

Elements of Quantum Physics involved in Photosynthesis

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« Quantum Biology » ?

Biological systems = interacting organic molecules

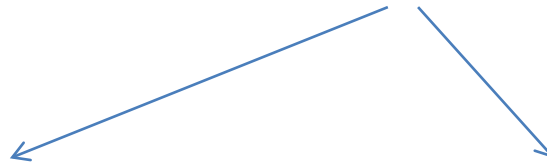
1) individual constituents = Molecules

=> nuclei/electrons cohesion => quantum mechanics => Quantum Chemistry

what is a molecule (quantum mechanically) ?

2) « Quantum Biology »

= Do biological systems exploit **quantum effects** to perform their function?



e.g.: **Quantum « coherence »**

« Particule-Wave duality »

« Interference »

« Superposition of Q. states »

Photosynthesis

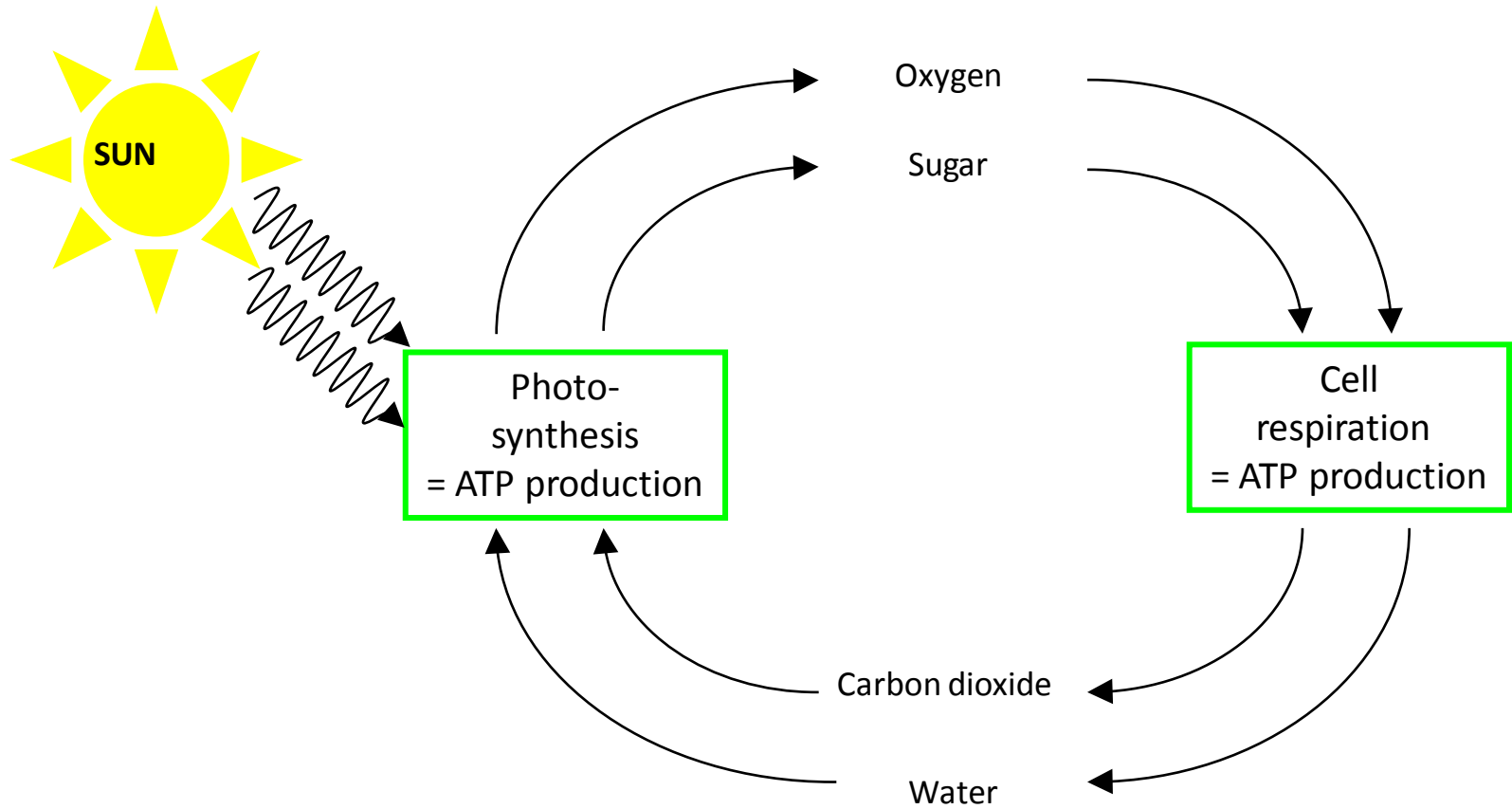
e.g.: « **Tunneling** »

=>Electron transfer in biology



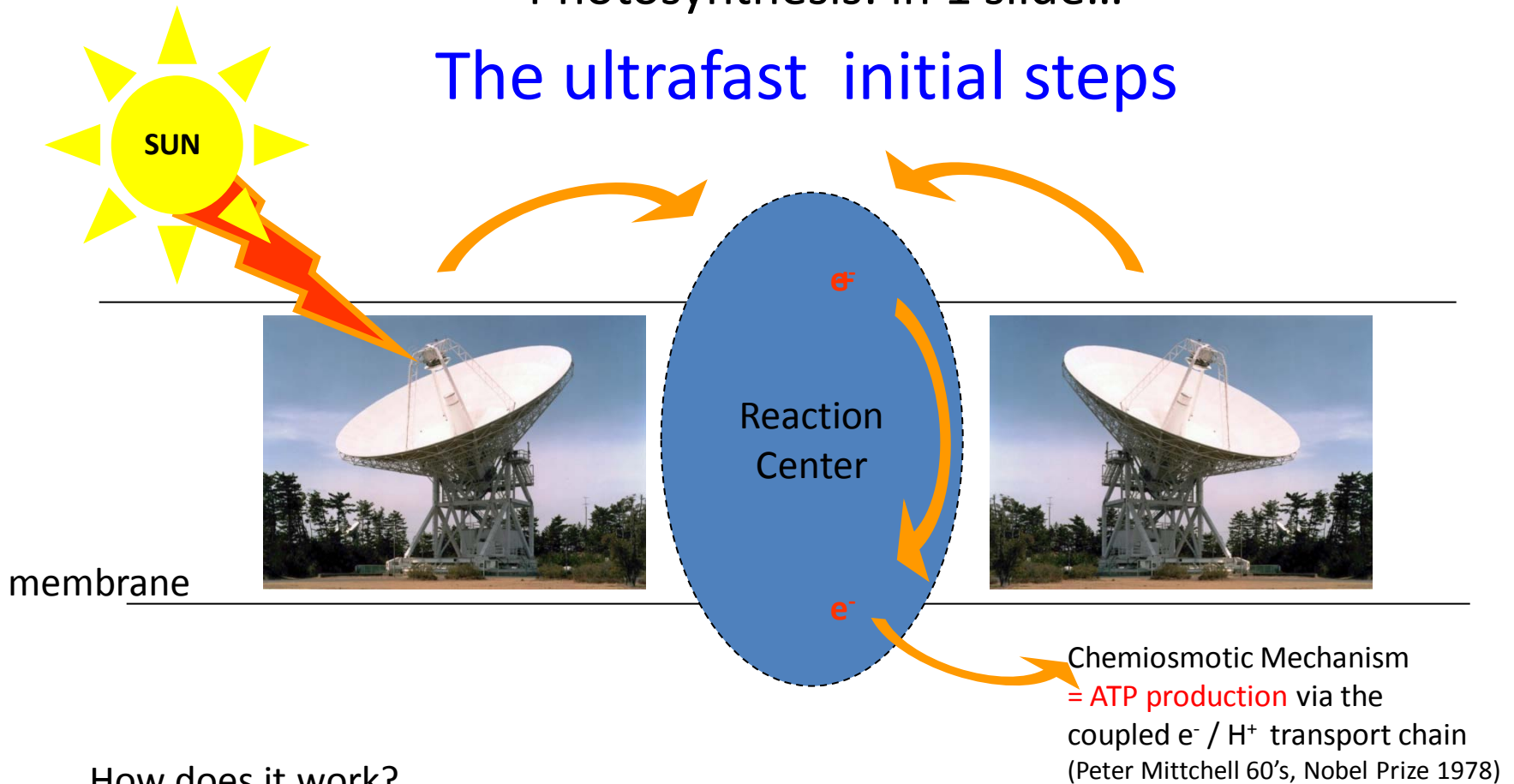
Prof. Spiros Skourtis
(in 40 minutes)

Photosynthesis: in 1 slide...



Photosynthesis: in 1 slide...

The ultrafast initial steps



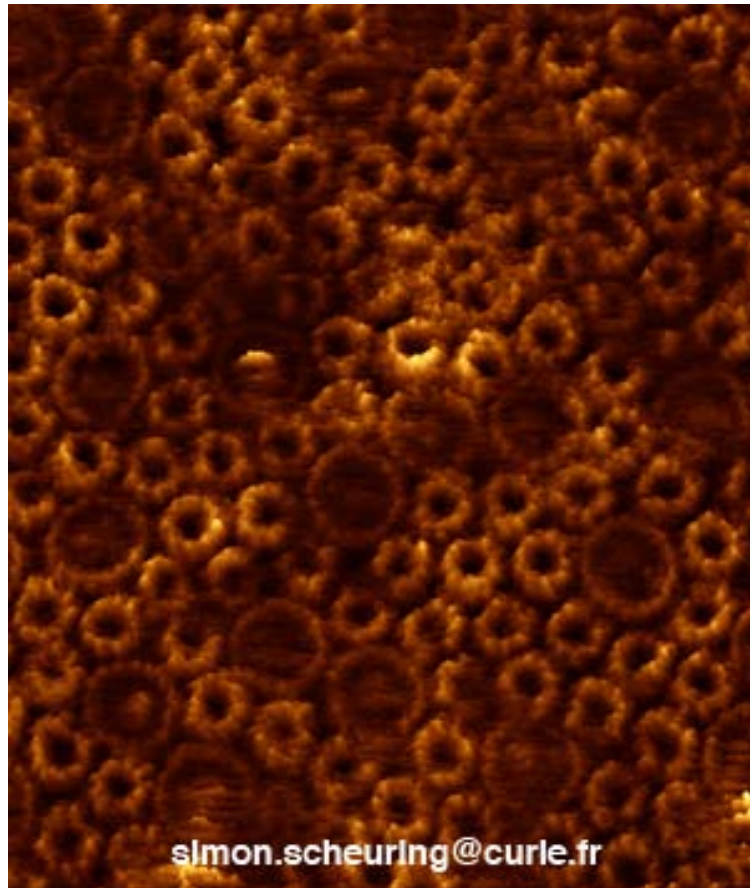
How does it work?

- 1) Antennas : Light collection - Energy transfer
- 2) Reaction Center : Electron transfer

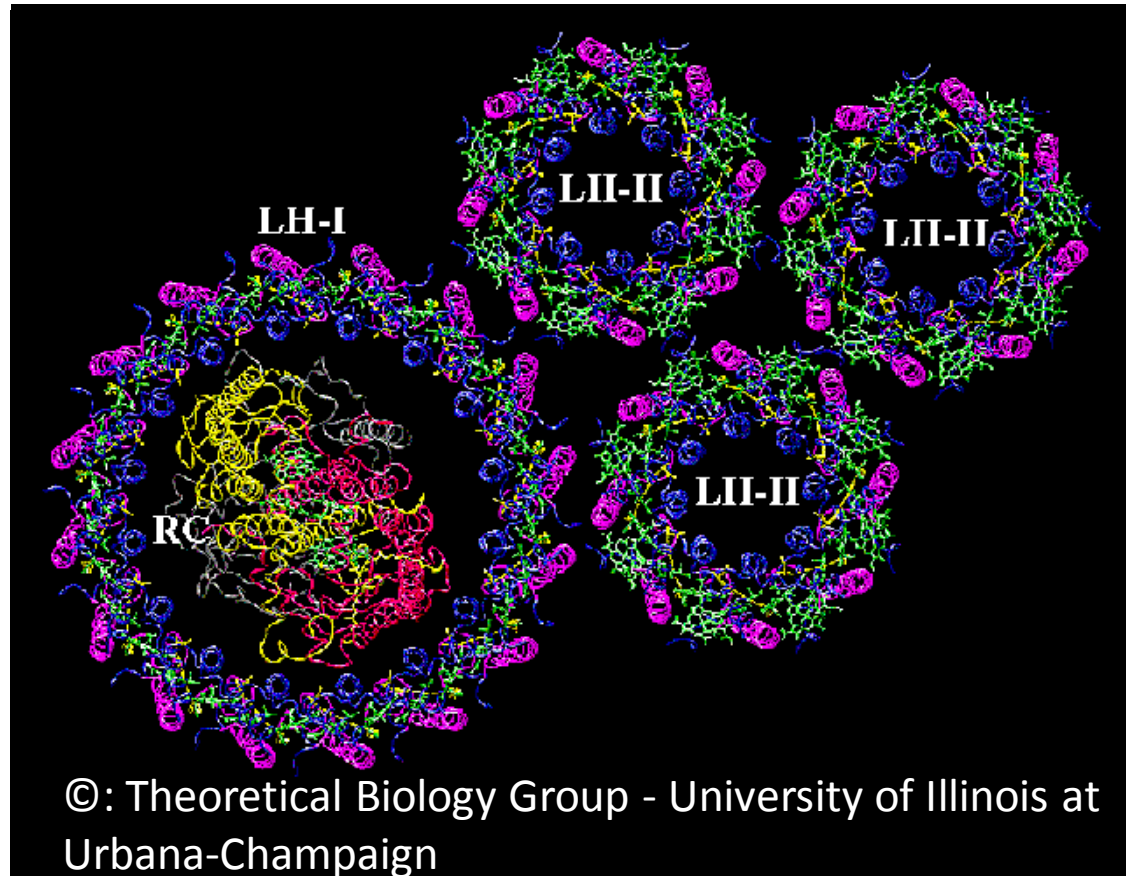
Overall quantum efficiency
> 90% !!!

Photosynthesis Step 1 : Light harvesting

Understood after structural determination of protein complexes



High-resolution AFM of native photosynthetic membranes of *Rhodospirillum rubrum*. (2004)



LH-2 structure (X-ray crystallography):

Rhodopseudomonas acidophila: McDermott et al. Nature **374**, 517 (1995)

Rhodospirillum rubrum: Koepke et al., Structure **4**, 581 (1996)

RC-LH1 structure (X-ray crystallography):

Rhodopseudomonas palustris: Roszak et al. Science **302**, 1969 (2003)

Light - Harvesting complexes: Efficient antennas for light collection

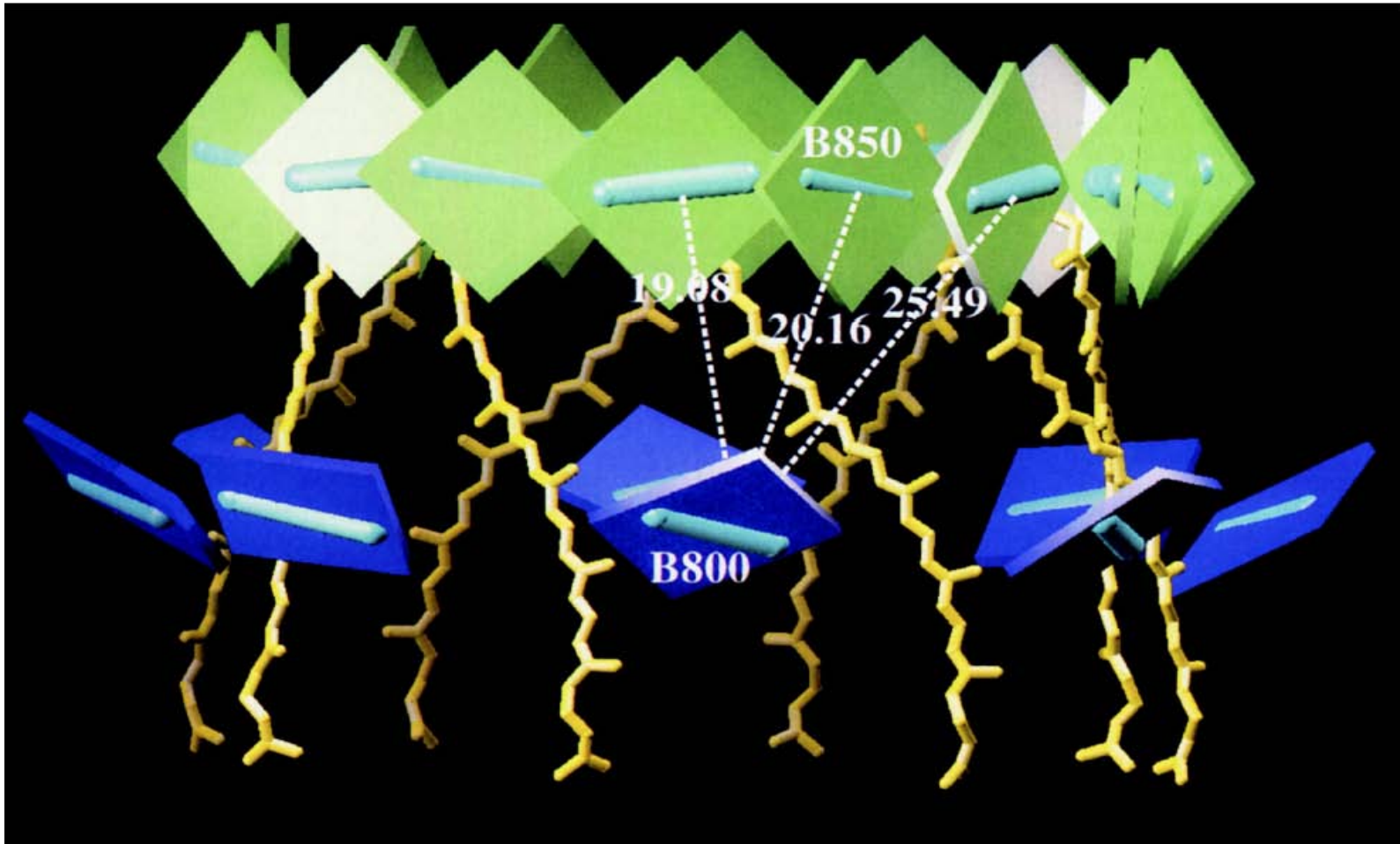


FIGURE 1. ARRANGEMENT OF BACTERIOCHLOROPHYLLS AND CAROTENOIDS in LH-II of *Rs. molischianum*.⁷ Bacteriochlorophylls (BChls) are represented as squares; 16 B850 BChls (green) are arranged in the top ring and 8 B800 BChls (violet) in the bottom ring. Carotenoids (yellow) are shown in a twig-like representation. Bars (cyan) connected with the BChls represent the transition dipole moments of individual BChls that are responsible for the 800 nm and 850 nm bands in the BChl absorption spectra. Representative distances between the central magnesium atoms of B800 BChl and B850 BChl are indicated (in angstroms).

Hu and Shulten, *Physics Today* August 1997

What is the (quantum) Physics of such molecular assemblies ?

« Quantum Biology » ?

Biological systems = interacting organic molecules in condensed phase (water)

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e.g.: Quantum « coherence »
« Particule-Wave duality »
« Interference »
« Superposition of Q. states »

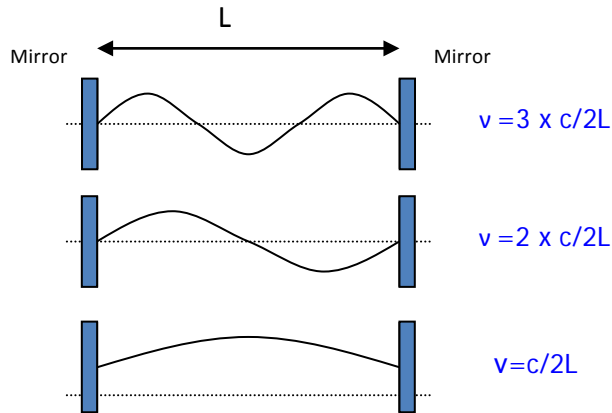
e.g.: « Tunneling »
=>Electron transfer in biology

relevant e.g. for Photosynthesis

Concept #1 Quantum interference

Wave-particle duality and Quantization

Interference in Optics....



photons \Rightarrow particules $E = h\nu$
 \Rightarrow **Travelling plane wave:** $\sin(2\pi\nu(t - z/c))$

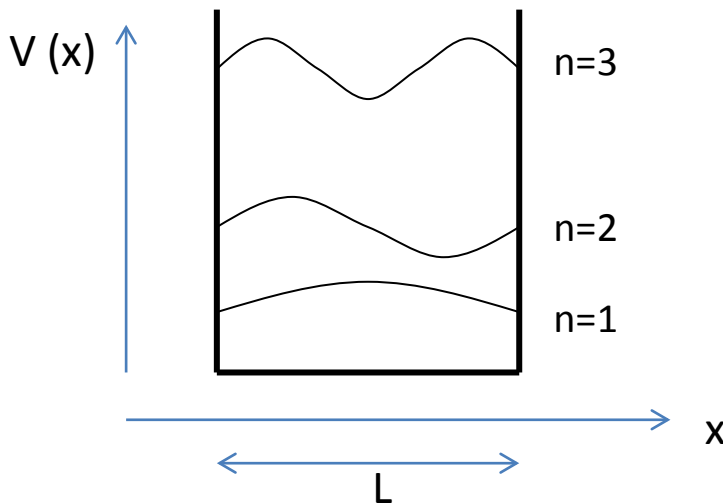
One round trip: $\Delta z = 2L$ $\sin(2\pi\nu(t - z/c)) + \sin(2\pi\nu(t - z/c - 2L/c))$

Constructive interference = « in-phase »
 $\Rightarrow \nu \times 2L/c = n$

discrete energy modes of the cavity : $\nu = n \times c/(2L)$

Interference in Quantum mechanics = same thing !

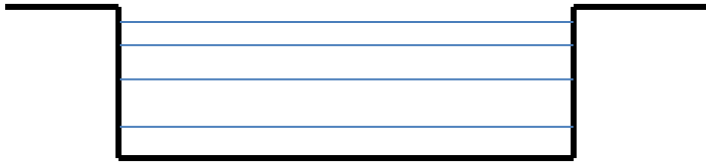
e.g. electrons in a box:



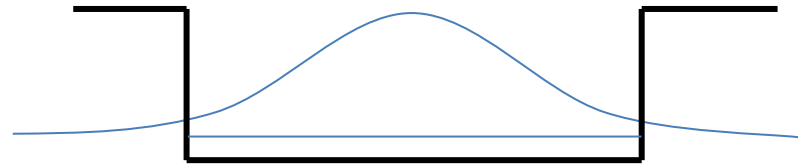
stationary wavefunction \Leftrightarrow **constructive interference**
 between electron travelling towards left and right
 \Rightarrow **Energy quantization**

Concept #2: Tunneling

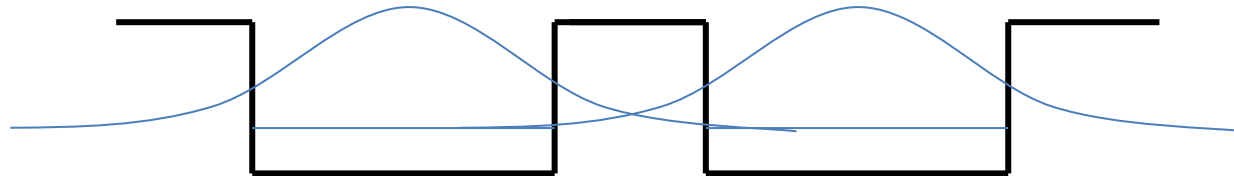
Finite potential depth



wave function extend beyond the region classically allowed
(cf evanescent waves)



two molecules next to each other:



wave functions may overlap = both electron systems interact

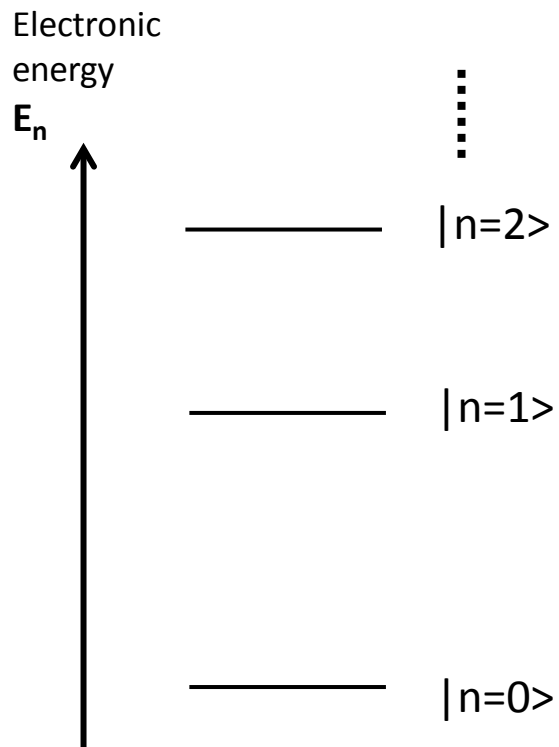
⇒ electron transfer through the barrier = « tunneling »

⇒ not allowed by classical physics (the only classical way is above the barrier)

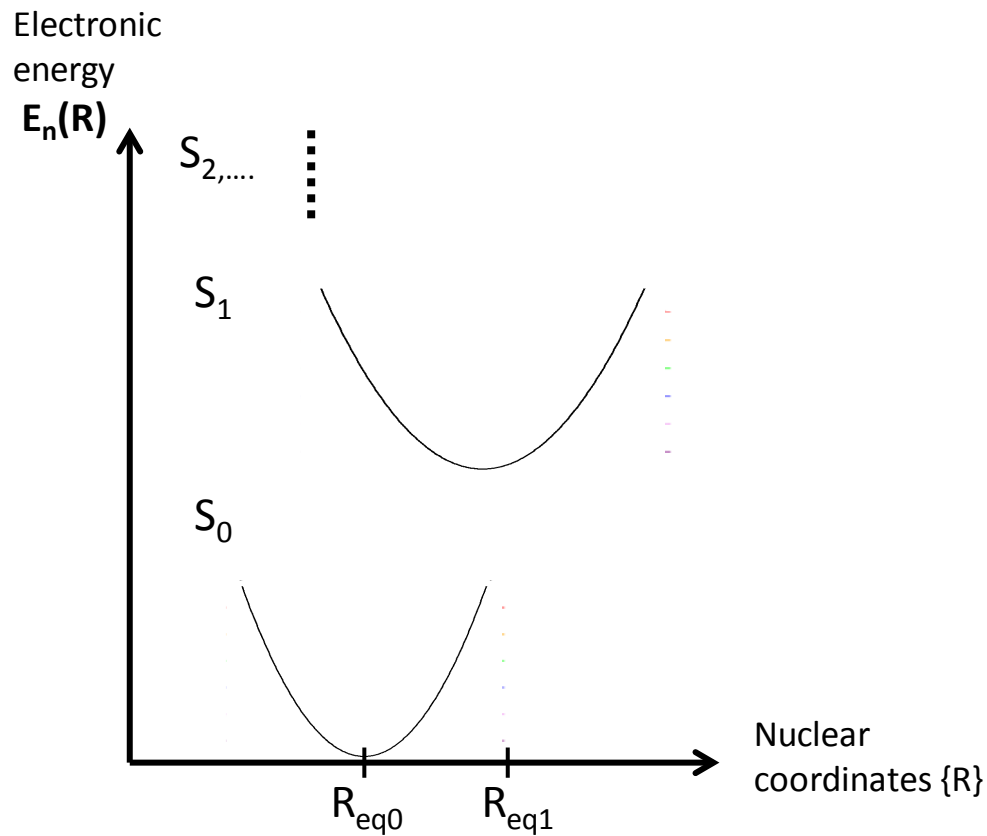
See Electron Transfer processes in biology => Spiros Skourtis

Quantum mechanical description of a molecule

Quantized energy levels



... but molecules have nuclei



Quantum mechanical description of a molecule

... but molecules have nuclei

Born-Oppenheimer approximation:

$$m_p/m_e \sim 1836$$

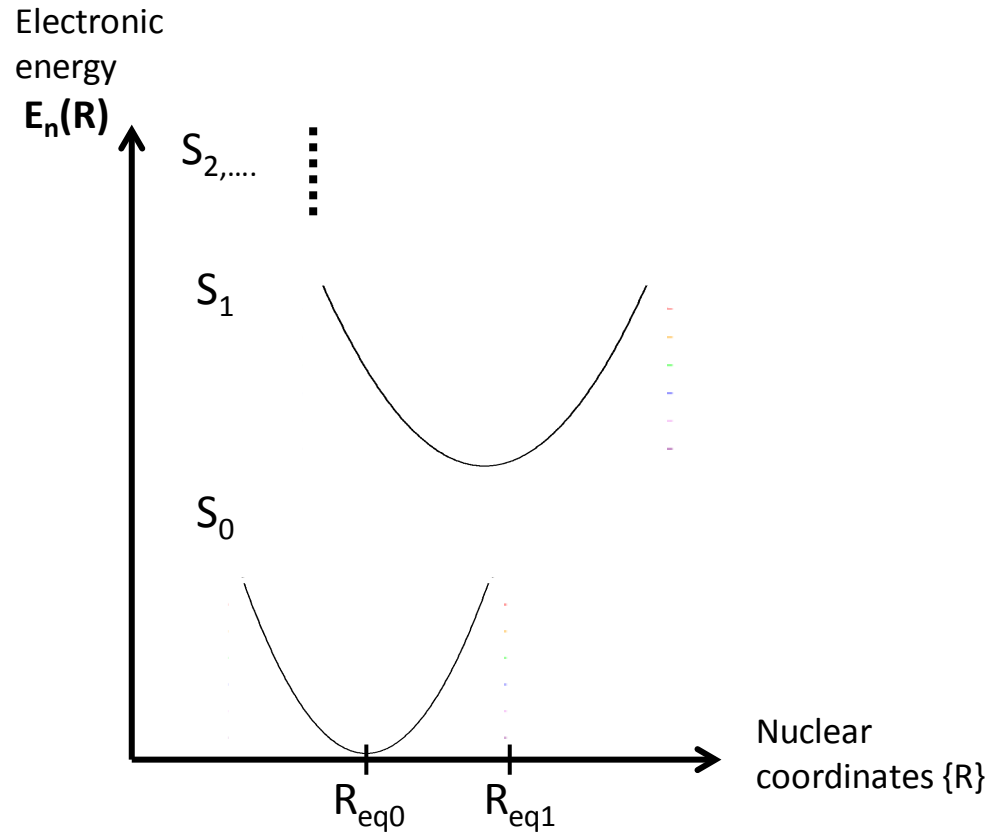
Nuclear motions are slow compared to electronic dynamics

Molecular wave function:

$$|\Psi\rangle = |\Phi_e\rangle \times |\chi_{e,v}\rangle$$

Electronic wave function
(electronic degrees of freedom)

Vibrational wave function
(nuclear degrees of freedom)



Quantum mechanical description of a molecule

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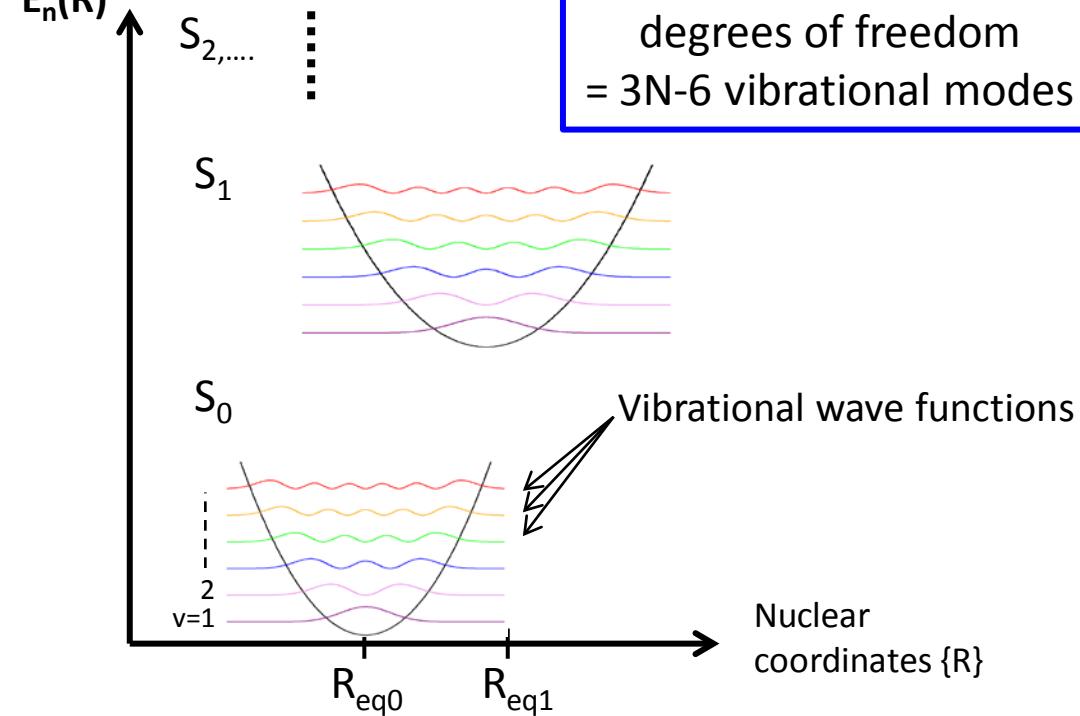
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... but molecules have nuclei

Electronic energy $E_n(\mathbf{R})$



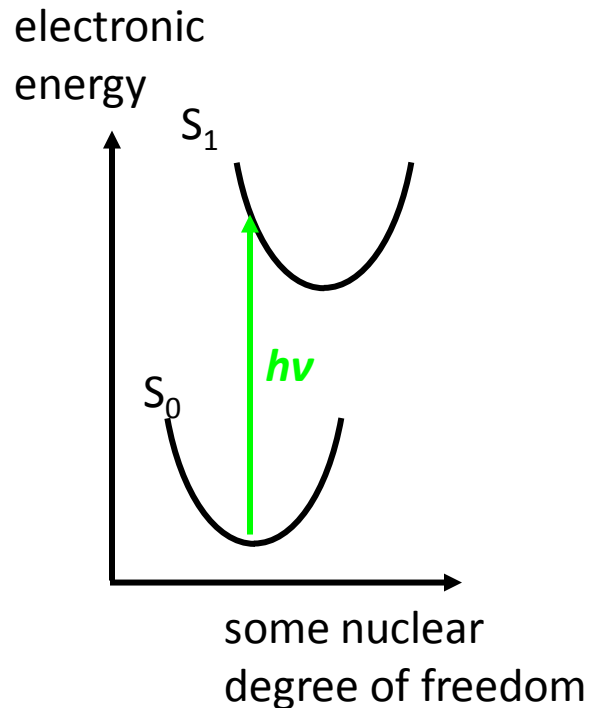
N atoms =
3N-6 internal
degrees of freedom
= 3N-6 vibrational modes

Vibrational wave functions

Nuclear coordinates $\{\mathbf{R}\}$

Orders of magnitude

light excites the **electronic** degrees of freedom



Electronic energy:

$E_1 - E_0$: example : optical transition = vis light:
500nm $\Rightarrow E = h\nu \Rightarrow T = 1/\nu = 1.5$ fs

Vibrational energy:

C=C stretch: $1500\text{ cm}^{-1} \Rightarrow T \sim 20$ fs

Lower frequency modes $\Rightarrow 100\text{ cm}^{-1} \Rightarrow T \sim 300$ fs

Thermal bath :

ambient temperature kT : $300\text{ K} \Leftrightarrow 200\text{ cm}^{-1}$

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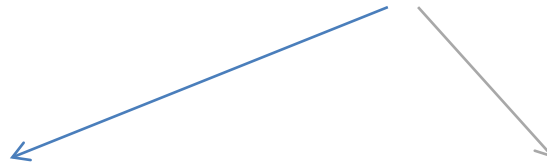
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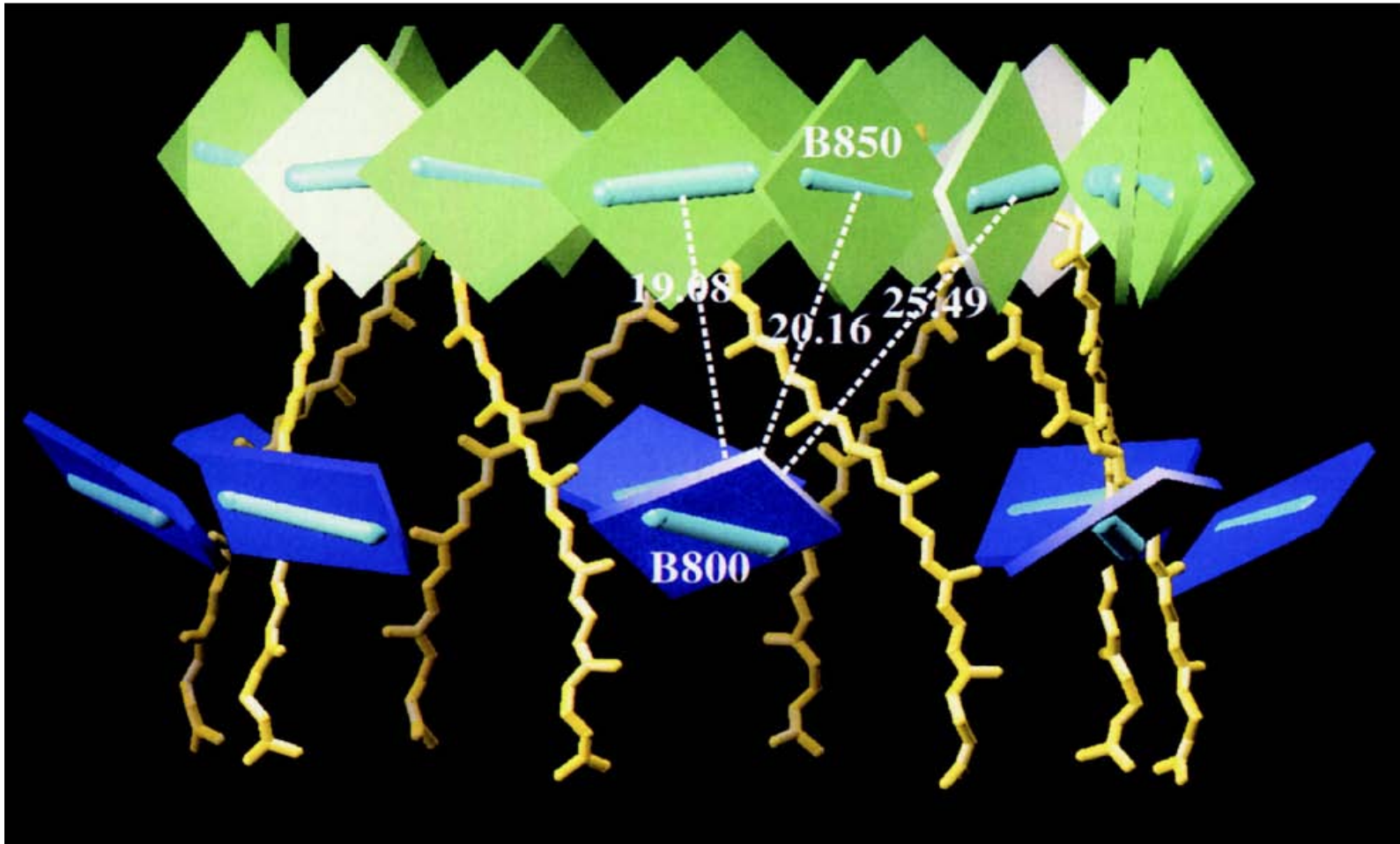


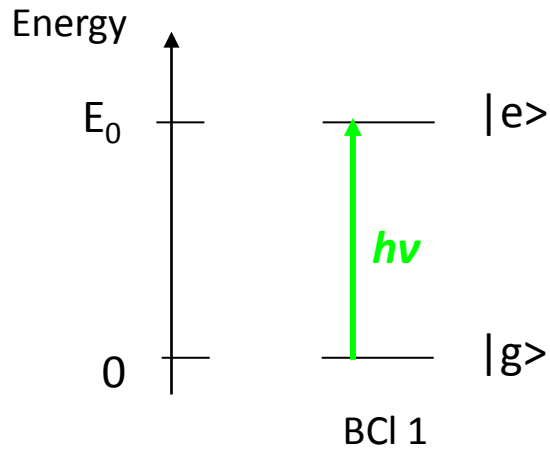
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Hu and Shulten, *Physics Today* August 1997

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Chromophores: (electronic degrees of freedom only)

1 Chromophore



Interaction with light:

$$-\vec{d} \cdot \vec{E}$$

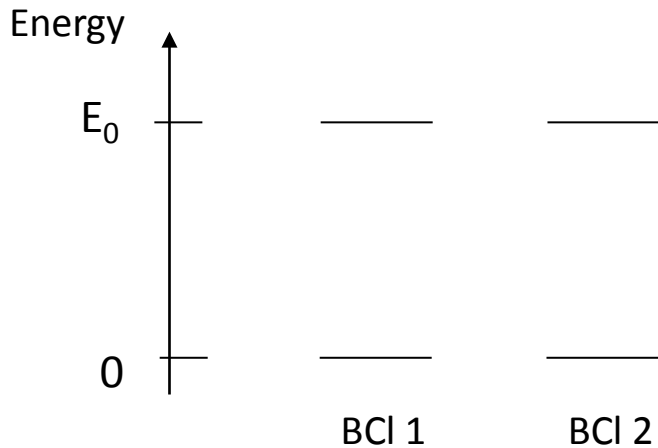
oscillating optical field

molecular dipole

=> photon absorption

Chromophores: (electronic degrees of freedom only)

2 Chromophores



if 1 photon is absorbed :

$|eg\rangle$ or $|ge\rangle$

2 possible excited states: BChl1 or BChl2

\Leftrightarrow 2 states of same energies

Interaction with light:

$$-\vec{d} \cdot \vec{E}$$



oscillating optical field

molecular dipole

=> photon absorption

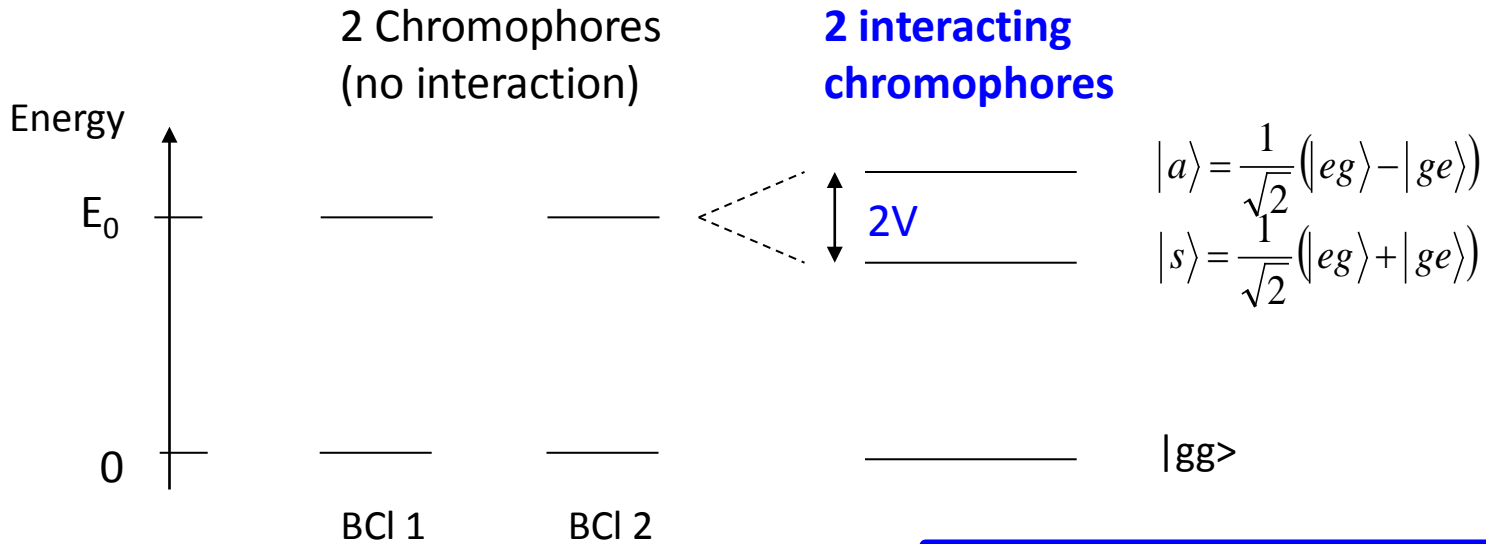
**interaction between
chromophores**

(e.g. dipole-dipole)

$$V = \frac{1}{4\pi\epsilon_0 R_{12}^3} (\vec{d}_1 \cdot \vec{d}_2 - 3d_{1z} d_{2z})$$

= coupling between $|eg\rangle$ and $|eg\rangle$

Chromophores: (electronic degrees of freedom only)



Interaction with light:

$$-\vec{d} \cdot \vec{E}$$



oscillating optical field

molecular dipole

=> photon absorption

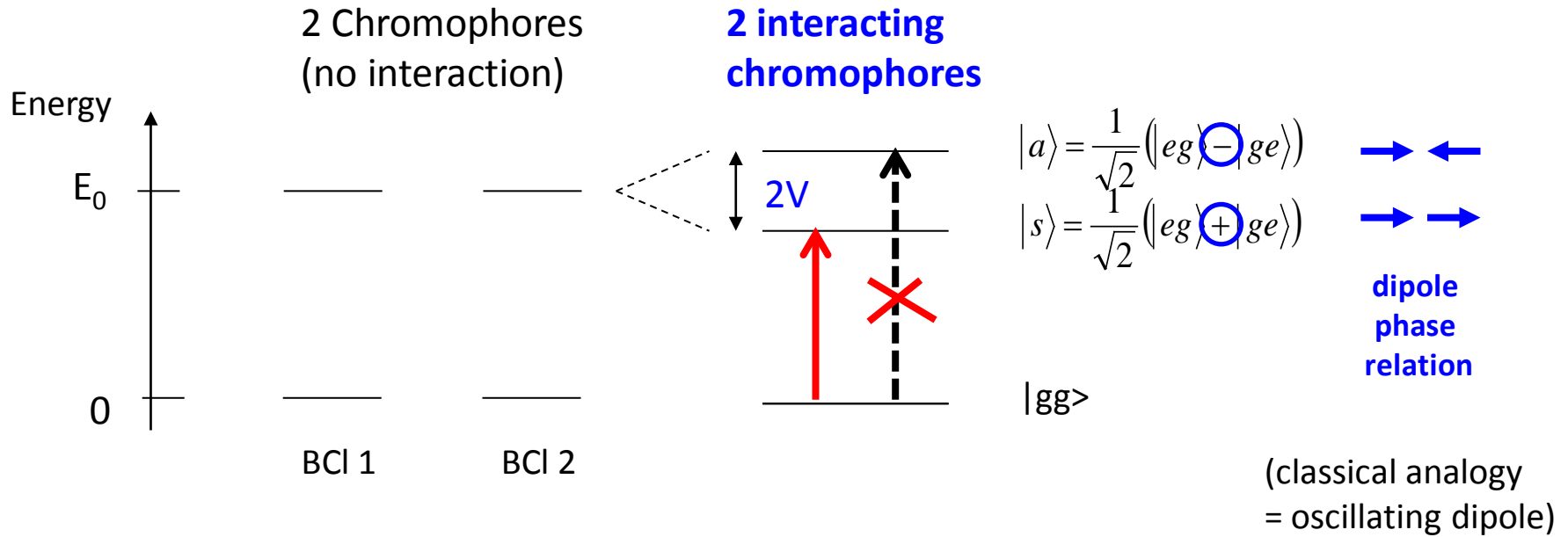
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$$V = \frac{1}{4\pi\epsilon_0 R_{12}^3} (\vec{d}_1 \cdot \vec{d}_2 - 3d_{1z}d_{2z})$$

= coupling between $|eg\rangle$ and $|eg\rangle$

Concept #3: Quantum Coherence



$|s\rangle$: in phase oscillation => quantum superposition = constructive interference
=> one single larger dipole

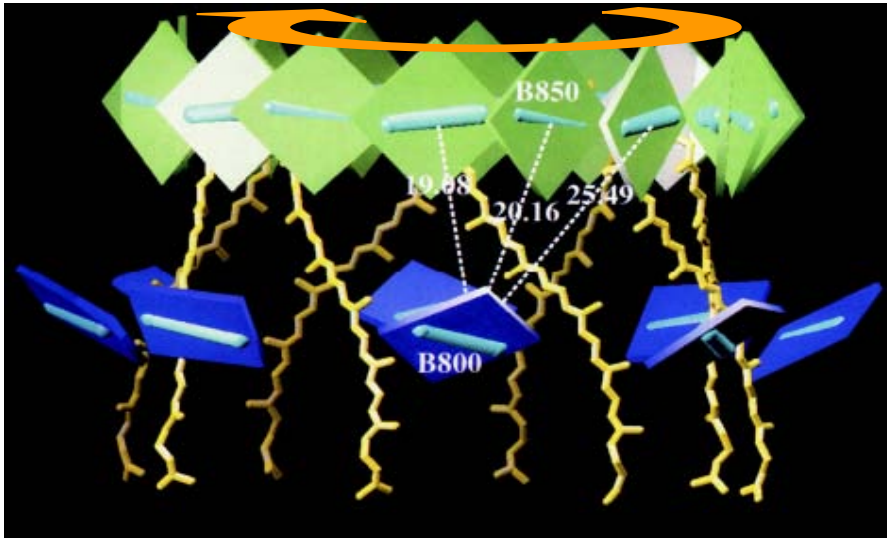
$|a\rangle$: out-of-phase oscillation => quantum superposition = destructive interference
=> zero dipole

**Defined Phase relation between both $|eg\rangle$ and $|ge\rangle$
= Quantum Coherence**

= Excitation is DELOCALIZED on both chromophores (exciton states)

Concept #3: Quantum Coherence

LH2: $2N = 16$ coupled BChl's



8 pairs of head-to-tails BChl's

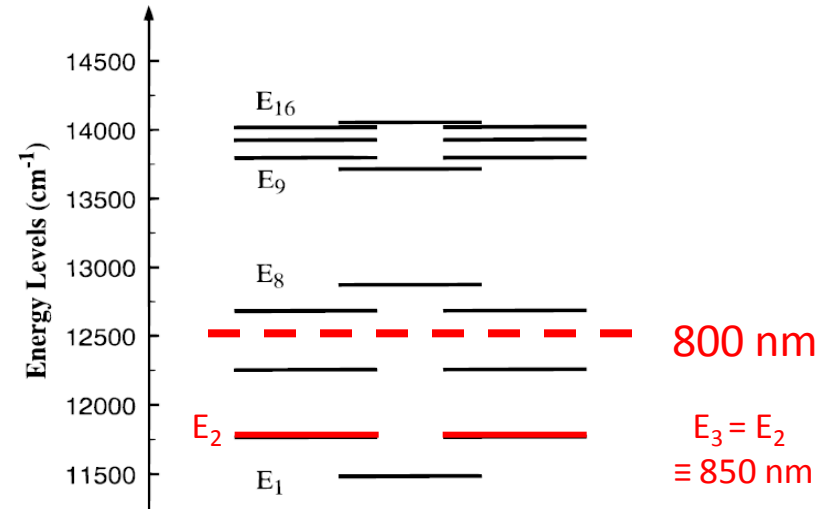


Figure 6. Energies associated with the eigenstates (exciton states) of the effective Hamiltonian describing the aggregate of B850 BChls in LH-II. The ϵ -value was chosen such that energies E_2, E_3 coincide with the spectral maximum of the circular aggregate at 850 nm.

from Hu et al. J. Phys. Chem. B, 1997

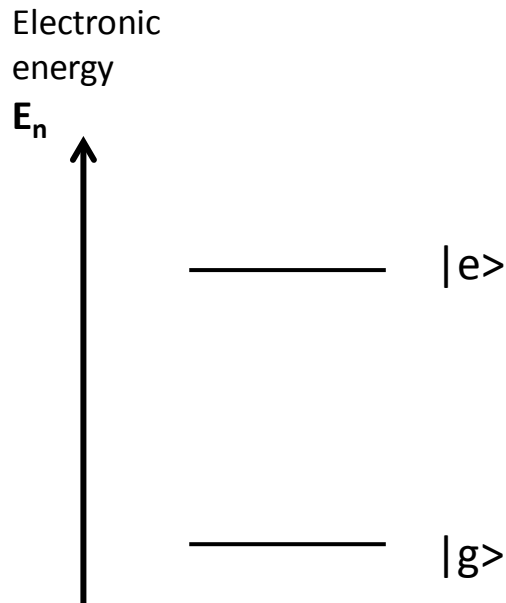
➤ Delocalized excitation

quantum superposition of 16 BChl's states with one of them being excited.

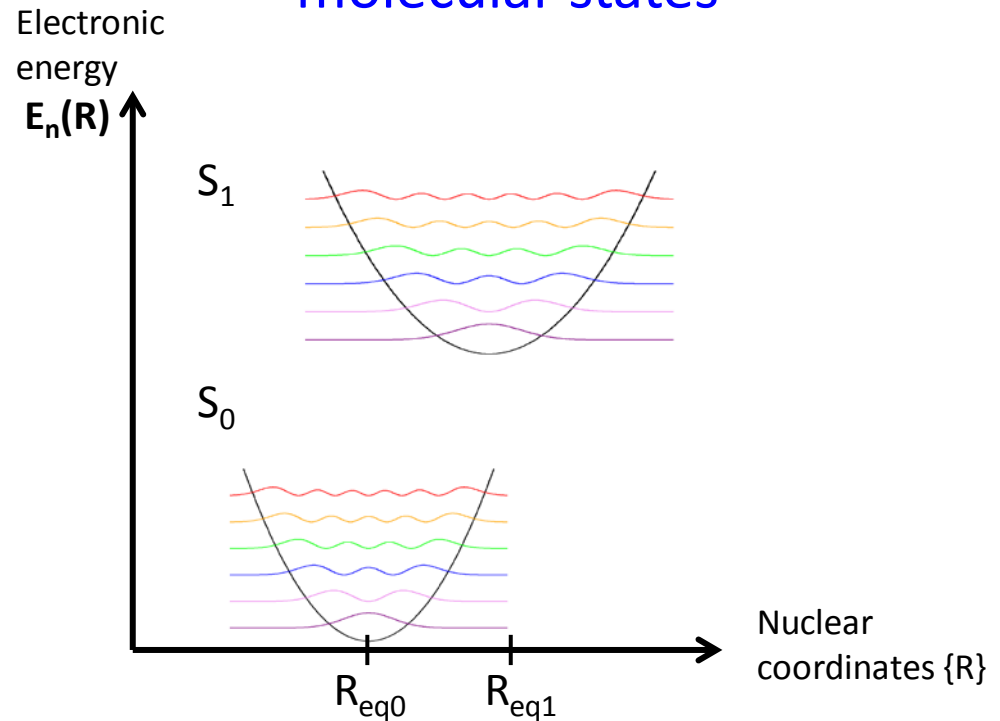
each of the 16 delocalized state correspond to a defined phase relation between individual dipoles

What is missing in our description?

We talked about
electronic states



We should rather discuss
molecular states



- **3N-6 vibrational degrees of freedom for each BCI,**
- **+ environment degrees of freedom (e.g. protein scaffold at 300K)**

= Thermal Bath

Back to Concept #3: Quantum Coherence


eigen states = stationary states

$$|a\rangle = \frac{1}{\sqrt{2}}(|eg\rangle - |ge\rangle) \quad (\varphi=\pi) \text{ (out-of-phase dipoles)}$$
$$|s\rangle = \frac{1}{\sqrt{2}}(|eg\rangle + |ge\rangle) \quad (\varphi=0) \text{ (in-phase dipoles)}$$

delocalized state :

$$|deloc.\rangle = \frac{1}{\sqrt{2}}(|eg\rangle + \boxed{\exp(i\varphi)}|ge\rangle)$$

phase factor



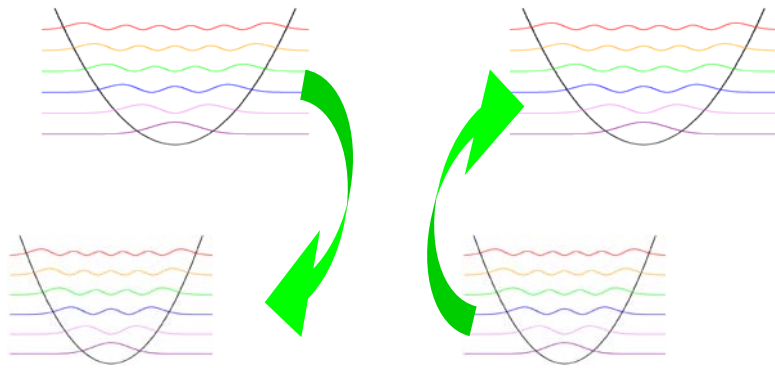
Interaction with the bath:

- => each individual BChl wavefunction has a **fluctuating phase** (e.g. collisions)
- ⇒ phase relation (i.e. quantum coherence) gets lost
- ⇒ no quantum superposition (i.e. no interference) survives
- ⇒ « **Decoherence** »
- => No delocalisation anymore : **excitation localized on one BChl**

⇒ « Incoherent » (i.e. classical) regime

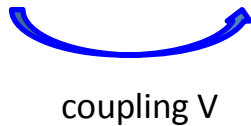
Concept #4: Incoherent Energy “hopping”

quantum coherence is lost due to fluctuating interaction with bath but the interaction (dipole-dipole coupling) still exists



$$|\text{BChl 1}\rangle = |e\rangle \times |\chi_{e,v1}\rangle$$

$$|\text{BChl 2}\rangle = |g\rangle \times |\chi_{g,v2}\rangle$$



FERMI Golden rule

- Transition from 1 initial state to a continuum of final states
- Energy conservation

Transition rate =

$$k_i = \frac{2\pi}{\hbar} \sum_f |V_{if}|^2 \delta(E_i - E_f)$$

statistical average
(thermal bath)

=> Förster Resonant Energy Transfer (FRET)

(1930's)

What about Quantum biology ?

1) Basic Expectation

Two time scales: τ_{rel} = time scale for equilibration via interaction with thermal bath
 τ_{trans} = time scale for energy transfer = \hbar/V (coupling)

$$\tau_{\text{trans}} \ll \tau_{\text{rel}}$$

fully quantum coherent:
delocalization over the entire antenna

« Exploring »
simultaneously all channels
for energy transfer to the
next antenna or to the RC
=> fastest possible energy
transfer to the RC (i.e. most
efficient)

Optimum efficiency

$$\tau_{\text{rel}} \ll \tau_{\text{trans}}$$

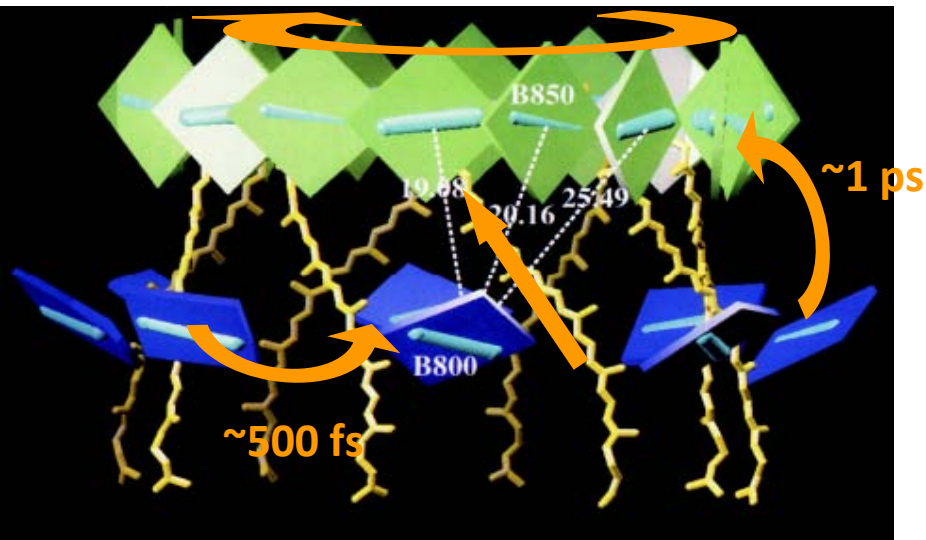
fully incoherent:
localization and energy hopping

Random walk
explore successively the different
channels
dissipation => may never arrive before
(energy loss or trap)

Less efficient

Back to Light Harvesting complexes

Within LH-2



Between antennas

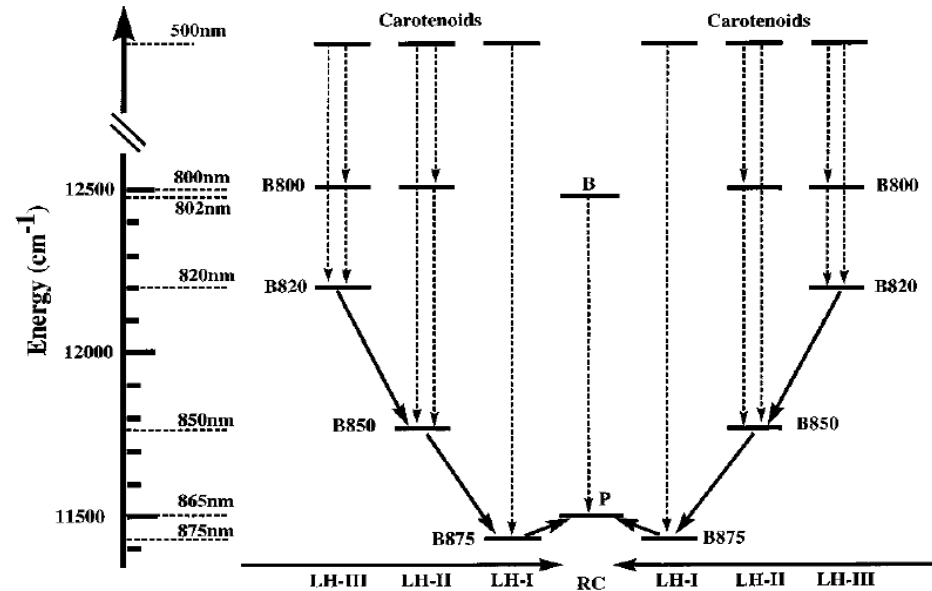
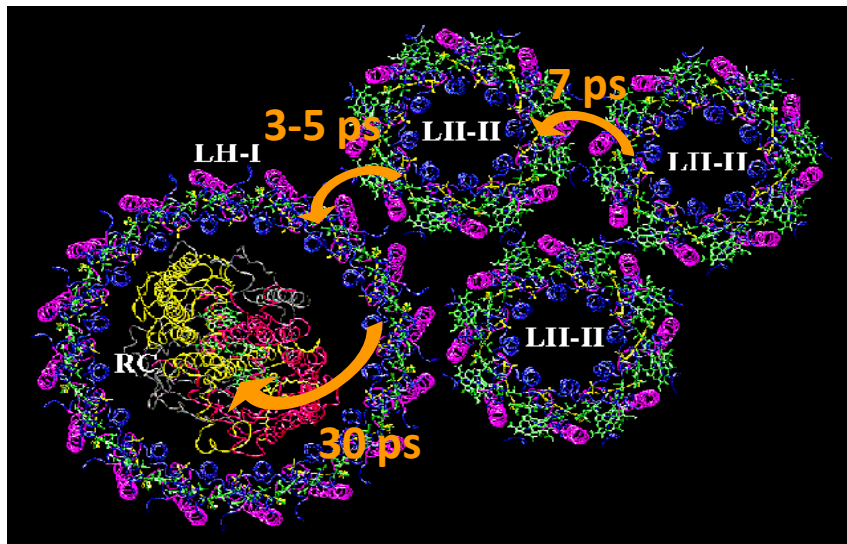


Figure 3. Energy levels of the electronic excitations in the PSU of purple bacteria with BChl-a. The diagram illustrates a funneling of excitation energy toward the photosynthetic reaction center (RC). The dashed lines indicate (vertical) intracomplex exciton transfer, the solid lines (diagonal) intercomplex energy transfer. LH-I exists in all purple bacteria; LH-II exists in most species; LH-III arises in certain species only.

from Hu et al. J. Phys. Chem. B, 1997

time scales : Sundström et al., J.Phys. Chem B 1999
van Grondelle et al., PCCP 2005,

What about Quantum biology ?

2) Observations

nature

Vol 446|12 April 2007|doi:10.1038/nature05678

LETTERS

Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

Gregory S. Engel^{1,2}, Tessa R. Calhoun^{1,2}, Elizabeth L. Read^{1,2}, Tae-Kyu Ahn^{1,2}, Tomáš Mančal^{1,2,†}, Yuan-Chung Cheng^{1,2}, Robert E. Blankenship^{3,4} & Graham R. Fleming^{1,2}
(University of California, Berkeley, USA)

nature

Vol 463|4 February 2010|doi:10.1038/nature08811

LETTERS

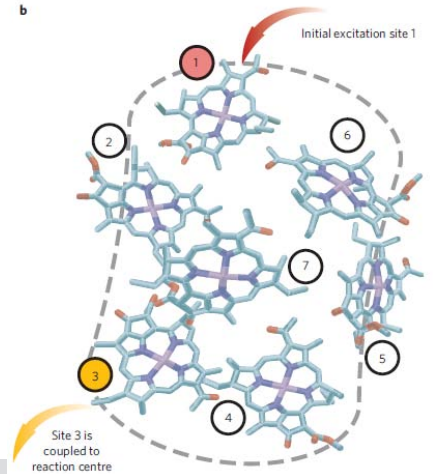
Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature

(University of Toronto, Canada)

Elisabetta Collini^{1*†}, Cathy Y. Wong^{1*}, Krystyna E. Wilk², Paul M. G. Curmi², Paul Brumer¹ & Gregory D. Scholes¹

See also: « Coherence in Energy Transfer and Photosynthesis »

Aurélia Chenu and Gregory D. Scholes, *Annu. Rev. Phys. Chem.* **2015**. 66:69–96

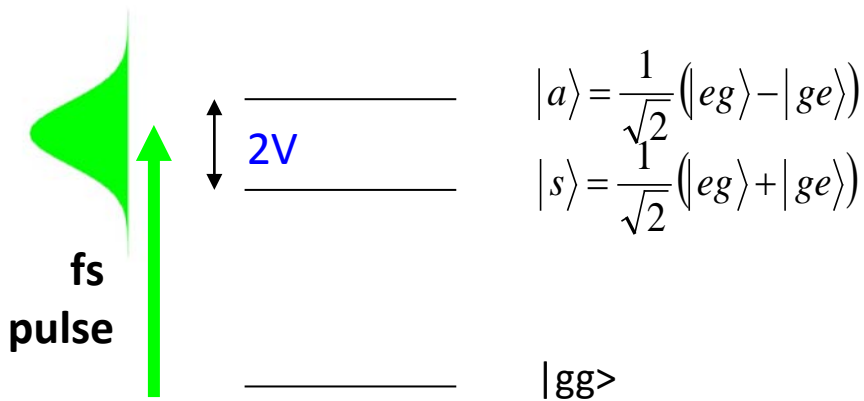


Fenna-Matthews-Olson (FMO) complex

What about Quantum biology ?

2) Observations

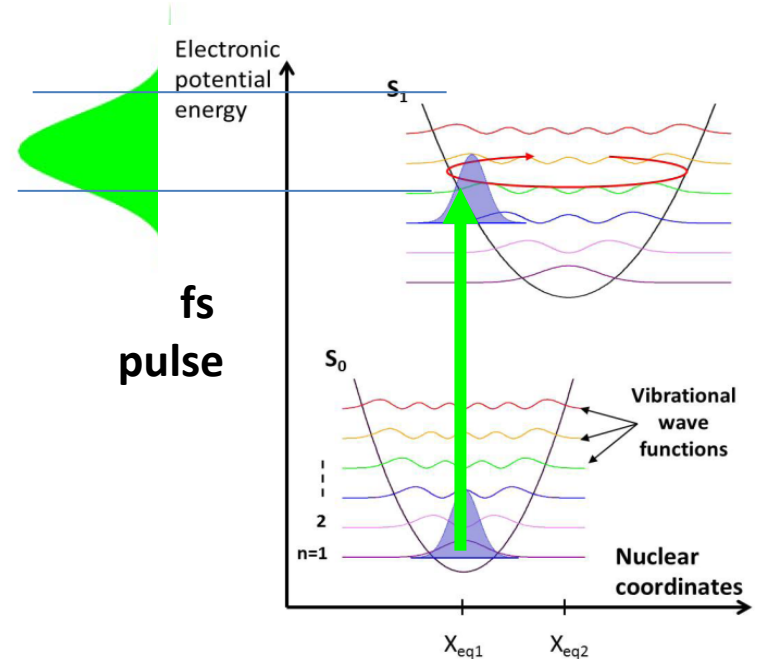
interacting chromophores
=
excitonic states



- ⇒ create a superposition of excitonic states
- ⇒ non-stationary **DELOCALIZED** excitonic state
- ⇒ oscillating spectroscopic signatures

**Interpretation of these oscillatory signals
in terms of electronic or vibrational coherences?**

one single chromophore
=
vibrational states



- ⇒ create a superposition of vibrational states
- ⇒ non-stationary **LOCALIZED** vibrational state
- ⇒ oscillating spectroscopic signatures
(cf Zewail in the 80's)

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in light harvesting complexes:

e.g.: **« Tunneling »**
=>Electron transfer in biology

✓intense theoretical development

coherent versus incoherent => **intermediate regimes**

electronic versus vibrational => coupled regimes

✓By how much quantum coherence may improve the efficiency?