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Correlation-function analysis of coherent optical transients and fluorescence from a quasi-two-level system

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A quasi-two-level system is a generalization of a two-level system where each of the single levels is replaced by a nearly degenerate multiplet. We develop the theory of the photon echo, the stimulated echo, and fluorescence emission for such systems when they are subjected to pulses of electromagnetic radiation that are short compared to the reciprocal (in frequency units) of the widths of the multiplets. The observable in each of these experiments is related to equilibrium time-correlation functions of the system in the absence of the radiation field. The correlation functions associated with these experiments involve more than two dynamical operators and more than two times, unlike the correlation functions for such processes as low-power optical absorption and neutron scattering. We introduce an exactly solvable factorization model for the transition moments, which includes as special cases the situation where either of the multiplets is a single state. We also consider the unitary model, which was introduced by Mims, and which leads to considerable simplification of the correlation functions. Several examples of these models are discussed to investigate the features of time-dependent fluorescence experiments and coherent optical transient experiments. In general, there is no simple connection between the time dependence of the decay of a photon echo and the Fourier transform of the low-power homogeneous absorption spectrum.

I. INTRODUCTION

Time-resolved fluorescence experiments and optical coherence experiments, especially two-pulse photon echoes are extremely valuable probes of spectral details that are obscured in normal absorption spectra by inhomogeneous broadening.[1-3] Modulation of the photon echo or quantum beats in the fluorescence emission provide one with information about energy-level splittings. On the other hand, monotonic decay of the photon echo is usually interpreted in terms of the homogeneous width of a spectral line. Modulated photon echoes arising from hyperfine interactions have been observed from ruby[4,5] and Pr^{3+}/LaF_3 crystals.[6,7] In gas phase NH_2D, Shoemaker and Hopf[8] have found that rotational Stark splittings cause a modulation of the echo. (Similar modulations have of course been observed in the electron[9-11] and nuclear[12] spin analogs.) Several groups have seen quantum beats in the time-resolved fluorescence signals from both atomic and molecular systems.[13-21] Other groups have observed unmodulated photon-echo decays from impurities in molecular crystals.[22,23]

Performance of these experiments typically involves subjecting the sample to an intense pulse of electromagnetic radiation. The pulse is strong enough to induce a nonlinear response of the sample to the pulse. For some experiments, such as absorption of weak incident radiation and single scattering of beams of radiation or neutrons, the formalism of linear-response theory and equilibrium time-dependent correlation functions[24-26] has been especially useful. Coherent transient experiments and time-dependent fluorescence intensity measurements do not fall into the class of experiments for which the time correlation function analysis has been traditionally applied. It is therefore of interest to inquire to what extent these experiments can be analyzed in terms of equilibrium correlation functions.

As photon-echo experiments are designed to extract information about the absorption spectrum that cannot be obtained directly because of inhomogeneous broadening, it is worthwhile to understand the connection between the photon-echo signal and the *homogeneous* line shape. It is often assumed that there is a direct relationship between the photon-echo amplitude and the Fourier transform of the homogeneous line shape. Such a relationship would imply that the nonlinear response of a system to the strong pulses of a

photon-echo experiment can be related to thermal fluctuations of the dipole moment in the absence of radiation, which through the fluctuation-dissipation theorem gives rise to the optical line shape.[24–26]

Most of the experimental systems that were cited in the opening paragraph fall into an important class of systems that we call quasi-two-level systems. A quasi-two-level system (QTLS) is a generalization of a two-level system where each of the single levels is replaced by a nearly degenerate multiplet. In this paper we investigate the theory of the photon echo, stimulated echo, and fluorescence experiments for QTLS's, with special attention to the relationship between these experiments and equilibrium correlation functions. One of our findings is that the nonlinear response of a system to a strong perturbation is in general different from thermal fluctuations, and hence in general there is no simple relationship between the photon-echo decay and the homogeneous line shape.

Important theoretical work on the modulation of coherent transient signals from QTLS's has been performed by Lambert *et al.*[4] and by Mims.[10] These authors obtained quite general expressions for the (two-pulse) photon-echo[4,10] and (three-pulse) stimulated-echo[10] intensities. Explicit results have been calculated for the special cases of a few nearly degenerate levels in each multiplet.[4,10,27] The theory of quantum beat fluorescence has been presented for the case of weak excitation pulses.[13,16,28–30] In this paper we extend these various results, show how the theoretical expressions can be written in terms of correlation functions, and discuss several examples.

We begin in Sec. II by considering a general QTLS and calculating the photon echo, stimulated echo, and fluorescence signals that occur as a result of excitation by short pulses of arbitrary intensity. In Sec. III we derive equilibrium time-correlation function expressions for these observables. The equilibrium time-correlation functions needed to describe the photon echo, stimulated echo, and fluorescence experiments are functions of 5, 7, and 4 dynamical variables, respectively, at 3, 4, and 2 times, respectively. Thus they are significantly more complicated than the two-time correlation functions that appear in experiments for which linear-response theory is adequate.

In Sec. IV we consider a more restricted class of QTLS's where the transition dipole matrix elements obey a certain factorization condition. For this model, the correlation function expressions of Sec. III are evaluated exactly. Important cases of physical interest that are subsumed by this model are those where either the ground or excited state is a single level. In Sec. V we consider another class of QTLS's, which has been discussed by Mims,[10] in which the number of states is the same in the two multiplets and the transition dipole moment matrix contains off-diagonal blocks that are unitary. For such systems the correlation function expressions of Sec. III can be simplified. These results are applicable to QTLS's that arise from the interaction of a two-level system having a transition moment with a set of additional degrees of freedom that do not have transition moments.

In Sec. VI we discuss special cases of our results where the energy-level distribution is continuous. In Sec. VI A we consider a system with a single ground state and an excited-state continuum. Such a system is very similar to the Bixon-Jortner[31] model of radiationless transitions in isolated molecules. In Sec. VI B we turn to a discussion of the photon echo from dilute impurities in molecular crystals, and conclude that it may not be correct to interpret these experiments[22,23] using optical line-shape theory.

II. GENERAL QUASI-TWO-LEVEL SYSTEM

In this section we calculate the photon echo, stimulated echo, and fluorescence signals from an inhomogeneous distribution of QTLS's. We consider a general QTLS where both the ground and excited states consist of multiplets, as studied by Lambert *et al.*[4] and shown in Fig. 1. The ground and excited states are denoted by $\{|a\rangle\}$ and $\{|b\rangle\}$, respectively.

Each QTLS represents the full (with the exception of the matter-radiation interaction) Hamiltonian for a particular system in the inhomogeneous distribution. That is, it includes the effect of any local electric or magnetic fields and (for crystals) the interaction between the impurity and host atoms or molecules. Formally, we write the Hamiltonian for a particular QTLS in the eigenstate

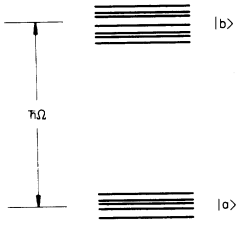

FIG. 1. A quasi-two-level system.

representation

$$H_0=\sum_a \hbar\omega_a \,|\, a\rangle\langle a \,|\, + \sum_b \hbar\omega_b \,|\, b\rangle\langle b \,|\, . \tag{2.1}$$

Without loss of generality we define an arbitrary zero of energy in the ground-state multiplet and associate the inhomogeneity with the excited-state frequencies ω_b. Thus we write

$$\omega_a = x_a \ , \tag{2.2}$$

$$\omega_b = \Omega + x_b + \delta \ , \tag{2.3}$$

where x_a is the deviation of level a from the zero of energy, Ω is the laser frequency, x_b is the average deviation of ω_b from Ω, and δ is the inhomogeneous deviation (of ω_b from Ω) with $\langle \delta \rangle = 0$. Throughout this section $\langle \cdots \rangle$ refers to an average over the inhomogeneous distribution. In the presence of a monochromatic laser field, the Hamiltonian is

$$H = H_0 + H_1 \ , \tag{2.4}$$

$$H_1 = -E\hat{\mu}\cos(\Omega t - kz) \ , \tag{2.5}$$

$$\hat{\mu} = \sum_{ab} (\mu_{ab} \,|\, a\rangle\langle b \,|\, + \mu_{ab}^* \,|\, b\rangle\langle a \,|\,) \ . \tag{2.6}$$

E is the magnitude of the electric field, polarized in the x direction, of a wave propagating in the z direction with wave vector k. $\hat{\mu}$ is the x component of the transition dipole operator. We assume that the above description of the laser field is valid for each excitation pulse and (in subsequent sections) that detectors measure light polarized in the x direction. Generalization to cases in which the excitation pulses have different directions[32] or polarizations[33] or in which the detector is polarized differently[28,33] is straightforward.

The equation of motion for the density matrix is the Liouville–von Neumann equation:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H,\rho] \ . \tag{2.7}$$

Transforming to a rotating frame by

$$\tilde{\rho} = \exp[iS(\Omega t - kz)]\rho \exp[-iS(\Omega t - kz)] \ , \tag{2.8}$$

$$S = \sum_b |\, b\rangle\langle b \,|\, , \tag{2.9}$$

and making the rotating wave approximation we obtain

$$\frac{\partial \tilde{\rho}}{\partial t} = -i[(\Delta - \chi/2), \tilde{\rho}], \tag{2.10}$$

where

$$\Delta = \sum_a x_a \,|\, a\rangle\langle a \,|\, + \sum_b (x_b + \delta) \,|\, b\rangle\langle b \,|\, \tag{2.11}$$

and

$$\chi = E\hat{\mu}/\hbar \ . \tag{2.12}$$

In what follows we assume that the ith laser pulse has an amplitude E for a duration τ_i, and further that we may neglect Δ in Eq. (2.10) during each pulse. Thus we require that

$$\Delta_{aa}\tau_i, \Delta_{bb}\tau_i << 1 \tag{2.13a}$$

for all a, b; that is, the pulse durations are short compared to the inverse frequency width of each multiplet. We also require that in some sense

$$\chi >> \Delta \ . \tag{2.13b}$$

(It is difficult to state a precise condition involving the matrix elements of χ without a detailed specification of the energy-level and transition-moment structures.) Although Eqs. (2.13a) and (2.13b) impose stringent requirements on the properties of the excitation pulses (which may in fact not be realized in some experimental situations), theoretical progress is greatly facilitated by these assumptions and hence we adopt them here. We also note that as long as the pulses are short, nonideal (nonsquare) pulses can be treated in a similar manner.[2,4] Under these conditions, during a pulse Eq. (2.10) can be formally solved to give

$$\tilde{\rho}(\tau) = V(\tau)\tilde{\rho}(0)V(-\tau) \ , \tag{2.14}$$

where

$$V(\tau) = \exp(i\chi\tau/2) \ . \tag{2.15}$$

In the absence of the laser field the solution similarly is

$$\tilde{\rho}(t) = U(t)\tilde{\rho}(0)U(-t) \ , \tag{2.16}$$

where

$$U(t) = \exp(-i\Delta t) \ . \tag{2.17}$$

A. Photon echo

The photon-echo sequence consists of a laser pulse of duration τ_1 followed at a time t_1 later by a second pulse of duration τ_2. After the second pulse, at time $t + t_1$, the density matrix is

$$\tilde{\rho}(t+t_1)=U(t)V(\tau_2)U(t_1)V(\tau_1)\tilde{\rho}(0) \times V(-\tau_1)U(-t_1)V(-\tau_2)U(-t) . \tag{2.18}$$

[Because of Eq. (2.13) we are permitted to neglect τ_1 and τ_2 in the argument of $\tilde{\rho}$.] The x component of the polarization of the medium, when averaged over the inhomogeneous distribution, is

$$p(t)=\langle \mathrm{Tr}[\hat{\mu}\rho(t)]\rangle . \tag{2.19}$$

Writing

$$p(t)=\tilde{p}(t)\exp[-i(\Omega t-kz)]+\text{c.c.} , \tag{2.20}$$

it is easy to see that

$$\tilde{p}(t)=\sum_{ab}\mu_{ab}\langle\tilde{\rho}_{ba}(t)\rangle . \tag{2.21}$$

Furthermore, for an optically thin sample the signal intensity $\mathcal{I}(t)$ is

$$\mathcal{I}(t)\propto|\tilde{p}(t)|^2 , \tag{2.22}$$

so the calculation reduces to evaluating the matrix elements of Eq. (2.18) and averaging over the inhomogeneous distribution.

We assume that initially the population of the states in the ground manifold is described by a Boltzmann distribution, so that

$$\tilde{\rho}(0)=\sum_a P_a|a\rangle\langle a| , \tag{2.23}$$

$$P_a=e^{-\beta\hbar\chi_a}\Big/\sum_a e^{-\beta\hbar\chi_a} , \tag{2.24}$$

and $\beta=1/k_BT$. Inserting complete sets of states $|c\rangle$ and $|c'\rangle$ in Eq. (2.18) and using Eq. (2.23) and the fact that $U(t)$ is diagonal, we obtain

$$\tilde{\rho}_{ba}(t+t_1)=\sum_{a'cc'}U_b(t)V_{bc}(\tau_2)U_c(t_1) \times V_{ca'}(\tau_1)P_{a'}V_{a'c'}(-\tau_1)U_{c'}(-t_1) \times V_{c'a}(-\tau_2)U_a(-t) . \tag{2.25}$$

(In this equation and the ones that follow, a,a',a'', . . . refer to ground multiplet levels, b,b',b'', . . . , refer to excited multiplet levels, and c,c',c'', . . . , refer to both sets of levels.) We are interested in times such that $\delta t,\delta t_1 >> 1$, so in averaging over δ, many terms vanish. Retaining only those terms that contribute to the echo at time $t=t_1$, we have

$$\tilde{p}(2t_1)=\sum_{aba'b'a''}\mu_{ab}\exp[-it_1(x_b-x_a-x_{b'}+x_{a'})] \times V_{ba'}(\tau_2)V_{a'a''}(\tau_1) \times P_{a''}V_{a''b'}(-\tau_1)V_{b'a}(-\tau_2) . \tag{2.26}$$

Recognizing that odd powers of χ only connect the $|a\rangle$ and $|b\rangle$ manifolds while even powers of χ only connect states within each manifold, we obtain

$$\tilde{p}(2t_1)=-i\sum_{aba'b'a''}\mu_{ab}\exp[-it_1(x_b-x_a-x_{b'}+x_{a'})]\langle b|\sin(\tfrac{1}{2}\chi\tau_2)|a'\rangle\langle a'|\cos(\tfrac{1}{2}\chi\tau_1)|a''\rangle P_{a''} \times\langle a''|\sin(\tfrac{1}{2}\chi\tau_1)|b'\rangle\langle b'|\sin(\tfrac{1}{2}\chi\tau_2)|a\rangle . \tag{2.27}$$

At sufficiently high temperatures all the states in the ground manifold will be equally populated and hence $P_{a''}=(N_0)^{-1}$, where N_0 is simply the number of states in the ground manifold. In this instance Eq. (2.27) reduces to the results obtained by Lambert *et al.*[4]:

$$\tilde{p}(2t_1)=-\frac{i}{2N_0}\sum_{aba'b'}\mu_{ab}\exp[-it_1(x_b-x_a-x_{b'}+x_{a'})] \times\langle b|\sin(\tfrac{1}{2}\chi\tau_2)|a'\rangle\langle a'|\sin(\chi\tau_1)|b'\rangle\langle b'|\sin(\tfrac{1}{2}\chi\tau_2)|a\rangle . \tag{2.28}$$

B. Stimulated echo

At a time t after the third pulse of a stimulated-echo sequence the density matrix is given by

$$\tilde{\rho}(t+t_2+t_1)=U(t)V(\tau_3)U(t_2)V(\tau_2)U(t_1)V(\tau_1)\tilde{\rho}(0)V(-\tau_1)U(-t_1)V(-\tau_2)U(-t_2)V(-\tau_3)U(-t) , \tag{2.29}$$

where τ_1, τ_2, and τ_3 are the durations of the first, second, and third pulses, and t_1 and t_2 are the time inter-

vals between the first and second, and second and third pulses, respectively. As in the calculation of the photon echo we consider the general QTLS shown in Fig. 1, and as before, to find the signal we must evaluate $\langle \tilde{\rho}_{ba}(t+t_1+t_2)\rangle$. Retaining only the terms which lead to an echo when $t=t_1$ and using the properties of χ discussed above, we obtain

$$\tilde{p}(2t_1+t_2)=-i\sum_{aba'b'a''''}\mu_{ab}\exp[-it_1(x_b-x_a-x_{b'}+x_{a'})]\langle a'|\cos(\tfrac{1}{2}\chi\tau_1)|a''''\rangle P_{a''''}\langle a''''|\sin(\tfrac{1}{2}\chi\tau_1)|b'\rangle$$
$$\times\Bigg[\sum_{a''a'''}\exp[it_2(x_{a''}-x_{a'''})]\langle b|\sin(\tfrac{1}{2}\chi\tau_3)|a'''\rangle$$
$$\times\langle a'''|\cos(\tfrac{1}{2}\chi\tau_2)|a'\rangle\langle b'|\sin(\tfrac{1}{2}\chi\tau_2)|a''\rangle\langle a''|\cos(\tfrac{1}{2}\chi\tau_3)|a\rangle$$
$$+\sum_{b''b'''}\exp[-it_2(x_{b''}-x_{b'''})]\langle b|\cos(\tfrac{1}{2}\chi\tau_3)|b''\rangle$$
$$\times\langle b''|\sin(\tfrac{1}{2}\chi\tau_2)|a'\rangle\langle b'|\cos(\tfrac{1}{2}\chi\tau_2)|b'''\rangle\langle b'''|\sin(\tfrac{1}{2}\chi\tau_3)|a\rangle\Bigg]. \quad (2.30)$$

C. Fluorescence

The fluorescence signal is observed after a single laser pulse. The calculation of this signal, however, is not directly analogous to the photon-echo calculation. In our semiclassical treatment the photon echo arises from an oscillating macroscopic polarization. Fluorescence, on the other hand, is an inherently quantum-mechanical spontaneous emission event, and as the experiments by Gibbs[34] have shown, it is necessary to use a quantized treatment of the radiation field. Here we are not interested in calculating the *radiative* decay rate; in fact, we assume its time scale is much longer than the one we are considering, and hence the fluorescence signal directly probes the *nonradiative* excited-state dynamics.

At a time t after the laser pulse the density matrix is

$$\tilde{\rho}(t)=U(t)V(\tau)\tilde{\rho}(0)V(-\tau)U(-t)\,. \quad (2.31)$$

In the Apppendix we give a rigorous derivation of the fluorescence signal using the quantum theory of radiation. Here we argue more heuristically that the intensity of fluorescence to a ground state $|a\rangle$ is proportional to the population of the excited state that can radiate to $|a\rangle$, namely, $\hat{\mu}|a\rangle$, and the total intensity is the sum of the intensities to all the ground levels, hence

$$\mathcal{I}_{\rm fl}(t)\propto\sum_a\langle a|\hat{\mu}\rho(t)\hat{\mu}|a\rangle \quad (2.32)$$
$$=\sum_{abb'}\mu_{ab}\mu^*_{ab'}\langle b|\tilde{\rho}(t)|b'\rangle\,. \quad (2.33)$$

Taking matrix elements of Eq. (2.31) we obtain the general result

$$\mathcal{I}_{\rm fl}(t)\propto\sum_{aba'b'}\mu_{ab}\mu^*_{ab'}\exp[-i(x_b-x_{b'})t]$$
$$\times\langle b|\sin(\tfrac{1}{2}\chi\tau)|a'\rangle P_{a'}$$
$$\times\langle a'|\sin(\tfrac{1}{2}\chi\tau)|b'\rangle\,. \quad (2.34)$$

In the limit of low power [for which $\sin(\frac{1}{2}\chi\tau)$ can be expanded in powers of χ and only the first term need be retained], at high temperatures we recover the expression derived by previous authors,[13,28,29]

$$\mathcal{I}_{\rm fl}(t)\propto\sum_{aba'b'}\mu_{ab}\mu_{ba'}\mu_{a'b'}\mu_{b'a}$$
$$\times\exp[-i(x_b-x_b')t]\,. \quad (2.35)$$

One immediately apparent feature of the general result, Eq. (2.34), is that the time dependence of the fluorescence intensity depends only on the *excited*-state level structure. For a three-level system this has been pointed out by Scully and Shea.[35] This observation is, however, at variance with calculations by other authors[4,5] based on the (incorrect) semiclassical treatment of the matter-radiation interaction.

D. The homogeneous absorption spectrum

Since we will be discussing the relationship between the homogeneous absorption spectrum and the various coherent transients, it is appropriate to write down the expression for the line shape for a general QTLS. Of course, the observed line shape

will show the effects of inhomogeneous broadening. By the homogeneous line shape, we mean the hypothetical spectrum from a collection of systems for which $\delta=0$. Using the definitions of Eqs. (2.1) and (2.23), and Fermi's golden rule, the spectrum is simply[24]

$$\mathscr{I}(\omega)\propto\sum_{ab}P_a\,|\mu_{ab}|^2\delta(\omega-(\Omega+x_b-x_a))\ . \tag{2.36}$$

III. EQUILIBRIUM CORRELATION FUNCTIONS

Given the usefulness of the time correlation function formalism for describing many processes including light and neutron scattering and the weak absorption of radiation in several branches of spectroscopy, it is natural to ask to what extent the nonlinear experiments that are of interest in this paper can be described by correlation functions. Surprisingly enough, we find that in all the cases considered, the nonlinear response to one or more strong radiation pulses can be described by *equilibrium* time correlation functions for fluctuations that occur in the absence of the radiation.

It is well known that the theoretical expression for the homogeneous line shape can be written in terms of the dipole-moment correlation function.[24] Here we sketch the derivation, since the ideas used are identical to those we need to derive the more complex expressions for the coherent transients and fluorescence.

Starting with the general formula for the line shape, Eq. (2.36), we use the integral representation of the delta function to write $\mathscr{I}(\omega)$ in the suggestive form

$$\mathscr{I}(\omega)\propto\int_{-\infty}^{\infty}dt\,e^{i\omega t}\sum_{ab}e^{-\beta\hbar x_a}e^{ix_at}\times\langle a|\hat{\mu}|b\rangle e^{-i(x_b+\Omega)t}\langle b|\hat{\mu}|a\rangle\ . \tag{3.1}$$

Using the definition of H_0, Eq. (2.1) (with $\delta=0$, since this is the homogeneous spectrum), this can be written as

$$\mathscr{I}(\omega)\propto\int_{-\infty}^{\infty}dt\,e^{i\omega t}\sum_{ab}\langle a|e^{-\beta H_0}e^{iH_0t/\hbar}\times\hat{\mu}e^{-iH_0t/\hbar}|b\rangle\langle b|\hat{\mu}|a\rangle\ . \tag{3.2}$$

Since $\hat{\mu}$ has no matrix element between states in the same manifold, the sum over b represents a complete set, and since $\hbar\Omega>>k_BT$, the sum over a is approximately a trace, so we obtain the usual correlation-function result

$$\mathscr{I}(\omega)\propto\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle\hat{\mu}(t)\hat{\mu}(0)\rangle_0\ , \tag{3.3}$$

where

$$\hat{\mu}(t)=e^{iH_0t/\hbar}\hat{\mu}e^{-iH_0t/\hbar} \tag{3.4}$$

and

$$\langle\cdots\rangle_0=\frac{\mathrm{Tr}(e^{-\beta H_0}\cdots)}{\mathrm{Tr}(e^{-\beta H_0})}\ . \tag{3.5}$$

Next we consider the general expression for the photon-echo amplitude, Eq. (2.27). Upon rearrangement and with the definition

$$B_i=E\tau_i/2\hbar\ , \tag{3.6}$$

Eq. (2.27) becomes

$$\tilde{p}(2t_1)=-i\sum_{aba'b'a''}P_{a''}e^{-ix_{a''}t_1}\langle a''|\sin(B_1\hat{\mu})|b'\rangle e^{i(x_{b'}+\Omega)t_1}\times\langle b'|\sin(B_2\hat{\mu})|a\rangle e^{ix_at_1}\langle a|\hat{\mu}|b\rangle e^{-i(x_b+\Omega)t_1}\times\langle b|\sin(B_2\hat{\mu})|a'\rangle e^{-ix_{a'}t_1}\langle a'|\cos(B_1\hat{\mu})|a''\rangle e^{ix_{a''}t_1}\ . \tag{3.7}$$

Using the definition of H_0 (with $\delta=0$) and Eq. (3.4), this can be rewritten as

$$\tilde{p}(2t_1)=-i\left[\sum_{a'''}\langle a'''|e^{-\beta H_0}|a'''\rangle\right]^{-1}\sum_{aba'b'a''}\langle a''|e^{-\beta H_0}\sin[B_1\hat{\mu}(-t_1)]|b'\rangle\times\langle b'|\sin[B_2\hat{\mu}(0)]|a\rangle\langle a|\hat{\mu}(t_1)|b\rangle\times\langle b|\sin[B_2\hat{\mu}(0)]|a'\rangle\langle a'|\cos[B_1\hat{\mu}(-t_1)]|a''\rangle\ . \tag{3.8}$$

Since $\sin[B_1\hat{\mu}(-t_1)]$ has no matrix elements between states in the same manifold, the sum over b' can be replaced by the unit operator. Similarly since $\sin[B_1\hat{\mu}(-t_1)]\sin[B_2\hat{\mu}(0)]$ has matrix elements *only* between states in the same manifold, the sum over a can be replaced by the unit operator, and so on for b and a'. Finally, since $\hbar\Omega >> k_BT$, the sums over a'' and a''' are each replaced by traces, and with Eq. (3.5) we obtain the correlation-function result

$$\tilde{p}(2t_1) = -i\langle \sin[B_1\hat{\mu}(-t_1)]\sin[B_2\hat{\mu}(0)]\hat{\mu}(t_1)\sin[B_2\hat{\mu}(0)]\cos[B_1\hat{\mu}(-t_1)]\rangle_0 . \tag{3.9}$$

We note that as for the spectrum, this is an *equilibrium* time correlation function for the *homogeneous* system in the absence of radiation.

Similarly, for the stimulated echo, Eq. (2.30) can be written as

$$\begin{aligned}\tilde{p}(2t_1+t_2) = -i\langle & \sin[B_1\hat{\mu}(-(t_1+t_2))] \\ & \times\{\sin[B_2\hat{\mu}(-t_2)]\cos[B_3\hat{\mu}(0)]\hat{\mu}(t_1)\sin[B_3\hat{\mu}(0)]\cos[B_2\hat{\mu}(-t_2)] \\ & + \cos[B_2\hat{\mu}(-t_2)]\sin[B_3\hat{\mu}(0)]\hat{\mu}(t_1)\cos[B_3\hat{\mu}(0)]\sin[B_2\hat{\mu}(-t_2)]\} \\ & \times\cos[B_1\hat{\mu}(-(t_1+t_2))]\rangle_0 .\end{aligned} \tag{3.10}$$

Finally for the fluorescence signal, Eq. (2.34) becomes

$$\mathcal{S}_{\rm fl}(t) \propto \langle \sin[B\hat{\mu}(0)]\hat{\mu}(t)\hat{\mu}(t)\sin[B\hat{\mu}(0)]\rangle_0 . \tag{3.11}$$

These correlation functions differ from the usual ones [e.g., Eq. (3.3)] in that they contain nonlinear functions of operators, and they involve more than two operators and more than two times. Thus comparing Eqs. (3.3) and (3.7) it is clear that in general the photon-echo amplitude is not simply related (e.g., via the Fourier transform) to the homogeneous spectrum.

We conclude this section by commenting on the general utility of correlation-function expressions. In deriving the results of Sec. II we have expressed the transition dipole operator in terms of the eigenstates of the Hamiltonian. For a complex interacting system (e.g., an impurity in a crystal) both the eigenstates and the transition dipole matrix elements are very difficult to obtain. Therefore the results of Sec. II may not be useful. However, it is often true that the system is conveniently described by a representation that does not diagonalize the Hamiltonian. The correlation-function expressions of the present section are well suited for this (or any other) representation. It is, for example, in this spirit that progress has been made in low-power (linear) absorption-line-shape theory of impurities in crystals[36] or molecules in liquids.[24] Thus we anticipate that the correlation-function expressions provided here will be useful in understanding nonlinear experiments from complex systems.

IV. THE FACTORIZATION MODEL

In Secs. II and III we derived general expressions for the time dependence of the coherent transients and fluorescence. The evaluation of these expressions is difficult due to the presence of the trigonometric functions of the dipole operator. Below, we consider a class of QTLS's that is exactly solvable for arbitrary numbers of levels in each multiplet. Important special cases in this class are systems in which either the ground or excited multiplet is a single level. The solvable nature of this latter case was recognized by Yeh and Eberly.[37]

The factorization model we consider in this section is defined by the assumption that the transition dipole moments have the special form

$$\mu_{ab} = m_a m_b^* . \tag{4.1}$$

Defining the states $|\phi_0\rangle$ and $|\phi_1\rangle$ by

$$|\phi_0\rangle = \sum_a m_a |a\rangle , \tag{4.2}$$

$$|\phi_1\rangle = \sum_b m_b |b\rangle , \tag{4.3}$$

the dipole operator [Eq. (2.6)] can be written in the form

$$\hat{\mu} = |\phi_0\rangle\langle\phi_1| + |\phi_1\rangle\langle\phi_0| . \tag{4.4}$$

The simplicity of the factorization model lies in the property that

$$\hat{\mu}^3 = D^2\hat{\mu} , \tag{4.5}$$

where

$$D^2 = D_0^2 D_1^2 , \tag{4.6}$$

$$D_0^2=\langle\phi_0|\phi_0\rangle=\sum_a |m_a|^2 , \tag{4.7}$$

$$D_1^2=\langle\phi_1|\phi_1\rangle=\sum_b |m_b|^2 . \tag{4.8}$$

If we define the "area" of the ith laser pulse by

$$A_i=DE\tau_i/\hbar , \tag{4.9}$$

then it is straightforward to show that

$$\sin[B_i\hat{\mu}(t)]=\sin(\tfrac{1}{2}A_i)\hat{\mu}(t)/D \tag{4.10}$$

and

$$\cos[B_i\hat{\mu}(t)]=1+[\cos(\tfrac{1}{2}A_i)-1][\hat{\mu}(t)/D]^2 , \tag{4.11}$$

where

$$\hat{\mu}(t)=|\phi_0(-t)\rangle\langle\phi_1(-t)| + |\phi_1(-t)\rangle\langle\phi_0(-t)| , \tag{4.12}$$

and

$$|\phi_j(t)\rangle=e^{-iH_0t/\hbar}|\phi_j\rangle \tag{4.13}$$

for $j=0,1$. With these simplifications we can now compute the various time-dependent signals from the correlation-function expressions.

A. Photon echo

With Eqs. (4.10) and (4.11) the correlation-function expression [Eq. (3.9)] for the photon-echo signal amplitude can be written as

$$\tilde{p}(2t_1)=-iG^2D_1D_0^{-1}\sin^2(\tfrac{1}{2}A_2)\sin(\tfrac{1}{2}A_1) \times|f_1(t_1)|^2f_0(t_1) \times\{g^*(t_1)+f_0^*(t_1)[\cos(\tfrac{1}{2}A_1)-1]\} , \tag{4.14}$$

where

$$f_0(t)\equiv\langle\phi_0(t)|\phi_0\rangle/\langle\phi_0|\phi_0\rangle \tag{4.15}$$

$$=D_0^{-2}\sum_a |m_a|^2\exp(itx_a) , \tag{4.16}$$

$$f_1(t)\equiv\langle\phi_1|\phi_1(t)\rangle/\langle\phi_1|\phi_1\rangle \tag{4.17}$$

$$=D_1^{-2}\sum_b |m_b|^2\exp[-it(x_b+\Omega)] , \tag{4.18}$$

$$g(t)\equiv\langle|\phi_0\rangle\langle\phi_0(t)|\rangle_0/\langle|\phi_0\rangle\langle\phi_0|\rangle_0 \tag{4.19}$$

$$=G^{-2}\sum_a P_a|m_a|^2\exp(itx_a) , \tag{4.20}$$

$$G^2\equiv\sum_a P_a|m_a|^2 . \tag{4.21}$$

Although this expression is still somewhat involved, the important point is that for any system, given the ground- and excited-state level structures and transition moments, it is very simple to evaluate.

Two important cases occur when either the ground or excited manifold is a single state. (The factorization model is rigorously valid in each of these cases.) For a system with a single excited state $|f_1(t)|^2=1$, while for a system with a single ground state $|f_0(t)|^2=f_0(t)g^*(t)=1$. The results of Eq. (4.14) simplify accordingly. When both the ground and excited manifolds are single states, we obtain the correct two-level result.

At high temperatures P_a is constant and Eq. (4.14) can be simplified to obtain

$$\tilde{p}(2t_1)=-\frac{iD}{2N_0}\sin(A_1)\sin^2(\tfrac{1}{2}A_2) \times|f_0(t_1)|^2|f_1(t_1)|^2 . \tag{4.22}$$

If we consider two systems, one with a single ground state and an excited-state multiplet, and another with the single level and the multiplet reversed, but with the same splittings and transition moments and with the temperature high enough to populate all the ground multiplet levels equally, Eq. (4.22) shows that apart from an uninteresting normalization factor the photon-echo signal will be identical for the two systems. In particular, if the multiplet is a doublet we recover the formulas of Lambert *et al.*[4] and Schenzle *et al.*[27]

B. Stimulated echo

Substituting Eqs. (4.10) and (4.11) into Eq. (3.10) we can express the stimulated echo amplitude in terms of the same functions we defined for the photon echo. The result is

$$\begin{aligned}\tilde{p}(2t_1+t_2)=&-iG^2D_1D_0^{-1}\sin(\tfrac{1}{2}A_1)\sin(\tfrac{1}{2}A_2)\sin(\tfrac{1}{2}A_3)\\ &\times[|f_1(t_1)|^2\{f_0(t_1+t_2)+f_0(t_1)f_0(t_2)[\cos(\tfrac{1}{2}A_3)-1]\}\\ &\times(g^*(t_1+t_2)+f_0^*(t_1+t_2)[\cos(\tfrac{1}{2}A_1)-1]+f_0^*(t_2)[\cos(\tfrac{1}{2}A_2)-1]\\ &\times\{g^*(t_1)+f_0^*(t_1)[\cos(\tfrac{1}{2}A_1)-1]\})\\ &+f_0(t_1)\{g^*(t_1)+f_0^*(t_1)[\cos(\tfrac{1}{2}A_1)-1]\}\{f_1(t_1+t_2)+f_1(t_1)f_1(t_2)[\cos(\tfrac{1}{2}A_3)-1]\}\\ &\times\{f_1^*(t_1+t_2)+f_1^*(t_1)f_1^*(t_2)[\cos(\tfrac{1}{2}A_2)-1]\}] .\end{aligned} \tag{4.23}$$

At high temperatures P_a is constant, and this simplifies somewhat to

$$\begin{aligned}\tilde{p}(2t_1+t_2)= &-(iD/2N_0)\sin(A_1)\sin(\tfrac{1}{2}A_2)\sin(\tfrac{1}{2}A_3)\\ &\times(|f_1(t_1)|^2\{f_0(t_1+t_2)+f_0(t_1)f_0(t_2)[\cos(\tfrac{1}{2}A_3)-1]\}\\ &\times\{f_0^*(t_1+t_2)+f_0^*(t_1)f_0^*(t_2)[\cos(\tfrac{1}{2}A_2)-1]\}\\ &+|f_0(t_1)|^2\{f_1(t_1+t_2)+f_1(t_1)f_1(t_2)[\cos(\tfrac{1}{2}A_3)-1]\}\\ &\times\{f_1^*(t_1+t_2)+f_1^*(t_1)f_1^*(t_2)[\cos(\tfrac{1}{2}A_2)-1]\})\ . \end{aligned} \tag{4.24}$$

This equation displays the symmetry between ground and excited multiplets that is evident in the high-temperature photon-echo results. Another feature of this result is that when t_2 is varied, the observed modulation will depend on t_1, as well as the pulse areas A_2 and A_3. In Sec. VI we will consider the case where the multiplet is a continuum; we will see that in special cases Eq. (4.24) simplifies dramatically.

Finally, we note that for a two-level system it is easy to verify that

$$\tilde{p}(2t_1+t_2)=(-iD/4)\sin(A_1)\sin(A_2)\sin(A_3)\ , \tag{4.25}$$

which is the correct result.

C. Fluorescence

Within the factorization model the fluorescence intensity becomes

$$\mathcal{I}_{\rm fl}(t)\propto D_1^2G^2\sin^2(\tfrac{1}{2}A)|f_1(t)|^2\ . \tag{4.26}$$

In contrast to the coherent transient results for this model, we see that the time dependence does not depend upon the power, A. Again it is clear that only the excited-state level structure determined the fluorescence modulation. In addition we note that the signal is maximized when a π pulse ($A=\pi$) is applied and thus the system is fully excited. This is in contrast to semiclassical calculations[4,5] that predicted the signal would be maximized by a $\pi/2$ pulse.

D. Relationship of the photon echo and fluorescence to the homogeneous line shape

For the factorization model we have been considering in this section it is straightforward to show that the homogeneous line shape, from Eq. (3.3), is given by

$$\mathcal{I}(\omega)\propto\int_{-\infty}^{\infty}dt\,e^{i\omega t}g(t)f_1(t)\ . \tag{4.27}$$

Comparing this equation with Eq. (4.14) for the photon echo it is clear that in general there is no simple relationship between the two.

To emphasize this point let us consider a QTLS with a single excited state $|b\rangle$; for simplicity we take $x_b=0$. At very low temperatures only the lowest level $|0\rangle$ in the ground-state multiplet is initially populated so that $P_a=\delta_{a0}$. The spectrum is simply a sharp line, as it depends only on $g(t)$. On the other hand, the photon echo depends on both $g(t)$ and $f_0(t)$, the latter of which is temperature independent. Therefore even at $T=0$ K the photon echo is modulated by ground-state splittings. It is clear that this conclusion does not depend on the exactly solvable model we have been considering in this section. Physically the result can be understood because a single coherent excitation pulse can transfer population from the lowest ground level, through the excited-state manifold, to *all* the ground-state levels.

Alternatively we can consider the high-temperature limit when P_a is constant, and thus $f_0(t)=g(t)$. Then from Eqs. (4.22) and (4.27) it can be seen that

$$\tilde{p}(2t_1)\propto\left|\int_{-\infty}^{\infty}d\omega\,e^{-i\omega t_1}\mathcal{I}(\omega)\right|^2\ , \tag{4.28}$$

and thus the photon-echo signal is directly related to the Fourier transform of the homogeneous spectrum. This high-temperature result, however, appears to depend on the factorization assumption.

The total fluorescence intensity arises from incoherent spontaneous emission, and its time dependence is caused only by the excited multiplet splittings. At $T=0$ K the line shape is also only affected by the excited multiplet splittings. Thus we find [from Eqs. (4.26) and (4.27)] that for the factorization model at $T=0$ K, the fluorescence intensity is proportional to the squared magnitude of

the Fourier transform of the homogeneous line shape.

V. THE UNITARY MODEL

The unitary model, which was introduced by Mims,[10] is another model for the dipole operator that leads to considerable simplification of the general results of Secs. II and III and that corresponds to situations of physical interest. In this model the number of states, N, in the ground and excited multiplets must be the same. The model is defined by

$$\mu_{ab}=\mu_0 M_{ab}\,, \tag{5.1}$$

where M is an N by N unitary matrix and μ_0 is a constant that is determined by the overall dipole strength. Such a structure of the transition dipole matrix arises when the system of interest consists of a two-level system coupled to another mechanical system (a bath) and all the transition moment arises from the transition moment in the two-level system. In addition, this coupling must not connect the two levels. The states of the combined system can therefore be written as products of bath states and two-level-system states. Furthermore the transition moment operator is a product of an off-diagonal operator for the two-level system and the unit operator for the bath. Calculation of the nonzero matrix elements of the transition moment involves calculating matrix elements of the unit operator between the bath states appropriate for the lower and upper states of the two-level system, and such a matrix is unitary.

The simplifications that follow from the unitary model are due to the fact that

$$\hat{\mu}^2=\mu_0^2\,, \tag{5.2}$$

and therefore

$$\sin[B_i\hat{\mu}(t)]=\sin(B_i\mu_0)\hat{\mu}(t)/\mu_0\,, \tag{5.3}$$

$$\cos[B_i\hat{\mu}(t)]=\cos(B_i\mu_0)\,. \tag{5.4}$$

Defining pulse areas by

$$A_i=\mu_0 E\tau_i/\hbar \tag{5.5}$$

the correlation-function expressions for the photon echo, stimulated echo, and fluorescence become, respectively,

$$\tilde{p}(2t_1)=(-i/2\mu_0^3)\sin(A_1)\sin^2(\tfrac{1}{2}A_2)\times\langle\hat{\mu}(-t_1)\hat{\mu}(0)\hat{\mu}(t_1)\hat{\mu}(0)\rangle_0\,, \tag{5.6}$$

$$\tilde{p}(2t_1+t_2)=(-i/8\mu_0^3)\sin(A_1)\sin(A_2)\sin(A_3)\times\{\langle\hat{\mu}(-t_1-t_2)\hat{\mu}(-t_2)\hat{\mu}(t_1)\hat{\mu}(0)\rangle_0+\langle\hat{\mu}(-t_1-t_2)\hat{\mu}(0)\hat{\mu}(t_1)\hat{\mu}(-t_2)\rangle_0\}\,, \tag{5.7}$$

$$\mathscr{I}_{\rm fl}(t)\propto\mu_0^{-2}\sin^2(\tfrac{1}{2}A)\langle\hat{\mu}(0)\hat{\mu}(t)\hat{\mu}(t)\hat{\mu}(0)\rangle_0\,. \tag{5.8}$$

Each observable is related to a four $\hat{\mu}$ correlation function that involves 3, 4, and 2 times, respectively.

VI. DISCUSSION

A. Bixon-Jortner model of radiationless transitions

As a special case of the factorization model discussed in Sec. IV, let us consider a QTLS with a single ground state, $|a\rangle$, and an excited-state multiplet whose levels form a continuum. Taking $x_a=0$, then $g(t)=f_0(t)=1$, and from Eq. (4.27) we see that $\mathscr{I}(\omega)$ and $f_1(t)$ are related by a Fourier transform. Since the excited multiplet is a continuum, $\mathscr{I}(\omega)$ is a smooth function of ω. Reasonable assumptions for $\mathscr{I}(\omega)$ of a Gaussian or a Lorentzian lead to a Gaussian or exponential decay of $f_1(t)$. Since many experimental decays are exponential, we focus on the Lorentzian assumption here:

$$\mathscr{I}(\omega)=(\Gamma/\pi)[(\omega-\Omega)^2+\Gamma^2]^{-1}\,. \tag{6.1}$$

With this choice of line shape $f_1(t)$ is simply

$$f_1(t)=\exp(-\Gamma|t|-i\Omega t)\,. \tag{6.2}$$

For instance, then, the fluorescence decay is [from Eq. (4.26)]

$$\mathscr{I}_{\rm fl}(t)\propto\exp(-2\Gamma t)\,. \tag{6.3}$$

This is precisely the result obtained by Bixon and Jortner in their model of radiationless transitions in isolated molecules.[31] In their model the excited-state manifold consists of a singlet electronic state with a transition moment to the ground state, coupled to a manifold of other excited states with no transition moments. When the full excited-state manifold is diagonalized they find an approximately Lorentzian homogeneous line shape. The fluorescence decay occurs because the fluorescing singlet state is not an eigenstate of the Hamiltonian. In the context of Mukamel's recent paper,[38] it is interesting that the time evolution of a superposition state looks like a T_1 process. To make the

correspondence with our model, we note that we work in the eigenstate representation; therefore the "singlet" state $\hat{\mu}\,|\,a\rangle$ is a superposition of eigenstates.

Using the exponential form of $f_1(t)$, Eq. (6.2), to evaluate the photon and stimulated-echo decays from Eqs. (4.22), (4.24), and (2.22), we find

$$\mathcal{I}_{\rm pe}(2t_1)\propto\exp(-4\Gamma t_1) \tag{6.4}$$

and

$$\mathcal{I}_{\rm se}(2t_1+t_2)\propto\exp(-4\Gamma t_1)[1+\exp(-2\Gamma t_2)]^2\ . \tag{6.5}$$

It is interesting to recognize that Eqs. (6.3)–(6.5) are precisely the forms of decay calculated from a strictly two-level system where the excited-state population is depleted with a rate 2Γ while the ground-state level is not repopulated.[39,40] Thus the preceding calculation provides theoretical support for the two-level phenomenology of radiationless transitions. Invoking such a two-level model including *radiative* decay, Wiersma *et al.*[40,41] have shown experimentally that one can find the radiationless contribution to the lifetime from the nonexponential decay of the stimulated echo.

We should also point out that Yeh and Eberly[37] have examined a model identical to the one discussed above. For a *single* system they found that there was no echo signal for times long compared to the inverse frequency width of the excited-state band. However, for the *inhomogeneous distribution* of systems that we have considered, we found that fluorescence, photon echo, and stimulated-echo signals do occur for times long compared to the inverse of the inhomogeneous frequency width, but *short* compared to the inverse of the single-system frequency width.

B. Photon echoes in molecular crystals

We conclude by speculating about the resolution of a puzzling aspect of the experiments by Cooper *et al.*[23] and Morsink *et al.*[22] on photon echoes and fluorescence from impurity molecules in molecular crystals. In these experiments, the laser pulse was tuned to the zero-phonon absorption line of the impurity molecules. Defining T_2 and T_1 by

$$\mathcal{I}_{\rm pe}(2t_1)\propto\exp(-4t_1/T_2)\ , \tag{6.6}$$

$$\mathcal{I}_{\rm fl}(t)\propto\exp(-t/T_1)\ , \tag{6.7}$$

both groups found that

$$1/T_2=1/2T_1+1/T_2'\ , \tag{6.8}$$

where $1/T_2'$ is nonzero even in the limit of zero concentration of impurities. Furthermore, recent experiments by the Fayer group[42] show that $1/T_2'$ is independent of temperature at low temperatures (below 1.8 K) and thus extrapolates to a nonzero value at $T=0$ K.

The usual way of interpreting photon-echo data when the zero-phonon line is excited is via the theory of the homogeneous line shape. The homogeneous line shape is related to the equilibrium dipole-moment autocorrelation function. By *assuming* that the long-time dependence of the echo amplitude is governed by that of the autocorrelation function, one concludes that the echo amplitude is related to a Fourier transform of the homogeneous line shape

$$\tilde{p}(2t_1)\propto\int_{-\infty}^{\infty}d\omega\,e^{-i\omega 2t_1}\mathcal{I}(\omega)\ . \tag{6.9}$$

For a Lorentzian zero-phonon line with linewidth $\Delta\nu$, this leads to

$$1/T_2=\pi\Delta\nu\ . \tag{6.10}$$

The linewidth has lifetime $(1/2\pi T_1)$ and nonlifetime $(\Delta\nu')$ contributions:

$$\pi\Delta\nu=1/2T_1+\pi\Delta\nu'\ . \tag{6.11}$$

Theoretical models of nonlifetime line broadening due to excitation-phonon coupling predict that $\Delta\nu'$ is very strongly temperature dependent at low temperatures and vanishes at $T=0$ K.[36,43–46] (A notable exception is the work[47,48] based on Krivoglaz's model[49] of linear excitation coupling to anharmonic phonons. However, in a later paper Krivoglaz[50] corrects an error in his original calculation and thus brings his work into qualitative agreement with other theoretical models.) Therefore if Eq. (6.10) is invoked there is a clear discrepancy between line-shape theory and the echo experiments.

The excitation-phonon model for impurities in a crystal involves a two-level system (the bare excitation) with a transition moment, coupled to bath degrees of freedom (the phonons) with no transition moment. This is precisely the situation described by the unitary model of Sec. V. Although the excitation-phonon model is not strictly a QTLS (because the phonon progression is of infinite extent), it is nevertheless tempting to apply our results. We found that the photon-echo amplitude is [Eq. (5.6)]

$$\tilde{p}(2t_1)\propto\langle\hat{\mu}(-t_1)\hat{\mu}(0)\hat{\mu}(t_1)\hat{\mu}(0)\rangle_0\ . \tag{6.12}$$

For times long compared to characteristic phonon correlation times it might be reasonable to assume that

$$\langle\hat{\mu}(-t_1)\hat{\mu}(0)\hat{\mu}(t_1)\hat{\mu}(0)\rangle_0 \approx \langle\hat{\mu}(-t_1)\hat{\mu}(0)\rangle_0 \times\langle\hat{\mu}(t_1)\hat{\mu}(0)\rangle_0 , \tag{6.13}$$

thus implying that

$$\tilde{p}(2t_1)\propto\left|\int_{-\infty}^{\infty}d\omega\, e^{-i\omega t_1}\mathcal{I}(\omega)\right|^2 , \tag{6.14}$$

which provides the connection between the photon echo and the homogeneous absorption line shape. We note that for a Lorentzian line shape this relation also leads to Eq. (6.10). The derivation of Eq. (6.12), however, depended on the assumption that the durations of the excitation pulses were short compared to the frequency widths of the multiplets. In this case the relevant frequency is ω_D, the Debye frequency. Thus we emphasize that the (admittedly tenuous) steps leading to the connection Eq. (6.14) are only valid for $\tau\omega_D << 1$, which are very short pulses indeed. For the pulse durations that are at present experimentally available ($\tau\omega_D >> 1$) it is not yet clear how to proceed, but it seems likely that even in this example the photon-echo decay will not be simply related to the homogeneous linewidth.

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APPENDIX: FULLY QUANTUM-MECHANICAL RESULT FOR THE TIME DEPENDENCE OF THE FLUORESCENCE INTENSITY

In this appendix, we derive Eq. (2.32) for the time dependence of the fluorescence from a QTLS after it has been subjected to a pulse of electromagnetic radiation. Since fluorescence is a spontaneous emission process, we use a quantum-mechanical treatment of the radiation field to obtain a correct description of the process. The method we use is equivalent to the usual quantum-mechanical theory of spontaneous emission with the exception that we consider the case in which the state of the matter before the emission process is a superposition of matter-energy eigenstates rather than a single eigenstate.

At the end of the excitation pulse, which for the purpose of this discussion we define to be $t=0$, the matter state is

$$|\psi(0)\rangle=\sum_a d_a|a\rangle+\sum_b d_b|b\rangle . \tag{A1}$$

In the absence of interaction with the radiation field, the time-dependent state would be

$$|\psi_0(t)\rangle=\sum_a d_a(t)|a\rangle+\sum_b d_b(t)|b\rangle , \tag{A2}$$

where

$$d_a(t)=d_a\exp(-ix_at) , \tag{A3}$$

$$d_b(t)=d_b\exp[-i(\Omega+\delta+x_b)t] . \tag{A4}$$

The elements of the density matrix are

$$\rho_{cc'}(t)\equiv d_c(t)d_{c'}^*(t) . \tag{A5}$$

Consider

$$\sum_a\langle a|\hat{\mu}\rho(t)\hat{\mu}|a\rangle=\sum_{abb'}\mu_{ab'}\rho_{b'b}(t)\mu_{ba} =\sum_{abb'}\mu_{ab'}\mu_{ba}d_{b'}d_b^* \times\exp[-i(x_{b'}-x_b)t] . \tag{A6}$$

This quantity is on the right-hand side of (2.32), and we wish to show that it is proportional to the time-dependent fluorescence intensity $\mathcal{I}_{\rm fl}(t)$.

To describe the effect of interaction of matter with radiation, we use the usual Hamiltonian

$$H=H_0+H_r+V , \tag{A7}$$

where H_0 is the matter Hamiltonian, with eigenvalues given in (2.1)–(2.3), H_r is the radiation Hamiltonian, and V is the interaction between radiation and matter. The eigenfunctions of H_r are the familiar vacuum state, 1 photon state, 2 photon states, etc. The interaction V is $-\hat{\mu}\hat{E}$, where $\hat{\mu}$ is the x component of the matter dipole-moment operator and $\hat{E}$ is the x component of the electric field operator. (We are interested in fluorescence polarized in the x direction.) The basis functions we use are denoted $|cr\rangle$, where c is a matter quantum number, with the same meaning as in Sec. II,

and r is a radiation quantum number. We will be concerned only with the vacuum ($r=0$) and one-photon ($r=q$) radiation states, where q denotes the wave vector of the photon. V has nonzero matrix elements between the vacuum and one-photon states:

$$\langle cq \mid V \mid c'0\rangle = -E_{q0}\mu_{cc'} . \tag{A8}$$

At time 0, the matter state is given by (A1) and the radiation state is a vacuum. Therefore the full state is

$$|\Psi(0)\rangle = \sum_a d_a \mid a0\rangle + \sum_b d_b \mid b0\rangle , \tag{A9}$$

where d_a and d_b have the same value as in (A1). We want to calculate $|\Psi(t)\rangle$ to first order in V. To zeroth order, the state is

$$|\Psi_0(t)\rangle = \sum_a d_a(t) \mid a0\rangle + \sum_b d_b(t) \mid b0\rangle , \tag{A10}$$

where $d_a(t)$ and $d_b(t)$ are given in (A3) and (A4). To first order in V, $|\Psi(t)\rangle$ can contain contributions from one-photon basis functions of the form $|aq\rangle$. We write the time-dependent state as

$$\begin{aligned}|\Psi(t)\rangle = &\sum_a d_{a0}(t)\exp(-ix_a t)\mid a0\rangle \\ &+\sum_b d_{b0}(t)\exp[-i(\Omega+\delta+x_b)t]\mid b0\rangle \\ &+\sum_{aq} d_{aq}(t)\exp[-i(x_a+\omega_q)t]\mid aq\rangle ,\end{aligned} \tag{A11}$$

where ω_q is the frequency of a photon with quantum number q, and

$$\begin{aligned} d_{a0}(0)&=d_a , \\ d_{b0}(0)&=d_b , \\ d_{aq}(0)&=0 . \end{aligned} \tag{A12}$$

The total probability that one photon exists at time t is the sum of the probabilities of being in the states $|aq\rangle$ or

$$\sum_{aq} |d_{aq}(t)|^2 .$$

The rate of fluorescence emission is just the time derivative of this, or

$$\mathcal{I}_{\rm fl}(t) = \frac{d}{dt}\sum_{aq} |d_{aq}(t)|^2 . \tag{A13}$$

We want to show that this is equal to the right-hand side of (A6).

To evaluate $d_{aq}(t)$, we note from (A11) that

$$d_{aq}(t) = \langle aq \mid \Psi(t)\rangle \exp[i(x_a+\omega_q)t] . \tag{A14}$$

It follows from Schrödinger's equation that

$$\dot{d}_{aq}(t) = (-i/\hbar)\langle aq \mid V \mid \Psi(t)\rangle \exp[i(x_a+\omega_q)t] , \tag{A15}$$

where we have used the fact that

$$\langle aq \mid (H_0+H_r) = \hbar(x_a+\omega_q)\langle aq \mid .$$

To evaluate this to first order in V, we replace $|\Psi(t)\rangle$ by $|\Psi_0(t)\rangle$ and obtain

$$\dot{d}_{aq}(t) = \frac{i}{\hbar}\sum_b \mu_{ab}E_{q0}d_b \exp[-i(\Omega+\delta+x_b-x_a-\omega_q)t] . \tag{A16}$$

Integrating this with regard to t, squaring, and substituting into (A13), we obtain

$$\mathcal{I}_{\rm fl}(t) = \frac{1}{\hbar^2}\frac{d}{dt}\sum_{abb'}\int_0^t dt'\int_0^t dt'' d_b^* d_{b'}\mu_{ab}^*\mu_{ab'}\exp[i(x_b-x_{b'})t']\exp[i(\Omega+\delta+x_{b'}-x_a)(t'-t'')]Q(t'-t'') , \tag{A17}$$

where

$$Q(t) = \sum_q |E_{q0}|^2 \exp(-i\omega_q t) . \tag{A18}$$

The Fourier transform of $Q(t)$ is

$$\hat{Q}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}Q(t) = 2\pi\sum_q |E_{q0}|^2\delta(\omega-\omega_q). \tag{A19}$$

$\hat{Q}(\omega)$ is a one-photon density of states, with the states weighted by their value of $|E_{q0}|^2$, which is a measure of the ease with which the states can be prepared from the vacuum by creation of one photon. The function $Q(t)$ is highly peaked when its argument is zero. Hence in (A17) we extend the t'' integral to $-\infty$ and $+\infty$. It follows that

$$\mathcal{I}_{\rm fl}(t)=\frac{1}{\hbar^2}\frac{d}{dt}\sum_{abb'}\hat{Q}(\Omega+\delta+x_{b'}-x_a)\times\int_0^t dt' d_b^* d_{b'}\mu_{ab}^*\mu_{ab'}\times\exp[i(x_b-x_{b'})t'] .$$

We assume that the one-photon density of states is slowly varying over frequency ranges of the order of Δ_{aa} and Δ_{bb}, and so we obtain

$$\mathcal{I}_{\rm fl}(t)=\frac{\hat{Q}(\Omega)}{\hbar^2}\sum_{abb'}d_b^* d_{b'}\mu_{ab}^*\mu_{ab'}\exp[i(x_b-x_{b'})t] ,$$

which is the same as the right-hand side of (A6) Q.E.D.

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