

Bacterial Photosynthesis

Szeged, 18 October, 2007

What is photosynthesis?

Photosynthesis is the most important biological process on Earth.



Photosynthesis

- has stored **energy** from the sun in petroleum, natural gas and coal,
- fills all of our **food** requirements and many of our needs for **fiber** and **building materials**,
- has transformed the world into the hospitable **environment**,
- research is critical to maintaining and improving our **quality of life**.

We can learn

- how to increase **crop yields** of food, fiber, wood, and fuel,
- how to better use our **lands**,
- how to provide new, efficient ways to collect and use **solar energy**,
- how to design new, faster, and more compact **computers**,
- how carbon dioxide and other "greenhouse gases" affect the global **climate** and
- how to come even to new **medical breakthroughs**.

Photosynthesis and energy storage



Our **major sources of energy** (coal, oil, natural gas etc.) are all derived from ancient plants and animals. Thus, most of the energy we use today originally **came from sunlight through photosynthesis!**

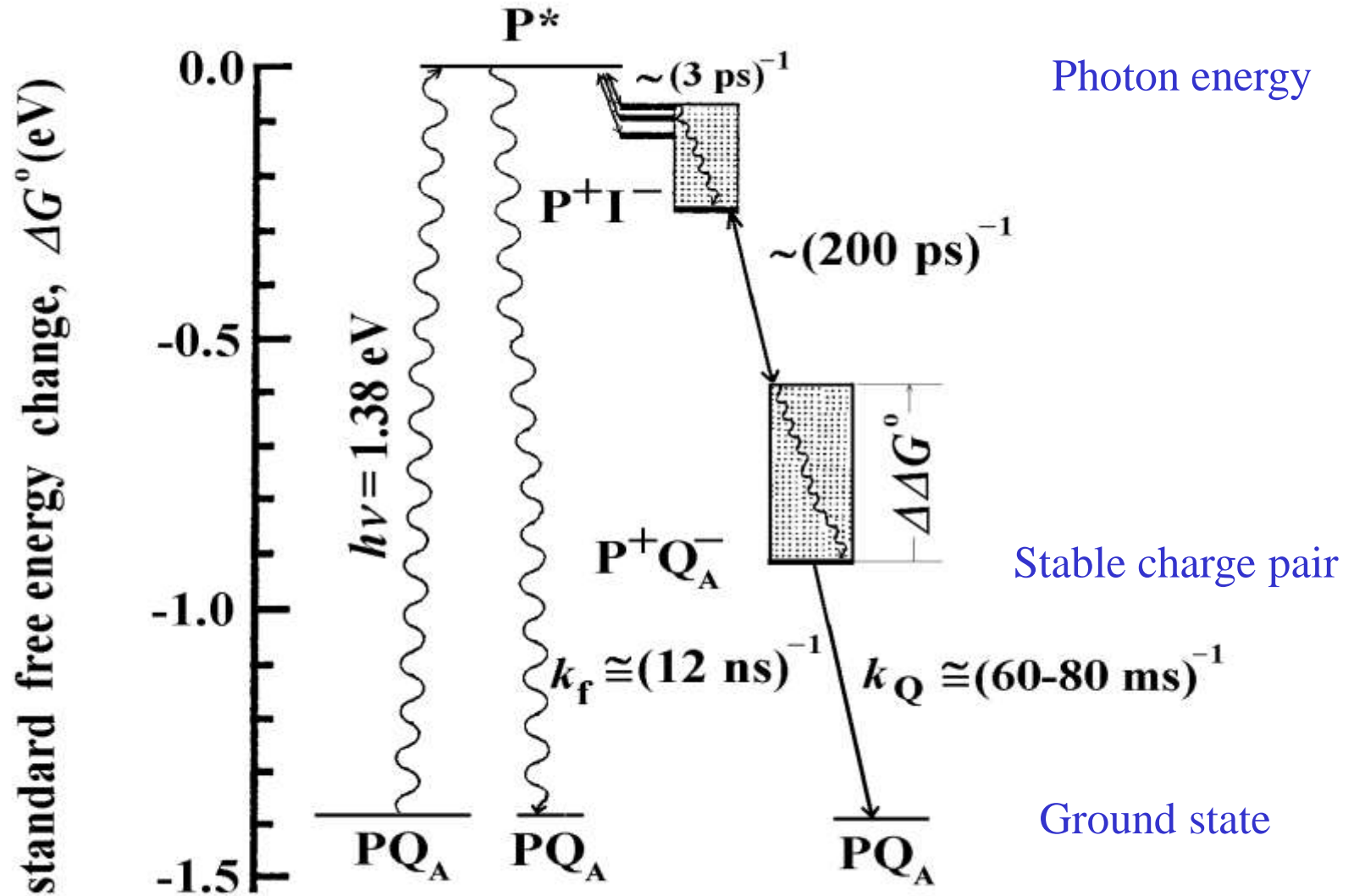
Efficiency of energy conversion.

- The overall photosynthesis process is **relatively wasteful**:
 - 0.2% for uncultivated plant life,
 - 1-2% of cultivated plant,
 - ~ 8% in sugar cane, which is one of the most efficient plants (8% of the light absorbed by the plant is preserved as chemical energy).

Many plants undergo a process called **photorespiration**. This is a kind of "short circuit" of photosynthesis that wastes much of the plants' photosynthetic energy.

- The early steps in the conversion of sunlight to chemical energy are **quite efficient**.

The yield of conversion of light energy to stable photochemical energy is $\sim 30\%$



Photosynthesis myths

- Only plants are phototrophs
 - At least 50% of photosynthesis is bacterial
- All phototrophs are green
 - Phototrophs come in all colors
- Photosynthesis produces Oxygen
 - Lots of anoxygenic photosynthesis
- All photosynthesis uses a multiprotein complex
 - Bacteriorhodopsin/Proteorhodopsin are single enzymes
- Photosynthesis is pretty well characterized
 - Many uncharacterized phototrophs in Oceans

Photosynthesis = Light \rightarrow Carbohydrates

Light \rightarrow (Chemical) Energy

Chlorophyll a / Bacteriochlorophyll

Other Pigments

Antenna/Reaction centers

Membranes

e^- and H^+ Transport

Bacteriorhodopsin/Proteorhodopsin

Oxygenic Photosynthesis

Plants

Algae

Cyanobacteria

Oxygen is a “Side-product”

Anoxygenic Photosynthesis

Mostly reduced sulfur-containing chemicals as reductants

Many Bacteria

Catching Light

Pigments

Chlorophyll

Mg-tetrapyrrole

Usually in membranes

Highly variable

Bacteriochlorophyll a

Absorbs other wavelengths than chlorophyll a (and many other Bacteriochlorophyll types)

„Special Pair” very **electropositive** (in the dark)

but very **electronegative** (in the light)

Photosynthetic Membranes

Thylakoid-membrane

Eukaryotes

Other membranes

Prokaryotes

Chlorosome

Other Pigments

Phycobilins

Phycobiliproteins - Light antenna in cyanobacteria and red Algae

Outside: Phycoerthrin (550 nm)

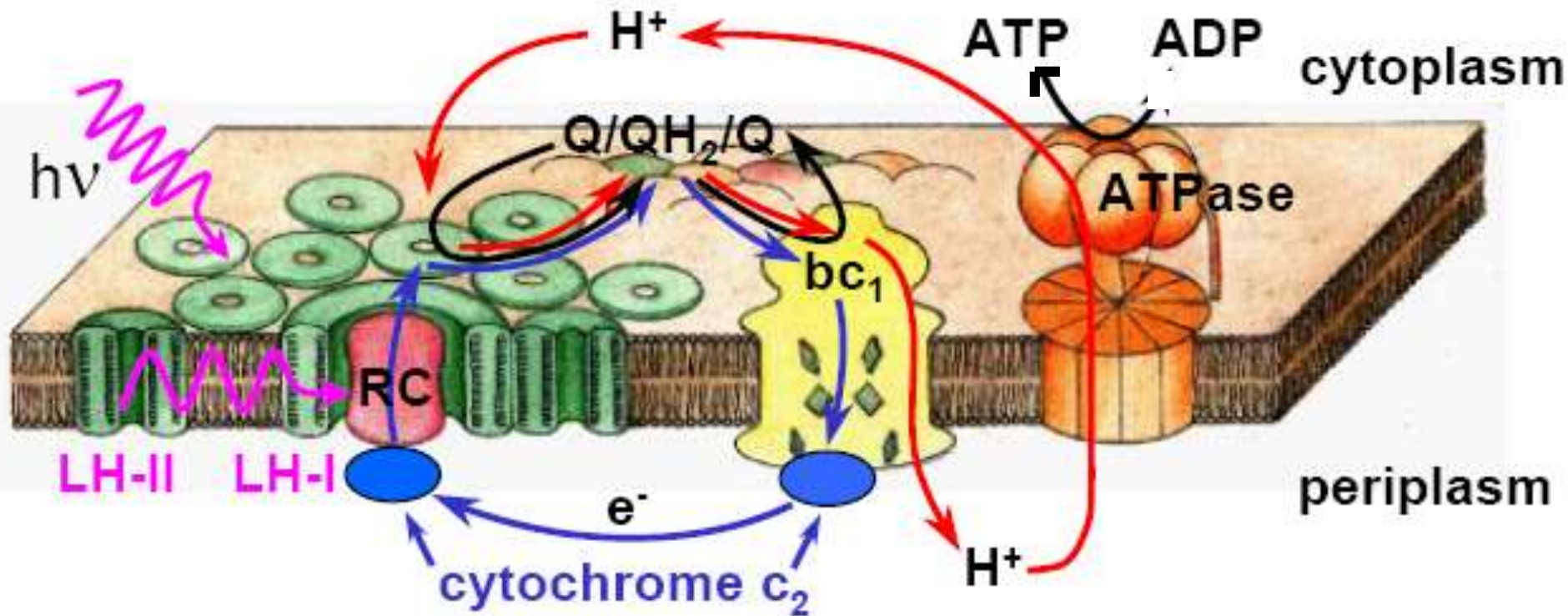
Middle: Phycocyanin (620 nm)

Inner: Allophycocyanin (650 nm)

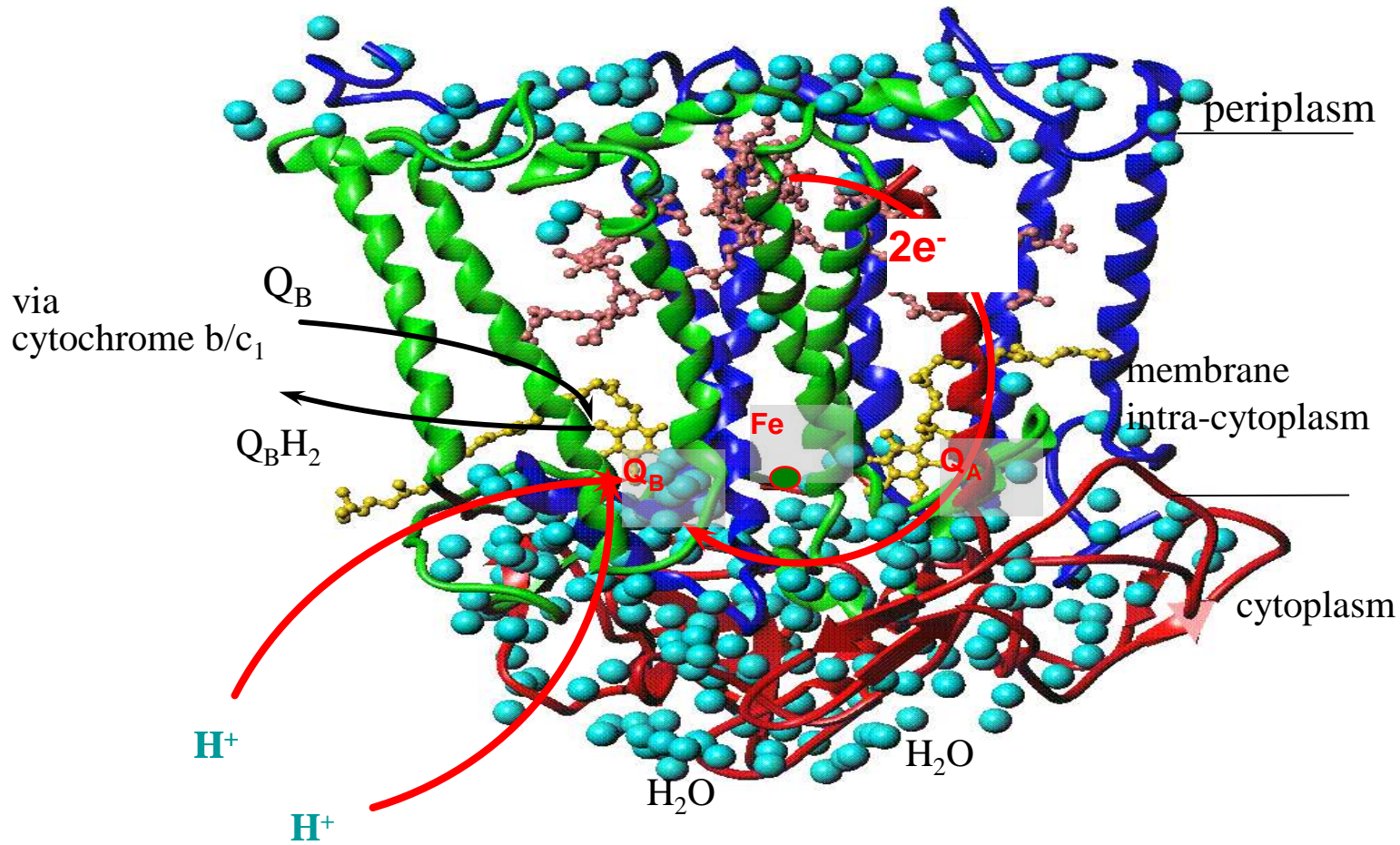
Chlorophyll a

More Phycobilisomes at low Light

Photosynthetic Apparatus of Purple Bacteria



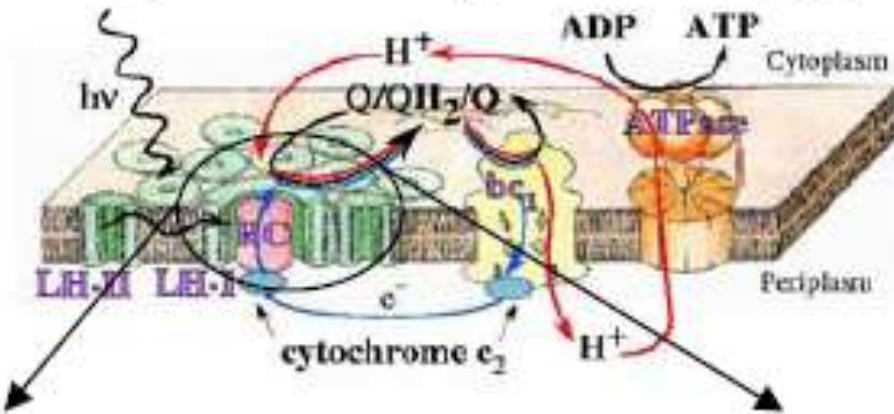
Structure and function of the RC from *Rba. sphaeroides*.
The bacterial RC is a redox protein.



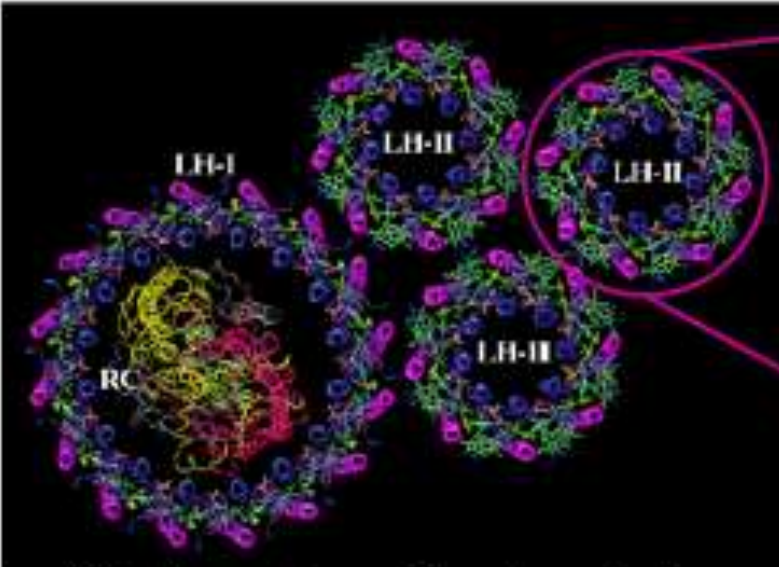
Stowell et al. (1997, pdb 1AIG).

Harvesting the Sun

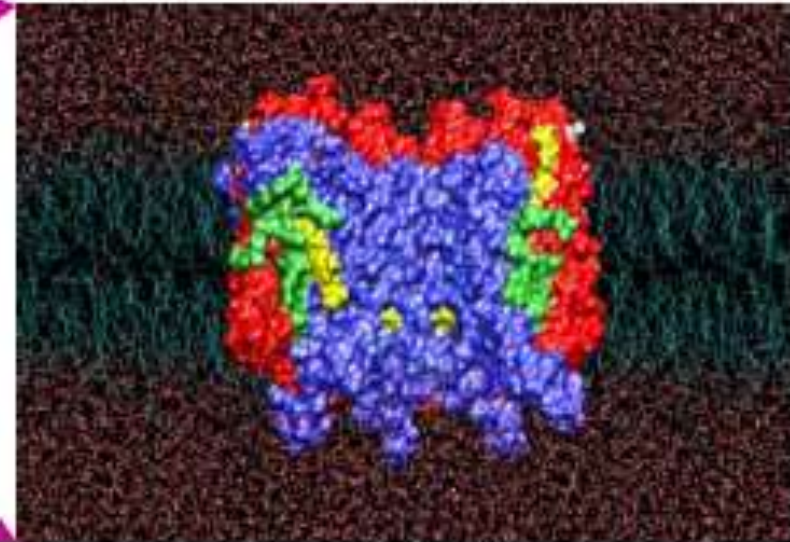
Photosynthetic membrane generates ATP using light energy



The light harvesting system displays a hierarchy of integral, functional units



Light harvesting unit funnels excitation energy to photosynthetic reaction center



Light harvesting complex II absorbs light and converts it into electronic excitations of BChls

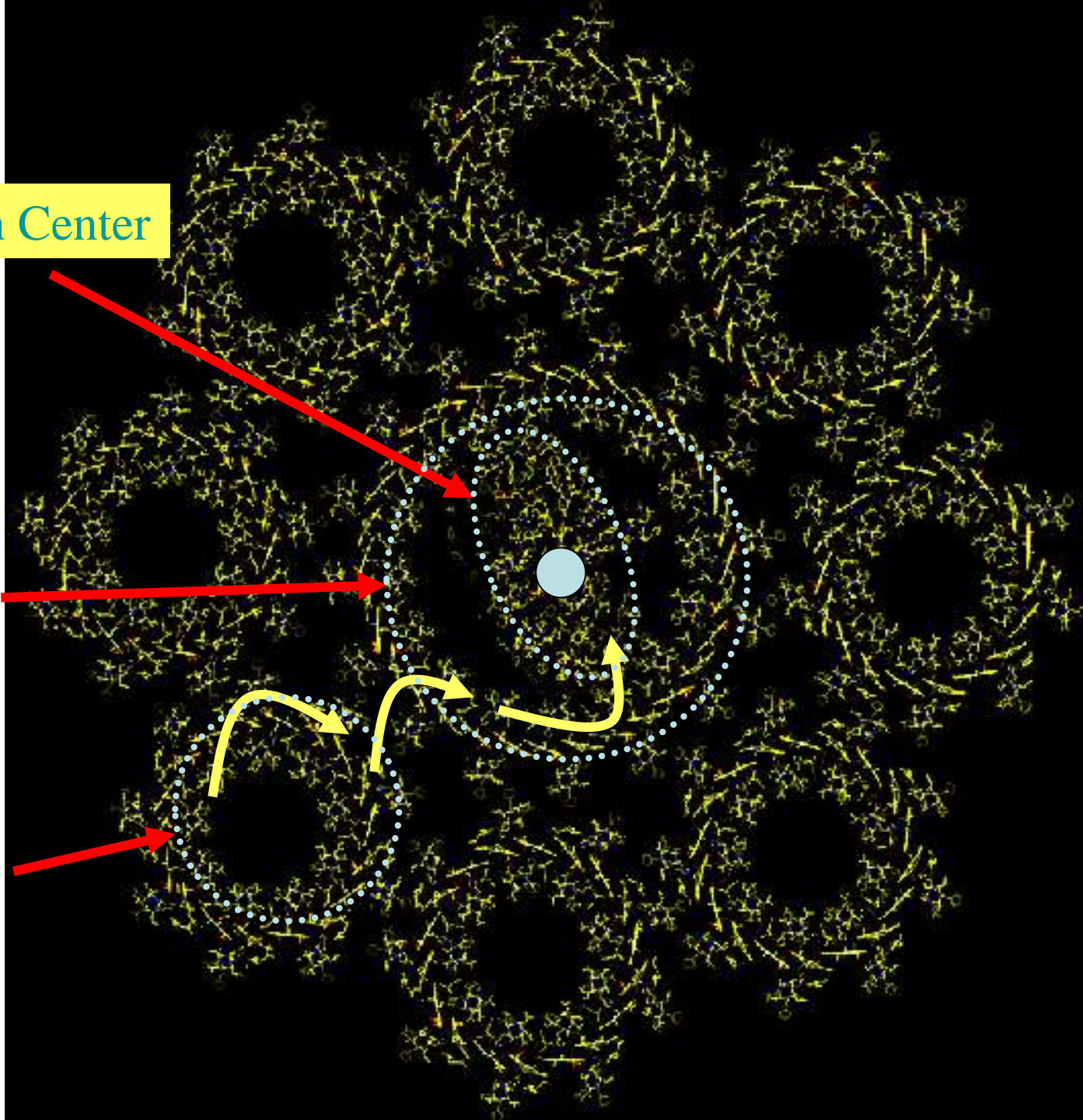
Molecular modeling of integral, functional units with more than 10^6 atoms necessary

Reaction Center

LH1

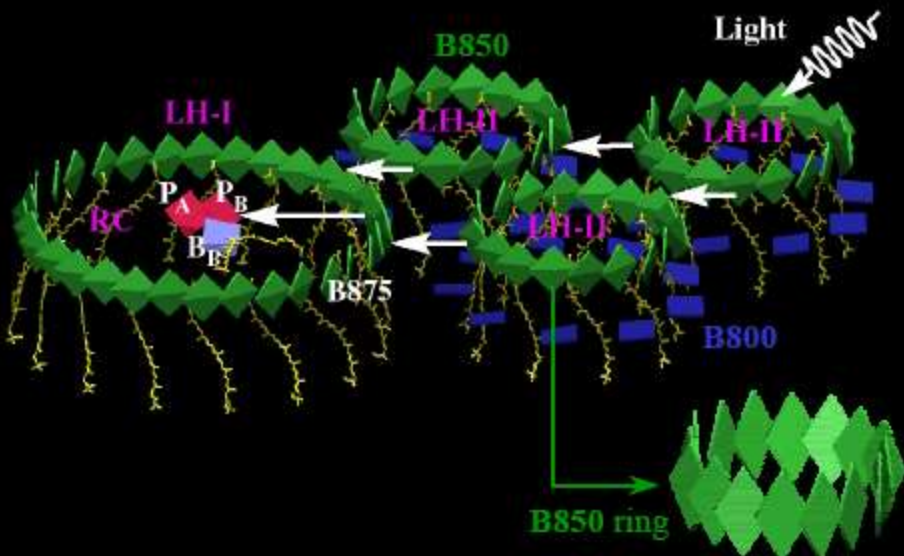
LH: light harvesting complex

LH2

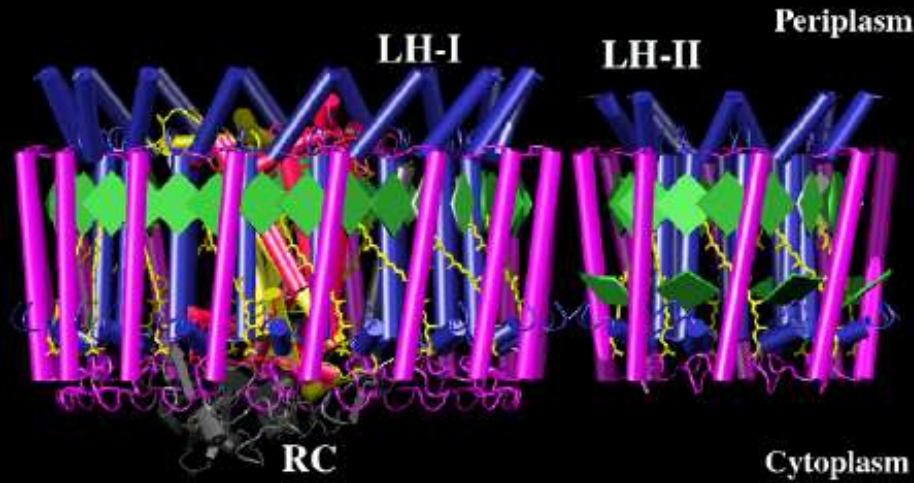


Harvesting the light. Absorption of the photon and migration of the electronic excitation energy to the RC.

Hierarchical aggregate of *chromophores*



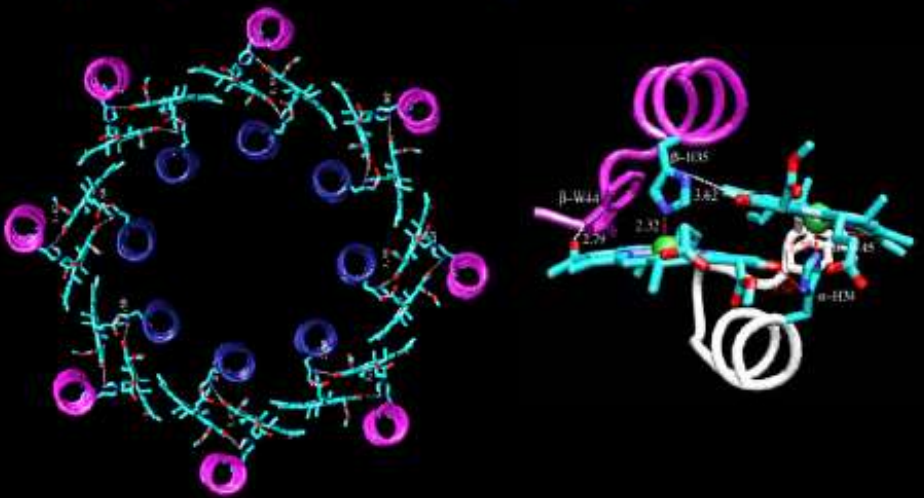
Pigment Organization in the Bacterial Photosynthetic Membrane



Note the conspicuous arrangement of chlorophyll rings!

B850 BChls of LH-II of *Rs. molischianum*

New aggregation pattern of chlorophylls, first discovered by R. Cogdell et al in LH-II of *Rps. acidophila*



Spectrum tuned through local and excitonic interactions as well as disorder

How does the Light Harvesting System function with thermal disorder?

How does Q/QH₂ pass through LH-I to/from RC within reasonable time (≈ 1 ms)?

Primary Absorption of a Photon

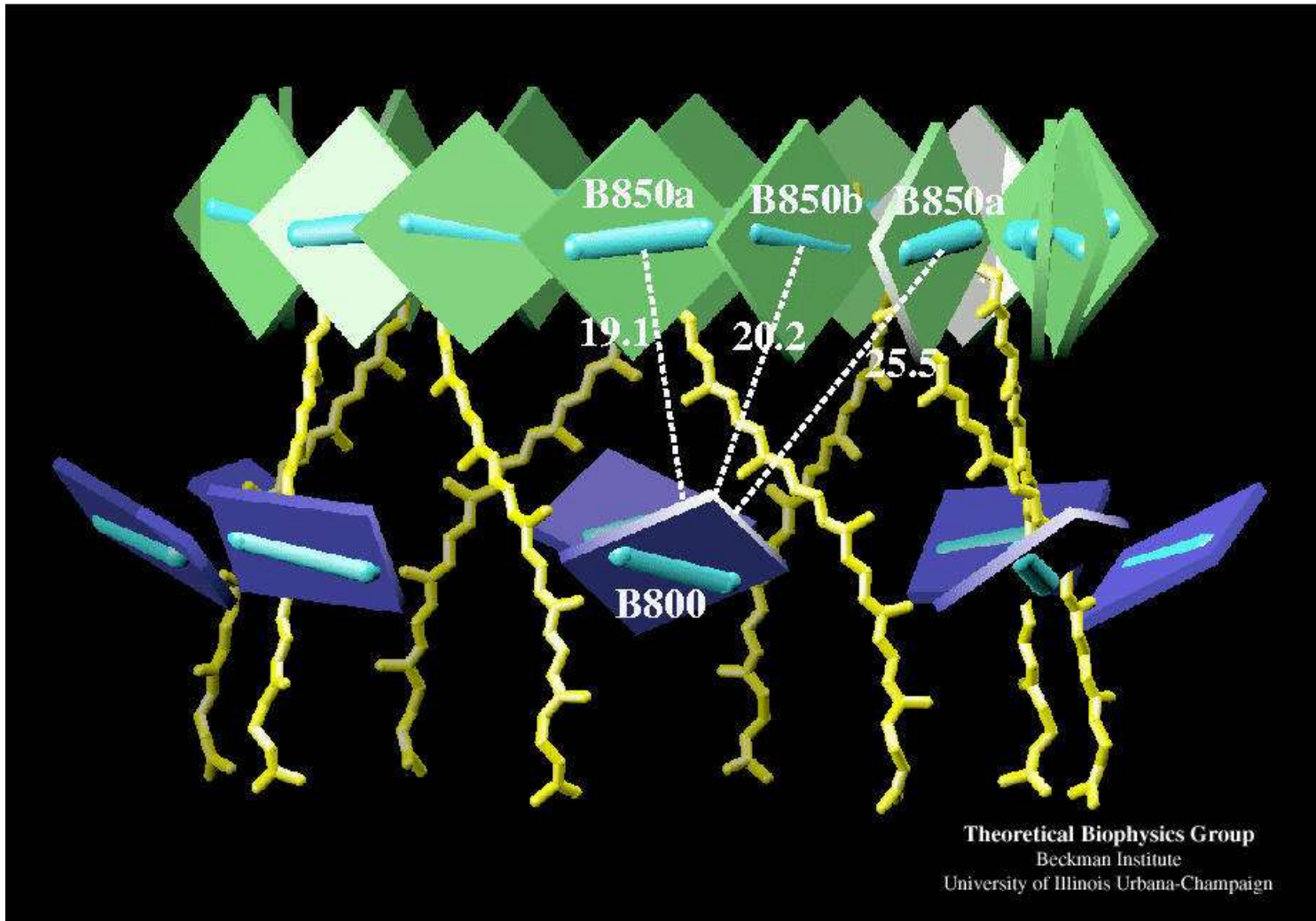
Purple bacteria have developed under relentless evolutionary pressure in a habitat below that of most plant life - that is, at the bottom of ponds or in topsoil, depending on the species. Only light left unharvested by plants penetrates to those depths, mainly at wavelengths at about 500 nm and above 800 nm.

Carotenoids in light-harvesting complexes of purple bacteria absorb at 500 nm.

Bacteriochlorophylls absorb at 800 - 875 nm. In LH-II, there exist two kinds of BChls.

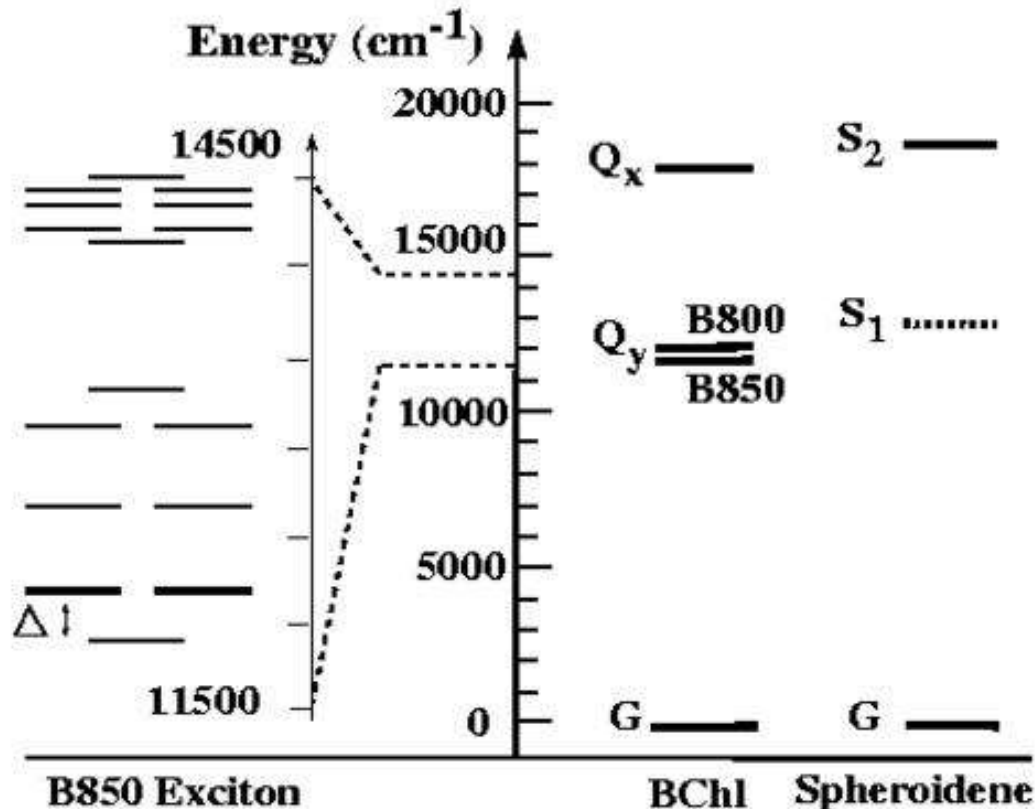


B800 BChls and B850 BChls, absorbing at 800 and 850 nm, respectively. B800 and B850 BChls are oriented perpendicular to each other so that they can absorb light from every direction. While the B800 BChls are spatially separated (center-to-center) by 20 Å, B850 BChls form a ring of close (around 9 Å) and, thus, tightly coupled BChls. To characterize the electronic properties of the excited states of a circular BChl aggregate, an effective Hamiltonian description have been established. The excited states of the aggregate, so-called **excitons**, are described as a superposition of single BChl Q_y excitations.



Optical Properties

The energies associated with the eigenstates (exciton states) of the effective Hamiltonian for the B850 BChl aggregate of LH-II of *Rs. molischianum* are shown below together with the energies of the excited states of single BChls and the carotenoid spheroidene. The two bands in the spectrum arise from a dimerization of the BChls in LH-II and LH-I, i.e., the distance between neighboring BChls within one heterodimer (9.2 \AA in LH-II), is different from the distance between neighboring BChls between heterodimers (8.9 \AA in LH-II).



The ring structure increases absorption

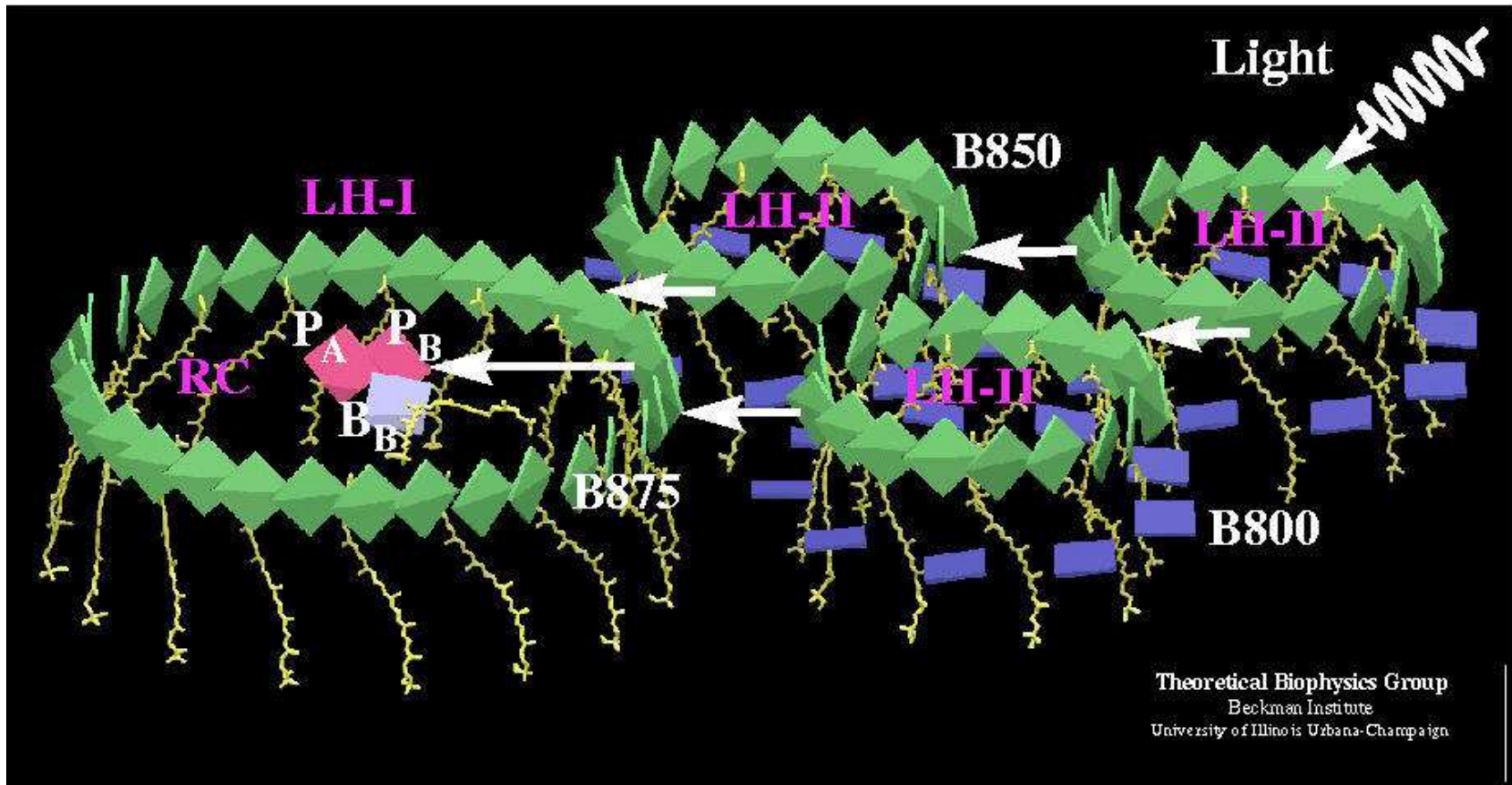
The distribution of oscillator strength can have important functional implications: excitation of the B850 BChl system would result, after thermal relaxation, in the preferential population of the energetically lowest exciton state $|1\rangle$ which is optically forbidden due to its vanishing oscillator strength and, hence, is prevented from wasteful fluorescence. The population of state $|1\rangle$ would depend sensitively on the actual energy difference between $|1\rangle$ and the energetically degenerate states $|2\rangle$, $|3\rangle$.

The ring structure generates an energy trap

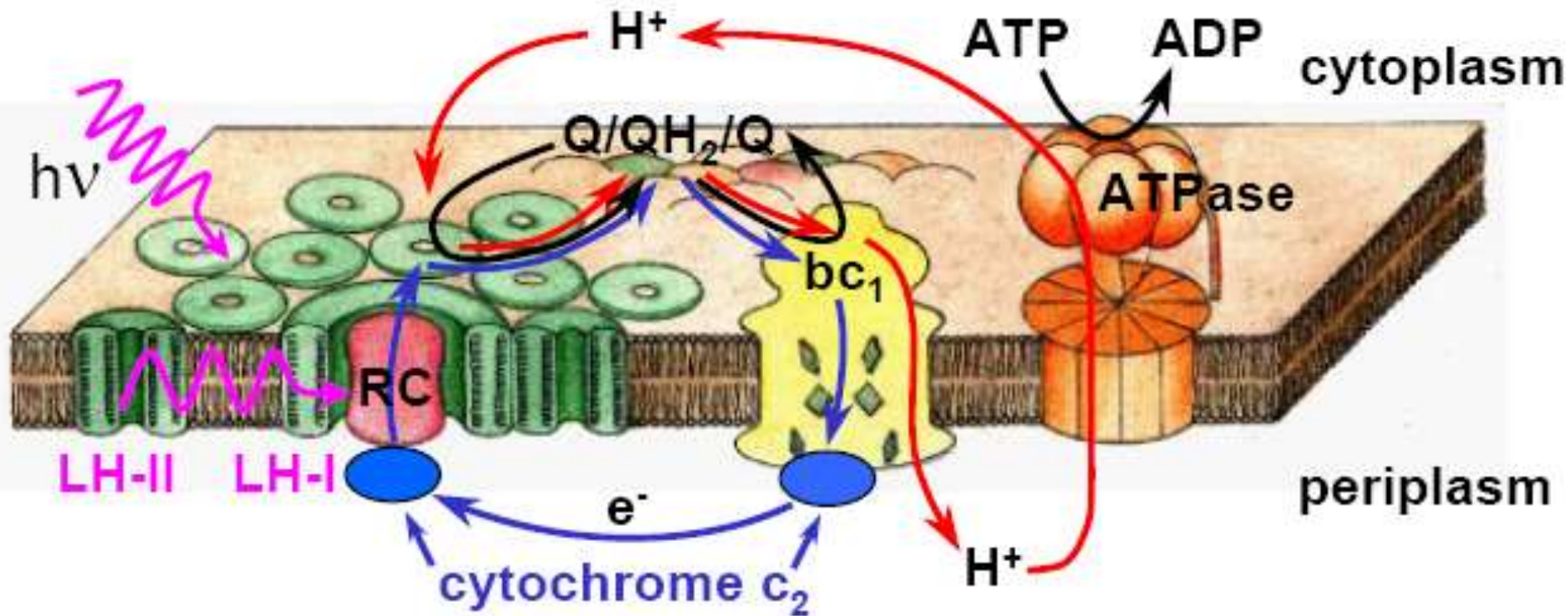
One must note that the properties of the B850 BChl system outlined hinge much on the ideal **eight-fold symmetry** axis of LH-II of *Rs. molischianum*. **Distortions** due to thermal motion or interruptions of the complete circle would alter the oscillator strength distribution. The characteristics of the exciton states due to a complete coherent spread of the excitations over the LH-II ring need to be studied in the presence of distortions. It is widely believed that the B850 BChl excited states, despite natural disorder, are delocalized, but the extent of delocalization is debated. The estimate for the number of coherently coupled BChls ranges from two BChl molecules to the entire length of the B850 BChl aggregate. The treatment of dynamic disorder for an exciton system like that of the Q_y excitons in LH-II is technically extremely difficult and essentially impossible.

Inter-Complex Excitation Transfer

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). PA and PB refer to the reaction center special pair, and BA, BB to the accessory bacteriochlorophylls. The figure exhibits clearly the co-planar arrangement of the B850 BChl ring in LH-II, the B875 BChl ring of LH-I, and the reaction center BChls PA, PB, BA, BB.



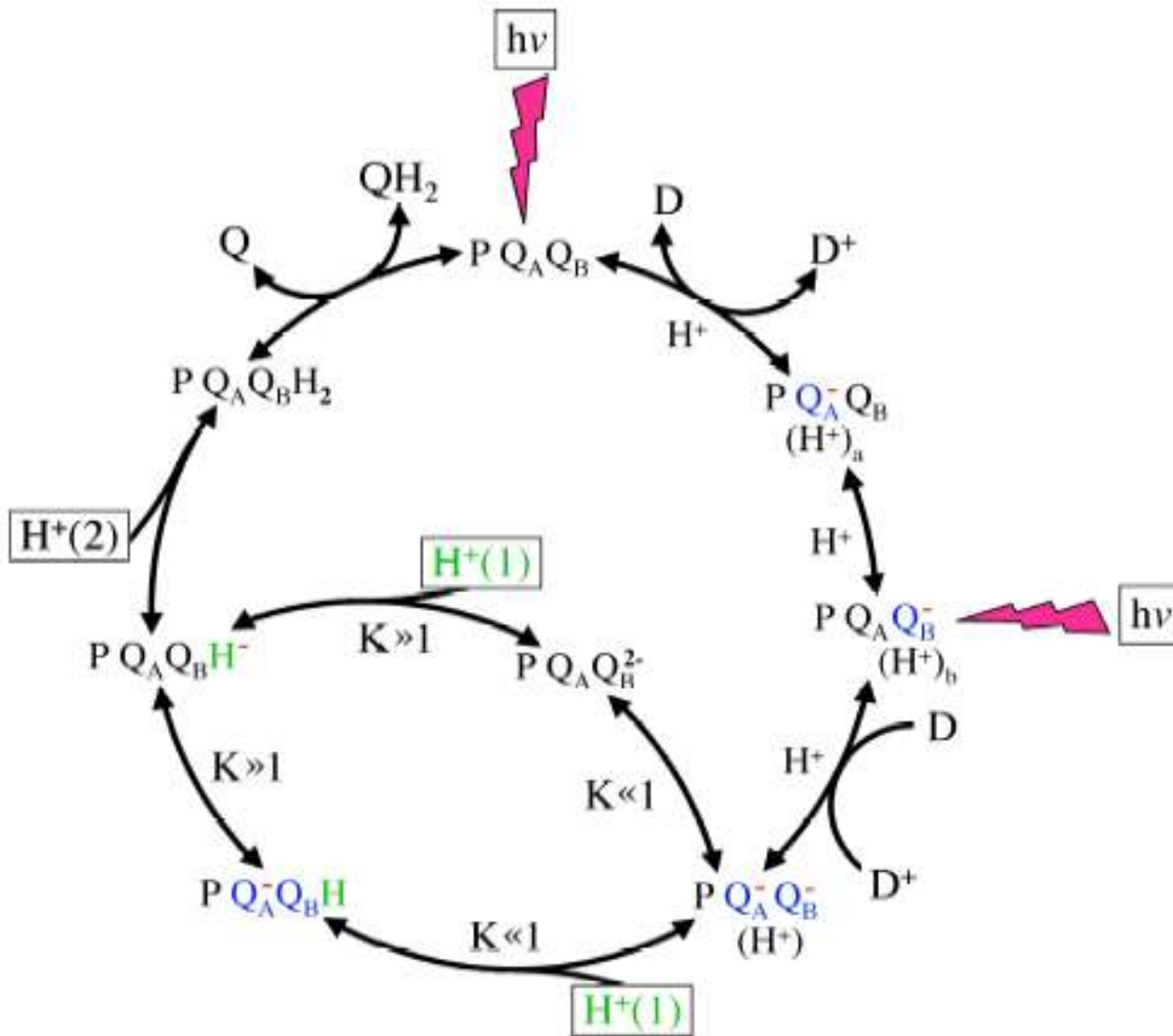
Natural way of proton translocation (proton pump)



RC - Photosynthetic Reaction Center

LH - Light Harvesting Complex

The photocycle in the RC. It is part of a proton pump.



1st photoactivation: the first electron is shared between the two quinones. The negative charges of the anionic semiquinones induce proton uptake to the protein, contributing to the partial shielding and stabilization of the semiquinones.

2nd photoactivation: the full reduction of Q_B is coupled with the delivery of two protons to the quinone head group, to form QH_2 , which unbinds and is replaced by an oxidized quinone. Two possible routes are shown for the proton-coupled second electron transfer - the lower path (PT/ET) is the active one.

Generation of protonmotive force in nanovesicles (artificial proton pump)

