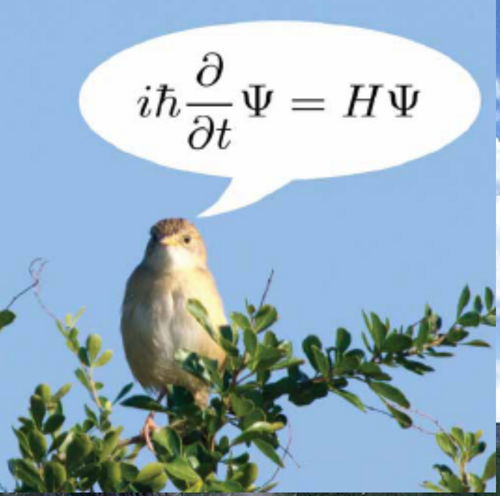
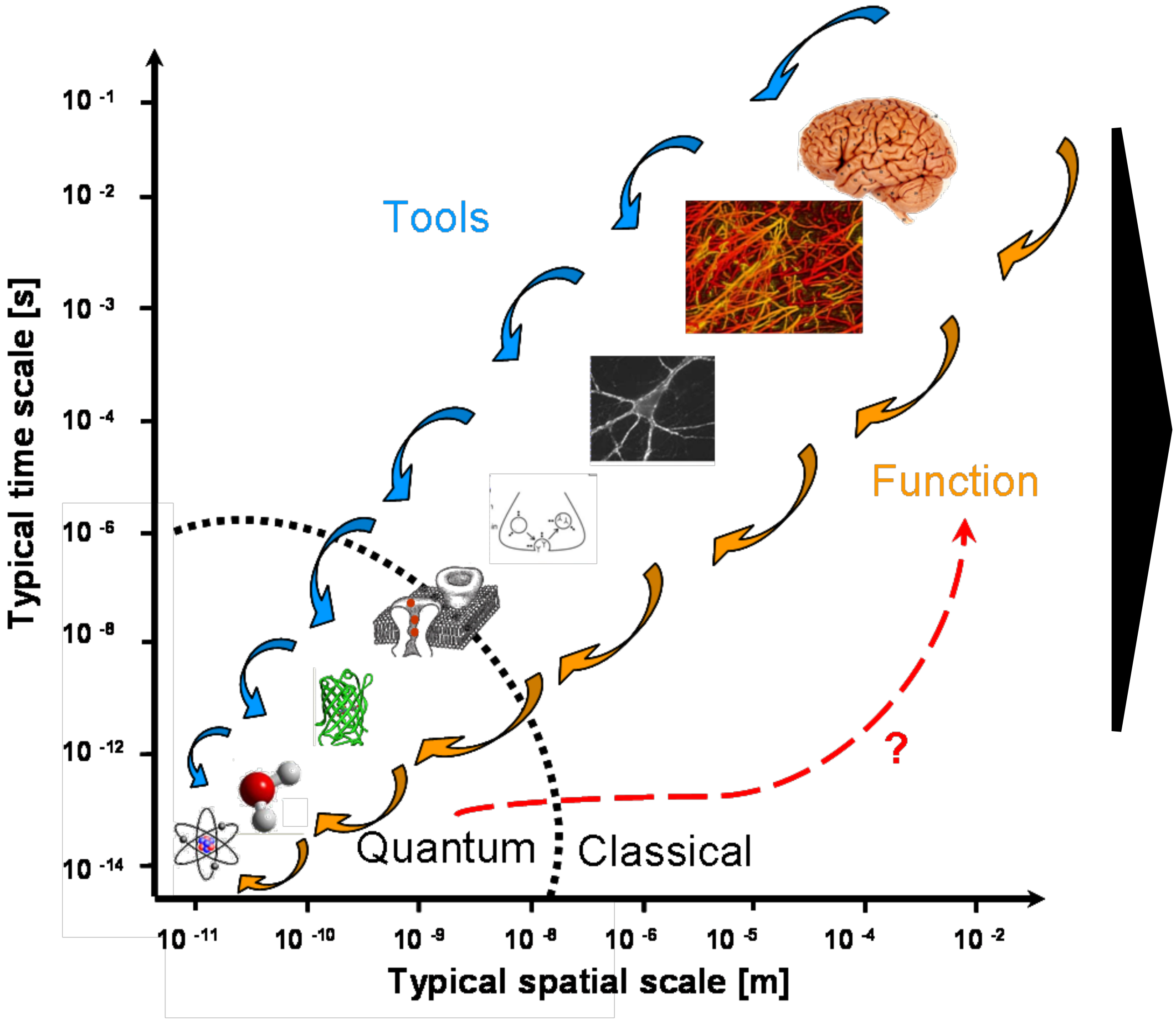


Quantum Mechanical Phenomena in Biology

K. Birgitta Whaley, UC Berkeley

Biological function across all time and size scales



Developing tools for studying biological structure and function at unprecedented spatial and temporal resolution

Can quantum coherence be relevant for biological function?

A. Vaziri
B. HHMI/U. Vienna

Quantum Biology has long roots:

- QM should apply to biology (life)
  Bohr, Jordan,··· 1929 onwards
- N. Timofeev-Resovsky (genetics)
  K. Zimmer (photobiology)
  M. Delbrück (quantum physics)

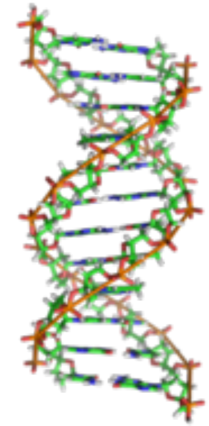
1935

probed genetic structure and mutations with X-rays

first quantum probe of biological structures and function, acknowledgement of need to understand detailed molecular structure of functional biological entities

- First Era: 1930 – 1950s (b.L.)

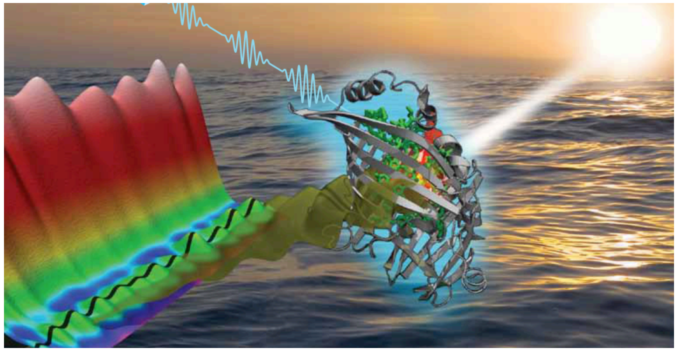
molecular structure and pathways, energetics, kinetics, stability – quantum nature of molecular energy levels, energy barriers… (Schrödinger *What is Life?* 1943)



DNA 1953

- Second Era:1960s onward (a.L.)

Quantum dynamical effects – new generations of dynamical probes, innovation via quantum science and technology…



Quantum Biology, second era

Experiments:

1963 Yoshizawa-Wald: photoisomerization in primary step of vision
(1991 fsec dynamics, 2010 conical intersection)

1966 DeVault-Chance: electron tunneling in photosynthesis

1997 Savikhin, Buck Struve: excitonic coherence in light harvesting

1989 Klinman et al.: hydrogen tunneling in enzyme reactions

2007 Fleming et al.: excitonic coherence in EET during light harvesting

2010 Engel et al., Scholes et al.: quantum coherence of EET in LHCs at ambient temperatures

Additional Proposals:

1995 Hameroff-Penrose: quantum coherence in brain microtubules

1996 Turin: inelastic electron tunneling in olfaction

1998 Schulten et al.: radical pair mechanism of bird navigation
(many subsequent experiments consistent with this theory)

2010 Vaziri-Plenio: quantum coherent transport in ion channels

Schrödinger and biology:

- 1943 "*What is Life*": genetic structure and stability determined by quantum nature of molecular energy levels, energy barriers between stable configurations; no consideration of i) tunneling, ii) quantum coherence or entanglement in such biological processes
- 1943 "*quantum indeterminacy* plays no biologically relevant role" in bodily events corresponding to activity of the mind, except possibly by enhancing accidental nature of meiosis, mutations, etc.

Quantum mechanics and biology today:

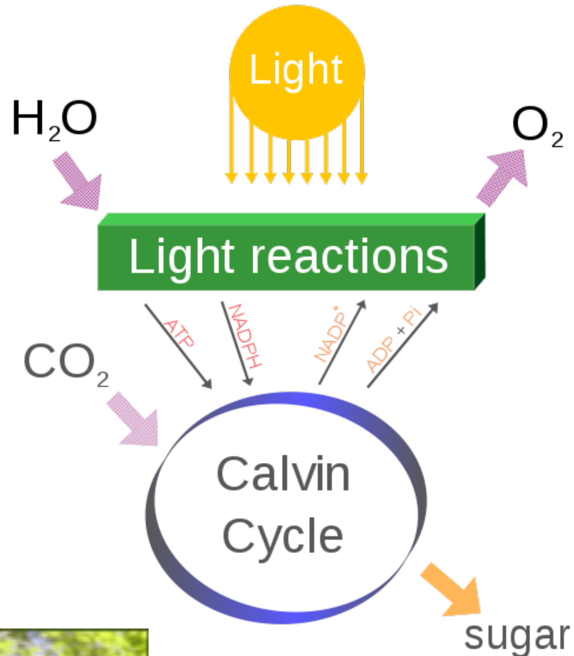
Solvay Congress 2010

Potential Quantum Dynamical Processes in Biology

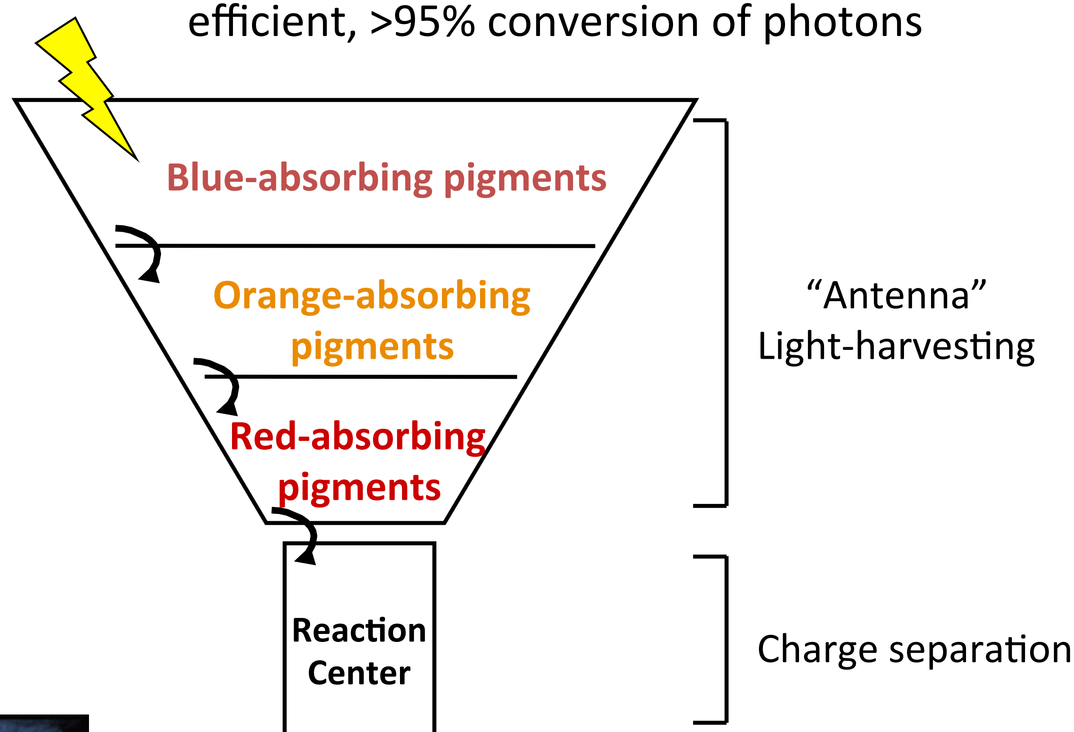
	Excited States	Light Particles	Radical Pairs
Biological Phenomena	Primary steps in photosynthesis Vision	Enzyme catalysis Photosynthesis	Bird navigation
Quantum Processes	Energy transfer Electron transfer Isomermization	Long-range electron tunneling H atom transfer Proton-coupled electron transfer	Reactions producing radical pairs

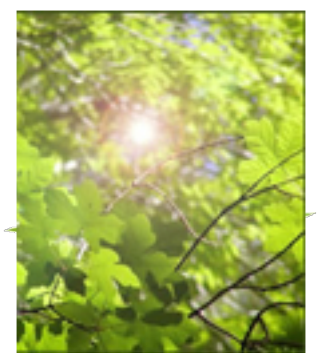
DARPA: Quantum Effects in Biological Environments

Photosynthesis

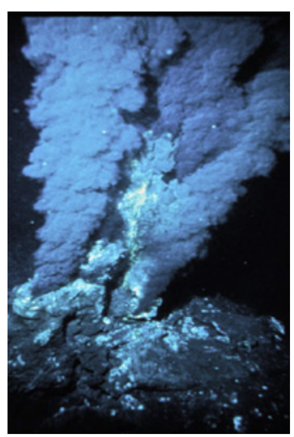


The "light" reactions are rapid and efficient, >95% conversion of photons





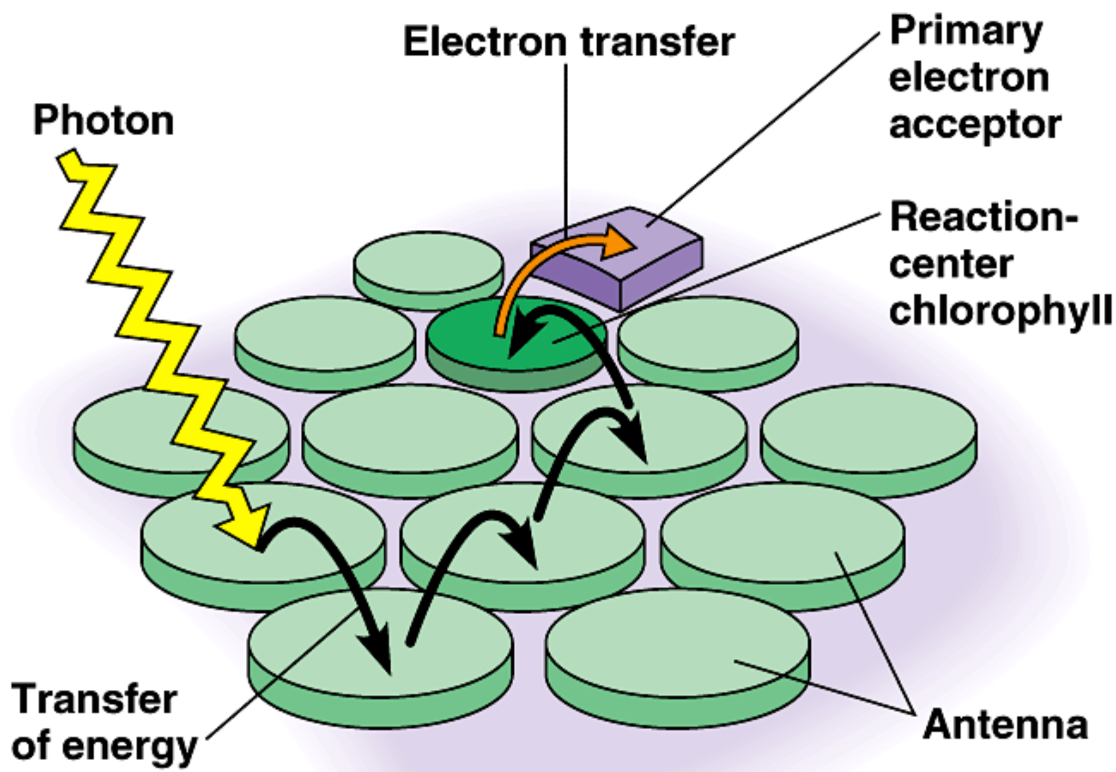
green plants



bacteria

…Secondary electron transfer reactions, Water splitting, Proton transport across thylakoid membrane, Reduction of $NADP^+$, ATP synthesis…

Photosynthetic Light Harvesting



at low light intensity

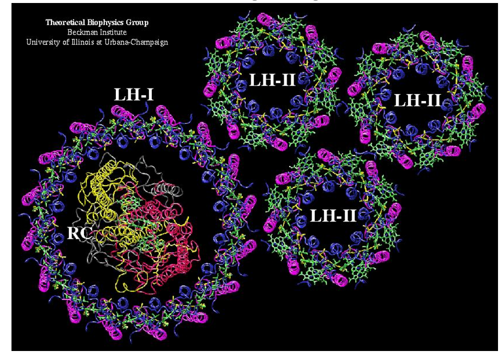
quantum yield ~ 100%

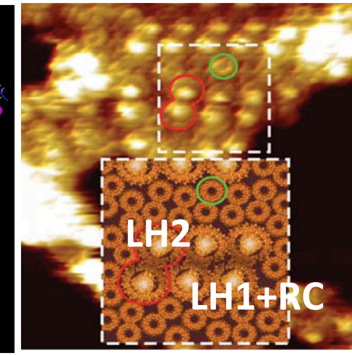
Each absorbed photon almost certainly reaches the reaction center and drives the charge separation.

Light Harvesting Complexes

- A bewildering variety of antennae
- All composed of densely packed chromophores (pigments, visible light absorbing molecules)
- The molecular aggregates are often but not always embedded in protein scaffolds

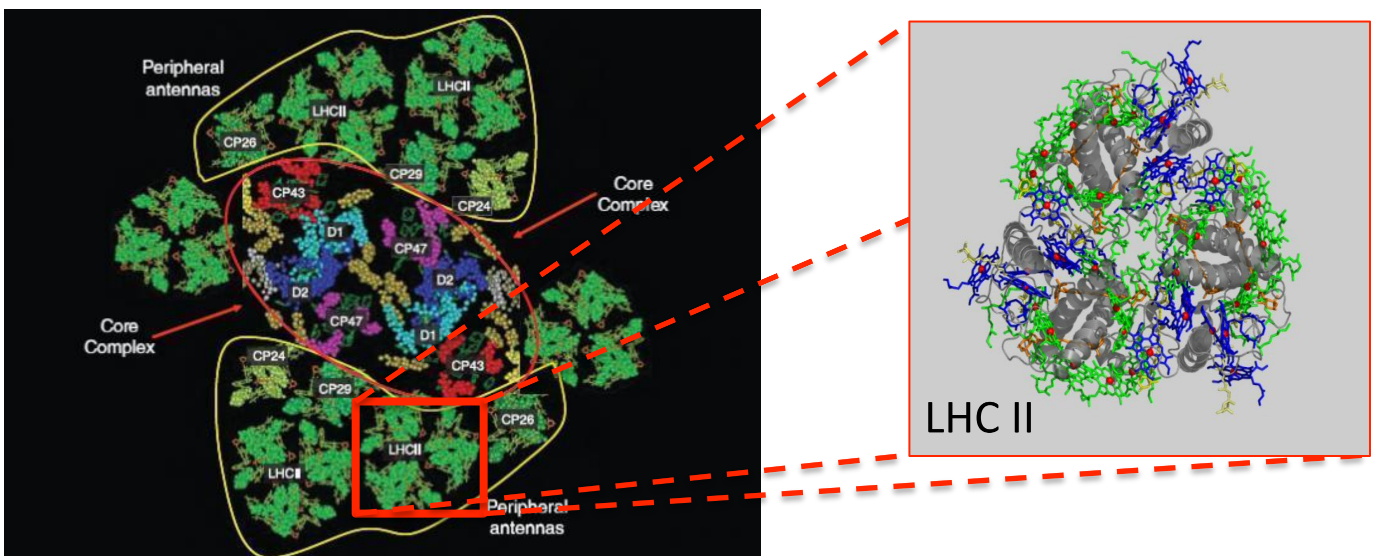
LH 1 and 2 in purple bacteria





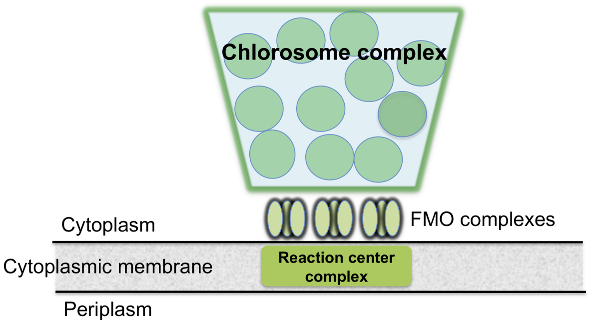
Bahatyrova et al., *Nature* **430**, 1058 (2004)

PS II of higher plants, blue-green algae, cyanobacteria



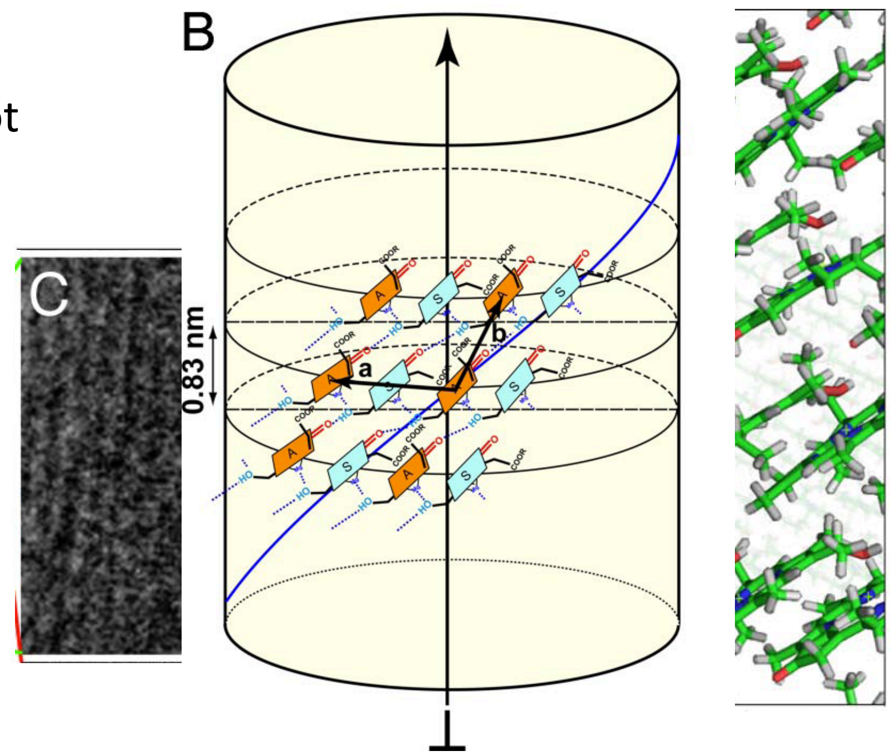
50% of green matter on earth uses PS II

Chlorosome of green sulfur bacteria



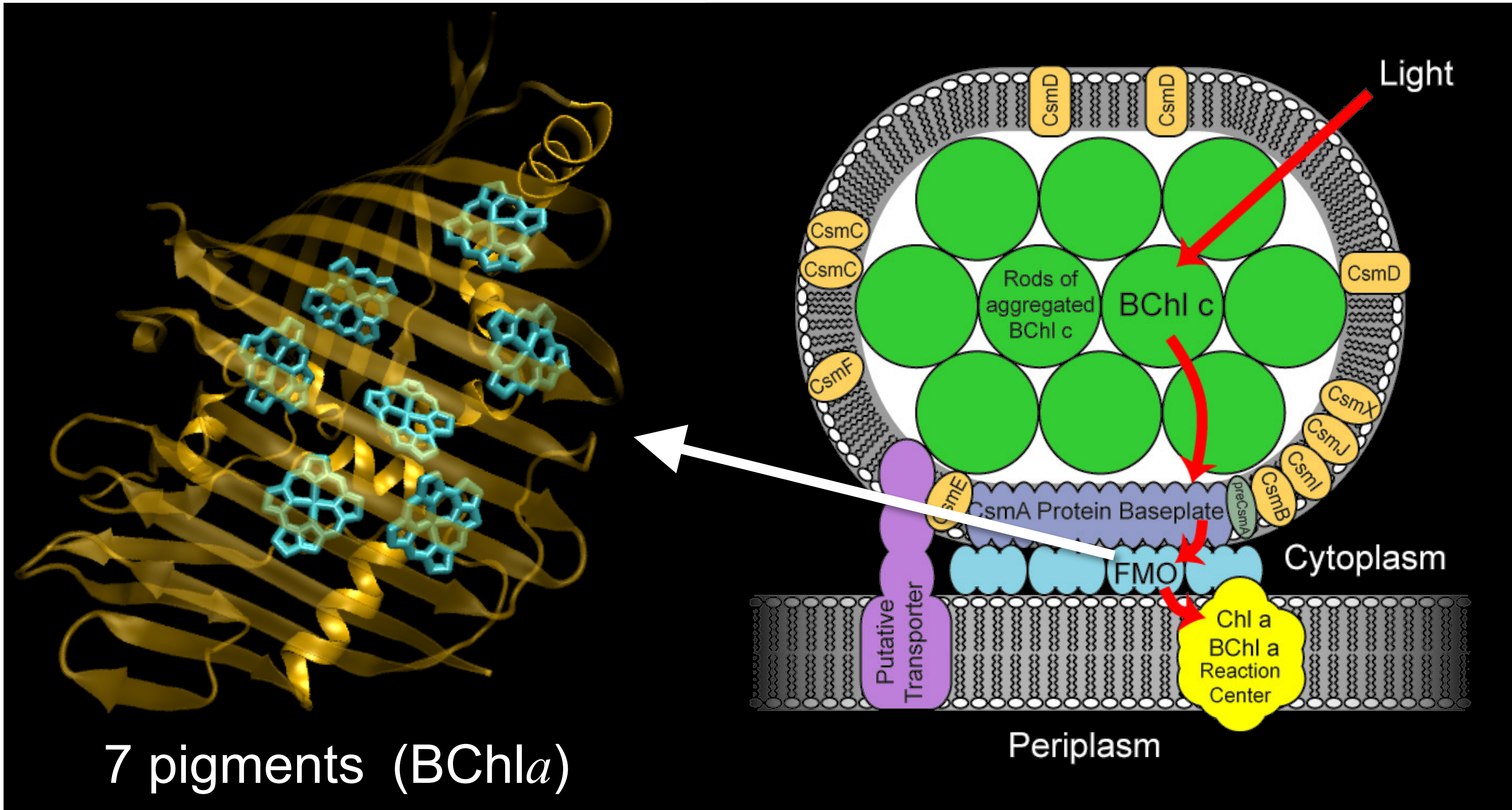
Antenna system of green sulfur bacteria

- Structure determined in 2009 for mutants (not WT)
- Chlorophyll stacks are self-assembled into concentric nanotubes
- Helical arrangement of chromophore transition moments implies helical exciton delocalization pathway
- Interaction between stacks allows T-T exciton interactions which provide photoprotection
- Evolutionarily optimized for low light intensity?



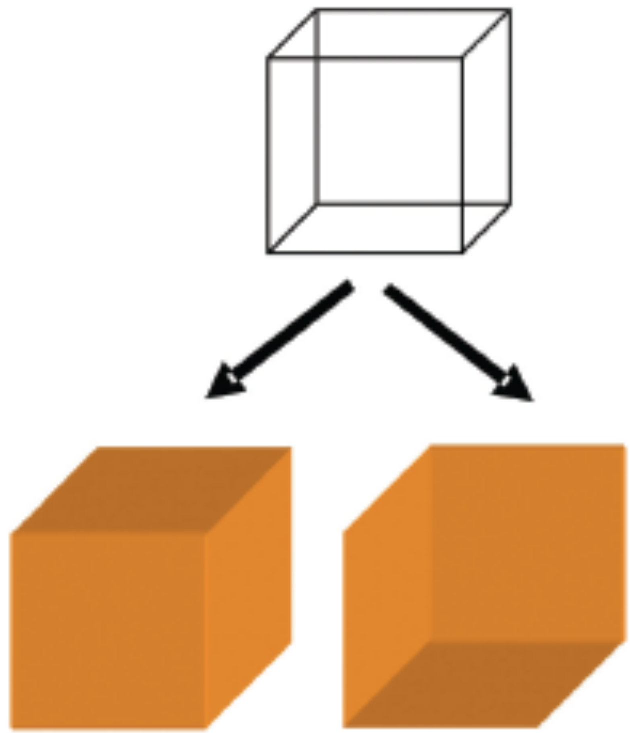
Fenna-Matthews-Olson Complex (FMO)

"Wire" connecting Chlorosome antenna to Reaction center



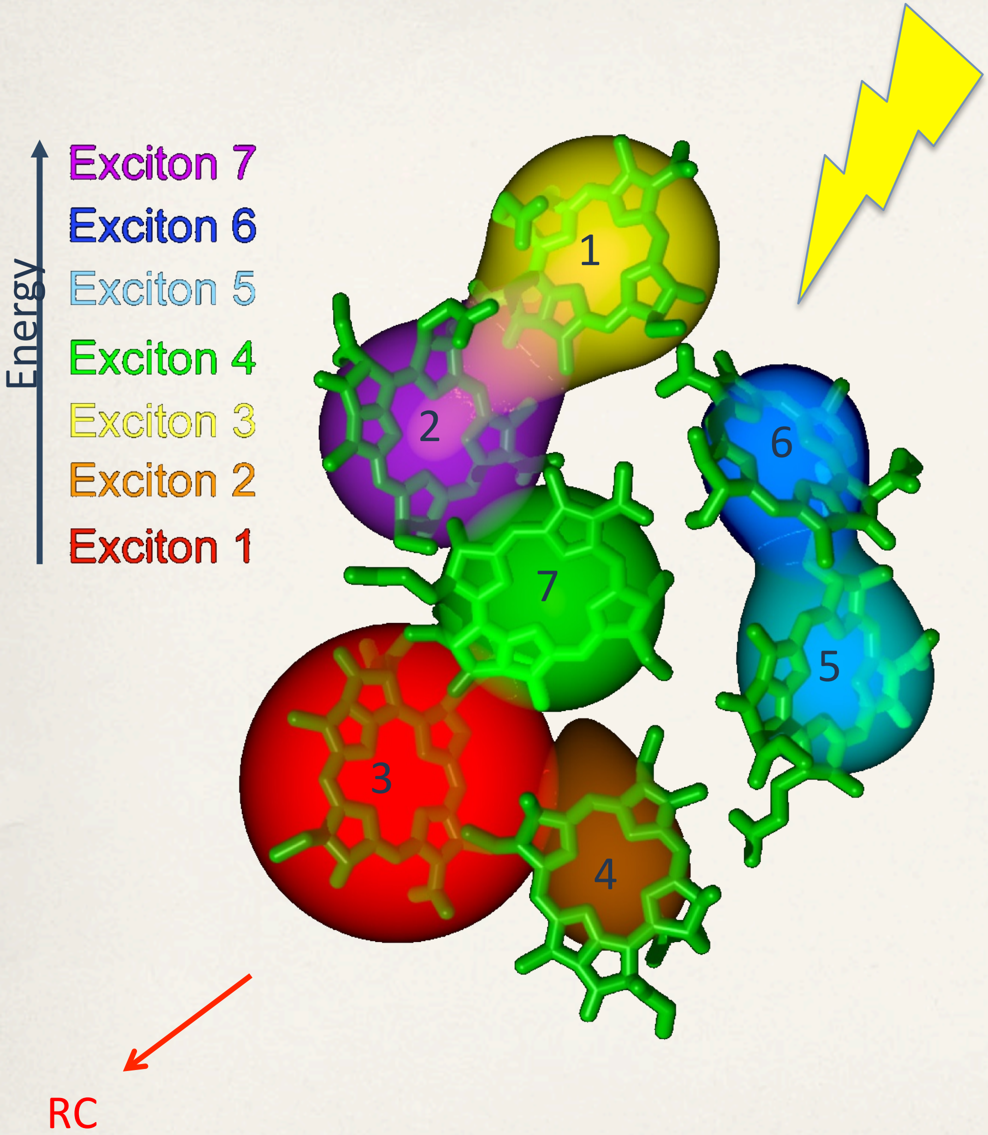
Quantum superposition:

visual representation with ambiguous cube



F.A. Wolf, *Taking the Quantum Leap: The New Physics for Nonscientists*, New York: Harper & Row (1989).

FMO Complex: (Frenkel) excitons



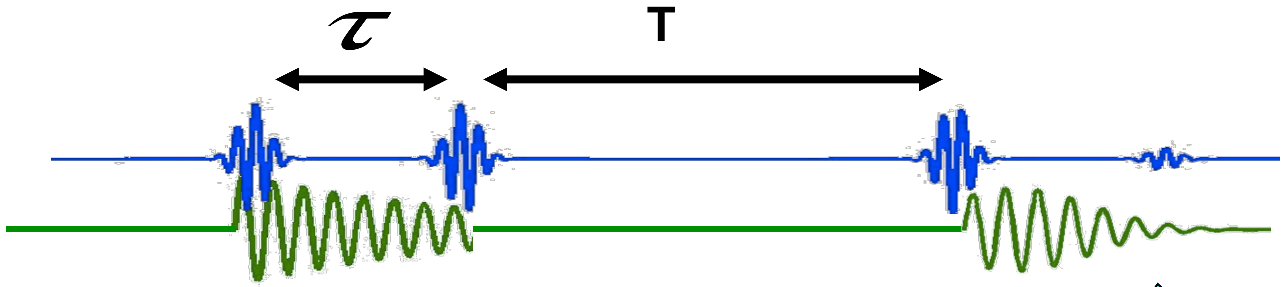
In vivo: electronic excitation transferred from (chlorosome) antenna via base plate

In vitro: Optical transitions to delocalized exciton states

- prototypical LH complex
- Well characterized by pump-probe experiments [1] and theoretical modeling [2]
- Mostly delocalized on two BChls
- Lowest energy exciton sits on BChl 3

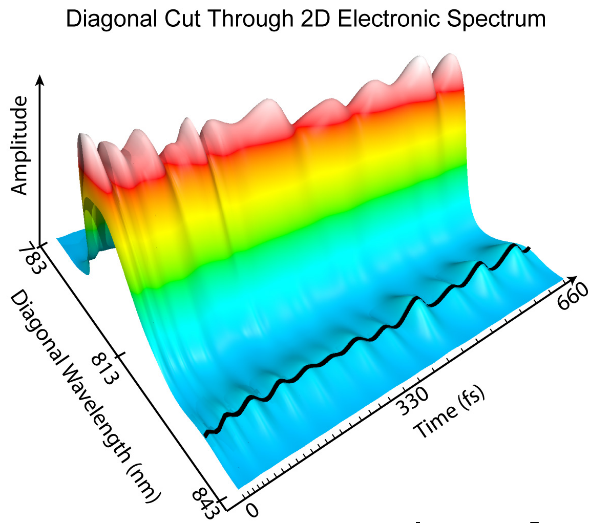
[1] A. Freiberg, S. Lin, K. Timpmann & R. E. Blankenship, J. Phys. Chem. B 101, 7211 (1997)
[2] J. Adolphs & T. Renger, Biophys. J. 91, 2778 (2006).

2D Spectrum probes energy transfer dynamics

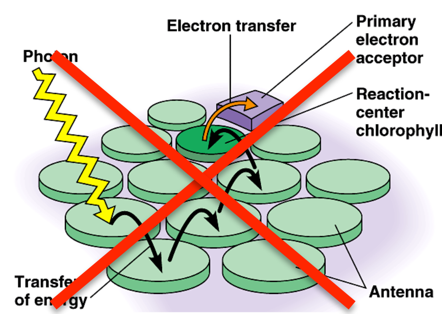


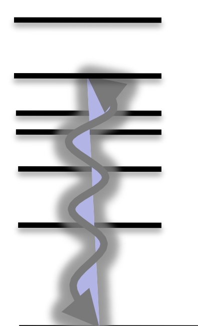
Fourier Transform

with Respect to τ



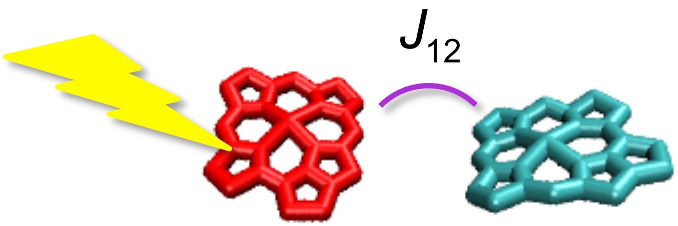
Spectrally resolved, heterodyne detected photon echo.





quantum coherent excitonic energy transport in light harvesting complexes (Engel, Scholes, Fleming)

Coupled pigment-protein dynamics:



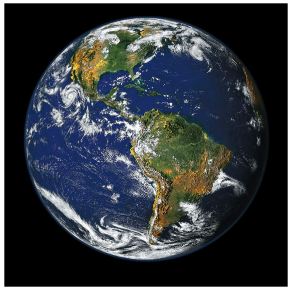
Modeling energy transfer is hard because multiple similiar energy scales – no small parameter…

4 similar energy scales:

- electronic energy transfer,
- coupling of electrons to protein vibrations,
- relaxation of protein vibrations, redistribution of energy
- energetic disorder in pigment (chromophore) energies

No accident! Energy transport in FMO appears to be optimized with respect to all parameters…

- **Has evolution highlighted/preserved non-trivial quantum effects to ensure optimization of some biological function critical for survival/ adaptation?**



- **Quantum information processing?**

When It Comes to Photosynthesis, Plants Perform Quantum Computation

The wavelike motion of energetic particles through photosynthetic systems enables plants to efficiently capture the sun's energy

Scientific American, April, 2007

Engel et al, Nature 2007: does FMO perform quantum search for reaction center?
Hoyer, Sarovar, KBW NJP 2010: no quantum speedup and no quantum computation

- **Coherence is accompanied by long ranged and long lived entanglement**
  Sarovar, Ishizaki, Fleming, KBW, Nature Physics 2010

- **Coherence contributes to high quantum efficiency of light harvesting?**
  Aspuru-Guzik et al, Plenio et al, Cao et al,... Yes

- **Coherence enhances unidirectionality of energy transport, can propagate between complexes and ratchet energy transfer up energy gradients**
  Hoyer, Ishizaki, KBW, Phys Rev E (2012)

Is photosynthesis performing a quantum search?

"…the system is essentially performing a single quantum computation, sensing many states simultaneously and selecting the correct answer... In the presence of quantum coherence transfer, such an operation is analogous to Grover's algorithm…"

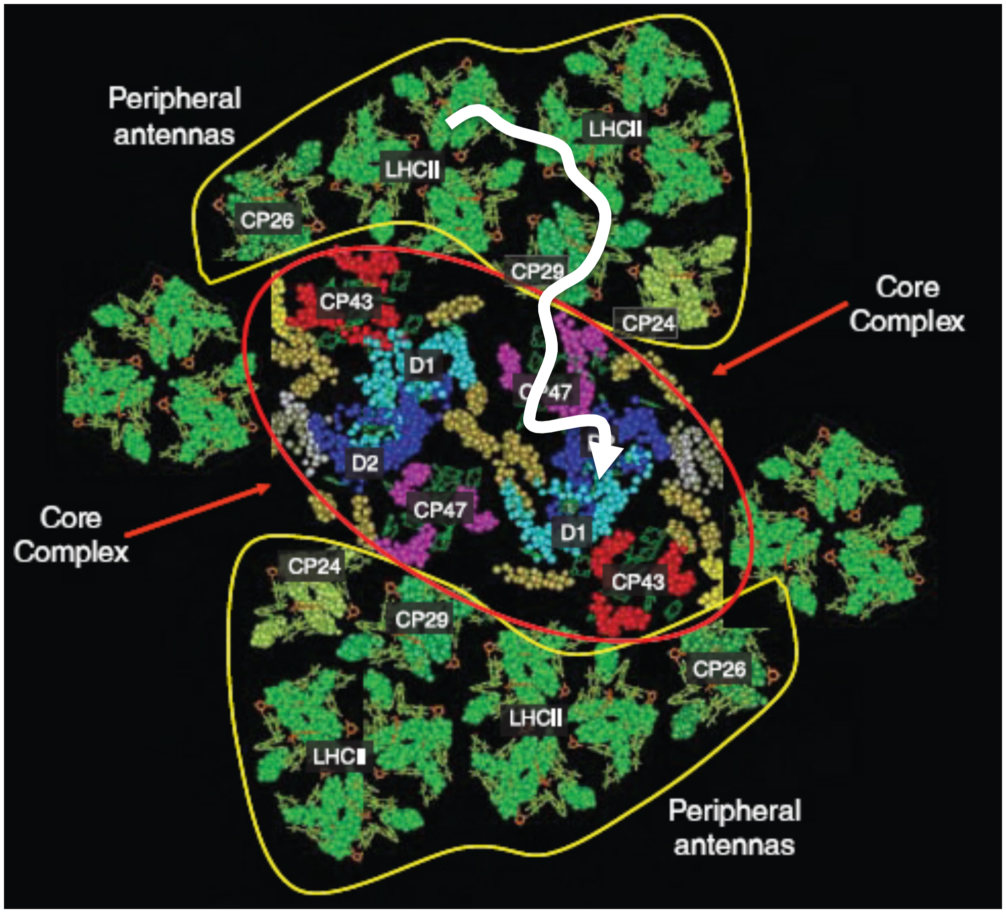
Engel *et al.*, Nature **446**, 782 (2007)

When It Comes to Photosynthes… Computation

The wavelike motion of energetic particles through photosynthetic systems enables pla… energy

Scientific American, April, 2007

Is quantum coherence relevant to truly long range energy transfer?



Photosystem II super-complex, courtesy of Roberto Bassi

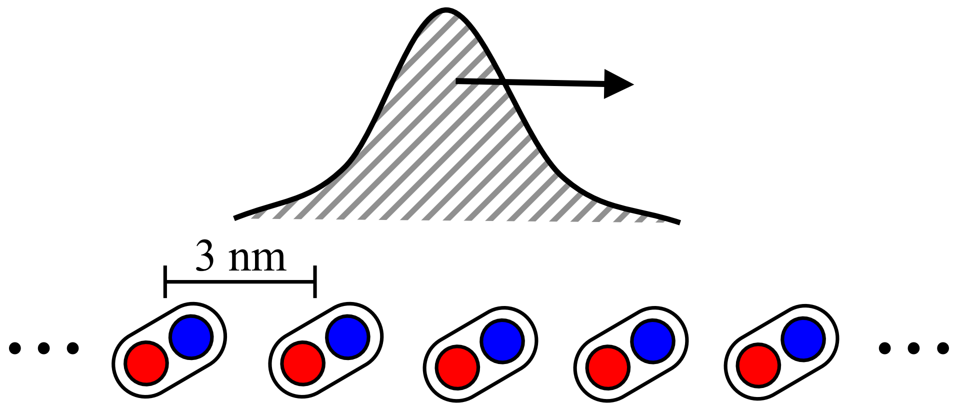
All coherence experiments to date show quantum beating in a single complex –

- Is coherence transmitted **between** complexes?
- If so, why? How might it help photosynthetic function?

Theory:

- coherence is transmitted
- enables unidirectional transport
- enables uphill transport

Enhanced unidirectionality from coherence-assisted uphill transport

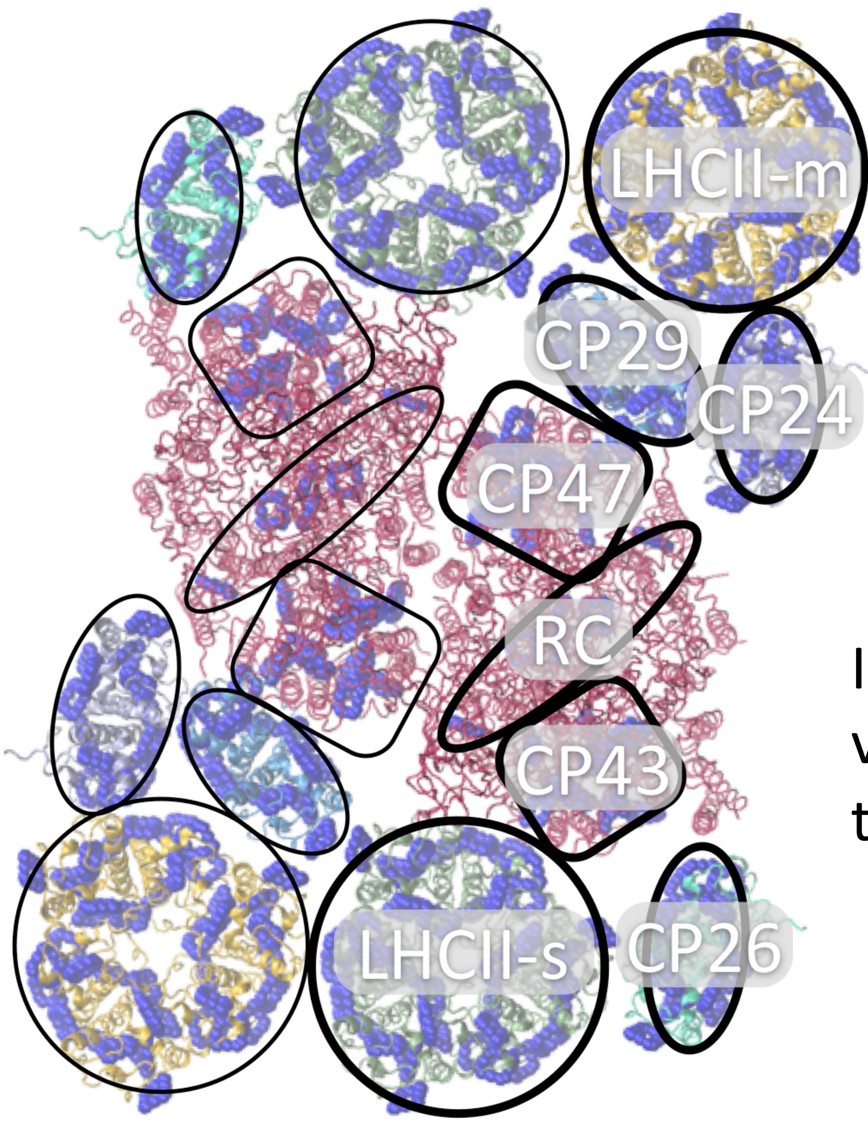


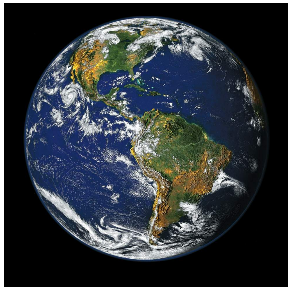
Proof of principle linked dimer model: asymptotic uphill bias in 1D random walk between asymmetric dimers, resulting from non-equilibrium initial conditions after each inter-dimer transfer and hence unbalanced left and right transfer rates at short times.

S. Hoyer, K. B. Whaley, 2010

quantum coherent ratcheting of energy transfer Hoyer et al. PRE 2012

Subcomplex analysis of PSII





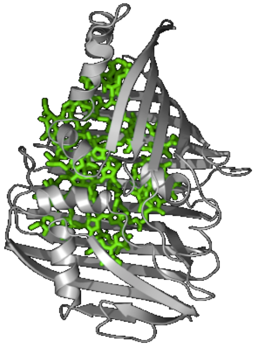
Green plants

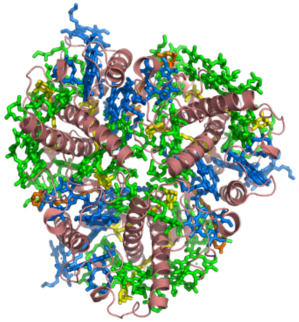
CP24-CP29 ~ 20-30 pigments
uphill step from here to RC

Is coherence transmitted from LHCII via several intermediate complexes to the reaction center (RC)?

Looking Forward

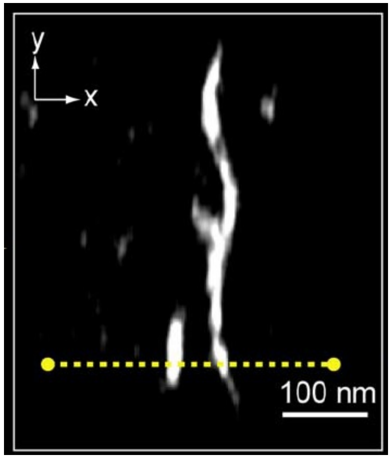
Multidimensional Electronic Spectroscopy of a Single Complex.





NMR of a Single Entity.

Spin Image of a Tobacco Mosaic Virus.

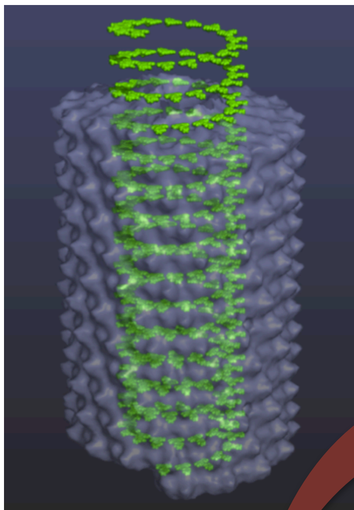


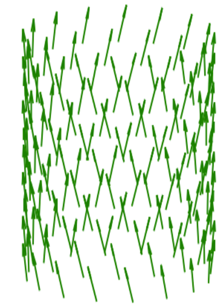
Degen,Poggio,Mamin, Rettner,Rugar , PNAS, **106**, 5, 1333, 2009.

Quantum Inspired Rational Design (QIRD) of TMV-templated light sensors

M Sarovar and K. B. Whaley, New J. Physics **15**, 013030 (2013).

Hypothesize structure





Electronic structure for individual and few coupled pigments

Molecular mechanics to describe aggregation and self-assembly

Effective theories for charge and energy transfer, and optical properties

Feedback and optimize

Collaboration with synthetic chemists (Matt Francis, UCB)

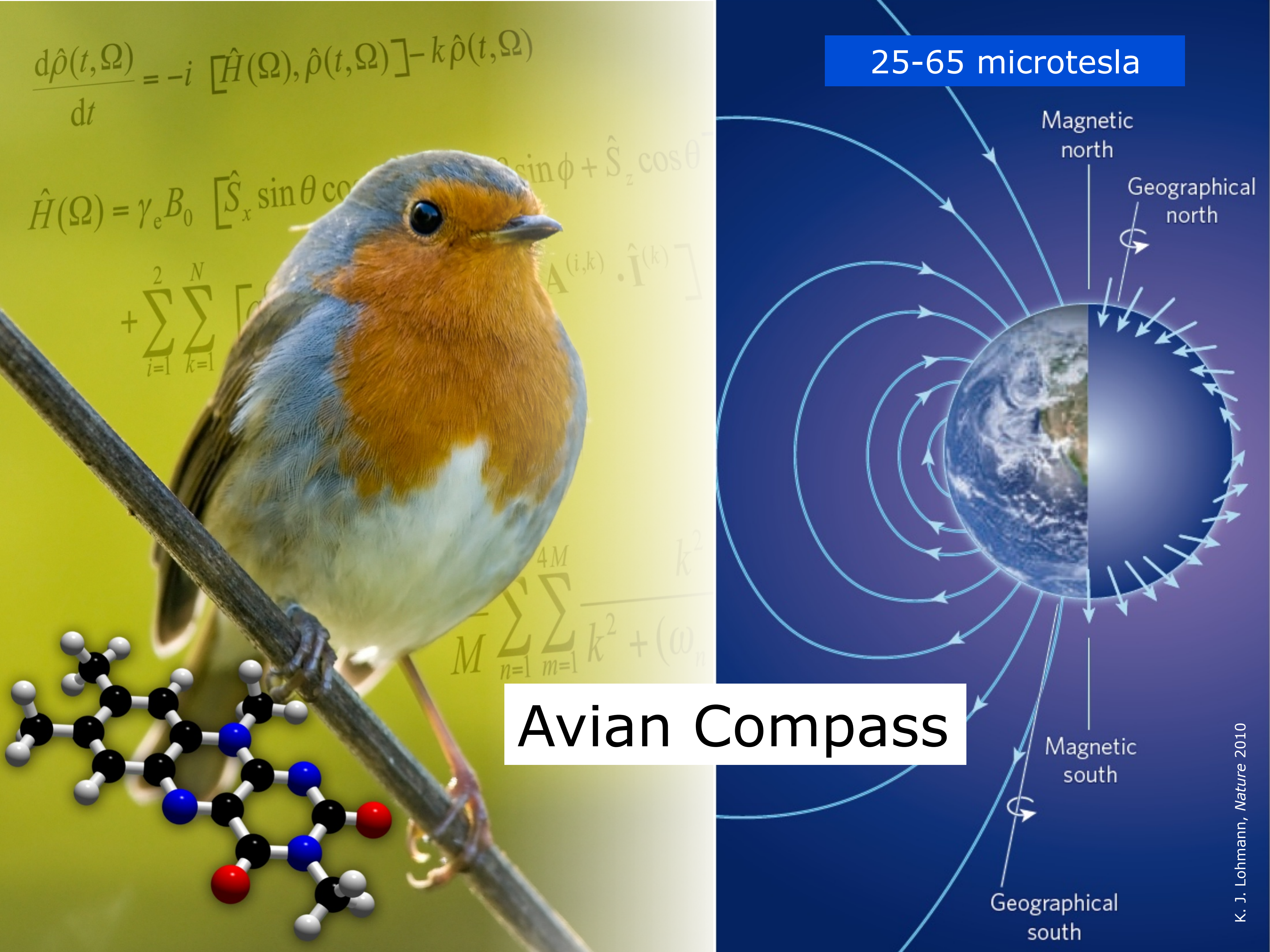
Assess light harvesting functionality

Quantum insights for Light Harvesting

- Quantum coherence in photosynthesis – observations in vitro, theory predicts long range entanglement
- Quantum advantage? Improved efficiency, facilitates uphill and long range energy transfer…

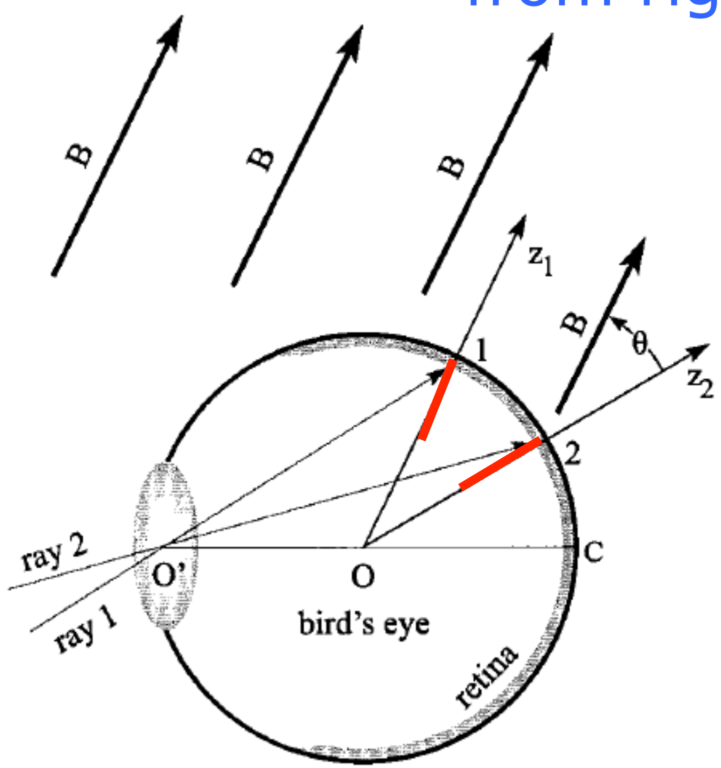
Current directions

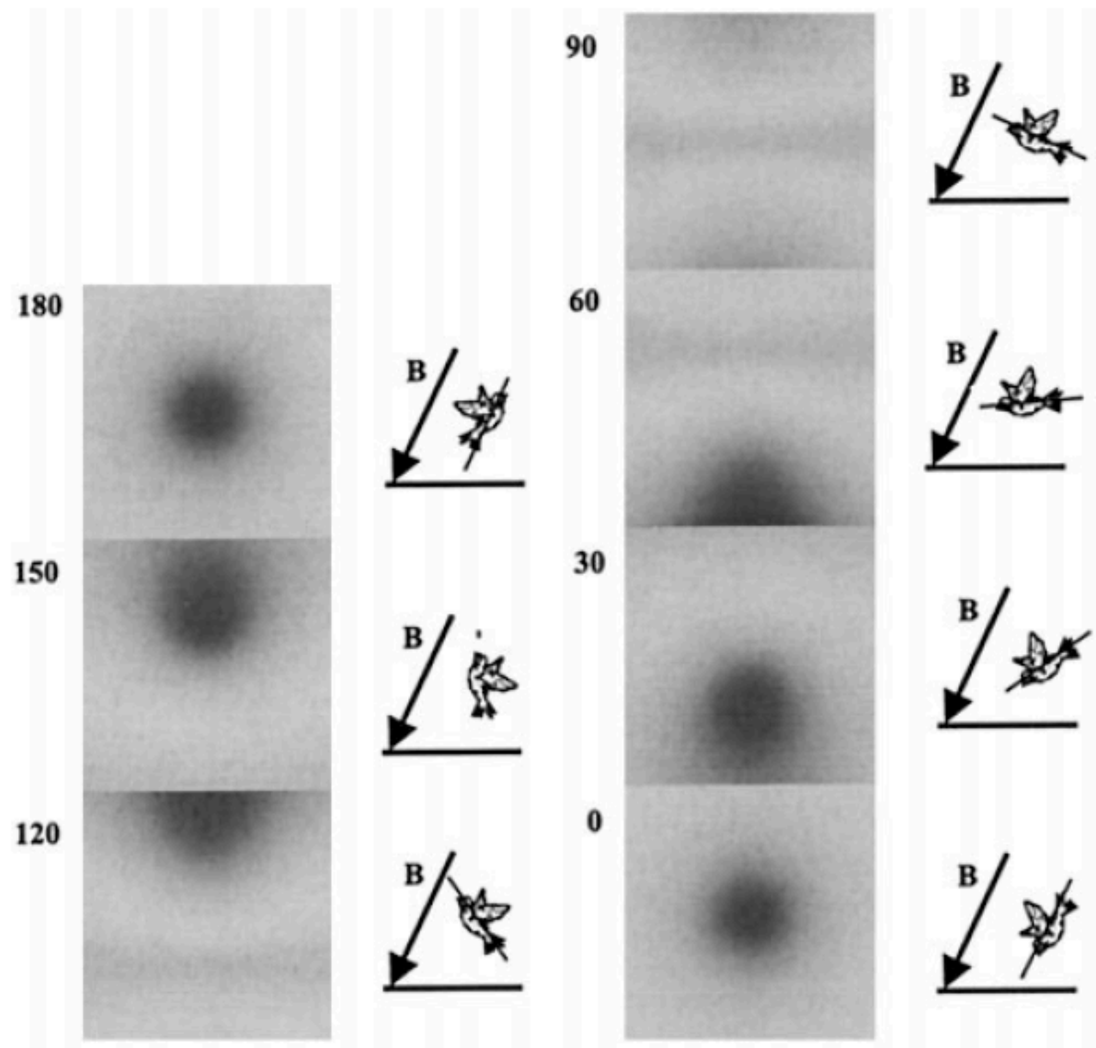
- What can coherent control of light fields add?
- Electronic vs vibrational quantum dynamics
- Single complex dynamics – fluorescence detected coherent spectroscopy in confocal microscopy…
- Harnessing quantum effects for biomimetic light harvesting with protein-templated molecular aggregates… potential for sensors, solar energy collection…
- Naturally robust quantum devices?...

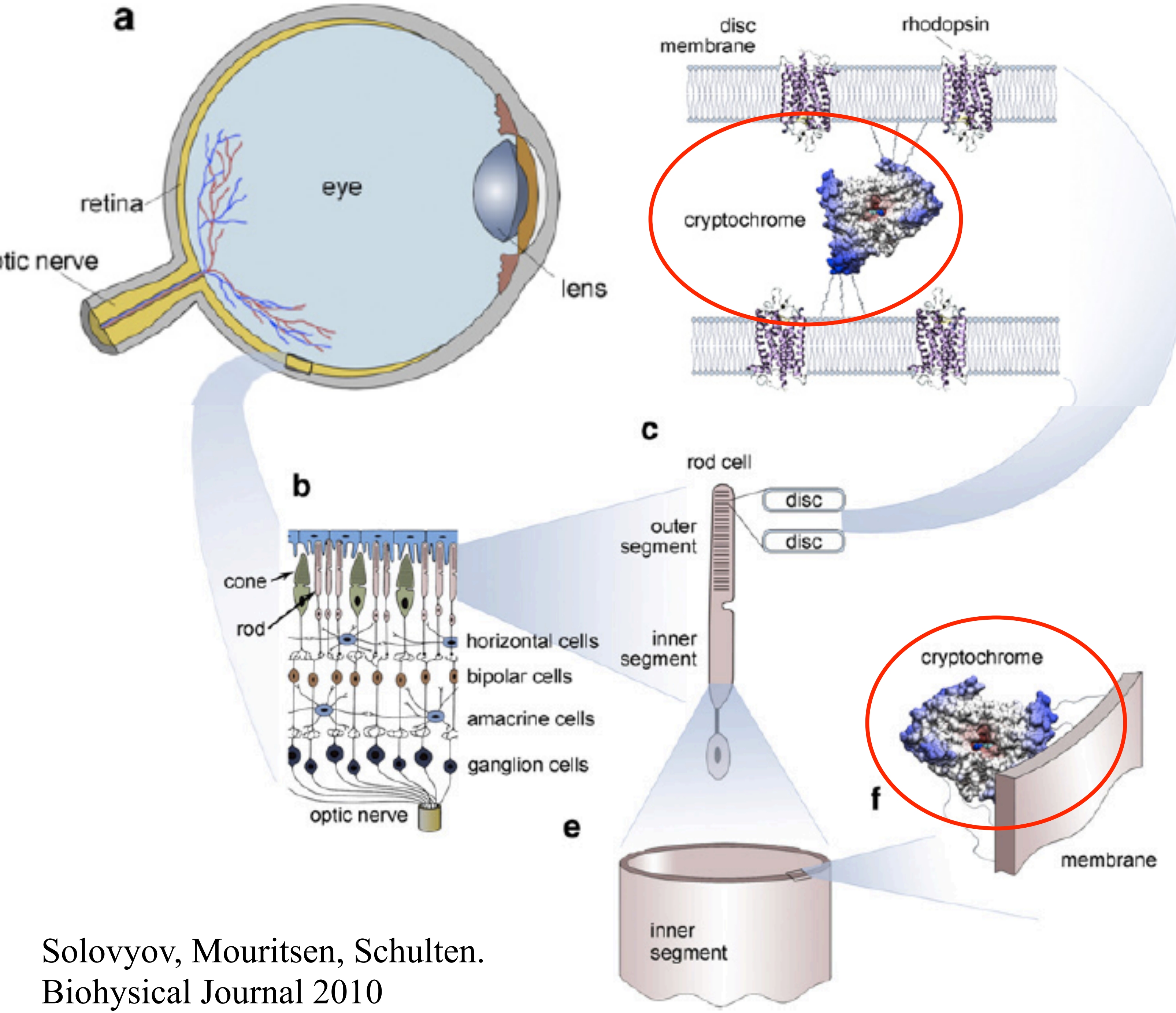


25-65 microtesla
Magnetic north
Geographical north
Magnetic south
Geographical south
Avian Compass
K. J. Lohmann, Nature 2010

Visual modulation pattern resulting from rigidly fixed receptor molecules

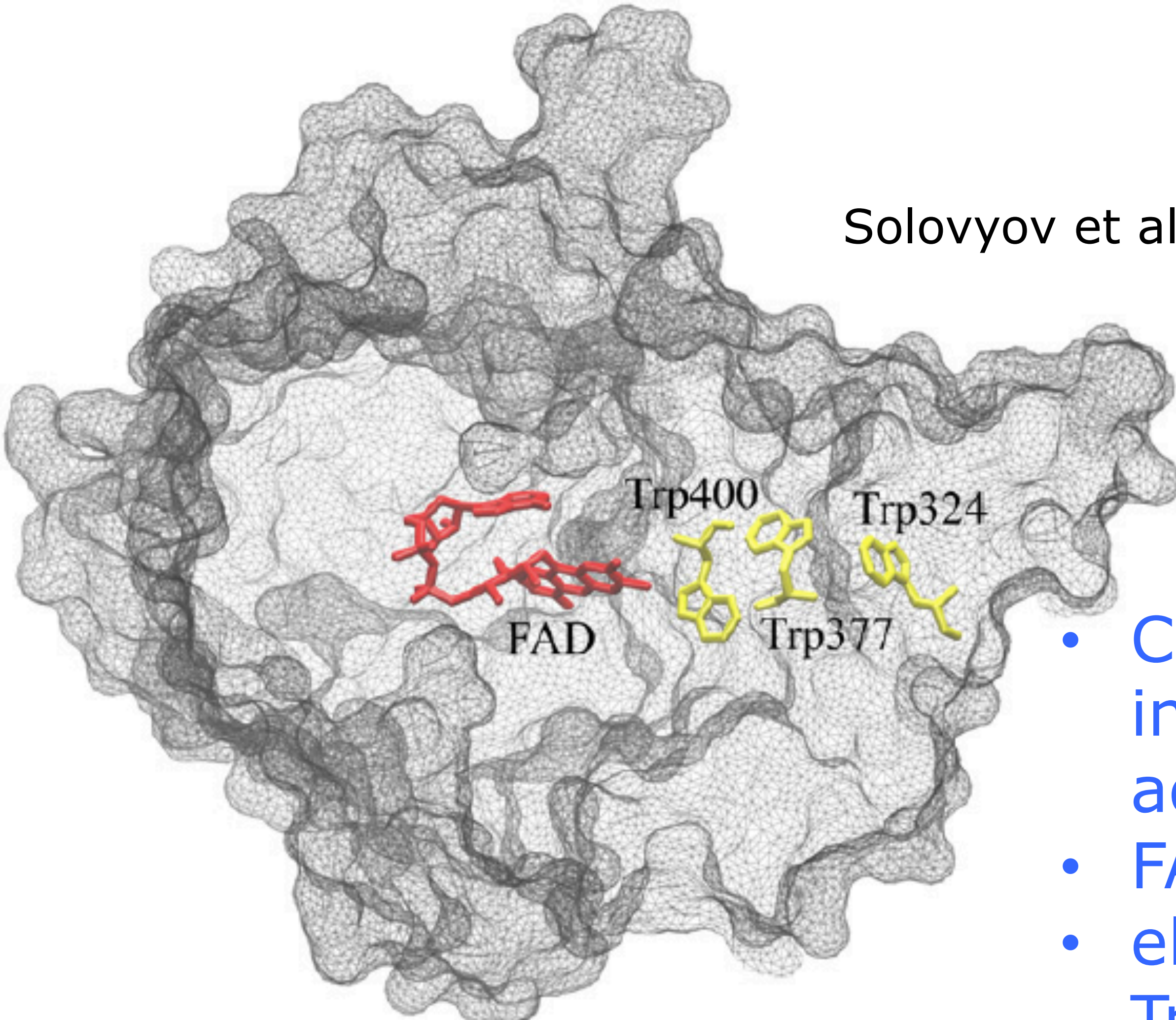






Solovyov, Mouritsen, Schulten.
Biohysical Journal 2010

Cryptochrome – candidate receptor system

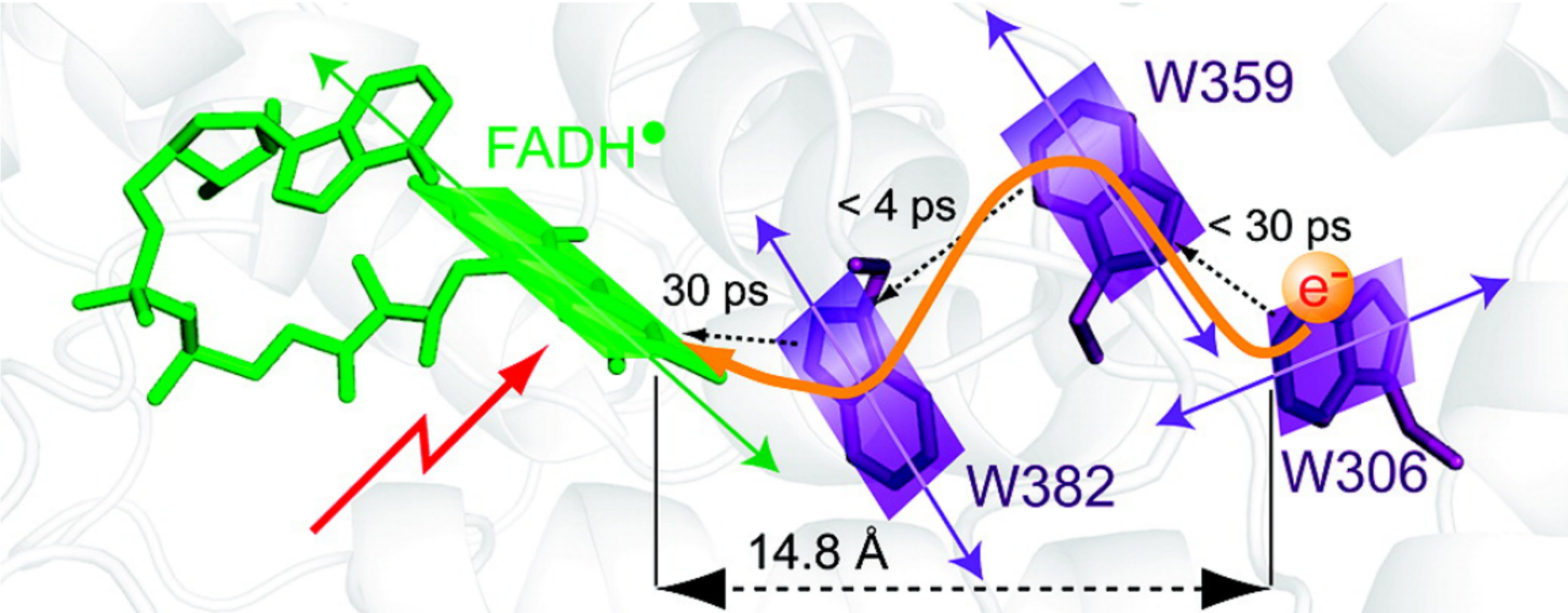


Solovyov et al. Biophys J, 2007

- Cryptochrome protein internally binds additional molecules
- FAD absorbs light
- electron transfer via Trp species generates radical pair

Radical pair = 2 electrons located on different molecules

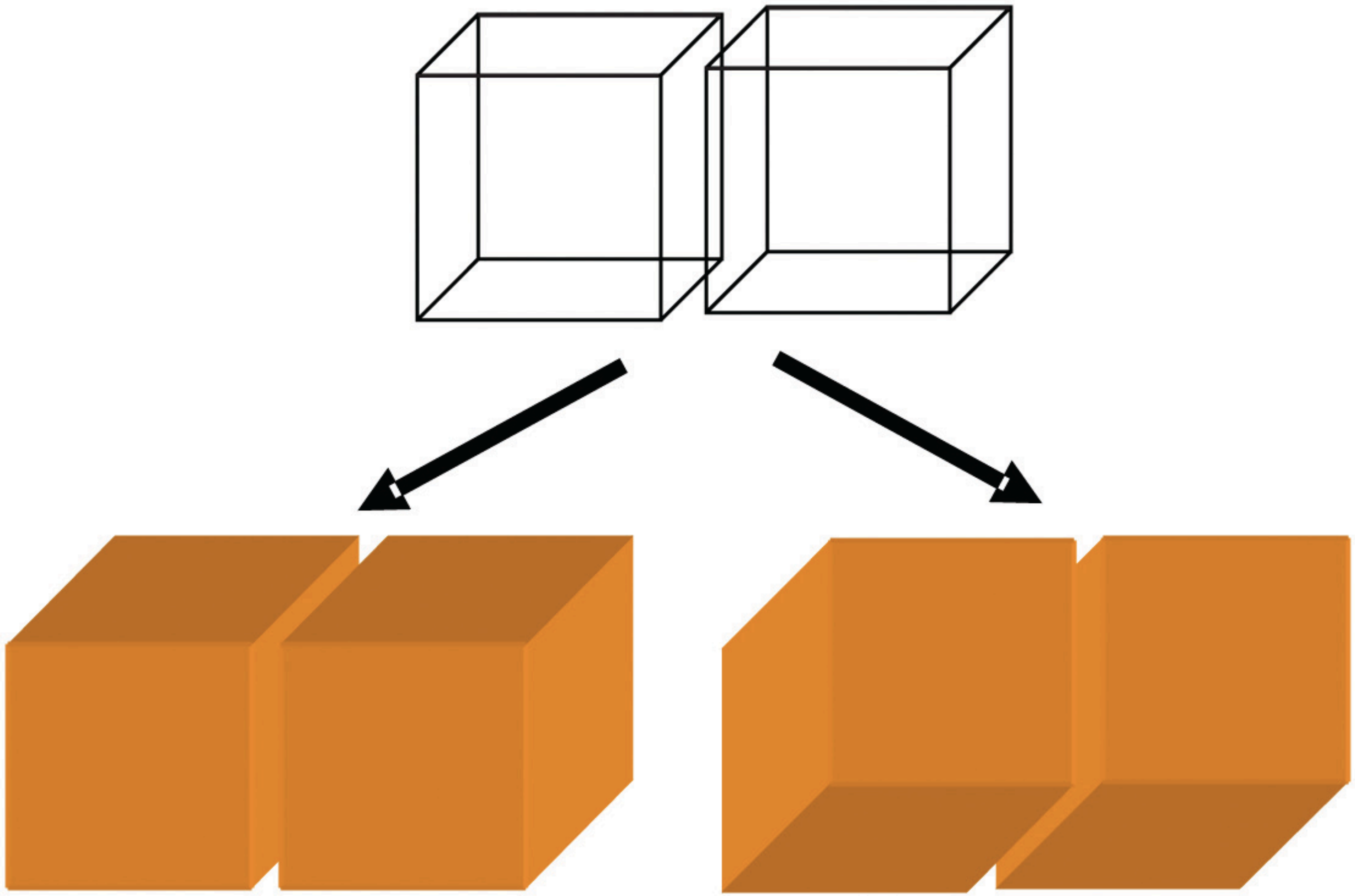
Lukacs et al., JACS Communications 130, 14394 (2008)



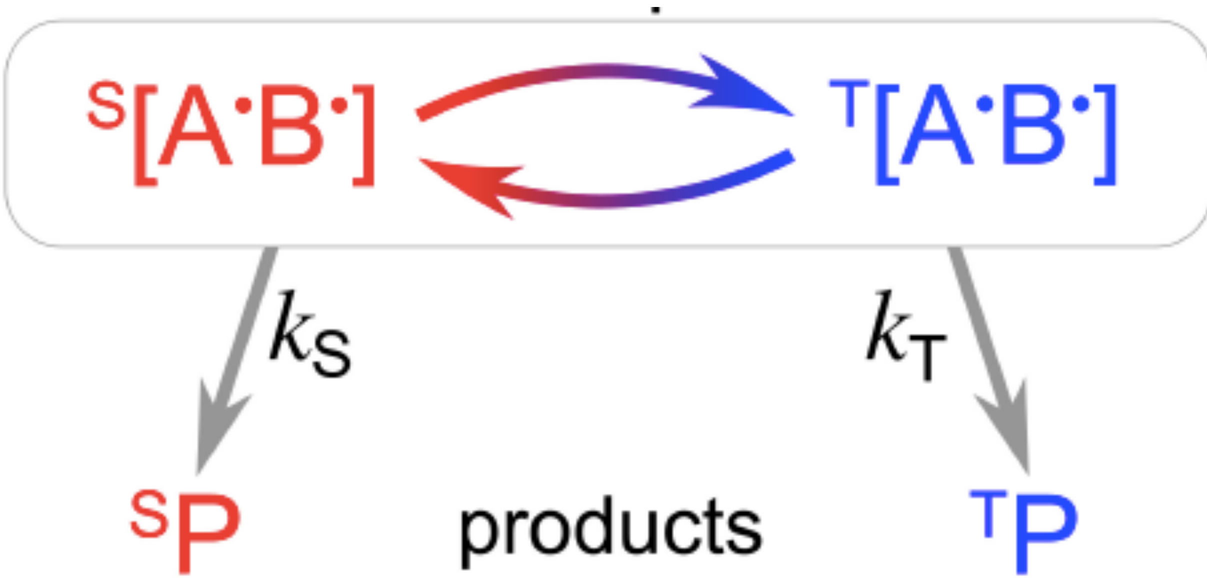
Radical pair of electrons have quantum correlated, ‘entangled’ spins

4 possible spin states: 1x S and 3 x T

Entanglement analog: we see correlations between boxes

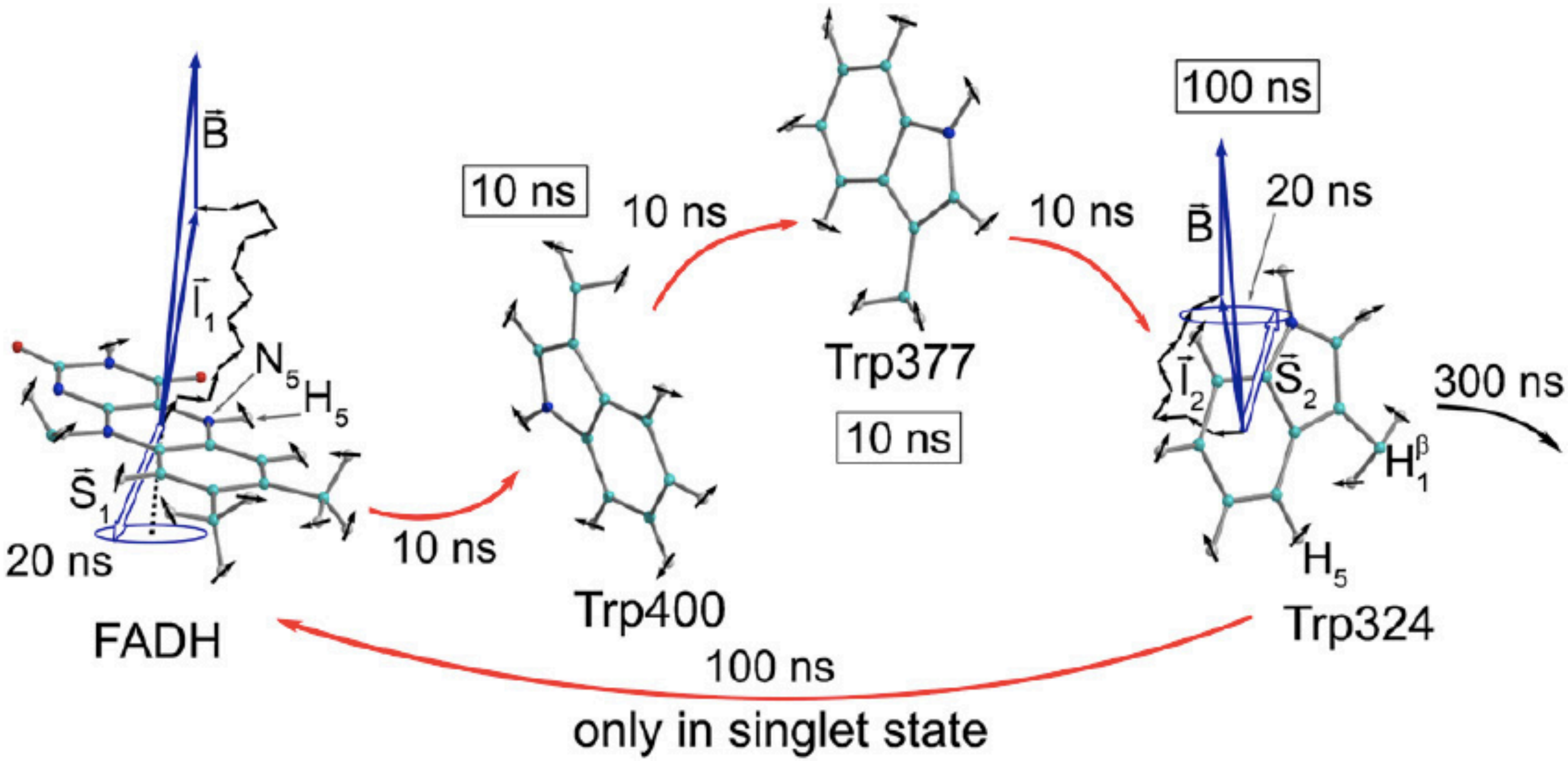


Radical Pair Mechanism



1. S and T radical pairs coherently interconvert in presence of local magnetic fields deriving from interactions of the electron spins with magnetic nuclei in the two radical partner molecule
2. Chemically distinct product yields controlled by interconversion and rates k_S, k_T
3. Interconversion rate also determined by weak magnetic field, e.g., Earth's magnetic field B ~ 50 μT
4. Anisotropic electron-nuclear interations give sensitivity to inclination of B

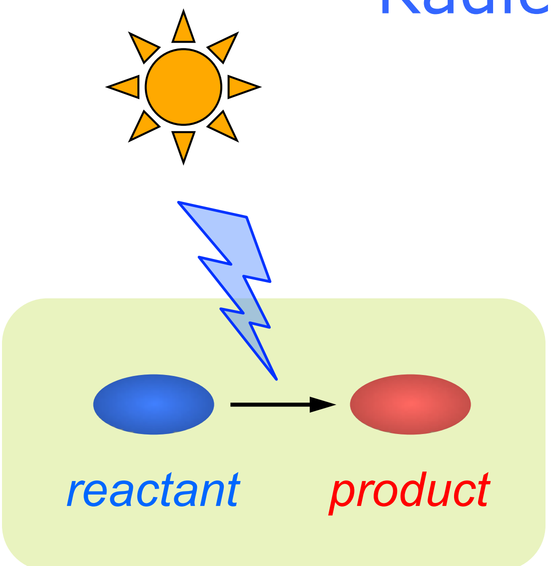
Possible cryptochrome radical pair formation and operation

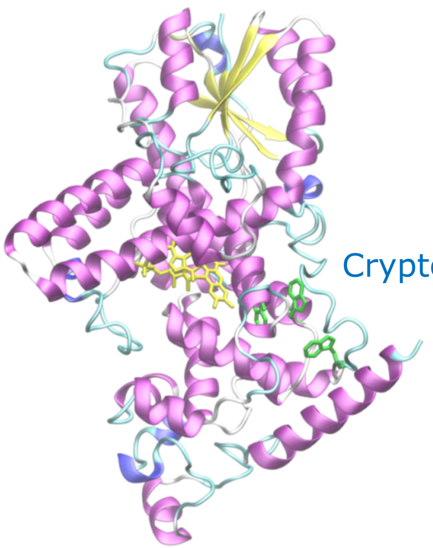


Solovyov et al. Biophys J, 2007

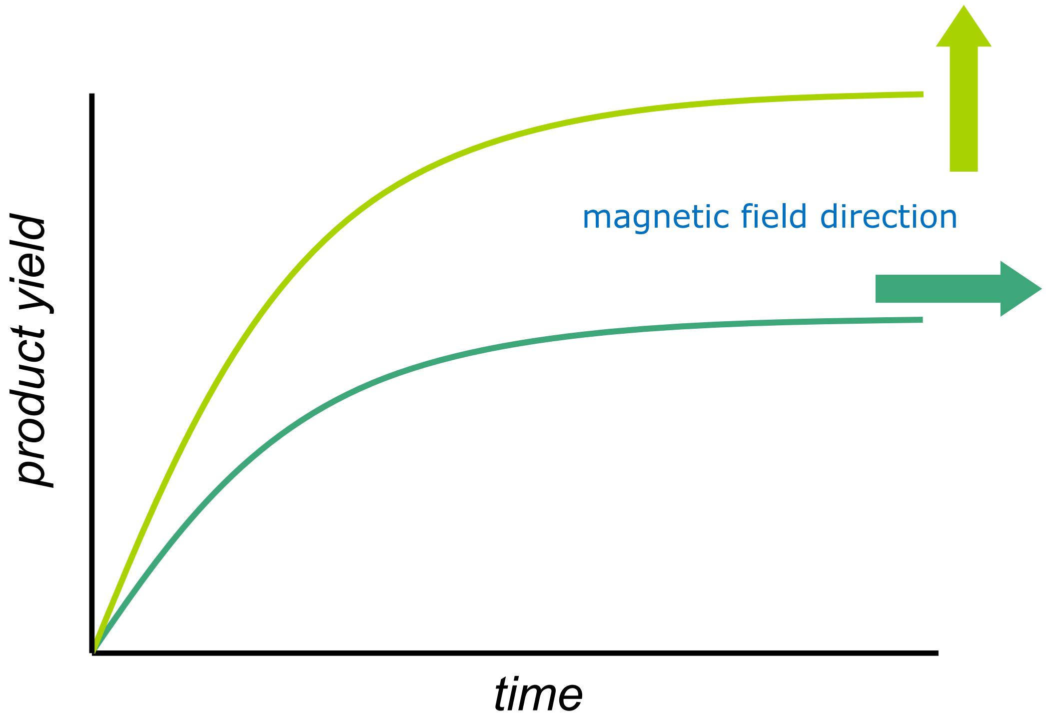
P. Hore

Radical pair magnetoreception



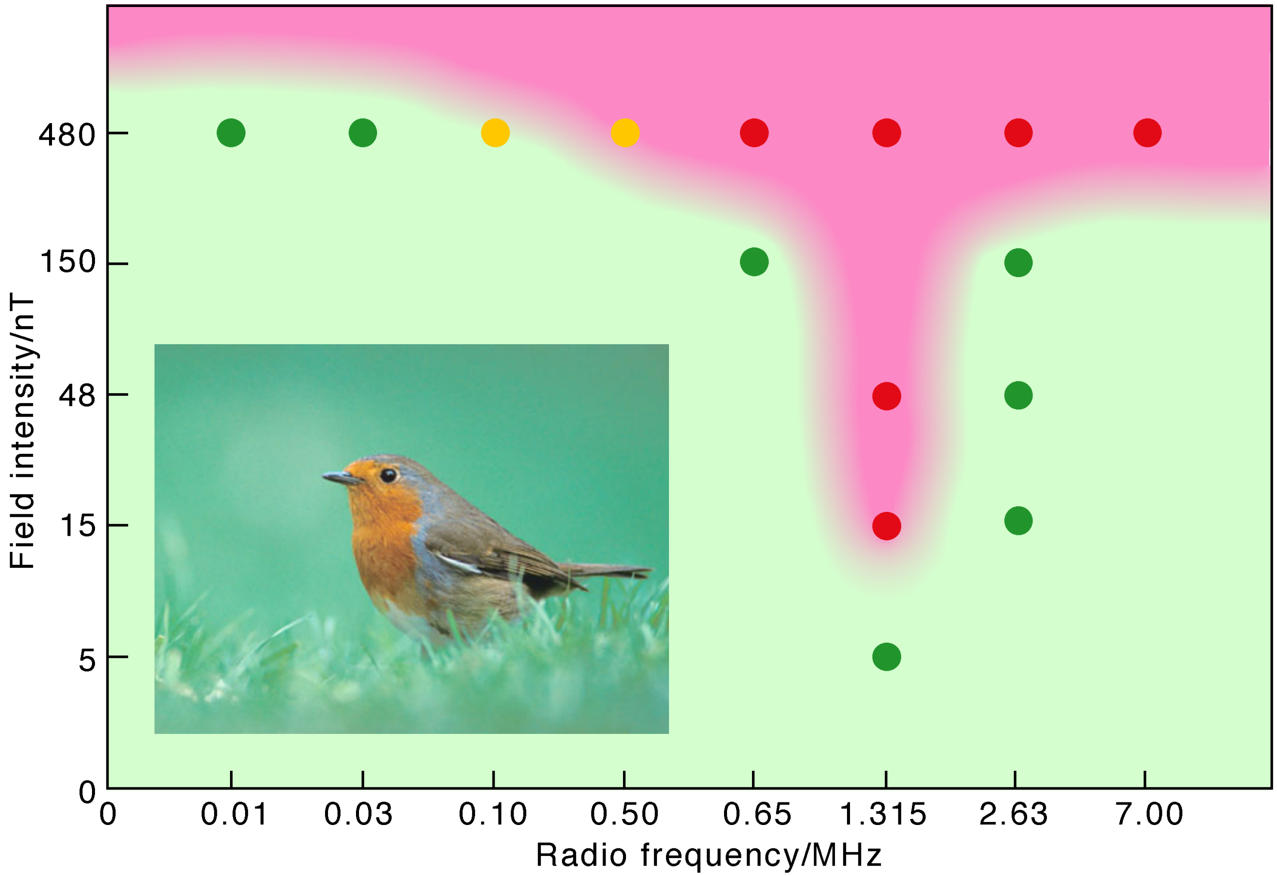


Ritz, Adem & Schulten, 2000



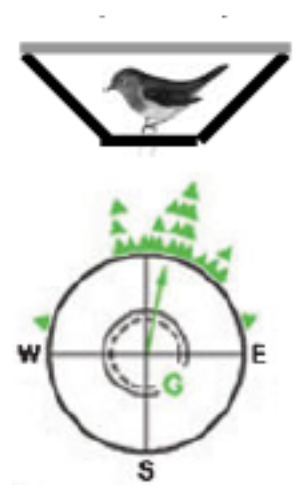
Schulten, Swenberg & Weller, 1978

Animal-detected magnetic resonance (ADMR)



disoriented

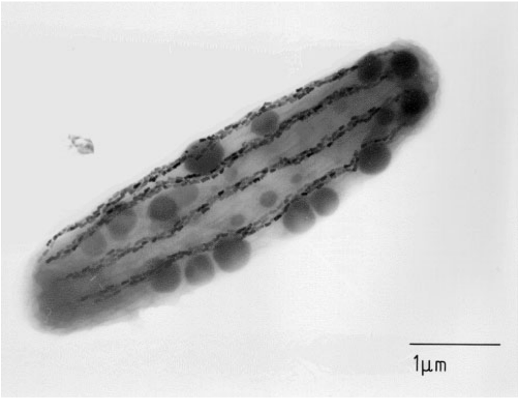
oriented



Ritz, Wiltschko, Hore, Rodgers, Stapput, Thalau, Timmel, Wiltschko, *Biophys. J.* (2009)

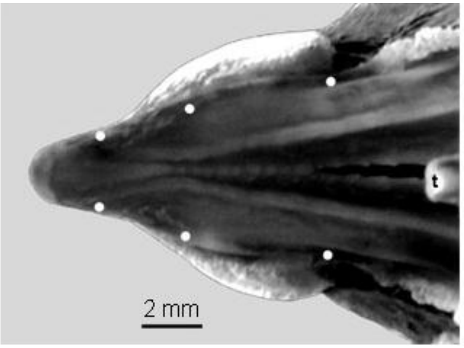
T. Ritz

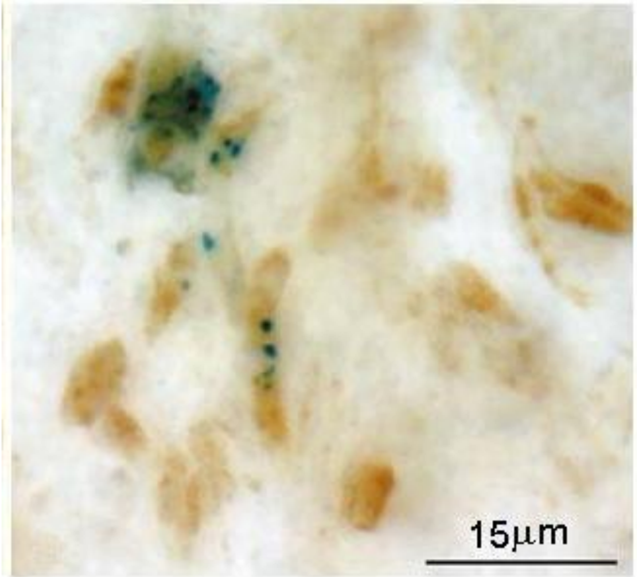
Magnetic Particles?



Magnetic (Magnetotactic) Bacteria

Magnetite-containing structures within neurofilaments in the skin of the upper beak of pigeons:



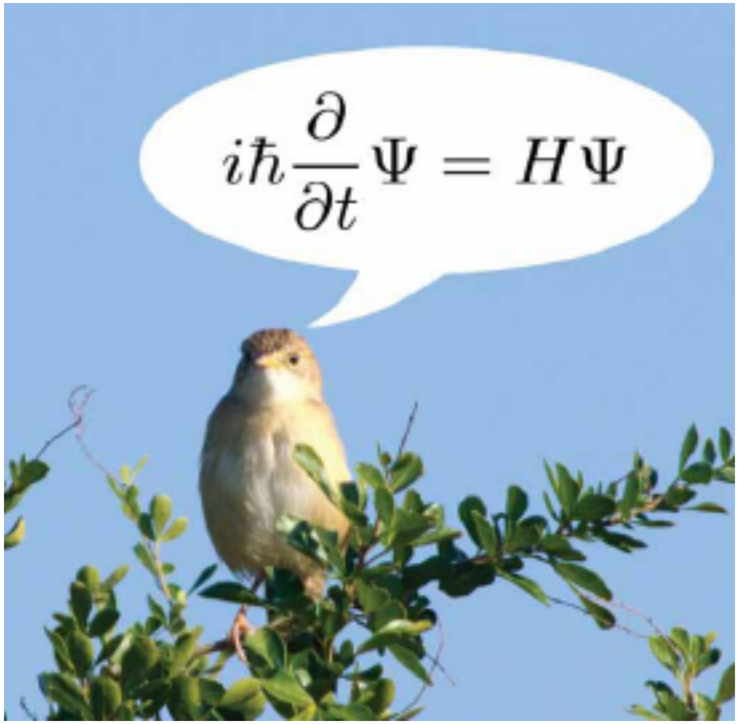


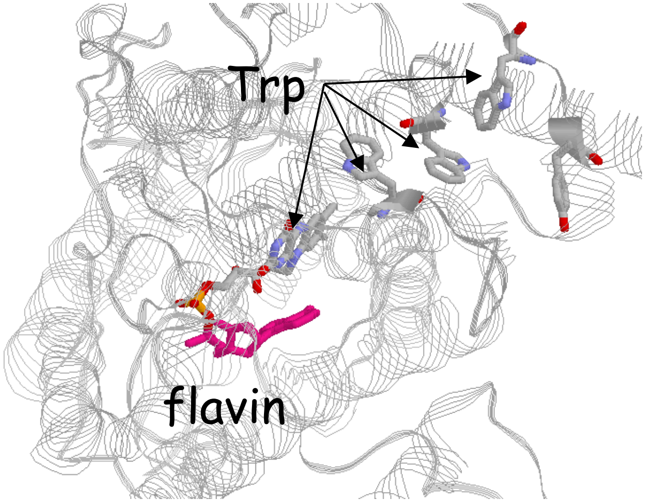
reconstruction based on histological sections:

(from Fleissner et al. 2003)

Quantum insights for Avian Compass:

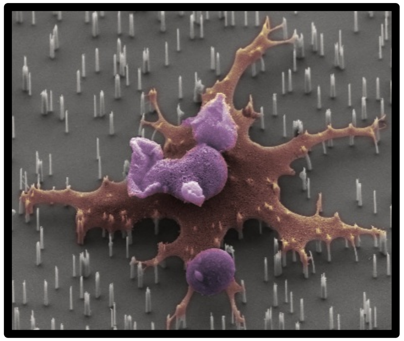
- Possible role of coherent dynamics of entangled electrons
- Needed - direct probe of coherence





Using tools of quantum science and nanotechnology to probe structure and dynamics of biological systems

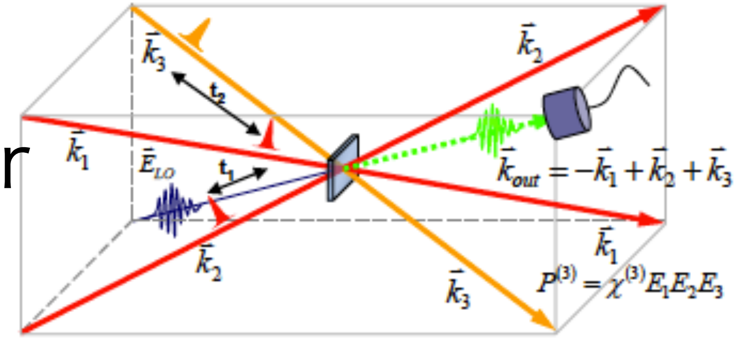
- Microscopic probes of living cells, cellular response, biochemical & electrical monitoring, biomolecule delivery…



Si nanorods offer cellular access: H. Park

NV centers: R. Walsworth, J. Wrachtrup, M. Lukin, H. Park, A. Jacoby....

- Ultrafast spectroscopy, quantum coherent control for electronic dynamics in biological systems



G. Fleming, G. Scholes, G. Engel, R. van Grondelle, N. van Hulst....