Excitation energy transfer in light-harvesting systems: effect of the initial state

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Abstract

Light harvesting is a problem that has attracted interest for a long time. It became active again in recent years stimulated by suggestions of quantum effects in energy transport. Recent experiments found evidence that BChla 1 and BChla 6 are the first ones to be excited in the Fenna–Matthews–Olson (FMO) protein; theoretical studies, however, are mostly restricted to considering the exciton in BChla 1 initially. In this paper, we study the energy transport in the FMO complex by taking different initial states into account. The decoherence rates are optimized for maximal transport efficiency. Dependence of the energy transfer efficiency on the initial states is given and discussed. Effects of fluctuations in the site energies and couplings are also examined.

1. Introduction

Knowledge of photosynthetic processes in bacteria and plants may provide deep insights into designing efficient and robust artificial light-harvesting systems, where the initial stages in the conversion of solar energy into chemical and other forms of energy can be described by exciton dynamics with trapping and decoherence. Recent experimental and computational studies suggest that environmental noise can assist the exciton transport and can be optimized for the maximal energy transfer efficiency [1–13]. In particular, special attention has been focused on the so-called Fenna–Matthews–Olson (FMO) complex which promotes the energy transfer from the main light-harvesting complex towards the chemical reaction centre in green sulfur bacteria.

As a small protein in green sulfur bacterium, the FMO complex is a highly efficient energy transfer wire that connects chlorosomes (i.e. light collecting pigment arrays) to photosynthetic reaction centres. In structure, the FMO protein is a trimer, each monomer contains seven bacteriochlorophyll-a (BChla) molecules embedded within a protein scaffold and is believed to function independently [14]. We shall refer to the individual BChla molecules as sites in this paper. Recent studies have determined the orientation of the FMO complex within the inter-membrane region between the chlorosome antenna and reaction centre [14, 15], evidence that photosynthetic systems exhibit quantum coherence at ambient temperature has been found, but the significance of these discoveries for biological energy transfer remains unclear. It is quite certain that the reaction centre is strongly coupled to BChla 3 and that the excitation energy enters an FMO monomer from the chlorosomes via BChla 1 or BChla 6.

Although a preliminary understanding of the complex dynamics of the excitation transfer has been made, the theory is still in its infancy. For example, most studies are restricted to one exciton limit and the initial exciton is supposed to be in only one of the seven sites. This paper addresses two open questions concerning the relevance of excitonic coherence to photosynthetic energy transfer. First, we present a theoretical framework which elucidates how decoherence could assist the excitation transfer; we optimize the decoherence rates for the maximal transfer efficiency and study the robustness
of the excitation transfer against the fluctuation of the on-site energy. Second, we present a study on the coherence in the initially excited states by showing the dependence of the transfer efficiency on the initial states. This paper is organized as follows. In section 2, we introduce the model to describe the FMO complex and the Markovian master equation for the dynamics of the exciton transport. In section 3, we optimize the decoherence rates for the maximal excitation energy transfer efficiency and explore how the efficiency depends on the initial state of the FMO. The fluctuations in the local on-site energy and in the site-site couplings affect the transfer efficiency; this effect is also studied in section 3. Finally, we conclude our results in section 4.

2. The model

In the following, we will briefly introduce the Hamiltonian model that we use to describe the FMO complex. For each site we take two electronic states into account. Since we restrict ourselves to a single electronic excitation, the so-called Frenkel exciton Hamiltonian

$$ H = \sum_{j=1}^{7} E_j |j\rangle \langle j| + \sum_{i<j=1}^{7} J_{ij} |i\rangle \langle j| + h.c. $$

(1)

can describe the reversible dynamics of the electronic degrees of freedom. Here $|j\rangle$ represents the state where only the jth site is excited and all other sites are in their electronic ground state. $E_j$ is the on-site energy of site $j$, and $J_{ij}$ denotes the excitonic coupling between sites $i$ and $j$. In the site basis, we follow [15] and employ the Hamiltonian matrix elements (in units of cm$^{-1}$) in the remainder of this paper.

$$ H = \begin{pmatrix}
215 & -104.1 & 5.1 & -4.3 & 4.7 & -15.1 & -7.8 \\
-104.1 & 220.0 & 32.6 & 7.1 & 5.4 & 8.3 & 0.8 \\
5.1 & 32.6 & 0.0 & -46.8 & 1.0 & -8.1 & 5.1 \\
-4.3 & 7.1 & -46.8 & 125.0 & -70.7 & -14.7 & -61.5 \\
4.7 & 5.4 & 1.0 & -70.7 & 450.0 & 89.7 & -2.5 \\
-15.1 & 8.3 & -8.1 & -14.7 & 89.7 & 330.0 & 32.7 \\
-7.8 & 0.8 & 5.1 & -61.5 & -2.5 & 32.7 & 280.0 \\
\end{pmatrix} $$

(2)

Here the zero energy has been shifted by 12 230 cm$^{-1}$ for all sites, corresponding to a wavelength of $\sim$800 nm. We note that in units of $h = 1$, we have 1 ps$^{-1} = 5.3$ cm$^{-1}$. Then by dividing $J_{ij}$ and $E_j$ by 5.3, all elements of the Hamiltonian are rescaled in units of ps$^{-1}$. We can find from the Hamiltonian $H$ that in the FMO complex there are two dominating exciton energy transfer pathways: $1 \rightarrow 2 \rightarrow 3$ and $6 \rightarrow (5, 7) \rightarrow 4 \rightarrow 3$. Although the nearest neighbour terms dominate the site-site coupling, significant hopping matrix elements exist between more distant sites. This indicates that coherent transport itself may not explain why the excitation energy transfer is so efficient.

We adopt the spin-boson model to describe the interactions between excitations and surrounding protein environments:

$$ H_{sb} = \sum_{i=1}^{7} \sum_{j} g_{ij} |\bar{i}\rangle \langle \bar{i}| (a_{j}^\dagger a_{j}) $$

(3)

where $g_{ij}$ represents the coupling constant between the site $i$ and the mode $j$ of the environment. The Hamiltonian $H_{sb}$ describes the modulation of the on-site energy by the environment in the linear case, where the on-site energy on the dimensionless environment coordinate is $q_j \sim (a_{j}^\dagger a_{j})$. Such a site–environment coupling can model the site–vibration interaction, leading to decoherence in the FMO. This decoherence can be described by the master equation. To derive the master equation, we adopt the following assumptions. (1) The time evolution of the whole system (the FMO + environment) is unitary, where the full Hamiltonian is assumed to be time independent and consists of three parts, namely the system Hamiltonian $H$, the bath Hamiltonian $H_b$, and the interaction Hamiltonian $H_{sb}$. The deviation of the master equation is equivalent to finding the dynamics of the FMO by tracing out the degrees of freedom of the environment. This is not always possible and we shall assume that (2) the system–environment interaction is sufficiently weak, so that perturbation theory is applicable. Moreover, we assume that (3) the whole system is in a product initial state, and (4) the environment has short memory in the sense that the correlation time is very short. For details, we refer the readers to [16, 17]. With these assumptions, we can derive a master equation to describe the dynamics of the FMO complex, which is given by

$$ \frac{d\rho}{dt} = -i[H, \rho] + \mathcal{L}(\rho) + \mathcal{L}_{38}(\rho), $$

(4)

where the Liouvillian takes

$$ \mathcal{L}(\rho) = \sum_{j=1}^{7} \gamma_j \left[ P_j \rho(t) P_j - \frac{1}{2} P_j \rho(t) P_j - \frac{1}{2} \rho(t) P_j \right], $$

$$ \mathcal{L}_{38}(\rho) = \Gamma \left[ P_{38} \rho(t) P_{38} - \frac{1}{2} P_{38} \rho(t) P_{38} - \frac{1}{2} \rho(t) P_{38} \right], $$

(5)

with $P_j = |j\rangle \langle j|$, $j = 1, 2, 3, \ldots, 7$ and $P_{38} = |3\rangle \langle 8| = P_{53}^\dagger$. $\mathcal{L}(\rho)$ describes exciton decoherence due to the site–environment couplings, and $\mathcal{L}_{38}(\rho)$ characterizes the excitation trapping at site 3 due to interactions with the reaction centre, labelled as site 8. The presence of this eighth BChl chromophore has been suggested in each subunit of the FMO complex by recent crystallographic data [18]. Furthermore, experimental data and theoretical studies indicated that the eighth BChl is the closest to the baseplate and should be the point at which energy flows into the FMO complex [19, 20].

We shall use the population $p_k$ at time $T$ in the reaction centre given by $p_k(T) = Tr(|k\rangle \langle k| \rho(T))$ to quantify the excitation transfer efficiency. Clearly, the Liouvillian $\mathcal{L}_{38}(\rho)$ plays an essential role in the excitation transfer; through this term the decoherence with rates $\gamma_j$ ($j = 1, 2, \ldots, 7$) can enhance the excitation transfer as we show in the next section.

3. Results

It is believed that the completely coherent dynamics is not the most ideal case for the excitation transfer, and the quantum coherence itself cannot explain the very high excitation transfer efficiency. Indeed, our numerical simulations show that $\Gamma$ can
be optimized to 87.14 with $\gamma_j = 0$ to obtain the maximal excitation transfer efficiency $p_8 = 0.6781$.

We optimize the decoherence rates $\Gamma$ and $\gamma_j$, ($j = 1, 2, \ldots, 7$), for the maximal excitation energy transfer efficiency and find that $\Gamma = 44$ and $\gamma_1 = 1.2, \gamma_2 = 24, \gamma_3 = 0.9333, \gamma_4 = 6.5333, \gamma_5 = 53.1, \gamma_6 = 1.8, \gamma_7 = 27$ yield a maximal transfer efficiency $p_8 = 0.9256$. With these decoherence rates, the population on each site as a function of time is plotted in figure 1. Two observations can be made from figure 1: (1) the population shows oscillatory behaviours during the first 0.5 ps and then they change in a smooth way; (2) the excitation on sites 1 and 2 dominates the population, while the population at site 3 is almost zero. The first observation can explain why the excitation transfer lasts longer than the quantum coherence (quantum oscillation), and the second observation suggests that sites 1 and 2 play an important role in the excitation energy transfer. The excitation on site 3 is trapped and transferred to the reaction centre almost immediately so as to obtain a high transfer efficiency, as figure 1 shows.

The spatial and temporal relaxation of exciton shows that site 1 and 6 were populated initially with a larger contribution [15]. Then it is interesting to study how the initial states affect the excitation transfer efficiency. In the following, we shall shed light on this issue. Two cases are considered. First, we calculate the excitation transfer efficiency with exciton initially in a superposition of sites 1 and 6, and study the effect of transfer efficiency on the initial states. Second, we extend this study to initial states where sites 1 and 2 are initially excited. These calculations are performed by numerically optimizing the decoherence rates for the maximal transfer efficiency at time $T = 5$ ps; selected results are shown in figures 2, 3 and 5.

In figure 2, we present the transfer efficiency as a function of $\theta$ and $\phi$, which characterizes the pure initial states of the FMO complex through $|\psi(t = 0)\rangle = \cos \theta |1\rangle + \sin \theta \exp(i\phi)|6\rangle$ (upper panel) and $|\psi(t = 0)\rangle = \cos \theta |1\rangle + \sin \theta |6\rangle$ (lower panel). We find that a properly coherent superposition of sites 1 and 6 (or 2) can enhance the exciton transfer. For exciton initially in a superposition of sites 1 and 6, the transfer efficiency is more sensitive to the population ratio (characterized by $\theta$) but not to the relative phase $\phi$. The transfer efficiency arrives at its maximum with $\theta = \frac{\pi}{2}$ and $\phi = 0$ (it is not unique), suggesting that exciton on site 6 is more...
on the mixing rate a different way, see figure 4. We observe from figure 4 that the transfer efficiency reaches its maximum with (in units of $\theta$) $\theta = \frac{\pi}{4}$ and $\phi = 0$. For exciton initially excited on sites 1 and 2, both the population ratio and the relative phase affect the energy transfer; the transfer efficiency reaches its maximum with $\theta = \frac{\pi}{4}$ and $\phi = 0$ and its minimum with $\theta = \frac{3\pi}{4}$ and $\phi = 0$.

Figure 3 shows the dependence of the transfer efficiency on the mixing rate $p$, where the initial state is a classical mixing of sites 1 and 6 (or 2). Obviously, the population mixing favours the transfer efficiency. In particular, the classical mixing of sites 1 and 6 (or site 2) always increase the transfer efficiency; this is different from the case where the mixing is performed in a different way, see figure 4. We observe from figure 4 that the transfer efficiency attains a minimal value at $\theta = \frac{\pi}{4}$ and $p = 1$ (upper panel) which is consistent with the observation that emerged from figure 2. As $p$ decreases, the transfer efficiency increases linearly. Similar features can be found from the lower panel of figure 4. These results suggest that the population on site 6 favours the energy transfer: if the mixing of sites 6 and 1 is classical, the transfer efficiency increases linearly with the population on site 6; otherwise, it depends on the mixing angle $\theta$ and the relative phase $\phi$.

We would like to note that the coherent superposition of exciton on the sites 1 and 6 (or 2) can help the energy transfer even when the decoherence is absent. For example, our numerical optimizations show that the transfer efficiency can be increased to 98% starting with an initial state $\cos(1.2632\pi)|1\rangle + \sin(1.2632\pi)|2\rangle$; however, this is not the case for classical mixing (or incoherent superposition) of sites 1 and 2 (or site 6) as the initial states. The transfer efficiency is always smaller than (or equal to) 67.81% (the efficiency in the case with exciton 100% on site 1 in the absence of decoherence) with initial states in the form $p|1\rangle|1\rangle + (1 - p)|2\rangle|2\rangle$. This suggests that the transfer enhancement by coherent superposition of exciton on sites 1 and 6 (or site 2) is a common feature for the energy transfer in the FMO complex regardless of the presence of decoherence. But the enhancement of the transfer efficiency by classical mixing works only in the presence of decoherence. This can be understood as the coherent cancellation or the coherent enhancement in the dynamics of the exciton transport.

It has been shown that the local decoherence can enhance the transfer efficiency [11] in the FMO, this can be understood as the fluctuation-induced broadening of energy levels, which bridges the on-site energy gap and the coupling between them. This gives rise to the following question: how do the fluctuations in the site energies and couplings affect the transfer efficiency? In the following, we will study this issue and show that the exciton transfer in the FMO complex
of Gaussian fluctuations, we introduce a Gaussian function in the on-site energies are Gaussian. To examine the effect on the transfer efficiency fluctuates greatly. (2) For fluctuations with zero mean in the site energies and couplings increase, the results suggest that the experimental results recorded for samples at low temperature would also be observable at higher temperatures.

We take the decoherence rates that maximize the transfer efficiency for the numerical simulation. Two types of fluctuations in the site energies and inter-site couplings are considered. The first one has zero mean, while the other has non-zero positive mean. For the fluctuations with zero mean, the Hamiltonian in equation (2) takes the following changes, $H_{12} \rightarrow H_{12}(1+r \cdot (\text{and} (1)-0.5))$ and $H_{\phi} \rightarrow H_{\phi}(1+r \cdot (\text{and} (1)-0.5))$. For the fluctuations with non-zero positive mean, the Hamiltonian takes the following changes, $H_{12} \rightarrow H_{12}(1+r \cdot (\text{and} (1)))$ and $H_{\phi} \rightarrow H_{\phi}(1+r \cdot (\text{and} (1)))$, where $r$ and $(\text{and} (1))$ denotes a random number between 0 and 1. So a 100% static disorder may appear in the on-site energies and inter-site couplings.

With these arrangements, we numerically calculated the transfer efficiency and present the results in figure 4. Each transfer efficiency is a result averaged over 20 fluctuations. Two observations are obvious. (1) As the fluctuations with zero mean in the site energies and couplings increase, the transfer efficiency fluctuates greatly. (2) For fluctuations with non-zero positive mean, the efficiency increases with $r_2$ but decreases with $r_1$. This can be interpreted as follows. The energy gap between neighbouring sites blocks the energy transfer, whereas the inter-site couplings that represent the overlap of different sites favour the transport. As a result of competition, the efficiency increases with $r_2$ but decreases with $r_1$. For the fluctuation with zero mean, the results are subtle, it depends seriously on each run, and the averaged transfer efficiency remains almost unchanged.

Adolphs and Renger [15] suggested that the fluctuations in the on-site energies are Gaussian. To examine the effect of Gaussian fluctuations, we introduce a Gaussian function $y(x|\sigma, \mu) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$, where $\mu$ is the mean while $\sigma$ denotes the standard deviation. Furthermore, we assume that the fluctuations enter into only the on-site energies, namely $H_{12}$ is replaced by $H_{12}(1+y(x|\sigma, \mu))$, $j = 1, 2, ..., 7$. With these notations, we plot the effect of fluctuations on the transfer efficiency in figure 6(a). We find that the efficiency is almost independent of the variation, but it decreases as the mean increases. This again can be understood as the blockage of energy transfer by the energy gap between the neighbouring sites. When these Gaussian fluctuations occur in both the on-site energies and couplings, we find from figure 6(b) that the transfer efficiency increases as the mean increases and the variation decreases. This is a result of a competition between the energy gaps and couplings of the neighbouring sites.

4. Conclusion

In this paper, we study the excitation transfer efficiency in light-harvesting complexes, in particular, the Fenna–Matthew–Olson (FMO) complex. This is a problem that has attracted interest for a long time, and is timely due to the recent activity sparked by suggestions of quantum effects in energy transport. It is well known that photosynthetic organisms operate at extremely low light levels, and the exciton initially excited in the FMO complex may occupy sites 1 and 6 (or site 2) simultaneously. This stimulates us to study the effects of the initial state on the transfer efficiency. Based on the Frenkel exciton Hamiltonian and the master equation, we have optimized the decoherence rates for the maximal energy transfer efficiency which can reach about 93% at time 5 ps. By considering different mixing of exciton on sites 1 and 6 (or site 2) as the initial states, we have examined the effect of initial states on the energy transfer efficiency. The results suggest that a classical mixing of sites 1 and 6 (or site 2) always enhances the energy transfer efficiency, whereas a coherent superposition of sites 1 and 6 (or site 2) increases the efficiency only for special initial states. This can be understood as the coherent cancellation or the coherent enhancement in quantum physics.

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References

[1] Engel GS, Calhoun T R, Read E L, Ahn T-K, Manal T, Cheng Y-C, Blankenship R E and Fleming G R 2007 Nature 446 782
[2] Lee H, Cheng Y-C and Fleming G R 2007 Science 316 1462
[3] Panitchayangkoon G, Hayes D, Fransted K A, Caram J R, Harel E, Wen J, Blankenship R E and Engel G S 2010 arXiv:1001.5108
[4] Collini E, Wong C Y, Wilk K E, Curmi P M G, Bruemer P and Scholes G D 2010 Nature 463 644
[5] Collini E and Scholes G D 2009 Science 323 369
[6] Gaab K and Bardeen C 2004 J. Phys. Chem. B 108 7813
[7] Olaya-Castro A, Lee C F, Olsen F P and Johnson N F 2008 Phys. Rev. B 78 085115
[8] Fassioli F, Nazir A and Olaya-Castro A 2010 J. Phys. Chem. Lett. 1 2139
[9] Plenio M B and Huelga S F 2008 New J. Phys. 10 113019
[10] Rebentrost P, Mohseni M, Kassal I, Lloyd S and Aspuru-Guzik A 2009 New J. Phys. 11 033003
