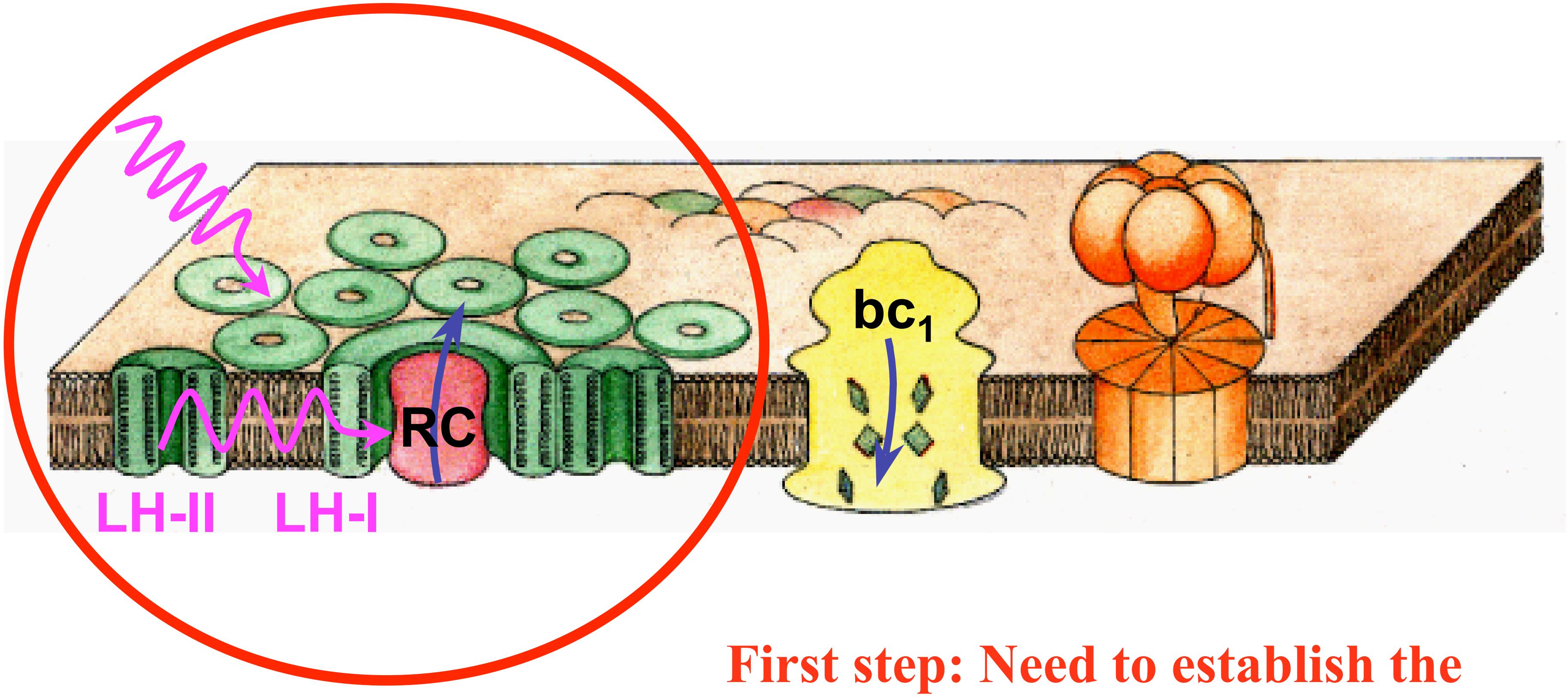
Light Harvesting in Photosynthesis

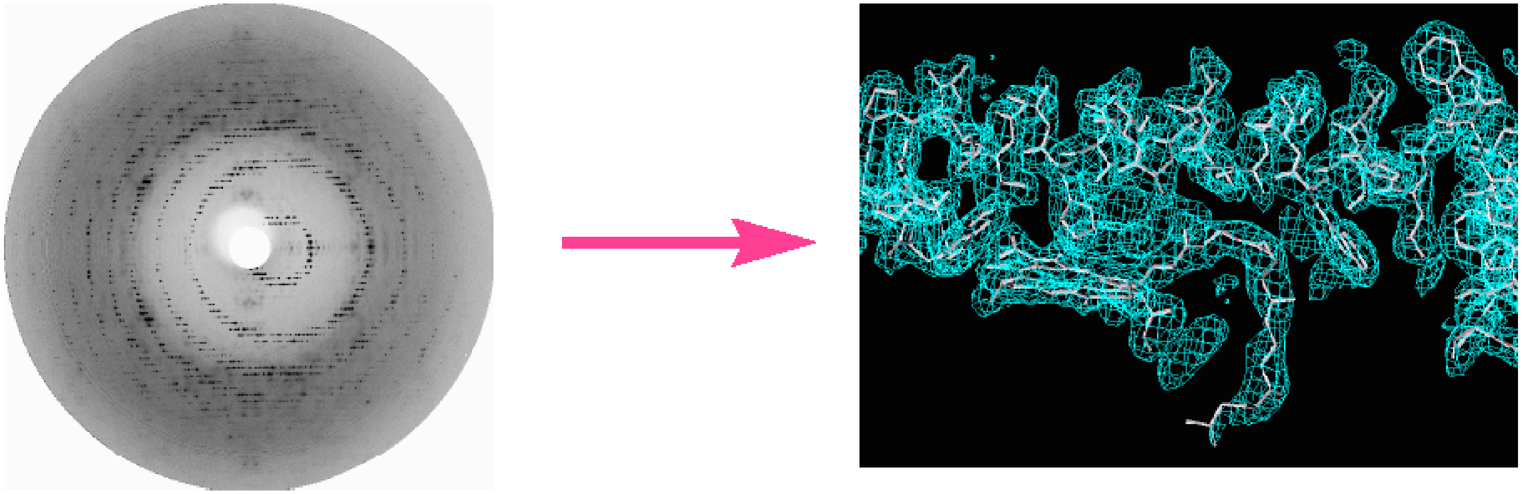


First step: Need to establish the structure of the underlying system

Phase Problem and Conventional Solutions

Phase Problem

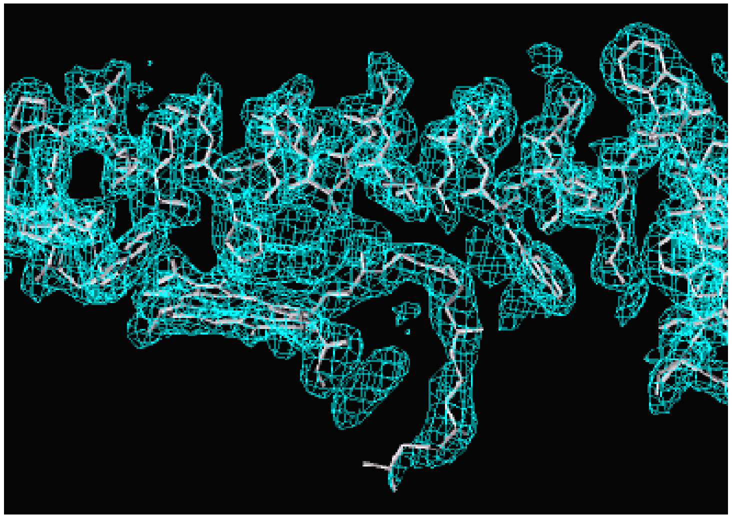
$$\rho(xyz) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F(hkl)\, e^{i\alpha(hkl)}\, e^{-2\pi i\,(hx+ky+lz)}.$$



Method	Requirement
Multiple Isomorphous Replacement	Two or more isomorphous heavy metal derivatives
Molecular Replacement	Known structure of highly homologous protein

Structure of LH-II of *Rs. molischianum* Obtained Through a Computationally Derived Search Model

molecular replacement through modeling



Summary of Crystallographic Data

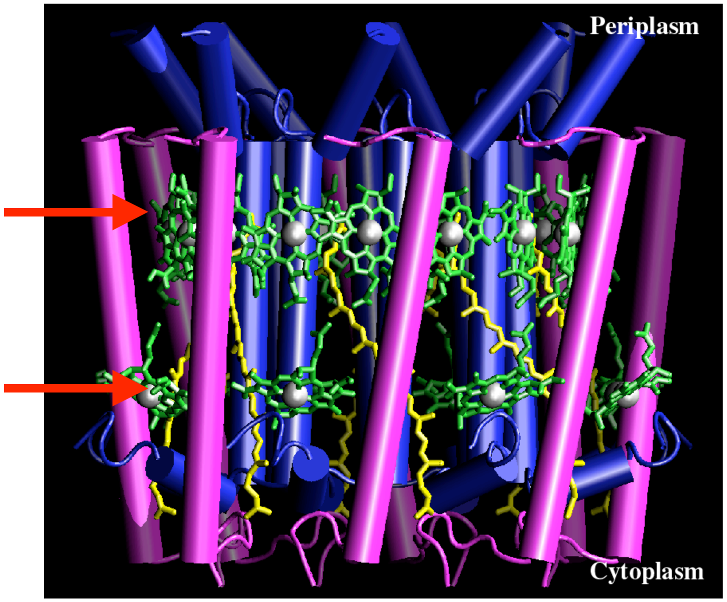
• space group	P4212
• resolution range	8-2.4 A
• unique reflection	30309
• completeness	87.2
• R-factor (%)	21.1
• free R-factor (%)	23.2

Koepke et al., Structure, **4**, 581 (1996)

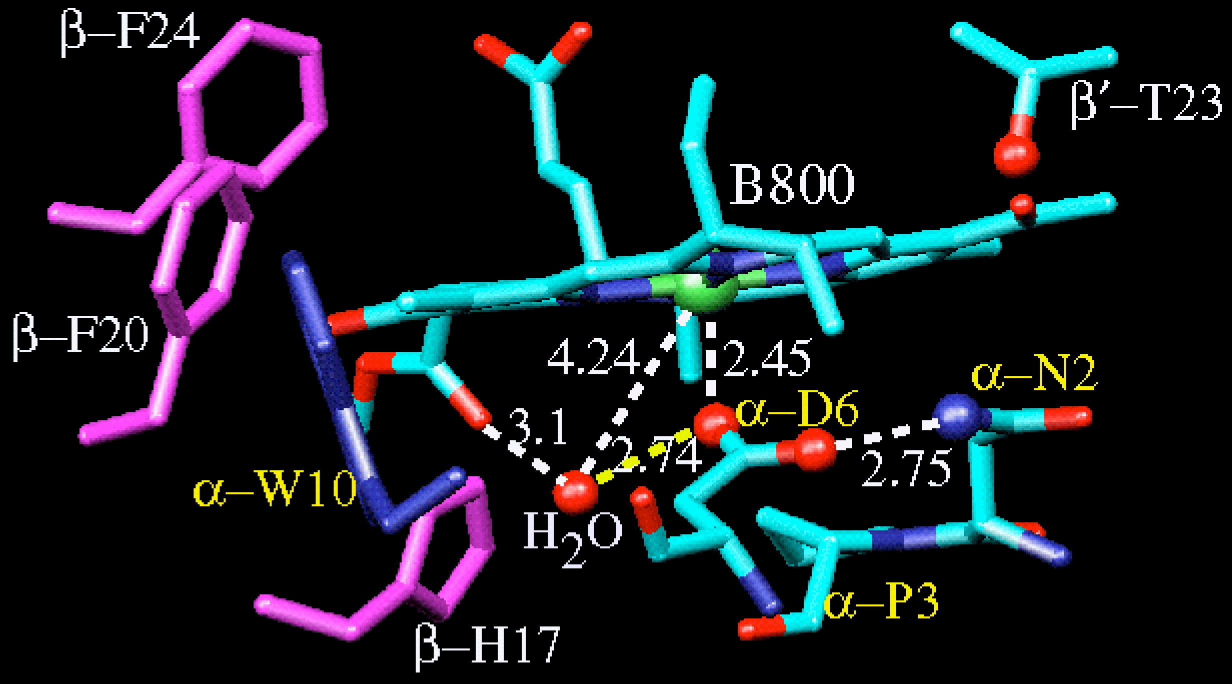
B850 band

B800 band

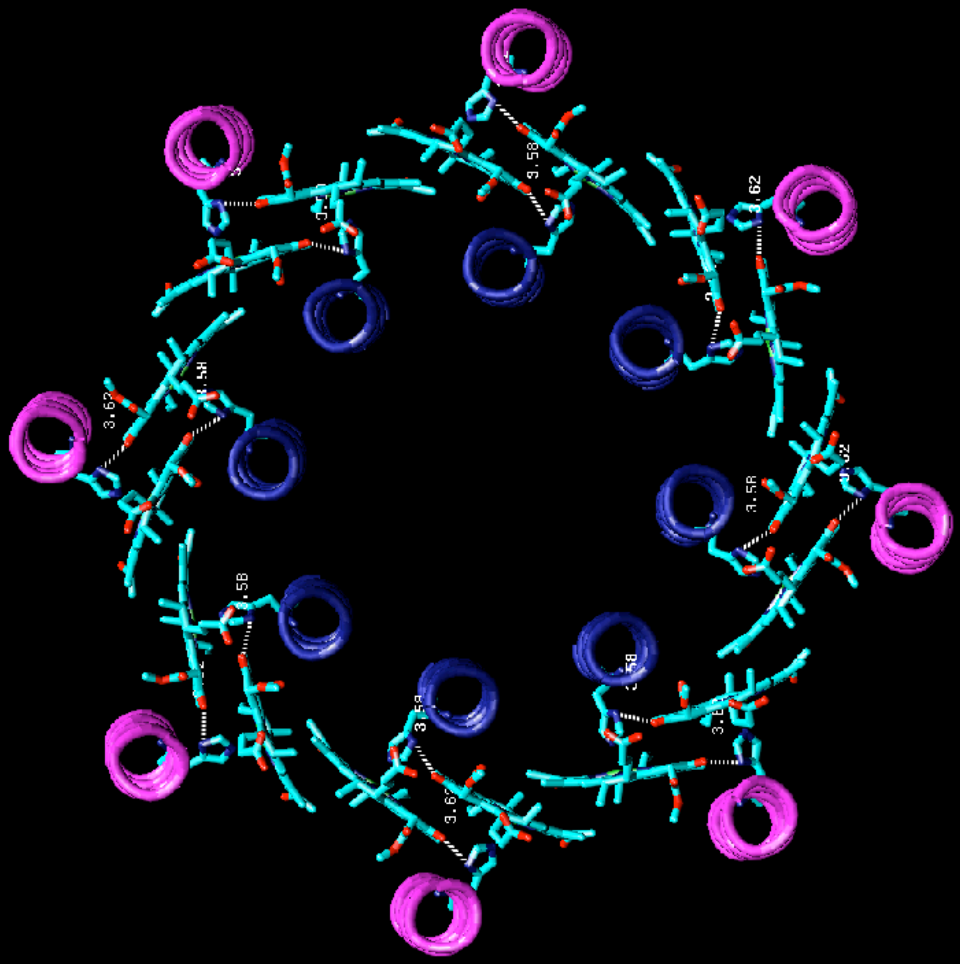
spectrum

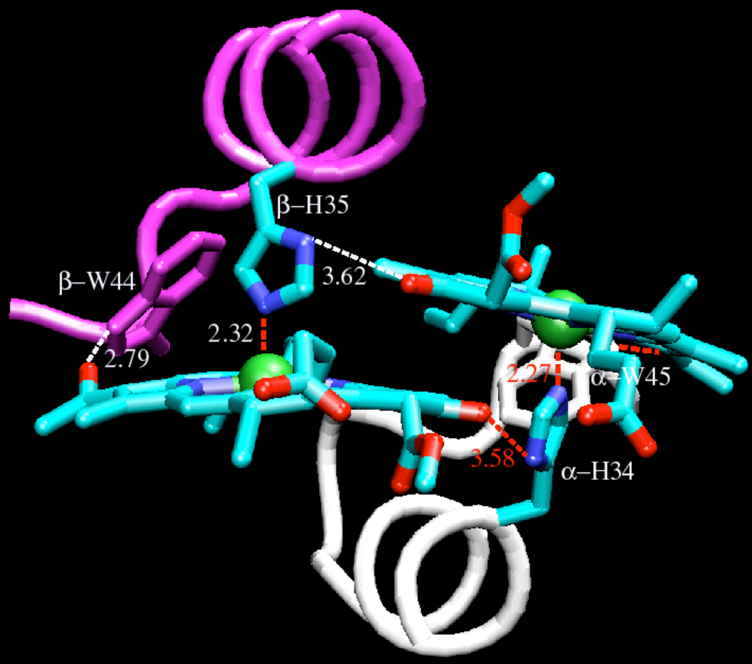


B800 BChl-a Binding Site



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



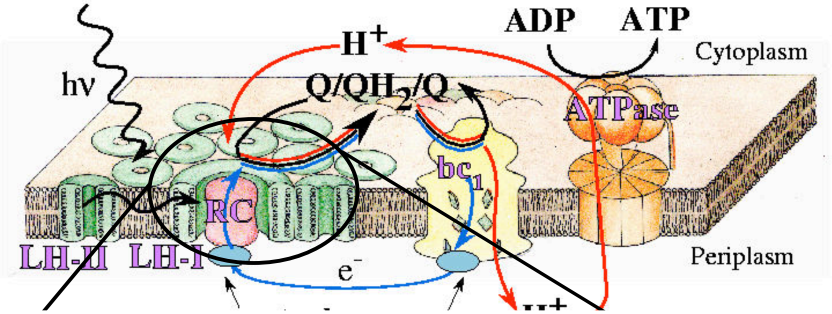


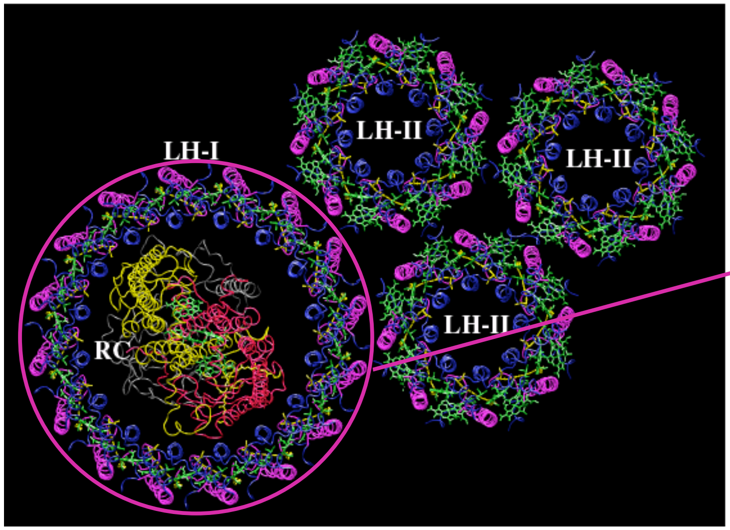
Spectrum tuned through local and excitonic interactions as well as disorder

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

Hu and Schulten, Biophys J., **75**, 683-694 (1998)
Ritz *et al*., **J. Lumin., 76-77**, 310-321 (1998)
Hu *et al*., PNAS, **95**, 5935-5941 (1998)
Koepke *et al*., Structure, **4**, 581-597 (1996)
Hu *et al*., J. Phys. Chem., **B 101**, 3854-3871 (1997)
Cory *et al*., J. Phys. Chem., **B 102**, 7640-7650 (1998)
Damjanovic *et al*., **Phys. Rev. E, 59**, 3293-3311 (1999)
Ritz *et al*., Photosyn. Res., 66:125–144, 2000.
Ritz *et al.,* J. Phys. Chem. B, 105:8259–8267, 2001.
Sener *et al.,* **Phys. Rev. E,** 65:031916, 2002.
Hu *et al.,* Quart. Rev. Biophys., 35:1–62, 2002.
Damjanovic *et al*., **Phys. Rev. E** 65: 031919, 2002.
Sener *et al*.. J. Phys. Chem. B. 106:7948–7960. 2002.

Photosynthetic membrane generates ATP using light energy





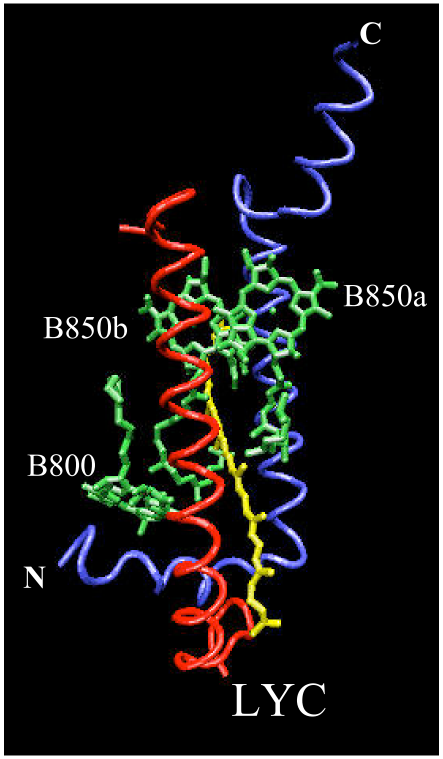
We need to know also the structure of the LH-I ring! We use again modeling, replacing subunit of LH-II by that of LH-I

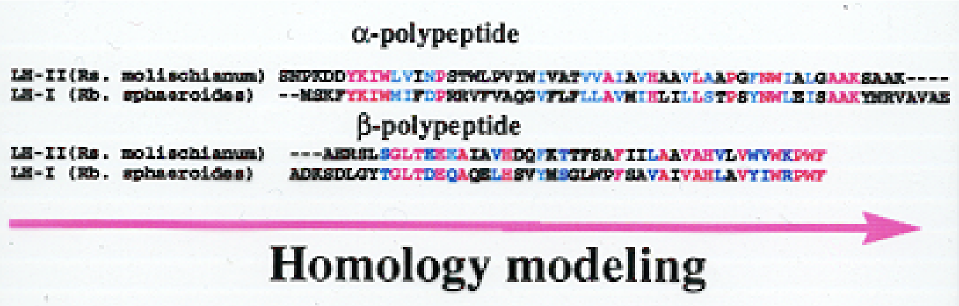
Molecular modeling of integral, functional units with more than 10^6 atoms necessary

Modeling the Structure of LH-I of *Rb. sphaeroides* (1)

subunit of LH-II

subunit of LH-I





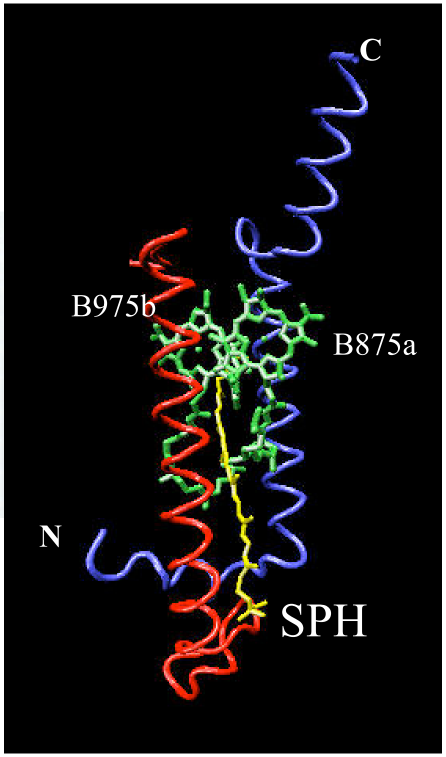
α-polypeptide

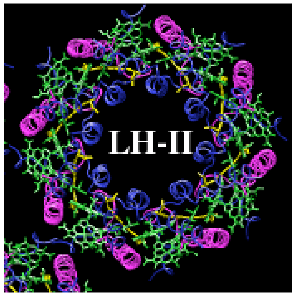
```
LH-II(Rs. molischianum) SNPKDDYKIWLVINPSTWLPVIWIVATVVAIAVHAAVLAAPGFNWIALGAAKSAAK----
LH-I (Rb. sphaeroides)  --MSKFYKIWMIFDPRRVFVAQGVFLFLLAVMIHLILLSTPSYNWLEISAAKYNRVAVAE
```

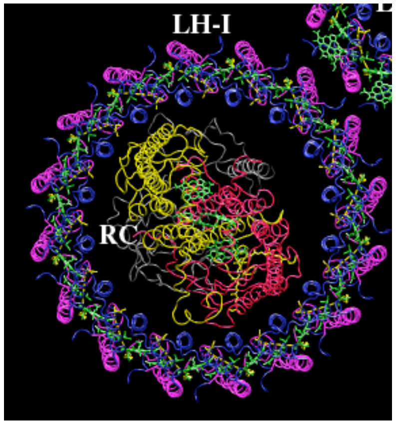
β-polypeptide

```
LH-II(Rs. molischianum)  ---AERSLSGLTEEEAIAVHDQFKTTFSAFIILAAVAHVLVWVWKPWF
LH-I (Rb. sphaeroides)   ADKSDLGYTGLTDEQAQELHSVYMSGLWPFSAVAIVAHLAVYIWRPWF
```

Homology modeling

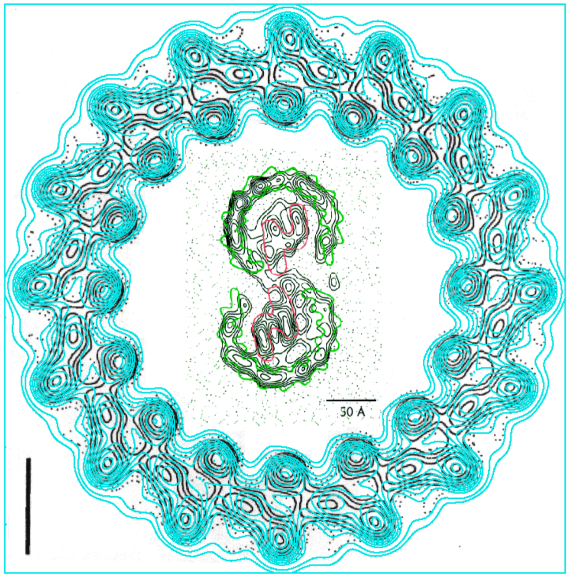


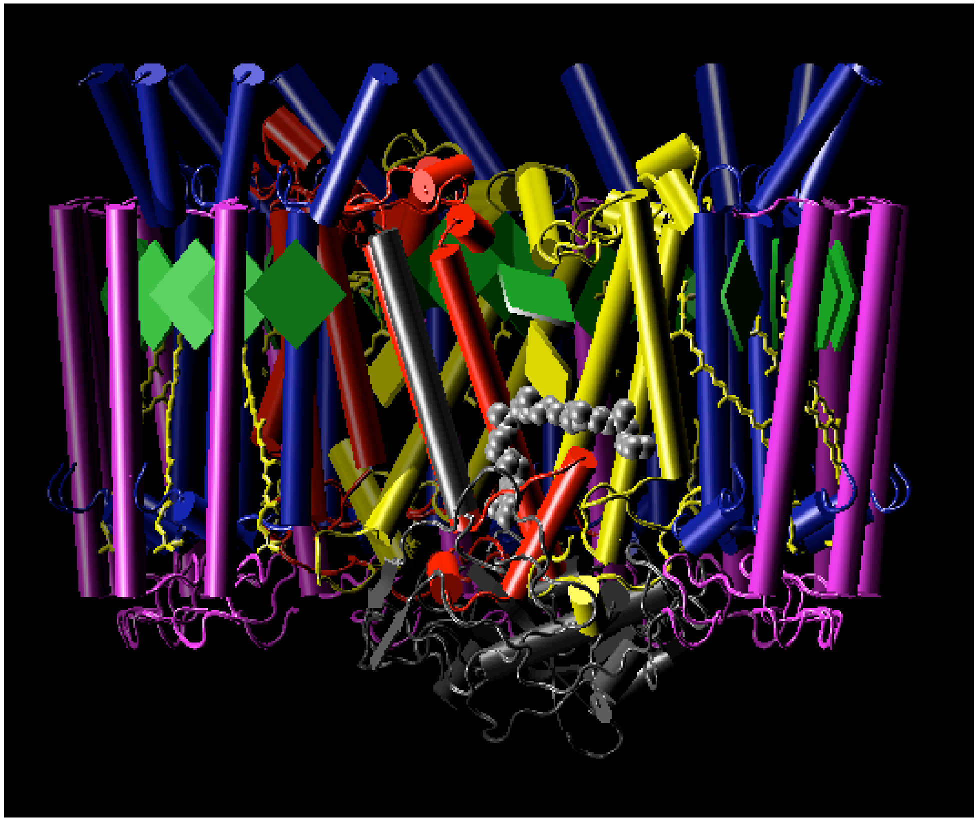


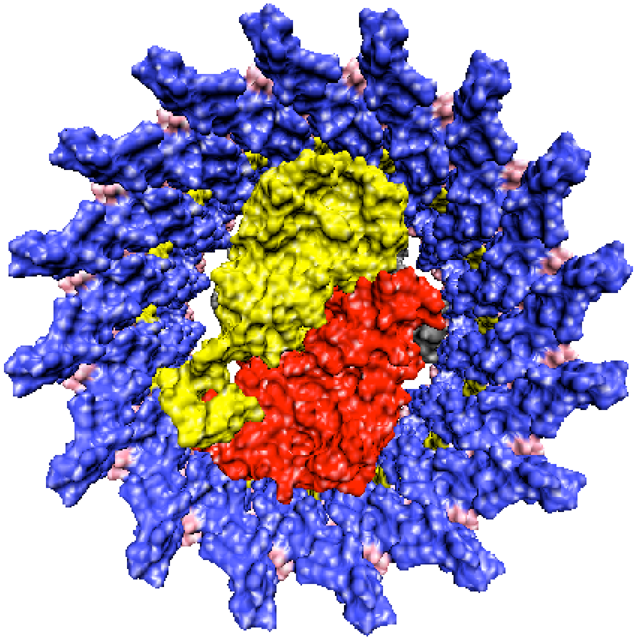


LH-I – RC Complex of *Rb. Sphaeroides*

Model agrees well with EM map



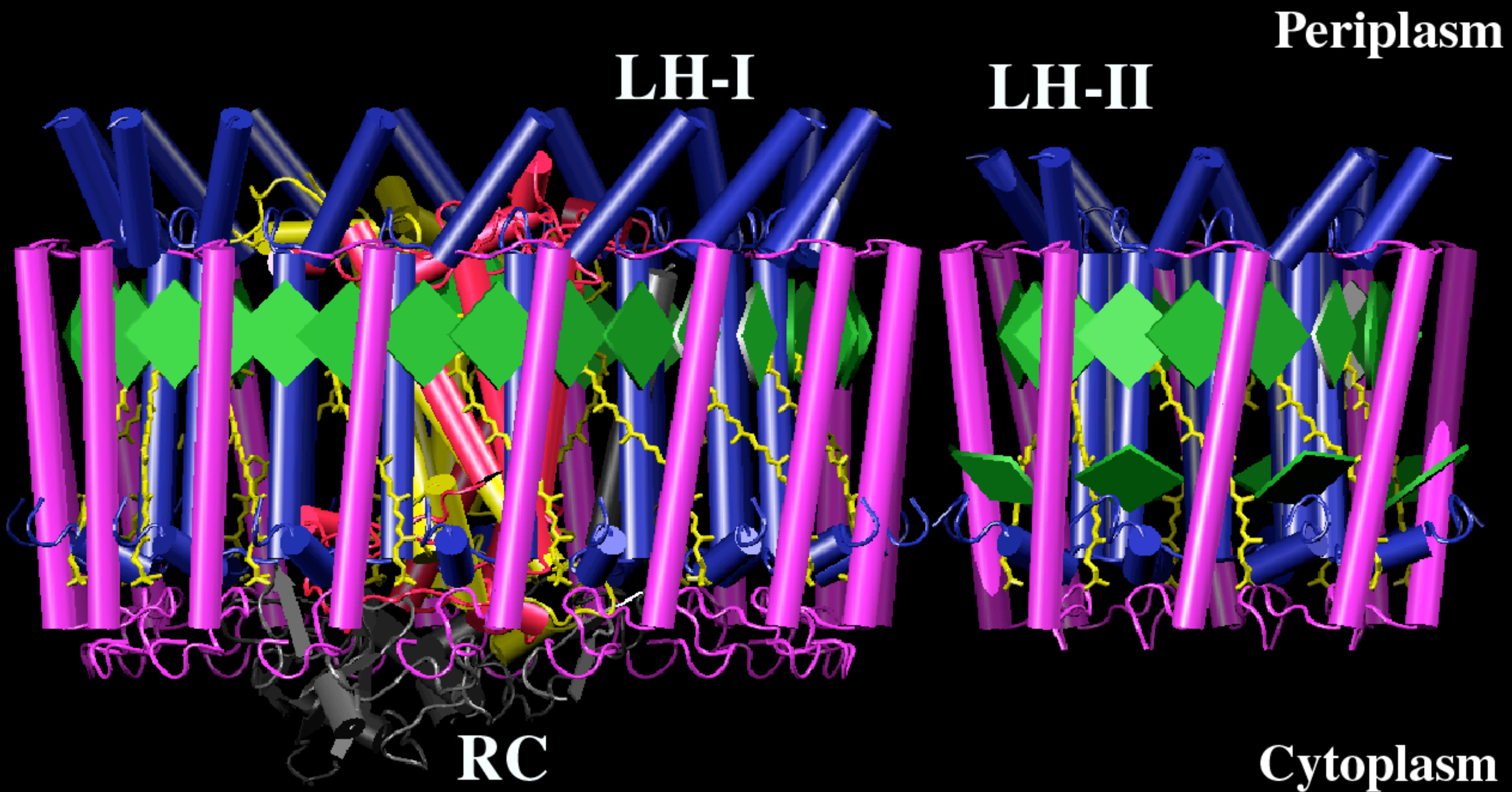




Xiche Hu

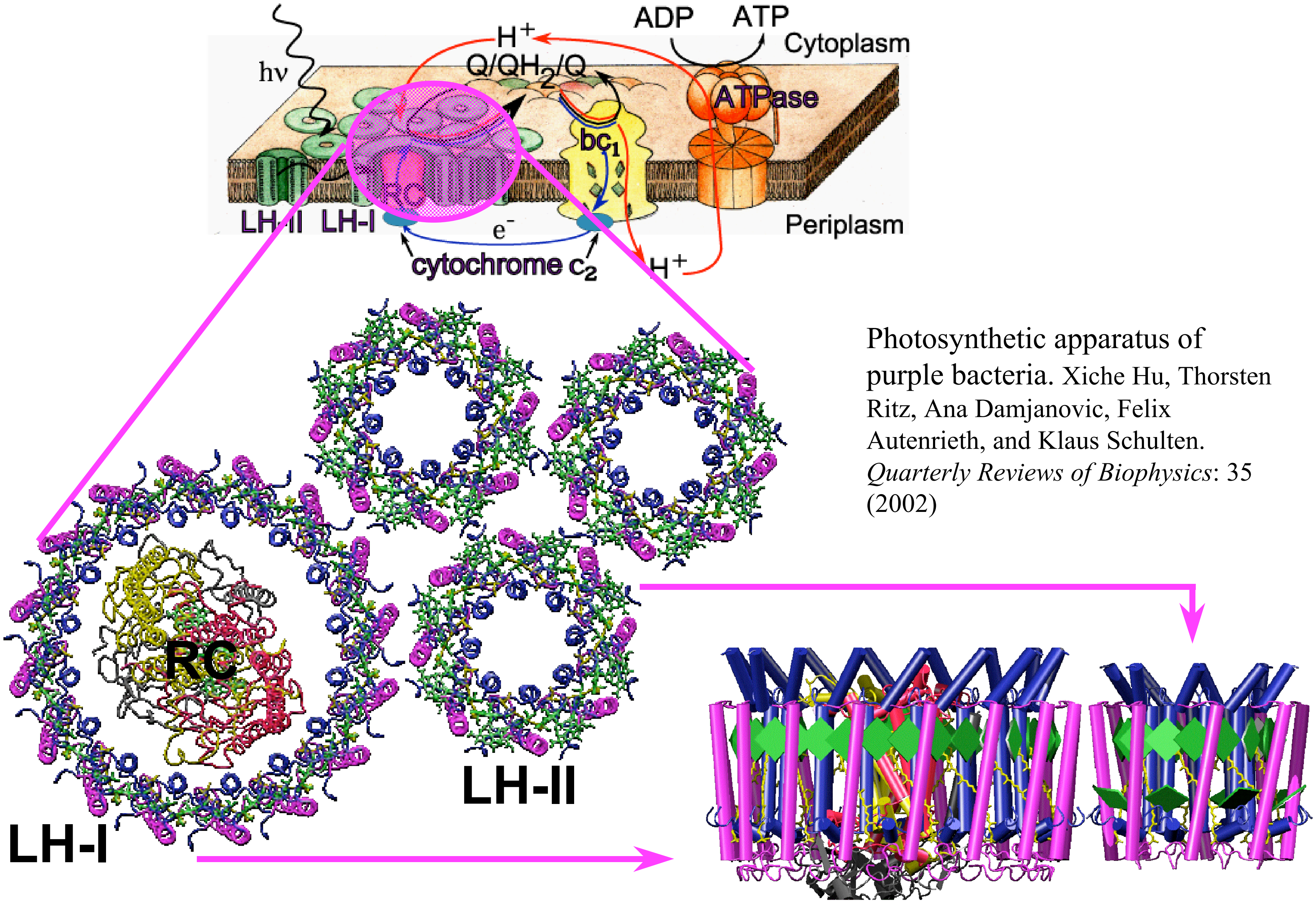
View from top

Pigment Organization in the Bacterial Photosynthetic Membrane



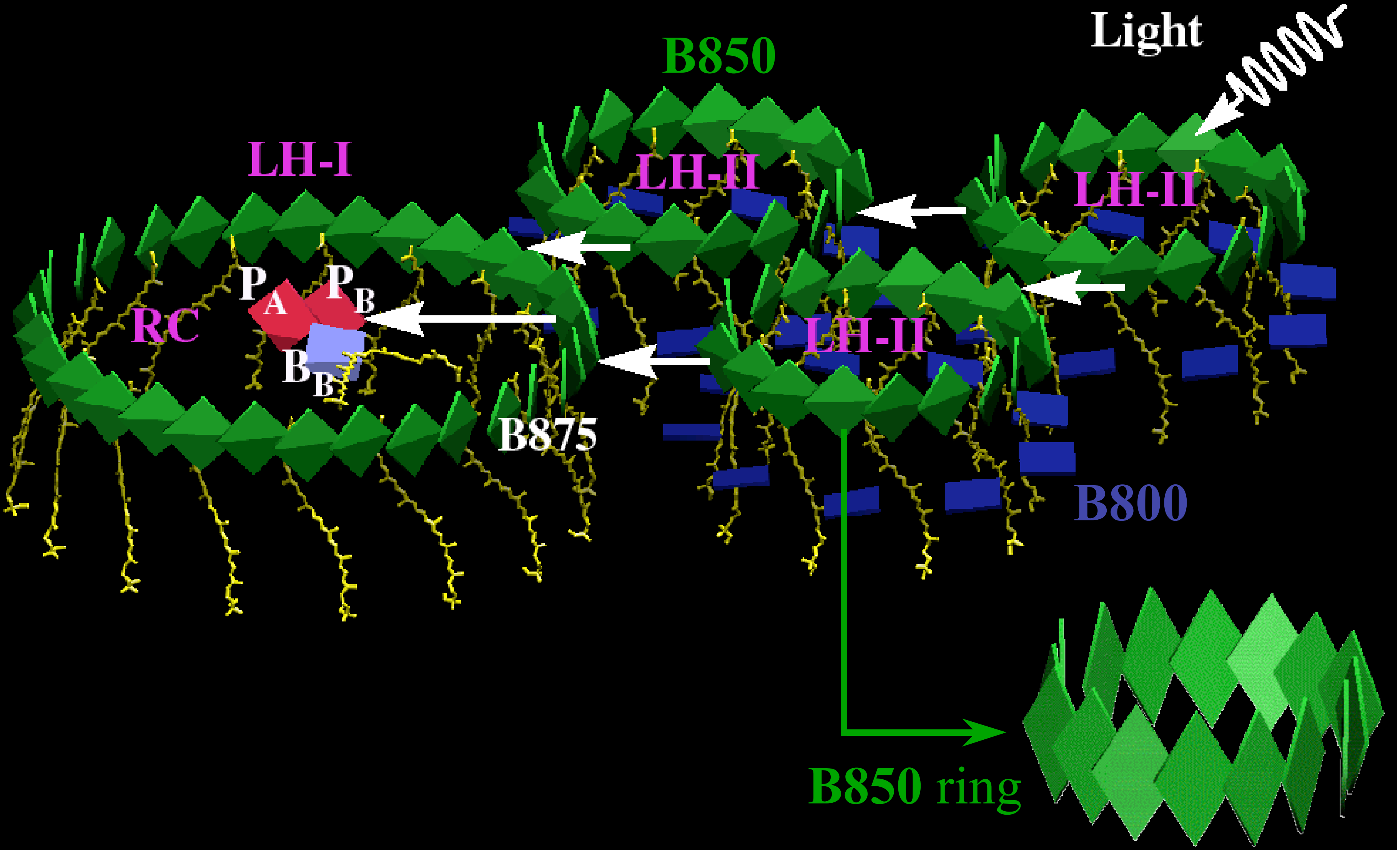
Note the conspicuous arrangement of chlorophyll rings!

Structure of Light Harvesting System

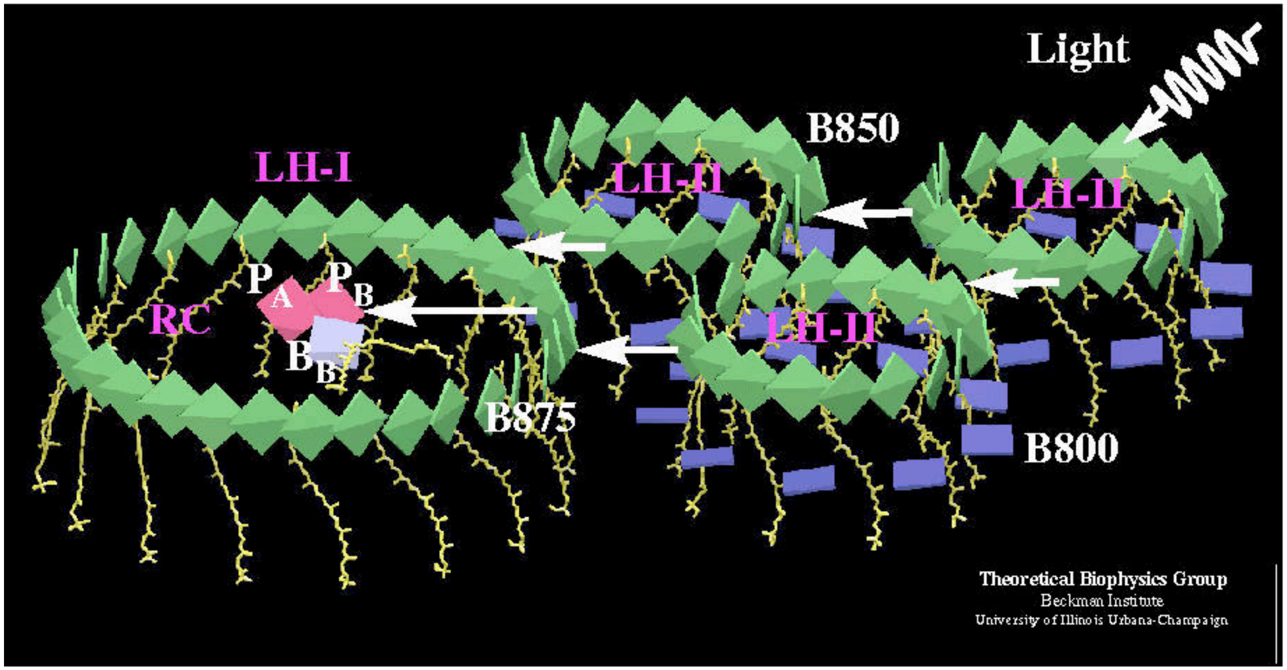


Photosynthetic apparatus of purple bacteria. Xiche Hu, Thorsten Ritz, Ana Damjanovic, Felix Autenrieth, and Klaus Schulten. *Quarterly Reviews of Biophysics*: 35 (2002)

Hierarchical aggregate of *chromophores*



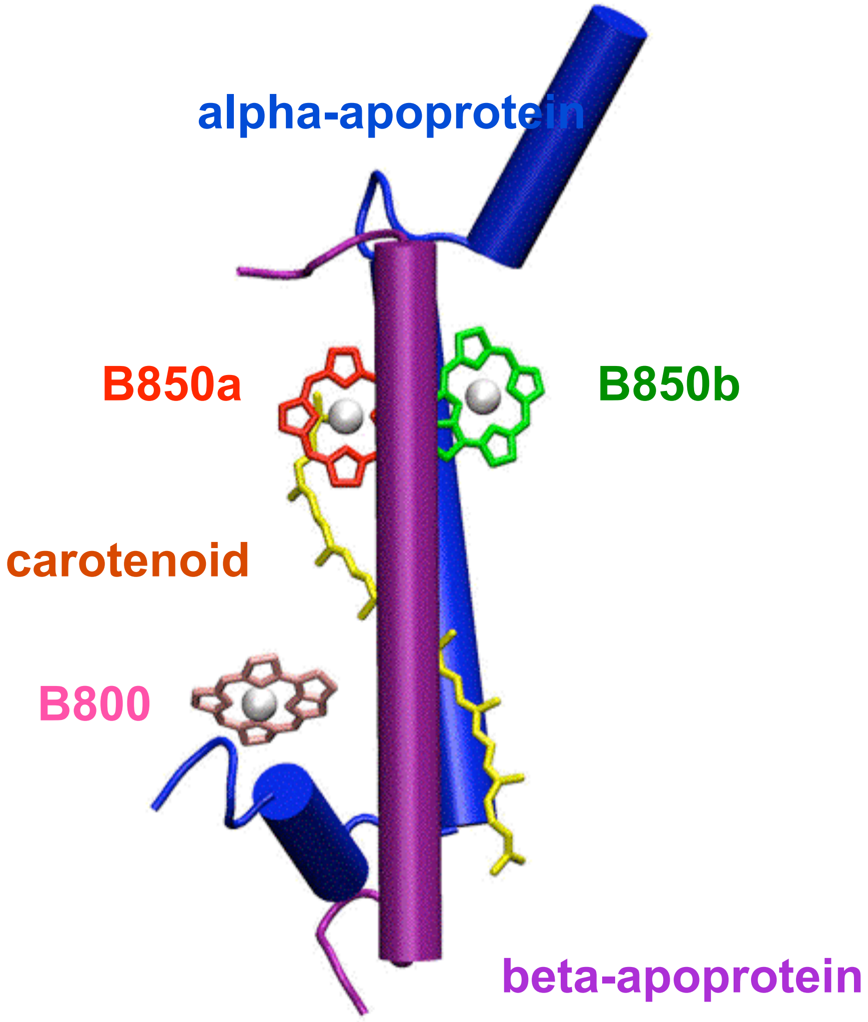
The Hard Earned Model

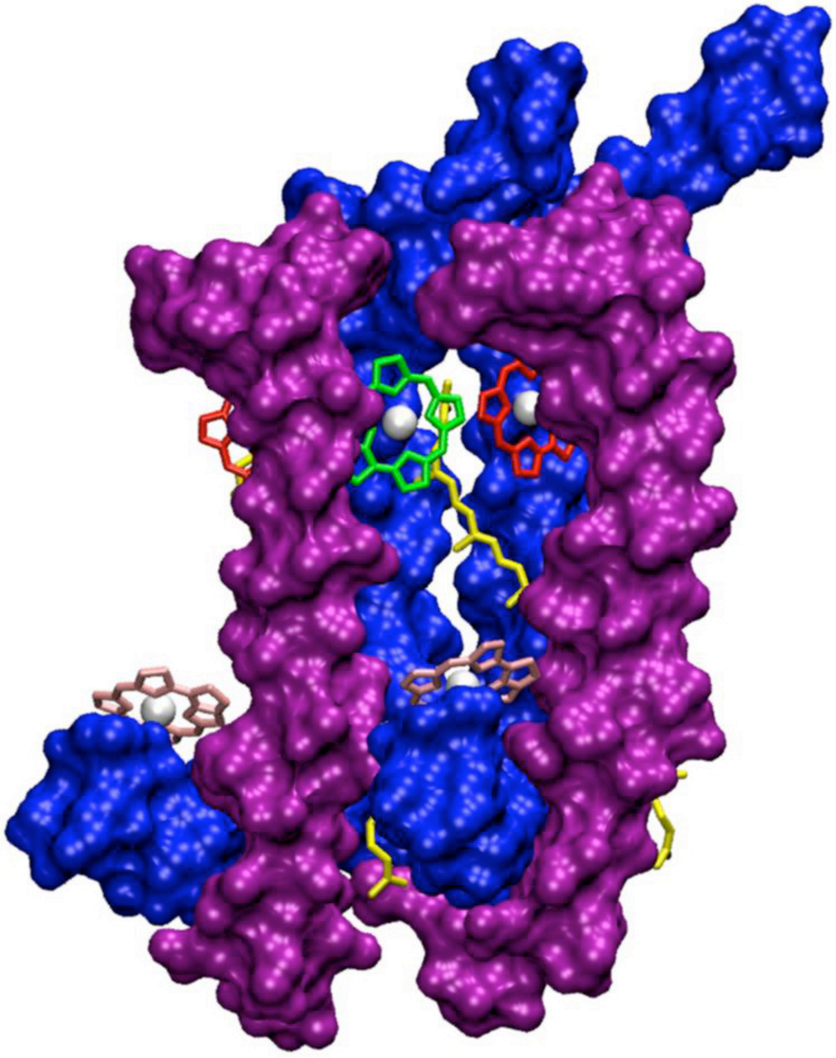


Here is a lesson to impatient physical scientists to learn: There is no royal road to the model! In the present case and many others, the model is arrived at not through superior inteligence of the physical scientist, but through long (2 years) collaboration with life scientists, in the present case crystallographers (Michel, Cogdell, Glasgow) and electron microscopists (Ghosh, Stuttgart).

Tutorial

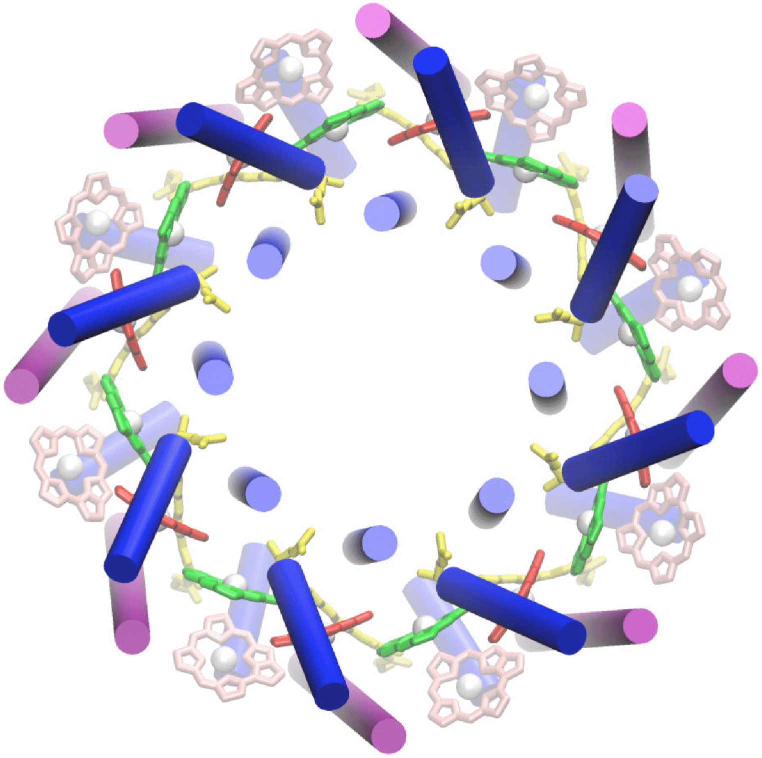
Structural unit of Light Harvesting Complex II (LH-II) from Rh. molischianum

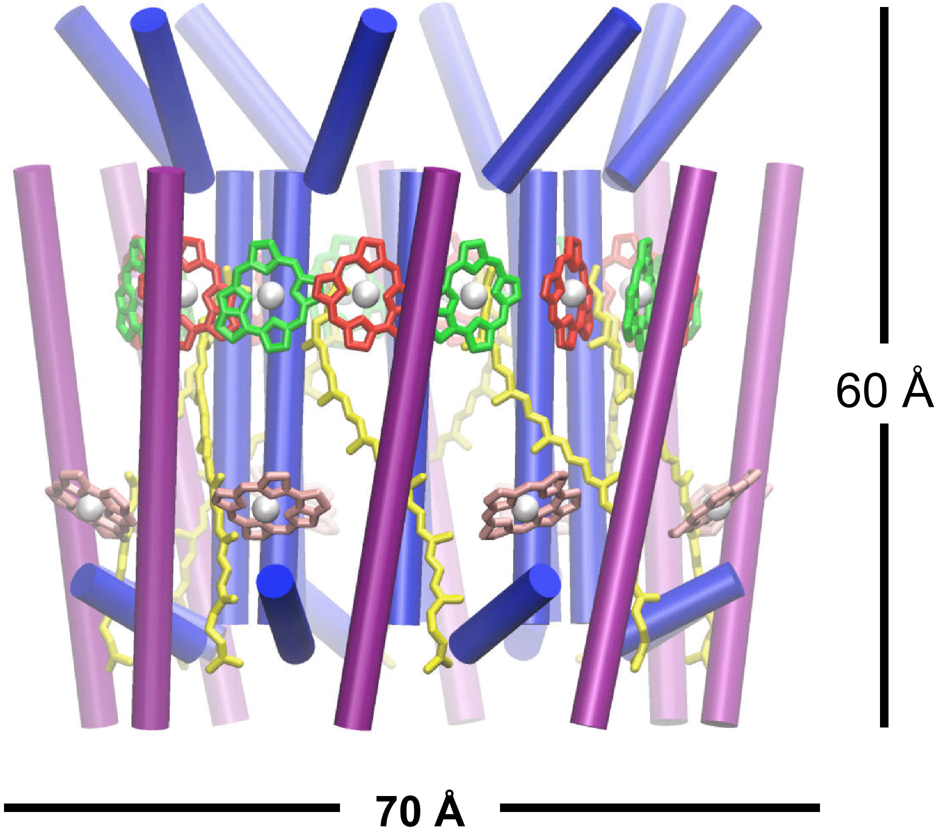




Tutorial

LH-II ring of 8 structural units

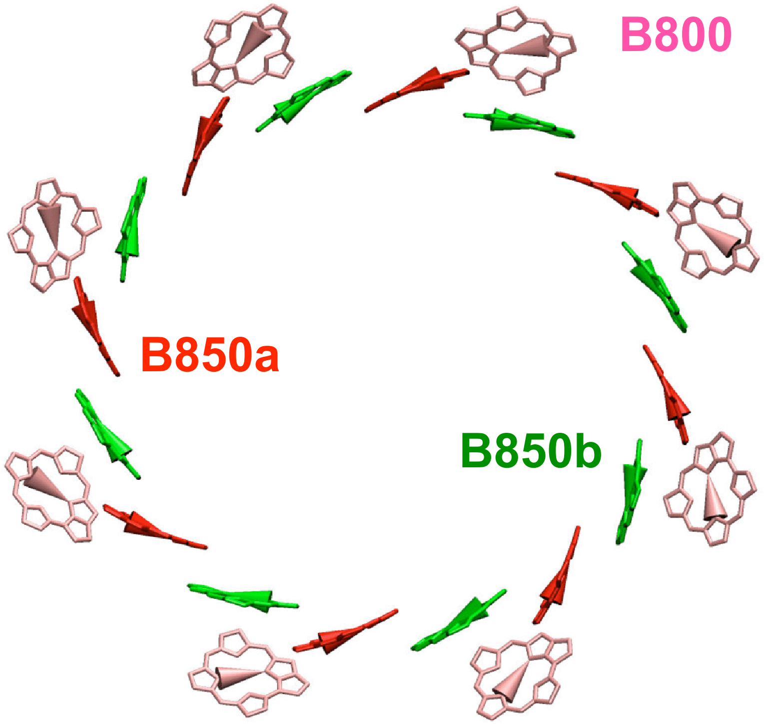




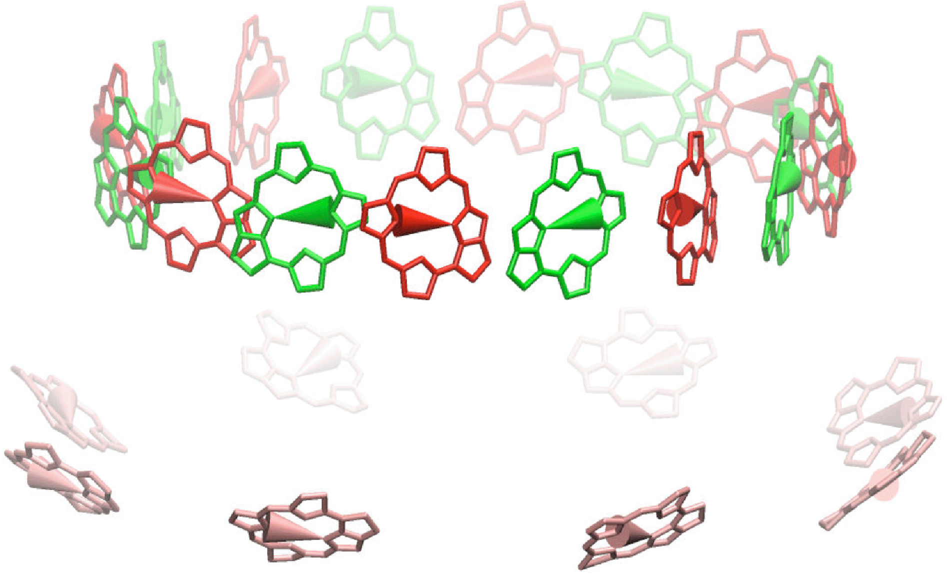
- 8 heterodimers (8 alpha-apoproteins, 8 beta-apoproteins)
- 24 BChls (8 B850a, 8 B850b and 8 B800)
- 8 carotenoids

Tutorial

24 Bacteriochlorophyls and their transition dipole moments in LH-II



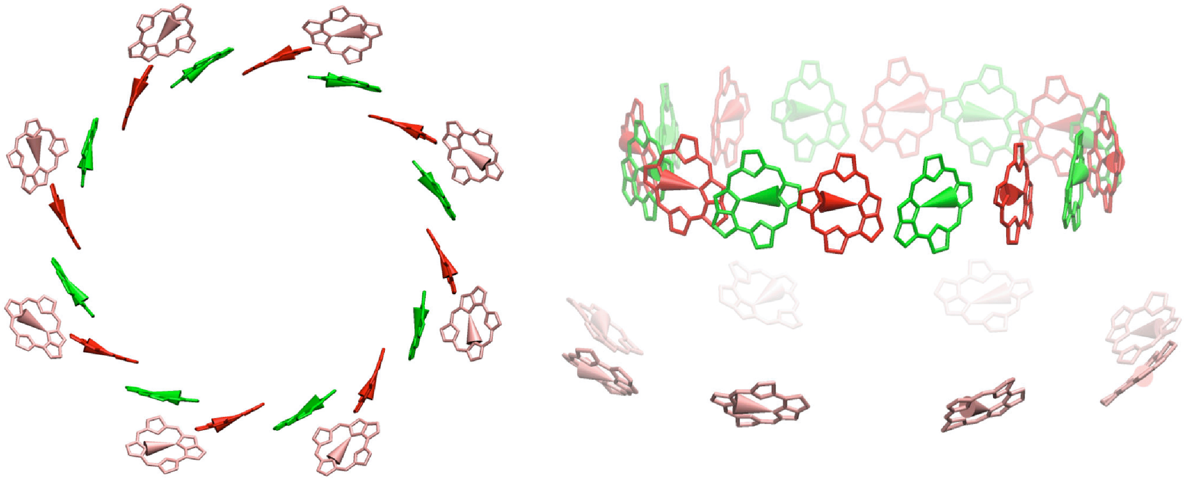
Ring of 16 B850a and B850b



Ring of 8 B800

Tutorial

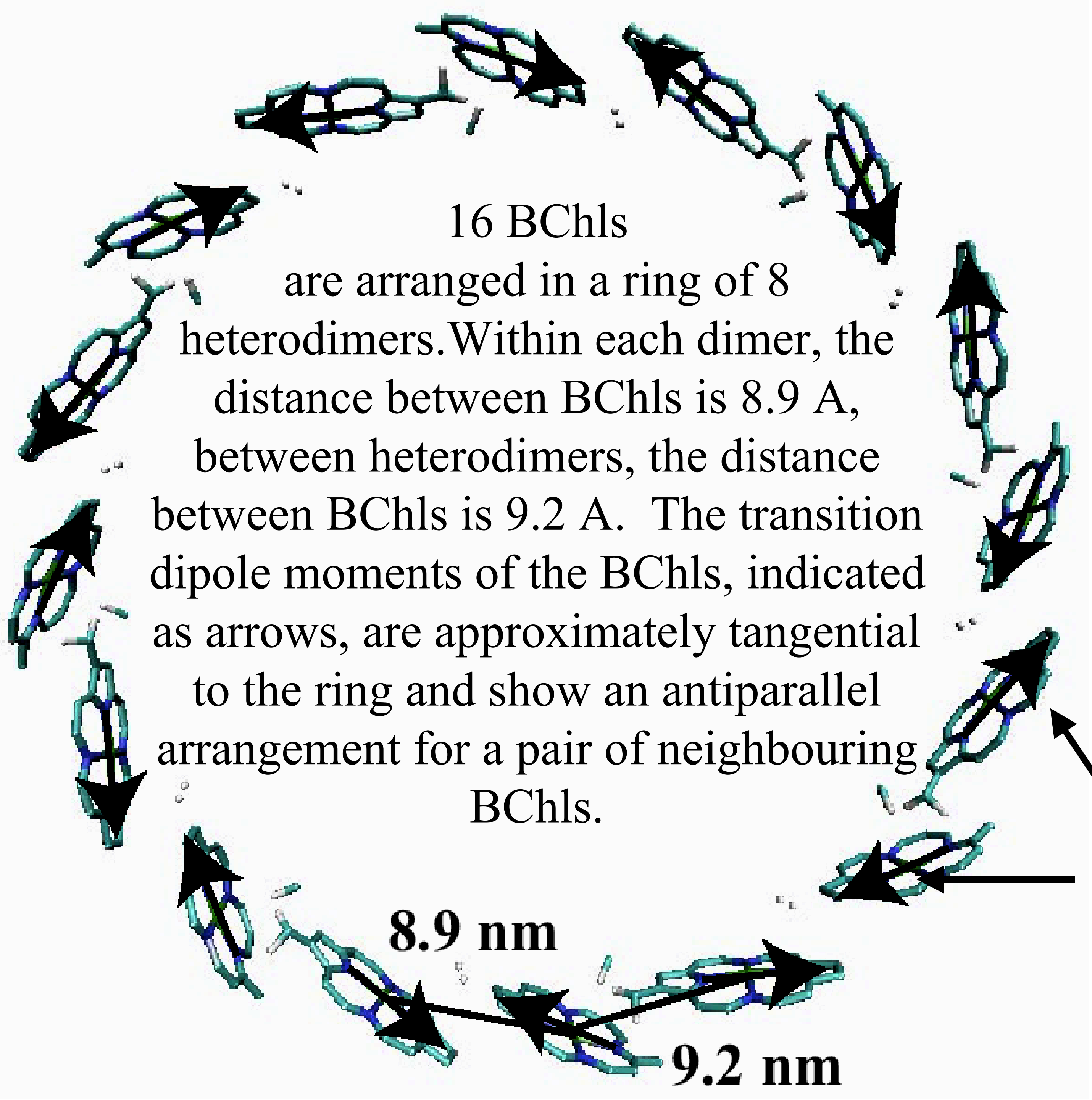
Rate of Excitation Transfer from BChl i to BChl j



Induced dipole-induced dipole interaction coupling between excited state of BChl i and ground state of BChl j

$$k_{ij} = \frac{2\pi}{\hbar}|U_{ij}|^2 J_{ij} \qquad U_{ij} = C\frac{[\hat{d}_i \cdot \hat{d}_j - 3(\hat{d}_i \cdot \hat{r}_{ij})(\hat{d}_j \cdot \hat{r}_{ij})]}{r_{ij}^3}$$

B850 BChl aggregate from LH-II of the purple bacterium Rs. molischianum



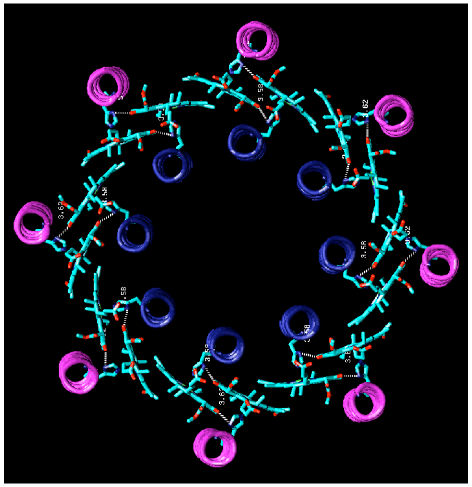
16 BChls are arranged in a ring of 8 heterodimers. Within each dimer, the distance between BChls is 8.9 A, between heterodimers, the distance between BChls is 9.2 A. The transition dipole moments of the BChls, indicated as arrows, are approximately tangential to the ring and show an antiparallel arrangement for a pair of neighbouring BChls.

transition dipole moments

Eigenvalue Problem for a Circular Dimerized Aggregate

Ring of 2N chlorophylls described by the basis states

$$|n\rangle = |\mathrm{BChl}_1, \mathrm{BChl}_2, \ldots, \mathrm{BChl}^*_n, \ldots, \mathrm{BChl}_{2N}\rangle \;,\; n = 1, \ldots, 2N$$



$$H = \left(\begin{array}{cccccccccc}
\varepsilon_0 & v_1 & W_{1,3} & W_{1,4} & \cdot & \cdot & \cdot & \cdot & W_{1,2N-1} & v_2 \\
v_1 & \varepsilon_0 & v_2 & W_{2,4} & \cdot & \cdot & \cdot & \cdot & W_{2,2N-1} & W_{2,2N} \\
W_{3,1} & v_2 & \varepsilon_0 & v_1 & \cdot & \cdot & \cdot & \cdot & W_{3,2N-1} & W_{3,2N} \\
W_{4,1} & W_{4,2} & v_1 & \varepsilon_0 & \cdot & \cdot & \cdot & & \cdot & \cdot \\
\cdot & & & & & & & & \cdot & \cdot \\
\cdot & \multicolumn{7}{c}{W_{jk} \;=\; C \left(\dfrac{\vec{d}_j \cdot \vec{d}_k}{{r_{jk}}^3} - \dfrac{3(\vec{r}_{jk} \cdot \vec{d}_j)\;(\vec{r}_{jk} \cdot \vec{d}_k)}{{r_{jk}}^5} \right)} & \cdot & \cdot \\
\cdot & & & & & & & & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \varepsilon_0 & v_2 & W_{2N-2,2N} \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & v_2 & \varepsilon_0 & v_1 \\
v_2 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & W_{2N,2N-2} & v_1 & \varepsilon_0
\end{array} \right)$$

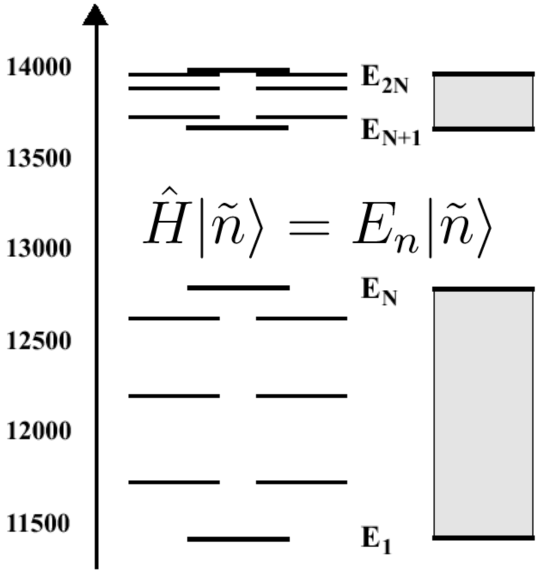
N fold axis

$$|\widetilde{n, \beta}\rangle \;=\; \frac{1}{\sqrt{N}} \sum_{k=1}^{N} \exp(2ikn\pi/N)\;|k, \beta\rangle$$

Dimerization: 2-D vectors

$$\begin{aligned}
E_1 &= \varepsilon_0 + 1.942 v_3 - \sqrt{0.576 {v_3}^2 + (v_1 + v_2 - 0.638 v_3)^2} \\
E_8 &= \varepsilon_0 - 1.513 v_3 - \sqrt{0.089 {v_3}^2 + (v_1 - v_2 + 0.038 v_3)^2}
\end{aligned}$$

$$\begin{aligned}
E_9 &= \varepsilon_0 - 1.513 v_3 + \sqrt{0.089 {v_3}^2 + (v_1 - v_2 + 0.038 v_3)^2} \\
E_{16} &= \varepsilon_0 + 1.942 v_3 + \sqrt{0.576 {v_3}^2 + (v_1 + v_2 - 0.638 v_3)^2}
\end{aligned}$$



$$\hat{H}|\tilde{n}\rangle = E_n|\tilde{n}\rangle$$

Quantum Chemical Determination of Aggregate

$$\hat{H} = \begin{pmatrix} c & v_1 & & & & v_2 \\ v_1 & c & v_2 & & & \\ & v_2 & c & v_1 & W_{i,j} & \\ & W_{i,j} & & \ddots & & \\ & & & & \ddots & \\ v_2 & & & & v_1 & c \end{pmatrix}$$

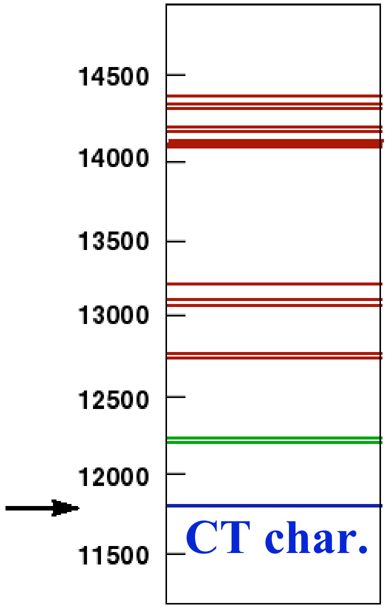
Effective Hamiltonian for Q_y excitations of the B850 ring

Due to circular symmetry and co-planar arrangement of transition dipole moments, degenerate electronic state $E_{2,3}$ carries almost all oscillator strength.

This establishes effective Hamiltonian!

no adjustable parameters

ZINDO/S calculations

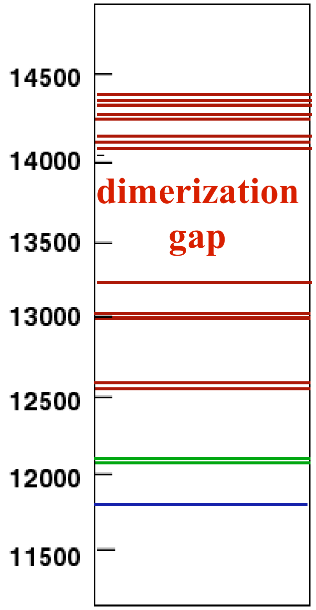


Zerner et al.

analytical solution

matched to quantum chemistry results

effective Hamiltonian calculations



Effective Hamiltonian

long range coupling narrows band

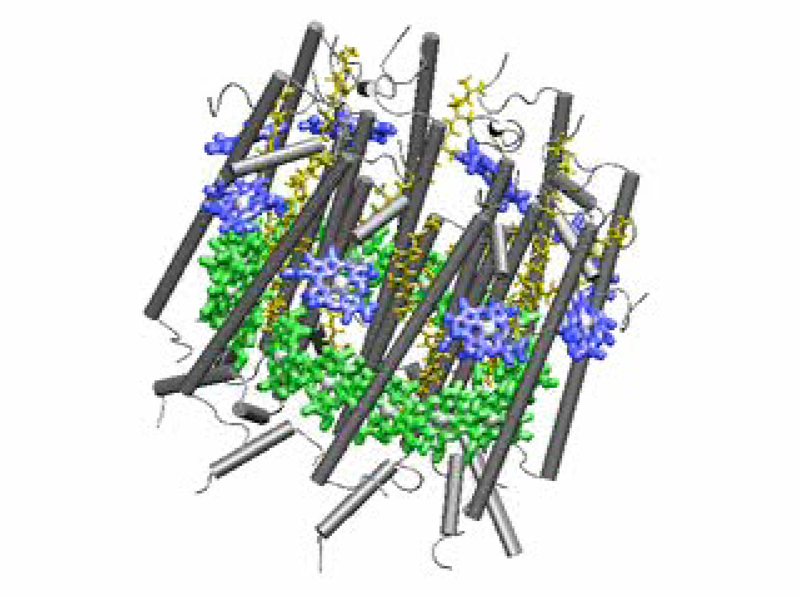
J. Phys. Chem., *B102*, 7640 (1998)
J. Phys. Chem., *B101*, 3854 (1997)
J. Lumin. *76-78*, 310 (1998)

allowed states

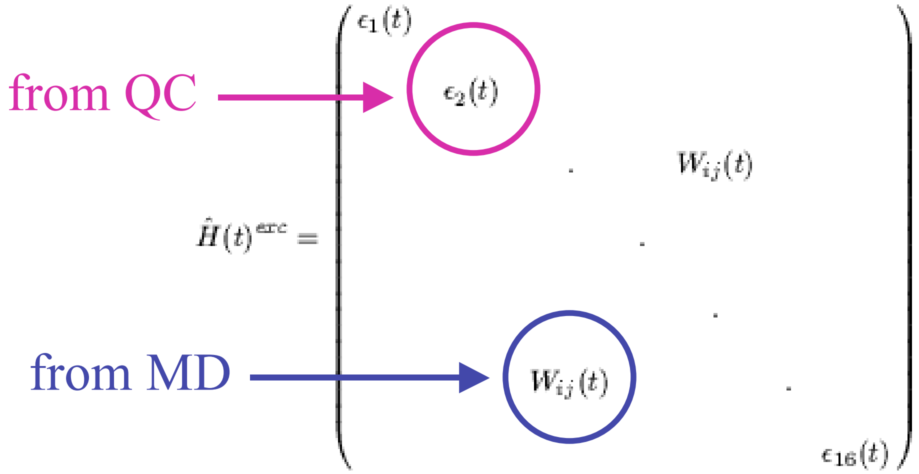
$$W_{jk} = C \left(\frac{\vec{d}_j \cdot \vec{d}_k}{r_{jk}{}^3} - \frac{3(\vec{r}_{jk} \cdot \vec{d}_j)\,(\vec{r}_{jk} \cdot \vec{d}_k)}{r_{jk}{}^5} \right)$$

The Effect of Dynamic Disorder

Molecular Dynamics (MD) Simulation



Gaussian 98, HF/CIS, STO-3G basis

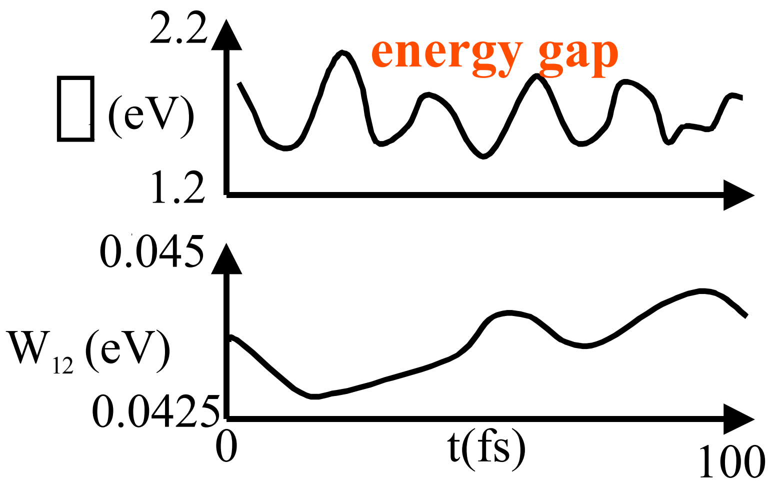


$$\hat{H}(t)^{exc} = \begin{pmatrix} \epsilon_1(t) & & & & \\ & \boxed{\epsilon_2(t)} & & W_{ij}(t) & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & \cdot \\ & \boxed{W_{ij}(t)} & & & \cdot \\ & & & & \epsilon_{16}(t) \end{pmatrix}$$

$$W_{jk} = C\left(\frac{\vec{d}_j \cdot \vec{d}_k}{{r_{jk}}^3} - \frac{3(\vec{r}_{jk}\cdot\vec{d}_j)\,(\vec{r}_{jk}\cdot\vec{d}_k)}{{r_{jk}}^5}\right)$$

LH2 in membrane: 85,000 atoms; equilibrated for 2ns with NAMD2; NpT ensemble; periodic boundary condition; full electrostatics (PME)

Followed by 0.8ps simulation, trajectory output every 2fs with quantum chemistry calc. of exc. energy, interpolated to “sample” every 0.5 fs



Ana Damjanovic, Ioan Kosztin, Ulrich Kleinekathoefer, and Klaus Schulten, Phys. Rev.E, 65:031919 (2002)

Polaron Coherence Length (one mode)

Polaron spectrum in leading order perturbation theory

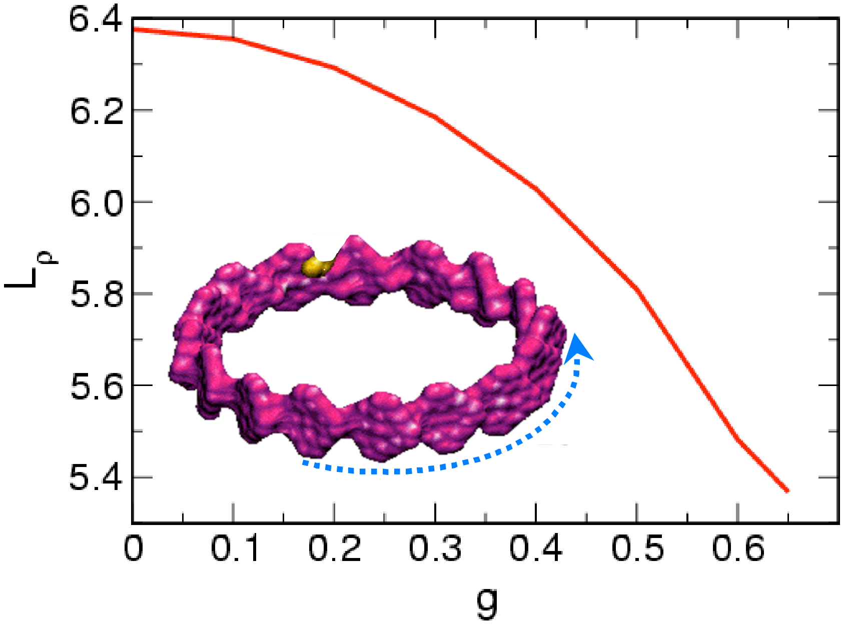
$$E_k = \epsilon_k + \frac{g^2\omega_0^2}{M}\sum_q \frac{1}{\epsilon_k - \epsilon_{k+q} - \omega_0}$$

$$|k;0) = |k;0\rangle + \frac{g\omega_0}{\sqrt{M}}\sum_q \frac{1}{\epsilon_k - \epsilon_{k+q} - \omega_0}|k+q;1_q\rangle$$

Exciton coherence size (inverse Participation ratio)

$$L_\rho = \left[\left(\sum_{ij}|\rho_{ij}|\right)^2\right]\left[M\sum_{ij}|\rho_{ij}|^2\right]^{-1}$$

$$\rho_{ij} = \sum_k C_k^*(i)C_k(j)\exp(-\beta E_k)$$



Dynamic disorder slightly reduces the coherence size of the exciton

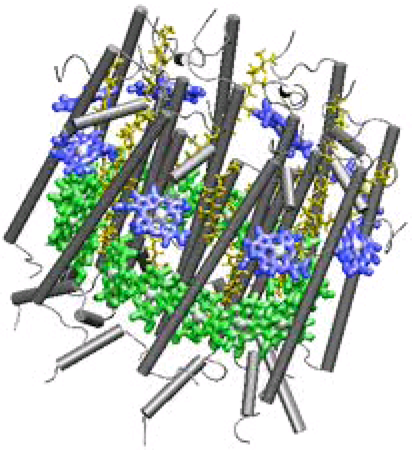
Ana Damjanovic, Ioan Kosztin, Ulrich Kleinekathoefer, and Klaus Schulten, Phys. Rev.E, 65:031919 (2002)

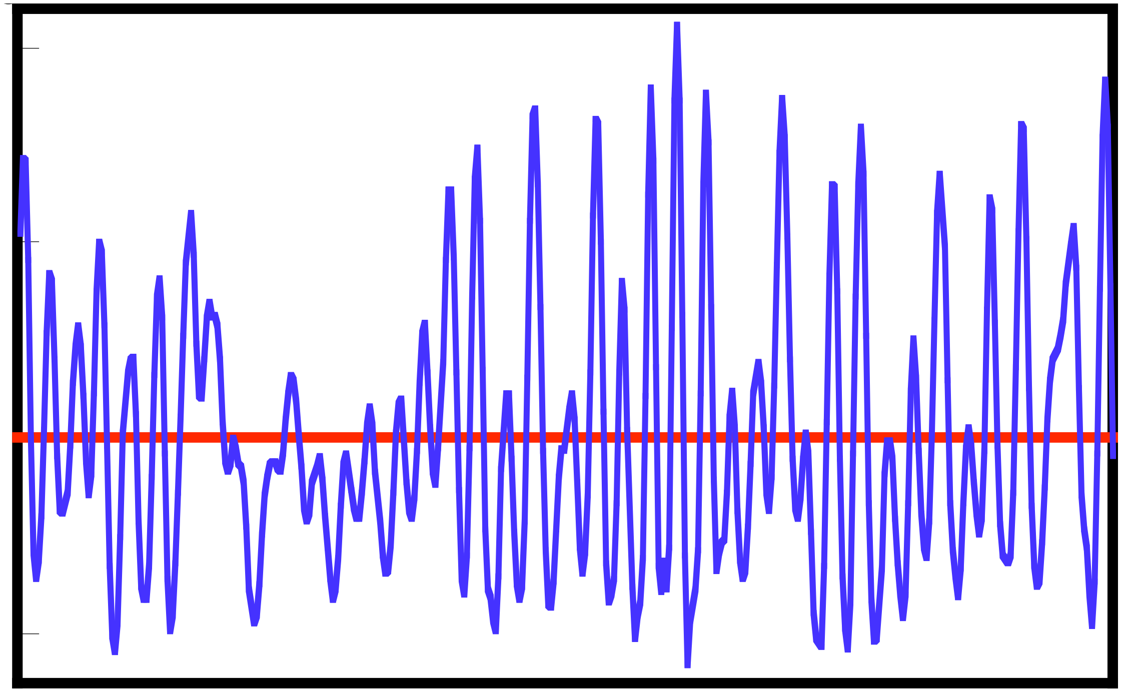
Absorption Spectrum – Polaron Model

Step 1: BChl energy gap fluctuations
from MD/QC simulations

$$\delta\epsilon(t) = \epsilon(t) - \epsilon_0$$

(all modes)





Ana Damjanovic, Ioan Kosztin, Ulrich Kleinekathoefer, and Klaus Schulten, Phys. Rev.E, 65:031919 (2002)

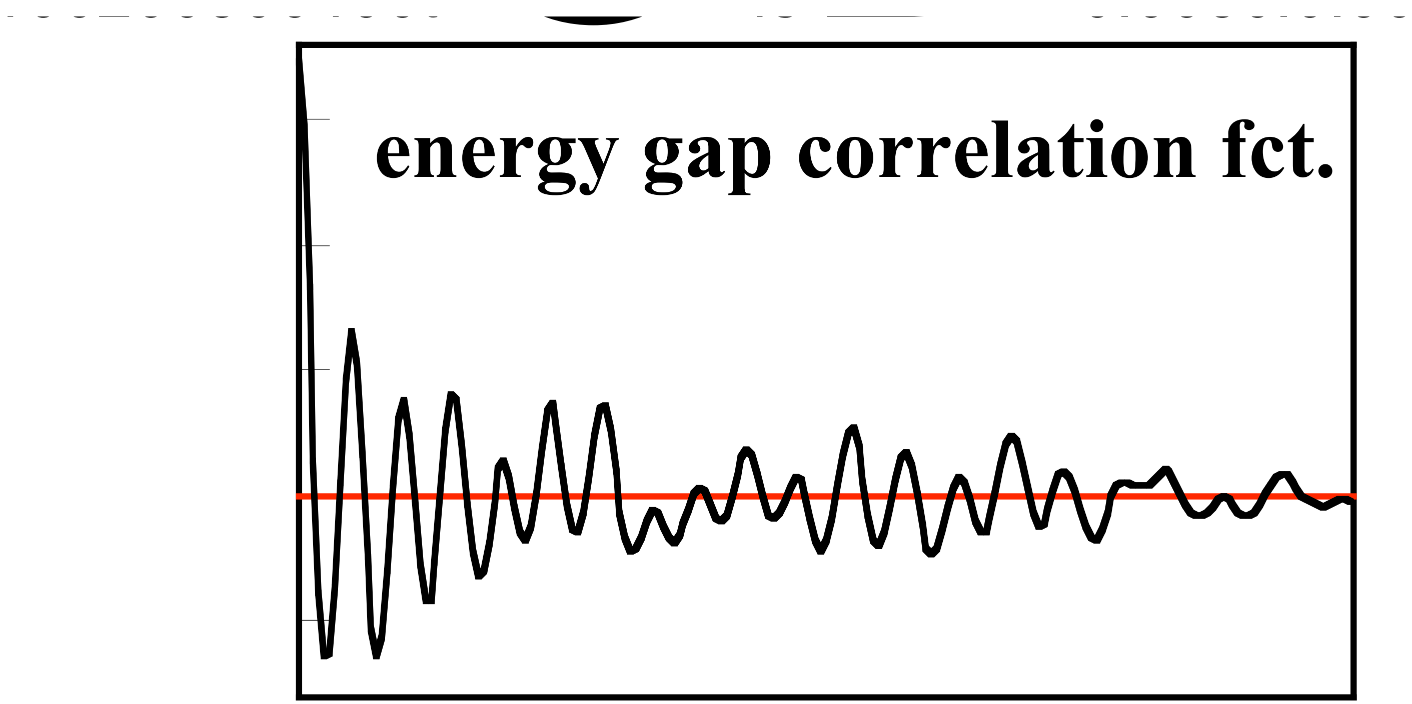
Absorption Spectrum – Polaron Model

Step 1: BChl energy gap fluctuations
from MD/QC simulations

$$\delta\epsilon(t) = \epsilon(t) - \epsilon_0$$

Step 2: Autocorrelation function

$$\mathcal{C}(t) = \langle \delta\epsilon(t)\delta\epsilon(0) \rangle$$



Ana Damjanovic, Ioan Kosztin, Ulrich Kleinekathoefer, and Klaus Schulten, Phys. Rev.E, 65:031919 (2002)

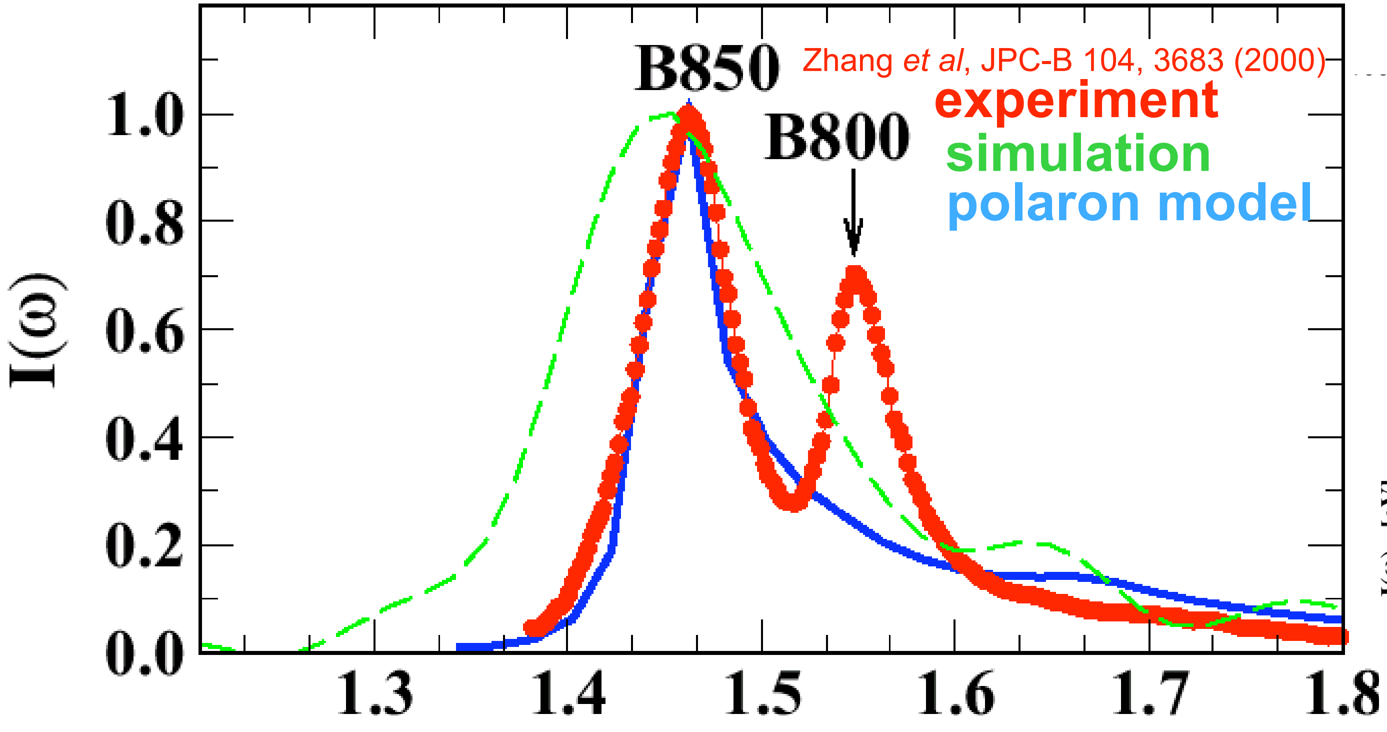
Absorption Spectrum – B850 Excitons

$$I(\omega) \propto \sum_k |d_k|^2 \int_0^\infty dt \exp[-\Phi'_k(t)] \cos[(\omega - \epsilon_k)t + \Phi''_k(t)]$$

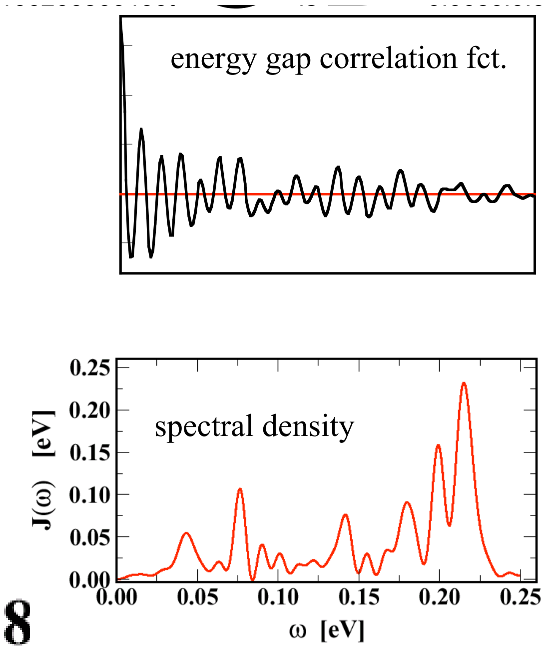
phonon contribution

$$\Phi_k(t) = \int_0^t d\tau (t-\tau) \mathcal{D}(\tau) F_k(\tau)$$

exciton contribution



From MD/QC simulation

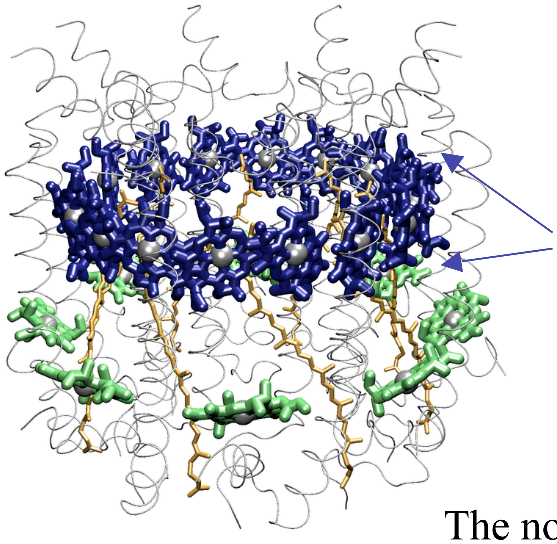


http://xxx.lanl.gov/abs/physics/0107064

Ana Damjanovic, Ioan Kosztin, Ulrich Kleinekathoefer, and Klaus Schulten, Phys. Rev. E, 65:031919 (2002)

Spectral Properties of Light-Harvesting Complexes and the Role of Static Disorder

Recall effective Hamiltonian description for a BChl ring:



$$H_0 = \begin{pmatrix} E_a & v_1 & W_{13} & W_{14} & \cdots & v_2 \\ v_1 & E_b & v_2 & W_{24} & \cdots & W_{2N} \\ W_{31} & v_2 & E_a & v_1 & \cdots & W_{3N} \\ W_{41} & W_{42} & v_1 & E_b & \cdots & W_{4N} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ v_2 & W_{N2} & W_{N3} & W_{N4} & \cdots & E_b \end{pmatrix}$$

E_a and E_b are the site energies.
$v1$ and $v2$ are nearest neighbor interactions.

The non-nearest neighbor interactions are given by a dipole-dipole term:

$$U_{ij} = C\frac{[\hat{d}_i \cdot \hat{d}_j - 3(\hat{d}_i \cdot \hat{r}_{ij})(\hat{d}_j \cdot \hat{r}_{ij})]}{r_{ij}^3}$$

Thermal (static) disorder as a random matrix ensemble:

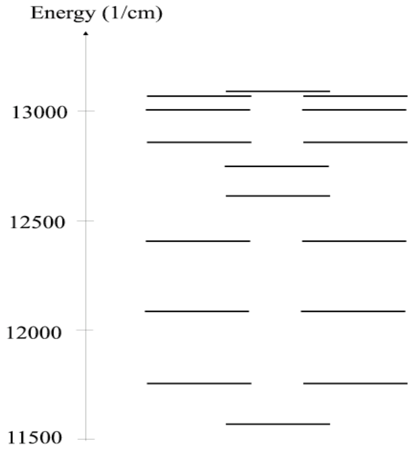
$$\boxed{H = H_0 + R}$$

deterministic + random

… where R is a matrix randomly choosen from a certain distribution.

Melih Sener and K. Schulten. Physical Review E, 65:031916 (2002)

We are interested in spectral properties:

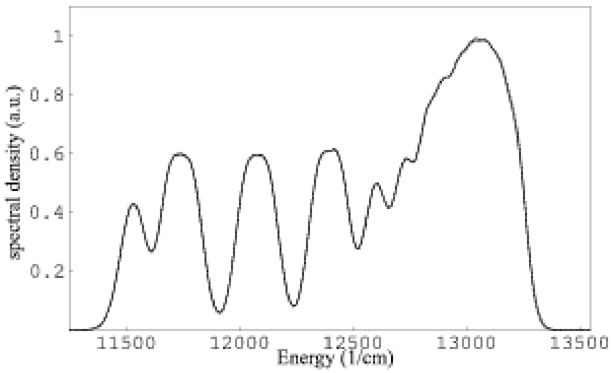


unperturbed spectrum

Ensemble average

1. Spectral density:

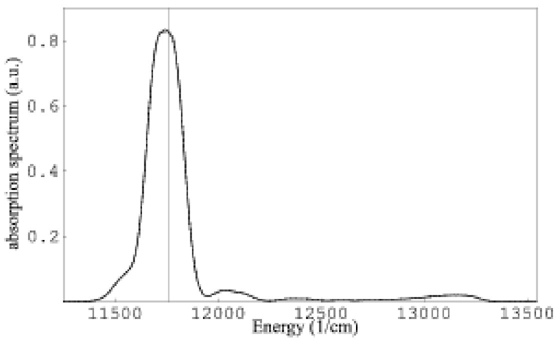
(i.e. the distribution of energy eigenvalues)



$$\rho(E) = \left\langle \sum_i \delta(E - E_i) \right\rangle$$

2. Absorption spectrum:

(i.e. the spectrum weighed by oscillator strengths)



$$A(E) = K E \left\langle \sum_i \mu_i \delta(E - E_i) \right\rangle$$

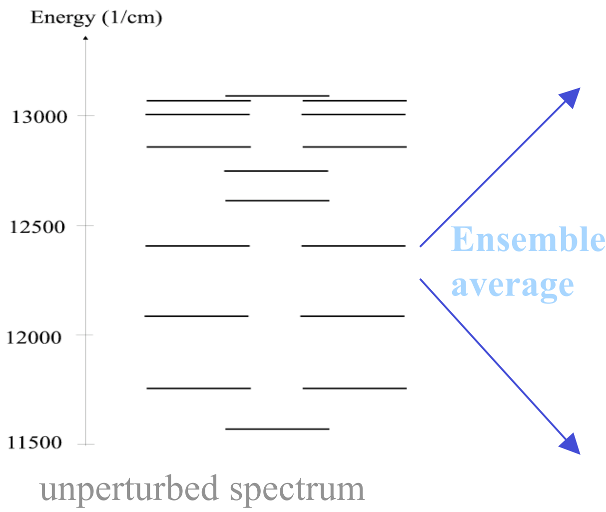
Note: Everything is averaged over the 'disorder` described by *R*.

$$\boxed{H = H_0 + R}$$

$$\langle \ldots \rangle \equiv \int d[R]\, P(R) \ldots$$

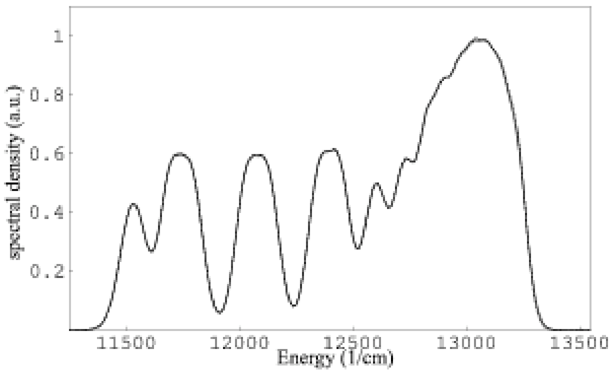
Melih Sener and K. Schulten. Physical Review E, 65:031916 (2002)

Independence of spectral density and absorption spectrum from type of random distribution (universality)

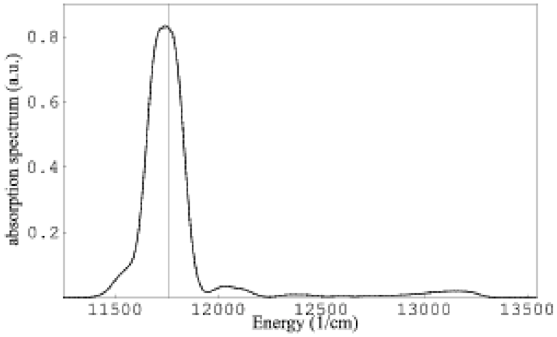


unperturbed spectrum

1. Spectral density:



2. Absorption spectrum:



- •Spectral fluctuations are model independent. (reminiscent of *Central Limit Theorem*.)
- • *Distribution* of R is largely irrelevant. (i.e. a Gaussian is as good as any other distribution.)
- • *Symmetry class* of R becomes irrelevant at *large N* (i.e. R can be real symmetric or complex hermitian.)
- •The *width* of R needs to be carefully taken into account.

$$\boxed{H = H_0 + R}$$

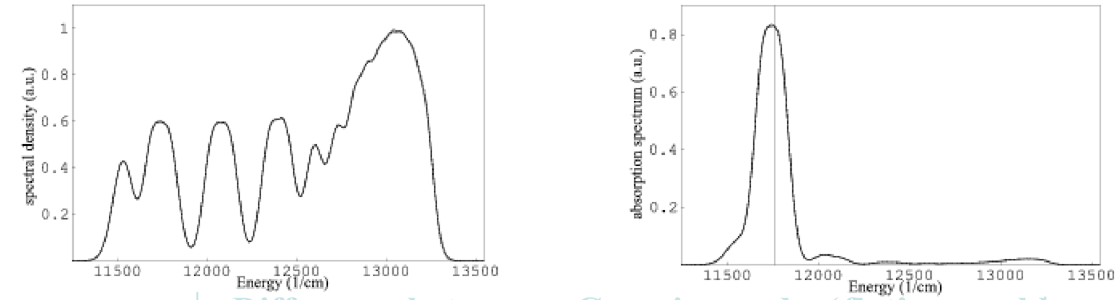
Universality means model independence!

$$\langle L \rangle \equiv \int d[R]\, P(R)\, L$$

Melih Sener and K. Schulten. Physical Review E, 65:031916 (2002)

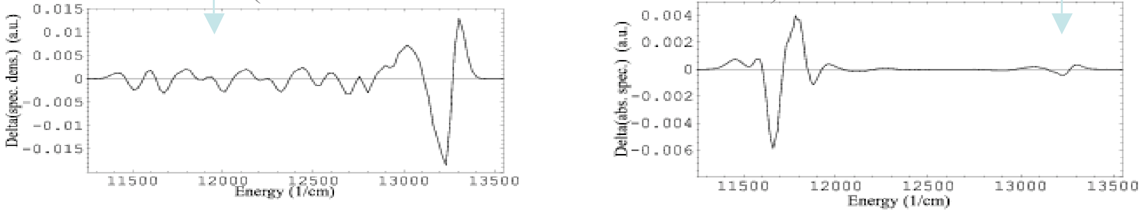
Independence of spectral density and absorption spectrum from type of random distribution (universality)

1. Spectral density: 2. Absorption spectrum:



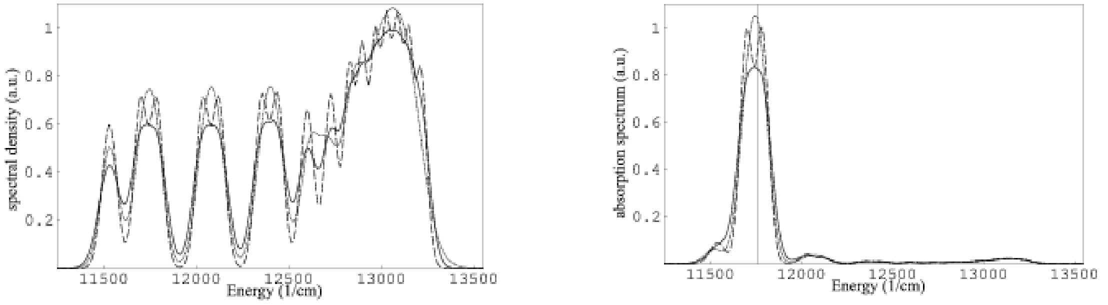
Difference between a Gaussian and a 'flat' ensemble

(not observable on full scale above)



Even across symmetry classes spectra remain robust.

(real symmetic: solid / complex hermitian: dashed / diagonal disorder: dotted)



- Spectral fluctuations are model independent. (reminiscent of *Central Limit Theorem*.)
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- ***Symmetry class*** of R becomes irrelevant at *large N* (i.e. R can be real symmetric or complex hermitian.)
- The *width* of R needs to be carefully taken into account.

$$\boxed{H = H_0 + R}$$

Universality means model independence!

$$\langle \dots \rangle \equiv \int d[R]\, P(R) \dots$$

Melih Sener and K. Schulten. Physical Review E, 65:031916 (2002)

Spectral density can be computed analytically in case of Gaussian unitary disorder

$$H = H_0 + R$$

$$\langle \ldots \rangle \equiv \int d[R]\, P(R) \ldots$$

$$P(R) = N_R \exp\left[-\frac{1}{2\sigma^2} Tr(R^+ R)\right]$$

$$\rho(\varepsilon) = \left\langle \sum_{i=1}^{N} \delta(\varepsilon - E_i) \right\rangle$$

$$\rho(\varepsilon) = \frac{1}{\pi} \mathrm{Im} \left\langle Tr \frac{1}{\varepsilon - i\eta - (H_0 + R)} \right\rangle$$

$$\rho(\varepsilon) = \frac{1}{2\pi} \frac{\partial}{\partial j}\bigg|_{j=0} \mathrm{Im}\, Z(j)$$

$$H_0 = U_0^+ \Lambda U_0$$

Λ is the diagonal part of H_0.

Partition function (NxN)

$$Z(j) = \int d[R]\, P(R) \frac{\det[\varepsilon - i\eta - (\Lambda + R) + j]}{\det[\varepsilon - i\eta - (\Lambda + R) - j]}$$

Hubbard-Stratonovitch transformation

Partition function (1+1)x(1+1)

$$Z(j) = \int d[\sigma] N_\sigma \exp\left[-\frac{1}{2\sigma^2} Str\, \sigma^2\right] \prod_{i=1}^{N} SDet^{-1}\left[\begin{pmatrix} \varepsilon - i\eta - \lambda_i - j & 0 \\ 0 & \varepsilon - i\eta - \lambda_i + j \end{pmatrix} - \sigma\right]$$

$$Z(j) = \int d[S]\, B^2(S) N_\sigma \prod_{i=1}^{N} SDet^{-1}[S + \lambda_i]\, I_u(S)$$

$$I_u(S) = \int d\mu(u) \exp\left[-\frac{1}{2\sigma^2} STr\left(uSu^+ + \begin{pmatrix} \varepsilon - i\eta - j & 0 \\ 0 & \varepsilon - i\eta + j \end{pmatrix}\right)^2\right]$$

This is an integral over a super-unitary group. It is known as a *Harish-Chandra-Itzykson-Zuber integral*.

Road Map:

- Express spectral density as an integral over matrices
- Reduce the (large) matrix integral to a (small) super-matrix integral (Hubbard-Stratonovitch transformation)
- Evaluate the super-matrix integral using harmonic analysis on super-groups (Harish-Chandra-Itzykson-Zuber integrals)
- The final expression is given in terms of the unperturbed spectrum, Λ.

Melih Sener and K. Schulten. Physical Review E, 65:031916 (2002)

Spectral density can be computed analytically in case of Gaussian unitary disorder

Final expression for the spectral density
in terms of the unperturbed spectrum:

$$\square(\square) = \frac{1}{\square^2}\underset{0}{\square} d\square\, B_0 B_1$$

$$B_0 = \underset{\square}{\square} d\square\, e^{\square\square^2}\,\mathrm{Im}\,\square\underset{i=1}{\overset{N}{\square}}\frac{1}{\square\square i\square\square\frac{1}{\sqrt{2\square}}\left(\square+\square^2\square\;\square\square_i\right)}\square$$

just integrating-by-parts
delta functions…

$$B_1 = \underset{\square}{\square} d\square\, e^{\square\square^2}\underset{i=1}{\overset{N}{\square}}\square i\square\square\frac{1}{\sqrt{2\square}}\left(\square+\square^2\square\;\square\square_i\right)\square$$

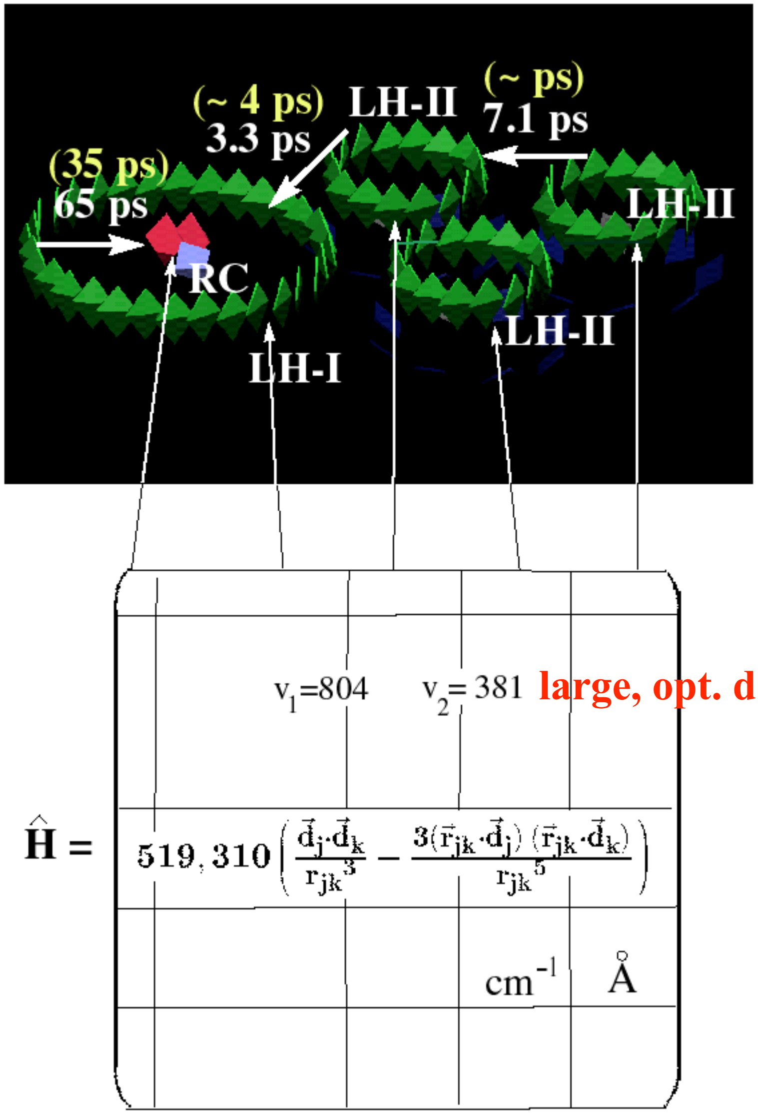
just a polynomial times
a gaussian…

… final symbolics is evaluated using *Mathematica*.

Melih Sener and K. Schulten.
Physical Review E, 65:031916
(2002)

When combined with *universality* this approach grants us analytical insight into the spectra of light-harvesting complexes.

Effective Hamiltonian for Entire Photosynthetic Unit



$$\hat{\mathbf{H}} = \quad 519{,}310\left(\frac{\vec{d}_j\cdot\vec{d}_k}{r_{jk}^{3}} - \frac{3(\vec{r}_{jk}\cdot\vec{d}_j)\,(\vec{r}_{jk}\cdot\vec{d}_k)}{r_{jk}^{5}}\right)$$

$v_1=804 \quad v_2=381$ **large, opt. dens.?**

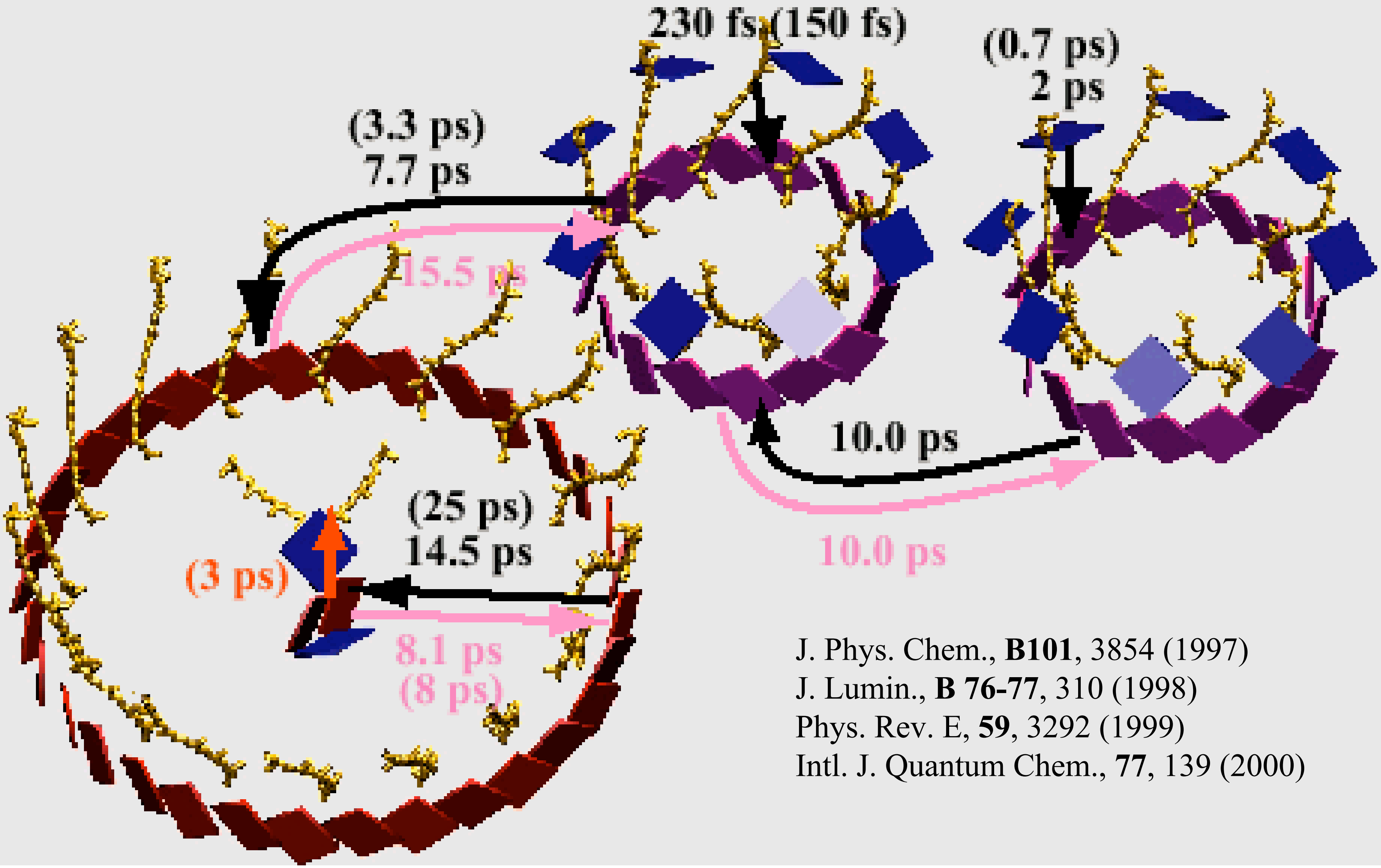
$\mathrm{cm}^{-1} \quad$ Å

$$k_{DA} = \frac{2\pi}{\hbar}|U_{DA}|^2 J_{DA}$$

$$J_{DA} = \int S_D(E) S_A(E)\, dE$$ **exp.**

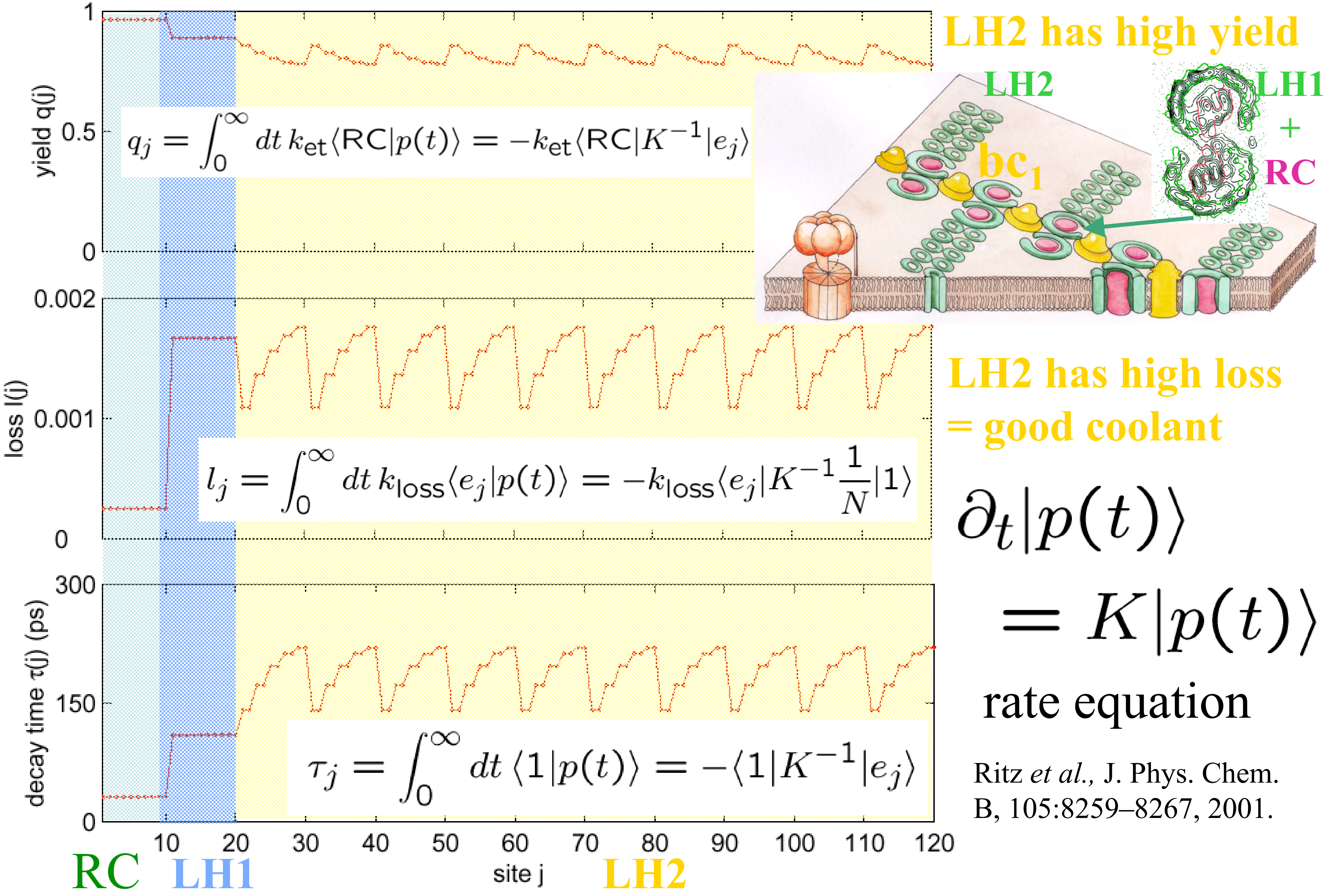
The effective Hamiltonian derived for an LH-II ring is extended to the entire system of light harvesting complexes. i.e., LH-I and LH-IIs, assuming LH-II nearest neighbour couplings and dipolar coupling for non-nearest neighbour interactions, for a geometry of closest packed LH-I and LH-II proteins.

Excitation Transfer in Photosynthetic Unit



J. Phys. Chem., **B101**, 3854 (1997)
J. Lumin., **B 76-77**, 310 (1998)
Phys. Rev. E, **59**, 3292 (1999)
Intl. J. Quantum Chem., **77**, 139 (2000)

Yield, Loss, and Overall Decay Rates in Light Harvesting System



$$q_j = \int_0^\infty dt\, k_{\mathrm{et}} \langle \mathrm{RC} | p(t) \rangle = -k_{\mathrm{et}} \langle \mathrm{RC} | K^{-1} | e_j \rangle$$

$$l_j = \int_0^\infty dt\, k_{\mathrm{loss}} \langle e_j | p(t) \rangle = -k_{\mathrm{loss}} \langle e_j | K^{-1} \frac{1}{N} | 1 \rangle$$

$$\tau_j = \int_0^\infty dt\, \langle 1 | p(t) \rangle = -\langle 1 | K^{-1} | e_j \rangle$$

LH2 has high yield

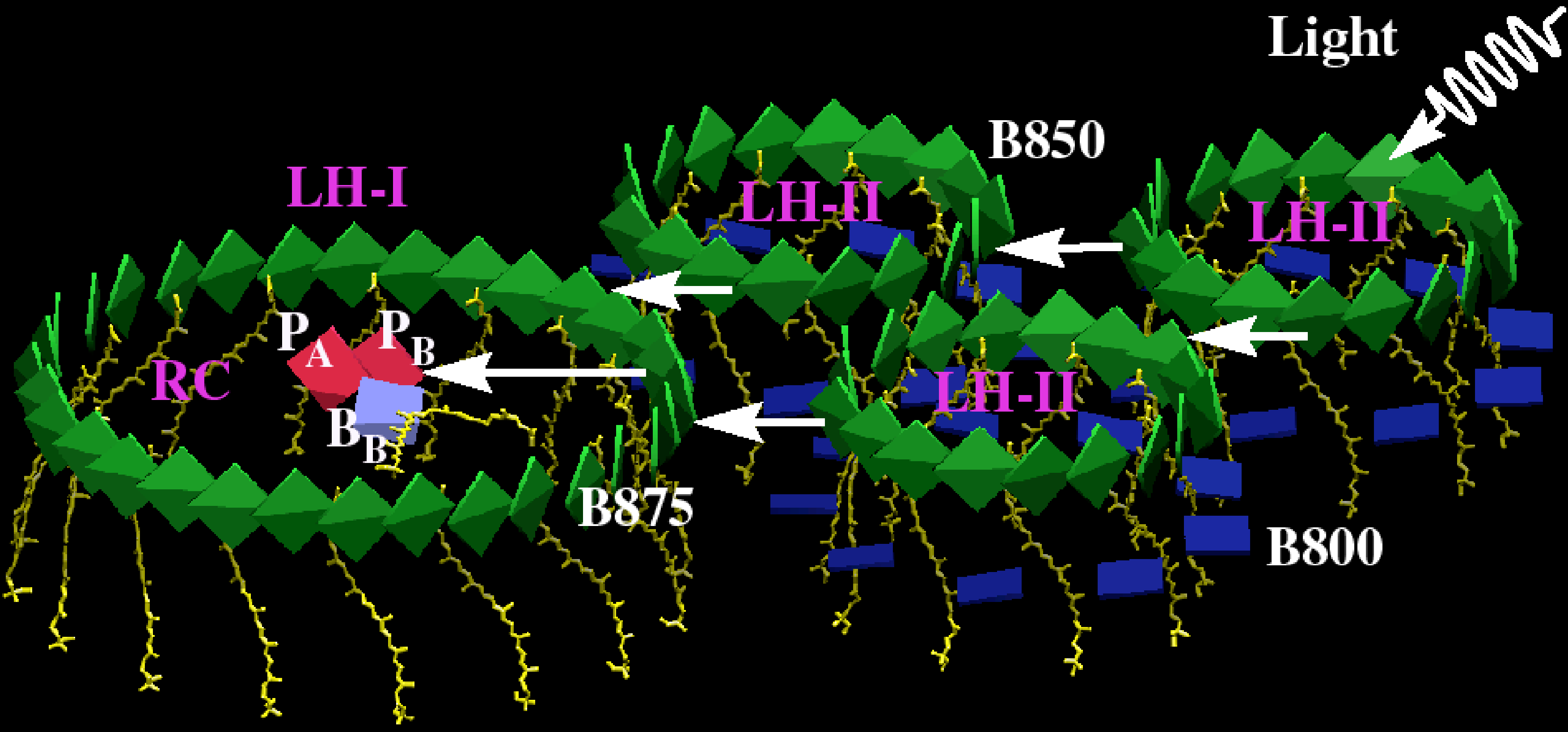
LH2 has high loss
= good coolant

$$\partial_t |p(t)\rangle = K |p(t)\rangle$$

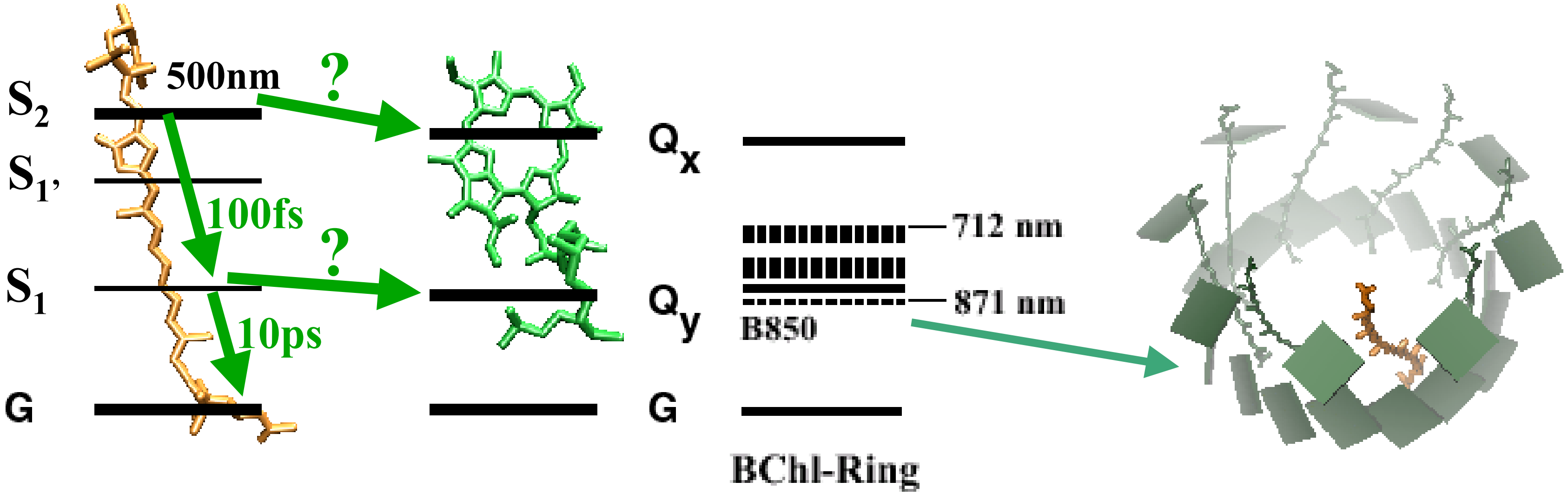
rate equation

Ritz *et al.*, J. Phys. Chem. B, 105:8259–8267, 2001.

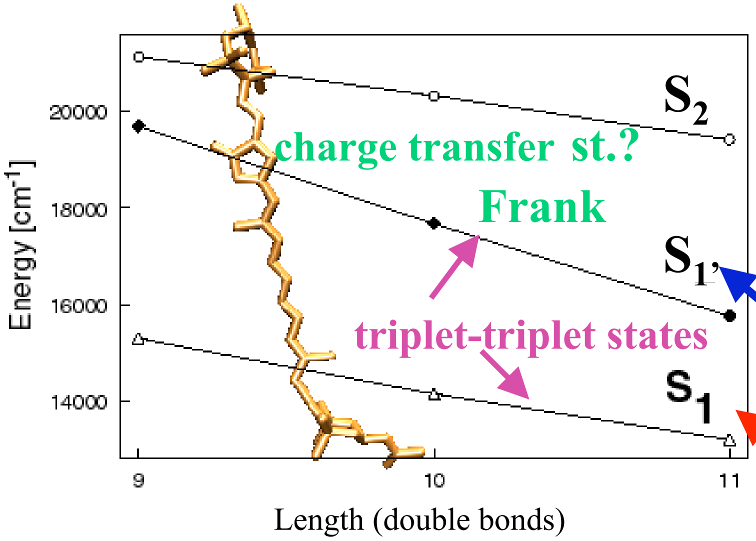
The Role of the Carotenoids in Light Absorption and Excitation Flow



Two Channels for Car-Chl Transfer



Electronic excitations in carotenoids



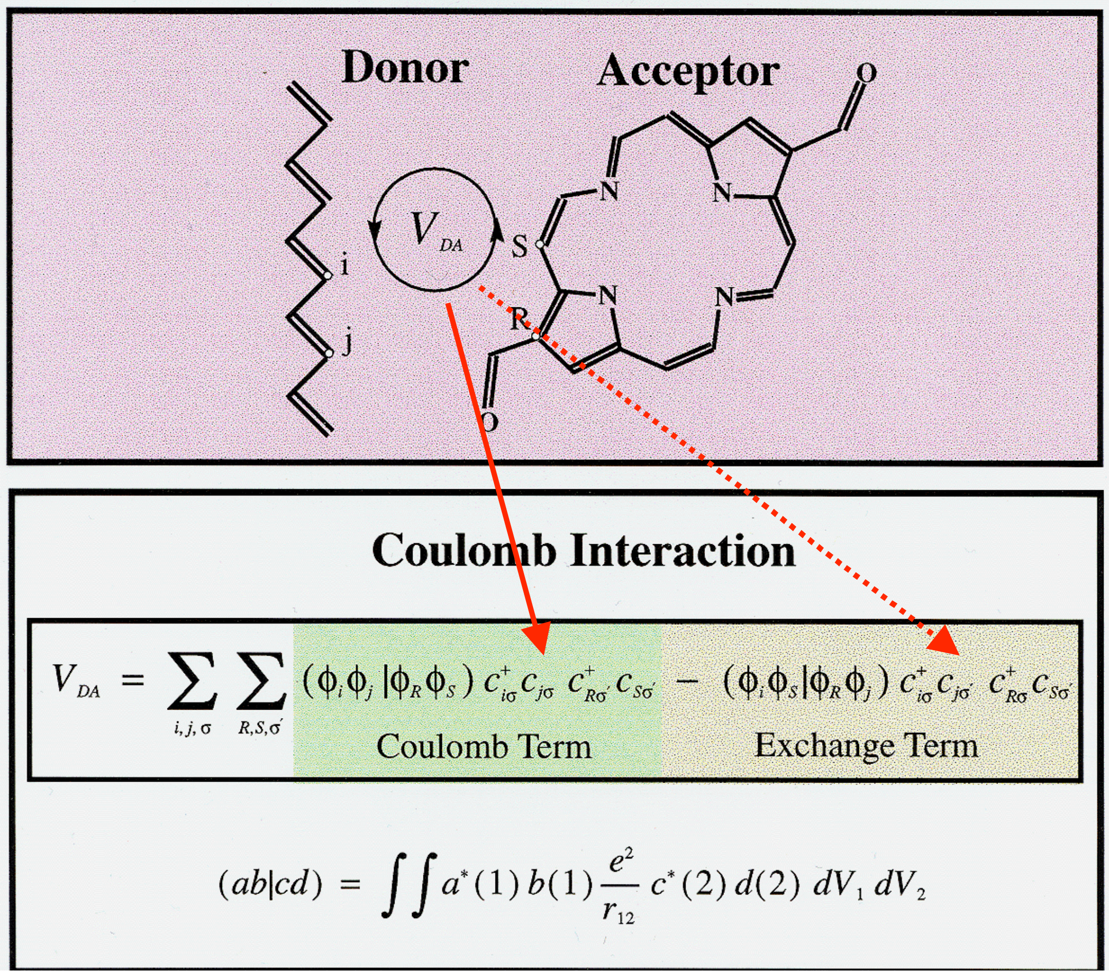
Correspondence: S_2 => $1B_u^+$ optically allowed

Car ↔ polyene states $S_{1'}$ => $1B_u^-$ optically forbidden

S_1 => $2A_g^-$ optically forbidden

Phys. Rev. B, 36, 4337 (1987) theor.
Chem. Phys. Lett., 299, 187 (1999) exp.
Chem. Phys. Lett., 290, 36 (1998) exp.
Chem. Phys. Lett. 14, 299, 305 (1972) exp., theor.

Hamiltonian



Coulomb Interaction

$$V_{DA} = \sum_{i,j,\sigma}\sum_{R,S,\sigma'} \underbrace{(\phi_i\phi_j|\phi_R\phi_S)\, c^+_{i\sigma} c_{j\sigma}\, c^+_{R\sigma'} c_{S\sigma'}}_{\text{Coulomb Term}} - \underbrace{(\phi_i\phi_S|\phi_R\phi_j)\, c^+_{i\sigma} c_{j\sigma'}\, c^+_{R\sigma} c_{S\sigma'}}_{\text{Exchange Term}}$$

$$(ab|cd) = \int\int a^*(1)\, b(1) \frac{e^2}{r_{12}} c^*(2)\, d(2)\, dV_1\, dV_2$$

Separation into donor, acceptor, and interaction contributions:

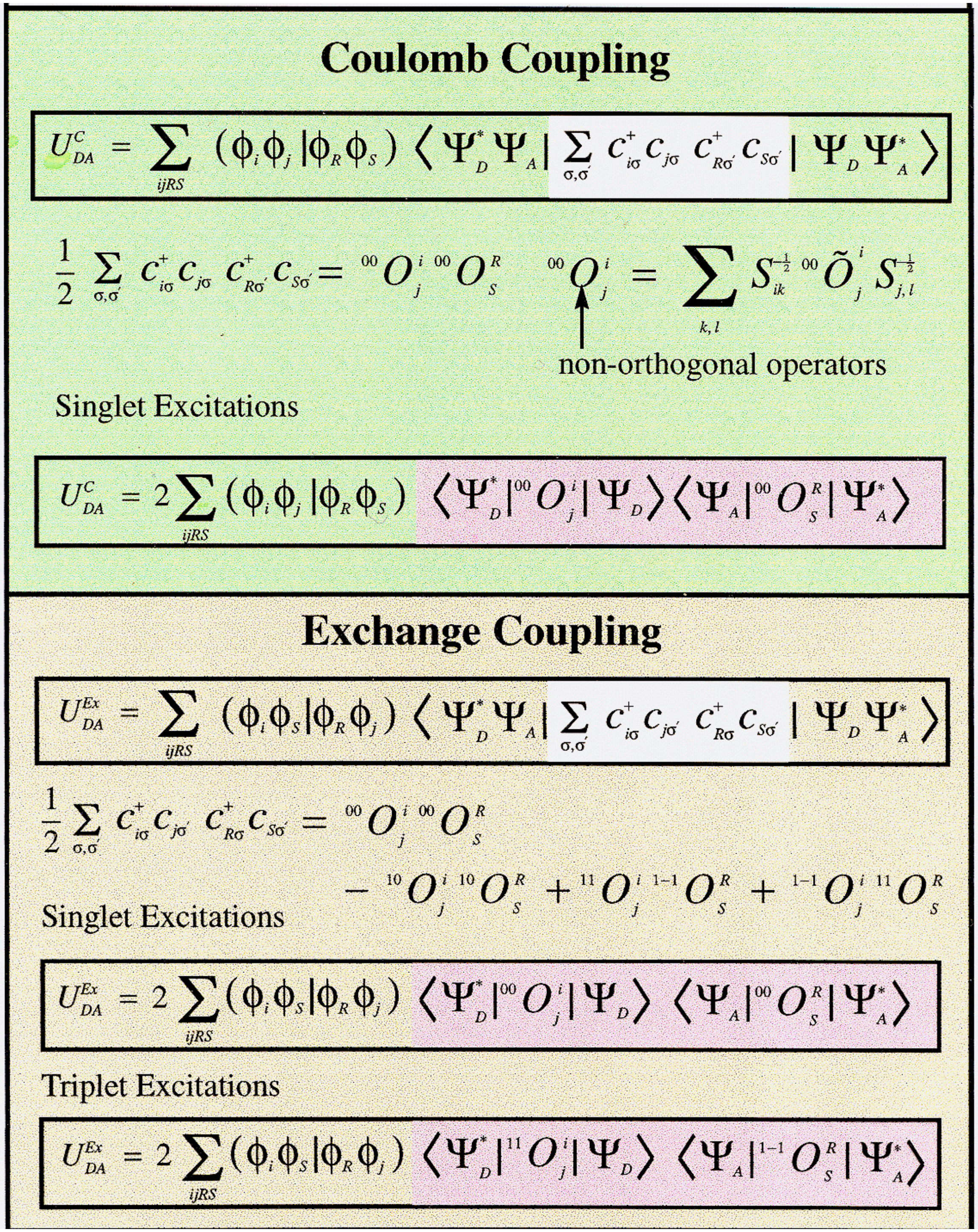
$$H = H_D + H_A + V_{DA}$$

(only π atomic orbtals included, no polarizability effects!)

Describe the effect of V_{DA} in perturbation theory, i.e., evaluate matrix elements accounting for transition of excitation from *donor* to *acceptor*

We relied considerably on N. Nagae,. Kakitani, T. Kato, M. Mimuro, J. Chem. Phys, 98, 10 (1993)

Transition Matrix Elements



Coulomb Coupling

$$\boxed{U^{C}_{DA} = \sum_{ijRS} (\phi_i\phi_j|\phi_R\phi_S)\left\langle \Psi^{*}_{D}\Psi_{A}\middle| \sum_{\sigma,\sigma'} c^{+}_{i\sigma}c_{j\sigma}\, c^{+}_{R\sigma'}c_{S\sigma'} \middle| \Psi_{D}\Psi^{*}_{A}\right\rangle}$$

$$\frac{1}{2}\sum_{\sigma,\sigma'} c^{+}_{i\sigma}c_{j\sigma}\, c^{+}_{R\sigma'}c_{S\sigma'} = {}^{00}O^{i}_{j}\,{}^{00}O^{R}_{S} \qquad {}^{00}O^{i}_{j} = \sum_{k,l} S^{-\frac{1}{2}}_{ik}\,{}^{00}\tilde{O}^{i}_{j}\,S^{-\frac{1}{2}}_{j,l}$$

non-orthogonal operators

Singlet Excitations

$$\boxed{U^{C}_{DA} = 2\sum_{ijRS} (\phi_i\phi_j|\phi_R\phi_S)\left\langle \Psi^{*}_{D}\middle|{}^{00}O^{i}_{j}\middle|\Psi_{D}\right\rangle\left\langle \Psi_{A}\middle|{}^{00}O^{R}_{S}\middle|\Psi^{*}_{A}\right\rangle}$$

Exchange Coupling

$$\boxed{U^{Ex}_{DA} = \sum_{ijRS} (\phi_i\phi_S|\phi_R\phi_j)\left\langle \Psi^{*}_{D}\Psi_{A}\middle| \sum_{\sigma,\sigma'} c^{+}_{i\sigma}c_{j\sigma'}\, c^{+}_{R\sigma}c_{S\sigma'} \middle| \Psi_{D}\Psi^{*}_{A}\right\rangle}$$

$$\frac{1}{2}\sum_{\sigma,\sigma'} c^{+}_{i\sigma}c_{j\sigma'}\, c^{+}_{R\sigma}c_{S\sigma'} = {}^{00}O^{i}_{j}\,{}^{00}O^{R}_{S} - {}^{10}O^{i}_{j}\,{}^{10}O^{R}_{S} + {}^{11}O^{i}_{j}\,{}^{1-1}O^{R}_{S} + {}^{1-1}O^{i}_{j}\,{}^{11}O^{R}_{S}$$

Singlet Excitations

$$\boxed{U^{Ex}_{DA} = 2\sum_{ijRS} (\phi_i\phi_S|\phi_R\phi_j)\left\langle \Psi^{*}_{D}\middle|{}^{00}O^{i}_{j}\middle|\Psi_{D}\right\rangle\left\langle \Psi_{A}\middle|{}^{00}O^{R}_{S}\middle|\Psi^{*}_{A}\right\rangle}$$

Triplet Excitations

$$\boxed{U^{Ex}_{DA} = 2\sum_{ijRS} (\phi_i\phi_S|\phi_R\phi_j)\left\langle \Psi^{*}_{D}\middle|{}^{11}O^{i}_{j}\middle|\Psi_{D}\right\rangle\left\langle \Psi_{A}\middle|{}^{1-1}O^{R}_{S}\middle|\Psi^{*}_{A}\right\rangle}$$

Express coupling in terms of 2nd quantization for non-orthogonal orbitals

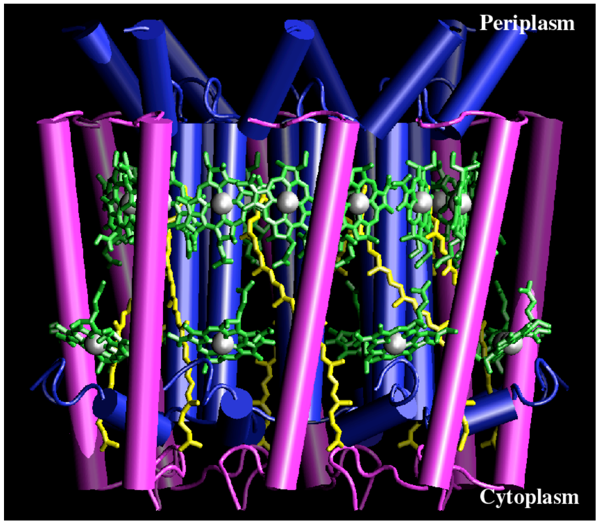
Factor coupling into donor and acceptor contributions:

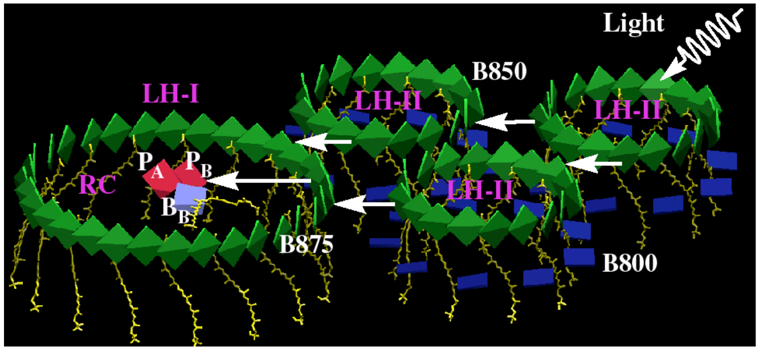
Coulomb coupling is rank zero tensor (singlet transitions only)

Exchange coupling is rank one tensor (singlet and triplet transitions)

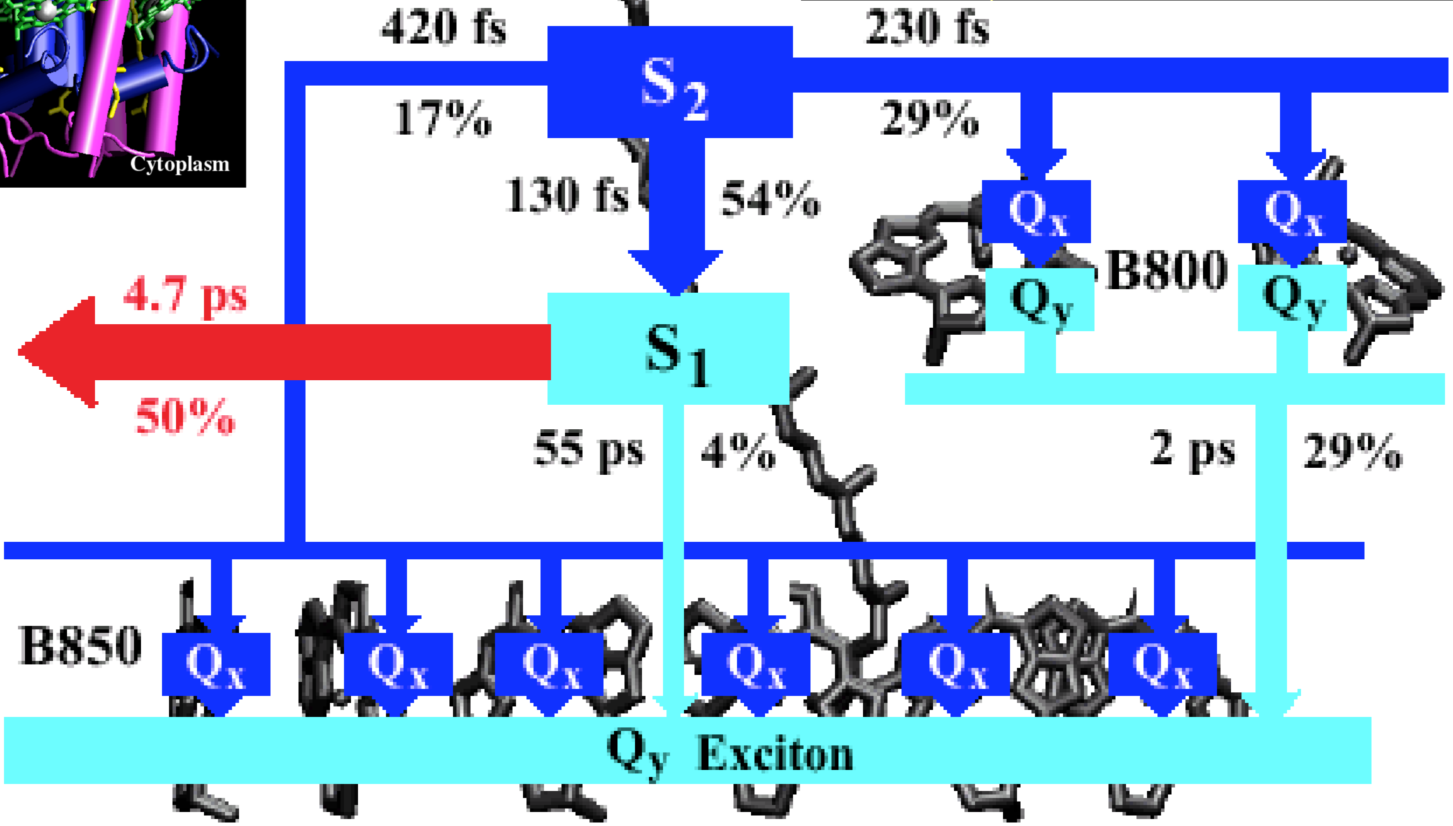
No triplet results will be shown!

Conversion times and efficiencies for photons absorbed into the **carotenoid (LYC)** S_2 state in LH2 of *Rs. molischianum*





LYC



420 fs

17%

S_2

230 fs

29%

130 fs

54%

Q_x

Q_x

B800

Q_y

Q_y

4.7 ps

50%

S_1

55 ps

4%

2 ps

29%

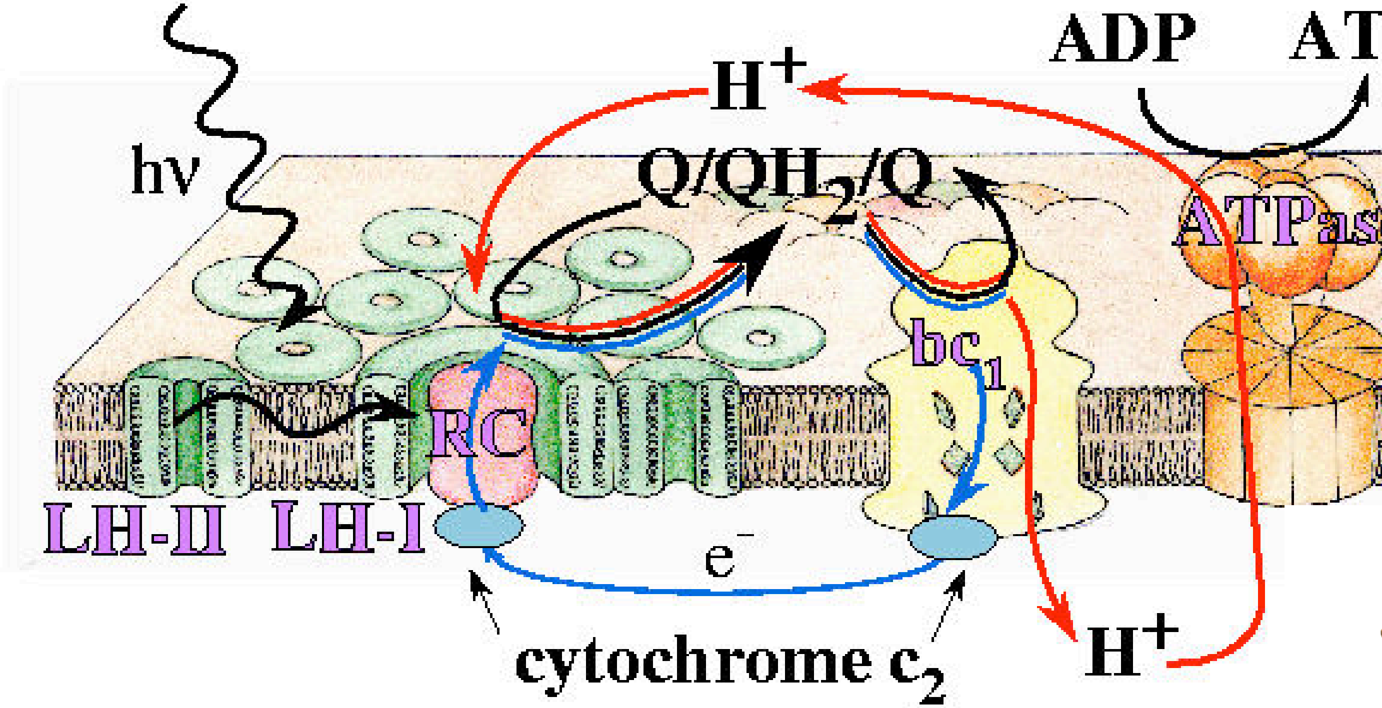
B850

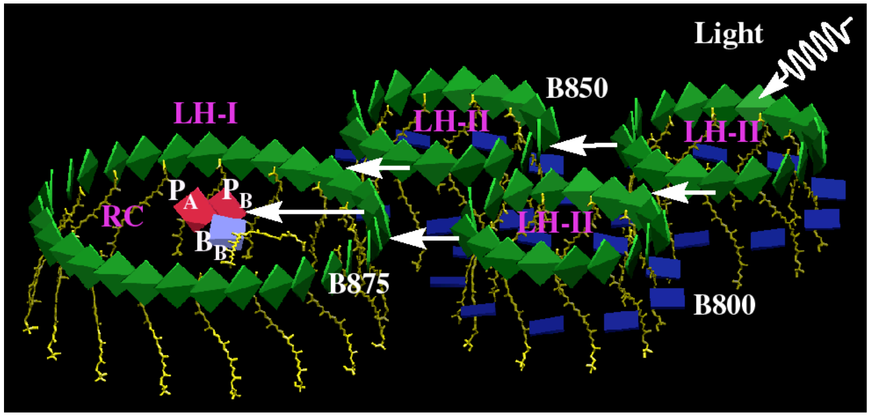
Q_x Q_x Q_x Q_x Q_x Q_x

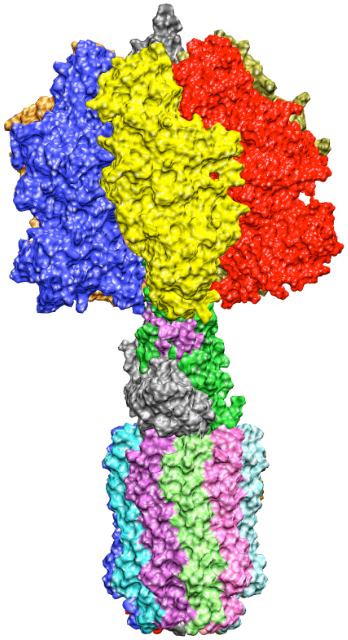
Q_y Exciton

Photosynthetic Apparatus of Purple Bacteria

Function Achieved Through Large Structures







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Deyu Lu, UIUC

Beckman Institute and Department of Physics U. Illinois

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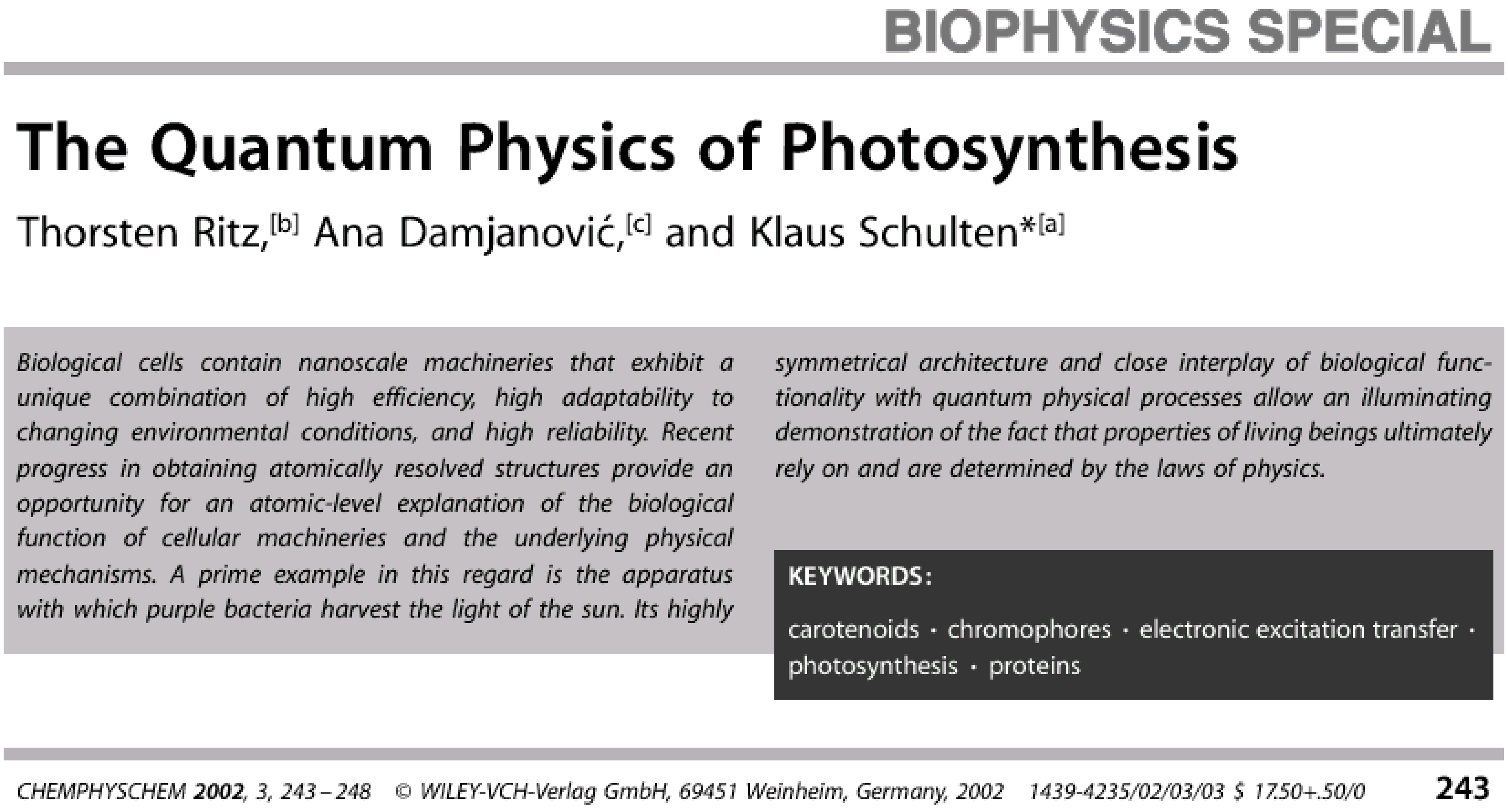
NIH Resource for Macromolecular Modeling and Bioinformatics Theoretical Biophysics Group, Beckman Institute, UIUC



BIOPHYSICS SPECIAL

The Quantum Physics of Photosynthesis

Thorsten Ritz,[b] Ana Damjanović,[c] and Klaus Schulten*[a]

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 atomically resolved 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

CHEMPHYSCHEM ***2002**, 3, 243 – 248* *© WILEY-VCH-Verlag GmbH, 69451 Weinheim, Germany, 2002* *1439-4235/02/03/03 $ 17.50+.50/0*

See also: www.ks.uiuc.edu