Probing biological light-harvesting phenomena by optical cavities

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We propose a driven optical cavity quantum electrodynamics (QED) setup aimed at directly probing energy transport dynamics in photosynthetic biomolecules. We show that detailed information concerning energy transfer paths and delocalization of exciton states can be inferred (and exciton energies estimated) from the statistical properties of the emitted photons. This approach provides us with a spectroscopic tool to interrogate biological systems in terms of quantum optical phenomena which have usually been studied in solid-state or atomic systems (e.g., semiconductor quantum dots and trapped atoms) and which are now extended to a broader range of spectroscopy experiments.

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I. INTRODUCTION

Plants and some types of bacteria can efficiently process solar light by converting photons into chemical energy. Light-harvesting protein complexes, which are responsible for this process, utilize Frenkel excitons as intermediate carriers to convert solar light into chemical energy. In particular, theoretical and experimental analysis of fundamental quantum photosynthesis,2–6 the analysis of exciton dynamics in light-harvesting complexes (LHCs) involved in natural photosynthesis, and the study of internal excitation energy transfer dynamics of biomolecules. We show that detailed information concerning energy transfer paths and delocalization of exciton states can be inferred (and exciton energies estimated) from the statistical properties of the emitted photons. This approach provides us with a spectroscopic tool to interrogate biological systems in terms of quantum optical phenomena which have usually been studied in solid-state or atomic systems (e.g., semiconductor quantum dots and trapped atoms) and which are now extended to a broader range of spectroscopy experiments.

The paper is organized as follows: In Sec. II we describe the experimental scheme we propose to probe excitation dynamics in light-harvesting complexes. As a specific example of LHC, we consider a Fenna-Matthews-Olson pigment protein complex. In Sec. III, we show that the LHC exciton structure and energy transfer paths can be mapped onto the statistical properties of cavity photons such as mean photon number and second-order correlation functions and later measured through light modes leaking out of the cavity. Inhomogeneous broadening effects are also discussed. Furthermore, we quantify the amount of quantum correlations between the cavity mode and the biological system and discuss the possibility of polariton formation for a single LHC in a cavity. Conclusions and final remarks are presented in Sec. IV.
In order to probe the exciton structure of biological systems, we essentially propose a pump-probe scheme in which the probe field is substituted by the cavity mode (see Fig. 1). The sample is assumed to be confined inside an optical cavity with resonance frequency \( \omega_c \). As an example of a LHC, we choose the Fenna-Matthews-Olson (FMO) pigment-protein complex involved in the natural photosynthesis of green-sulphur bacteria. The FMO subunit has seven strongly coupled \( BChl \) molecules (sites). It can be described by the Hamiltonian

\[
H_c = \sum_j \omega_j \hat{\sigma}_j^+ \hat{\sigma}_j^- + \sum_{j \neq l} v_{j,l} (\hat{\sigma}_j^- \hat{\sigma}_l^+ - \hat{\sigma}_j^+ \hat{\sigma}_l^-),
\]

where \( \omega_j \) is the site energy, \( v_{j,l} \) denotes the coherently coupling between the corresponding sites. Single exciton transitions within the FMO complex are estimated to be in the range of 12 150 to 12 750 cm\(^{-1}\). The EET dynamics in the FMO can be described by a general Liouville-von Neumann equation for the density matrix \( \rho = -i[H, \rho] + L(\rho) \), where the total Hamiltonian \( H \) includes the FMO Hamiltonian Eq. (2), the cavity Hamiltonian \( H_{cav} = \omega_c \hat{a}^\dagger \hat{a} \), the interactions between FMO and the cavity Eq. (1), and also the coupling between the FMO and an external field \( E(\omega_c, t) \) given by

\[
H_f(t) = -\sum_i \mu_i E(\omega_c, t) \hat{\sigma}_i^+ + H.c.
\]

The dephasing and relaxation channels in the isolated FMO system impose an irreversible dynamics of an initially created exciton state. The simplest way to introduce these noise processes into the dynamics is using a Lindblad form for \( L(\rho) \). In particular, the FMO environmental noise can be described by pure dephasing (with rate \( \gamma \)) in terms of site-energy fluctuations (phenomenological Haken-Strobl-Reineker model). This analysis, although based on a simplified theoretical
model, allows us to bring out the basic principles of our proposal for a broad range of spectroscopy experiments. Extensions to non-Markovian effects which can arise from strong coupling and/or the form of the environment spectral function\textsuperscript{13,14,40–43} as well as other cavity setups involving additional laser fields, the role of multiple excitations, and other generalizations will be investigated in a forthcoming paper.

In the site basis, the Hamiltonian of the FMO pigment-protein complex, $H_s$, is

\[
H_s = \begin{pmatrix}
215.0 & -119.0 & 6.8 & -7.2 & 8.6 & -18.1 & -14.9 \\
-119.0 & 305.0 & 36.9 & 9.3 & 2.1 & 16.3 & 6.9 \\
6.8 & 36.9 & 0.0 & -69.8 & -1.5 & -11.5 & 3.7 \\
-7.2 & 9.3 & -69.8 & 200.0 & -78.3 & -21.3 & -75.9 \\
8.6 & 2.1 & -1.5 & -78.3 & 425.0 & 110.3 & -6.4 \\
-18.1 & 16.3 & -11.5 & -21.3 & 110.3 & 315.0 & 43.0 \\
-14.9 & 6.9 & 3.7 & -75.9 & -6.4 & 43.0 & 265.0
\end{pmatrix},
\] (4)

where the diagonal elements are the site energies—shifted from the base line $\omega_{\text{base}} = 12.195 \text{ cm}^{-1}$ corresponding to a wavelength of $\cong 820 \text{ nm}$—while the off-diagonal elements are the intersite coupling rates (all numbers are given in units of $\text{cm}^{-1} = 1.988 \times 10^{-3} \text{ N m} = 1.2414 \times 10^{-3} \text{ eV}$). The off-diagonal terms of the Hamiltonian were calculated in a dipole-dipole approximation and the site energies were taken from the Poisson-Boltzmann quantum chemistry model of Ref. 44. The intensities of the electronic transitions in the computed absorption spectrum (top inset in Fig. 2) are proportional to $|\mu_z|^2$, and the spectrum is averaged over different spatial orientations of the FMO complex. The relaxation and dephasing caused by the surrounding environment can be described by the following local Lindblad terms:

\[
\mathcal{L}^\text{relax}_S(\hat{\rho}) = \sum_{j=1}^{7} \Gamma_j / 2 [\{\hat{\sigma}_j^+ \hat{\sigma}_j^-\hat{\rho}, \hat{\rho}\} + 2\hat{\sigma}_j^- \hat{\rho} \hat{\sigma}_j^+]],
\] (5)

\[
\mathcal{L}^\text{deph}_S(\hat{\rho}) = \sum_{j=1}^{7} \gamma_j / 2 [\{\hat{\sigma}_j^+ \hat{\sigma}_j^-\hat{\rho}, \hat{\rho}\} + 2\hat{\sigma}_j^+ \hat{\sigma}_j^- \hat{\rho} \hat{\sigma}_j^+]],
\] (6)

with $\Gamma_j$ and $\gamma_j$ being the relaxation and dephasing rates at the site $j$, respectively. In the following, we choose for simplicity uniform dephasing rates (i.e., equal $\gamma_j$ and so simply labeled as $\gamma$). Moreover, here we neglect exciton relaxation processes because the 1 ns excitation lifetime\textsuperscript{45} is much longer than the time scale we look at. Let us point out that some relaxation is also present indirectly through the interaction with the cavity which has a damping channel described by the Lindbladian term

\[
\mathcal{L}^C_\text{relax}(\hat{\rho}) = (\Gamma_C / 2) [\{\hat{a}^\dagger \hat{a}, \hat{\rho}\} + 2\hat{a} \hat{\rho} \hat{a}^\dagger],
\] (7)

where $\Gamma_C$ is the damping rate of the cavity modes due to the photon leakage (i.e., $\Gamma_C = \omega_C / Q$ with $Q$ being the quality factor of the cavity). Note that we have also included the presence of dissipation inside the FMO complex in our numerical simulations and it turns out that exciton relaxation through the cavity mode is much more efficient, although direct exciton recombination process can be relevant on a 45-ps timescale. For a self-consistent model we use the same transition dipoles to construct interactions between BChl molecules in the FMO Hamiltonian and also for the coupling with the cavity and external fields. The positions and the relative directions of the dipoles are extracted from the structure of the FMO complex.\textsuperscript{46} The positions $R_i$ of the seven sites (BChl), taken as a middle point between four nitrogen atoms in each BChl, are

\[
[R_i] = \begin{pmatrix}
53.08 & 58.26 & 20.64 \\
56.04 & 54.79 & 32.40 \\
49.57 & 44.77 & 45.39 \\
38.81 & 42.25 & 43.06 \\
34.15 & 47.78 & 31.26 \\
41.44 & 47.82 & 22.61 \\
47.53 & 43.95 & 33.22
\end{pmatrix},
\] (8)

The directions the three components (in some reference frame) of the seven induced-transition dipoles $\mu_i$ are

\[
[\mu_i] = \begin{pmatrix}
-0.026 & 0.286 & -0.958 \\
-0.752 & 0.601 & -0.271 \\
-0.935 & 0.061 & 0.349 \\
-0.001 & 0.393 & -0.919 \\
-0.739 & 0.672 & 0.048 \\
0.859 & 0.371 & -0.353 \\
0.176 & -0.042 & -0.983
\end{pmatrix},
\] (9)

where the absolute values of the transition dipoles are taken as a phenomenological parameter $\mu_0 = 6 \text{ D}$, which accounts for effects of screening and induced charges.\textsuperscript{44} The exciton energies corresponding to the Hamiltonian (4) are $E_1 - E_7 = [-31.0, 129.4, 148.7, 254.6, 310.1, 394.5, 518.6] \text{ cm}^{-1}$ and the absolute values of the electronic transition dipoles of the FMO chromophores are $|\mu_1| - |\mu_7| = [6.4, 13.8, 3.7, 11.3, 7.2, 4.0, 5.6] \text{ D}$. Finally, we assume a continuous-wave laser pumping exciton transitions in the LHC. The laser field is coupled to the
cavity modes through the trapped biosample only. The value of the external (pump) field can be estimated as 

\[ E = \sqrt{2I/(c\varepsilon_0)} \] 

where \( I \) is the laser field intensity, \( c \) is the speed of light, and \( \varepsilon_0 \) is the vacuum permittivity. For example, the intensity of a cw laser field used in Raman spectroscopy is about 5 mW. In these experiments the laser beam is focused on a 5 \( \mu \)m\(^2\) spot. This corresponds to \( I = 100 \, \text{kW/cm}^2 \) or the field \( E = 27 \times 10^5 \, \text{V/m} \). This value is much smaller than the peak field value used in femtosecond pulse lasers. However, a cw would result in a heat accumulation, thus stronger fields could damage a sample.

III. RESULTS AND DISCUSSION

A. Cavity mean photon number

In Fig. 2, we show the mean photon number in the cavity in the stationary state and as a function of the driving field and of the cavity mode frequencies together with the electron excitation spectrum of FMO. This 2D map is obtained 45 ps after a strong laser driving field of intensity \( I \approx 110 \, \text{kW/cm}^2 \) has been turned on. The estimated values of electronic transition dipoles of the FMO chromophores are in the range of 3 to 14 D. Thus, the maximal coupling energy between the driving field and the excitons is of the order of 1 to 7 cm\(^{-1}\) = 30 to 210 GHz and the exciton-cavity coupling is about five times smaller. The cavity photon population saturates to a stationary regime on 20 ps timescale showing a set of peaks that are clearly associated with the exciton frequencies of the FMO complex (fine structure on the diagonal is due to computational resolution). Indeed, in analogy to 2D spectroscopy, diagonal peaks are in correspondence of the FMO exciton energies, and off-diagonal features appear due to energy transfer between different exciton states. The diagonal line in the spectra is due to both a coherent and an incoherent transfer of the photons from the laser field into the cavity. The former process is similar to the Raman scattering and goes through coherence pathways without generating an exciton population in LHC, while the latter process can be considered as light absorption by the LHC with the following spontaneous emission of a same-frequency photon into the cavity.
FIG. 5. (Color online) Stationary mean photon number of the cavity mode as a function of the cavity ($Q = 10^4$) resonance frequency $\omega_c$ (vertical axis) and the pump laser frequency $\omega_l$ (horizontal), both in units of cm$^{-1}$—shifted by 12 195 cm$^{-1}$. The dephasing rates are $\gamma = 1, 50, 100$ cm$^{-1}$ (from top to bottom).

The horizontal lines in the spectra (off-diagonal peaks) are due to population transfer between different excitons. Weaker optical fields would result in a similar set of peaks.

FIG. 6. (Color online) Stationary mean photon number of the cavity mode as a function of the cavity ($Q = 10^3$) resonance frequency $\omega_c$ (vertical axis) and the pump laser frequency $\omega_l$ (horizontal), both in units of cm$^{-1}$—shifted by 12 195 cm$^{-1}$. The dephasing rate is $\gamma = 10$ cm$^{-1}$, but the stationary regime would be achieved on a longer timescale. For the particular case shown in Fig. 2, the noise strength is $\gamma = 10$ cm$^{-1}$ $\sim 2$ ps$^{-1}$. The symmetry of the 2D spectrum with respect to the main diagonal ($\omega_l = \omega_c$) is recovered when the quality factor $Q$ is increased. Our intuitive explanation of the present asymmetry is that the cavity field is subjected to a leakage process, which is not present for the laser field. In all our simulations, we include an isotropic averaging of the measured quantities over completely random orientations of FMOs in the cavity. In the presence of an oriented sample these quantum features would be further enhanced. Stronger, albeit (biological-) structure preserving, laser driving fields can result in a resolvable fine structure of diagonal peaks. This effect is similar to a level anticrossing.

FIG. 7. (Color online) Stationary mean photon number of the cavity mode as a function of the cavity ($Q = 10^4$) resonance frequency $\omega_c$ (vertical axis) and the pump laser frequency $\omega_l$ (horizontal), both in units of cm$^{-1}$—shifted by 12 195 cm$^{-1}$. The dephasing rate is $\gamma = 50$ cm$^{-1}$, the pump field is $E = 0.01$ cm$^{-1}/D$, and the cavity coupling coefficient is $g = 0.01$ cm$^{-1}/D$. 

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or a hole burning—see Fig. 3. Indeed, the relatively strong coupling with the pump laser field leads to a splitting of the exciton level into two dressed states corresponding to two new peaks in the mean-photon-number 2D map. The behavior of the anticrossing effect within a diagonal peak as a function of the laser field coupling can be observed in Fig. 4. Qualitatively, this picture remains valid for values of $\gamma$ within the range 1 to 100 cm$^{-1}$ (Fig. 5), for a lower-quality ($Q = 10^3$) cavity (Fig. 6), and also for a weaker (state-of-the-art) cavity-coupling rate (Fig. 7) according to the present stage of technology. Finally, we show the effect of static disorder (i.e., disorder in the site energies) on the mean-photon-number 2D spectra, averaged over full random orientation disorder as well (as always done in this work); see Fig. 8 for a disorder of 50 cm$^{-1}$. As observed in 2D spectroscopy, it leads to the presence of inhomogeneous broadening for the diagonal peaks.

B. Second-order correlation function

In order to characterize quantum properties of the generated cavity photon state in its stationary state, we compute the second-order photon coherence function$^{48}$ at zero time delay $g^{(2)}(0) = \langle \hat{a}^\dagger \hat{a} \hat{a} \hat{a}^\dagger \rangle / \langle \hat{a} \hat{a} \rangle^2$. In Fig. 9 we show a full-range contour plot for the second-order coherence function at time delay zero $g^{(2)}(0)$ of the stationary cavity mode as a function of the cavity and pump frequencies, for different cavity parameters. In general, we obtain a nonclassical photon state generation [$g^{(2)}(0) < 1$] for most of the laser and cavity frequencies except on the diagonal line with $\omega_c = \omega_l$ where a coherent state [$g^{(2)}(0) = 1$] and a thermal state [$g^{(2)}(0) > 1$] can be observed. Moreover, it turns out, as in Fig. 10, that $g^{(2)}(0)$ depends on the amount of dephasing noise in the dynamics, and this might become a tool to estimate the strength of interaction between the biological molecule and the external environment. Notice also that the photon mode population...
is more sensitive to the dephasing noise, as compared to $g^{(2)}(0)$. Furthermore, $g^{(2)}(0)$ simply degrades with $\gamma$, except for a nondiagonal peak. Considering $g^{(2)}(0)$ as a measure of nonclassicality, higher values at intermediate noise levels would point toward noise being instrumental in maintaining long-lived coherence. Finally, we analyze the time evolution of the second-order coherence function at time delay zero $g^{(2)}(0)$ of the stationary cavity mode for diagonal and off-diagonal peaks—see Fig. 11. Although the time scale that we consider here is not feasible to be investigated with the current photon detector technology, it could be in a near future or even nowadays with other natural or artificial light-harvesting systems where this behavior takes place in a longer time due to different system parameters.

As a possible signature of polariton formation, we quantify the amount of quantum correlations between the FMO sample and the cavity mode, as measured by the logarithmic negativity.\(^4^9\) It turns out that this quantity reaches a maximum at about 800 fs and around the main two diagonal peaks in the 2D map in Fig. 2—see Fig. 12. Note that the lifetime of these correlations is around 2 ps\(^{-1}\), which is the time scale of the fastest decay process due to the presence of dephasing noise. Therefore, the coupling between the quantum cavity and the confined sample leads to the creation of nonclassical correlations between these two systems.

C. Polariton physics

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In our analysis it is important to trap the biological sample inside the cavity. Although several techniques are known in this respect, in this section we show by a simple and elementary argument the feasibility of such process by using an external electric field. In particular, let us apply an additional cw laser field $E_0$ polarized along the axis $\vec{e}$ with carrier frequency $\omega_0$ interacting with the FMO complex as the pump laser field. The corresponding interaction energy is

$$\Delta = \sum_{i=1}^{7} \left| \vec{\mu}_i \cdot \vec{e} \right| E_0 |^2 \omega_0 - \omega_i$$

and shows a minimum by varying the orientation of the polarization axis $\vec{e}$. In particular, we consider a spatial profile for the electric field given by a Gaussian function peaked in the center of the cavity as $E_0(x) = \bar{E}_0 e^{-x^2/(2\lambda^2)}$, where $\lambda = 800$ nm. In Fig. 13, we show the trapping potential $\Delta(x)$ and the corresponding trapping force as a function of the position $x$ for the optimal orientation of the polarization axis, $\omega_0 = -5000$ cm$^{-1}$, and $\bar{E}_0 = 5$ cm$^{-1}$/$D$. The trapping force is about 20 times larger than the gravitational force to which a single FMO is subjected, assuming that it has a mass of around 80 kDa $\sim 15 \times 10^{-23}$ kg (including the protein scaffolding).\textsuperscript{50}

In this regime, the amount of electronic excitation in the FMO complex is very small—see inset to Fig. 13. Moreover, we have found that the trapping force can be even several orders of magnitude larger than the gravitational one, allowing a very tiny amount of excitation in the FMO system induced by the presence of the laser irradiation. Therefore, following this simple argument, it seems that it is possible to trap a sample of FMO complexes inside the cavity, without perturbing the system (i.e., leaving it in its ground state), and then experimentally apply a driving laser field.

**D. Trapping LHCs inside cavity**

**E. Entangling biosamples in separate cavities**

Finally, we propose a possible scheme (in Fig 14) for a probabilistic creation of quantum correlations (i.e., entanglement) between two FMO samples confined in spatially separate cavities following Refs. 51 and 52 where such a protocol was introduced for trapped ions. In other terms, after applying the pump laser fields to the two separate samples, the outgoing photons from the cavities are mixed on a 50/50 beam splitter and one applies a projection of the two-photon state into a Bell state of the form $(1/\sqrt{2})(|\text{click, no click}\rangle + |\text{no click, click}\rangle)$. Then, after the projection, the composite system of the two LHC samples has a chance to be left in an entangled state with some finite probability. Therefore, we measure the entanglement (by logarithmic negativity) between the two samples after the projection for the two-cavity mode into the Bell state. This quantity is shown in Fig. 15. We find that one can probabilistically entangle the two biological samples (entangled polaritons) with a nonvanishing probability. This type of experiment would provide an striking demonstration of ability of these complexes to sustain quantum coherence.

**IV. CONCLUSIONS AND OUTLOOK**

We have extended the rich physics of cavity quantum electrodynamics to biological molecules, in particular light-harvesting complexes involved in natural photosynthesis. As an example, we have considered a sample of the Fenna-Matthews-Olson (FMO) pigment-protein complex inside an optical cavity and driven transversally by a laser field. Our main result is that the emission spectrum from the coupled FMO-cavity system reflects coherent energy transfer into the...
cavity through delocalized exciton states, as well as exciton dynamics within the FMO complex. Moreover, we have found that a strong laser field driving the exciton dynamics in the pigment-protein complex can burn a hole in the emission spectrum resulting in an additional structure of resonance peaks. Besides, the generation of quantum states of light inside the cavity due to the interaction with the confined biological complexes was also observed. Finally, we contrast the proposed technique to other methods in use in molecular spectroscopy. Cavity ring-down spectroscopy (CRDS) can be employed for detection of molecular species in the gas and liquid phases, as well as interfaces. In contrast to the proposed microcavity-based spectroscopy that aims for the strongest possible molecular-cavity coupling, CRDS is designed to use large cavities that support different frequencies and usually involves long path lengths. Microcavities have been used to detect molecules based on the frequency shift of the cavity itself. In contrast, this technique employs cavities resonant with the molecular transitions to interrogate the molecules optically. We believe that the spectroscopic tool proposed here can efficiently probe both static and dynamical (system-environment) properties of natural and artificial photosynthetic structures and provide additional experimental support for the coherent dynamics unveiled by nonlinear spectroscopy experiments. This combined evidence is expected to further elucidate the role that quantum coherence may play in the remarkably robust energy transport phenomena involved in natural photosynthesis.

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24. A. Very recently, it has been discovered that the FMO subunit has eight pigments. However, this should not affect the analysis we propose here for a generic light-harvesting system.