Stochastic theory of line shape and relaxation

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This paper is a generalization of Kubo's stochastic theory of spectroscopic line shapes which appeared in 1962 under the same title. Using a stochastic, Hermitian Hamiltonian to phenomenologically incorporate absorber-perturber interactions resulting from molecular collisions, we are able to reproduce Kubo's derivation of the simple Lorentzian line shape: $I(\omega)=\pi^{-1}\Gamma[(\omega-\omega_0)^2+\Gamma^2]^{-1}$ in which the width Γ is related to the mean-square strength, Q_3, of a diagonal stochastic Hamiltonian by $\Gamma=2Q_3$. Our generalization of this line shape is $I(\omega)=(1/\pi)\{1+(1-\omega/\Omega)[(\Gamma_2-\Gamma_1)/2\Gamma]\}\Gamma/[(\omega-\Omega)^2+\Gamma^2]^{-1}$, where Γ_1 and Γ_2 measure the degree of anisotropy in the off-diagonal part of the stochastic Hamiltonian. With perfect isotropy their contribution vanishes, but we are still left with additional corrections to the simple Lorentzian: $\Gamma=2Q(1+\omega_0^2/\epsilon^2)^{-1}+2Q_3$ and $\Omega=\omega_0+\Delta$, where $\Delta=2Q(\omega_0/\epsilon)(1+\omega_0^2/\epsilon^2)^{-1}$. Our result does reduce to Kubo's in the absence of off-diagonal stochastic terms. The parameter ϵ measures the non-Markovianness of the stochastic Hamiltonian and yields white noise in the limit $\epsilon\rightarrow\infty$. Our results are valid for this limit regime. The frequency shift Δ is a measure of the non-Markovianness.

I. INTRODUCTION

The problem of spectral line-shape broadening has received a great deal of attention over the years. Theories which treat radiative and Doppler broadening are well established, but collisional broadening has taken longer to understand as thoroughly. The latter is an intrinsically more difficult problem because it is a many-body problem.

The problem deals with the absorption of light by a given system, the absorber, which is continuously subjected to a multitude of complex forces. These forces originate in the interaction of the absorber with a large number of particles, the perturbers which form the medium in which the absorber is immersed. Therefore, one has to deal with two distinct but simultaneous interactions. The first one is the well-defined interaction between the absorber and the radiation field. The difficulty resides in the second interaction, the one between the perturbers and the absorber, which influences significantly the time evolution of the latter. The general quantum-mechanical perturbation expansion for the density matrix of the combined system, absorber plus radiation, and subsequently the relevant entities for an n-photon process, are well defined, but the computation of the probability of transition from one state of the system to another in such a process is rendered extremely difficult by the presence of the perturber-absorber interactions.

Physically, we expect this interaction to make the system undergo transitions between the various states, as well as disturb the spectrum of energy levels. In other words, this interaction should not simply commute with the Hamiltonian of the isolated system, i.e., it ought not to be diagonal in the basis of the states that span the Hilbert space of the isolated absorber. Mathematically and physically, the exact expression of this interaction is of great complexity, and any statistical method dealing with this problem has to overcome this complexity by performing, in one way or another, some kind of an averaging over the effects of the bath of perturbing particles.

The averaged effect of the bath is to cause relaxation. One question we address is how this relaxation is produced. In some theories, it is not produced, but introduced phenomenologically, as in the Bloch equations.[1-3] In these equations, the effect of the bath is incorporated by the addition of phenomenological relaxation parameters to the quantum Liouville equation for the isolated absorber plus radiation field. A traditional description of the absorber in the bath, by a non-Hermitian Hamiltonian, can produce these parameters. This treatment has predicted a simple Lorentzian form for the spectral line shape for single-photon processes. However, non-Lorentzian line shapes are observed also, and therefore the sources of their features are missing from such a theory. We shall point out later what these features are, as well as what we have found their sources to be.

Other methods have attempted the direct approach by starting from the quantum Liouville equation with the explicit presence of the interaction between the absorber and the perturbers, in order to produce the relaxation.[4-8] In many of these theories, approximations like adiabaticity, or binary form, are needed to build an extremely intricate mathematical bridge between the potential of interaction and the spectral line shape. Some have succeeded in reproducing the form of various experimental line shapes. However, often, if not always, the final step of the theory, which is to compute the form of the line, has to be handled numerically, and the link between a physical feature of the potential of interaction and the characteristics of the line shape it ultimately influences is lost in the complicated equations. As for the kind of averaging used, it usually is the projection operator technique or the tracing over the bath degrees of freedom. The role of statistical mechanics is explicitly recognized with the use of a canonical distribution for the perturbers.[4]

There is also a stochastic approach, as first developed by Kubo.[9–11] A full discussion of this theory comes later; it is closely related to our own. As Kubo pointed out, any effective method for many-body systems uses somewhere an assumption which is essentially of a stochastic nature.

The idea behind a stochastic approach is to represent the perturbation by a Hermitian, time-dependent stochastic Hamiltonian. This interaction potential is not given an explicit form but is characterized by a set of stochastic properties, e.g., Gaussian stochastic processes are characterized by their first and second moments.[12] Denoting a Gaussian stochastic Hamiltonian by $\tilde{H}(t)$, the stochastic properties are

$$\langle \tilde{H}_{ij}(t)\rangle = \hbar C_{ij} \; , \tag{1.1}$$

$$\langle \tilde{H}_{ij}(t)\tilde{H}_{kl}(s)\rangle = \hbar^2 Q_{ijkl} f_{ijkl}(\,|t-s|\,) \; . \tag{1.2}$$

The first moments, the C's, are the constant mean values of the matrix elements. The second moments, or autocorrelations, are products of strength constants, the Q's, and correlation functions, the f's, which are a measure of the "length in time" of the correlation between two matrix elements. For stationary processes, these functions depend on the absolute value of the time difference only.[13]

Physically, the correlation function of any random process has to have a finite width. However, this width can be so small compared to the other natural time scales of the problem that it can be considered infinitesimally small, in which case the correlation function is represented by a Dirac delta function. This is the white noise or Markovian limit. If this does not hold, one has to simulate colored noise, i.e., a non-Markovian process, by using a correlation with a finite width. We shall use the following form:

$$f_{ijkl}(\,|t-s|\,) = (\epsilon_{ijkl}/2)\exp(-\epsilon_{ijkl}\,|t-s|\,) \; , \tag{1.3}$$

in which ϵ is a positive constant, the inverse of which measures the lifetime of the correlation function. One reason for choosing this particular function is that it tends to a Dirac delta function when ϵ tends to infinity.

We have characterized the whole perturbation with a set of phenomenological parameters, the C's, Q's, and ϵ's. However, it should be clear that these parameters are fundamentally different from the phenomenological parameters added to incorporate *ad hoc* relaxation as is done in some theories. For one thing, they do not directly represent the relaxation of the absorber induced by the bath. They characterize the interaction only, and are expected to produce the relaxation on the average. Furthermore, any interaction potential, whatever its form and complexity might be, has to induce such a set of parameters, the values of which undoubtedly depend on those of the "natural" parameters, like the constants that fix the form and strength of the interaction potential, number density of the medium, etc. Finding out what that dependence is would certainly be interesting, but, from our point of view, the first and most important task is to link each parameter we have defined to the features of the spectral line shape it influences. The main features that can be observed in an ordinary line shape are the broadening, the shift from the natural frequency, and the asymmetry about the line center.

To illustrate these concepts, we shall study the simplest possible system which can give physical insight into the phenomenon of relaxation: a two-state spin system (1) in a fixed magnetic field, (2) perturbed by a randomly modulated magnetic field, and (3) interacting with a radiation field. In this introduction we introduce terminology and list a variety of results. The details of the derivations are to be found in Secs. II and III, and in the Appendix.

The entire system is described by the following Hamiltonian:

$$H(t) = H_0 + \tilde{H}(t) + V(t) \; , \tag{1.4}$$

where

$$H_0 = \left[\frac{e\hbar}{2mc}B\right]\sigma_3 \tag{1.5}$$

is the Hamiltonian of the isolated system, the spin in the fixed magnetic field $\mathbf{B}$ along the z axis;

$$\tilde{H}(t) = \left[\frac{e\hbar}{2mc}\right]\tilde{\mathbf{B}}(t)\cdot\boldsymbol{\sigma} \tag{1.6}$$

is the stochastic interaction between the spin and the fluctuating magnetic field $\tilde{\mathbf{B}}(t)$; and

$$V(t) = i\left[\frac{e\hbar}{2mc}\right]\left[\frac{2\pi\hbar c^2}{V\omega}\right]^{1/2}(ae^{-i\omega t} - a^{\dagger}e^{i\omega t})(\mathbf{k}\times\mathbf{e})\cdot\boldsymbol{\sigma} \tag{1.7}$$

is the purely magnetic interaction of the spin with a single-mode radiation field. The density matrix obeys the quantum Liouville equation

$$i\hbar\frac{\partial}{\partial t}\rho(t) = [L_0 + \tilde{L}(t) + L_v(t)]\rho(t) \; , \tag{1.8}$$

where the Liouvillian operators are defined by "commutator operators,"

$$L_0 \equiv [H_0, \cdot\,] \; , \tag{1.9}$$

$$\tilde{L}(t) \equiv [\tilde{H}(t), \cdot\,] \; , \tag{1.10}$$

$$L_v(t) \equiv [V(t), \cdot\,] \; . \tag{1.11}$$

The formal solution of (1.8) is

$$\rho(t) = \underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds[L_0 + \tilde{L}(s) + L_v(s)]\right]\rho(0) \; , \tag{1.12}$$

in which we have used the time-ordered exponential, defined by[12]

$$\underset{\leftarrow}{T}\exp\left[\int_0^t M(s)ds\right]\equiv 1+\sum_{n=1}^{\infty}\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n\, M(t_1)M(t_2)\cdots M(t_n)\,.$$

The order of the factors in the integrand is crucial because, in general, $M(t_l)$ and $M(t_k)$ do not commute for $t_l\neq t_k$.

We are concerned with a single-photon process, and the corresponding spectral line shape. What seems to be the natural approach is to use the well-defined quantum formalism, i.e., the interaction picture with respect to $V(t)$ by rewriting (1.12) as follows:

$$\rho(t)=U(t,0)\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,\hat{L}_v(s)\right]\rho(0)\,, \quad (1.13)$$

where

$$\hat{L}_v(t)\equiv U^{\dagger}(t,0)L_v(t)U(t,0) \quad (1.14)$$

and

$$U(t,s)\equiv \underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_s^t d\tau[L_0+\tilde{L}(\tau)]\right]\,, \quad (1.15a)$$

$$U^{\dagger}(t,s)\equiv \underset{\rightarrow}{T}\exp\left[\frac{i}{\hbar}\int_s^t d\tau[L_0+\tilde{L}(\tau)]\right]\,. \quad (1.15b)$$

Then we expand (1.13) in terms of $L_v(t)$, and extract the probability of transition in the single-photon process. We must average this probability in order to take into account the average effect of the stochastic Hamiltonian. In the Appendix we present the calculation involved in this method and show that it runs into difficulty which can be best pictured by the following two inequalities:

$$\left\langle \prod_{i=1}^{p\,(\geq 2)}\exp\left[\int_{t_i}^{t_i'}dt\,\tilde{\omega}_i(t)\right]\right\rangle \neq \prod_{i=1}^{p\,(\geq 2)}\left\langle \exp\left[\int_{t_i}^{t_i'}dt\,\tilde{\omega}_i(t)\right]\right\rangle \quad (1.16)$$

or

$$\left\langle \prod_{i=1}^{p\,(\geq 2)}\underset{\leftarrow}{T}\exp\left[\int_{t_i}^{t_i'}dt\,\tilde{O}_i(t)\right]\right\rangle \neq \prod_{i=1}^{p\,(\geq 2)}\left\langle \underset{\leftarrow}{T}\exp\left[\int_{t_i}^{t_i'}dt\,\tilde{O}_i(t)\right]\right\rangle\,, \quad (1.17)$$

where the $\tilde{\omega}(t)$'s and $\tilde{O}(t)$'s are randomly modulated functions and operators, respectively, and the brackets stand for the stochastic averaging. Using this traditional method one is faced with the averaging of a product of exponentials of the form above. The individual factors in the products on the right-hand side of (1.16) and (1.17) can be computed with the cumulant method,[14–16] but no such method exists to compute the average of the products on the left-hand side. The cumulant method for this type of problem was developed by Kubo to handle the stochastic averaging of a single exponential of the form

$$\left\langle \exp\left[\int_{t_1}^{t_2}dt\,\tilde{\omega}(t)\right]\right\rangle\,, \quad (1.18)$$

where $\tilde{\omega}(t)$ is a stochastic function.[16] Fox generalized the method to handle the following form:

$$\left\langle \underset{\leftarrow}{T}\exp\left[\int_{t_1}^{t_2}dt\,\tilde{O}(t)\right]\right\rangle\,, \quad (1.19)$$

where $\tilde{O}(t)$ is a stochastic operator.[14,15]

In the Appendix, we show that this mathematical difficulty with the natural approach to the problem goes away in the particular instance where the fluctuating magnetic field $\tilde{\mathbf{B}}(t)$ is along the same direction as the fixed magnetic field $\mathbf{B}$, i.e., along the z axis. [In more general terms, this is the case whenever the stochastic Hamiltonian $\tilde{H}(t)$ commutes with the isolated system Hamiltonian H_0, and therefore is diagonal in the basis of the eigenstates of H_0.] In this special case, one is left with the stochastic averaging of a single exponential of the form (1.18). We then find that the formal expression for the line shape agrees with the one Kubo used in his stochastic approach to spectral line broadening based on the oscillator model,[9,10] and which predicts a simple Lorentzian line shape, centered at the natural frequency, in the weakly non-Markovian case. We should then expect that shifts and asymmetries of line shapes are effects of off-diagonal terms of the stochastic perturbation. Our approach will prove this is so.

We are faced with the question of how to handle the stochastic averaging in the presence of a non-diagonal stochastic perturbation. Firstly, it should be understood that it is the density-matrix formalism which ought to be used in this problem. The basic reason is that if the Schrödinger equation is used, the averaged values of the time-dependent coefficients of the expansion for the state of the system in terms of the eigenstates would be studied. The quantum-mechanical expectation values of arbitrary operators would then involve bilinear combinations of these averaged values. This would lead to incorrect and unphysical results, including the decay of total probability, because products of averages do not equal averages of products. The density-matrix description directly involves the average values of bilinear products of the expansion coefficients, and, thereby, avoids this mistake. Secondly, there are two interaction pictures available in this problem. In our approach, we shall use them both in the following order: (a) Use the interaction representation with respect to $\tilde{H}(t)$, (b) Perform the stochastic averaging on the density matrix, (c) Use the interaction representation with respect to $V(t)$, (d) Expand the averaged density matrix in terms of $V(t)$, (e) Extract the averaged probability of transition in a single photon process. This procedure permits one to take into account the effect of the stochastic perturbation to all orders. The stochastic averaging is handled by the cumulant method applied to a single time-ordered exponential, the argument of which is a superoperator. No diagonal assumption for the stochastic Hamiltonian is required to perform this averaging. The details are found in Sec. II and we list below several salient features in the analysis.

In mathematical language, the five steps of our process are depicted as follows.

(a) Rewrite (1.12) as

$$\rho(t)=U(t,0)\,\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,\tilde{L}_I(s)\right]\rho(0)\ , \tag{1.20}$$

where

$$\tilde{L}_I(t)\equiv U^\dagger(t,0)\tilde{L}(t)U(t,0) \tag{1.21}$$

and

$$U(t,s)\equiv \underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_s^t d\tau[L_0+L_v(\tau)]\right]\ , \tag{1.22a}$$

$$U^\dagger(t,s)\equiv \underset{\rightarrow}{T}\exp\left[\frac{i}{\hbar}\int_s^t d\tau[L_0+L_v(\tau)]\right]\ . \tag{1.22b}$$

(b) Average (1.20) to obtain

$$\langle\rho(t)\rangle=\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds[L_0+R(s)+L_v(s)]\right]\rho(0)\ , \tag{1.23}$$

where $R(t)$ is the relaxation tetradic.

(c) Rewrite (1.23) as

$$\langle\rho(t)\rangle=G(t,0)\,\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,\hat{L}_v(s)\right]\rho(0)\ , \tag{1.24}$$

where

$$\hat{L}_v(t)\equiv G^\dagger(t,0)L_v(t)G(t,0) \tag{1.25}$$

and

$$G(t,s)\equiv \underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_s^t d\tau[L_0+R(\tau)]\right]\ , \tag{1.26a}$$

$$G^\dagger(t,s)\equiv \underset{\rightarrow}{T}\exp\left[\frac{i}{\hbar}\int_s^t d\tau[L_0+R(\tau)]\right]\ . \tag{1.26b}$$

(d) Expand (1.24),

$$\langle\rho(t)\rangle=\sum_{n=0}^{\infty}\langle\rho^{(n)}(t)\rangle\ , \tag{1.27}$$

where

$$\langle\rho^{(0)}(t)\rangle=G(t,0)\rho(0)\ , \tag{1.28}$$

$$\langle\rho^{(n)}(t)\rangle=\left[-\frac{i}{\hbar}\right]^n\int_0^t ds_1\int_0^{s_1}ds_2\cdots\int_0^{s_{n-1}}ds_n\,G(t,s_1)L_v(s_1)G(s_1,s_2)\cdots L_v(s_n)G(s_n,0)\rho(0)\ . \tag{1.29}$$

The density matrix $\langle\rho^{(n)}(t)\rangle$ is of order n in $L_v(t)$, and we shall refer to it as the "partial" averaged density matrix of order n. G is the super Green's function which governs the time behavior of the system in the absence of the radiation. Therefore, the series (1.27) is the generalization in form of the usual expansion of the density matrix of a nonperturbed system interacting with a radiation field, where the super Green's function would simply be

$$G(t,s)=\exp\left[-\frac{i}{\hbar}(t-s)L_0\right] \tag{1.30}$$

and indeed the general expression for G, (1.26a), does reduce to (1.30) in the absence of the relaxation tetradic R.

(e) The relevant partial averaged density matrix for a single-photon process is the one of second order. If the initial and final states of the combined system, spin plus radiation, for the single-photon process are $|i\rangle$ and $|f\rangle$, respectively, then the averaged probability of transition at time t is

$$\langle P(t)\rangle=\langle f\,|\,\langle\rho^{(2)}(t)\rangle\,|f\rangle \tag{1.31}$$

with

$$\rho(0)=|\,i\rangle\langle i\,|\ . \tag{1.32}$$

Having outlined the program applicable to all the problems of this nature, let us define the constants and phenomenological parameters relevant for the special case treated here. First, we rewrite (1.5)–(1.7) as follows:

$$H_0=\tfrac{1}{2}\hbar\omega_0\sigma_3\ , \tag{1.33}$$

$$\tilde{H}(t)=\sum_{i=1}^{3}\hbar\tilde{\phi}_i(t)\sigma_i\ , \tag{1.34}$$

$$V(t)=i\hbar\gamma(ae^{-i\omega t}-a^\dagger e^{i\omega t})\sigma_2\ , \tag{1.35}$$

where

$$\omega_0=\left[\frac{e}{mc}\right]B\ , \tag{1.36}$$

$$\tilde{\phi}_i(t)=\left[\frac{e}{2mc}\right]\tilde{B}_i(t)\ , \tag{1.37}$$

$$\gamma=\left[\frac{e}{mc}\right]\left[\frac{\pi\hbar\omega}{2V}\right]^{1/2}\ , \tag{1.38}$$

a and $a^\dagger$ are the annihilation and creation operators, respectively, of a photon of frequency ω. The wave vector $\mathbf{k}$ and the polarization vector $\mathbf{e}$ are along the third and first directions, respectively, σ_1, σ_2, and σ_3 are the Pauli matrices. ω_0 is the natural frequency, and $\tilde{\phi}_i(t)$ is a randomly modulated function relative to the ith component of the stochastic magnetic field $\tilde{\mathbf{B}}(t)$. The off-diagonal terms of the perturbation come from the transverse components of the latter. Note that $\tilde{H}(t)$ is manifestly Hermitian since the $\tilde{\phi}(t)$'s are real functions.

The stochastic properties of $\tilde{H}(t)$ are

$$\langle \tilde{\phi}_i(t) \rangle = 0 , \tag{1.39}$$

$$\langle \tilde{\phi}_i(t)\tilde{\phi}_j(s) \rangle = Q_i \delta_{ij} (\epsilon_i/2) \exp(-\epsilon_i \, | t-s |) . \tag{1.40}$$

Each stochastic function $\tilde{\phi}_i(t)$ is assumed to be Gaussian. The setting of the first moments to zero is a simplifying but not necessary assumption which represents the physical assumption of an averaged value of zero for the stochastic force acting on the system. The presence of the Kronecker delta function in (1.40) is also a simplifying but not necessary assumption. We have found that its absence, permitting the most general form for the autocorrelations, is of virtually no consequence on the conclusions drawn from the theory, and the expressions of certain entities are only slightly modified. The parameters, Q's and ϵ's, have the dimension of a frequency.

In Sec. II we study the influence of the stochastic perturbation on the time behavior of the spin system, and establish the creation of relaxation. In Sec. III the interaction with the radiation field is added. The expression (1.27) for the averaged density matrix and the spectral line shape are derived, and each phenomenological parameter we introduced is linked to the features of the spectral line shape it influences.

The averaging of the density matrix introduces the relaxation tetradic in which all the statistically averaged effects of the stochastic perturbation are contained. This tetradic term in the differential equation for the averaged density matrix cannot be written as a commutator. This means there is no Schrödinger equation equivalent to the averaged density matrix equation, i.e., there is no "average" Hamiltonian, Hermitian or not, that could describe the perturbed system and reproduce the effects stated hereafter. This confirms the claim that our theory is fundamentally different from several other phenomenological theories which are based on the Schrödinger-equation level of description.

We end this introduction by stating the long list of main results. As we pointed out, there are two regimes for a stochastic process: the white-noise regime, and the colored-noise regime. The problem is not analytically solvable in the second regime, except at the one end of the "noise spectrum" closest to the white-noise regime, i.e., in the weakly colored noise case. The problem is exactly solvable in the white-noise regime, and therefore this case is treated first.

A. Markovian case

This is the white-noise regime where all the ϵ's in (1.40) are made infinite, so that all the correlation functions are Dirac delta functions.

1. Isotropic stochastic properties

To start with the simplest case, we assume that all the correlation strengths are equal, i.e.,

$$Q_1 = Q_2 = Q_3 = Q . \tag{1.41}$$

We find that the population of the two states exhibit the following time behavior:

$$\tfrac{1}{2} \pm \tfrac{1}{2} e^{-\Gamma_0 t} . \tag{1.42}$$

The + sign corresponds to the state initially populated. This introduces the concept of "lifetime." Whatever state is initially populated, the relaxation drives the spin system towards an equilibrium where statistically the total probability is equally shared by the two states. Γ_0^{-1} can be referred to as the lifetime of the two coupled states. In the following paragraphs, it is shown that a stochastic coupling between the two states is absolutely necessary for a nonzero value of the relaxation parameter Γ_0. If the stochastic perturbation does not couple the two states, but only disturbs the energy levels by making these levels fluctuate about their natural positions, then the energies of the two eigenstates are only randomly modulated. The latter remain stationary in the usual quantum-mechanical sense.

As for the coherence between the two states, it exhibits the following time behavior:

$$\langle \rho_{12}(t) \rangle = \rho_{12}(0) e^{(i\omega_0 - \Gamma)t} . \tag{1.43}$$

In the isotropic stochastic properties, Markovian case, and only in this case, the two relaxation parameters Γ and Γ_0 are equal,

$$\Gamma_0 = \Gamma = 4Q . \tag{1.44}$$

It is worth noting that a simple phenomenological approach that assigns an imaginary energy to the upper, or excited, state because of the perturbation produces this form for the coherence. Γ would be the imaginary part of the energy, but Γ^{-1} would also be the lifetime of the excited state as usually conceived since the population of this state would be given by $e^{-2\Gamma t}$. As this simple approach would predict, we find also the line shape to be a simple unshifted Lorentzian,

$$I(\omega) = \frac{1}{\pi} \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} . \tag{1.45}$$

The conclusion that would then be drawn is that the inverse of the observed width of the line shape is the lifetime of the excited state. In fact, one should conclude from our approach that, in this particular case, the inverse of the observed width measures the lifetime of the states as defined by (1.42). Shortly, we shall see that this is the only instance where this identification is precise.

2. Nonisotropic stochastic properties

Now the Q's are assumed to be all different. The populations have the same time behavior as before,

$$\tfrac{1}{2} \pm \tfrac{1}{2} e^{-\Gamma_0 t} . \tag{1.46}$$

But the time behavior of the coherence is now found to be

$$\langle\rho_{12}(t)\rangle=\rho_{12}(0)\left[\cos(\Omega t)+i\frac{\omega_0}{\Omega}\sin(\Omega t)\right]e^{-\Gamma t}+\rho_{21}(0)\left[\frac{\Gamma_1-\Gamma_2}{2\Omega}\right]\sin(\Omega t)e^{-\Gamma t}, \quad (1.47)$$

where

$$\Gamma_i=2Q_i,\ \ i=1,2,3 \quad (1.48)$$

$$\Gamma=\tfrac{1}{2}(\Gamma_1+\Gamma_2)+\Gamma_3, \quad (1.49)$$

$$\Omega=\left[\omega_0^2-\left[\frac{\Gamma_1-\Gamma_2}{2}\right]^2\right]^{1/2}. \quad (1.50)$$

The coherence and its complex conjugate are coupled by the anisotropy between the two transverse directions. This anisotropy shifts the frequency at which the coherence oscillates from the natural frequency ω_0. As for the relaxation parameter Γ_0 in (1.46), it is given by

$$\Gamma_0=\Gamma_1+\Gamma_2. \quad (1.51)$$

This proves the claim that Γ_0 and Γ are different in general, and that a coupling between the two states is necessary for a finite lifetime. If the isotropy of the transverse space is assumed, i.e.,

$$Q_1=Q_2=Q\neq Q_3, \quad (1.52)$$

one recovers the time behavior of the coherence found previously,

$$\langle\rho_{12}(t)\rangle=\rho_{12}(0)e^{(i\omega_0-\Gamma)t}, \quad (1.53)$$

but the two relaxation parameters Γ_0 and Γ are still different,

$$\Gamma=2Q+2Q_3, \quad (1.54)$$

$$\Gamma_0=4Q. \quad (1.55)$$

Only the isotropy of the full space makes them equal. Note that if the off-diagonal part of the stochastic Hamiltonian is dropped altogether, the time behavior (1.53) for the coherence is preserved, and would induce an unshifted Lorentzian form for the line shape. The two states would remain stationary since Γ_0 would be equal to zero. It is the decay rate Γ of the coherence that sets the width of the line, and not the inverse of the lifetime Γ_0.

For the nonisotropic stochastic properties, Markovian case, we find the line shape to have the following form:

$$I(\omega)=\frac{1}{\pi}\left[1+\left[1-\frac{\omega}{\Omega}\right]\left[\frac{\Gamma_2-\Gamma_1}{2\Gamma}\right]\right]\frac{\Gamma}{(\omega-\Omega)^2+\Gamma^2}. \quad (1.56)$$

The decay rate Γ of the coherence measures the width of the line, but is different from the inverse of the lifetime Γ_0. The shifted frequency Ω at which the coherence oscillates defines the center of the line. The amount of anisotropy of the transverse space measures the asymmetry about the center of the line, as well as the amount of shift of this center from the natural frequency ω_0.

The connection between off-diagonal terms of the stochastic Hamiltonian and the shift and asymmetry of a line shape is manifest. In the Markovian case, the isotropy of the transverse stochastic properties annihilates both the shift and the asymmetry of the line, and reduces the latter to a simple unshifted Lorentzian.

We are reminded that the results above are exact (as is demonstrated in Secs. II and III) since the problem is exactly solvable in the white-noise regime. The line shape (1.56) is depicted in Fig. 1 and Fig. 2 for various values of the parameters.

B. Non-Markovian case

This is the colored-noise regime where all the ϵ's in (1.40) are finite. For arbitrary values of the ϵ's the solution to the problem is not analytically tractable. However, the problem can be solved in the weakly colored noise case. The ϵ's, although finite, are considered to be very large compared to the natural frequency ω_0. This is the end of the noise spectrum closest to the Markovian case. The results stated hereafter are expected to, and do, reduce to the previous ones as $\epsilon\rightarrow\infty$.

The populations of the states have the same time behavior as before,

$$\tfrac{1}{2}\pm\tfrac{1}{2}e^{-\Gamma_0 t}. \quad (1.57)$$

The coherence exhibits the following time behavior:

$$\langle\rho_{12}(t)\rangle=\rho_{12}(0)\left[\cos(\Omega t)+\frac{i}{\Omega}\left[\omega_0+\frac{\Delta_1+\Delta_2}{2}\right]\times\sin(\Omega t)\right]e^{-\Gamma t}+\rho_{21}(0)\frac{1}{2\Omega}[\Gamma_1-\Gamma_2+i(\Delta_1-\Delta_2)]\sin(\Omega t)e^{-\Gamma t}, \quad (1.58)$$

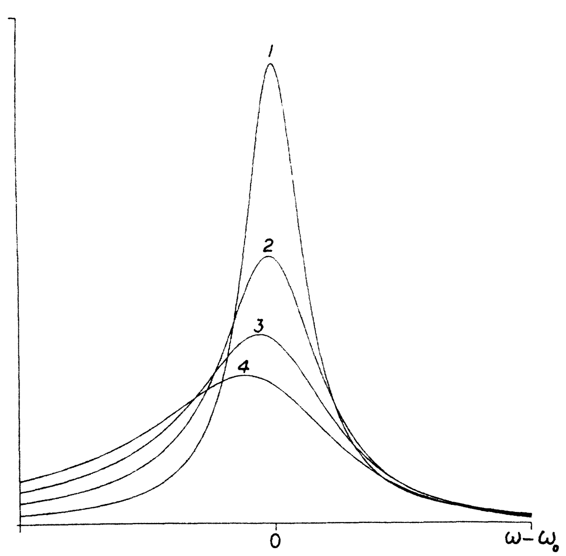

FIG. 1. $\Gamma_1/\omega_0=0.1$, (1) $\Gamma_2/\omega_0=0.1$, (2) $\Gamma_2/\omega_0=0.3$, (3) $\Gamma_2/\omega_0=0.5$, (4) $\Gamma_2/\omega_0=0.7$.

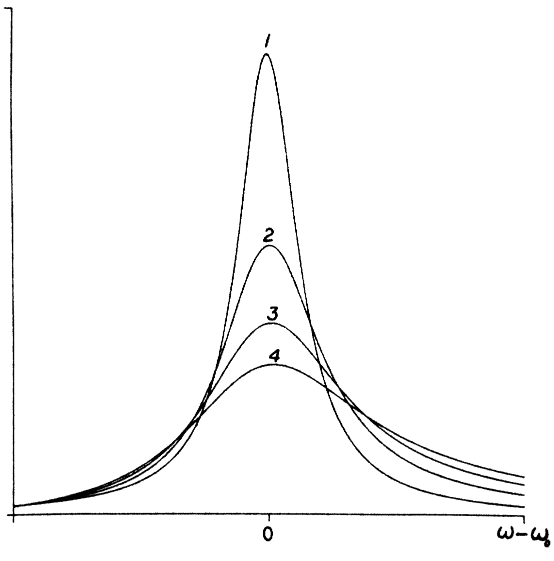

FIG. 2. $\Gamma_2/\omega_0=0.1$, (1) $\Gamma_1/\omega_0=0.1$, (2) $\Gamma_1/\omega_0=0.3$, (3) $\Gamma_1/\omega_0=0.5$, (4) $\Gamma_1/\omega_0=0.7$.

where

$$\Gamma_i=2Q_i(1+\omega_0^2/\epsilon_i^2)^{-1},\quad i=1,2 \tag{1.59}$$

$$\Gamma_3=2Q_3 \ , \tag{1.60}$$

$$\Delta_i=2Q_i(\omega_0/\epsilon_i)(1+\omega_0^2/\epsilon_i^2)^{-1},\quad i=1,2 \tag{1.61}$$

and

$$\Gamma_0=\Gamma_1+\Gamma_2 \ , \tag{1.62}$$

$$\Gamma=\frac{1}{2}(\Gamma_1+\Gamma_2)+\Gamma_3 \ , \tag{1.63}$$

$$\Omega=\left[\omega_0^2+\omega_0(\Delta_1+\Delta_2)+\Delta_1\Delta_2-\left[\frac{\Gamma_1-\Gamma_2}{2}\right]^2\right]^{1/2} . \tag{1.64}$$

The difference between the two relaxation parameters Γ and Γ_0 is again clear; but now, not even the isotropy of the entire space, i.e.,

$$Q_1=Q_2=Q_3=Q \ , \tag{1.65a}$$

$$\epsilon_1=\epsilon_2=\epsilon_3=\epsilon \tag{1.65b}$$

can reduce them to the same value since they would then be given by

$$\Gamma=2Q(1+\omega_0^2/\epsilon^2)^{-1}+2Q \ , \tag{1.66}$$

$$\Gamma_0=4Q(1+\omega_0^2/\epsilon^2)^{-1} \ . \tag{1.67}$$

This is a consequence of the fact that the widths ϵ_1 and ϵ_2 of the transverse correlation functions have a bearing on the relaxation, and the width ϵ_3 of the longitudinal correlation function does not.

The coherence and its complex conjugate are again coupled by the anisotropy between the two transverse directions. As in the Markovian case, this anisotropy shifts the frequency at which the coherence oscillates from the natural frequency ω_0. But here, there is a further shift induced purely by the colored noise, and which is not annihilated by the isotropy of the transverse space. Indeed, when

$$Q_1=Q_2=Q \ , \tag{1.68a}$$

$$\epsilon_1=\epsilon_2=\epsilon \ , \tag{1.68b}$$

the coherence given by (1.58) reduces to

$$\langle\rho_{12}(t)\rangle=\rho_{12}(0)e^{i(\omega_0+\Delta)t}e^{-\Gamma t} \ , \tag{1.69}$$

where

$$\Gamma=2Q(1+\omega_0^2/\epsilon^2)^{-1}+2Q_3 \ , \tag{1.70}$$

$$\Delta=2Q(\omega_0/\epsilon)(1+\omega_0^2/\epsilon^2)^{-1} \ . \tag{1.71}$$

This leads to a line shape with a shifted Lorentzian form

$$I(\omega)=\frac{1}{\pi}\frac{\Gamma}{(\omega-\omega_0-\Delta)^2+\Gamma^2} \ . \tag{1.72}$$

If the noise is tuned closer and closer to the Markovian regime, the expression (1.71) shows that Δ tends to zero, as expected.

For the nonisotropic stochastic properties, non-Markovian case with a weakly colored noise, the line shape has the following form:

$$I(\omega)=\frac{1}{\pi}\left[1+\left[1-\frac{\omega}{\Omega}\right]\left[\frac{\Gamma_2-\Gamma_1}{2\Gamma}\right]\right]\frac{\Gamma}{(\omega-\Omega)^2+\Gamma^2} \ , \tag{1.73}$$

where the various parameters are defined by (1.59)–(1.64). Again, it is the decay rate Γ and the frequency Ω of the coherence that define the width and the center of the line, respectively. The shift of this center from the natural frequency ω_0 has two sources: the colored noise, and the anisotropy of the transverse space, which also induces the asymmetry about the center of the line.

If the off-diagonal part of the stochastic Hamiltonian is dropped altogether, simply by setting

$$Q_1=Q_2=0 \ , \tag{1.74}$$

the expression (1.73) reduces to a simple unshifted Lorentzian with a width given by

$$\Gamma=2Q_3 \ . \tag{1.75}$$

This agrees with Kubo's result we mentioned earlier [see Eq. (A21) in the Appendix]. Let us stress once again that (1.74) implies

$$\Gamma_0=0 \ . \tag{1.76}$$

The eigenstates remain stationary because the stochastic perturbation does not couple them. The width of the line, Γ, measures nothing but the decay rate of the coherence between the two states.

In conclusion, the connection between off-diagonal terms of the stochastic perturbation and the shift and asymmetry of a line shape is also manifest in this case. But here, the isotropy of the transverse stochastic properties only annihilates the asymmetry of the line, and reduces the latter to a simple, shifted, Lorentzian. The source of the shift that persists is the colored-noise correlation lifetime, and the observed energy shift is a measure of the non-Markovianness of the process.

The statement of these results concludes our introduction and the next sections contain many of the details required to justify these results.

II. MAGNETIC RELAXATION

In this section the spin system in the constant magnetic field is made to interact with the stochastic magnetic field, and the effects the latter has on the time behavior of the spin are derived. The total Hamiltonian is

$$H(t)=H_0+\widetilde{H}(t)\ , \tag{2.1}$$

where

$$H_0=\hbar\frac{\omega_0}{2}\sigma_3\ , \tag{2.2}$$

$$\widetilde{H}(t)=\sum_{i=1}^{3}\hbar\widetilde{\phi}_i(t)\sigma_i\ , \tag{2.3}$$

ω_0 and $\widetilde{\phi}_i(t)$ are defined by (1.36) and (1.37), respectively. The stochastic properties are

$$\langle\widetilde{\phi}_i(t)\rangle=0\ , \tag{2.4}$$

$$\langle\widetilde{\phi}_i(t)\widetilde{\phi}_j(s)\rangle=Q_i\delta_{ij}(\epsilon_i/2)\exp(-\epsilon_i\,|\,t-s\,|\,)\ . \tag{2.5}$$

The $\widetilde{\phi}$'s are real functions with the dimension of a frequency, $\widetilde{H}(t)$ is manifestly Hermitian, and the Q's and ϵ's are real positive constants with the dimension of a frequency.

The time evolution of the system is governed by the following quantum Liouville equation:

$$i\hbar\frac{\partial}{\partial t}\rho(t)=[L_0+\widetilde{L}(t)]\rho(t)\ , \tag{2.6}$$

where

$$L_0\equiv[H_0,\cdot]\ , \tag{2.7}$$

$$\widetilde{L}(t)\equiv[\widetilde{H}(t),\cdot]\ . \tag{2.8}$$

The tetradic elements of a commutator operator, or superoperator, of the form

$$[O,\cdot]=O\cdot-\cdot O\ , \tag{2.9}$$

where O is an operator, are

$$[O,\cdot]_{ijkl}=O_{ik}\delta_{lj}-\delta_{ik}O_{lj}\ . \tag{2.10}$$

A. Averaged density matrix and relaxation tetradic

From (2.6) it follows that

$$\rho(t)=\exp\left[-\frac{i}{\hbar}tL_0\right]\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,\widetilde{L}_I(s)\right]\rho(0)\ , \tag{2.11}$$

where

$$\widetilde{L}_I(t)\equiv\exp\left[\frac{i}{\hbar}tL_0\right]\widetilde{L}(t)\exp\left[-\frac{i}{\hbar}tL_0\right] \tag{2.12}$$

is the stochastic Liouville operator in the interaction representation. The averaging of the time-ordered exponential in (2.11) is handled with the cumulant method,[12]

$$\left\langle\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,\widetilde{L}_I(s)\right]\right\rangle=\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\sum_{m=1}^{\infty}\int_0^t ds\,C^{(m)}(s)\right]\ , \tag{2.13}$$

where $C^{(m)}(t)$ is the mth cumulant. For a Markovian process, all cumulants beyond the second vanish identically.[12] For a weakly non-Markovian process, the series of cumulants may be truncated at the second one since the magnitude of higher cumulants is generally much smaller than that of the second cumulants. The first two cumulants are given by

$$C^{(1)}(t)=\langle\widetilde{L}_I(t)\rangle\ , \tag{2.14}$$

$$C^{(2)}(t)=-\frac{i}{\hbar}\int_0^t ds[\langle\widetilde{L}_I(t)\widetilde{L}_I(s)\rangle-\langle\widetilde{L}_I(t)\rangle\langle\widetilde{L}_I(s)\rangle]\ . \tag{2.15}$$

The stochastic property (2.4), with the help of (2.8) and (2.12), implies that the first cumulant vanishes. Therefore, the expression for the averaged density matrix $\langle\rho(t)\rangle$ is

$$\langle\rho(t)\rangle=\exp\left[-\frac{i}{\hbar}tL_0\right]\times\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,C^{(2)}(s)\right]\rho(0)\ , \tag{2.16}$$

which implies

$$\frac{\partial}{\partial t}\langle\rho(t)\rangle=-\frac{i}{\hbar}[L_0+R(t)]\langle\rho(t)\rangle \tag{2.17}$$

or

$$\langle\rho(t)\rangle=G(t,0)\rho(0)\ , \tag{2.18}$$

where G, the super Green's function that governs the time behavior of the averaged density matrix, is given by

$$G(t,s)=\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_s^t d\tau[L_0+R(\tau)]\right]\ , \tag{2.19}$$

where $R(t)$ is the relaxation tetradic, defined by

$$R(t)=-\frac{i}{\hbar}\int_0^t ds\left\langle\widetilde{L}(t)\exp\left[-\frac{i}{\hbar}(t-s)L_0\right]\times\widetilde{L}(s)\exp\left[\frac{i}{\hbar}(t-s)L_0\right]\right\rangle\ . \tag{2.20}$$

This general expression for the relaxation tetradic takes on the following form in this problem:

$$R(t)=\sum_{i=1}^{3} R_i(t)\ , \tag{2.21}$$

where

$$R_i(t)\equiv -i\hbar Q_i \int_0^t ds \frac{\epsilon_i}{2} e^{-\epsilon_i(t-s)}[\sigma_i,\cdot] \times \exp\left[-\frac{i}{\hbar}(t-s)L_0\right][\sigma_i,\cdot] \times \exp\left[\frac{i}{\hbar}(t-s)L_0\right] . \tag{2.22}$$

Furthermore, since $\langle \rho(t)\rangle$ is a 2×2 matrix, it can be expanded in terms of Pauli matrices,

$$\langle \rho(t)\rangle = \tfrac{1}{2}\sigma_0 + \sum_{i=1}^{3} M_i(t)\sigma_i\ . \tag{2.23}$$

The coefficients of the expansion are given by

$$M_i(t)=\tfrac{1}{2}\,\mathrm{Tr}[\sigma_i\langle \rho(t)\rangle]\ . \tag{2.24}$$

They obey the following system of coupled differential equations

$$\frac{d}{dt}M_i(t)=-\frac{i}{2\hbar}\sum_{j=1}^{3}\mathrm{Tr}\{\sigma_i[L_0+R(t)]\sigma_j\}M_j(t)\ . \tag{2.25}$$

From (2.23) one can read what the averaged density matrix elements are, for populations,

$$P_1(t)=\langle \rho_{11}(t)\rangle=\tfrac{1}{2}-M_3(t)\ , \tag{2.26a}$$

$$P_2(t)=\langle \rho_{22}(t)\rangle=\tfrac{1}{2}+M_3(t)\ , \tag{2.26b}$$

1 and 2 denote the lower and upper states, respectively, and for the coherence,

$$C_{12}(t)=\langle \rho_{12}(t)\rangle = M_1(t)+iM_2(t)=C_{21}^*(t)\ . \tag{2.27}$$

Finally, since the super Green's function G is a tetradic, (2.18) is to be read as

$$\langle \rho_{ij}(t)\rangle=\sum_{k,l} G_{ijkl}(t,0)\rho_{kl}(0)\ . \tag{2.28}$$

In the cases studied hereafter, (2.22) is used to compute the relaxation tetradic, which, when put into (2.25), allows one to compute the coefficients of the averaged density-matrix expansion. These coefficients are used in (2.26) and (2.27) to derive the time behavior of the density matrix elements. Finally, (2.28) is used to find the expression of nonvanishing tetradic elements of G in each case.

B. Markovian case

All the correlation functions are taken to be Dirac delta functions, i.e., all the ϵ's are considered infinite since

$$\lim_{\epsilon\to\infty}[(\epsilon/2)\exp(-\epsilon\,|\,t-s\,|\,)]=\delta(t-s)\ . \tag{2.29}$$

Then, the relaxation tetradic, defined by (2.21), is independent of time

$$R=-i\hbar\sum_{i=1}^{3} Q_i(\cdot-\sigma_i\cdot\sigma_i)\ . \tag{2.30}$$

1. Isotropic stochastic properties

The simplest case comes about by considering all the autocorrelation strengths equal, then

$$R=-i\hbar Q\sum_{i=1}^{3}(\cdot-\sigma_i\cdot\sigma_i) \tag{2.31}$$

and (2.25) gives

$$\frac{d}{dt}M_1(t)=-\omega_0 M_2(t)-\Gamma M_1(t)\ , \tag{2.32a}$$

$$\frac{d}{dt}M_2(t)=\omega_0 M_1(t)-\Gamma M_2(t)\ , \tag{2.32b}$$

$$\frac{d}{dt}M_3(t)=-\Gamma_0 M_3(t)\ , \tag{2.32c}$$

where

$$\Gamma_0=\Gamma=4Q\ . \tag{2.33}$$

The averaged density matrix elements are found to be given by

$$P_1(t)=\langle \rho_{11}(t)\rangle = \tfrac{1}{2}[P_1(0)+P_2(0)]+\tfrac{1}{2}[P_1(0)-P_2(0)]e^{-\Gamma_0 t}\ , \tag{2.34a}$$

$$P_2(t)=\langle \rho_{22}(t)\rangle = \tfrac{1}{2}[P_1(0)+P_2(0)]-\tfrac{1}{2}[P_1(0)-P_2(0)]e^{-\Gamma_0 t}\ , \tag{2.34b}$$

$$C_{12}(t)=\langle \rho_{12}(t)\rangle=\rho_{12}(0)e^{(i\omega_0-\Gamma)t}\ . \tag{2.34c}$$

From these expressions and (2.28), we find that the nonvanishing tetradic elements of G are

$$G_{1111}(t,s)=G_{2222}(t,s)=\tfrac{1}{2}+\tfrac{1}{2}e^{-\Gamma_0(t-s)}\ , \tag{2.35a}$$

$$G_{1122}(t,s)=G_{2211}(t,s)=\tfrac{1}{2}-\tfrac{1}{2}e^{-\Gamma_0(t-s)}\ , \tag{2.35b}$$

$$G_{1212}(t,s)=G_{2121}^*(t,s)=e^{(i\omega_0-\Gamma)(t-s)}\ . \tag{2.35c}$$

2. Nonisotropic stochastic properties

If the autocorrelation strengths are all different, the relaxation tetradic R, given by (2.30), is to be used in (2.25) which then gives

$$\frac{d}{dt}M_1(t)=-\omega_0 M_2(t)-(\Gamma_2+\Gamma_3)M_1(t)\ , \tag{2.36a}$$

$$\frac{d}{dt}M_2(t)=\omega_0 M_1(t)-(\Gamma_1+\Gamma_3)M_2(t)\ , \tag{2.36b}$$

$$\frac{d}{dt}M_3(t)=-(\Gamma_1+\Gamma_2)M_3(t)\ , \tag{2.36c}$$

where

$$\Gamma_i=2Q_i,\quad i=1,2,3 \tag{2.37}$$

with the following definitions:

$$\Gamma_0=\Gamma_1+\Gamma_2\ , \tag{2.38}$$

$$\Gamma=\tfrac{1}{2}(\Gamma_1+\Gamma_2)+\Gamma_3\ , \tag{2.39}$$

$$\Omega=\left[\omega_0^2-\left[\frac{\Gamma_1-\Gamma_2}{2}\right]^2\right]^{1/2} . \tag{2.40}$$

The populations of, and the coherence between, the two states then exhibit the following time behavior:

$$P_1(t)=\langle\rho_{11}(t)\rangle =\tfrac{1}{2}[P_1(0)+P_2(0)] +\tfrac{1}{2}[P_1(0)-P_2(0)]e^{-\Gamma_0 t}\ , \tag{2.41a}$$

$$P_2(t)=\langle\rho_{22}(t)\rangle =\tfrac{1}{2}[P_1(0)+P_2(0)] -\tfrac{1}{2}[P_1(0)-P_2(0)]e^{-\Gamma_0 t}\ , \tag{2.41b}$$

$$C_{12}(t)=\langle\rho_{12}(t)\rangle =\rho_{12}(0)\left[\cos(\Omega t)+i\frac{\omega_0}{\Omega}\sin(\Omega t)\right]e^{-\Gamma t} +\rho_{21}(0)\left[\frac{\Gamma_1-\Gamma_2}{2\Omega}\right]\sin(\Omega t)e^{-\Gamma t}\ . \tag{2.41c}$$

With the help of (2.28) and these expressions, one finds that in this case the nonvanishing tetradic elements of G are

$$G_{1111}(t,s)=G_{2222}(t,s)=\tfrac{1}{2}+\tfrac{1}{2}e^{-\Gamma_0(t-s)}\ , \tag{2.42a}$$

$$G_{1122}(t,s)=G_{2211}(t,s)=\tfrac{1}{2}-\tfrac{1}{2}e^{-\Gamma_0(t-s)}\ , \tag{2.42b}$$

$$G_{1212}(t,s)=G^*_{2121}(t,s) =\left[\cos[\Omega(t-s)]+i\frac{\omega_0}{\Omega}\sin[\Omega(t-s)]\right]e^{-\Gamma(t-s)}\ , \tag{2.42c}$$

$$G_{1221}(t,s)=G^*_{2112}(t,s) =\frac{1}{2\Omega}(\Gamma_1-\Gamma_2)\sin[\Omega(t-s)]e^{-\Gamma(t-s)}\ . \tag{2.42d}$$

C. Non-Markovian case

Now the correlation functions have a finite width. The relaxation tetradic is defined by (2.21)

$$R(t)=\sum_{i=1}^{3}R_i(t)\ , \tag{2.43}$$

where $R_i(t)$, for $i=1$ or 2, is given by

$$\begin{aligned}R_i(t)=&\frac{\hbar}{2}\left[\frac{\Delta_i}{2}\right][\sigma_3,\cdot]+i\frac{\hbar}{2}\left[\frac{\Delta_i}{2}\right]\alpha_i(\sigma_1\cdot\sigma_2+\sigma_2\cdot\sigma_1)\\ &-i\frac{\hbar}{2}\Gamma_i(\cdot-\sigma_i\cdot\sigma_i)\left[1-\left[\cos(\omega_0 t)-\frac{\omega_0}{\epsilon_i}\sin(\omega_0 t)\right]e^{-\epsilon_i t}\right]\\ &+i\frac{\hbar}{2}\left[\frac{\Gamma_i}{2}\right]\{i[\sigma_3,\cdot]-\alpha_i(\sigma_1\cdot\sigma_2+\sigma_2\cdot\sigma_1)\}\left[\sin(\omega_0 t)+\frac{\omega_0}{\epsilon_i}\cos(\omega_0 t)\right]e^{-\epsilon_i t}\ ,\end{aligned} \tag{2.44}$$

with

$\alpha_1=1$ and $\alpha_2=-1$.

$R_3(t)$ is given by

$$R_3(t)=-i\frac{\hbar}{2}\Gamma_3(\cdot-\sigma_3\cdot\sigma_3)(1-e^{-\epsilon_3 t})\ . \tag{2.45}$$

The various constants are defined by

$$\Gamma_i=2Q_i(1+\omega_0^2/\epsilon_i^2)^{-1},\ \text{for } i=1,2 \tag{2.46}$$

$$\Delta_i=2Q_i(\omega_0/\epsilon_i)(1+\omega_0^2/\epsilon_i^2)^{-1},\ \text{for } i=1,2 \tag{2.47}$$

$$\Gamma_3=2Q_3\ . \tag{2.48}$$

For weakly non-Markovian noise, we consider the ϵ's, although finite, to be very large compared to ω_0, and therefore, we can neglect the time-dependent terms in the relaxation tetradic. Then,

$$R=\frac{\hbar}{2}\left[\frac{\Delta_1+\Delta_2}{2}\right][\sigma_3,\cdot] +i\frac{\hbar}{2}\left[\frac{\Delta_1-\Delta_2}{2}\right](\sigma_1\cdot\sigma_2+\sigma_2\cdot\sigma_1) -i\frac{\hbar}{2}\sum_{i=1}^{3}\Gamma_i(\cdot-\sigma_i\cdot\sigma_i)\ . \tag{2.49}$$

The system (2.25) then takes on the following form:

$$\frac{d}{dt}M_1(t)=-(\omega_0+\Delta_2)M_2(t)-(\Gamma_2+\Gamma_3)M_1(t)\ , \tag{2.50a}$$

$$\frac{d}{dt}M_2(t)=(\omega_0+\Delta_1)M_1(t)-(\Gamma_1+\Gamma_3)M_2(t)\ , \tag{2.50b}$$

$$\frac{d}{dt}M_3(t)=-(\Gamma_1+\Gamma_2)M_3(t)\ , \tag{2.50c}$$

with the following definitions:

$$\Gamma_0=\Gamma_1+\Gamma_2\ , \tag{2.51}$$

$$\Gamma=\frac{1}{2}(\Gamma_1+\Gamma_2)+\Gamma_3\ , \tag{2.52}$$

$$\Omega=\left[\omega_0^2+\omega_0(\Delta_1+\Delta_2)+\Delta_1\Delta_2-\left[\frac{\Gamma_1-\Gamma_2}{2}\right]^2\right]^{1/2} . \tag{2.53}$$

The populations and the coherence are given by

$$P_1(t)=\langle\rho_{11}(t)\rangle=\tfrac{1}{2}[P_1(0)+P_2(0)]+\tfrac{1}{2}[P_1(0)-P_2(0)]e^{-\Gamma_0 t}\ , \tag{2.54a}$$

$$P_2(t)=\langle\rho_{22}(t)\rangle=\tfrac{1}{2}[P_1(0)+P_2(0)]-\tfrac{1}{2}[P_1(0)-P_2(0)]e^{-\Gamma_0 t}\ , \tag{2.54b}$$

$$C_2(t)=\langle\rho_{12}(t)\rangle=\rho_{12}(0)\left[\cos(\Omega t)+\frac{i}{\Omega}\left[\omega_0+\frac{\Delta_1+\Delta_2}{2}\right]\sin(\Omega t)\right]e^{-\Gamma t}\ ,$$
$$+\rho_{21}(0)\frac{1}{2\Omega}[\Gamma_1-\Gamma_2+i(\Delta_1-\Delta_2)]\sin(\Omega t)e^{-\Gamma t}\ . \tag{2.54c}$$

And finally, the nonvanishing tetradic elements of G are deduced from these expressions with the help of (2.28),

$$G_{1111}(t,s)=G_{2222}(t,s)=\tfrac{1}{2}+\tfrac{1}{2}e^{-\Gamma_0(t-s)}\ , \tag{2.55a}$$

$$G_{1122}(t,s)=G_{2211}(t,s)=\tfrac{1}{2}-\tfrac{1}{2}e^{-\Gamma_0(t-s)}\ , \tag{2.55b}$$

$$G_{1212}(t,s)=G^*_{2121}(t,s)$$
$$=\Bigg[\cos[\Omega(t-s)]+\frac{i}{\Omega}\left[\omega_0+\frac{\Delta_1+\Delta_2}{2}\right]\times\sin[\Omega(t-s)]\Bigg]e^{-\Gamma(t-s)}\ , \tag{2.55c}$$

$$G_{1221}(t,s)=G^*_{2112}(t,s)$$
$$=\frac{1}{2\Omega}[\Gamma_1-\Gamma_2+i(\Delta_1-\Delta_2)]\times\sin[\Omega(t-s)]e^{-\Gamma(t-s)}\ . \tag{2.55d}$$

When the ϵ's are made infinite, these expressions tend to their counterparts in Sec. II B 2 of the Markovian case as expected. Equation (2.47) shows that Δ_i is of order $Q(\omega_0/\epsilon)$, and vanishes in the limit $\epsilon\to\infty$. In the fully Markovian limit, there are no Δ_i energy shifts.

III. LINE SHAPES

Having shown how the relaxation enters into the time behavior of the spin system, we now make the latter interact with a radiation field to see the effects of this relaxation on the spectral line shapes.

A. Second-order partial averaged density matrix

The total Hamiltonian is now given by

$$H(t)=H_0+\tilde{H}(t)+V(t)\ , \tag{3.1}$$

where

$$H_0=\hbar\frac{\omega_0}{2}\sigma_3\ , \tag{3.2}$$

$$\tilde{H}(t)=\sum_{i=1}^{3}\hbar\tilde{\phi}_i(t)\sigma_i\ , \tag{3.3}$$

$$V(t)=i\hbar\gamma(ae^{-i\omega t}-a^{\dagger}e^{i\omega t})\sigma_2\ . \tag{3.4}$$

ω_0, $\tilde{\phi}_i(t)$, and γ are defined by (1.36), (1.37), and (1.38), respectively. The stochastic properties of $\tilde{H}(t)$ are given by (1.39) and (1.40).

The Liouville equation for the density matrix $\rho(t)$ is now

$$i\hbar\frac{\partial}{\partial t}\rho(t)=[L_0+\tilde{L}(t)+L_v(t)]\rho(t)\ , \tag{3.5}$$

where

$$L_0\equiv[H_0,\cdot]\ , \tag{3.6}$$

$$\tilde{L}(t)=[\tilde{H}(t),\cdot]\ , \tag{3.7}$$

$$L_v(t)\equiv[V(t),\cdot]\ . \tag{3.8}$$

Let us define

$$U(t,s)\equiv \underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_s^t d\tau[L_0+L_v(\tau)]\right]\ , \tag{3.9a}$$

$$U^{\dagger}(t,s)=\underset{\rightarrow}{T}\exp\left[\frac{i}{\hbar}\int_s^t d\tau[L_0+L_v(\tau)]\right]\ . \tag{3.9b}$$

From (3.5) it follows that

$$\rho(t)=U(t,0)\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,\tilde{L}_I(s)\right]\rho(0)\ , \tag{3.10}$$

where

$$\tilde{L}_I(t)=U^{\dagger}(t,0)\tilde{L}(t)U(t,0) \tag{3.11}$$

is the stochastic Liouvillian in the interaction representation. The averaging of the time-ordered exponential in

(3.10) is again handled by the cumulant method, and is identical in form to the one that had to be performed in Sec. II [see (2.13)]. Therefore, the averaged density matrix is now found to obey the following differential equation:

$$\frac{\partial}{\partial t}\langle\rho(t)\rangle=-\frac{i}{\hbar}[L_0+R(t)+L_v(t)]\langle\rho(t)\rangle\ , \tag{3.12}$$

where the relaxation tetradic $R(t)$ is defined by

$$R(t)\equiv-\frac{i}{\hbar}\int_0^t ds\langle\widetilde{L}(t)U(t,s)\widetilde{L}(s)U^{\dagger}(t,s)\rangle\ . \tag{3.13}$$

The expression (3.13) can be rewritten

$$R(t)=\sum_{i=1}^{3}R_i(t)\ , \tag{3.14}$$

where

$$R_i(t)\equiv-i\hbar Q_i\int_0^t ds\left[\frac{\epsilon_i}{2}\right]e^{-\epsilon_i(t-s)}\times[\sigma_i,\cdot]U(t,s)[\sigma_i,\cdot]U^{\dagger}(t,s)\ . \tag{3.15}$$

In the case of white noise, the ϵ's are infinite, and therefore the correlation functions are Dirac delta functions. (3.15) then gives very simply

$$R=-i\hbar\sum_{i=1}^{3}Q_i(\cdot-\sigma_i\cdot\sigma_i)\ . \tag{3.16}$$

The presence of the unit superoperator in the photon space is implicit, and therefore, this relaxation tetradic is simply the extension to the full Hilbert space of the relaxation tetradic in the absence of the radiation field given by (2.30). We recall that in the Markovian case, the truncation of the series of cumulants is exact, and therefore, the expression (3.16) and the results derived hereafter for this case are exact.

By comparing (3.14) to (2.21), we see that in the non-Markovian case the relaxation tetradic in this problem is not a simple extension to the full Hilbert space of the relaxation tetradic in the absence of the radiation field. However, we can write the superoperator $U(t,s)$, given by (3.9), as follows:

$$U(t,s)=\exp\left[-\frac{i}{\hbar}(t-s)L_0\right]-\frac{i}{\hbar}\int_s^t d\tau\exp\left[-\frac{i}{\hbar}(t-\tau)L_0\right]L_v(t)\times\exp\left[-\frac{i}{\hbar}(\tau-s)L_0\right]+\cdots\ . \tag{3.17}$$

This expression can be used to write $R(t)$ as a series in the Liouvillian operator $L_v(t)$. All terms of the series involving the latter represent the feedback influence of the radiation field on the relaxation induced by the stochastic magnetic field. The effect of these terms on the spectral line shape is expected, and found, to be small compared to the effect of the one term of zeroth order in $L_v(t)$, which represent the "direct" relaxation of the spin system. We shall therefore approximate the expression (3.14) by

$$R(t)=\sum_{i=1}^{3}R_i(t)\ , \tag{3.18}$$

where

$$R_i(t)=-i\hbar Q_i\int_0^t ds\frac{\epsilon_i}{2}e^{-\epsilon_i(t-s)}[\sigma_i,\cdot]\times\exp\left[-\frac{i}{\hbar}(t-s)L_0\right][\sigma_i,\cdot]\times\exp\left[\frac{i}{\hbar}(t-s)L_0\right]\ , \tag{3.19}$$

which is the extension to the full Hilbert space of the relaxation tetradic given by (2.21).

Thus the formal solution of the differential equation (3.12) is

$$\langle\rho(t)\rangle=\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds[L_0+R(s)+L_v(s)]\right]\rho(0)\ , \tag{3.20}$$

where $R(t)$ is the extension to the full Hilbert space of the relaxation tetradic in the absence of the radiation field. This holds for both the Markovian and non-Markovian cases.

Using now the "interaction picture" with respect to $V(t)$, $\langle\rho(t)\rangle$ can be rewritten as follows:

$$\langle\rho(t)\rangle=\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds[L_0+R(s)]\right]\times\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,\hat{L}_v(s)\right]\rho(0)\ , \tag{3.21}$$

where

$$\hat{L}_v(t)\equiv\underset{\rightarrow}{T}\exp\left[\frac{i}{\hbar}\int_0^t ds[L_0+R(s)]\right]L_v(t)\times\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds[L_0+R(s)]\right]\ . \tag{3.22}$$

By expanding the second time-ordered exponential on the right-hand side of (3.21), one can write

$$\langle\rho(t)\rangle=\sum_{n=0}^{\infty}\langle\rho^{(n)}(t)\rangle\ , \tag{3.23}$$

where

$$\langle \rho^{(0)}(t) \rangle = G(t,0)\rho(0) , \quad (3.24)$$

$$\langle \rho^{(n)}(t) \rangle = \left[-\frac{i}{\hbar} \right]^n \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n\, G(t,s_1)L_v(s_1)G(s_1,s_2) \cdots G(s_{n-1},s_n)L_v(s_n)G(s_n,0)\rho(0) . \quad (3.25)$$

We refer to $\langle \rho^{(n)}(t) \rangle$ as the partial averaged density matrix of order n. G is precisely the super Green's function which governs the time behavior of the spin system in the absence of the radiation field,

$$G(t,s) = \underset{\leftarrow}{T} \exp \left[-\frac{i}{\hbar} \int_s^t d\tau [L_0 + R(\tau)] \right] . \quad (3.26)$$

The series (3.23) is the generalization in form of the usual expansion of the density matrix of a nonperturbed system interacting with a radiation field, where the super Green's function would simply be

$$G(t,s) = \exp \left[-\frac{i}{\hbar}(t-s)L_0 \right] . \quad (3.27)$$

In the applications to photon processes, the physical observables are obtained from the density matrix using even orders of the interaction $V(t)$. Therefore, the relevant partial averaged density matrix for a single-photon process is the one of second order,

$$\langle \rho^{(2)}(t) \rangle = -\frac{1}{\hbar^2} \int_0^t ds_1 \int_0^{s_1} ds_2\, G(t,s_1)L_v(s_1) \times G(s_1,s_2)L_v(s_2) \times G(s_2,0)\rho(0) . \quad (3.28)$$

The averaged probability of transition in a single-photon absorption process is then

$$\langle P(t) \rangle = \langle \bar{n}-1 | \, \langle 2 | \, \langle \rho^{(2)}(t) \rangle \, | 2 \rangle \, | \bar{n}-1 \rangle \quad (3.29)$$

and the initial density matrix is

$$\rho(0) = | 1 \rangle \langle 1 | \otimes | \bar{n} \rangle \langle \bar{n} | , \quad (3.30)$$

where $\bar{n}$ is the number of photons, and $|1\rangle$ represents the ground state of the two level system. It was established in Sec. II that the tetradic elements of G have the following properties:

$$G_{iijk} = G_{iijj}\delta_{jk} , \quad (3.31a)$$

$$G_{ikjj} = G_{iijj}\delta_{ik} , \quad (3.31b)$$

$$G^*_{iijj} = G_{iijj} , \quad (3.31c)$$

$$G_{ijkl} = G_{ijkl}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \text{ for } i \neq j \text{ or } k \neq l , \quad (3.31d)$$

$$G_{ijij} = G^*_{jiji} , \quad (3.31e)$$

$$G_{ijji} = G^*_{jiij} , \quad (3.31f)$$

Using the expression (3.28) for the second-order partial averaged density matrix and the properties (3.31a), (3.31b), and (3.31d), the explicit form of the averaged probability of transition $\langle P(t) \rangle$ is

$$\langle P(t) \rangle = -\frac{1}{\hbar^2} \sum_{\substack{i,k,l,\\ m,n,p}} \int_0^t ds_1 \int_0^{s_1} ds_2 \langle \bar{n}-1 | [G_{22ii}(t,s_1)L_{viikl}(s_1)G_{klmn}(s_1,s_2)L_{vmnpp}(s_2)G_{pp11}(s_2,0) | \bar{n} \rangle \langle \bar{n} |] | \bar{n}-1 \rangle ,$$

$$\langle P(t) \rangle = -\frac{1}{\hbar^2} \sum_{\substack{i,k,l,\\ m,n,p}} \int_0^t ds_1 \int_0^{s_1} ds_2 G_{22ii}(t,s_1)G_{klmn}(s_1,s_2)G_{pp11}(s_2,0) \times \langle \bar{n}-1 | [L_{viikl}(s_1)L_{vmnpp}(s_2) | \bar{n} \rangle \langle \bar{n} |] | \bar{n}-1 \rangle . \quad (3.32)$$

Using the identity

$$L_{vijkl}(t) = [V(t), \cdot]_{ijkl} = V_{ik}(t)\delta_{jl} \cdot - \cdot \delta_{ki} V_{lj}(t) \quad (3.33)$$

one finds

$$\langle \bar{n}-1 | [L_{viikl}(s_1)L_{vmnpp}(s_2) | \bar{n} \rangle \langle \bar{n} |] | \bar{n}-1 \rangle = -\bar{n}\hbar^2\gamma^2(\sigma_2)_{lk}(\sigma_2)_{mn}(\delta_{il}\delta_{mp}e^{-i\omega(s_1-s_2)} + \delta_{np}\delta_{ki}e^{i\omega(s_1-s_2)}) . \quad (3.34)$$

Since σ_2 is purely nondiagonal, (3.32) can be written as follows:

$$\langle P(t)\rangle=\bar{n}\gamma^2\sum_{\substack{k,l\\k\neq l}}\sum_{\substack{m,n\\m\neq n}}(\sigma_2)_{lk}(\sigma_2)_{mn}\int_0^t ds_1\int_0^{s_1}ds_2\, G_{22ll}(t,s_1)e^{-i\omega s_1}G_{klmn}(s_1,s_2)e^{i\omega s_2}G_{mm11}(s_2,0)$$
$$+\bar{n}\gamma^2\sum_{\substack{k,l\\k\neq l}}\sum_{\substack{m,n\\m\neq n}}(\sigma_2)_{lk}(\sigma_2)_{mn}\int_0^t ds_1\int_0^{s_1}ds_2\, G_{22kk}(t,s_1)e^{i\omega s_1}G_{klmn}(s_1,s_2)e^{-i\omega s_2}G_{nn11}(s_2,0)\;. \tag{3.35}$$

Given the properties (3.31c)–(3.31f), by interchanging the indices k and l, and m and n in the second term on the right-hand side of (3.35), it is easily seen that the latter is the complex conjugate of the first term. Then

$$\begin{aligned}\langle P(t)\rangle=&\left[\bar{n}\gamma^2\int_0^t ds_1\int_0^{s_1}ds_2\, G_{2222}(t,s_1)e^{-i\omega s_1}G_{1212}(s_1,s_2)e^{i\omega s_2}G_{1111}(s_2,0)+\text{c.c.}\right]\\&+\left[\bar{n}\gamma^2\int_0^t ds_1\int_0^{s_1}ds_2\, G_{2211}(t,s_1)e^{-i\omega s_1}G_{2121}(s_1,s_2)e^{i\omega s_2}G_{2211}(s_2,0)+\text{c.c.}\right]\\&-\left[\bar{n}\gamma^2\int_0^t ds_1\int_0^{s_1}ds_2\, G_{2222}(t,s_1)e^{-i\omega s_1}G_{1221}(s_1,s_2)e^{i\omega s_2}G_{2211}(s_2,0)+\text{c.c.}\right]\\&-\left[\bar{n}\gamma^2\int_0^t ds_1\int_0^{s_1}ds_2\, G_{2211}(t,s_1)e^{-i\omega s_1}G_{2112}(s_1,s_2)e^{i\omega s_2}G_{1111}(s_2,0)+\text{c.c.}\right]\;.\end{aligned} \tag{3.36}$$

The diagonal tetradic elements of G are of the form

$$G_{iijj}(t,s)=\tfrac{1}{2}\pm\tfrac{1}{2}e^{-\Gamma_0(t-s)}\;. \tag{3.37}$$

All terms in (3.36) that involve the exponentials above tend to a constant when t tends to infinity. Therefore,

$$\lim_{t\to\infty}\frac{d}{dt}\langle P(t)\rangle=\frac{\bar{n}}{4}\gamma^2\lim_{t\to\infty}\left[\frac{d}{dt}\int_0^t ds_1\int_0^{s_1}ds_2\{e^{-i\omega s_1}[G_{1212}(s_1,s_2)+G_{2121}(s_1,s_2)-G_{1221}(s_1,s_2)-G_{2112}(s_1,s_2)]e^{i\omega s_2}+\text{c.c.}\}\right] \tag{3.38}$$

and the normalized spectral line shape is given by

$$I(\omega)=\frac{1}{2\pi}\lim_{t\to\infty}\left[\int_0^t ds\{e^{-i\omega t}[G_{1212}(t,s)+G_{2121}(t,s)-G_{1221}(t,s)-G_{2112}(t,s)]e^{i\omega s}+\text{c.c.}\}\right]\;. \tag{3.39}$$

This general expression is evaluated for various special cases in the Secs. III B and III C.

B. Markovian case

1. Isotropic stochastic properties

The nonvanishing tetradic elements of G which appear in (3.39) are given by (2.35c),

$$G_{1212}(t,s)=G^*_{2121}(t,s)=e^{(i\omega_0-\Gamma)(t-s)}\;. \tag{3.40}$$

ω is tuned to the vicinity of the natural frequency ω_0, therefore $G_{2121}(t,s)$ will produce an antiresonant term which can be neglected. The line shape is given by

$$I(\omega)=\frac{1}{\pi}\frac{\Gamma}{(\omega-\omega_0)^2+\Gamma^2}\;, \tag{3.41}$$

where Γ is defined by (2.33).

2. Nonisotropic stochastic properties

All the tetradic elements of G which appear in (3.39) do not vanish in this case, and are given by (2.42c) and (2.42d). The line shape takes on the following form:

$$I(\omega)=\frac{1}{\pi}\left[1+\left[1-\frac{\omega}{\Omega}\right]\left[\frac{\Gamma_2-\Gamma_1}{2\Gamma}\right]\right]\frac{\Gamma}{(\omega-\Omega)^2+\Gamma^2}\;. \tag{3.42}$$

Γ and Ω are given by

$$\Gamma=\frac{1}{2}(\Gamma_1+\Gamma_2)+\Gamma_3\;, \tag{3.43}$$

$$\Omega=\left[\omega_0^2-\left[\frac{\Gamma_1-\Gamma_2}{2}\right]^2\right]^{1/2} \tag{3.44}$$

with Γ_1, Γ_2, and Γ_3 defined by (2.37).

C. Non-Markovian case

Now the tetradic elements of G in (3.39) are given by (2.55c) and (2.55d). The line shape is again given by

$$I(\omega)=\frac{1}{\pi}\left[1+\left[1-\frac{\omega}{\Omega}\right]\left[\frac{\Gamma_2-\Gamma_1}{2\Gamma}\right]\right]\frac{\Gamma}{(\omega-\Omega)^2+\Gamma^2}\;. \tag{3.45}$$

Here Γ and Ω are given by

$$\Gamma=\frac{1}{2}(\Gamma_1+\Gamma_2)+\Gamma_3 , \quad (3.46)$$

$$\Omega=\left[\omega_0^2+\omega_0(\Delta_1+\Delta_2)+\Delta_1\Delta_2-\left[\frac{\Gamma_1-\Gamma_2}{2}\right]^2\right]^{1/2} , \quad (3.47)$$

where the Γ_i's and Δ_i's are defined by (2.46)–(2.48). For isotropic stochastic properties, (3.45) reduces to

$$I(\omega)=\frac{1}{\pi}\frac{\Gamma}{(\omega-\omega_0-\Delta)^2+\Gamma^2} , \quad (3.48)$$

where

$$\Delta=\Delta_1=\Delta_2 . \quad (3.49)$$

Finally, we shall note that for the isotropic stochastic properties, non-Markovian case, a long and difficult computation has shown that, to lowest order in ϵ^{-1}, the correction to the approximate relaxation tetradic (3.18), relevant to the single-photon process, does not influence the line shape. The effect is to replace the coupling-strength constant γ between the spin system and the radiation field by a larger coupling strength constant γ_{eff} given by

$$\gamma_{\text{eff}}=\gamma(1+2Q/\epsilon)^{1/2}\simeq\gamma(1+Q/\epsilon) . \quad (3.50)$$

Physically, this means the instability of the states induced by the stochastic coupling between them increases the probability of transition in the photon-absorption process.

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APPENDIX

Here we present the various steps of what we have referred to as the natural approach. Starting with the quantum Liouville equation

$$i\hbar\frac{\partial}{\partial t}\rho(t)=[L_0+\tilde{L}(t)+L_v(t)]\rho(t) , \quad (A1)$$

where the three Liouvillian operators are defined by (1.9)–(1.11), this equation has the formal solution

$$\rho(t)=\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds[L_0+\tilde{L}(s)+L_v(s)]\right]\rho(0) . \quad (A2)$$

Using the interaction picture with respect to $V(t)$, the expression (A2) is rewritten as

$$\rho(t)=U(t,0)\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,\hat{L}_v(s)\right]\rho(0) , \quad (A3)$$

where

$$\hat{L}_v(t)\equiv U^\dagger(t,0)L_v(t)U(t,0) , \quad (A4)$$

$$U(t,s)\equiv\underset{\leftarrow}{T}\exp\left[-\frac{i}{\hbar}\int_s^t d\tau[L_0+\tilde{L}(\tau)]\right] , \quad (A5a)$$

$$U^\dagger(t,s)\equiv\underset{\rightarrow}{T}\exp\left[\frac{i}{\hbar}\int_s^t d\tau[L_0+\tilde{L}(\tau)]\right] . \quad (A5b)$$

The expansion of (A3) in terms of $L_v(t)$ defines the partial density matrix of order n, $\rho^{(n)}(t)$, as follows:

$$\rho(t)=\sum_{n=0}^{\infty}\rho^{(n)}(t) , \quad (A6)$$

where

$$\rho^{(0)}(t)=U(t,0)\rho(0) , \quad (A7)$$

$$\rho^{(n)}(t)=\left[-\frac{i}{\hbar}\right]^n\int_0^t ds_1\int_0^{s_1}ds_2\cdots\int_0^{s_{n-1}}ds_n\,U(t,s_1)L_v(s_1)U(s_1,s_2)\cdots L_v(s_n)U(s_n,0)\rho(0) . \quad (A8)$$

The probability of transition, in a single-photon absorption process, is given by

$$P(t)=\langle 2|\,\langle\bar{n}-1|\,\rho^{(2)}(t)\,|\bar{n}-1\rangle\,|2\rangle$$

$$P(t)=-\frac{1}{\hbar^2}\int_0^t ds_1\int_0^{s_1}ds_2\langle\bar{n}-1|\,\langle 2|\,[U(t,s_1)L_v(s_1)U(s_1,s_2)L_v(s_2)U(s_2,0)\,|1\rangle\langle 1|\otimes|\bar{n}\rangle\langle\bar{n}|\,]\,|2\rangle\,|\bar{n}-1\rangle \quad (A9)$$

or in explicit form

$$P(t)=-\frac{1}{\hbar^2}\sum_{\substack{i,j,k,l,\\ m,n,p,q}}\int_0^t ds_1\int_0^{s_1}ds_2\langle\bar{n}-1|\,[U_{22ij}(t,s_1)L_{vijkl}(s_1)U_{klmn}(s_1,s_2)L_{vmnpq}(s_2)U_{pq11}(s_2,0)\,|\bar{n}\rangle\langle\bar{n}|\,]\,|\bar{n}-1\rangle . \quad (A10)$$

The tetradic elements of U cannot be computed if the stochastic Hamiltonian $\widetilde{H}(t)$ has off-diagonal terms. The expressions (A9) or (A10) cannot be averaged since we are dealing with the average of a product of the form (1.17).

In the special case where $\widetilde{H}(t)$ is diagonal, we have

$$H_0+\widetilde{H}(t)=\hbar\frac{\omega_0}{2}\sigma_3+\hbar\widetilde{\phi}_3(t)\sigma_3 \tag{A11}$$

or

$$H_0+\widetilde{H}(t)=\hbar[\omega_2(t)\,|\,2\rangle\langle 2\,|+\omega_1(t)\,|\,1\rangle\langle 1\,|\,]\ , \tag{A12}$$

where

$$\omega_2(t)=\frac{\omega_0}{2}+\widetilde{\phi}_3(t)\ , \tag{A13a}$$

$$\omega_1(t)=-\frac{\omega_0}{2}-\widetilde{\phi}_3(t)\ . \tag{A13b}$$

In this case, we can consider, as Kubo did, the system as an oscillator with a randomly modulated frequency since

$$\omega_2(t)-\omega_1(t)=\omega_0+\widetilde{\omega}(t)\ , \tag{A14}$$

where

$$\widetilde{\omega}(t)=2\widetilde{\phi}_3(t) \tag{A15}$$

is the fluctuation in frequency. Then, the tetradic elements of U can be computed,

$$U_{ijkl}(t,s)=\exp\left[-i\int_s^t d\tau[\omega_i(\tau)-\omega_j(\tau)]\right]\delta_{ik}\delta_{jl}\ . \tag{A16}$$

This implies that the first and the last tetradic elements in (A10) reduce to unity, and the probability of transition reduces to

$$P(t)=\bar{n}\gamma^2\int_0^t ds_1\int_0^{s_1}ds_2\left[e^{-i(\omega-\omega_0)(s_1-s_2)}\times\exp\left[i\int_{s_1}^{s_2}d\tau\,\widetilde{\omega}(\tau)\right]+\text{ c.c.}\right]. \tag{A17}$$

The averaging of a single exponential can be handled by the cumulant method, and therefore, (A17) can be averaged.

$$I(\omega)\sim\lim_{t\to\infty}\frac{d}{dt}\langle P(t)\rangle\ ,$$

$$I(\omega)=\frac{1}{2\pi}\int_0^\infty ds\left[e^{-i(\omega-\omega_0)s}\left\langle\exp\left[i\int_0^s d\tau\,\widetilde{\omega}(\tau)\right]\right\rangle+\text{c.c.}\right], \tag{A18}$$

or, equivalently,

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^\infty ds\,e^{-i(\omega-\omega_0)s}\left\langle\exp\left[i\int_0^s d\tau\,\widetilde{\omega}(\tau)\right]\right\rangle . \tag{A19}$$

As an application of the fluctuation-dissipation theorem, the expression (A19) was used by Kubo as the basis of his stochastic approach to line broadening, based on the oscillator model.[9,10]

Given the stochastic properties of $\widetilde{\phi}_3(t)$ [(1.39) and (1.40)], the cumulant method gives

$$\begin{aligned}\left\langle\exp\left[i\int_0^s d\tau\,\widetilde{\omega}(\tau)\right]\right\rangle &=\exp\left[-\tfrac{1}{2}\int_0^s d\tau_1\int_0^s d\tau_2\langle\widetilde{\omega}(\tau_1)\widetilde{\omega}(\tau_2)\rangle\right]\\ &=\exp\left[-2Q_3\epsilon_3\int_0^s d\tau(s-\tau)e^{-\epsilon_3\tau}\right].\end{aligned}$$

For weakly colored noise,

$$\left\langle\exp\left[i\int_0^s d\tau\,\widetilde{\omega}(\tau)\right]\right\rangle=e^{-2Q_3 s} \tag{A20}$$

and therefore, the expression (A19) gives for the spectral line shape

$$I(\omega)=\frac{1}{\pi}\frac{\Gamma}{(\omega-\omega_0)^2+\Gamma^2} \tag{A21}$$

with

$$\Gamma=2Q_3\ . \tag{A22}$$

Finally, let us note that even in this particular case [$\widetilde{H}(t)$ diagonal], this method cannot handle a multiphoton process. For example, a two-photon absorption process in a three-state system would lead to a probability of transition of the form

$$\begin{aligned}P(t)\sim &\int_0^t ds_1\int_0^{s_1}ds_2\int_0^{s_2}ds_3\int_0^{s_3}ds_4\left[e^{-i(\omega-\omega_{32})(s_1-s_3)}\exp\left[i\int_{s_3}^{s_2}d\tau\,\widetilde{\omega}_{32}(\tau)\right]\times e^{-i(\omega-\omega_{21})(s_2-s_4)}\exp\left[i\int_{s_4}^{s_2}d\tau\,\widetilde{\omega}_{21}(\tau)\right]+\text{c.c.}\right]\\ &+\int_0^t ds_1\int_0^{s_1}ds_2\int_0^{s_2}ds_3\int_0^{s_3}ds_4\left[e^{-i(\omega-\omega_{32})(s_1-s_2)}\exp\left[i\int_{s_2}^{s_1}d\tau\,\widetilde{\omega}_{32}(\tau)\right]\times e^{-i(\omega-\omega_{21})(s_4-s_3)}\exp\left[i\int_{s_4}^{s_3}d\tau\,\widetilde{\omega}_{21}(\tau)\right]+\text{c.c.}\right]\\ &+\int_0^t ds_1\int_0^{s_1}ds_2\int_0^{s_2}ds_3\int_0^{s_3}ds_4\left[e^{-i(\omega-\omega_{32})(s_1-s_2)}\exp\left[i\int_{s_2}^{s_1}d\tau\,\widetilde{\omega}_{32}(\tau)\right]\times e^{-i(\omega-\omega_{21})(s_4-s_3)}\exp\left[i\int_{s_3}^{s_4}d\tau\,\widetilde{\omega}_{21}(\tau)\right]+\text{c.c.}\right],\end{aligned} \tag{A23}$$

which cannot be averaged.

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