

Exceptional service in the national interest



The meeting of quantum physics and biology

Mohan Sarovar

Sandia National Laboratories, Livermore, USA



Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Outline of talk

- The relevance of quantum mechanics to biology
 - Functional timescales and importance of non-equilibrium dynamics
- Examples & links to quantum information
 - Primary processes in photosynthesis
 - Avian magnetoreception

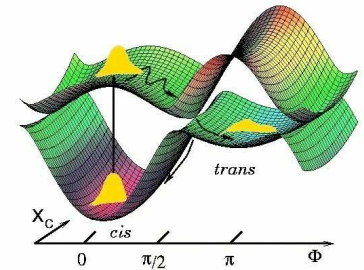
Three classes of QM influence in biology

1. **The trivial:** QM dictates energies, molecular orbitals, etc.

2. **Molecular dynamics and chemical kinetics:**

e.g.

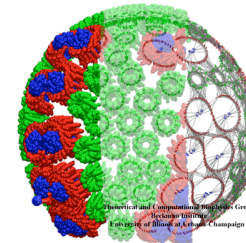
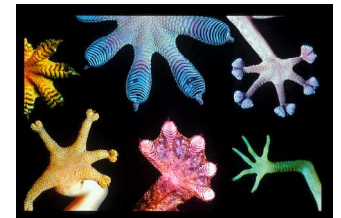
- Ultra-fast molecular transitions through conical intersections
- Chemical reactions involving electron & proton tunneling



3. **Functional necessity:**

e.g.

- Exploitation of van der Waals forces in Gecko feet adhesion*
- Magneto-reception in birds*
- Olfaction (vibration assisted electron tunneling)*
- **Photosynthetic light harvesting**



* Preliminary experimental evidence only

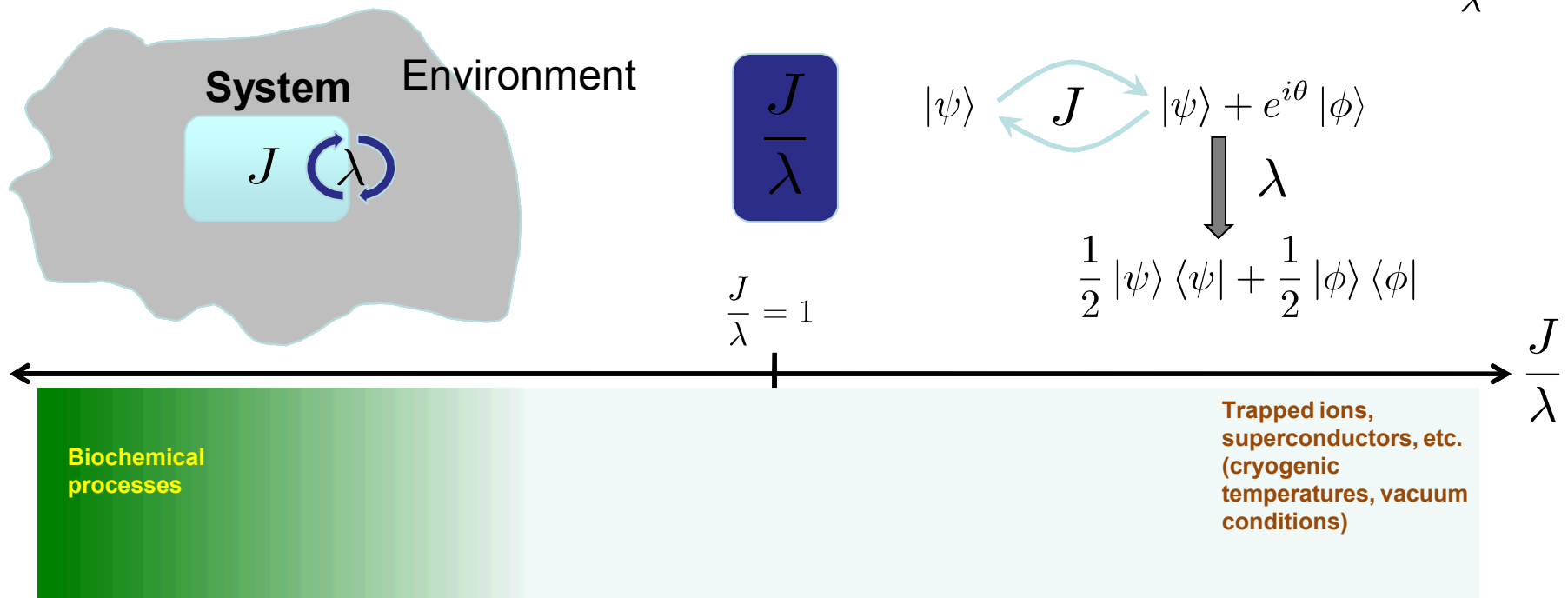
What is so surprising about quantum behavior in biology?

1. $\hbar\omega < k_B T$ Thermal energy overwhelms signatures of energy quantization

2. Decoherence theory: W. Zurek et al.

Coherent evolution timescale: $\tau_c \propto \frac{1}{J}$

Decoherence timescale: $\tau_D \propto \frac{1}{\lambda}$



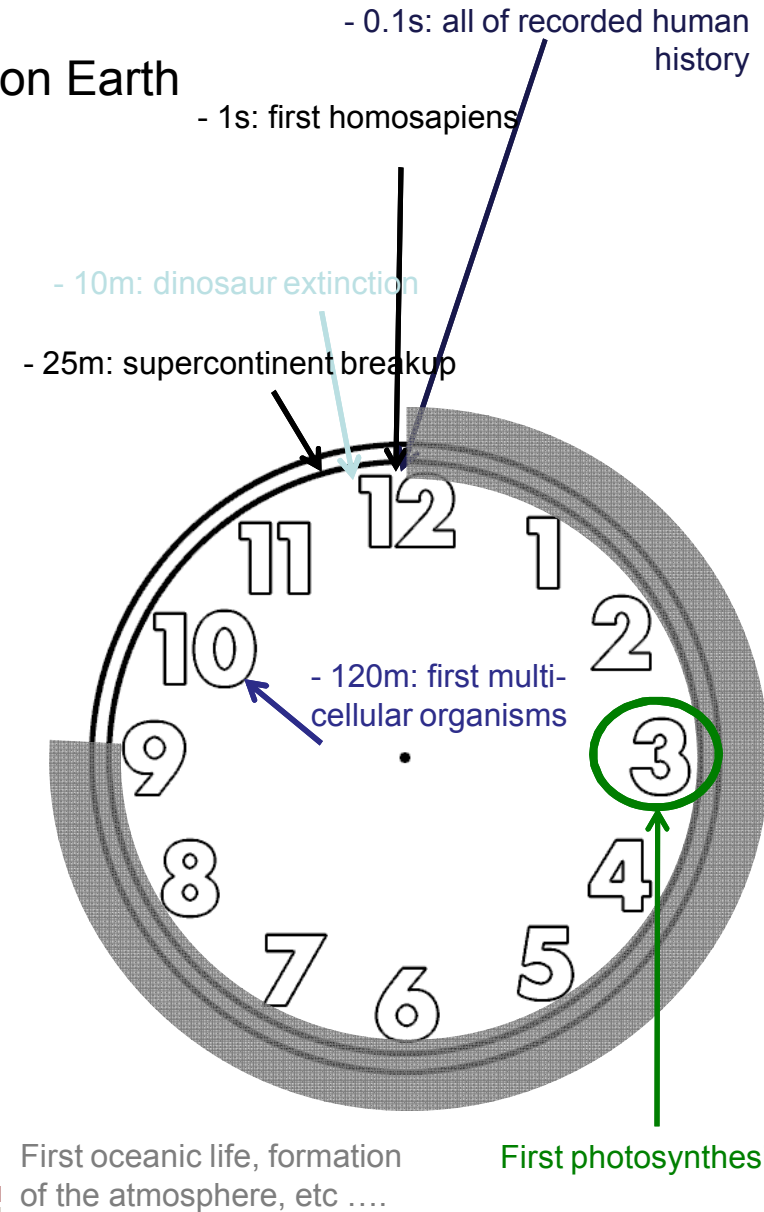
Non-equilibrium dynamics

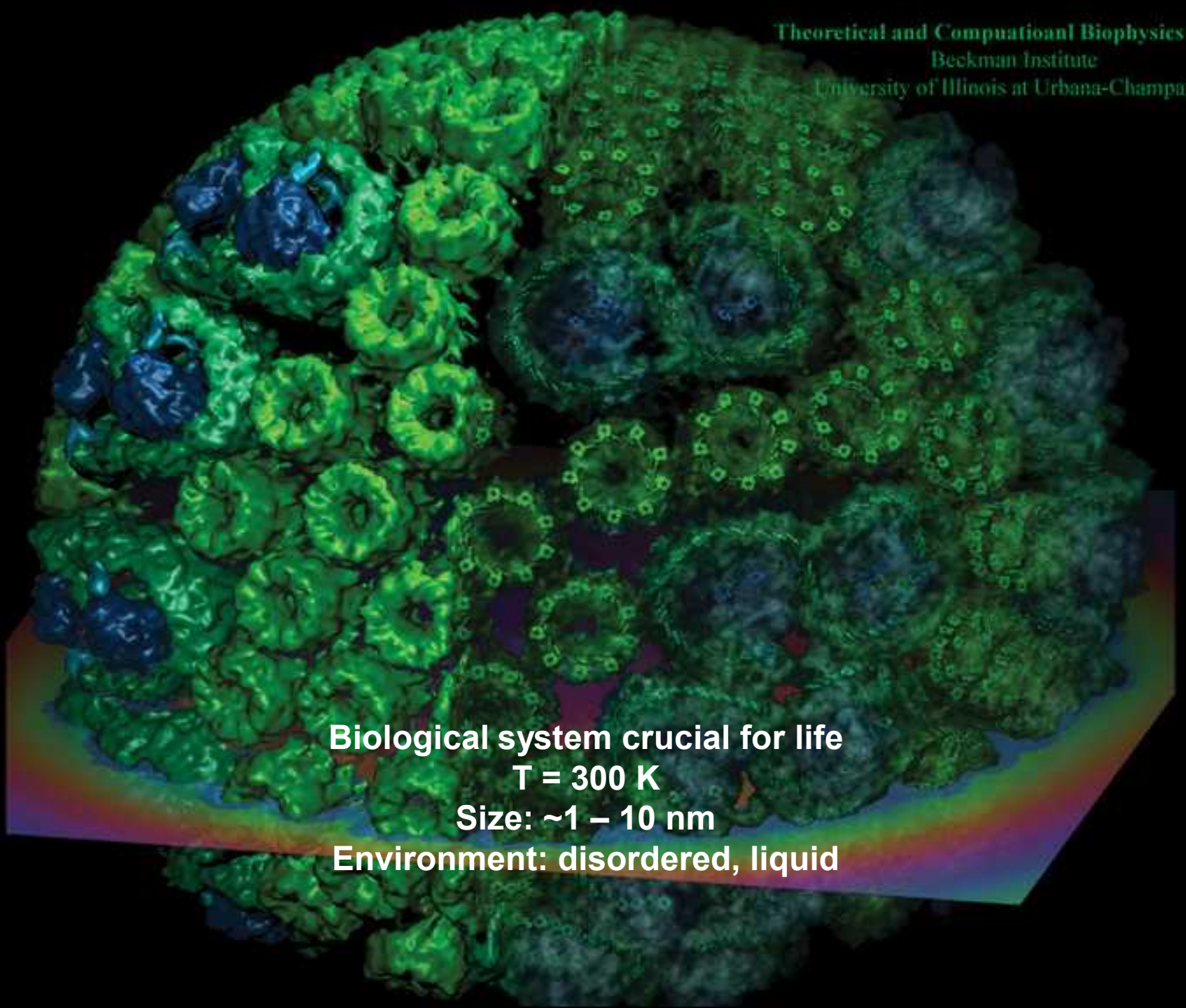
Quantum effects can dominate before equilibration

Primary processes in photosynthesis

Photosynthesis

- Arguably the **most important** biological process on Earth
 - converts CO₂ to oxygen
 - ultimately responsible for all food, most fuel
 - performed by plants, algae, bacteria
- One of the **oldest** biological processes on Earth
 - at least 3.25 to 2.7 billion years old, (c.f. Earth 4.5 billion years old first multi-cellular organisms appear 0.65 billion years ago)
 - has had a long time to evolve and has been under extreme evolutionary pressure





Biological system crucial for life

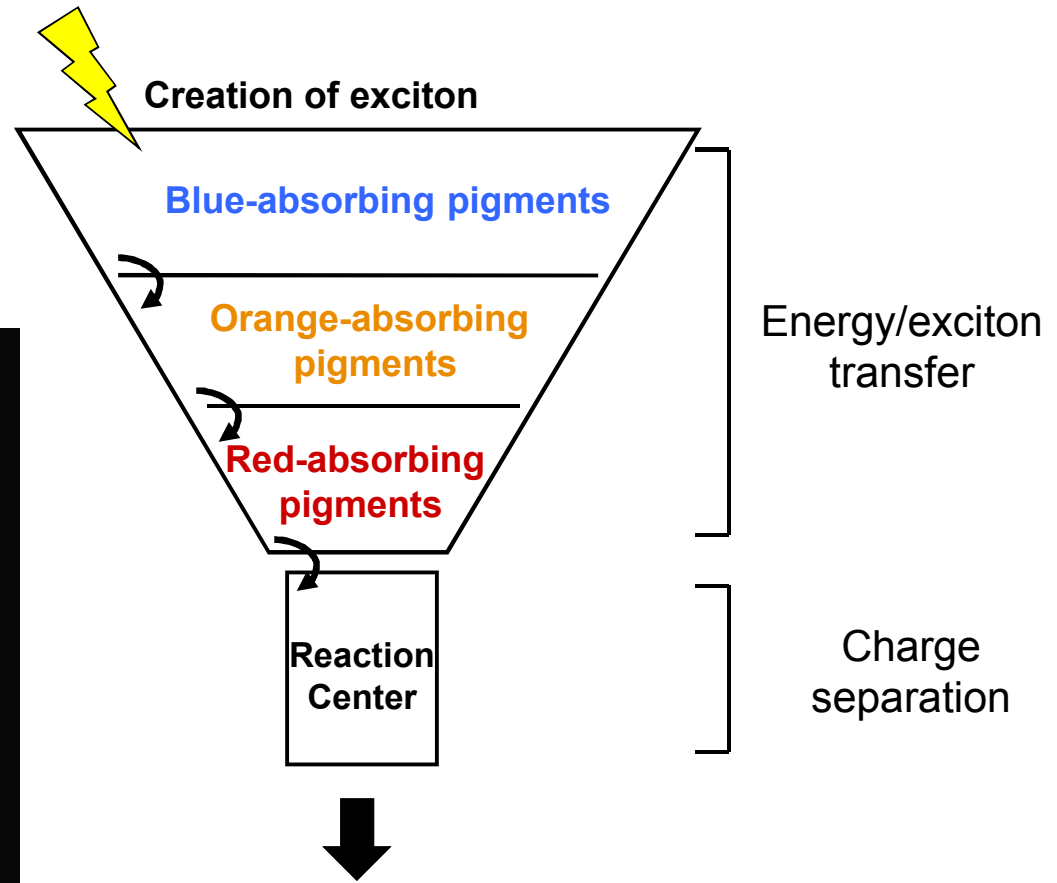
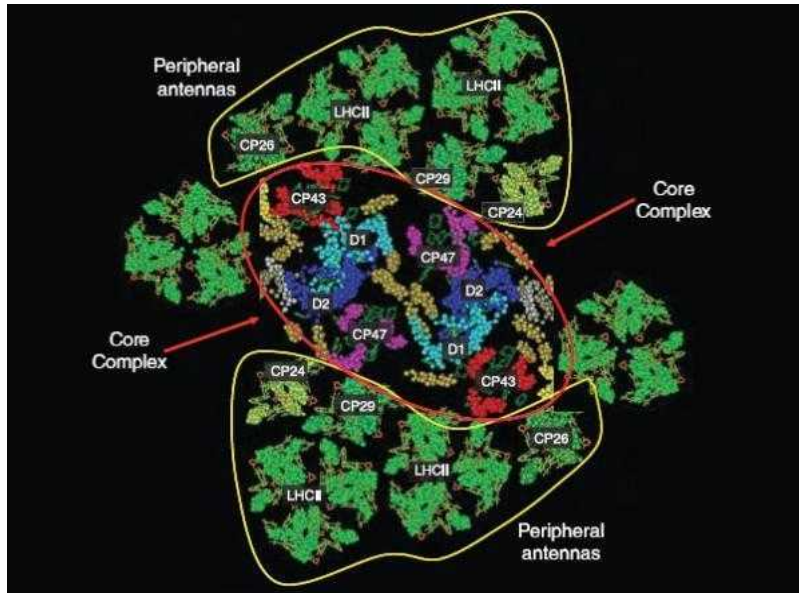
$T = 300 \text{ K}$

Size: $\sim 1 - 10 \text{ nm}$

Environment: disordered, liquid

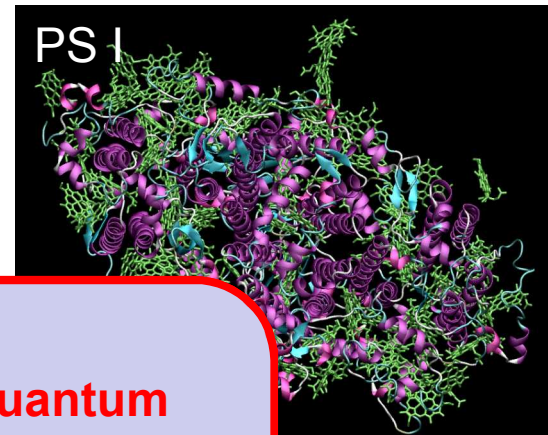
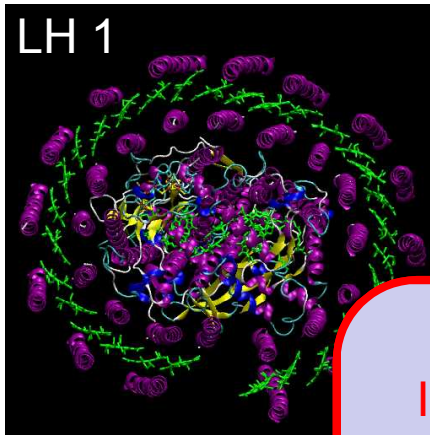
The initial stages of photosynthesis

Light harvesting complex (LHC)



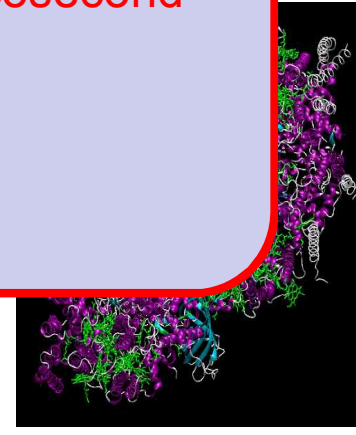
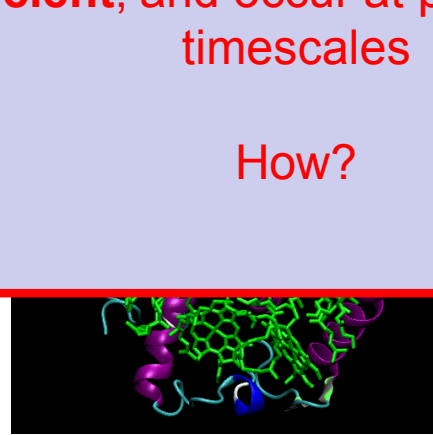
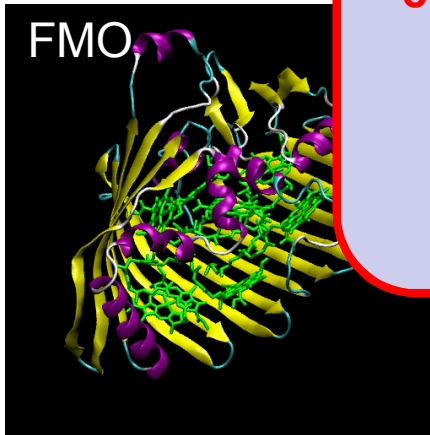
...Secondary electron transfer reactions, Water splitting, Proton transport across thylakoid membrane, Reduction of NADP⁺, ATP synthesis...

Light harvesting complexes



Initial stages are **>95% quantum efficient**, and occur at picosecond timescales

How?



Pictures from
D. Noy

- A large variety of light harvesting antennae
- All composed of densely packed pigment molecules
- The molecular aggregates are often embedded in protein scaffolds, and always within membranes

Theoretical modeling of energy transfer Sandia National Laboratories

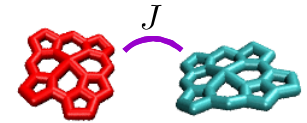
Electronic degrees of freedom:

Frenkel Hamiltonian (tight-binding, single particle model)

$$H_{\text{el}} = \sum_n E_n |n\rangle \langle n| + \sum_{n \neq m} J_{nm} |n\rangle \langle m|$$

pigment electronic transition energies

Coulomb coupling (e.g. dipole-dipole)



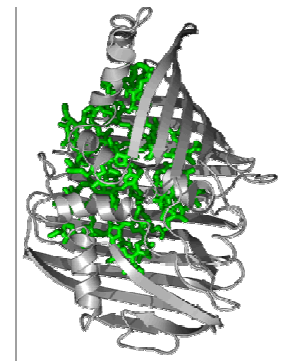
Pigment-protein interactions: open system dynamics

$$H = H_{\text{el}} + H_{\text{el-ph}} + H_{\text{ph}}$$

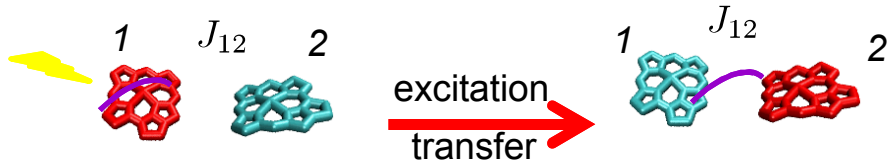
reduced dynamics

$$\frac{d\rho_{\text{el}}}{dt} = \dots$$

master equation

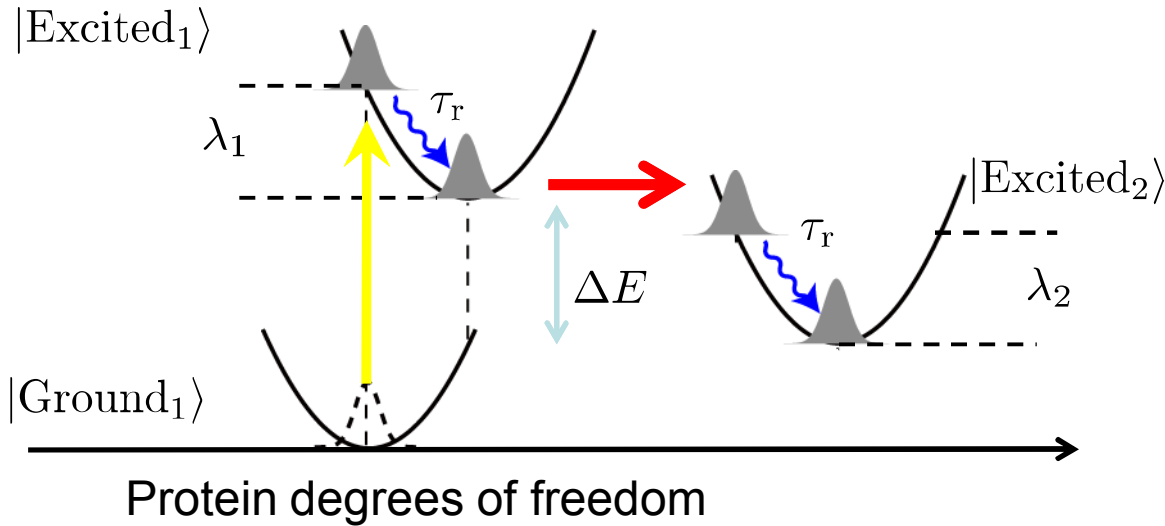


Theoretical modeling of energy transfer



$$|1\rangle \equiv |\text{Excited}_1\rangle \otimes |\text{Ground}_2\rangle$$

$$|2\rangle \equiv |\text{Ground}_1\rangle \otimes |\text{Excited}_2\rangle$$



Several energy scales

Pigment coupling	J_{12}
Reorganization energy of protein bath	λ
Protein relaxation timescale	$\frac{\hbar}{\tau_r}$
Pigment energy difference	ΔE
Temperature	$k_B T$

Theoretical modeling of energy transfer Sandia National Laboratories

Typical photosynthetic Systems

$$J_{12} \sim \lambda \sim \frac{\hbar}{\tau_r} \sim \Delta E \sim k_B T$$

Capturing both coherent and incoherent dynamics is important

Several energy scales

Pigment coupling	J_{12}
Reorganization energy of protein bath	λ
Protein relaxation timescale	$\frac{\hbar}{\tau_r}$
Pigment energy difference	ΔE
Temperature	$k_B T$

Reduced models

Forster theory:

$$J_{12} \ll \lambda, \quad \tau_r \approx 0$$

Redfield theory:

$$J_{12} \gg \lambda, \quad \tau_r \approx 0$$

Haken-Strobl:

$$k_B T \gg \Delta E$$

Temperature independent Lindblad:

$$J_{12} \gg \lambda, \quad k_B T \gg \Delta E$$

Generalized Bloch-Redfield:

$$\lambda \not\gg J_{12}, \quad \frac{\hbar}{\tau_r} \not\gg J_{12}$$

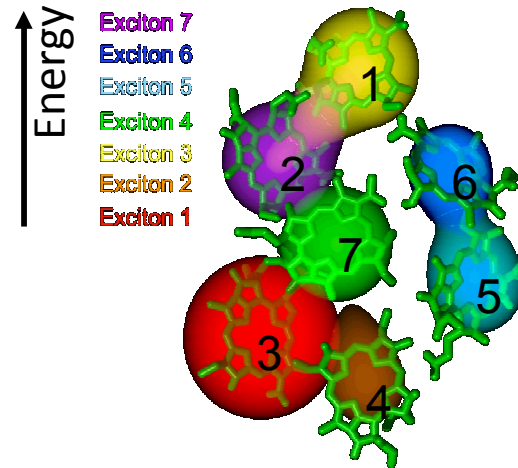
Reduced hierarchy equations approach:

Gaussian distributed fluctuations

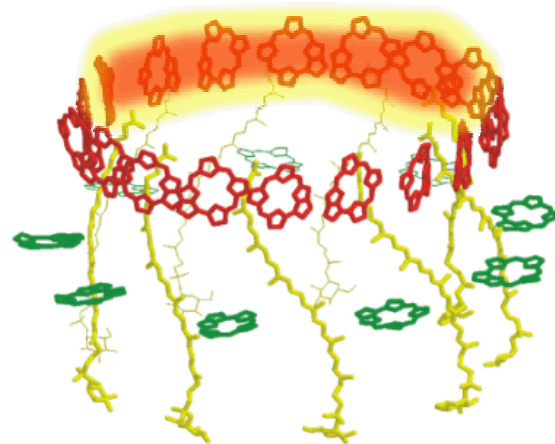
“Static” coherence in LHCs

Electronic excited state (excitons)
delocalized across several pigments

Green sulfur bacteria

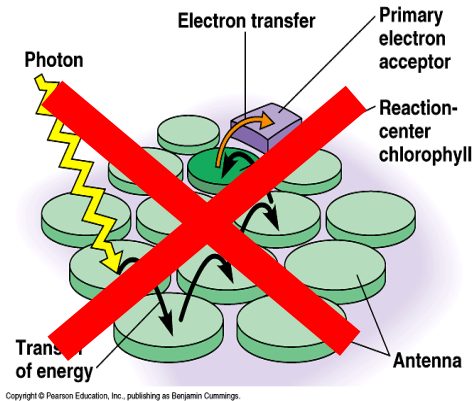


Purple bacteria

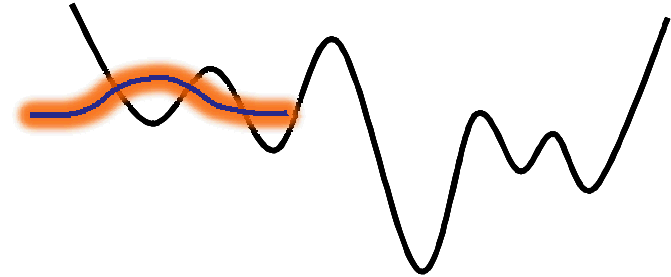


Dynamics of light harvesting: cartoon

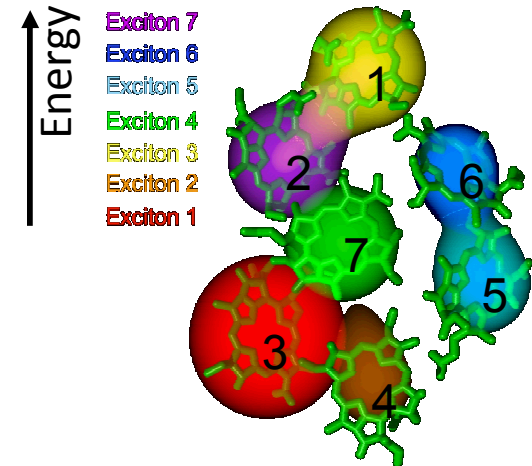
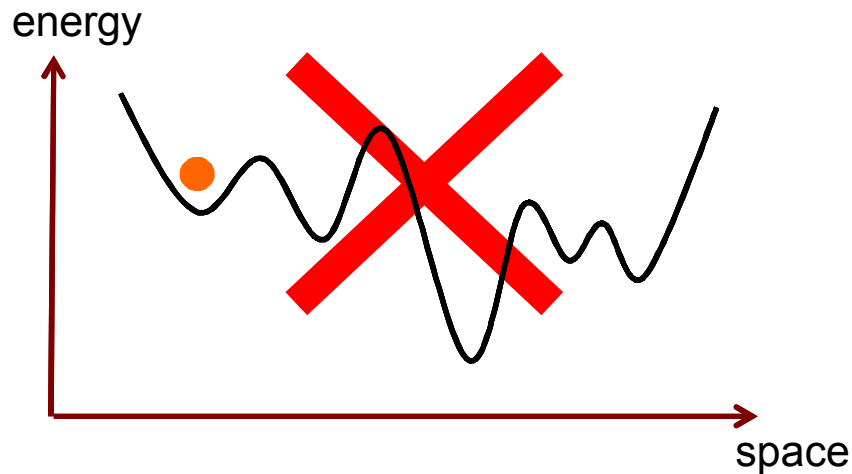
The conventional model



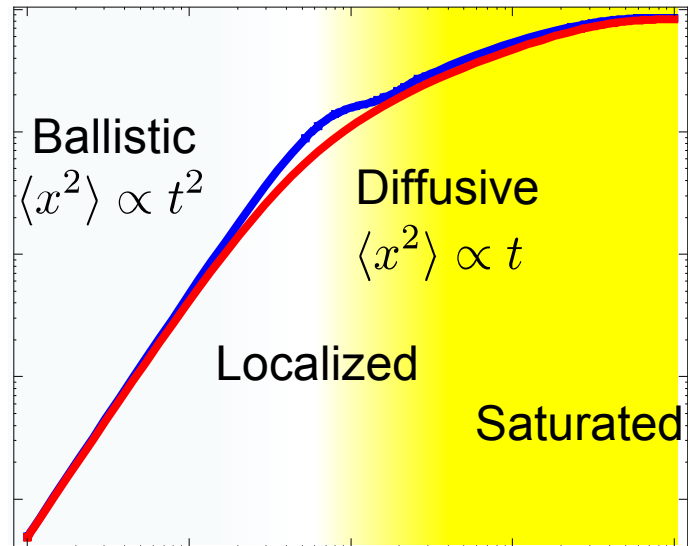
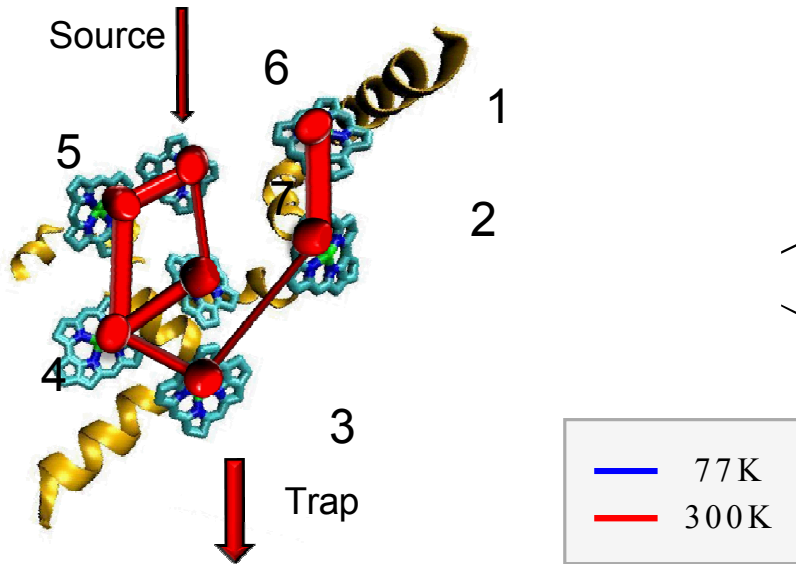
Revised model



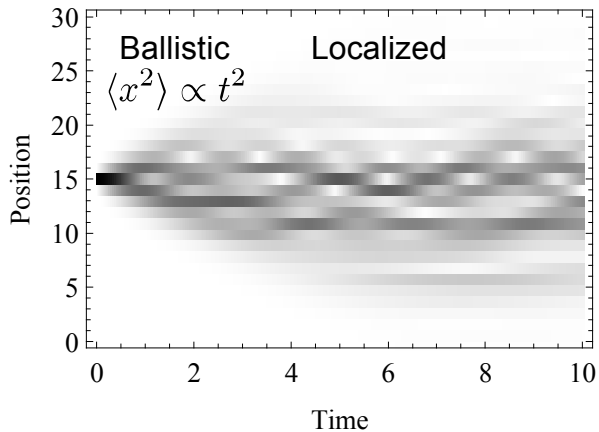
Electronic excited state (excitons) delocalized across several pigments



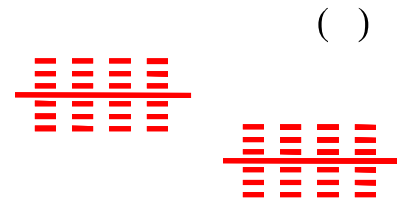
Example: dynamics in FMO



Anderson localization

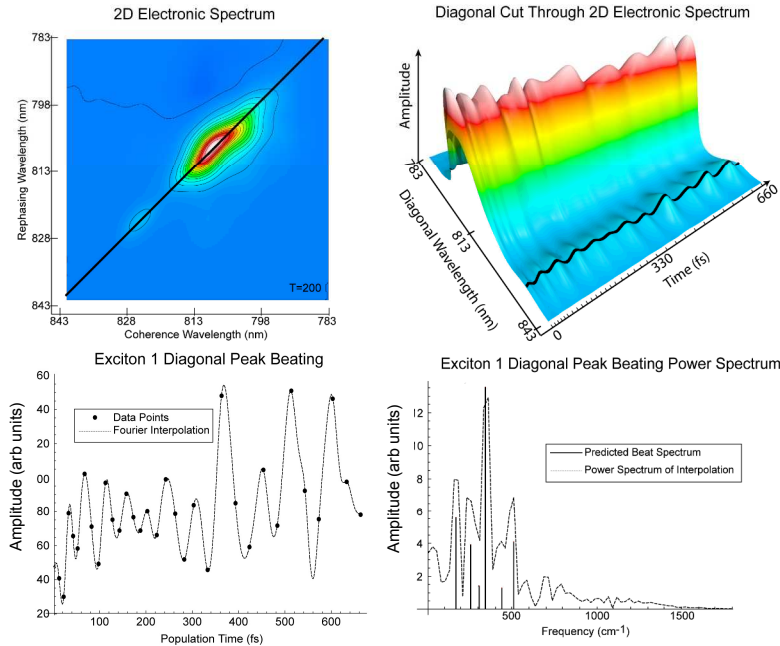


Any variation in site energies lead to localization



Dephasing allows escape from Anderson localization but makes overall transport sub-ballistic

Experimental evidence of partially coherent transport in LHCs



“Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems”, G.S. Engel, *et al.*, *Nature* **446**, 782 (2007)

Green sulfur bacteria (7 pigments)

Fenna Matthews Olson (FMO) complex:

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

Marine algae – phycobiliproteins (8 pigments)

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

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

Purple bacteria (2-3 pigments)

Reaction center:

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

Higher plants (14 pigments)

LHC-II:

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

Optimality of transport

Typical photosynthetic Systems

$$J_{12} \sim \lambda \sim \frac{\hbar}{\tau_r} \sim \Delta E \sim k_B T$$

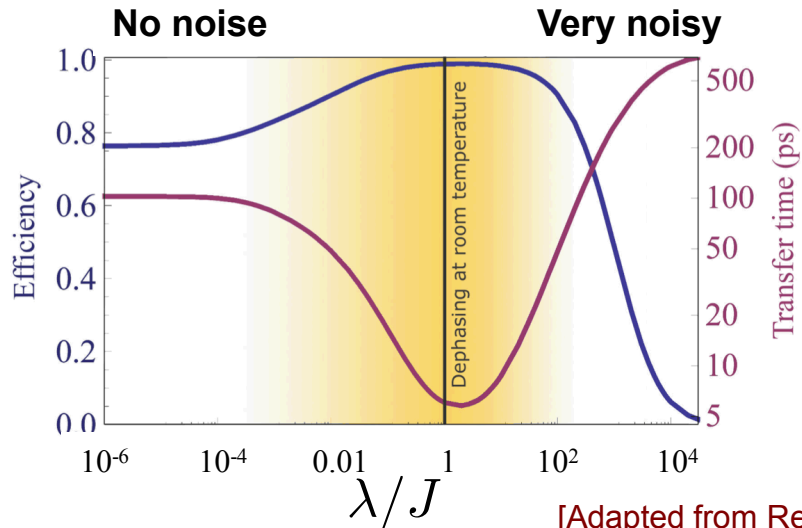
J : inter-pigment coupling

λ : pigment-protein/solvent coupling
(reorganization energy)

Rebentrost, P., *et al.* *New J. Phys.* **11**, 033003 (2009).

Kim, J.-H. & Cao, J. *J. Phys. Chem. B* **114**, 16189–16197 (2010).

Mohseni, M., Shabani, A., Lloyd, S. & Rabitz, H. *arXiv:1104.4812* (2011).



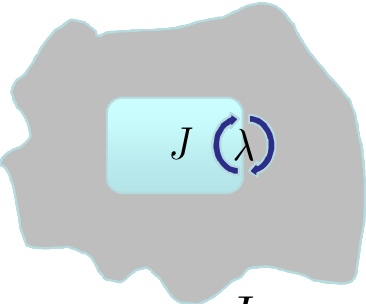
[Adapted from Rebentrost et al., 2009]

Balance between coherent dynamics and environmental coupling essential for efficient transport.

Only coherent -> wave-like transport, but no appreciable capture of energy

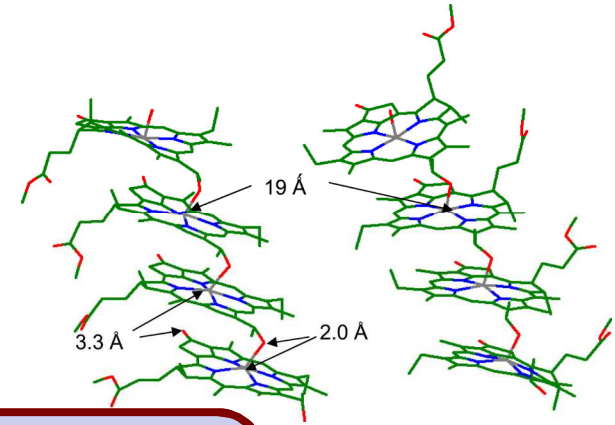
Only decoherent -> slow, diffusive transport

Maintaining the delicate balance



J : inter-pigment coupling

- Densely packed molecular aggregates
- Precisely oriented complexes



T
y
p
i
c
a
l
l
y
,

$$\frac{J}{\lambda} \ll 1$$

λ : pigment-phonon

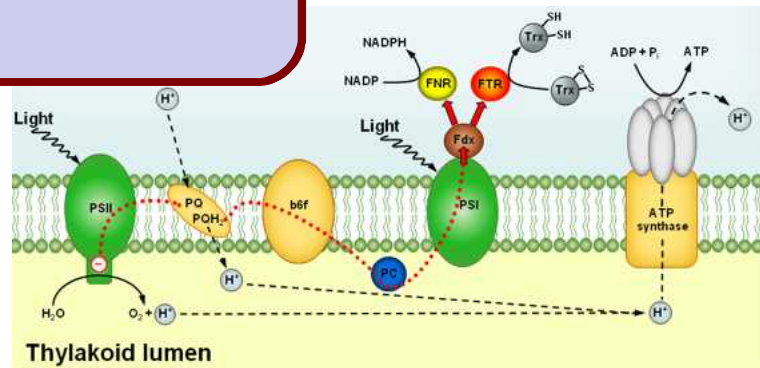
Structure is crucial!

Controlled environment (membrane embedded):

weaker electron-phonon coupling

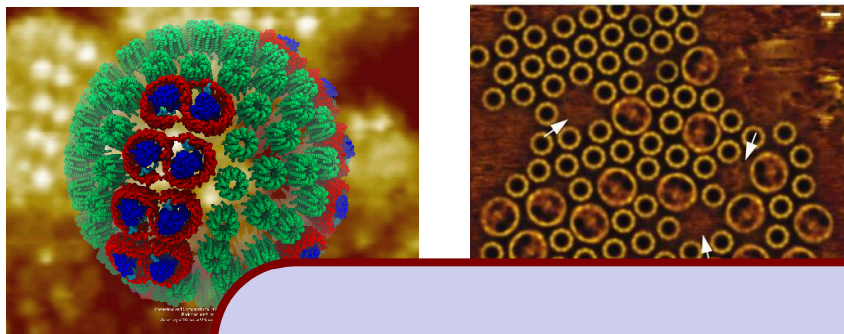
Typical reorganization energies of pigments in solution:
200 – 2000 cm^{-1} [Gilmore & McKenzie 2008]

c.f. Reorganization energy of FMO LHC: 35cm^{-1}



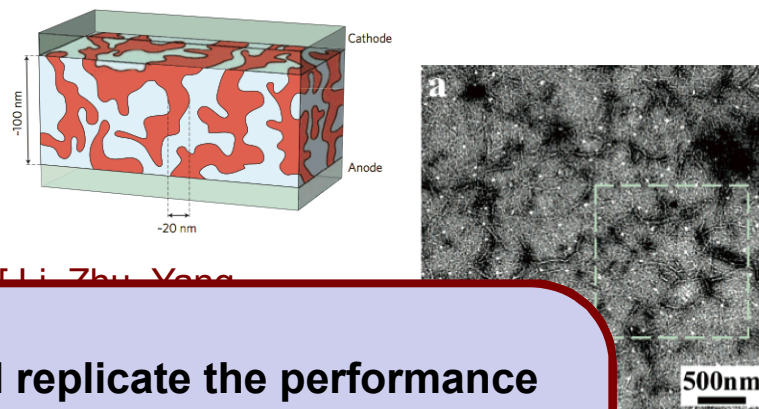
Natural and artificial light harvesting

LH I and LH II light harvesting complexes in purple bacteria



[Beckmann
Illinois]
[Scheuring
2004]

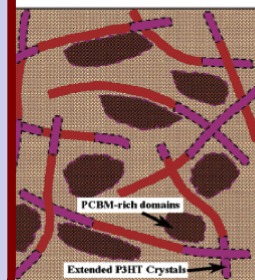
P3HT:PCBM bulk-heterojunction organic solar cell



[Li, Zhu, Yang

Can we mimic the structure and replicate the performance of natural LHCs in an artificial system? (quantum efficiency, tunability of absorption)

Need to control assembly of pigments at the nanoscale



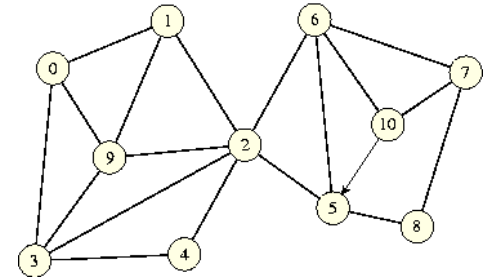
- Hierarchical structure
- Ordered and strict spatial structure
- Energetic structure (gradient)

- Random morphology, orientation
- No energy gradient on fine scale

Quantum walks in the presence of decoherence

e.g.

$$H = - \sum_{[i,j]} \Delta_{ij}(t) (c_i^\dagger c_j + c_i c_j^\dagger) + \sum_j \epsilon_j(t) c_j^\dagger c_j$$



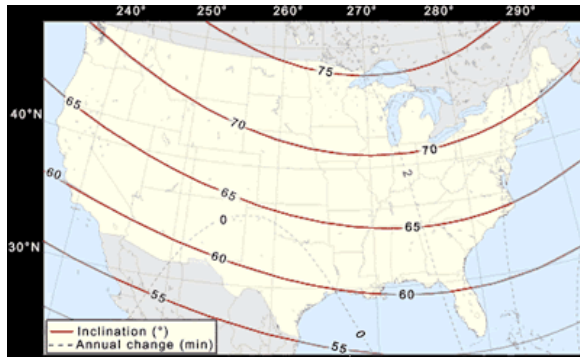
Accurate model of decoherence important.

[MS et. al., 2008]: The precise model of the decoherence matters greatly, sometimes more than the rate of decoherence (hypercube).

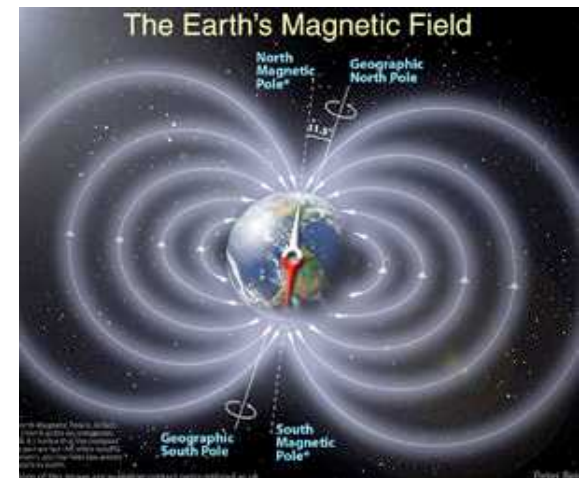
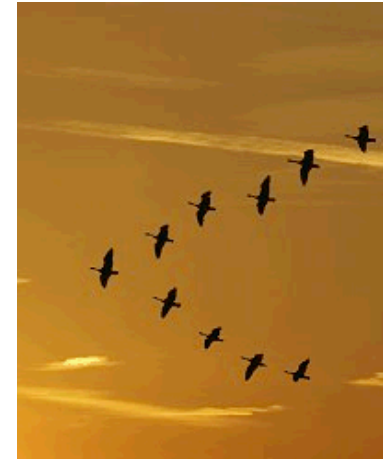
The avian chemical compass

Avian magnetoreception

- Migrating birds navigate using the Earth's magnetic field
- From experiments (W. Wiltschko & R. Wiltschko) we know:
 - birds are sensitive to magnetic field inclination



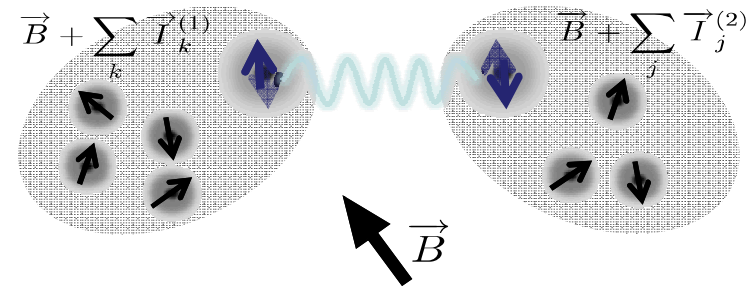
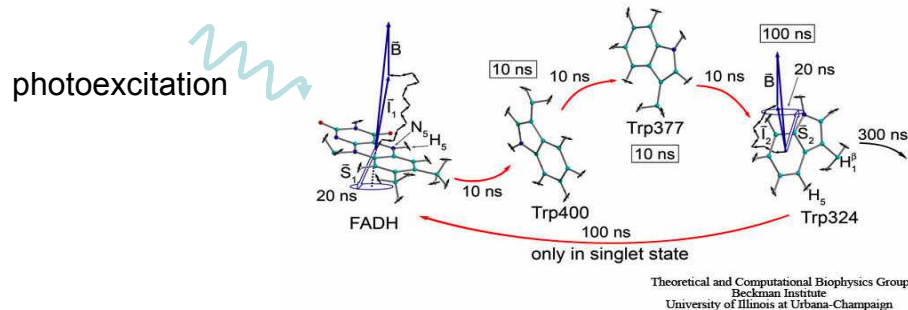
- require light above a threshold wavelength to sense magnetic fields
- sensing works for a narrow range of magnetic field strengths (matching the Earth's field $\sim 30 - 60 \mu\text{T}$)



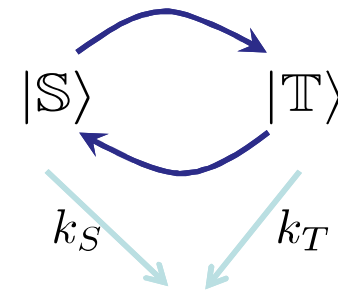
The radical pair mechanism

First proposed by K. Schulten & C. Swenberg (1978).

Developed by **Schulten**, Ritz, Hore, Wiltschko, Rodgers ...



$$|S\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle |\downarrow\rangle + |\downarrow\rangle |\uparrow\rangle)$$



Singlet-triplet inter-conversion dependent on **B** and the local magnetic moments.

Radical pair recombination (chemical end product) is spin dependent: will recombine if in singlet state, will not if in triplet.

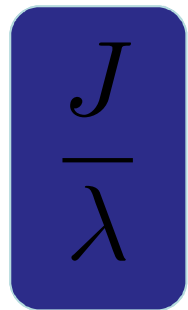
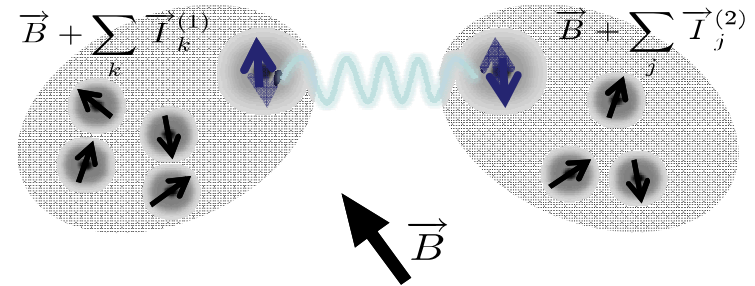
=> Biochemical signals bird receives dependent on **B**.

Quantum mechanics of the avian compass

$$H^{(1)} = g\mu_B \vec{B} \cdot \vec{S}^{(1)} + \sum_k \lambda_k \vec{I}_k \cdot \vec{S}^{(1)}$$

J : the magnetic field coupling

λ : the couplings to local nuclear magnetic moments



- (1) Entanglement in the initial two-electron state (e.g. singlet state) increases sensitivity of mechanism
- (2) The loss of initial entanglement is the key dynamic (entangled states useful for metrology)
- (3) $\frac{J}{\lambda} \approx 1$ necessary for high sensitivity to B

Mechanism agrees with experimental data, but unconfirmed as yet.

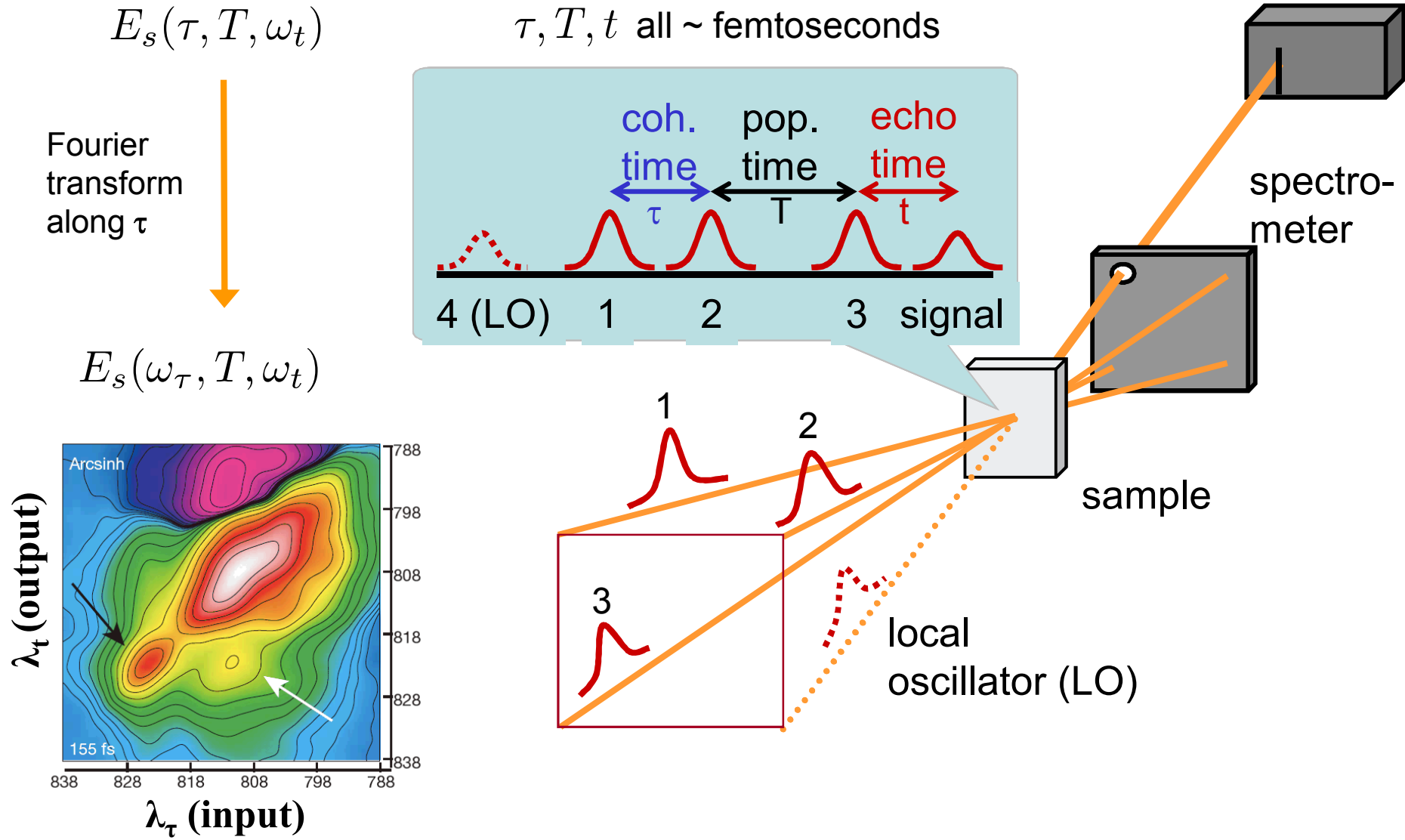
C. Rodgers & P. Hore. PNAS, **106**, 353 (2009)
T. Ritz *et al.* Biophysical J., **96**, 3451 (2009)
J. Cai *et al.* arXiv:0906.2383 [quant-ph] (2009)
E. Rieper *et al.* arXiv:0906.3725 [quant-ph] (2009)

Connection to quantum information

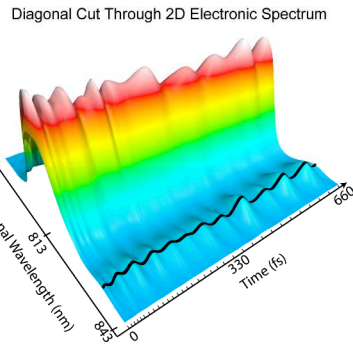
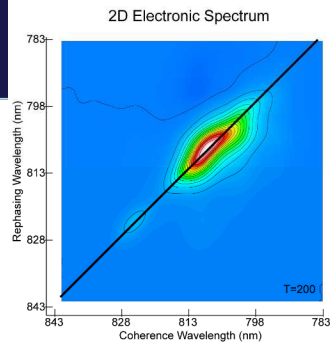
Essentially a parameter estimation problem

Backup slides

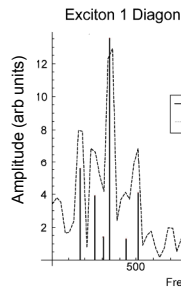
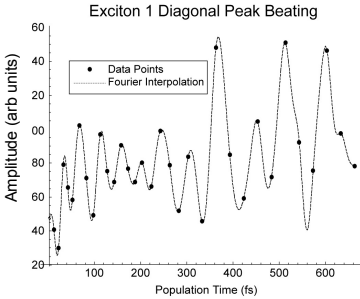
Probing the ultrafast



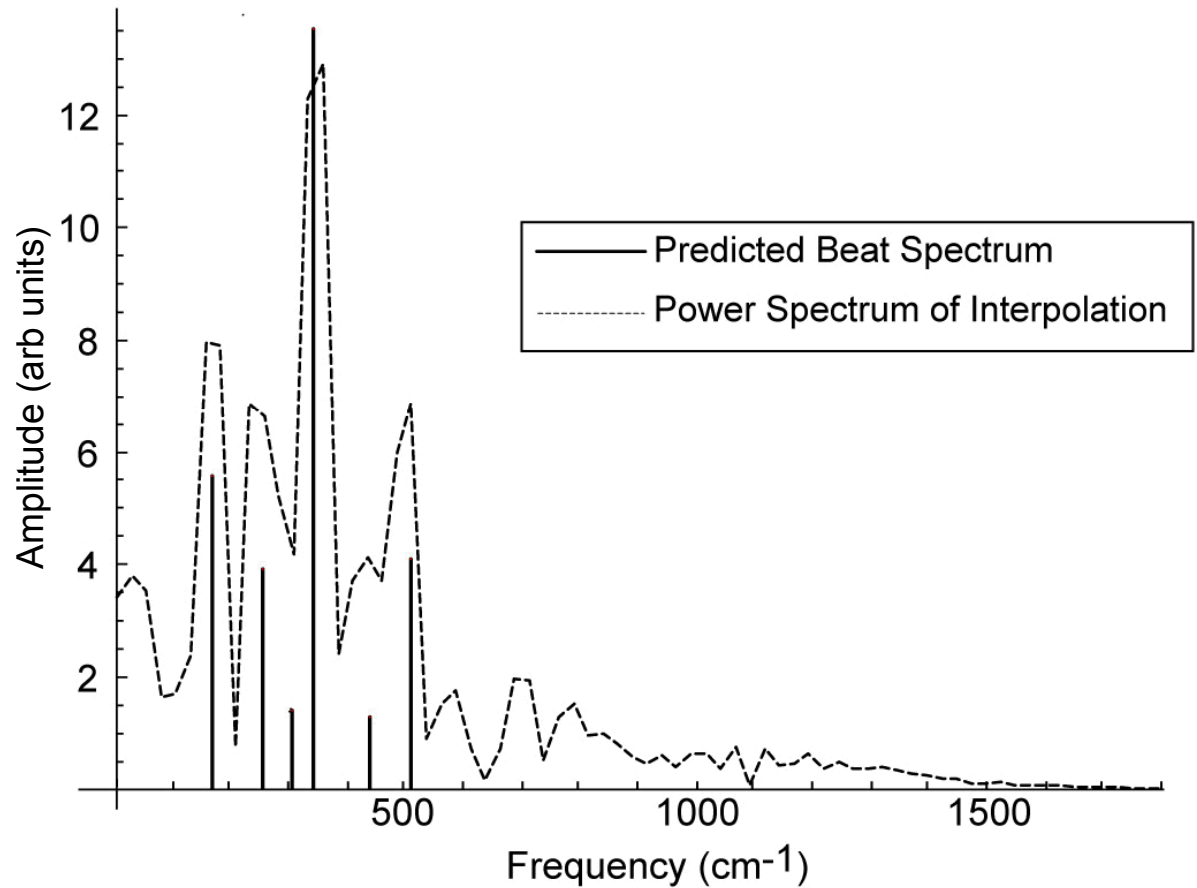
Difference in FMO (77K)



I Cut Through 2D Electronic Spectrum



Exciton 1 Diagonal Peak Beating Power Spectrum



- Oscillatory signal
- Electronic population relation
- Strong evidence

Rephasing Wavelength

“Evidence for wavelike energy systems”, G.S. Engel, T.R. (R.E. Blankenship, and G. R