Importance of Excitation and Trapping Conditions in Photosynthetic Environment-Assisted Energy Transport

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ABSTRACT: It has been argued that excitonic energy transport in photosynthetic complexes is efficient because of a balance between coherent evolution and decoherence, a phenomenon called environment-assisted quantum transport (ENAQT). Studies of ENAQT have usually assumed that the excitation is initially localized on a particular chromophore, and that it is transferred to a reaction center through a similarly localized trap. However, these assumptions are not physically accurate. We show that more realistic models of excitation and trapping can lead to very different predictions about the importance of ENAQT. In particular, although ENAQT is a robust effect if one assumes a localized trap, its effect can be negligible if the trapping is more accurately modeled as



Förster transfer to a reaction center. Our results call into question the suggested role of ENAQT in the photosynthetic process of green sulfur bacteria and highlight the subtleties associated with drawing lessons for designing biomimetic light-harvesting complexes.

INTRODUCTION

Mechanisms of energy transport in photosynthetic systems¹ have attracted renewed attention²⁻⁴ in recent years because of the experimental observation of long-lived coherences in bacterial and algal light-harvesting complexes.⁵⁻⁸ Indeed, it has been suggested that coherent quantum effects may play an important role in energy transport in photosynthetic complexes.⁹⁻¹⁵

In particular, it has been proposed that the high efficiency of photosynthetic energy transport arises out of the interplay between coherent evolution and environmentally induced noise, an effect dubbed environment-assisted quantum transport (ENAQT)¹⁶ or dephasing-assisted energy transport.^{17,18} In coherent systems, disorder can cause localization and thus inhibit transfer. In those cases, ENAQT can be understood as the suppression of coherent localization through noise, which helps the excitation move through the disordered photosynthetic complex and toward its destination, the reaction center (RC), where the energy is used to power the first chemical steps of photosynthesis.

Although it has been shown that ENAQT can occur in a wide variety of quantum¹⁶⁻²² and classical²³⁻²⁵ transport systems, these findings are usually based on specific assumptions that have been challenged. In particular, in most models, it is assumed that the system starts out with only one pigment molecule initially excited and that only one pigment molecule (the "trap") is responsible for the ultimate exciton transfer to the RC. These assumptions might be incorrect: unless the system is so disordered that each eigenstate is effectively localized on one site, both the initial state and the trap state will be at least partially delocalized.

Here we examine ENAQT in situations where both the excitation and the trapping are treated in more physically realistic ways. Most importantly, we show that the description of the coupling to the RC significantly influences the magnitude and, consequently, the importance of the predicted ENAQT. If the trap is localized at a particular site, as it has been assumed previously, we show that ENAQT persists under almost all excitation conditions, including excitation transfer from an antenna complex. However, ENAQT is either absent or negligible if the coupling to the RC is treated as Förster transfer (as we argue it should be), meaning that it is unlikely to be important for influencing the biological function of light-harvesting complexes.

THEORETICAL METHODS

We consider the dynamics of excitons in a network of N chromophores (or sites). Under the usual weak illumination, it is rare to find more than one exciton in a single complex. Therefore, we restrict ourselves to the single-exciton manifold, with state $|i\rangle$ indicating that the exciton is on site *i*. The system is then described by a tight-binding Hamiltonian (see May and Kühn,²⁶ section 9.2)

$$H_{\rm s} = \sum_{i=1}^{N} \varepsilon_i |i\rangle \langle i| + \sum_{i(1)$$

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where ε_i are the excitation energies of the molecules and V_{ij} the intermolecular couplings. We will denote the eigenstates of H_s as $|e_i\rangle$, with energies E_i

$$H_{s}|e_{i}\rangle = E_{i}|e_{i}\rangle \tag{2}$$

We will also denote the state where no excitons are present as $|g\rangle$ and the state where the exciton has been transferred to a reaction center as $|RC\rangle$. Neither $|g\rangle$ nor $|RC\rangle$ are coupled to the states $|i\rangle$ through $H_{\rm s}$.

The interaction of a photosynthetic system with its environment is in general complicated and non-Markovian.^{22,26,27} However, because this work is about qualitative features of ENAQT, we will use a Markovian model that, although simplistic, captures the essential physics.^{16–18} We assume that the system–bath interaction can be modeled using a Lindblad (or, equivalently, Redfield²⁸) master equation for the system density matrix ρ^{28}

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H_{\rm s}, \rho] + \mathcal{L}_{\rm deph}[\rho] + \mathcal{L}_{\rm diss}[\rho] + \mathcal{L}_{\rm RC}[\rho] \tag{3}$$

where the various nonunitary contributions are denoted \mathcal{L} . In particular

$$\mathcal{L}_{deph}[\rho] = \sum_{i=1}^{N} 2\gamma_{i} \left(|i\rangle \langle i|\rho|i\rangle \langle i| - \frac{1}{2} \{|i\rangle \langle i|, \rho\} \right)$$
(4)

where $\{\cdot,\cdot\}$ is the anticommutator, describes a pure dephasing process that attenuates the coherence between different sites at a site-dependent rate γ_i . It can be thought of as being caused by bath-induced fluctuations in the site energies (see May and Kühn,²⁶ section 9.3). For present purposes, the important aspect of eq 4 is that it acts in the site basis, a feature it shares with most models of chromophoric noise, even the non-Markovian ones.

The remaining two terms in eq 3 describe two mechanisms by which the excitation can be lost. First, the exciton can recombine at each site at rate Γ_i :

$$\mathcal{L}_{\text{diss}}[\rho] = \sum_{i=1}^{N} 2\Gamma_{i}\left(|g\rangle\langle i|\rho|i\rangle\langle g| - \frac{1}{2}\{|i\rangle\langle i|, \rho\}\right)$$
(5)

If this happens, the exciton's energy is lost to the environment. Second, $\mathcal{L}_{RC}[\rho]$ describes the (unidirectional) transfer of excitations to the RC. Because it also causes exciton disappearance from the $|i\rangle$ -manifold, it will have a form similar to eq 5, with details depending on the trapping conditions discussed below. In any case, the exciton will eventually either dissipate or be transferred to the RC, which motivates the definition of the *efficiency* η as the probability that the energy will arrive at the RC rather than being dissipated:

$$\eta = \lim_{t \to \infty} \langle \mathrm{RCl}\rho(t) | \mathrm{RC} \rangle \tag{6}$$

Our main result is that η is sensitive to how we describe the exciton transfer \mathcal{L}_{RC} from the complex to the RC. The usual approach has been to use

$$\mathcal{L}_{\rm RC}[\rho] = \mathcal{L}_{\rm RC}^{\rm local}[\rho] = 2\Gamma_{\rm RC} \left(|{\rm RC}\rangle \langle k|\rho|k\rangle \langle {\rm RC}| - \frac{1}{2} \{|k\rangle \langle k|, \rho\} \right)$$
(7)

where only one site, denoted k, transfers excitation to the RC (hence the superscript "local"). The underlying assumption is that k is closest to the RC and, consequently, that it is the only

site appreciably coupled to it. In that case, the efficiency can also be written as

$$\eta = 2\Gamma_{\rm RC} \int_0^\infty \mathrm{d}\tau \, \left\langle k | \rho(\tau) | k \right\rangle \tag{8}$$

Equations 7 and 8 have been used to describe several environment-assisted transport processes in photosynthetic complexes^{16,17} and in ordered systems.²⁰

However, the localized transfer model does not always correctly describe exciton transfer between a photosynthetic complex and the RC. Below, we will discuss the example of the Fenna–Matthews–Olson complex of green sulfur bacteria, whose separation from the RC is ~2 nm.^{29,30} This is a large distance compared with the interpigment distances in FMO (4-11 Å),³¹ indicating that the two complexes are weakly coupled to each other.³²

Exciton transfer between weakly coupled complexes is an incoherent process that can be modeled using a multichromophoric generalization of Förster resonant energy transfer (FRET).^{13,33–38} Although the chromophores within the donor and/or the acceptor may be strongly coupled leading to delocalized excitons—the transfer between the two complexes is nevertheless given by Fermi's golden rule (see May and Kühn,²⁶ section 9.6.4)

$$\kappa = \frac{2\pi}{\hbar} \sum_{D_i, A_i} \sum_{D_f, A_f} g_D(D_i) g_A(A_i) |\langle D_i A_i | J | D_f A_f \rangle|^2$$
$$\times \delta(E_{D_i} + E_{A_i} - E_{D_f} - E_{A_f})$$
(9)

where the sums are over the *eigenstates* D_i and A_i of the (excited) donor and the (de-excited) acceptor and D_f and A_f of the (de-excited) donor and the (excited) acceptor. The initial populations of donor and acceptor states are g_D and g_A , and the coupling $\langle D_i A_i | J | D_f A_i \rangle$ is the matrix element of the complete donor-acceptor Coulomb interaction *J*.

We stress that FRET is a transfer between populations of donor and acceptor eigenstates and *not sites*. This is true whether one uses the generalized multichromophoric theory referred to above^{13,33-38} or whether the donor and acceptor are each treated as one supermolecule for the purposes of the original Förster theory (which becomes accurate for large interaggregate distances). A localized state has coherences in the energy basis, and the corresponding oscillations would average to zero in the long-time limit characteristic of weakly coupled aggregates (this is the essence of the secular approximation). Instead, if the coupling J only involves site k in the donor—as we assume for the sake of the argument—the localized state $|k\rangle$ ought to be decomposed into eigenstate components, each of which contributes to an independent incoherent rate in eq 9. In the present case, this means replacing $\mathcal{L}_{\rm BC}^{\rm local}$ with

$$\mathcal{L}_{\mathrm{RC}}^{\mathrm{FRET}}[\rho] = 2\Gamma_{\mathrm{RC}} \sum_{i=1}^{N} |\langle e_i | k \rangle|^2 \\ \times \left(|\mathrm{RC}\rangle \langle e_i | \rho | e_i \rangle \langle \mathrm{RC}| - \frac{1}{2} \{ |e_i\rangle \langle e_i |, \rho \} \right)$$
(10)

The efficiency can still be calculated using eq 6, or eq 8 can be modified to

$$\eta = 2\Gamma_{\rm RC} \int_0^\infty \mathrm{d}\tau \, \sum_{i=1}^N |\langle e_i | k \rangle|^2 \langle e_i | \rho(\tau) | e_i \rangle \tag{11}$$

In the following, we will show results of calculations using both \mathcal{L}_{RC}^{local} and \mathcal{L}_{RC}^{FRET} in order to relate this work to previous studies and to highlight the importance of correctly modeling the system–RC coupling.

The choice of an initial state for eq 3 involves similar concerns. In particular, we emphasize that the excitation of photosynthetic complexes is *not* impulsive, except in ultrafast experiments. Rather, excitation occurs through a *steady* state, ^{15,39–41} where an external energy source—whether light or an antenna complex—continuously pumps the systems and where the excitation energy is continuously lost to either the environment or the RC.

In a steady-state context, the natural definition of efficiency is the ratio of exciton (or energy) flux to the RC to the incoming flux that pumps the system. Consequently, eqs 6, 8, and 11 may seem inappropriate. However, Jesenko and Žinidarič have shown that the efficiency of a steady-state process is equal to the efficiency of the corresponding impulsive case,⁴² as we will illustrate in examples below. We will use eqs 8 and 11 here to better relate our results to the existing body of work.

We will consider three excitation regimes: localized excitation, excitation by transfer from an antenna complex, and photoexcitation.

The simplest model of initial excitation is localized excitation of a single site, which has been considered in numerous studies of excitonic energy transfer and ENAQT.^{10,14,16–18,20,21,40} Without loss of generality, we will call the initial site "1", writing

$$\rho_{\text{local}} = |1\rangle\langle 1| \tag{12}$$

Using this initial state is equivalent, in the sense of Jesenko and Žnidarič,⁴² to a steady-state system whose master equation includes an additional term that transfers population from the ground state to $|1\rangle$

$$\mathcal{L}_{\text{pump}}[\rho] = 2\Gamma_{\text{pump}}\left(|1\rangle\langle g|\rho|g\rangle\langle 1| - \frac{1}{2}\{|g\rangle\langle g|, \rho\}\right)$$
(13)

In many photosynthetic architectures, an exciton is harvested by peripheral antenna complexes before being transferred to the RC via other intermediate complexes. For instance, in the case of green sulfur bacteria, light absorbed by the chlorosome antenna is first transferred through the baseplate⁴³⁻⁴⁵ to the FMO complex before reaching the RC. This naturally raises the question of what is the appropriate "initial" state for an intermediate complex that is excited by an antenna complex.

In green sulfur bacteria, the distances both between the chlorosome and the baseplate $(\sim 2 \text{ nm})$,^{43,44,46} and between the baseplate and FMO $(\sim 1.5 \text{ nm})^{44}$ are so large that exciton transfer should be described by FRET. If the FMO site closest and most strongly coupled to the baseplate is 1, FRET would populate excitonic eigenstates in proportion in which they occur at site 1, giving the "initial" state

$$\rho_{\text{ant}} = \sum_{i=1}^{N} |\langle 1|e_i \rangle|^2 |e_i \rangle \langle e_i|$$
(14)

The corresponding continuous pumping term is easily written down in analogy to eq 13.

When a light-harvesting complex is excited by light, one must distinguish the cases of coherent and incoherent illumination. $^{15,39,41,47-50}$

If the incoming light is incoherent (as is sunlight), various frequencies only excite populations of the eigenstates with which they are resonant and not coherences between them.^{39,47,48} If we assume, somewhat crudely, that each transition has the same oscillator strength, incoherent light will create a mixture of eigenstates in proportion to the intensity of the light spectrum at the transition frequency. For thermal light, such as sunlight, one obtains pumping from the ground state to

$$\rho_{\rm incoh} = \frac{1}{N} \sum_{i=1}^{N} I(E_i) |e_i\rangle \langle e_i|$$
(15)

where $I(\omega)$ is the Planck distribution for the thermal light (we use T = 5800 K, the effective temperature of the Sun, in calculations below) and N is the normalization constant. This is the correct "initial" state, in the sense of Jesenko and Žnidarič,⁴² for what is in reality a steady-state process.

If, on the other hand, the complex were excited by a coherent, transform-limited laser pulse, one would obtain a superposition instead of a mixed state.^{39,47,48} The state will depend on details such as the spectrum, duration, intensity, and polarization of the pulse. However, to enable comparison with eq 15, we assume the same spectrum and that all eigenstates acquire the same phase, so we write the initial state as

$$\rho_{\rm coh} = |\psi\rangle\langle\psi|, \quad \text{where } |\psi\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \sqrt{I(E_i)} |e_i\rangle$$
(16)

RESULTS AND DISCUSSION

In the calculations that follow, we have used as the model system a single unit of the Fenna–Matthews–Olson (FMO) complex of *Prosthecochloris aestuarii*. It is composed of seven coupled bacteriochlorophyll (BChl) molecules supported by a protein scaffold, as shown in Figure 1. We used the site energies



Figure 1. Arrangement of the bacteriochlorophyll molecules of a single unit of the Fenna–Matthews–Olson (FMO) complex³¹ (drawn using PyMOL⁵¹).

 ε_i and couplings V_{ij} given by Adolphs and Renger (Tables 2 and 4).⁵² In FMO, BChl 3 is believed to be closest to the reaction center,⁵² giving k = 3. We follow previous authors^{17,53} in estimating $\Gamma_{\rm RC} = 1 \text{ ps}^{-1}$. Furthermore, we assume that the dissipative rates are the same for all molecules, $\Gamma_i = \Gamma = 5.0 \times 10^{-4} \text{ ps}^{-1.54}$ as are the dephasing rates, $\gamma_i = \gamma$, which we take to be an adjustable parameter.

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Figure 2. Energy transfer efficiency in FMO as a function of the dephasing rate, assuming different initial states and different trapping mechanisms. (a) Calculated using localized transfer to the reaction center (RC), as had been assumed in most previous work, eq 7. The efficiency is shown for four initial states: (i) ρ_{local} transfer into site 1, eq 12 (solid line), (ii) ρ_{ant} , incoherent transfer from an antenna complex, eq 14 (dashed line), (iii) ρ_{incoh} incoherent photoexcitation, eq 15 (dotted line), (iv) ρ_{coh} coherent photoexcitation, eq 16 (dash-dotted line). Regardless of the manner of initial excitation, coherent evolution leads to localization of the excitation at low dephasing, resulting in transport efficiencies of about 70–90%. With increasing dephasing, localization is suppressed and the efficiency grows to almost 100%, the signature of ENAQT. Finally, for strong noise, energy transfer to the RC is modeled as Förster resonant energy transfer (FRET), which is more physically realistic, see eq 10. Note the enlarged scale on the vertical axis. ENAQT can now be seen to occur with only some initial conditions, and to be very small in those cases. In the most physically relevant case (transfer from antenna complex, dashed line), the magnitude of ENAQT is at most several percent, making it doubtful that the natural dephasing rate has been fine-tuned by natural selection. (d) Same as (c), but with 1000 randomly chosen initial states, showing that the four initial states above are typical.

We have calculated the efficiency η of excitonic transport through FMO using both the localized model of coupling to the RC and the FRET model (eqs 7 and 10, respectively), as well as using all of the initial excitation conditions given above. In all cases, we calculated the efficiency as a function of the dephasing rate γ , which discloses the presence or absence of ENAQT. The results are shown in Figure 2, a and c.

To verify that the results for particular initial states hold in general, we also computed the efficiency with 1000 random pure initial states, sampled from the uniform distribution on the \mathbb{C}^7 Hilbert space. The results are shown in the shaded bands in Figure 2, b and d. If the initial state were mixed, the efficiency would still lie within these bands because the efficiency, being a linear function of the initial state, is a convex combination of the component pure-state efficiencies.

The results in Figure 2a,b are drastically different from those in panels c and d, indicating that it is crucial to describe the process of transfer to the RC correctly. We discuss the two cases separately.

If \mathcal{L}_{RC}^{local} is used to model exciton transfer from FMO to the RC, Figure 2a,b shows that ENAQT survives under all initial

conditions, including the biologically relevant transfer from antenna complex and excitation by incoherent light. The only exception would be if the exciton were initialized directly at the trap, which would give maximum efficiency at infinite dephasing.

As pointed out previously, whether ENAQT occurs depends on a competition of time scales.^{54–56} In particular, the fact that $\Gamma_{\rm RC} \gg \Gamma$ implies that any excitation that can reach the trap will be caught, increasing the efficiency. The excitation can only be dissipated if it gets stuck away from the trap by some means.

If dephasing (or other noise) is weak or absent, it is most appropriate to think of transport in the basis of the eigenstates of the Hamiltonian (see May and Kühn,²⁶ section 9.6). If dephasing is completely absent, the trapping at rate $\Gamma_{\rm RC}$ will quickly remove the exciton population at the trap site, leaving behind a state with no support at the trap. Because of the finite exciton lifetimes, the eigenstate linewidths will broaden and partially overlap, allowing excitons to again flow to the trap site. However, because the dissipation is weak and the line broadening correspondingly small, this process will be slow, allowing a substantial fraction of the population to be dissipated at the slower rate Γ . In the presence of weak noise, the time-dependent environmental fluctuations behave as perturbations that can shift populations between different eigenstates (as in Redfield theory). The effect will be to shift excitons among various sites as well, allowing almost all of them to reach the trapping site (and therefore be trapped) during the dissipative lifetime Γ^{-1} . This explains the peak in efficiency at intermediate levels of dephasing.

If the dephasing becomes very strong, the Zeno effect prevents excitons from moving between sites at all. Because excitons at nontrap sites will all be dissipated, the efficiency is simply the initial population at the trap site multiplied by the branching ratio $\Gamma_{\rm RC}/(\Gamma + \Gamma_{\rm RC})$.

By contrast, if exciton transfer to the RC is modeled using $\mathcal{L}_{\text{RC}}^{\text{FRET}}$, Figure 2c,d shows that ENAQT is either much reduced or vanishes altogether. At most, the dephasing-induced enhancement of the transfer rate is about 4%.

The efficiency is uniformly high in this case, always exceeding 96%. As noted above, $\Gamma_{\rm RC} \gg \Gamma$ means that the only way to get a low efficiency is if the exciton is somehow prevented from reaching the trap. If the trap is localized—as when $\mathcal{L}_{\rm RC}^{\rm local}$ is used—this can be achieved by also localizing the exciton. By contrast, $\mathcal{L}_{\rm RC}^{\rm FRET}$ traps population from all eigenstates (albeit with different rates), meaning that the exciton has nowhere to hide.

The difference between the two regimes is most pronounced at high dephasing. With a local trap, the Zeno effect completely suppresses the motion of the exciton to the trapping site, which is not a problem in the FRET model because all sites contribute to FRET.

We note that similar results about exciton transport in FMO were obtained by Pelzer et al.⁵⁷ using the Keldysh formalism and assuming the exciton source is an incoherent antenna complex. In their model there is also no ENAQT, in that the probability that an exciton injected into FMO reaches the RC monotonically increases with the dephasing rate. The differences between their results and ours follow from different descriptions of the antenna complex and the RC. Pelzer et al. represented both the antenna complex and the RC as individual sites that are resonant with the highest and lowest exciton energies in FMO, respectively. One consequence of this model is that the exciton flux from the antenna complex to FMO decreases with the dephasing rate. By contrast, we assumed that the antenna complex spectrum is broad and that it can drive various transitions in FMO via FRET.

CONCLUSIONS

In this paper, we have shown that ENAQT depends not only on the initialization of the photosynthetic complex⁵⁶ but also on how the final exciton transfer to the RC is modeled. Although ENAQT is a robust effect that occurs with all initial states if one assumes localized trapping, it mostly vanishes if the transfer to the RC is described as a Förster transfer.

As we argued above, the FRET trapping model will usually be the one that correctly captures the physics of excitonic transfer between weakly coupled complexes. The fact that the FRET model allows only very small ENAQT calls into question the suggestion that, at least in FMO, natural selection has optimized the interplay between quantum dynamics and noise in order to achieve a highly efficient photosynthetic energy transport. Although we focused on the example of FMO, we expect similar results in other photosynthetic complexes. The only exception would be if individual sites were so energetically misaligned that each eigenstate were essentially localized, giving $\mathcal{L}_{RC}^{local} \approx \mathcal{L}_{RC}^{FRET}$. In that situation, the complex would act as a simple energy funnel, and ENAQT would be more pronounced because noise would assist the migration of excitons from the initially populated eigenstate(s) to the spatially remote trap eigenstate(s). However, such a situation may be rare in nature owing to the relatively strong couplings in many complexes.

We have used a simplified Markovian model in this work to emphasize the relevant physics, especially the importance of considering whether the noise and the trapping operate in the site basis or the eigenbasis. Although more complicated models describing the full system—bath dynamics might be used to calculate the efficiency of energy transfer,^{58,59} we expect to observe the same behavior, provided that they involve variablestrength noise acting in the site basis (as most noise models do). Indeed, simulations of ENAQT in FMO using sophisticated noise models did not find qualitatively important differences from the results obtained in the pure-dephasing model.^{19,22} Finally, although non-Markovian effects can affect transport efficiency,^{22,27} this is not a concern in steady-state systems—such as natural or artificial light-harvesting—where equivalent Markovian baths can be used.⁴²

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Notes

The authors declare no competing financial interest.

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