Coherent excitation transferring via dark state in light-harvesting process

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We study the light absorption and energy transferring in a donor-acceptor system with a bionic structure. In the optimal case with uniform couplings, it is found that the quantum dynamics of this seemingly complicated system is reduced as a three-level system of A-type. With this observation, we show that the dark state based electromagnetically-induced transparency (EIT) effect could enhance the energy transfer efficiency, through a quantum interference effect suppressing the excited population of the donors. We estimate the optimal parameters of the system to achieve the maximum output power. The splitting behavior of maximum power may be used to explain the phenomenon that the photosynthesis systems mainly absorb two colors of light.

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To tackle the global problem of energy source people may learn lots from the natural process of light-harvesting in plants, algae and bacteria. The energy transfer mechanism of high efficiency in light-harvesting process would help to design the new generation of clean solar energy sources. Recently, the long-time coherent properties of excitation in light-harvesting systems have been observed in experiments. This coherence can be preserved in these structures for a long time, even in room temperature. It seems that the high efficiency of light conversion is related to these coherent properties even with quantum natures. Therefore, the physical mechanism of photosynthesis assisted by (somehow quantum) coherence attracts much more attention from both experimental and theoretical aspects.

An inherent mechanism for high efficiency energy transferring may be due to the optimizing of spatial structure of light-harvesting systems. The X-ray analysis has revealed some common elements shared by different light-harvesting complexes in nature, one of which is a ring structure with a centered reaction center. It is well-known that the nature selection rules always keep the most adaptable feature in the biological system for the present environment. Therefore, it is believed that this kind of structure takes advantage in the light-harvesting process. The mechanism behind this optimal structure may account for the high efficiency of the natural light-harvesting process. Thus the investigation of mechanism of similar system would be heuristic to design artificial light-harvesting systems with self-assembling molecular array or the quantum dot array in top-down-semiconductor fabrication in the future.

In this letter, we will study a generic model, which is similar to the light harvesting complex of type I (LHC I), a centralized acceptor surrounded by the coupled donors arranged in a ring. In natural light-harvesting process, the light-capture process and excitation transferring happen simultaneously. To mimic the natural process, we include light capture process in the model by coupling the donors with photons in single mode. By showing the present model with homogeneous coupling could be reduced into the well-studied three-level A system, we find that the overall transfer efficiency is insensitive to the decay of the donors when the eigen-frequency of the acceptor is resonant with the light. This discovery implies that the dark state effect suppresses the excitation population on the noisy donors so that the energy transferring efficiency is dramatically improved. Otherwise, the loss of donor excitations will largely decrease the transferring efficiency to the acceptor.

As illustrated in Fig.(a), our model concerning light capture and coherent excitation transfer, is similar to the structure of LHC I. The one-dimensional circle array consists N donors which is also analogous to the ring structures in the LHC II, such as B800 or B850 ring. Similar to the pigment molecules in natural LHC I ring, each donor can be modeled as a two-level system (TLS) $|e_i\rangle$ and $|g_i\rangle$ with energy level spacing $\epsilon_i$ $(i = 1, \ldots, N)$. TLS is a proper approximation for single excitation case in practice. In most natural conditions, the LHCs always have only one excitation, thus our discussion only concerns the zero and one-excitation subspaces. The acceptor is placed at the center of ring. Since the hoping between the non-adjacent sites would be weak, we consider only the adjacent hopping of excitation on the ring with strength $g$. As we know, the visible light takes main
part of the energy of the solar spectrum and the corresponding wavelength is about $5 \times 10^8$ Å. In the cell of photosynthesis bacteria, the B800 and B850 ring usually have the radius about 4–6 nm \cite{17}. Thus, the BCHl molecules, the unit of B800 and B850 ring, are coupled uniformly to the incident light of frequency $\omega$ which is described by the creation (annihilation) operator $b^\dagger(b)$. To mimic the major function of natural process, we adopt the uniform couplings in the present model, namely, $\epsilon_i = \epsilon$. Then the model Hamiltonian reads as

$$H = H_D + e_A A^\dagger A + H_{DA} + \omega b^\dagger b + J \sum_{i=1}^N (e_i^\dagger b + h.c.) , \quad (1)$$

where $H_D = \sum_{i=1}^N \left[ \epsilon_i e_i + g \left( e_i^\dagger e_{i+1} + h.c. \right) \right]$ and $H_{DA} = \sum_{i=1}^N t_0 \left( e_i A^\dagger + h.c. \right)$ with $e_i^\dagger = |e_i\rangle \langle g|$ and $A^\dagger = |e\rangle_A \langle g|$. The physical implementation of the present structure could be quantum dot, which has the size about 2–10 nm and distance about 10 nm \cite{19}. The recent experimental synthesis of 12-porphyrin ring \cite{20} also opens up the possibilities of designing resemblance of natural light-harvesting element. The generic model with $N$ donors and $M$ acceptors has been discussed with the master equation \cite{3}. The similar setup with all donors and acceptors in a chain has also been discussed to reveal the optimal constitution of the two components \cite{13}.

In this letter, we only consider the effective transferring process and explore the advantage of the spatial configuration of the ring type. The collective excitation of the donor ring is described by the Fourier transformation $e_j = \sum_k e^{ikj} \hat{e}_k / \sqrt{N}$ and $e_j^\dagger = \sum_k e^{-ikj} \hat{e}_k^\dagger / \sqrt{N}$, where $\hat{e}_k (\hat{e}_k^\dagger)$ is the annihilation (creation) operator of the collective mode with definite momentum $k$. Here, the summation is over all the discrete momentum $k_n = 2\pi (n-1)/N$, with $n = 1, \ldots, N$. Indeed, in the large $N$ limit, we can show that $|\hat{e}_k, \hat{e}_k^\dagger \rangle \rightarrow \delta_{kk'}$, thus the collective excitations behave as bosons \cite{21}. In terms of the boson-like operators $\hat{e}_k (\hat{e}_k^\dagger)$, the donor Hamiltonian is seemingly diagonalized as $H_D = \sum_k (\epsilon + 2g \cos k) \hat{e}_k^\dagger \hat{e}_k$, which represents an energy band with $N$ sub-energy-levels. We note that interaction term is rewritten as $H_{DA} = \sqrt{N} \epsilon_0 (\hat{e}_0 A^\dagger + h.c.)$, which shows that only the zero mode excitation with $k = 0$ is coupled to the acceptor while the others described by $\hat{e}_k (\hat{e}_k^\dagger) \quad (k \neq 0)$ are decoupled with the acceptor. Therefore, the above Fourier transformation separates the total Hamiltonian into two un-coupled parts, $H' = H_D - (\epsilon + 2g) \hat{e}_0^\dagger \hat{e}_0$ and

$$H_{\text{eff}} = \omega_0 \hat{e}_0^\dagger \hat{e}_0 + \omega b^\dagger b + \omega_A A^\dagger A + \sqrt{N} [t_0 \hat{e}_0^\dagger A + J \hat{e}_0^\dagger b + h.c.] , \quad (2)$$

where $\omega_0 = \epsilon + 2g - i\kappa$ and $\omega_A = \epsilon_A - i\Gamma$. We need to point out that the dissipation rates $\kappa$ and $\Gamma$ have been phenomenologically introduced to describe the loss of excitations from the donors and the acceptor respectively.

Next we give two remarks on the implication of the above effective Hamiltonian: 1. the zero mode excitation described by $\hat{e}_0^\dagger$ has the energy $E_{k=0} = \epsilon + 2g$. Acting on the ground state $|0\rangle = |g_1, g_2, \ldots, g_N\rangle$, $\hat{e}_0^\dagger$ gives a uniform superposition $|1\rangle = |1_{k=0}\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^N |1_j\rangle$ of the single localized excitations $|1_j\rangle = |g_1, \ldots, g_j-1, e_j, g_{j+1}, \ldots, g_N\rangle$ in the $j$th donor ($j = 1, 2, \ldots, N$). It is similar to the single magnon state in the spin wave system. It has been numerically proved that the collective excited initial state $|1_{k=0}\rangle$ would result in the maximum efficiency with respect to any other mode \cite{4}. 2. In single excitation subspace, the photon-assisted donor-acceptor system could be described as a three-level $\Lambda$ system as illustrated in Fig.2(b). The dash-boxed area is the corresponding single excitation subspace. Interestingly, the incident light only couples to the zero mode of the donor ring. Since all other modes are decoupled from the capture process, they do not contribute to the light-harvesting process, thus the excitation energy is transferred to the acceptor only through the zero mode channel. Therefore, the transferring efficiency will be improved dramatically, if the nature light-harvesting systems were optimized to emerge a zero mode.

In the single excitation case, the evolution of excitation is constrained in the subspace spanned by $|1_k\rangle = |1, 0, 0\rangle, |1_D\rangle = |0, 1, 0\rangle$ and $|1_A\rangle = |0, 0, 1\rangle$ for the direct product state $|a, b, c\rangle = |a\rangle \otimes |b\rangle \otimes |c\rangle$ of the photon, donor in zero-mode and acceptor respectively. Let $|\phi(t)\rangle$ be the single excitation wave function with corresponding amplitudes $u(t), v(t)$ and $w(t)$ to the above basis vectors. The Schrödinger equation is reduced into $i\dot{V}(t) = MV(t)$ for $V(t) = [u(t), v(t), w(t)]^T$ and

$$M = \begin{pmatrix} \omega & \sqrt{N} & 0 \\ \sqrt{N} & \omega_0 & \sqrt{N} \omega_A \\ 0 & \sqrt{N} \omega_0 & \omega_A \end{pmatrix} . \quad (3)$$

The energy transfer is usually understood as the decay from the donors in excited states $|1_k\rangle$ \cite{1, 14}, thus the overall transfer efficiency is given by an integral $\eta = \int_0^\infty 2\pi |v(t)|^2 dt$. In practice, with the hopping from the donor to the acceptor, the rate of transferring excitation to outside agent should be larger than that only by the dissipation from the excited donors, i.e., $\sqrt{N} \tau_0 \gg \kappa$ and $\Gamma \gg \kappa$. Typically, we will choose the parameters \cite{17} here as $\epsilon_A / \tau_0 = 10$, $g / \tau_0 = 0.3$ and $\Gamma / \tau_0 = 0.3$ with $\tau_0 \approx 10 \text{ps}^{-1}$. In most cases, we set the total donor number $N = 8$. We illustrate the dependence of efficiency on detuning $\omega - \epsilon_A$ and dissipation parameter $\kappa/\Gamma$ in Fig.2(a). There exists a high peak at $\omega = \epsilon_A$ for given $\kappa/\Gamma$ with the peak value of efficiency almost unchanged. This observation reflects the efficiency is insensitive to the decay of the donor ring. At resonance, the excitation amplitude of the donor is highly suppressed, as
where sensitive to the donor decay rate $\kappa$. The slow change of peak value indicates that the efficiency at resonance is insensitive to the donor decay rate $\kappa$. The amplitude evolution $|u(t)|$, $|v(t)|$ and $|w(t)|$, the Rabi frequencies $\omega$ and dissipation parameter $\kappa = \Gamma/3$.

illustrated in Fig. 2(b). For the system comprises only the donor and the acceptor with initial excitation on the donor, there is a up-bound for the overall transfer efficiency $\eta'_{\text{max}} = \Gamma / (\Gamma + \kappa)$. In the present discussion with the light capture included, the efficiency actually goes beyond the up-bound.

The above discovery that the transfer efficiency is insensitive to the noisy of the donors at resonance can be explained according to the dark state, which has been widely investigated in quantum optics. To this end, we write the dark state $|D_0(t)\rangle = \cos \theta(t) |1_b\rangle - \sin \theta(t) |1_A\rangle$ in the single-excitation subspace for $\Gamma = 0$, where $\theta(t) = \arctan \left[ J/t_0 \exp \left[ -i (\epsilon_A - \omega) t \right] \right]$. $|D_0(t)\rangle$ is an eigenstate with vanishing eigen-value, namely, $H_{\text{eff}}(D_0(t)) = 0$. It has been demonstrated that the perfect transfer of population between the two low-lying energy levels can be achieved by adiabatically tuning the Rabi frequencies $J$ and $t_0$. In this process, the excitation on the upper energy level is suppressed to avoid the dissipation of excitations.

This dark stated based mechanism persists in the present artificial system with bionic structure. For this system, the evolution wave function is

$$|\phi(t)\rangle = \sum_{i=1}^{3} e^{-i \epsilon_i t} \sqrt{N_i} |E_i\rangle,$$  

where $|E_i\rangle = N_i^{-1/2} \left[ (x_i - \omega_0) |x_i - \omega_A\rangle - N t_0^2 |1_B\rangle - \sqrt{N} J (x_i - \omega_A) |1_D\rangle + N J t_0 |1_A\rangle \right]$ is an eigenstate with a normalized constant $N_i^2 = N^2 J^2 t_0^2 + N J^2 (x_i - \omega_A)^2 + (x_i - \omega_0) (x_i - \omega_A) - N t_0^2$; $x_i$ is the corresponding eigenvalue of the matrix $M$, whose expressions are not explicitly written down since they are too lengthy. If we choose the parameters as previous $\epsilon_A/t_0 = 10$, $g/t_0 = 0.3$, $\kappa/t_0 = 0.1$, $\Gamma/t_0 = 0.3$ and $J/t_0 = 0.1$, the eigen states at resonance $\omega = \epsilon_A$ are written as

$$|E_1\rangle \simeq -0.995 |1_b\rangle + 0.01 i |1_D\rangle + 0.01 |1_A\rangle,$$

$$|E_2\rangle \simeq 0.07 |1_b\rangle + (0.7 + 0.03 i) |1_D\rangle + 0.7 |1_A\rangle,$$

$$|E_3\rangle \simeq 0.07 |1_b\rangle + (-0.7 + 0.03 i) |1_D\rangle + 0.7 |1_A\rangle.$$  

Here, $|E_1\rangle$ is the dark state with very small component in donor excitation, which is proportional to $J \epsilon / \sqrt{N} t_0^2$. The initial one photon state can be rewritten with the above eigenstates as the basis, i.e., $|1\rangle_b = 0.995 |E_1\rangle + 0.07 |E_2\rangle + 0.07 |E_2\rangle$.

The component of dark state in the initial state is approximate $pe_1 = t_0 / \sqrt{t_0^2 + J^2}$, which is almost 1 under the practical condition $J \ll t_0$. In the capture and transferring process, the population on excited donors is suppressed to be small in avoiding dissipation, as illustrated in Fig. 2(b). On the dark state, the system decays very slowly at the rate $\gamma_0 \simeq \Gamma / (J/t_0)^2$, while it dissipates quickly on the bright state ($|E_2\rangle$, $|E_3\rangle$) at rate $\gamma_B \simeq (\kappa + \Gamma)/2$. Thus, for large time scale $t_B > 1/\gamma_B$, the main contribution of transferring is carried on by the dark state. We demonstrate the ratio of populations on the photonic state and on acceptor in Fig. 2(c). The asymptotic value of this ratio for long time is approximately $t_0 / \sqrt{t_0^2 + J^2}$, which is the one of dark state in the initial state.

In the transferring process, another important quantity is the average transfer time, which is defined as $\tau = \eta^{-1} \int_0^\infty 2 \Gamma t |v(t)|^2 dt$. To effectively utilize the energy, the excitation should be transferred with a high efficiency and also within a short time scale. In the previous discussions, we have proved that the efficiency can be improved via the dark state mechanism. However, we have illustrated that the decay rate of photon at resonance is suppressed by a factor $(J/t_0)^2$, while the efficiency is proportional to $[1 + (J/t_0)^2]^{-1/2}$. We meet a dilemma that the efficiency and the average transfer time can not be optimized simultaneously. In Fig. 3(a), we demonstrate the average transfer time as a function of the dissipation rate of the donor and the detuning. The small peak in the center hints that the transfer time is not optimal at resonance $\omega = \epsilon_A$. It is readily seen in Fig. 3(a) that the optimal frequencies of quick transfer are not at resonance $\omega = \epsilon_A + 2g$ but split into two, which is known as the Rabi splitting in quantum optics. The two peaks can be determined by exactly diagonalizing the photon assisted donor-acceptor system in single excitation subspace as $\omega_{\pm} = (\epsilon_A + 2g + \epsilon)/2 \pm [(\epsilon + 2g - \epsilon_A)^2 + 4N t_0^2]^{1/2}/4$. The transfer time reaches its minimum optimal point when $\omega = \omega_\pm$, while the efficiency is not at its maximum as illustrated in Fig. 3.

In fact, such dilemma has been met in many investigations about heat engines: the Carnot heat engine converts the heat into work with maximum efficiency, while it takes infinite long time. In practice, one would
concern more about the output power, which characterizes the output energy within unit time. In the present case, we introduce a similar quantity \( \mathcal{P} = \eta/\tau \) characterizing the ability of the excitation energy transfer, which is called the mean transfer power. In Fig.3 (b), we demonstrate the mean power \( \mathcal{P} \) as a function of detuning between the incident light frequency and the acceptor excitation energy for different donor dissipation rates \( \kappa = \Gamma, 1.5\Gamma \) and 2.0\( \Gamma \).

The optimal frequency is \( \omega = 9.1t_0 \) and \( \omega = 14.7t_0 \), which are different from the optimal value of both efficiency and average transfer time. Actually, we have observed that the photosynthesis systems choose to absorb sunlight mainly from two domains of the solar spectrum. For example, the green plants mainly use red and blue color photons. The present model can be utilized to justify this observation. However, for the practical system, the estimation of the exactly frequency goes beyond the scope of the present model because it concerns very complicated biological environments.

In summary, we have studied the light capture and excitation transfer process in a generic model consisted of donor and acceptor assisted by photons. By optimizing this artificial photosynthesis system to realize an effective three-level \( \Lambda \) configuration evolving dark state, we demonstrated the coherent population transferring through the dark state channels, where the dissipation from donors is effectively suppressed. In the present studies, we deal with the dissipation of the excitation by phenomenologically introducing an imaginary part to the Hamiltonian of the donor. However, in reality, this dissipation is always connected to the vibration degrees of freedom, which may be account for the dimerized structure as discussed in the LHC I and LHC II [13]. And also, it is worth to investigate effect of vibrations in designing some artificial light-harvesting systems. For the present model, we can also discuss the quantum or classical correlations of the output excitations with more than one photon, which could be used to explain the mechanism of the light-harvesting system avoiding the damage from high intensity light source.

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