A Classical Approach to Multichromophoric Resonance Energy Transfer

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Enhanced rates in multichromophoric resonance energy transfer are shown to be well described by a classical theory based on classical electrodynamics. 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, \(N_A N_D\). As an example, the theory, applied to the transfer rate in LH II, gives results in excellent agreement with experiment.

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 LH III) 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 formulae, 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 LH III 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 Multichromoporic 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

\[
k_F = \frac{J^2}{2 \pi \hbar} \int_{-\infty}^{\infty} d\omega \ E_D(\omega) I_A(\omega) \tag{1}
\]

where \(J\) is the electronic coupling between \(D\) and \(A\), \(E_D(\omega)\) is related to the normalized emission lineshape 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. Therefore, use of the rate expression (1) 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.

Motivated by these facts, a general quantum Förster-like rate expression for a set of \(D_j\) \((j = 1, \ldots, N_D)\) donors and \(A_k\) \((k = 1, \ldots, N_A)\) acceptors with intra-D and intra-A coherences was formulated in Ref. [5]. The expression can be cast as

\[
k_{\text{MC}} = \sum_{j,j' \neq k,k'} \frac{N_A}{2 \pi \hbar^2} \int_{-\infty}^{\infty} d\omega \ E_D^{j'j}(\omega) I_A^{k'k}(\omega), \tag{2}
\]

with the obvious generalization of the notation in Eq. (1). 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]). However, as shown below, the rate is well described by classical electrodynamics, and results in the
observed enhanced chromophoric energy transfer.

Classical Multichromoporic Förster’s Resonance Energy Transfer—For the relevant configurations involved in light-harvesting systems, the distance between molecules is at most a few nanometers, while the relevant wavelength of light is on the order of several hundred nanometers. Hence energy transfer will primarily be due to non-radiative contributions, justifying a point dipole approximation. Moreover, the known inverse sixth-power distance dependence of the transfer mechanism owes its origin to the quadratic dependence of the rate on a coupling of transition electric dipoles [13, 14]. In the quantum description of the donor-acceptor energy transfer, deexcitation of the donor is followed by emission of a virtual photon that is absorbed by the acceptor [14].

Classically, the donor is envisioned as an oscillating dipole of frequency $\omega_D$, and the acceptor as an absorber with oscillation frequency $\omega_A$. The donor radiates an electric field that permeates the acceptor and the acceptor absorbs energy from this field [13, 15]. Adopting this view, Kuhn [16] and Silbey et al. [15] derived, in the 1970’s, 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 [15, 16]. Here we significantly extend Refs. [15] and [16] to obtain a classical description of multichromophoric energy transfer.

To do so, consider a set of $D_j$ ($j = 1, \ldots, N_D$) donor molecules and $A_k$ ($k = 1, \ldots, N_A$) acceptor molecules, located at $r_{D_j}$ and $r_{A_k}$, respectively. In the frequency domain, the polarization of each molecule is proportional to the applied field (linear response) $p_{D_j}(\omega) = \epsilon_0 \chi_{D_j}(\omega) E(r_{D_j}, \omega)$, $p_{A_k}(\omega) = \epsilon_0 \chi_{A_k}(\omega) E(r_{A_k}, \omega)$, where $E(r_{D_j}, \omega)$ is the $\omega$ frequency component of the total electric field at the position of the donor (similarly for the acceptor) and $\chi(\omega)$ is the polarizability tensor of the molecule. The electric field at position $r$ can be decomposed into an externally incident field $E^{\text{ext}}$ and the sum of the fields produced by all others molecules in the aggregate. In the non-radiative approximation, the electric field at point $r$ due to the presence of a dipole $p$ at point $r_0$ is

$$E(r, \omega) = \frac{3\hat{n}\hat{n} - 1}{4\pi\epsilon_0|r-r_0|^3} \cdot p(\omega) \equiv \Phi(r-r_0) \cdot p(\omega),$$

where $\hat{n}$ is the unit vector directed from $r_0$ to $r$. Note that $p(\omega)$ is a vector comprising all donors and acceptors. If the external field is zero in the region of the acceptors, the polarization of each of the donor and acceptor molecules is $p_{D_j}(\omega) = \epsilon_0 \chi_{D_j}(\omega) E^{\text{ext}}(r_{D_j}, \omega)$, $p_{A_k}(\omega) = \epsilon_0 \chi_{A_k}(\omega) E^{\text{ext}}(r_{A_k}, \omega)$, and $p_{A_k}(\omega) = \epsilon_0 \chi_{A_k}(\omega) \sum_{k' \neq k} N_0 \Phi_{kk'} \cdot p_{A_k'}(\omega) + \epsilon_0 \chi_{A_k}(\omega) \sum_{j=1}^{N_D} \Phi_{kj} \cdot p_{D_j}(\omega)$, where $\Phi_{kk'}$ is the dipolar coupling between $D_j$ and $A_k$, $\Phi_{kj}$ is the dipolar coupling between $D_j$ and $A_k$, $\Phi_{kk'}$ is the dipolar coupling between $D_j$ and $A_k$, and $A_k'$, the $A_k$ and $A_k'$ intra-A coupling. Here $E^{\text{ext}}$ is the external field applied only to the donors.

To expose the interplay between donors and acceptors, it is convenient to substitute the expression for $p_{D_j}(\omega)$ into $p_{A_k}(\omega)$, giving

$$p_{A_k} = \epsilon_0 \chi_{A_k} \sum_{k' \neq k} N_0 \Phi_{kk'} \cdot p_{A_k'} + \epsilon_0 \sum_{j=1}^{N_D} \chi_{A_k} \Phi_{kj} \cdot \chi_{D_j} E^{\text{ext}}(r_{D_j})$$

$$+ \epsilon_0 \sum_{j=1}^{N_D} \chi_{A_k} \Phi_{kj} \cdot \chi_{D_j} \Phi^{D}_{jj'} \cdot p_{D_{j'}} + \epsilon_0 \sum_{j=1}^{N_D} \chi_{A_k} \Phi_{kj} \cdot \chi_{D_j} \sum_{k'=1}^{N_A} \Phi_{jk'} \cdot p_{A_{k'}}.$$ (4)

where the $\omega$ dependence of $p_{D_j}$, $p_{A_k}$, $\chi_{D_j}$, and $\chi_{A_k}$ is implicit. Further iterations are, of course, possible but Eq. (4) already displays a number of processes that enhance the polarizability at $A_k$, and hence can affect the energy transfer. (i) The first term in Eq. (4) will mediate the transfer of energy between $A_k'$ and $A_k$ via the interaction term $\Phi_{kk'}$. (ii) In the second term, the electric field $E^{\text{ext}}(r_{D_j})$ excites the donor $D_j$ which can transfer part of the energy of the field to the acceptor $A_k$ via the interaction term $\Phi_{kj}$. (iii) The third term describes how energy in donor $D_{j'}$ can flow into donor $D_j$ due to the interaction term $\Phi_{jj'}$, and how part of this energy can transfer to acceptor $A_k$ via the interaction term $\Phi_{kj}$. (iv) The last term describes transfer of energy stored in acceptor $A_{k'}$ to donor $D_j$, assisted by the interaction $\Phi_{jk'}$, and the subsequent transfer from $D_j$ to $A_k$ mediated by $\Phi_{kj}$. Processes (i) and (ii) are first order in the interactions (via $\Phi^A_{kk'}$ and $\Phi_{kj}$, respectively), while (iii) and (iv) are second order in the interactions (via $\Phi_{kj} \Phi_{jj'}$ and $\Phi_{kj} \Phi_{jk'}$, respectively). If, in addition, the external field $E^{\text{ext}}$ is allowed to interact with the acceptors (a situation not relevant for the present discussion), energy can flow directly into the acceptors, and higher order processes in the transfer of energy from the field to acceptors will contribute.

Although this description of energy transfer 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 \( \chi \). In the symmetric configuration, \( \Phi_{kk'}^A = \Phi^A \), with identical acceptor response \( \chi_A = \chi \), the first term in Eq. (4) is \( \epsilon_0 \chi \rho(0 - 1) \Phi^A \cdot p_{Akk} \). Despite the fact that this term already predicts an enhancement of the polarization of the \( k \)-acceptor, we show below that this interaction need not be the one responsible for the dramatic enhancement of the transfer rate. Rather, it is the second term in Eq. (4) that allows every acceptor to interact with every donor that is often significant.

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 \( \dot{\bar{u}}(\mathbf{r}, t) = -\nabla \cdot \mathbf{S} \) and, using Maxwell’s equations and integrating over a volume enclosing the acceptor region, the rate of energy flow absorbed by the acceptors is [17–19]

\[
\dot{Q}(t) = \sum_{k=1}^{N_A} \mathbf{E}(\mathbf{r}_{Ak}, t) \cdot \mathbf{p}_{Akk}(t) . \tag{5}
\]

By contrast to Eq. (5), \( \mathbf{p}_{Akk}(t) \) denotes here the polarizability in the time domain. The electric field \( \mathbf{E}(\mathbf{r}_{Ak}, t) \) labels the total electric field at the position of the \( k \)-th acceptor in the time domain obtained by Fourier transforming the total electric field in Eq. (3).

Equation (5) provides the time dynamics of energy transfer. To see how, for example, Eq. (5) relates to Förster rate theory [15], consider a set of \( N_D \) donors and \( N_A \) acceptors. If each dipole is polarizable along a single axis and the external field is applied along this axis, then the acceptor polarization equation, in the frequency domain, can be written in term of scalar quantities as \( p_{Akk}(\omega) = \epsilon_0 \chi_A(\omega) \sum_{k' \neq k} \Phi_{kk'}^A \cdot \mathbf{p}_{Akk}(\omega) + \epsilon_0 \chi_A(\omega) \sum_{j=1}^{N_D} \Phi_{kj} \cdot \mathbf{p}_{Dj}(\omega) \). Defining the vectors \( \mathbf{p}_D(\omega) \), \( \mathbf{p}_A(\omega) \) and \( \mathbf{E}^{\mathrm{ext}}(\omega) \) with components \( p_{Dj}(\omega) \), \( p_{Akk}(\omega) \) and \( E^{\mathrm{ext}}(\mathbf{r}_{Dj}, \omega) \), respectively, and the matrices \( \Phi^A \), \( \Phi(\omega) \), \( \Phi^A(\omega) \) and \( \Phi \) with components \( \Phi_{kk'}^A \), \( \chi_A(\omega) \Phi_{kj} \), \( \chi_A(\omega) \Phi_{kk'}^A \) and \( \Phi_{kj} \), respectively, the above equation can be rewritten as \( \mathbf{p}_A(\omega) = \epsilon_0 \Phi^A(\omega) \mathbf{p}_A(\omega) + \epsilon_0 \Phi(\omega) \mathbf{p}_D(\omega) \). Hence, the linear relationship of the acceptor polarization to the donor’s is \( \mathbf{p}_A(\omega) = \left[ 1 - \epsilon_0 \Phi^A(\omega) \right]^{-1} \epsilon_0 \Phi(\omega) \mathbf{p}_D(\omega) \).

The rate of energy flow absorbed by the acceptors within this configuration is \( \dot{Q}(t) = [\Phi^A \cdot \mathbf{p}_A(t) + \Phi \cdot \mathbf{p}_D(t)] \cdot \mathbf{p}_A(t) \). In order to compare with Förster’s rate, the time dependent rate [Eq. (5)] is transformed into the frequency domain \( \dot{\bar{Q}}(\omega) \), the oscillations in the transfer rate integrated out and the average value of the rate \( \dot{\bar{Q}}(0) \) obtained [18]. Here \( \dot{\bar{Q}}(0) = 2 \epsilon_0 \int_0^\infty d\omega \omega \Phi \mathbf{p}_D(\omega) \cdot (\text{Im}\{1 - \epsilon_0 \Phi^A(\omega)^{-1} \Phi(\omega)\}) \mathbf{p}_D(\omega) \)+

\[
2 \int_0^\infty d\omega \omega \left[ \Phi^A \mathbf{p}_A(\omega) \right] \cdot \mathbf{p}_A(\omega), \text{ or, written explicitly}
\]

\[
\dot{\bar{Q}}(0) = \sum_{j} \sum_{kk'} \epsilon_0 \Phi_{kj} \Phi_{kj'} \int_0^\infty d\omega \omega I_{kk'}^A(\omega) E_{Dj'}(\omega)
\]

with \( I_{kk'}^A(\omega) = \text{Im}\{1 - \epsilon_0 \Phi^A(\omega)^{-1} \chi_A''(\omega)\} \) and \( E_{Dj'}(\omega) = p_{Dj'}(\omega) p_{Dj'}(\omega) \) related to the emission and absorption spectrum of the donors and acceptors. The first term recovers the form of the multichromophoric Förster expression (2). The second term is related to the enhancement due to intra-acceptor interaction and appears here [and not in Eq. (2)] because there, the transfer rate was derived for the particular case when no excitations are present at \( t = 0 \) in acceptor sector. As in Eq. (2), the intra-donor interaction in Eq. (1) is encoded in the definition of \( I_{kk'}^A(\omega) \) and \( E_{Dj'}(\omega) \). Additionally, if only a single acceptor and a single acceptor are present, Eq. (1) coincides with a single donor transferring energy to a single acceptor (see Ref. [18]).

To show in detail how classical electrodynamics gives the same transfer rate enhancement as predicted by quantum arguments, first consider a molecular aggregate model comprised of two donors and two acceptors in the configuration shown in the lower inset of Fig. 1. The main panel of Fig. 1 shows the energy \( E_A(t) \) absorbed by the acceptors with a single excited state and Lorentzian lineshapes \( \chi(\omega) = 2(\epsilon_0 \hbar)^{-1} \omega_0 |\mu|^2 / [(\omega - \omega_0 + i\gamma/2)(\omega + \omega_0 + i\gamma/2)] \), where \( \mu \) is the transition dipole moment of the molecule, \( \omega_0 \) its transition frequency and \( \gamma \) is radiative decay rate. 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 ($\Phi_{jk} = \Phi_{j'k'} = \Phi_{k'k} = \Phi$) 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 interaction is present (the so-called "direct transfer" case, $\Phi_{jk} = \Phi_{j'k'} = 0$; 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 are larger as well. Thus, Fig. 1 shows that classical electrodynamics predicts the same enhancement of a factor of two as found in quantum approaches of excitonic energy transfer [1, 3].

To understand the origin of this enhancement, it is illustrative to compare to the case when there are no intra-interactions between donor or between acceptors, but where each acceptor can interact with each donor ($\Phi_{jk} = \Phi$, $\Phi_{kj} = \Phi_{k'k'} = 0$; red dotted line). For this case, the enhancement of the transfer rate is seen to be virtually identical to the case where intra-interactions are allowed. Therefore, 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) Forster 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 intra-donor or intra-acceptor interactions helping the energy transfer pathway.

To test the predictions of this classical theory, the transfer rate of the Light Harvesting complex II is calculated below.

Light Harvesting Complex II—LH II 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 as the acceptors), and the other nine the B800 ring (as the donor). The LH II complex is described here by a set of interacting dipoles. Specifically, 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 modelled as a single dipole [21]. The alternating transition dipole moment orientations within the B850 ring, which gives rise to the nine-fold symmetry, is nicely shown in Fig. 1 of Ref. [23], as is the donor location. Interdimer, intradimer coupling and site energies in the B850 ring are set as in [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 $\Phi_{2n-1,2n} = \Phi_{2n,2n-1} = 363 \text{ cm}^{-1}$ and the interdimer coupling is $\Phi_{2n+1,2n} = \Phi_{2n,2n+1} = \Phi_{1,18} = \Phi_{18,1} = 320 \text{ cm}^{-1}$ ($n = 1, \ldots, 9$). Intercomplex couplings between the elements comprising B850 are calculated using the point dipole approximation with a transition dipole strength of 6.1 D.

Within linear response theory, the environmental influence is included through the response function [24, 25] $\chi_\lambda(\omega) = 2(\epsilon_0 \hbar)^{-1} \omega_i |\mu_i|^2 / [-\omega^2 - i \omega \gamma(\omega) + \omega_i^2]$, where $\mu_i$ is the transition dipole moment of molecule $i$, $\omega_i$ its transition frequency and $\gamma(\omega)$ is the Laplace transform of the damping kernel, related to the spectral density $J(\omega)$ of the bath modes by $\gamma(t) = \frac{2}{\epsilon_0 \hbar} \omega_i |\mu_i|^2 \int_0^{\infty} \frac{d\omega}{\pi} J(\omega) \cos(\omega t)$. For donor and acceptor molecules, independent identical baths are assumed and characterized by a Drude-Lorentz spectral density, $\hbar J(\omega) = 2\lambda\Lambda / (\omega^2 + \Lambda^2)$, where $\Lambda$ is the site reorganization energy of the donor (acceptor) and $\lambda$ is the inverse bath correlation time [21]. Setting $\lambda_0 = 40 \text{ cm}^{-1}$, $\lambda_A = 200 \text{ cm}^{-1}$ and $\Lambda = 0.01 \text{ fs}^{-1}$ reproduces the B800 and B850 absorption spectra at $T = 300 \text{ K}$ [22].

Figure 2 shows the energy absorbed by the acceptors when a delta pulse in time excites the donor. The blue shading results from high frequency oscillations. To define a transfer rate, the result of the simulation is best fit to a double exponential decay $(e^{-\kappa t} + e^{-\kappa s t})/(2 + c)$ with a fast component $\kappa_f = 1.31 \text{ ps}^{-1}$, a slow component $\kappa_s = 8.14 \text{ ps}^{-1}$, and the normalization constant $c = 1.43 \times 10^{-3}$. The rate constant can be associated with an average incoherent energy transfer rate $\kappa_f$ and a process stabilization rate $\kappa_s$, respectively. 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 multi-chromophoric energy transfer rate in Eq. (2), reported in Ref. [21], is $\kappa_{\text{qntm}} = 0.7 \text{ ps}^{-1}$. Hence, the classical result obtained here of 1.31 ps$^{-1}$ predicts a transfer rate very close to the experimental rate. Indeed, it is somewhat more accurate than the results predicted by the quantum calculation.
The fact that classical theory provides better results than does the quantum result arises from the dynamic character of the classical description [see Eq. (6)] versus the kinematic character of the quantum approach [see Eq. (2)]. Specifically, the classical simulation predicts the transfer rate on the basis of the time dynamics while the multichromophoric rate equation adopts a number of approximations (see Ref. [22] for details) and is calculated at $t \to \infty$. Thus, the main dynamical features, such as the correct transfer rate, are not incorporated into the quantum description. This suggests that a full dynamic quantum calculation for the LH II, at the same level of the classical one performed here, would be of interest.

Comments — It is of some interest to comment on the relationship of this approach to the quantum view of multichromophoric energy transfer.

(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 $\gamma_{D\to A} \sim |\mu_{D} \cdot \mu_{A}|^{2}$. Hence, for a pair of identical donors and a pair of identical acceptors the total rate reads $\Gamma_{D\to A}^{inc} = 2\gamma_{D\to A}$. However, if local coherence is present and the donor is in the symmetric ground state $(\mu_{1D} + \mu_{1D})/\sqrt{2}$ and communicates with the corresponding state on the acceptor, the total rate $\Gamma_{D\to A}^{coh} \sim |(\mu_{1D} + \mu_{2D}) \cdot (\mu_{1A} + \mu_{2A})|^{2} / 4$, or explicitly,

$$\Gamma_{D\to A}^{coh} \sim \frac{1}{4} \left| \mu_{1D} \cdot \mu_{1A} + \mu_{1D} \cdot \mu_{2A} + \mu_{2D} \cdot \mu_{1A} + \mu_{2D} \cdot \mu_{2A} \right|^{2},$$

so that $\Gamma_{D\to A}^{coh} = 2\Gamma_{D\to A}^{inc}$. Thus, the enhancement of the coherent rate $\Gamma_{D\to A}^{coh}$ 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 obtained above based on classical electrodynamics is precisely the one predicted by supertransfer [1, 3] and corresponds to the second term in Eq. (4). Specifically, this term contains $N_{D}$ donor contributions to each acceptor polarization. A total number of $N_{A}$ such acceptor terms contribute to the rate [Eq. (5)], so that the overall enhancement effect is a function of $N_{A}N_{D}$. Note that the classical theory formulated here also predicts additional processes that may enhance or diminish energy transfer [see discussion below Eq. (4)].

(b) Equations for the polarizations $p_{D,i}(\omega)$ and $p_{A,k}(\omega)$ can be solved via the matrix equation $A^{-1}p = E_{ext}$, where $E_{ext}$ is the external applied field on each polarized molecule $p_{i}$, and the polarizability matrix $A$ is defined as $A_{ij} = \left[ \frac{\Phi_{ij}}{\hbar\omega} \right]$. Here $i$ and $j$ indices run over all the aggregate molecules. The polarizability matrix depends solely on the properties of the aggregate. The presence of off-diagonal elements $A_{ij}$ implies that individual chromophores cannot be excited independently. Therefore, the excitation at one site spreads over other sites and this tendency can be viewed as exciton delocalization. Indeed, although delocalization is often referred to as quantum coherence, we see that delocalization is present in the classical realm and enhances the energy transfer rate up to the number of interacting molecules (see Eq. (4)).

Summary — A theory of multichromophoric electronic energy transfer based on classical electrodynamics is developed here and shown capable of producing the enhancement predicted by quantum-based approaches. The approach constitutes the classical formulation of the quantum multichromophoric theory and 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 intra-coupling in donors and acceptor chromophores. When applied to model light harvesting systems, such as LH II, the results for the transfer rate are similar to those that are based on quantum calculations. Results from the classical theory derived here suggest that the mechanisms such as supertransfer may be robust against certain types of decoherence, since they have a classical origin. Further, they suggest examination of a wide variety of cases, now ongoing, to reveal the role of various contributions in Eq. (4) to energy transfer.

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