Beckman Institute

NSF Summer School UIUC 2003

Molecular Machines of the Living Cell : Photosynthetic Unit from Light Absorption to ATP Synthesis

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Ana Damjanovic

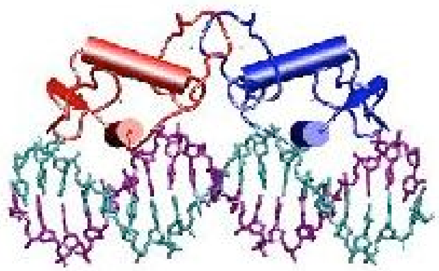
Theoretical Biophysics Group

(also Sanghyun Park, Deyu Lu, and Ulrich Kleinekathoefer)

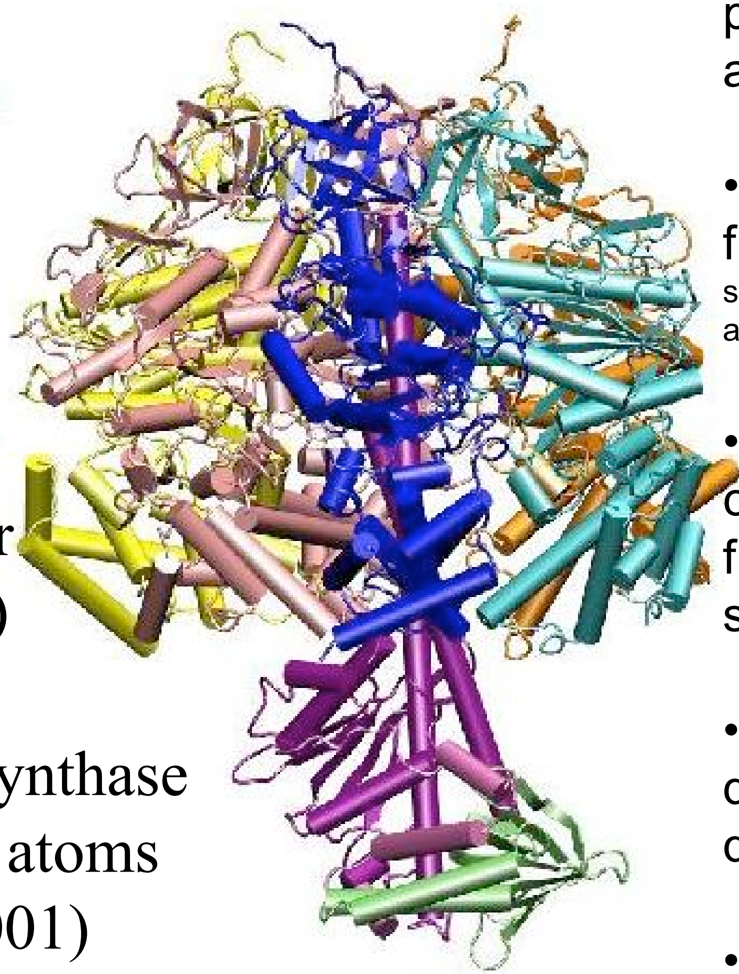
Research Opportunities in the Teraflop Era

Towards Larger Molecules

BPTI
3K atoms



Estrogen Receptor
36K atoms (1996)



ATP Synthase
327K atoms
(2001)

- Studying protein-protein and protein-nucleic acid recognition and assembly.

- Investigating integral functional units (membrane proteins, signal transduction, motors, bioenergetic apparatus).

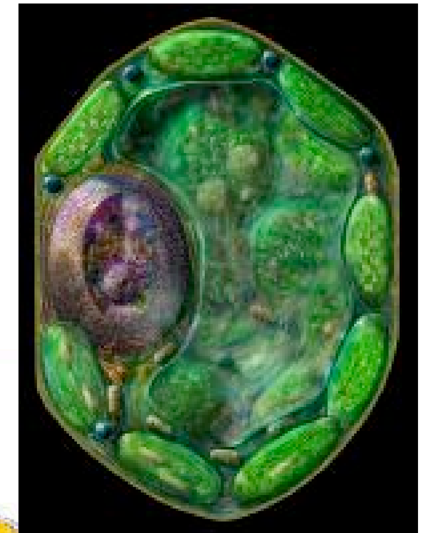
- Bridging the gap between computationally feasible and functionally relevant time scales.

- Combining classical molecular dynamics simulations with quantum chemical forces.

- Describing integral cell functions.

Molecular Machines of the Living Cell

Animal cell

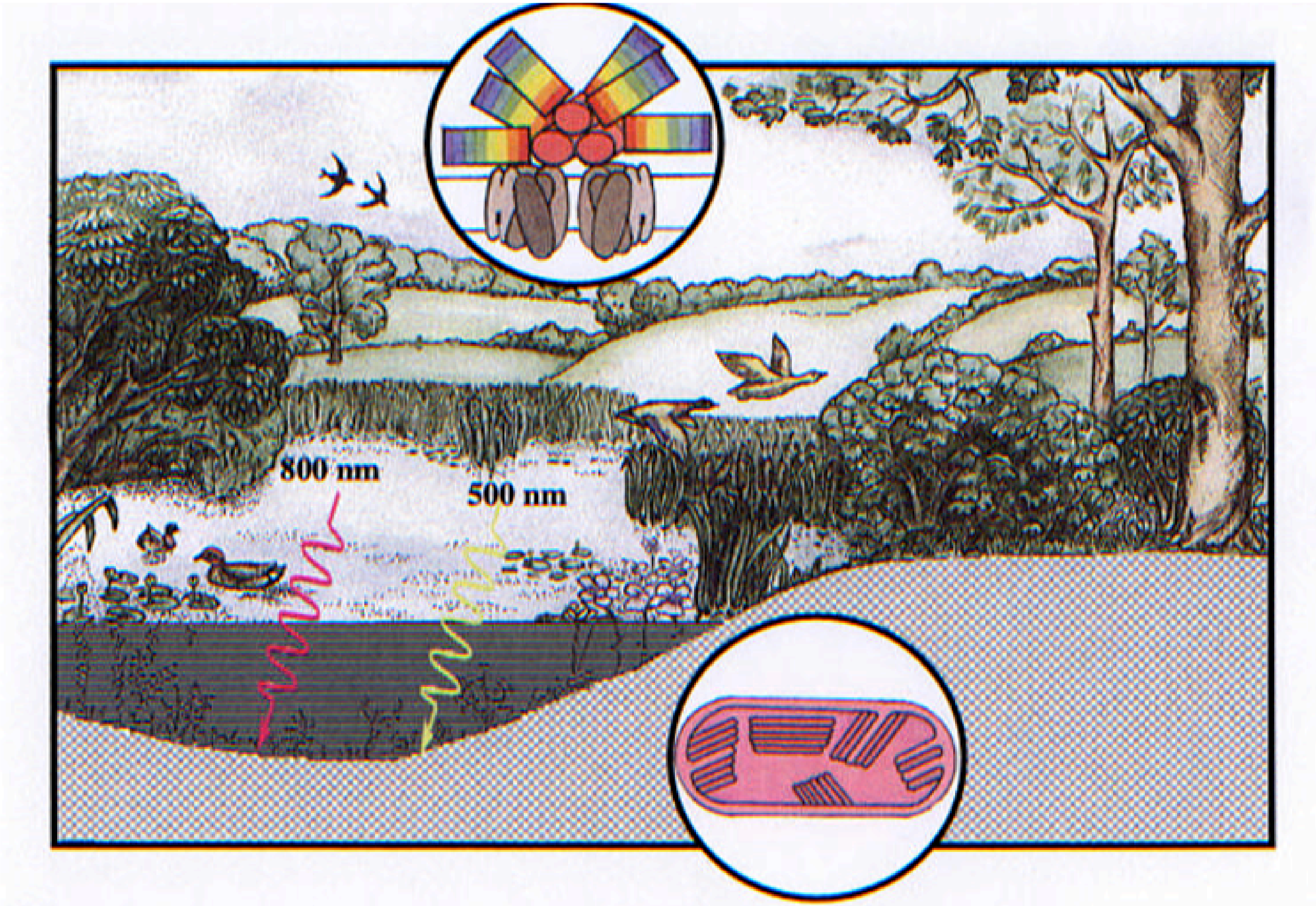


Plant cell

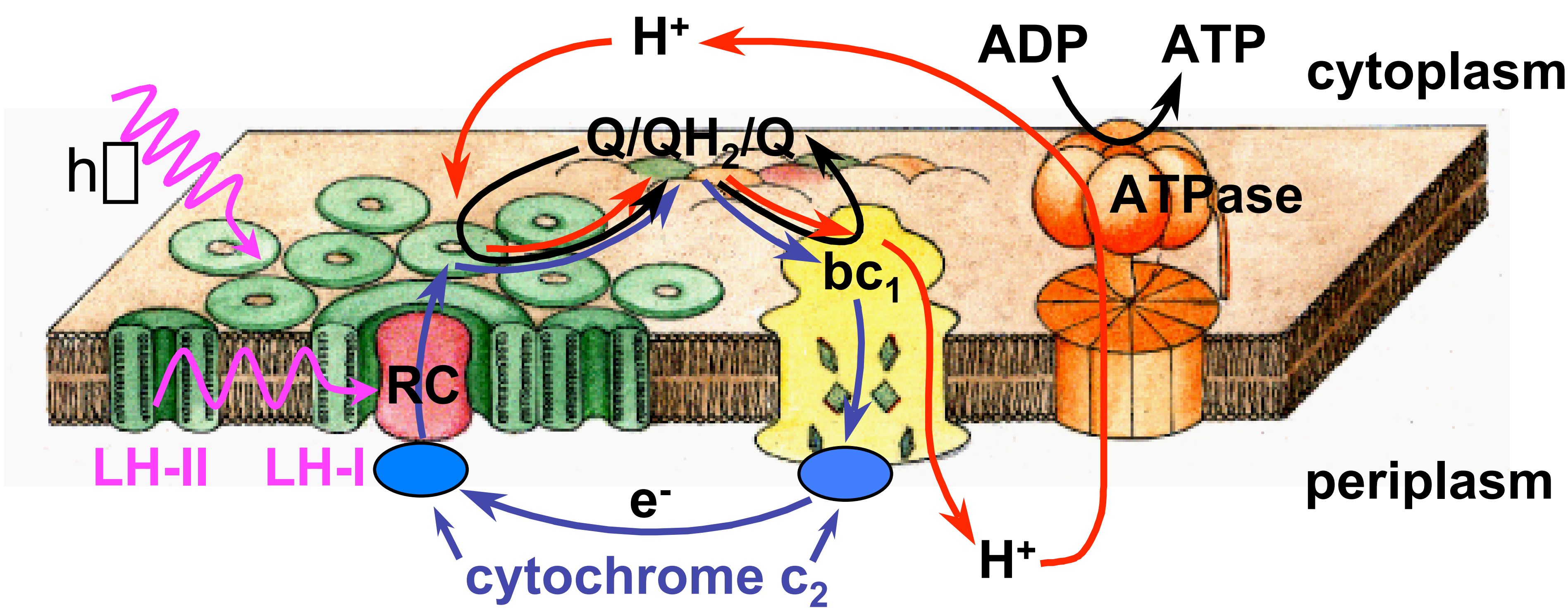
Study of integral cell functions:

gene storage, regulation, and expression; protein synthesis and degradation; energy conversion and storage; cell motion; cell signaling; metabolic pathways; …

Habitats of Photosynthetic Life Forms



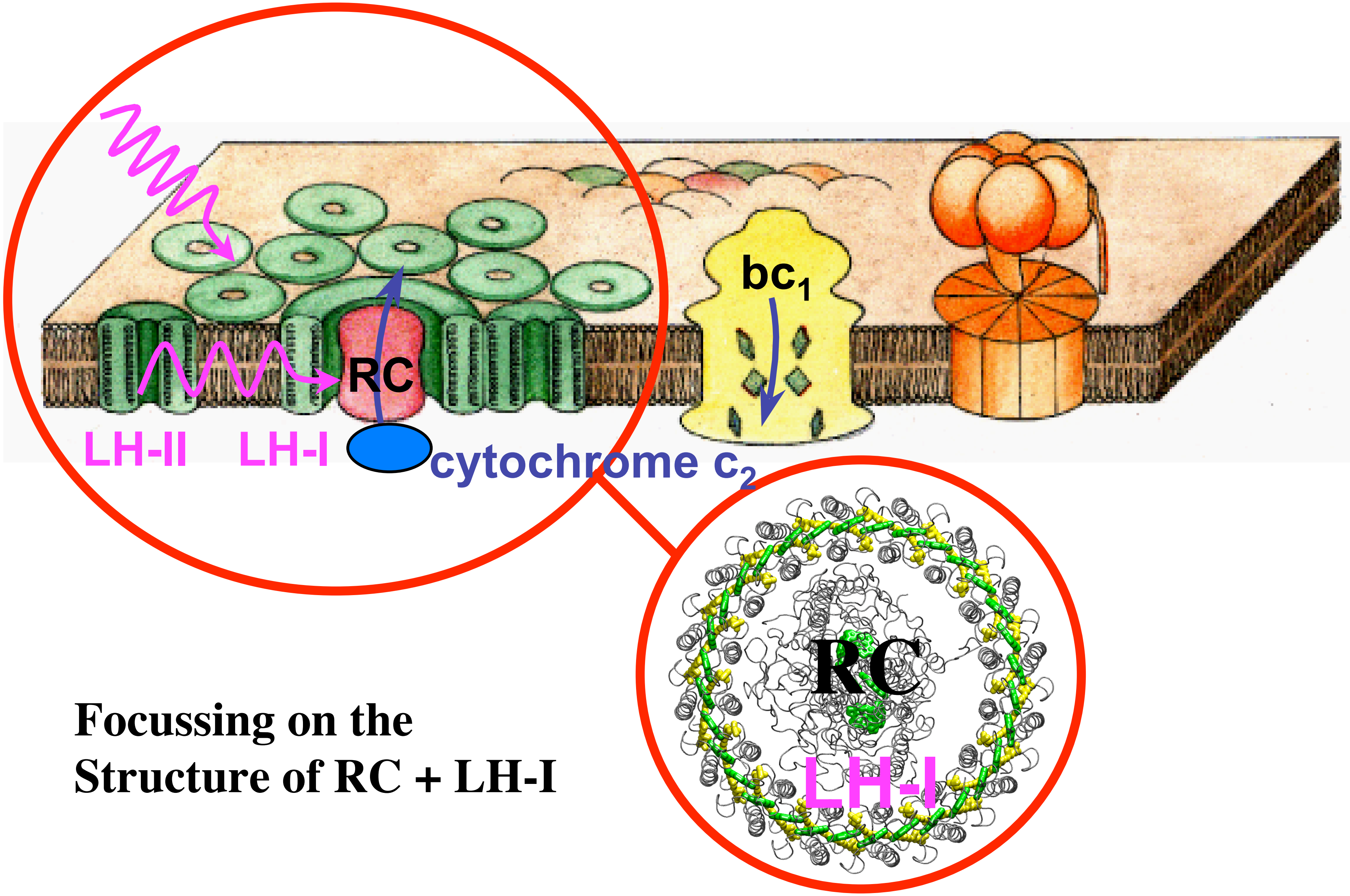
Photosynthetic Apparatus of Purple Bacteria



RC - Photosynthetic Reaction Center

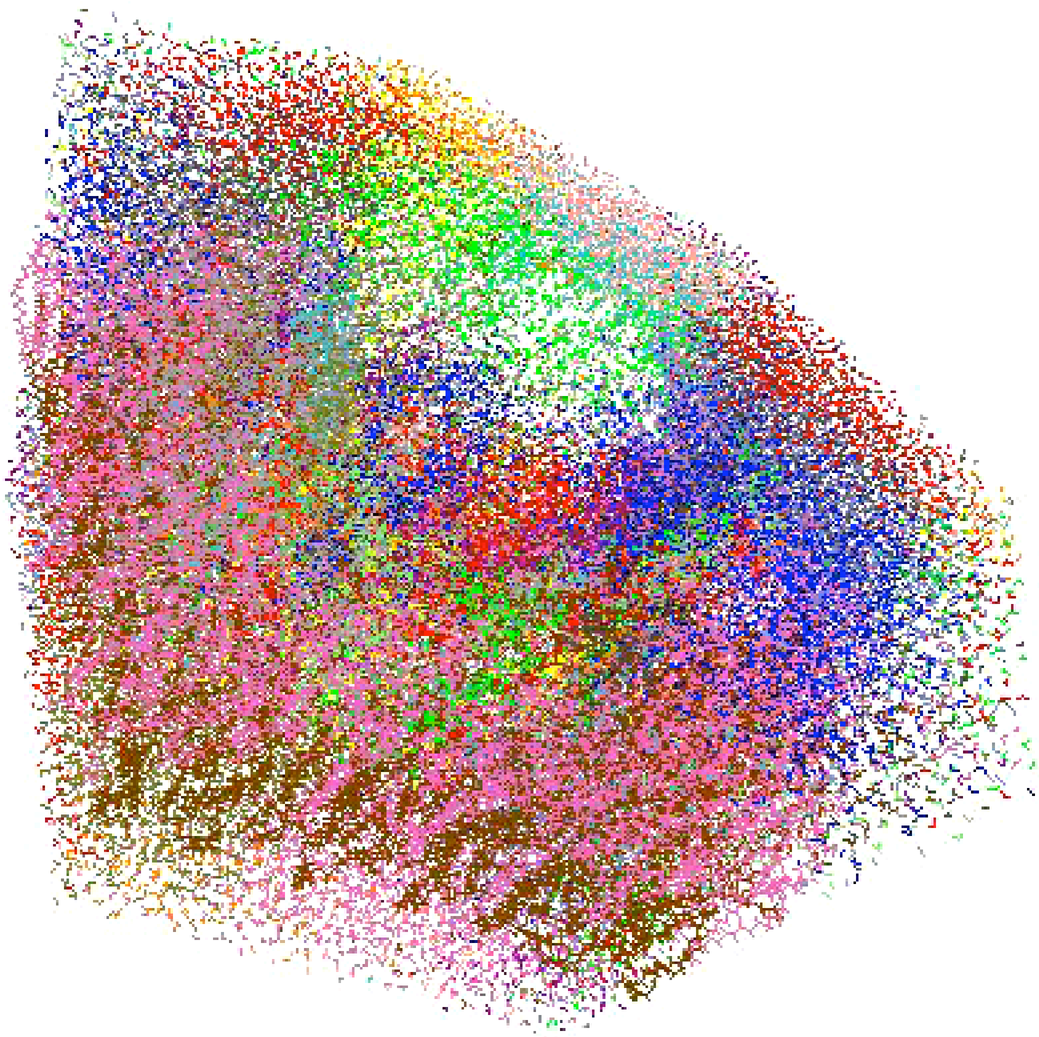
LH – Light Harvesting Complex

Structure of RC+LH-I+Cyt System



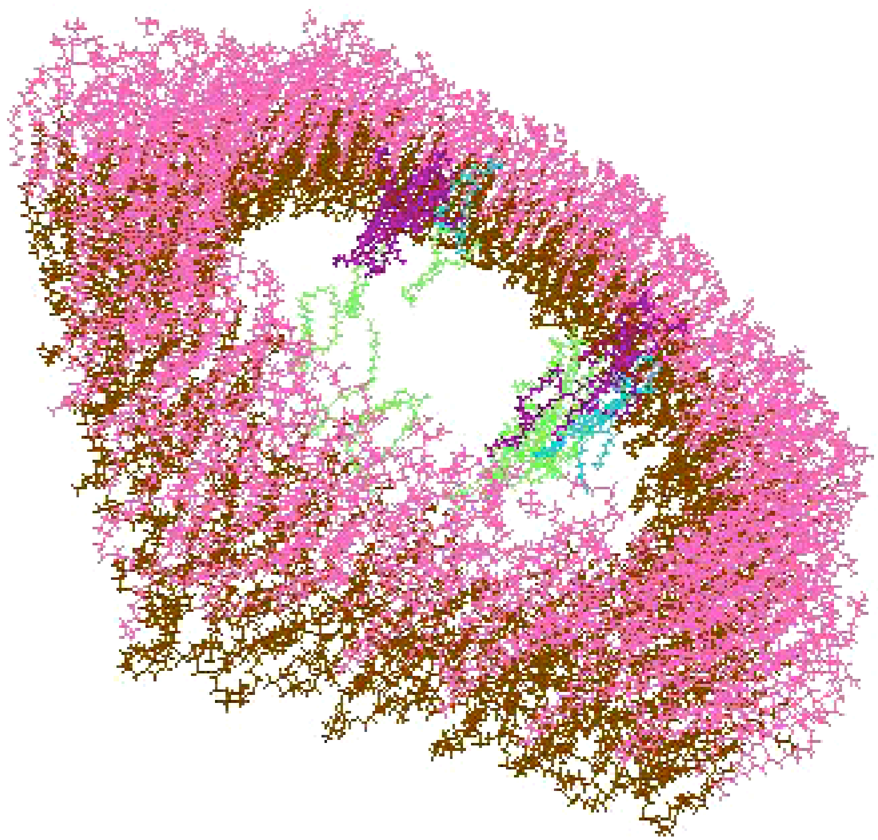
Focussing on the Structure of RC + LH-I

Focussing on the Structure of RC+LH-I+Cyt



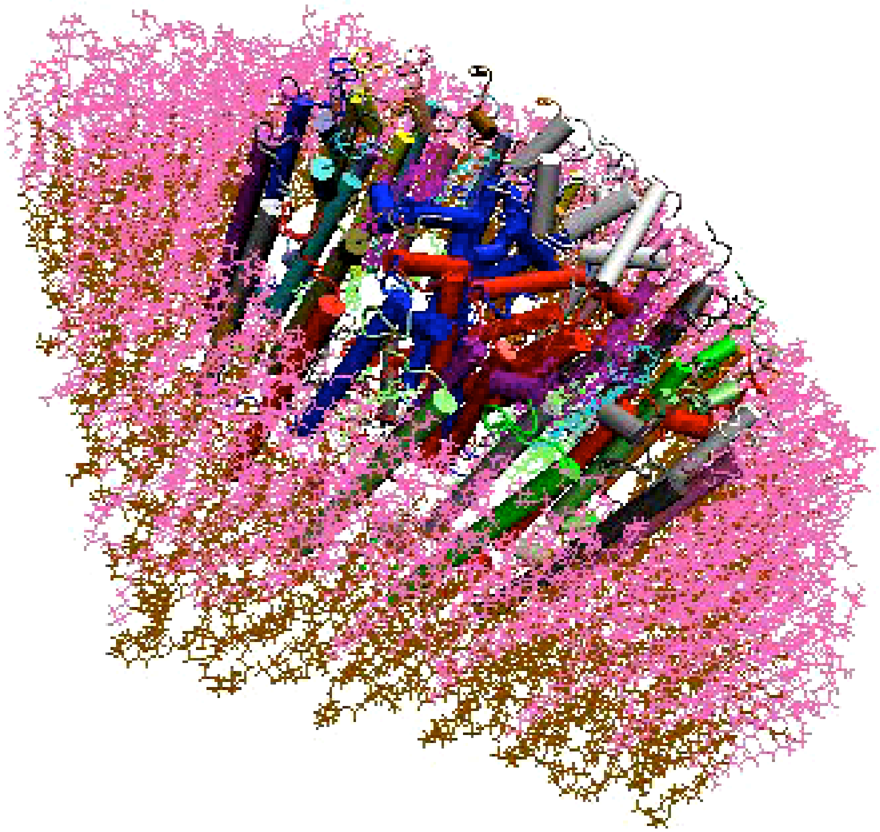
System of Water - Lipids - Protein

Focussing on the Structure of RC+LH-I+Cyt



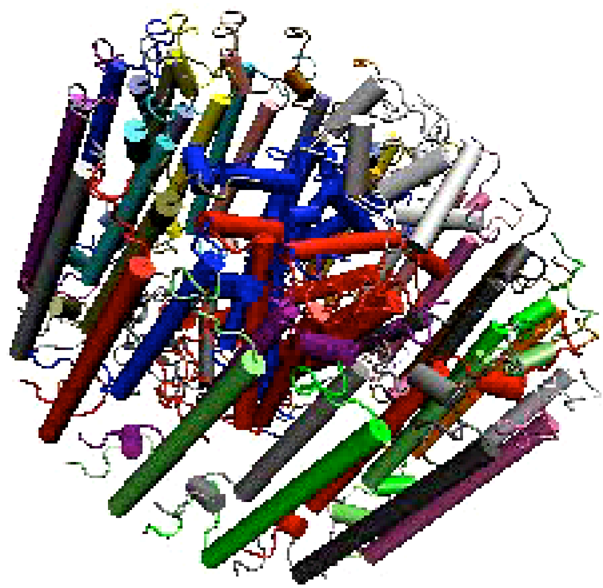
Lipids only

Focussing on the Structure of RC+LH-I+Cyt



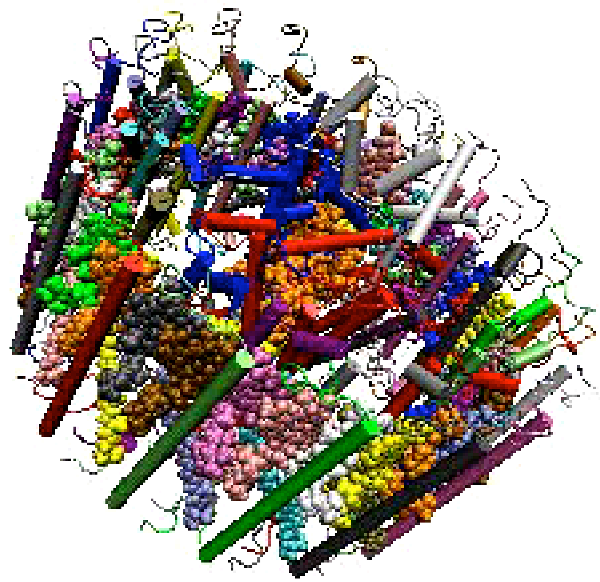
Lipids and Proteins

Focussing on the Structure of RC+LH-I+Cyt



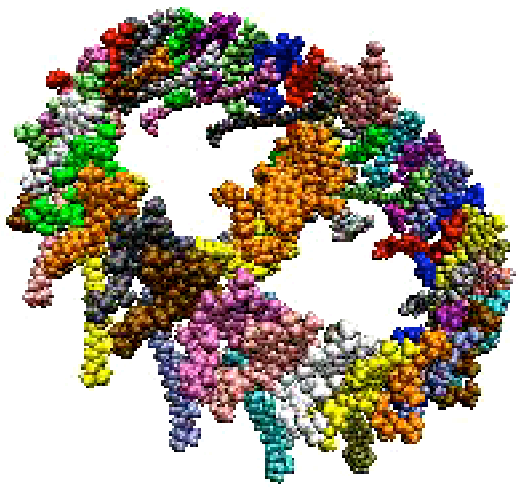
Proteins only

Focussing on the Structure of RC+LH-I+Cyt



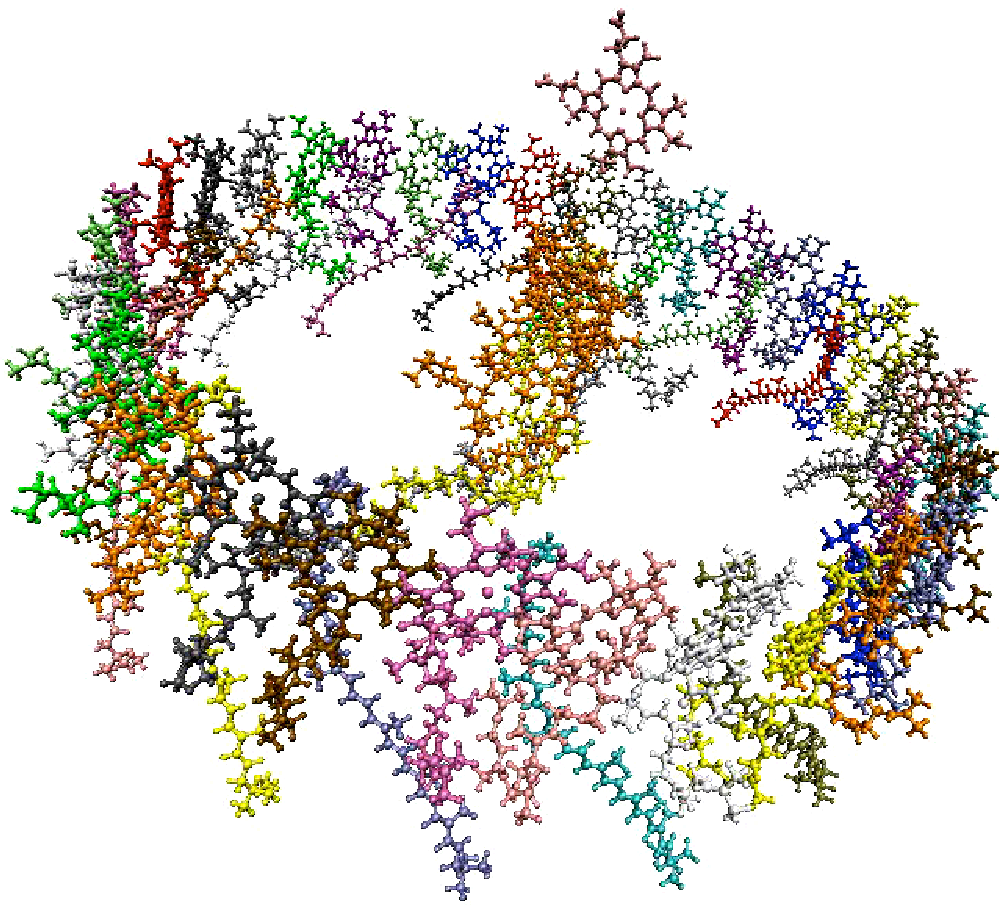
Proteins and Chromophores

Focussing on the Structure of RC+LH-I+Cyt



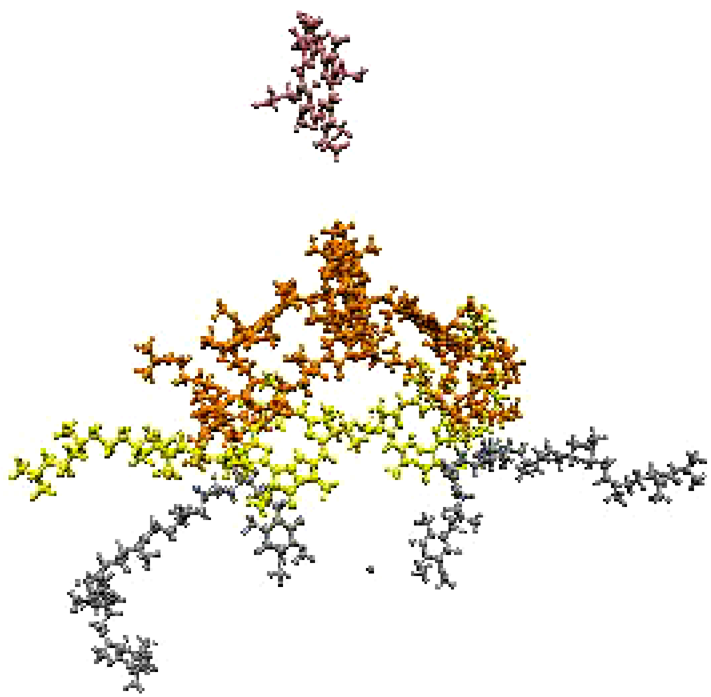
Chromophores only

Focussing on the Structure of RC+LH-I+Cyt

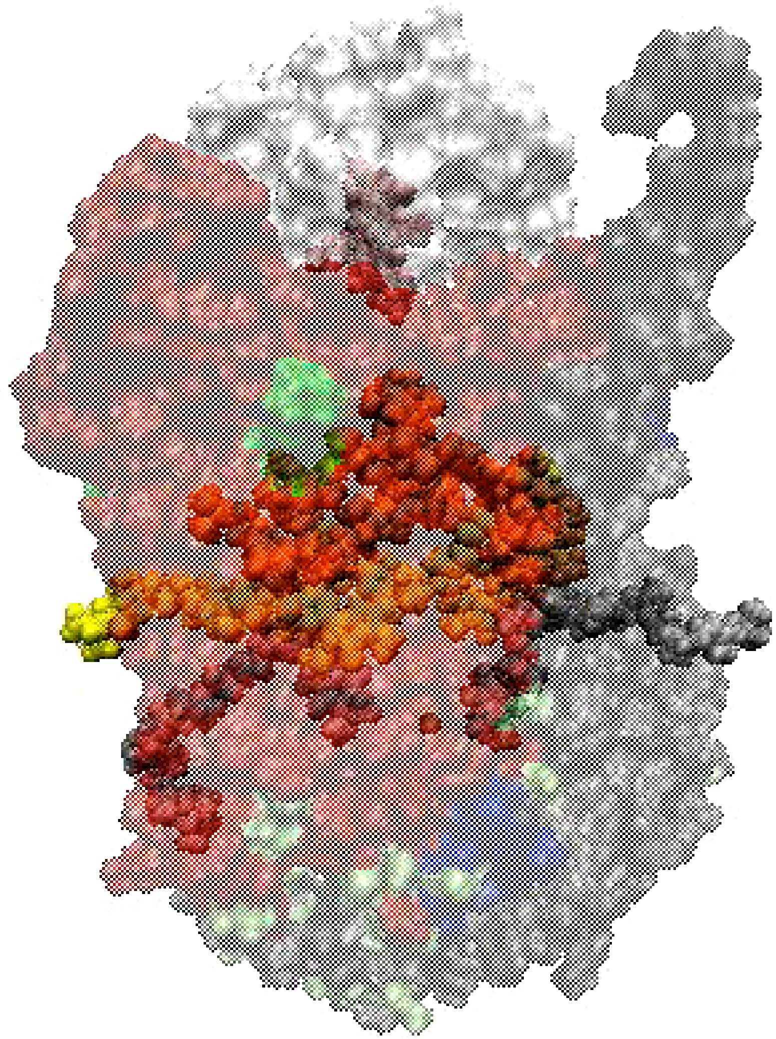


Chromophores only

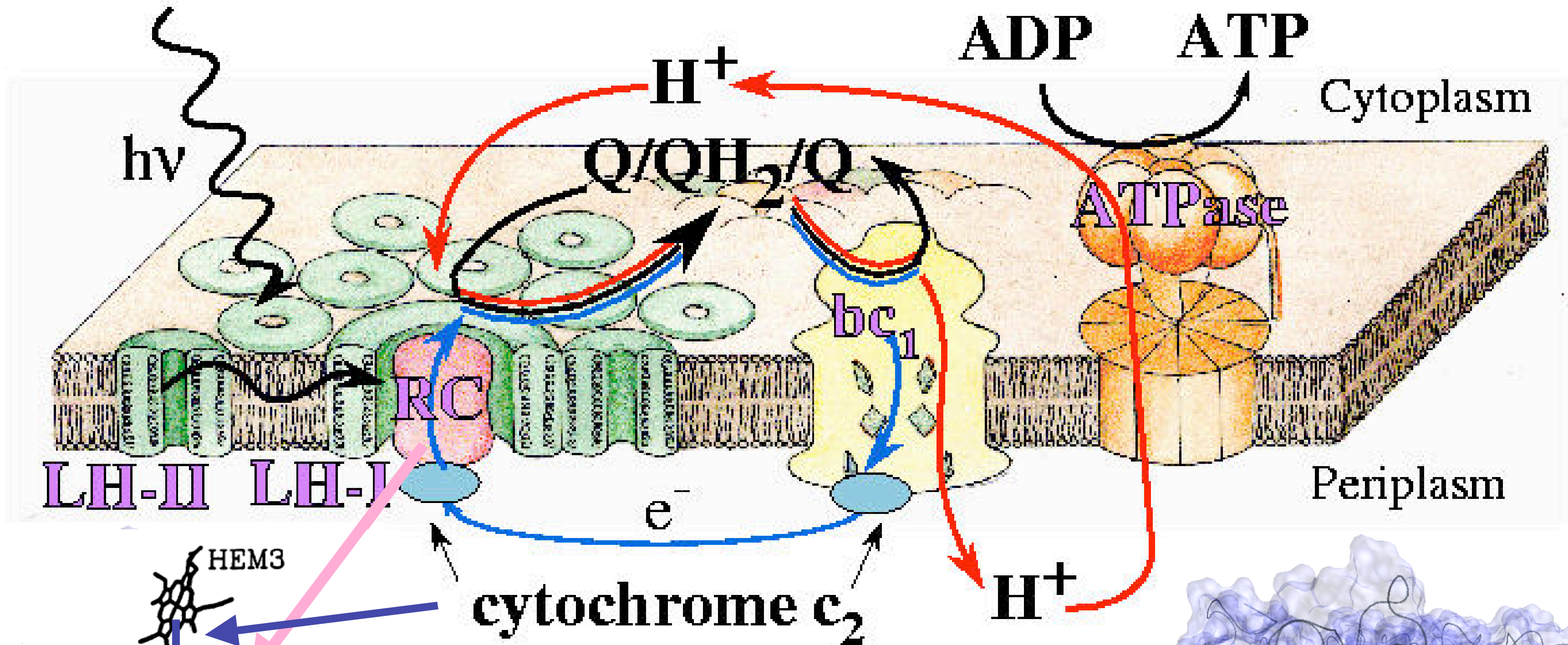
Electron Transfer Chain in RC + Cyt c Complex

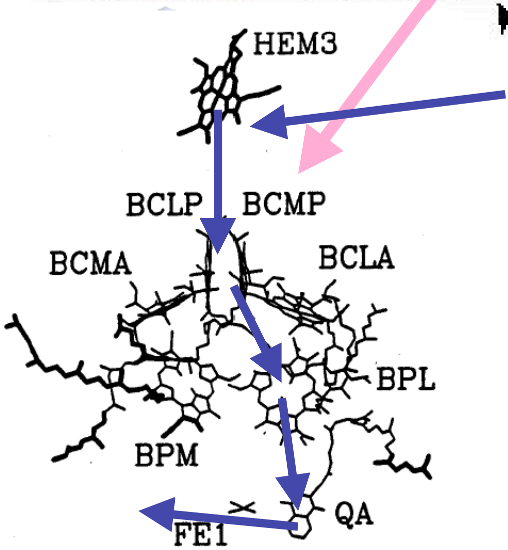


Role of the Protein Matrix on Electron Transfer

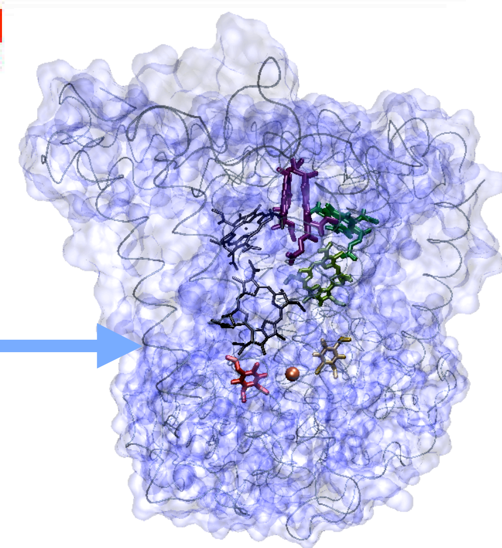


Role of Thermal Disorder on Electron Transfer in the Photosynthetic Reaction Center





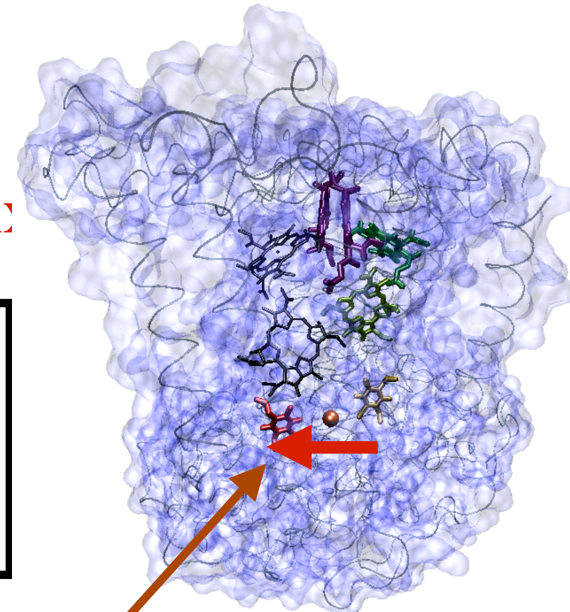
We wanted to describe how electron transfer is coupled to the thermal motion of the surrounding protein.



Electron Transfer Process Coupled to the Protein Matrix

We assumed that the electron transfer

$Q_A^- Q_B$ -> $Q_A Q_B^-$ is coupled to an **ensemble of oscillators representing the protein matrix**



Hamiltonian $$\hat{H}_{\mathrm{qo}}^{(s)} = \begin{pmatrix} \hat{H}_r^{(s)} & v \\ v & \hat{H}_p^{(s)} + E \end{pmatrix}$$

Protein matrix is a bath of oscillators linearly coupled to the electron transfer according to

$$\hat{H}_r = \sum_j \left(\frac{\hat{p}_j^2}{2M_j} + \frac{1}{2} M_j \omega_j^2 q_j^2 \right)$$

$$\hat{H}_p = \sum_j \left(\frac{\hat{p}_j^2}{2M_j} + \frac{1}{2} M_j \omega_j^2 \left(q_j - \frac{c_j}{M_j \omega_j^2} \right)^2 \right)$$

Dong Xu and Klaus Schulten. Chemical Physics, 182: 91--117, 1994.

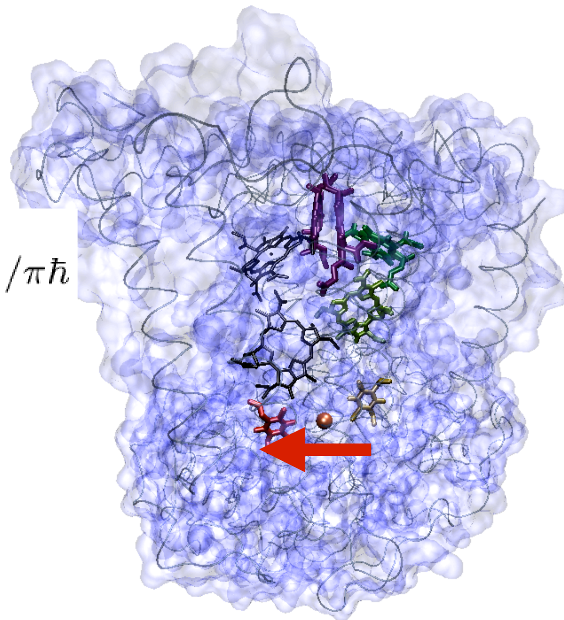
Klaus Schulten. In D. Bicout and M. J. Field, editors, Proc. Ecole de Physique des Les Houches, pp 85--118, Les Editions de Physique, Springer, Paris, 1995.

Klaus Schulten. Science, 290:61--62, 2000.

Electron Transfer Process Coupled to the Protein Matrix

Rate for an ensemble of oscillators (spin boson model, Legett et al)

$$k_{qb}(R \to P) = \frac{v^2}{\hbar^2} \int_{-\infty}^{+\infty} dt \; e^{itE/\hbar} \; e^{iQ_1(t)/\pi\hbar} \; e^{-Q_2(t)/\pi\hbar}$$



Relaxation rate

$$k_{\rm rel} = \frac{2v^2}{\hbar^2} \int_0^{+\infty} dt \cos(\quad tE/\hbar) \cos(Q_1(t)/\pi\hbar) \; e^{-Q_2(t)/\pi\hbar}$$

$$Q_1(t) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\hbar\omega_j^3} \sin\omega_j t$$

$$Q_2(t) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\hbar\omega_j^3} \coth\frac{\hbar\omega_j}{2kT} \left[1 - \cos(\omega_j t)\right]$$

But we didn't know all the coupling constants c_j ? All we needed to know was J

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j)$$

$$Q_1(t) = \int_0^{\infty} d\omega \, \omega^{-2} J(\omega) \sin\omega t$$

$$Q_2(t) = \frac{\pi}{2} \int_0^{\infty} d\omega \, \omega^{-2} J(\omega) \coth\frac{\hbar\omega}{2kT} (1 - \cos\omega t)$$

Electron Transfer Process Coupled to the Protein Matrix

Relaxation rate

$$k_{\rm rel} = \frac{2v^2}{\hbar^2} \int_0^{+\infty} dt \cos(\ tE/\hbar) \cos(Q_1(t)/\pi\hbar) \, e^{-Q_2(t)/\pi\hbar}$$

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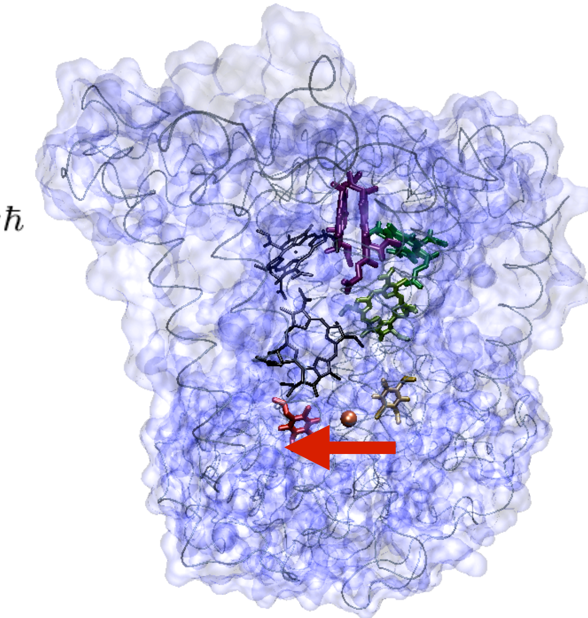


1994

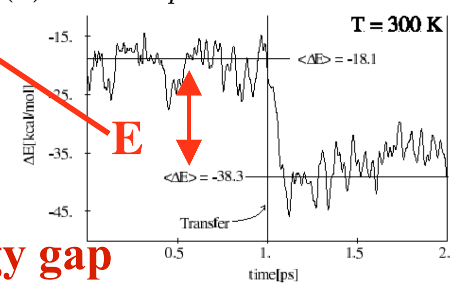
$$\frac{J(\omega)}{\omega} = \frac{\sigma^2}{k_B T} \int_0^{\infty} dt \, C(t) \cos \omega t$$

$$C_{\epsilon\epsilon}(t) = \frac{\langle \, (\epsilon(t) - \langle\epsilon\rangle) \, (\langle\epsilon(0) - \langle\epsilon\rangle) \, \rangle}{\langle\epsilon(0) - \langle\epsilon\rangle \, \rangle^2}$$

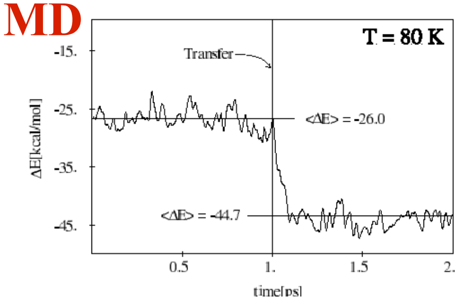
energy gap correlation function

σ **rms deviation of energy gap**

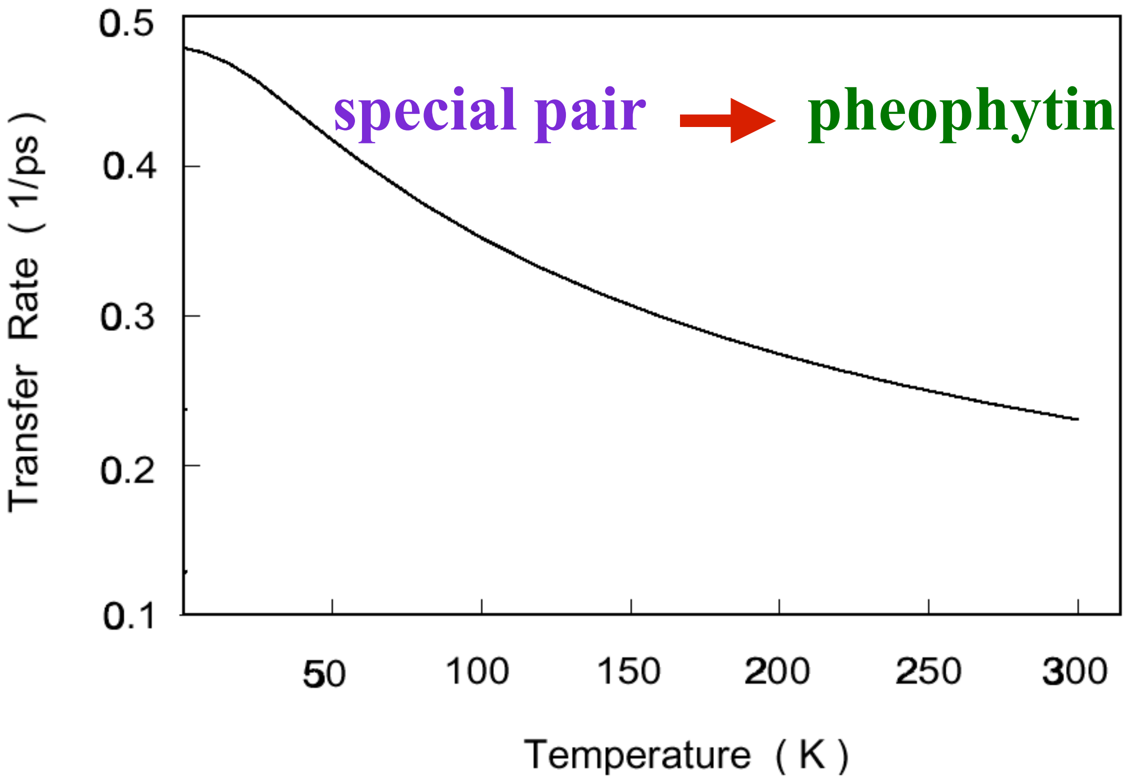
$$\epsilon(t) = \hat{H}_p - \hat{H}_r + E$$

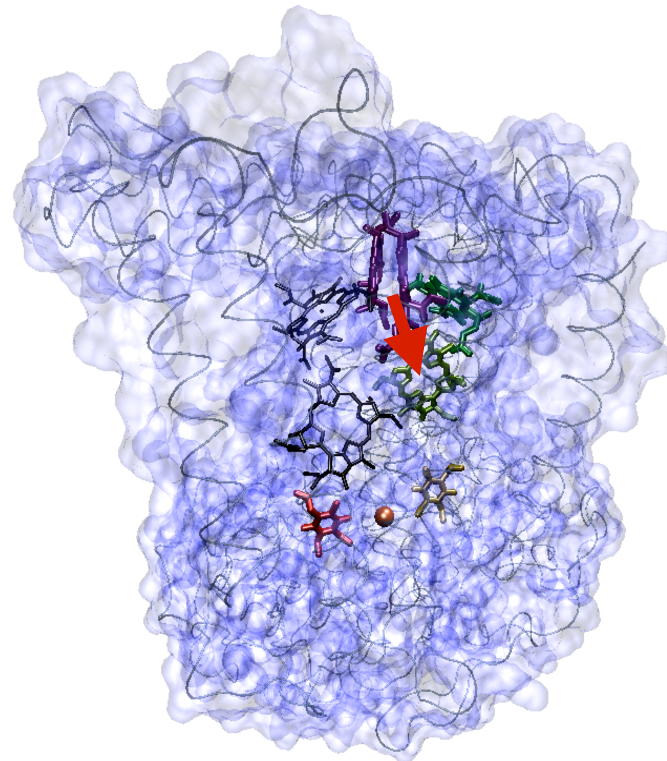


energy gap from MD 1989



Temperature Dependence of Electron Transfer Rate





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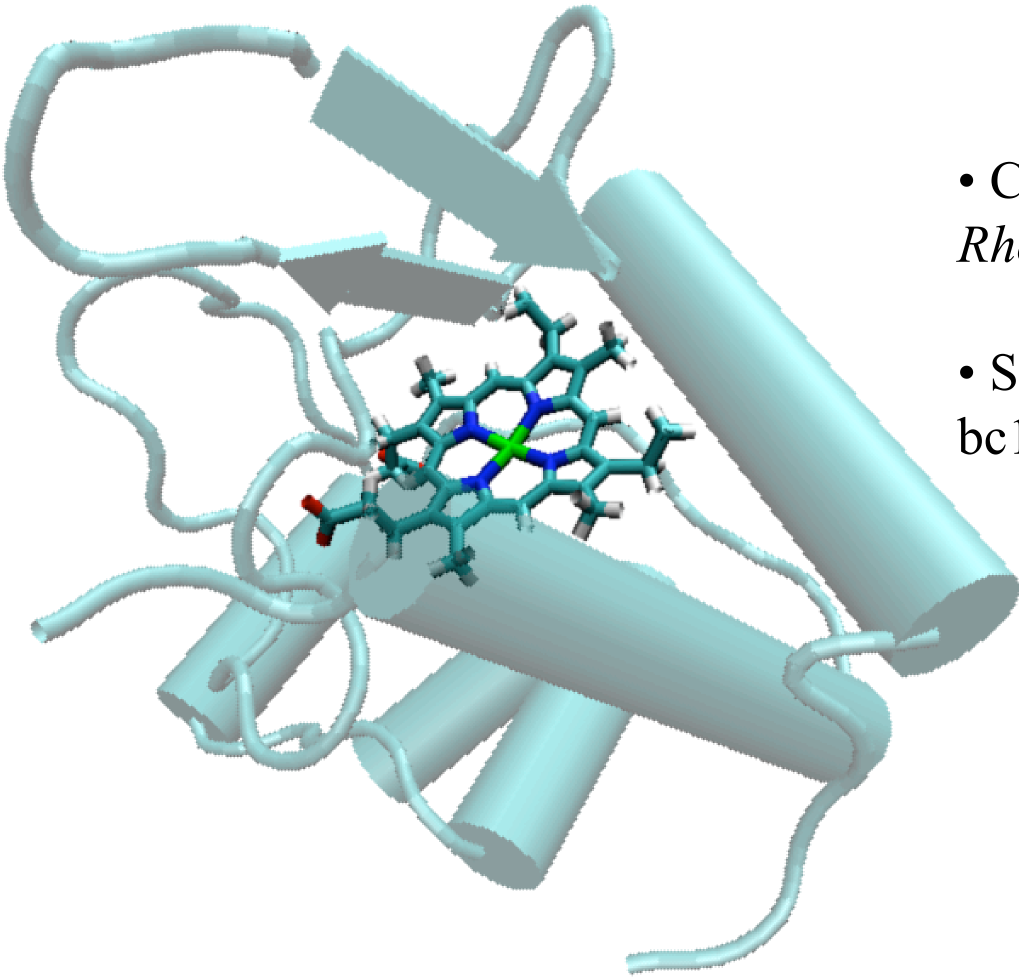
Klaus Schulten. Science, 290:61--62, 2000.

Electron Transfer

Coupling protein motion to electron transfer via MD

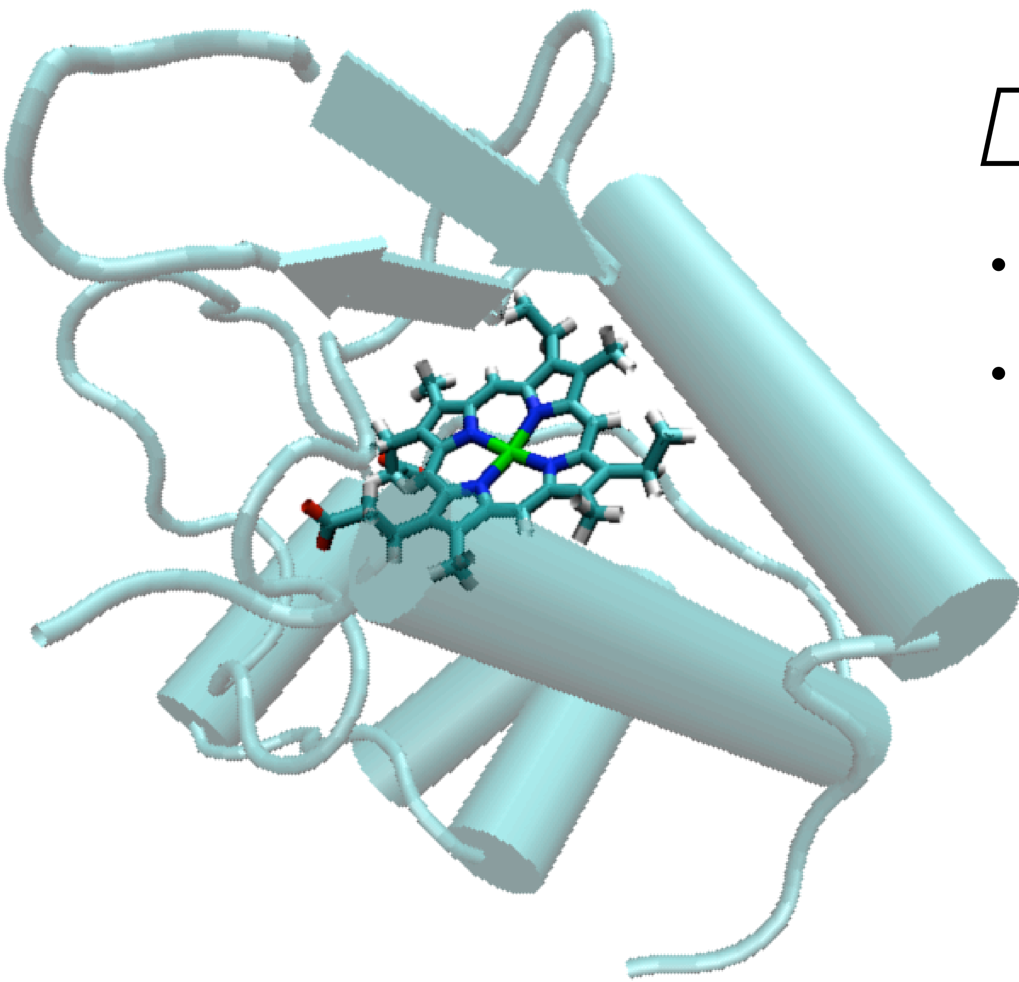


- Cytochrome c_2 from purple bacterium *Rhodobacter sphaeroides*.
- Serves as electron carrier between bc1-complex and reaction center

When the gene encoding cytochrome c_2 is deleted from *Rb. sphaeroides*, the bacterium is unable to grow photosynthetically.

Electron Transfer

The energy gap function



$$\Delta(t) = E_P(t) - E_R(t)$$

- *R:* reactant state (reduced)
- *P:* product state (oxidized)

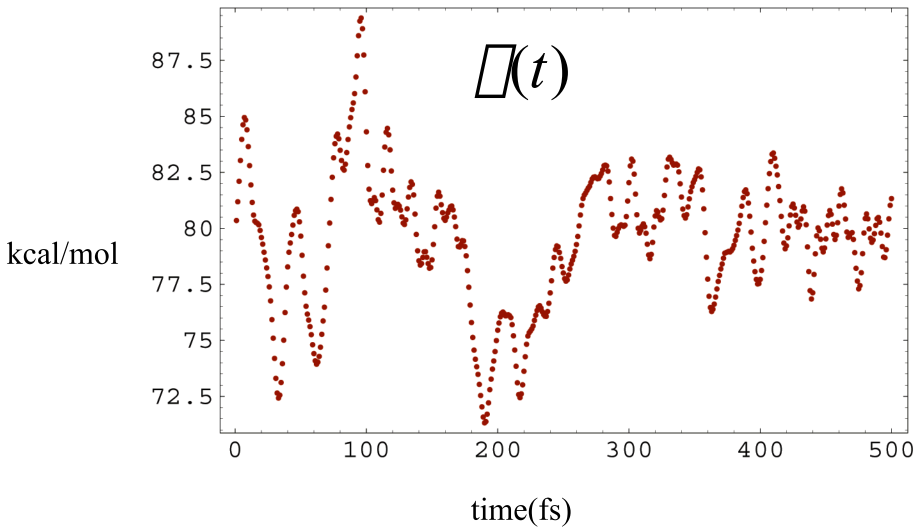
Tutorial:

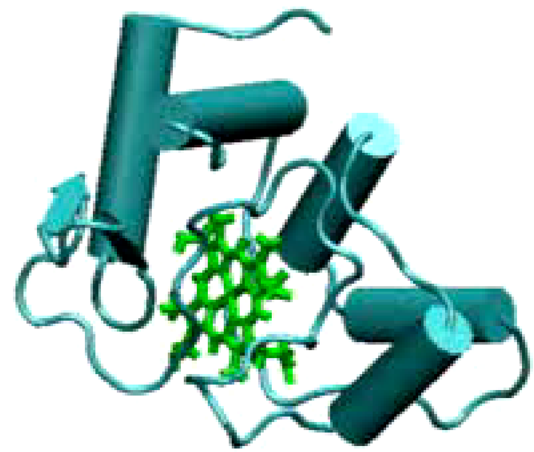
You will do two consecutive NAMD runs.

- obtain an MD trajectory
- evaluate $\Delta(t)$ at each frame of the first trajectory through a second NAMD run

Electron Transfer

MD simulation of the electron transfer process



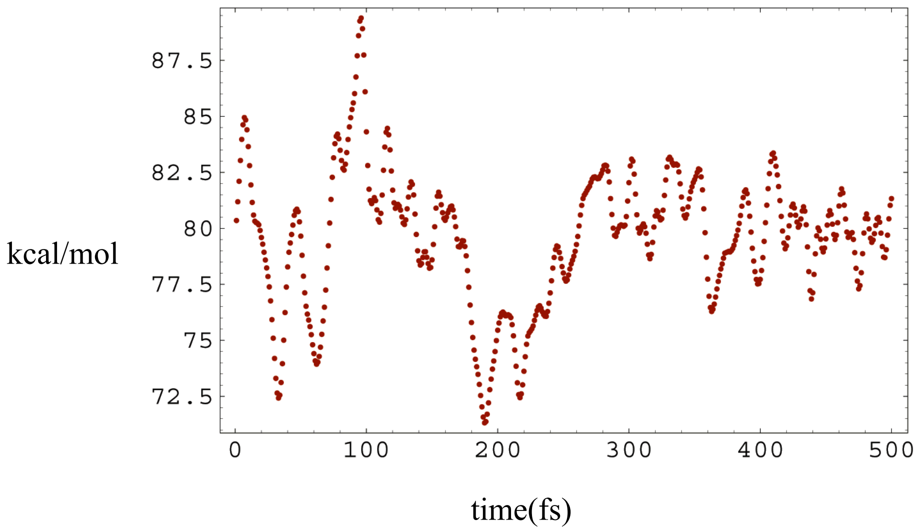


- ~12000 atoms solvated system
- Already minimized and equilibrated
- You will continue from a restart file

  (so, you do not need to worry about velocity relaxation)

Electron Transfer

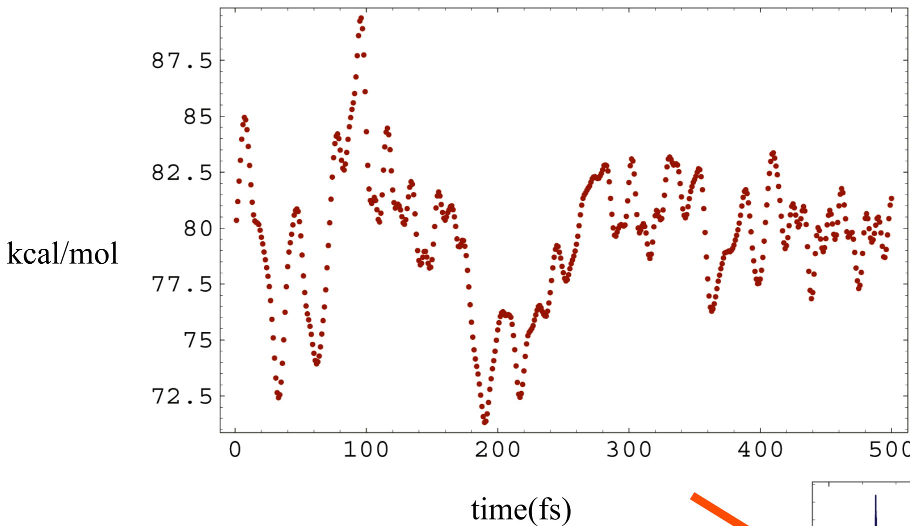
The energy gap function



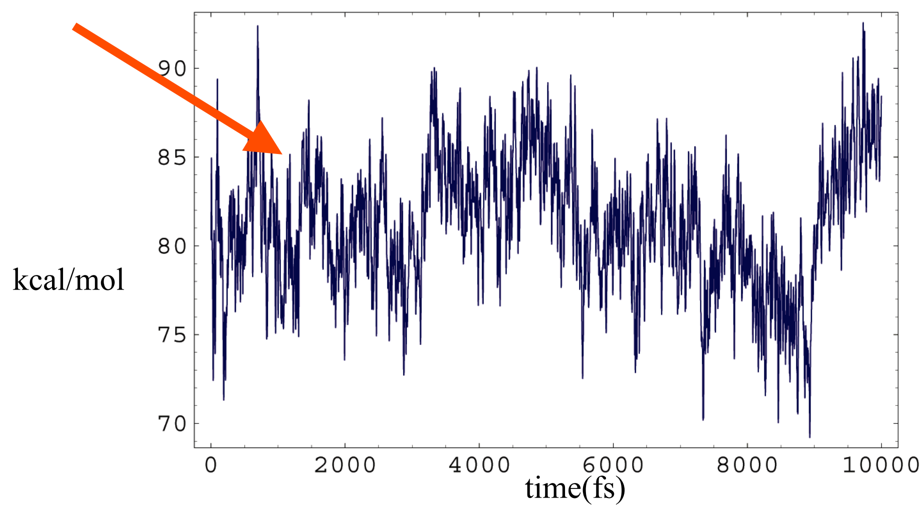
Result from the first 500fs

Electron Transfer

The energy gap function

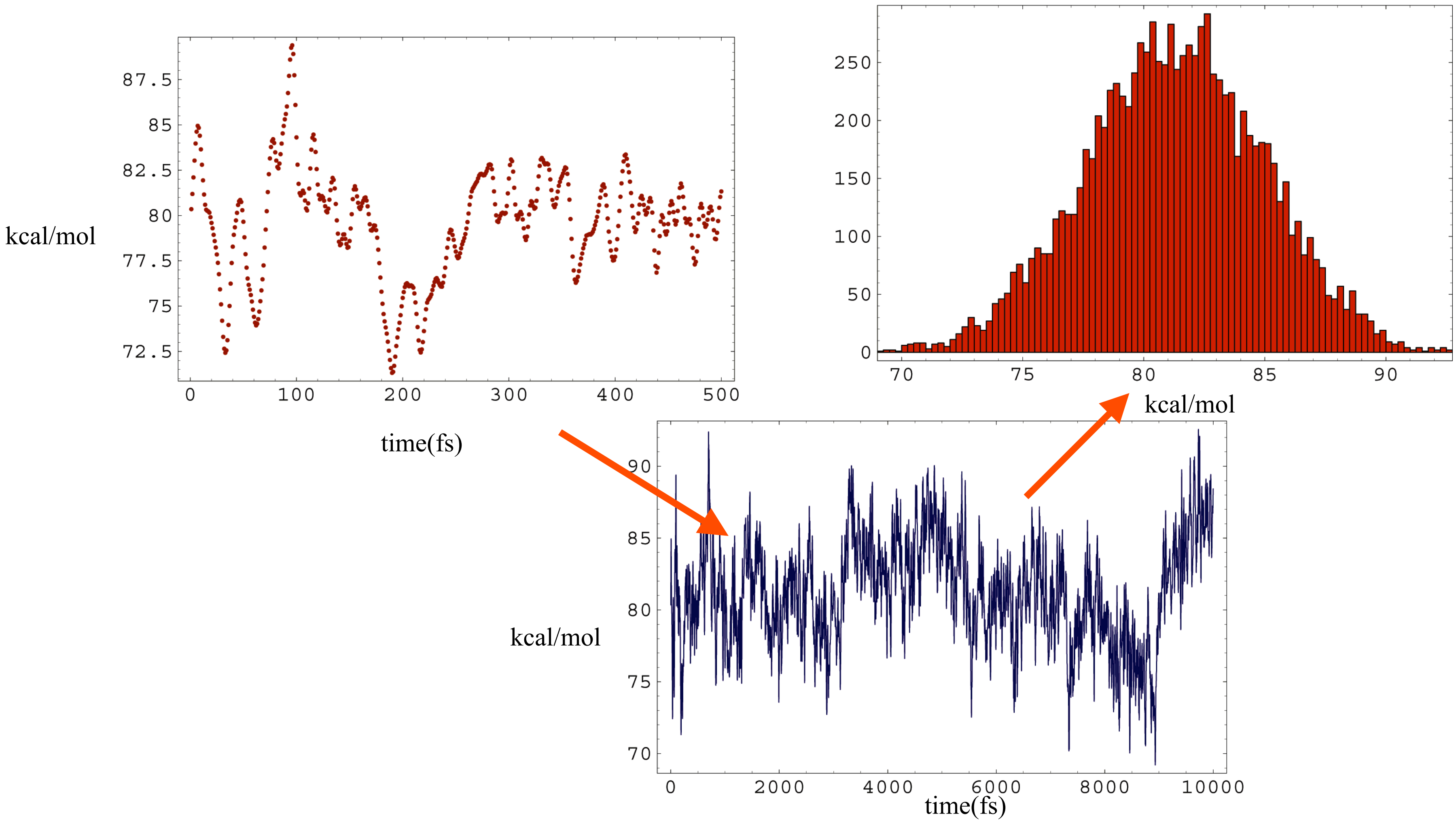


You will be given a longer trajectory…



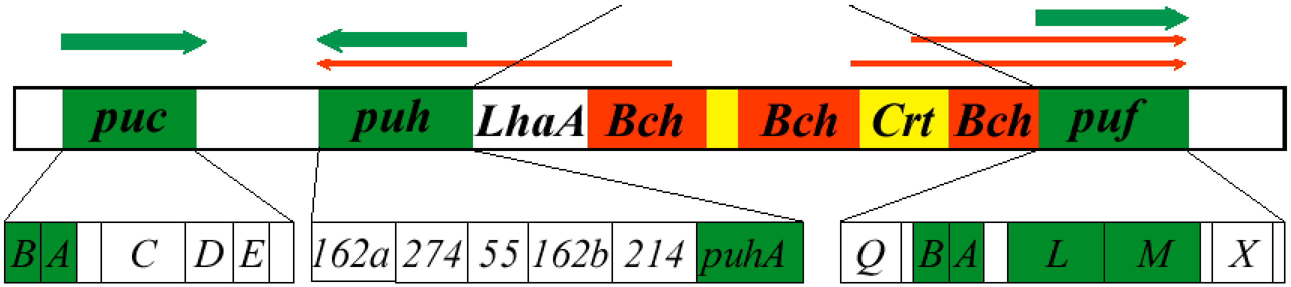
Electron Transfer

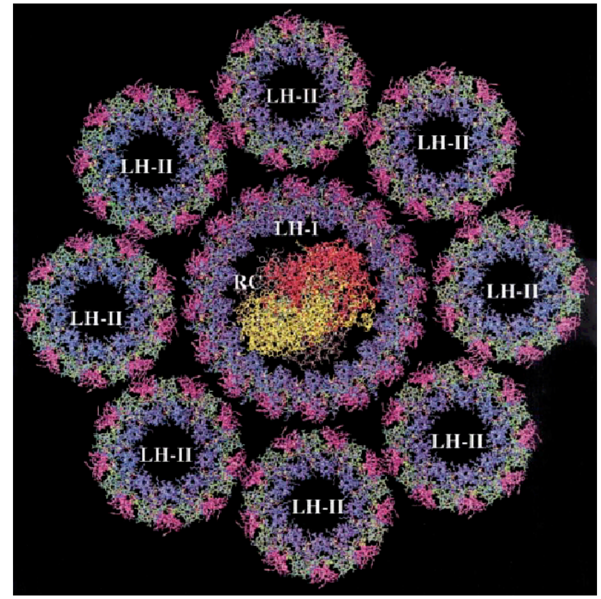
The energy gap function



Genomic Organization of the Light Harvesting Complexes

- BChla metabolism
- carotenoid metabolism



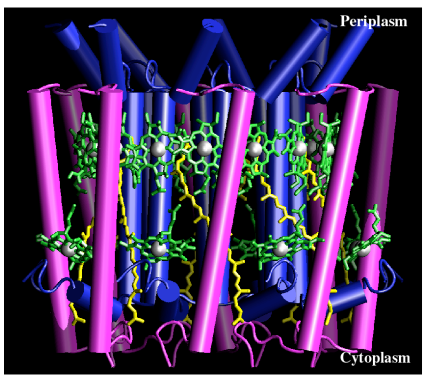


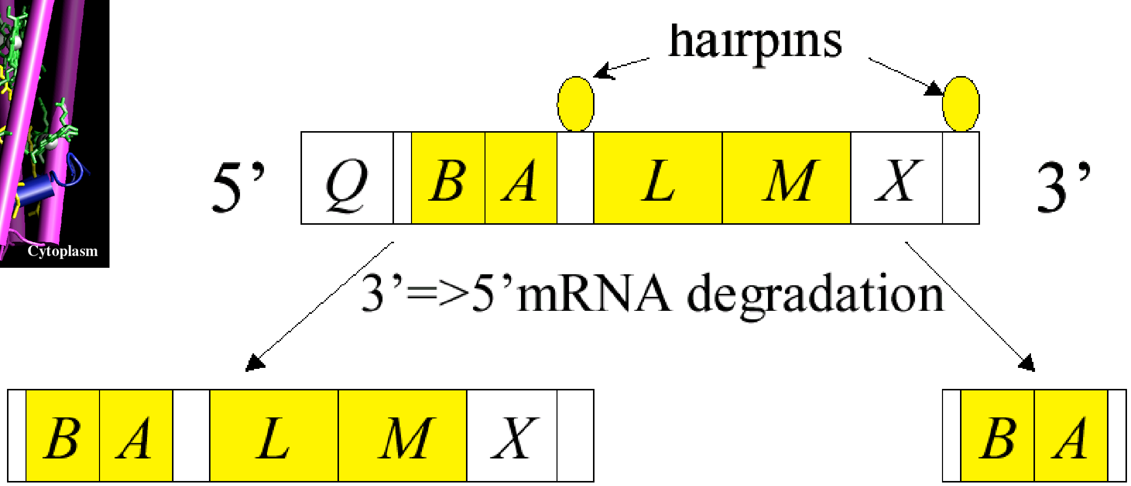
- LH2 apoproteins
- PucC, D, E

- H-subunit
- 5 ORFs

LhaA = light-harvesting complex assembly

- LH1apoproteins
- L-subunit
- M-subunit
- PufQ, PufX





- half-life 8 min
- half-life > 20 min

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Photosynthetic apparatus of purple bacteria

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