Theory of optical spectra of photosynthetic pigment-protein complexes: From structure to function

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Introduction: light-harvesting

Theory of spectra and excitation energy transfer

Calculation of parameters

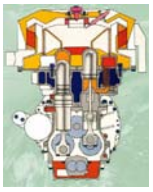
Applications: B777-complex, B820-complex, WSCP, FMO-Protein, Photosystem I

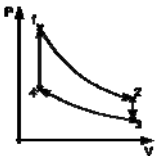
Harvesting sun light

http://www.en.tibet.cn

Solar thermal power

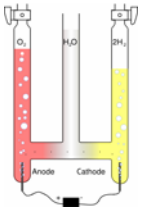
Sterling engine

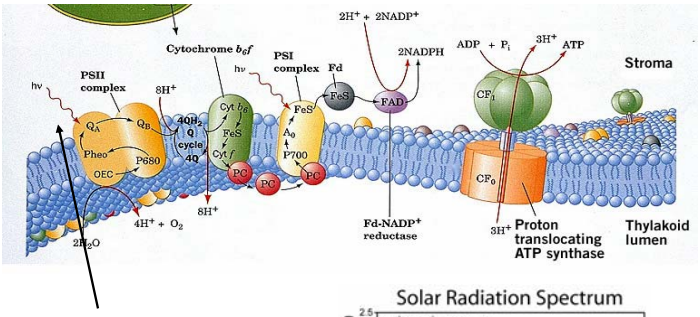


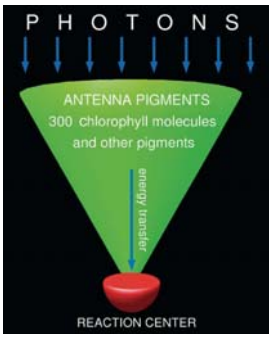


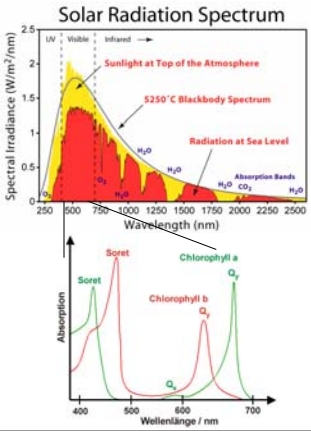
Using thermal power to generate electricity

Using electricity to split water and store energy as hydrogen fuel (1 kg H_2 per day)



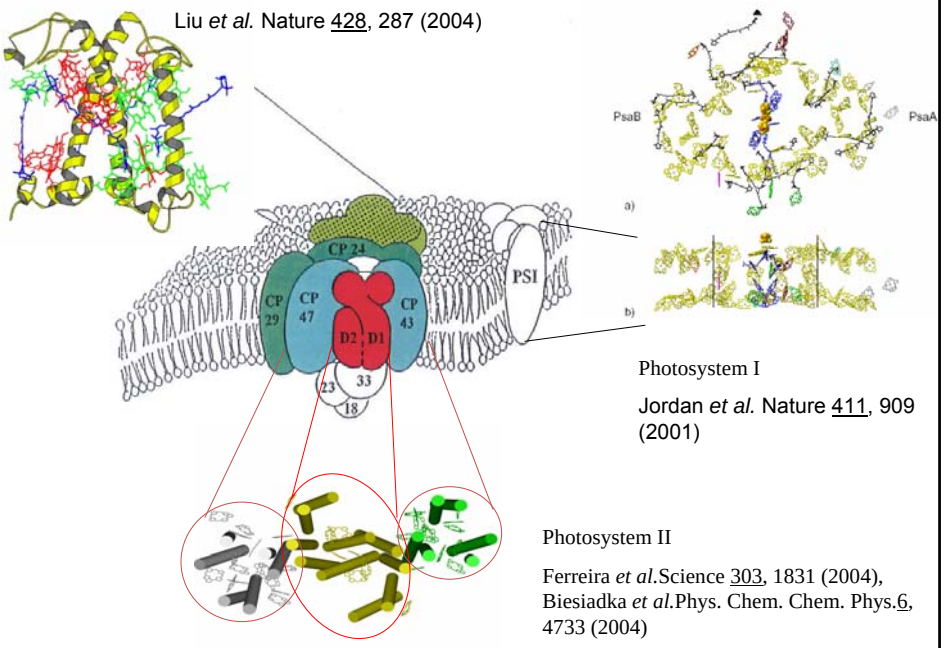






LHC-II

Liu *et al.* Nature 428, 287 (2004)

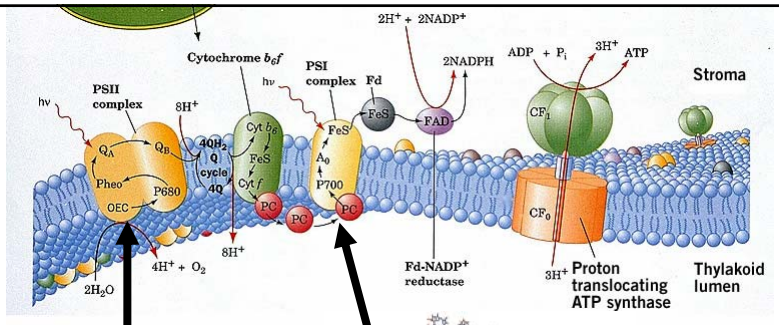


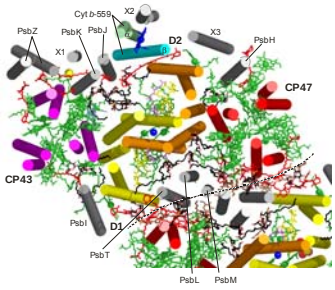
Photosystem I

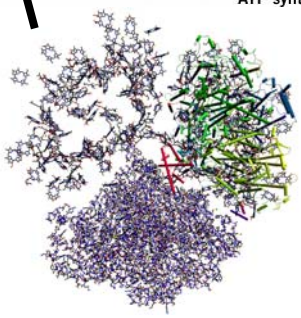
Jordan *et al.* Nature 411, 909 (2001)

Photosystem II

Ferreira *et al.*Science 303, 1831 (2004), Biesiadka *et al.*Phys. Chem. Chem. Phys.6, 4733 (2004)







Question:

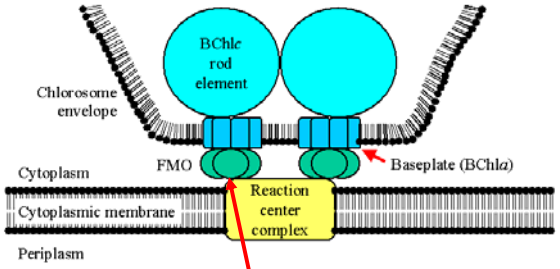
How do proteins trigger excitation energy transfer ?

Photosystem II
-Loll, Kern, Saenger, Zouni, Biesiadka Nature 2005

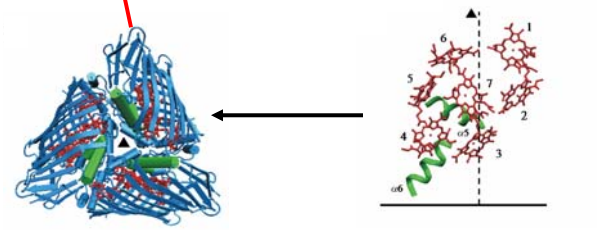
Photosystem I
-Jordan, Fromme, Witt, Klukas, Saenger, Krauss, Nature 2005

Light harvesting in green sulfur bacteria:

The role of pigment-protein coupling



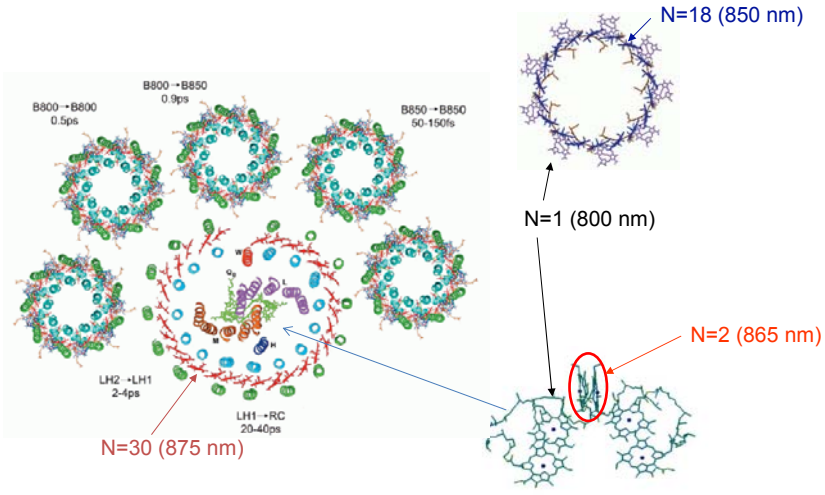
- Fenna *et al. Nature* 1975,
- Tronrud *et al.*
  J. Mol. Biol. 1986 (1.9 Å)



Question: How is excitation energy flow directed in the FMO protein ?

Light-harvesting in purple bacteria:

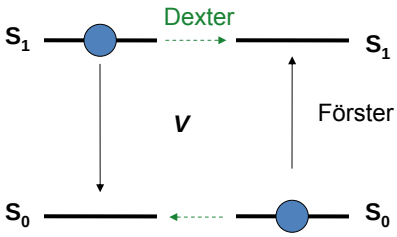
The role of pigment-pigment coupling



Question: Why is excitation energy of special pair (N=2) so low?

Interactions in Pigment-Protein Complexes

Pigment-Pigment Coupling

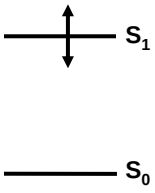


-Excitation energy transfer

-Delocalized excited states

-Coupling to charge transfer states

Pigment-Protein Coupling



-Different site energies

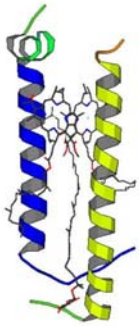
-Dynamic modulation of site energies

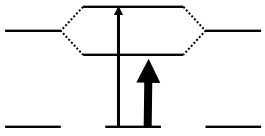
-Static disorder

Model systems

B777 complex

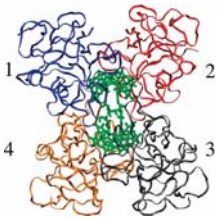
B820 complex

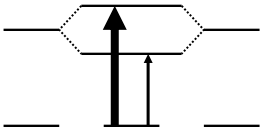




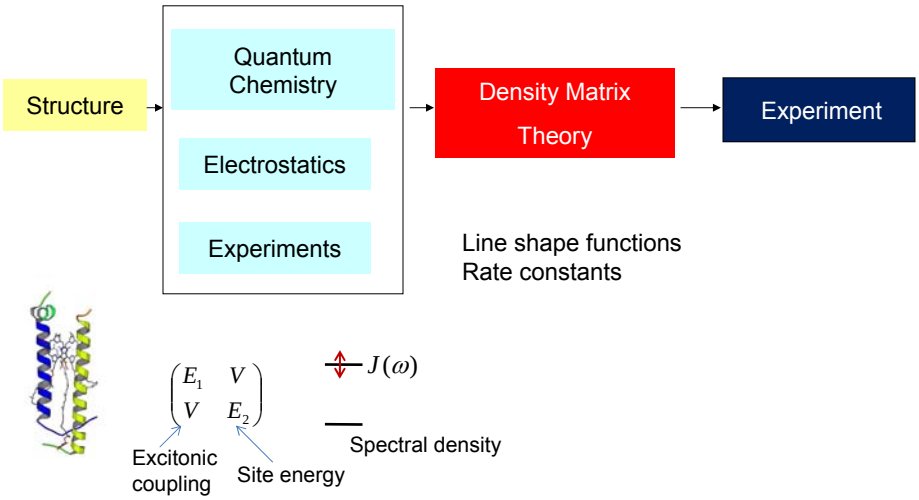
IIB-WSCP

Horigome *et al.*
J. Biol. Chem. 2007

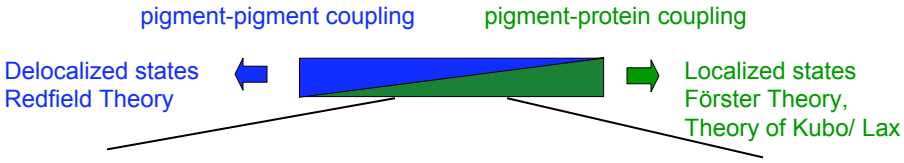




Development of theory and calculation of parameters



Theories of optical spectra and excitation energy transfer



- Generalized Förster Theory (Fetisova et al. 1996, Sumi et al. 1999, Jang et al. 2004, Raszewski, Renger *et al.* 2005, Raszewski and Renger 2008), ***Transfer between aggregates***

- Modified Redfield Theory (Mukamel and coworkers 1998, Yang und Fleming 2002, Renger und Marcus 2003, ...), ***Excitonic potential energy surfaces***

- Non-Markovian Density Matrix Theory (Zwanzig 1960, van Kampen 1974, Renger and May 2001, Renger and Marcus 2002, Jang and Silbey 2003, Renger 2004), ***Vibrational sidebands and life time broadening, dynamic localization***

Non-Markovian Expressions for Linear Absorption

COP-Theory (Renger and May, Phys. Rev. Lett. 84, 5228 (2000))

$$D_M(\omega) = \frac{\Gamma_M(\omega)}{(\omega - \tilde{\omega}_M)^2 + (\Gamma_M(\omega))^2}$$

$$\Gamma_M(\omega) = \sum_K \gamma_{MK} \pi (\omega - \omega_{K0})^2 \left\{ (1 + n(\omega - \omega_{K0})) J(\omega - \omega_{K0}) + n(\omega_{K0} - \omega) J(\omega_{K0} - \omega) \right\}$$

POP-Theory (Renger and Marcus, J. Chem. Phys. 116, 9997 (2002))

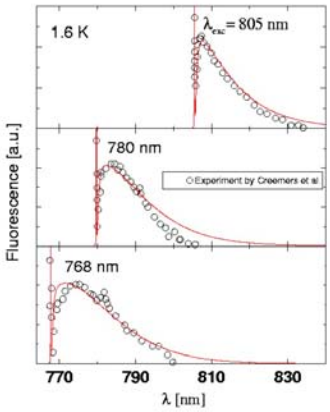
$$D_M(\omega) = \Re \int_0^\infty dt e^{i(\omega - \tilde{\omega}_M)t} e^{G_M(t) - G_M(0)} e^{-t/\tau_M}, \qquad \tau_M^{-1} = \Gamma_M(\omega_{M0})$$

$$G_M(t) = \gamma_{MM} \int_0^\infty d\omega J(\omega) \{ (1 + n(\omega)) e^{-i\omega t} + n(\omega) e^{i\omega t} \}$$

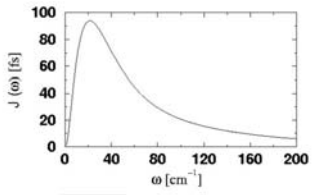
Extraction of Spectral Density of Monomer Complex

B777 Complex

FLN Spectra



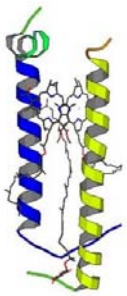
Spectral Density

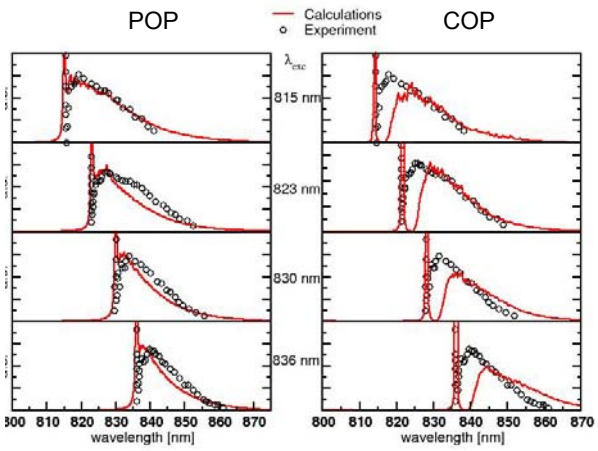


Renger and Marcus, J. Chem. Phys. 116, 9997 (2002)

Calculation of Fluorescence Line Narrowing Spectra of Dimer Complex

B820 Complex

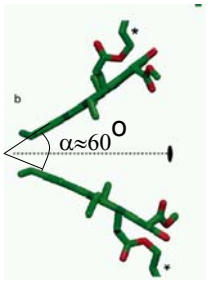


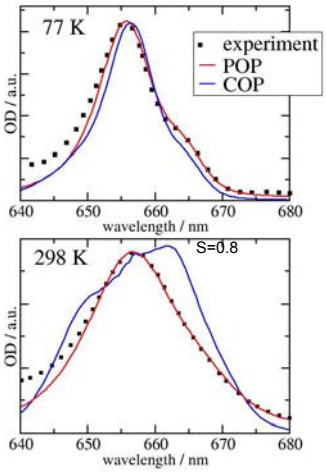


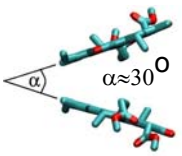
Renger and Marcus, J. Chem. Phys. 116, 9997 (2002)

Structure Prediction of WSCP

Structural model for IIA-WSCP-complex with Chl *a* / Chl *a* of cauliflower







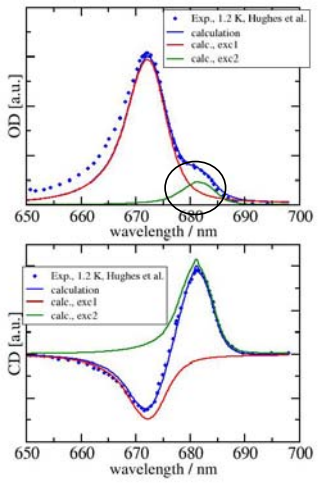
Structural model for IIA-WSCP-complex with Chl *b* / Chl *b* of cauliflower

Hughes et al., JACS (2006)

Renger, Trostmann *et al.* JPCB (2007)

Chla-Chla WSCP Revisited

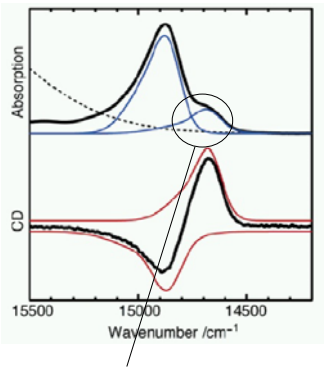
$\alpha = 25^o$



Renger, Trostmann *et al.* JPCB (2007)

Hughes *et al.* , JACS (2006)

$\alpha = 60^o$



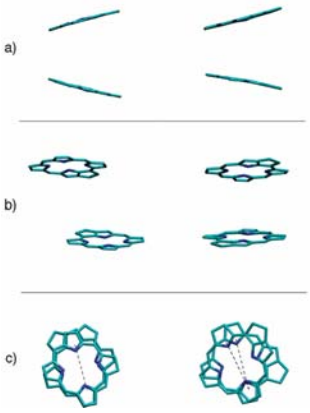
Neglect of homogenous broadening !

Comparison theoretical prediction of IIA-WSCP - crystal structure of IIB-WSCP

$\alpha = 27^o$

Crystal structure of Chla/Chla dimer in IIB WSCP-complex

Horigome *et al.*
J. Biol. Chem. (2007)



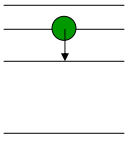
$\alpha = 25^o$

Structural model for Chla/Chla dimer in IIA-WSCP-complex of cauliflower

Renger, Trostmann *et al.*
JPCB (2007)

-> IIA-WSCP and IIB-WSCP share the same Chl binding motif

Rate Constant for Transitions between Delocalized States- Redfield Theory



Exciton relaxation

$$k_{M\to N} = 2\pi\gamma_{MN}\omega_{MN}^2\left\{J(\omega_{MN})[1+n(\omega_{MN})]+J(\omega_{NM})n(\omega_{NM})\right\}$$

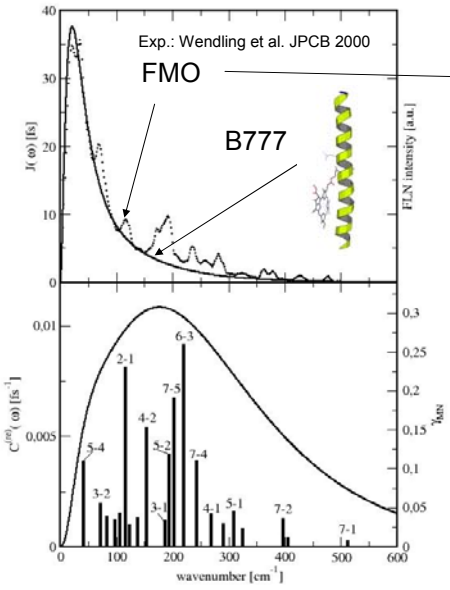
$$\gamma_{MN} = \sum_m |c_m^{(M)}|^2 |c_m^{(N)}|^2$$

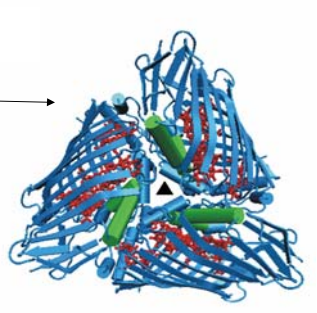
Lineshape function for optical excitation (Markov approximation)

$$D_M(\omega) = \frac{\tau_M^{-1}}{(\omega-\tilde{\omega}_M)^2+\tau_M^{-2}} \qquad \tau_M^{-1} = \frac{1}{2}\sum_N k_{M\to N}$$

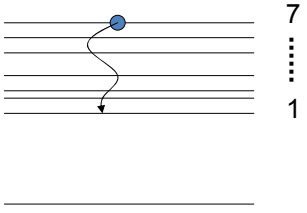
e.g. Renger, May and Kühn, Physics Rep. 343, 137 (2001)

Spectral density and exciton relaxation



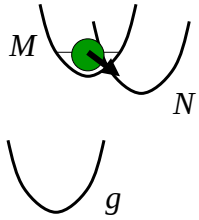


Exciton relaxation



Adolphs and Renger, Biophysical J. (2006)

Modified Redfield Theory



-Non-perturbative treatment of diagonal part of exciton vibrational coupling (excitonic PES)

-Brownian oscillators: Mukamel and coworkers (1998), Yang and Fleming (2002)

-Harmonic oscillators: Renger and Marcus (2003)

Rate Constant in Modified Redfield Theory

$$k_{M\to N} = \int_{-\infty}^{\infty} dt e^{i\omega_{MN}t} e^{\phi_{MN}(t)-\phi_{MN}(0)} [(\frac{\lambda_{MN}}{\hbar} + G_{MN}(t))^2 + F_{MN}(t)]$$

with

$$\phi_{MN}(t) = \phi_0(t)\sum_m (|c_m^{(M)}|^2 - |c_m^{(N)}|^2)^2$$

$$G_{MN}(t) = -i\dot{\phi}_0(t)\sum_m ((c_m^{(M)})^3 c_m^{(N)} - (c_m^{(N)})^3 c_m^{(M)})$$

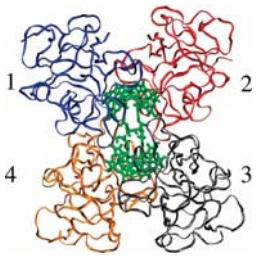
$$F_{MN}(t) = -\ddot{\phi}_0(t)\sum_m |c_m^{(M)}|^2 |c_m^{(N)}|^2$$

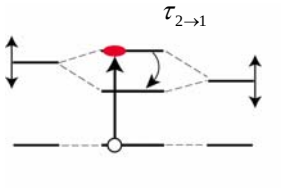
$$\lambda_{MN} = \frac{\lambda}{2}\sum_m ((c_m^{(M)})^3 c_m^{(N)} + (c_m^{(N)})^3 c_m^{(M)}))$$

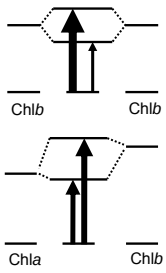
$$\phi_0(t) = \int_{-\infty}^{\infty} d\omega\, J(\omega)\{(1+n(\omega))e^{-i\omega t} + n(\omega)e^{i\omega t}\}$$

Renger and Marcus J. Phys. Chem. A 107, 8404 (2003)

Exciton relaxation in WSCP





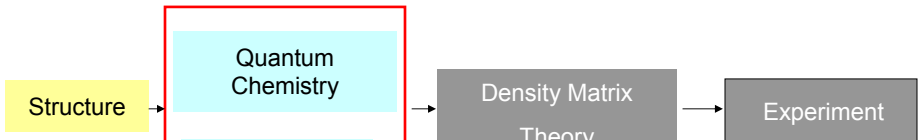


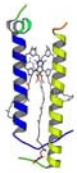
	Mod. Redfield (Renger *et al.* 2007)	**Redfield** (Renger *et al.* 2007)	**Experiment** (Theiss et al. 2007)
Chl*b*/ Chl*b*	**60 fs**	**80 fs**	**< 150 fs**
Chl*a*/ Chl*b*	**450 fs**	**5400 fs**	**400 fs**

Multi vibrational quanta-transitions included

Only one quantum-Transitions included

Calculation of parameters





$$\begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix}$$

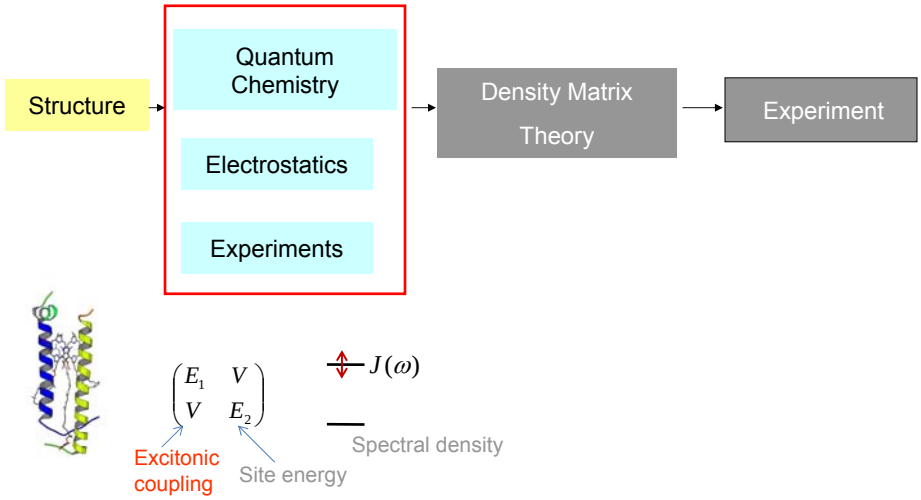
Excitonic coupling

Site energy

$J(\omega)$

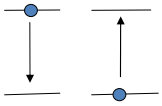
Spectral density

Calculation of parameters

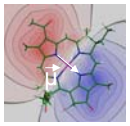


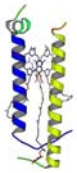
Excitonic coupling

Point dipole approximation

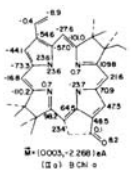


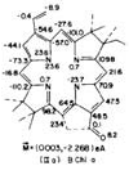
$$V_{mn} = f\left(\frac{\vec{\mu}_m\vec{\mu}_n}{R_{mn}^3} - 3\frac{(\vec{\mu}_m\vec{R}_{mn})(\vec{\mu}_n\vec{R}_{mn})}{R_{mn}^5}\right)$$





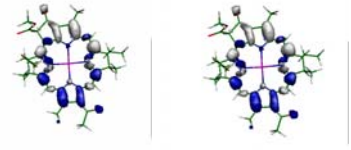
Transition monopole method (Weiss 1972, Chang 1977)





$$V_{mn} = f\sum_{I,J}\frac{q_I^{(m)}q_J^{(n)}}{|\vec{R}_I - \vec{R}_J|}$$

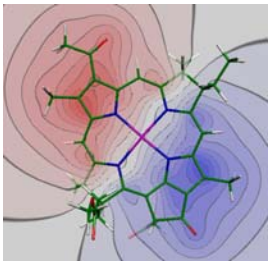
Transition density cube (TDC) method (Krüger, Scholes, Fleming 1998)



$$V_{mn} = f\int d^3r_1 d^3r_2 \rho_m(\vec{r}_1)\frac{1}{|\vec{r}_1 - \vec{r}_2|}\rho_n(\vec{r}_2)$$

Transition charges from electrostatic potential (TrEsp) method

ESP of transition density
BChl *a* (TDDFT/B3LYP)

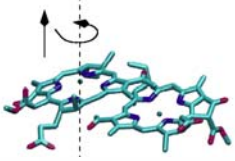


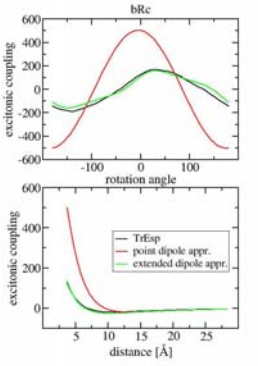
Fit of ab-initio ESP of transition density by atomic partial charges

$$V_{mn} = f \sum_{I,J} \frac{q_I^{(m)} q_J^{(n)}}{|\vec{R}_I - \vec{R}_J|}$$

Madjet, Abdurahman, Renger, JPC B (2006)

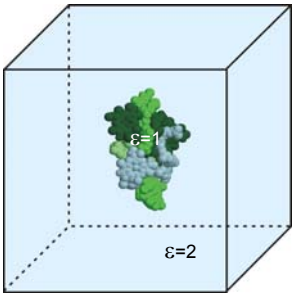
Special pair coupling in bRc





Dipole extent: 8.8 Å

Influence of the dielectric medium on excitonic couplings



Continuum electrostatics calculations on FMO protein

- BChls treated as cavities with transition monopole charges in dielectric of protein/ solvent, ε = 2
- $|\mu_{vac}|^2$ = 37 D^2 (Knox and Spring 2003)

$$\nabla[\varepsilon(\vec{r})\nabla\phi_m(\vec{r})] = -4\pi\sum_I q_I \delta(\vec{r} - \vec{R}_I^{(m)})$$

$$V_{mn} = \sum_I q_I \phi_m(\vec{R}_I^{(n)})$$

effective dipole strength

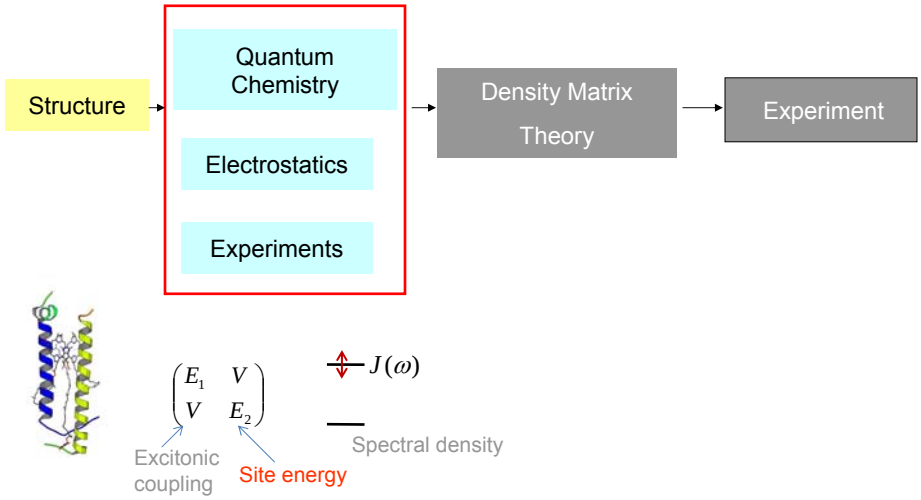
$$V_{mn}(\varepsilon = 2) = f \; V_{mn}^{(\mathrm{vac})}$$

f: screening / local field correction

Result for FMO: *f* = 0.8 -> $|\mu_{eff}|^2$ = 30 D^2

Renger and Adolphs, Biophys. J. 2006

Calculation of parameters



Site energies from fit of optical spectra

Louwe *et al.* 1997 (FMO, N=7)

Vulto *et al.* 1998 (FMO, N=7)

Wendling *et al.* 2002 (FMO, N=7)

Adolphs and Renger 2006 (FMO, N=7)

Raszewski, Renger et al. 2005 (D1D2cyt*b*559, N=8)

Novoderezhkin et al. 2005 (LHC-II, N=14)

Byrdin et al. 2002 (PSI, N=96)

Brueggemann et al. 2004 (PSI, N=96)

⋮

many more

$$\begin{pmatrix} E_1 & & V_{mn} & \\ & E_2 & & \\ & & \ddots & \\ V_{mn} & & & E_N \end{pmatrix}$$

Advantage: Spectra agree with experiment

Disadvantages: We do not know how the protein tunes the site energies

There may be more than one solution

Direct calculation of site energies

Quantum chemical calculations

Eccles and Honig 1983 (model study)

Gudowska-Nowak, Newton, Fajer 1990 (FMO, N=7)

Damjanovic, Vaswani, Fromme, Fleming 2002 (PS-I, N=96)

No long-range electrostatic interactions with the protein included

$$\begin{pmatrix} E_1 & & V_{mn} & \\ & E_2 & & \\ & & \ddots & \\ V_{mn} & & & E_N \end{pmatrix}$$

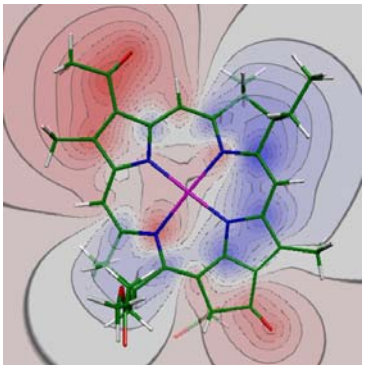
Yin, Dahlbom, Canfield, Hush, Kobayashi, Reimers 2007 (PS-I, N=96)

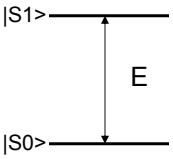
Protein included by classical point charges-electron leakage problems

Quantum chemical/ electrostatic approach

Müh, Renger *et al.* 2007, Adolphs, Renger et al. 2008

Tuning of site energies by the protein

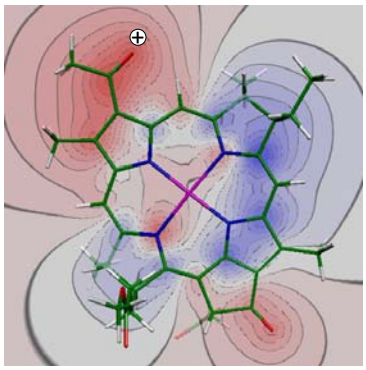


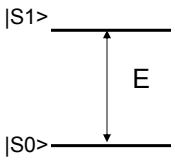


ϕ(S1)-ϕ (S0), BChl *a*

Madjet, Abdurahman, Renger, JPC B 2006

Tuning of site energies by the protein

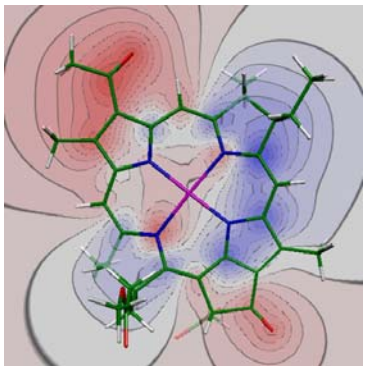


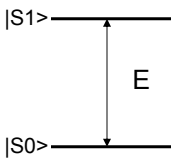


ϕ(S1)-ϕ (S0), BChl *a*

Madjet, Abdurahman, Renger, JPC B 2006

Tuning of site energies by the protein

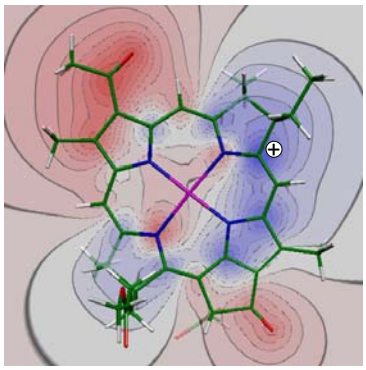




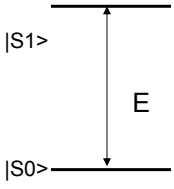
ϕ(S1)-ϕ (S0), BChl *a*

Madjet, Abdurahman, Renger, JPC B 2006

Tuning of site energies by the protein



ϕ(S1)-ϕ (S0), BChl *a*

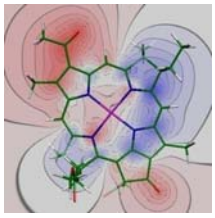


Madjet, Abdurahman, Renger, JPC B 2006

Excitation energy transfer in the FMO-protein

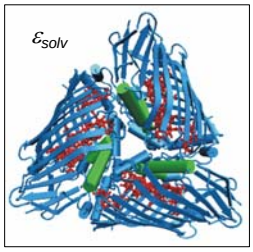
The role of the pigment-protein coupling

Quantum Chemistry



ϕ(S1)-ϕ (S0), BChl *a*
(TDDFT/B3LYP)

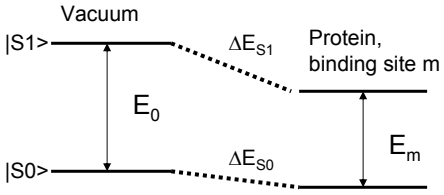
Atomic Electrostatics



FMO-Protein

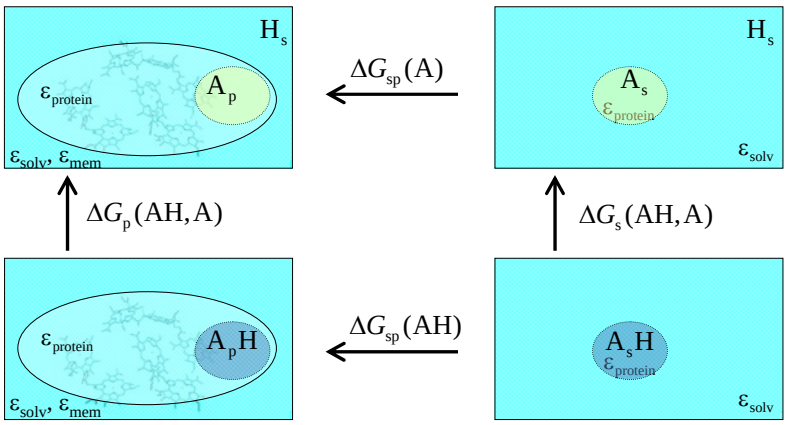
-Electrostatic free energy calculations

-Average over protonation states of titratable groups



Thermodynamic cycle for protonation

Residue in protein | Model compound in solvent



$$\Delta G_{\mathrm{p}}(\mathrm{AH,A}) = \Delta G_{\mathrm{sp}}(\mathrm{A}) - \Delta G_{\mathrm{sp}}(\mathrm{AH}) + RT\ln 10\, pK_{\mathrm{mod}}$$

from electrostatic calculations — from experiment

Continuum electrostatics calculations

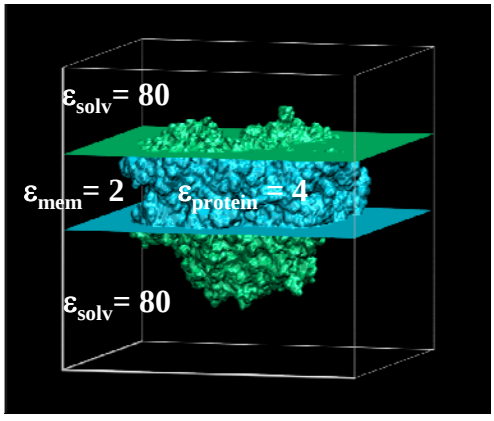
$$\nabla[\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})] = -4\pi\rho(\mathbf{r}) + \kappa^2(\mathbf{r})\phi(\mathbf{r})$$

-solving the linearized Poisson-Boltzmann equation numerically

-calculation of $\Delta G_{\mathrm{sp}}(\mathrm{A})$, $\Delta G_{\mathrm{sp}}(\mathrm{AH})$ and interaction matrix W_{ij} between titratable groups :

$$\Delta G_{\mathrm{p}}(\mathrm{AH,A}) = \Delta G_{\mathrm{sp}}(\mathrm{A}) - \Delta G_{\mathrm{sp}}(\mathrm{AH}) + RT\ln 10\, pK_{\mathrm{mod}}$$

$\Delta G_{\mathrm{p}}(\mathrm{AH,A})$, $\mathrm{W_{ij}}$



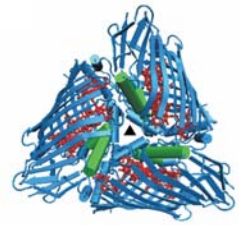
Protonation probability

$$\langle x_i \rangle_{\mathrm{proton}} = \sum_{x_1 \cdots x_N = 0,1} e^{-\frac{\Delta G(x_1 \cdots x_N)}{kT}} x_i$$

$$\Delta G(x_1 \cdots x_N) = \mathrm{f}\,(\mathrm{pH}, \Delta G_p^{(i)}(\mathrm{AH, A}), \{W_{ij}\})$$

average performed numerically by Monte Carlo method

Results for the FMO-Protein

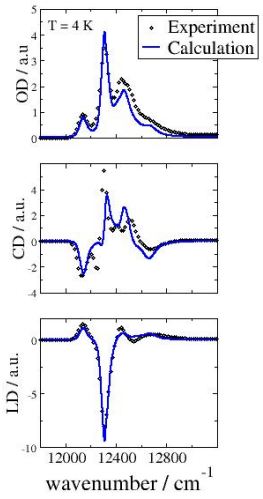


Dominating contributions to site energy shifts

-hydrogen bonds (<150 cm^{-1})

-charged amino acid side chains (<180 cm^{-1})

-backbone of two α-helices (-340 cm^{-1} at Bchla 3)



Experiment:

Wendling *et al.* Photos. Res. 2002

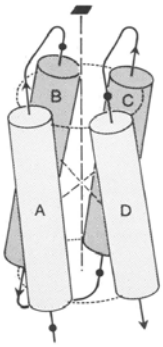
Müh, Renger *et al.* PNAS 2007

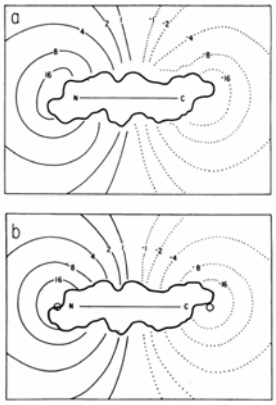
Proc. Natl. Acad. Sci. USA
Vol. 79, pp. 4545–4549, August 1982
Biochemistry

α-Helix dipole model and electrostatic stabilization of 4-α-helical proteins

(electrostatic interactions/protein structure)

ROBERT P. SHERIDAN*, RONALD M. LEVY*†, AND F. R. SALEMME‡§

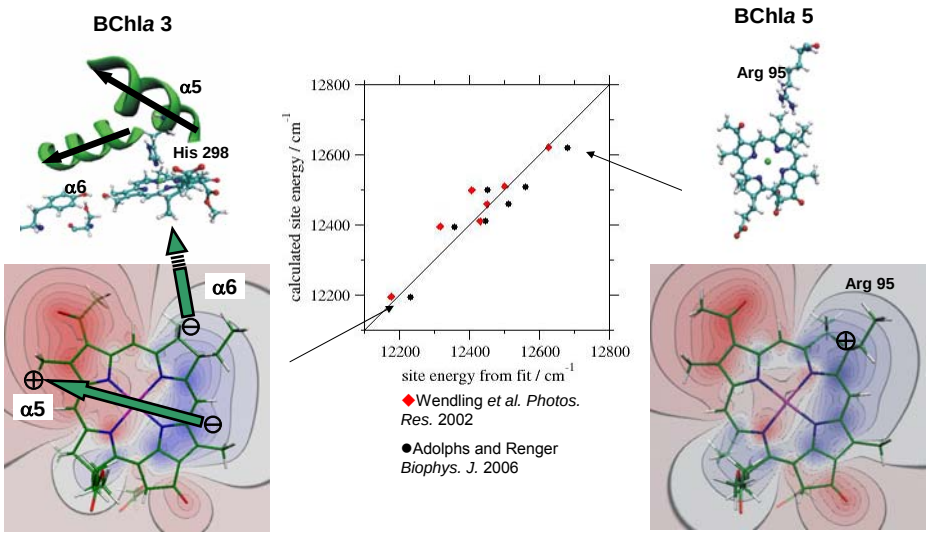




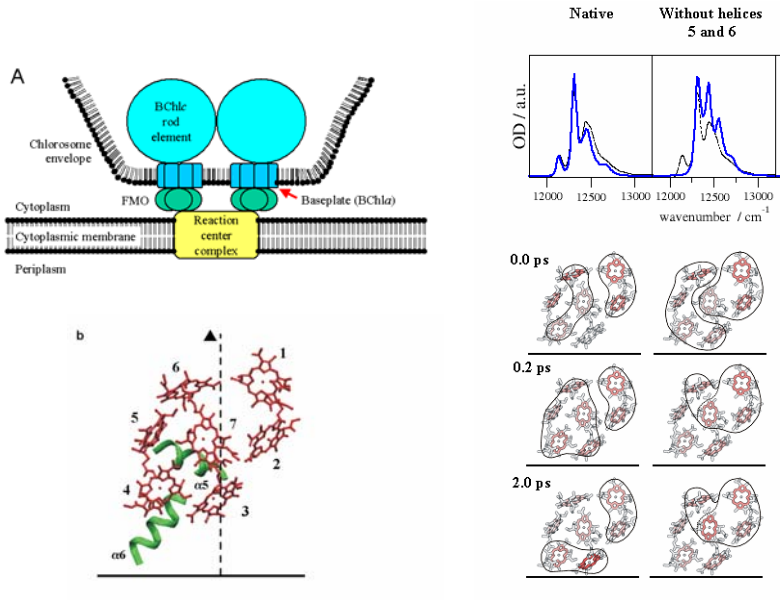
ESP of α-helix

ESP of extended dipole, $|\delta q|$=0.5 e

Correlation between fitted site energies and direct calculations

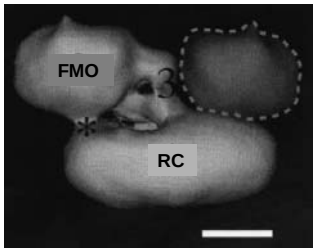


Exciton relaxation between baseplate and reaction center

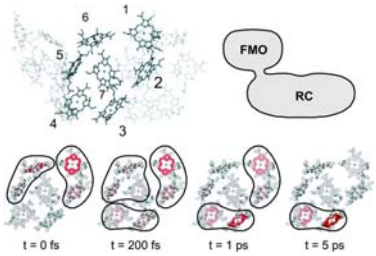


Müh, Renger *et al.* PNAS 2007

Prediction of orientation of FMO-complex



Remigy et al. J. Mol. Biol. 1999

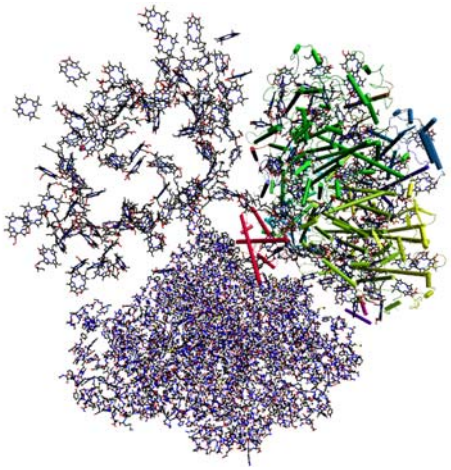


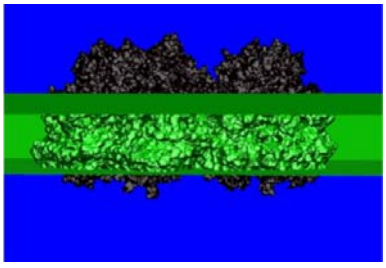
Adolphs and Renger Biophys. J. 2006

Adolphs and Renger (Biophys. J. 2006): ,, Efficient transfer of excitation energy to the reaction center requires BChl 3 and 4 to be the linker pigments."

Wen, Blankenship et al. (PNAS 2009): Membrane orientation of the FMO antenna protein from Chlorobaculum tepidum as determined by mass spectrometry-based footprinting: ,,The large differences in the modification of certain peptides show that the Bchl *a* #3 side of the FMO trimer interacts with the cytoplasmic membrane, which is consistent with recent theoretical predictions**.** "

Application to Photosystem I

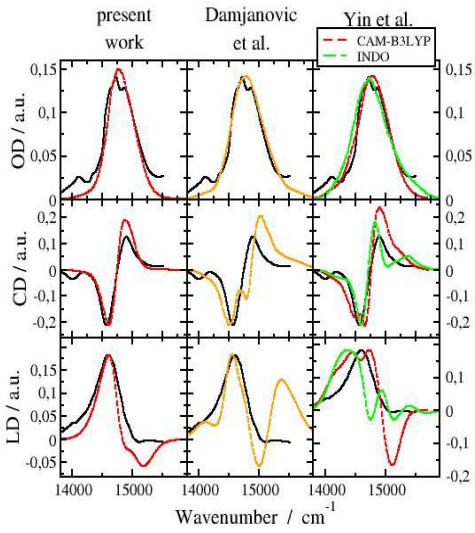




Regions of different dielectric constants

N_{Chl} = 96 * 3

Comparison of present approach with quantum chemical calculations from the literature



Damjanovic et al. J. Phys. Chem. B 2002

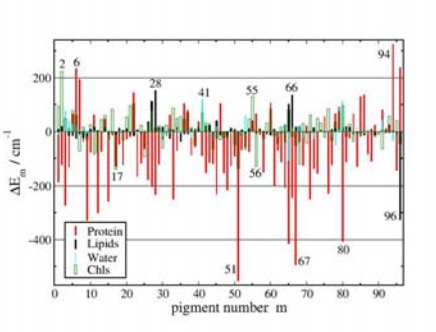
Yin et al. J. Phys. Chem. B 2007

Present work: Adolphs, Müh, Madjet, Schmidt am Busch, Renger submitted

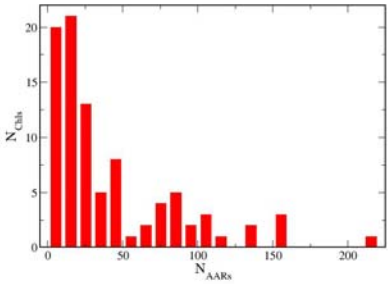
***Experiment (black):* Byrdin et al. Biophys. J. 2002**

Cause of site energy shifts

Protein-induced shifts dominate

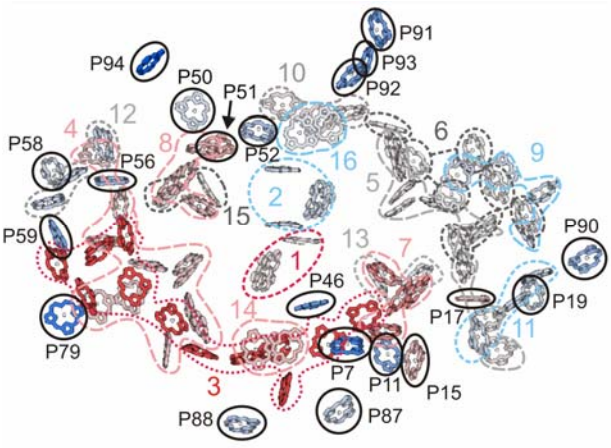


Long-range electrostatic interactions are important



Number of Chls N_{Chl}, for which N_{AAR} residues contribute significantly to site energy shift

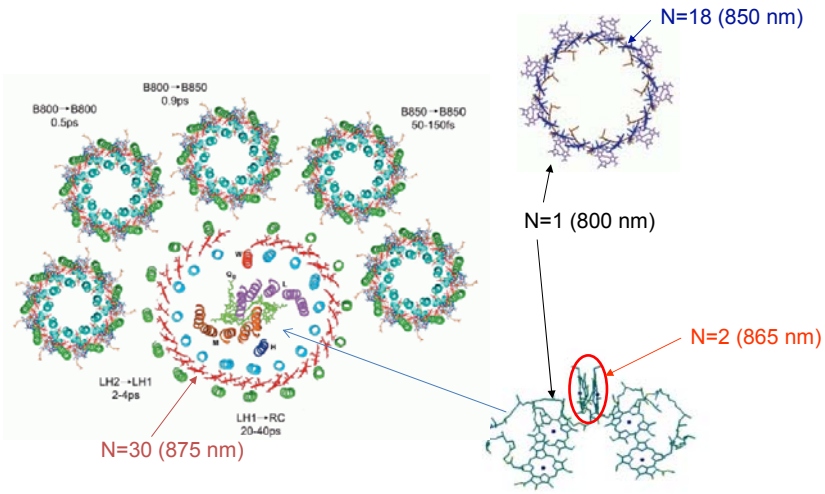
Location of low-energy exciton states



Concentration of low-energy states is higher at the side of the A-branch of the reaction center

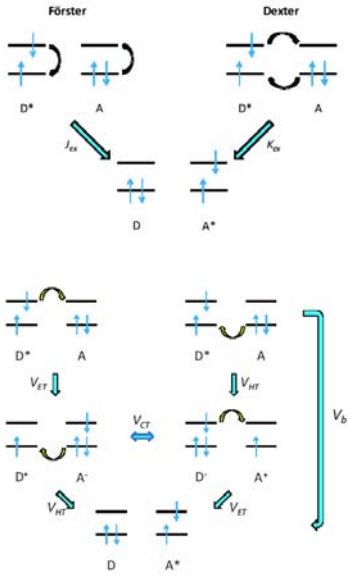
Asymmetric light-harvesting

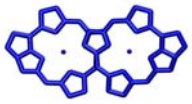
Analysis of short-range effects



Question: Why is excitation energy of special pair (N=2) so low?

Analysis of short-range interactions between chlorophylls





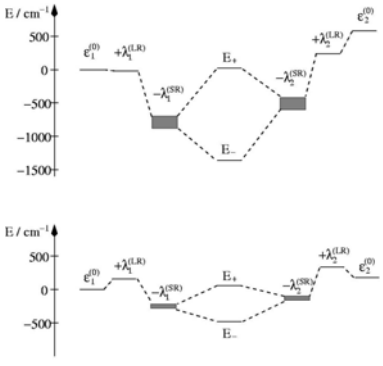
Special pair of purple bacteria

$$H_2 = \begin{pmatrix} \varepsilon_1^{(0)} + \lambda_1^{(LR)} + \lambda_1^{(SR)} & V_{LR} + V_{SR} \\ V_{LR} + V_{SR} & \varepsilon_2^{(0)} + \lambda_2^{(LR)} + \lambda_2^{(SR)} \end{pmatrix}$$

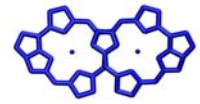
Effective 2-state Hamiltonian relating monomer and dimer quantum chemical calculations

Madjet, Müh, Renger J. Phys. Chem. B 2009

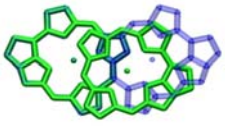
Analysis of short-range effects in special pairs of purple bacteria and photosystem I



bRC



PSI

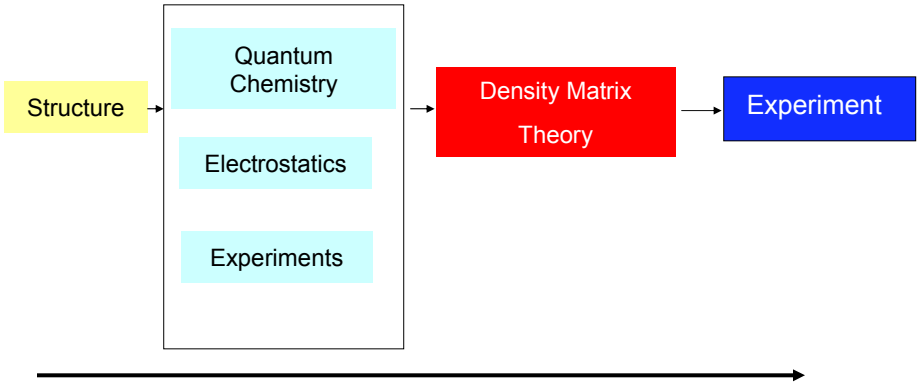


Short-range effects create excitation energy sink in the special pairs

Madjet, Müh, Renger J. Phys. Chem. B 2009

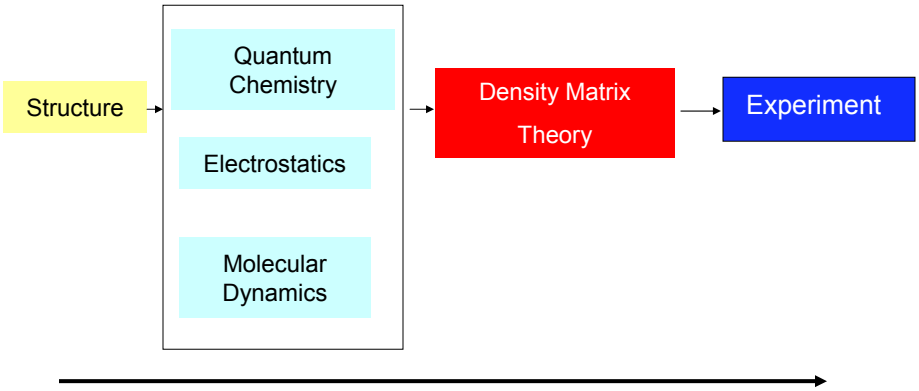
Summary

Development of theory and calculation of parameters



-structure prediction for IIa-WSCP
-α-helices direct excitation energy flow in FMO-protein
-prediction of orientation of FMO-protein relative to reaction center
-asymmetry in light-harvesting of photosystem I
-short-range effects create excitation energy sinks in special pairs of purple bacteria and photosystem I

Outlook



-Calculation of spectral density
-Calculation of site energies of PS II
-Application to color tuning and signal transduction in photoreceptors
-Application to simulate FRET experiments on conformational transitions of proteins

-Non-perturbative description of excitonic and exciton-vibrational coupling

Acknowledgement

Theory of optical spectra:	V. May (Humboldt Universität zu Berlin) R. Marcus (Caltech, Pasadena)
Quantum chemical calculations:	M. E. Madjet, Qchem-Developers (Y. Shao, S. T. Brown)
Electrostatic calculations:	E. W. Knapp, G. Kieseritzky (FU Berlin) F. Müh, J. Adolphs (FU Berlin) M. Schmidt am Busch (JKU)
Calculation of spectra:	J. Adolphs, G. Raszewski
Experiments, WSCP:	I. Trostmann (Mainz), C. Theiss (TU Berlin)
Experiments, PS-I:	E. Schlodder (TU-Berlin)

Financial support: Deutsche Forschungsgemeinschaft

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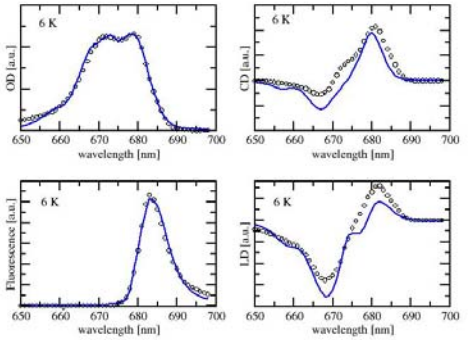
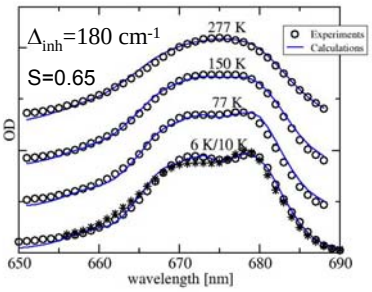
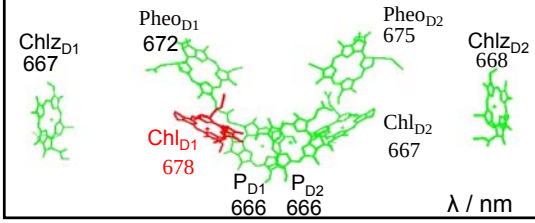
Optical properties of photosystem II reaction centers

Experiments: Germano et al. (2001)





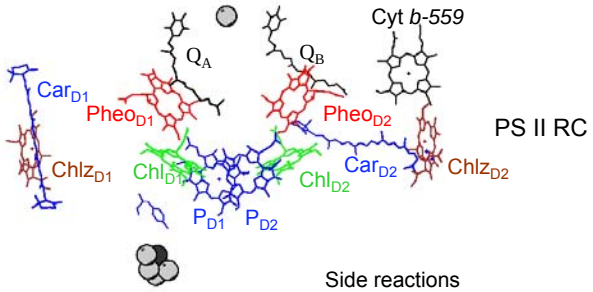


-primary electron donor is Chl$_{D1}$

G. Raszewski, W. Saenger and Th. Renger, Biophysical J. (2005)

In agreement with pump-probe data (Groot et al. PNAS 2005, Holzwart et al. PNAS 2006)

Electron transfer in photosystem II



PS II RC

Primary reactions

$P_{680}^{*} \rightarrow P_{680}^{+}Pheo_{D1}^{-}$

$Pheo_{D1}^{-}Q_A \rightarrow Pheo_{D1}Q_A^{-}$

$Q_A^{-}Q_B \rightarrow Q_AQ_B^{-}$

Side reactions

$P_{680}^{+}Pheo_{D1}^{-} \rightarrow {}^{3}\left[P_{680}^{+}Pheo_{D1}^{-}\right] \rightarrow {}^{3}Chl^{*}Pheo_{D1}$

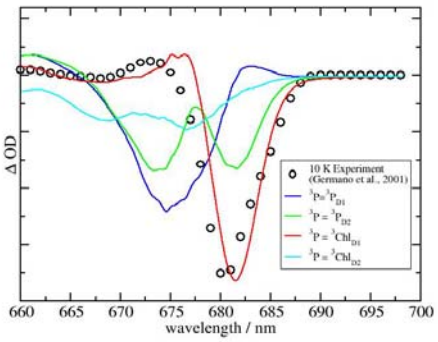
${}^{3}Chl^{*} + O_2 \rightarrow Chl + {}^{1}O_2^{*}$

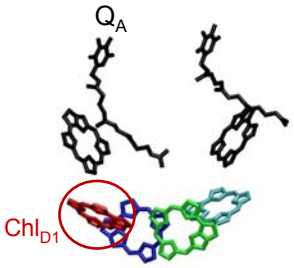
$P_{680}^{+}Car \rightarrow P_{680}Car^{+}$

Questions: Nature of P_{680}^{*}, P_{680}^{+}, ${}^{3}Chl^{*}$, Car^{+}
Photoprotective mechanisms,

Localization of the triplet state

Triplet minus singlet absorbance difference





Photoprotection: $^3Chl_{D1}{}^*Q_A^- \rightarrow Chl_{D1}Q_A^-$

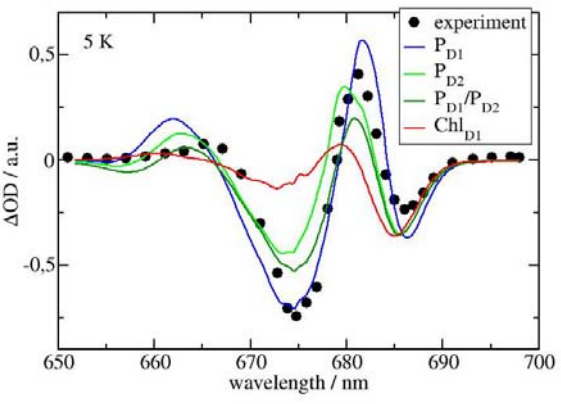
-Triplet localized at Chl_{D1}

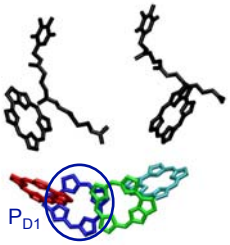
-in agreement with EPR measurements by Rutherford et al. 1991, T-S spectra on mutants by Schlodder, Renger et al. 2008

Theory: G. Raszewski, W. Saenger and Th. Renger, Biophysical J. (2005)

Identity of P_{680}^+

$P^+Q_A^-$ - PQ_A absorbance difference of PS-II Core-Complexes of T. elongatus





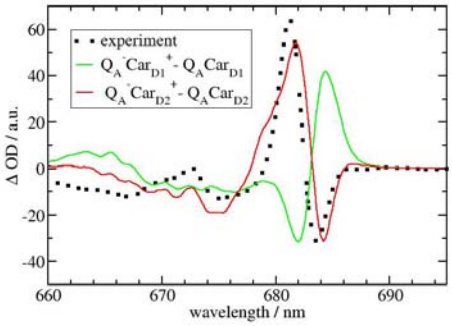
Hole stabilizes at P_{D1}

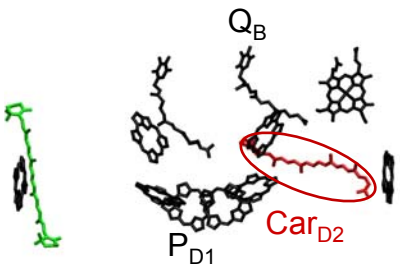
-in agreement with EPR measurements by Zech et al. 1997

-$P^+Q_A^-$-PQ_A spectra on mutants by Diner and Schlodder et al. (2001)

Experiment: Hillmann and Schlodder Biochemistry (1995)
Theory: Raszewski, Diner, Schlodder, Renger Biophys. J. (2008)

Identity of Car^+



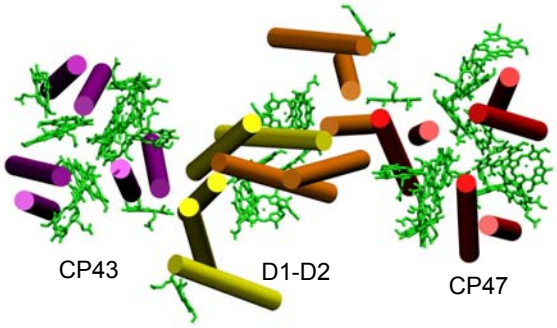


Hole transfer along Car_{D2}

Photoprotection: $P_{D1}^+Car_{D2}Q_B^- \rightarrow P_{D1}Car_{D2}^+Q_B^- \rightarrow P_{D1}Car_{D2}Q_B$

Experiment and theory: Schlodder, Renger et al. Biochemistry (2008)

Light-harvesting in PS-II core complexes

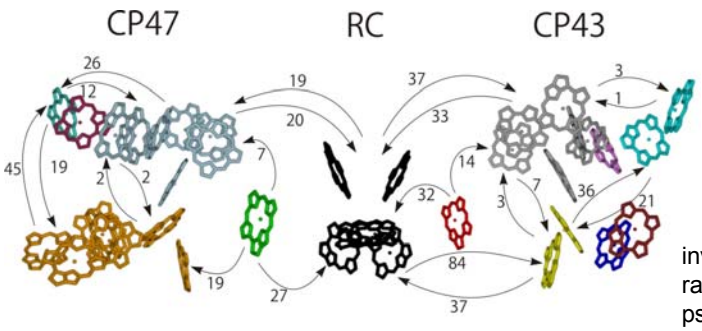


-Site energies obtained from fit of optical spectra of the subunits

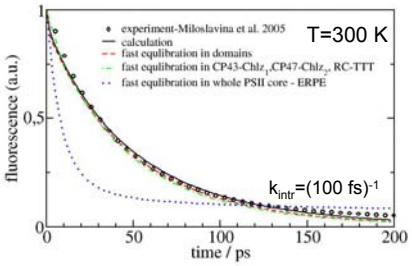
-Site energies of CP43 and CP47 verified by calculation of pump-probe spectra and comparison with experimental data

-Question: What limits the decay of excited states ?

Raszewski and Renger JACS (2008)

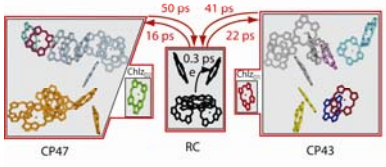


inverse rate constants / ps



Raszewski and Renger JACS (2008)

Minimal model



Light harvesting is limited by the transfer to the trap