Theory of motional narrowing of EPR spectral density of magnetic ions

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A theory of the EPR line shape of a magnetic impurity coupled to a lattice is presented that is capable of treating both the "slow" and "fast" regimes. A self-consistent equation of motion for the propagator of the ion motion is obtained under the assumption that the fluctuations of the lattice are not affected by the presence of the impurity. The equation is shown to correspond to the choice of the lowest-order term in a renormalized perturbation theory for the "self-energy" operator of the system. A diagrammatic representation of the perturbation theory is given which one may readily use to include higher-order corrections. The lowest-order approximation is analogous to the mode-coupling, or independent-mode approximation in extended systems, and is equivalent to the Kubo-Tomita approximation in the "fast" regime. A solution of a model problem that exhibits the motional-narrowing phenomenon is given. The theory may be generalized to arbitrary finite-dimensional systems coupled to a bath.

I. INTRODUCTION

Recent EPR experiments[1] on Fe^{3+}-V_0 impurity centers introduced into $SrTiO_3$ have been interpreted in such a way as to provide a measurement of the width of the central peak in the spectral density of the soft optical mode of the lattice vibrations at the structural phase transition.[2] The interpretation is clouded by the lack of an adequate theory to describe the measurements in the "slow" regime, near the critical point. The Kubo-Tomita theory of motional narrowing has been used for this purpose,[3] but is adequate only in the "fast" regime, where the fluctuations of the lattice responsible for the observed EPR linewidth have a characteristic frequency much greater than the observed width. When the characteristic frequency of the fluctuations becomes comparable to the linewidth that the fluctuations produce, the interaction of the mode in question with the fluctuations is strongly modified. The Kubo-Tomita theory is based upon a second-order perturbation result, and as a consequence, uses in the calculation of the linewidth, the unperturbed motion of the mode, i.e., the motion of the mode in the absence of the fluctuations. It cannot treat, therefore, the modification of the interaction when the time scales of the fluctuation and of the decay of the mode become comparable, i.e., the "slow" regime. A manifestation of this is the fact that the Kubo-Tomita theory predicts a Gaussian line shape in the "slow" regime, whatever the actual distribution of the fluctuating fields. The purpose of this note is to provide a calculable theory, adequate in both regimes. We will obtain a self-consistent equation for the linewidth in the "slow" regime that goes over into the Kubo-Tomita result in the "fast" regime.

This equation is the result of taking the lowest-order diagram in a diagrammatic expansion that provides, in principle, a complete solution of the problem and, in practice, a systematic way of obtaining more accurate solutions. The lowest-order solution is analogous to the independent-mode approximation in extended systems.[4] We will restrict the discussion to a magnetic impurity coupled to a lattice, but the method may be applied to any motional-narrowing problem. Similar methods have also been used in the theory of turbulence in plasmas.[5]

II. DERIVATION OF EQUATION OF MOTION

The system under consideration can be described by the Hamiltonian

$$H = H_I + H_{I-L} + H_L \,, \tag{1}$$

where H_I describes the magnetic impurity ion, H_L the lattice, and H_{I-L} the interaction between the two. We will assume that the interaction is so weak in the region of the phase space of the lattice modes that are important that we can neglect its effect on the lattice. This assumption may be questioned in the particular example we are considering since the Fe^{3+}-V_0 complex does produce local distortion of the lattice. However, the relative strong coupling to the short-wavelength lattice modes implied should not affect the critical behavior, which depends upon the coupling to the long-wavelength modes. We shall, in any case, make this assumption.

Define

$$U(t, t_0) = e^{+i(\mathcal{L}_I + \mathcal{L}_{I-L} + \mathcal{L}_L)(t-t_0)}\,\theta(t - t_0)\,, \tag{2}$$

where $\mathcal{L}O = (1/\hbar)[H, O]$, $\theta(t) = 1$ if $t > 0$, 0 otherwise, and

$$\overline{U}(t, t_0) = \mathrm{Tr}^L \rho_L^{eq} U(t, t_0), \quad \rho_L^{eq} = e^{-\beta H_L}/\mathrm{Tr}^L e^{-\beta H_L} . \quad (3)$$

Tr^L denotes a trace over the lattice states only. U is an operator in the space V consisting of all bounded linear operators on the Hilbert space of the system. We denote by V, $V_I \otimes V_L$ where V_I and V_L are the spaces of linear operators on the ion and lattice Hilbert space, respectively. $\overline{U}$ is an operator on V_I, since the trace in (3) is over the states of the lattice only. If the spin of the ion is of magnitude S, then $\overline{U}$ is a $(2S+1)^2$-dimensional operator. A convenient basis in the space of linear operators is provided by the states $|X^{nm}\rangle$ where the operators (on the Hilbert space of the spins) associated with the states (in V_I) are defined by

$$\sum_{m=-n}^{+n} X^{nm} t^m = [-tS^- + 2S^z + (1/t)S^+]^n, \quad n = 0, \ldots, 2S. \quad (4)$$

An innerproduct on V_I can be defined by

$$\langle A | B \rangle = \mathrm{Tr}\, A^\dagger B . \quad (5)$$

This innerproduct is appropriate for the EPR problem when the temperature is sufficiently high that $\beta H_I \ll 1$. The theory is readily generalized to include the effect of finite temperatures.[4] We find

$$\langle X_{nm} | X_{n'm'} \rangle = \delta_{nn'} \delta_{mm'} C_{nm} , \quad (6)$$

where

$$C_{nm} = \frac{(2S+1+n)!(n!)^2 2n!}{(2n+1)!(2S-n)!(n-m)!(n+m)!/2S+1} , \quad (7)$$

so that the states $|A_{nm}\rangle = C_{nm}^{-1/2} |X_{nm}\rangle$ are an orthonormal basis. The EPR line shape is determined by $\langle S^+ | \overline{U}(t, t_0) | S^+ \rangle$, but we will of necessity derive an equation of motion for the complete matrix associated with $\overline{U}$.

U satisfies

$$\frac{\partial}{\partial t} U(t, t_0) - i(\mathfrak{L}_I + \mathfrak{L}_{I\text{-}L} + \mathfrak{L}_L) U(t, t_0) = \delta(t - t_0) . \quad (8)$$

On taking the trace over ρ_L^{eq}, which we denote by either a bar over the averaged quantities, or angular brackets $\langle\ \rangle$, and observing that $\mathrm{Tr} \rho_L^{eq} \mathfrak{L}_L U = 0$, we obtain

$$\frac{\partial}{\partial t} \overline{U}(t, t_0) - i(\mathfrak{L}_I + \overline{\mathfrak{L}}_{I\text{-}L}) \overline{U}(t, t_0) - i \langle \mathfrak{L}_{I\text{-}L}(I - A) U(t, t_0) \rangle = \delta(t - t_0) , \quad (9)$$

where the operator A indicates that the average is taken over every operator to the right. We have also, by subtracting (9) from (8),

$$\frac{\partial}{\partial t}(I-A)U - i\,\mathfrak{L}_I (I-A)U - i(I-A)\mathfrak{L}_{I\text{-}L}(I-A)U - i\mathfrak{L}_L (I-A)U = -i\Delta\mathfrak{L}_{I\text{-}L}\overline{U} , \quad (10)$$

where

$$\Delta\mathfrak{L}_{I\text{-}L} = \mathfrak{L}_{I\text{-}L} - \overline{\mathfrak{L}}_{I\text{-}L} .$$

Integrating (10) and substituting in (9), we obtain

$$\frac{\partial}{\partial t} \overline{U}(t, t_0) - i(\mathfrak{L}_I + \overline{\mathfrak{L}}_{I\text{-}L}) \overline{U}(t, t_0) + \left\langle \Delta\mathfrak{L}_{I\text{-}L} \int_{t_0}^{t} U'(t, t') \Delta\mathfrak{L}_{I\text{-}L} \right\rangle \overline{U}(t', t_0)\, dt' = \delta(t - t_0) , \quad (11)$$

where

$$\frac{\partial}{\partial t} U'(t, t_0) - i[\mathfrak{L}_I + (I-A)\mathfrak{L}_{I\text{-}L}(I-A) + \mathfrak{L}_L] U'(t, t_0) = \delta(t - t_0) . \quad (12)$$

Equation (11) is an exact expression.

If the coupling term were negligible in (12), we could obtain a solution of the form $U'(t, t_0) = U_I(t, t_0) U_L(t, t_0)$ with $U_I(t, t_0) = e^{i\mathfrak{L}_I(t-t_0)}$ and $U_L(t, t_0) = e^{i\mathfrak{L}_L(t-t_0)}$. If in addition, the coupling term were of the form $H_{I\text{-}L} = O_I \Phi_L$, i.e., the spin system is coupled to a single lattice field, the left-hand side of Eq. (11) could be written $(\tilde{\phi}_L = \phi_L - \langle \phi_L \rangle)$

$$\frac{\partial}{\partial t} \overline{U}(t, t_0) - i(\mathfrak{L}_I + \overline{\mathfrak{L}}_{I\text{-}L}) \overline{U}(t, t_0) + \int_{t_0}^{t} K(t, t') \overline{U}(t', t_0) \langle \tilde{\Phi}_L(t) \tilde{\Phi}_L(t') \rangle\, dt' , \quad (13)$$

where

$$K(t, t')\overline{U}(t', t_0) = [O_I, e^{i(\mathfrak{L}_I + \overline{\mathfrak{L}}_{I\text{-}L})(t-t')} [O_I, \overline{U}(t', t_0)]] .$$

If $\langle \Phi_L(t) \Phi_L(t') \rangle$ decays rapidly compared to $\overline{U}$, the upper limit may be replaced by infinity in the integrals and the result is equivalent to the Kubo-Tomita theory. This is the "fast" regime. In the "slow" regime, the effect of the operator $\mathfrak{L}_L$ is reduced and the coupling terms become important. The simplest generalization of (13) that includes the effect of the modification of the ion spectral density due to its interaction with the lattice is obtained by making the approximation

$$U'(t, t_0) \simeq \overline{U}(t, t_0) U_L(t, t_0) . \quad (14)$$

This results in a closed, self-consistent equation for $\overline{U}$:

$$\frac{\partial}{\partial t} \overline{U}(t, t_0) - i(\mathfrak{L}_I + \overline{\mathfrak{L}}_{I\text{-}L}) \overline{U}(t, t_0) + \left\langle \Delta\mathfrak{L}_{I\text{-}L} \int_{t_0}^{t} \overline{U}(t, t') U_L(t, t') \Delta\mathfrak{L}_{I\text{-}L} \right\rangle \overline{U}(t', t_0)\, dt' = \delta(t - t_0). \quad (15)$$

The significance of Eq. (14) can be more readily seen by introducing an explicit representation for the operators on V in terms of which we can obtain a diagrammatic interpretation of Eq. (15). Let us choose a basis in V_I for which $\mathfrak{L}_I + \overline{\mathfrak{L}}_{I\text{-}L}$ is diagonal, the elements of which we will denote by $|i\rangle$, and which are associated with operators O_i. In this basis let $\langle i|\overline{U}(t,t_0)|j\rangle \equiv \overline{V}_{ij}(t,t_0)$. The operator $\Delta\mathcal{L}_{I-L}$ can be represented by

$$(\Phi_L - \langle\Phi_L\rangle)\Delta_{ij} = \langle i|\Delta\mathcal{L}_{I-L}|j\rangle = \mathrm{Tr}\,O_i[O_I, O_j](\Phi_L - \langle\Phi_L\rangle) \quad (16)$$

and Eq. (15) can be written

$$\frac{\partial}{\partial t}\overline{V}_{ij}(t,t_0) - i\mathcal{L}_i\overline{V}_{ij}(t,t_0) + \int_{t_0}^{t} K_{ik}(t,t')\langle\tilde{\Phi}(t)\tilde{\Phi}(t')\rangle\overline{V}_{kj}(t',t_0)\,dt' = \delta(t-t_0)\ , \quad (17)$$

where

$$K_{ij}(t,t') = \Delta_{ik}\overline{V}_{kl}(t,t')\Delta_{lj} \quad (18)$$

and

$$(\mathcal{L}_I + \overline{\mathcal{L}}_{I-L})|i\rangle = \mathcal{L}_i|i\rangle\ . \quad (19)$$

Once the matrix Δ, the eigenvalues $\mathcal{L}_i$ and the function $\langle\Phi_L(t)\Phi_L(t')\rangle$ are given, Eq. (17) may be readily solved by numerical integration.

To obtain a diagrammatic expansion with which to interpret this result, consider rewriting Eq. (12) in the interaction representation, and iterating it to obtain a solution. We would have then

$$U'(t,t_0) = e^{i(\mathcal{L}_I+\overline{\mathcal{L}}_{I-L}+\mathcal{L}_L)(t-t_0)}\left(1 + \int_{t_0}^{t}\Delta\mathcal{L}^I(t')\,dt' + \int_{t_0}^{t}\int_{t_0}^{t'}\Delta\mathcal{L}^I(t')\Delta\mathcal{L}^I(t'')\,dt'\,dt'' + \cdots\right), \quad (20)$$

where

$$\Delta\mathcal{L}^I(t') = e^{-i(\mathcal{L}_I+\overline{\mathcal{L}}_{I-L}+\mathcal{L}_L)(t'-t_0)}(I-A) \times \Delta\mathcal{L}_{I-L}(I-A)e^{i(\mathcal{L}_I+\overline{\mathcal{L}}_{I-L}+\mathcal{L}_L)(t'-t_0)}\ . \quad (21)$$

Ignoring for the moment the projection operator $I-A$, we can associate with each of the factors $\Delta\mathcal{L}$ in the perturbation expansion the vertex shown in Fig. 1(a). As long as we do not admit the effects of the interaction on the lattice dynamics, this is the only vertex we need consider. The contribution from the second-order term in Eq. (20) to $[\Delta\mathcal{L}U'(t,t_0)\Delta\mathcal{L}]_{ij}$ can then be represented diagrammatically as shown in Fig. 1(b) where the horizontal lines linking the vertices represent the propagator $e^{i(\mathcal{L}_I+\mathcal{L}_{I-L})(t-t_0)}$. Note that the diagram is still an operator in V_L, corresponding to the factor $\tilde{\Phi}(0)\tilde{\Phi}(t-t')\tilde{\Phi}(t-t'')\tilde{\Phi}(t-t_0)$. When the average is taken in order to calculate $\langle\Delta\mathcal{L}U'(t,t_0)\Delta\mathcal{L}\rangle$, the diagrams that can be obtained will be as shown in Figs. 2(a)–2(d). The wavy lines in Figs. 2(a)–2(c) linking vertices t_1 and t_2 are equal to $\langle\tilde{\Phi}_L(t_1)\times\tilde{\Phi}_L(t_2)\rangle$, and arise from the part of the average of the four-spin operators that can be factored. Figure 2(d) arises from the cumulant of the average of the four-spin operators, and indicates that, in general, the response of the ionic system in the slow motion regime cannot be determined from knowledge of $\langle\tilde{\Phi}_L(t_1)\tilde{\Phi}_L(t_2)\rangle$ alone, but depends on higher-order correlation functions as well. The exception to this statement is the case in which the higher-order correlations vanish; i.e., the field variables have Gaussian statistics for all times.

In fact diagram 2(a) would not exist because of the projection operator $I-A$, that we temporarily ignored. These serve to eliminate all diagrams that have the structure shown in Fig. 3. The diagram for $\langle(\Delta\mathcal{L}U'(t,t_0)\Delta\mathcal{L})_{ij}\rangle$ is, quite generally, of the form shown in Fig. 4(a), where the shaded box contains all possible diagrams with an arbitrary number of vertices that do not reduce to an intermediate state without any field lines present. The

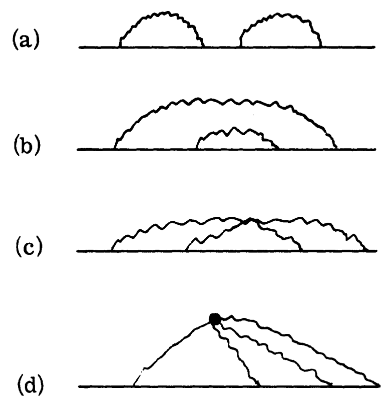

FIG. 2. All possible fourth-order contributions to $\langle\Delta LU\,\Delta L\rangle$. Wavy lines joining two points represent $\langle\tilde{\Phi}(t_1)\,\tilde{\Phi}(t_2)\rangle$. Wavy lines joining four points represent $\langle\tilde{\Phi}(t_1)\,\tilde{\Phi}(t_2)\,\tilde{\Phi}(t_3)\,\tilde{\Phi}(t_4)\rangle_C$.

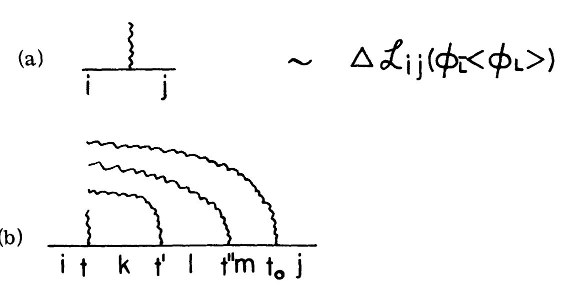

FIG. 1. (a) Vertex diagram and associated analytic expression. (b) Fourth-order contribution to $\Delta LU\Delta L$.

FIG. 3. Diagram eliminated by projection operator I-A in the definition of U'.

approximation we have used in the "fast" regime, that corresponds to the Kubo-Tomita theory is shown in Fig. 4(b). If we represent $\overline{U}_{ij}(t, t_0)$ by a thick line, then the approximations we have used for the entire range of rates for the fluctuation of the fields is shown in Fig. 4(c). It should be evident that this is indeed the simplest generalization of Fig. 4(b) to include the effects of the interaction on the ions in the intermediate states. It is analogous to the mode-coupling approximation in extended systems.[4] We note that some of the effect of the ion on the lattice fluctuations can be accounted for by renormalizing the wavy line, but as we expect these effects to be small, and as it increases greatly the computational difficulty to do this, we will not attempt this in the present work.

III. SOLUTION OF MODEL PROBLEM

As an example that can be solved by the method outlined above, we will consider the simple case of a spin-1 system in a magnetic field, interacting with the lattice through a term $D(S^z)^2\Phi$, and we will assume that the correlation function of the field decays exponentially with a time constant (γ) we will allow to vary. We assume $\langle\Phi\rangle = 0$ and $\langle\Phi^2\rangle = 1$. The Hamiltonian is

$$\mathcal{H} = -HS^z + D(S^z)^2\Phi + H_L \ . \quad (22)$$

There are nine operators needed to span V_I, and $\mathcal{L}_I$ is already diagonal in the basis generated in (6) with

$$\mathcal{L}_I\,|X_{nm}\rangle \approx -H[S^z, X_{nm}] \approx -Hm\,|X_{nm}\rangle \ . \quad (23)$$

The interaction matrix is

$$\langle A_{nm}|\Delta\mathcal{L}|A_{n'm'}\rangle = \frac{D\,\mathrm{Tr}X^{\dagger}_{nm}[(S^z)^2, X_{n'm'}]}{C^{1/2}_{nm}\,C^{1/2}_{n'm'}\,\tilde{\Phi}_L} \ .$$

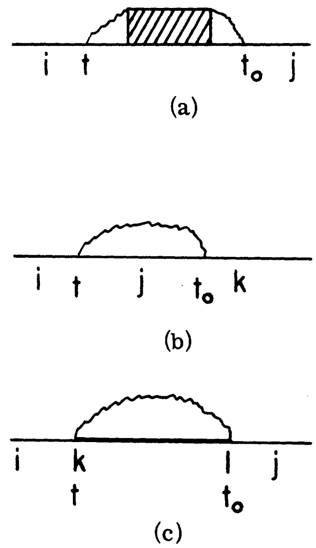

FIG. 4. (a) Diagramatic representation of $\langle\langle\Delta L U'(t, t_0) \times \Delta L\rangle_{ij}\rangle$. (b) Lowest-order perturbation result for $\langle\langle\Delta L U'(t, t_0)\Delta L\rangle_{ij}\rangle$. Equivalent to the Kubo-Tomita theory in the fast limit. (c) Lowest-order self-consistent approximation. Diagram represents $\langle\Delta L\overline{U}(t, t_0)\,\Delta L\rangle_{ij}$.

Since we are interested only in the $\langle A_{1,+1}|\overline{U}(t) \times|A_{1,+1}\rangle$ matrix element, $\mathrm{Tr}[S^-(t)S^+(0)]/\frac{2}{3}S(S+1)$, we do not need to calculate the entire matrix. In fact, the interaction couples only $|A_{1,+1}\rangle$ and $|A_{2,+1}\rangle$ so that we need only consider a 2×2 matrix equation.

The only nonvanishing matrix elements of $\Delta\mathcal{L}$ in this subspace are

$$\langle A_{1,+1}|\Delta\mathcal{L}|A_{2,+1}\rangle = \langle A_{2,+1}|\Delta\mathcal{L}|A_{1,+1}\rangle = D(\Phi_L - \langle\Phi_L\rangle) \ . \quad (24)$$

Equation (17) is then explicitly

$$\frac{\partial}{\partial t}\begin{pmatrix}\overline{U}_{11}(t) & \overline{U}_{12}(t)\\ \overline{U}_{21}(t) & \overline{U}_{22}(t)\end{pmatrix} - i\begin{pmatrix}-H & 0\\ 0 & -H\end{pmatrix}\begin{pmatrix}\overline{U}_{11}(t) & \overline{U}_{12}(t)\\ \overline{U}_{21}(t) & \overline{U}_{22}(t)\end{pmatrix} + \int_0^t D^2 e^{-\gamma(t-t')}\begin{pmatrix}\overline{U}_{22}(t-t') & \overline{U}_{21}(t-t')\\ \overline{U}_{12}(t-t') & \overline{U}_{11}(t-t')\end{pmatrix}\begin{pmatrix}\overline{U}_{11}(t') & \overline{U}_{12}(t')\\ \overline{U}_{21}(t') & \overline{U}_{22}(t')\end{pmatrix} dt' = \delta(t) \ . \quad (25)$$

Note that the symmetry of the equation is such that $\overline{U}_{11} = \overline{U}_{22}$ and $\overline{U}_{12} = \overline{U}_{21}$, so that (25) may be written

$$\frac{\partial}{\partial t}\overline{U}(t) - i\mathcal{L}_I\overline{U}(t) + \int_0^t D^2 e^{-\gamma(t-t')}\overline{U}(t-t')\overline{U}(t')\,dt' = \delta(t) \ . \quad (26)$$

Defining $\overline{U}_I(t) = e^{-i\mathcal{L}_I t}\overline{U}(t)$, we have

$$\frac{\partial \overline{U}_I(t)}{\partial t} + \int_0^t D^2 e^{-\gamma(t-t')}\overline{U}_I(t-t')\overline{U}_I(t')\,dt' = \delta(t) \ . \quad (27)$$

It is evident that $\overline{U}_I(t)$ remains a diagonal matrix for all t. In the limit that $D^2/\gamma \ll \gamma$, the fast regime,

$$\overline{U}_I(t) = e^{-D^2 t/\gamma}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \ ,$$

which is the Kubo-Tomita result. The EPR line shape, which is just the real part of the Fourier transform of $\overline{U}_I(t)$, is a Lorentzian. In the opposite limit, $\gamma^2 \ll D^2$, the equation can be solved by La-

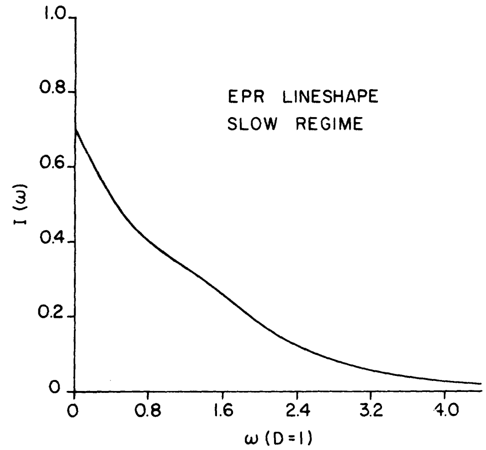

FIG. 5. Solution of self-consistent equations for a simple model: $I(\omega)=R_e(\overline{U}_I)_{11}(\omega)=\int_0^\infty \cos(\omega+H)t\,\mathrm{Tr}[S^-(t) \times S^+(0)]\,dt/\frac{2}{3}S(S+1)$.

place transforming and replacing the factor $e^{-\gamma(t-t')}$ by unity. The result for $\mathrm{Re}(\overline{U}_I)_{11}=\mathrm{Re}(\overline{U}_I)_{22}$ is

$$\mathrm{Re}(\overline{U}_I)_{11}(\omega)=\frac{-\omega}{2D^2}+\frac{1}{2D}\left(\frac{\omega^4}{D^4}+16\right)^{1/4} \times \cos\left(\frac{1}{2}\tan^{-1}\frac{4D^2}{\omega^2}\right). \quad (28)$$

In Fig. 5 we show the spectral density Eq. (28) (EPR line shape). The half-width at half-maximum is $1.06D$. Comparing this with the halfwidth in the fast regime, we see that the crossover will occur when $\gamma \simeq D$, as expected.[1]

The fact that we obtain a solution in the slow-motion regime that is independent of the probability distribution of the field, depending only on $\langle\Phi^2\rangle$, is a limitation of our approximation. This is most easily seen if the perturbation is taken to be $\delta H S^z \Phi$, with $\langle\Phi\rangle = 0$ and Φ time independent. $\langle S^+ | \overline{U} | S^+\rangle$ is readily calculated and is

$$\langle S^+ | \overline{U}(t) | S^+\rangle = \int e^{i(H+\delta H\Phi)t}\rho(\Phi)\,d\Phi\ , \quad (29)$$

so that $\overline{U}_I(t)$ is just the characteristic function of the distribution of field values $\rho(\Phi)$. Our method would yield a line shape as shown in Fig. 5, independent of $\rho(\Phi)$. The difficulty lies in the neglect of higher-order graphs in the approximate expression we have used for $\langle\Delta\mathcal{L}U'\Delta\mathcal{L}\rangle$. As has been pointed out above, it is only by inclusion of graphs such as Fig. 2(d) and similar ones in higher order that the specific distribution $\rho(\Phi)$ has an effect. Even if there are no graphs such as Fig. 2(d), i.e., $\rho(\Phi)$ is Gaussian, it would be necessary to include all the irreducible graphs of higher order in $\langle\Delta\mathcal{L}U'\Delta\mathcal{L}\rangle$ in order to have a Gaussian for the solution of Eq. (17). In particular, the approximation we have used, when Eq. (17) is iterated does not produce a term that corresponds to the diagram in Fig. 3. The moments of the spectral density are the coefficients in the expansion of $\langle S^+ | \overline{U}_I(t) | S^+\rangle$ in powers of t.[6] The omission of a diagram such as Fig. 3 implies that the fourth moment of the solution will be incorrect. As long as the coupling is linear in the field, it also implies that the effective distribution $\tilde{\rho}(\Phi)$, i.e., the distribution that would actually lead to the solution of (17) in the "slow" limit, if calculated exactly, has an incorrect value for $\langle\Phi^4\rangle$. The equations may be improved to include these terms by approximating $\langle\Delta\mathcal{L}U'\Delta\mathcal{L}\rangle$ by the sum of the expressions corresponding to Figs. 4(c) and 6. The resultant solution would then have the correct fourth moments if $\rho(\Phi)$ were a Gaussian, and the solution analogous to Eq. (28) will have 3 as the ratio of the fourth moment to the second-moment squared, as is appropriate for a Gaussian, but the higher moments will still not be those of a Gaussian.

IV. CONCLUSION

Although the methods we have presented do not provide a closed form solution of the motional-narrowing problem in the slow limit, they do make clear the essential difficulties and provide a systematic means of obtaining approximate solutions. For the case of a general distribution of field values $P(\phi)$, the method yields a solution in terms of an infinite set of graphs associated with cumulant averages $\langle\phi^n\rangle_c$, and there is no prospect of reducing the problem to closed form. For a Gaussian random process, the graphs have a relatively simple structure, and are all functionals only of $\langle\Phi(t)\,\Phi(0)\rangle$, so that it may prove possible to obtain a closed solution. This is certainly possible when $[H_{I-L}, H_I]=0$. In any event, the graphs have a sufficiently simple structure that numerical solutions of the equations of motion with a finite number of terms kept in the perturbation expansion of the self-energy are feasible, and lead to solutions with a corresponding number of the moments correct. Since the lowest-order graph already provides a description of the cross-

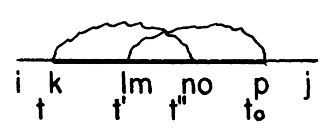

FIG. 6. Next correction in renormalized perturbation series to $\langle\Delta LU'\,\Delta L\rangle$ in the case that $\langle\Phi(t_1)\,\Phi(t_2) \times\Phi(t_3)\,\Phi(t_4)\rangle_C$, the cumulant average, is zero.

over phenomenon between the slow and fast regimes, we expect that the higher-order terms will serve to increase the accuracy of the line shape, but will not significantly alter the dependence of the linewidth in the slow regime on the parameters of the problem.

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[6]This statement will be true whenever the Kramers-Kronig relation holds, which it does not in the model solution, since there is a branch cut with a branch point at the origin. The second moment of the line shape does not in fact exist, since the spectral density falls off as ω^{-3}. In this case, for nth moment one should read the nth term in the Taylor-series expansion.