Revisiting the Excitation Energy Transfer in the Fenna-Matthews-Olson Complex

X. X. Yi\textsuperscript{1,2}, X. Y. Zhang\textsuperscript{1}, and C. H. Oh\textsuperscript{2}
\textsuperscript{1}School of Physics and Optoelectronic Technology
Dalian University of Technology, Dalian 116024 China
\textsuperscript{2}Centre for Quantum Technologies and Department of Physics,
National University of Singapore, 117543, Singapore
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I. INTRODUCTION

In 1962, John Olson isolated a water-soluble bacteriochlorophyll (BChl a) protein from green sulfur bacteria \textsuperscript{1}. In 1975, Roger Fenna and Brian Matthews resolved the X-ray structure of this protein (Fenna-Matthews-Olson (FMO)) from Prosthecochloris aestuarii and found that the protein consists of three identical subunits related by C\textsubscript{3} symmetry, each containing seven BChl a pigments \textsuperscript{2}. In photosynthetic membranes of green sulfur bacteria, this protein channels the excitations from the chlorosomes to the reaction center. Since it was the first photosynthetic antenna complex of which the X-ray structure became available, it triggered a wide variety of studies of spectroscopic and theoretical nature, and it therefore has become one of the most widely studied and well-characterized pigment-protein complexes.

The excitation-energy transfer can be elucidated with 2D echo-spectroscopy using three laser pulses which hit the sample within several femtoseconds time spacings. The experimentally measured 2D echo-spectra of the chlorophores. They are in general complex from the aspect of quantum mechanics, regardless it is difficult to calculate. In this paper, we will shed light on the effects of complex inter-site couplings by addressing the following questions. First, we present a theoretical framework which elucidates how complex couplings could assist the excitation transfer. We optimize the relative phases in the couplings for maximal transfer efficiency and study the robustness of excitation transfer against the fluctuations of the on-site energy and inter-site couplings. 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 Sec. II, we introduce the model to describe the FMO complex for the dynamics of the exciton transport. In Sec. III, we optimize the phases phenomenologically introduced in the couplings for 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 inter-site couplings affect the transfer efficiency, this effect is studied in Sec. IV. Finally, we conclude in Sec. V.

II. MODEL

Since the FMO complex is arranged as a trimer with three different subunits interacting weakly with each other, we restrict our study to a single subunit which contains eight bacteriochlorophyll molecules (BChls)\textsuperscript{[21, 22]}. The presence of the 8th BChl chromophore has just been suggested by the recent crystallographic data\textsuperscript{[21]}, and the recent experimental data and theoretical studies indicated that the 8th BChl is the closest site to the baseplate and should be the point at which energy flows into the FMO complex\textsuperscript{[22, 23]}. However, the eighth BChl is loosely bound, it usually detaches from the others when the system is isolated from its environment to perform experiments. Thus we do not take the eighth into account.

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We describe the FMO complex by a generic one-dimensional Frenkel exciton model, consisting of a regular chain of 7 optically active sites, which are modeled as two-level systems with parallel transition dipoles. The corresponding Hamiltonian reads,

\[
H = \sum_{j=1}^{7} E_{j} |j\rangle\langle j| + \sum_{i>j=1}^{7} (J_{ij}|i\rangle\langle j| + J'_{ij}|j\rangle\langle i|),
\]

where \(|j\rangle\) represents the state where only the \(j\)-th 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 \(j\), \(J_{ij} = J'_{ji}\). The on-site and the inter-site energies from Ref.\textsuperscript{[3]} (in units of cm\(^{-1}\)) will be adapted to study the quantum dynamics of the FMO. As aforementioned, a phase \(\phi_{ij}\) is added to the inter-site coupling \(J_{ij}\) stronger than 15 cm\(^{-1}\),

\[
H = \begin{pmatrix}
215 & -104.1e^{i\phi_{12}} & 5.1 & -4.3 & 4.7 & -15.1e^{i\phi_{16}} & -7.8 \\
-104.1e^{-i\phi_{12}} & 220.0 & 32.6e^{i\phi_{23}} & 7.1 & 5.4 & 8.3 & 0.8 \\
5.1 & 32.6e^{-i\phi_{23}} & 0.0 & -46.8e^{i\phi_{34}} & 1.0 & -8.1 & 5.1 \\
-4.3 & 7.1 & -46.8e^{-i\phi_{34}} & 125.0 & -70.7e^{i\phi_{45}} & -14.7 & -61.5e^{i\phi_{47}} \\
4.7 & 5.4 & 1.0 & -70.7e^{-i\phi_{45}} & 450.0 & 89.7e^{i\phi_{56}} & -2.5 \\
-15.1e^{-i\phi_{16}} & 8.3 & -8.1 & -14.7 & 89.7e^{-i\phi_{56}} & 330.0 & 32.7e^{i\phi_{67}} \\
-7.8 & 0.8 & 5.1 & -61.5e^{-i\phi_{47}} & -2.5 & 32.7e^{-i\phi_{67}} & 280.0
\end{pmatrix}.
\]}

Here the zero energy has been shifted by 12230 cm\(^{-1}\) for all sites, corresponding to a wavelength of \(~800nm\). We note that in units of \(\hbar = 1\), we have 1 ps\(^{-1}\)=5.3 cm\(^{-1}\). Then by dividing \(|\rho\rangle\) and \(E_{j}\) by 5.3, all elements of the Hamiltonian are rescaled by units of ps\(^{-1}\). We can find from the Hamiltonian \(H\) that in the Fenna-Matthews-Olson complex (FMO), there are two dominating exciton energy transfer (EET) pathways: \(1 \rightarrow 2 \rightarrow 3\) and \(6 \rightarrow (5, 7) \rightarrow 4 \rightarrow 3\). Although the nearest neighbor terms dominate the site to 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 phenomenologically introduce a decoherence scheme to describe the excitation population transfer from site 3 to the reaction center (site 8). The master equation to describe the dynamics of the FMO complex is then given by,

\[
\frac{dp}{dt} = -i[H, \rho] + L_{38}(\rho),
\]

where \(L_{38}(\rho) = \Gamma \left[ P_{38}(t)P_{38} - \frac{1}{2} P_{38} \rho(t) - \frac{1}{2} \rho(t)P_{38}\right]\) with \(P_{38} = |3\rangle\langle 8| = P_{83}\) characterizes the excitation trapping at site 8 via site 3.

We shall use the population \(P_{8}\) at time \(T\) in the reaction center given by \(P_{8}(T) = \text{Tr}(|8\rangle\langle 8|\rho(T))\) to quantify the excitation transfer efficiency. Clearly, the Liouvillian \(L_{38}(\rho)\) plays an essential role in the excitation transfer. With this term, we will show in the next section that the complex inter-site coupling can enhance the excitation energy transfer.

III. SIMULATION RESULTS

It has been shown that the Hamiltonian with real inter-site couplings can not give high excitation energy transfer efficiency. Indeed, the previous numerical simulations shown that \(\Gamma\) can be optimized to 87.14 with all \(\phi_{ij} = 0\) to obtain the highest excitation transfer efficiency \(p_{8} = 0.6781\) in this case\textsuperscript{[24]}.

With complex inter-site couplings, the EET efficiency can reach almost 90% by optimizing the phases added to \(J_{ij}\). In units of \(\pi\), these phases are \(\phi_{12} = 1.2566, \phi_{16} = 3.3510, \phi_{23} = 1.8850, \phi_{34} = 1.8850, \phi_{45} = 1.8850, \phi_{47} = 0.8378, \phi_{56} = 3.1416, \phi_{67} = 0.3142\). With these phases,
the population on each site as a function of time is plotted in Fig. 1. Two observations can be made from Fig. 1: (1) The population shows oscillatory behavior in the whole energy transfer process, this is different from the situation where decoherence dominates the mechanism of EET [24], (2) the excitation on site 1 and 2 dominates the population, while the population at site 3 is almost zero. The first observation can be understood as the quantum coherence lasts the whole EET, and the second observation suggests that the site 1 and site 2 play important role in the excitation energy transfer. The excitation on site 3 is trapped and transferred to the reaction center almost immediately as to obtain a high transfer efficiency, as Fig. 1 shows.

Spatial and temporal relaxation of exciton shows that the site 1 and 6 were populated initially with large contribution [5]. 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 site 1 and 6 and analyze 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 analyses are performed by numerically calculate the transfer efficiency at time $T = 5\text{ps}$, selected results are shown in Fig. 2 and Fig. 3.

In Fig. 2 we present the transfer efficiency as a function of $\theta$ and $\phi$, which characterize 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 $|\psi(t = 0)\rangle = \cos \theta |1\rangle + \sin \theta \exp(i\phi) |2\rangle$ (lower panel). We find the FMO complex efficient to transfer excitation initially at site 1 is not good at EET with site 6 occupied. Namely, coherent superposition of sites 1 and 6 decreases the exciton transfer efficiency. For exciton initially in a superposition of 1 and 6, the transfer efficiency is more sensitive to the population ratio (characterized by $\theta$) but not to the relative phase $\phi$. For exciton initially excited on site 8 represents the reaction center. The phases are optimized for the EET efficiency. The exciton is assumed initially on the site 1. The upper panel shows the population without decoherence, while the bottom panel shows that with $\gamma_2 = 2.4$ and $\gamma_{j\neq 2} = 0$, see Eq.(3). $\Gamma = 44$ is chosen throughout this paper.
1 and 2, both the population ratio and the relative phase affect the energy transfer, the transfer efficiency reaches its maximum with $\theta = \frac{3}{4} \pi$ and $\phi = \frac{1}{4} \pi$ and it arrives at its minimum with $\theta = \frac{5}{4} \pi$ and $\phi = \frac{1}{4} \pi$. This observation suggests that a properly superposition of site 1 and site 2 can enhance the EET, although the increase of efficiency is small.

Fig. 3 shows the dependence of the transfer efficiency on the mixing rate $p$, where the initial state is a classical mixing of site 1 and 6 (or 2). Obviously, the population mixing of site 1 and site 6 does not favors the transfer efficiency. While the classical mixing of site 1 and site 2 increase the transfer efficiency a little bit (not clear from the figure).

It is recently suggested that decoherence is an essential feature of EET in the FMO complex, where decoherence arises from interactions with the protein cage, the reaction center and the surrounding environment. Further examination shown that dephasing can increase the efficiency of transport in the FMO, whereas other types of decoherence (for example dissipation) block the EET. These effects of decoherence can be understood as the fluctuation-induced-broadening of energy levels, which bridges the on-site energy gap and changes equivalently the coupling between the sites.

We now examine if the decoherence can further increase the EET efficiency with the complex inter-site couplings. The decoherence can be described by an added Liouvillian term

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

(5)

to Eq. 4 with $P_j = \langle j | j \rangle$, $j = 1, 2, 3, ..., 7$. The decoherence may come from site-environment couplings, where the environment models the thermal phonon bath and radiation fields. Optimizing the decoherence rates $\gamma_j$, $(j = 1, 2, ..., 7)$ with $\Gamma = 44$ for the EET efficiency, we find $\gamma_2 = 2.4$ and $\gamma_j = 0, (j \neq 2)$ yields a transfer efficiency $P_8 = 0.9344$, see Fig. 4. Non-zero $\gamma_j, (j = 1, 3, 4, 5, 6, 7)$ can increase the EET efficiency, but the amplitude of the increase is not evident, for example, $\gamma_1 = 2.4, \gamma_3 = 2.0, \gamma_6 = 1.8$, the other $\gamma_j = 0$ and $\Gamma = 44$ yields $P_8 = 0.9374$.

### IV. EFFECT OF FLUCTUATIONS

The site energies are among the most debated properties of the FMO complex. These values are needed for exciton calculations of the linear spectra and simulations of dynamics. They depend on local interactions between the BChl a molecule and the protein envelope and include electrostatic interactions and ligation. Since the interactions are difficult to identify and even harder to quantify, the site energies are usually treated as independent parameters obtained from a simultaneous fit to several optical spectra. There are many approaches to obtain the site energies by fitting the spectra. One of the main differences between those approaches is whether they restrict the interactions to BChl a molecules within a subunits or whether they include interactions in the whole trimer. Since the site energies and inter-site couplings may be different and fluctuate due to the couplings to its surroundings, it is interesting to ask how 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 remains essentially unaffected in the presence of random variations in site energies and inter-site couplings. This strongly suggests that the experimental results recorded for samples at low temperature would also be observable at higher temperatures.

To be specific, we consider two types of fluctuations in the site energies and inter-site couplings. In the first one, it has zero mean, while the another type of fluctuations has nonzero positive mean. For the fluctuations with zero mean, the Hamiltonian in Eq. 3 takes the following changes, $H_{jj} \rightarrow H_{jj}(1 + r_1 \cdot \text{rand}(1))$ and $H_{ij, \neq j} \rightarrow H_{ij, \neq j}(e^{i\phi_{ij}} + r_2 \cdot \text{rand}(1))$. For the fluctuations with nonzero positive mean, the Hamiltonian takes the following changes, $H_{jj} \rightarrow H_{jj}(1 + r_1 \cdot \text{rand}(1))$ and $H_{ij, \neq j} \rightarrow H_{ij, \neq j}(e^{i\phi_{ij}} + r_2 \cdot \text{rand}(1))$, where rand(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 Fig. 4. Each value of transfer efficiency is a result averaged over 20 fluctuations. From the numerical simulations, we notice that the results for fluctuations with non-zero mean are almost the same as those for zero-mean fluctuations, we hence present here only the results for zero-mean fluctuations. Two observations are obvious. (1) With zero-mean fluctuations in the site energies and couplings increase, the transfer efficiency fluctuates greatly. (2) The efficiency decreases with both $r_2$ and $r_1$. Moreover, the EET efficiency is sensitive to the fluctuations in the site energy more than that in the inter-site couplings.

These feature can be interpreted as follows. Since the
network with Hamiltonian Eq.(3) is optimal for EET efficiency, any changes in the site-energy and inter-site couplings would diminish the excitation energy transfer, leading to the decrease in the EET efficiency. This feature is different from the case that the decoherence dominates the mechanism of EET. As Ref. 24 shown, the efficiency increases with $r_1$ but decreases with $r_2$. The physics behind this difference is as follows. For the case that the decoherence dominates the mechanism of EET, the energy gap between neighboring sites blocks the energy transfer, whereas the inter-site couplings (representing the overlap of different sites) together with the decoherence favor the transport. Whereas for the present case the phases in the inter-site couplings need to match the energy spacing between sites. As a result, any mismatches would results in decrease in the EET efficiency.

It was 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. We assume that the fluctuations enter only into the on-site energies, namely, $H_{jj}$ is replaced by $H_{jj}(1 + y(x|\sigma, \mu))$, $j = 1, 2, \ldots, 7$. With these notations, we plot the effect of fluctuations on the transfer efficiency in Fig. 6 (upper panel). We find that the dependence of the efficiency on the variation is subtle: When the mean is zero, the efficiency reach its maximum at $\sigma = 0.5$, while when the mean is large, small variation favors the EET efficiency. Moreover, we find that the efficiency decreases as the mean increases. This again can be understood as mismatch between the site energy and the inter-site couplings caused by the fluctuations. When these Gaussian fluctuations occur in both the on-site energies and the couplings, we find from Fig 6 (bottom panel) that the transfer efficiency decreases as the mean and variation increases.

Absorption spectroscopy and 2D echo-spectroscopy are used to study time-resolved processes such as energy transfer or vibrational decay as well as to measure intermolecular couplings strengths. They provide a tool that gives direct insight into the energy states of a quantum system. In turn, the eigenenergies are essential to calculate the absorption spectroscopy and 2D echo-spectroscopy. It is easy to find that the eigenenergies and energy gaps for the FMO with complex inter-site couplings, given by (96.2851, 62.2958, 61.4307, 48.2046, 22.6379, 18.9438, -4.1374), are almost the same as in the system with real inter-site couplings given by (96.8523, 62.6424, 57.9484, 50.6357, 22.8218, 19.2387, -4.4789). The maximal difference is at the 7th eigenenergy, it is about 8.25% to its eigenenergy. This suggests that the absorption spectroscopy and 2D echo-spectroscopy may not change much due to the introduced phases in the inter-site couplings.

V. CONCLUSION

Excitation energy transfer (EET) has been an interesting subject for decades not only for its phenomenal efficiency but also for its fundamental role in Nature. Recent studies show that the quantum coherence itself cannot explain the very high excitation energy transfer efficiency in the Fenna-Matthews-Olson Complex. In this paper, we show that this is not the case when the inter-site couplings are complex. Based on the Frenkel exciton Hamiltonian and the phenomenologically introduced de-
coherence, we have optimized the phases in the inter-site couplings for maximal energy transfer efficiency, which can reach about 89.72% at time 5ps without decoherence and 93.44% with only dephasing at site 2. By considering different mixing of exciton on site 1 and site 6 (site 2) as the initial states, we have examined the effect of initial states on the energy transfer efficiency. The results suggest that any mixing of site 1 and site 6 decreases the energy transfer efficiency, whereas a coherent superposition (or classically mixing) of site 1 and site 2 does not change much the EET efficiency. The fluctuations in the site energies and inter-site couplings diminish the EET due to the mismatch caused by the fluctuations.

Finishing this work, we have noticed a closely related preprint [25]. While they focus on bi-pathway EET in the FMO (i.e., neglecting the inter-site couplings weaker than $15 \text{cm}^{-1}$) and a general representation for complex network, we are mainly concerned about the phases added to the inter-site couplings, initial excitations and fluctuations in the site energies and inter-site couplings. In this respect, both works are complementary to each other.

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