HOW NATURE HARVESTS SUNLIGHT

Specialized molecular aggregates in purple bacteria exploit subtle quantum physics to collect and convert light energy for photosynthesis.

Xiche Hu and Klaus Schulten

It is through photosynthesis that Earth's biosphere derives its energy from sunlight. Photosynthetic organisms—plants, algae and photosynthetic bacteria—have developed efficient systems to harvest the light of the Sun and to use its energy to drive their metabolic reactions, such as the reduction of carbon dioxide to sugar. The ubiquitous green color of plants is testimony to the key molecular participant in the light harvesting of plants, chlorophyll.[1] More hidden in this respect, but no less widespread, is a second participating molecule, carotenoid. In green leaves, the color of the carotenoids is masked by the much more abundant chlorophylls, whereas in ripe tomatoes or the petals of yellow flowers, the carotenoids predominate. Chlorophyll molecules exist in slightly different chemical structures in various photosynthetic organisms, as chlorophyll *a* or *b* in plants or algae, and as bacteriochlorophyll *a* or *b* in photosynthetic bacteria. Molecules such as chlorophyll and carotenoid that absorb light and impart color to living matter and other materials are called pigments.

In general, biological pigments are noncovalently bound to proteins, forming the so-called pigment–protein complexes. Light harvesting in plants, as well as in bacteria, is carried out by protein-bound chlorophyll–carotenoid aggregates and involves a hierarchical interplay of the pigments' electronic excitations. In the early 1930s, Robert Emerson and William Arnold[2] demonstrated that it took on average 2480 chlorophylls to reduce one molecule of CO$_2$ under saturating flash light intensity. When the quantum requirement for the reaction (10 quanta per CO$_2$ reduction) is properly taken into account, this number is reduced tenfold to about 250 chlorophylls. To explain the cooperative action of this set of chlorophylls, it had been postulated that only very few chlorophylls in the so-called photosynthetic reaction center[3] (RC) directly take part in photochemical reactions. Most chlorophylls serve instead as light-harvesting antennas capturing the sunlight and funneling the electronic excitation toward the RC. Louis Duysens was the first to observe directly the postulated transfer of electronic excitation between different chlorophylls: Light absorbed by one type of pigment sensitized emission from a spectrally distinctive and energetically lower-lying pigment.[4]

The excitation of the RC induces an electron transfer reaction that charges the membrane. (See Graham Fleming and Rienk van Grondelle's article, "The Primary Steps of Photosynthesis," PHYSICS TODAY, February 1994, page 48.) As its name implies, the RC forms the center of the light-conversion system, transforming light energy to fuel the metabolism. (Since we are presently concerned with the light-harvesting process and not with the actual utilization of the light energy, no further explanation of the RC will be given here.)

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The pigment organization in which multiple light-harvesting antennas serve the RC seems to have been adopted by all photosynthetic organisms. With it, they can collect light from a broader spectral range and use energy much more efficiently. In particular, light-harvesting antennas enlarge the RC's cross section for capturing sunlight. For although the RC possesses light-absorbing chlorophylls itself, photons absorbed by the RC chlorophylls are not sufficient to saturate its maximum turnover rate. When exposed to direct sunlight, chlorophylls absorb at a rate of at most 10 Hz and, in dim light, at a rate of 0.1 Hz. However, the chemical reaction of the RC can "turn over" at 1000 Hz. By feeding the RC with excitation energy, the light-harvesting complexes keep the RC running at an optimal rate. Light-harvesting antennas minimize the investment of the organism's metabolic energy for the biosynthesis of the pertinent proteins: It is more economical for the bacterium to synthesize the relatively small proteins that can provide a scaffold for the light-harvesting pigments than to produce many copies of the large RC and its associated electron transfer proteins.

According to this rationale, photosynthesis is initiated by electronic excitation of an aggregate of light-harvesting pigments and by transfer of the excitation to the RC. These processes are the subject of this article, in which we focus on those purple bacteria with a well-characterized photosynthetic system.

Purple bacteria are great masters of harvesting light. They developed their virtuosity under relentless evolutionary pressure in a habitat below that of most plant life—that is, at the bottom of ponds or in topsoil, depending on the species. Only light left unharvested by plants penetrates to these depths, mainly at wavelengths of about 500 nm and above 800 nm. To harvest this light efficiently, the bacteria exploit elegant quantum physics, the workings of which were fully understood only recently, after the discovery of the structure of the pigment–protein complexes that make the light-harvesting process possible. (Space limitations do not allow us to do justice to the many researchers who have contributed to this field.)

Light-harvesting complex II

In most purple bacteria, the photosynthetic membranes contain two types of light-harvesting complex—light-harvesting complex I (LH-I) and light-harvesting complex II (LH-II). LH-I surrounds the RC, whereas LH-II is not directly associated with the RC but transfers energy to the RC by way of LH-I.[1,5] The number of LH-IIs varies according to growth conditions such as light intensity and temperature.

Two research groups, using x-ray crystallographic techniques, have recently elucidated the structures of LH-II from two different but closely related purple bacte-

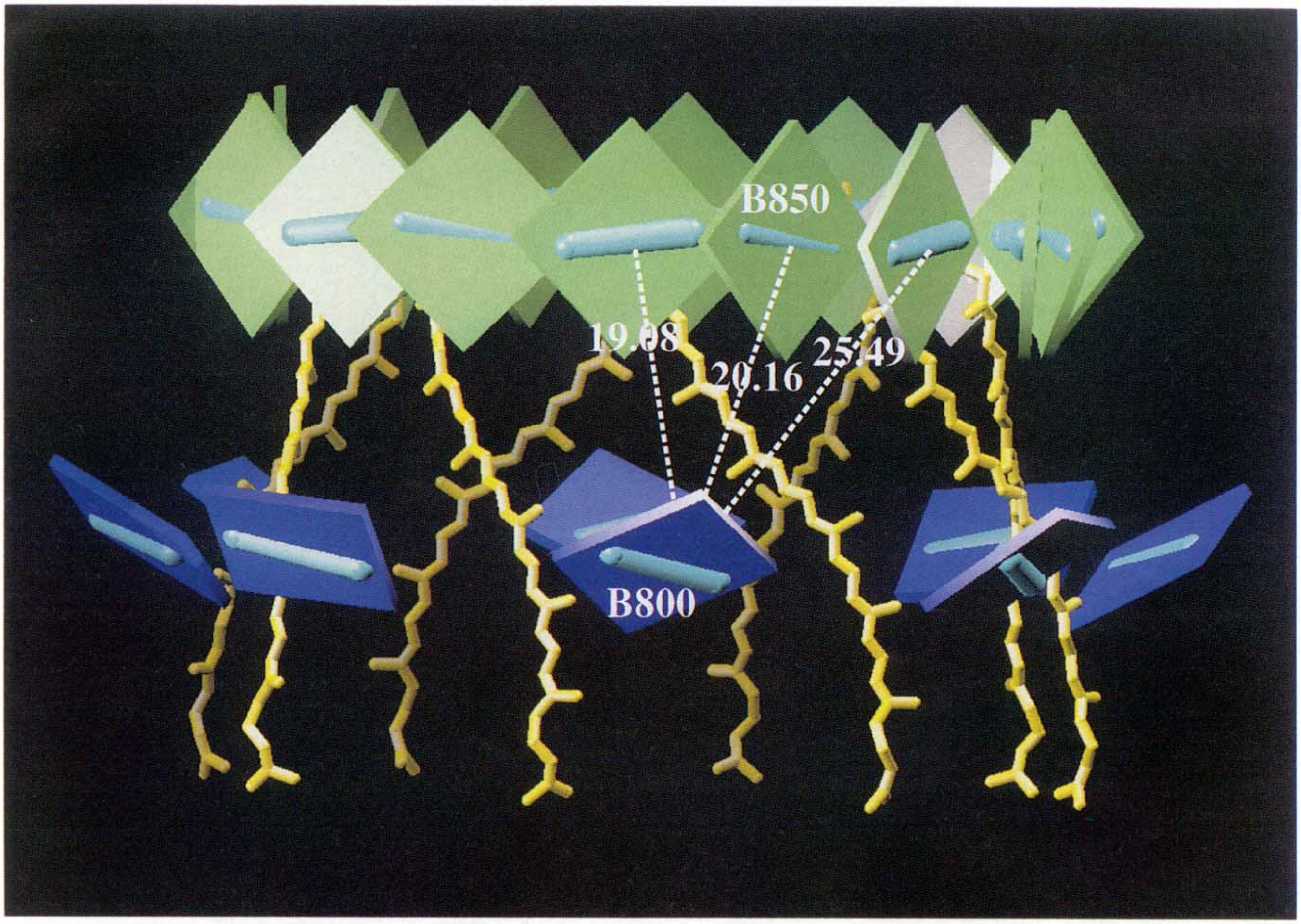


FIGURE 1. ARRANGEMENT OF BACTERIOCHLOROPHYLLS AND CAROTENOIDS in LH-II of *Rs. molischianum*.[7] Bacteriochlorophylls (BChls) are represented as squares; 16 B850 BChls (green) are arranged in the top ring and 8 B800 BChls (violet) in the bottom ring. Carotenoids (yellow) are shown in a twig-like representation. Bars (cyan) connected with the BChls represent the transition dipole moments of individual BChls that are responsible for the 800 nm and 850 nm bands in the BChl absorption spectra. Representative distances between the central magnesium atoms of B800 BChl and B850 BChl are indicated (in angstroms).

ria that contain bacteriochlorophyll *a* (BChl-*a*), *Rhodospirillum* (*Rs.*) *molischianum* and *Rhodopseudomonas* (*Rps.*) *acidophila*.[6,7] The crystal structure of LH-II in *Rps. acidophila* was solved by Richard Cogdell and coworkers.[6] And in collaboration with Hartmut Michel's group in Frankfurt, Germany, we solved the structure of LH-II in *Rs. molischianum* to a resolution of 0.24 nm.[7] It turned out that the LH-II of both bacteria adopts a highly symmetrical and beautiful ring shape, with a radius of about 7 nm. In the case of *Rps. acidophila* the ring has a ninefold symmetry axis, and in LH-II from *Rs. molischianum* the ring has an eightfold symmetry axis.

LH-II of *Rs. molischianum* is actually built of 48 independent components that self-aggregate in the bacterial membrane to form the ring-shaped complex seen on the cover of this issue: eight identical α-helices of 56 amino acids (called the α-apoproteins, shown in blue), eight identical α-helices of 45 amino acids (called the β-apoproteins, magenta), 24 BChls (green) and eight carotenoids (yellow). The complex can be considered an aggregate of eight building blocks, commonly referred to as the $\alpha\beta$-heterodimers, each consisting of an α-apoprotein, β-apoprotein, three BChls and a carotenoid.

The 24 BChls and 8 carotenoids in LH-II actually harvest the light, and the role of the remaining part of the complex is that of a scaffold to hold the aggregate properly positioned in the membrane of the bacterium. Figure 1 depicts the 24 BChl molecules and 8 carotenoid molecules, viewed from the side and with all other components stripped away. Sixteen of the BChls, commonly referred to as B850 BChls, form a tight ring-shaped aggregate (top in figure 1), and the remaining 8 BChls, commonly referred to as B800 BChls, form a loose ring-shaped aggregate (bottom in the figure). The 8 carotenoids are arranged such that each carotenoid touches 2 BChls, as clearly shown. This figure illustrates the part of the structure relevant for an explanation of the physical mechanisms underlying the light-harvesting process.

The discovery of this highly symmetric aggregate immediately posed the question of how far the geometry of the bacteriochlorophyll–carotenoid aggregate and the electronic properties of the BChls and carotenoids serve the process of harvesting light. The subsequent investigations into the electronic excitations of the aggregate, done by us and others, revealed physical properties that ideally support the biological function. First, the most conspicuous structural element, the ring of 16 B850 BChls, has been found in quantum chemical calculations of its electronic excitations to exhibit two bands of excitons; the band splitting reflects a weakly dimerized form of the aggregate (the bacteriochlorophyll–bacteriochlorophyll distances alternate slightly along the ring).[8] Most remarkable is the property of the excitons that stems from the fact that they extend coherently over the entire BChl ring: Photons are absorbed only by 2 of the 16 exciton states—namely, the second and the third energetically lowest states, the corresponding exciton states actually being energetically degenerate. (See box 1 on page 31.) Since the lowest excited state is optically forbidden and does not fluoresce, the BChl rings in the structure act as energy storage rings, preserving excitation energy until it is forwarded to other rings and ultimately to the RCs.

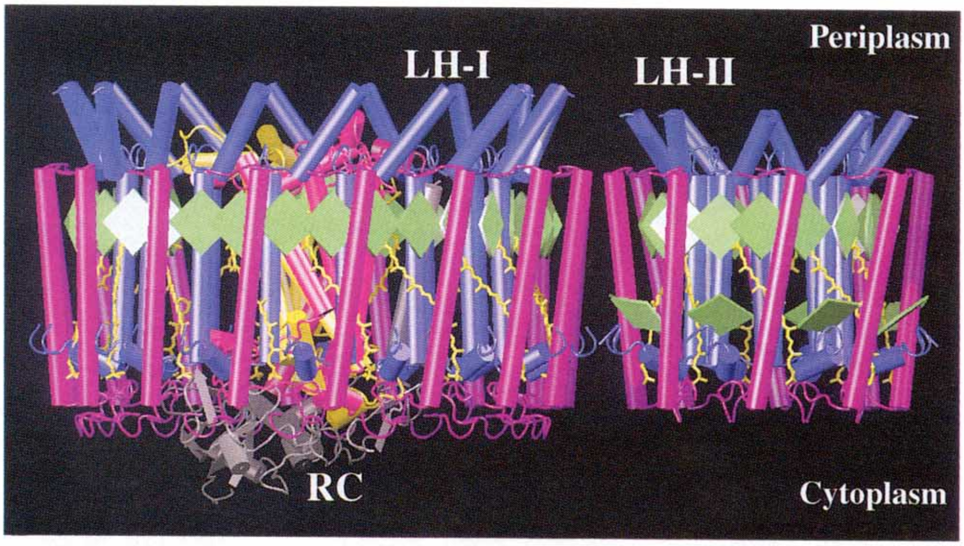


FIGURE 2. THE MODELED PHOTOSYNTHETIC UNIT showing the arrangement of its main pigment–protein complexes—namely, LH-II, LH-I and the photosynthetic reaction center (RC). The unit has been constructed using the model structure of the *Rb. sphaeroides* LH-I[8] and the crystal structures of the *Rb. sphaeroides* RC and *Rs. molischianum* LH-II.[7] We note that recent electron microscopy data suggest that the LH-II of *Rb. sphaeroides* contains 9 $\alpha\beta$-heterodimers instead of 8 as in the LH-II of *Rs. molischianum*. The α-helices are represented as cylinders with the α-apoproteins of both LH-I and LH-II shown in blue and the β-apoproteins in magenta, respectively. The RC is a complex of three protein subunits shown in different colors. The pigment molecules—that is, the BChls and carotenoids—are shown in green and yellow, respectively. The figure is actually to scale, with the relative positions of LH-1 and LH-II being derived by optimizing the LH-II's interaction with LH-1.

The 8 B800 BChls shown in blue and the carotenoids shown in yellow in figure 1 act as antennas, which absorb the sunlight and funnel its energy to the ring of 16 B850 BChls, shown in green in figure 1. This role is rather straightforward in the case of the 8 B800 BChls. They absorb light near 800 nm and transfer the resulting electronic excitation of the individual BChls to the top BChl ring (in figure 1) through the so-called Förster mechanism, which had actually been proposed independently by Robert Oppenheimer[9,10] and Theodor Förster.[11] (See box 2 on page 32). Quantum mechanical calculations predict that this transfer should proceed within 700 femtoseconds, a time that agrees with spectroscopic observation.[8]

More intricate is the role of the carotenoids that absorb light at 500 nm. The corresponding excited state of carotenoid decays within 200 fs to an optically forbidden electronic state in resonance with the BChl excitations in the 800–850 nm range. The state is well known from the physics of highly correlated one-dimensional electron systems and involves two triplet magnons coupled to an overall singlet state.[12] The optically forbidden character of the state precludes its coupling to the BChl ring (top in figure 1) through the mechanism suggested by Oppenheimer and Förster, which involves interaction between induced dipoles. However, the same optically forbidden character permits coupling through higher-order multipoles, as well as through electron exchange—that is, through the so-called Dexter mechanism. (See box 2.) The Dexter mechanism requires the molecules to be in van der Waals contact, which, as the structure in figure 1 shows, is indeed the case. Through the electron exchange mechanism, the carotenoids also protect the BChls and the entire bacterium against the detrimental effects of BChl triplet states, which arise with a small but finite probability and can generate highly reactive singlet oxygen according to the reaction

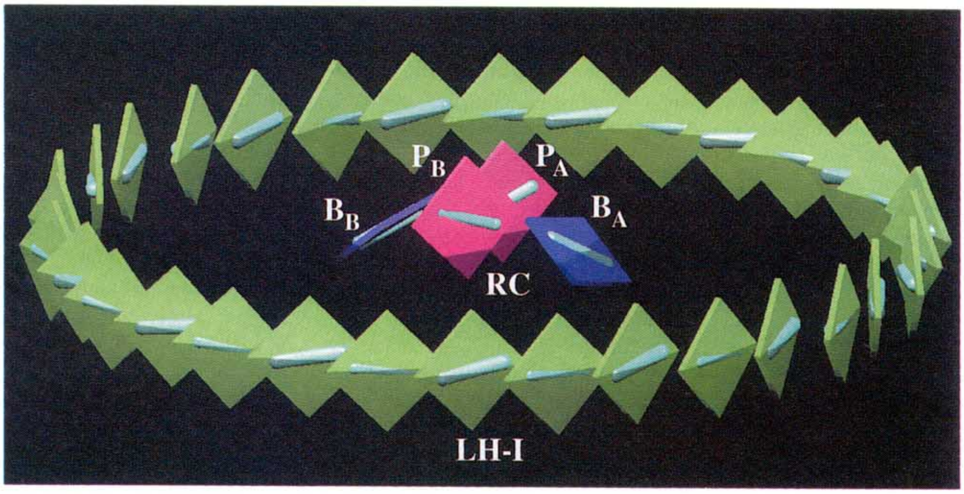
ground state (triplet) O_2 + triplet BChl → excited state (singlet) O_2 + ground state (singlet) BChl.

The carotenoids quench the bacteriochlorophylls' triplet states. As a result, electronic excitation of O_2 is prevented and with it the damaging properties of this compound in its reactive singlet form.

Light-harvesting complex I

To understand how the energy deposited in LH-IIs, as described in the previous section, is actually channeled

FIGURE 3. ARRANGEMENT OF BChls in the complex consisting of LH-I and the photosynthetic reaction center (RC), with all other components stripped away. The BChls are represented as squares with the B875 BChls of LH-I shown in green, and the special pair (P_A and P_B) and the accessory BChls (B_A and B_B) of the RC shown in red and blue, respectively. Cyan bars represent transition dipole moments of individual BChls. This spatial arrangement is ideally suited to transfer excitation energy and to store it.



into the metabolism of photosynthetic bacteria, one needs to examine the relevant components of the bacterial membrane—the LH-II, the LH-I mentioned above and the RC. The RC accepts excitation energy through two BChls that form a strongly interacting dimer, the so-called special pair.[3] Two additional BChls, in close proximity to the special pair, are also present in the RC. The function of these two, the so-called accessory BChls, has been hotly debated. They were considered as "voyeurs" of the initial electron transfer process

$$\mathrm{P + H \rightarrow P^+ + H^-}$$

in the RC from the special pair P to a pheophytin H. (A pheophytin is a chlorophyll-like molecule without a central magnesium atom.) Alternatively, they were considered as a "stepping stone" in the scheme

$$\mathrm{P + BChl + H \rightarrow P^+ + BChl^- + H \rightarrow P^+ + BChl + H^-}.$$

As stated above, the RC is surrounded by the pigment–protein complex LH-I, which is remarkably similar to LH-II but is about twice its size. LH-I consists of 16 building blocks—namely, the $\alpha\beta$-heterodimers mentioned above. Electron micrographs have shown that the RC is ringed tightly by LH-I, which in turn is surrounded by LH-IIs. In some bacteria, such as *Rs. molischianum*, the association of LH-I and the RC is so strong that LH-I cannot be separated from the RC without losing its spectral properties. However, in other species such as *Rhodobacter (Rb.) sphaeroides*, pure and homogeneous LH-I complexes can be isolated.

Photosynthetic bacteria have evolved a pronounced energetic hierarchy in the light-harvesting system. Pigments of outer light-harvesting complexes absorb at a higher energy than do inner ones. For example, the LH-II complex, which surrounds LH-I, absorbs maximally at 800 nm and 850 nm. LH-I, which in turn surrounds the RC, absorbs at a lower energy (875 nm).[1] The energy cascade serves to funnel electronic excitations from the LH-IIs through LH-I to the RC. Over billions of years of evolution, nature has adopted a variety of ways to shift the spectral maxima for light absorption. This shifting can be done directly by using different kinds of pigments that absorb maximally at different wavelengths.[1] However, a more elegant way is achieved in the bacterial photosynthetic unit whose constituents, LH-II, LH-I and RC, all contain BChl-*a* as the major pigment. Although the absorption spectra of monomeric BChl-*a* peaks at 772 nm in organic solvent, in the photosynthetic unit the peak positions redshift by various amounts—that is, to 800–900 nm. Quantum chemical calculations suggest that excitonic interactions are responsible for a major part of the spectral redshift.[8] In addition, BChl–protein interactions shift the site energies of individual BChls, and thus contribute to the spectral shift. For example, the B800 and B850 BChls of LH-II are held by different protein side groups, with the binding environment of B800 being more polar than that of B850.[6,7]

Box 1. Excitons of Circular Aggregate of Bacteriochlorophylls

The B850 BChls of LH-II can be represented as circular aggregates of $2N$ BChls, where $N = 8$ and $N = 9$ for LH-II from *Rs. molischianum* and *Rps. acidophila*, respectively. These aggregates exhibit only N-fold symmetry axes due to a dimerization of the BChls—reflected in their structures[6,7]—and to interactions between the electronic excitations of the individual BChls[8]

$$| j \rangle \;=\; |\mathrm{Chl}_1, \mathrm{Chl}_2, \ldots, \mathrm{Chl}_j^*, \ldots, \mathrm{Chl}_{2N}\rangle, \qquad (1)$$

$$\mathrm{j} = 1, 2, \ldots, 2\mathrm{N}.$$

Due to the stated interactions, stationary states of the aggregates are coherent superpositions, so-called excitons,[17] of the lowest energy (Q_y) excited states of individual BChls. Naturally, the electronic excitations of neighboring BChls interact most strongly, and in the simplified description presented here all other interactions are neglected. Furthermore, we assume a $2N$-fold symmetry axis, neglecting the observed dimerization of BChl in the aggregates. The resulting exciton states are

$$|\widetilde{n}\rangle = \frac{1}{\sqrt{2N}} \sum_{j=1}^{2N} e^{ijn\pi/N} \, | j \rangle \qquad (2)$$

with energies

$$\epsilon_n = E_o + 2\, V_o \cos \frac{\pi n}{N} \qquad (3)$$

$$[\mathrm{n} = -N + 1, -N + 2, \ldots, N].$$

Ev represents the (Q_y) excitation energy of the individual BChls and V_0 the interaction energy between neighboring BChls. The state of the lowest energy, for $V_0 > 0$, is

$$\epsilon = \epsilon_N = E_o - 2\, V_o. \qquad (4)$$

The transition dipole moments associated with the excitons are

$$\langle \mathrm{ground} \,|\, \vec{\mathcal{D}} \, |\widetilde{n}\rangle = \frac{1}{\sqrt{2N}} \sum_{j=1}^{2N} e^{ijn\pi/N} \, \vec{D}_j. \qquad (5)$$

Here $\vec{D}_j$ denotes the transition dipole moments of the individual BChls, which are oriented within the plane of the membrane and can be represented as

$$\vec{D} = D_0 \begin{pmatrix} \cos \phi_j \\ \sin \phi_j \\ 0 \end{pmatrix}, \; \phi_j = \frac{\pi j (N+1)}{N}, \; j = 1, 2, \ldots 2N, \qquad (6)$$

From (5) one obtains for the oscillator strength of the ground state $\rightarrow |\widetilde{n}\rangle|$ transition

$$| \langle \mathrm{ground} | \vec{\mathcal{D}} \, |\widetilde{n}\rangle |^2 = N D_o^2 \, (\delta_{n,-N+1} + \delta_{n,N-1}). \qquad (7)$$

Only two excitons with degenerate energies

$$\epsilon \pm = E_o - 2\, V_o \cos \frac{\pi}{N} \qquad (8)$$

carry oscillator strength. These are actually the second and third lowest electronic excitations of the aggregate. An effective Hamiltonian governing interactions between the states $| j \rangle$ had been constructed based on quantum-chemical calculations by Michael Zerner of the University of Florida.[8] The excitonic states resulting from this Hamiltonian exhibit the same pattern of oscillator strength as the simplified description above.

The energetic hierarchy described furnishes a cascade of electronic excitations that "gravitate" from LH-II through excitation transfer and thermal relaxation toward the RC, with the key link being LH-I. This scheme was known for decades, but a deeper understanding could only emerge once the structure of LH-I was known. Luckily, a coincidence expedited further work. It turned out, that for the bacterium *Rb. sphaeroides*, the 16 building blocks of the LH-I complex are genetically close to the building blocks of the LH-II complex of *Rs. molischianum*. That allowed us to develop a computer model of LH-I in which the building block, an $\alpha\beta$-heterodimer as in LH-II, was constructed by homology modeling with the $\alpha\beta$-heterodimer of LH-II of *Rs. molischianum* as a template.[8] The $\alpha\beta$-heterodimers prepared in this way were then aggregated into a circular hexadecameric complex by simulating the molecular dynamics and by minimizing the energy under the constraint of 16-fold symmetry. The resulting LH-I model superimposed perfectly on an electron density projection map observed by electron microscopy,[13] leading us to believe that the model has a good chance of being correct not only in its overall geometry, but also in its details.

Here, the modeling technique was the same as that employed earlier to build the structure of LH-II, except that for LH-II the model could be verified by x-ray diffraction data.[7] The accuracy of the modeled LH-I structure is also supported by the fact that the RC fits into its core. Moreover, this LH-I model is apparently consistent with a drawing provided by Papiz *et al.*,[14] who have geometrically placed 16 $\alpha\beta$-heterodimers of LH-II from *Rps. acidophila* into contour peaks of the observed electron density projection map.[13]

Figure 2 presents LH-I with the RC at its center and an LH-II complex placed next to it in a position determined by optimizing the LH-II's interaction with LH-I. The molecular complex shown encompasses all the components of the electronic excitation funnel, the carotenoids (yellow) and the BChls (blue) capturing 500 nm photons and 800 nm photons, respectively, and the coplanar rings of 16 and 32 BChls in LH-II and LH-I with graded excitation energies at 850 nm and 875 nm, respectively. The RC bacteriochlorophylls, however, are not visible in figure 2. Instead, they are shown in figure 3, in which P_A and P_B label the special pair BChls and B_A and B_B label the accessory BChls; the 32 BChls of LH-I are also shown, but all other components have been stripped away.

Figure 3 illustrates that the spatial relationship of the LH-I and RC BChls is ideally suited to excitation transfer. It is evident that LH-I also functions as a storage ring for excitation energy, serving as an intermediary in transferring light energy from the LH-II complexes to the P_A and P_B BChls. A quantum mechanical analysis suggests that the accessory BChls B_A and B_B provide a tunneling path for the excitation transfer, which accelerates the transfer significantly.[8] Accordingly, the accessory BChls may serve as "stepping stones" for the electronic excitation to reach the RC's special pair, dividing into two 3.6 nm and 1.1 nm segments the relatively wide distance of 4.2–5.1 nm, which exists between the LH-I BChls and the RC special pair P_A and P_B.[8]

In figure 4 we present the arrangement of three LH-II complexes surrounding an LH-I combined with an RC, displaying only BChls. The actual photosynthetic apparatus contains about 30 to 300 BChls per RC, depending on growth conditions. This implies that the maximum number of LH-IIs associated with the LH-I–RC complex is about 10. The RC + LH-I + (LH-II)$_n$ (n = 1,10) aggregate constitutes a nanometric structure in the bacterial membrane specialized in efficient light absorption and energy transfer. The arrows in figure 4 indicate the path of excitation transfer in the apparatus.

The two most prominent features of the pigment organization are the ringlike architecture of the BChl aggregate within individual pigment–protein complexes LH-II and LH-I, and the coplanar arrangement of the B850 BChls of LH-II, the B875 BChls of LH-I, as well as the BChls inside the RC. Such a planar organization of BChls in the bacterial photosynthetic unit is optimal for energy transfers based on the delocalized exciton model.[8]

Box 2. Excitation Transfer Mechanisms

Excitation transfer between a donor D and an acceptor A, $D^* + A \rightarrow D + A^*$, is a radiationless transition process. Assuming that only two electrons—one on D and another on A—are involved in the transition, the properly antisymmetrized total wave functions of the system ($D \ldots A$) before and after the transition can be represented by

$$\Psi_{D^*A} = \frac{1}{\sqrt{2}}\,[\psi_{D^*}(1)\cdot\psi_A(2) - \psi_{D^*}(2)\cdot\psi_A(1)] \qquad (9)$$

and

$$\Psi_{DA^*} = \frac{1}{\sqrt{2}}\,[\psi_D(1)\cdot\psi_{A^*}(2) - \psi_D(2)\cdot\psi_{A^*}(1)]. \qquad (10)$$

The transition probability between the two states Ψ_{D^*A} and Ψ_{DA^*} is governed by the resonance integral

$$U = \langle \Psi_{D^*A} \,|\, V_{DA} \,|\, \Psi_{DA^*} \rangle, \qquad (11)$$

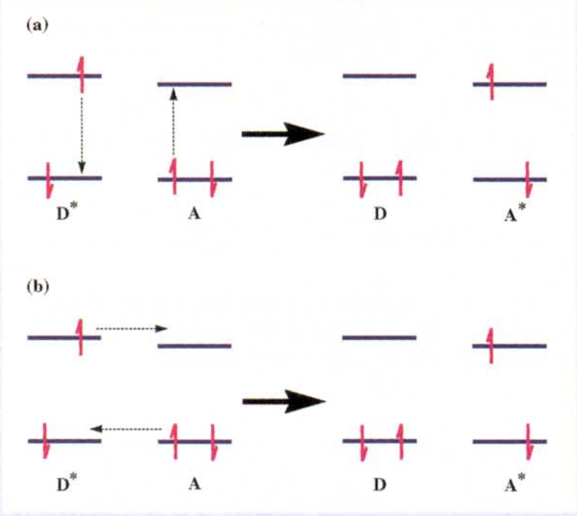
where V_{DA} represents the Coulombic interaction that caused the transition. U has two terms: the Coulomb term

$$U_C = \langle \psi_{D*}(1)\psi_A(2) \,|\, V_{DA} \,|\, \psi_D(1)\psi_{A*}(2) \rangle \qquad (12)$$

and the exchange term

$$U_{EX} = \langle \psi_{D*}(1)\psi_A(2) \,|\, V_{DA} \,|\, \psi_D(2)\psi_{A*}(1) \rangle. \qquad (13)$$

Depicted in the following drawing are the transfer mechanisms (a) due to the Coulomb term suggested by Oppenheimer[9,10] and Förster,[11] and (b) due to the exchange term suggested by Dexter[18]:



The two mechanisms differ significantly in their operative range. While the Coulomb mechanism is effective over distances of typically 2-5 nm, the exchange mechanism is effective only in case of sufficient overlap of the wavefunctions of D^* and A, i.e., for distances of a few tenths of a nanometer. The Coulomb mechanism, for optically allowed transitions, has an R^{-6} distance dependence reflecting its close relationship to the van der Waals interaction.[11] The exchange mechanism decays exponentially with distance. As a consequence of selection rules, the Coulomb mechanism applies only to transfer of singlet excitations (assuming singlet ground states A and D), whereas the exchange mechanism is applicable also to transfer of triplet excitations.

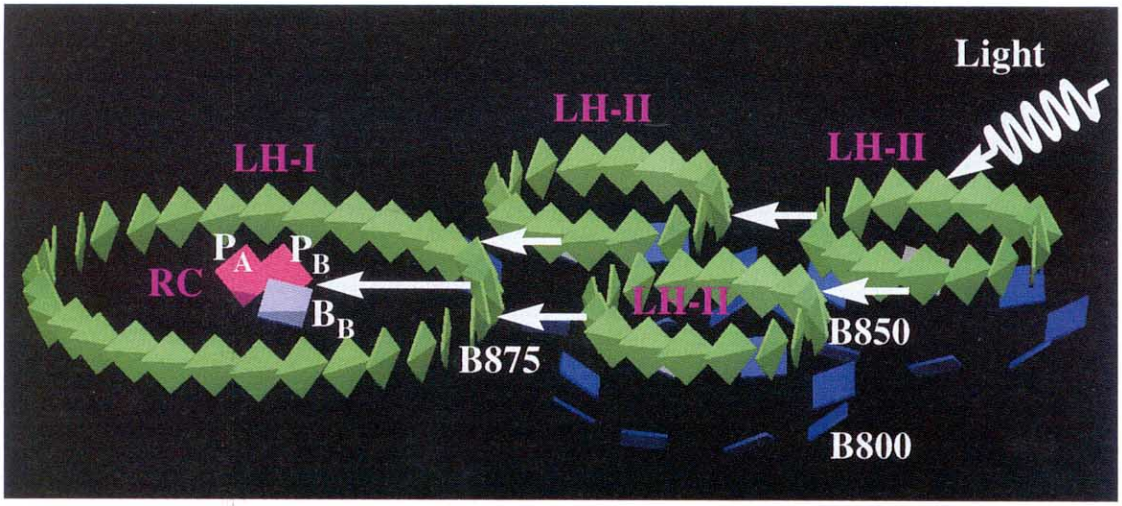


FIGURE 4. EXCITATION TRANSFER in the bacterial photosynthetic unit. LH-II contains two types of BChls commonly referred to as B800 (dark blue) and B850 (green), which absorb at 800 nm and 850 nm, respectively. BChls in LH-I absorb at 875 nm, and are labeled as B875 (green). P_A and P_B refer to the (photosynthetic reaction center) RC special pair, and B_A, B_B to the accessory bacteriochlorophylls. The figure clearly shows the coplanar arrangement of the B850 BChl ring in LH-II, the B875 BChl ring of LH-I, and the RC BChls P_A and P_B, B_A, B_B.

For the circular aggregate of BChls, the second and the third exciton states carry all the oscillator strength. (See box 1.) The oscillator strength of each of the two states is thus enhanced by a factor of N compared to a single BChl, with $2N$ being the number of BChls in the circular aggregate. Furthermore, the transition dipole moments of the optically allowed degenerate (second and third) exciton states are oriented in the two dimensional plane that encompasses all the BChls of the LH-IIs, LH-I and RC.

The excitation transfer LH-II → LH-I → RC occurs within 100 picoseconds at about 95% efficiency. To look in more detail, time-resolved spectroscopy has been used to determine the time constants for the individual excitation transfer steps.[15,16] There are many potential pathways for photons to be absorbed and for the subsequent excitations to reach the RC. One path originates from excitation of the 800 nm photons by LH-II. (See figure 4.) It requires, in general, four sequential steps for the respective excitations to be transferred to the RC: B800 (LH-II) → B850 (LH-II) → B850 (LH-II) → LH-I → RC. Time-resolved picosecond and femtosecond spectroscopy revealed that excitation transfer from B800 → B850 proceeds within about 700 fs. Two-color pump-probe femtosecond measurements determined a time constant of 3–5 ps for the B850 → LH-I step. The final LH-I → RC transfer step requires about 35 ps, making it the slowest step.[15,16] The rate for intercomplex LH-II → LH-II transfer has not been determined yet. However, picosecond absorption and excitation spectra measurements on *Rb. sphaeroides* have revealed a time constant of 12 ± 1 ps for the B800 excitation to be transferred all the way to the LH-I ring. Discounting the well-characterized B800 → B850 time constant of 0.7–2.0 ps and the B850 → LH-I time constant of 3–5 ps, one can estimate a time constant of at most a few picoseconds for the intercomplex LH-II → LH-II transfer.

An effective Hamiltonian can be constructed that describes the exciton system of the entire aggregate shown in figure 4. (See box 1.) Using a perturbation scheme, this Hamiltonian allows one to calculate the transfer rates between the different components, LH-II → LH-II, LH-II → LH-I, and LH-I → RC.[8] The nature of the pigment system, specifically its extensive system of electronic excitations, makes the aggregate shown the ideal target for spectroscopic studies that can monitor in great detail the excitation flow in the system. It turns out that the predictions based on the effective Hamiltonian description agree closely with observation.

Looking ahead

The integral structure of the photosynthetic unit, along with time-resolved spectroscopic measurements and an effective Hamiltonian description, explain a remarkable number of features of the light-harvesting process in purple bacteria on the basis of fundamental physics. However, many questions remain unanswered and new questions are raised. One of the new questions concerns the way in which the light-harvesting complexes aggregate in the photosynthetic membrane and how the size of the rings is determined. The crystal structures of LH-II display circular aggregates of identical building blocks. Although functionally the structure of the exciton levels of the ring-shaped BChl aggregates, as described in box 1, is independent of ring size, it is tempting to ask why LH-II of *Rs. molischianum* forms a complex of eight building blocks while LH-II of *Rps. acidophila* and *Rb. sphaeroides* form complexes of nine building blocks. What is the effect of static and dynamic disorder on the delocalized excitons? Static disorder is caused by structural heterogeneity, and dynamic disorder involves off-diagonal disorder through the thermal fluctuation of BChl position and orientation. Can dynamic disorder dephase the coherency underlying the excitonic states of the circular BChl aggregates? (See box 1.) What is the mechanism by which the photosynthetic unit regulates light absorption and excitation transfer under intense light to avoid burning the RC?

The guiding principles governing light harvesting of purple bacteria should be generally applicable to other photosynthetic organisms. In this regard, it should be noted that the structures of several other light-harvesting systems have already been solved, including the water-soluble BChl-*a* pigment–protein complex of the green sulfur bacterium *Prostechochloris aestuarii*, the water-soluble pigment–protein complex from the cyanobacterium *Mastigocladus laminosus*, LHC-II of green plants and Photosystem

I of plants, as well as the peridinin–chlorophyll–protein from *Amphidinium carterae*. Comparing these systems shows that light-harvesting in photosynthesis has evolved toward one goal—namely, maximizing efficiency—but has been realized differently in different organisms: Only bacteria evolved ringtype chlorophyll aggregates.

The determination of a structural model of the light-harvesting system of purple bacteria has been the achievement of many researchers. It amounts to a significant step toward understanding the physical mechanisms that photosynthetic life-forms selected in establishing life on Earth. Knowing the structure of light-harvesting complexes will advance our understanding of the primary excitation transfer process, just as the structure of the RC revolutionized the study of the primary electron transfer processes. Spectroscopic data of light harvesting will be interpreted on the solid basis of an atomic structure, and new experiments can be suggested. These developments coincide with important technical advances in time-resolved femtosecond laser spectroscopy[15] (see "Ultrafast Reaction Dynamics" by Martin Gruebele and Ahmed Zewail in PHYSICS TODAY, May 1990, page 24) and in molecular genetics.[5] The advances in laser spectroscopy promise to probe dynamics of excitation transfers on time scales comparable to intrinsic atomic motions. The advances in molecular genetics make possible the site-directed mutation of the light-harvesting complexes for probing functionally and structurally important residues. More practically, it is possible that the physical principles governing the light-harvesting and electron transfer processes, having been selected and optimized over billions of years of evolution, one day will be applied to engineer solar cells.

To sum up, the work yet to come will combine research in physics and biology to elucidate further the interplay of life and light.

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References

1. H. Scheer, ed., *Chlorophylls*, CRC Press, Boca Raton, Fla. (1991).
2. R. Emerson, W. Arnold, J. Gen. Physiol. **16**, 191 (1932).
3. J. Deisenhofer, O. Epp, K. Miki, R. Huber, H. Michel, Nature **318**, 618 (1985).
4. L. N. M. Duysens, "Transfer of Excitation Energy in Photosynthesis," PhD thesis, Univ. Utrecht (1952).
5. R. E. Blankenship, M. T. Madigan, C. E. Bauer, eds., *Anoxygenic Photosynthetic Bacteria*, Kluwer Academic Publishers, Dordrecht, Germany (1995).
6. G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell, N. W. Isaacs, Nature **374**, 517 (1995).
7. J. Koepke, X. Hu, C. Muenke, K. Schulten, H. Michel, Structure **4**, 581 (1996).
8. X. Hu, T. Ritz, A. Damjanovic, K. Schulten, J. Phys. Chem. B **101**, 3854 (1997).
9. J. R. Oppenheimer, Phys. Rev. **60**, 158 (1941).
10. W. Arnold, J. R. Oppenheimer, J. Gen. Physiol. **33**, 423 (1950).
11. T. Förster, Ann. Phys. (Leipzig) **2**, 55 (1948).
12. P. Tavan, K. Schulten, Phys. Rev. B **36**, 4337 (1987).
13. S. Karrasch, P. A. Bullough, R. Ghosh, Eur. Mol. Biol. J. **14**, 63, (1995).
14. M. Z. Papiz, S. M. Prince, A. M. Hawthornthwaite-Lawless, G. McDermott, A. A. Freer, N. W. Isaacs, R. J. Cogdell, Trends in Plant Science **1**, 198 (1996).
15. T. Pullerits, V. Sundstrom, Acc. Chem. Res. **29**, 381 (1996).
16. R. van Grondelle, J. Dekker, T. Gillbro, V. Sundstrom, Biochim. Biophys. Acta, **1187**, 1, (1994).
17. R. S. Knox, *Theory of Excitons*, Academic Press, New York (1963).
18. D. L. Dexter, J. Chem. Phys. **21**, 836 (1953). ■