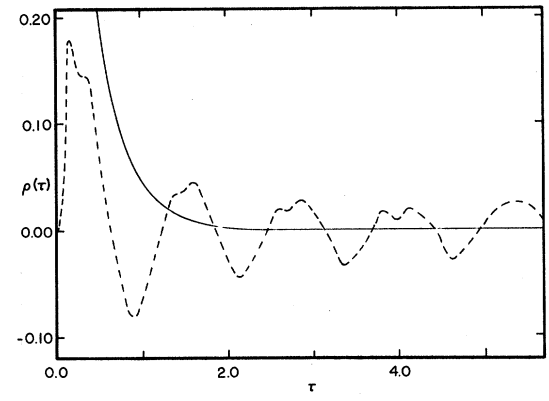

FIG. 8. A study of Eq. (44) with $\sigma = 0.1$ and $(v\mu - E)/E = \frac{1}{2}$. The solid line refers to the purely exponential term, and the dashed line refers to the nonexponential contributions.

It was also our intention to determine whether the appearance of nonexponential modes of decay was due to the particular model studied, the two-level atom, or whether nonexponential behavior would emerge from the study of other models as well. Therein lies the interest of the spin system studied in this paper, since oscillations were observed in the solution of Eq. (44) as well.

It is important to recognize that the sequence of slowly damped oscillations which arises in the solution of the master equation for the two models studied here may not be observable experimentally. To investigate this point, as well as to test the reasonableness of the model introduced here for spin-lattice relaxation, we have estimated the relaxation time of cerium ethyl sulfate using Eq. (44). This estimate can be correlated with experiment since the relaxation times for various rare-earth salts, including 0.2% cerium in lanthanum ethyl sulfate, have been studied experimentally by Scott and Jeffries.[21] To begin, we recall the definition of σ. We choose as a value for v the velocity of sound in the lattice 2×10^5 cm/sec, the value used by Scott and Jeffries. Sears in his study of the heat capacity of cerium ethyl sulfate estimates the cou-

pling parameter ϵ to be $\frac{1}{2}$. For simplicity, we shall assume here that ϵ does not change appreciably when we have 0.2% cerium ethyl sulfate in lanthanum ethyl sulfate. For the difference in frequency of the two lowest energy levels for cerium ethyl sulfate we choose 10^{11} sec^{-1}.[15,19] Finally, the density of lattice sites can be estimated from the crystallographic data of Johnson and Meyer.[22] For cerium ethyl sulfate we obtain a density of 10^{18} cm^{-3}. Using these estimates, we obtain a value of 10^{-4} for σ. From the structure of Eq. (44) and on the basis of the numerical work presented in Figs. 7–9, it is reasonable to conclude that the dominant contribution to $\rho(\tau)$ will be given by the exponential term in that equation. Furthermore, in view of the small value of σ the exponential term itself can be approximated by

$$e^{-4\sigma E t}$$

If we define the relaxation time T to be

$$T = 1/4\sigma E ,$$

then with the choice of σ and ϵ cited above, we estimate the relaxation time of cerium ethyl sulfate to be 10^{-8} sec. Scott and Jeffries observe a relaxation time of the order of 10^{-4} sec in 0.2% cerium ethyl sulfate. From the dependence of the relaxation time on temperature they conclude that the observed relaxation is due to the Orbach and Raman mechanisms. The estimate of T for the relaxation time for the direct-process relaxation mechanism is consistent with their observation, since at very low temperatures the direct process is known to be faster than either the Raman or Orbach processes. In fact, for 1% praseodynium in lanthanum double nitrate, a non-Kramers salt for which the direct process can be distinguished from the Raman process at low temperatures, one observes a relaxation time for the direct process of 10^{-6} sec and for the Raman process of 10^{-2} sec. Hence, at least for the spin problem a partial answer can be given to the question raised earlier, namely, whether it might be possible to observe experimentally the sequence of slowly damped oscillations found in solving the master equation. For, if one is prepared to accept that the calculations presented here, which refer to a model defined at zero temperature, have some relevance to real systems (and, in particular, to cerium ethyl sulfate at $\sim 3\,^{\circ}$K), and if one agrees that the relaxation time of the direct process is not faster than 10^{-8} sec, then a direct experimental observation of nonexponential decay for this system is not precluded, given the magnetic resonance equipment currently available. Should it be possible to observe such an effect, it would be fair to say that the underlying mathematical structure of the Prigogine-Résibois master equation provides a framework within which the Zwanzig suggestion can be understood, and this, in the view of the authors, assumes an importance that cannot be overstressed.

ACKNOWLEDGMENTS

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APPENDIX

We define

$$\sigma(N, z) = \int_0^\infty dt\, e^{izt}\rho(N, t) .$$

Beginning with Eq. (14),

$$\rho_0(N, 0) = [\psi(z) + iz]\sigma(N, z) ,$$

we retain terms proportional to g_λ and $g_\lambda^\dagger$ in the Hamiltonian, obtaining

$$\begin{aligned}\rho_0(N, 0) = iz\sigma(N, z) + \frac{4z}{i\hbar^2}\sum_\lambda \Big\{ & |h_\lambda|^2 \frac{1}{z^2 - (c|k_\lambda| - E)^2}\,[(N_\lambda + 1)\delta^{\mathrm{Kr}}(N_p - 2)\,(\sigma(N, z) - \sigma(N_p - 1, N_\lambda + 1, \{N_\mu\}, z)) \\ & + N_\lambda \delta^{\mathrm{Kr}}(N_p - 1)\,(\sigma(N, z) - \sigma(N_p + 1,\ N_\lambda - 1, \{N_\mu\}, z))] \\ & + |g_\lambda|^2 \frac{1}{z^2 - (c|k_\lambda| + E)^2}\,[N_\lambda \delta^{\mathrm{Kr}}(N_p - 2)\,(\sigma(N, z) - \sigma(N_p - 1, N_\lambda - 1, \{N_\mu\}, z)) \\ & + (N_\lambda + 1)\delta^{\mathrm{Kr}}(N_p - 1)\,(\sigma(N, z) - \sigma(N_p + 1, N_\lambda + 1, \{N_\mu\}, z))]\Big\} . \end{aligned} \tag{47}$$

For the particular choice (which we shall call $\mathfrak{N}$) of N variables,

$$N_p = 2, \quad N_\mu = 0 ,$$

for all modes μ, this becomes

$$1 = iz\sigma(\mathfrak{N}, z) + \frac{4z}{i\hbar^2} \sum_{\lambda} |h_\lambda|^2 \frac{1}{z^2 - (c|k_\lambda| - E)^2} [\sigma(\mathfrak{N}, z) - \sigma(\lambda, z)] . \quad (48)$$

For a second choice of N variables, $N_p = 1$, $N_\lambda = 1$, $N_{\mu \neq \lambda} = 0$, the equation becomes

$$0 = iz\sigma(\lambda, z) + \frac{4z}{i\hbar^2} |h_\lambda|^2 \frac{1}{z^2 - (c|k_\lambda| - E)^2} [\sigma(\lambda, z) - \sigma(\mathfrak{N}, z)] + \frac{4z}{i\hbar^2} \sum_{\mu \neq \lambda} |g_\mu|^2 \frac{1}{z^2 - (c|k_\mu| - E)^2}$$

$$\times [\sigma(\lambda, z) - \sigma(\mathfrak{N}, \lambda, \mu, z)] + \frac{4z}{i\hbar^2} |g_\lambda|^2 \frac{1}{z^2 - (c|k_\lambda| - E)^2} [\sigma(\lambda, z) - \sigma(\mathfrak{N}, 2\lambda, z)] . \quad (49)$$

For an infinite system we have

$$(8\pi^3/L_1L_2L_3) \sum_\lambda \to 2 \int d\vec{k} .$$

Keeping in mind the expressions for $|h_\lambda|^2$ and $|g_\lambda|^2$ given in Sec. II, we proceed to the infinite-system limit and neglect terms proportional to $(L_1L_2L_3)^{-1}$. The first equation becomes

$$1 = iz\sigma(\mathfrak{N}, z) - \frac{4iz\alpha c^2}{\pi} \int_0^\infty dk \frac{k}{z^2 - (ck - E)^2}$$

$$\times [\sigma(\mathfrak{N}, z) - \sigma(k, z)] . \quad (50)$$

The second equation becomes

$$0 = iz\sigma(k, z) - \frac{4iz\beta c^2}{\pi} \int_0^\infty dk' \frac{k'}{z^2 - (ck' - E)^2}$$

$$\times [\sigma(k, z) - \sigma(\mathfrak{N}, k, k', z)] . \quad (51)$$

We note that this second equation does not contain $\sigma(\mathfrak{N}, z)$ and merely links $\sigma(k, z)$ to a new quantity $\sigma(\mathfrak{N}, k, k', z)$ involving a state with the atom excited and two photons present. Since the left-hand side of this equation is zero, this is a homogeneous relation between $\sigma(k, z)$ and $\sigma(\mathfrak{N}, k, k', z)$, and we have a hierarchy of equations with higher terms being given by the equations

$$0 = iz\sigma(\mathfrak{N}, k, k', z) - \frac{4iz\beta c^2}{\pi} \int_0^\infty dk'' \frac{k''}{z^2 - (ck'' - E)^2}$$

$$\times [\sigma(\mathfrak{N}, k, k', z) - \sigma(k, k', k'', z)] \quad (52)$$

and

$$0 = iz\sigma(\mathfrak{N}, k, k', k'', z) - \frac{4iz\beta c^2}{\pi} \int_0^\infty dk''' \frac{k'''}{z^2 - (ck''' - E)^2}$$

$$\times [\sigma(\mathfrak{N}, k, k', k'', z) - \sigma(k, k', k'', k''', z)] . \quad (53)$$

It is clear that a solution to this hierarchy is

$$\sigma(k, z) = \sigma(\mathfrak{N}, k, k', z) = \sigma(k, k', k'', z)$$

$$= \sigma(\mathfrak{N}, k, k', k'', k''', z) = \cdots = 0 .$$

With this solution for $\sigma(k, z)$ our first equation becomes

$$1 = iz\sigma(\mathfrak{N}, z) - \frac{4iz\alpha c^2}{\pi} \int_0^\infty dk \frac{k}{z^2 - (ck - E)^2} \sigma(\mathfrak{N}, z) , \quad (54)$$

which is merely Eq. (19). Now the existence of the operator $[\psi(z) + iz]^{-1}$ requires that the hierarchy of equations have only one solution.[23] We find, therefore, that for the specific initial condition corresponding to spontaneous emission and spin-lattice relaxation at zero temperature, in weak coupling in the thermodynamic limit, non-energy-conserving terms proportional to $|g_\lambda|^2$ do not play a role in the time evolution of the system.

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"Overlap" Contributions to the Electric-Field-Gradient Components at the Fe^{3+} Site in FeOCl

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Using the simple Sawatzky model, we have made an evaluation of the "overlap" contributions to the electric-field-gradient (EFG) components at the non-axially-symmetric Fe^{3+} site in FeOCl. The modifications to the EFG components calculated previously by lattice-sum methods are considerable. For O^{2-} and Cl^- polarizibility α values of 1.0 Å^3, it was possible both to match the experimental asymmetry parameter η value of 0.32 and to get a $Q(Fe^{57m})$ value of 0.19 b, close to the ferrous consensus.

Recently there appeared a determination of the Fe^{57m} nuclear-quadrupole coupling parameters pertinent to the non-axially-symmetric Fe^{3+} site in FeOCl.[1] Unfortunately, the fit of a self-consistent monopole–point-dipole lattice-sum electric-field-gradient (EFG) calculation to these data was not very satisfactory. The dipole contributions to the EFG, for O^{2-} and Cl^- polarizibilities α varying over the range 1–3 Å^3, were at times comparable to the monopole sums (cation polarizibility was neglected). The only way that the EFG asymmetry parameter η could be properly fitted within the α range used was to set $\alpha_O = \alpha_{Cl} = 1$. However, this led to a calculated $Q(Fe^{57m})$ of 0.33 b, which, in the light of recent analyses,[2] is probably much too large. We present in this paper an evaluation, in this system, of the EFG contributions due to the overlap distortion of the Fe^{3+} closed-shell orbitals by the ligands. Such calculations have recently been made in α-Al_2O_3 and α-Fe_2O_3 by Sawatzky and associates[3] and by Sharma.[4] From their analyses in sapphire-type geometries, these authors have obtained values for $Q(Al^{27})$ and $Q(Fe^{57m})$ which agree very well with other data. We use the more simple Sawatzky formulation here.

Clearly, the non-axially-symmetric Fe^{3+} site in FeOCl provides a more searching test of theoretical EFG calculations than the symmetric Fe^{3+} site in α-Fe_2O_3. Also, unlike α-Fe_2O_3, the lattice-sum calculations in FeOCl are relatively insensitive to variations in crystallographic parameters.[1] However, as noted above, anion polarizibility enters relatively prominently here. Before proceeding further, we summarize the FeOCl Mössbauer-effect results. The quadrupole splitting ΔE_Q was found to be 0.916 ± 0.001 mm/sec; the η value was 0.32 ± 0.03; and the x, y, z principal axes of the EFG were parallel to the crystallographic c, b, a axes, respectively ($c < a < b$) with V_{zz} negative.

In this system, Fe^{3+} is octahedrally coordinated, having as nearest neighbors two oxygen ions at 1.964 Å, another two oxygens at 2.100 Å, and two chlorines at 2.368 Å. In calculating the overlap integrals, we have noted the arguments of Sawatzky and associates in assessing the relative magnitudes of various contributions to the overlap. Therefore, we consider here the overlap of the Fe^{3+} $2p$ and $3p$ orbitals with (i) the oxygen $2p$ orbitals and (ii) the chlorine $3p$ orbitals. The basic equation for the EFG contribution $(V'_{zz})_k$ from each *set* k of 2