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Communication: The origin of many-particle signals in nonlinear optical spectroscopy of non-interacting particles

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Nonlinear spectroscopy signals detected by fluorescence from dilute samples of N non-interacting molecules are usually adequately described by simply multiplying the single molecule response by N . We show that signals that scale with higher powers of N are generated by the joint detection of several particles. This can be accomplished by phase sensitive detection such as phase cycling, photo-acoustic modulation, or by Hanbury-Brown Twiss photon coincidence. Such measurements can dissect the ensemble according to the number of excited particles. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4960049>]

The nonlinear optical response of assemblies of N noninteracting particles is essentially a single molecule problem that can be fully addressed in the single particle phase space.¹ This note discusses macroscopic multi-particle signals that go beyond this simple picture. Cascading^{1,2} is a well-known process that creates heterodyne detected signals that scale quadratically with N . In that process, the molecules interact via the exchange of a photon. Here we do not consider cascading since we exclude any type of intermolecular interaction. The number of molecules excited by weak fields in an ensemble has a Poisson distribution but this distribution is immaterial to ordinary single-body observables such as the polarization in conventional nonlinear spectroscopy. We show that in order to observe multiparticle signals that scale nonlinearly with N , we must look at observables involving several particles such as the joint probability that two or more molecules are excited. Possible multiparticle detection modes include phase sensitive detection of fluorescence as offered, e.g., by phase cycling,^{3–5} photo-acoustic phase modulation,^{6,7} or photon coincidence.⁸

The many-body state of an ensemble of noninteracting particles driven by external fields is described by the density matrix,

$$\rho(t) = \prod_j (\rho_{g_j} + \delta\rho_j(t)), \quad (1)$$

where ρ_{g_j} is the equilibrium density matrix of particle j and $\delta\rho_j(t)$ is the change induced by the driving fields. By expanding this product in powers of $\delta\rho_j$ we obtain

$$\begin{aligned} \rho^{(1)}(t) &= \sum_j \rho_j' = \delta\rho_j(t), \\ \rho^{(2)}(t) &= \sum_{j,k} \rho_{jk}' \delta\rho_j \delta\rho_k, \end{aligned} \quad (2)$$

etc. Here ρ' represents the state of all particles other than those specified by the indices in their ground state, i.e.,

$$\begin{aligned} \rho_j' &= \prod_{m \neq j} \rho_{g_m}, \\ \rho_{jk}' &= \prod_{m \neq j,k} \rho_{g_m}, \end{aligned} \quad (3)$$

and so forth. Conservation of probability implies

$$\text{Tr} \delta\rho_j(t) = 0. \quad (4)$$

Because of this, if we observe the expectation value of a single article operator $A^{(1)} = \sum_j A_j$, we get

$$\text{Tr} A^{(1)} \rho^{(1)} = \sum_j \text{Tr}(A_j \delta\rho_j) = N \text{Tr}(A_j \delta\rho_j) \quad (5)$$

and

$$\text{Tr} A^{(1)} \rho^{(n)} = 0, \quad n > 1 \quad (6)$$

In the last equality in Eq. (5), we have assumed identically driven particles. The key point is that this signal only depends on $\rho^{(1)}$. In a similar manner, if we observe a two particle operator

$$A^{(2)} = \sum_{j \neq k} A_j A_k, \quad (7)$$

then

$$\text{Tr} A^{(2)} \rho^{(2)} = \sum_{j \neq k} (\text{Tr} A_j \delta\rho_j) (\text{Tr} A_k \delta\rho_k) = N(N-1) (\text{Tr} A_j \delta\rho_j). \quad (8)$$

This solely depends on $\rho^{(2)}$. Higher order n -particle observables can be calculated similarly. To probe many-particle projections of the ensemble, we must therefore simultaneously observe several particles. Any observation of particle j alone is unaffected by the presence of particle k ; for interpreting a measurement made on particle j , we need not worry about what another noninteracting particle does. This is consistent with the principle of local reality as formulated by Einstein–Podolsky–Rosen (EPR).⁹ Life will be very confusing otherwise.

We now use these arguments to examine the recent double-quantum-coherence reported by Bruder, Binz, and Steinkemeier.⁷ In these novel experiments, phase-sensitive detection of fluorescence induced by a pair of short pulses with variable delay T in ensembles of noninteracting particles

had revealed harmonics $n\omega_{eg}$ of the fundamental molecular frequency in the Fourier transform of the signal with respect to T . These were labeled multiple quantum coherence (MQC) resonances.

To describe these signals, we consider an ensemble of two level particles $|e_j\rangle, |g_j\rangle$, all initially in their ground state, which interact with a field made of two short pulses with delay T and controlled phases (Fig. 1),

$$E(t) = E_1(t) \exp(-i\omega_1 t - i\phi_1) + E_2(t - T) \exp(-i\omega_2 t - i\phi_2) + c.c., \quad (9)$$

where ϕ_n is the phase of the field E_n . The fluorescence is proportional to the probability that particle j is in the excited state which is given by the expectation value of $A_j = |e_j\rangle\langle e_j|$.

The fluorescence signal is proportional to the number of particles in the excited state, given by

$$P_e^{(1)}(T) = \sum_j \langle A_j \rangle = N \langle A_j \rangle. \quad (10)$$

Assuming short impulsive pulses $E_n(\tau) = \delta(\tau)$, we obtain using the diagram in Fig. 1

$$\langle A_j \rangle = a + b \cos(\phi_{12} + (\omega_{eg} - \omega_1)T). \quad (11)$$

Here $\phi_{12} = \phi_1 - \phi_2$ and the coefficients a and b depend on the pulse amplitudes E_n . To second order in perturbation theory,

$$a = |\mu_{eg}|^2 (E_1^2 + E_2^2), \quad b = |\mu_{eg}|^2 2E_1 E_2.$$

Since a is phase-independent, the two-particle signal, $P_e^{(2)}(T)$, will possess contributions proportional to

$$\exp(\pm in(\phi_{12} + (\omega_{eg} - \omega_1)T)) \text{ with } n = 0, 1, 2.$$

The contribution with $n = 2$ is unique for $P_e^{(2)}(T)$. However, the terms with $n = 0, 1$ contribute to both $P_e^{(1)}(T)$ and $P_e^{(2)}(T)$. By selecting the signal component with phase ϕ_{12} through phase cycling or photoacoustic modulation, we get

$$\langle A_j \rangle = |\mu_{eg}|^2 E_1 E_2 \exp(-i(\omega_{eg} - \omega_1)T - i\phi_{12}). \quad (12)$$

Fourier transform of Eq. (10) together with Eq. (12) with respect to the time delay T gives

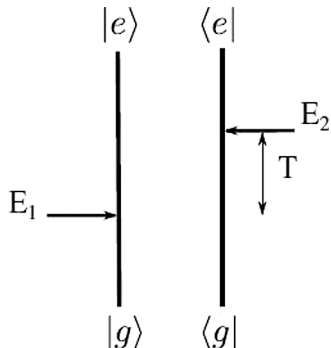


FIG. 1. The excited state population (Eqs. (10) and (12)) induced by a pair of phase controlled pulses with time delay T .

$$P_e^{(1)}(\Omega) = -i \int_0^\infty dT P_e^{(1)}(T) \exp(i\Omega T) = E_1 E_2 N |\mu_{eg}|^2 \exp(-i\phi_{12}) \frac{1}{\Omega - \omega_{eg} + \omega_1 + i\varepsilon}. \quad (13)$$

Phase sensitive detection of fluorescence thus reflects $\rho^{(1)}$ and only shows single quantum $\Omega = \omega_{eg}$ resonances.

The joint probability that two particles are excited is obtained by detecting a two-particle operator $A_{jk} = |e_j\rangle\langle e_j| \times |e_k\rangle\langle e_k|$. This is related to $\rho^{(2)}$,

$$P_e^{(2)}(t) = N(N-1) \langle A_j \rangle \langle A_k \rangle, \quad (14)$$

with $\langle A_j \rangle$ given by Eq. (12). We then get for identically driven molecules

$$\langle A_j \rangle \langle A_k \rangle = |\mu_{eg}|^4 E_1^2 E_2^2 \exp(-2i(\omega_{eg} - \omega_1)T - 2i\phi_{12}). \quad (15)$$

This will generate a signal with phase $2\phi_{12}$. The product $\langle A_j \rangle \langle A_k \rangle$ oscillates as $\exp(-2i(\omega_{eg} - \omega_1)T)$. Fourier transform then gives double quantum $\Omega - 2\omega_{eg}$ resonances,

$$P_e^{(2)}(\Omega) = E_1^2 E_2^2 N(N-1) |\mu_{eg}|^4 \times \exp(-2i\phi_{12}) \frac{1}{\Omega - 2\omega_{eg} + 2\omega_1 + i\varepsilon}. \quad (16)$$

Phase selection thus allows us to dissect the ensemble; detecting a phase $n\phi_{12}$ for this model amounts to probing n particle excitations as represented by $\rho^{(n)}$. Of course, there is no new information in the double quantum coherences of Eq. (16) since Eq. (14) is simply given by products of single particle coherences. Alternatively a two-photon coincidence measurement^{8,10} will reveal two particle excitations described by $\rho^{(2)}$ and will lead to identical two-body resonances.¹¹ In the setup considered here, the phase serves as a convenient bookkeeping device for the number of excited particles allowing us to selectively detect and sort out n particle events. A phase $n\phi_{12}$ implies that we measure a state with n excited particles as given by $\rho^{(n)}$. Only single molecule diagrams (Fig. 1) are required in order to calculate Eq. (8). We need not work in the many-body space. However, had we chosen to do so, we would need a large number of diagrams that maintain unnecessary bookkeeping of time orderings of field interactions with different particles. These eventually cancel out once the signal is calculated and assumes the factorized form of Eq. (14).

Note that Eq. (11) only applies to well-separated pulses acting on two level systems. Additional contributions to $P_e^{(1)}(T)$ and $P_e^{(2)}(T)$ must be taken into account for temporally overlapping pulses or for three level systems where emission can occur from state $|e\rangle$ or from the third level $|f\rangle$. These must be carefully sorted out, which complicates the analysis.

In summary, the recently observed multi-quantum coherence signals in the phase sensitive detection of fluorescence from ensembles of molecules⁷ represent macroscopic, rather than microscopic, coherence. These signals arise from products of single quantum coherences in individual molecules rather than from a genuine microscopic multi-quantum coherence and therefore carry no many-body information. Ordinary coherent optical signals are given by a *sum* of single particle contributions and depend solely on the density

matrix of a single particle. Only when we look at observables involving several particles (e.g., the joint probability that two or more molecules are excited) then the signal will depend on *products* of single particle quantities which scale nonlinearly with N . By imprinting a phase $n\phi_{12}$ in the signal, we can separately record the various terms in the expansion of Eq. (1).

How does it come that $\rho^{(2)}$ does not contribute to the fluorescence of particle j even though it involves an excitation of the j particle? When particle j is excited, the possible two particle states are $|e_j g_k\rangle$ and $|e_j e_k\rangle$. $\rho^{(2)}$ moves some population from $|e_j g_k\rangle$ to $|e_j e_k\rangle$. However, it does not affect the total population of $|e_j\rangle$ and the total fluorescence from particle j . By measuring the $2\phi_{12}$ phase component, we observe $|e_j e_k\rangle$ and not $|e_j g_k\rangle$ which shows the two particle resonance. The above discussion assumed noninteracting particles. If the particles do interact,¹² the collective signals will carry new information about multiexciton states. We then need to calculate the signal in the n particle space. It should be interesting to develop perturbative expansion of signals in inter-particle interactions based on the present expansion. It should further be noted that when using stationary fields ($E_m(t)$ independent on t) with no control over their time ordering, the collective resonances cancel out by interference.¹³ In that case, these resonances can be recovered by using quantum or entangled light.^{10,11,14–16}

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