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Förster energy transfer theory as reflected in the structures of photosynthetic light harvesting systems

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Abstract

Förster's theory of resonant energy transfer underlies a fundamental process in nature, namely the harvesting of sunlight by photosynthetic life forms. The theoretical framework developed by Förster and others describes how electronic excitation migrates in the photosynthetic apparatus of plants, algae, and bacteria from light absorbing pigments to so-called reaction centers where light energy is utilized for the eventual conversion into chemical energy. The demand for highest possible efficiency of light harvesting appears to have shaped the evolution of photosynthetic species from bacteria to plants which, despite a great variation in architecture, display common structural themes founded on the quantum physics of energy transfer as described first by Förster. In this review, Förster's theory of excitation transfer is summarized including recent extensions, and the relevance of the theory to photosynthetic systems as evolved in purple bacteria, cyanobacteria, and plants is demonstrated. In an Appendix, Förster's energy transfer formula, as used widely today in many fields of science, is derived.

1 Introduction

Most life on Earth is powered, directly or indirectly, by photosynthetic light harvesting. Photosynthetic organisms feature supra-molecular assemblies containing hundreds of cooperating protein subunits that convert the short-lived electronic excitation resulting from the absorption of a photon into increasingly more stable forms of energy, ultimately into the form of stable chemical bonds [1–4]. Light energy is generally not utilized at the pigment molecule at which it is absorbed, but is instead transferred, often over hundreds of Ångströms, to a reaction center (RC) where it initiates electron transfer, resulting in a membrane potential. The basis of this energy migration process is fluorescence resonance energy transfer (FRET) as described by Förster in 1946 and 1948 and often named after him [5, 6].

The cooperative energy harvesting of pigment molecules in photosynthesis was first reported in the pioneering work of Emerson and Arnold in 1932 [7] who observed that in green algae many chlorophyll (Chl) molecules (see Fig. 1) cooperate to produce one oxygen molecule. The physical basis of the related energy transfer process was discussed in 1941 by Oppenheimer [8], whose brief publication, which did not explicitly state a FRET formula for

a donor-acceptor pair, went largely unnoticed. (See [9] for a brief history of the development of energy transfer theory.) Förster reported the expression for FRET between two pigments (Eq. 4 below and the Appendix) in terms of the spectral overlap (resonance) between the donor and acceptor states, the intermolecular distance, and the relative orientation of the so-called transition dipole moments of the molecules [5, 6]. An early application to purple bacterial energy harvesting was reported by Duysens [10]. Förster's formulation has since been widely adopted for describing energy transfer not only between the pigments of a single protein [9, 11–21], but among extensive light harvesting networks containing hundreds of proteins and thousands of pigments [22, 23]. FRET has also been adopted as a commonly used methodology in experimental laboratories today in a wide range of disciplines, particularly in the life sciences [24, 25].

The ramifications of Förster's formula (Eq. 4) are apparent as structural motifs in photosynthetic systems found in nature. The Förster formula appears to have played the role of a design constraint shaping the evolution of photosynthetic organisms [1, 2, 26, 27]. Consequently, most photosynthetic species share, as a common feature, a photosynthetic unit (PSU) containing peripheral pigment-protein (antenna) complexes surrounding RCs. Initial absorption of sunlight in peripheral pigments creates excitons, electronic excitations spread over several neighboring pigments exhibiting strong quantum mechanical coherence as reported over a decade ago [12, 28–30]. The energy stored in the form of an exciton remains untapped until it is harvested at a RC. Efficient harvesting of light energy demands transfer of excitons to RCs well within the decay time of excitons (around a nanosecond), typically within tens of picoseconds. At the RC, the excitation energy is transformed into a more stable form through electron transfer [31, 32]. The need for rapid migration of energy among pigments, as governed by Förster's formalism, imposes constraints on inter-pigment separation as well as on the pigment energy levels. Additionally, nature appears to have adapted to actively utilize the thermal disorder existing at physiological temperature: this disorder facilitates efficient excitation transfer between pigments by maintaining a broad spectral resonance, a key factor in Förster's formulation [13, 33, 34].

In recent decades, the architecture of PSUs and their constituent proteins has been determined for several species (see Fig. 2), reflecting collectively the aforementioned structural motifs based on Förster theory. Here, light harvesting systems that are ubiquitous in nature and have been studied exhaustively are considered. In oxygenic photosynthetic species such as cyanobacteria and plants, two pigment-protein complexes, photosystem I (PSI) [35–37] and photosystem II (PS2) [38–40], cooperate to use light reactions and water to produce oxygen and the molecules ATP and NADPH that drive cellular processes and reactions. In anoxygenic purple bacteria, the PSU contains the peripheral light harvesting complex II (LH2) [41–43], excitonically coupled to a RC-light harvesting complex I (RC-LH1) core complex [44–46]; these pigment-protein complexes are sometimes augmented by additional satellite complexes that are expressed depending on physiological conditions [47]. In both oxygenic and anoxygenic species, a charge separation [48, 49] is initiated at the RC. The resulting charge gradient is eventually utilized for ATP production at the ATP synthase [50, 51]. The supramolecular organization of the PSU in purple bacteria has recently been determined based on AFM [52–54] and EM [55] data, providing the geometrical detail needed for a description of energy transfer according to Förster across an entire photosynthetic membrane containing thousands of bacterichlorophylls (BChls) [22, 23].

The organization of this article is as follows. First, Förster's theory of excitation transfer, as applicable to biological pigments, is summarized. Second, structures of several photosynthetic pigment-protein complexes are examined in terms of their Förster energy transfer characteristics. Common structural motifs among light harvesting proteins are discussed in relation to the physics of the energy harvesting process. In an Appendix, a

derivation of the Förster formula is provided for the benefit of the reader who seeks to understand the physics of fluorescent energy transfer.

2 Förster's theory of fluorescent resonant energy transfer in pigment-protein complexes

Light absorption and the subsequent transfer of energy in a biological system is governed by quantum physics that incorporates the Coulomb interaction between electrons belonging to spatially separated pigments. Förster approximated the interaction between pigments that are sufficiently separated in terms of a transition dipole-transition dipole term as the leading multipole order of the relevant Coulomb interaction [5, 6]. Due to this interaction, an electronically excited pigment P_i^* (the donor) undergoes the transition back to its ground state P_i , $P_i^* \rightarrow P_i$, characterized through a transition dipole moment $\mathbf{d}_i$ and excitation energy ε_i , while a ground state pigment P_j (the acceptor) undergoes the transition to its electronically excited state, i.e., $P_j \rightarrow P_j^*$, characterized through a transition dipole moment $\mathbf{d}_j$ and excitation energy ε_j . The joint transition $P_i^*P_j \rightarrow P_iP_j^*$ is induced by the interaction energy

$$V_{ij} = \frac{\mathbf{d}_i \cdot \mathbf{d}_j}{r_{ij}^3} - \frac{3(\mathbf{r}_{ij} \cdot \mathbf{d}_i)(\mathbf{r}_{ij} \cdot \mathbf{d}_j)}{r_{ij}^5}, \quad (1)$$

where $\mathbf{r}_{ij}$ is the vector connecting the center of P_i to the center of P_j (see the Appendix for derivation). If the pigments are too close (typically less than 10 Å as measured by the Mg-Mg distance) the multipole expansion underlying Eq. 1 breaks down and, furthermore, electron exchange becomes relevant [56], requiring a complementary description of the FRET coupling V_{ij} [57].

The rate of excitation transfer between donor pigment i and acceptor pigment j is given by

$$k_{ij} = \frac{2\pi}{\hbar} |V_{ij}|^2 J_{ij}, \quad J_{ij} = \int S_i^D(E) S_j^A(E) dE, \quad (2)$$

where $S_i^D(E)$ and $S_j^A(E)$ are the spectra for donor (i) emission and acceptor (j) absorption, respectively, determined by the coupling of the pigment to vibrational states due to thermal motion. The integral J_{ij} accounts for the spectral overlap. Here the spectra are normalized through $\int S(E) dE = 1$. For identical pigments, emission and absorption spectra are generally related to one another by the so-called Stokes Shift [58]. After averaging over all possible orientations of $\mathbf{d}_i$ and $\mathbf{d}_j$ in Eq. 1, the transfer rate, Eq. 2, can be written (see Appendix) [6]

$$k_{ij} = \frac{4\pi}{3\hbar} \frac{d_i^2 d_j^2}{r_{ij}^6} J_{ij}. \quad (3)$$

In Förster's original formulation [6], this transfer rate is expressed elegantly as

$$k_{ij} = \frac{1}{\tau_0} \left(\frac{R_0}{r_{ij}} \right)^6, \quad (4)$$

where τ_0 is chosen as the relevant fluorescence lifetime of participating pigments, typically a nanosecond, and R_0 is

$$R_0 = \left(\frac{4\pi}{3\hbar} d_i^2 d_j^2 \tau_0 J_{ij} \right)^{1/6}. \quad (5)$$

The term R_0 , now called the Förster radius, is the inter-pigment separation (approximately 90 Å for Chls) at which energy transfer is 50 % likely to succeed without loss due to fluorescence or internal conversion.

Energy migration in pigment networks and extension of Förster's theory

Förster's original theory [5, 6] has been extended for systems containing clusters of strongly interacting pigments [11, 12, 16, 20–23, 29, 33, 57, 59–62]. The clusters are described through an effective Hamiltonian matrix, the elements of which account for the coupling energy between electronic excitations in cluster pigments, typically those held together by a single light harvesting complex in a PSU with many light harvesting complexes. To express the effective Hamiltonian, its basis states need to be introduced. For example, for a two pigment cluster, the Hamiltonian H is a 2×2 matrix acting on basis states $|1\rangle$ and $|2\rangle$

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (6)$$

In the case of a cluster of N Chls or BChls, the Hamiltonian H is an $N \times N$ matrix acting on states $|1\rangle, |2\rangle, \dots, |N\rangle$. State $|i\rangle$ describes the cluster in which all pigments are in their ground state, except for pigment i which is in the lowest electronic excited state. For Chl and BChl molecules, the lowest excited state is the so-called Q_y state [58] which has a transition dipole moment approximately along the vector connecting the N_B and N_D atoms of the Chl porphyrin ring (see Fig. 1). The effective Hamiltonian H can be written [4, 12, 28, 63]

$$H = \sum_{i=1}^N \varepsilon_i |i\rangle \langle i| + \sum_{i \neq j}^N V_{ij} |i\rangle \langle j|, \quad (7)$$

where ε_i is the energy for the Q_y -excited state of Chl i ; V_{ij} are the coupling energies given in Eq. 1.

Due to coupling terms V_{ij} , excitation of a single Chl rapidly leads to a coherent sharing of excitations among all N Chls. These coherent states are the excitons defined as the eigenstates $|\tilde{n}\rangle$ of the Hamiltonian matrix H and are described by $H |\tilde{n}\rangle = E_n |\tilde{n}\rangle$ where E_n are the eigenvalues. The Hamiltonian, Eq. 7, determines also the time evolution of exciton

states through the formula $|\psi(t)\rangle = \sum_{n=1}^N \alpha_n \exp(-\frac{i}{\hbar} E_n t) |\tilde{n}\rangle$ where α_n are coefficients that

depend on the initial excitation, e.g., on which one of the N Chls was initially excited. This description neglects couplings of the electronic excitation to the internal motion of the pigments and their protein environment as described below. Thermal motion prevalent under physiological conditions causes exciton states $|\psi(t)\rangle$, normally spread over N Chls, to localize over a few pigments [30] and the population of the eigenstates $|\tilde{n}\rangle$ to approach, due to system-bath coupling only approximately, the Boltzmann distribution with occupancies $\rho_n = \exp(-E_n/k_B T) / \sum_m \exp(-E_m/k_B T)$ [20].

In the weak coupling limit where excitons become localized to individual Chls, energy migration in a pigment network can be described as a stochastic sequence of energy transfer events between individual Chls governed by Förster theory. In such a Chl-Chl hopping formulation, the probability $p_i(t)$ that Chl i is electronically excited at time t is given by a so-called master equation [13, 59]

$$\begin{aligned} \frac{d}{dt} p_i(t) &= \sum_j \mathcal{K}_{ij} p_j(t), \\ \mathcal{K}_{ij} &= k_{ji} - \delta_{ij} \left(\sum_k k_{ik} + k_{diss} + \delta_{i,RC} k_{CS} \right). \end{aligned} \quad (8)$$

Here k_{ij} are given by the Förster formula, Eq. 2, k_{diss} is the exciton dissipation rate due to internal conversion or fluorescence, k_{CS} is the charge separation rate at the RC, and $\delta_{i,RC}$ equals 1 if Chl i belongs to a RC and 0 otherwise. Accordingly, the initial excitation migrates stochastically, generally proceeding from higher energy pigments to lower energy ones, until reaching a RC and causing a charge separation event. Notably, some photosynthetic proteins such as PS1 contain Chls that absorb light at energies lower than the RC Chls that participate in charge separation [64, 65] which nonetheless remain excitonically connected to the RC at physiological temperatures. Using Eq. 8 one can compute the average excitation lifetime τ and the quantum efficiency q (the probability that an excitation leads to charge separation) [13, 59]

$$\tau = -\frac{1}{N} \langle \mathbf{1} | \mathcal{K}^{-1} | \mathbf{0} \rangle, \quad (9)$$

$$q = -\frac{1}{N} k_{CS} \langle RC | \mathcal{K}^{-1} | \mathbf{0} \rangle, \quad (10)$$

where $|\mathbf{0}\rangle$ denotes the initial state, $|\mathbf{1}\rangle \equiv \sum_i |i\rangle$, and $|RC\rangle \equiv \sum_i \delta_{i,RC} |i\rangle$.

The aforementioned Chl-Chl hopping model fails to properly describe excitation migration when typical interpigment couplings are large (i.e., greater than 100 cm^{-1} ; energies given in reciprocal wavelength). In a system containing such strongly coupled Chl clusters, e.g., the purple bacterial LH2 discussed in the next section (Fig. 2Ai, Bi), it becomes necessary to take into account the delocalization of excitons over multiple Chls. In the case where Förster energy transfer is considered between two or more Chl clusters, namely, when intra-cluster pigment coupling is strong, but the inter-cluster coupling is weak, the transfer of energy between the clusters is described according to modified Förster theory, where a Boltzmann equilibrium of donor cluster states is assumed prior to the transfer to the acceptor cluster. Accordingly, the energy transfer rate $k_{D,A}$ between a donor pigment cluster $\mathcal{D}$ and an acceptor

pigment cluster $\mathcal{A}$, akin to the transfer rate between two individual pigments k_{ij} (Eq. 2), is given by [33, 59, 66]

$$k_{\mathcal{D}\mathcal{A}} = \frac{2\pi}{\hbar} \sum_{m \in \mathcal{D}} \sum_{n \in \mathcal{A}} \frac{e^{-E_m^{\mathcal{D}}/k_B T}}{\sum_{l \in \mathcal{D}} e^{-E_l^{\mathcal{D}}/k_B T}} |V_{mn}^{\mathcal{D}\mathcal{A}}|^2 \int dE S_m^{\mathcal{D}}(E) S_n^{\mathcal{A}}(E), \quad (11)$$

where $V_{mn}^{\mathcal{D}\mathcal{A}}$ is the electronic coupling energy between donor exciton state m and acceptor exciton state n , $E_m^{\mathcal{D}}$ and $E_l^{\mathcal{D}}$ are the energy levels of the donor and acceptor pigment clusters, and $S_m^{\mathcal{D}}(E)$ and $S_n^{\mathcal{A}}(E)$ denote the associated emission and absorption spectra.

In a network consisting of M pigment clusters, the excitation lifetime can be expressed similarly to Eq. 9, namely,

$$\tau = -\frac{1}{M} \langle \mathbf{1} | \mathcal{K}_{cl}^{-1} | \mathbf{0} \rangle. \quad (12)$$

where the $M \times M$ matrix $\mathcal{K}_{cl}$ is defined similar to Eq. 8 in terms of the inter-cluster transfer rates $k_{\mathcal{D}\mathcal{A}}$ given in Eq. 11. In this extension of Förster theory, formulated a decade ago [33, 59, 66], energy migration among pigment clusters is described analogously to the case of individual weakly coupled pigments, accounting for quantum mechanical coherent sharing of excitation among pigments in a cluster. The physiological role of quantum coherent states have been pointed out at length already in 1997 when the structures of the first light harvesting complexes were determined [28]. Recently, quantum mechanical coherent sharing of excitations has attracted attention again [67, 68].

Detrapping and sharing of excitations among reaction centers

In general, not every excitation that arrives at a RC results in a charge separation event. It may instead escape back to the antenna array and possibly be captured at a different RC. Energy transfer away from the RC competes against the charge separation process at the RC, both processes having similar time constants of a few picoseconds. For example, in purple bacterial RC-LH1 complexes the corresponding probability of an exciton detrapping from the RC back into the pigment array is around 20–30 % [69]. Detrapping events generally result in a loss of light harvesting efficiency. However, the sharing of detrapped excitations by other RCs is advantageous if the RC, where the excitation is initially received, is nonfunctional [22]; excitation sharing among all Chls in the PSU also reduces radiation damage as it spreads its effect over many pigments.

The description of energy migration in a system with multiple RCs must be augmented to account for repeated detrapping and retrapping events. For a pigment network containing multiple RCs, the probability Q_{ij}^x that an excitation, which was detrapped at RC_j will be retrapped at RC_i , is [13, 33]

$$Q_{ij}^x = -k_{cs} \langle RC_i | \mathcal{K}_{cl}^{-1} | T_j \rangle, \quad (13)$$

where $|T_j\rangle$ is the state following the detrapping event at RC_j . These detrapping probabilities determine the sharing of excitation among dozens of RCs within an entire photo-synthetic

vesicle [22]. Detrapping and retrapping events are summed up in the so-called sojourn expansion [13, 33].

Förster theory of energy transfer in the presence of thermal motion

Photosynthetic life forms exist at physiological temperature and are subject to disorder due to thermal motion. Photosynthetic organisms have evolved means for not only coping with thermal disorder, but for utilizing it in maintaining high light harvesting efficiency. For example, the quantum efficiency in the PS1 complex (Fig. 2A.iv, B.iv), which is over 0.9 at physiological temperature, drops to 0.5 or less and becomes wavelength dependent at cryogenic temperatures [13, 33, 34, 70, 71]. This drop in efficiency is a result of weakened resonances J_{ij} , a key factor in the Förster formula (Eq. 3), when spectral lineshapes become narrower at lower temperatures; long wavelength-pigments become excitonic traps and excitation transfer rates to neighboring pigments reduce significantly.

Spectral properties of photosynthetic systems are particularly sensitive to thermal effects. The absorption spectrum of a pigment-protein complex at a finite temperature can be described in terms of the effective Hamiltonian H (Eq. 7). One such description is given in terms of the so-called dynamic disorder model of site energy fluctuations such as those reported in molecular dynamics trajectories [30, 63]; another model, referred to as static disorder, describes thermal effects in terms of the ensemble average over many realizations of a system [60].

In order to describe the effects of thermal motion on energy transfer between pigments, one must account for the coupling between pigments and the environment. For this purpose, one adds to the system Hamiltonian H (Eq. 7) a thermal bath of harmonic oscillators [30, 72–75], namely the Hamiltonian

$$H_B = \sum_{\xi=0}^{\infty} \left(\frac{p_{\xi}^2}{2m_{\xi}} + \frac{m_{\xi}\omega_{\xi}^2 x_{\xi}^2}{2} \right), \quad (14)$$

along with a system-bath coupling given by the Hamiltonian

$$H_{SB} = \sum_{j=1}^K W_j \sum_{\xi=0}^{\infty} c_{j\xi} x_{\xi}, \quad (15)$$

where W_j are coupling operators that describe K independent forms of coupling between system and environment. The vibrational states x_{ξ} model the thermal motions of the environment surrounding the pigment. As such, they are responsible for the donor emission and acceptor absorption spectra, and in turn influence the spectral overlap in Eq. 2. The time evolution of the exciton states is then described in terms of a reduced density matrix $\rho(t)$ obtained by averaging over the bath degrees of freedom [20]

$$\rho(t) = \text{tr}_B \left\{ \exp \left(-\frac{i}{\hbar} \int_0^t ds \mathcal{L}_T(s) \right) e^{-\beta H_B} / \text{tr}_B(e^{-\beta H_B}) \right\} \rho(0), \quad (16)$$

where $\mathcal{L}_T = [H_T, \cdot]$ and $H_T = H + H_B + H_{SB}$ and $\beta = 1/k_B T$. The time evolution of the reduced density matrix $\rho(t)$ is calculated by performing the trace over the bath degrees of freedom of

the total system propagator $\exp(i \int \mathcal{L}_T(s) ds/\hbar)$, assuming a Boltzmann distribution of bath vibrational states [20].

Perturbative techniques are typically utilized to solve Eq. 16. In a system where inter-pigment couplings are weak compared to pigment-environment coupling, Förster theory holds, whereas when pigment-environment coupling is weak compared to inter-pigment coupling, Redfield theory holds [16, 76–81]. In a typical pigment-protein complex, where there is coherence between nearby pigments, both Förster and Redfield approximations have limited applicability and a non-perturbative and non-Markovian formalism is needed [16, 82–85]. In recent years, a fully non-Markovian description of quantum dynamics in a noisy environment has been characterized to arbitrary order in system-environment coupling by utilizing a hierarchy of auxiliary density matrices [20, 86, 87]. This method has been used to study the coherence dynamics in the Fenna-Matthews-Olsen pigment-protein complex of green sulphur bacteria [88, 89], DNA [90], and pigment-protein complexes of purple bacteria [20, 91–93]. The calculations show, for example, that light absorbing Chls in a cluster spread the excitation coherently over the cluster and relax within 1–2 ps to the Boltzmann distribution of populated exciton states that underlie the cluster-cluster rate given in Eq. 11 [20]. Use of the cluster-cluster rate implies immediate relaxation; the short calculated relaxation time reported in [20] implies that Eq. 11 should represent excitation migration in the purple bacterial PSU rather well.

3 Architecture of light harvesting systems and the influence of Förster energy transfer

Photosynthetic species display a remarkable variety in their physiology as well as in structure and supramolecular organization of their constituent light harvesting proteins (see Figs. 2, 3, and 4) [1, 2]; yet common structural motifs reflecting Förster's theory of energy transfer are discernible. The key characteristics in the Förster formula are geometrical properties κ (Eq. 35), R_0 (Eq. 5), and rapid, i.e., r^{-6} , decay (Eq. 4), as well as optical ones, namely the spectral overlap J_{ij} (Eq. 8). The geometrical term κ accounts for the effect of pigment orientation on transfer rate (see Appendix); the Förster radius R_0 (approximately 90 Å for Chls) along with the r^{-6} decay of transfer efficiency place bounds on pigment separation and associated pigment packing density; the resonance term J_{ij} requires that pigments are spectrally matched for efficient transfer.

In the remainder of this section the structural features and light harvesting characteristics of exemplary photosynthetic systems from cyanobacteria, plants, and purple bacteria are compared (Fig. 2). In particular, the supramolecular architecture of purple bacterial light harvesting systems are inspected, selected here and in the authors' research because of their great simplicity. Excitation transfer properties of photosynthetic proteins are dependent especially on the geometry of constituent pigments that are located in the trans-membrane region; BChl transition dipole moments in purple bacterial systems are organized in an orderly array (Fig. 3i and ii), whereas Chls in higher organisms such as cyanobacteria feature more complex, seemingly random networks (Fig. 3iii).

Light harvesting complexes from purple bacteria

The purple bacterial PSU consists mainly of two pigment-protein complexes, LH2 and LH1, the latter surrounding an RC to form an RC-LH1 complex (see Fig. 2, A.i–iii, B.i–iii). LH2 and LH1 display a cylindrical arrangement of transmembrane helices that form a scaffold of BChls and carotenoids [9]. The LH2 subunits assemble in an eight-fold [42] or nine-fold [94, 95] symmetry, depending on species. The simplicity of this modular, symmetric organization of purple bacterial light harvesting proteins stands in stark contrast to their

counterparts in cyanobacteria and plants [35, 37, 39] discussed below. The LH2 complex of the purple bacterium *Rhodobacter (Rh.) sphaeroides* (shown in Fig. 2A.i, B.i, modeled after the *Rhodospseudomonas acidophila* LH2 complex [43]) features 9 subunits containing a total of 27 BChls [96], divided into two rings. These so-called B850 and B800 rings are named after their absorption peaks of 850 nm and 800 nm, containing 18 and 9 BChls, respectively. The LH1 BChls form only a single ring that absorbs at 875 nm. The reader can view movies of all light harvesting systems featured in Figs. 2 and 4 (Supplementary Material).

The BChl rings in the LH2 and LH1 system exhibit excitonic behavior investigated in numerous theoretical [20, 28, 30, 59, 60, 69] and experimental [97–102] studies. The theoretical studies were based on crystallographic structures of LH2 [41–43] that showed two BChl rings and on models of LH1 [103] that exhibit a single BChl ring. Both LH2 and LH1 show a ring of closely packed BChls with a nearest neighbor Mg-Mg distance of about 10 Å; LH2 shows a second ring of greater separation (Mg-Mg distance of approximately 20 Å) and, therefore, weakly coupled, pigments. In the case of LH2, the BChl electronic excitations were described by full quantum chemical calculations [104], as well as through effective Hamiltonians as shown in Eq. 7 [28]. In the latter case, as neighboring B850 ring BChls, i.e., those labeled $j, j + 1$, are in direct contact, the respective coupling energies $V_{j,j+1}$, which are in the range of 300 cm^{-1} [105–107], need to be determined by quantum chemistry methods [57, 104, 107]; however, the remaining V_{ij} can be determined according to Eq. 1. The B850 ring BChls clearly exhibits excitonic behavior as demonstrated theoretically in [28] and verified in optical experiments [97, 100]. Electronic excitations in the LH1 B875 ring behave very similarly to those in the LH2 B850 ring as shown theoretically [59, 69] and experimentally [98, 108]. In LH2, excitons are quickly, within 1 ps, transferred from B800 to B850 BChls; transfer between B850 rings in two neighboring LH2 complexes as well as the transfer from an LH2 to a nearby LH1 typically takes place within 5–10 ps; the transfer from the LH1 ring to the RC occurs within 30–50 ps [20, 59, 69, 98, 109, 110]. Excitation migration in the modified Förster formalism among a network containing hundreds of these proteins is discussed below for the purple bacterial chromatophores.

The circular architecture of pigments, such as in LH2 and LH1 (Fig. 2i, ii and Fig. 3i, ii), has multiple benefits for efficient light harvesting. It allows excitation transfer between neighboring proteins to occur without directional preference, providing a robustness with respect to protein orientations in the photosynthetic membrane. A notable property of the B850 and B875 rings is the opposite orientation of the transition dipole moments of neighboring BChls (Fig. 3i, ii). The alternating orientation along with coherent delocalisation of excitation in the exciton states enhances light harvesting by making the excitonic ground state of LH2 optically inactive [111], i.e., making fluorescence weak, which increases the lifetime of LH2 and LH1 excitations. Additionally, the stated orientation of BChls renders the exciton states of 850 nm (LH2) and 875 nm (LH1) superradiant, i.e., all absorption and excitation transfer strength is accumulated in these excitons, improving light absorption and excitation transfer characteristics in the purple bacterial light harvesting systems [28, 112].

Light harvesting complexes from cyanobacteria and plants

In oxygenic photosynthetic species, the structure of individual proteins as well as the organization of the corresponding thylakoid membrane are more complex than their purple bacterial counterparts. The modularity and symmetry of components in purple bacteria is replaced by a complex, seemingly random network of pigments. The cyanobacterial PS1 [35] (Fig. 2iv; Fig. 3iii), containing 96 Chls, is organized in the form of a trimeric complex. The corresponding plant PS1 [37] (Fig. 2v) preserves the position and orientation of most of the Chls found in the cyanobacterial system, its evolutionary precursor. However, plant PS1

features additional pigments in accompanying Lhca subunits for a total of more than 160 Chls [37, 113–115]. The cyanobacterial PS2 (Fig. 2vi) shares some structural similarity with PS1 featuring a total of 35 Chls as well as a unique oxygen evolving manganese complex [38–40].

The greater size and complexity, compared with purple bacteria, of the oxygenic light harvesting proteins make it more challenging to compute energy transfer characteristics. For the purple bacterial pigment networks introduced above, such as those in LH2, the related effective Hamiltonians are defined in terms of a handful of independent parameters due to the symmetry of the system [41–43]. In contrast, for cyanobacterial PS1 with its disordered Chl network, there are 96 site energies that have to be determined independently in a costly computation [15] and many inter-pigment couplings need to be computed [13].

An excitation lifetime of 28 ps was determined for cyanobacterial PS1 with a corresponding quantum efficiency of 0.97 based on the master equation approach (Eq. 9) [13]. A study of the trimeric PS1 complex reveals that Förster transfer between individual monomers is weak [14, 33]; the excitation sharing probability between the RCs of different monomers (the cross-trapping probability, Eq. 13) is only about 4 % [33]. Not surprisingly, a comparison of the light harvesting network of plant PS1 with that of cyanobacterial PS1 reveals significant similarities, with the exception of the presence of the Lhca subunits which increase the total absorption cross-section of the system as well as the overall excitation lifetime (50 ps) due to the longer average exciton path length [66]. The average excitation transfer time from the Lhca subunits to the PS1 core in the plant system was calculated to be 2–5 ps [66]. However, a parameter sensitivity analysis has revealed that these transfer times cannot be determined reliably in the absence of accurate site energy assignments for Lhca Chls. The stated computations of exciton kinetics and quantum efficiency reproduce observations [71, 116–118] at room temperature, but they generally fail to account for low temperature exciton dynamics; the latter is sensitive to effective Hamiltonian parameters such as individual Chl site energies.

Oxygenic photosystems, when compared to their purple bacterial counterparts (Fig. 2), display a greater packing density of pigments along with a complex geometrical arrangement which appear to facilitate more efficient harvesting of light, in agreement with the Förster formula.

Supramolecular organization of the purple bacterial photosynthetic unit

Recently, the supramolecular organization of entire PSUs in purple bacteria were determined for the pseudo-spherical chromatophore vesicles [22, 23] of *R. sphaeroides*, for the lamellar, i.e., flat, chromatophore system in *Rsp. photometricum* [119], and for the tubular vesicles found in LH2-minus mutants [55, 92]. The structural models shown in Fig. 4 were derived through a combination of atomic force microscopy [52, 54, 103, 120, 121], cryo-electron microscopy [55, 122–126], and linear dichroism spectra [120], as well as through the atomic-level structures of the constituent proteins introduced in Fig. 2. The photo-synthetic vesicles feature hundreds of light harvesting proteins and thousands of pigments, distributed over a membrane vesicle 50–70 nm wide. Notably, some of the components essential for function, such as the ATP synthase or the bc_1 complex, are still missing in the available data [52–54, 127, 128] and, therefore, are not accounted for in the models. The stoichiometry of constituent proteins is dependent on the growth conditions, especially light intensity [23].

Due to the large size of chromatophore vesicles, energy transfer properties can currently only be studied in the context of the modified Förster formalism (Eq. 11), i.e., in terms of pairwise energy transfer events between the neighboring pigments clusters of LH2, LH1,

and RC. The average excitation lifetime in the spherical chromatophore (Fig. 4A), thus computed, is around 100 ps [23] with a corresponding quantum efficiency of 0.9. The computed lifetime is larger than the observed values of 60–80 ps [98, 108, 109, 129–132], partly due to the vesicle model being constructed for a system grown in low light, featuring more peripheral LH2 complexes and a longer average exciton path length. Substantial excitation sharing between RCs arises in spherical chromatophores as the probability (Eq. 13) for a detrapped excitation to be recaptured at the same RC is only 13 % on average [22].

The lamellar chromatophore shown in Fig. 4B represents an arrangement of LH2 and RC-LH1 complexes in photosynthetic membranes of *Rsp. photometricum* [119]. Currently, no structural information is known for the proteins in *Rsp. photometricum*. The LH2 and RC structures shown correspond instead to the structures for *Rps. acidophila* [43], while the LH1 monomer is a homology model based on the LH2 crystal structure of *Rh. molischianum* [42]. The average excitation lifetime in the lamellar chromatophore, computed similarly to the aforementioned spherical chromatophore in *R. sphaeroides* [23], is 77ps, with a corresponding quantum efficiency of 0.92.

For the tubular chromatophore (Fig. 4C), the symmetry of the structure (given by the wallpaper group **p2** [133]) makes possible the computation of the overall excitation transfer behavior from a small number of parameters describing adjacent (inter-cluster) Förster transfers; the computation yields an average excitation lifetime of about 70 ps [92] with a corresponding quantum efficiency of 0.93. It is currently not known if the tubular vesicles present in LH2-minus mutants are photosynthetically active.

The supramolecular organization seen in purple bacterial chromatophores demonstrates how the light harvesting efficiency is achieved through modularity of architecture: first, the subunits within individual proteins are identical, facilitating easy assembly and strong inter-pigment couplings; second, light harvesting proteins within the chromatophore are interchangeable, likely aggregating spontaneously under self-induced curvature [96, 134–137]. The resulting network containing thousands of BChls achieves highly efficient energy transfer to RCs while still permitting a window of separation between light harvesting proteins to facilitate diffusion of quinones necessary for the overall physiological mechanism [23, 54].

Fluorescent energy transfer as a physical constraint shaping the organization of photosynthetic systems

Several features critical in Förster's energy transfer theory, such as orientation of pigments, inter-pigment separation and spectral resonance, are prominent in the organization of photosynthetic systems and appear to have influenced the evolution of photosynthetic species. Below, common structural motifs, seen in the light of Förster theory, are enumerated.

First and foremost, a high energy transfer efficiency according to Eq. 4, demands a small (compared to R_0) inter-pigment separation, i.e., a large pigment density. As can be seen in Fig. 2, plant and cyanobacterial PS1 features a greater pigment density than its purple bacterial counterpart. Furthermore, less protein content is used for the scaffolding of comparable pigment networks in the oxygenic systems; in fact, cyanobacterial PS1 features 1 Chl per 27 amino acids whereas a comparable purple bacterial assembly of a RC-LH1 complex with two accompanying LH2s feature 1 BChl per 40 amino acids, which are also distributed over a larger volume [4].

Second, the geometry of pigment networks in cyanobacterial PS1 features, despite the apparent disorder, an optimality with respect to Chl orientations and site energy fluctuations

and a robustness against damaged pigments when overall excitation transfer efficiency is used as a fitness criterion [13, 15, 138, 139]. At physiological temperature, the interval over which the quantum efficiency fluctuates due to perturbations of the PS1 Chl network is rather narrow (0.95–0.97) [13]. However, within this narrow interval of efficiency the actual pigment geometry gives rise to nearly the highest possible efficiency value, indicating an optimality [13] which is most prevalent in the pigments that immediately surround the RC [139].

Third, thermal disorder is actively utilized in photosynthetic systems for the broadening of pigment absorption profiles [30, 60, 63]; the broadening is essential for maintaining strong resonance values J_{ij} necessary for high energy transfer efficiency. Additionally, photosystems employ a variety of pigments with different absorption peaks to harvest light energy over a broad range of wavelengths, resulting in a funnel-like energy flow. Furthermore, virtually all pigments absorb light at the edge of the water absorption spectrum [140], largely overlapping with the visible spectrum, since for species that evolve in water, wavelengths of light absorbed by water are inaccessible.

Fourth, RCs and their associated electron transfer chains (ETCs) are typically surrounded in light harvesting systems by a *cordon sanitaire*, i.e., an absence of non-ETC pigments in the immediate vicinity of the ETC [27, 141, 142]. This appears to be necessary for maintaining high electron transfer efficiency along the ETC following the charge separation at the RC: ‘leaking’ of electrons out of the ETC would require an overlap of electronic wavefunctions and, thus, falls off exponentially with pigment distance [56], whereas energy transfer into the RC has an r^{-6} dependence (c.f. Eq. 4) on pigment distance [6] which wins over greater distances; therefore, efficient energy transfer into the RC can be maintained while loss of electrons can be prevented [4, 27]. The pigment gap is readily discerned in Fig. 2, ii, iv, v, and vi, and the respective movies (Supplementary Material).

Further physics-based design principles appear to be prevalent in the evolution of photosynthetic systems such as protection from photodamage (demanding proximity between Chls and carotenoids [57]), associated repair, modularity of components, assembly of supramolecular aggregates, and graceful degradation with unavoidable radiation damage [27]. Energy transfer as described by Förster is not the only fundamental process essential for physiological function. Nonetheless, it appears to have profoundly influenced photosystem architecture.

4 Discussion

Förster’s pioneering work [5, 6] enabled several generations of scientists to study, in ever increasing detail, the harvesting of light energy in nature. As outlined above, Förster’s original work has since been expanded upon in scope as well as detail; his approximation scheme has been replaced in time by more accurate methods which are computationally more intensive. What is perhaps surprising is how well Förster’s theory manages to capture the essential physics of the energy migration process in photosynthetic light harvesting. Duysens [10] and others could apply Förster’s theory to describe energy transfer in photosynthetic species even before detailed structures of the constituent proteins were available. Today, Förster theory is used to study energy transfer not only in massive networks of photosynthetic proteins found in nature and resolved in atomic level structure, but also in artificial light harvesting systems [141, 142].

Notably, nature herself appears to be influenced in the evolution of photosynthetic life forms by the physics of the FRET process as described by Förster. For today’s scientists, the idea that living matter should be studied with the same laws of physics as inanimate matter is

obvious. In retrospect, at the time when Förster's work was published, Schrödinger's seminal book [143] stating that physical theory be applied to describe biological processes was still fairly new; Förster's work applying quantum physics to describe a fundamental biological process was pioneering. Förster has shown, in retrospect not surprisingly, that quantum physics reigns in all photosynthetic lifeforms on Earth. The beautiful colors due to plants, algae, and photosynthetic bacteria are a telling sign of Förster theory and quantum physics at work, fueling life on Earth with the energy of sunlight. While Förster realized that excitation transfer among pigments is essential in photosynthetic light harvesting, we see today that pigments, scaffolded by intricate protein structures, carry out the role in amazing hierarchical assemblies. Förster stated that quantum effects rule how nature harvests sunlight; today we know that he was definitely right, but that the real role of quantum physics is even more beautiful than he could envision.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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A Appendix

In Förster energy transfer, an excited electron on the donor molecule D in orbital φ_{D^*} drops in energy to a ground state orbital φ_D , while an electron on the acceptor molecule A is simultaneously excited from its ground state orbital φ_A to its excited state orbital φ_{A^*} . This process, depicted in Fig. 5, is often written as $D^*A \rightarrow DA^*$, where $*$ is used to indicate which molecule is excited (Fig. 5).

A simple example is furnished when both A and D are hydrogen atoms and an electron in the $2P_z$ state on donor (D) hydrogen atom transfers its excitation to the acceptor (A) hydrogen atom. In this case, the ground state orbitals, φ_D and φ_A , are then the $1S$ orbitals of each hydrogen atom and the excited state orbitals, φ_{D^*} and φ_{A^*} , are the $2P_z$ orbitals of each hydrogen atom. In this appendix, the expression for the excitation transfer rate is derived.

Fermi's golden rule [144]

$$k = \frac{2\pi}{\hbar} V_{DA}^2 \delta(E_D - E_A), \quad (17)$$

gives us the prescription for calculating the rate k of excitation transfer between two pigments with excitation energies E_D and E_A . Due to the vibrational motion of the surrounding environment at finite temperature, the δ -function is replaced by the spectral overlap integral

$$J_{DA} = \int dE S_D(E) S_A(E), \quad (18)$$

where S_D is the emission spectrum of pigment i and S_A is the absorption spectrum of pigment j (see text above for normalization). The spectral overlap Eq. 18 assumes each pigment having independent thermal environments, i.e., no correlated fluctuations. The presence of correlated fluctuations between pigment environments may enhance or suppress the transfer between the donor and acceptor pigments depending on the nature of the correlations [145, 146].

To determine k , the interaction energy V_{DA} between the excited states of pigments D and A needs to be calculated, which is given by the Coulomb interaction integral (Fig. 6)

$$V_{DA} = \int d\mathbf{r}_D \int d\mathbf{r}_A \frac{\rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A)}{r_{AD}}, \quad (19)$$

where r_{AD} is the distance from the electron on donor D to the electron on acceptor A and

$$\rho_D(\mathbf{r}_D) = e\varphi_{D^*}(\mathbf{r}_D)\varphi_D(\mathbf{r}_D) \quad (20)$$

$$\rho_A(\mathbf{r}_A) = e\varphi_{A^*}(\mathbf{r}_A)\varphi_A(\mathbf{r}_A). \quad (21)$$

We emphasize that ρ_D and ρ_A do not denote charge densities, but so-called the transition densities for ground state to excited state transitions

Indeed, we note that due to the orthogonality of orbital pairs $\varphi_D(\mathbf{r}_D)$, $\varphi_{D^*}(\mathbf{r}_D)$ and $\varphi_A(\mathbf{r}_D)$, $\varphi_{A^*}(\mathbf{r}_D)$ holds

$$c_D = \int d\mathbf{r}_D \rho_D(\mathbf{r}_D) = 0 \quad (22)$$

$$c_A = \int d\mathbf{r}_A \rho_A(\mathbf{r}_A) = 0. \quad (23)$$

The vector connecting the electrons of D and A can be written

$$\mathbf{r}_{AD} = (\mathbf{R}_D - \mathbf{R}_A) + (\mathbf{r}_D - \mathbf{r}_A). \quad (24)$$

Assuming $|\mathbf{R}_D - \mathbf{R}_A| \gg |\mathbf{r}_D - \mathbf{r}_A|$, the factor $1/r_{AD}$ in Equation (19) can be expanded [140]

$$\frac{1}{r_{AD}} = \frac{1}{R} - \frac{\mathbf{r} \cdot \mathbf{R}}{R^3} + \frac{3(\mathbf{r} \cdot \mathbf{R})^2 - r^2 R^2}{2R^5} + O\left(\frac{1}{R^4}\right), \quad (25)$$

where $\mathbf{R} = \mathbf{R}_D - \mathbf{R}_A$, $\mathbf{r} = \mathbf{r}_D - \mathbf{r}_A$, $R = |\mathbf{R}|$ and $r = |\mathbf{r}|$. Taking only the three leading terms of Equation (25) into account, Equation (19) can be re-written

$$V_{DA} = V_1 + V_2 + V_3, \quad (26)$$

where

$$V_1 = \int d\mathbf{r}_D \int d\mathbf{r}_A \rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A) / R \quad (27)$$

$$V_2 = \int d\mathbf{r}_D \int d\mathbf{r}_A \rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A) \mathbf{r} \cdot \mathbf{R} / R^3 \quad (28)$$

$$V_3 = \int d\mathbf{r}_D \int d\mathbf{r}_A \rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A) [3(\mathbf{r} \cdot \mathbf{R})^2 - r^2 R^2] / (2R^5). \quad (29)$$

The leading term V_1 can be calculated readily

$$V_1 = \int d\mathbf{r}_D \rho_D(\mathbf{r}_D) \int d\mathbf{r}_A \rho_A(\mathbf{r}_A) / R = c_D c_A / R, \quad (30)$$

and is found not to contribute to the interaction energy due to $c_D = c_A = 0$. Likewise, V_2 also does not contribute to the interaction energy as is shown by the calculation

$$\begin{aligned} V_2 &= \int d\mathbf{r}_D \int d\mathbf{r}_A \rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A) \mathbf{r} \cdot \mathbf{R} / R^3 \\ &= \int d\mathbf{r}_D \int d\mathbf{r}_A \rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A) (\mathbf{r}_D - \mathbf{r}_A) \cdot \mathbf{R} / R^3 \\ &= \int d\mathbf{r}_A \rho_A(\mathbf{r}_A) \int d\mathbf{r}_D \rho_D(\mathbf{r}_D) \mathbf{r}_D \cdot \mathbf{R} / R^3 - \int d\mathbf{r}_D \rho_D(\mathbf{r}_D) \int d\mathbf{r}_A \rho_A(\mathbf{r}_A) \mathbf{r}_A \cdot \mathbf{R} / R^3 \\ &= c_A (\mathbf{d}_D \cdot \mathbf{R}) / R^3 - c_D (\mathbf{d}_A \cdot \mathbf{R}) / R^3, \end{aligned} \quad (31)$$

where the definition of the transition dipole moment,

$$\mathbf{d}_{A/D} = e \int d\mathbf{r} \varphi_{A^*/D^*}(\mathbf{r}) \mathbf{r} \varphi_{A/D}(\mathbf{r}) \quad (32)$$

has been used. Lastly, V_3 is calculated

$$\begin{aligned} V_3 &= \int d\mathbf{r}_D \int d\mathbf{r}_A \rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A) \left\{ [3(\mathbf{r}_D - \mathbf{r}_A) \cdot \mathbf{R}]^2 - |\mathbf{r}_D - \mathbf{r}_A|^2 R^2 \right\} / (2R^5) \\ &= \int d\mathbf{r}_D \int d\mathbf{r}_A \rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A) \left\{ 3 \left[(\mathbf{r}_D \cdot \mathbf{r})^2 + (\mathbf{r}_A \cdot \mathbf{r})^2 - 2(\mathbf{r}_D \cdot \mathbf{R})(\mathbf{r}_A \cdot \mathbf{R}) \right] - (|\mathbf{r}_D|^2 + |\mathbf{r}_A|^2 - 2\mathbf{r}_D \cdot \mathbf{r}_A) R^2 \right\} / (2R^5) \\ &= \int d\mathbf{r}_D \int d\mathbf{r}_A \rho_D(\mathbf{r}_D) \rho_A(\mathbf{r}_A) \left\{ 3 \left[-2(\mathbf{r}_D \cdot \mathbf{R})(\mathbf{r}_A \cdot \mathbf{R}) + (2\mathbf{r}_D \cdot \mathbf{r}_A) R^2 \right] \right\} / (2R^5) \\ &= \left\{ (\mathbf{d}_D \cdot \mathbf{d}_A) R^2 - 3(\mathbf{d}_D \cdot \mathbf{R})(\mathbf{d}_A \cdot \mathbf{R}) \right\} / R^5, \end{aligned} \quad (33)$$

and is found to be the leading non-zero contribution to the interaction energy V in Eq. (25).

By using V_3 for the interaction energy, the well-known Förster formula for fluorescence resonance energy transfer is obtained

$$k = \frac{2\pi}{\hbar} |\mathbf{d}_D|^2 |\mathbf{d}_A|^2 \left[(\widehat{\mathbf{d}}_D \cdot \widehat{\mathbf{d}}_A) - 3(\widehat{\mathbf{d}}_D \cdot \widehat{\mathbf{R}})(\widehat{\mathbf{d}}_A \cdot \widehat{\mathbf{R}}) \right]^2 R^{-6} J_{DA}, \quad (34)$$

where we have defined $\widehat{\mathbf{R}} = \mathbf{R}/R$, $\widehat{\mathbf{d}}_D = \mathbf{d}_D/|\mathbf{d}_D|$ and $\widehat{\mathbf{d}}_A = \mathbf{d}_A/|\mathbf{d}_A|$. The term

$$\kappa = (\widehat{\mathbf{d}}_D \cdot \widehat{\mathbf{d}}_A) - 3(\widehat{\mathbf{d}}_D \cdot \widehat{\mathbf{R}})(\widehat{\mathbf{d}}_A \cdot \widehat{\mathbf{R}}), \quad (35)$$

accounts for the effect of D and A orientation on energy transfer. For example, when $\mathbf{R}$ is in the same direction as $\mathbf{d}_D$ then κ depends simply on the component of $\mathbf{d}_A$ along $\mathbf{d}_D$. The term κ is often averaged over all possible orientations of $\widehat{\mathbf{d}}_D$ and $\widehat{\mathbf{d}}_A$ to give $\kappa^2 = 2/3$, which simplifies the Förster formula to

$$k = \frac{4\pi}{3\hbar} \frac{d_D^2 d_A^2}{R^6} J_{DA}. \quad (36)$$

Figure 1. Structure of chlorophyll *a* molecule. The transition dipole moment of the lowest (Q_y) state lies approximately in the plane of the porphyrin ring, along the vector connecting the N_B and N_D atoms.

Figure 2.

Pigment organization across different photosynthetic systems. (A) Top view (perpendicular to the membrane plane) and (B) side view (along the membrane plane) of pigment-protein complexes (i to vi) LH2 [42], RC-LH1 monomer [43], RC-LH1 dimer model [69], cyanobacterial PS1 [35], plant PS1 with Lhca subunits [37], and PS2 [38], respectively. Protein components are shown as transparent blue traces to highlight the Chls and BChls (green; shown only as porphyrin rings) and the carotenoids (orange). (See Supplementary Material for movies of these systems.)

Figure 3. Orientations of the transition dipole moments of the constituent BChl and Chl molecules. (A) Top view (perpendicular to the plane of the membrane) and (B) side view (along the plane of the membrane); (i) LH2 [42], (ii) monomeric RC-LH1 [43, 147], and (iii) cyanobacterial PS1 [35].

Figure 4.

Structural models for (A) spherical [22, 23], (B) lamellar [121], and (C) tubular [55, 92] photosynthetic chromatophores from purple bacteria. Shown above are the constituent proteins: LH2 complexes (green) and RC-LH1 complexes (LH1 in red; RC in blue). Shown below are the associated BChl networks. The lamellar patch (B) is shown embedded in a lipid membrane, containing a total of nearly 23 million atoms including water (not shown). (See Supplementary Material for movies of these systems.)

Figure 5.

The excitation transfer process $D^*A \rightarrow DA^*$. Here, ϕ_D and ϕ_A are the ground state orbitals of the donor and acceptor electrons and ϕ_{D^*} and ϕ_{A^*} are the excited state orbitals of the donor and acceptor electrons, respectively.

Figure 6. Positions of donor pigment $\mathbf{R}_D$ and donor electron $\mathbf{r}_D$ and of acceptor pigment $\mathbf{R}_A$ and acceptor electron $\mathbf{r}_A$.