

Classical Approach to Multichromophoric Resonance Energy Transfer

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A classical formulation of the quantum multichromophoric theory of resonance energy transfer is developed on the basis of classical electrodynamics. The theory allows for the identification of a variety of processes of different order in the interactions that contribute to the energy transfer in molecular aggregates with intracoupling in donors and acceptor chromophores. Enhanced rates in multichromophoric resonance energy transfer are shown to be well described by this theory. Specifically, in a coupling configuration between N_A acceptors and N_D donors, the theory correctly predicts an enhancement of the energy transfer rate dependent on the total number of donor-acceptor pairs. As an example, the theory, applied to the transfer rate in light harvesting II, gives results in excellent agreement with experiment. Finally, it is explicitly shown that as long as linear response theory holds, the classical multichromophoric theory formally coincides with the quantum formulation.

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Introduction.—Aspects of modern research on electronic resonant energy transfer in photosynthetic light-harvesting systems have focused on energy transfer as a coherent collective phenomenon. This feature has been highlighted as central to several transfer mechanisms, such as super transfer [1] and a network renormalization scheme [2], and predicts dramatic enhancements of energy transfer rates [3]. Qualitative arguments explaining such behavior often rely on interactions within donors and acceptors that induce delocalization of the excitation and establish quantum correlations, such as entanglement, between chromophores. As a consequence, this observed unexpected rate enhancement has been widely attributed to quantum coherence of acceptors and donors.

This purportedly quantum behavior at ambient conditions in photosynthetic light-harvesting systems has contributed to the view that quantum effects play an important role in enhancing transport efficiency in photosynthesis, and that these effects are somehow favored by evolutionary selection. For example, arguments to explain transfer rate enhancements and irreversibility in light harvesting complexes [such as the light harvesting II (LHII)] as quantum processes involving superposition and process coherence have been proposed [4–8], and the extent to which enhancement is quantum, and is therefore incapable of being accounted for classically, is being extensively discussed [3,7,9].

In this Letter we demonstrate that such enhanced rates are readily explained by a classical theory that is reliant solely upon classical electrodynamics. The resultant expressions retain the simplicity of Förster energy transfer formulas, while allowing a straightforward interpretation of

the origin of the enhanced energy transfer rates. We apply this approach to calculate the energy transfer rate in both a model system and in LHII and show that it accurately describes enhanced multichromophoric energy transfer rates. Since multichromophoric electronic energy transfer is also prevalent in a large range of studies on molecular systems such as DNA [10] and proteins [11], the theory is expected to be useful in a wide variety of applications.

Quantum multichromophoric Förster's resonance energy transfer.—Note first the current quantum perspective on multichromophoric electronic energy transfer. Consider the pairwise transfer of excitation from chromophore D to A : $D^* + A \rightarrow D + A^*$, where D^* (D) is the excited (ground) state donor and A (A^*) is the ground (excited) state acceptor. From the single chromophoric Förster theory, the rate of energy transfer from D to A is given by $k_F = (J^2/2\pi\hbar) \int_{-\infty}^{\infty} d\omega E_D(\omega) I_A(\omega)$, where J is the electronic coupling between D and A , $E_D(\omega)$ is related to the normalized emission line shape of the donor D , and $I_A(\omega)$ to the linear absorption cross section of the acceptor A [12].

As long as the D and A molecules are well separated from one another, inter- D - A distances are larger than intra- D and intra- A distances, and well-defined D and A sites exist, so that the use of the rate expression k_F is justified. However, application of this single chromophoric theory to multichromophoric systems leads to errors because transfer involves more than one pair of excitations, and because intra- D and intra- A coherences that allow exciton delocalization over multiple chromophores are neglected.

These facts motivated a general quantum Förster-like rate expression for a set of D_j ($j = 1, \dots, N_D$) donors and

A_k ($k = 1, \dots, N_A$) acceptors with intra- D and intra- A coherences, formulated in Ref. [5]. The expression can be cast as

$$k_F^{\text{MC}} = \sum_{j'j''}^{N_D} \sum_{k'k''}^{N_A} \frac{J_{j'k'} J_{j''k''}}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\omega E_D^{j''j'}(\omega) I_A^{k''k'}(\omega), \quad (1)$$

with $I_A^{k''k'}(\omega)$ and $E_D^{j''j'}(\omega)$ the absorption of acceptors and the stimulated emission of donors, respectively. The intra- D and intra- A coherences are said to be quantum, arising from a superposition of energy eigenstates, and to be responsible for the enhanced transfer rate (e.g., Ref. [6]).

Classical multichromophoric Förster's resonance energy transfer.—Classically, the donor is envisioned as an oscillating dipole of frequency ω_D , and the acceptor as an absorber with oscillation frequency ω_A . The donor radiates an electric field that permeates the acceptor and the acceptor absorbs energy from this field [13,14]. Adopting this view, Kuhn [15] and Silbey *et al.* [13] derived, in the 1970s, Förster's transfer rate using a completely classical approach. Specifically, they showed that the rate of energy transfer of a set of classically interacting dipoles can be recast in a form identical to that of Förster theory [13,15]. Here we significantly extend Refs. [13] and [15] to obtain a classical description of multichromophoric energy transfer.

To do so, consider as above a set of N_D donor molecules and N_A acceptor molecules, located at $\mathbf{r}_{D_j}$ and $\mathbf{r}_{A_k}$, respectively. The polarization of the n th molecule, at position $\mathbf{r}_n$, is proportional to the applied field (linear response), $\mathbf{p}_n(\omega) = \epsilon_0 \chi_n(\omega) \mathbf{E}(\mathbf{r}_n, \omega)$, where $\mathbf{E}(\mathbf{r}_n, \omega)$ is the ω frequency component of the total electric field at $\mathbf{r}_n$ and $\chi_n(\omega)$ is the polarizability tensor of the n th molecule ($n = D_1, \dots, D_{N_D}, A_1, \dots, A_{N_A}$). The electric field at position $\mathbf{r}$ can be decomposed into an externally incident field $\mathbf{E}^{\text{ext}}$ and the sum of the fields produced by all others molecules in the aggregate. In the nonradiative approximation, the electric field at point $\mathbf{r}$ due to the presence of a dipole $\mathbf{p}$ at point $\mathbf{r}_0$ is $\mathbf{E}(\mathbf{r}, \omega) = [(3\hat{\mathbf{n}}\hat{\mathbf{n}} - 1)/4\pi\epsilon_0|\mathbf{r} - \mathbf{r}_0|^3] \mathbf{p}(\omega) \equiv \Phi(\mathbf{r} - \mathbf{r}_0) \mathbf{p}(\omega)$, where $\hat{\mathbf{n}}$ is the unit vector directed from $\mathbf{r}_0$ to $\mathbf{r}$. The polarization of each of the donor and acceptor molecules is

$$\mathbf{p}_n(\omega) = \epsilon_0 \chi_n(\omega) \mathbf{E}^{\text{ext}}(\mathbf{r}_n, \omega) + \epsilon_0 \chi_n(\omega) \sum_{n'} \Phi_{nn'} \mathbf{p}_{n'}(\omega), \quad (2)$$

where $\Phi_{nn'}$ is the dipolar orientational coupling between molecules n and n' spanned by four blocks: the $\Phi_{jj'}^D$ block (denoted Φ^D below) describes intra- D coupling between D_j and $D_{j'}$ (for $j, j' = 1, \dots, N_D$), the block $\Phi_{kk'}^A$ (denoted Φ^A below) related to intra- A coupling between A_k and $A_{k'}$ (for $k, k' = 1, \dots, N_A$) and the Φ_{jk}^{DA} block (denoted Φ^{DA}) are the

D_j and A_k interaction. Here, the external field is only applied to the donors, so that $\mathbf{E}^{\text{ext}}(\mathbf{r}_n, \omega) = 0$ for $n = A_1, \dots, A_{N_A}$. The case when the field impulsively excites all donors and acceptors can be found in the Supplemental Material [16].

Although Eq. (2) is formulated in the frequency domain, it is clear that in the time domain these processes are oscillatory (see below) and that the lifetime of the oscillations depends upon the structure and values of χ . For example, in a symmetric configuration in which the acceptors have the same constant coupling $\Phi_{kk'}^A = \phi^A$, with identical acceptor response $\chi_{A_k} = \chi_A$, the term related to the intra- A interactions in Eq. (2) is $\epsilon_0 \chi_A (N_A - 1) \phi^A \mathbf{p}_{A_k}$. Despite the fact that this term already predicts an enhancement of the polarization of the k acceptor, it is shown below that this interaction need not be the one responsible for the dramatic enhancement of the transfer rate. Rather, it is the term in Eq. (2) that allows every acceptor to interact with every donor that is often significant (see Supplemental Material [16] for further details).

Within classical electrodynamics, the Poynting vector $\mathbf{S} = \mathbf{E} \times \mathbf{H}$ describes the energy flux density of the electromagnetic field. The rate of energy to or from a unit volume free of current or charges is $\dot{u}(\mathbf{r}, t) = -\nabla \cdot \mathbf{S}$ and, using Maxwell's equations and integrating over a volume enclosing the acceptor region, the rate of energy flow absorbed by the acceptors is

$$\dot{Q}(t) = \sum_{k=1}^{N_A} \mathbf{E}(\mathbf{r}_{A_k}, t) \cdot \dot{\mathbf{p}}_{A_k}(t), \quad (3)$$

and similarly for donors. Here $\mathbf{p}_{A_k}(t)$ denotes the polarizability in the time domain [17–19] and $\mathbf{E}(\mathbf{r}_{A_k}, t)$ labels the total electric field at the position of the k th acceptor at time t . $\dot{Q}(t)$ provides the time dynamics of energy transfer. To see how it relates to Förster rate theory [13], consider a set of N_D donors and N_A acceptors. If each dipole is polarizable along a single axis, then $\mathbf{p}_n = p_n \hat{\mathbf{n}}_n$, $\chi_n = \chi_n \hat{\mathbf{n}}_n \hat{\mathbf{n}}_n$ and if the external field is applied along this axis, $\mathbf{E}_{\text{ext}}(\mathbf{r}_n) = E_{n,\text{ext}} \hat{\mathbf{n}}_n$, then the polarization equation (2), in the frequency domain, can be conveniently expressed as $\mathbf{F}^{-1} \mathbf{p} = \mathbf{E}^{\text{ext}}$, where the polarizability matrix $\mathbf{F}^{-1}$ is defined as $\mathbf{F}_{nn'}^{-1} = [(\delta_{nn'}/\epsilon_0 \chi_n) - \Phi_{nn'}]$, and the polarization vector is $\mathbf{p} = [\mathbf{p}_D, \mathbf{p}_A]^T$ with the scalar components $p_n(\omega)$, and the external applied field vector $\mathbf{E}^{\text{ext}}$ has scalar components $E_{n,\text{ext}}$ (for $n, n' = D_1, \dots, D_{N_D}, A_1, \dots, A_{N_A}$). The presence of off-diagonal elements $\mathbf{F}_{ij}$ implies that individual chromophores cannot be excited independently. Therefore, the excitation at one site spreads over other sites, which can be viewed as exciton delocalization within the classical picture.

The rate of energy flow absorbed by the acceptors within this configuration is $\dot{Q}(t) = [\Phi^A \mathbf{p}_A(t) + \Phi^{DA} \mathbf{p}_D(t)] \cdot \dot{\mathbf{p}}_A(t)$.

In order to compare with Förster's rate, $\dot{Q}(t)$ is transformed into the frequency domain, $\tilde{Q}(\omega)$, the oscillations in the transfer rate integrated out and the average value of the rate $\tilde{Q}(0)$ obtained [18]. Specifically, as shown in the Supplemental Material [16] $\tilde{Q}(0) = 2\epsilon_0 \text{Im} \int_0^\infty d\omega \omega \Phi^{DA} \mathbf{p}_D^*(\omega) \cdot [(\chi_A^{-1}(\omega)/\epsilon_0 - \Phi^A)^{-1} \Phi^{DA} \mathbf{p}_D(\omega)]$, or, written explicitly

$$\tilde{Q}(0) = \sum_{jj'} \sum_{kk'} 2\epsilon_0 \Phi_{kj}^{DA} \Phi_{k'j'}^{DA} \int_0^\infty d\omega I_A^{kk'}(\omega) E_D^{jj'}(\omega) \quad (4)$$

with $I_A^{kk'}(\omega) = \omega \text{Im}[\chi_A^{-1}(\omega)/\epsilon_0 - \Phi^A]_{kk'}^{-1}$ and $E_D^{jj'}(\omega) = p_{Dj}^*(\omega) p_{Dj'}(\omega)$ related to the emission and absorption spectrum of the donors and acceptors. This expression recovers the form of the multichromophoric Förster expression (1). As in Eq. (1), the intradonor interaction in the Förster rate k_F is encoded in the definition of $I_A^{kk'}(\omega)$ and $E_D^{jj'}(\omega)$. Additionally, if only a single donor and a single acceptor are present, Eq. (4) coincides with a single donor transferring energy to a single acceptor [18].

To show how classical electrodynamics gives the same transfer rate enhancement as predicted by quantum arguments, consider a molecular aggregate model comprised of two donors and two acceptors at the vertices of a tetrahedron, as shown in the lower inset of Fig. 1. The main panel of Fig. 1 shows the normalized energy absorbed by the acceptors [Eq. (3), here denoted $Q_A(t)$] with a single excited state and with Lorentzian line shapes $\chi(\omega) = 2(\epsilon_0 \hbar)^{-1} \omega_0 |\mu|^2 / [(\omega_0 - \omega - i\gamma/2)(\omega_0 + \omega + i\gamma/2)]$, where μ is the transition dipole moment of the molecule, ω_0 its transition frequency, γ is radiative decay rate, and

$E_{\text{abs}} = 4\pi^2 \omega_0 |\mu|^2 N_D / \hbar$ is the total energy absorbed by the donors from the electric field. The donors are excited with a delta pulse in time. Each molecule is polarized along a single polarization axis and all fields applied to the molecule are along this axis of polarization.

The rate of energy transfer when the excitation is symmetrically delocalized over the interacting dipoles, i.e., when the dipoles all interact ($\Phi_{kj}^{DA} = \phi$ and $\Phi_{jj'}^D = \Phi_{kk'}^A = \phi'$, ϕ and ϕ' constants) is shown as a dashed blue line, and is seen to be twice as fast as the case where the dipoles only communicate individually; i.e., no donor and no acceptor interactions are present (the so-called “direct transfer” case, $\Phi_{kj}^{DA} = \phi \delta_{kj}$, $\Phi_{jj'}^D = \Phi_{kk'}^A = 0$: continuous black line). Moreover, in the former fully connected case, not only is the frequency of the energy oscillation (transfer rate) faster but the amplitude of the energy oscillations is larger as well. Thus, Fig. 1 shows that classical electrodynamics predicts the same enhancement of a factor of 2 as found in quantum approaches of excitonic energy transfer [1,3].

To understand the origin of this enhancement, we compare to the case when there are no intra-interactions between donor or between acceptors, but where each acceptor can interact with each donor ($\Phi_{jk}^{DA} = \phi$, $\Phi_{jj'}^D = \Phi_{kk'}^A = 0$: red dotted line). The enhancement of the transfer rate is seen to be virtually identical to the case where intra-interactions are allowed. That is, the enhancement here originates from the fact that all donors transfer to all acceptors and not from the intra-interactions between acceptors or between donors, an observation consistent with quantum results using the “diagonal (secular) Förster rate” model [5,20,21].

In the upper inset of Fig. 1, the case of vanishing intra-acceptor (or donor) interactions in the presence of intra-donor (or acceptor) interactions is depicted by the dashed cyan curve (or dot-dashed green curve). Although the effect here is small, it is clear that the transfer rate may indeed benefit from the lack of intradonor or intra-acceptor interactions helping the energy transfer pathway.

Light harvesting complex II.—To test the predictions of this classical theory, it is applied to calculate the transfer rate of LHII. This complex is formed by 27 bacteriochlorophylls (BChls) arranged in two rings: eighteen of them form the B850 ring with nine forming $\alpha\beta$ -heterodimer subunits (here referred to as the acceptors), and the other nine the B800 ring (as the donor). The LHII complex is described here by a set of interacting dipoles. The couplings between the BChls in the B800 ring are much smaller than those in the B850 ring [4,22] implying a monomeric structure for the B800 ring; hence the donor is usually modeled as a single dipole [21]. The alternating transition dipole moment orientations within the B850 ring giving rise to the ninefold symmetry is well depicted in Ref. [23], as is the donor location. Interdimer, intradimer coupling

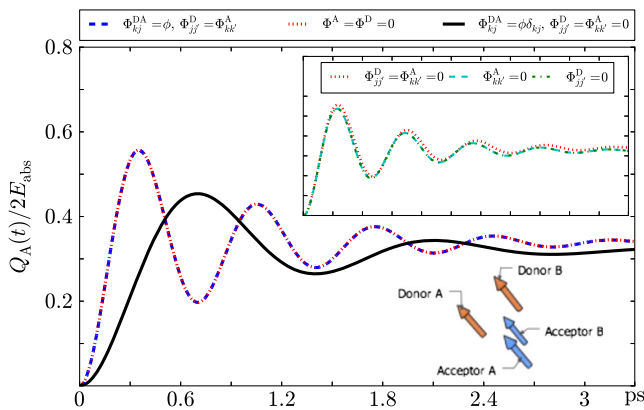


FIG. 1 (color online). Normalized total energy in the acceptors for donors and acceptors in resonance at $\omega_0 = 13\,317.2\text{ cm}^{-1}$ with dipole moments of $2.6 D$. All dipoles are separated 1 nm from each other. The radiative decay rate is $\gamma = (0.8\text{ ps})^{-1}$ for all dipoles. Note that the blue dashed curve and dotted red curve lie atop one another. Values of the parameters are typical for light-harvesting systems.

and site energies in the B850 ring are set as in Ref. [21]. The site energy of the two $\alpha\beta$ -heterodimer subunits are $E_{2n-1} = 12406 \text{ cm}^{-1}$ and $E_{2n} = 12602 \text{ cm}^{-1}$, the intradimer coupling is $J_{2n-1,2n} = J_{2n,2n-1} = 363 \text{ cm}^{-1}$ and the interdimer coupling is $J_{2n+1,2n} = J_{2n,2n+1} = J_{1,18} = J_{18,1} = 320 \text{ cm}^{-1}$ ($n = 1, \dots, 9$). Intercomplex couplings between the elements comprising B850 are calculated using the point dipole approximation with a transition dipole strength μ of $8.3 D$ and are related to the dipolar orientational coupling $\Phi_{nn'}$ by $J_{nn'} = \mu^2 \Phi_{nn'}$.

The environmental influence is included through the linear response function [24,25] $\chi_j(\omega) = 2(\epsilon_0 \hbar)^{-1} \omega_j \mu_j^2 / [-\omega^2 - i\omega\tilde{\gamma}(\omega) + \omega_j^2]$, where μ_j is the transition dipole moment of molecule j , ω_j its transition frequency, and $\tilde{\gamma}(\omega)$ is the Laplace transform of the damping kernel, related to the spectral density $\mathcal{J}(\omega)$ of the bath modes by $\tilde{\gamma}(\omega) = \coth(\frac{1}{2}\hbar\omega\beta)\mathcal{J}(\omega)$. For donor and acceptor molecules, independent identical baths are assumed and characterized by the spectral density, $\hbar\mathcal{J}(\omega) = 2\lambda\Lambda\omega/(\omega^2 + \Lambda^2)$, where λ is the site reorganization energy of the donor (acceptor) and Λ is the inverse bath correlation time [21]. Setting $\lambda_D = 40 \text{ cm}^{-1}$, $\lambda_A = 200 \text{ cm}^{-1}$, $\Lambda = 0.01 \text{ fs}^{-1}$, and using a zero-mean-Gaussian-distributed energetic disorder of $\sigma_D = 55 \text{ cm}^{-1}$ in the donor and $\sigma_A = 290 \text{ cm}^{-1}$ in the acceptors, reproduces the B800 and B850 absorption spectra at $T = 300 \text{ K}$ [22].

Figure 2 shows the normalized energy emitted by the donor [denoted $Q_D(t)$] when excited initially with a delta pulse, for an ensemble of 10^4 complexes. The result of the simulation is best fit to a double exponential decay $(ae^{-\kappa_f t} + be^{-\kappa_{uf} t} + c)/(a + b + c)$ with an ultrafast component $\kappa_{uf} = 22.36 \text{ ps}^{-1}$, a fast component $\kappa_f = 0.92 \text{ ps}^{-1}$, and the normalization constants $a = 0.05$, $b = 0.12$, and $c = 0.1$. The ultrafast component is associated with the sudden energy absorption from the single-dipole donor to the acceptor ring. If the entire donor ring is included, the intradonor dynamics modifies the transfer rates and it is expected that the ultrafast component will be slower and the

fast component's rate increases. Work along this line is in progress.

The experimental transfer rate was reported to be $\kappa_{\text{exp}} \sim 1.25 \text{ ps}^{-1}$ [26] while the quantum prediction, based on a diagonal representation of multichromophoric energy transfer rate in Eq. (1), reported in Ref. [21], is $\kappa_{\text{qntm}} = 0.7 \text{ ps}^{-1}$. Hence, the classical result obtained here of 0.92 ps^{-1} predicts a transfer rate close to the experimental rate, and is more accurate than the results predicted by the quantum calculation. The fact that classical theory provides somewhat better results than does the quantum result may arise from the fact that the classical transfer rate is obtained from the time dynamics directly, whereas the multichromophoric rate equation includes a number of approximations (see Ref. [22] for details) and is calculated at $t \rightarrow \infty$. Thus, the main dynamical features, such as the correct transfer rate, are not directly incorporated into the quantum description. This suggests that a full dynamic quantum calculation for the LHII, at the same level of the classical one performed here, would be of interest. Furthermore, since it is shown above that Eqs. (1) and (4) coincide, if no additional approximations are introduced, then both the quantum and classical results should coincide.

The quantum-classical transition is discussed in the Supplemental Material [16]. There it is shown that the two coincide when the assumption of the linear response is valid and that the classical multichromophoric enhancement is still present in an effective single exciton regime considered by normalizing the energy in the entire aggregate.

Comments.—(a) To reconcile the above result with the supertransfer mechanism [1], note the standard quantum argument which proceeds as follows: if coherence is not present within the donor region, the incoherent Fermi golden rule rate of a donor to transmit energy to the acceptor is $\gamma_{D \rightarrow A} \sim |\mu_D \cdot \mu_A|^2$. Hence, for a pair of identical donors and a pair of identical acceptors the total rate reads $\Gamma_{D \rightarrow A}^{\text{inc}} = 2\gamma_{D \rightarrow A}$. However, if local coherence is present and the donor is in the symmetric ground state $(\mu_{1D} + \mu_{2D})/\sqrt{2}$ and communicates with the corresponding state on the acceptor, the total rate $\Gamma_{D \rightarrow A}^{\text{coh}} \sim \frac{1}{4} |\mu_{1D} \cdot \mu_{1A} + \mu_{1D} \cdot \mu_{2A} + \mu_{2D} \cdot \mu_{1A} + \mu_{2D} \cdot \mu_{2A}|^2$, so that $\Gamma_{D \rightarrow A}^{\text{coh}} = 2\Gamma_{D \rightarrow A}^{\text{inc}}$. Thus, the enhancement of the coherent rate $\Gamma_{D \rightarrow A}^{\text{coh}}$ comes from the terms $\mu_{1D} \cdot \mu_{2A}$ and $\mu_{2D} \cdot \mu_{1A}$, which include the interactions between all donors and all acceptors. Therefore, the enhancement that we obtained above, based on classical electrodynamics, is precisely the one predicted by supertransfer [1,3] and corresponds to these terms in Eq. (2). Note that the classical theory formulated here also predicts additional processes that may enhance or diminish energy transfer (see Supplemental Material [16]).

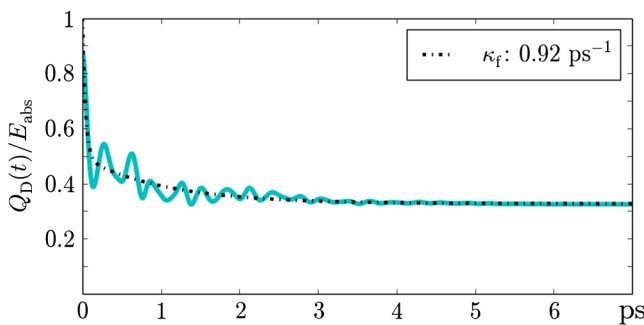


FIG. 2 (color online). Normalized total energy within the B800 ring (donor) in LHII, initially excited with a delta pulse. Dashed curve is a best fit to the oscillatory (cyan) result.

(b) We note that the treatment in this Letter has adopted a “site basis” approach, focusing on each dipole. A generalized formulation could be used to study global donor or acceptor bright or dark states, which would be obtained as eigenstates of the $\mathbf{F}$ matrix, and used to define the initial conditions for the subsequent dynamical evolution.

In summary, a classical theory of multichromophoric electronic energy transfer was developed and shown capable of producing the enhancement predicted by quantum-based approaches, and that, as long as linear response holds, the classical approach coincides formally with the quantum description. Excellent results were also obtained for the LHII case of one donor and multiple acceptors. Further studies are under way to display the utility of this approach in a variety of other energy transfer scenarios.

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