Communications: Signatures of quasiparticle entanglement in multidimensional nonlinear optical spectroscopy of aggregates

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Excitons represent collective optical excitations in which the motions of electrons belonging to different chromophores are correlated. We discuss the utility of the notion of entanglement commonly used in quantum information processing, in the description of these excitations. A distinction is made between some apparent entanglement effects associated with the linear response that may be removed by a transformation of coordinates and can be handled classically, and genuine entanglement that is fundamentally quantum in nature and shows up only in the nonlinear optical response. © *2010 American Institute of Physics*. [doi:10.1063/1.3454657]

The role of quantum effects in exciton dynamics and transport in molecular aggregates is of considerable current interest. This controversial question is both fundamental and has practical implications to, e.g., the efficiency of photosynthetic light harvesting in biological complexes and the design of biomimetic solar cells.[1–5] For this debate to be meaningful it is necessary to clearly define a proper reference classical system and identify deviations from it as "quantum effects."

Exciton models have long been used to describe electronic excitations and optical properties of molecular crystals and aggregates. In this picture each chromophore is viewed as a localized oscillator. The actual electronic excitations are collective (delocalized) and this gives rise to several characteristics in their linear spectroscopy: Redistributed oscillator strengths among different transitions and cooperative spontaneous emission (super-radiance). Convenient measures of the degree of delocalization are provided by various types of participation ratios.[6–11] The same underlying issue of coherence among particles is addressed in the field of quantum information processing but from a very different angle.[12–14] Quantum computing algorithms are based on the manipulation of many-body systems into an entangled state by performing local operations on individual chromophores. Entanglement is a purely quantum concept. The wave function of an assembly of N two-level systems (q-bits) contains 2^N independent coefficients, provided the state is entangled (i.e., its wave function may not be factorized into a product of functions of the various q-bits). This provides an exponentially large memory capacity. However, it should be noted that entanglement is not an objective property of the state of the system but rather depends on the choice of degrees of freedom used to describe it. In a given state certain types of degrees of freedom could be entangled but sometimes the entanglement may be removed by a simple transformation of coordinates.

To illustrate this point let us consider a system of N coupled harmonic coordinates q_α described by a quadratic Hamiltonian. This Hamiltonian can be diagonalized by constructing normal modes via the transformation, $Q_j = \Sigma S_{j\alpha} q_\alpha$. Using these collective coordinates we can write the eigenstates as direct products,

$$\psi = \prod_{j=1}^{N} \psi_j(Q_j). \tag{1}$$

Obviously, in this state the normal modes undergo independent motions and are not entangled. This will not be the case had we used the original q_α coordinates which obviously are entangled. We can thus choose between two types of descriptions of the same state of the system: Either in terms of independent normal modes or as entangled local motions. The former is classical and by far simpler. This issue never arises in quantum processing applications where there is no ambiguity as to the choice of the relevant degrees of freedom. In those applications the entanglement must be invariant under local unitary transformations and controlled by simple (e.g., two q-bit) operations.[7–9] It is for this reason that entanglement is then measured in the site basis, rather than the delocalized exciton basis. However, if we are merely looking for a simple physical description for optical excitations in aggregates we have some freedom in defining our coordinates.

In this article we argue that the linear response can always be mapped onto a collection of unentangled quasiparticle exciton coordinates and all observables related to linear spectroscopy may thus be treated classically. Quantum entanglement then shows up only in nonlinear spectroscopy. In the following analysis we should keep in mind some important differences from quantum computing applications. These use strong saturating $(\pi, \pi/2)$ pulses in order to manipulate the entire ensemble of q-bits. Signatures of entanglement are imprinted in the many-body eigenstates. A system of N q-bits has 2^N such states which can be completely manipulated by elementary one and two q-bit operations. Nonlinear spectroscopy of complex chromophores, on the other hand, uses weak fields in order to avoid undesirable photophysical and photochemical processes that can take place at high degrees of excitations. The system remains mostly in the ground state

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but its wave function acquires small contributions from higher states. We thus typically consider separately groups of states with successively larger number of quasiparticles rather than the entire 2^N manifold.

We start with the effective exciton Hamiltonian representing N chromophores,[15,16]

$$H = \sum_n \varepsilon_n B_n^+ B_n + \sum_{n_1 m} J_{nm} B_n^+ B_m + \sum K_{nmn'm'} B_n^+ B_m^+ B_{n'} B_{m'}.$$

(2)

B_n^+ (B_n) are Boson operators that create (annihilate) an excitation on the nth chromophore and satisfy the commutation relations $[B_n, B_m^+] = \delta_{nm}$. When the Hamiltonian (2) is derived microscopically we naturally obtain operators which satisfy different commutation rules. For example, for two-level chromophores we have the Pauli commutation rule $[B_n^+, B_m] = \delta_{nm}[1 - 2B_n^+ B_n]$ Three-level chromophores have different rules.[11] If we start with the microscopic many-electron Hamiltonian as is commonly done in semiconductors, then the elementary exciton operators create electron hole pairs. The exciton operators are composite Bosons with more complex commutations.[16–18] Nevertheless, it is possible to recast the Hamiltonian in terms of Boson operators. In the case of Frenkel excitons we can define a physical space of states and modify the Hamiltonian [i.e., the parameters K in Eq. (2) or higher order terms if needed] so that its eigenstates coincide with the physical space of interest. Stated differently, excitons interact in two ways: via their commutation rules (Pauli blocking) and by direct coupling. It is possible to eliminate the former and use simple Boson commutations and compensate for that by adding interaction terms to the Hamiltonian. This is essential for developing the quasiparticle picture. For example, to represent two-level chromophores we add an interaction term $\Delta_n B_n^+ B_n^+ B_n B_n$. Δ_n is an energy penalty that shifts the double exciton states on the nth chromophore. By sending $\Delta_n \rightarrow \infty$ the shift is so large that the state becomes decoupled from the physical space of states and may be ignored. Each chromophore thus behaves as a two-level system. A similar approach can be used for multilevel chromophores. Many other elaborate Bosonization schemes have been developed for including all interaction effects in the Hamiltonian.[17,18] They can all be used to recast the Hamiltonian with different levels of sophistication in terms of elementary Boson operators. By doing so the system can be represented as a collection of anharmonic oscillators.

Hereafter we consider aggregates made out of two-level chromophores. The exciton levels form distinct n-particle manifolds. There is one ground state, N single-particle excitations, $N(N-1)/2$ two-particle excitations, etc., to a total of 2^N states. Linear spectroscopy only accesses the single-particle manifold, $|e\rangle = \sum_n c_{en} B_n^+ |g\rangle$. We now define the collective exciton coordinates by the following transformation:

$$B_e = \sum_n c_{en} B_n.$$

(3)

The Boson commutations are preserved $[B_e, B_{e'}^+] = \delta_{ee1}$ and a classical-oscillator picture of the system may be obtained by

using the corresponding dimensionless coordinates and momenta,

$$Q_e = \frac{1}{\sqrt{2}}(B_e + B_e^+), \quad P_e = \frac{i}{\sqrt{2}}(B_e^+ - B_e).$$

(4)

The single-exciton manifold and all linear optical properties can be fully described by the effective harmonic Hamiltonian which diagonalizes the first two terms in Eq. (2),

$$H = \sum_e \varepsilon_e B_e^+ B_e.$$

(5)

The single-exciton states $B_e^+ |g\rangle$ have a direct-product form in this coordinate system and show no entanglement. All entanglement effects such as exciton delocalization[7,10,11] are now incorporated through these coordinates and the single-exciton eigenstates can be a described in terms of these nonentangled normal modes. If we couple this Boson quasiparticle system linearly to an optical field via the interaction $E(t)[B_e + B_e^+]$, the driven wave function will be given at all times by the coherent state,

$$|\psi(t)\rangle = \exp\left(\sum_e c_e(t) B_e^+\right)|g\rangle.$$

(6)

Again, this factorized direct-product state shows no entanglement.

Equation (6) represents the exact driven state of the original Hamiltonian Eq. (2) only in the single-exciton space where $|\psi(t)\rangle \cong |g\rangle + \sum_e c_e B_e^+ |g\rangle$, but breaks down in the higher spaces. We thus conclude that single-particle excitations that determine the linear response can be handled classically. Technically the chromophores are entangled but this entanglement can be easily removed by the transformation to quasiparticle coordinates. In contrast, the entanglement may not be generally eliminated for multiparticle states. The first signatures of entanglement appear at the two-particle excitation level. For noninteracting quasiparticles the two-exciton eigenstates are given by the direct-product nonentangled form,

$$|f_o\rangle = B_{e_1}^+ B_{e_2}^+ |g\rangle.$$

(7)

More generally, however, the two-exciton eigenstates are entangled

$$|f\rangle = \sum_{e_1 e_2} c_{f,e_1 e_2} B_{e_1}^+ B_{e_2}^+ |g\rangle.$$

(8)

Two-exciton states may be directly accessed by nonlinear four wave mixing techniques. The two-exciton entanglement has distinct signatures in two-dimensional (2D) double-quantum-coherence spectroscopy.[15,19] This time-domain technique uses four short pulses with wavevectors $\mathbf{k_1}$, $\mathbf{k_2}$, $\mathbf{k_3}$, and $\mathbf{k_4}$ (in chronological order) to generate the signal in the direction $\mathbf{k_4} = \mathbf{k_1} + \mathbf{k_2} - \mathbf{k_3}$. The wave function of the optically driven system is given by

$$|\psi(t)\rangle = |g\rangle + \sum_e R_e(t) B_e^+ |g\rangle + \sum_f R_f(t) D_f^+ |g\rangle,$$

(9)

where we have introduced creation operators for the two-exciton states,
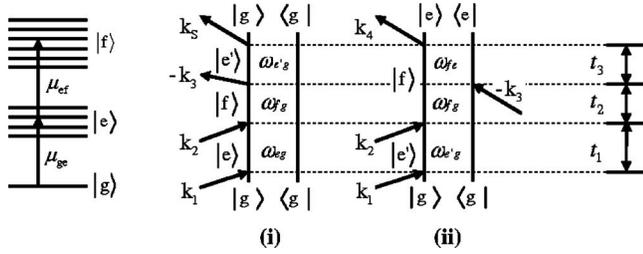
FIG. 1. Left: Many-body states and transition dipoles of the exciton model of four coupled two-level chromophores. Shown is the ground state g, the single-exciton manifold e, and the two-exciton manifold f. Right: The two Feynman diagrams contributing to the double-quantum coherence signal. t_j are the time delays between laser pulses. For uncoupled quasiparticles the two diagrams exactly cancel and the signal vanishes.

$$D_f^+ = \sum_{e_1 e_2} c_{f,e_1 e_2} B_{e_1}^+ B_{e_2}^+. \tag{10}$$

The time-dependent coefficients R_e and R_f depend on details of the pulse envelopes. The 2D spectra given by the Feynman diagrams shown in Fig. 1 project this wave function into many-body states that may be resolved by their energies. The signal can be recorded versus the three delay periods between pulses t_1, t_2, and t_3. 2D plots are obtained by a double Fourier transform with respect to two of these variables, holding the other fixed consider, for example, the signal,

$$S(\Omega_1, \Omega_2, t_3) = \int_o^\infty dt_1 \int_o^\infty dt_2 \, \exp(i\Omega_1 t_1 + i\Omega_2 t_2) S(t_1, t_2, t_3). \tag{11}$$

Ω_2 contains $|f\rangle\langle g|$ resonances at ω_{fg} and shows the two-exciton manifold. Ω_1 shows the $|e\rangle\langle g|$ resonances at ω_{eg}. Similarly in a different projection of the same signal, $S(t_1, \Omega_2, \Omega_3)$ Ω_3 will show both $|e\rangle\langle g|$ and $|f\rangle\langle e|$ resonances. This signal vanishes for a system of noninteracting excitons [Eq. (5)] due to destructive interference of the two diagrams. It is thus induced by correlations. For weakly coupled excitons we can calculate the signal using first order perturbation theory: The eigenstates are unperturbed and show no entanglement. However, the eigenvalues are shifted which makes the signal finite (the two diagrams no longer cancel). We see $N(N-1)/2$ possible $|f\rangle$ peaks along Ω_2 each having two peaks along Ω_1. The total number of peaks in the 2D spectrum is therefore $N(N-1)$. This is illustrated for $N=4$ in Fig. 2. For a strongly entangled system we can fill the entire
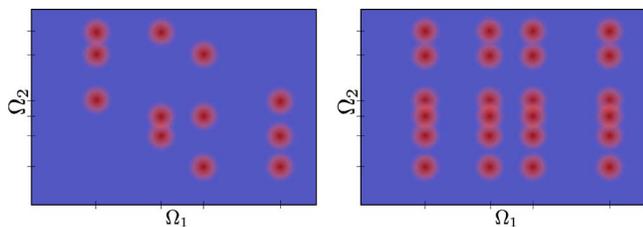

FIG. 2. Schematic 2D double-quantum-coherence spectra of the model in Fig. 1 with four single-exciton and δ two-exciton states. Left: No entanglement. There are six two-exciton states shown along Ω_2, each made out of two excitons and has two peaks along Ω_1, for a total of twelve peaks. Right: Strongly entangled states. Now each two-exciton state can project into all four single excitons giving 24 possible peaks.

grid which gives $N^2(N-1)/2$ possible peaks. We next consider the $S(t_1, \Omega_2, \Omega_3)$ signal. Here we have again $N(N-1)/2$ peaks at ω_{fg} along Ω_2, but along Ω_3 we have $N^2(N-1)/2$ $|f\rangle\langle e|$ peaks at ω_{fe} and N $|e\rangle\langle g|$ peaks at ω_{eg}. These signals thus carry direct information about the two-exciton states and their degree of entanglement.

More generally, a coherent n-quantum coherence optical signal can directly reveal the state of entanglement of n quasiparticle degrees of freedom by properly correlating the time evolutions during selected and controlled delay periods. The peak pattern becomes much richer for states with higher numbers of particles. Consider, for example, the $\chi^{(5)}$ signal generated at $3\mathbf{k}_1 - 2\mathbf{k}_2$ which carries information on three excitons. We will denote the $\binom{N}{2} = \frac{1}{6}N(N-1)(N-2)$ three-exciton states as h. With the first delay period between $\mathbf{k}_1$ and $\mathbf{k}_2$ we will see ω_{hg} resonances in Ω_1 corresponding to the various three-exciton states. Along the frequency associated with the second delay (Ω_2) between $\mathbf{k}_2$ and the detected signal we can see resonances of the types ω_{eg}, ω_{fe}, and ω_{hf}. The rich peak pattern will show how the h states project into various products of f and e states thus revealing three-exciton entanglement.

The fact that exciton states may be delocalized among chromophores is obviously interesting and implies quantum communication between them, provided it survives decoherence effects due to the surrounding medium. One could then justifiably argue that the chromophores are entangled and that the dynamics is profoundly quantum in nature. However, as shown here, these quantum effects can be easily eliminated by basing the description on the delocalized exciton modes.

Quantum mechanics clearly enters into the definition of the quasiparticle oscillators, but once this is done, the dynamics can be described in purely classical terms. This is reminiscent of the normal mode description of harmonic molecular vibrations [Eq. (4)] where technically, the different atoms in the molecule are entangled; however an equivalent description in terms of independent normal modes is much simpler. In the normal modes different atoms move in well defined phases and all "quantum coherence" effects are included in these phases. Oscillatory "quantum beats" in the linear response can be fully understood with the classical-oscillator picture. Once we identify our natural coordinates for the many-body states based on the linear response, we can then ask the following: Are these coordinates entangled in higher (two, three particle, etc.) excited eigenstates? As demonstrated here, this question can be unambiguously answered by nonlinear spectroscopy where genuine quantum entanglement effects show up. Entanglement at the single-exciton level can always be eliminated, leaving it only to two excitons and higher. 2D spectroscopy provides a direct access to the entanglement of these coordinates in various many-body states as selected by the 2D axes. Interactions with the optical pulses can only manipulate one chromophore at a time and create intramolecular coherences. Many-body coherences build up during the free evolution periods between optical pulses due to chromophore interactions.

To fully exploit the oscillator picture, the optical response of aggregates can be described by equations of motion for variables which represent different numbers of quasiparticles. These *nonlinear exciton equations*[20–24] can be truncated to the desired order in optical fields. To the linear order they give the Drude oscillator model but additional oscillator modes are needed to represent higher nonlinerarities. In the quasiparticle picture, optical nonlinearities are attributed to exciton scattering that results either from direct coupling (nonlinearities in the Hamiltonian) or Pauli exclusion (the non-Boson commutation relations). The scattering matrix which can be accessed via the nonlinear optical response provides a convenient measure for genuine entanglement of multiple excitons.

Finally we note that the present analysis was limited to conventional spectroscopy with classical light where chromophore entanglement is created solely by their interactions. Spectroscopy with entangled photons is an exciting recent development.[25] Following the interaction with entangled photons the chromophores may become entangled even when they do not interact with each other. This could open up new possibilities for creating and manipulating the entanglement and may give rise to new collective entanglement-induced resonances[26] in nonlinear spectroscopy.

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