Photon echoes as a probe for long-range spatial correlations

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A microscopic correlation-function expression for the photon-echo signal in systems with long-range spatial correlations is developed. In general, the signal is given by an eight-point correlation function of the dipole operator involving two particles. In the absence of long-range spatial correlations, this correlation function may be factorized into a product of two four-point, single-particle correlation functions. Only under these conditions is the signal proportional to the absolute square of the ensemble-averaged nonlinear polarization. We predict that photon echoes may be used to probe the long-range spatial correlations near critical points.

Coherent, nonlinear optical signals are usually calculated in two steps. First, the material system is assumed to interact with the incident light fields, creating a nonlinear polarization with a specified wave vector and frequency. Subsequently, this polarization is substituted into Maxwell's equations and generates the signal field. This procedure is used both for steady-state and for transient (e.g., free-induction decay, photon echoes) observables.[1–5] In the absence of long-range spatial correlations, the coherent nonlinear process is characterized by an *amplitude* (proportional to the nonlinear polarization averaged over any thermal bath), and the signal intensity is given by the absolute square of this amplitude. Consequently, the conventional treatments of nonlinear coherent transients focus on calculating the ensemble-averaged nonlinear polarization.[1–5] However, more general treatments of superfluorescence and stimulated Raman scattering use Langevin equations and require an ensemble averaging over the signal (amplitude square) rather than over the amplitude.[6] In this paper we develop a microscopic correlation-function expression for the photon-echo signal. 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 nonlinear medium, this correlation function may be factorized into a product of two four-point, single-particle correlation functions. Only under these conditions is the signal given by an amplitude square.[5,6,9–13] We predict, however, that, when long-range correlations exist (e.g., near critical points), this factorization will break down, and the present, more general expression will need to be used. The effects of line broadening on the photon-echo signal are shown to be dramatically different for short-range and long-range mechanisms. In an ideal photon-echo experiment, the material system interacts with two short laser pulses. We shall denote the frequency, wave vector, and electric-field amplitude of the first pulse by ω_1, $\mathbf{k}_1$, and E_1, respectively, and those of the second pulse by ω_2, $\mathbf{k}_2$, and E_2. The first pulse acts at time $t = 0$, and the second at time T. The photon echo is a coherent transient observed at time t ($t > T$) in the direction $\mathbf{k}_s = 2\mathbf{k}_2 - \mathbf{k}_1$. We have solved for the echo signal in a model system consisting of N two-level absorbers (with states $|a_\alpha\rangle$ and $|b_c\rangle$, $\alpha = 1, 2, \ldots N$), which interact with a thermal bath but not with each other. The $\mathbf{k}_s$ mode of the radiation field was treated quantum mechanically, and the signal is defined as the rate of change of the occupation number of this mode, i.e., the expectation value of $\mathrm{d}/\mathrm{d}t a_s^\dagger a_s$, where $a_s^\dagger$ (a_s) are the creation (annihilation) operators for the s mode. The calculation was made by using the tetradic (Liouville-space) scattering theory.[7,9,13] The result for the signal at time t, to lowest order in E_1 and E_2, is given by the eight-point, two-particle correlation function[14]:

$$S(t, T) = 8\pi|E_1|^2|E_2|^4 \sum_{\alpha,\beta=1}^{N} \langle V_{ab}{}^{\alpha}(-T)V_{ba}{}^{\alpha}(0)V_{ab}{}^{\beta}(0) \times V_{ba}{}^{\beta}(t-T)V_{ab}{}^{\alpha}(t-T)V_{ba}{}^{\alpha}(0)V_{ab}{}^{\beta}(0)V_{ba}{}^{\beta}(-T)\rangle \times \exp[i(2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_s)\cdot(\mathbf{r}_\alpha - \mathbf{r}_\beta)]. \tag{1}$$

Here α and β denote two particles located at $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$, respectively. The angle brackets $\langle \ldots \rangle$ denote a trace over all degrees of freedom (absorbers and baths), and V is the dipole interaction

$$V_{ab}{}^{\alpha}(t) \equiv \mu_{ab} \exp(iH_0 t)|a_\alpha\rangle\langle b_\alpha| \exp(-iH_0 t), \tag{2}$$

where μ_{ab} is the transition dipole between states $|a_\alpha\rangle$ and $|b_\alpha\rangle$, H_0 being the material Hamiltonian (in the absence of the radiation field). V_{ba} is the Hermitian conjugate of V_{ab}. In Eq. (1) we have used the invariance of the correlation function to translation in time. The normalization of Eq. (1) is in arbitrary units. If particles α and β are uncorrelated, we can factorize the two-particle correlation function in Eq. (1) into a product of two single-particle correlation functions corresponding to particles α and β. Let us introduce the polarization of particle α, i.e.,

$$\langle P_\alpha(t, T)\rangle = 2E_1|E_2|^2\langle V_{ab}{}^{\alpha}(-T)V_{ba}{}^{\alpha}(0)V_{ab}{}^{\alpha}(t-T)V_{ba}{}^{\alpha}(0)\rangle. \tag{3}$$

Equation (1) can then be rearranged as

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$$S(t, T) = 2\pi|E_1E_2{}^2|^2 \sum_{\alpha,\beta} \langle P_\alpha(t, T)\rangle\langle P^*{}_\beta(t, T)\rangle \times \exp[i(2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_s)\cdot(\mathbf{r}_\alpha - \mathbf{r}_\beta)]. \quad (4)$$

Since in this case $\langle P_\alpha(t, T)\rangle$ does not depend on $\mathbf{r}_\alpha$, i.e., $\langle P_\alpha\rangle = \langle P_\beta\rangle = \langle P\rangle$, we can perform the α, β summations immediately, resulting in

$$S(t, T) = (2\pi)^4(N^2/\Omega)|\langle P(t, T)\rangle|^2\delta(2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_s), \quad (5)$$

where N is the number of particles that contribute to the nonlinear optical response, Ω is the volume of the active nonlinear medium, and $\langle P\rangle$ is given by Eq. (3). 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. (4). In that case, we have to evaluate the eight-point correlation function [Eq. (1)], which semiclassically (when V^α and V^β commute) can be recast as the two-particle average $\langle P_\alpha(t, T)P^*{}_\beta(t, T)\rangle$.

We now illustrate Eq. (1) by considering the following model: The material system consists of a collection of two-level systems denoted $|a_\alpha\rangle$ and $|b_\alpha\rangle$, each having a frequency $\omega_{ba}{}^\alpha$. We assume two line-broadening mechanisms and write

$$\omega_{ba}{}^\alpha = \omega_\alpha + \delta\omega_\alpha(t), \quad (6)$$

where $\delta\omega_\alpha(t)$ and ω_α represent dynamic and static (inhomogeneous) broadening mechanisms, respectively. We assume that $\delta\omega_\alpha(t)$ is a random variable with zero mean $\langle\delta\omega_\alpha(t)\rangle = 0$ and that its correlation function is[15]

$$\langle\delta\omega_\alpha(t)\delta\omega_\alpha(0)\rangle = \Delta^2\exp(-\Lambda t), \quad (7a)$$

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 that

$$\langle\delta\omega_\alpha(t)\delta\omega_\beta(0)\rangle = \Phi(\mathbf{r}_{\alpha\beta})\Delta^2\exp(-\Lambda t). \quad (7b)$$

$\Phi(\mathbf{r}_{\alpha\beta})$ is finite over a correlation length ξ and is zero otherwise. In addition, we assume that the static frequency ω_α has an inhomogeneous Gaussian distribution, i.e.,

$$W(\omega_\alpha) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[\frac{(\omega_\alpha - \omega_\alpha{}^0)^2}{2\sigma^2}\right]. \quad (8)$$

For simplicity, we take the inhomogeneous part to be uncorrelated for different particles. This does not affect our result since the inhomogeneous part cancels for the echo signal. For this model we may evaluate S [Eq. (1)], resulting in[14]

$$S(t, T) = A(N^2/\Omega)\exp[-2\gamma t - \sigma^2(t - 2T)^2] \times \int_0^R \mathrm{d}\mathbf{r}\,\exp\{-[1 - \Phi(\mathbf{r})]f(t, T)\}\exp(i\Delta\mathbf{k}\cdot\mathbf{r}). \quad (9)$$

Here, R is the radius of the nonlinear medium $\Omega = 4\pi R^3/3$, $2\gamma \equiv 1/T_1$ is the inverse lifetime of the excited state, $A = 8\pi|\mu_{ab}|^8|E_1|^2|E_2|^4$, $\Delta\mathbf{k} \equiv 2\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{k}_s$,

$$f(t, T) = 4g(t - T) + 4g(T) - 2g(t), \quad (10)$$

and

$$g(\tau) = (\Delta/\Lambda)^2[\exp(-\Lambda\tau) - 1 + \Lambda\tau]. \quad (11)$$

Equation (9) 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 $\Phi(\mathbf{r})$. A reasonable model for $\Phi(\mathbf{r}_{\alpha\beta})$ is $\sim\exp(-\mathbf{r}_{\alpha\beta}/\xi)$. For simplicity, we take

$$\Phi(\mathbf{r}_{\alpha\beta}) = \begin{cases}1, & |\mathbf{r}_{\alpha\beta}| < \xi \\ 0, & \text{otherwise}\end{cases}. \quad (12)$$

When the frequency modulations $\delta\omega_\alpha(t_1)$ and $\delta\omega_\beta(t_2)$ at two different sites $\alpha \neq \beta$ are *uncorrelated*, i.e., $\xi = 0$, we have $S(t, T) = S_u(t, T)\delta(\Delta\mathbf{k})$, where

$$S_u(t, T) = (2\pi)^3A(N^2/\Omega)\exp[-2\gamma t - f(t, T) - \sigma^2(t - 2T)^2]. \quad (13)$$

In the other extreme ($\xi \to \infty$), the line broadening originating from the modulation disappears, since both particles are fully correlated and the contribution of fluctuations in the frequency of particle α cancels those of particle β in Eq. (1). This two-particle cancellation is lost once the eight-point correlation function is factorized [Eq. (4)]. We thus get for $\xi \to \infty$, $S(t, T) = S_c(t, T)\delta(\Delta k)$, where

$$S_c(t, T) = (2\pi)^3A(N^2/\Omega)\exp[-2\gamma t - \sigma^2(t - 2T)^2]. \quad (14)$$

In the general case (arbitrary ξ) we get

$$S(t, T) = F_R(\Delta\mathbf{k})S_u(t, T) + F_\xi(\Delta\mathbf{k})[S_c(t, T) - S_u(t, T)], \quad (15)$$

where

$$F_r(\Delta\mathbf{k}) = \frac{[\sin(\Delta\mathbf{k}\cdot\mathbf{r}) - (\Delta\mathbf{k}\cdot\mathbf{r})\cos(\Delta\mathbf{k}\cdot\mathbf{r})]}{2\pi^2(\Delta k)^3}, \qquad r = R, \xi \quad (15a)$$

and where $\Delta k \equiv |\Delta\mathbf{k}|$ and $r \equiv |\mathbf{r}|$. For $\Delta\mathbf{k}\cdot\mathbf{r} \gg 1$, F_r becomes a Dirac δ function, i.e.,

$$F_r(\Delta\mathbf{k}) \to \delta(\Delta\mathbf{k}), \quad (15b)$$

whereas for $\Delta\mathbf{k}\cdot\mathbf{r} \ll 1$ we have

$$F_r(\Delta\mathbf{k}) \to (2\pi)^{-3}4\pi r^3/3 \equiv r^3/6\pi^2. \quad (15c)$$

Ordinarily R is a macroscopic length, say, 10^{-3} cm, whereas ξ is short range and microscopic $\sim 10^{-6}$ 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. (15c)]. The signal under these conditions is given by the first term in Eq. (15). When the correlation length ξ becomes longer, the second term increases. 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., $R^{-1} \ll \Delta\mathbf{k} \ll \xi^{-1}$, we see only the second term in Eq. (15). This term is induced by the spatial correlations in the sample. Making use of Eqs. (13)–(15), we get in this case

$$S(t, T) = F_\xi(\Delta\mathbf{k})[S_c(t, T) - S_u(t, T)] = AN^2(\Omega_c/\Omega)\exp[-2\gamma t - \sigma^2(t - 2T)^2] \times \{1 - \exp[-f(t, T)]\}, \quad (16)$$

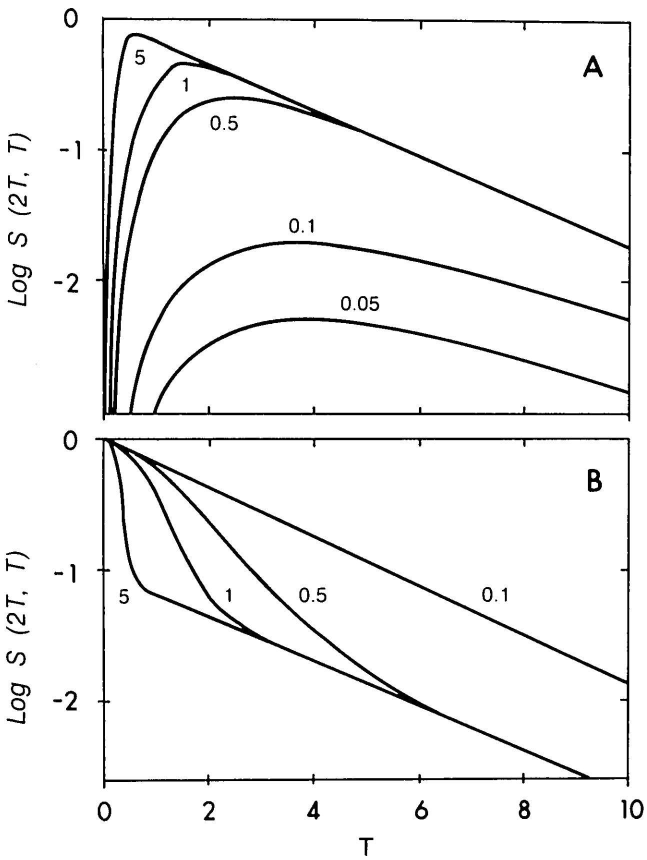

Fig. 1. A, The induced photon-echo signal $\log_{10} S(2T, T)$ [Eq. (16)] for $R^{-1} \ll |\Delta \mathbf{k}| \ll \xi^{-1}$. $\gamma = 0.1$, $\Lambda = 1$, and Δ was varied, as shown in the figure. B, The photon-echo signal $\log_{10} S(2T, T)$ [Eq. (17)] in the direction of exact phase matching. Parameters are the same as in A. $\Omega_c/\Omega = 0.1$.

where we have used Eq. (15c) for $F_\xi(\Delta \mathbf{k})$ and defined the correlation volume $\Omega_c = 4\pi\xi^3/3$. The echo signal is usually observed at $t = 2T$, whereby the inhomogeneous broadening {i.e., the $\exp[-\sigma^2(t - 2T)^2]$ term} vanishes. In Fig. 1A, we display $S(2T, T)$ [Eq. (16)] for several values of Λ/Δ.

In the direction of perfect phase matching $\Delta \mathbf{k} = 0$ we have, using Eqs. (13)–(15),

$$S(t, T) = AN^2 \exp[-2\gamma t - \sigma^2(t - 2T)^2] \times \{[1 - (\Omega_c/\Omega)]\exp[-f(t, T)] + (\Omega_c/\Omega)\}. \quad (17)$$

$S(2T, T)$ [Eq. (17)] is displayed in Fig. 1B for several values of Λ/Δ. The signal in Fig. 1A has a maximum, and its shape is sensitive to the nature of the line-broadening mechanism as given by $f(2T, T)$. In this figure we show several curves with the same value of Λ and various values of Δ. In the fast modulation limit ($\Lambda/\Delta \gg 1$, $\Delta = 0.05, 0.1, 0.2$) the maximum of the curve is at

$$T = (4\hat{\Gamma})^{-1} \log \frac{\gamma + \hat{\Gamma}}{\gamma}, \quad (17')$$

where $\hat{\Gamma} \equiv \Delta^2/\Lambda$. As Δ decreases, the maximum shifts toward longer times, and the magnitude of the signal decreases. Since this signal is induced by the correlated dephasing of two particles, it will vanish in the absence of dephasing $\Delta \to 0$. The appearance of this signal and its spatial dependence on $\Delta \mathbf{k}$ are a measure of the correlated dynamics in the sample and of the correlation length ξ. Figure 1B displays similar curves for the exact phase-matching condition $\langle \Delta \mathbf{k} \rangle = 0$ [Eq. (17)]. For $\Delta = 1$ the curve starts at short times as a Gaussian (for regions of time $T < \Lambda^{-1}$). Then it becomes exponential with a rate of $\sim 4(\hat{\Gamma} + \gamma)$, and in the long-time limit it decays with a slower rate of 4γ. As Δ increases, the short-time behavior becomes more dominant. The relative magnitude of the short- and long-time components is a measure of Ω_c/Ω [see Eq. (17)]. It should be noted that usually (far from critical points) $\Omega_c/\Omega \ll 1$. Under these conditions, $S(t, T)$ [Eq. (17), Fig. 1B] is essentially S_u. As $|\Delta \mathbf{k}|$ is varied, we expect the time dependence of the signal to change continuously from that of Fig. 1A to that of Fig. 1B. The $|\Delta \mathbf{k}|$ range under which this transition occurs is $\sim \xi^{-1}$. We predict that photon echoes (and other four-wave mixing techniques)[11,13,14] should provide a sensitive probe for the dynamics of systems near critical points,[16] whereby ξ diverges and $\Omega_c/\Omega \sim 1$.

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