Robustness and Optimality of Light Harvesting in Cyanobacterial Photosystem I

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Abstract

As most biological species, photosynthetic lifeforms have evolved to function optimally, despite thermal disorder and with fault tolerance. It remains a challenge to understand how this is achieved. To address this challenge the function of the protein-pigment complex photosystem I (PSI) of the cyanobacterium *Synechococcus elongatus* is investigated theoretically. The recently obtained high resolution structure of this complex exhibits an aggregate of 96 chlorophylls that are electronically coupled to function as a light-harvesting antenna complex. This paper constructs an effective Hamiltonian for the chlorophyll aggregate to describe excitation transfer dynamics and spectral properties of PSI. For this purpose, a new kinetic expansion method, the sojourn expansion, is introduced. Our study shows that at room temperature fluctuations of site energies have little effect on the calculated excitation lifetime and quantum yield, which compare favorably with experimental results. The efficiency of the system is found to be robust against ‘pruning’ of individual chlorophylls. An optimality of the arrangement of chlorophylls is identified through the quantum yield in comparison with an ensemble of randomly oriented chlorophylls, though, the quantum yield is seen to change only within a narrow interval in such an ensemble.
1 Introduction

Photosynthesis is the main source of energy in our biosphere. Although light-harvesting systems show a great variety in their design and function, most of them are membrane proteins comprised of a network of pigment antennae surrounding a reaction center [1]. The antenna complex is responsible for the absorption of light and the transfer of the resulting electronic excitation to a so-called special pair of chlorophylls in the reaction center, where a charge separation across the cell membrane is initiated. This charge separation is later utilized by the cell to store energy through synthesis of ATP in a more stable form.

Oxygenic photosynthetic species employ two transmembrane protein-pigment complexes for light-harvesting, named photosystems I and II. Photosystem I (PSI) is a ubiquitous protein-pigment complex found in green plants, algae and cyanobacteria. Located in the bacterial membrane, it absorbs sunlight and uses its energy to transfer electrons across the cell membrane. PSI is remarkable in that it contains the antenna complex, reaction center and the electron transfer chain all within the same protein. For a recent review on PSI physiology and function we refer the reader to Refs. [2, 3, 4].

A high resolution atomic structure was recently obtained for PSI from the cyanobacterium Synechococcus (S.) elongatus [5]. The structure exhibits an aggregate of 96 chlorophyll molecules, including the special pair, P700, at which the primary charge separation takes place. This finding opens up the opportunity to study in detail the light-harvesting function of PSI, i.e., one can computationally examine the light-harvesting pathway from initial absorption of a photon to the transfer of electrons by the special pair. In the past, a similar leap in structural information on the peripheral light-harvesting complexes LH1 and LH2 of purple bacteria resulted in the photosynthetic unit of purple bacteria being the best understood antenna complex today [6, 7, 8, 9, 10].

It is of interest to compare the structure and function of PSI to the photosynthetic unit of purple bacteria. Both systems contain on the order of a hundred chromophores per reaction center. In purple bacteria these chromophores are organized in highly symmetric ring-like structures [11, 12, 13]. In contrast, the chlorophyll aggregate in PSI forms a rather random array surrounding the reaction center (see Fig. 1), the only hint of order being a pseudo-\(C_2\) symmetry apparent in the structure.
Purple bacteria have the oldest known photosynthetic apparatus, while cyanobacteria and their relatives are evolutionarily more recent \[14, 15\]. It is of interest to compare the light-harvesting systems of these lifeforms and to elucidate the drive toward a more efficient system in the more recently developed light-harvesting complexes.

A related issue is whether the peculiar arrangement of chlorophylls found in the reported structure is essential for the functioning of PSI or whether the system can be described successfully assuming some degree of randomness. For example, is every single chlorophyll essential for the proper functioning of the system? This question also constitutes a modeling challenge. Due to its circular symmetry and repetitive elements a purple bacterial light-harvesting complex can be modeled with only a few physical parameters describing chlorophyll site energies and electronic couplings \[10, 16, 17\]. PSI, on the other hand, features 96 chlorophylls that show few regularities and seemingly require a large number of parameters for their description.

There are two possible ways to approach the complexity of the chlorophyll aggregate in PSI. In one approach, typically taken in chemistry, one strives for an ever increasing accuracy in a model through a large number of specific parameters. This approach implies that the specific properties of every one of the 96 chlorophylls in PSI matter. In another approach, typically taken in physics, one identifies a minimal set of characteristics, e.g., average properties of the 96 chlorophylls, relevant for the description of function and observed spectra.

The most relevant functional property of PSI is its high efficiency in using excitation energy for charge separation in the reaction center despite thermal disorder and ever present internal damage. One seeks to know how robust PSI is against perturbations such as ‘pruning’ or ‘bleaching’ of individual chlorophylls or changes in the protein that effect chlorophyll site energies. Robustness in biology is not a new concept. The issue was addressed earlier in Refs. \[18, 19\] and, recently in the study of biochemical networks involved in bacterial chemotaxis \[20, 21\]. These studies suggest that biological networks exhibit a high degree of insensitivity to fine-tuning of physical parameters.

Another issue of interest is the optimality of the design of the chlorophyll aggregate in PSI. Is it possible to rearrange or reorient the pigments in PSI to achieve a better quantum yield or did evolution establish an optimal arrangement? This is likely easier to
answer *in silico* than *in vivo*.

While the issues of robustness and optimality can be addressed well by the physicists’ approach, details of the low temperature excitation transfer dynamics and spectral features are likely better studied by the chemists’ approach. The longest wavelength features of the spectrum attributed to so-called ‘red chlorophylls’ are an example of this. Red chlorophylls are responsible for broadening the absorption profile of PSI, but their role is not fully understood. For a review we refer the reader to Ref. [2].

In order to answer the questions raised above we study ensembles of various chlorophyll arrangements. This permits us to investigate the dependence of the light harvesting function of PSI in detailed or coarse descriptions as well as the robustness and optimality of the system. For this purpose, we use the high resolution structure reported in [5] as a starting point to describe the spectral and excitation transfer characteristics of PSI. The structure reveals the relative orientation of chlorophyll molecules, which makes it possible to construct an effective Hamiltonian for the chlorophyll aggregate. The resulting quantum yield for charge separation and the average excitation lifetime is determined based on this Hamiltonian.

We also investigate the excitation transfer dynamics that results after the absorption of a photon by PSI. Besides determining the overall lifetime of an excitation and the quantum yield (the probability that photon absorption leads to electron transfer from the special pair), one wishes to know how excitation migrating through PSI repeatedly reaches and escapes the special pair, i.e., engages in sojourns from the special pair into the chlorophyll pool. We suggest a kinetic expansion method, the sojourn expansion, to account for the outlined excitation migration in a light-harvesting complex.

The organization of this paper is as follows: In the next section we introduce the effective Hamiltonian for the chlorophyll aggregate of PSI. Sec. 3 utilizes this Hamiltonian to discuss candidates for the red chlorophyll states. In Sec. 4 we discuss the effect of thermal disorder on the spectral properties of PSI in terms of random matrix theory. In Sec. 5 we introduce the general theoretical framework for the study of excitation transfer dynamics, including the sojourn expansion, and apply it to PSI. The robustness of the efficiency of the system is investigated under the effects of the fluctuations in chlorophyll site energies and the pruning of individual chlorophylls. In Sec. 6 we examine the opti-
mality of the arrangement of chlorophylls in PSI. Sec. 7 contains a general discussion and our conclusions. In an appendix we summarize our method to compute inter-chlorophyll couplings.

2 Effective Hamiltonian for chlorophyll aggregate

In this section we construct an effective Hamiltonian for the aggregate of chlorophyll molecules in PSI defined in a basis of single chlorophyll excitations. Isolated cyanobacterial PSI is known to exist \textit{in vivo} mostly as a trimer \cite{5}. In this paper we will examine the behavior of the monomeric complex. Of the 96 chlorophylls present in PSI, 95 are chlorophyll \textit{a} molecules and one of the special pair chlorophylls is a chlorophyll \textit{a’}. For computational simplicity, we will assume below all chlorophylls to be of chlorophyll \textit{a} type.

The lowest excited state of a chlorophyll molecule is the \textit{Q}$_y$ state \cite{23}. A set of basis states for an effective Hamiltonian is then given by

\begin{equation}
|i\rangle = |\phi_1 \phi_2 \cdots \phi_i^* \cdots \phi_N\rangle, \quad i = 1, 2, \ldots N,
\end{equation}

in which the \textit{i}th chlorophyll is \textit{Q}$_y$-excited, all the other chlorophylls being in their ground states. The total number of chlorophylls is \(N = 96\). By using this basis, an effective Hamiltonian can be written as

\begin{equation}
H_0 = \begin{pmatrix}
\epsilon_1 & W_{12} & W_{13} & \cdots & W_{1N} \\
W_{21} & \epsilon_2 & W_{23} & \cdots & W_{2N} \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
W_{N1} & W_{N2} & W_{N3} & \cdots & \epsilon_N
\end{pmatrix}.
\end{equation}

Here, \(\epsilon_i\) denotes the chlorophyll site energy for the \textit{Q}$_y$ state of the \textit{i}th chlorophyll, which needs to be determined later, and \(W_{ij}\) denotes the coupling between the \textit{i}th and the \textit{j}th chlorophylls.

The electronic coupling, \(W_{ij}\), between excited states of two chlorophyll molecules has two contributions

\begin{equation}
W_{ij} = W_{ij}^c + W_{ij}^{ex},
\end{equation}

where \(W_{ij}^c\) corresponds to a direct Coulomb term \cite{24} and \(W_{ij}^{ex}\) corresponds to an electron exchange term \cite{25}. In PSI, almost all of the chlorophylls are at a Mg-Mg distance of
greater than 7 Å, a range in which Coulomb interaction dominates \cite{26}; therefore we keep only the contribution of the direct Coulomb term, $W_{ij}^c$, in the remainder of the paper.

The electronic couplings due to the direct Coulomb interaction are calculated through two approaches. In the first (approximate) approach, the couplings are determined assuming a dipole-dipole interaction between transition dipole moments of the chlorophyll $Q_y$ states. In this approximation, the couplings are given by (see, for example, Ref. \cite{26})

$$W_{ij} = C \left( \frac{\mathbf{d}_i \cdot \mathbf{d}_j}{r_{ij}^3} - \frac{3(r_{ij} \cdot \mathbf{d}_i)(r_{ij} \cdot \mathbf{d}_j)}{r_{ij}^5} \right)$$

where $\mathbf{d}_i$ are unit vectors along transition dipole moments from the ground state to the $Q_y$ state of the $i$th chlorophyll and $r_{ij}$ is the vector connecting the Mg atoms of chlorophylls $i$ and $j$; the transition dipole moments for the $Q_y$ state are taken to be along the vector connecting the N$_B$ and N$_D$ atoms. The latter assumption is seen to be valid by comparing the transition dipole moment unit vectors thus computed to the ones obtained in the course of the full Coulomb semi-empirical method introduced below. The atomic positions are taken from crystallographic data \cite{5}. The parameter $C = 116000$ Å$^3$ cm$^{-1}$ in Eq. (4) is determined by enforcing asymptotic agreement at large distances with the full Coulomb couplings introduced below \cite{26}. Full Coulomb couplings in turn are fixed by the oscillator strength of the $Q_y$ transition, which is taken to be 23 Debye$^2$ \cite{27}. Since the transition dipole moment vectors are computed simply from geometry, application of Eq. (4) has a low computational cost. Naturally, the dipolar approximation is the more accurate, the larger the distance between the chlorophylls.

The second approach, following Ref. \cite{26}, computes electronic couplings using a semi-empirical Pariser-Parr-Pople (PPP) Hamiltonian as utilized in Refs. \cite{26, 28}. In this approach, the contribution of all orders of multipoles are included, i.e., not only the dipole-dipole contribution. Therefore, we will refer to this description as the full Coulomb (FC) approach. The details of this approach are outlined in the appendix.

In Fig. 2 are illustrated the first five eigenstates of the effective Hamiltonian (2) with full Coulomb couplings and identical site energies. Excitons are localized typically only over a few chlorophylls, in some cases coinciding with strongly coupled pairs.
3 Red chlorophyll candidates for photosystem I

A number of chlorophyll molecules in PSI of *S. elongatus* are known to absorb light at longer wavelengths than the special pair P700. The number of these ‘red chlorophylls’ is suggested to be between seven and eleven [29, 30]. In Ref. [30] individual absorption peaks for the red chlorophyll states were observed for 4 K at wavelengths 708 nm, 715 nm, and 719 nm. Among possible causes for this red shift in the absorption peak of these chlorophylls are the effect of the local protein environment on the site energies and the effect of excitonic splitting due to a strong coupling between pairs of chlorophylls.

In Ref. [5] candidates for the red chlorophylls were suggested based on the orientation of chlorophylls and the assumption of a strong excitonic splitting as the cause of the spectral red shift. In Ref. [30] a match between these candidates and the experimentally resolved red absorption peaks were suggested. In this section we extend this discussion by comparing the dipolar couplings with the corresponding full Coulomb couplings. In Ref. [5] a trimer (B31-B32-B33) and three dimers (A32-B7, B37-B38, A38-A39) of chlorophylls were given as red chlorophyll candidates (see Fig. [3] nomenclature of Ref. [5] is used for naming chlorophylls). Indeed in the framework of the dipolar couplings these chlorophylls form the strongest coupled pairs. However, in the framework of the full Coulomb couplings a different picture emerges. This may not be surprising as the two approaches tend to disagree over short distances, such as the inter-chlorophyll distances within strongly coupled pairs.

In the full Coulomb description the couplings of the chlorophyll pairs in the trimer B31-B32-B33 are significantly (more than a factor 3) smaller than their corresponding dipolar couplings. Since there are chlorophyll pairs with much stronger couplings in PSI, the trimer loses its position as a red chlorophyll candidate in the full Coulomb picture.

Furthermore, a strong coupling is not enough to cause a red shift in the absorption spectrum. Viewed as a two state system, a chlorophyll pair will have one higher energy excitonic state and one lower energy excitonic state, each with a certain oscillator strength. A red shift can be associated only with a case where the lower energy excitonic state has a higher oscillator strength than the higher energy excitonic state. Otherwise, there needs to be a significant shift in the chlorophyll site energies due to the protein environment to account for the red shift. It turns out that the two strongest coupled pairs, B37-B38 and
A38-A39, have most of their oscillator strength in the higher energy state. Therefore, we leave them out of the list of red chlorophyll candidates.

Four pairs of chlorophylls, which have the strongest couplings as well as the higher oscillator strength in the lower lying state, are suggested as red chlorophyll candidates (highlighted in Table I and Fig. 3). A match between the observed red absorption peaks and the suggested candidates cannot be done reliably without knowledge of the site energies. However, matching the furthest red shift with the strongest coupling we tentatively suggest that A32-B7 is responsible for the 719 nm absorption peak, A33-A34 and A24-A35 for the 715 nm peak, and B22-B34 for the 708 nm peak.

It must be noted that excitonic splitting alone cannot be the only cause for observed red shifts. For example, in case of two identical chlorophylls, which have their $Q_y$ absorption peaks at 675 nm, a coupling of about 900 cm$^{-1}$ would be needed to place the lower energy excitonic state at 719 nm. This suggests that the red chlorophyll states are caused by the contribution of both excitonic splitting and site energy shifts due to the local protein environment. Furthermore, any isolated chlorophyll may contribute to the red chlorophyll band of the PSI spectrum solely due to its site energy shift, a possibility which is totally neglected in our present picture.

The trimer of chlorophylls, B31-B32-B33, deserves a closer inspection than presented thus far. As seen in Fig. 4, the atomic structure indicates that the three chlorophylls are connected to each other by water molecules, suggesting that they might have to be treated computationally as a supermolecule. In regard to the possible failure of our description, we note that the His residue coordinating chlorophylls B31-B32-B33 is absent in Synechocystis, which exhibits a weaker long wavelength absorption band. Indeed, the close packing of chlorophylls B31-B32-B33 is reminiscent of J-aggregates [31], which are known to have red shifted spectra compared to the spectra of their building blocks. We may suggest, hence, that the chlorophylls B31-B32-B33 may yet be responsible for red absorption, despite the weak couplings emerging from our description.

4 Effect of thermal disorder on spectral properties

Spectral properties and excitation transfer dynamics of a photosynthetic system are two complementary sources of information. Both are determined by the Hamiltonian describ-
ing the system. However, the spectral properties are influenced more by chlorophyll site energies, i.e., the diagonal entries of the effective Hamiltonian, whereas the excitation transfer dynamics more directly reflects the role of inter-chlorophyll couplings.

A reconstruction of the (low temperature) absorption spectrum from the Hamiltonian is not possible without a knowledge of the site energies. This is seen, for example, in the much smaller seven chlorophyll system of the FMO complex \[32\]. Similarly the inverse problem of using the spectrum to reconstruct the site energies (assuming the couplings are known) is ill posed, since with as many parameters as the number of chlorophylls in the system one cannot unambiguously assign the site energies. Indeed it is a very important test for any calculation of the chlorophyll site energies to faithfully reproduce the experimentally observed absorption spectrum, especially at low temperatures.

Nevertheless spectral data can provide valuable information on the general distribution of chlorophyll site energies if not on individual sites. Therefore, we study the spectral properties of PSI in the light of the effective Hamiltonian introduced in Sec. 2, before we proceed with a detailed discussion of excitation transfer dynamics.

### 4.1 Random matrix theory as a description of thermal disorder

Both the spectral features and the excitation transfer dynamics in a photosynthetic system need to be described in the presence of strong thermal disorder. Standard zero-temperature quantum theory remains inadequate in this respect. Below we present a method, based on random matrix theory \[33, 34, 35\], to study static disorder in a system described by an effective Hamiltonian, such as the one given in Sec. 2. For a more detailed account of the application of random matrix theory to the description of static disorder in photosynthetic systems the reader is referred to Ref. \[36\]. For a discussion of dynamic disorder in a light-harvesting complex the reader is referred to Refs. \[37, 38\].

We consider an ensemble of Hamiltonians that describes a set of photosynthetic systems in thermal equilibrium. In contrast to a canonical ensemble from statistical mechanics, whose members are points in the phase space of one Hamiltonian, we consider an ensemble of Hamiltonians each of which represents another copy of the photosynthetic system in question. We will be interested in spectral properties as averaged over this ensemble.
For a description of this ensemble, we employ the sum of the noise-free effective Hamiltonian, $H_0$, based on the crystal structure, and a random part, $R$, representing thermal fluctuations

$$H = H_0 + R.$$  

(5)

Here the matrix $R$ is drawn from a certain probability distribution, $P(R)$, representing the effects of thermal disorder. All relevant spectral quantities are defined in terms of an ensemble average over the random part, $R$, with respect to the weight function, $P(R)$.

The density of states and the directionally averaged absorption spectrum for (5) are defined by

$$\rho(\omega) = \langle \sum_{i=1}^{N} \delta(\omega - E_i) \rangle,$$  

(6)

$$\alpha(\omega) = \frac{4\pi^2 \omega n}{3c} \langle \sum_i |D_i|^2 \delta(\omega - E_i) \rangle,$$  

(7)

where $< \ldots > \equiv \int d[R] P(R) \ldots$ and $E_i$ are the eigenvalues of $H = H_0 + R$. The transition dipole moments for eigenstates, $D_i = \sum_m c_i(m)d_m$, are given in terms of the transition dipole moment unit vectors of individual sites, $d_m$, and the expansion coefficients, $c_i(m)$, of eigenstates.

These definitions for the average spectral behavior are superior to the ‘Gaussians on sticks’ approach sometimes utilized, where Gaussian envelopes are put around the eigenvalues of $H_0$ to reconstruct the spectrum. Especially in cases where there is a significant overlap between the envelopes of multiple eigenvalues, the average spectral properties are seen to deviate significantly. As an extreme example one can consider a case of $N$ degenerate eigenvalues [34]. In this case a sum of Gaussian envelopes gives another Gaussian with the same width, whereas the width of the average spectrum should be proportional to $\sqrt{N}$.

The nature of the probability distribution, $P(R)$, as a function of temperature is not easy to determine. However, studies in random matrix theory have shown that many average spectral features are largely independent of the exact shape of $P(R)$ and instead depend mainly on its width [33]. This kind of independence from the specific probability distribution is akin to the central limit theorem and is known as random matrix univ-
sality. This universality allows one to make simplifying assumptions on the nature of \( P(R) \) [35].

 Although most results on random matrix universality are based on the limit where the matrix size becomes large, remarkable spectral similarity persists even for mesoscopically sized ensembles. In an earlier investigation, we have applied random matrix universality to the peripheral light-harvesting complex, LH2, of purple bacteria [36], which has 16 strongly coupled bacteriochlorophylls. It was seen that, when the width of the disorder term, \( P(R) \), is taken into account the average density of states and the absorption spectrum are rather insensitive to the changes of \( P(R) \). Analytical formulae for the density of states at finite temperature as a function of the zero temperature spectrum were derived for a simple form of \( P(R) \) in Ref. [36].

 In the following we take the probability distribution, \( P(R) \), to describe diagonal disorder

\[
P_{\text{diag}}(R) = N_{\text{diag}} \prod_i \exp \left( -\frac{1}{2\nu_{\text{diag}}^2} R_{ii}^2 \right) \prod_{i\neq j} \delta(R_{ij}).
\] (8)

For the width of the distribution (8) we take \( \nu_{\text{diag}} = 70 \text{ cm}^{-1} \) at 4 K [39, 40]. A similar description has been used in Ref. [10] for the light harvesting system of purple bacteria. We use the parameter \( \nu_{\text{diag}} \) to numerically evaluate the absorption spectrum as defined in (8). In Fig. [4] is shown the absorption spectrum at 4 K based on the effective Hamiltonian with full Coulomb couplings and homogeneous site energies corresponding to 675 nm. Ignoring the red chlorophyll band of the spectrum, a width for the bulk of about 230 cm\(^{-1}\) (corresponding to a FWHM of 550 cm\(^{-1}\)) at 4 K is reported in Ref. [30]. However, the width for the 4 K spectrum in Fig. [4] measures only about 140 cm\(^{-1}\). The mismatch can be attributed to our neglect of the site energy heterogeneity.

 Though it is not possible to reconstruct the chlorophyll site energies from the spectrum, one can obtain an estimate on the width of the distribution of site energies. In order to accomplish this we will ignore for the moment the red chlorophyll band of the spectrum and instead concentrate on the main peak as given in Ref. [30]. The width of the absorption spectrum for the actual (inhomogeneous) site energies, \( W_{\text{inhom}} \), the width of the absorption spectrum for the homogeneous site energies, \( W_{\text{hom}} \), and the width of the distribution of site energies (heterogeneity), \( W_e \), are approximately related to each other.
by

\[ W_{inhom}^2 = W_{hom}^2 + W_\epsilon^2. \] (9)

As discussed above, assuming \( W_{inhom} = 230 \text{ cm}^{-1} \) and \( W_{hom} = 140 \text{ cm}^{-1} \) results in a site energy distribution width of about \( W_\epsilon = 180 \text{ cm}^{-1} \) (FWHM of 430 cm\(^{-1}\)). The validity of this assertion can be numerically verified by generating an ensemble of Hamiltonians with the same full Coulomb couplings but with random site energies for the given value of \( W_\epsilon \). This value will be utilized later in the discussion of excitation transfer dynamics.

5 Excitation transfer dynamics in photosystem I

In this section we construct the excitation transfer rates between chlorophylls using Förster theory [24]. We will follow the methodology suggested in Ref. [41]. The excitation transfer rate from chlorophyll \( i \) to chlorophyll \( j \) is [24, 25]

\[ T_{ij} = \frac{2\pi}{\hbar}|H_{ij}|^2J_{ij}, \quad J_{ij} = \int S_i^D(E)S_j^A(E)dE, \] (10)

where \( H_{ij} \) is the coupling between the chlorophylls and \( J_{ij} \) is the spectral overlap between the emission spectrum, \( S_i^D(E) \), of the donor chlorophyll \( i \) and the absorption spectrum, \( S_j^A(E) \), of the acceptor chlorophyll \( j \). Following Refs. [42, 41] we approximate these spectra by Gaussians

\[ S_i^D(E) = \frac{1}{\sqrt{2\pi\nu}} \exp\left(-\frac{(E_i - S - E)^2}{2\nu^2}\right), \]

\[ S_j^A(E) = \frac{1}{\sqrt{2\pi\nu}} \exp\left(-\frac{(E_j - E)^2}{2\nu^2}\right), \] (11)

where \( E_i \) and \( E_j \) are the absorption peaks for the chlorophylls and \( S \) is the Stokes shift. We take the Stokes shift to be equal to \( 160 \text{ cm}^{-1} \) at room temperature [23] and \( 20 \text{ cm}^{-1} \) at 4 K [43]. We have assumed identical widths for the emission and absorption spectra of \( 240 \text{ cm}^{-1} \) at room temperature [23]. In the case of identical site energies, rates for forward transfer and back transfer are equal, \( T_{ij} = T_{ji} \), but this is not the case when the site energies differ. The network of excitation transfer rates between chlorophylls of PSI for identical site energies are shown in Fig. 6 for both the full Coulomb and dipolar Hamiltonians.
The largest transfer rate away from a given chlorophyll suggests the average excitation lifetime at that chlorophyll. Fig. 7 shows the largest excitation transfer rates for all 96 chlorophylls. It can be seen that these rates correspond to an average largest transfer rate between chlorophylls of about 11 ps$^{-1}$.

Using the transfer rates between the chlorophylls, a master equation can be constructed for the rate of change of probabilities, $p_i(t)$, describing the likelihood that the chlorophyll $i$ is electronically excited at time $t$. The corresponding rate equation is

$$\frac{d}{dt} p_i(t) = \sum_j K_{ij} p_j(t),$$

(12)

where $K_{ij}$ = $T_{ji} - \delta_{ij} \left( \sum_k T_{ik} + k_{\text{diss}} + \delta_{i,P700} k_{\text{CS}} \right)$,

(13)

where $k_{\text{diss}}$ denotes the dissipation (internal conversion) rate, which is assumed to be uniform among the chlorophylls, $k_{\text{CS}}$ denotes the charge separation rate at the special pair P700 and $\delta_{i,P700}$ is equal to 1 when $i$ is one of the two chlorophylls in the special pair and zero otherwise. The dissipation and charge separation rates are not known to great accuracy. Inspired by the purple bacterial light-harvesting systems \[41\] we assume a dissipation rate of $k_{\text{diss}} = (1 \text{ ns})^{-1}$. The charge separation rate at P700 is observed to be between 1 ps$^{-1}$ and (3 ps)$^{-1}$ \[44, 45, 46\]. In the following we will assume a charge separation rate of $k_{\text{CS}} = (1.5 \text{ ps})^{-1}$.

Given an initial distribution, $p_i(0)$, the formal solution to Eq. (12) can be written

$$|p(t)\rangle = \exp(Kt) |p(0)\rangle.$$

(14)

Using this expression, explicit formulae for the average excitation lifetime, the quantum yield, and overall dissipation rate can be given \[41\].

Let us define a uniform (non-normalized) state, $|1\rangle := \sum_i |i\rangle$, describing equally likely occupation probabilities for all chlorophylls. If we assume this uniform distribution for the initial state, i.e., $|p(0)\rangle = N^{-1}|1\rangle$, then the average excitation lifetime, $\tau$, the quantum yield, $q$, and the overall dissipation probability, $d$, are all given in terms of similar expressions \[41\]

$$\tau = -\frac{1}{N} \langle 1 | K^{-1} | 1 \rangle,$$

(15)

$$q = -\frac{1}{N} k_{\text{CS}} \langle P700 | K^{-1} | 1 \rangle = 1 - d,$$

(16)
where $|P700\rangle \equiv \sum_i \delta_{i,P700} |i\rangle$.

Average excitation lifetimes and the quantum yields for various models are provided in Table 2. The data in the first three rows are based on an effective Hamiltonian that assumes identical site energies for the two chlorophylls of the P700 pair. The site energies were chosen such that the P700 excitonic state with the highest oscillator strength coincides with the 698 nm (14327 cm$^{-1}$) absorption peak at 4 K. Since one of the two P700 chlorophylls is a chlorophyll $a'$, the identical site energy assumption for the P700 is likely to be unrealistic, however it shall be adequate for an approximate description of the excitation transfer dynamics. For full Coulomb couplings the highest oscillator strength lies at the higher energy excitonic state (see Table 1); since the respective coupling between the two P700 chlorophylls is 47.6 cm$^{-1}$, the P700 site energy is chosen to be 14279 cm$^{-1}$. For dipolar couplings the highest oscillator strength lies at the lower energy excitonic state (the sign of the coupling is different for the two methods); the coupling between the two P700 chlorophylls is 272 cm$^{-1}$ requiring a P700 site energy of 14599 cm$^{-1}$. The site energies for the remaining chlorophylls are placed at 675 nm (14815 cm$^{-1}$) unless otherwise noted.

The efficiency of 97.3 % and the average excitation lifetime of 27.4 ps for full Coulomb couplings, given in the first row of Table 2, are in general agreement with the near unit efficiency and the 20-40 ps lifetime reported for PSI at room temperature [2, 47, 48, 49, 50, 51]. A recent estimate of the average excitation lifetime reported for trimeric PSI in S. elongatus is 35.8 ps [47]. A comparison between the first and the last rows in Table 1 shows the importance of having P700 chlorophylls at a lower energy than the bulk of the chlorophylls in order to decrease the trapping time and to increase efficiency.

In Fig. 8 are provided the distribution of quantum yield and average excitation lifetime across an ensemble of Hamiltonians with full Coulomb couplings, P700 tuned to the observed absorption peak, and all other chlorophyll site energies randomly distributed with a width of 180 cm$^{-1}$ around 675 nm (thus the ensemble covers different realizations of heterogeneity, not static disorder). Fig. 8 reveals that, at room temperature, fluctuations in the site energies (heterogeneity) have no considerable effect on efficiency. This allows us to reconstruct room temperature excitation transfer dynamics with reasonable accuracy.
even without detailed knowledge of the chlorophyll site energies. However, at 4 K, the line shapes of individual chlorophylls become so narrow that the spectral overlap integrals in Eq. (10) become unrealistically small for misplaced site energies. Also at low temperatures the broadening of spectral line shapes due to electron-phonon couplings need to be taken into account as this broadening is likely to effect the overlap integrals in the context of Förster theory. We find it impossible to construct a reliable picture of the low temperature excitation transfer dynamics with the current data.

It is of interest to know in how far low energy chlorophylls control the excitation transfer dynamics and trapping in PSI. In this regard, one may construct models in which the red chlorophyll candidates given in Sec. 3 are used to refine the assignment of chlorophyll site energies. However, it must be kept in mind that an accurate assignment of an individual chlorophyll pair to an observed red chlorophyll state cannot be done reliably without a precise knowledge of site energies. It is seen that the room temperature excitation transfer dynamics is not effected greatly by the inclusion of this extra information in a model where all other site energies are unknown or taken to be random. Fig. 8 supports this claim. As a result we find it rather unfruitful to proliferate the multitude of models already given in Table 2. At room temperature the role of low energy chlorophylls appear to be simply to extend the absorption profile to longer wavelengths rather than to have a profound effect on the excitation transfer dynamics. However, at low temperatures red chlorophylls may function as effective traps and could serve as probes to investigate the excitation transfer dynamics of PSI in detail.

5.1 Effect of removal of individual chlorophylls on excitation transfer dynamics

One way to probe the function of individual chlorophylls in PSI as well as the degree of robustness in its design is to examine the effect of the removal of chlorophylls on the efficiency of the system. To this end we remove various chlorophylls one at a time and examine the quantum yield of the remaining system.

Fig. 9 shows the quantum yield as a function of the removed chlorophyll. The two P700 chlorophylls are not removed in this study. Although the effect of the removal of the other four reaction center chlorophylls on the quantum yield are shown, it is hard to test
their effect directly, since they are also a part of the electron transfer chain. Therefore, we will concentrate on the remaining 90 chlorophylls.

It is interesting to note that, except for the four reaction center chlorophylls which are immediate neighbors to the P700, removal of a chlorophyll hardly has any effect on the quantum yield. In fact, for most of the chlorophylls a deletion results in an increase in the quantum yield. This is a consequence of the relative yield being defined with respect to the remaining chlorophylls, not with respect to the unperturbed system.

Thus it is seen that, outside the reaction center, no chlorophylls play the role of a gatekeeper for excitation transfer, whose removal would have an adverse effect on the yield. Instead the individual chlorophylls contribute to the overall cross-section of the antenna complex. Outside the electron transfer chain, the four chlorophylls with the highest impact on efficiency (A26, B24, B39 and A40) are the nearest neighbors of the six reaction center chlorophylls. These chlorophylls, especially A40 and B39, appear to link the antenna system to the reaction center and are therefore referred to as connecting chlorophylls. As an extreme example one may consider the removal of all four of these chlorophylls simultaneously. Even in this case the quantum yield reduces to only 96.85 % from the value of 97.25 % for the unperturbed complex with the same Hamiltonian; the average excitation lifetime increases from 27.4 ps to 31.5 ps upon removal. These results agree with some of the simulations reported in Ref. [52].

5.2 An expansion of the average lifetime in terms of return times to the reaction center

The average excitation lifetime, \( \tau \), can be expanded in terms of processes describing the initial delivery of excitation to the special pair and possible subsequent returns following detrapping. In order to establish such an expansion, we rewrite the excitation transfer rates (12) in a form where the P700 is treated as a single excitonically coupled unit as opposed to two separate chlorophylls.

A two state Hamiltonian for P700 is given by

\[
H_{P700} = \begin{pmatrix} \epsilon_1 & U_{P700} \\ U_{P700} & \epsilon_2 \end{pmatrix},
\]  

(18)

where \( \epsilon_1 \) and \( \epsilon_2 \) are the site energies for the two P700 chlorophylls and \( U_{P700} \) denotes the coupling between them. Not knowing the values of the site energies it will be assumed
below that $\epsilon_1 = \epsilon_2$. However, the expansion below can be readily applied to nonidentical site energies.

Let us denote the eigenvalues of the two state system (18) by $E_1$ and $E_2$ and the corresponding eigenfunctions by

$$
\Psi_{P700}^1 = c_{1,1} |1\rangle + c_{1,2} |2\rangle,
$$

$$
\Psi_{P700}^2 = c_{2,1} |1\rangle + c_{2,2} |2\rangle,
$$

respectively. Then the coupling of any of the other chlorophylls, $j = 3, \ldots, N$, to any eigenstate, $m = 1, 2$, of P700 is

$$
\tilde{H}_{mj} = \tilde{H}_{jm} = \sum_{\alpha=1}^{2} c_{m,\alpha} H_{j\alpha},
$$

where $H_{j\alpha}$ are the elements of the original effective Hamiltonian (2).

We will assume that thermal equilibration between eigenstates of P700 have been achieved before excitation transfer out of P700 occurs. This is likely to be a reasonable assumption at room temperature for full Coulomb couplings, where $k_B T = 209 \text{ cm}^{-1}$ is larger than the interchlorophyll couplings. The expansion outlined below can also be formulated for a reaction center where multiple chlorophylls without a strong excitonic character are responsible for charge separation, making the thermal equilibration assumption invalid. However, in that case the final formulation of the expansion cannot be written as succinctly as Eq. (31) below.

The excitation transfer from P700 to any other chlorophyll is given by a Boltzmann weighted sum

$$
\tilde{T}_{P700,j} = \sum_{m=1}^{2} \tilde{T}_{mj},
$$

$$
\tilde{T}_{mj} = \frac{2\pi}{\hbar} \sum_{n=1}^{2} e^{-E_n/k_B T} |\tilde{H}_{mj}|^2 \int S_m^D(E) S_j^A(E) dE,
$$

where we assume an identical line shape for the eigenstates of P700, chosen equal to the lineshape of all other chlorophylls in PSI. The excitation transfer rate from another chlorophyll to P700 is

$$
\tilde{T}_{j,P700} = \sum_{m=1}^{2} T_{j,m},
$$
where $T_{j,m}$ are given by Eq. (10), except that $m = 1, 2$ now denotes an eigenstate of P700 as given in Eq. (19).

A reduced $(N - 1) \times (N - 1)$ transfer rate matrix, $\tilde{T}$, can be constructed using these rates. The corresponding matrix, $\tilde{K}$, that enters in Eq. (12) governing the kinetics of PSI, is

$$
\tilde{K}_{ij} = \tilde{T}_{ji} - \delta_{ij} \left( \sum_k \tilde{T}_{ik} + k_{\text{diss}} + \delta_{i,P700} k_{CS} \right).
$$

(23)

Average excitation lifetime, $\tau$, and quantum yield of the system are defined as in Eqs. (15) and (16), e.g.,

$$
\tau = -\frac{1}{N-1} \langle 1 | \tilde{K}^{-1} | 1 \rangle,
$$

(24)

where $|1\rangle = |P700\rangle + \sum_{j=3}^{N} |j\rangle$ denotes the (nonnormalized) uniform initial state (in the basis of this reduced Hamiltonian $|P700\rangle$ denotes the vector with a one in the first column and zeroes everywhere else).

We introduce now the expansion of the average excitation lifetime. The terms that arise in this expansion are introduced and explained in Fig. 10. For the purpose of this expansion we separate from $\tilde{K}$ the operator, $\Delta$, that describes detrapping

$$
\tilde{K} \equiv \kappa + \Delta,
$$

$$
\Delta \equiv \begin{pmatrix}
0 & 0 & \cdots & 0 \\
\tilde{T}_{P700,3} & 0 & \cdots & 0 \\
\tilde{T}_{P700,4} & 0 & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots \\
\tilde{T}_{P700,N} & 0 & \cdots & 0
\end{pmatrix}.
$$

(25)

The inverse, $\tilde{K}^{-1}$, that enters in Eq. (24), can be expressed through Taylor expansion in $\Delta$

$$
\tilde{K}^{-1} = (\kappa + \Delta)^{-1} = \left(1 + \kappa^{-1} \Delta\right)^{-1} \kappa^{-1}
$$

$$
= \kappa^{-1} - \kappa^{-1} \Delta \kappa^{-1} + \kappa^{-1} \Delta \kappa^{-1} \Delta \kappa^{-1} - \cdots
$$

(26)

where $\mathbf{1}$ is the $(N - 1) \times (N - 1)$ identity matrix. The validity of this expansion can be proven by noting that the absolute value of the eigenvalues of $\kappa^{-1} \Delta$ are less than one.
Substituting this expansion into Eq. (24) results in a decomposition of the lifetime into a series

$$\tau \equiv \tau_0 + \tau_1 + \tau_2 + \cdots,$$

where

$$\begin{align*}
\tau_0 &= -\frac{1}{N-1} \langle 1 | \kappa^{-1} | 1 \rangle, \\
\tau_1 &= +\frac{1}{N-1} \langle 1 | \kappa^{-1} \Delta \kappa^{-1} | 1 \rangle, \\
\tau_2 &= -\frac{1}{N-1} \langle 1 | \kappa^{-1} \Delta \kappa^{-1} \Delta \kappa^{-1} | 1 \rangle, \\
&\vdots
\end{align*}$$

(28)

One can simplify Eq. (28) by noting that $\Delta$ can be expressed as $\Delta = W_D |T\rangle \langle P700|$ where $W_D = \sum_{j=3}^{N} T_{P700,j}$ is the total detrapping rate from the special pair, P700, and where $|T\rangle = W_D^{-1} \sum_{j=3}^{N} T_{P700,j} |j\rangle$ is a transient state representing the occupation probabilities right after a detrapping event has occurred. Substituting $\Delta$, thus factored, into Eq. (28) the expansion terms for the average excitation lifetime can be written

$$\begin{align*}
\tau_1 &= q_1 \tau_{soj}, \\
\tau_2 &= q_1 q_T \tau_{soj}, \\
\tau_3 &= q_1 q_T^2 \tau_{soj}, \\
&\vdots
\end{align*}$$

(29)

where the defining parameters are

$$\begin{align*}
\tau_{soj} &= -\langle 1 | \kappa^{-1} | T \rangle, \\
q_1 &= -\frac{W_D}{N-1} \langle P700 | \kappa^{-1} | 1 \rangle, \\
q_T &= -W_D \langle P700 | \kappa^{-1} | T \rangle.
\end{align*}$$

(30)

The terms appearing in Eq. (29) can be summed to give

$$\tau = \tau_0 + \frac{q_1}{1 - q_T} \tau_{soj}.$$  

(31)

The expansion decomposes the average excitation lifetime in terms of multiple escapes and returns (sojourns) to the reaction center, and hence, we call it the sojourn expansion.
Terms arising in the sojourn expansion for an effective Hamiltonian with full Coulomb couplings (see row 1 of Table 2) is provided in Table 3. It can be seen that the time for a first delivery of excitation to P700, approximately given by $\tau_0$, constitutes less than half of the average excitation lifetime at room temperature.

6 How optimal is the design of photosystem I?

At first glance the arrangement of chlorophylls in PSI appear to be random except for a pseudo-$C_2$ symmetry (see Fig. 1). Especially when compared to the regular circular aggregates found in purple bacterial photosynthetic systems, this brings up the question of whether the particular arrangement of chlorophylls in PSI is optimal in some way.

Even though the fitness landscape over which a photosynthetic apparatus should be judged is many dimensional, a crude measure of optimality is given by the quantum yield of the system. Ignoring all other concerns for optimality from an evolutionary perspective such as assembly, aggregation and interaction with other biomolecules in the cell, we examine whether the chlorophyll aggregate in PSI can be rearranged to result in a better quantum yield.

In order to keep the number of parameters to be varied at a manageable level, the chlorophyll positions (as defined by their Mg atoms) as well as the chlorophyll site energies are kept fixed. Instead we consider an ensemble of alternate PSI’s formed by random independent reorientations of constituent chlorophylls.

It is costly to repeat the semi-empirical computation of full Coulomb couplings between chlorophylls for a large ensemble of chlorophyll arrangements. Therefore, we revert to dipolar couplings for this study. The ensemble in question is formed by taking the vector for the transition dipole moment at each chlorophyll and multiplying it by a randomly generated $SO(3)$ rotation matrix, thus reorienting it. A new effective Hamiltonian is then computed using the couplings between these new transition dipole moment vectors as explained in Sec. 2, while keeping the same site energies as before. The effective Hamiltonians thus generated are used to compute the quantum yield and the average excitation lifetime at room temperature. For this study identical site energies (675 nm) for all chlorophylls are chosen except for P700, the site energies of which are chosen in such a way as to coincide with the observed absorption peak, as explained in Sec. 5.
Therefore the results of this study should be compared with the original arrangement of chlorophylls given in row 2 of Table 2.

Fig. 11 contains a histogram of quantum yields and average excitation lifetimes for this ensemble at room temperature. The values for the original arrangement of chlorophylls are indicated by an arrow. It is seen that the original chlorophyll arrangement is nearly at the top of the distribution, though a few arrangements can be found to have a better quantum yield. It does not necessarily imply, however, that the efficiency of PSI can be easily improved upon. Not only is the study of quantum yields outlined above approximate in nature, but also there is no way to accurately model the constraints which had to be satisfied over the course of the evolution of this system. Nevertheless, it is impressive to find the original chlorophyll arrangement at near top efficiency.

The relatively small variation in the quantum yield across the ensemble seen in Fig. 11 brings up the question as to whether the apparent optimality is an artifact that will disappear in a more accurate computation. This small variation is a result of the nearly three orders of magnitude difference between the dissipation and charge transfer rates. As an ultimate test, full Coulomb couplings need to be computed for each system in an ensemble of randomly oriented chlorophyll aggregates and the effect of individual site energies also need to be taken into account. This is beyond the scope of this study due to prohibitively high computational costs. Nevertheless, as a consistency check, the ensemble described in Fig. 11 may be replaced by one with an alternate (random) set of site energies. It is seen that at room temperature the result of near optimal efficiency changes little under an assumption of different site energies (not shown). This is because the transfer rates at room temperature are influenced more strongly by couplings than by site energies, unless site energy variations are large enough to be comparable to the spectral width of individual chlorophylls (see Eq. 11). Also, the similarity between the networks of excitation transfer pathways for dipolar and full Coulomb couplings seen in Fig. 8 seems to suggest that the general properties of excitation transfer dynamics and therefore also the optimality will not be greatly effected by going from the dipolar to the full Coulomb couplings.
7 Conclusion

The availability of a high resolution structure of the cyanobacterial photosystem I provides new opportunities to investigate the mechanism of light harvesting in this large pigment-protein complex. In this study, the excitation transfer dynamics at room temperature has been examined starting from an effective Hamiltonian based on interactions between chlorophylls.

As a first approximation the effect of chlorophyll-protein interactions on the site energies has been ignored. However, we have used the available spectral data to construct a more refined Hamiltonian with limited information on site energies. Also, a prediction on the overall heterogeneity of site energies is made.

The calculated quantum yield and average excitation lifetime at room temperature compare favorably with experimental results. The sojourn expansion method resolves details of excitation migration in PSI, namely repeated approaches to and escapes from the reaction center. Studying an ensemble of Hamiltonians corresponding to copies of PSI with varying site energies, it is seen that the yield and the lifetime are influenced largely by inter-chlorophyll couplings and not so much by fluctuations of the site energies at room temperature. The sojourn expansion reveals that the time for a first delivery of excitation to P700 contributes less than half of the average excitation lifetime. At room temperature, about two thirds of the lifetime results from detrapping events.

However, the low temperature behavior of PSI is more difficult to describe accurately than the room temperature behaviour. Not only is the low temperature absorption spectrum impossible to reproduce without a knowledge of chlorophyll site energies, but also overlap integrals contributing to the excitation transfer rates become much more sensitive to the difference between the donor and the acceptor site energies due to the smaller linewidths at low temperatures. Furthermore, the broadening of lineshapes due to electron-phonon couplings also need to be carefully taken into account at low temperatures as this effect may have a significant impact on the overlap integrals in the framework of Förster theory. Ignoring these contributions results in an unrealistic picture of excitation transfer dynamics at low temperature.

The robustness and optimality of the chlorophyll arrangement in PSI has been examined by means of various computational experiments. On the one hand, it is seen that
the efficiency of the chlorophyll network of PSI is robust against perturbations such as 
the pruning of individual chlorophylls or fluctuations of chlorophyll site energies. On the 
other hand, a study of an ensemble of alternate PSI’s with randomly reoriented chloro-
phyll aggregates shows that the original arrangement actually has a near optimal quantum 
yield.

Note added in revision

After submission of this paper we have been informed of a recent calculation of chlorophyll 
site energies for cyanobacterial PSI [59]. When these site energy values are substituted 
in the computations outlined above we obtain at room temperature an average excitation 
lifetime of 33.9 ps and a quantum yield of 96.6 %, which compare favorably with the results 
given in this paper. The overall width of the distribution of site energies, including the 
red chlorophylls and P700, is around 260 cm$^{-1}$, which is larger than the estimate made 
in this paper of 180 cm$^{-1}$ based on the bulk of the low temperature spectrum. These new 
results support our suggestion that the room temperature excitation transfer dynamics 
of PSI can be described well without detailed knowledge of site energies. Repeating the 
optimality study discussed in section 6 also for the set of site energies in Ref. [59] yields 
results similar to those shown in Fig. [11].

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A Full Coulomb computation of inter-chlorophyll couplings

Here we outline the method employed to compute the electronic couplings, $W_{\alpha\beta}$, between 
two chlorophylls semi-empirically. This section follows Ref. [26] to which the reader is 
referred for a more detailed treatment.
The electronic coupling between a donor and an acceptor molecule can be written

\[ W_{\alpha\beta} = \sum_{i,j \in I_D} \sum_{R,S \in I_A} C^c_{ij,RS} \times \langle \psi^{*\alpha}_i | 00 O^j_R | \psi_\alpha \rangle \times \langle \psi_\beta | 00 O^R_S | \psi^{*\beta}_j \rangle, \]  

(32)

where \( I_D \) and \( I_A \) denote the set of atomic orbital indices of the donor and acceptor chlorophylls, and \( C^c_{ij,RS} \) describe the Coulomb integrals involving atomic orbitals labeled by \( i, j, R \) and \( S \). The spin tensors \( 00 O^j_R \) and \( 00 O^R_S \) prompt the intramolecular transitions \( |\psi_\alpha\rangle \rightarrow |\psi^{*\alpha}_i\rangle \) and \( |\psi^{*\beta}_j\rangle \rightarrow |\psi_\beta\rangle \). The Coulomb interaction has zero rank, as denoted by the 00 superscript. Therefore it only proceeds through singlet-singlet transitions. The Coulomb integral \( C^c_{ij,RS} \) can be approximated \[42\] as

\[ S_{ij} \cdot \frac{e^2}{R_{ij,RS}} \cdot S_{RS}, \]

where \( S_{ij} \) and \( S_{RS} \) are the atomic-orbital overlap integrals, and \( R_{ij,RS} \) is the distance between the midpoint of atoms \( i \) and \( j \) and the midpoint of the atoms \( R \) and \( S \). As suggested in \[53\], \( S_{ij} \) is taken to be 1 when \( i = j \), 0.27 when atoms \( i \) and \( j \) are joined by a chemical bond, and zero otherwise.

To evaluate the transition density matrix elements, one requires the description of the chlorophyll electronic states involved in the excitation transfer process. We choose a semi-empirical description for the chlorophyll electronic states as provided by the Pariser-Parr-Pople (PPP) Hamiltonian \[54, 55\], which has been used earlier in \[26, 28\]. The PPP Hamiltonian

\[ H_{PPP} = \sum_{i < j} Z_i Z_j R_{ij} + \sum_{i,\sigma} \left( -I_i - \sum_{j \neq i} Z_j R_{ij} \right) n_{i\sigma} + \sum_{i \neq j,\sigma} t_{ij} c^+_i c_j + \frac{1}{2} \sum_{i,j,\sigma,\delta} R_{ij} n_{i\sigma} n_{j\delta}, \]  

(33)

involves orbitals of \( \pi \)-type only. The creation and annihilation operators, \( c^+_i \) and \( c_j \), act on mutually orthogonal atomic \( \pi \)-orbitals. The corresponding number operator is given by \( n_{i\sigma} = c^+_i c_i \). \( R_{ij} \) is the effective electron-electron repulsion integral between an electron in atomic obital at site \( i \) and one in orbital at site \( j \) and \( t_{ij} \) denotes the resonance integral between atoms \( i \) and \( j \). \( I_i \) is the effective ionization potential of an orbital at site \( i \). \( Z_i \) is the net charge of the core at atom \( i \) which was chosen to be 1. The resonance integral, \( t_{\alpha\beta} \), is evaluated according to the empirical formula \[56\]

\[ t_{\alpha\beta} = \gamma_0 + 3.21(r_{ij} - 1.397\AA), \]  

(34)

where \( \gamma_0 \) is a constant and \( r_{ij} \) is the distance between the nuclear sites \( i \) and \( j \). The
effective electron-electron repulsion integral, $R_{ij}$, is calculated through the Ohno formula \[57, 58\],

$$R_{ij} = 14.397 \text{ eV} \left[ \left( \frac{2 \times 14.397 \text{ eV}}{R_{ii} + R_{jj}} \right)^2 + \frac{r_{ij}^2}{\AA^2} \right]^{-\frac{1}{2}}. \quad (35)$$

Assuming the same values of the semiempirical parameters as in Ref. \[26\] (listed in Table 4), we perform a SCF-CI calculation, including all single excited $\pi$-orbitals, for the singlet states of a chlorophyll.

The chlorophyll electronic structure calculations are based on geometries of a simplified chlorophyll analog, displayed in Fig. 12 (solid line). In this analog, the double bond of ring II (dotted line in Fig. 12) is taken out. Thus the chlorophyll is almost symmetric about the magnesium atom except that there is a carbon atom at one end and an oxygen atom at the opposite end. For the calculations performed on the analog structure, the $Q_x$ and $Q_y$ states are easy to identify. However, for the calculations based on the real chlorophyll structure, where the electronic states are mixed, this identification is difficult. A fully symmetric analog, with both oxygen atoms at the end, was also proposed in \[28\] based on the same consideration and the error arising from the simplified chlorophyll analog was shown to be insignificant compared to the systematic errors.

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Figure 1: Photosystem I of the cyanobacterium *Synechococcus elongatus* and its 96 chlorophylls. The special pair P700 is shown in blue. The remaining four reaction center chlorophylls are shown in red. For clarity, neither the chlorophyll tails nor other cofactors are shown. The chlorophyll pool surrounding the reaction center displays a pseudo-$C_2$ symmetry. Figure produced with VMD [22].
Figure 2: Excitonic (de)localization in PSI. The first five eigenstates of the effective Hamiltonian with full Coulomb couplings and identical site energies are shown. The radius of the sphere around a chlorophyll is proportional to its occupation probability in the respective state. Excitons are delocalized typically over no more than a few chlorophylls. Figure produced with VMD [22].
Figure 3: Red chlorophyll candidates. Chlorophylls suggested to be engaged in red absorption are highlighted in red. Red chlorophyll candidates are chosen to be the four chlorophyll pairs, which exhibit the strongest couplings in the full Coulomb description as well as a higher oscillator strength in the lower lying excitonic state. In yellow are shown chlorophyll pairs with strong couplings in the dipolar approximation that are suggested to be not responsible for the red absorption in the full Coulomb description (see also text, Table 1 and Fig. 4). Figure produced with VMD [22].
Figure 4: Chlorophyll trimer B31-B32-B33. Shown are these three closely spaced chlorophylls connected by two water molecules and coordinated by a His residue. The structure suggests that the trimer be described as a supermolecule. Figure produced with VMD [22].
Figure 5: Absorption spectrum. Shown is the low temperature (4 K) spectrum for an effective Hamiltonian with full Coulomb couplings and homogeneous site energies (675 nm). The spectrum is generated for an ensemble with diagonal disorder corresponding to 70 cm$^{-1}$. A comparison of the width of this spectrum with that of the experimental absorption spectrum [30] allows the prediction of the heterogeneity in the site energies.
Figure 6: Network of excitation transfer pathways in PSI. The networks at room temperature for full Coulomb couplings (top) and dipolar couplings (bottom) are shown. The thickness of bonds connecting chlorophylls are proportional to the transfer rates between them. Only the 130 largest transfer rates are presented. The transfer rates are computed for a system with identical site energies at room temperature. Figure produced with VMD [22].
Figure 7: Largest excitation transfer rate from PSI chlorophylls. Shown are rates for all 96 PS1 chlorophylls as a function of the donor chlorophyll. The horizontal line indicates the average value of 11.1 ps$^{-1}$. The excitation transfer rates are computed for a Hamiltonian with full Coulomb couplings and homogeneous site energies for all chlorophylls, except P700 (c.f. row 1, Table 2).
Figure 8: Effect of fluctuations of the site energies (heterogeneity) on excitation transfer dynamics. Shown are the distributions of quantum yield and lifetime at room temperature for an ensemble of effective Hamiltonians with full Coulomb couplings. The ensemble consists of systems where P700 was tuned to the observed absorption peak and with the rest of the chlorophyll site energies chosen randomly with a width of 180 cm$^{-1}$ around 675 nm. The histograms were generated from an ensemble of 1000 systems.
Figure 9: Quantum yield for pruned chlorophylls. Shown is the quantum yield resulting after pruning of individual chlorophylls. The chlorophylls whose deletion has the highest impact on quantum yield are labeled. Chlorophylls (eC-xx), numbered 3 to 6, are part of the reaction center. Chlorophylls A26, A40, B24, and B39 are connecting chlorophylls situated closest to the reaction center (see inset). The horizontal line denotes the efficiency of the unperturbed system (97.25 %), which is described by the effective Hamiltonian with full Coulomb couplings, identical site energies, and P700 tuned to the observed absorption spectrum (c.f. row 1, Table 2).
Figure 10: Processes contributing to the overall excitation lifetime. The excitation in a uniform initial state $|1\rangle$ (see text) after reaching the special pair $|P_{700}\rangle$ either causes a charge separation (CS) or, with detrapping probability $q_1$, returns to the surrounding chlorophylls through the transient state $|T\rangle$ (see text). From the transient state excitation migrates through PSI to return to $|P_{700}\rangle$ after which charge separation occurs or, again with detrapping probability, $q_T$, the transient state $|T\rangle$ is reached once more. The process of migration, return to $|P_{700}\rangle$, possibly charge separation or renewed detrapping is repeated. The first usage time, $\tau_0$, is the sum of the delivery-to-trap time starting from a uniform state, $|1\rangle$ and of the charge separation time. $\tau_0$ represents the average time it takes for charge separation to take place if no detrapping events occur. The sojourn time, $\tau_{soj}$, is the sum of the delivery-to-trap time starting from the transient state, $|T\rangle$ and of the charge separation time. After subtracting the charge separation time, $\tau_{soj}$ may be viewed as the return time back to P700 after a detrapping event. Dissipation processes are not shown.
Figure 11: Optimality of PSI. The distributions of quantum yield and average excitation lifetime for an ensemble of randomly generated chlorophyll aggregates at room temperature are shown. Chlorophyll couplings are computed in the dipolar approximation to reduce computational cost. P700 site energies are tuned to the observed absorption peak and the remaining site energies are taken to be identical (675 nm). The histograms are generated from an ensemble of 1000 systems. The results for the original arrangement (c.f. row 2, Table 2) of chlorophylls are indicated by an arrow.
Figure 12: Schematic representation of the conjugated double bonds of the chlorophyll analog (in solid line) used in the calculations of the couplings. Part of ring II (dotted line) has been removed from the structure (see text).
Table 1: Key chlorophyll pairs in PSI and their couplings. Pairs shown in boldface are the suggested red chlorophyll candidates according to the excitonic splittings computed in the full Coulomb picture (see text for details). FC: full Coulomb couplings, DP: dipolar couplings, $O_{lo}/O_{hi}$: ratio of oscillator strengths for the lower and higher excitonic states for full Coulomb couplings. The couplings are given in units of cm$^{-1}$. The pair ecA1-ecB1 is the special pair P700. Note that the dipolar approximation generally overestimates the value of the coupling at short distances. The parentheses around the full Coulomb couplings for the special pair and the trimer B31-B32-B33 indicate that these chlorophyll groups might have to be treated as supermolecules, making the full Coulomb description inaccurate (see text and Fig. [4]).

| chlorophyll pair | $|H_{ij}|$ (FC) | $|H_{ij}|$ (DP) | $O_{lo}/O_{hi}$ |
|------------------|----------------|----------------|----------------|
| B37-B38          | 179            | 242            | 0.225          |
| A38-A39          | 162            | 199            | 0.171          |
| A32-B7           | 161            | 255            | 10.6           |
| A33-A34          | 153            | 193            | 14.3           |
| A24-A35          | 131            | 88.6           | 3.69           |
| B22-B34          | 127            | 92.6           | 3.50           |
| ecA1-ecB1        | (47.6)         | 272            | 0.31           |
| B31-B32          | (88.8)         | 301            | 191            |
| B32-B33          | (55.5)         | 276            | 75.9           |
Table 2: Average excitation lifetime and quantum yield. *Model A*: Full Coulomb couplings with P700 tuned (see text) to the observed absorption peak and with identical site energies (675 nm) for the chlorophyll pool. *Model B*: Dipole-dipole couplings with P700 tuned to the observed absorption peak and with identical site energies (675 nm) for the chlorophyll pool. (The difference in lifetimes for models A and B are mainly due to the difference of site energy assignments for P700 for dipolar and full Coulomb models.) *Model C*: Full Coulomb couplings with P700 tuned to the observed absorption peak, but with random site energies (centered around 675 nm with a width of 180 cm$^{-1}$) for the chlorophyll pool. (Ensemble average value is given here. For more detail see Fig. 8.) *Model D*: Full Coulomb couplings with identical site energies (675 nm) for all chlorophylls, including P700.

| model | lifetime (ps) | quantum yield |
|-------|--------------|---------------|
| A     | 27.4         | 97.3 %        |
| B     | 45.9         | 95.4 %        |
| C     | 28.8         | 97.1 %        |
| D     | 75.3         | 92.5 %        |
Table 3: Characteristics of sojourn expansion. The quantities given (for definition see Fig. 10 and Eq. (31)) have been evaluated for the effective Hamiltonian with full Coulomb couplings and adjusted P700 site energies (row 1, Table 2).

| $\tau$  | $\tau_0$ | $\tau_{soj}$ | $q_1$    | $q_T$    |
|---------|---------|-------------|--------|--------|
| 27.6 ps | 11.8 ps | 4.55 ps     | 77.2 % | 77.8 % |
Table 4: Semiempirical parameters of the PPP Hamiltonian as defined in expressions (33), (34), and (35).

|                | Carbon(C)          | Oxygen(O)          | Nitrogen(N)         |
|----------------|--------------------|--------------------|---------------------|
| $I_k$          | 11.16 eV           | $I_k$ = 17.70 eV   | $I_k$ = 14.12 eV    |
| $R_{kk}$       | 11.13 eV           | $R_{kk}$ = 15.23 eV| $R_{kk}$ = 12.34 eV |
| $\gamma_0$    |                    |                    |                     |
|                | $\gamma_0$ = -2.43 eV |                    |                     |
|                | $Z_k$ = 1.0        |                    |                     |
| $r_{k,k\pm1}$ |                    | 1.35 Å (double bonds) |                     |
|                |                    | 1.46 Å (single bonds) |                     |