Four-wave mixing using partially coherent fields in systems with spatial correlations

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A microscopic correlation function expression for the signal in four-wave mixing is developed. Both stationary and transient (i.e., photon-echo) experiments with coherent or incoherent radiation fields are considered. In general, these observables are described by an eight-point correlation function of the dipole operator involving two particles, and the signal cannot be written as an amplitude squared. Conditions under which the correlation function may be factorized into a product of two four-point, single-particle correlation functions are specified. In this case the conventional approach, based on calculating a nonlinear polarization and substituting it as a source in Maxwell's equations, is justified. However, in the presence of long-range spatial correlations in the sample (e.g., near critical points) the conventional formulation breaks down and the present theory should be used.

I. INTRODUCTION

Four-wave-mixing (4WM) signals are usually calculated in two steps. First, the material system is assumed to interact with three incident light fields, creating a nonlinear polarization with a specified wave vector and frequency. This polarization can be expressed in terms of the nonlinear susceptibility $\chi^{(3)}$. Subsequently, this polarization is substituted as a source into Maxwell's equations and generates the signal field.[1–6] This procedure is used both for steady-state and for transient (e.g., free-induction decay, photon echoes) observables. Within this framework, the coherent nonlinear process is always characterized by an amplitude (averaged over any thermal bath), and the coherent signal intensity is given by the absolute square of this amplitude. In this article we shall develop a microscopic correlation-function expression for the signal in four-wave mixing which does not use the above procedure. We show that the signal is, in general, given in terms of an eight-point, two-particle correlation function of the dipole operator.[7,8] In the absence of long-range spatial correlations in the sample, this correlation function may be factorized into a product of two four-point, single-particle correlation functions. Under these conditions, the conventional procedure holds, $\chi^{(3)}$ is given by the four-point, single-particle correlation function, and the signal may be expressed as by an amplitude squared.[5,6,9–11] We predict, however, that in the presence of long-range spatial correlations (e.g., near critical points) this approximation breaks down, and the present, more general expression, needs to be used. Applications are made to photon echoes[12] and to stationary 4WM with incoherent light sources.[13–15] The latter technique was shown recently to yield a femtosecond temporal resolution by using two incoherent fields with a variable delay between them. Our general expression for this experiment involves an eight-point correlation function of the dipole operator and a six-point correlation function of the radiation field.

II. THE FOUR-WAVE-MIXING SIGNAL: A PROBE FOR AN EIGHT-POINT CORRELATION FUNCTION

Our microscopic model for four-wave mixing consists of four parts: a system of noninteracting absorbers, each having a few levels, a thermal bath of particles which do not interact directly with the radiation field but do interact with the absorbers, three classical external electromagnetic fields which are parametrically mixed in the 4WM process, and, finally, a fourth mode of the electromagnetic field, which is vacant initially and is being generated in the process. This mode will be treated quantum mechanically in order to account properly for spontaneous emission. The total model Hamiltonian is

$$H=H_S+H_B+H_{SB}+\sum_{n=1}^{4} V_n(t)\ . \tag{1}$$

Here, H_S, H_B, and H_{SB} denote the system Hamiltonian, the bath Hamiltonian, and their interactions, respectively. $V_n(t)$ is the interaction of the system with the nth mode of the electromagnetic field. For the input classical modes ($n=1,2,3$), we have[1–6]

$$V_n(t)=E_n(t)\sum_{\alpha=1}^{N}[\,V_+^{n\alpha}(t)\exp(-i\mathbf{k}_n\cdot\mathbf{r}_\alpha)+V_-^{n\alpha}(t)\exp(i\mathbf{k}_n\cdot\mathbf{r}_\alpha)]\ , \tag{2a}$$

where

$$V_+^{n\alpha}(t)=\mu^\alpha\exp(i\omega_n t)\ , \tag{2b}$$

$$V_-^{n\alpha}(t)=\mu^\alpha\exp(-i\omega_n t)\ . \tag{2c}$$

Here, ω_n and k_n denote the frequency and wave vector of the nth field $n=1,2,3,4$, E_n is the amplitude of the (classical) nth field $n=1,2,3$, μ^α denotes the dipole operator of the α particle, and $V_\pm$ stands for the positive and negative frequency parts of the fields. For steady-state 4WM, $E_n(t)$ is time independent. Otherwise it contains the temporal profile of the incident pulses and also effects of field incoherence via a stochastic modulation. For the fourth mode ($n=4$), which is treated quantum mechanically, we have

$$V_4(t)=\sum_{\alpha=1}^{N}[V_+^{4\alpha}(t)\exp(-i\mathbf{k}_4\cdot\mathbf{r}_\alpha)+V_-^{4\alpha}(t)\exp(i\mathbf{k}_4\cdot\mathbf{r}_\alpha)]\ , \tag{3a}$$

where

$$V_+^{4\alpha}(t)=C\mu^\alpha a_4^\dagger\exp(i\omega_4 t)\ , \tag{3b}$$

$$V_-^{4\alpha}(t)=C^*\mu^\alpha a_4\exp(-i\omega_4 t)\ . \tag{3c}$$

Here, $a_4^\dagger(a_4)$ is the creation (annihilation) operator for the fourth mode, and

$$C=-i\omega_4\left[\frac{4\pi\hbar}{2\omega_4 L^3}\right]^{1/2}\ , \tag{3d}$$

where we adopt a box normalization, and L is the size of the box. For subsequent manipulations we shall also define

$$\overline{V}(t)\equiv\sum_{n=1}^{4}V_n(t) \tag{4a}$$

and

$$V(t)\equiv\sum_{n=1}^{3}V_n(t)\ . \tag{4b}$$

In this article we shall use the Liouville-space (tetradic) notation,[9,10] whereby an ordinary operator is represented by a ket $|B\rangle\rangle$. The total density matrix ρ obeys the Liouville equation

$$\frac{d\rho}{dt}=-iL\rho\ , \tag{5a}$$

where we have set $\hbar=1$, and where

$$L\equiv[H,\dots]\ . \tag{5b}$$

Equation (5b) implies that $LA\equiv[H,A]$ for any operator A, etc. We shall also define

$$\mathscr{V}(t)\equiv[V(t),\dots]\ , \tag{6a}$$

$$\mathscr{V}_n(t)\equiv[V_n(t),\dots]\ , \tag{6b}$$

$$\overline{\mathscr{V}}(t)\equiv[\overline{V}(t),\dots]\ . \tag{6c}$$

We are now in a position to introduce the formal definition of the signal in 4WM. We shall be interested in a parametric process, whereby the generated field ω_4 satisfies the phase-matching condition, which implies that the signal is proportional to $\delta(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3-\mathbf{k}_4)$. The generated coherent signal may be defined by considering the rate of emission of photons into mode 4. The operator representing this rate is

$$B\equiv\frac{d}{dt}a_4^\dagger a_4=i[V_4(t),a_4^\dagger a_4]\ , \tag{7}$$

which in Liouville-space notation assumes the form

$$|B\rangle\rangle\equiv i\mathscr{V}_4(t)|a_4^\dagger a_4\rangle\rangle\ . \tag{8}$$

The photon-emission rate at time t into mode 4 is the expectation value of $|B\rangle\rangle$, i.e.,

$$\langle\langle B|\rho(t)\rangle\rangle\equiv\mathrm{Tr}[B^\dagger\rho(t)]\ . \tag{9}$$

where $\rho(t)$ is the total density matrix (system plus field plus bath) at time t. Since we shall consider only contributions to Eq. (9) which satisfy the phase-matching condition $\delta(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3-\mathbf{k}_4)$, we may integrate the signal over all ω_4 without any loss of information. Our definition for the four-wave-mixing signal (rate of change of the intensity of field 4) will, therefore, be

$$S=\int d\omega_4\langle\langle B|\rho(t)\rangle\rangle\ , \tag{10}$$

or, using Eq. (8),

$$S=-i\int d\omega_4\langle\langle a_4^\dagger a_4|\mathscr{V}_4(t)|\rho(t)\rangle\rangle\ . \tag{11}$$

In order to proceed further, we need to expand $\rho(t)$ to the necessary order in $\overline{\mathscr{V}}(t)$. Initially at $t\rightarrow-\infty$ we have

$$|\rho(-\infty)\rangle\rangle=|\rho_S(-\infty)\rangle\rangle\,|\rho_B(-\infty)\rangle\rangle\,|\rho_4(-\infty)\rangle\rangle\ ; \tag{12}$$

the system and bath are in thermal equilibrium and mode 4 is in the vacuum state

$$|\rho_4(-\infty)\rangle\rangle=|\mathrm{vac},\mathrm{vac}\rangle\rangle\ . \tag{13}$$

Equation (13) is the Liouville-space notation for

$$\rho_4(-\infty)=|\mathrm{vac}\rangle\langle\mathrm{vac}|\ . \tag{13a}$$

It is clear that in order for the trace over ω_4 in Eq. (11) not to vanish, we need to apply $\mathscr{V}_4$ twice, one $\mathscr{V}_4$ acting from the left and the other from the right. If these two interactions occur with two different particles (say α and β), we shall get a factor $\exp[-i\mathbf{k}_4\cdot(\mathbf{r}_\alpha-\mathbf{r}_\beta)]$ [Eq. (3)]. If $\alpha=\beta$, i.e., both interactions occur with the same particle, then we lose all information about $\mathbf{k}_4$, and the process will not be phase-matched. It is, therefore, clear that we need at least two different material particles in order to achieve the phase matching. The simplest way this may be accomplished is by expanding Eq. (11) to eighth order[7,8] in $\overline{\mathscr{V}}(t)$, whereby each field 1,2,3,4 interacts once with atom α and once with atom β, resulting in the spatial factor

$$\exp[i(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3-\mathbf{k}_4)\cdot(\mathbf{r}_\alpha-\mathbf{r}_\beta)]\ .$$

When this factor is summed over $\mathbf{r}_\alpha,\mathbf{r}_\beta$, it will result in the necessary phase-matching condition. Another way to rationalize why we need our expression to eighth order in $\overline{\mathscr{V}}$ is by noting that we are looking for a four-photon process whose amplitude is fourth order in $\overline{\mathscr{V}}$ and intensity (amplitude squared) must be eighth order in $\overline{\mathscr{V}}$. The density matrix $\rho(t)$ must, therefore, be expanded to seventh order in $\overline{\mathscr{V}}(t)$ (second order in $\mathscr{V}_1$, $\mathscr{V}_2$, and $\mathscr{V}_3$, and first order in $\mathscr{V}_4$) in order to obtain S to eighth order. We, therefore, finally get

$$S=-i\int d\omega_4\langle\langle a_4^\dagger a_4|\mathscr{V}_4(t)|\rho^{(7)}(t)\rangle\rangle\ . \tag{14}$$

Making use of standard perturbation theory, we then have

$$S=(-i)^8\int d\omega_4\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\cdots\int_{-\infty}^{\tau_6}d\tau_7\langle\langle a_4^\dagger a_4\,|\,\mathscr{V}_4(t)G(t-\tau_1)\overline{\mathscr{V}}(\tau_1)G(\tau_1-\tau_2)\overline{\mathscr{V}}(\tau_2)\cdots$$
$$\times G(\tau_6-\tau_7)\overline{\mathscr{V}}(\tau_7)\,|\,\rho(-\infty)\rangle\rangle\ , \tag{15}$$

where each $\overline{\mathscr{V}}_n$, $n=1,\ldots,4$, appears twice in Eq. (15). $G(\tau)$ is the Green's function for the material system

$$G(\tau)\equiv\exp(-iL_0\tau)\ , \tag{16}$$

where

$$H_0\equiv H_S+H_B+H_{SB} \tag{17a}$$

and

$$L_0\equiv[H_0,\ldots]\ . \tag{17b}$$

In Eq. (15) there are two $\mathscr{V}_4$ factors. One of them is $\mathscr{V}_4(t)$, which corresponds to the latest time. Let us assume that the other one is at τ_p, i.e.,

$$\overline{\mathscr{V}}(\tau_p)=\mathscr{V}_4(\tau_p)\ , \tag{18}$$

where $p=1,2,\ldots,7$. The only ω_4 dependence of the integrand in Eq. (15) will come from $\mathscr{V}_4(\tau_p)$ and $\mathscr{V}_4(t)$. Since the field 4 is initially in the $|\text{vac}\rangle\langle\text{vac}|$, the only nonvanishing contributions to S will come from

$$a_4^\dagger(t)\,|\,\text{vac}\rangle\langle\text{vac}\,|\,a_4(\tau_p) \tag{19}$$

or

$$a_4^\dagger(\tau_p)\,|\,\text{vac}\rangle\langle\text{vac}\,|\,a_4(t)\ . \tag{20}$$

This implies that the ω_4 dependence of Eq. (15) is of the form $\exp[\pm i\omega_4(t-\tau_p)]$. The ω_4 integration in Eq. (15) can thus be performed, resulting in

$$\int\exp[-i\omega_4(t-\tau_p)]d\omega_4=2\pi\delta(t-\tau_p)\ . \tag{21}$$

Since the times τ_n are fully ordered, this implies that τ_p has to be the time closest to t, i.e., $\tau_p=\tau_1$. Utilizing Eq. (21), the τ_1 integration in Eq. (15) can also be made. In other words, the only terms contributing to 4WM do so when the last two interactions are $\mathscr{V}_4$ and occur at the same time at the end of the process. Using this and changing integration variables, we finally get

$$S=2\pi\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\cdots\int_{-\infty}^{\tau_5}d\tau_6\langle\langle a_4^\dagger a_4\,|\,\mathscr{V}_4(t)\mathscr{V}_4(t)G(t-\tau_1)\mathscr{V}(\tau_1)G(\tau_1-\tau_2)\mathscr{V}(\tau_2)$$
$$\times G(\tau_2-\tau_3)\mathscr{V}(\tau_3)G(\tau_3-\tau_4)\mathscr{V}(\tau_4)$$
$$\times G(\tau_4-\tau_5)\mathscr{V}(\tau_5)G(\tau_5-\tau_6)\mathscr{V}(\tau_6)\,|\,\rho(-\infty)\rangle\rangle\ . \tag{22}$$

Equation (22) is the main formal result of this article and provides the basis for the description of a variety of 4WM processes. The following points should be noted regarding Eq. (22).

(1) The eight interaction terms in Eq. (22) represent two interactions with each of the four modes.

(2) The times $t\geq\tau_1\geq\cdots\geq\tau_6$ are completely ordered. Therefore, we first make six interactions with fields 1,2,3 (in all orders in time), and the last two interactions are with mode 4. There are $6!/(2!)^3=90$ permutations of the relative order in time of the six interactions with fields 1, 2, and 3.

(3) Consider the last two interactions $\mathscr{V}_4$; one of them has to be from the left and the other from the right in order to get the phase matching. There are $2^6=64$ possibilities of acting with the other six interactions from the left or the right. Overall, we have $90\times64=5760$ terms in Eq. (22). Many of them will be negligible within the rotating-wave approximation and will not contribute, in practice.

(4) We should consider two different system particles, located at $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$. Each field will interact once with α and once with β. This will result in the overall spatial factor

$$\exp[i(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3-\mathbf{k}_4)\cdot(\mathbf{r}_\alpha-\mathbf{r}_\beta)]\ .$$

This factor, under certain conditions, will result in the phase matching.

(5) The conventional procedure for calculating nonlinear optical signals[1-6] is based on calculating a nonlinear polarization, which is then substituted as a source term in the Maxwell equations. The signal is then written as a square of an amplitude. The present derivation shows that S, in general, cannot be factorized into an amplitude squared, and, therefore, the range of applicability of the Bloch-Maxwell equation is limited. In general, we need a theory for the signal, *not for the amplitude.* The conditions for factorizing S [Eq. (22)] as an amplitude squared, whereby the Bloch-Maxwell equations apply, will be discussed in the coming sections.

III. APPLICATION TO PHOTON ECHOES

The photon echo is the simplest 4WM observable. In this case, the number of terms in Eq. (22) reduces enormously.[3,4,10,11] We consider two short pulses at times t_1 and t_2, i.e.,

$$E_1(t)=\overline{E}_1\delta(t-t_1)\ ,$$
$$E_2(t)=E_3(t)=\overline{E}_2\delta(t-t_2)\ . \tag{23}$$

The echo signal has a wave vector $\mathbf{k}_4=2\mathbf{k}_2-\mathbf{k}_1$, so that in our previous notation we should take

$$\mathbf{k}_1 \to -\mathbf{k}_1 \,, \qquad \mathbf{k}_2 = -\mathbf{k}_3 \,. \tag{24}$$

We shall denote the separation (in time) between the pulses by

$$T \equiv t_2 - t_1 \,. \tag{25}$$

In order to generate the echo signal, we take the first two interactions in Eq. (22) [$\mathscr{V}(\tau_6)$ and $\mathscr{V}(\tau_5)$] to occur with E_1, and the last four [$\mathscr{V}(\tau_4), \ldots, \mathscr{V}(\tau_1)$] to occur with E_2. Upon the substitution of Eqs. (23) in Eq. (22), we note that Eq. (22) now contains six δ functions, all integrations can be performed immediately, and the time ordering is also fixed. Using Eqs. (22) and (23), the echo signal at $\mathbf{k}_4 = 2\mathbf{k}_2 - \mathbf{k}_1$ is then given by

$$S(t,T) = 2\pi |\overline{E}_1|^2 |\overline{E}_2|^4 |C|^2 \sum_{\alpha,\beta} \langle\langle a_4^\dagger a_4 | \mathscr{V}_-^{4\beta}(t) \mathscr{V}_+^{4\alpha}(t) G(t-t_2) \mathscr{V}_+^{2\beta}(t_2) \mathscr{V}_+^{2\beta}(t_2) \mathscr{V}_-^{2\alpha}(t_2) \mathscr{V}_-^{2\alpha}(t_2) G(t_2-t_1)$$
$$\times \mathscr{V}_-^{1\beta}(t_1) \mathscr{V}_+^{1\alpha}(t_1) | \rho(-\infty) \rangle\rangle \exp[i(2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_4)\cdot(\mathbf{r}_\alpha - \mathbf{r}_\beta)] \,. \tag{26}$$

Note that the choice of $\mathscr{V}_\pm$ was dictated uniquely by the phase-matching requirement, i.e., the factor

$$\exp[i(2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_4)\cdot(\mathbf{r}_\alpha - \mathbf{r}_\beta)] \,.$$

Equation (22) contains many more terms which do not contain this factor and will thus appear in a different direction in space. Equation (26) can be rearranged in a more compact form. Let us assume that each of the absorbers (α) is a two-level system with levels $|a_\alpha\rangle$ and $|b_\alpha\rangle$. The dipole operator is then given by

$$\mu^\alpha = \mu_{ab} |a_\alpha\rangle\langle b_\alpha| + \mu_{ba} |b_\alpha\rangle\langle a_\alpha| \,. \tag{27}$$

Within the rotating-wave approximation, we consider only slowly varying components of $V(t)$. Equations (2) thus assume the form

$$V_+^{n\alpha}(t) = \mu_{ab} |a_\alpha\rangle\langle b_\alpha| \exp(i\omega_n t) \tag{28}$$

and

$$V_-^{n\alpha}(t) = \mu_{ba} |b_\alpha\rangle\langle a_\alpha| \exp(-i\omega_n t) \,. \tag{29}$$

We shall further introduce the definitions

$$V_{ab}^\alpha(t) \equiv \langle a_\alpha | \exp(iH_0 t) \mu^\alpha \exp(-iH_0 t) | b_\alpha \rangle \,. \tag{30}$$

Equation (26) contains eight $\mathscr{V}$ factors; each one is a commutator and can act either from the left or from the right. Altogether, there are $2^8 = 256$ terms in this equation. Within the rotating-wave approximation [Eq. (28)], however, the $\mathscr{V}(t_1)$ and $\mathscr{V}(t)$ terms can act only once. Regarding the four $\mathscr{V}(t_2)$ terms, two of them act from the left and two from the right. There are four ways to do that, resulting in four identical terms. Equation (26) can then be written in the form

$$S(t,T) = 8\pi |\overline{E}_1|^2 |\overline{E}_2|^4 |C|^2 \sum_{\alpha,\beta} \langle V_{ab}^\alpha(-T) V_{ba}^\alpha(0) V_{ab}^\beta(0) V_{ba}^\beta(t-T) V_{ab}^\alpha(t-T) V_{ba}^\alpha(0) V_{ab}^\beta(0) V_{ba}^\beta(-T) \rangle$$
$$\times \exp[i(2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_4)\cdot(\mathbf{r}_\alpha - \mathbf{r}_\beta)] \,. \tag{31}$$

In Eq. (31) we have used the invariance of the correlation function with respect to a translation in time, and have shifted all time arguments by $-T$.

The Feynman diagram corresponding to Eq. (31) is shown in Fig. 1. This diagram displays the relative order in time of the various interactions as well as their nature (with which particle they occur and whether they act from the left or from the right). If particles α and β are uncorrelated, we can factorize the two-particle correlation function in Eq. (31) into a product of two single-particle correlation functions, corresponding to particles α and β. Let us introduce the polarization of particles α and β, i.e.,

$$\langle P_\alpha(t,T) \rangle = 2\overline{E}_1 |\overline{E}_2|^2 C \times \langle V_{ab}^\alpha(-T) V_{ba}^\alpha(0) V_{ab}^\alpha(t-T) V_{ba}^\alpha(0) \rangle \,, \tag{32a}$$

$$\langle P_\beta^*(t,T) \rangle = 2\overline{E}_1^* |\overline{E}_2|^2 C^* \times \langle V_{ab}^\beta(0) V_{ba}^\beta(t-T) V_{ab}^\beta(0) V_{ba}^\beta(-T) \rangle \,. \tag{32b}$$

Equation (31) can then be rearranged as

$$S = 2\pi \sum_{\alpha,\beta} \langle P_\alpha(t,T) \rangle \langle P_\beta^*(t,T) \rangle \times \exp[i(2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_4)\cdot(\mathbf{r}_\alpha - \mathbf{r}_\beta)] \,. \tag{33}$$

Since in this case $\langle P_\alpha \rangle$ does not depend on $\mathbf{r}_\alpha$, we can set $\langle P_\alpha \rangle = \langle P_\beta \rangle = \langle P \rangle$ and perform the α,β summations immediately, resulting in

$$S(t,T) = (2\pi)^4 (N^2/\Omega) |\langle P(t,T) \rangle|^2 \delta(2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_4) \,, \tag{34}$$

where N is the number of particles, and $\langle P(t,T) \rangle$ is given by Eq. (32a). This is the condition for validity of the conventional Bloch-Maxwell procedure.[1-6] However, in the presence of long-range spatial correlations in the sample, we can no longer invoke the factorization of Eq. (33). In

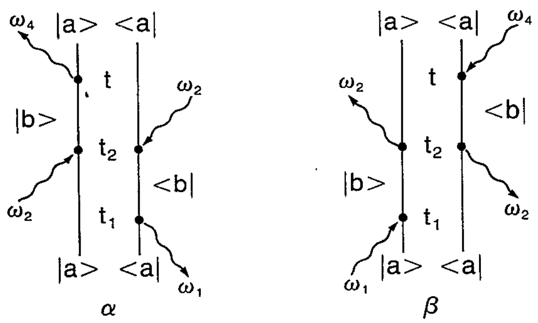

FIG. 1. The two-particle Feynman diagram corresponding to Eq. (31). The diagram shows the time ordering of the interactions of the α and β particles with the two incident fields (ω_1,ω_2) and with the echo mode (ω_4). For each particle the left (right) vertical line represents the bra (ket). The diagram uses the conventional notation (Ref. 3).

that case, we have to evaluate the eight-point correlation function [Eq. (31)], which amounts to the two-particle average $\langle P_\alpha(t,T)P^*_\beta(t,T)\rangle$.

IV. PHOTON ECHOES IN THE PRESENCE OF LONG-RANGE SPATIAL CORRELATIONS

We shall now illustrate Eq. (31) by considering the following model:[12] The material system consists of a collection of two-level systems, denoted $|a_\alpha\rangle$ and $|b_\alpha\rangle$, each having a frequency ω^α_{ba}. We assume two line-broadening mechanisms. The first is an inhomogeneous broadening with a distribution

$$W(\omega_{ba})=\frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(\omega_{ba}-\omega^0_{ba})^2}{2\sigma^2}\right]. \tag{35}$$

In addition, each molecular frequency undergoes a stochastic Gaussian modulation,[9,11,16] i.e.,

$$\omega^\alpha_{ba}=\omega_{ba}+\delta\omega_\alpha(t)\ . \tag{36}$$

$\delta\omega_\alpha(t)$ is a random variable with zero mean,

$$\langle\delta\omega_\alpha(t)\rangle=0\ . \tag{37a}$$

Its correlation function is

$$\langle\delta\omega_\alpha(t)\delta\omega_\alpha(0)\rangle=\Delta^2\exp(-\Lambda t)\ , \tag{37b}$$

where Δ represents the amplitude of the stochastic modulation, and Λ^{-1} is its correlation time. The modulation of different particles may be correlated. We thus assume

$$\langle\delta\omega_\alpha(t)\delta\omega_\beta(0)\rangle=\Phi(\mathbf{r}_{\alpha\beta})\Delta^2\exp(-\Lambda t),\quad \alpha\neq\beta\ . \tag{38}$$

$\Phi(\mathbf{r}_{\alpha\beta})$ is finite over a correlation length ξ and is zero otherwise. Two reasonable models for Φ are

$$\Phi(\mathbf{r}_{\alpha\beta})=\begin{cases}1 & \text{for } |\mathbf{r}_{\alpha\beta}|<\xi\ ,\\ 0 & \text{otherwise}\ ,\end{cases} \tag{39}$$

or

$$\Phi(\mathbf{r}_{\alpha\beta})=\exp(-|\mathbf{r}_{\alpha\beta}|/\xi)\ . \tag{40}$$

Making use of Eq. (31), the photon-echo signal for this model is given by

$$S(t,T)=A\sum_{\alpha,\beta}\exp[-\sigma^2(t-2T)^2]\times\left\langle\exp\left[-i\int_T^t[\delta\omega_\alpha(\tau)-\delta\omega_\beta(\tau)]d\tau+i\int_0^T[\delta\omega_\alpha(\tau)-\delta\omega_\beta(\tau)]d\tau\right]\right\rangle\exp(-2\gamma t)\exp[i\Delta\mathbf{k}\cdot(\mathbf{r}_\alpha-\mathbf{r}_\beta)]\ , \tag{41}$$

where 2γ is the inverse lifetime of the excited state (i.e., $2\gamma\equiv1/T_1$) and we have denoted

$$A\equiv8\pi|\mu_{ab}|^8|\bar{E}_1|^2|\bar{E}_2|^4|C|^2\ , \tag{42}$$

and

$$\Delta\mathbf{k}\equiv2\mathbf{k}_2-\mathbf{k}_1-\mathbf{k}_4\ . \tag{43}$$

In order to evaluate Eq. (41), we shall switch from the summation over α,β to integration, i.e.,

$$\sum_{\alpha,\beta=1}^N\to(N^2/\Omega)\int_0^R d\mathbf{r}_{\alpha\beta}\ , \tag{44}$$

where Ω is the volume of the active nonlinear medium with the radius R, i.e.,

$$\Omega\equiv4\pi R^3/3\ . \tag{45a}$$

For subsequent manipulations we shall also introduce the correlation volume Ω_c, i.e.,

$$\Omega_c\equiv4\pi\xi^3/3\ . \tag{45b}$$

For this model we may evaluate S, Eq. (41), resulting in

$$S(t,T)=A(N^2/\Omega)\exp[-\sigma^2(t-2T)^2-2\gamma t]\times\int_0^R d\mathbf{r}\exp\{-[1-\Phi(\mathbf{r})]f(t,T)\}\exp(i\Delta\mathbf{k}\cdot\mathbf{r})\ . \tag{46}$$

where

$$f(t,T)=4g(t-T)+4g(T)-2g(t)\ , \tag{47}$$

and

$$g(\tau)=(\Delta/\Lambda)^2[\exp(-\Lambda\tau)-1+\Lambda\tau]\ . \tag{48}$$

Equation (46) is our general result for the photon echo in the presence of long-range correlations. We note that $S(t,T)$ is a direct probe for the spatial correlation function $\Phi(\mathbf{r})$.

When the frequency modulations $\delta\omega_\alpha(t_1)$ and $\delta\omega_\beta(t_2)$ at different sites $\alpha\neq\beta$ are *uncorrelated*, i.e., $\xi=0$, we have, using Eqs. (41) and (44),

$$S(t,T)=S_u(t,T)\delta(\Delta\mathbf{k})\ , \tag{49}$$

where

$$S_u(t,T)=(2\pi)^3 A(N^2/\Omega)\times\exp[-2\gamma t-\sigma^2(t-2T)^2-f(t,T)]\ . \tag{50}$$

In the other extreme ($\xi\to\infty$), the line broadening due to the stochastic modulation disappears, since both particles are fully correlated, and we get

$$S(t,T)=S_c(t,T)\delta(\Delta\mathbf{k})\ , \tag{51}$$

where

$$S_c(t,T)=(2\pi)^3 A(N^2/\Omega)\exp[-2\gamma t-\sigma^2(t-2T)^2]\ . \tag{52}$$

In the general case (arbitrary ξ), we get

$$S(t,T)=F_R(\Delta\mathbf{k})S_u(t,T)+F_\xi(\Delta\mathbf{k})[S_c(t,T)-S_u(t,T)]\ , \tag{53}$$

where we denote $\Delta k\equiv|\Delta\mathbf{k}|$, $r\equiv|\mathbf{r}|$, and

$$F_r(\Delta\mathbf{k})=\frac{[\sin(\Delta k\,r)-(\Delta k\,r)\cos(\Delta k\,r)]}{2\pi^2(\Delta k)^3}\ . \tag{54}$$

For $\Delta kr\gg1$, F_r becomes a Dirac δ function, i.e.,

$$F_r(\Delta\mathbf{k})\to\delta(\Delta\mathbf{k})\ , \tag{55}$$

whereas for $\Delta kr\ll1$, we have

$$F_r(\Delta\mathbf{k})\to(2\pi)^{-3}4\pi r^3/3\ . \tag{56}$$

Ordinarily, R is a macroscopic length, say 10^{-3} cm, whereas ξ is short range and microscopic, $\sim10^{-6}$ cm. Under these conditions of short-range correlations, F_R is strongly peaked around the exact phase-matching condition $\Delta\mathbf{k}=0$, and F_ξ is negligible [Eq. (56)]. The signal is given in this case by the first term in Eq. (53). As the correlation length ξ becomes longer, the second term in Eq. (53) grows. F_ξ is also peaked around $\Delta\mathbf{k}=0$, but it is much broader than F_R, since $\xi\ll R$. If we look at a direction slightly off the exact phase matching, i.e., $R^{-1}\ll\Delta k\ll\xi^{-1}$, we shall see only the second component, which will be proportional to the "correlation volume" $F_\xi(\Delta\mathbf{k})=(2\pi)^{-3}\Omega_c$ [Eq. (56)]. This component is induced by the spatial correlations in the sample. Making use of Eqs. (49)–(53), we get in this case

$$S(t,T)=AN^2(\Omega_c/\Omega)\exp[-\sigma^2(t-2T)^2-2\gamma t]\times\{1-\exp[-f(t,T)]\}\ . \tag{57}$$

In the direction of perfect phase matching, $\Delta\mathbf{k}=0$, we have, using Eqs. (49)–(53),

$$S(t,T)=AN^2\exp[-\sigma^2(t-2T)^2-2\gamma t]\times\{[1-(\Omega_c/\Omega)]\exp[-f(t,T)]+(\Omega_c/\Omega)\}\ . \tag{58}$$

The echo signal is usually observed at $t=2T$, whereby the contribution of the inhomogeneous broadening (i.e., the $\exp[-\sigma^2(t-2T)^2]$ factor) has a maximum. In the fast-modulation ($\Lambda\gg\Delta$) limit, we have

$$f(t,T)=2\hat{\Gamma}t\ , \tag{59a}$$

where

$$\hat{\Gamma}=\Delta^2/\Lambda\ . \tag{59b}$$

In this case we get, using Eqs. (50), (52), and (59),

$$S_u(2T,T)\sim\exp[-4(\gamma+\hat{\Gamma})T] \tag{60a}$$

and

$$S_c(2T,T)\sim\exp(-4\gamma T)\ , \tag{60b}$$

whereas in the slow-modulation ($\Lambda\ll\Delta$) limit we have

$$f(t,T)=\Delta^2(t-2T)^2\ . \tag{61}$$

In this case, the line is only inhomogeneously broadened, and the echo signal decays with the T_1 rate [Eqs. (50), (52), and (61)]:

$$S_u(2T,T)=S_c(2T,T)\sim\exp(-4\gamma T)\ . \tag{62}$$

The effect of the long-range spatial correlations should be particularly significant near critical points, whereby ξ diverges.[12,17] The existence of highly activated soft modes near critical points results in dephasing processes which are correlated over a long range. In general, the phase-matching condition $\delta(\Delta\mathbf{k})$ strictly holds only in the two limits of independent, uncorrelated fluctuations [Eq. (49)] or for completely correlated fluctuations [Eq. (51)]. For intermediate values of the correlation length ξ, the temporal and spatial profiles of $S(t,T)$ are coupled, and the $\delta(\Delta\mathbf{k})$ function broadens. It should be emphasized that within the conventional formulation, based on the Bloch-Maxwell equations,[1–6] the effects of long-range spatial correlations cannot be incorporated, and these equations will always result in Eq. (34). This points to a fundamental limitation of the conventional formulation of nonlinear spectroscopy.

V. STATIONARY FOUR-WAVE MIXING WITH INCOHERENT LIGHT SOURCES

In this section we shall assume that the thermal bath is classical. In this case, the operators $V^\alpha(\tau)$ and $V^\beta(\tau)$ are classical functions of the bath variables, and they commute. It is, therefore, convenient to change the time variables $\tau_1,\ldots,\tau_6$ in Eq. (22) as follows: We denote the time for the three interactions with particle α by $t_1\ge t_2\ge t_3$ and those with particle β and $s_1\ge s_2\ge s_3$. We can then rewrite Eq. (22) as follows:

$$S=2\pi\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\int_{-\infty}^{t}ds_1\int_{-\infty}^{s_1}ds_2\int_{-\infty}^{s_2}ds_3\sum_{\alpha,\beta}\langle P_\alpha(t,t_1,t_2,t_3)P_\beta^*(t,s_1,s_2,s_3)\rangle_b\times\exp[i(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3-\mathbf{k}_4)\cdot(\mathbf{r}_\alpha-\mathbf{r}_\beta)]\ , \tag{63}$$

where

$$P_\alpha(t,t_1,t_2,t_3)=\sum_{(p,q,r=1,2,3)}\langle\langle\mu^\alpha|\,G(t-t_1)\mathscr{V}^{p\alpha}(t_1)G(t_1-t_2)\mathscr{V}^{q\alpha}(t_2)\times G(t_2-t_3)\mathscr{V}^{r\alpha}(t_3)\,|\rho(-\infty)\rangle\rangle_s\exp[-i(\omega_1-\omega_2+\omega_3-\omega_4)t] \tag{64a}$$

and

$$P_\beta(t,s_1,s_2,s_3)=\sum_{(p,q,r=1,2,3)}\langle\langle\mu^\beta|\,G(t-s_1)\mathscr{V}^{p\beta}(s_1)G(s_1-s_2)\times\mathscr{V}^{q\beta}(s_2)G(s_2-s_3)\mathscr{V}^{r\beta}(t_3)\,|\rho(-\infty)\rangle\rangle_s\exp[-i(\omega_1-\omega_2+\omega_3-\omega_4)t]\,. \tag{64b}$$

Here the subscript s indicates a trace over the system degrees of freedom, and P_α and P_β are still functions of the bath variables. The subscript b in $\langle\cdots\rangle_b$ indicates averaging over the bath variables. The total trace in Eq. (22) is thus made here in two steps, first over the system [Eqs. (64)] and then over the bath [Eq. (63)]. The sum over p,q,r involves the six permutations of these indexes with 1,2,3 corresponding to all possible orders in time in which the three fields 1,2,3 can act. $\mathscr{V}^{p\alpha}$ is taken to be either $\mathscr{V}_+^{p\alpha}$ or $\mathscr{V}_-^{p\alpha}$ depending on the permutation, so as to yield the correct phase matching,

$$\exp[i(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3-\mathbf{k}_4)\cdot\mathbf{r}_\alpha]\,.$$

There are many more terms in S [Eq. (22)], and we picked the ones with the desired phase-matching factor. We shall now consider several limiting cases of Eq. (63).

A. Stationary four-wave mixing using coherent light sources in the absence of long-range spatial correlations

Let us assume that particles α and β each interact with its own bath, and that they are uncorrelated. In this case, we can factorize the average $\langle P_\alpha P_\beta^*\rangle$ in Eq. (63) into a product of averages $\langle P_\alpha\rangle\langle P_\beta^*\rangle$. We further assume that the three incident fields are stationary and monochromatic; therefore,

$$E_n(t)=E_n,\quad n=1,2,3 \tag{65}$$

where $E_n(t)$ was defined in Eq. (2a). We now introduce the nonlinear susceptibility

$$\chi^{(3)}E_1E_2^*E_3\equiv\int_{-\infty}^{0}dt_1\int_{-\infty}^{t_1}dt_2\times\int_{-\infty}^{t_2}dt_3\langle P_\alpha(0,t_1,t_2,t_3)\rangle_b\,. \tag{66}$$

Note that $\chi^{(3)}$ in this case does not depend on α. Using Eqs. (63) and (66), we finally get

$$S=(2\pi)^4(N^2/\Omega)\,|E_1E_2^*E_3|^2\,|\chi^{(3)}|^2\delta(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3-\mathbf{k}_4)\,. \tag{67}$$

Only under these conditions can we define a nonlinear susceptibility and express the signal as its magnitude squared, in accordance with the Bloch-Maxwell equations.[1-6] General expressions of $\chi^{(3)}$ for the stochastic modulation model were derived recently and analyzed in detail for various physical situations.[9,10,18]

B. Four-wave mixing using incoherent laser sources

It has been demonstrated recently[13-15] that stationary 4WM with an incoherent laser source may be used to achieve an ultrafast (femtosecond) temporal resolution of relaxation processes. The technique starts with an incoherent laser source. This laser beam is split into two beams with wavevectors $\mathbf{k}_1$ and $\mathbf{k}_2$. The $\mathbf{k}_2$ beam is then delayed for a duration T with respect to the $\mathbf{k}_1$ beam. The signal in this experiment is obtained by recording the stationary emission in the direction $2\mathbf{k}_2-\mathbf{k}_1$ as a function of the delay time T. In order to derive an explicit expression for the signal in this case, let us introduce the positive and negative frequency parts of the electromagnetic field, i.e.,

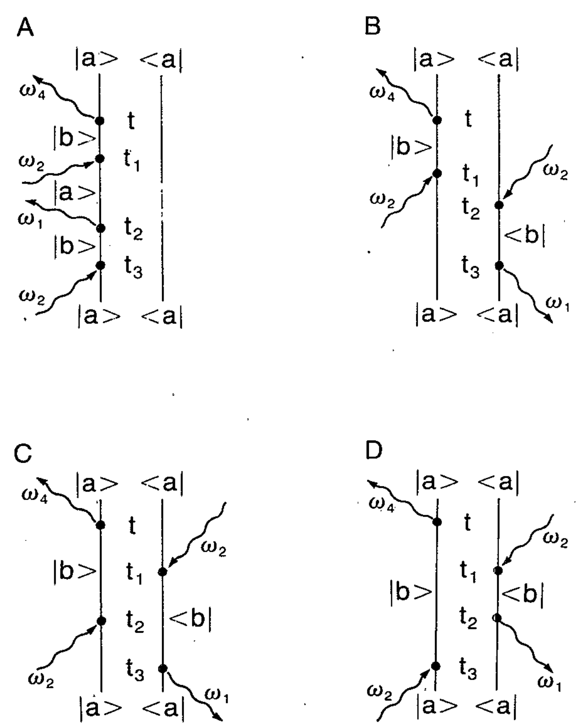

FIG. 2. The four Feynman diagrams corresponding to the polarization P_α [Eq. (69)]. Diagrams A, B, C, and D correspond to $P_{\alpha A}$, $P_{\alpha B}$, $P_{\alpha C}$, and $P_{\alpha D}$, respectively. The diagrams use the conventional notation (Ref. 3).

$$E(t)=\tilde{R}(t)\exp(-i\omega t)+\tilde{R}^*(t)\exp(i\omega t)$$
$$\equiv R(t)+R^*(t)\ . \tag{68}$$

Here, $R(t)$ is a stochastic function of time defined by its correlation functions. These will be introduced later [Eq. (73)]. The polarization function P_α in the rotating-wave approximation has four contributions displayed in the diagrams labeled A, B, C, and D in Fig. 2. Using Eq. (64a) and Fig. 2, we then get

$$P_\alpha(t,t_1,t_2,t_3)=\{[P_{\alpha A}R_A+P_{\alpha B}R_B]Q_1+[P_{\alpha C}R_C+P_{\alpha D}R_D]Q_2\}\ , \tag{69}$$

where

$$P_{\alpha A}(t,t_1,t_2,t_3)Q_1\equiv\langle V_{ab}^\alpha(t)V_{ba}^\alpha(t_1)V_{ab}^\alpha(t_2)V_{ba}^\alpha(t_3)\rho(-\infty)\rangle_s=\exp\left[-i\int_{t_1}^{t}\delta\omega_\alpha(\tau)d\tau-i\int_{t_3}^{t_2}\delta\omega_\alpha(\tau)d\tau\right]Q_1\ , \tag{70a}$$

$$P_{\alpha B}(t,t_1,t_2,t_3)Q_1\equiv\langle V_{ab}^\alpha(t)V_{ba}^\alpha(t_1)\rho(-\infty)V_{ab}^\alpha(t_3)V_{ba}^\alpha(t_2)\rangle_s=\exp\left[-i\int_{t_1}^{t}\delta\omega_\alpha(\tau)d\tau+i\int_{t_3}^{t_2}\delta\omega_\alpha(\tau)d\tau\right]Q_1\ , \tag{70b}$$

$$P_{\alpha C}(t,t_1,t_2,t_3)Q_2\equiv\langle V_{ab}^\alpha(t)V_{ba}^\alpha(t_2)\rho(-\infty)V_{ab}^\alpha(t_3)V_{ba}^\alpha(t_1)\rangle_s=P_{\alpha B}(t,t_1,t_2,t_3)Q_2\ , \tag{70c}$$

$$P_{\alpha D}(t,t_1,t_2,t_3)Q_2\equiv\langle V_{ab}^\alpha(t)V_{ba}^\alpha(t_3)\rho(-\infty)V_{ab}^\alpha(t_2)V_{ba}^\alpha(t_1)\rangle_s=P_{\alpha A}(t,t_1,t_2,t_3)Q_2\ . \tag{70d}$$

We have further defined the auxiliary quantities

$$R_A(t,t_1,t_2,t_3)=R_D(t,t_1,t_2,t_3)=R^*(t_1)R(t_2+T)R^*(t_3)\ , \tag{71a}$$

$$R_B(t,t_1,t_2,t_3)=R_D(t,t_1,t_2,t_3)=R^*(t_1)R^*(t_2)R(t_3+T)\ , \tag{71b}$$

$$Q_1(t,t_1,t_2,t_3)=Q_2(t,t_2,t_1,t_3)=\exp[-\gamma(t-t_1+t_2-t_3)]\ . \tag{72}$$

Making use of Eqs. (63) and (69)—(72), we finally get

$$S(T)=2\pi\int_{-\infty}^{0}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\int_{-\infty}^{0}ds_1\int_{-\infty}^{s_1}ds_2\int_{-\infty}^{s_2}ds_3\sum_{\alpha,\beta}(S_{\mathrm{I}}+S_{\mathrm{II}}+S_{\mathrm{III}}+S_{\mathrm{IV}})Q\ , \tag{73}$$

where

$$S_{\mathrm{I}}=\langle P_{\alpha A}(0,t_1,t_2,t_3)P_{\beta A}^*(0,s_1,s_2,s_3)\rangle_b\langle R_A(0,t_1,t_2,t_3)R_A^*(0,s_1,s_2,s_3)\rangle\ , \tag{73a}$$

$$S_{\mathrm{II}}=\langle P_{\alpha A}(0,t_1,t_2,t_3)P_{\beta B}^*(0,s_1,s_2,s_3)\rangle_b\langle R_A(0,t_1,t_2,t_3)R_B^*(0,s_1,s_2,s_3)\rangle\ , \tag{73b}$$

$$S_{\mathrm{III}}=\langle P_{\alpha B}(0,t_1,t_2,t_3)P_{\beta A}^*(0,s_1,s_2,s_3)\rangle_b\langle R_B(0,t_1,t_2,t_3)R_A^*(0,s_1,s_2,s_3)\rangle\ , \tag{73c}$$

$$S_{\mathrm{IV}}=\langle P_{\alpha B}(0,t_1,t_2,t_3)P_{\beta B}^*(0,s_1,s_2,s_3)\rangle_b\langle R_B(0,t_1,t_2,t_3)R_B^*(0,s_1,s_2,s_3)\rangle\ , \tag{73d}$$

$$Q=[Q_1(0,t_1,t_2,t_3)+Q_2(0,s_1,s_2,s_3)][Q_1(0,t_1,t_2,t_3)+Q_2(0,s_1,s_2,s_3)]\ . \tag{74}$$

The angular brackets in the R terms ($\langle R_AR_A^*\rangle$, etc.) in Eqs. (73) denote averaging over the stochastic realizations of the electromagnetic field. The simplest model is to assume that $R(t)$ is a Gaussian Markovian process with a δ-function correlation,[13] although other models may be used as well.

C. Four-wave mixing with incoherent laser sources in the absence of long-range spatial correlations

When particles α and β are uncorrelated, it is possible to carry out the averaging of Eq. (73) explicitly. This calculation was done recently for general four-wave mixing with coherent laser sources.[18] Let us introduce the following quantities:

$$\langle P_{\alpha A}(t,t_1,t_2,t_3)\rangle_b=\exp[-f_-(t,t_1,t_2,t_3)]\ , \tag{75a}$$

$$\langle P_{\alpha B}(t,t_1,t_2,t_3)\rangle_b=\exp[-f_+(t,t_1,t_2,t_3)]\ , \tag{75b}$$

where

$$f_\pm(t,t_1,t_2,t_3)=g(t-t_1)+g(t_2-t_3)\pm[g(t-t_3)-g(t_1-t_3)-g(t-t_2)+g(t_1-t_2)]\ , \tag{76}$$

and where $g(t)$ was defined in Eq. (48). Equations (73) and (75) result in

$$S(T)=(2\pi)^4 A(N^2/\Omega)\int_{-\infty}^{0}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\int_{-\infty}^{0}ds_1\int_{-\infty}^{s_1}ds_2\int_{-\infty}^{s_2}ds_3$$
$$\times\{\exp[-f_-(0,t_1,t_2,t_3)-f_-(0,s_1,s_2,s_3)]\langle R^*(t_1)R(t_2+T)R^*(t_3)R(s_1)R^*(s_2+T)R(s_3)\rangle$$
$$+\exp[-f_-(0,t_1,t_2,t_3)-f_+(0,s_1,s_2,s_3)]\langle R^*(t_1)R(t_2+T)R^*(t_3)R(s_1)R(s_2)R^*(s_3+T)\rangle$$
$$+\exp[-f_+(0,t_1,t_2,t_3)-f_-(0,s_1,s_2,s_3)]\langle R^*(t_1)R^*(t_2)R(t_3+T)R(s_1)R^*(s_2+T)R(s_3)\rangle$$
$$+\exp[-f_+(0,t_1,t_2,t_3)-f_+(0,s_1,s_2,s_3)]\langle R^*(t_1)R^*(t_2)R(t_3+T)R(s_1)R(s_2)R^*(s_3+T)\rangle\}$$
$$\times Q\delta(2\mathbf{k}_2-\mathbf{k}_1-\mathbf{k}_4)\ . \tag{77}$$

Equation (77) is a generalization of the result of Morita and Yajima,[13] to include a general stochastic line-broadening mechanism. It will reduce to the result of Morita and Yajima in the following limit:

(i) We assume the fast-modulation limit ($\Lambda/\Delta \gg 1$), i.e.,

$$f_\pm(t,t_1,t_2,t_3)=\hat{\Gamma}(t-t_1+t_2-t_3) \tag{78}$$

where

$$\hat{\Gamma}=\Delta^2/\Lambda\ . \tag{78a}$$

(ii) The T_1 relaxation model is changed. In Eq. (77) we have assumed that the excited-state lifetime is γ^{-1}. This results in the following expression for Q:

$$Q(t,t_1,t_2,t_3,s_1,s_2,s_3)=\exp[\gamma(t_1-t_2+t_3)+\gamma(s_1-s_2+s_3)]\{1+\exp[-2\gamma(t_1-t_2)]\}\{1+\exp[-2\gamma(s_1-s_2)\}\ . \tag{79}$$

Morita and Yajima[13] considered a closed T_1 relaxation of a two-level system, whereby level $|b\rangle$ decays into level $|a\rangle$. For their model we have

$$Q=\exp[\gamma(t_1-t_2+t_3)+\gamma(s_1-s_2+s_3)]\exp[-2\gamma(t_1-t_2+s_1-s_2)]\ . \tag{80}$$

Equation (77) together with Eqs. (78) and (80) is identical to the previous result.[13]

VI. CONCLUDING REMARKS

In this article we have analyzed the generation of the signal in four-wave-mixing processes from a microscopic point of view. The present treatment generalizes the conventional procedure commonly used in nonlinear optics, which is based on the Bloch-Maxwell equations.[1–6] That procedure assumes that coherent nonlinear processes may always be characterized by amplitudes and nonlinear susceptibilities, that there are no long-range correlations among the absorbers, and that the bath correlation time is very rapid (the fast-modulation limit). Our current derivation establishes the conditions for the validity of these assumptions and offers an alternative formulation which is less restrictive and holds when the Bloch-Maxwell procedure fails. In Sec. II we introduced the model system consisting of an active nonlinear medium interacting with three classical modes of the radiation field. The 4WM signal was defined in terms of the rate of change of the occupation number of a fourth mode $\mathbf{k}_4$ of the radiation field. Our general expression for the signal S, Eq. (22), is given in terms of an eight-point correlation function of the dipole operator. The system interacts twice with each of the three incoming fields and then interacts twice with the signal mode $\mathbf{k}_4$. The importance of Eq. (22) is that it demonstrates that the signal cannot be simply represented in general as a square of an amplitude. This is in contrast to the conventional formulation of the nonlinear optical response, which is based on calculating a nonlinear polarization via $\chi^{(3)}$, which is related to the amplitude of the signal. Equation (22) allows us to analyze the conditions of validity of the conventional formulation and make specific predictions when that formulation no longer holds.

In Sec. III we analyzed in detail an example of a time-domain 4WM, namely the generation of the photon echo. The echo signal is expressed in terms of an eight-point, two-particle correlation function of the dipole operator [Eq. (31)]. In the absence of long-range spatial correlations in the sample, this correlation function may be factorized into a product of two four-point, single-particle correlation functions. In this case, the signal is given by the absolute square of the nonlinear polarization [Eq. (34)], in agreement with the conventional formulation.[1–6] In Sec. IV we evaluated Eq. (31) for a general stochastic model, and Eq. (46) shows how the signal is a probe for the spatial correlation function $\Phi(r)$. When $\Phi(r)$ is long range, e.g., near critical points, we expect that the phase-matching condition $\delta(\Delta\mathbf{k})$ will break down, and that a broad signal, which is induced by the spatial correlations, will be seen. Equations (53), (57), and (58) allow us to study how the echo signal is modified in the presence of long-range spatial correlations. Our analysis suggests that conducting coherent nonlinear experiments near critical points could be very useful in probing the temporal and spatial correlations which dominate the critical dynamics. Further analysis of this case is presented elsewhere.[12] In Sec. V we considered the novel spectroscopic technique of correlation 4WM spectroscopy, whereby two delayed incoherent fields are used to generate the 4WM signal. We have derived a general formula for this signal which includes stochastic fields, stochastic line broadening, and long-range spatial correlations. This formula [Eq. (77)] generalizes the recent work of Morita and Yajima[13] and agrees with their result in the proper limits.

In summary, the present approach and Eq. (22) provide a general microscopic formulation for any type of 4WM (both in the time domain or in the frequency domain). The examples presented in this article demonstrate the two-body nature of the 4WM signal, which makes it an ideal tool with which to study long-range spatial correlations. This two-body aspect is absent in the conventional formulations of 4WM, which are based on the Bloch-Maxwell equations.

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