The Quantum Physics of Photosynthesis

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Abstract

Biological cells contain nanoscale machineries that exhibit a unique combination of high efficiency, high adaptability to changing environmental conditions, and high reliability. Recent progress in obtaining atomic resolution structures provide an opportunity for an atomic level explanation of the biological function of cellular machineries and the underlying physical mechanisms. A prime example in this regard is the apparatus with which purple bacteria harvest the light of the sun. Its highly symmetrical architecture and close interplay of biological functionality with quantum physical processes allow an illuminating demonstration of the fact that properties of living beings ultimately rely on and are determined by the laws of physics.

Keywords: carotenoids, chromophores, electronic excitation transfer, photosynthesis, proteins

Photosynthetic organisms can transform the energy contained in sunlight into chemical energy. Pigment molecules - chlorophylls and carotenoids - are excited upon light absorp-

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The light energy is then transferred, in the form of electronic excitation, in a series of steps to the so-called photosynthetic reaction center (RC), where it is used to induce a charge transfer and, thus, generate an electrostatic potential. This potential is used for further chemical reactions leading to the synthesis of ATP, which provides the free energy for all metabolic reactions in a cell. The apparatus that contains the RC together with surrounding chlorophylls and carotenoids, the latter organized in pigment-protein complexes, is termed the photosynthetic unit (PSU) [1]. The PSU is the biological equivalent of a solar cell and is working with high efficiency and high adaptability. In the PSU, the energy of the sun light is converted within 100 ps and with a quantum yield of 95% into a membrane potential that provides the energy for further metabolic processes. Various protection mechanisms prevent damage of the apparatus under intense light conditions in which excess energy needs to be dissipated. On the other hand, the PSU provides sufficient energy for the survival of a purple bacterium even under continuous low intensity irradiation. Through which mechanisms and strategies can this functionality be achieved?

To answer this question, one first has to note that nature chose to organize the PSU in a combination of RC’s and pigment-protein complexes instead of building only multiple copies of RC’s. This multi-component architecture provides many options to control the flow of energy in the PSU. To understand the control mechanisms employed, one needs to elucidate the physical mechanism by which energy can be transferred between two
pigment molecules.

In a seminal contribution, the physical chemist Theodor Förster showed that electronic excitation can be transferred by means of an incoherent, radiationless scattering process from a donor to an acceptor molecule, if the excited states of donor and acceptor are in resonance [2]. Since the coupling between donor and acceptor in this mechanism is weak, resonance of the participating excited states is an important condition for this mechanism to be efficient. For optically allowed states, i.e., states that are capable of absorbing and emitting light, Förster was able to connect the rates of excitation transfer with the absorption and emission spectra of the participating molecules. His rate equation is widely used today in the fluorescence resonance energy transfer (FRET) technique to determine the distance between two molecules by measuring the excitation transfer rates and absorption and emission spectra of pigment molecules.

Today, fifty years later, the structures of all components of the PSU of purple bacteria are known at atomic resolution. The structure of the RC was determined through X-ray crystallography and shows that an RC contains only four bacteriochlorophyll (BChl) molecules, an insufficient number to absorb sun light at an optimal rate. Further BChl’s are needed and in fact organized in so-called light-harvesting complexes.

In one such complex, LH1, 24 to 32 BChl’s and 12 to 16 carotenoids are arranged in a ring or ring fragment surrounding the RC. The BChl’s in LH1 are termed B875 BChl’s according to their absorption maximum at 875 nm. The structure of LH1 was deter-
Figure 1: The photosynthetic unit (PSU) is the biological equivalent of a solar cell. The PSU consists of the photosynthetic reaction center (red) and of circular light harvesting complexes surrounding the RC. A protein scaffold (black and white cylinders) fixes the pigments in the light harvesting complexes: carotenoids are shown in yellow, bacteriochlorophylls are colored according to their absorption maxima in blue, purple, and red (cf. Fig. 3).
Figure 2: Schematic illustration of the excitation flow in the photosynthetic unit. Light can be absorbed by carotenoids (yellow), B800-BChls (blue) or BChl rings (B850: purple, B875: dark red). The absorbed energy is transferred, in form of electronic excitation from the LH2 antenna complexes via the LH1 complex to the reaction center.
mined through molecular modelling on the basis of low-resolution electron microscopy data [3]. In some purple bacteria, additional LH2 antenna complexes surround the LH1 complex. The structure of LH2 was resolved through X-ray crystallography for two species of purple bacteria. In LH2 from \textit{Rhodospirillum (Rs.) molischianum}, sixteen B850-BChl’s form a closely connected ring with their molecule planes arranged perpendicular to the membrane plane [4]. A second ring is formed by the remaining eight B800-BChl’s whose molecular planes lie parallel to the membrane plane and which are clearly separated from each other. The arrangement of BChl’s in LH2 from \textit{Rhodopseudomonas (Rps.) acidophila} is analogous to that of \textit{Rs. molischianum} but eighteen B850 and nine B800 BChl’s are employed, resulting in a nine-fold symmetry axis instead of the eight-fold symmetry axis of \textit{Rs. molischianum} [5]. Under low light conditions, purple bacteria replace LH2 complexes by LH1 complexes that contain B820 BChl’s instead of B850 BChl’s, thus increasing the yield of energy transformation (see below). The organization of LH2 and LH1 complexes within the PSU is not known. In Figure 1, the structure of a minimal PSU consisting of one LH1 and three LH2 complexes is shown. A schematic illustration of the flow of excitation in this PSU is presented in Figure 2. The distances between the complexes in the modeled PSU were determined through energy minimization [6, 7]. The atomic resolution geometries of pigments in the PSU reveal a much more complicated picture than the one treated by Förster who assumed that the PSU contains
Figure 3: Optically active electron systems of the pigments in LH2 from *Rs. molischianum*. B800 BChl’s (blue) are separated from each other, while the electron systems of the 16 B850 BChl’s (purple) form an overlapping ring. Carotenoids (yellow) are in close contact to B800 and B850 BChl’s. Only four of the eight B800 BChl’s and one of the eight carotenoids present in LH2 are shown for clarity.
identical copies of individual pigment molecules. As shown in Figure 3, the PSU actually contains three types of pigments. Only a small part of the pigments are individual BChl’s, the larger part is organized in rings of closely coupled BChl’s. A third type of pigments, the carotenoids, are in close contact with both individual BChl’s and BChl rings.

This new picture of hundreds of pigment molecules organized in a hierarchical and symmetrical arrangement challenged physicists to achieve a description of the excitation transfer through application of quantum physics. In the following we will provide an overview of the results from the research agenda thus initiated, which is reviewed in more detail in [8]. Tracing the path of electronic excitation following absorption of a photon through the PSU, we will describe at each step in which way purple bacteria utilize the laws of quantum physics to control the biological functionality of its light harvesting apparatus. Our current understanding has been achieved through an extremely fruitful interplay between theory and experiments. Novel experimental methods that have been instrumental in characterizing the photosynthetic apparatus include, but are not limited to, hole-burning spectroscopy, time-resolved femtosecond spectroscopy [9], nonlinear absorption spectroscopy [10], high-resolution fluorescence spectroscopy [11] as well as single molecule spectroscopy [12]. Theoretical methods range from bioinformatics and structure prediction [3, 4] to molecular dynamics [13], quantum chemistry [14], the theory of exciton systems [15], stochastic quantum mechanics [16, 17], and advanced
condensed matter theory [18].

Collecting Photons The BChl system in the PSU exhibits a hierarchical arrangement in which BChl’s with higher energies are placed further away from the RC with the isolated B800 BChl’s being the most distant BChl’s. Since the geometry and spectral properties of the BChl’s are known, one can apply the Förster equation to calculate the excitation transfer time from B800 to individual B850 BChl’s. Surprisingly, the measured time of 700 fs for the B800 → B850 transfer step is an order of magnitude shorter than predicted by Förster theory (7.2 ps). How does the bacterium achieve this acceleration? Calculations reveal that the quantum states of the B850-BChl rings play a key role [6, 7]. Due to the strong couplings between BChl molecules excitation is coherently delocalized over a significant part of the ring and so-called exciton states are formed. For an idealized, i.e., symmetric, geometry, only two of the exciton states absorb light, whereas further optically forbidden exciton states spread over an energy range from 871 nm to 712 nm (cf. Fig. 4). Higher-lying exciton states are in better resonance with the B800 BChl’s than the BChl states at 850 nm, thus accelerating B800 → B850 excitation transfer. Excitation in the higher-lying exciton states relaxes very fast into the lower lying states until a Boltzmann distribution is reached. Thus, higher-lying exciton states become depopulated and cannot be used for back-transfer of excitation, which leads to a dramatic slowdown of back-transfer. Virtually all excitation
energy is funneled from the B800 BChl’s to the B850 BChl system. B800 BChl’s act as accessory pigments, enlarging the spectral range of light harvesting from the near infrared to the red.

![Diagram showing excitation energies of pigments in photosynthetic unit](image)

Figure 4: Excitation energies of the pigments in the photosynthetic unit. Full lines denote optically allowed states, broken lines indicate optically forbidden states. Excitation transfer can only occur between resonant states. In BChl rings, numerous optically forbidden exciton states improve resonance with B800 BChl and carotenoid states.

**Light-Harvesting and Photoprotection Through Carotenoids** A second class of accessory pigments are the carotenoids, which absorb light in the green range of the visual spectrum at about 500 nm. How can excitation from the high-lying carotenoid state be transferred to the BChl states at 800 and 850 nm, being far out of resonance?
Bacteria employ for this purpose a high-lying BChl state and a low-lying carotenoid state (cf. Figure 4). After absorption into the high-lying carotenoid state, excitation relaxes within 200 fs into the low-lying state which is forbidden in polyenes and symmetric carotenoids and is thus not able to absorb or fluoresce light.

Figure 5: Mechanisms of radiationless excitation transfer $D^* A \rightarrow DA^*$ from a donor $D$ to an acceptor $A$. (a) Coulomb mechanism: de-excitation of the donor ($D^* \rightarrow D$) is coupled through coulomb interaction to simultaneous excitation of the acceptor ($A \rightarrow A^*$). (b) Exchange mechanism: excitation is transferred via an exchange of electrons between donor and acceptor.

Photosynthetic bacteria with an efficient Car-BChl transfer are capable of transferring excitation within less than 10 ps from the optically forbidden carotenoid state to the BChl system [19]. The mechanism of this transfer step remained obscure till very re-
cently. Because of the close contact between carotenoids and BChl’s it was suggested that excitation could be transferred via an electron exchange mechanism. Alternatively, excitation could be transferred by means of higher-order multipole-multipole Coulomb couplings. Figure 5 illustrates (a) the Coulomb and (b) the electron exchange mechanism.

Quantum mechanical calculations show that only the Coulomb mechanism can furnish an efficient pathway for a transfer on a picosecond scale. Generally, the Coulomb coupling is stronger for optically allowed carotenoid states, i.e., even for closely spaced systems the dipole-dipole coupling terms dominate the Coulomb coupling.

Figure 6: Symmetries in the carotenoid C_{10}H_{20}. C_{2h}-symmetry: Identity under rotation by 180° around the shown axis. ’Alternancy’ symmetry: C-atoms can be separated in two disjunct and equivalent sets, denoted here through white and black disks.

To characterize the electronic properties of the carotenoid states, one needs to account for correlation effects between the π-electrons in the linear, conjugated systems of carotenoids. Two symmetries determine whether a carotenoid state is optically allowed or forbidden, the C_{2h}-symmetry and the so-called ’alternancy’ symmetry. Carotenoids
with $C_{2h}$-symmetry are invariant under rotation by 180° around the molecular symmetry axis (cf. Fig. 6). This symmetry can be broken through twisting and bending of the carotenoid, e.g., due to the interaction with the protein scaffold. The alternancy symmetry, which holds only approximately in carotenoids, arises from a topological feature of alternant hydrocarbons, according to which it is possible to divide the unsaturated carbon atoms into two disjunct and equivalent sets of atoms (cf. Fig. 6). The latter symmetry will be broken when the equivalence between the atoms is lifted, e.g., through functional side groups or a polarizing protein environment. Only if both symmetries are broken, the low-lying carotenoid excited state becomes allowed, and thus the Coulomb coupling is increased, resulting in faster transfer rates from this state.

Because of these symmetry properties, photosynthetic organisms can control the efficiency of carotenoid → BChl transfer through the choice of the carotenoid employed. The stronger the symmetries are broken, the more efficient the transfer pathway through the low-lying carotenoid states will be [19]. Polar side groups induce very strong symmetry breaking, which is used for example in the light-harvesting apparatus of a dinoflagellate in which the highly asymmetric carotenoid peridinin is the most abundant pigment [20]. Photosynthetic organisms can also control carotenoid → BChl transfer rates through changes in the geometrical arrangement. As calculations for LH2 complexes of different purple bacteria show, differences of less than 1 Å in the positions can determine whether excitation from a carotenoid is primarily transferred directly to the
B850 BChl ring or to the B800 BChl’s [21, 22].

In addition to their light harvesting role, carotenoids have a second, possibly even more important role. They protect photosynthetic organisms from harmful oxidation products. Under high-intensity light, excess excitation in BChl’s can relax into a low-lying triplet state, which in turn can excite singlet oxygen according to the reaction $^3\text{BChl}^* + ^3\text{O}_2 \rightarrow ^1\text{BChl} + ^1\text{O}_2^*$. Singlet oxygen $^1\text{O}_2^*$ is highly reactive and will oxidize conjugated double bonds, which ultimately leads to the death of the organism. Carotenoids prevent the generation of singlet oxygen by ”quenching” the BChl-triplet states according to the reaction $^3\text{BChl}^* + ^1\text{Car} \rightarrow ^1\text{BChl} + ^3\text{Car}$. The energy of the carotenoid triplet state $^3\text{Car}$ decreases with an increase in the length of conjugated system. For carotenoids with nine or more conjugated double bonds, the energy of $^3\text{Car}$ is low enough to efficiently prevent formation of singlet oxygen. The reaction $^3\text{BChl}^* + ^1\text{Car} \rightarrow ^1\text{BChl} + ^3\text{Car}$ is mediated through the electron exchange interaction [23]; corresponding calculations elucidate the reaction pathways by which carotenoids prevent photo-oxidative damage [14].

A Bacteriochlorophyll Excitation Reservoir Carotenoids and B800 BChl’s funnel their excitation energy into the BChl ring systems. In addition to the already mentioned acceleration of these transfer processes, the delocalized exciton states fulfil further roles. In the idealized case of circular LH2 aggregates, only the exciton states at 850 nm are
optically allowed. Below this pair of states, a further, optically forbidden, exciton state is located at 871 nm (cf. Fig. 4). Due to this particular electronic structure, BChl-rings can act as a short-term energy trap. Excitation from the high-lying exciton states relaxes into the lowest, optically forbidden exciton state, thus minimizing energy losses through fluorescence.

Figure 7: Times for excitation transfer between the various pigments in the photosynthetic unit. All times were determined through quantum mechanical calculations on the basis of the atomic level structures [22]. Experimentally measured times are shown for comparison in parentheses.

Excitation transfer between BChl-rings involves not only the optically allowed, but also the forbidden exciton states. The influence of the optically forbidden states becomes evident when comparing the forward to back-transfer rates as shown in Fig. 7. Excitation
transfer from an individual B850 BChl in LH2 to an individual B875 BChl molecule in LH1 is, according to the Förster rate equation $\tau_\text{←} = \tau_\text{→} \times e^{\Delta E/kT}$, expected to be six times faster than the corresponding back-transfer at room temperature. The effect of the optically forbidden exciton states is to speed up the back-transfer and thus to shift the LH2 ↔ LH1 transfer equilibrium to the side of LH2 as compared to a system in which no exciton exists.

Fig. 7 reveals an important organization principle of the PSU. Forward and back-transfer rates between different BChl aggregates are very similar and not biased strongly in the direction of the RC. In particular, back-transfer from the RC to LH1 occurs faster than the forward transfer LH1 → RC [24]. In earlier work, the PSU has often been described as an energy funnel with pigments lying at higher energies the more distant they are to the RC, thus ensuring that excitation is funneled quickly and efficiently towards the RC. However, the transfer times shown in Figure 7 reveal that this picture is inappropriate. The PSU is better described as a reservoir in which electronic excitation is distributed more or less evenly throughout the whole system with no bias towards the RC. This organization has a photoprotective function. Excess excitation, that is not used in an RC to induce an electron transfer, is transferred back to LH1 and the antenna LH2 complexes, where it is either dissipated or - in the ideal case - transferred on to another RC. Although this organization appears to be rather inefficient, calculations and measurements show that excitation is trapped within less than 200 ps at an RC [25].
This trapping time is small compared to the high fluorescence loss time of 1000 ps, which is achieved in part due to the energy trap function of circular BChl aggregates. Thus, the yield of excitation trapping in the RC remains high, namely above 85%. Only when the bacterium “starves” from a shortage of light through a long period of low irradiation, the genetic program of the cell is switched and LH2 complexes are replaced through LH3-complexes with a higher-lying excitation at 820 nm. The increase in energy results in an acceleration of forward transfer rates and, thus, in the construction of an excitation funnel under low light conditions.

Reliability in the Presence of Fluctuations Figure 7 represents a remarkable conceptual achievement. Through the application of quantum mechanics and using the known atomic geometries, times of excitation transfer between the various pigments can be calculated almost quantitatively. However, so far it has been neglected that the PSU, just like any other biological apparatus, operates at physiological temperatures, and is therefore subject to thermal fluctuations. The question how thermal disorder influences the quantum states in BChl aggregates has been a matter of intense debate and investigation. A recent answer to this question is given by a combination of quantum mechanical calculations and classical molecular dynamics simulations on the BChl aggregate in LH2 from *Rs. molischianum*. Figure 8 shows the thermal fluctuations of the local B850 BChl excitation energies as calculated
in [18]. The variation in excitation energy is comparable to the size of the coupling between BChl’s. One therefore expects that the excitations in the B850 aggregate, which are delocalized over the complete BChl aggregate in an ideal ordered arrangement of identical units, become localized over a small number of B850 BChl molecules due to the influence of the fluctuations [26].

![Figure 8: Fluctuations of excitation energies of an individual B850 BChl. The energies shown were determined through coupled molecular dynamics and quantum chemical calculations of the B850 BChl system in LH2 from Rs. molischianum [18].](image)

It remains to be understood how thermal fluctuations and noise affect the optical properties of BChl aggregates and excitation transfer rates. This question arises not only in the context of the light harvesting apparatus, but also applies to the electron transfer steps in the RC [13, 27]. Ultimately, all molecular machineries in biological cells consist of soft matter and are thus subject to strong thermal fluctuations. How do these machineries then achieve their functionality given that small changes in the geometrical
arrangement of the interacting components can result in dramatic changes in reaction
rates and yields, e.g., due to quantum-mechanical interferences? Answering this question
remains one of the most fascinating challenges in modern biophysics, which is second to
none in conceptual importance and mathematical difficulty.

One recent approach to meet this challenge considered the role of static disorder on the
B850 chlorophyll system [17]. Numerical calculations of level densities and spectra of
the disordered exciton system described by a Hamiltonian $H = H_0 + R$, demonstrated a
high degree of universality with respect to different models of disorder encapsulated in
$R$, generalizing in this regard earlier investigations of infinite systems in physics to finite
size systems in biology. For the case of Gaussian disorder of the elements of $R$, describing
the deviations from the ideal Hamiltonian $H_0$, supersymmetric calculus borrowed from
modern mathematical physics permitted the derivation of analytical expressions for the
density of exciton levels that can be employed independent of the size and geometry of
the chromophore cluster.

Dynamic disorder in the B850 chlorophyll system has also been approached successfully
merging advanced biomolecular simulation techniques, combined molecular dynamics
and quantum chemistry calculations, with advanced methods in condensed matter the-
ory, solutions to the polaron model in the intermediate coupling regime [18]. Simulated
excitation energy fluctuations as shown in Figure 8 yielded a spectral density that de-
scribes the coupling between electronic excitations and chromophore - protein vibrational
modes; this density was employed in the framework of the polaron model of vibronic coupling to yield without any adjustable parameters an excellent match to observed exciton spectra. A similar advance had been achieved earlier when the thermal effects on photoinduced electron transfer in the RC was described, combining – through use of 19th century theory of sound – energy gap fluctuations obtained from simulation with the spin-boson model of vibronic coupling in condensed matter systems [13, 27].

The photosynthetic apparatus of purple bacteria with its multi-component organization and wealth of accumulated experimental data is a likely candidate to play a key role in furthering our understanding of how cellular machineries work in general, comparable to the role of the hydrogen atom in developing an understanding of inorganic systems a century earlier.

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References


[22] T. Ritz, *The Quantum Physics of the Bacterial Photosynthetic Unit*, Der Andere Verlag, Osnabrück, **2001**.


