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Quantum transport in the FMO photosynthetic light-harvesting complex

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Abstract The very high light-harvesting efficiency of natural photosynthetic systems in conjunction with recent experiments, which showed quantum-coherent energy transfer in photosynthetic complexes, raised questions regarding the presence of non-trivial quantum effects in photosynthesis. Grover quantum search, quantum walks, and entanglement have been investigated as possible effects that lead to this efficiency. Here we explain the near-unit photosynthetic efficiency without invoking non-trivial quantum effects. Instead, we use non-equilibrium Green's functions, a mesoscopic method used to study transport in nano-conductors to compute the transmission function of the Fenna–Matthews–Olson (FMO) complex using an experimentally derived exciton Hamiltonian. The chlorosome antenna and the reaction center play the role of input and output contacts, connected to the FMO complex. We show that there are two channels for which the transmission is almost unity. Our analysis also revealed a dephasing-driven regulation mechanism that maintains the efficiency in the presence of varying dephasing potentials.

Keywords Photosynthesis · FMO complex · Quantum transport · Non equilibrium Green's Functions · NEGF

1 Introduction

Living organisms convert solar energy to forms they can use and store by capturing photons by pigments in their photosynthetic antennae and transporting the resulting excitons through protein complexes to the reaction centers, where ATP and NADPH are produced. Photosynthesis has been perfected by evolution and has a remarkable, near-unity efficiency [1]. Furthermore, phototrophic organisms can regulate the photosynthetic process in cases where incident photons exceed their photosynthetic ability,



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to avoid possible damage [1, 2]. Recent experiments provided evidence for the presence of unexpectedly long-time quantum coherences in energy transport through photosynthetic complexes [3-5]. Green sulfur bacteria were used as prototype organisms and the coherent transport was observed in the Fenna-Matthews-Olson (FMO) bacteriochlorophyll complex, which serves as a conductor, connecting the chlorosome antenna to the reaction center. Coherent transport is a strong indication that quantum mechanical phenomena may play a role in photosynthesis [2, 6], especially in achieving the almost perfect efficiency. Theoretical studies investigated the possible role of non-trivial quantum effects in photosynthesis, such as Grover quantum search [3], quantum walks [7, 8], and entanglement [9-12]. The presence of these quantum effects has been criticized. Quantum search was criticized in [7], quantum walks in [13], and entanglement in [14]. The presence of non-trivial quantum mechanical effects in photosynthesis remains an open question. Furthermore, theoretical studies provide strong evidence that coherence in electronic energy transfer in the FMO complex is evident at the classical level [15] and that classical electrodynamics can reproduce the results of quantum mechanical calculations [16]. The aim of this paper is to show that if quantum methods are to be used to explain the high-efficiency photosynthetic process, then there is no need to invoke non-trivial quantum effects. We use the non-equilibrium Green's function (NEGF) method to describe the phenomenon effectively. Our study also revealed a regulation mechanism that maintains the efficiency of the photosynthetic process.

2 Quantum transport in the FMO complex

Here we take a different approach to the study of transport in photosynthetic complexes. We use the non-equilibrium Green's functions (NEGF) method [17, 18], which is an established and accurate method for computing the transmission of nanoconductors and especially of organic nano-conductors [19, 20]. The contacts of the nano-conductor play a crucial role in electron transport and cannot be ignored [17, 18, 21]. The NEGF method takes into account the effects of contacts on electron transmission through nano-conductors. To use the NEGF method for the study of photosynthetic systems, we model the FMO complex as a nano-conductor connected to the chlorosome antenna and the reaction center, as shown in Fig. 1. The FMO complex contains seven electronically coupled bacteriochlorophyll- α chromophores (BChls), which are numbered from 1 (BChl1) to 7 (BChl7).

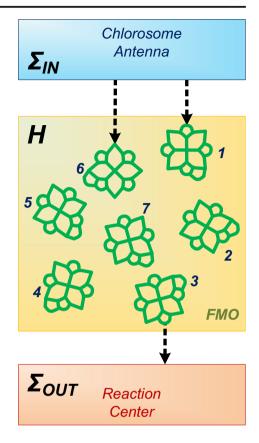
We compute the transmission, of the "Chlorosome antenna – FMO – Reaction center" system as a function of energy, T(E). Transmission is the conductance G(E) divided by the quantum of conductance $(2e^2/h)$ and is given by [17, 21]:

$$T(E) = \frac{G(E)}{2e^2/h} = Trace \left[\Gamma_{IN} \ G^R \ \Gamma_{OUT} \ G^A \right]$$
 (1)

 G^R and G^A are the retarded and advanced Green's functions and are quantum mechanical propagators that describe, in general, the propagation of excitations in space-time. Γ_{IN} and Γ_{OUT} are the broadening factors of the "Chlorosome antenna – FMO" contact and of the "FMO – Reaction center" contact, respectively. The retarded Green's function is given by:



Fig. 1 The FMO complex is modeled as a nano-conductor described by the Hamiltonian H. The seven BChls are numbered from 1 to 7. FMO is connected to the chlorosome antenna, described by the self-energy $\Sigma_{\rm IN}$ and the reaction center, described by the self-energy $\Sigma_{\rm OUT}$. Excitonic energy enters the FMO complex through BChl1 and BChl6 and exits through BChl3



$$G^{R} = [EI - H - \Sigma_{IN} - \Sigma_{OUT}]^{-1}$$
 (2)

E is the energy, I is the unit matrix, Σ_{IN} and Σ_{OUT} are the self-energies of the two contacts and H is the FMO excitonic Hamiltonian, which has been obtained by fitting to experimental data using a genetic algorithm [22, 23]. The broadening factors are connected to the self-energies by:

$$\Gamma_{IN,OUT} = i \cdot \left[\Sigma_{IN,OUT} - \Sigma^{\dagger}_{IN,OUT} \right] \tag{3}$$

The advanced Green's function G^A is given by:

$$G^{A} = \left(G^{R}\right)^{+} \tag{4}$$

The almost perfect efficiency of photosynthesis allows us to assume that the "Chlorosome antenna – FMO" and the "FMO – Reaction center" contacts are very well matched. This means that there is no excitonic energy reflection at these interfaces. We therefore compute the self-energies Σ_{IN} and Σ_{OUT} by assuming a semi-infinite repetition of BChl1, BChl6, and their connections towards the chlorosome antenna and a semi-infinite repetition of BChl3 towards the reaction center [17, 21]. The Hamiltonian is a site-basis Hamiltonian, where BChls are the sites, and we use it with an offset of 1.514 eV (12,210 cm⁻¹0) [13, 23].



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The surface Green's function G^n is computed from:

$$G^n = G^R \sum^{in} G^A \tag{5}$$

 Σ^{in} is given by:

$$\sum^{in} = f_{IN} \Gamma_{IN} + f_{OUT} \Gamma_{OUT} \tag{6}$$

where f_{IN} and f_{OUT} are the electron electrochemical potentials in the chlorosome antenna and the reaction center. The spectral function, A, is computed from:

$$A = i(G^R - G^A) \tag{7}$$

Dephasing is described by Σ_0 , which includes the interactions along the FMO complex [17, 21]. In this case:

$$\Sigma = \Sigma_{IN} + \Sigma_{OUT} + \Sigma_0$$

$$\Gamma = \Gamma_{IN} + \Gamma_{OUT} + \Gamma_0$$
(8)

and

$$\Sigma_0 = D G^R
\Gamma_0 = D A$$
(9)

The element $D_{i,j}$ of the matrix D represents the correlation between dephasing potentials at sites i and j.

The computation results are shown in Fig. 2a. Figure 2a shows the transmission function of the "Chlorosome antenna – FMO – Reaction center" system as a function of energy. The transmission is equal to 0.9579 for a channel with energy equal to 0.0293 eV (or 1.5433 eV without the offset). This channel is marked with A and we call it henceforth the A channel. About 0.002 eV above the A channel there is another channel with transmission equal to 0.4. This channel is very near the A channel and we consider it as part of the A channel. There is also another channel, the B cannel, with energy equal to 0.0082 eV, the transmission of which is equal to 0.2231. Our computations confirmed that excited electrons enter the FMO complex through both BChl1 and BChl6. The transmission function was almost zero for all energies when the other BChls were used as inputs, including BChl6 alone. When only BCHl1 was used as input, the transmission of the A channel was 0.712 and the transmission of the B channel was almost zero.

A part of the FMO Hamiltonian stems from the thermal fluctuations of the protein scaffold in which the BChls are embedded. Thermal fluctuations are represented by a dephasing potential energy [5, 7, 9, 14]. In the NEGF method, dephasing is treated as an external energy source acting on all BChl sites [17, 21]. We computed the transmission function of the "Chlorosome antenna – FMO – Reaction center" system for various dephasing potential energies. Figure 2b shows the transmission function of the system in the case of a dephasing potential energy equal to 0.0008 eV. The transmission of the A channel is 0.9550 and the transmission of the B cannel is 0.4893. We computed the transmissions of the A and B channels for dephasing potential energies from -0.0015 eV to +0.0015 eV (or from 1.5125 eV to 1.5155 eV without the offset). The results are shown in Fig. 3.



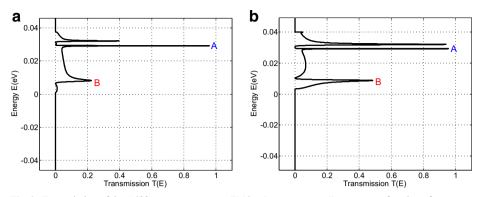
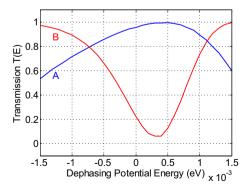


Fig. 2 Transmission of the "Chlorosome antenna – FMO – Reaction center" system as a function of energy. **a** The dephasing potential energy is zero and **b** the dephasing potential energy is 0.0008 eV

The transmission of the A channel is equal to unity (0.9962) when the dephasing potential energy is 0.0005 eV. For this energy, the transmission of the B channel is 0.1285. The transmission of the B channel for dephasing energies -0.0015 eV and 0.0015 eV is 0.9730 and 0.9965, respectively. The corresponding transmissions of the A channel are 0.5356 and 0.5990. For dephasing potential energies less than -0.0015 eV and larger than 0.0015 eV the transmissions of both channels fall abruptly to values near to 0.2.

From Fig. 3 it is evident that the transmissions of the A and B channels complement each other when the dephasing potential energy varies because of environmental fluctuations. This regulation mechanism maintains the near-unity efficiency in the presence of environmental fluctuations. As mentioned above, when BChl1 was considered to be the only input, only the A channel was conducting with transmission equal to 0.712 and when BChl6 was also considered as input the B channel appeared and was conducting with transmission equal to 0.2231. It is therefore reasonable to assume that although the cause of this regulation mechanism is not known, its source is probably the coupling between BChl1 and BChl6.

Fig. 3 Transmission of the A and B channels as a function of the dephasing potential energy





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3 Conclusions

We used NEGF, a mesoscopic method, to study energy transmission through the FMO photosynthetic complex. Contrary to Grover quantum search, quantum walks and entanglement based analyses, the effect of the contacts of the FMO complex with the chlorosome antenna and the reaction center was taken into account. Within bounds, decoherence induced by the environment was found to regulate and not inhibit the transmission of the FMO complex. We confirmed that excited electrons enter the FMO complex through both BChl1 and BChl6 and hypothesized that the source of the dephasing-driven regulation mechanism stems from the coupling between these two sites.

Compliance with ethical standards

Conflict of interest The author declares that he has no conflict of interest.

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