Manipulation of two-photon-induced fluorescence spectra of chromophore aggregates with entangled photons: A simulation study

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The nonclassical spectral and temporal features of entangled photons offer new possibilities to investigate the interactions of excitons in photosynthetic complexes and to target the excitation of specific states. Simulations of fluorescence in the bacterial reaction center induced by entangled light demonstrate a degree of selectivity of double-exciton states which is not possible using classical stochastic light with the same power spectrum.

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I. INTRODUCTION

Apart from their evident importance in experimental tests of the foundations of quantum mechanics, entangled photons promise many applications to quantum information processing [1,2], secure quantum communication [3–5], lithography [6–9], or metrology [10–12]. In addition, their nonclassical frequency and time correlations could also open up novel spectroscopic applications [13,14]. Entanglement-induced two-photon transparency [15] and the linear scaling of two-photon-induced fluorescence with the pump intensity [16] constitute two basic nonclassical effects observed with entangled photon pairs. This scaling makes it possible to carry out nonlinear optical measurements with much lower light intensity compared to classical light, as we will discuss in Sec. III. More generally, entangled photons offer new control parameters for nonlinear spectroscopy [17] and can be used to distinguish quantum entanglement with the pump intensity [16] and the linear scaling of two-photon-induced fluorescence [15]. In the rotating-wave approximation, the interaction Hamiltonian reads

\begin{equation}
H_{\text{int}}(t) = V(t)E^\dagger(t) + V^\dagger(t)E(t),
\end{equation}

where we have introduced the positive-frequency component of the dipole operator,

\begin{equation}
V(t) = \sum_e \{\mu_{eg}|g\rangle\langle e|e^{-i\omega_{egt}t} + \sum_f \mu_{fe}|e\rangle\langle f|e^{-i\omega_{fe}t}t),
\end{equation}

in which $\omega_{eg} = (E_e - E_g)/\hbar$ are matter transition frequencies and $\mu_{eft}$ are the dipole moments. The corresponding negative-frequency part of the electromagnetic field operator is given by

\begin{equation}
E(t) = \sum_s \left( \frac{2\pi \omega_s}{\Omega} \right)^{1/2} a_s^\dagger e^{i\omega_st},
\end{equation}

where $\Omega$ denotes the quantization volume, $a_s^\dagger$ is the creation operator for mode $s$, and $s$ runs over all possible pathways that reach the double-exciton state (see Fig. 1). In contrast, with classical fields the bandwidths of the two beams add up and create a large uncertainty in the sum. Our simulations show that the nonclassical distributions could be detected by the fluorescence signal. The control parameters of the entangled light can be used to stretch the signal in two-dimensional plots, which could reveal additional information about the matter.

II. THE MODEL

We consider a chromophore aggregate interacting with the electromagnetic field and described by the Hamiltonian

\begin{equation}
H = H_0 + H_F + H_{\text{int}},
\end{equation}

where $H_0$, $H_F$, and $H_{\text{int}}$ represent the aggregate, the field, and their coupling, respectively. The electronic states group into well-separated manifolds, which are denoted as $e$ manifold (single-exciton), $f$ manifold (double-exciton), etc. The field couples to the system via the dipole operator, which induces transitions between these manifolds. In the rotating-wave approximation, the interaction Hamiltonian reads

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where $T$ photon. The broad bandwidth allows us to access the entire manifold manner. The matrix element $\langle e_i, e_j \rangle$ of the single-exciton block of the density matrix is given by

$$
\rho_{e_i e_j}(t) = \text{tr}[|e_j(t)\rangle\langle e_i(t)|\rho(t)],
$$

where $\rho(t)$ denotes the density matrix of the entire matter-field system. In a superoperator Liouville space representation, the formal solution of the Heisenberg equation is given by the Dyson series [23]

$$
\rho(t) = T \exp\left(-\frac{i}{\hbar} \int_0^t dt' H_{\text{int}}(t')\right)\rho(-\infty),
$$

where $T$ is the time-ordering operator, and the superoperator $H_{\text{int}}$ is defined through $A\rho = \rho A - [A, \rho]$ in the interaction picture with respect to $H_0 + H_F$. For weak fields we can expand the exponential, and the leading (second) order contribution to Eq. (5) yields

$$
\rho'_{e_i, e_j}(t; \Gamma) = -\left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 \times\left[\langle V(t_1)A_{ij}(t)V(t_2)\rangle\langle V(t_1)\rangle\langle V(t_2)\rangle\right],
$$

where $A_{ij}(t) \equiv |e_j(t)\rangle\langle e_i(t)|$ and $\Gamma$ denotes the set of control parameters that govern the excitation, e.g., frequencies, pulse envelopes, etc. The angle brackets $\langle \cdot \cdot \cdot \rangle$ denote the quantum-mechanical expectation value with respect to the initial state $\rho(-\infty)$,

$$
\rho(-\infty) = |g\rangle\langle g| \otimes \rho_{\text{field}}.
$$

The fourth-order processes that end in the $|e\rangle$ manifold can be represented by diagrams I and II in Fig. 2 (for diagram rules, see [24]). These can be divided into two classes: Raman type that only involve single-exciton resonances (diagram I) and two-photon absorption type (diagram II) that involve the double-exciton manifold. We have to take two additional diagrams into account, in which three interactions occur on the right-hand side. Apart from the projector $|e_j(t)\rangle\langle e_i(t)|$, these are simply the complex conjugates of diagrams I and II in Fig. 2. We can thus write them as

$$
\rho_{e_i, e_j}(t; \Gamma) = -\left(-\frac{i}{\hbar}\right)^4 \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 \int_{-\infty}^t dt_3 \int_{-\infty}^t dt_4 \times\left[\langle V(t_1)A_{ij}(t)V(t_2)V(t_3)\rangle\langle V(t_1)\rangle\langle V(t_2)\rangle\langle V(t_3)\rangle\right].
$$

FIG. 1. (Color online) (a) Two-photon transitions with entangled photons. The broad bandwidth allows us to access the entire manifold $|e\rangle$; at the same time the manifold $|f\rangle$ is well resolved due to the narrow distribution of $\omega_1 + \omega_2$. (b) Transitions with classical light. Bandwidths of $\omega_1$ and $\omega_2$ now add up, and the $f$ manifold cannot be resolved.

\[ q_{f_i f_j m}(\tau; \Gamma) = \left( \frac{i}{\hbar} \right)^4 \int_{-\infty}^{\tau_4} d\tau_4 \int_{-\infty}^{\tau_3} d\tau_3 \int_{\tau_2}^{\tau_3} d\tau_2 \int_{\tau_1}^{\tau_2} d\tau_1 \times \langle V(\tau_3)V(\tau_2)B_i(\tau)V^\dagger(\tau_2)V^\dagger(\tau_1) \rangle \times \langle E^\dagger(\tau_3)E^\dagger(\tau_2)E(\tau_2)E(\tau_1) \rangle, \] 

(11)

where \( B_i(\tau) \equiv |f_i(\tau)\rangle \langle f_i(\tau)|. \) Equations (9)-(11) enable us to evaluate the density matrix for arbitrary states of the radiation field once we specify its four-point field correlation function.

### III. LIGHT SOURCES

#### A. The twin-photon state

Extensive research effort has focused on producing and detecting pairs of entangled photons. Numerous schemes have been employed for the generation of entangled photon pairs, including parametric down conversion [25], biexciton decay in semiconductors [26,27], or four wave mixing in optical fibers [28,29].

We consider a type of entangled light known as twin photons [30]. It is created by type-II parametric down conversion with a cw-pump laser of frequency \( \omega_p. \) When the pump beam is sufficiently weak, it predominantly produces temporally nonoverlapping pairs of entangled photons. The state of the field can then be expanded perturbatively in the interaction Hamiltonian of the pump beam with the nonlinear crystal [30],

\[
|\psi\rangle = E_p \int d\vec{k}_1 \int d\vec{k}_2 \sin[(k_1 - k_1 - k_2) L/2] 
\times e^{i(k_1 - k_2) z L/2} \delta(k_1 x + k_2 y) 
\times \delta(\omega(\vec{k}_1) + \omega(\vec{k}_2) - \omega_p)|\vec{k}_1 \vec{k}_2\rangle, \tag{12}
\]

where \( E_p \) is the pump field amplitude. The state is not normalized. Here, the length along the optical axis is denoted \( L, \) while it is assumed to be infinitely large in the other two directions. In the setup depicted in Fig. 3, one collects the light in two outgoing directions, \( \theta_1 \) and \( \theta_2, \) with respect to the optical axis, thus fix the central frequencies \( \omega_1 \) and \( \omega_2. \) Normalization requires that \( L \) be infinite.

\[
\text{FIG. 3. (Color online) Parametric down-conversion setup to produce twin photons: A high-energy pump of frequency } \omega_p \text{ creates two beams of entangled photons with central frequencies } \omega_1 \text{ and } \omega_2, \text{ such that } \omega_p = \omega_1 + \omega_2. \text{ The central frequencies are determined by the relative angles between the direction of propagation.}
\]

For short \( T, \) Eq. (12) leads to the broad power spectrum

\[
n_{\text{twin}}(\omega) = \int_{-\infty}^{\infty} dt_1 dt_2 e^{-i\omega(t_2 - t_1)} \langle E^\dagger(t_1) E(t_2) \rangle 
= n_0 |E_p|^2 \left[ \frac{\sin^2 \left( \frac{\omega - \omega_1}{2} T \right)}{\sin^2 \left( \frac{\omega - \omega_2}{2} T \right)} \right], \tag{13}
\]

which is depicted in Fig. 4. To evaluate the normally ordered correlation functions in Eq. (10), we note that it can be separated into

\[
\langle E^\dagger(t_3) E^\dagger(t_2) E(t_2) E(t_1) \rangle 
= \langle \psi | E^\dagger(t_3) E^\dagger(t_2) |0\rangle \langle 0 | E(t_2) E(t_1) |\psi\rangle, \tag{14}
\]

where [30]

\[
\langle 0 | E(t_2) E(t_1) |\psi\rangle 
= CE_p \operatorname{rect} \left( \frac{t_2 - t_1}{T} \right) (e^{-i\omega_1 t_1 - i\omega_2 t_2} + e^{-i\omega_1 t_1 + i\omega_2 t_2}). \tag{15}
\]

Here, \( C \) is a constant and we have defined the rectangular function

\[
\operatorname{rect}(x) = \begin{cases} 
1 & \text{for } x < 1, \\
0 & \text{otherwise.} 
\end{cases} \tag{16}
\]

The nonclassical nature of the quantum state produced by this setup has been verified in numerous experiments [31–38]. One important feature that follows from Eqs. (14) and (15) is that the four-point correlation function of the fields scales linearly with the pump intensity \( |E_p|^2, \) while classically it scales quadratically [39]. This scaling behavior can be utilized in
experiments to determine intensity regimes, in which Eq. (12) can account for the produced signal. In practice, we expect this linear scaling of fourth-order signals with a crossover to a quadratic classical scaling at higher intensities. The light beam can be considered to be made of pairs of photons. At weak intensities the pairs are temporally well separated, and the process is induced by two photons of the same pair. At higher intensities it becomes statistically more plausible for the two photons to come from different pairs, which are not entangled, and the classical scaling is recovered. This crossover has been demonstrated experimentally [35–38]. For instance, in Ref. [35] the authors detect it at an intensity (of the entangled photon flux) of 1.5 µW in a periodically poled potassium titanyl phosphate crystal, which was obtained by a pump intensity of less than 2.5 W. The linear scaling of the two-photon absorption was also demonstrated experimentally for organic porphyrin dendrimers [36,37].

Entangled photon sources are weak, but at the same time weak intensities are required to see the effect of entanglement. Nonlinear spectroscopy and imaging with weak fields should allow us to limit the damage to biological samples.

B. Stochastic light with the same power spectrum

To highlight the effects of entanglement, we consider a classical reference state of the field with the same power spectrum. To that end, we introduce the frequency decomposition of a classical field,

\[ E_i(t) = \sum_\omega \int d\omega A_1(\omega) e^{-i\omega t - i\phi_1(\omega)}, \]

where \( A_1 \) and \( \phi_1 \) are real functions representing the amplitude and the phase of the various modes. To reproduce the power spectrum, Eq. (13), we took

\[ A_1(\omega) = A_0 \text{sinc}[(\omega - \omega_1)T/2] e^{-i\phi(\omega)}, \]

\[ A_2(\omega) = A_0 \text{sinc}[(\omega - \omega_2)T/2] e^{-i\phi(\omega+\pi/2)}. \]

With this choice \( \phi(\omega) \) does not affect the power spectrum and will be chosen to obtain stationary stochastic light (rather than a pulse). We assume that \( \phi(\omega) \) is a random function, so there is no well-defined phase relation between the different frequencies. The quantum-mechanical expectation value in correlation functions such as \( \langle E^\dagger(t_1) E(t_2) E^\dagger(t_3) E(t_4) \rangle \) then needs to be replaced by an average over the distribution of \( \phi(\omega) \):

\[ \langle E^\dagger(t_1) E^\dagger(t_2) E(t_3) \rangle = \int d\omega_1 \int d\omega_2 \int d\omega_3 \int d\omega_4 A(\omega_1) A(\omega_2) A^*(\omega_3) A^*(\omega_4) e^{-i\phi(\omega_1+\phi(\omega_2)-\phi(\omega_3)-\phi(\omega_4))}. \]

Assuming that \( \phi \) is uniformly distributed in the interval \([0, 2\pi]\), we find that \( E \) is a stationary Gaussian process:

\[ \langle E^\dagger(t_3) E^\dagger(t_4) E(t_2) E(t_1) \rangle = \langle E^\dagger(t_3) E(t_2) \rangle \langle E^\dagger(t_4) E(t_1) \rangle + \langle E^\dagger(t_3) E(t_2) E(t_4) E(t_1) \rangle. \]

Thus, classical light only shows correlations on the level of intensities, i.e., \( \langle E^\dagger E \rangle \). By substitution of Eqs. (18) and (19) we then obtain

\[ \langle E^\dagger(t_3) E^\dagger(t_4) E(t_2) E(t_1) \rangle = N^4 \sum_{\omega_1, \omega_2} \left[ \text{tri} \left( \frac{t_1 - t_2}{T} \right) \text{tri} \left( \frac{t_2 - t_4}{T} \right) \right] \times e^{-i\omega_1(t_1-t_3)} e^{-i\omega_2(t_2-t_4)} + \text{tri} \left( \frac{t_1 - t_4}{T} \right) \text{tri} \left( \frac{t_2 - t_3}{T} \right) \times e^{-i\omega_1(t_1-t_2)} e^{-i\omega_2(t_3-t_4)}, \]

where the summations run over \( \omega_1 \) and \( \omega_2 \) and \( \text{tri}(x) \) is the triangular function as defined in Eq. (A2). This correlation function represents stationary, stochastic light since it only depends on time differences, just like the one produced by entangled photons with a stationary pump [see Eq. (15)]. However, there is one crucial difference. The quantum-mechanical expectation value can be factorized in Eq. (14) and only depends on \( t_1 - t_3 \) and \( t_2 - t_4 \). The correlation function (22) depends on \( t_1 - t_3, t_2 - t_4, t_1 - t_4, \) and \( t_2 - t_3 \).

IV. SINGLE- AND DOUBLE-EXCITON DENSITY MATRICES IN THE BACTERIAL REACTION CENTER

We now present simulations of the exciton density matrices produced by entangled and stochastic light with the same spectral density in a model of the bacterial reaction center (RC) of purple bacteria Blastochloris viridis [41]. The primary steps in photosynthesis involve excitation energy transfer towards and charge separation within RCs. The RC of purple bacteria utilizes the high-intensity near-IR region of the solar irradiation and transforms the energy into a chemical potential gradient with near-unity efficiency. In bacterial RC the charge separation occurs in the active branch of the protein on the subpicosecond to low-picosecond time scale [42,43]. The quenching of the excited-state special pair population has been demonstrated experimentally in time-resolved emission measurements [44,45].

The electronic Hamiltonian \( H_0 \) describes the optically bright chromophore excitations and dark charge-separated states in the active branch of the RC in a tight-binding formulation. It includes 12 single- and 41 double-exciton states, as depicted in Fig. 5(c). To construct \( H_0 \), we start with the x-ray structural data for \( B. \ viridis \) (Protein Data Bank code: 1PRC) [40]. The \( Q_y \) transition dipole moments are placed at the center of bacteriochlorophylls (BChls) and bacteriopheophytins (BPs). The excitation energies of BChls and BPs are taken from Ref. [46]. Förster couplings are calculated in the dipole approximation, except for the special pair where a value of 852 cm\(^{-1}\) was chosen, allowing us to reproduce the circular dichroism spectra of \( B. \ viridis \). The energy of the primary charge-separated (CS) state is fixed relative to the lowest special pair exciton state [47,48], which yields a reference point for the additional CS energies of the active branch. The Hamiltonian is given in detail in Ref. [41]. Dephasing effects and incoherent population transport were neglected. To model the absorption spectrum shown in Fig. 5, we assume the same lifetime broadening \( \gamma = 200 \text{ cm}^{-1} \).
for all single-exciton states, which agrees reasonably with more detailed simulations [41]. In Fig. 5(b), we mark the single-exciton states \( \epsilon \) by vertical lines, whose length is proportional to their oscillator strength \( |\mu_{\text{osc}}|^2 \). The spectrum is dominated by six states corresponding to molecular Frenkel excitations of the constituents of the RC. The other six charge transfer states are dark and cannot be accessed spectroscopically.

The exciton density matrix induced by entangled or stochastic light is block diagonal in the \( \epsilon \) and \( f \) manifolds since a coherence between the two manifolds can be related to field correlation functions of the kind \( \langle \epsilon^\dagger \epsilon E \rangle \) or \( \langle E^\dagger \epsilon E \rangle \), which vanish for any Fock state or stationary Gaussian process. In Fig. 6 we depict the absolute values of the density-matrix elements of the double-exciton states from \( f_1 \) to \( f_5 \) for \( \omega_p = 22160 \) and 24 200 cm\(^{-1}\). Entangled light excites a pure double-exciton state, \( \sum_f T_{gf}(t)|f\rangle \) [see Eq. (A8)]. Consequently, the purity of the density matrices in Figs. 6(a) and 6(b) is \( \text{tr}_f|\rho_f|^2 = 1 \). The density matrix induced by stochastic light [Figs. 6(c) and 6(d)] is not in a pure state; we obtain \( \text{tr}_f|\rho_f|^2 \approx 0.24 \) independent of the pump frequency. Furthermore, it is apparent that by tuning the pump frequency, we can select the excitation of certain states. Figure 6(a) shows strong excitation of states \( f_{11}, f_{25}, \) and \( f_{26} \), while in Fig. 6(b) the states between \( f_{27} \) and \( f_{50} \) are most strongly excited. This selectivity allows us to manipulate of the fluorescence signal, as will be shown in the next section. While the density matrices in Figs. 6(a) and 6(b) strongly depend on the pump frequency, our calculations of the corresponding density matrices produced by stochastic light indicate no such selectivity. The results are plotted in Figs. 6(c) and 6(d). For both pump frequencies (\( \omega_\epsilon + \omega_f = 22160 \) and 24 200 cm\(^{-1}\)), the excitation is distributed among the bright states \( f_{11}, f_{15}, f_{22}, f_{25}, f_{27}, \) and \( f_{50} \).

Figure 7 shows the single-exciton manifold density matrices [Eq. (A5)] for the same pump frequencies 22 160 and 24 200 cm\(^{-1}\). Our results qualitatively resemble the ones for the double-exciton manifold. By varying \( \omega_p \) we can enhance [Fig. 7(a)] or suppress [Fig. 7(b)] the excitation of \( \epsilon_5 \) (and, vice versa, of \( \epsilon_6 \) and \( \epsilon_7 \)), while stochastic light always creates very similar density matrices. For both frequencies, the population is mainly distributed between states \( \epsilon_3 \) and \( \epsilon_7 \).

The total population of the single-exciton manifold \( \sum_\epsilon \rho_{\epsilon \epsilon} \) calculated to second order in the matter-field interaction [Eq. (A3)] is displayed in Fig. 8 vs the frequencies \( \omega_p \) and \( \omega_f \). Due to the broadband nature of the beams, none of the peaks of the absorption spectrum in Fig. 5(b) can be resolved. This population only depends on the spectral density, is identical for stochastic and entangled light, and is not susceptible for the nonclassical features of entangled light.

The total double-exciton population \( \sum_f \rho_{ff} \) created by Eq. (A8) is plotted in Fig. 9(a). The distribution of the single-exciton states to fourth order (see diagram II in Fig. 2) looks almost identical since Eq. (10) includes an excitation to the double-exciton manifold, and it is not shown. It depends only

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**FIG. 5.** (Color online) (a) Arrangement of the six chromophores of the bacterial RC (Protein Data Bank code: 1PRC) [40]. (b) The absorption spectrum of the RC. The lifetime broadening of the excited states is taken to be 200 cm\(^{-1}\). The gray dashed line shows the power spectrum of Fig. 4, the single exciton states are indicated by red lines, and their heights are proportional to their transition dipole moments \( |\mu_{\text{tr}}|^2 \). (c) Level scheme of the RC. The 12 single-exciton states are marked in red, and the 41 double-exciton states in blue.

**FIG. 6.** (Color online) The double-exciton manifold density matrix upon excitation by entangled light with (a) \( \omega_p = 22160 \) cm\(^{-1}\) and (b) 24 200 cm\(^{-1}\). (c) and (d) The same as (a) and (b), but for stochastic light. Only the dominant states \( f_{10} \cdots f_{30} \) are shown.
weakly on $\omega_2$, reflecting the energy uncertainty due to the time entanglement. Thus, the central frequency of each beam is not important, and in the following we set $\omega_2 = 11\,000\,\text{cm}^{-1}$. Two broad resonance bands, at $22\,000$–$23\,000\,\text{cm}^{-1}$ (band $a$) and at $23\,000$–$24\,000\,\text{cm}^{-1}$ (band $b$), dominate the distribution. From our previous discussion of the density matrix, we anticipate that states $f_{11}$, $f_{15}$, and $f_{16}$ dominate band $a$, whereas states $f_{23}$–$f_{27}$ seem to make up band $b$ (see Fig. 6). The signal induced by stochastic light [Fig. 9(b)] shows no such structure. Due to the broad bandwidth, the level structure of the RC cannot be resolved at all.

To get a more detailed picture of this state distribution, we depict the contribution of various double-exciton state populations to the distribution [Eq. (A8)] in Fig. 10(a). The distributions are normalized at each $\omega_p$. States $f_{11}$, $f_{15}$, and $f_{16}$ dominate band $a$, whereas band $b$ is dominated by states $f_{23}$, $f_{24}$, and $f_{25}$. At higher pump frequency, states $f_{27}$, $f_{30}$, and $f_{32}$ are the most pronounced. In general, the regions of the leading contribution group around the states‘ energies, but the distributions may be asymmetric because of the presence of other states. We next turn to the distribution of single-exciton states [Fig. 10(b)]. Since the single excitons are obtained by emission from a two-exciton state, the distribution closely resembles the double-exciton distribution in Fig. 10(a). For instance, when $\omega_p \sim 22\,200\,\text{cm}^{-1}$, the double-exciton state $f_{11}$ is on resonance. It decays primarily into the single-exciton state $e_3$, and accordingly, the contribution of this state increases around the same value of the pump frequency. The same holds for, e.g., the double-exciton state $f_{30}$ and the single-exciton state $e_{10}$. However, in most cases the different contributions overlap, and the relation between the single-exciton and the double-exciton states is more complex.

V. TWO-PHOTON-INDUCED FLUORESCENCE

Having discussed our simulations of the excited-state distribution created by entangled light, we now turn to the question whether it may be possible to detect fingerprints of these distributions in experiments. To that end, we calculate the dispersed fluorescence signal. This involves transitions between double- and single-exciton states as well as transitions between single-exciton states and the ground state, i.e.,

$$ S_f(\omega; \Gamma) = \sum_{e,f} |\mu_{fe}|^2 p_f(\tau; \Gamma) \delta(\omega_f - \omega_e - \omega_s), \quad (23) $$

$$ S_e(\omega; \Gamma) = \sum_{e} |\mu_{eg}|^2 p_e(\tau; \Gamma) \delta(\omega_e - \omega_s). \quad (24) $$

Here, $\omega_s$ is the emitted fluorescence frequency, and $p_f$ ($p_e$) is the population of state $f$ ($e$) given by Eq. (11) [Eq. (10)]. More elaborate detection (gated time and frequency, photon statistics) is possible [49] but will not be considered here.

In Fig. 11, we display this signal vs the pump frequency $\omega_p$ and the emission frequency $\omega_s$. The $\delta$ functions in Eqs. (23) and (24) were replaced by a Lorentzian, which means the width of the peaks in horizontal direction of Fig. 11 is instrumental. In analogy to the distributions shown in Fig. 9, the fluorescence simulation with entangled photons [Fig. 11(a)] shows two distinct resonances along the $\omega_p$ axis, pertaining to bands $a$ and $b$, respectively (see also Fig. 13). Along $\omega_s$ (horizontal axis), it contains two contributions, one around $\omega_s \sim 10\,000\,\text{cm}^{-1}$ and a higher-energy part between 12 000 and 13 000 cm$^{-1}$, reminiscent of the absorption spectrum. This pronounced structure can be exploited to enhance or suppress certain features, as will be demonstrated in the following.

FIG. 7. (Color online) Same as Fig. 6, but for the single-exciton manifold. Only dominant states $e_3 \cdots e_{10}$ are shown.

FIG. 8. (Color online) Second-order contribution to the total single-exciton manifold population $\sum_e \rho_e(\tau)$, Eq. (7), with $T = 30\,\text{fs}$. (b) Excitation by entangled light with $T = 30\,\text{fs}$. (b) Excitation by stochastic light.
The simulation of the stochastic signal in Fig. 11(b) shows no structure along the $\omega_p$ axis and, consequently, does not allow a manipulation of the fluorescence signal. The dispersed fluorescence simulation for $\omega_p = 22\,160$ cm$^{-1}$ is shown in Fig. 12(a). Most of the peaks can be directly attributed to the energy of single-exciton states; the transition thus corresponds to fluorescence either from the single-exciton manifold or from double-exciton states, whose energies closely match the sum of two single-exciton states. However, the simulations also show side peaks of the resonance at 10\,245 cm$^{-1}$, which cannot be assigned to single-exciton energies. The strongest of these peaks is highlighted by the black arrow in Fig. 12(b). It corresponds to the $f_{11} \rightarrow e_7$ transition. Since state $f_{11}$ is most strongly excited at the given pump frequency [see Fig. 10(a)], this peak is most pronounced. At pump frequency 22\,500 cm$^{-1}$ resonantly excited states $f_{15}$ and $f_{16}$ show different transitions into the single-exciton state $e_6$ [see Fig. 12(c)]. The simulation with stochastic light shown in Figs. 12(d) and 12(e) cannot resolve any of these side peaks due to its broadband nature.

VI. CONCLUSIONS

We derived expressions for the single- and double-exciton density matrices of quantum systems interacting with arbitrary light sources perturbatively in the field. These were used to simulate the excitation of matter via entangled twin photons and stochastic light with the same power spectrum. Applications to the reaction center of purple bacteria show that the populations strongly depend on the nature of the light, and we indicated how these properties could be observed in the frequency-resolved fluorescence measurements. The nonclassical spectral profile of entangled light allows us to target specific double-exciton states and to explore all the excitation pathways to this state in a single shot. This shows up perspicuously in the fluorescence action spectrum in Fig. 13. The spectrum reveals the level structure of the double-exciton manifold, whereas the stochastic light cannot resolve this structure. For completeness, we also plot the action spectrum created by two cw laser beams with frequencies $\omega_1$ and $\omega_2$ at the peaks of the spectral density. Even though the narrow bandwidth of these beams allows for a good $\omega_p$ resolution, this signal is most pronounced when one of the laser beams
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APPENDIX A: EXCITATIONS INDUCED BY TWIN PHOTONS

Using Eq. (12), the field correlation function of the leading-order contribution, given by Eq. (7), yields

$$\langle E_i(t)E_j(t) \rangle = C \text{tri} \left( \frac{t_2 - t_1}{T} \right) \exp \left( -i \omega_1 (t_2 - t_1) + e^{-i \omega_2 (t_2 - t_1)} \right),$$


(A1)

where we have defined the triangular function

$$\text{tri}(x) = \begin{cases} 1 - |x| & \text{for } |x| < 1, \\ 0 & \text{otherwise.} \end{cases}$$

(A2)

Expanding the matter correlation function into a sum-over-states expression, we obtain

$$\varrho_{e,e}(t; \Gamma) = \frac{i \mu_{ge}^2 \mu_{eg}^2}{4 \hbar^2 (\omega_{ee} + 2i\gamma_e)} \left[ \text{sinc} \left( (\omega_1 - \omega_{eg} + i\gamma_e) T/2 \right) + \text{sinc} \left( (\omega_2 - \omega_{eg} - i\gamma_e) T/2 \right) \right],$$

(A3)

where we dropped the constant factor $C$. The matrix element of the dipole operator connecting states $g$ and $e$ is denoted $\mu_{ge}$, the energy difference is given by $\omega_{eg}$, and the lifetime broadening is denoted by $\gamma_e$. We can assume that $\gamma_e \approx \gamma_f$. Since the entanglement time $T$ is short relative to other time scales in the system ($T \sim 10^{-3}$ cm), this contribution to the single-exciton states depends weakly on the pump frequency $\omega_p$.

The field correlation function of Eq. (9) can be recast as a normally ordered term plus a commutator term, which we neglect. Using Eq. (15) and dropping the constant factor $C$, we obtain for the populations

$$\varrho_{e,e}(t; \Gamma) = \text{Re} \left\{ \sum_{e,e} \sum_{a,b,c,d} \frac{\mu_{ge}^2 \mu_{eg}^2}{\hbar^2} \left[ \frac{\mu_{fa} \mu_{eg}}{\omega_1 + \omega_2 - \omega_{fg} + i\gamma_f} \left( e^{-i(\omega_a - \omega_{eg} + i\gamma_e) T} - 1 \right) \frac{\mu_{fd} \mu_{ge}}{\omega_1 - \omega_{eg} + i\gamma_e} \left( e^{-i(\omega_a - \omega_{eg} - i\gamma_e) T} - 1 \right) \right. \right.$$

$$\left. - \frac{\mu_{fa} \mu_{eg}}{\omega_1 + \omega_2 - \omega_{fg} + i\gamma_f} \frac{\mu_{fd} \mu_{ge}}{\omega_1 - \omega_{eg} - i\gamma_e} \frac{\mu_{fa} \mu_{eg}}{\omega_1 + \omega_2 - \omega_{fg} + i\gamma_f} \frac{\mu_{fd} \mu_{ge}}{\omega_1 - \omega_{eg} + i\gamma_e} \right] \right\}. $$

$$\text{(A5)}$$

This contribution is proportional to the entanglement time $T$, reflecting the fact that in Eq. (9) the time pairs $(t_1, t_3)$ and $(t_2, t_4)$ are correlated. This means that the entire process has to happen within the entanglement time $T$. Since this time is very short with respect to other time scales in the system, $\varrho_{e,e}$ can be neglected. The only fourth-order contribution to the single-exciton manifold is thus given by Eq. (10). In a sum-over-states expression, it reads...
where the summations $a$, $b$, $c$, and $d$ run over $\omega_1$ and $\omega_2$. It is apparent that the single-exciton peaks are multiplied by phase factors of the kind $e^{i(\omega_{a}-\omega_{e}+i\gamma_{e})T}/(\omega_{a}-\omega_{e}+i\gamma_{e})$, while the two-exciton peak is not. Additionally, taking into account

$$e^{i(\omega_{a}-\omega_{e}+i\gamma_{e})T}/(\omega_{a}-\omega_{e}+i\gamma_{e}) \approx 2iT e^{i(\omega_{a}-\omega_{e})T/2} \text{sinc}[(\omega_{a}-\omega_{e})T/2],$$

(A6)

the single-exciton peaks have a structure very similar to Eq. (A3) and depend weakly on $\omega_p$. Thus, $\varrho_{e,e}(t)$ is dominated by the Lorentzian $1/(\omega_{a} + \omega_{b} - \omega_{fg} + i\gamma_{f})$, and this in turn means that spectroscopy with entangled photons can be used to probe the two-exciton manifold of aggregates.

We further note that Eq. (11) can be recast as the product of transition amplitudes $T_{fg}(t)$, given by

$$T_{fg}(t) = \left(\frac{\hbar}{i}\right)^2 \int_{-\infty}^{t} dt \int_{t}^{t} dt' \langle f(t)|V(t')|g(t')\rangle \langle g(t')|\psi\rangle$$

$$\times E(t')E(t')|\psi\rangle$$

(A7)

$$\varrho_{e,e}(t;\Gamma) = \frac{1}{8\hbar^4} \sum_{a,b} \sum_{c,d} \mu_{ge} \mu_{ef} \text{sinc}^2[(\omega_{a} - \omega_{e})T/2] \text{sinc}^2[(\omega_{b} - \omega_{f})T/2]$$

$$\times \left[ \frac{1}{(\omega_{fg} - \omega_{e} - \omega_{e} + i\gamma_{f})(\omega_{fg} - \omega_{e} - \omega_{e} + i\gamma_{f})} - \frac{1}{(\omega_{e} - 2i\gamma_{e})(\omega_{e} - 2i\gamma_{e})} \right]$$

$$+ \frac{\mu_{ge} \mu_{ef}}{(\omega_{fg} - \omega_{e} - \omega_{e} + i\gamma_{f})(\omega_{fg} - \omega_{e} - \omega_{e} + i\gamma_{f})}$$

$$- \frac{1}{(\omega_{e} - 2i\gamma_{e})(\omega_{e} - 2i\gamma_{e})} \right].$$

(B1)

$$\varrho_{fi,fj}(t;\Gamma) = \frac{1}{16\hbar^2} \sum_{a,b} \sum_{c,d} \mu_{ge} \mu_{ef} \mu_{ge} \mu_{fj} \text{sinc}^2[(\omega_{a} - \omega_{e})T/2] \text{sinc}^2[(\omega_{b} - \omega_{f})T/2]$$

$$\times \left[ \frac{1}{(\omega_{fi} - \omega_{e} - \omega_{e} + i\gamma_{f})(\omega_{fi} - \omega_{e} - \omega_{e} + i\gamma_{f})} - \frac{1}{(\omega_{e} + 2i\gamma_{e})(\omega_{fj} - 2i\gamma_{f})} \right].$$

(B2)

where we neglect the small imaginary part of the $\text{sinc}^2$ functions. The summations $a$ and $b$ run over $\omega_1$ and $\omega_2$, and we can assume that $\gamma_{e} \approx \gamma_{e}$. In comparison with the excitations induced by entangled photons, we observe that the single-exciton peaks in Eqs. (A5) and (A8) have a very similar structure to Eqs. (B1) and (B2), respectively. However, Eqs. (10) and (11) also contain Lorentzian factors that depend on $\omega_1 + \omega_2$, which dominate the signal. Those resonances are replaced by a constant background contribution in the second lines of Eqs. (B1) and (B2).
