

*Exceptional service in the national interest*



# Quantum biology unveiling the quantum tricks up nature's sleeve

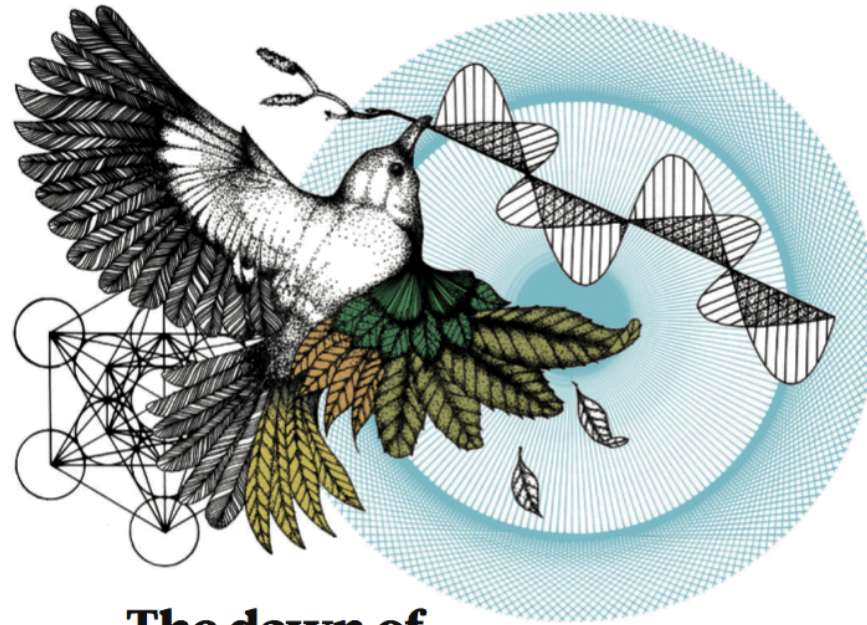
Mohan Sarovar

Scalable and Secure Systems Research

Sandia National Laboratories, Livermore, USA



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The dawn of  
**quantum**  
biology

*The key to practical  
quantum computing  
and high-efficiency  
solar cells may lie in  
the messy green world  
outside the physics lab.*

BY PHILIP BALL

Nature 474:272-274 (2011)

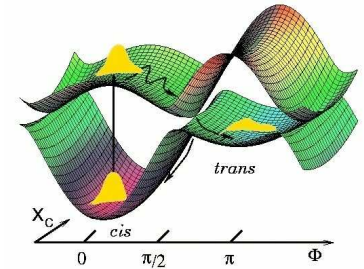
# Three classes of QM influence in biology

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

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

e.g.

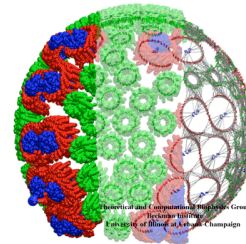
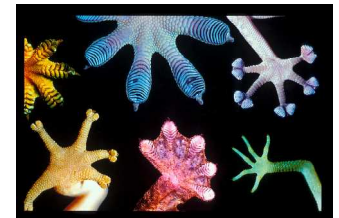
- Ultra-fast molecular transitions through conical intersections
- Chemical reactions involving electron & proton tunneling



3. **Functional necessity:**

Possible e.g.

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



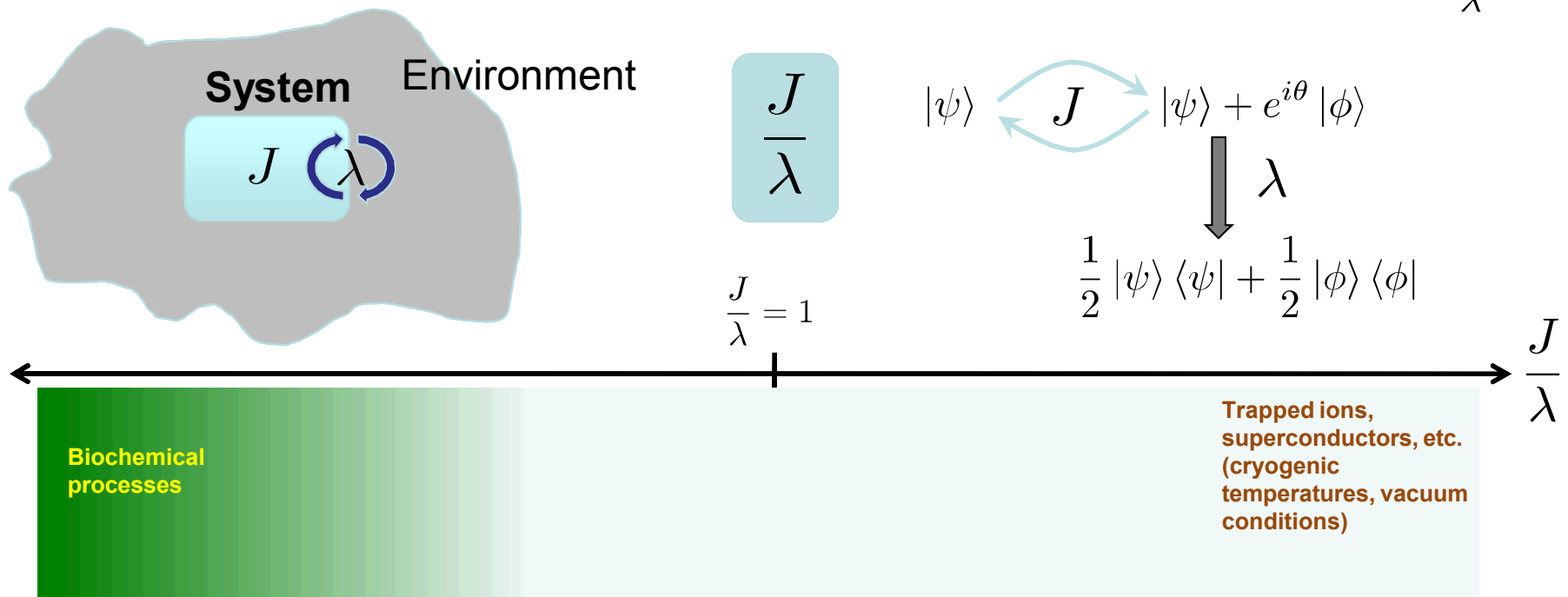
# What is so surprising about quantum behavior in biology?

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

2. Decoherence theory: W. Zurek et al.

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

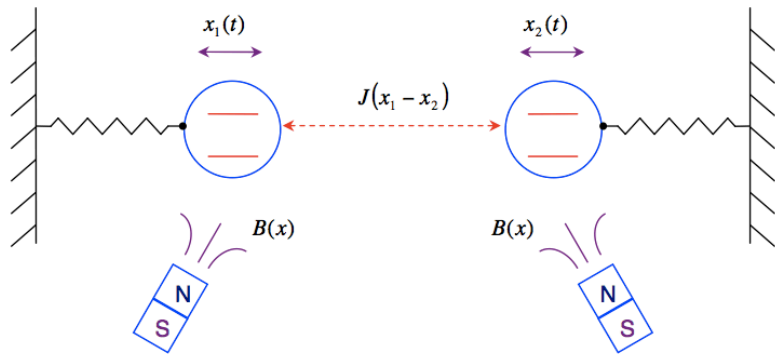
Decoherence timescale:  $\tau_D \propto \frac{1}{\lambda}$



# Non-equilibrium dynamics

Quantum effects can be prevalent before equilibration.

An example: Cai et al. Phys. Rev. E **82** 021921 (2010)  
 Guerreschi et al. New J. Phys. **14** 053043 (2012)

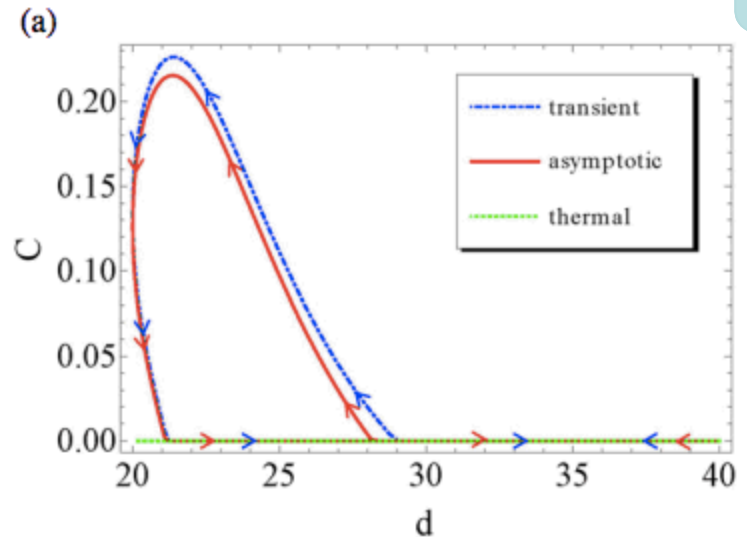


Entanglement can be generated continuously through periodic motion even when no entanglement would exist in equilibrium

$$H(t) = \omega_1 \sigma_z^1 + \omega_2 \sigma_z^2 + J(t) \sigma_x^1 \sigma_x^2$$

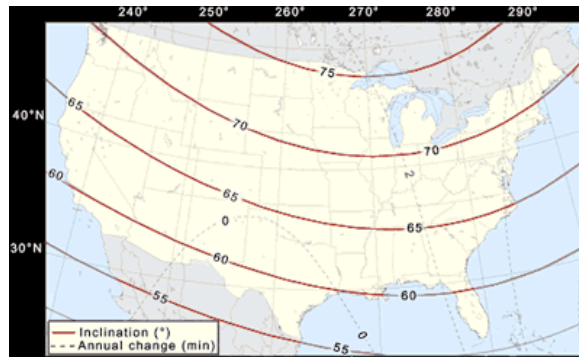
Each spin also coupled to a bosonic thermal bath ( $\lambda$ )

$$\frac{J}{\lambda}$$

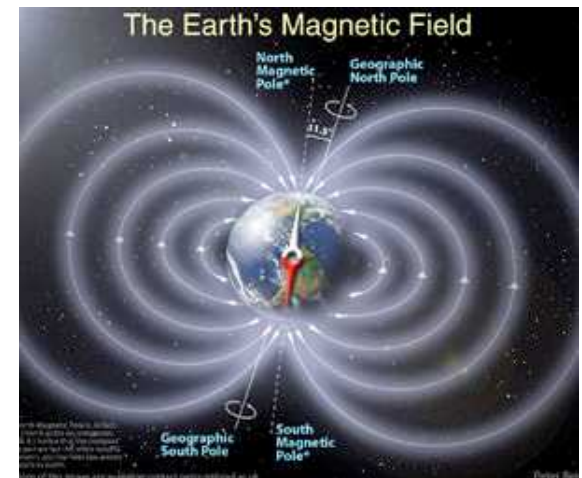
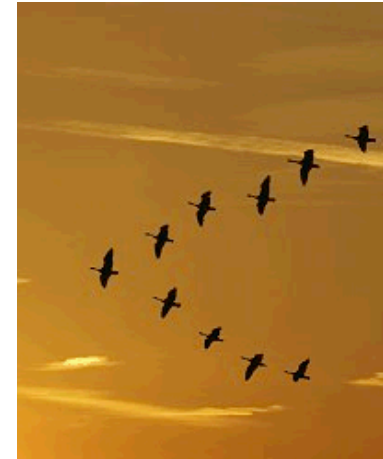


# Avian magnetoreception

- Migrating birds navigate using the Earth's magnetic field
- From experiments (W. Wiltschko & R. Wiltschko) we know:
  - birds are sensitive to magnetic field inclination (not polarity)



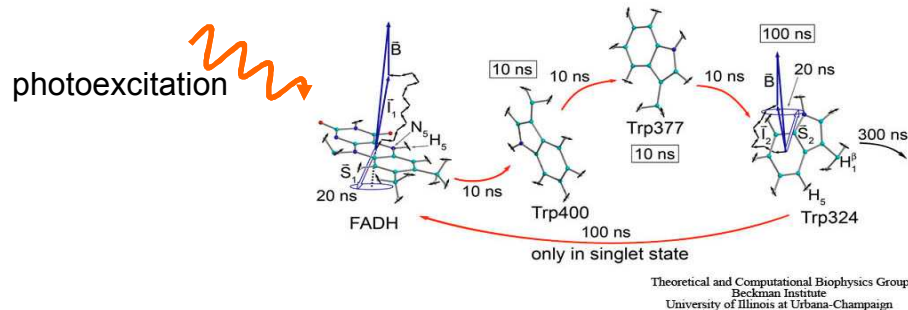
- require light above a threshold wavelength to sense magnetic fields (green to UV)
- sensing works for a narrow range of magnetic field strengths (matching the Earth's field  $\sim 30 - 60 \mu\text{T}$ )



# The radical pair mechanism

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

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

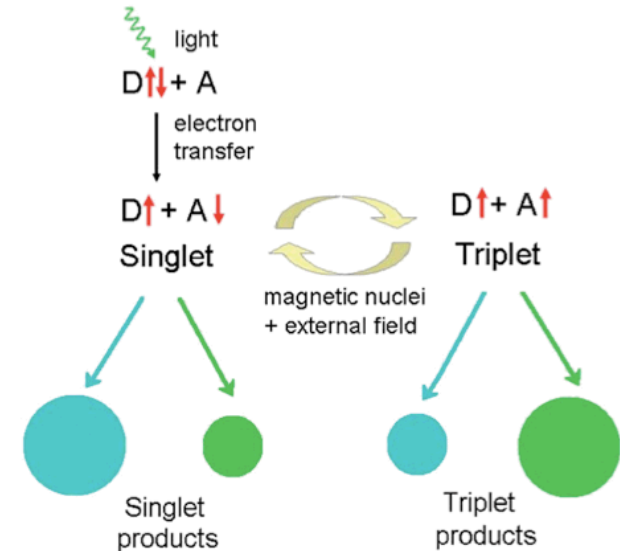


$$|S\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

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.

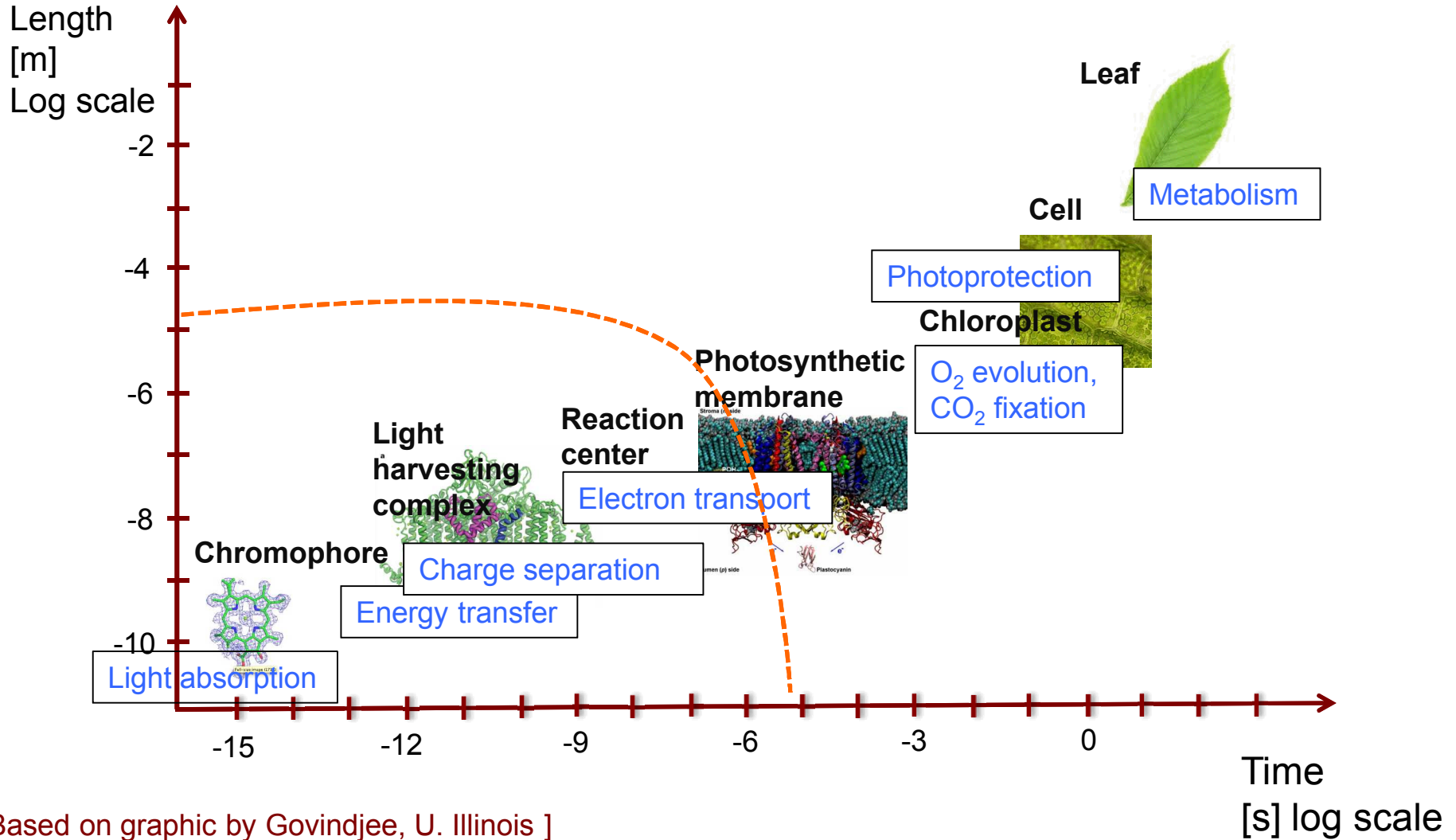
=> Biochemical signals bird receives dependent on **B**.



Ritz et al. *Biophys. J.* **96** 3451 (2009)

# Primary processes in photosynthesis

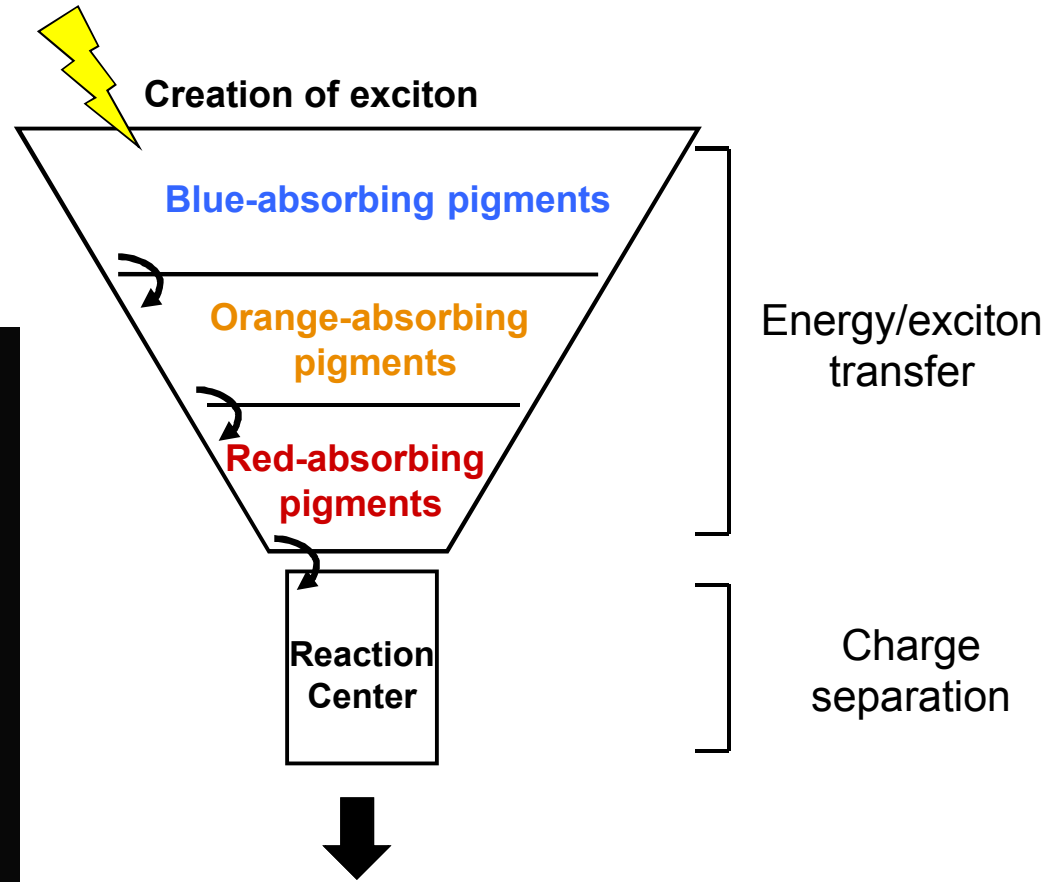
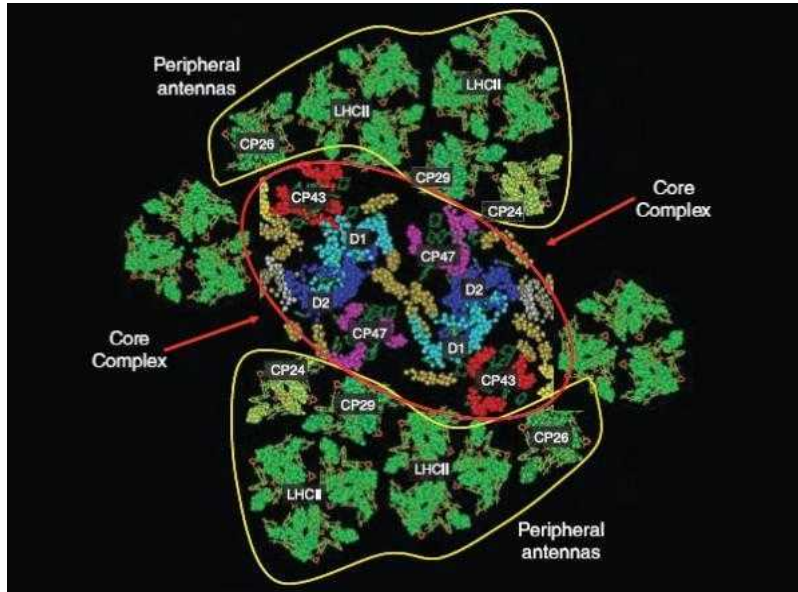
# Time & length scales in photosynthesis





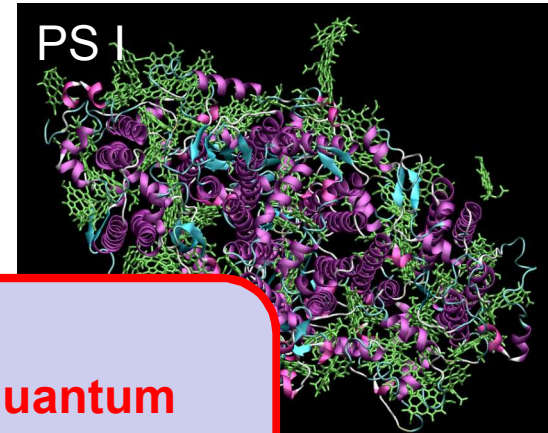
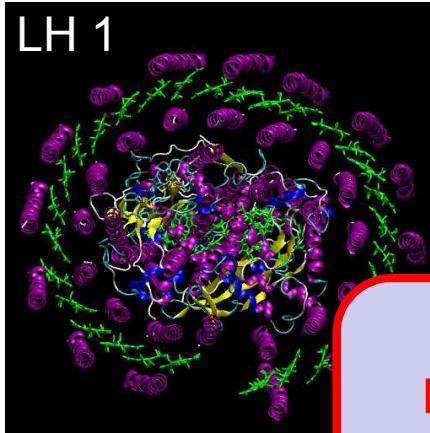
# The initial stages of photosynthesis

Light harvesting complex (LHC)

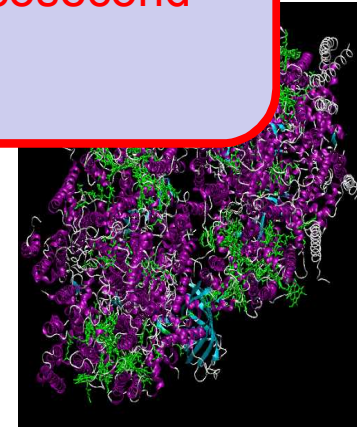
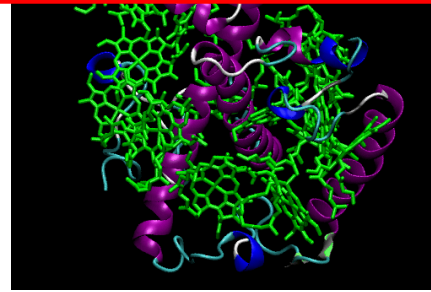


...Secondary electron transfer reactions, Water splitting, Proton transport across thylakoid membrane, Reduction of  $\text{NADP}^+$ , ATP synthesis...

# Light harvesting complexes



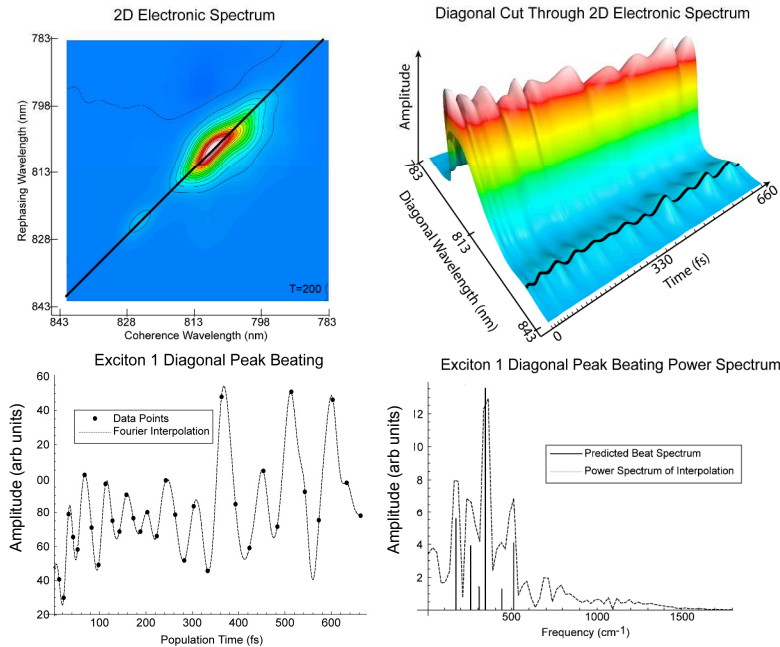
Initial stages are **>95% quantum efficient**, and occur at picosecond timescales



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

# Dynamic coherence 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:

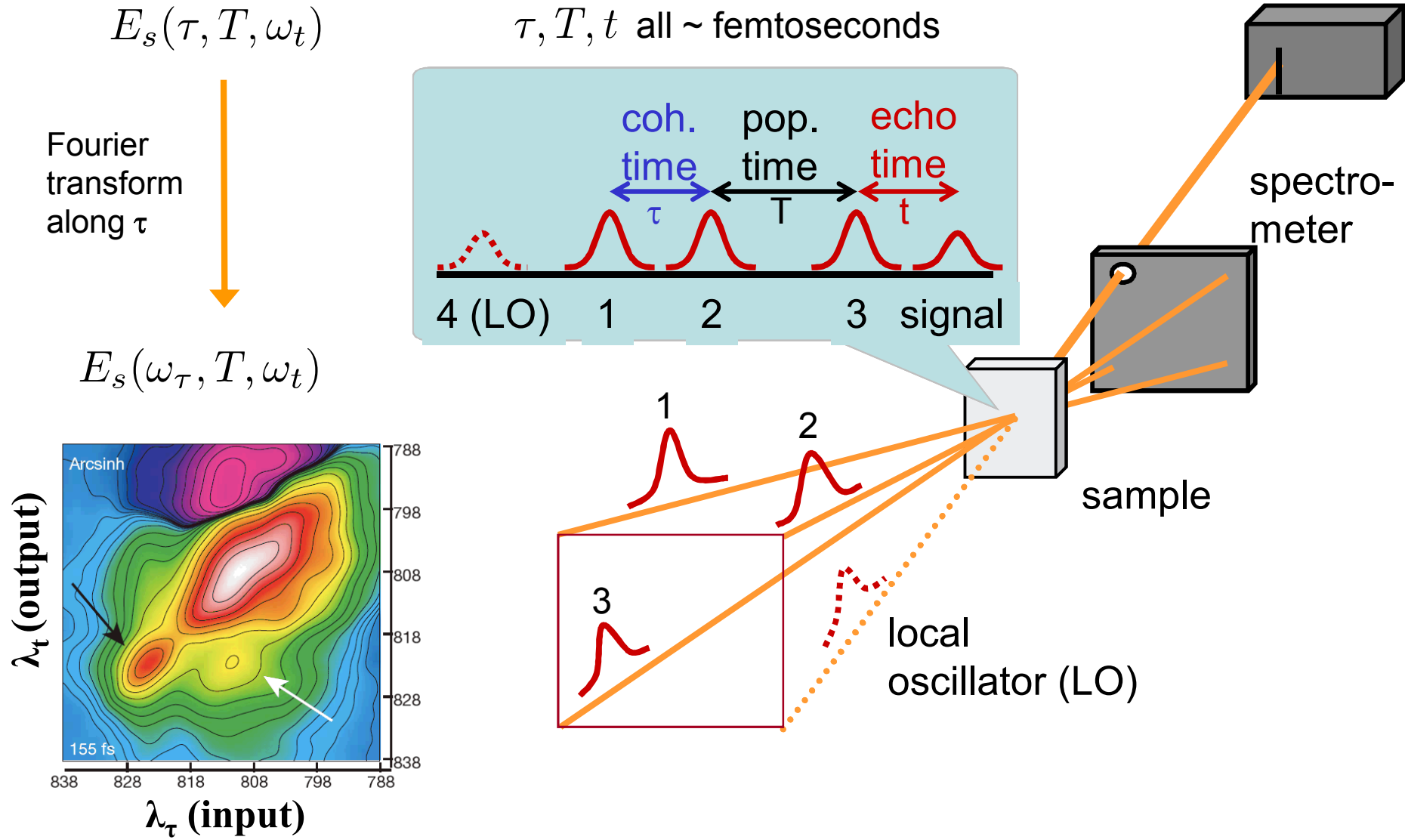
Lee *et al.*, *Science*, **316**, 1462 (2007)

## Higher plants (14 pigments)

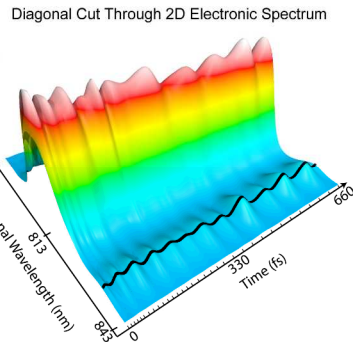
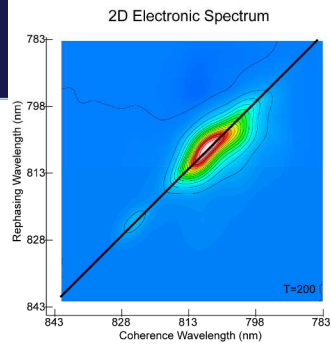
LHC-II:

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

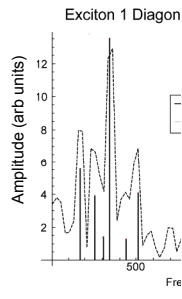
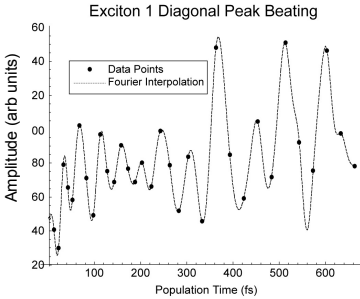
# Probing the ultrafast



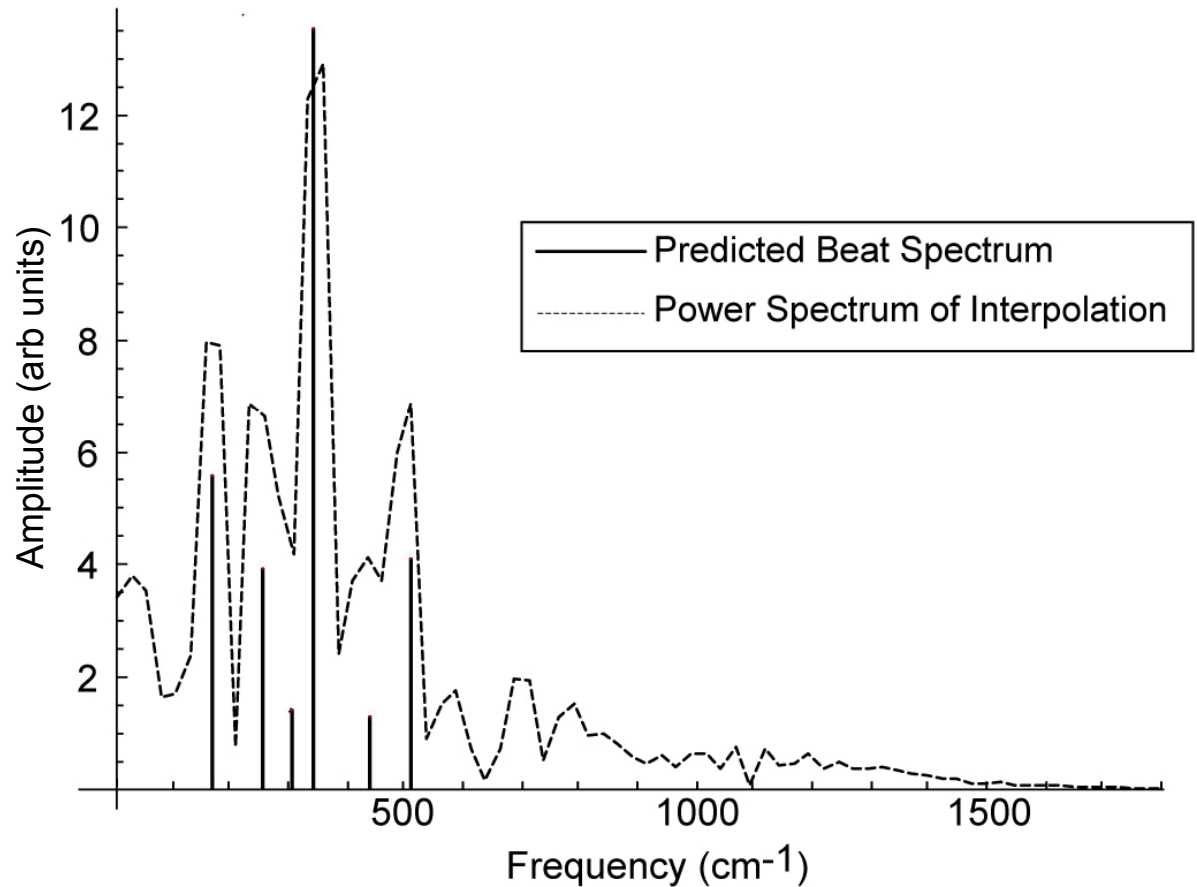
# Difference in FMO (77K)



## 1 Cut Through 2D Electronic Spectrum



## Exciton 1 Diagonal Peak Beating Power Spectrum



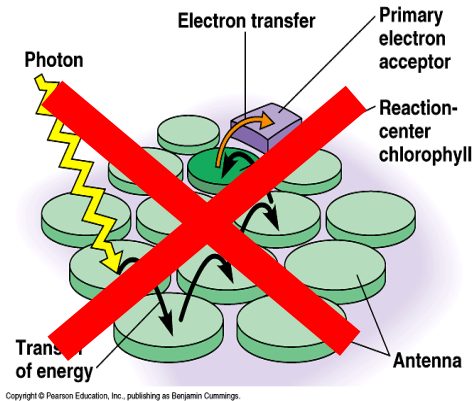
- Oscillatory signal
- Electronic population relation
- Strong evidence

Repeating Wavelength

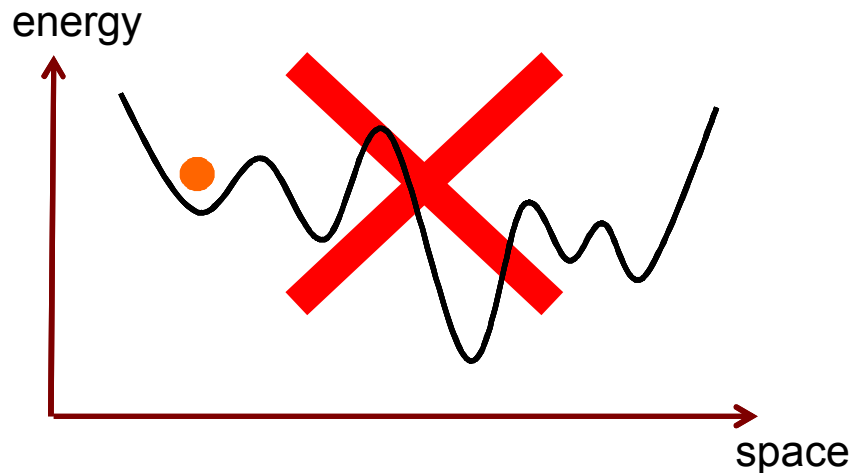
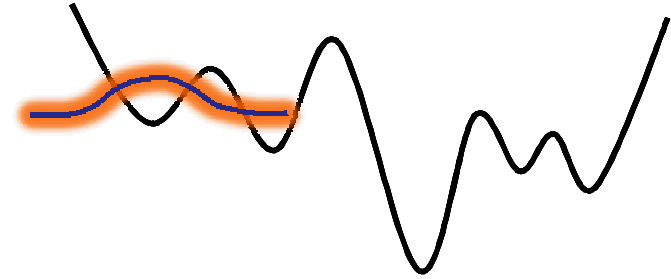
“Evidence for wavelike energy systems”, G.S. Engel, T.R. ( R.E. Blankenship, and G. R

# Dynamics of light harvesting: cartoon

## The conventional model

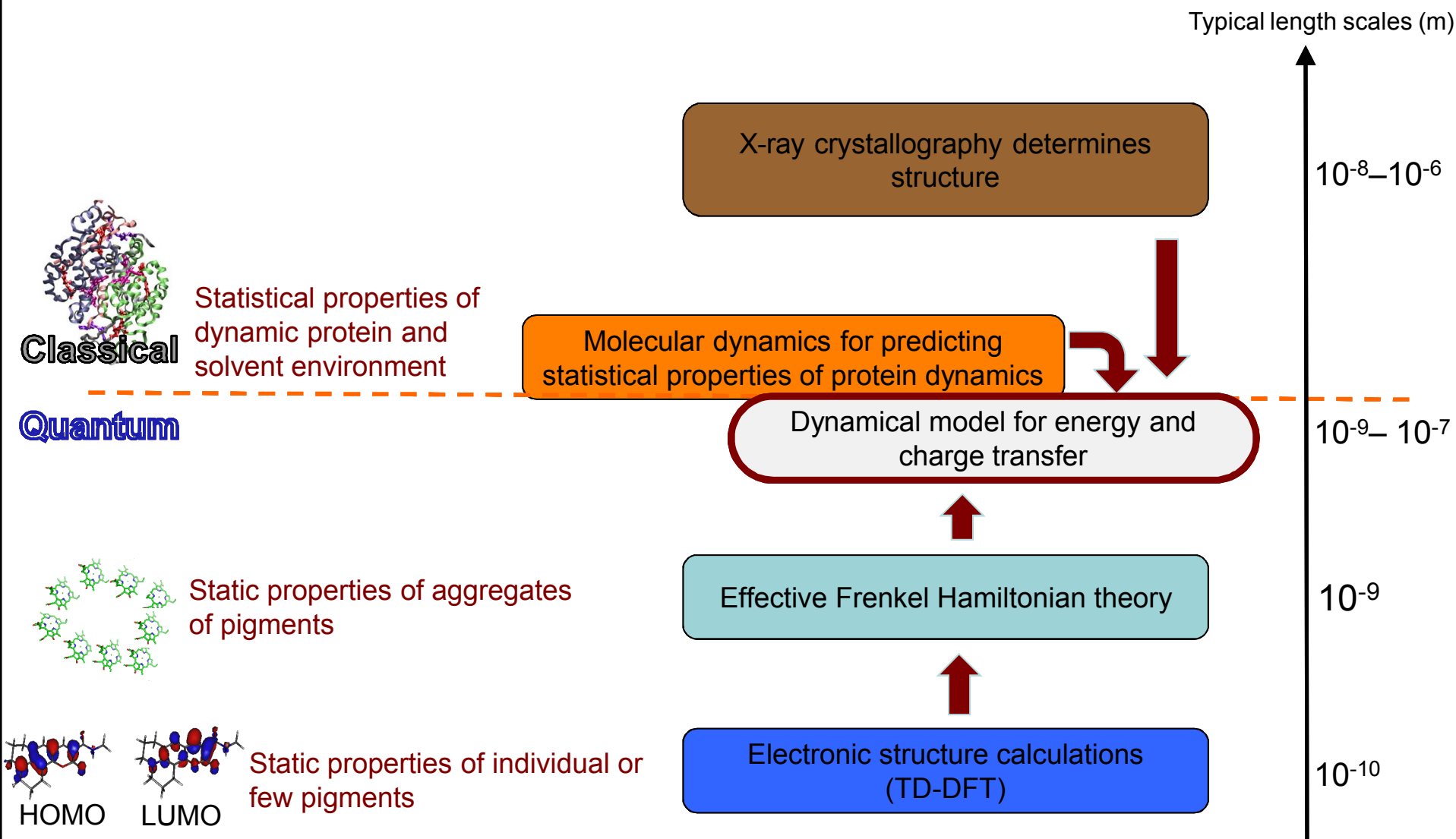


## Revised model



Electronic excited state (excitons) delocalized across several pigments even in the presence of the environmental coupling

# Current approach to modeling LHCs



# Theoretical modeling of energy transfer Sandia National Laboratories

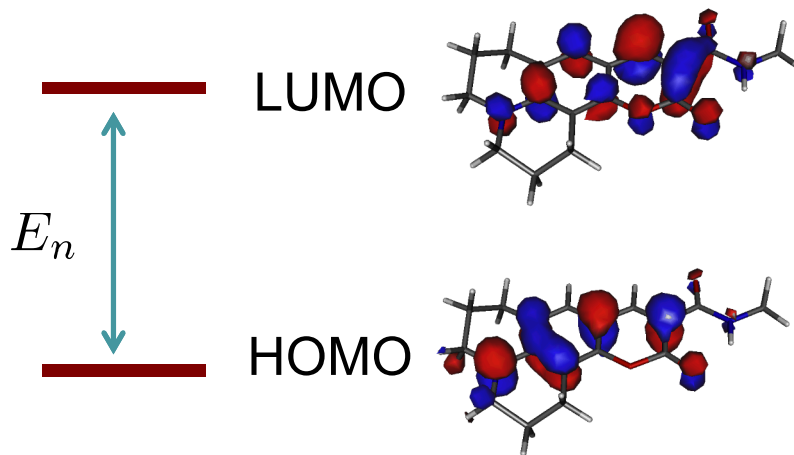
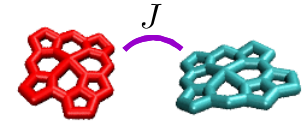
Electronic degrees of freedom:

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)



# Theoretical modeling of energy transfer Sandia National Laboratories

Pigment-protein interactions: open system dynamics

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

reduced dynamics

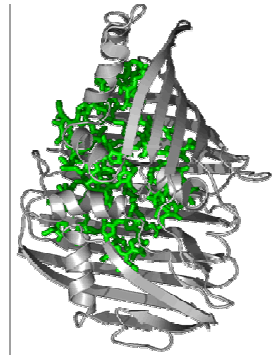
$$\frac{d\rho_{\text{el}}}{dt} = \dots$$

master equation

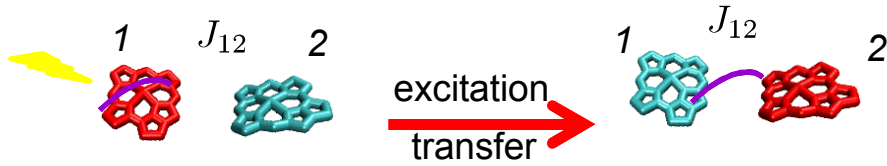
$$H_{\text{el-ph}} = \sum_n |n\rangle\langle n| \sum_i \xi_i (b_i + b_i^\dagger)$$

$$H_{\text{ph}} = \sum_i \omega_i b_i^\dagger b_i$$

Harmonic approximation good because of the large number of protein and solvent degrees of freedom

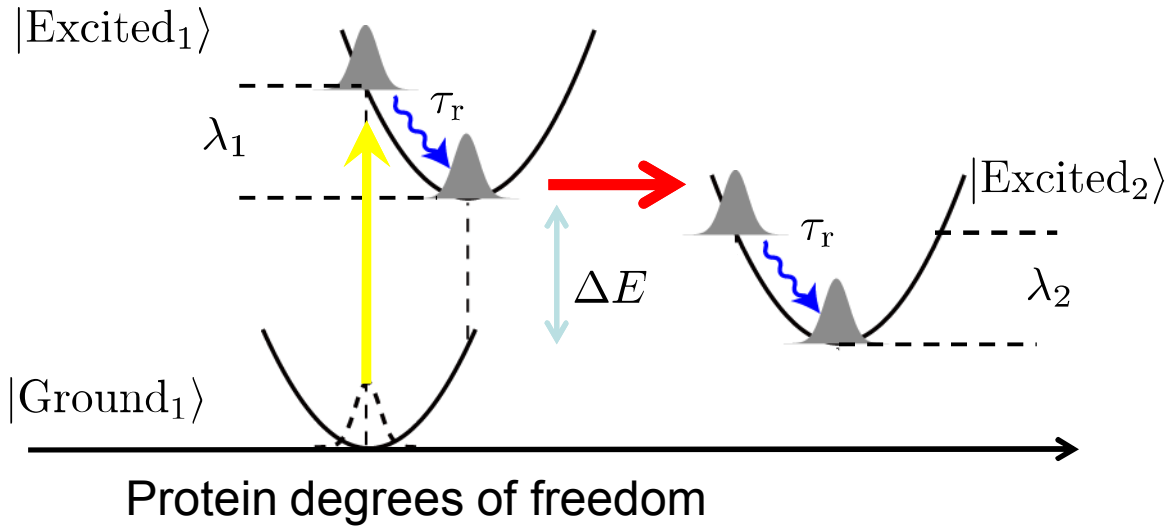


# Theoretical modeling of energy transfer Sandia National Laboratories



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

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



## Several energy scales

Pigment coupling	$J_{12}$
Reorganization energy of protein bath	$\lambda$
Protein relaxation timescale	$\frac{\hbar}{\tau_r}$
Pigment energy difference	$\Delta E$
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	$\lambda$
Protein relaxation timescale	$\frac{\hbar}{\tau_r}$
Pigment energy difference	$\Delta E$
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:

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

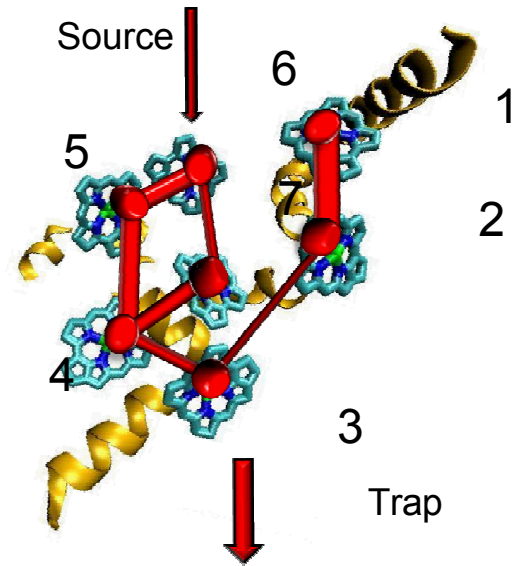
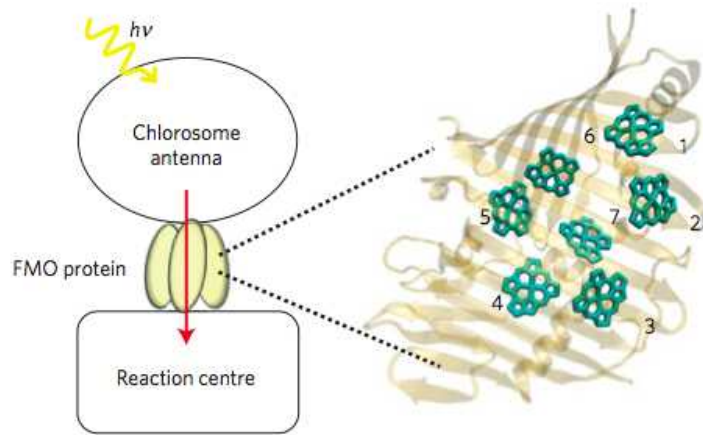
Generalized Bloch-Redfield:

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

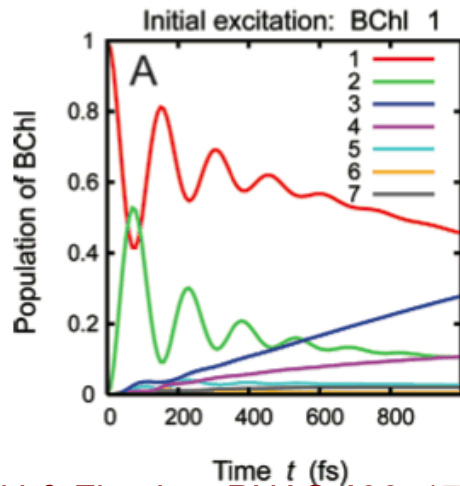
Reduced hierarchy equations approach:

Gaussian distributed fluctuations

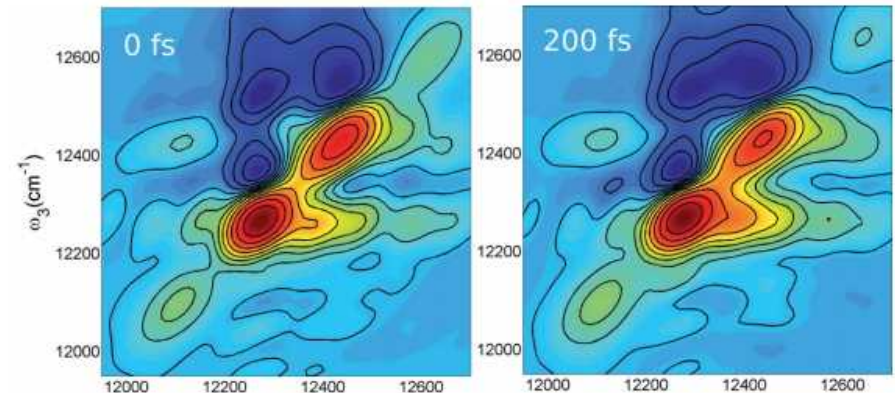
# Example: dynamics in FMO



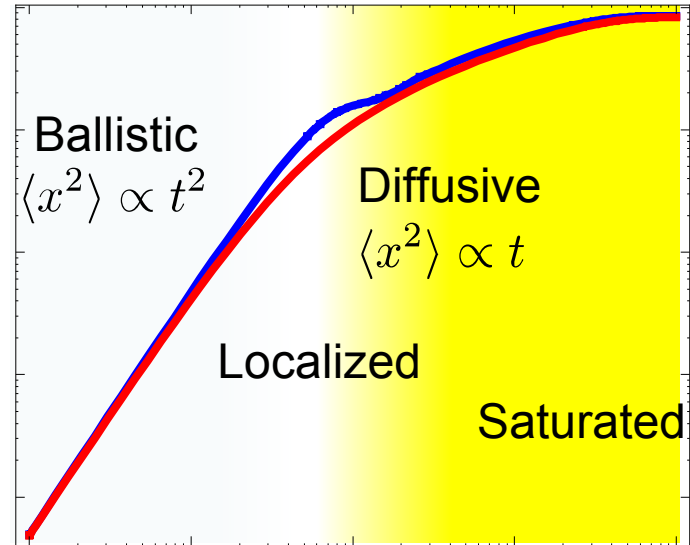
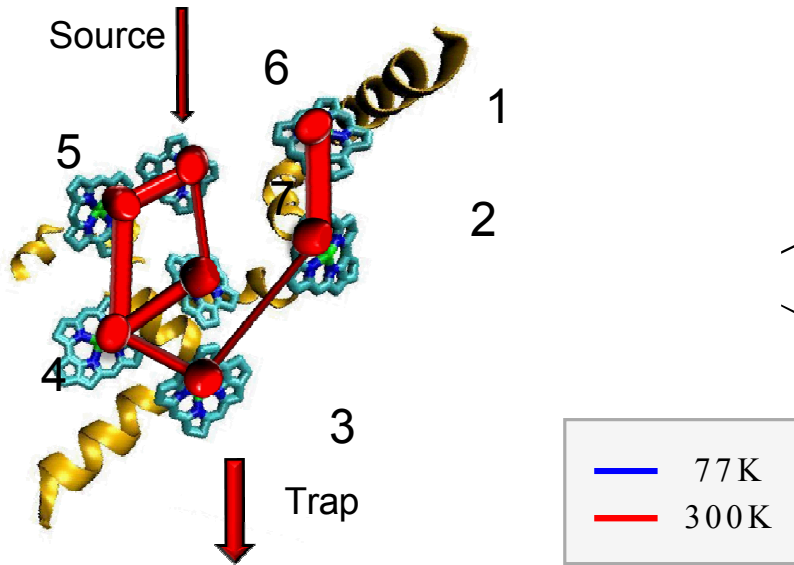
## Model dynamics within complex



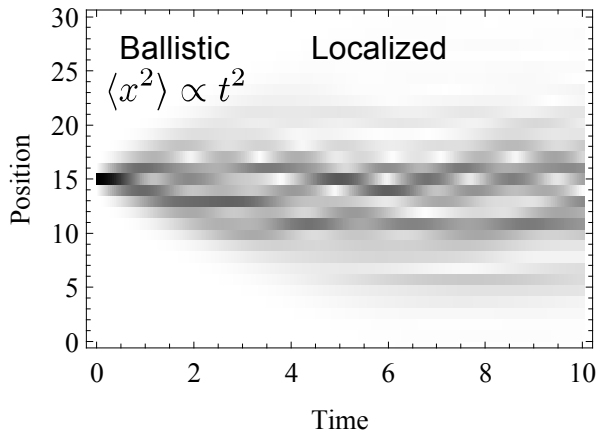
## Reproduce experimental signatures



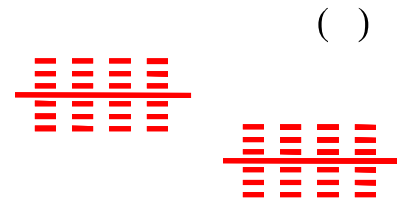
# Example: dynamics in FMO



## Anderson localization

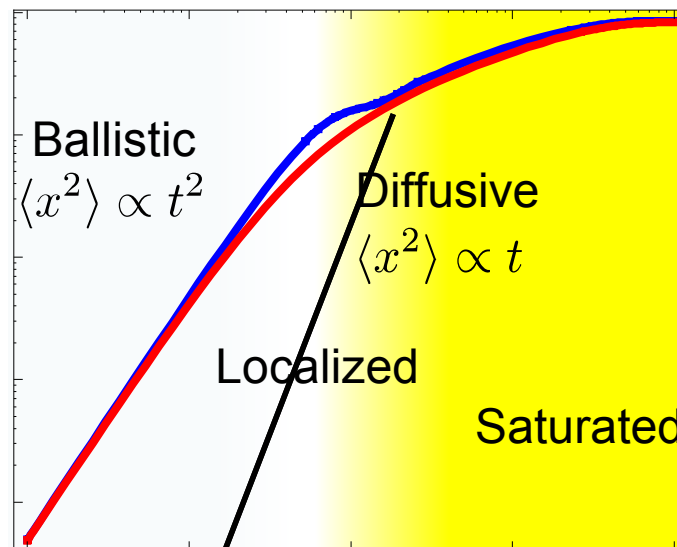
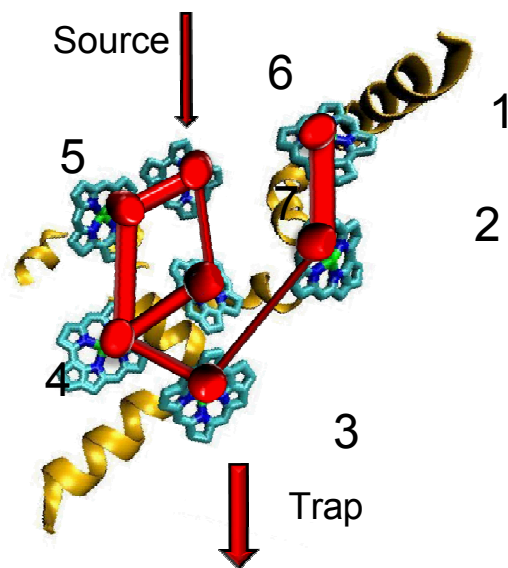


Any variation in site energies lead to localization



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

# Example: dynamics in FMO

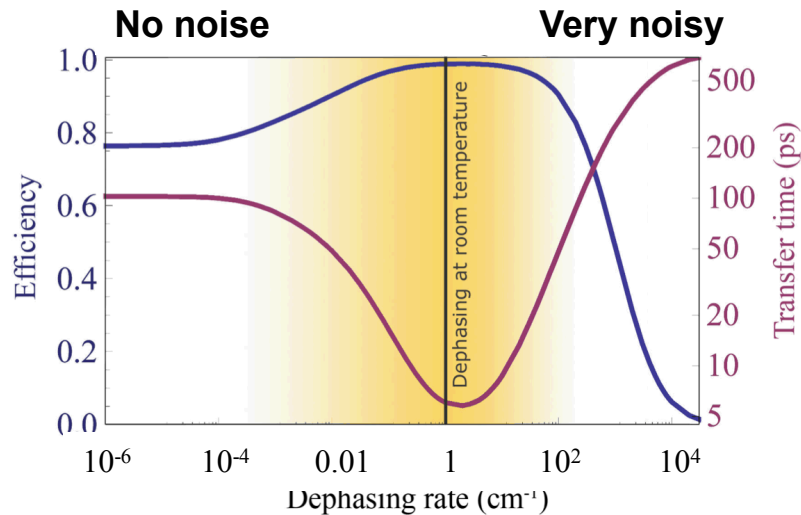


Exciton remains delocalized across multiple pigments throughout

Sarovar et al., Nature Phys. 6 462 (2010)

# Functional role for coherence?

- Efficiency of energy transfer



**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

[Adapted from Rebentrost et al., *New J. Phys.* **11** 033003 (2009)]

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

Plenio & Huelga, *New J. Phys.* **10**, 113109 (2008)

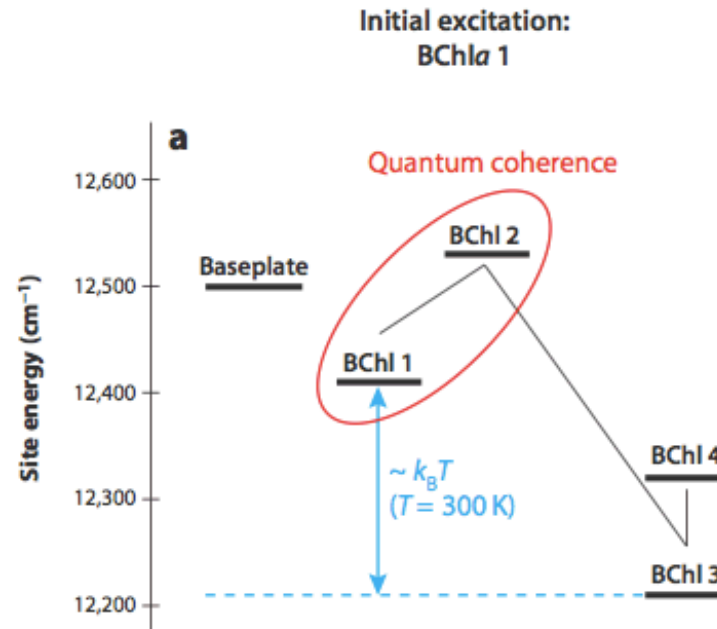
Kim, J.-H. & Cao, J. *J. Phys. Chem. B* **114**, 16189 (2010)

Mohseni, M *et al.* *arXiv:1104.4812* (2011)

...

# Functional role for coherence?

- Uni-directionality of energy transfer



From: Ishizaki & Fleming, *Ann. Rev. Condens. Matter Phys.* **3** (2011)

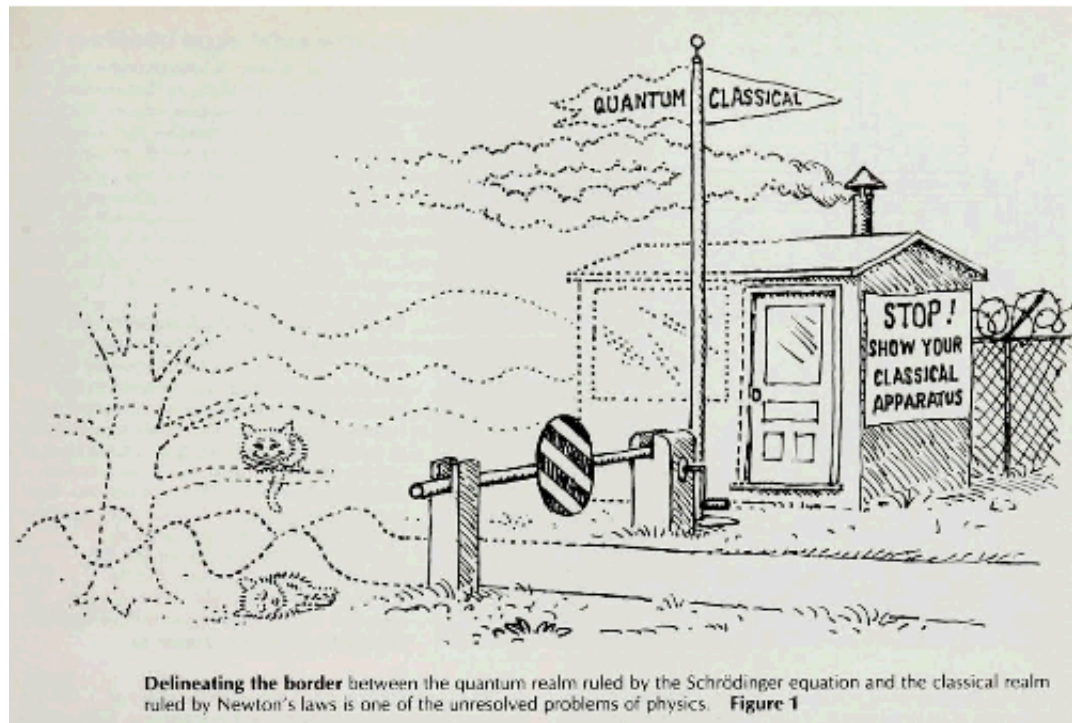
Ishizaki & Fleming, *PNAS* **106** 17255 (2009)  
Hoyer *et al.* *Phys. Rev. E* **86** 041911 (2012)

# Ongoing work

- Establish whether oscillations in 2D electronic spectroscopy are due to purely electronic or vibronic coherence  
[Jonas, Fleming, Scholes, Engel, ...]
- Establish functional role and/or evolutionary selection of coherence  
[Scholes, ...]
- Use lessons learned from natural light harvesting systems to construct artificial light harvesting devices (photovoltaics, sensors)
  - Nanoscale structure is critical for high quantum efficiencies at room temperature
  - Design principles (e.g. balance coherent and incoherent transfer)  
[Scholes et al. Nature Chem. **3**, 763 (2011)]  
[Sarovar & Whaley, New J. Phys. **15** 013030 (2013)]

# Conclusions

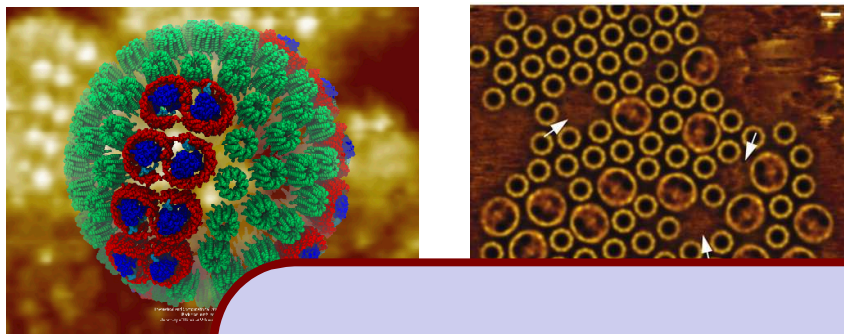
- Although definitive conclusions are immature at this time, there is mounting evidence (e.g. photosynthesis, avian magnetoreception) that non-equilibrium quantum coherent dynamics plays a non-trivial role in some key processes in biology



[W. Zurek, Physics Today, October 1991]

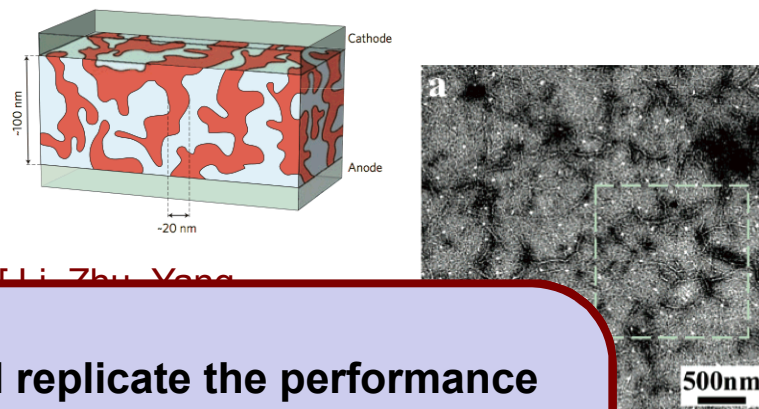
# Natural and artificial light harvesting

## LH I and LH II light harvesting complexes in purple bacteria



[ Beckmann  
Illinois ]  
[ Scheuring  
2004 ]

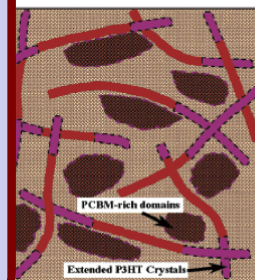
## P3HT:PCBM bulk-heterojunction organic solar cell



[ 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



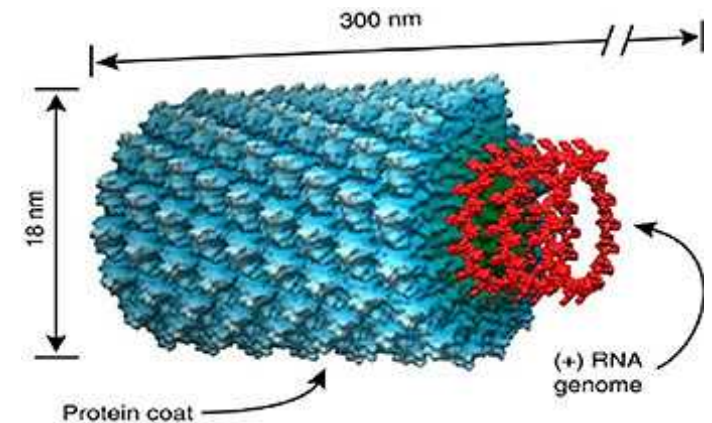
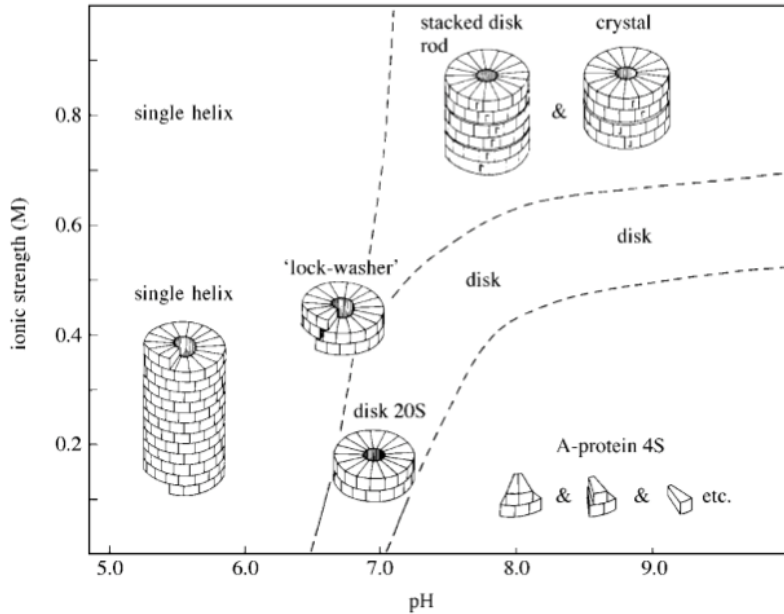
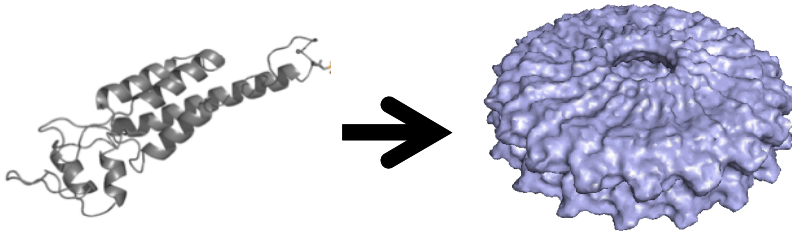
- Hierarchical structure
- Ordered and strict spatial structure
- Energetic structure (gradient)

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

# The tobacco mosaic virus

- Extensively studied virus – structure and properties well known
- Robust and well-known self-assembly process

## Tobacco Mosaic Virus (TMV) capsid

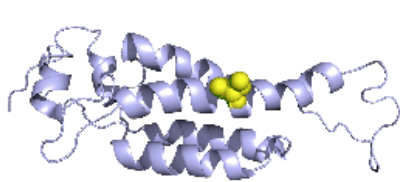
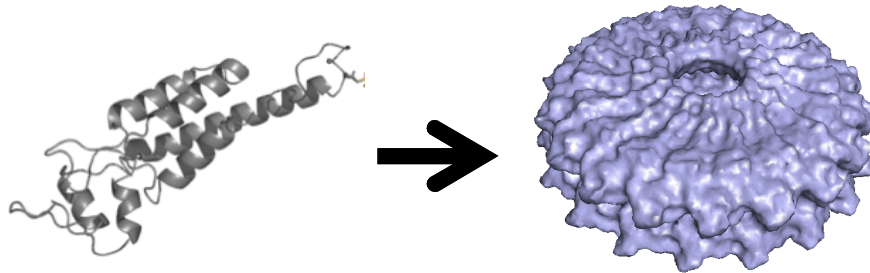


TMV self assembly  
“phase diagram”  
[Klug 1999]

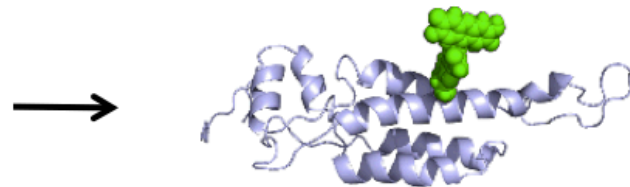
# Building synthetic LHCs from viruses

A route to tailoring nanoscale structure: use self-assembling proteins as scaffolds

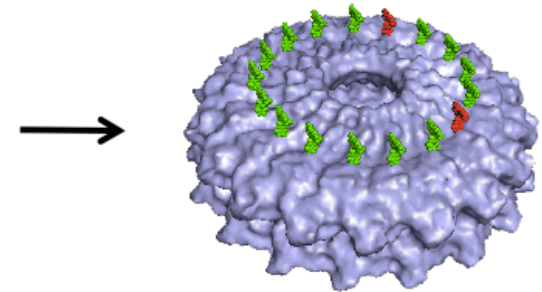
## Tobacco Mosaic Virus (TMV) capsid



TMVP with S123C  
mutation  
(from bacteria or plants)



TMVP labeled with  
chromophore using linker

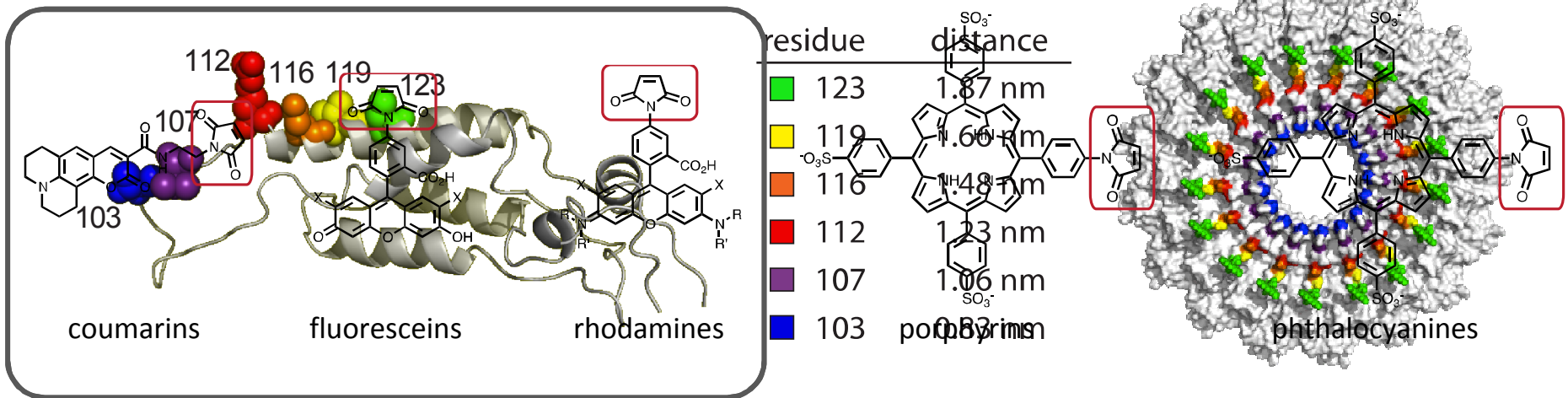


light harvesting disks  
(17 nm)

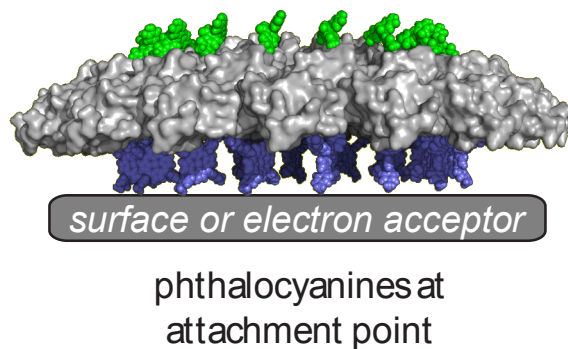
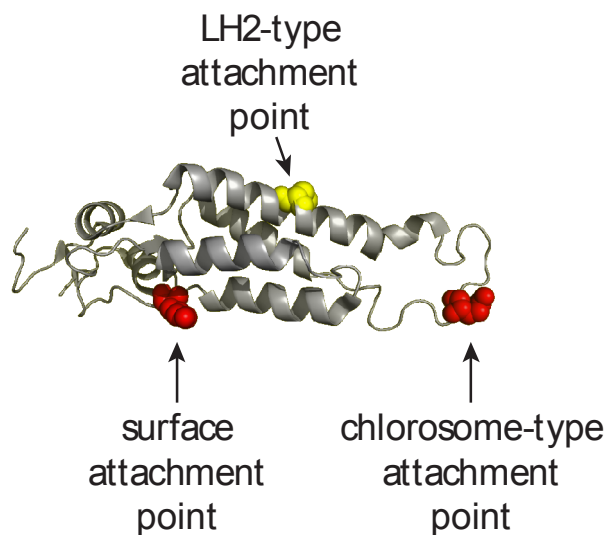
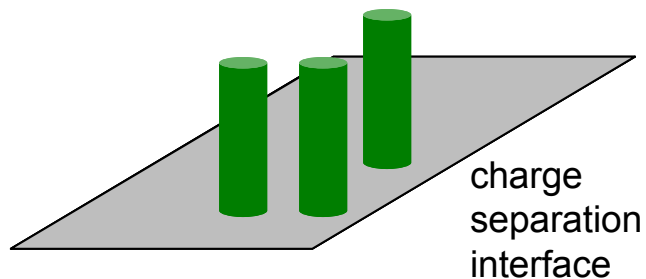
# TMV-templated light harvesting

## Advantages:

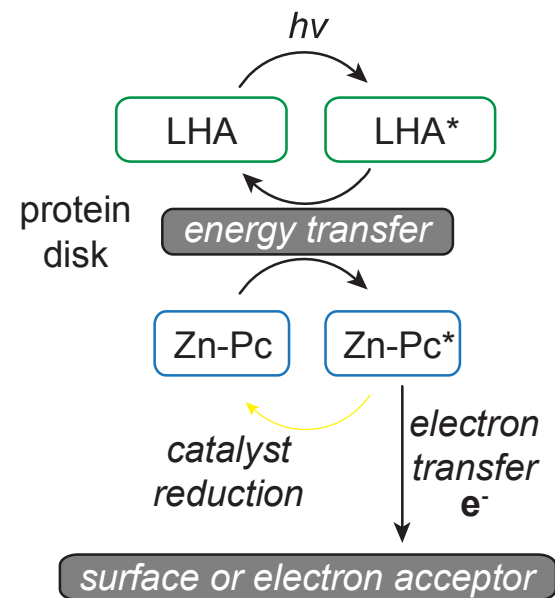
1. The spectral properties of the chromophores can be readily changed
2. The distances between the chromophores can be altered systematically
3. TMV-based complexes are highly stable and available in gram quantities



# TMV-templated light harvesting



electron transfer scheme:



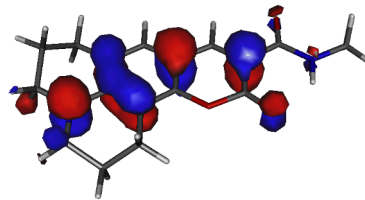
[Michel Dedeo and Dan Finley, UC Berkeley]

# Microscopic modeling of TMV-templated assemblies

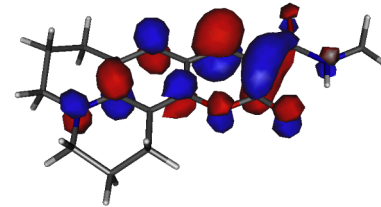
Electronic structure calculations  
(TD-DFT)

To obtain static properties of individual or few pigments

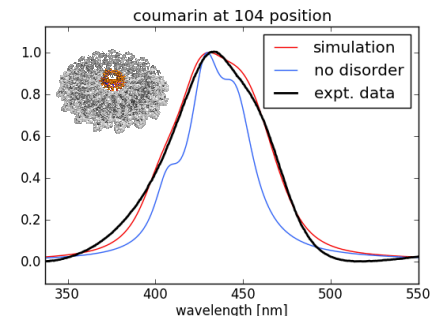
Coumain-343  
pigment



HOMO

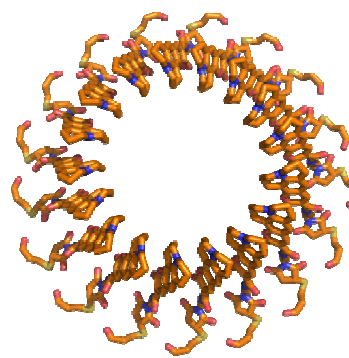
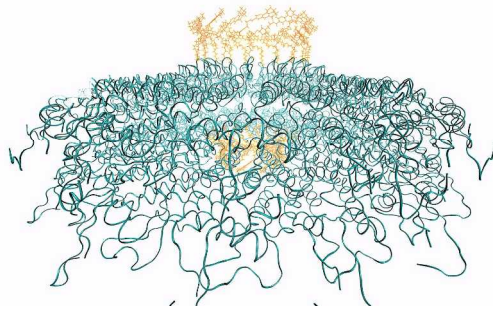


LUMO

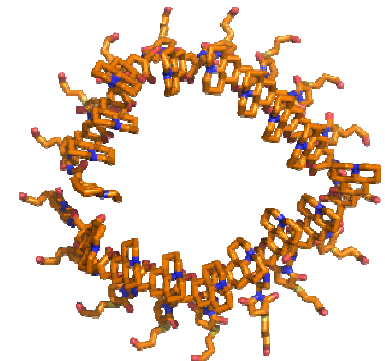


Molecular mechanics energy  
minimization for predicting self-  
assembled structures

To obtain structure imposed by  
self-assembly of functionalized  
TMV



Initial state

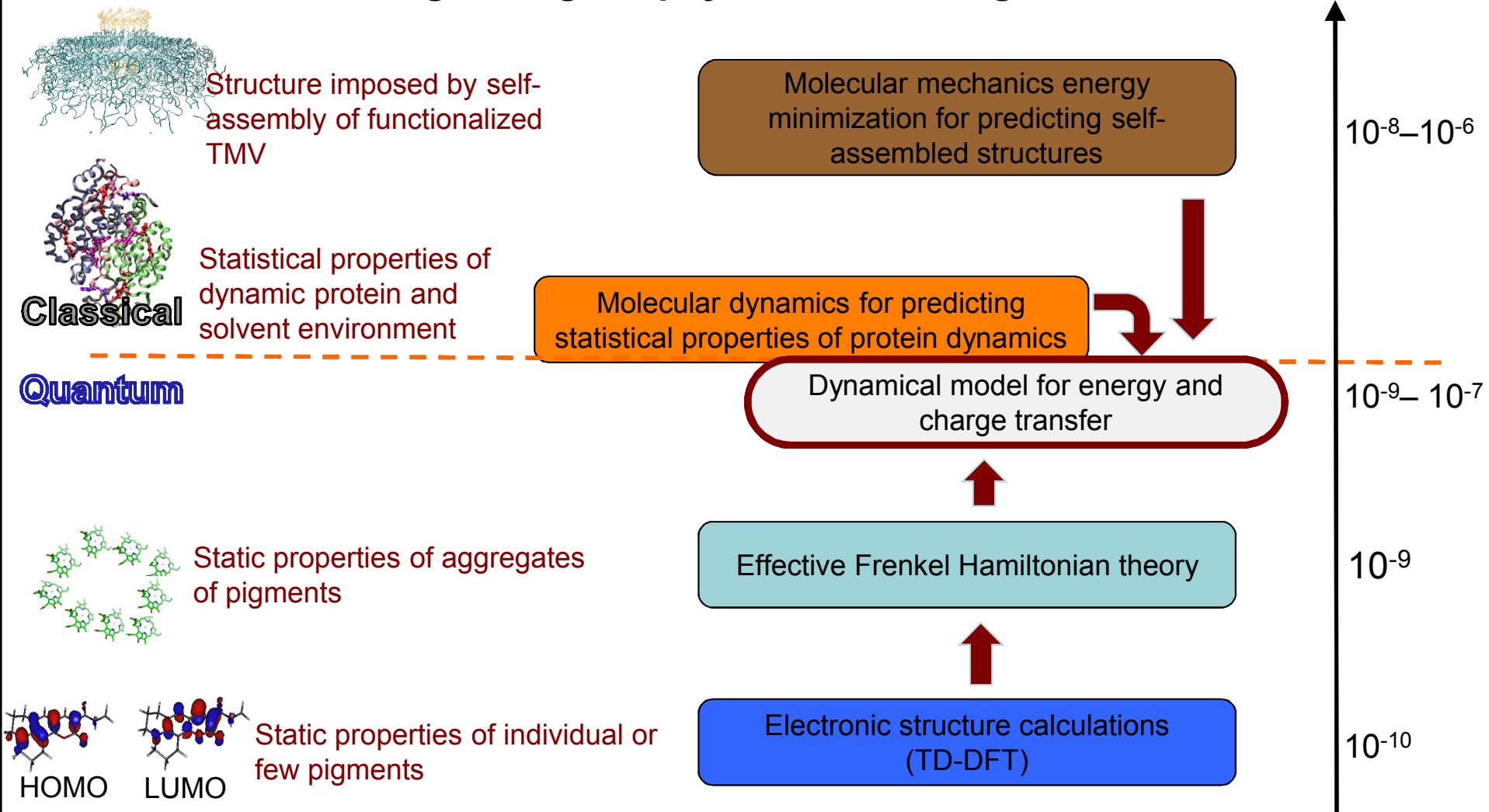


After energy minimization

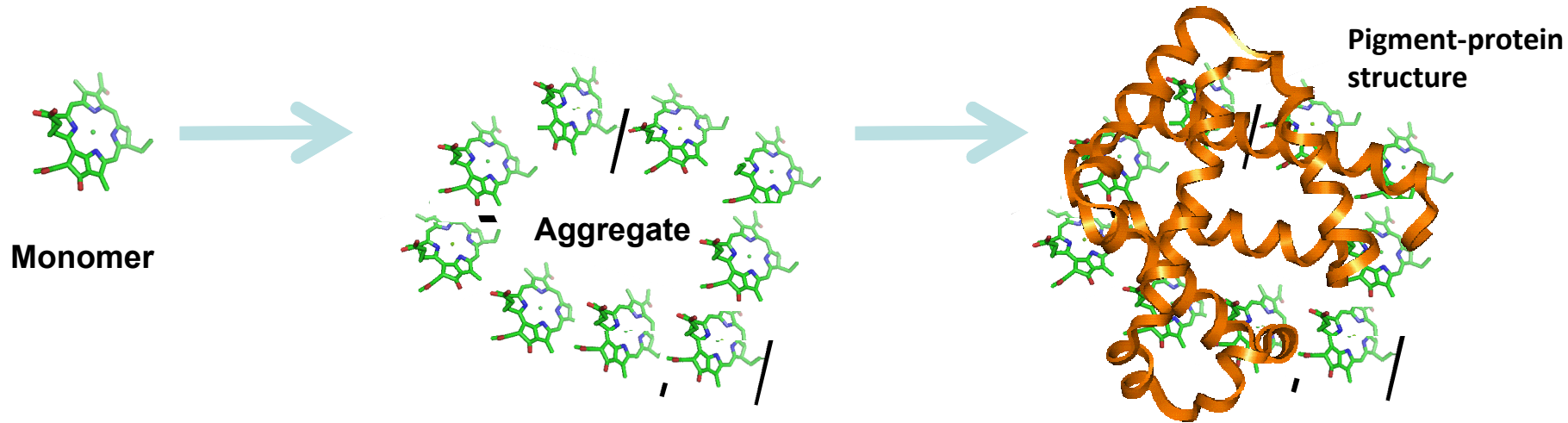
# Modeling TMV-templated light harvesting

**Challenge: integrate physics across length scales**

Typical length scales (m)



# Rational design of synthetic LHCs



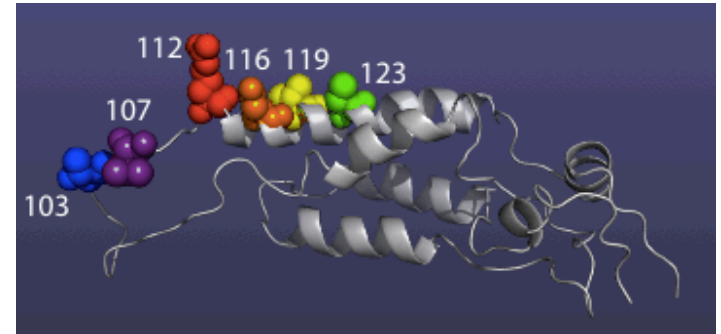
**Modeling, simulation and large-scale optimization** of TMV-templated structures

→ predict which structures are optimal for light harvesting to provide guidance to experiment

## Structure-function questions

- Which structural features determine the quantum behavior? Influence of:
  - Pigment density, pigment orientations, choice of pigments, etc.
- Can light harvesting performance be enhanced by suitable design?
- How does molecular aggregation control exciton dynamics and optical properties

# Rational design of synthetic LHCs



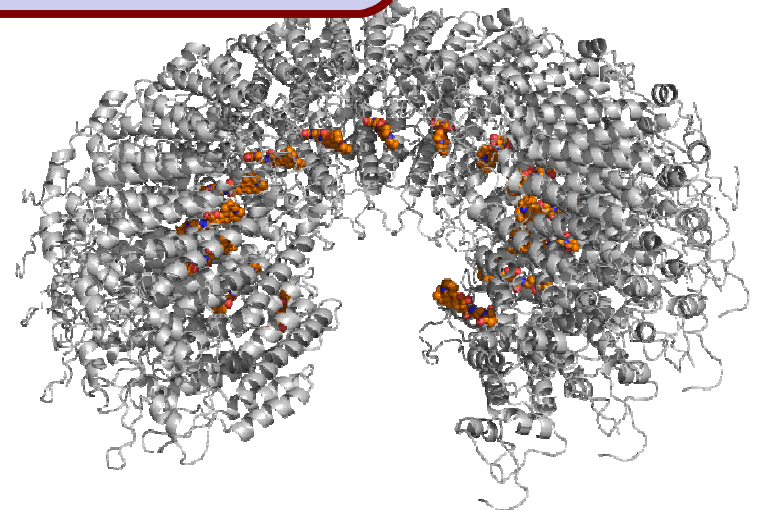
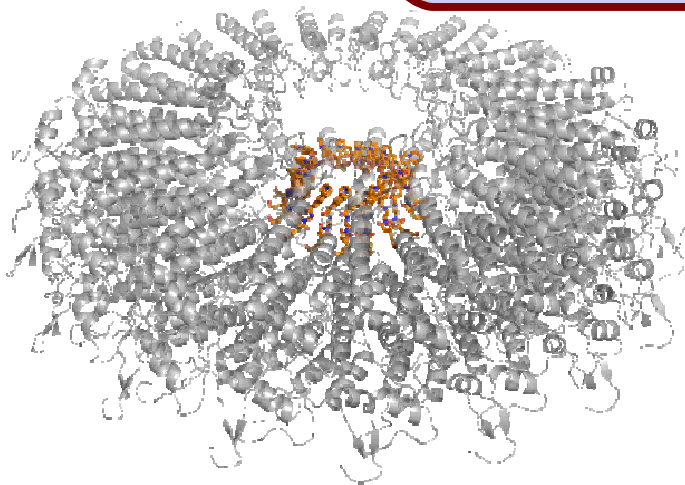
**Example:** compare two structures

TMV103

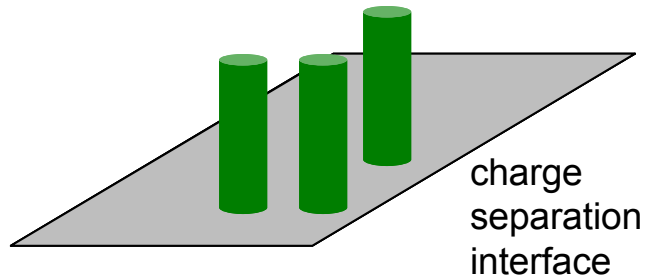
8-10 Å pigment separation  
Strong coupling, quantum effects prominent

Which has “best” light harvesting performance?

larger separation  
quantum effects less prominent



# Rational design of synthetic LHCs



## Objectives:

- (1) As wide an absorption window as possible
- (2) Fast transport to charge separation interface

Light harvesting intrinsically a **multi-objective optimization**

- In natural systems also
- Competing objectives?

# Multi-objective optimization

Optimization with multiple objectives:

$$\max_{\mathbf{x}} \mathbf{F}(\mathbf{x}) = [F_1(\mathbf{x}), F_2(\mathbf{x}), \dots, F_k(\mathbf{x})]^T$$

with constraints on  $\mathbf{x}$

**Ubiquitous in complex systems and nature.** Almost every natural system has to optimize multiple objectives. **Trade-offs**/compromises between objectives necessary.

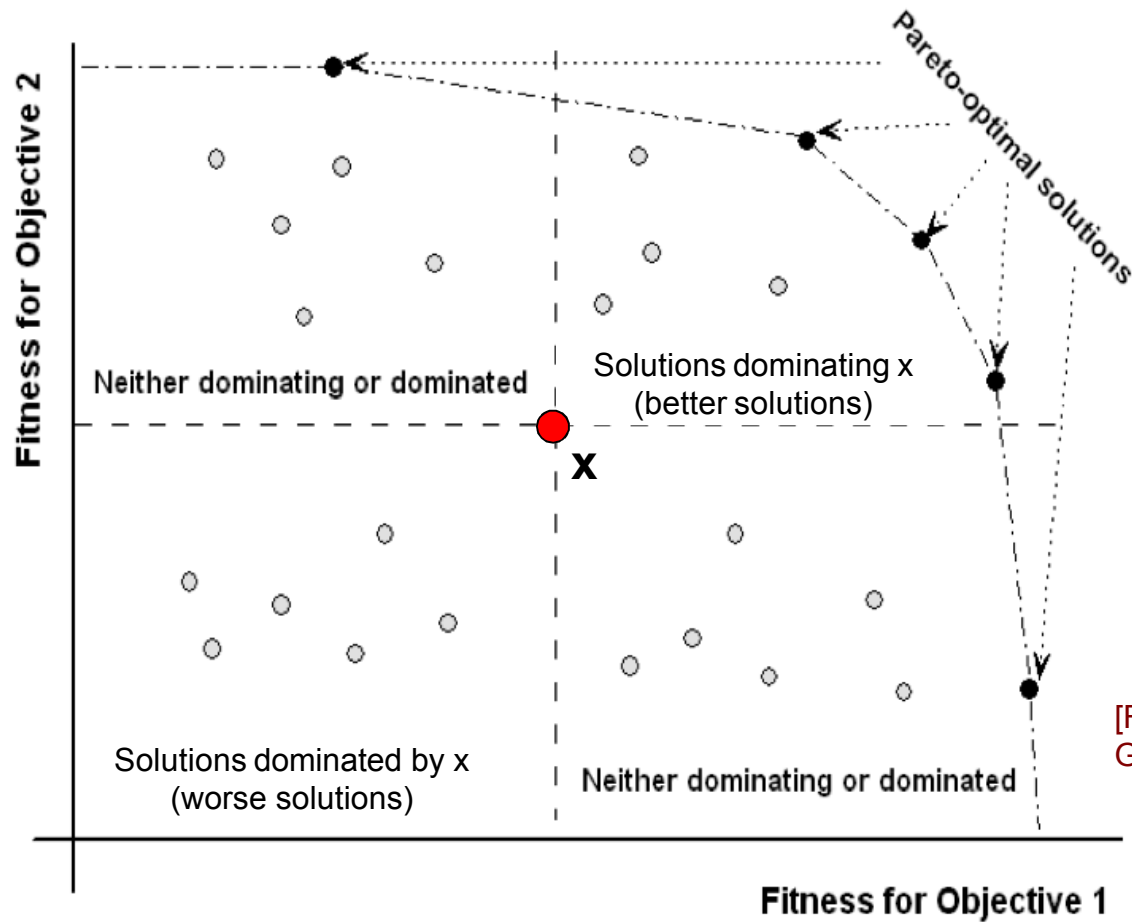
Common heuristic: can combine into one objective:

$$J(\mathbf{x}) = \alpha_1 F_1(\mathbf{x}) + \alpha_2 F_2(\mathbf{x}) + \dots + \alpha_k F_k(\mathbf{x})$$

But this presumes we know the relative importance of the objectives and thus assumes one particular trade-off.

Often in design problems we want to know exactly how this trade-off works. How do the objectives compete? This is characterized by the **Pareto frontier** of solutions.

# Multi-objective optimization: Pareto front



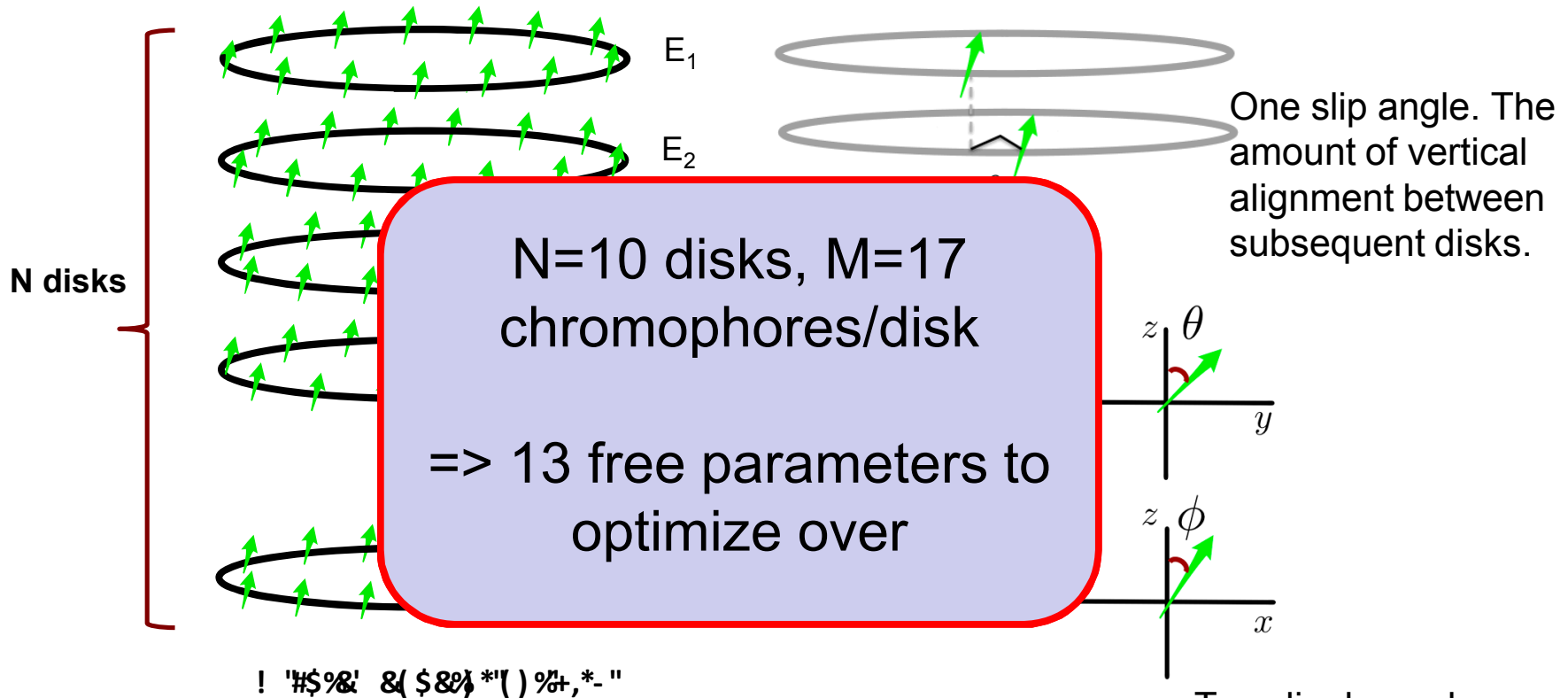
Typically find Pareto front by using **genetic optimization** techniques

[From Abraham, Jain & Goldberg, 2003]

**What are the trade-offs involved in light harvesting? Fundamental?**

# Structural model

## A reduced model:



One slip angle. The amount of vertical alignment between subsequent disks.

$N=10$  disks,  $M=17$  chromophores/disk  
 $\Rightarrow$  13 free parameters to optimize over

Two dipole angles. All chromophores in the structure form the same angles with the disk.

Energies of all chromophores on each disk.  
Chosen in the range: 400nm – 450nm

**TMV103 or TMV123**

# Dynamical model

Structures will be large and have some extent of disorder. Need simulation technique that is **efficient** as well as **accurate** across a **large range of parameters** (must capture quantum effects).

## Modified Redfield Theory

[Zhang, Meier, Chernyak, Mukamel & Yang, Fleming]

Similar to Redfield theory master equation but with no secular approximation and all reorganization effects captured non-perturbationively

Results in a rate equation for exciton **populations**: 
$$\frac{d\vec{P}}{dt} = R\vec{P}$$

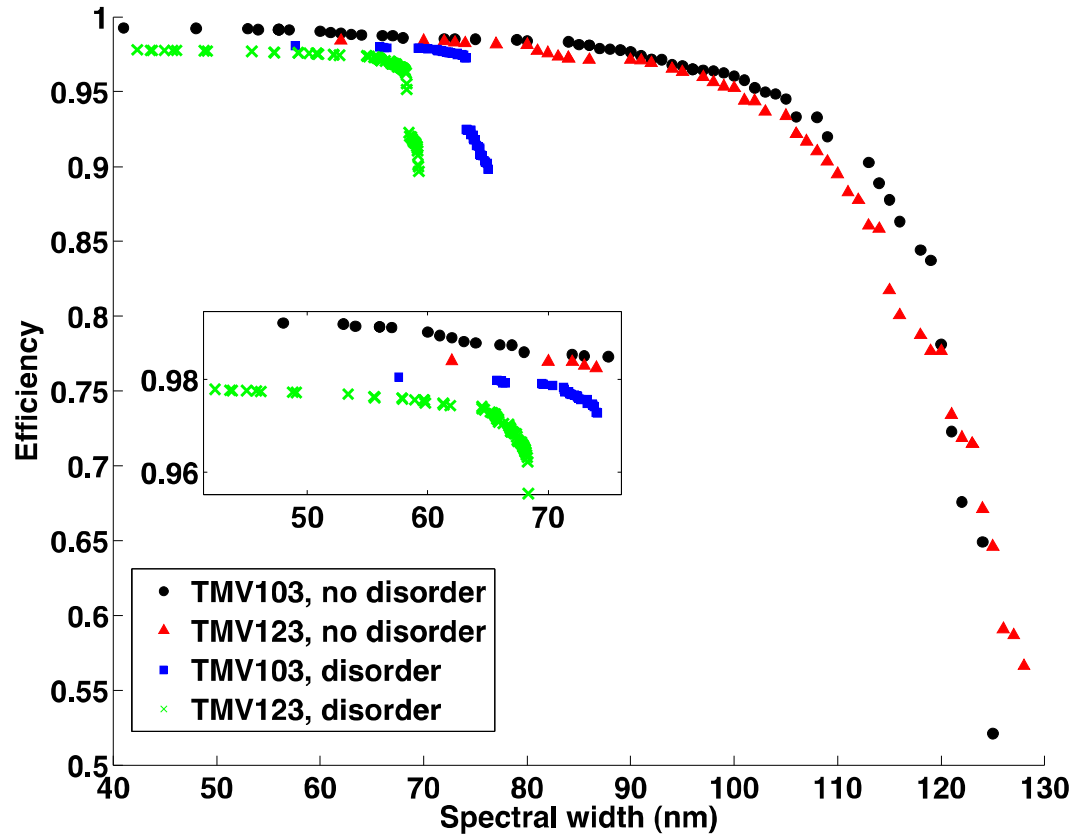
### Benefits:

efficient (rate equation); accurate representation of bath, temp, thermalization; respects fluctuation-dissipation

### Main limitation:

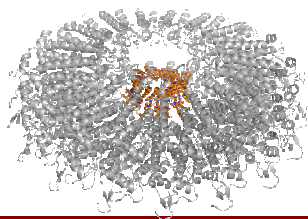
cannot model coherences in the exciton basis, but these are of minor significance for the asymptotic efficiencies calculated here

# Rational design and evaluation of structure

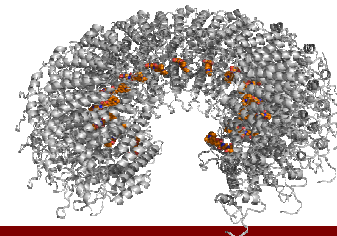


- TMV103 – no disorder
- ▲ TMV123 – no disorder
- TMV103 – disorder
- ✕ TMV123 – disorder

TMV103

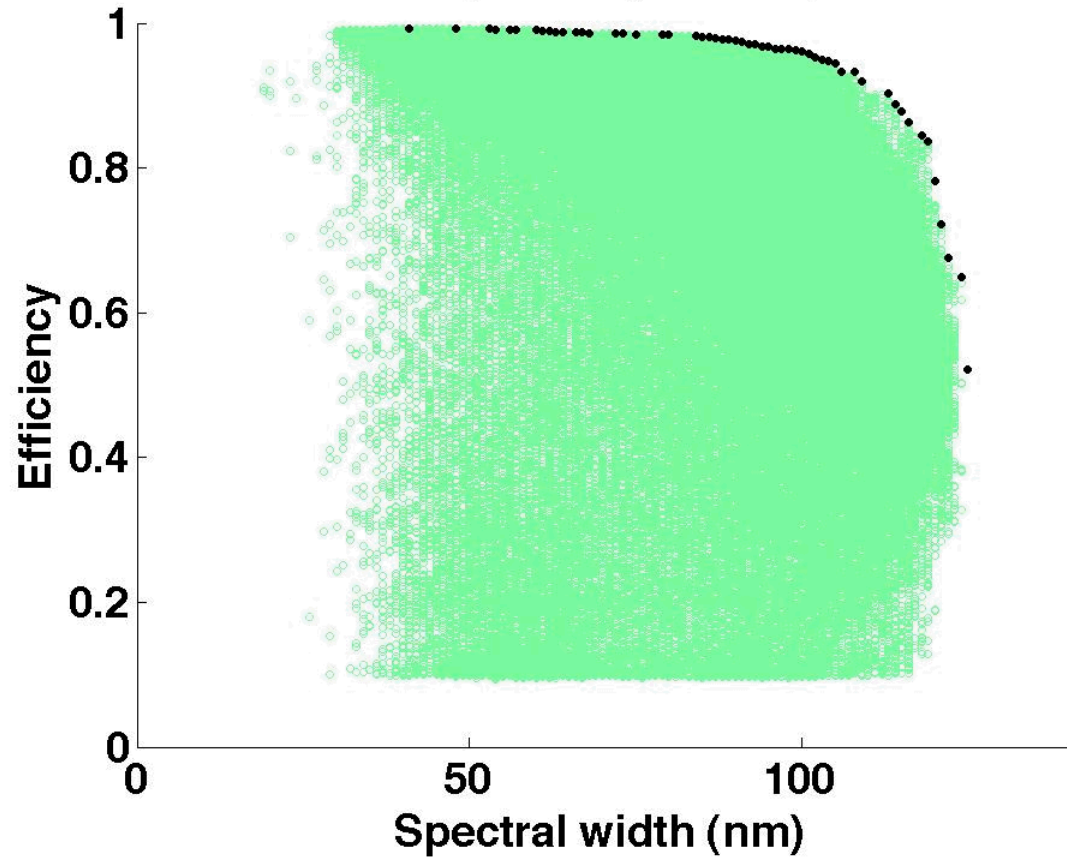


TMV123



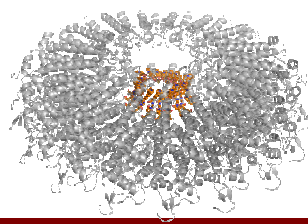
# Rational design and evaluation of structure

Landscape in objective space

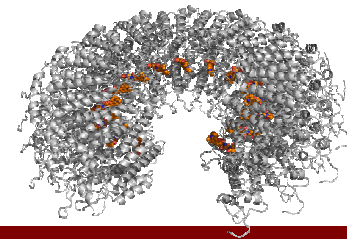


● TMV103 – no disorder

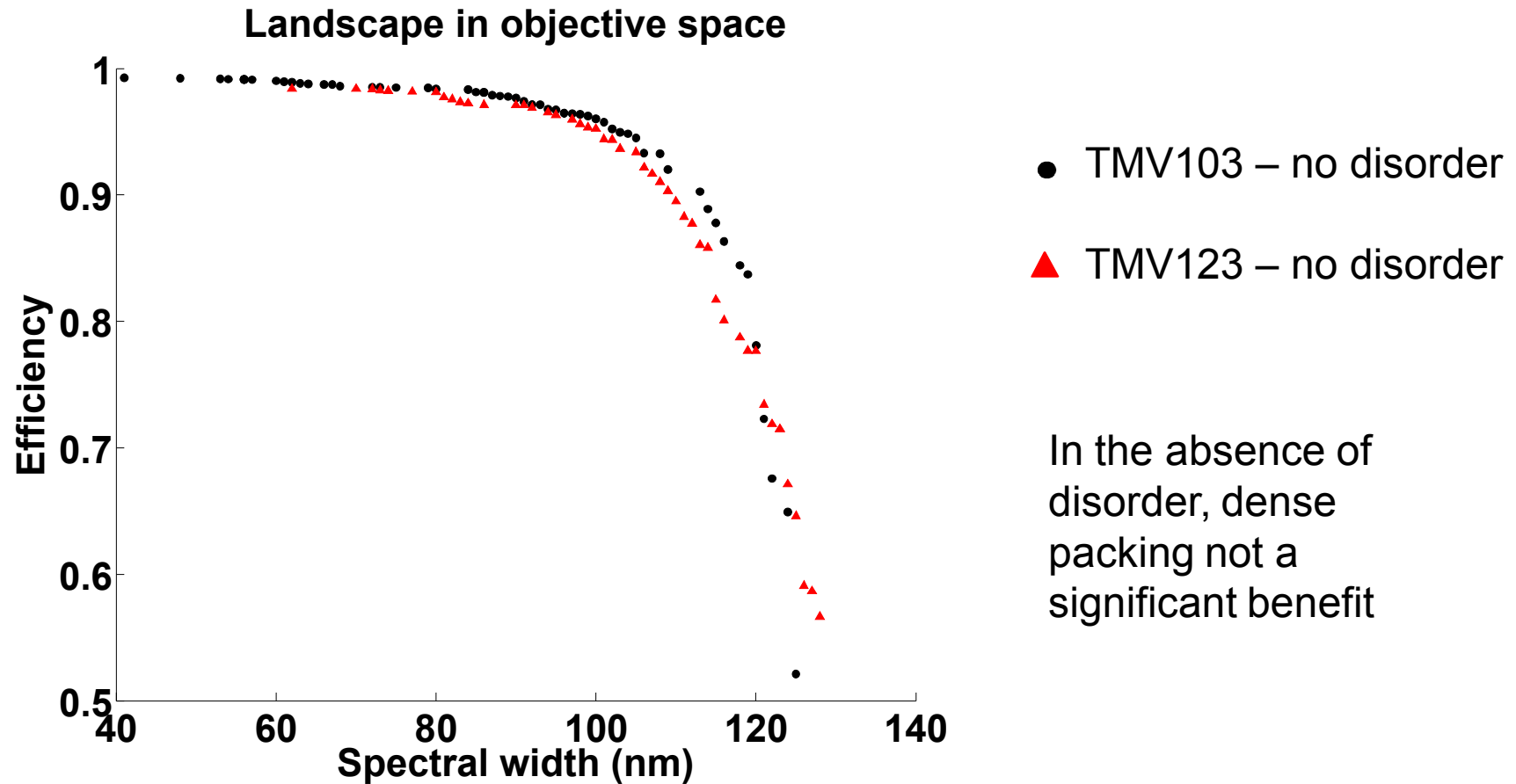
TMV103



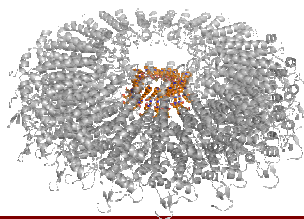
TMV123



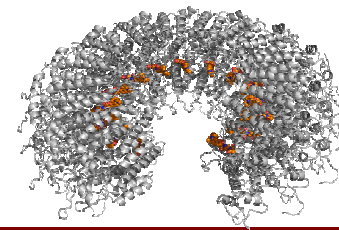
# Pareto fronts



TMV103

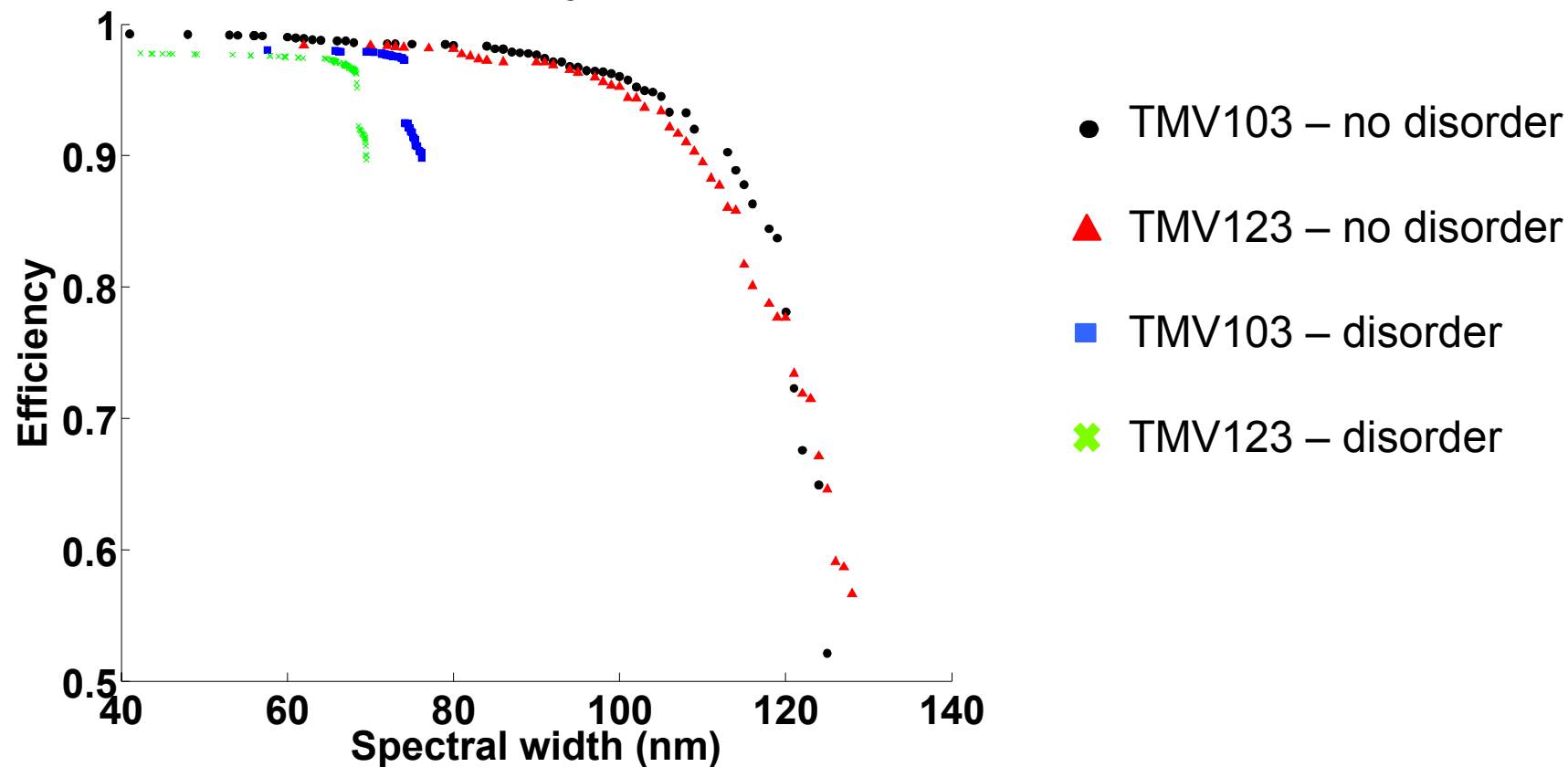


TMV123

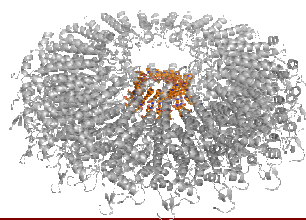


# Pareto fronts

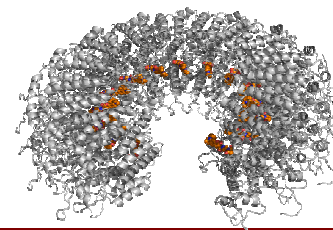
Landscape in objective space



TMV103

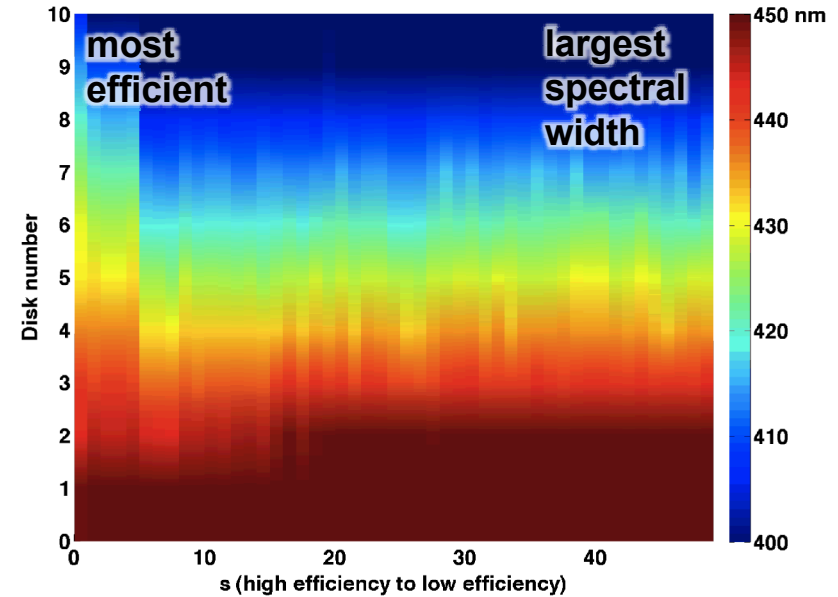
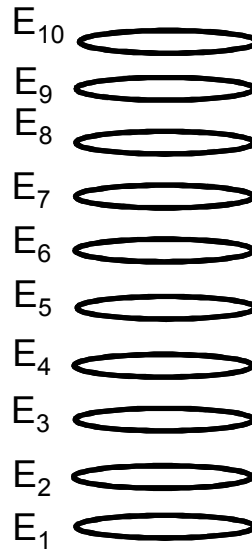
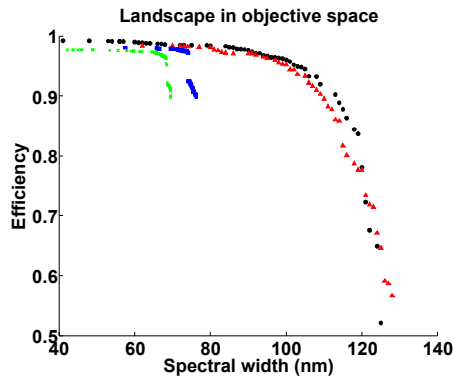


TMV123



# Optimal parameters and structures

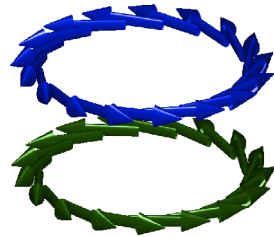
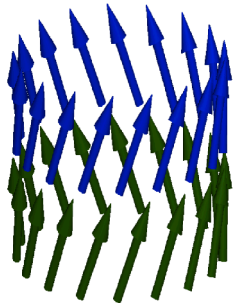
## E.g. TMV103 with disorder



Most efficient

Largest spectral width

Only two disks out of ten in cylinder shown for clarity

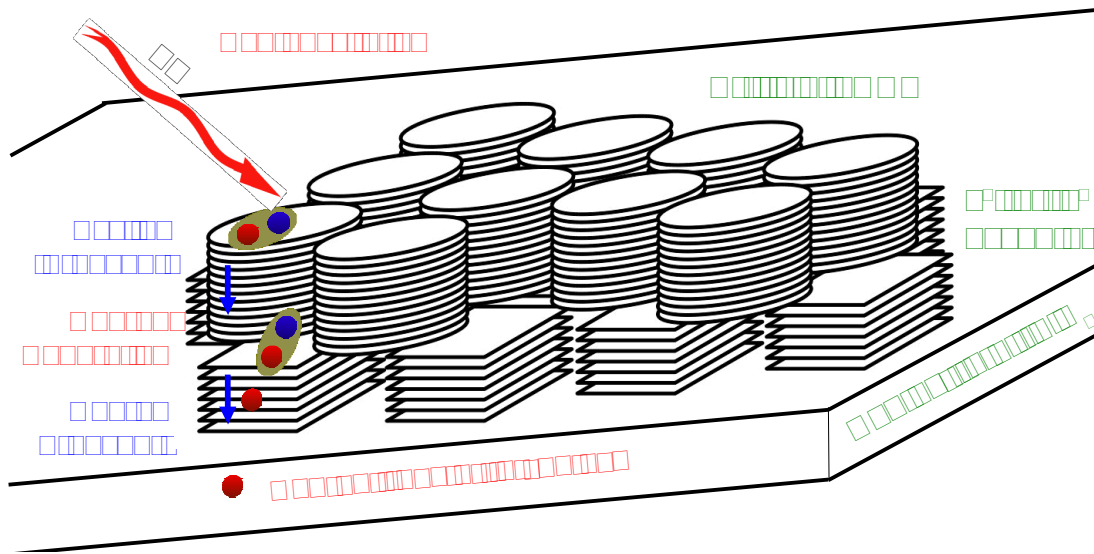


Possible to rationalize all these features (energetic, structural), and ascertain ways to optimize function by tuning structure

# Light harvesting design principles

1. A **trade-off** between efficiency and spectral width **exists** for cylindrical LHCs. Not possible to maximize both simultaneously
2. Optimal structures for efficiency or spectral width change dramatically depending on the amount of structural and energetic **disorder** present
3. An **energy funnel** is desirable in all situations, and essential in the presence of disorder
4. An **increased density of pigments** is not necessary in the absence of disorder, but it helps when there is disorder, especially to balance trade-offs
5. Strong electronic coupling, facilitated by densely packed pigments (e.g. TMV103), does not help in itself. The **spatial direction of the strong coupling** has to be controlled by chromophore orientation

# Continuing work



A biomimetic  
light harvesting  
device

- Understand structural disorder in assembled structures better and how to control it
- QM/MM simulations of TMV-templated chromophore assemblies in order to understand protein environment (will allow more precise statistical modeling)
- Non-linear spectra required to get more information about exciton transport timescales, exciton delocalization lengths, etc.
- Understand charge separation stage in more detail

# Acknowledgements



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Joonho Lee

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Prof. K. Birgitta Whaley



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Daniel Finley

Dr. Michel Dedeo

Prof. Graham R. Fleming