What Role does Quantum Mechanics play in Biology?

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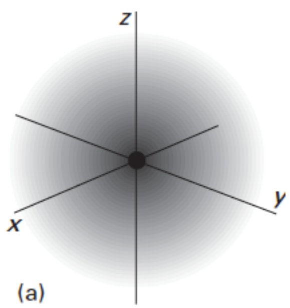
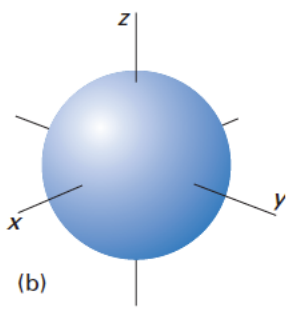
Overview

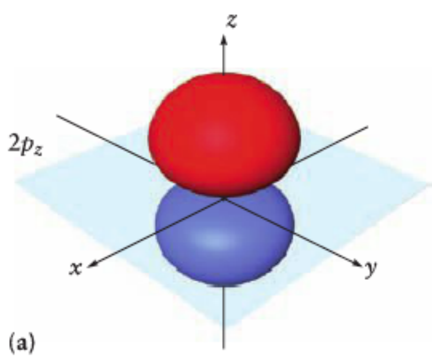
- Quantum biology – old roots and new shoots
- Quantum coherence in photosynthesis
- Implications for physics -quantum/classical transition?
- Implications for biology – functional role for coherence?
- Other quantum dynamical effects in biology
- Coherence and the evolution of photosynthesis...

- Outlook

A Paradigm Quantum System







- Electron in H atom (1s, 2p,…)

$$\left.\begin{matrix} \Psi \\ \\ |\Psi\rangle \end{matrix}\right\} \text{Quantum state}$$

$\psi(\vec{r})$ wavefunction

$$|\psi|^2(x) \equiv probability$$

$$\hat{H}(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$$

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)

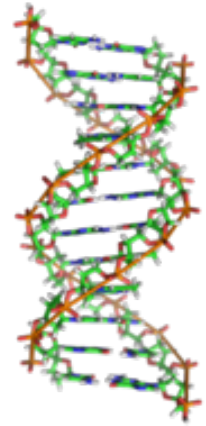
1935

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.)

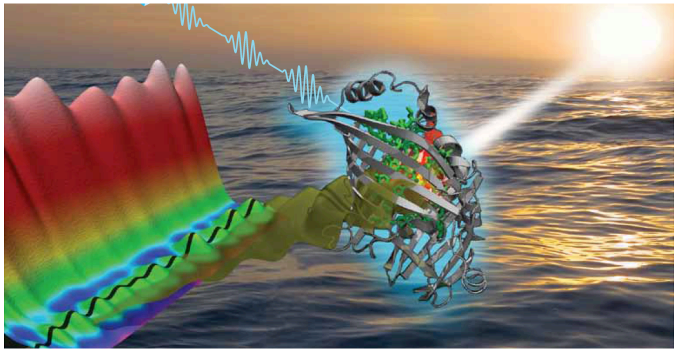
molecular structure and pathways, energetics, kinetics, stability – quantum nature of molecular energy levels, energy barriers… (Schrödinger *What is Life?* 1943)



DNA 1953

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

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



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.

Chemical/Molecular Biology

- molecules are quantum mechanical
  - energy levels, spin (fermi) statistics (essential!)
- chemical reaction rates
  - energy barriers and stability understood in terms of quantum analysis of molecular structure
  - tunneling through these can contribute to rates
- spectroscopy is quantum mechanical

All these features are manifest in biology

Schrödinger: no discussion of tunneling or coherence

1914 Marcelin: potential energy surface for chemical reactions
1926 Schrödinger: wave mechanics
1927 Heisenberg, Dirac: resonance/exchange phenomena
1927 Heitler-London: quantum mechanical theory of chemical bond
1927 Born-Oppenheimer: structure of molecular energy levels
1927 Hund
1928 Mulliken
molecular orbital theory
1928 Gamow: alpha particle tunneling
1933 Journal of Chemical Physics established
1933 Bell: hydrogen tunneling in chemical reactions
1935 Einstein-Podolsky-Rosen: non-local quantum correlations
1935 Schrödinger: identifies entanglement (Verschränkung) as "*the characteristic trait of quantum mechanics*"
1935 Delbrück et al.: mutation and genetic structure
1935 Eyring, Evans-Polanyi: quantum statistical theory of chemical reaction rates (precursors - Marcelin, Rice, Herzfeld, Tolman…)
1943 Schrödinger: "What is Life" lectures

Quantum behaviors…

- Quantized energies (eigenenergies)
- Discrete absorption of light
- Wave like behavior of quantum states (eigenstates)
- Superposition – coherences
- Interference (double slit)
- Multiple particles – entanglement

non-local quantum correlations

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

Quantum mechanics and biology today:

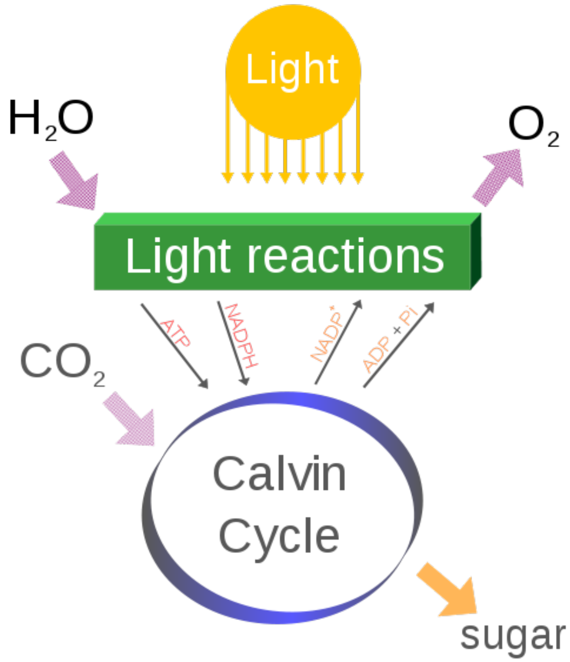
Solvay Congress 2010

Potential Quantum Dynamical Processes in Biology

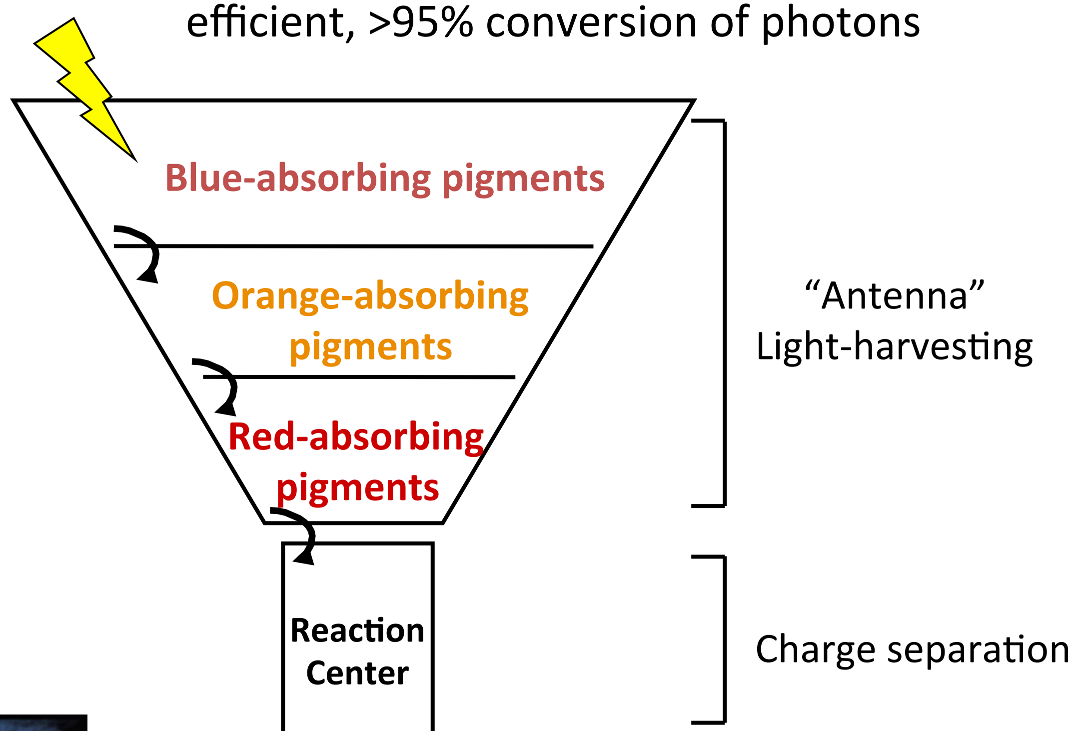
	Excited States	Light Particles	Radical Pairs
Biological Phenomena	Primary steps in photosynthesis Vision	Enzyme catalysis Photosynthesis	Bird navigation
Quantum Processes	Energy transfer Electron transfer Isomermization	Long-range electron tunneling H atom transfer Proton-coupled electron transfer	Reactions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

DARPA: Quantum Effects in Biological Environments

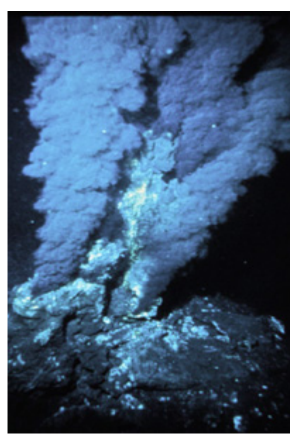
Photosynthesis



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…

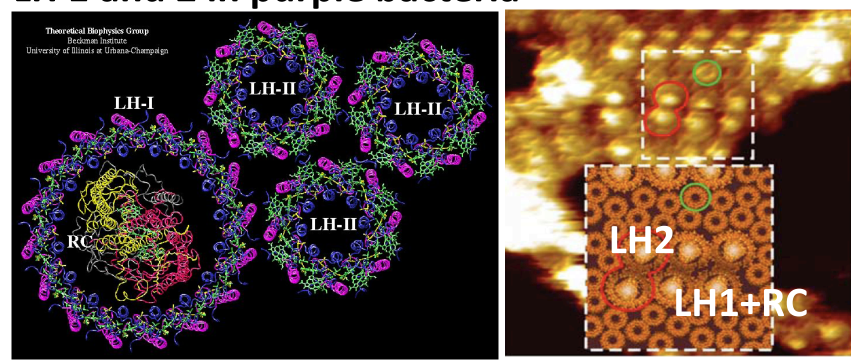
Light Harvesting Complexes

- A bewildering variety of antennae

- All composed of densely packed chromophores (pigments, visible light absorbing molecules)

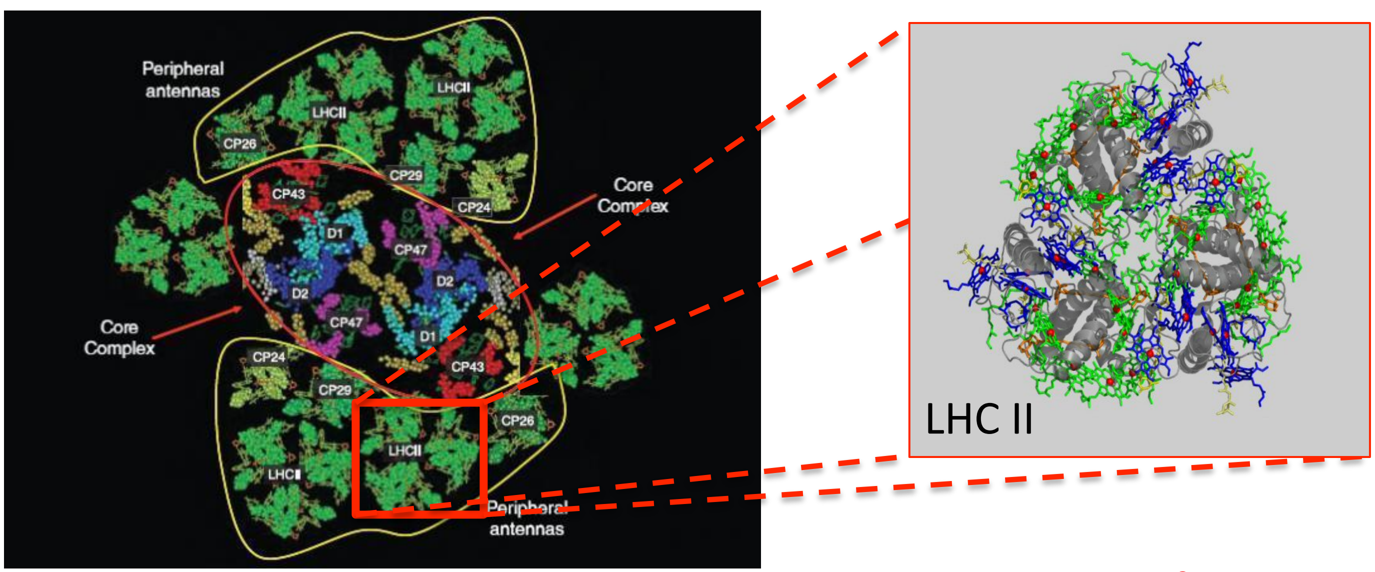
- The molecular aggregates are often but not always embedded in protein scaffolds

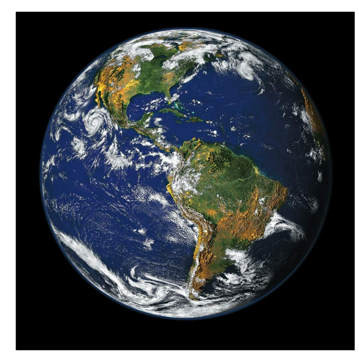
LH 1 and 2 in purple bacteria



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

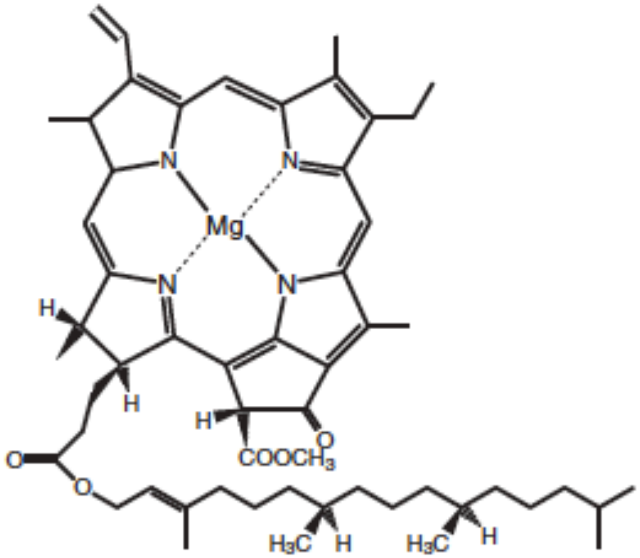
PS II of higher plants, blue-green algae, cyanobacteria





50% of green matter on earth uses PS II

Light absorption by Chlorophyll molecules:



chlorophyll *a*

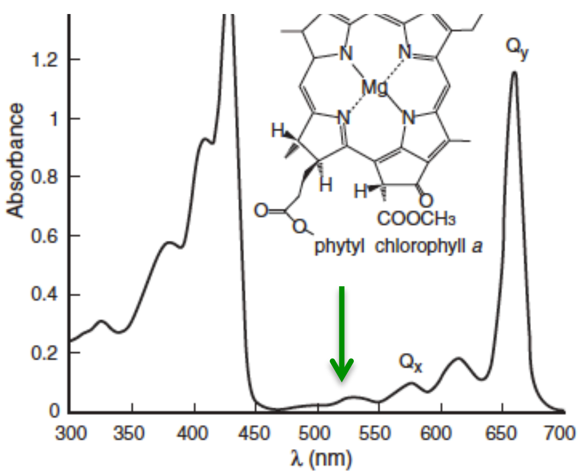
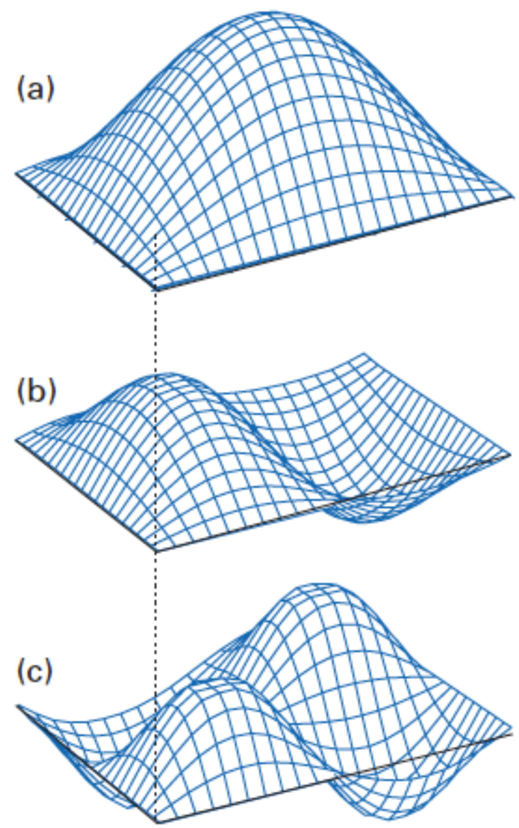
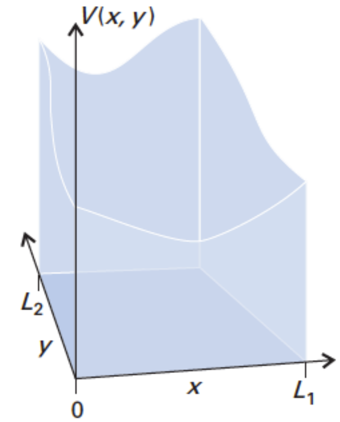


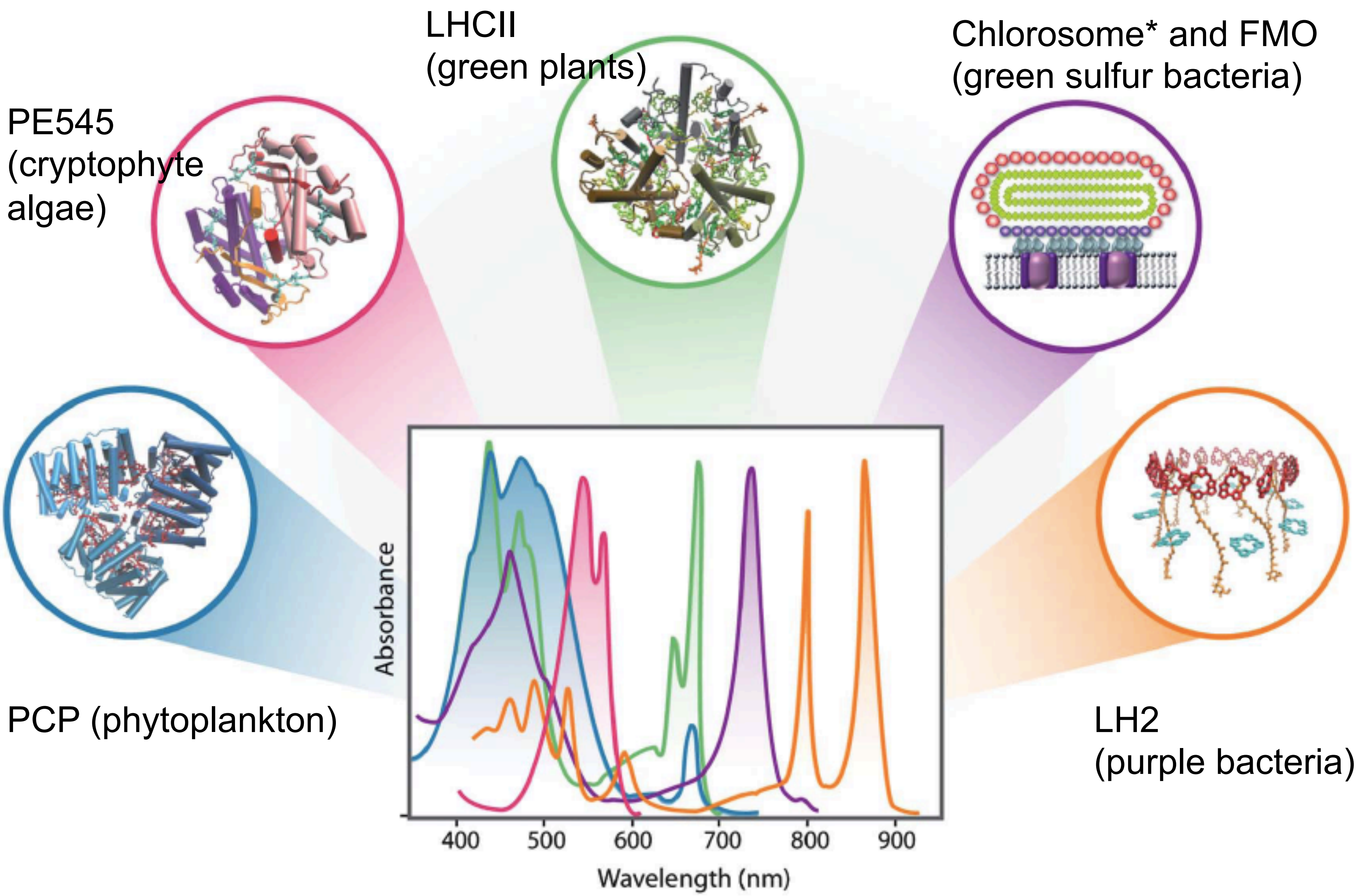
Figure 4.6 Absorption (left) and fluorescence (right) spectra of chloro



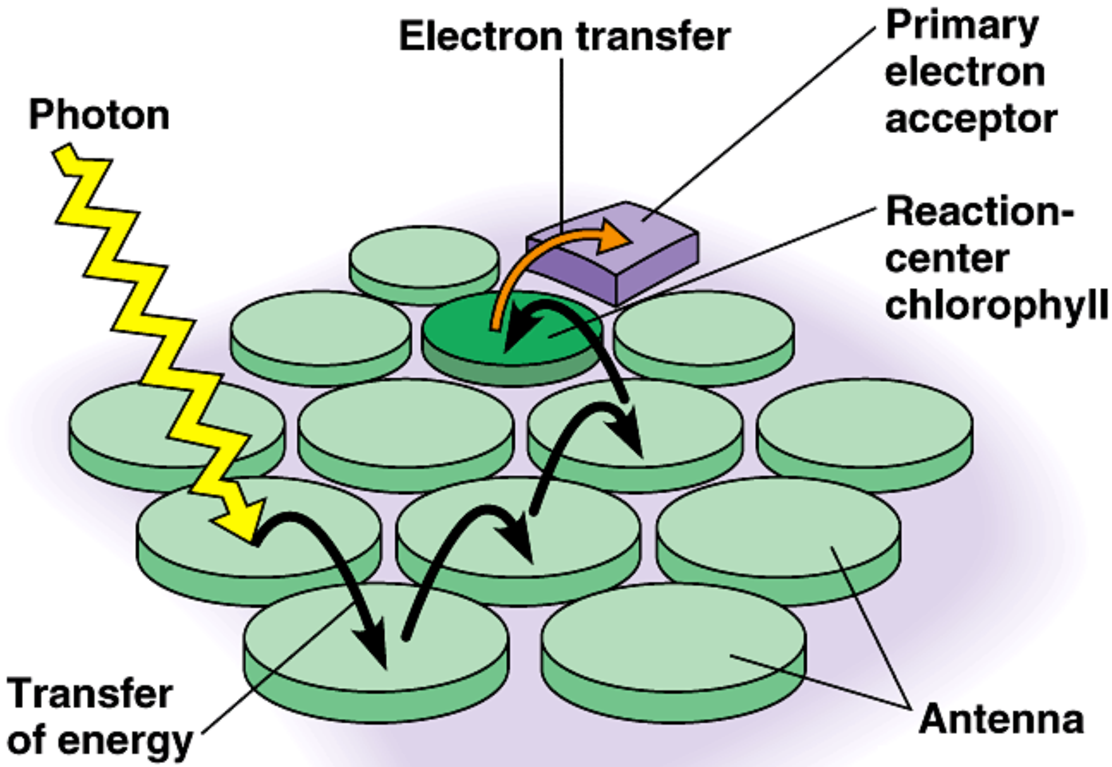


2D particle in box quantum model - rationalize spectral lines

Antenna Structures: pigment-protein complexes



Photosynthetic Light Harvesting

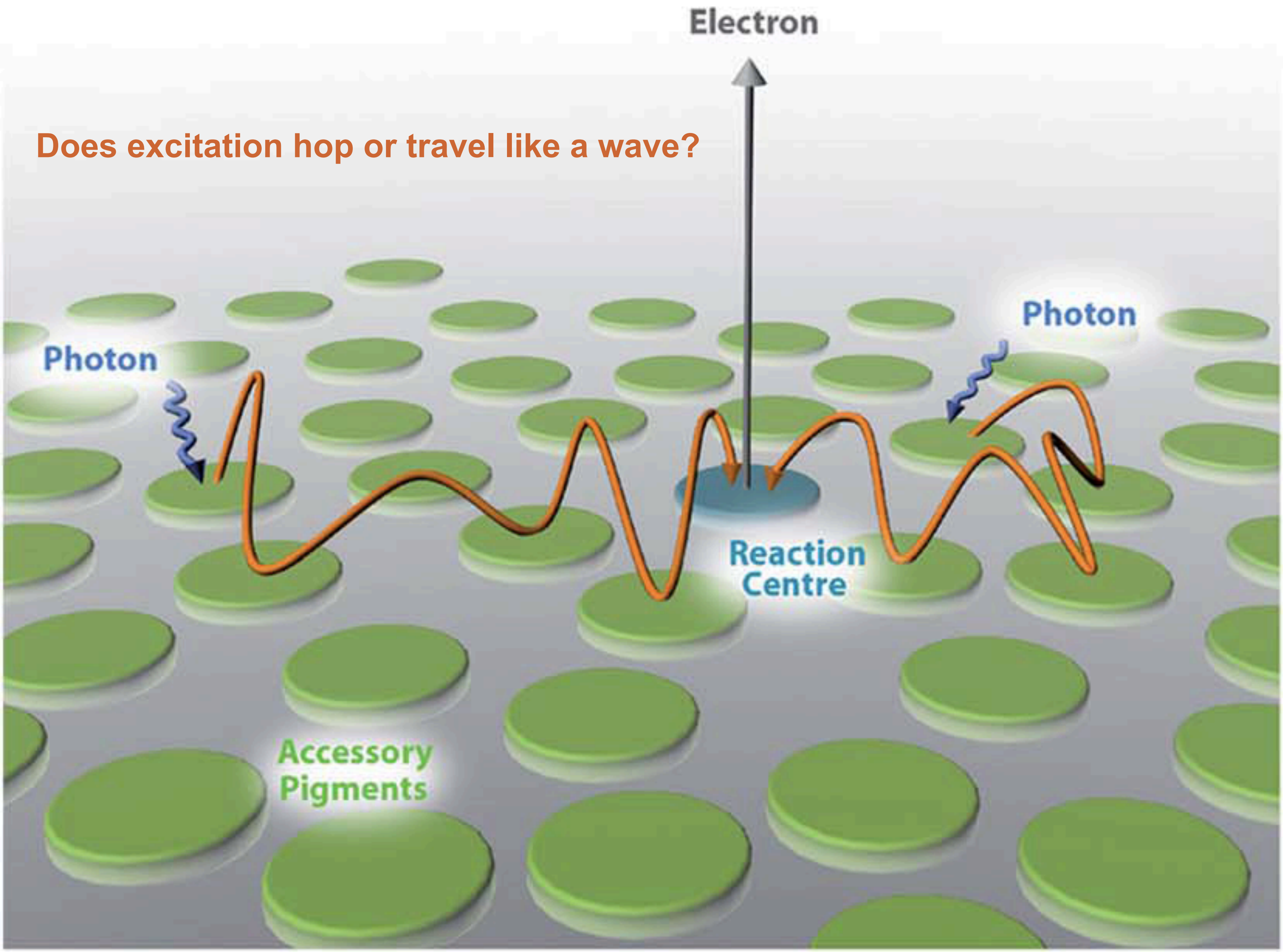


at low light intensity

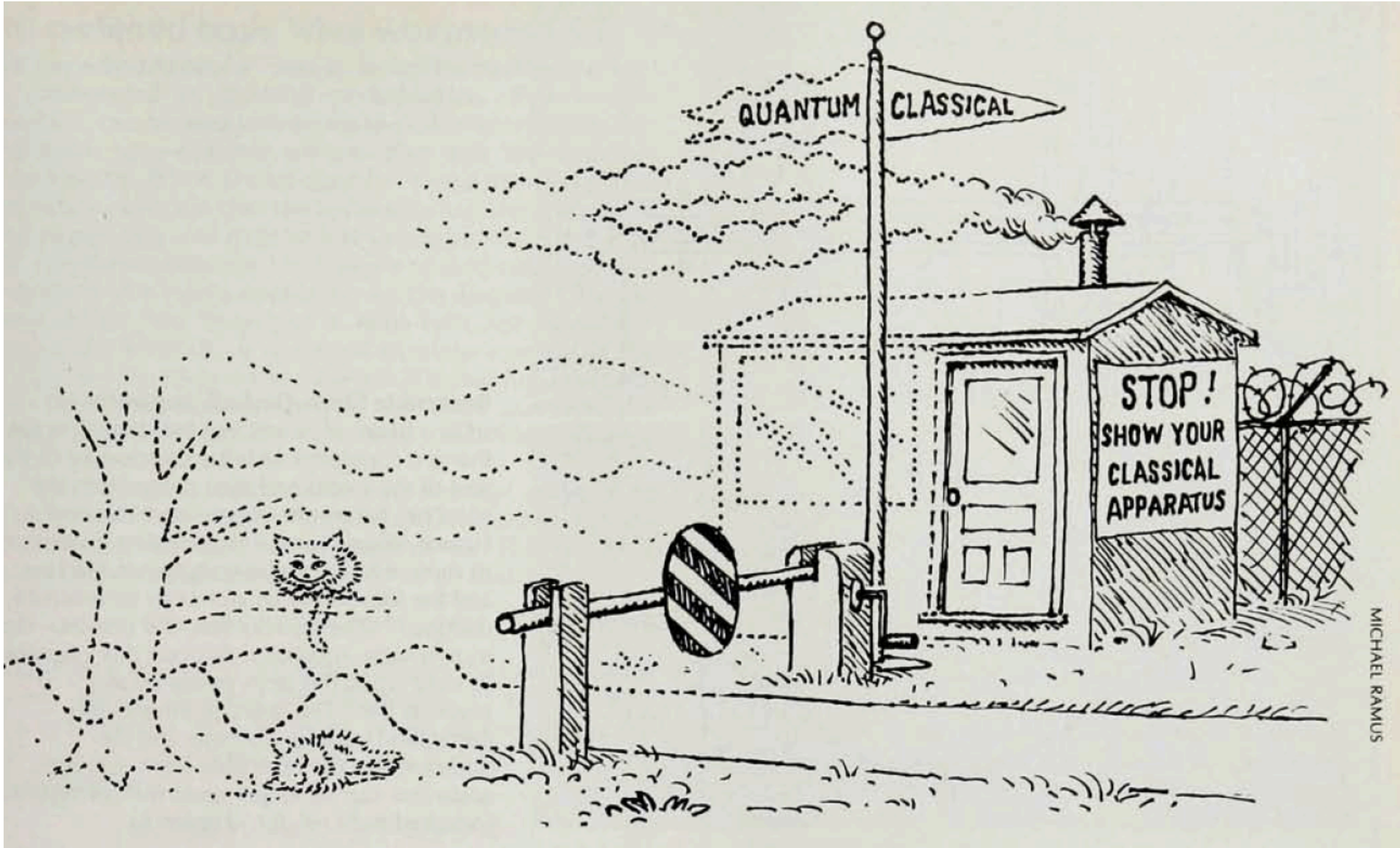
quantum yield ~ 100%

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

Does excitation hop or travel like a wave?



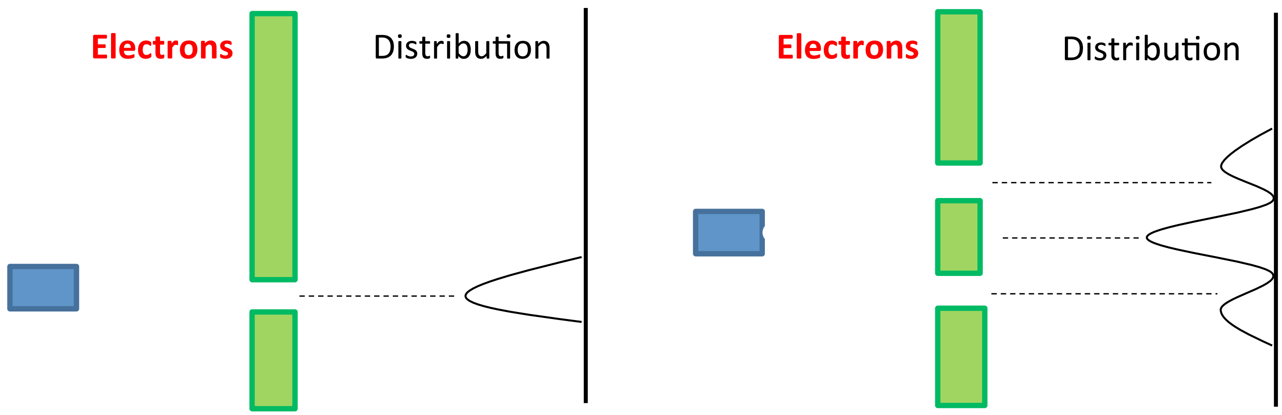
Quantum vs Classical ?



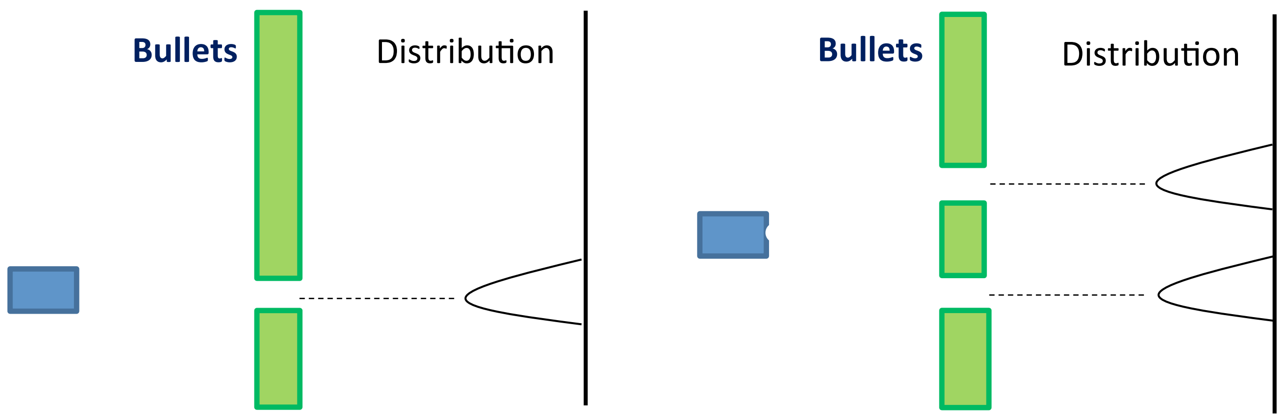
Delineating the border between the quantum realm ruled by the Schrödinger equation and the classical realm ruled by Newton's laws is one of the unresolved problems of physics.

W. H. Zurek, Physics Today, Oct. 1991

Quantum wave superposition



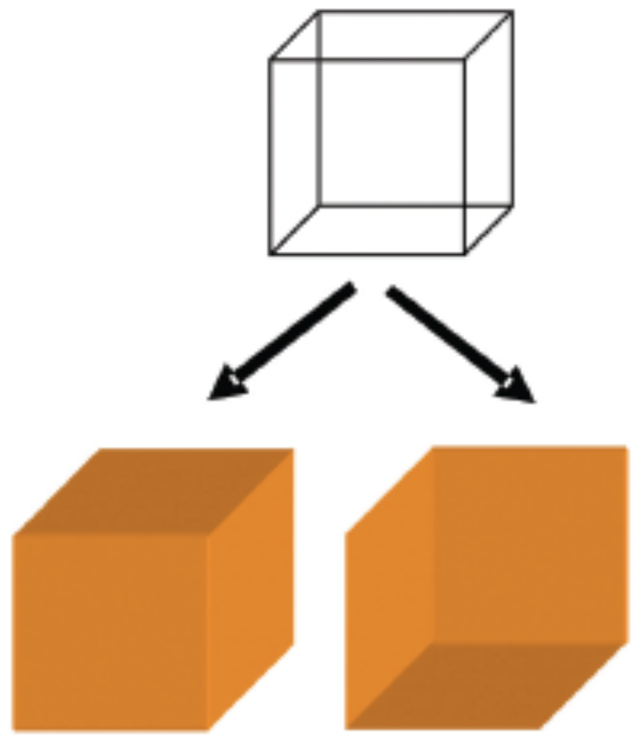
Boundary between quantum and classical



Classical addition

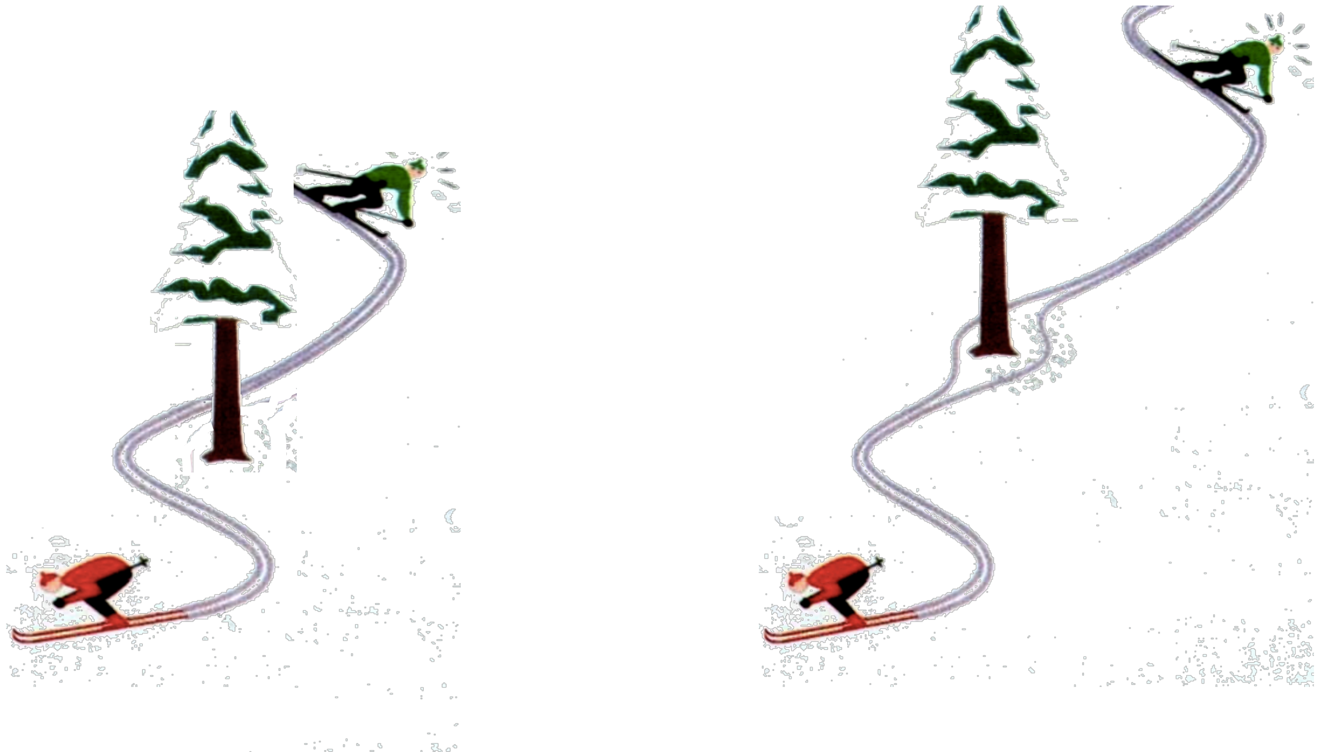
Quantum superposition:

visual representation with ambiguous cube



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

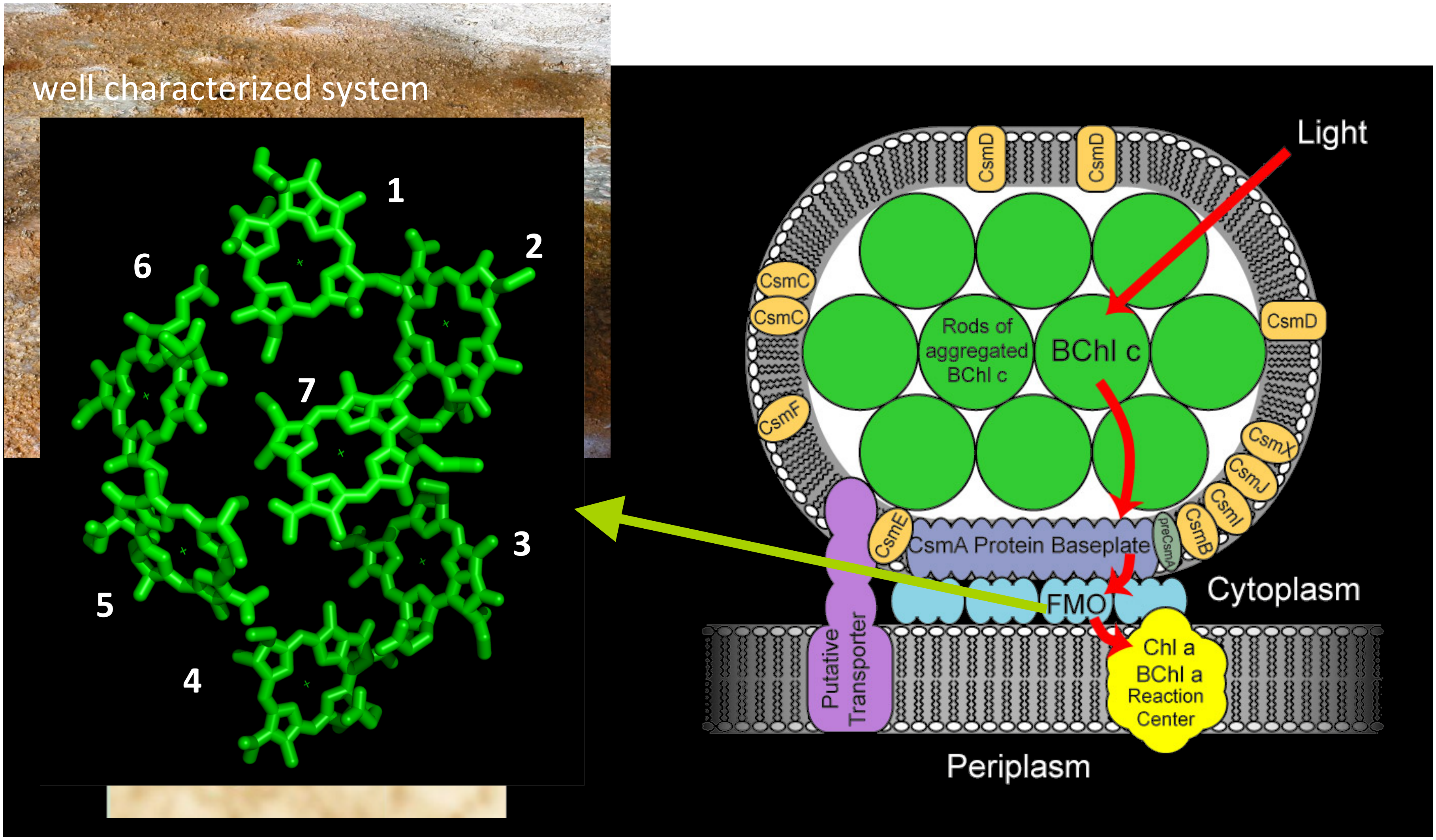
What limits quantum superpositions?



- Size? Complexity? Other?
- Boundary between classical and quantum
- Fundamental implications for nature of reality

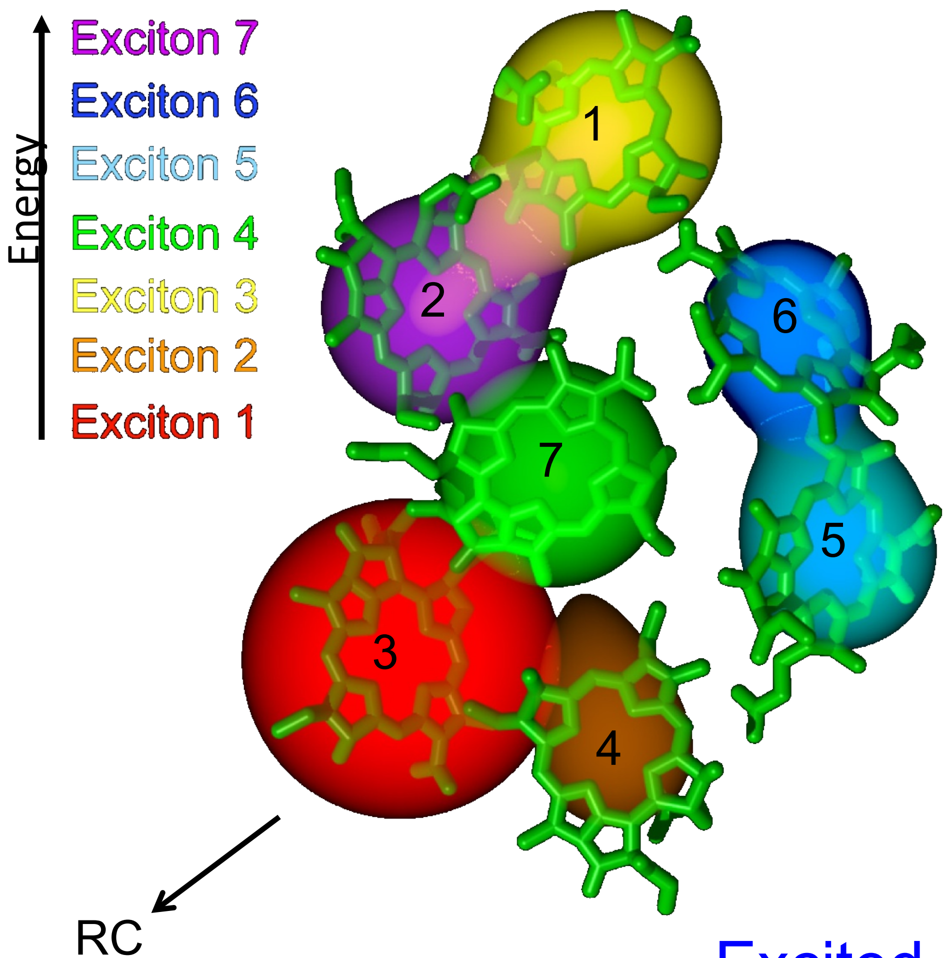
Light harvesting apparatus of green sulfur bacteria

FMO: energy 'wire' connecting chlorosome to reaction center



James Allen *et al.*, Photosynth. Res., **75**, 49 (2003)

Electronic excited states in FMO

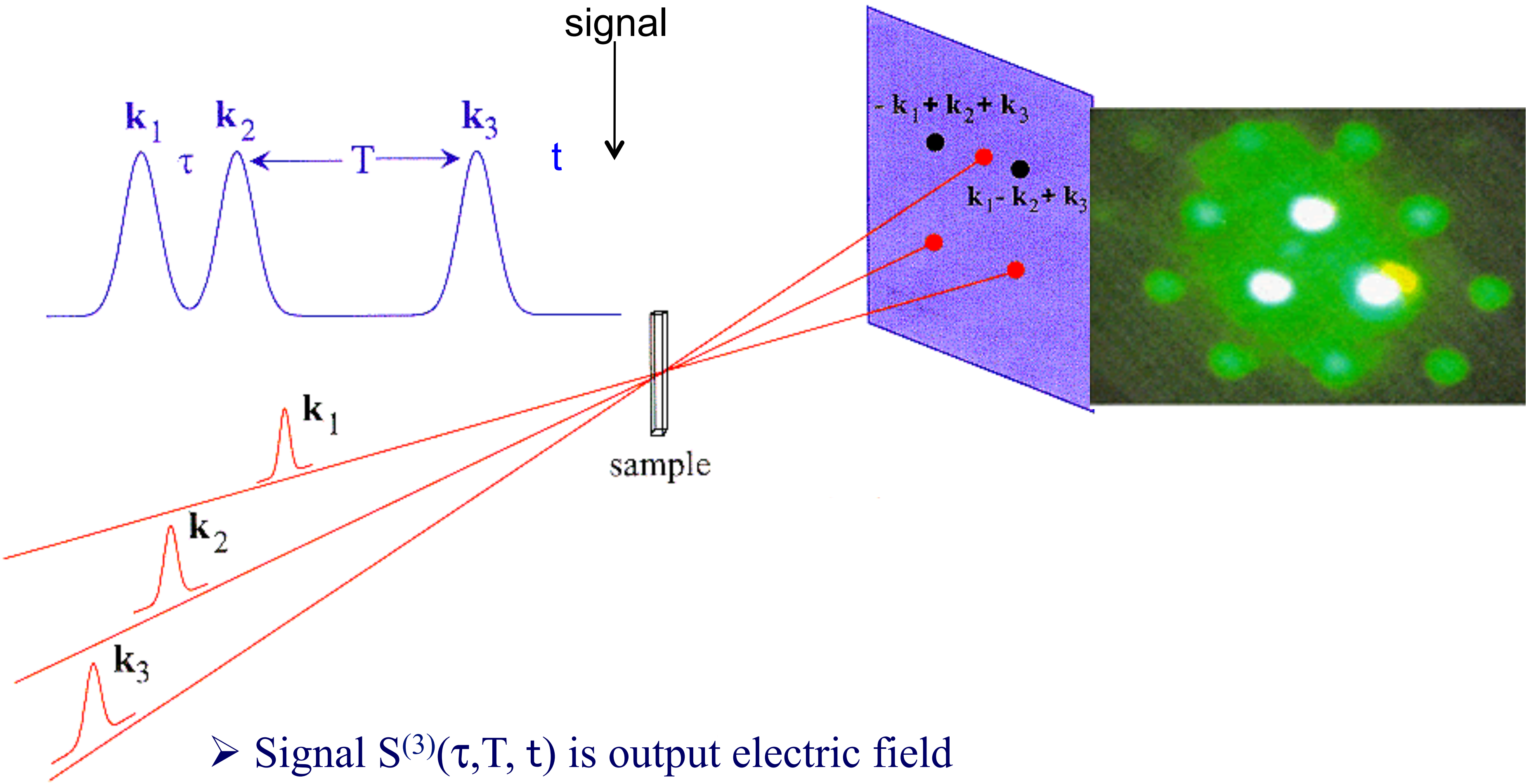


Optical transitions to delocalized excited states of electrons = **excitons**

- Mostly delocalized on two BChls
- Lowest energy exciton sits on BChl 3
- Electronic energy is transferred through FMO to the RC within a few ps

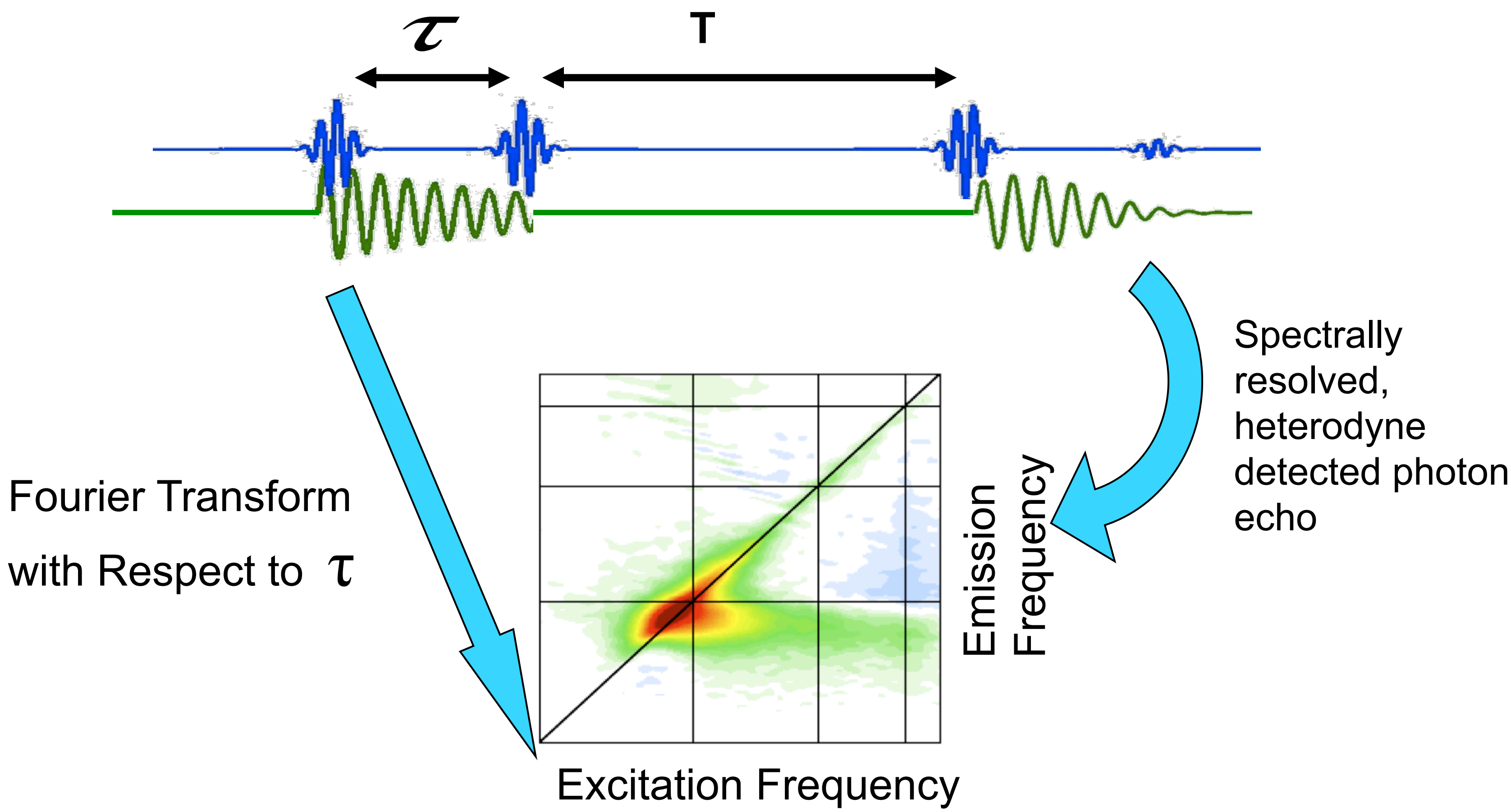
Excited electronic states delocalized over multiple molecules - what consequence for **dynamics and function**?

2D Femtosecond spectroscopy



- Signal $S^{(3)}(\tau,T, t)$ is output electric field
- Obtain $S^{(3)}(w_1,T, w_3)$ by double Fourier Transformations in τ and t
- Retrieves correlation between absorption and emission frequencies
- Echo technique can remove inhomogeneous broadening

2D Electronic Correlation Spectrum

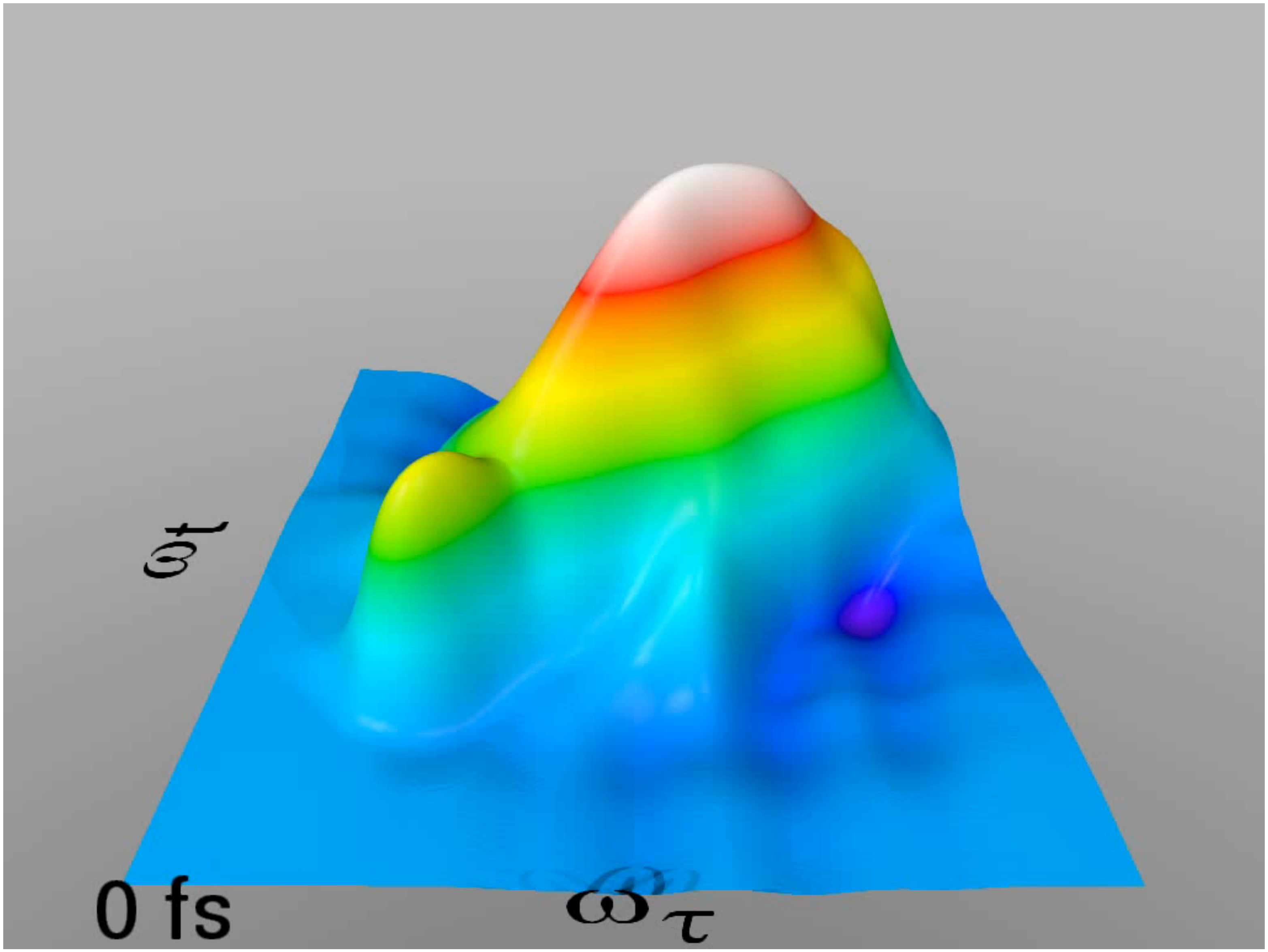


A 2D spectrum is a correlation map between the initial and final excitations and coherences

The correlation depends on the processes occurring during time T

Chlorobium tepidum FMO:

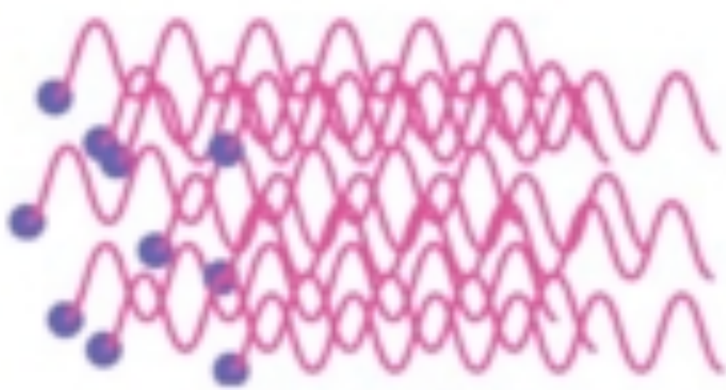
2D fsec spectra



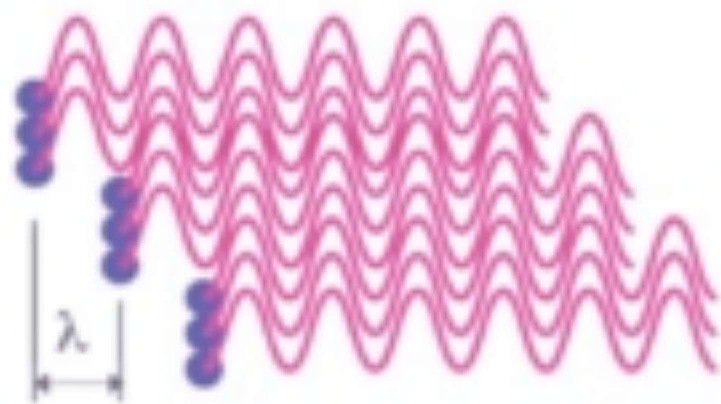
Fleming et al.
2007

What is coherence?

All together now!
Pedalling in step

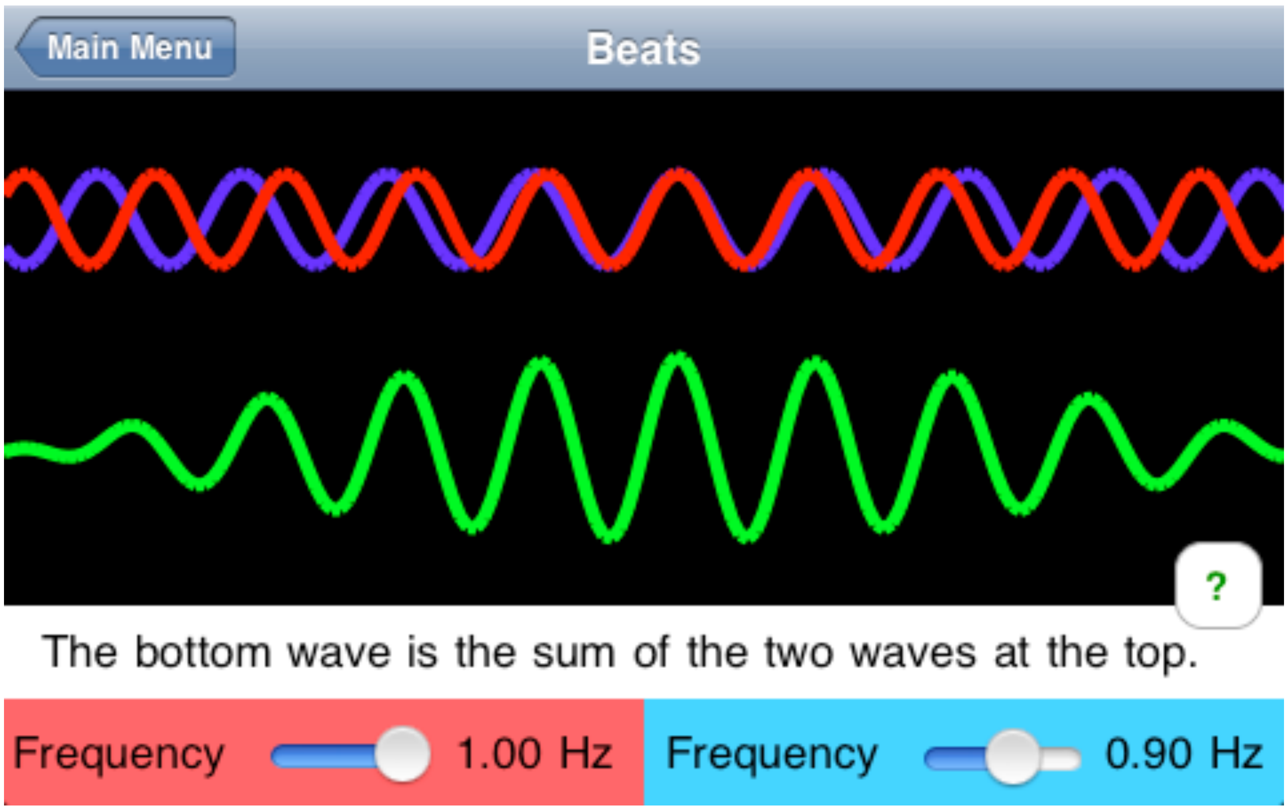


Incoherent waves



Coherent waves

Coherent addition of waves of different frequencies gives beats

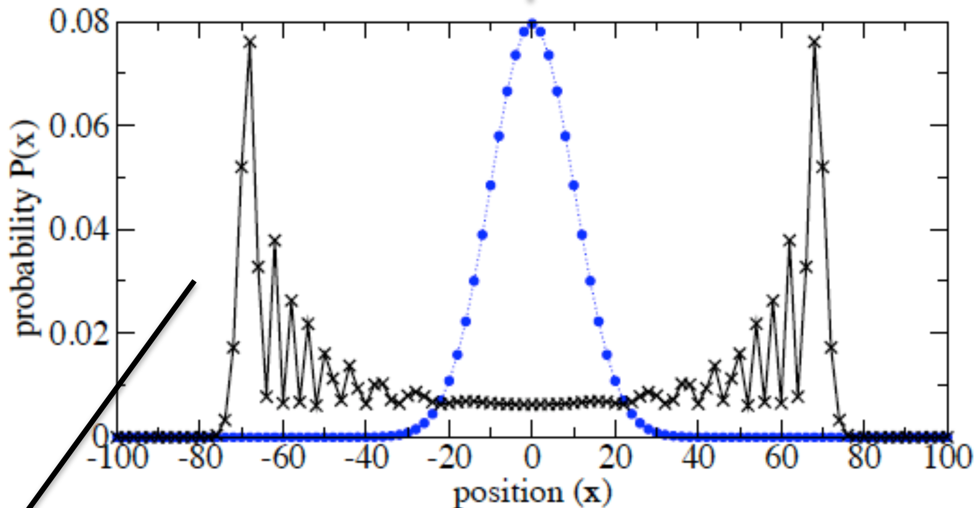


interference phenomenon

hopping versus wave motion

Drunken sailor moving in a straight line, randomly hopping left/right

diffusive motion $\langle x^2(t) \rangle \propto t$



Wave spreading out from origin and reflecting from walls

coherent motion, interference possible $\langle x^2(t) \rangle \propto t^2$

Quantum speedup - makes search algorithms more efficient

Shenvi et al. 2003

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)

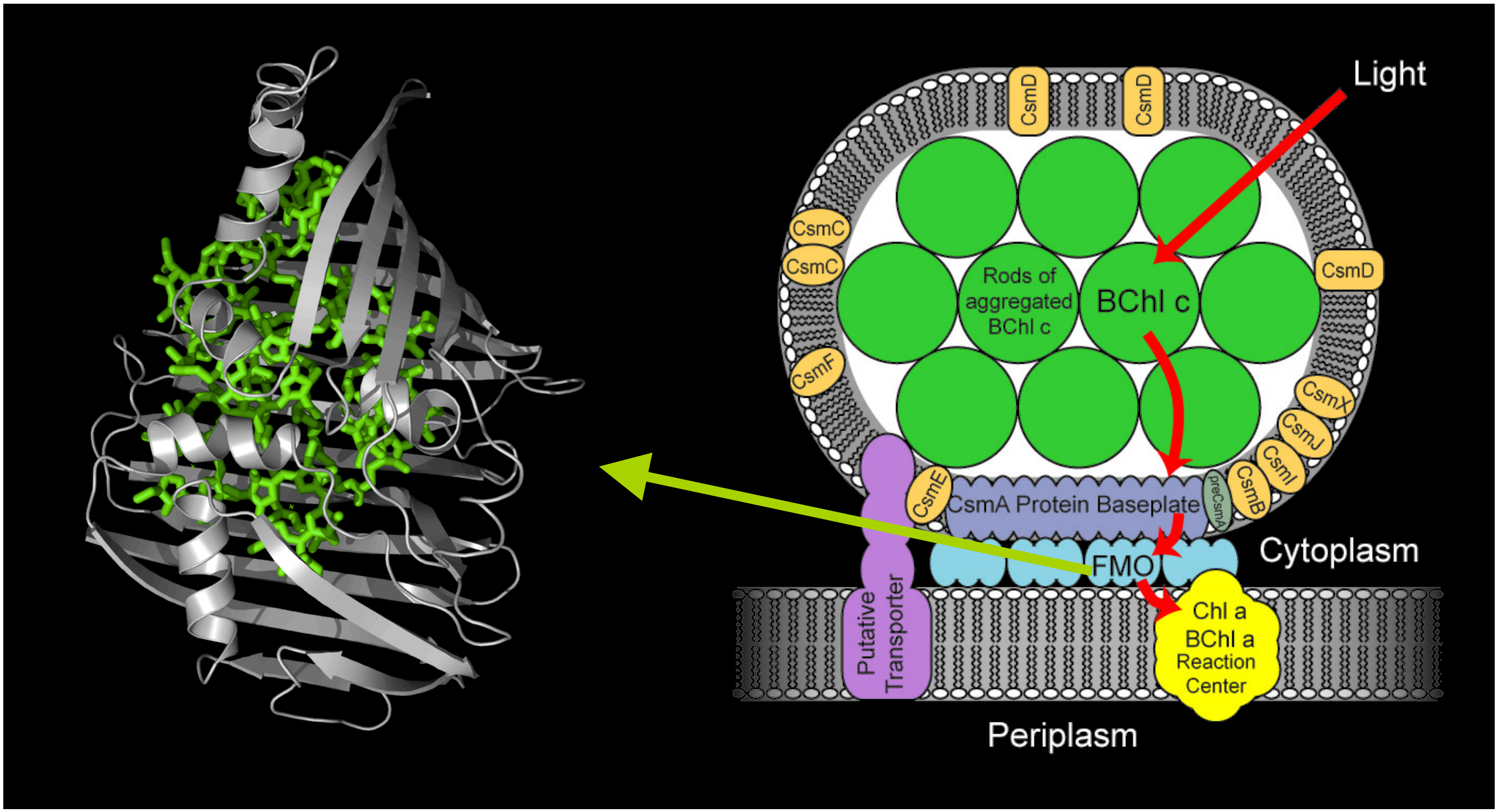
When It Comes to Photosynthes
Computation

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

Scientific American, April, 2007

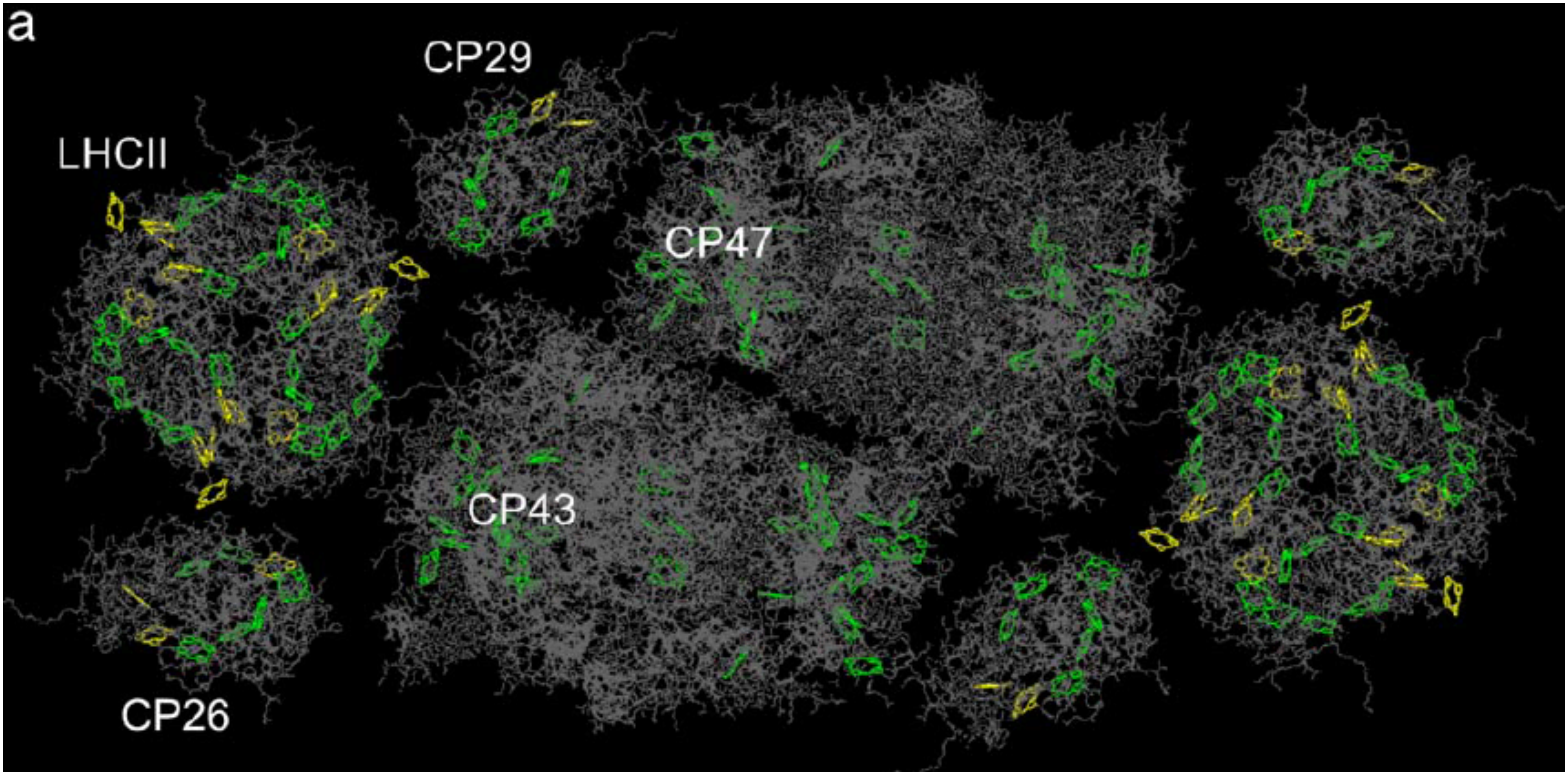
Light harvesting apparatus of green sulfur bacteria

FMO: energy 'wire' of chlorophyll embedded in protein scaffold

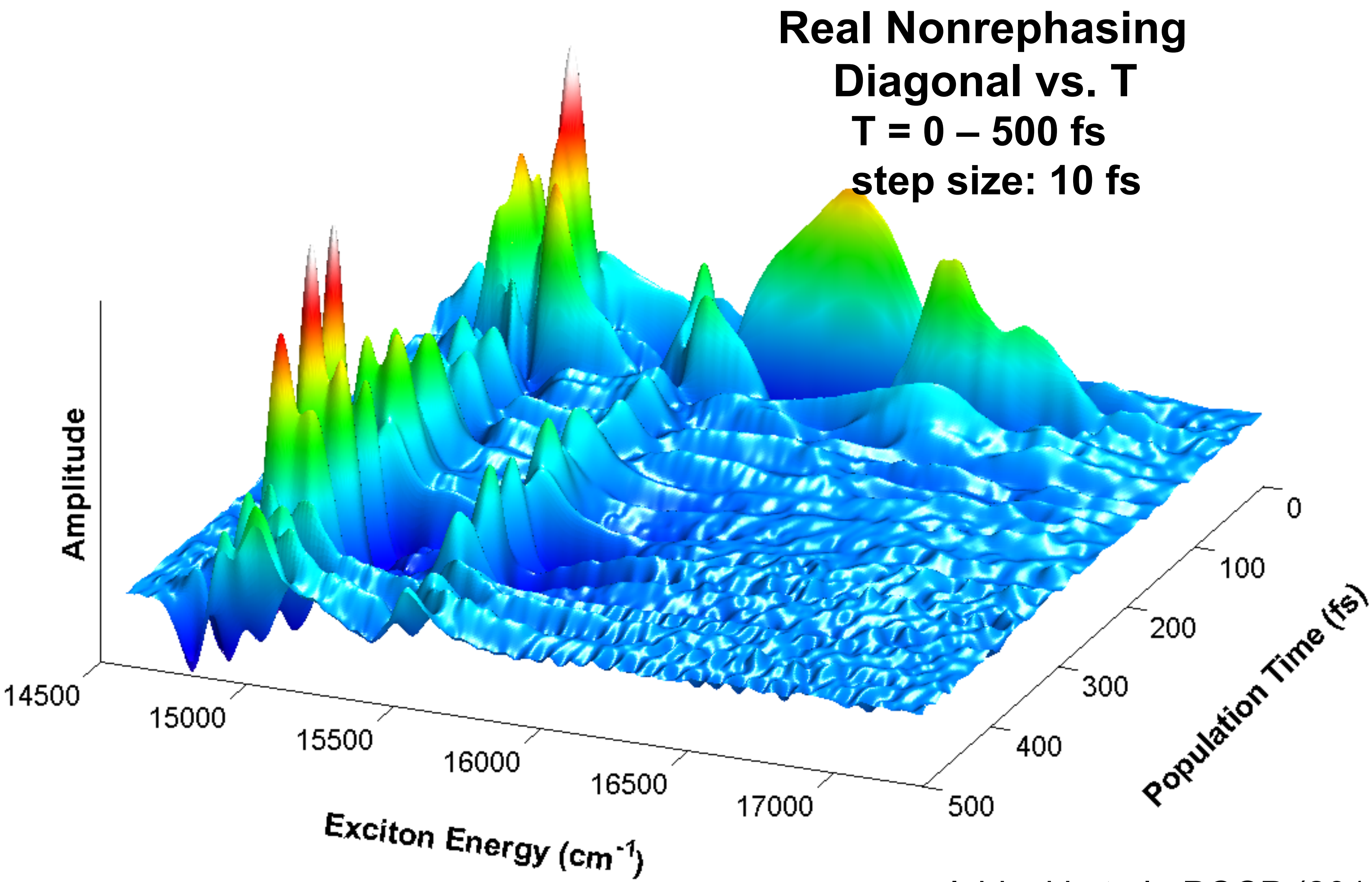


James Allen *et al.*, Photosynth. Res., **75**, 49 (2003)

Photosystem II – green plants



LHCII Excitonic Coherence



Ishizaki et al., PCCP (2010)

Natural Light Harvesting Systems: experimental evidence for quantum coherence effects

Green sulfur bacteria

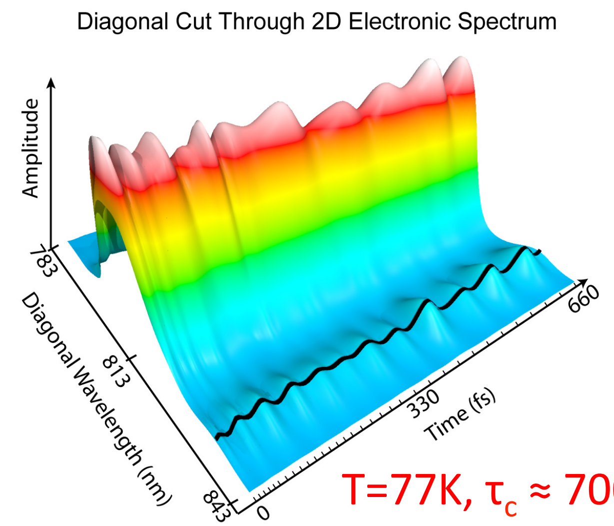
FMO (dynamics):

Engel et al., Nature, **446**, 782 (2007) (T=77K)

Engel et al., PNAS 107, 12766 (2010) (T=277K)

Chlorosome (exciton dephasing times):

Prokhorenko et al., Biophys. J. **79**, 2105 (2000)



T=77K, $\tau_c \approx 700$ fs

Marine algae – phycobiliproteins

Collini et al., Nature, **463**, 644 (2010) (T=294K);

Womick et al., JCP **133**, 024507 (2010)

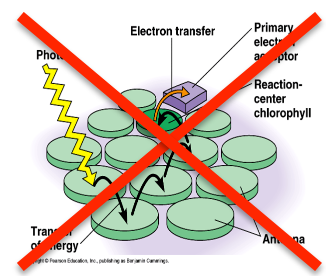
Purple bacteria

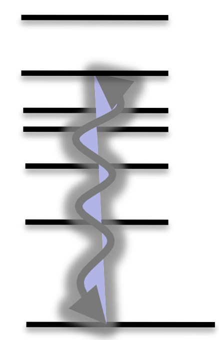
LH1/LH2 (static, dynamics):

Many studies – e.g: Monshouwer et al., Chem. Phys. Lett. **246**, 341 (1995); van Oijen et al., Science **285** 400 (1999)

Reaction center (dynamics):

Lee et al., Science, **316,** 1462 (2007)





Higher plants

LHC-II (dynamics):

Calhoun et al., J. Phys. Chem. B, **113**, 16291 (2009)

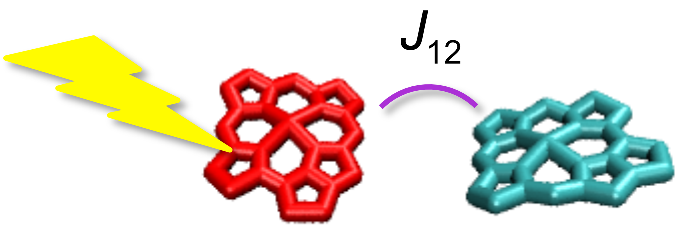
Features we usually associate with manifestations of quantum:

- Simple not complex systems
- Isolation, no environment
- Low temperatures
- but – biological systems are warm, wet, not isolated and manifestly complex…

What is the system and what is the environment?

- Conventional view:
  - Excitations = system
  - Protein = environment
- time scale for decoherence?
- what if environment has memory?
- what about intramolecular modes?
- correlated protein vibrations?
- non-adiabatic electronic/vibrational effects?
- need to revise conventional view…

Coupled pigment-protein dynamics:



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

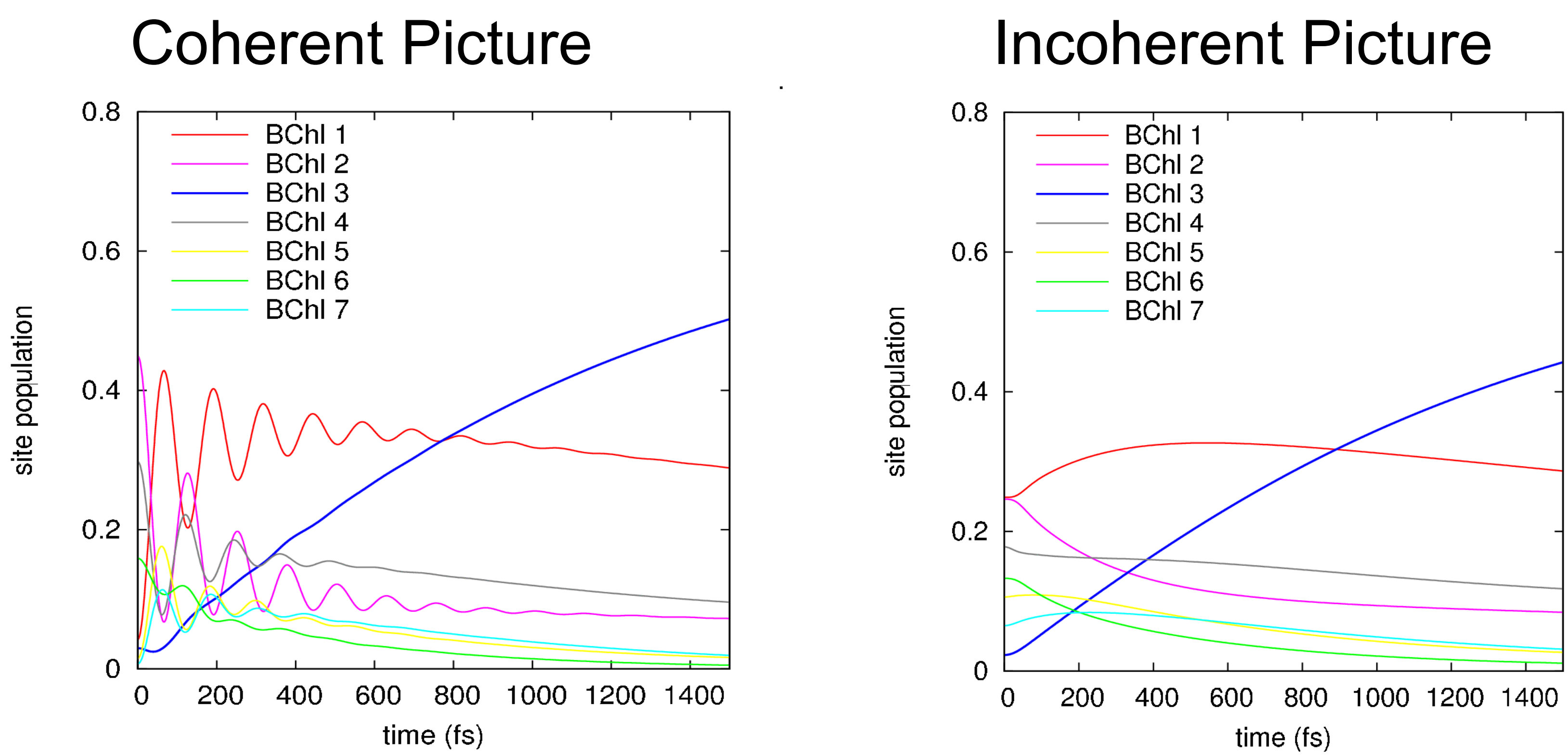
4 similar energy scales:

- 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…

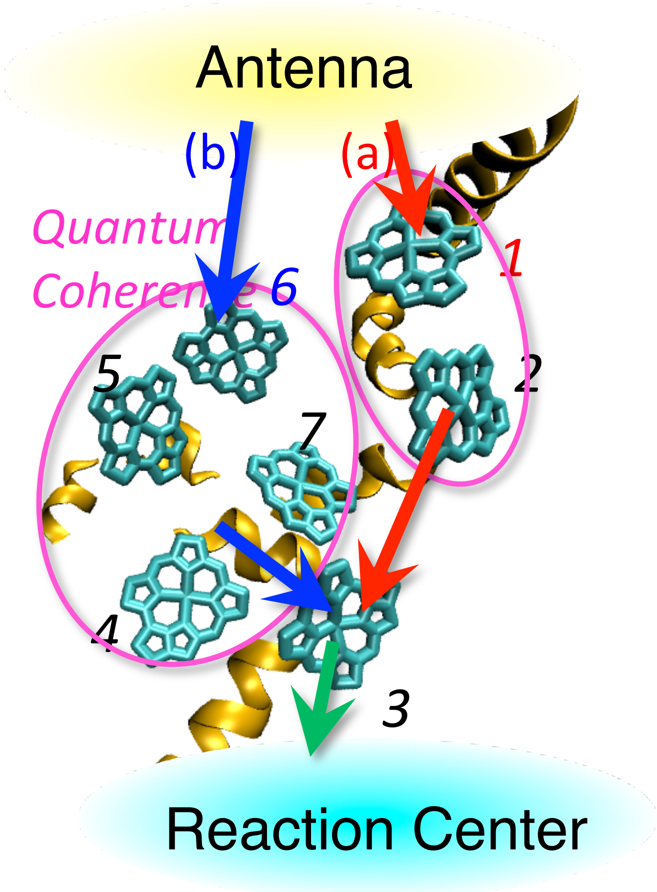
Coherent vs Incoherent Dynamics in the Site Basis

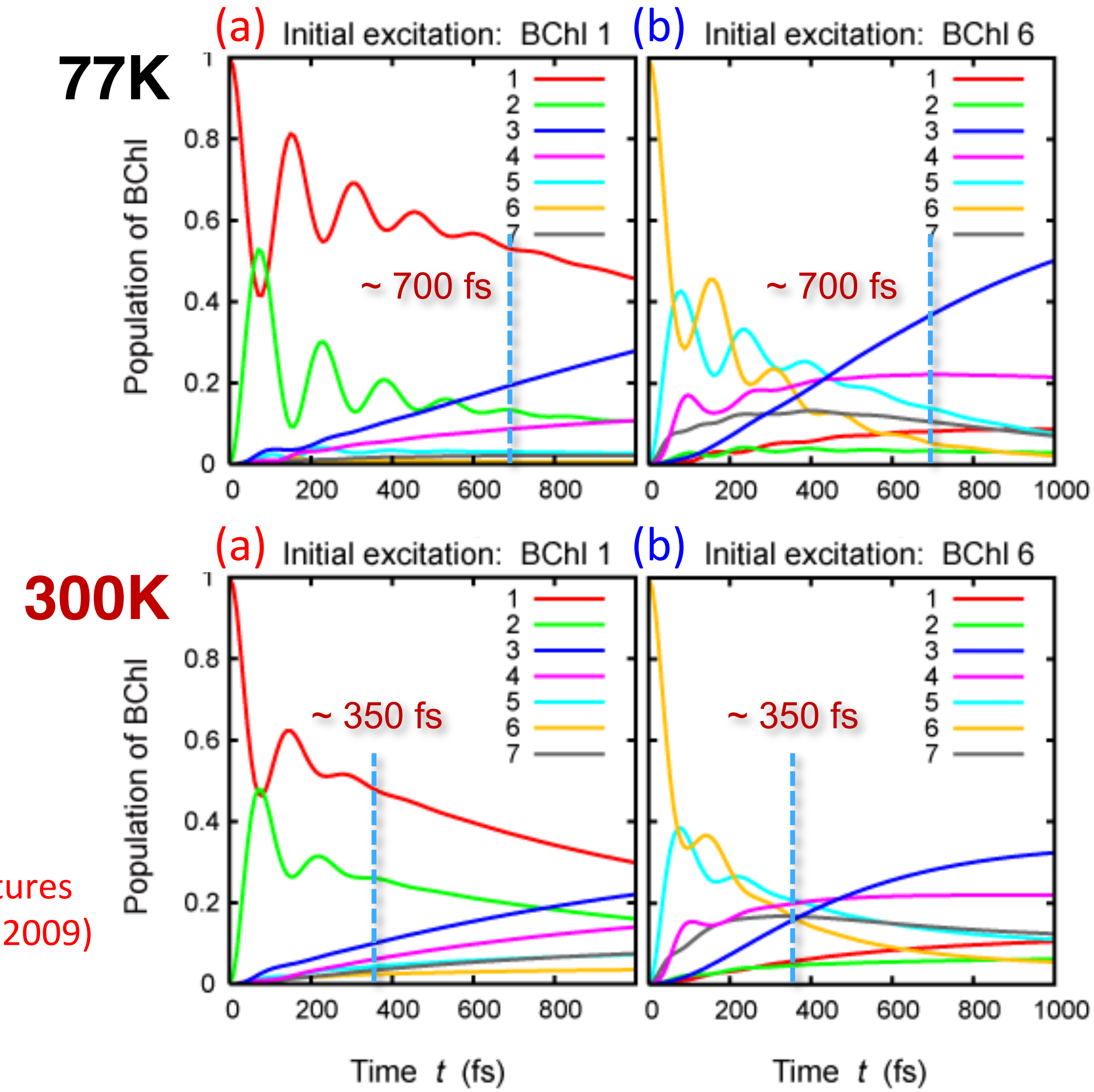
E. Read, Y. C. Cheng (Fleming group)



population redistribution in space shows interference effects due to coherence

2CTNL simulations of EET for FMO:

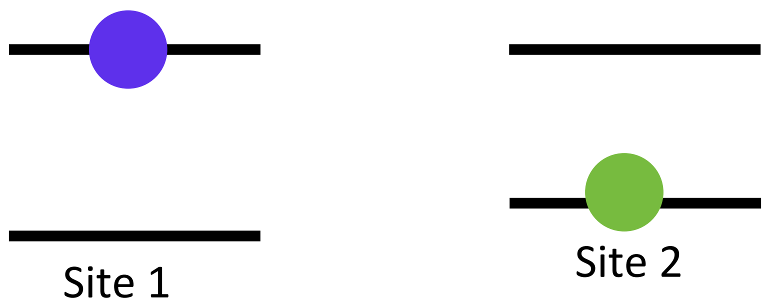




Coherences at physiological temperatures
Ishizaki & Fleming, PNAS 106, 17255 (2009)
Confirmed by experiments at 277 K
Engel et al. PNAS 107, 12766 (2010)

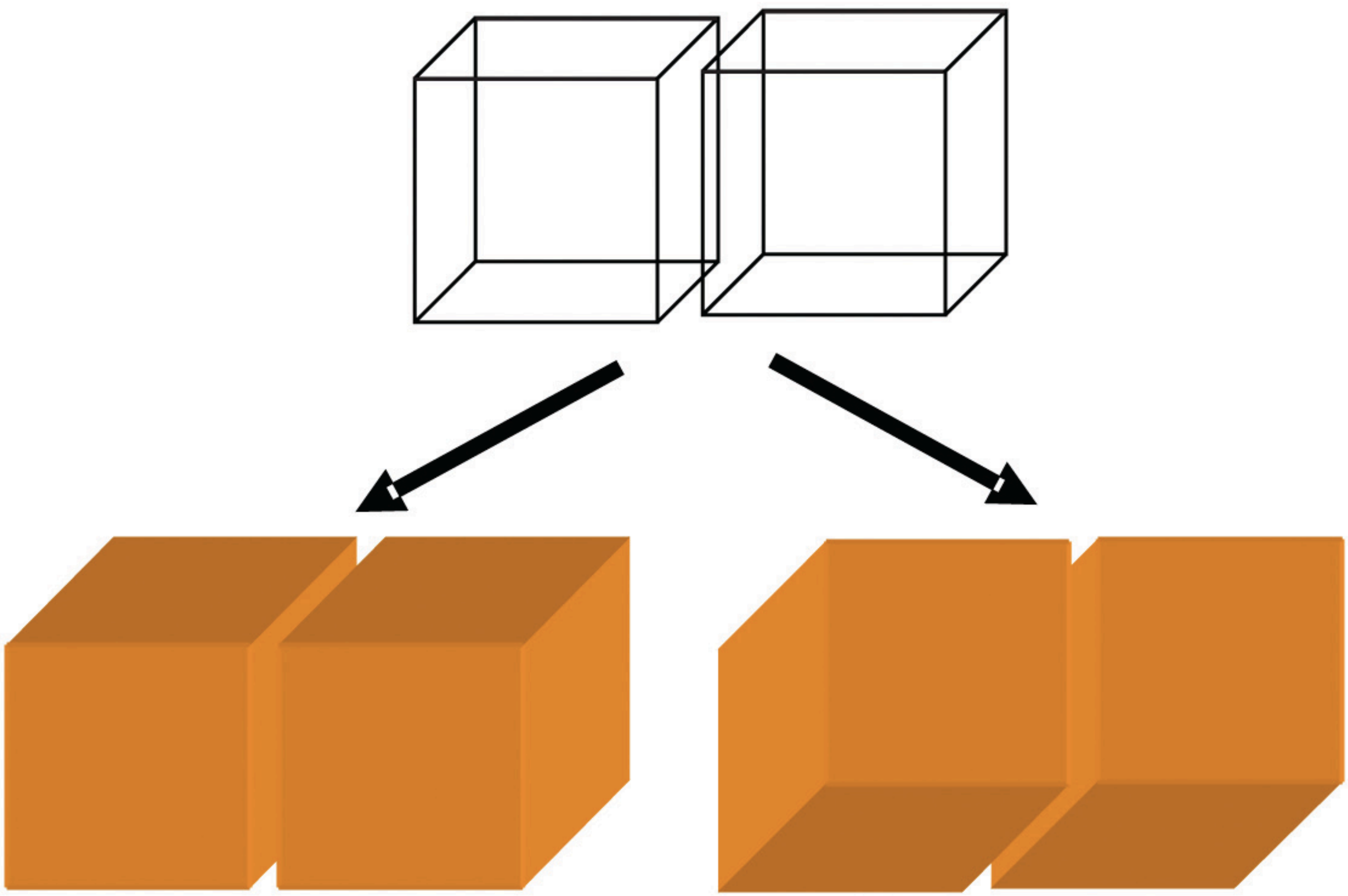
Electronic entanglement

Non-local quantum correlations between molecular electronic states



$$|\psi\rangle \equiv |g\rangle_1|e\rangle_2 + |e\rangle_1|g\rangle_2$$

Entanglement analog with ambiguous cube:
perceive orientational correlations between boxes



Electronic entanglement in Light Harvesting Systems:

M. Sarovar, A. Ishizaki,
G. R. Fleming, KBW,
Nature Physics **6**, 462 (2010)

- FMO studies (7 chromophores)
- global and bipartite entanglement
- significant entanglement for long times.
- “Long-range” across complex (~28 Å)
- many subsequent related theoretical studies

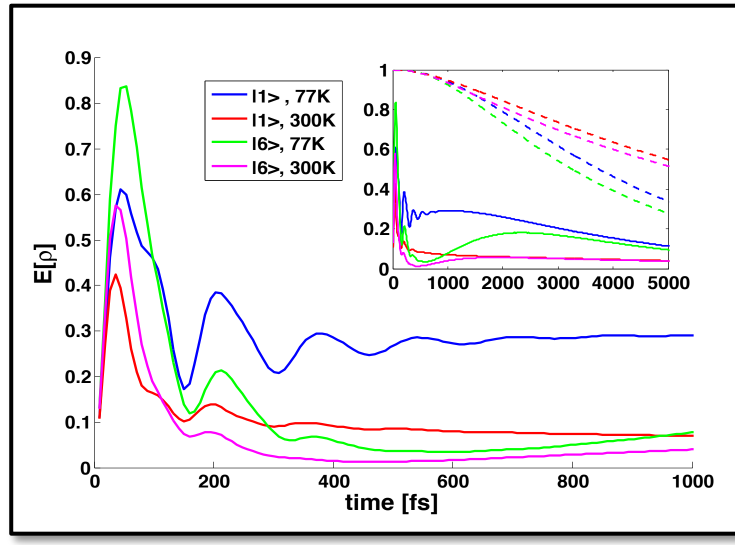
Non-local quantum correlations between molecular electronic states

Site 1

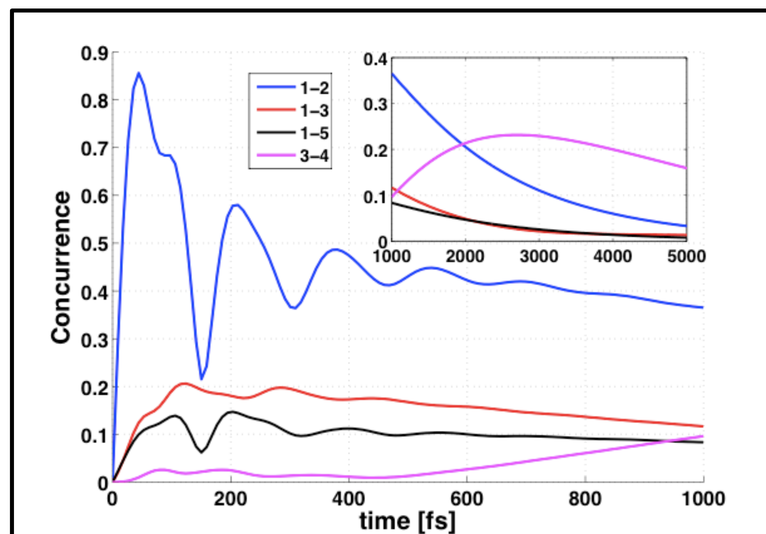
Site 2

$$|\psi\rangle \equiv |g\rangle_1|e\rangle_2 + |e\rangle_1|g\rangle_2$$

77K Global entanglement



Chromophore-chromophore entanglement

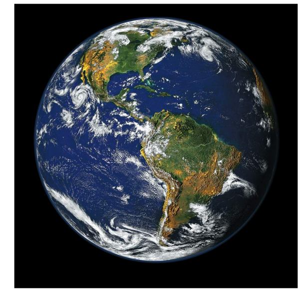


Why coherence despite protein environment?

- Driven open quantum system showing non-equilibrium quantum dynamics
- “Decoherence evasion”
- Is coherence purely electronic? Or vibronic?
- What is the protein doing? It has memory, generates coherence, interacts actively with system…
- Coherence helps quantum efficiency
- Functionally important $t_c > t_{eet}$
- Persistent (controllable?) entanglement with biological function
- Functional significance?

Possible functional roles of quantum coherence

- **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

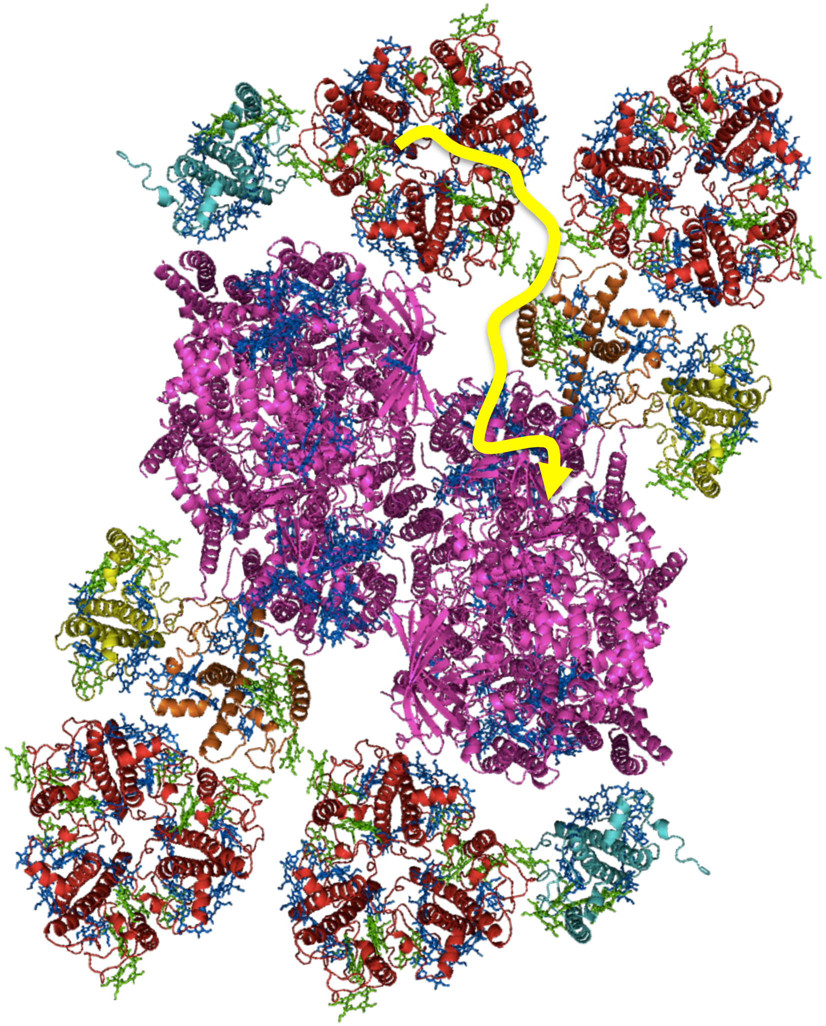
Engel et al, Nature 2007: does FMO perform quantum search for reaction center?
Hoyer et al, NJP 2010: **no quantum speedup and no quantum computation**

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

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

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

Is quantum coherence relevant to long range energy transfer?



Photosystem II super-complex, courtesy of Roberta Croce

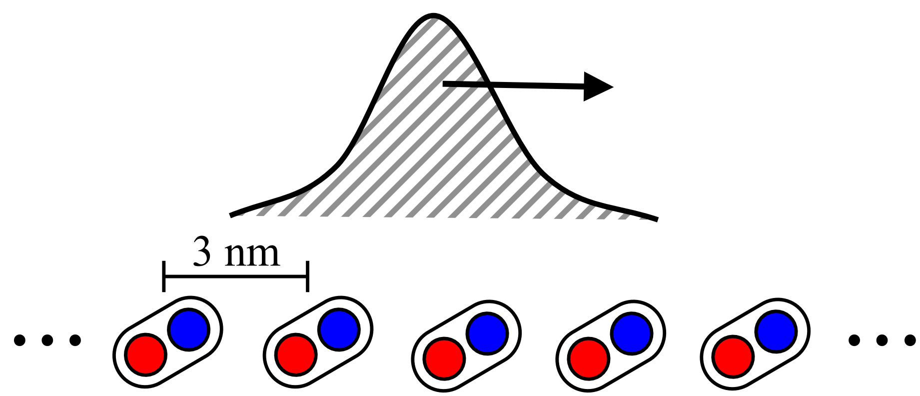
All coherence experiments to date show quantum beating in a single complex –

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

Hoyer et al. PRE (2012)

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

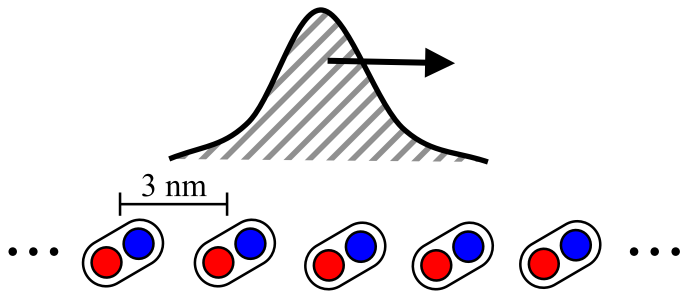
Coherence-assisted uphill transport



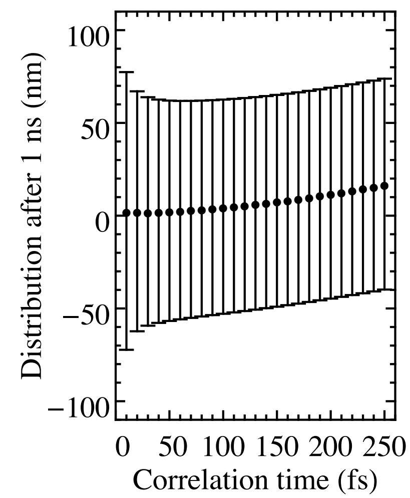
- asymptotic uphill bias in 1D random walk between asymmetric dimers
  - **non-equilibrium initial conditions** after each inter-dimer transfer
  - unbalanced left and right transfer rates at short times

quantum coherent ratcheting of energy transfer
Hoyer, Ishizaki, KBW, PRE 2012

Coherent quantum ratcheting of exciton transport: II

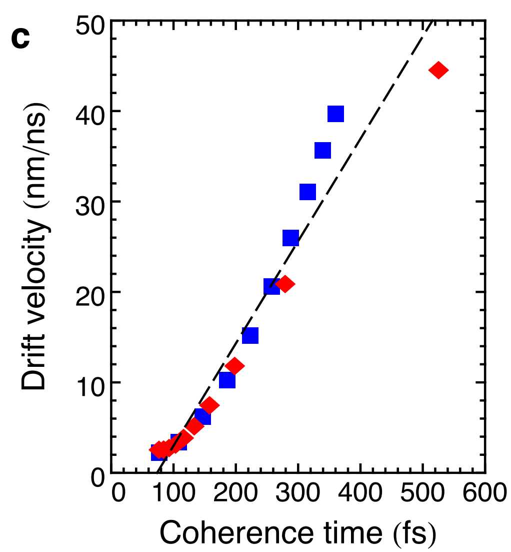


• construct random walk from inter-dimer transition probabilities $F_{\epsilon,\delta}(t)$,
sample space-time shifts $\xi_{\epsilon,\delta} = (\delta, t_{\epsilon,\delta})$



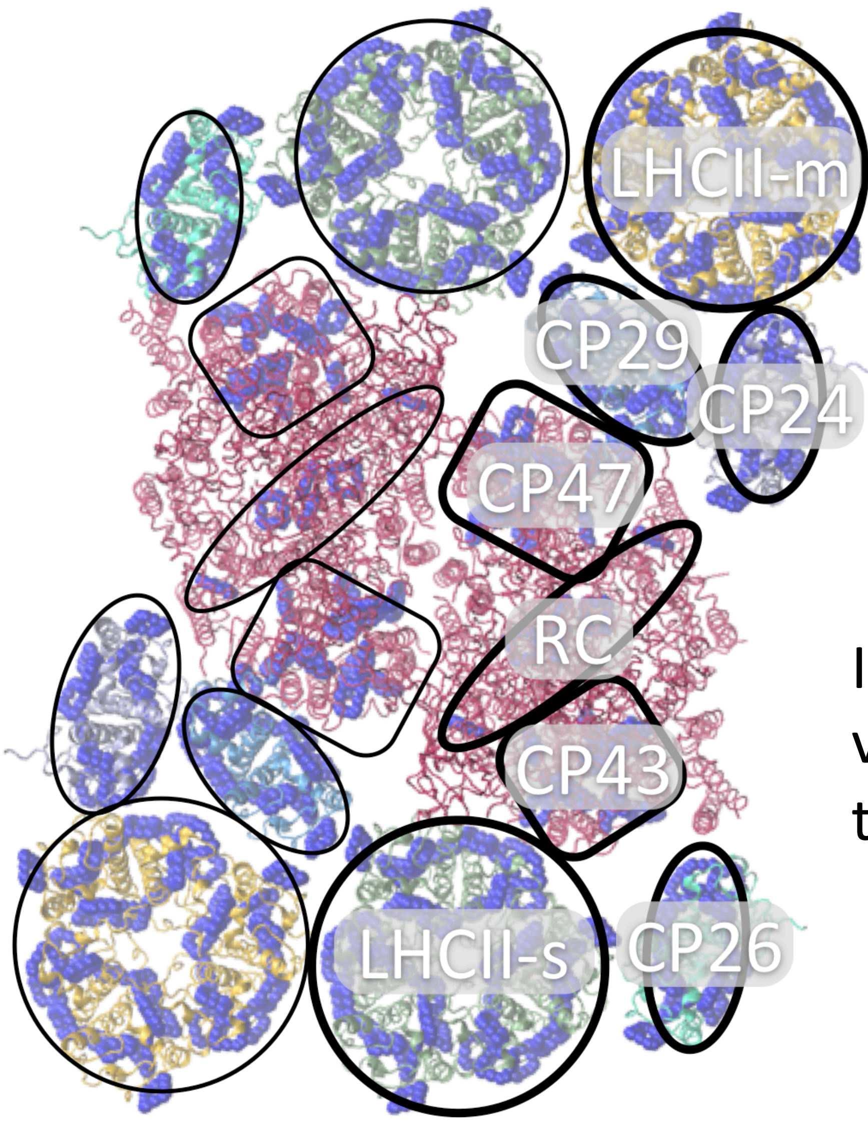
• random walk shows asymptotic spatial bias in uphill direction

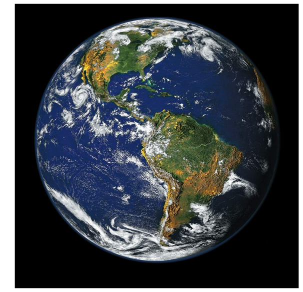
• drift velocity $v = E(n_T)/T$, with $E(n_T) = \bar{n}T/\bar{t}$
and $\bar{\xi} = (\bar{n}, \bar{t})$ from average over limiting distribution of step type and moment of step transition time $t_{\epsilon,\delta}$



• asymptotic bias and drift velocity increases as coherence of intra-dimer dynamics increases (vary by spatial and/or time correlations of bath)

Subcomplex analysis of PSII

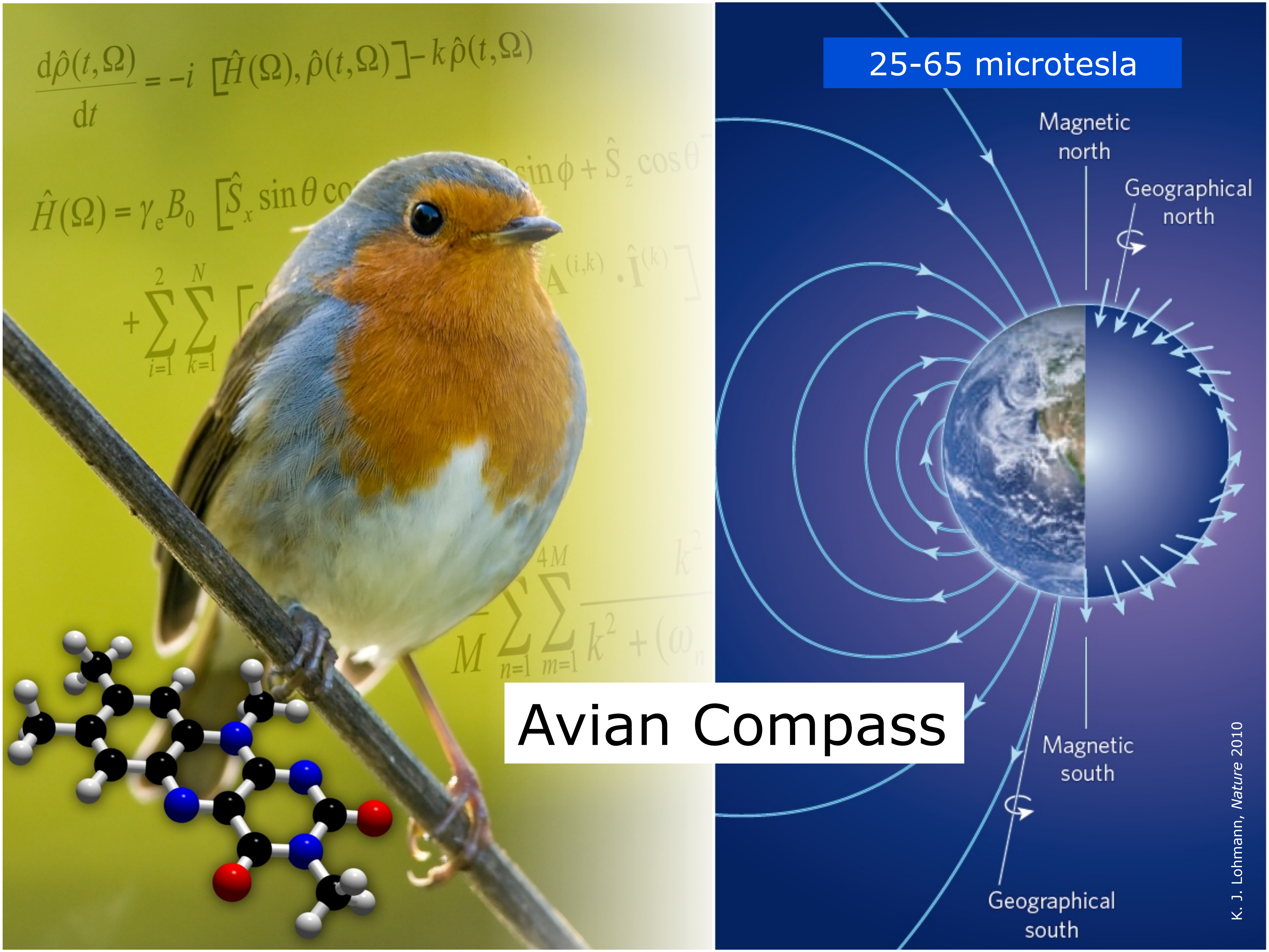




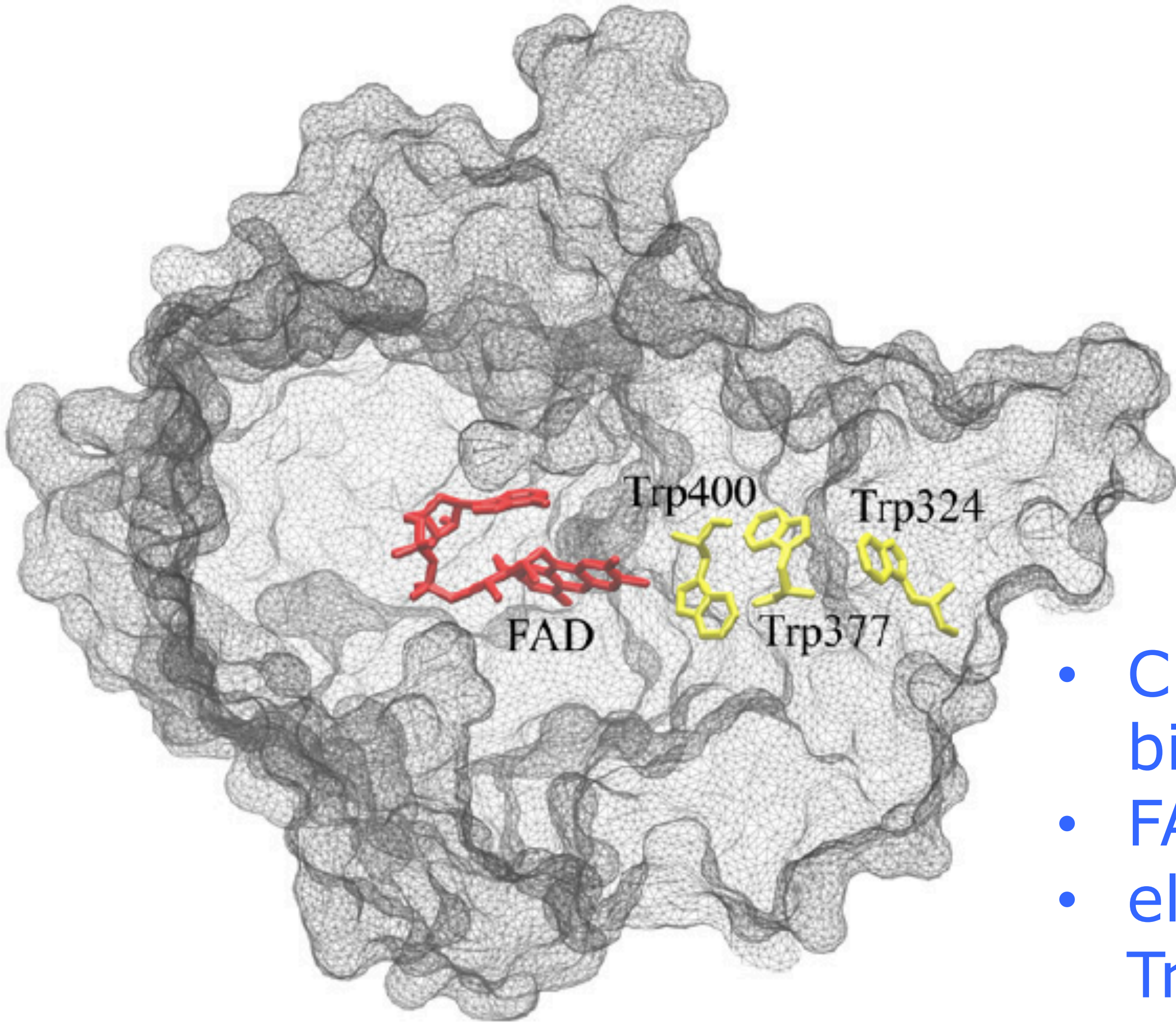
Green plants

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)?


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

Cryptochrome – photo receptor system

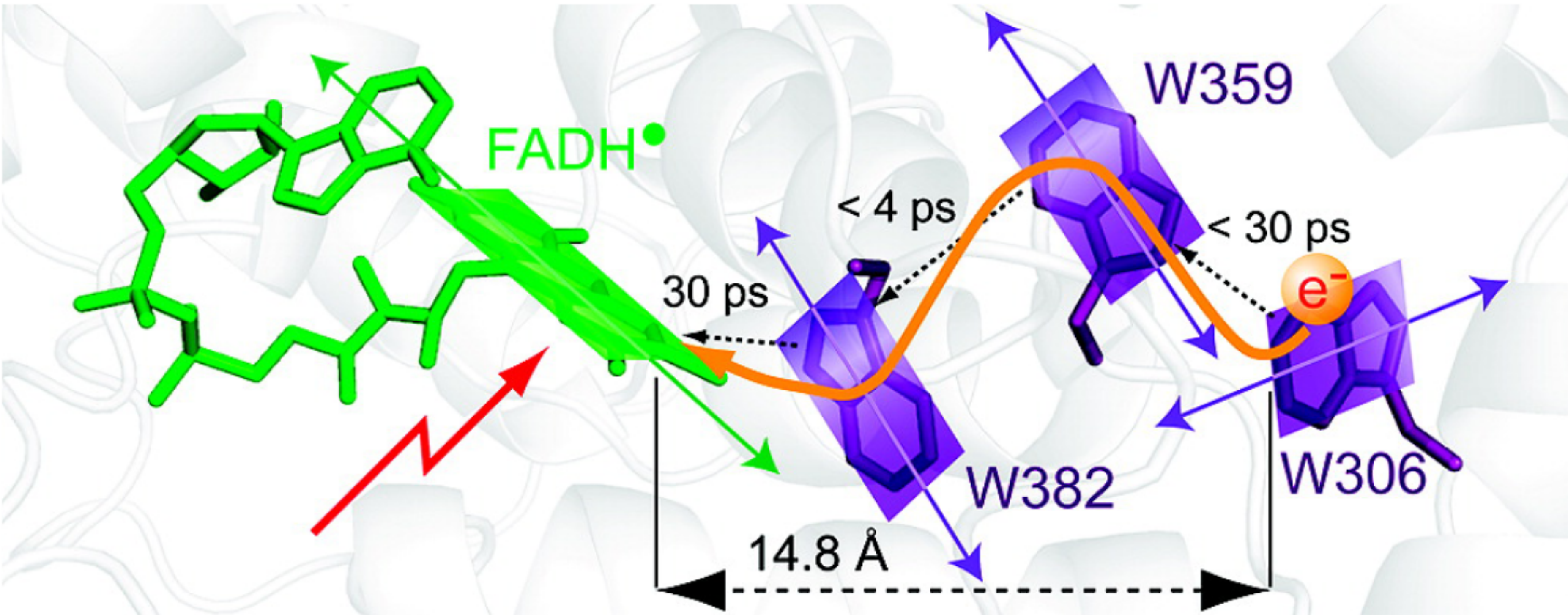


Are quantum correlated dynamics of radical pair electrons involved in the avian compass?

- Cryptochrome protein binds cofactor FAD
- FAD absorbs light
- electron transfer via Trp species generates long lived radical pair

Radical pair = 2 electrons located on different molecules

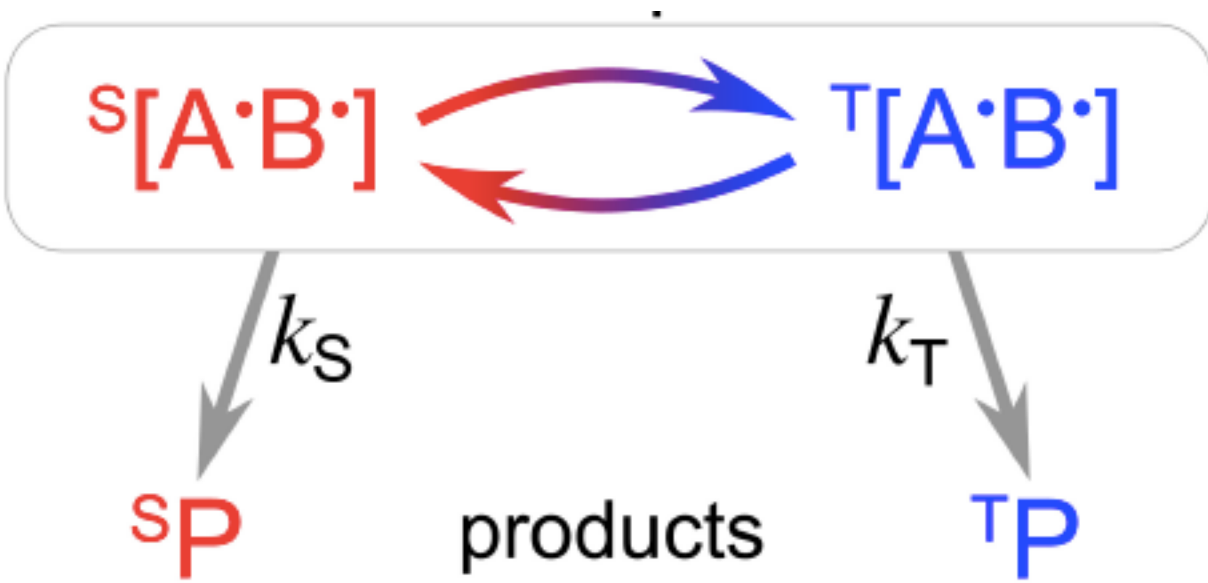
Cryptochrome electron transfer chain



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

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

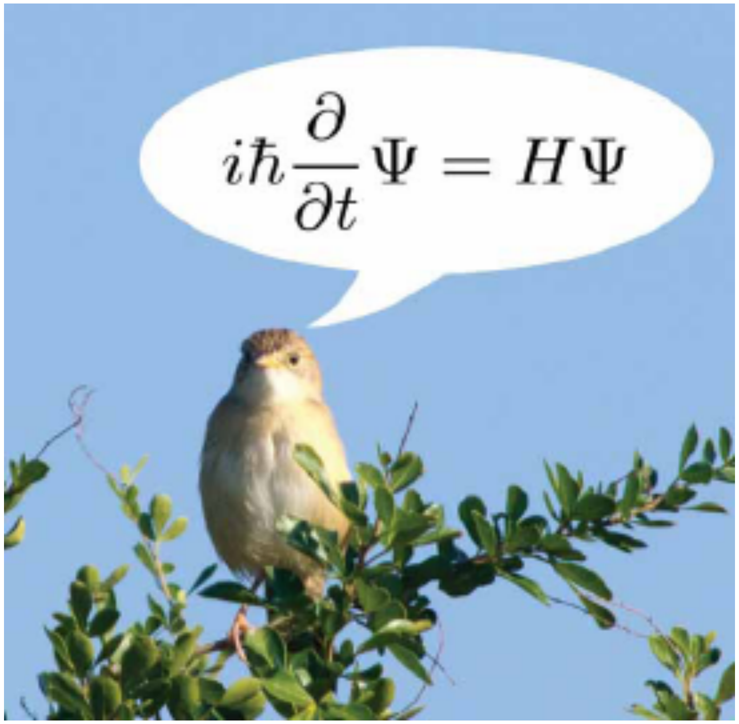
Radical Pair Mechanism

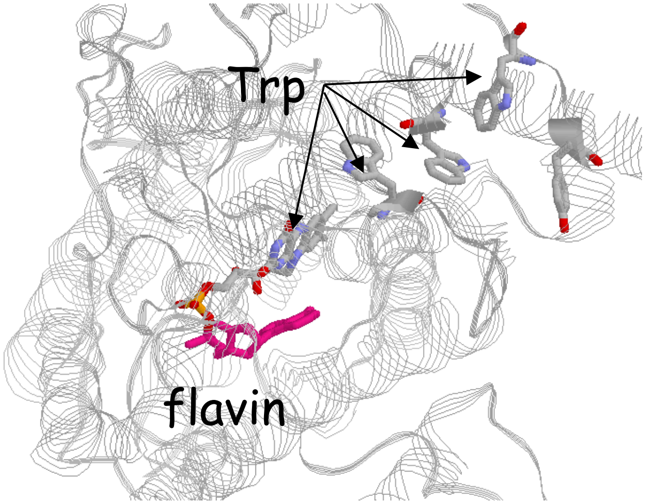


1. S and T radical pairs coherently interconvert in presence of local magnetic fields deriving from interactions of the electron spins with magnetic nuclei in the two radical partner molecule
2. Chemically distinct product yields controlled by interconversion and rates k_S, k_T
3. Interconversion rate 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

Quantum insights for Avian Compass:

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

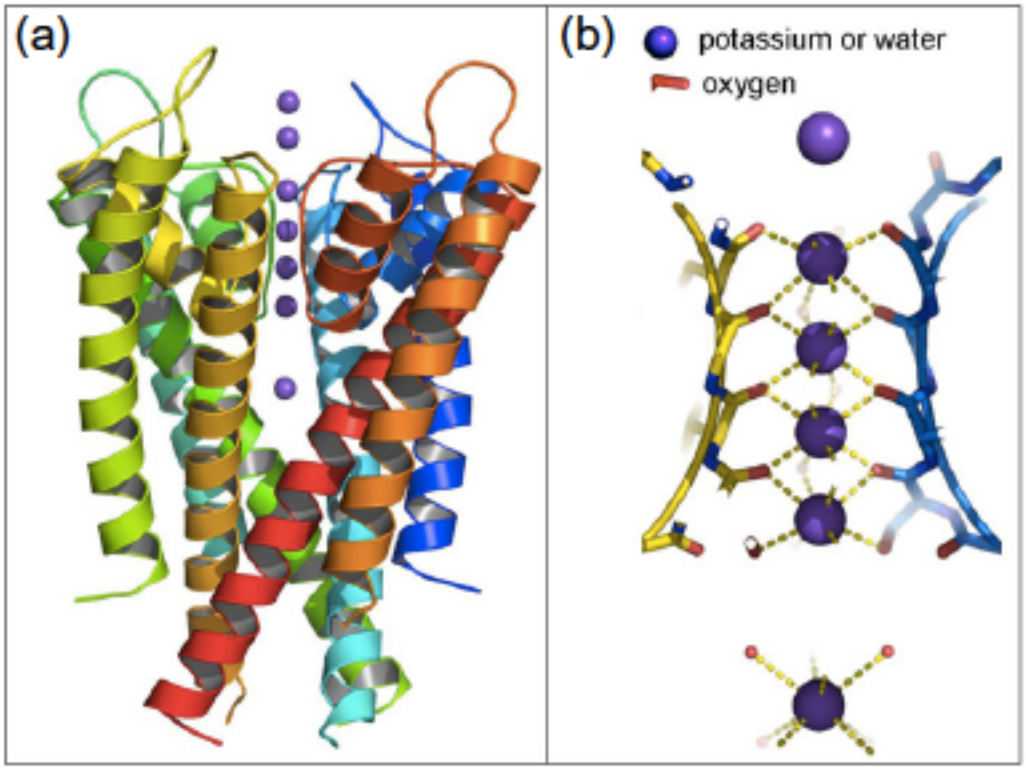




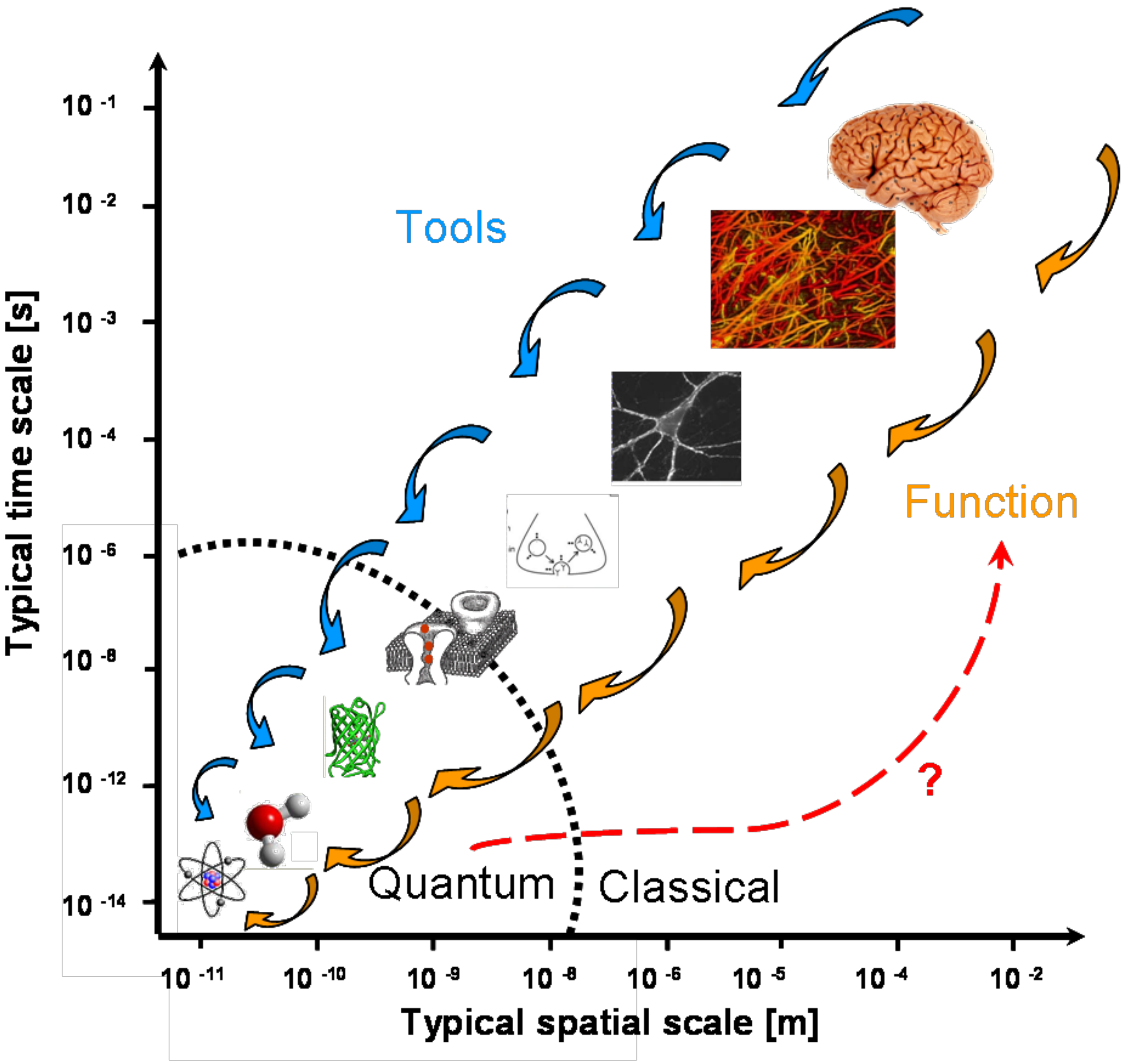
Coherence in ion channels

Does coherent collective vibration of CO groups enhance
K+ motion through channel?

A. Vaziri et al.
B. NJP 2010, 2011



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

Photosynthesis and evolution

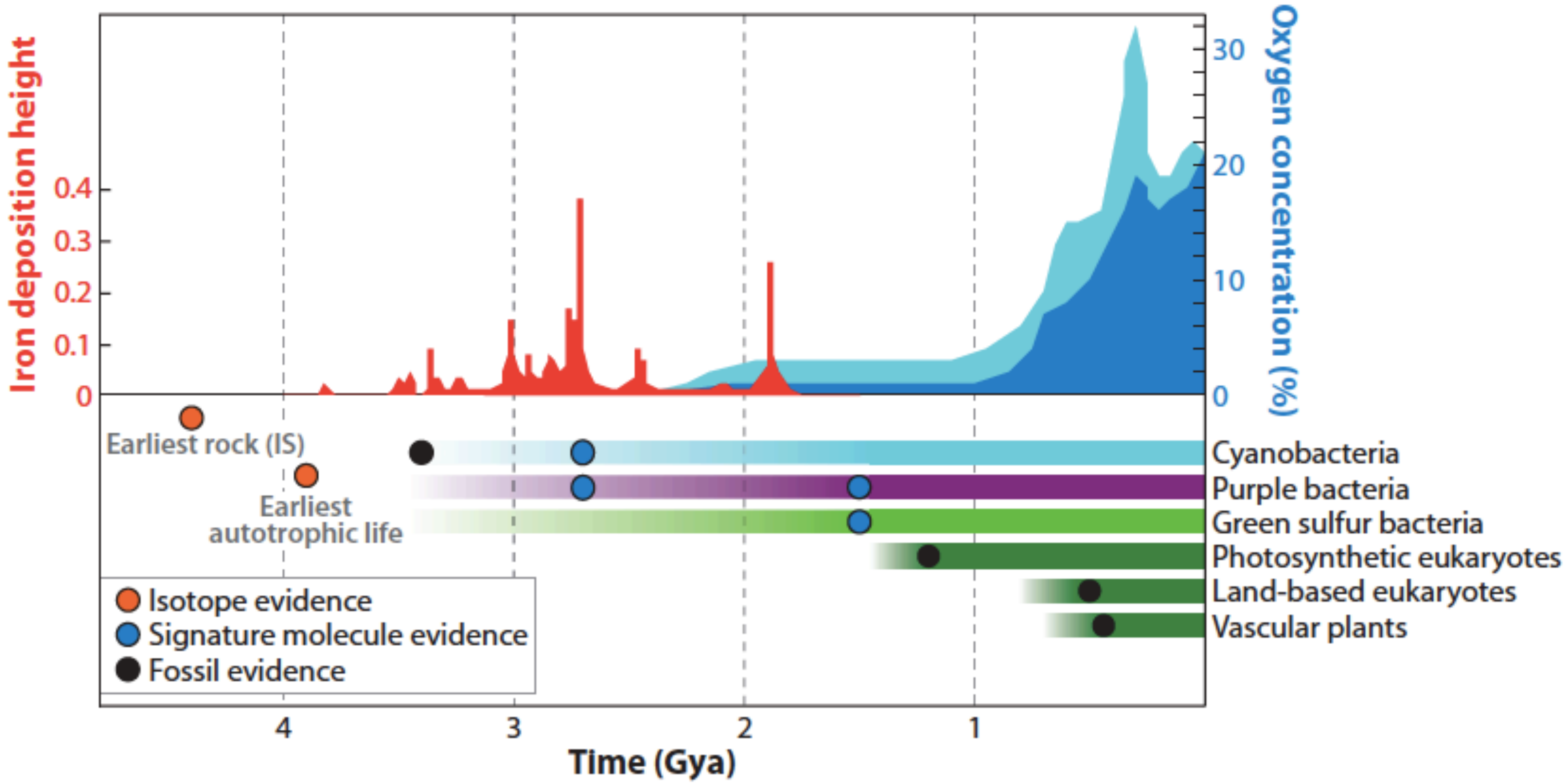
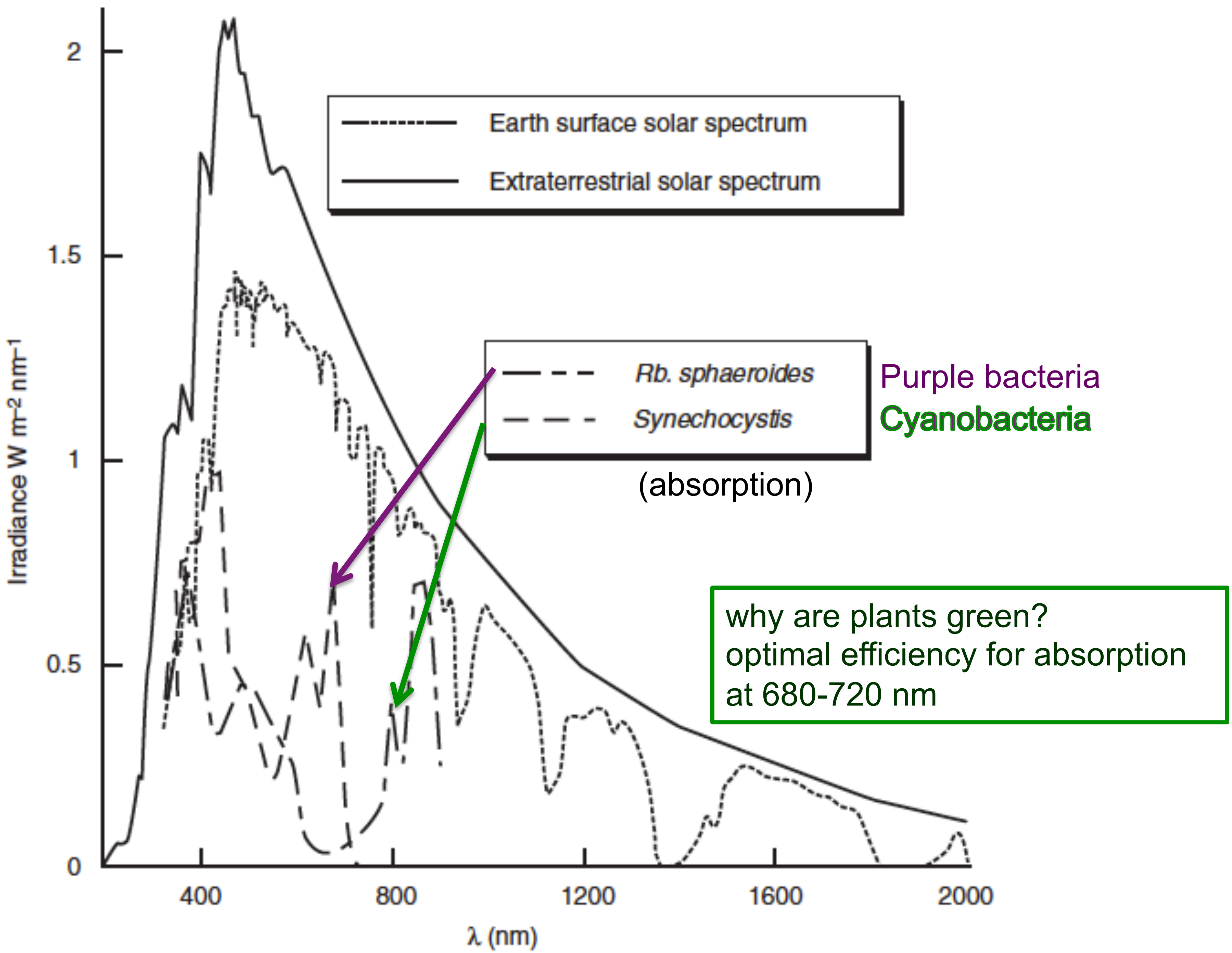


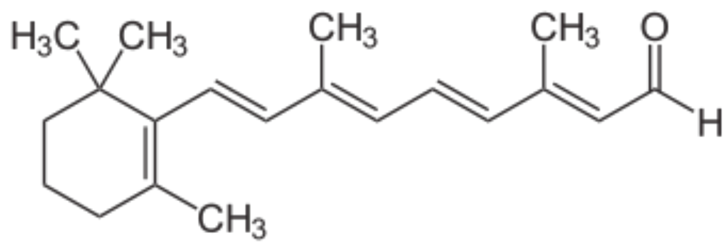
Figure 2

Evolution of life and photosynthesis in geological context, highlighting the emergence of groups of photosynthetic organisms. Minimum and maximum estimates for oxygen concentration are indicated by dark blue and light blue areas, respectively. Oxygen concentration data from Reference 80; banded iron formations data from Reference 87.

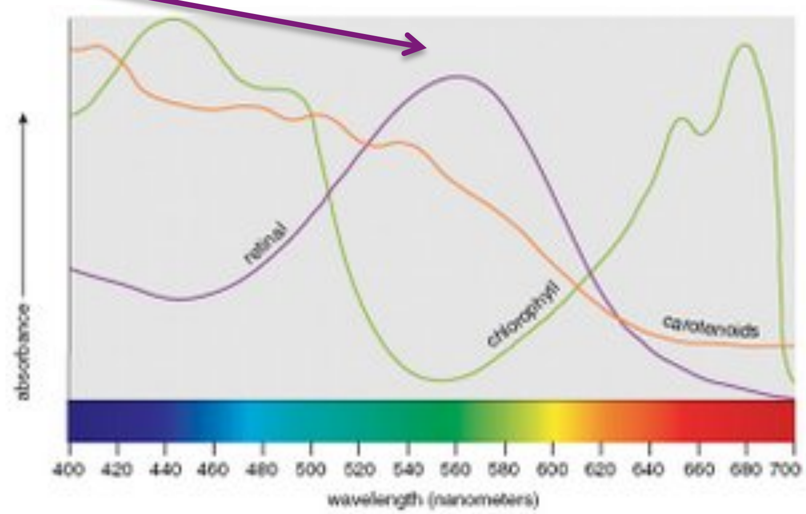


Earth surface solar spectrum
Extraterrestrial solar spectrum
Rb. sphaeroides
Synechocystis
Purple bacteria
Cyanobacteria
(absorption)
why are plants green?
optimal efficiency for absorption
at 680-720 nm
Irradiance W m-2 nm-1
λ (nm)
0
0.5
1
1.5
2
400
800
1200
1600
2000

An evolutionary biology question:

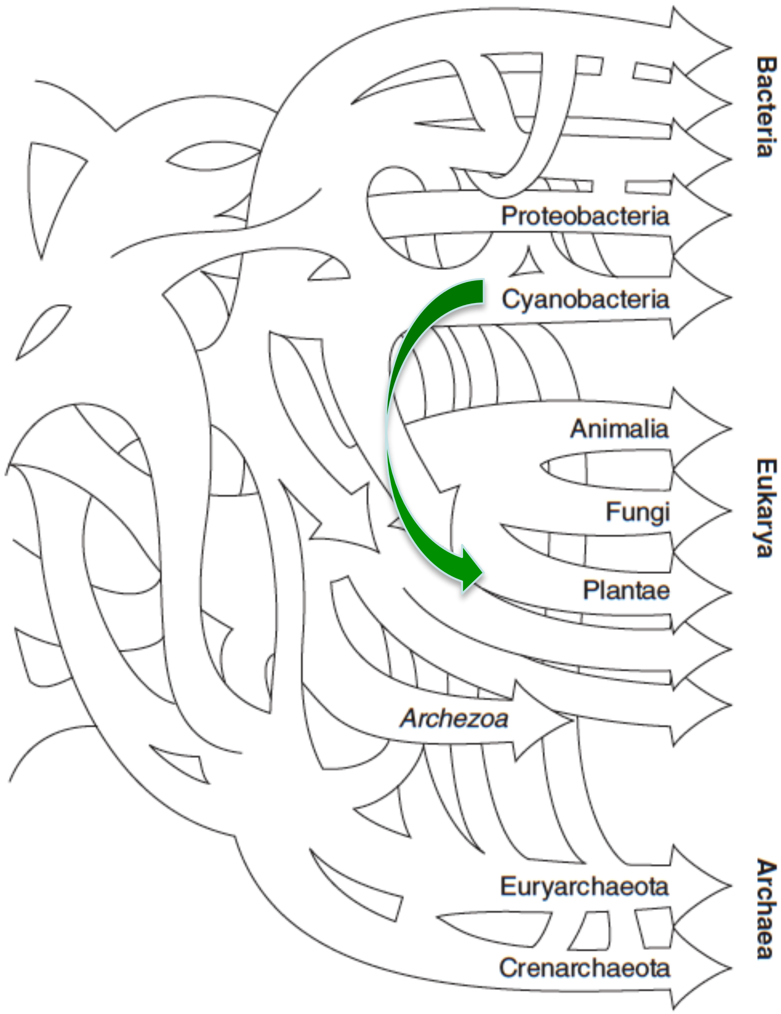


Retinal, found today in halobacteria (ancient organisms), absorbs green light



Were the first photosynthetic organisms purple?

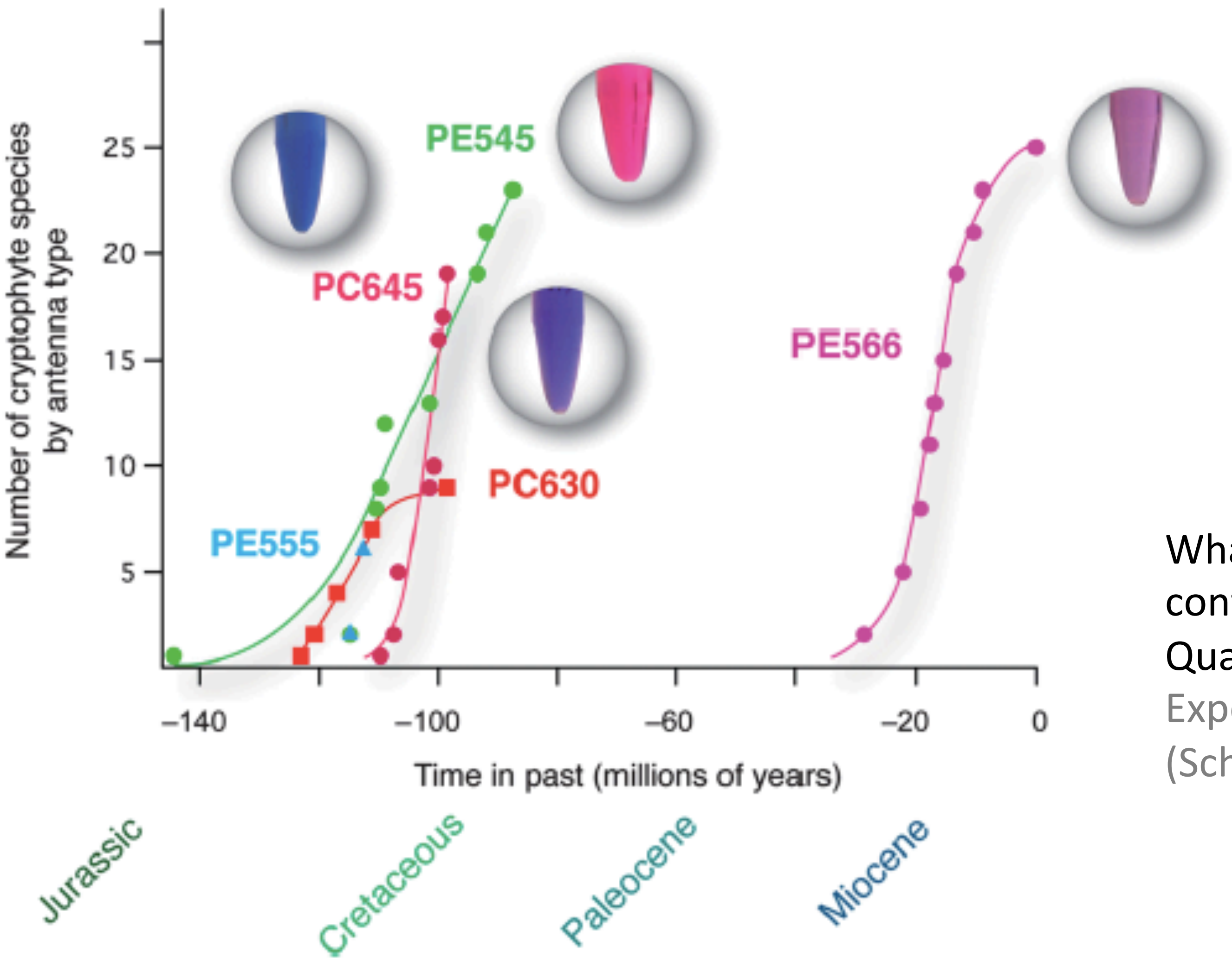
“Multistalked bush of life” shows extensive lateral gene transfer



changes in DNA give new proteins

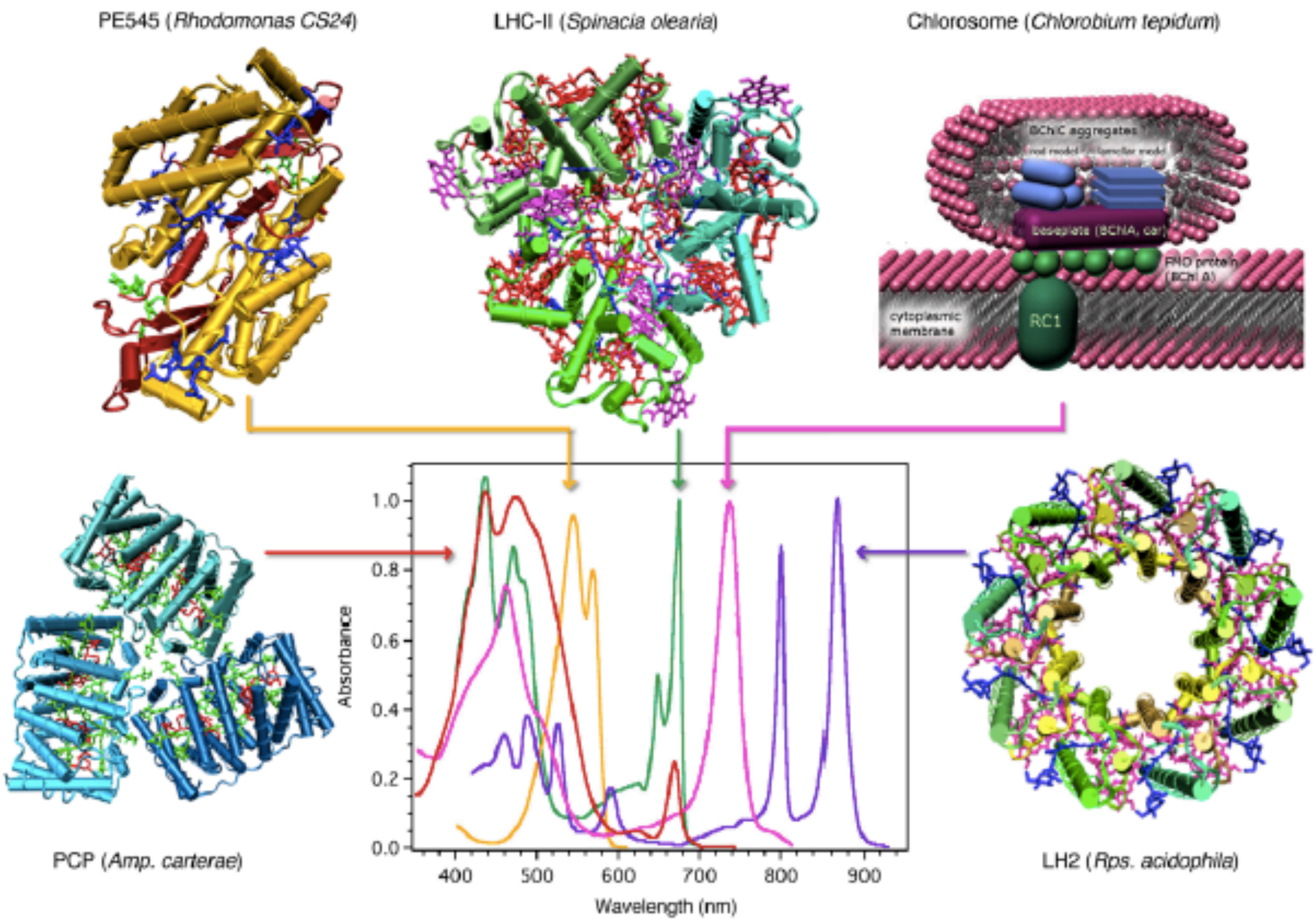
- gene duplication, fusion, splitting…
- lateral gene transfer - have components of light harvesting apparatus been exchanged between organisms?
- reaction centers, core antennas
- rhodopsin vs chlorophyll
- transition anoxygenic to oxygenic photosynthesis
- …

Speciation of cryptophytes according to antenna type



What advantage each confers in its habitat?
Quantum enhancement?
Experiments in progress (Scholes, Toronto)

Light-harvesting complexes: what accounts for the structures?



Antenna development

- Optimization depends on habitat, weather, competing organisms
- Different pigments/proteins consistent with multiple evolutionary origins
- Evolutionary relationships within classes
- Antenna design an innovation – each new type correlates with species diversification (requires significant gene evolution)

Light acclimation

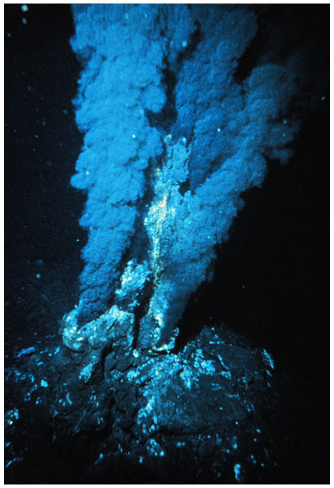
- High light conditions (plants)
  – energy dissipation, removal of oxygen
- Low light conditions (aquatic ecosystems)
  – maximise light absorption

Quantum efficiency is high in both situations

At what rate does a chlorophyll molecule in different conditions receive light?

full sunlight : 1100 photons per second
microbial mats (Yellowstone): 300 photons per second
80m under Black Sea: 1 photon every 8 hours*

Green sulfur bacteria – performs photosynthesis on black body (thermal) radiation emitted by hydrothermal vents 2500m under the ocean surface, use infrared light (800-1000 nm), intensity similar to its Black Sea variant – **BIG ANTENNA**



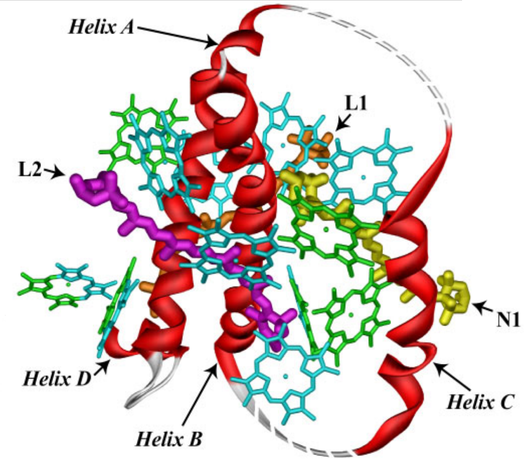
**equivalent to light from a small candle at 50m*

An antenna is not enough…

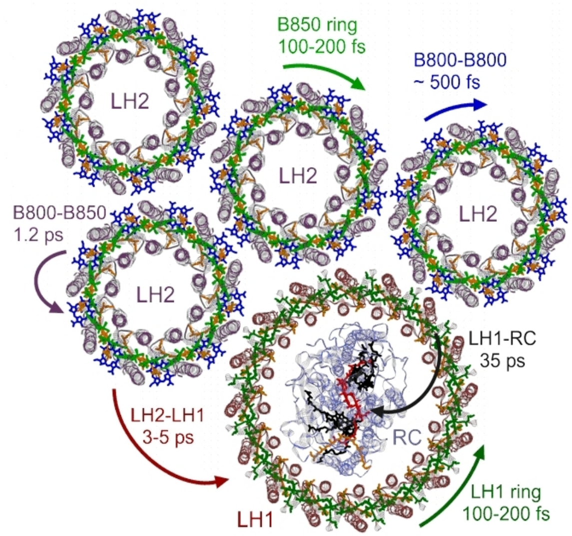
- photosynthesis is optimized for survival
- light harvesting is one of many factors
- in plants overall energetic efficiency correlates with growth fitness (Arntz et al. 2000)
- competition for light, protection from excess light and oxygen…
- access to nutrients (esp. aquatic ecosystems)
- quantum efficiency may be sacrificed to fend off competitors by e.g., dissipating energy as heat…

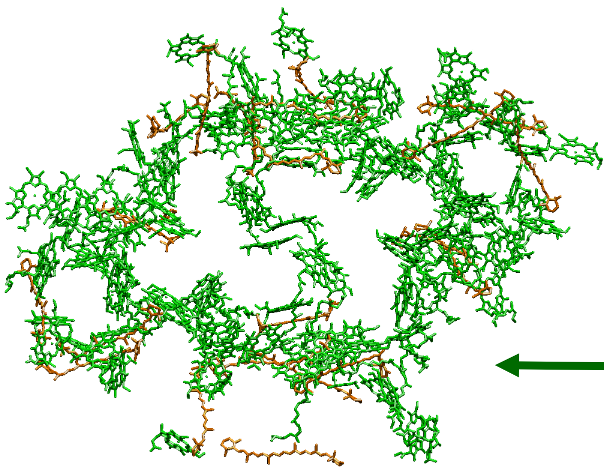
The Architecture of Photosynthesis is Optimized to:

Cover the solar spectrum
Protect against photochemical damage



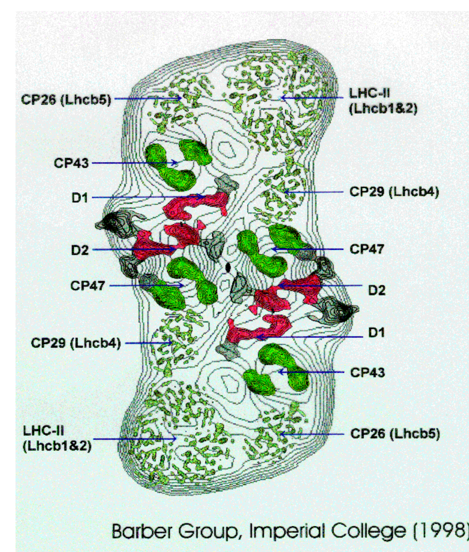
Separate energy and electron transfer (e.g., antenna)





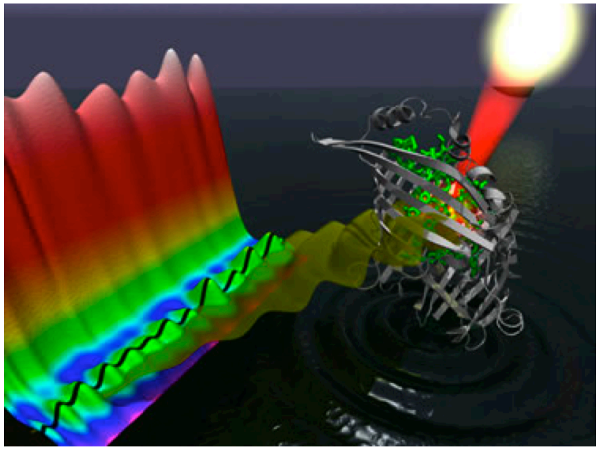
Transmit excitation to the reaction center with near unit quantum efficiency (light harvesting system)

Regulate the efficiency of light harvesting and repair damage (PSII)



Photosynthesis: what next?

- fundamental understanding of quantum effects in efficient energy conversion for life, role in biology
- control of natural quantum processors, develop natural quantum devices
- potential spin-off: new design of artificial devices for effective ‘quantum’ conversion of sunlight into chemical energy without competing biological constraints

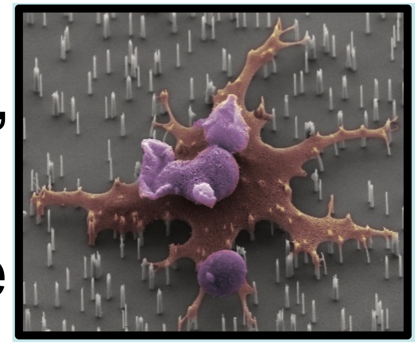


an “evolved” natural quantum processor?

→ design rules for robust quantum devices and efficient transduction of solar energy?

Quantum Biology: tools of quantum science and nanotechnology give new probes of structure and dynamics of biological systems

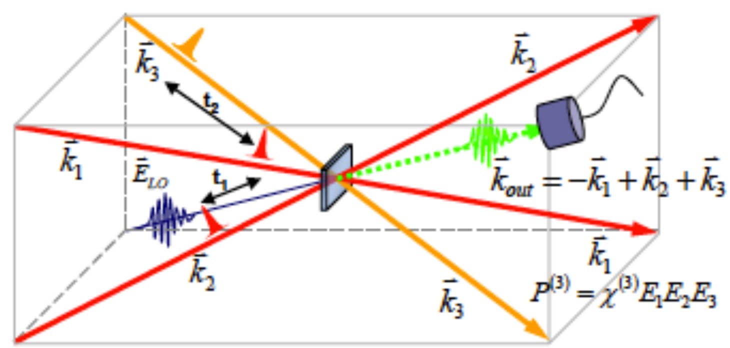
Microscopic probes of living cells, cellular response, biochemical & electrical monitoring, biomolecule delivery…



Si nanorods offer cellular access: H. Park

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

Ultrafast spectroscopy, e.g., for quantum dynamics of electronic energy transfer in photosynthesis



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

?

One can best feel in dealing with living things how primitive physics still is

Albert Einstein

Sit down before fact like a little child, and be prepared to give up every preconceived notion, follow humbly wherever and to whatever abyss Nature leads or you shall learn nothing

Thomas Henry Huxley