

**Quantum Entanglement  
for  
Complex Systems**

**Sabre Kais**

**Department of Chemistry  
Purdue University**

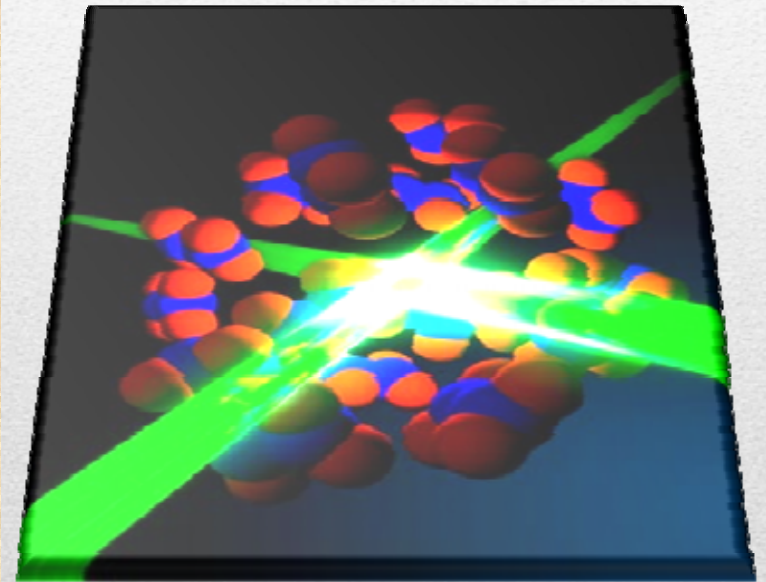
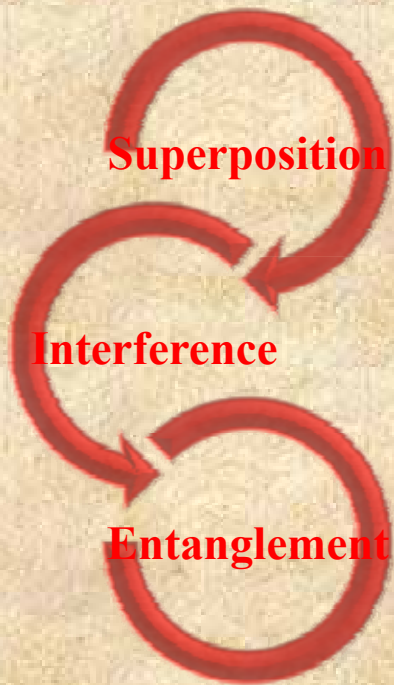
**West Lafayette, IN 47907**

**<http://www.chem.purdue.edu/kais>**

---

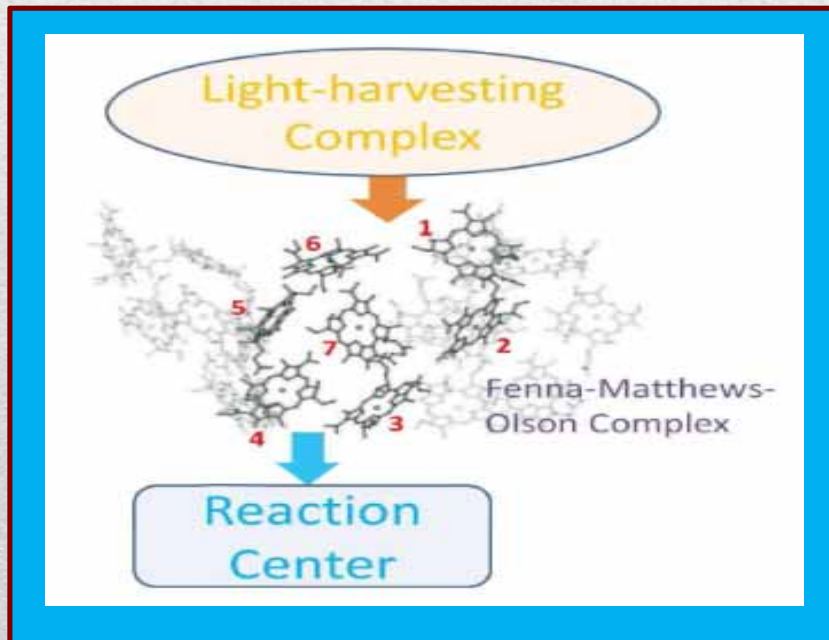
# What if there is never a quantum computer?

We learn about chemistry from the perspective of quantum information!



# Quantum Information for Chemical and Biological Systems

To understand the role of **coherence and entanglement in photosynthesis**, **mechanism with which birds determine magnetic north** and chemical reactions



## How are special quantum features useful in quantum computing?

- ◆ **Quantum Superposition**: helps the Quantum Computer hold large numbers of values simultaneously in a single register made up of relatively few qubits.
  - ◆ **Quantum Interference**: helps to determine a result that depends on all intermediate results, without having to reveal those intermediate results (avoid premature collapse of wavefunction)
  - ◆ **Entanglement**: enables the linkage of quantum registers so that whenever an answer  $f(x)$  appears in one register, we can always determine the  $x$  that generated it
-

# What is Entanglement?

**Schrodinger:** For an Entangled state "the best possible knowledge of the whole does not include the best possible knowledge of its parts"

**Einstein-Podolsky-Rosen:** An entangled wavefunction does not describe the physical reality in a complete way

**Bell:** A correlation that is stronger than any classical correlation

**Peres:** A trick that quantum magicians use to produce phenomena that cannot be imitated by classical magicians

**Bennett:** A resource that enables quantum teleportation

**Shor:** A global structure of the wavefunction that allows for faster algorithms

**Ekert:** A tool for secure communication

# Einstein-Podolsky-Rosen (EPR) Paradox (1935)

*Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?*

**The principle of reality**: individual particles possess definite properties even when they're not being observed.

**The locality principle**: information from a measurement in one of two isolated systems cannot produce real change in the other, especially superluminally (faster than  $c$ ).



*The quantum-mechanical description of reality given by the wave function is not complete, that is, there must be*

**Hidden Variables** *that we don't know about and hence don't measure that cause the uncertainty.*

---

## Local realism is out

John Bell showed in a 1964 paper entitled "On the Einstein Podolsky Rosen paradox," that local realism leads to a series of requirements—known as [Bell's inequalities](#)



John Bell (1928-1990)



Alain Aspect (1947-)

Alain Aspect has performed numerous beautiful experiments, proving conclusively that our universe violate Bell's Inequalities big time. And quantum mechanics explains the effects quite nicely

# Quantum Entanglement and Electron Correlation in Molecular Systems

Hefeng Wang and Sabre Kais\*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

The configuration interaction (CI) wave function is entangled since it violates Bell's inequality. Entanglement is related to electron correlation and might be used as an alternative measure of the electron correlation in quantum chemistry calculations.

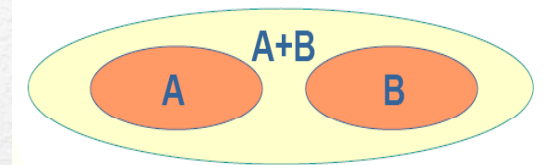
$$E(a b - a c + b d + c d) = E(a, b) - E(a, c) + E(b, d) + E(c, d) \leq 2$$

where  $E(a, b)$  is the mean value of the product of the outcomes of two spin measurements along the direction  $a$  and  $b$



# Entanglement

- The state of a composite quantum system is the **tensor product** of subsystems



$$\begin{aligned} |\psi\rangle &= (\alpha |0\rangle + \beta |1\rangle) \otimes (\gamma |0\rangle + \delta |1\rangle) \\ &= \alpha\gamma |00\rangle + \alpha\delta |01\rangle + \beta\gamma |10\rangle + \beta\delta |11\rangle \end{aligned}$$

- There exist states of many-qubit systems that **cannot be broken down** into a tensor product  
e.g there does not exist :

$$|\psi\rangle = \mu |00\rangle + \nu |11\rangle \neq (\alpha |0\rangle + \beta |1\rangle) \otimes (\gamma |0\rangle + \delta |1\rangle)$$

- We call these kinds of states **entangled states**
-

# Measuring Entangled State

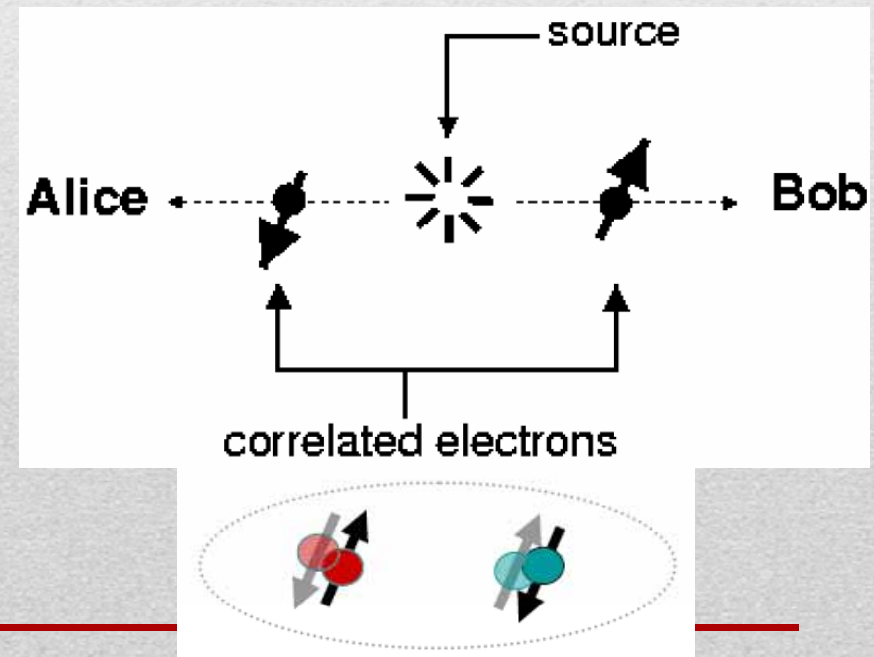
- ◆ For a two-qubit system, there are four entangled states named **Bell states**:

$$|\Psi^{\pm}\rangle = \frac{1}{\sqrt{2}}(|01\rangle \pm |10\rangle)$$

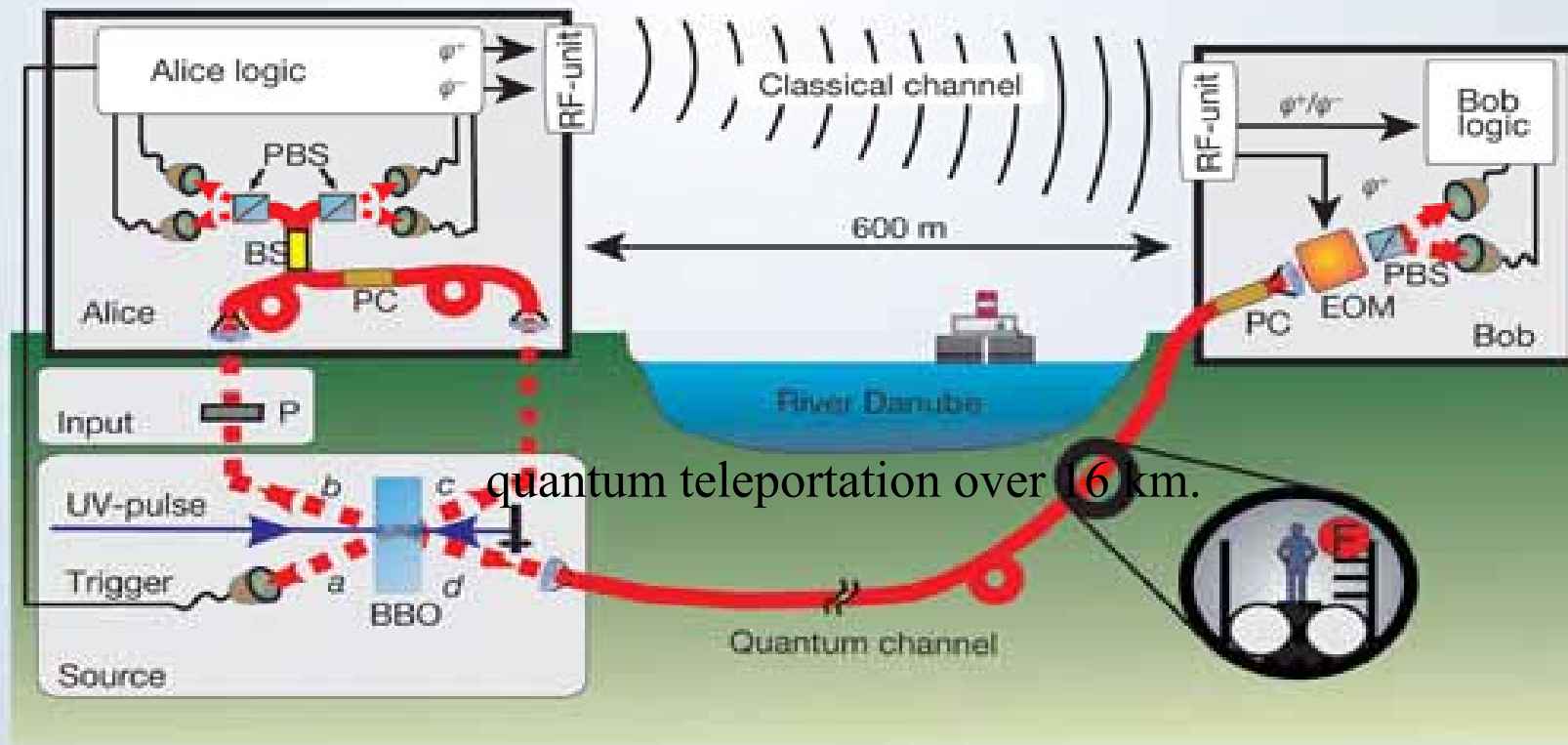
$$|\Phi^{\pm}\rangle = \frac{1}{\sqrt{2}}(|00\rangle \pm |11\rangle)$$

- ◆ After measuring an entangled pair for the first time, the outcome of the second measurement is known 100%

$$|\Psi^{+}\rangle = \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle)$$



# Quantum Teleportation Across the Danube



A real-world experiment marks a step towards worldwide quantum communication.

**Anton Zeilinger et. al.** *Nature* 430, 849 (2004)

**Xian-Min Jin, et. Al.** *Nature Photonics* (2010)

(Quantum Teleportation over 16 km)

# Requirements for Entanglement Measures

**Separability:** If  $\rho$  is separable, then  $E(\rho) = 0$ .

**Normalization:** The entanglement of a maximally state of two  $d$ -dimensional systems is given by  $E = \log(d)$ .

**No Increase Under Local Operations:** Applying local operations and classically communicating cannot increase  $E$ .

**Continuity:** In the limit of vanishing distance between two density matrices the difference between their entanglement should tend to zero.

**Additivity:** A certain number  $N$  of identical copies of the state  $\rho$  should contain  $N$  times the entanglement of one copy.

**Subadditivity:** the entanglement of the tensor product of two states should not be larger than the sum of the entanglement of each of the states.

**Convexity:** The entanglement measure should be a convex function.

---

*Von Neumann Entropy*

# Quantify Entanglement

(Entanglement of Formation)

- The pure state entanglement can be defined as the von Neumann entropy of either of the two subsystem A and B

$$E(\phi) = -\text{Tr}(\rho_A \log_2 \rho_A) = -\text{Tr}(\rho_B \log_2 \rho_B)$$

$$\rho_A = \text{Tr}_B(\rho), \quad \rho = |\phi\rangle\langle\phi|$$

- Concurrence is the simply expression of Entanglement

$$E(\rho) = \mathcal{E}(C(\rho)) \quad \mathcal{E} = h\left(\frac{1 + \sqrt{1 - C^2}}{2}\right)$$

$$h(x) = -x \log_2 x - (1 - x) \log_2 (1 - x)$$

$$C(\rho) = \max\{0, \lambda_1 - \lambda_2 - \lambda_3 - \lambda_4\}$$

$$R \equiv \sqrt{\sqrt{\rho} \tilde{\rho} \sqrt{\rho}} \quad \tilde{\rho} = (\sigma_y \otimes \sigma_y) \rho^* (\sigma_y \otimes \sigma_y)$$

## Recipe for Concurrence

*A Measure of Pairwise Entanglement*

$C = 0$  means no entanglement

$C = 1$  means maximum entanglement

1. Construct **density matrix**,  $\rho$
2. Construct **flipped density matrix**,  $\tilde{\rho}$
3. Construct **product matrix**,  $\rho\tilde{\rho}$
4. Find **eigenvalues**  $\lambda_1, \lambda_2, \dots$  of  $\rho\tilde{\rho}$
5. Calculate **Concurrence** from square roots of eigenvalues via

$$C = \max[0, \sqrt{\lambda_1} - \sqrt{\lambda_2} - \dots]$$

W. K. Wootters, Phys. Rev. Lett. 80, 2245 (1998)

# Hamiltonian

$$\hat{H} = \hbar \sum_i \omega_i \sigma_i^z + \hbar \sum_{i \neq j} \Omega_{ij} \sigma_i^x \sigma_j^x$$

$\hbar\omega_i$  = **Transition energy between qubit state  $|0\rangle$  and  $|1\rangle$  on site  $i$**

$\hbar\Omega_{ij}$  = **Dipole – Dipole interaction energy between site  $i$  and  $j$**

$\hbar = \mathbf{h}/2\pi$  = **Planck's constant**

For  $N = 2$ , use basis  $|00\rangle, |01\rangle, |10\rangle, |11\rangle$ :

$$\hat{H} = \begin{bmatrix} 0 & 0 & 0 & \Omega \\ 0 & \omega & \Omega & 0 \\ 0 & \Omega & \omega & 0 \\ \Omega & 0 & 0 & 2\omega \end{bmatrix}$$

Schrödinger Equation

$$\hat{H}\psi = E\psi$$

---



# Eigenvalues and Eigenvectors

$$\left\{ \begin{array}{ll} E_1 = \omega - \sqrt{\omega^2 + \Omega^2} & \psi_1 = \frac{1}{\sqrt{1 + \alpha_+^2}} (|11\rangle - \alpha_+ |00\rangle) \\ E_2 = \omega - \Omega & \psi_2 = \frac{1}{\sqrt{2}} (|10\rangle - |01\rangle) \\ E_3 = \omega + \Omega & \psi_3 = \frac{1}{\sqrt{2}} (|10\rangle + |01\rangle) \\ E_4 = \omega + \sqrt{\omega^2 + \Omega^2} & \psi_4 = \frac{1}{\sqrt{1 + \alpha_-^2}} (|11\rangle - \alpha_- |00\rangle) \end{array} \right.$$

$$\text{Where } \alpha_{\pm} = \frac{\omega \pm \sqrt{\omega^2 + \Omega^2}}{\Omega}$$

---

$$\Psi_2 = 1/\sqrt{2} (|10\rangle - |01\rangle)$$

$$\rho = |\psi_2\rangle\langle\psi_2| = \frac{1}{2} (|10\rangle - |01\rangle)(\langle 10| - \langle 01|)$$

$$= \begin{array}{c} |00\rangle \\ |01\rangle \\ |10\rangle \\ |11\rangle \end{array} \begin{array}{cccc} \langle 00| & \langle 01| & \langle 10| & \langle 11| \\ \left( \begin{array}{cccc} 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 \end{array} \right) \end{array}$$

$$\rho = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\Psi_2 = 1/\sqrt{2} (|10\rangle - |01\rangle)$$

$$R = \rho \tilde{\rho} = -\frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

**Eigenvalues :**  $\lambda_1 = 1, \lambda_2 = \lambda_3 = \lambda_4 = 0$

**Concurrence :**

$$C_{12} = \max [0, \sqrt{\lambda_1} - \sqrt{\lambda_2} - \sqrt{\lambda_3} - \sqrt{\lambda_4}] = 1$$

**Using the same method,**

**we can get the concurrence for  $\psi_3$**

$$C_{12} = 1$$

---

$$\Psi_1 = 1/\sqrt{1+\alpha_+^2}(|11\rangle - \alpha_+|00\rangle)$$

$$\rho = |\psi_1\rangle\langle\psi_1| = \frac{1}{1+\alpha_+^2} (|11\rangle - \alpha_+|00\rangle)(\langle 11| - \alpha_+\langle 00|)$$

$$= \frac{1}{1+\alpha_+^2} \begin{bmatrix} \alpha_+^2 & 0 & 0 & -\alpha_+ \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -\alpha_+ & 0 & 0 & 1 \end{bmatrix}$$

$$\tilde{\rho} = \frac{1}{1+\alpha_+^2} \begin{bmatrix} 1 & 0 & 0 & -\alpha_+ \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -\alpha_+ & 0 & 0 & \alpha_+^2 \end{bmatrix}$$

$$\Psi_1 = 1/\sqrt{(1+\alpha_+^2)}(|11\rangle - \alpha_+|00\rangle)$$

$$R = \rho \tilde{\rho} = \frac{1}{(1+\alpha_+^2)^2} \begin{bmatrix} 2\alpha_+^2 & 0 & 0 & -2\alpha_+^3 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -2\alpha_+ & 0 & 0 & 2\alpha_+^2 \end{bmatrix}$$

**Eigenvalues :**  $\lambda_1 = \frac{4\alpha_+^2}{(1+\alpha_+^2)^2}$ ,  $\lambda_2 = \lambda_3 = \lambda_4 = 0$

**Concurrence :**

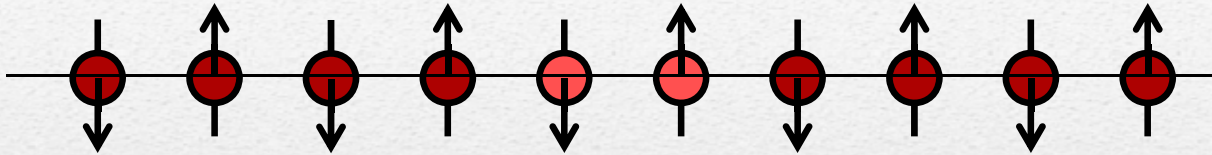
$$C_{12} = \max\left(0, \sqrt{\lambda_1} - \sqrt{\lambda_2} - \sqrt{\lambda_3} - \sqrt{\lambda_4}\right) = \frac{2\alpha_+}{1+\alpha_+^2}$$

**Using the same method,  
we can get the concurrence for  $\psi_4$**

$$C_{12} = \frac{2|\alpha_-|}{1+\alpha_-^2}$$

# Spin Systems

- ◆ A Spin Chain with nearest neighbor interaction

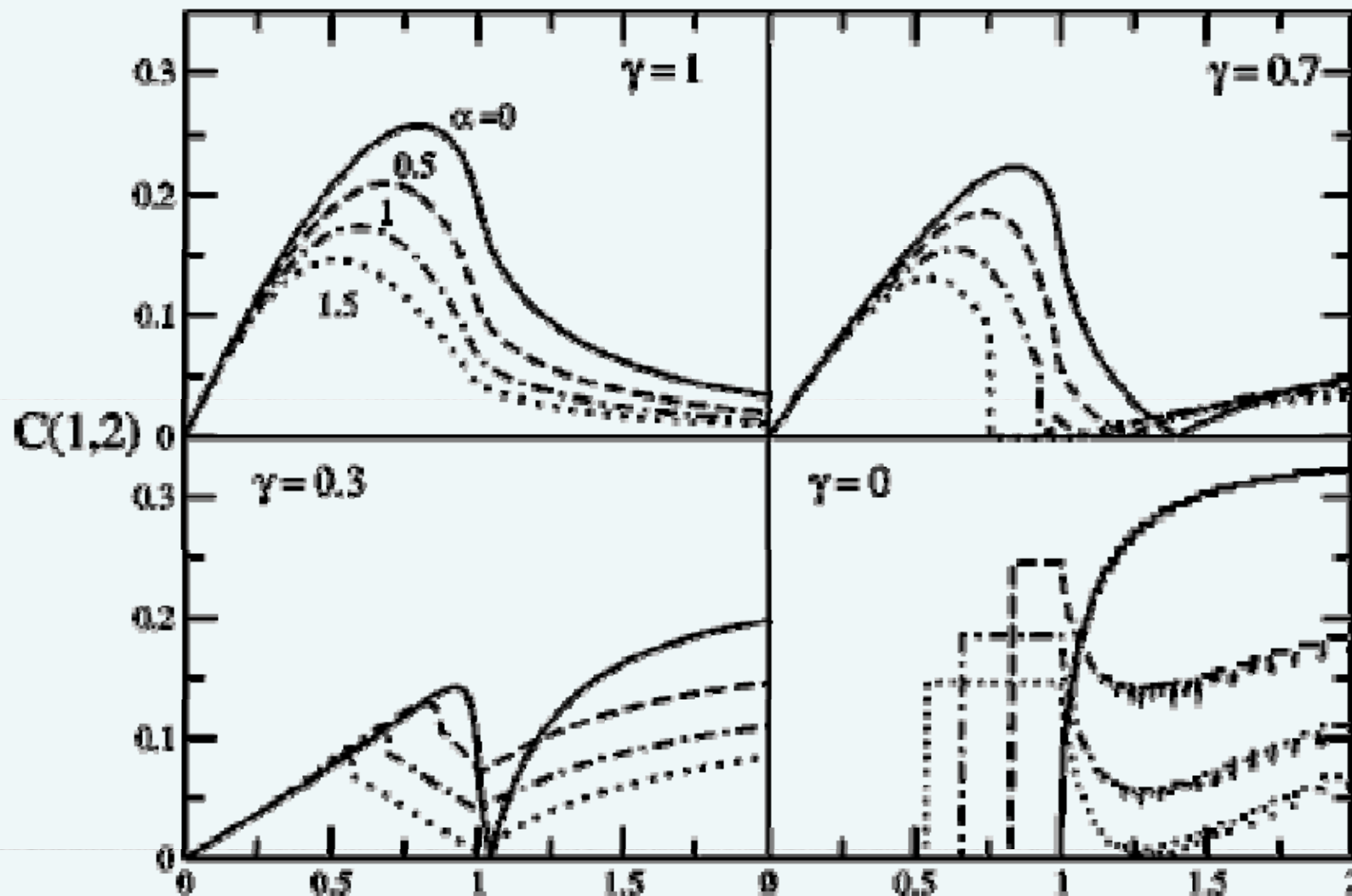


- ◆ Hamiltonian

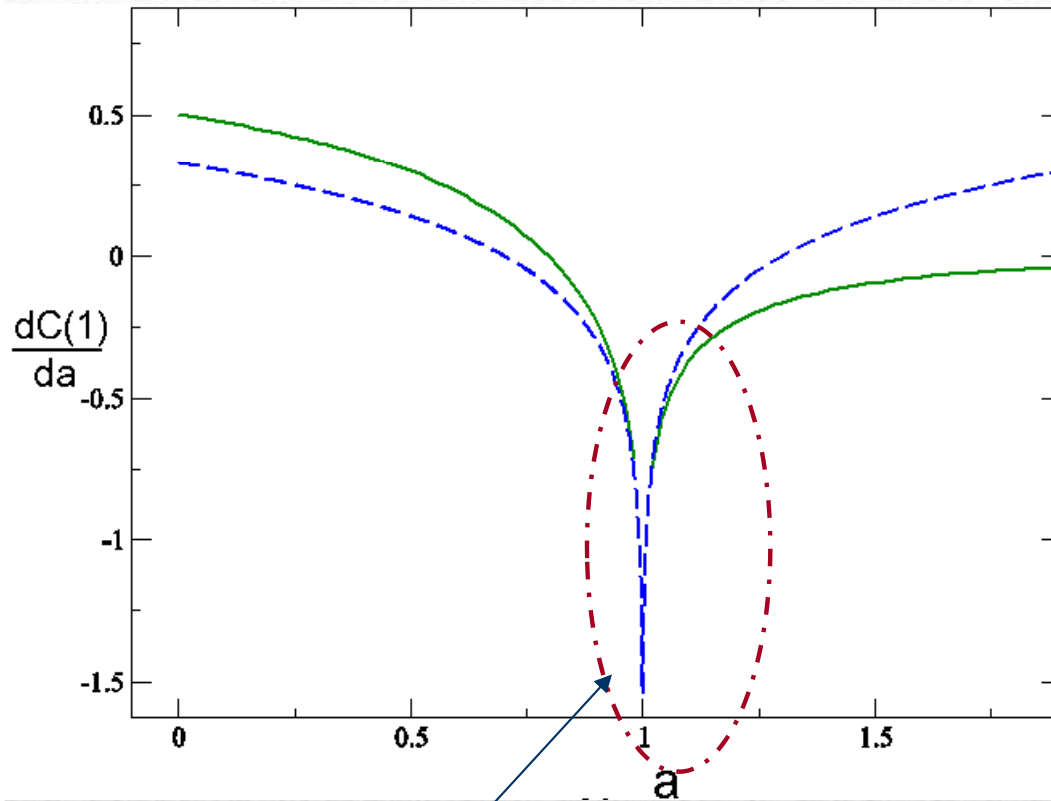
$$H = -\frac{1+\gamma}{2} \sum_{i=1}^N J_{i,i+1} \sigma_i^x \sigma_{i+1}^x - \frac{1-\gamma}{2} \sum_{i=1}^N J_{i,i+1} \sigma_i^y \sigma_{i+1}^y - \sum_{i=1}^N h_i \sigma_i^z$$

$N$  is total spin number,  $\gamma$  is the anisotropy parameter,  $J_{i,i+1} = J(1+\alpha)$  is the coupling constant between impure site and it is  $J$  for other sites,  $h_z$  is the interaction between external magnetic field and spin,  $\sigma$  is the Pauli matrix,  $\lambda = J/2h$

# Tuning Entanglement in Magnetic System



The system exhibit a quantum phase transition at a dimensionless coupling constant =1



As the system is tuned across a quantum critical point, the ground state and its correlations undergo qualitative changes

The same is true of the entanglement in the ground state

Entanglement can be used to characterize/classify phase transitions

$$\partial_a C(1) \approx \frac{8}{3\pi} \ln|a - a_c|$$



# Entanglement Calculations for Quantum Dots

- ◆ Hubbard Hamiltonian of quantum dots

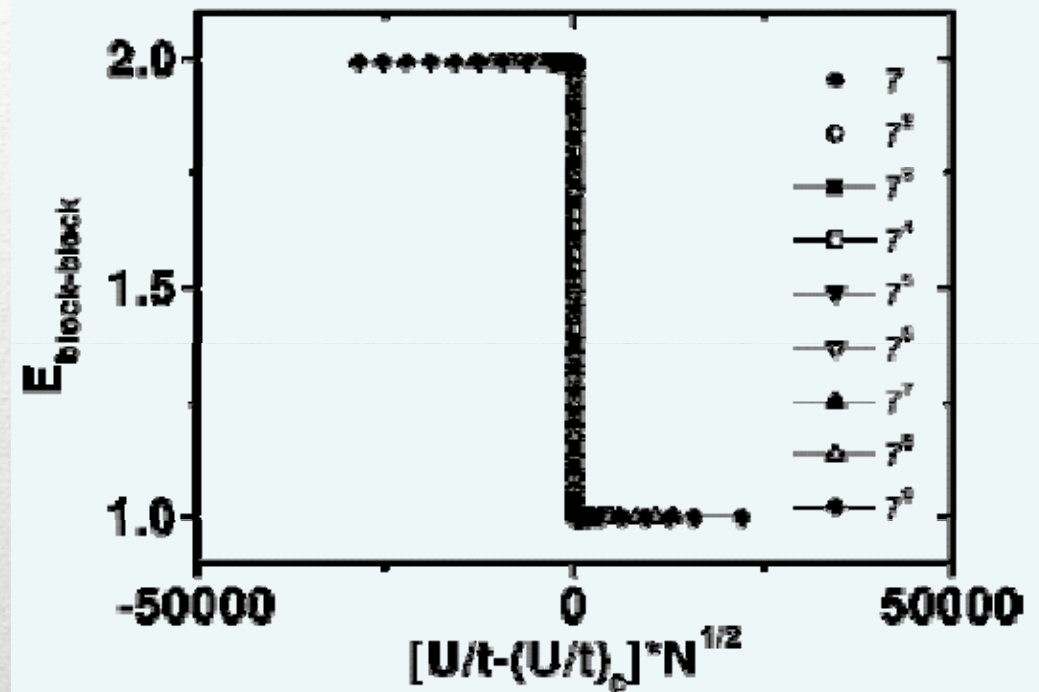
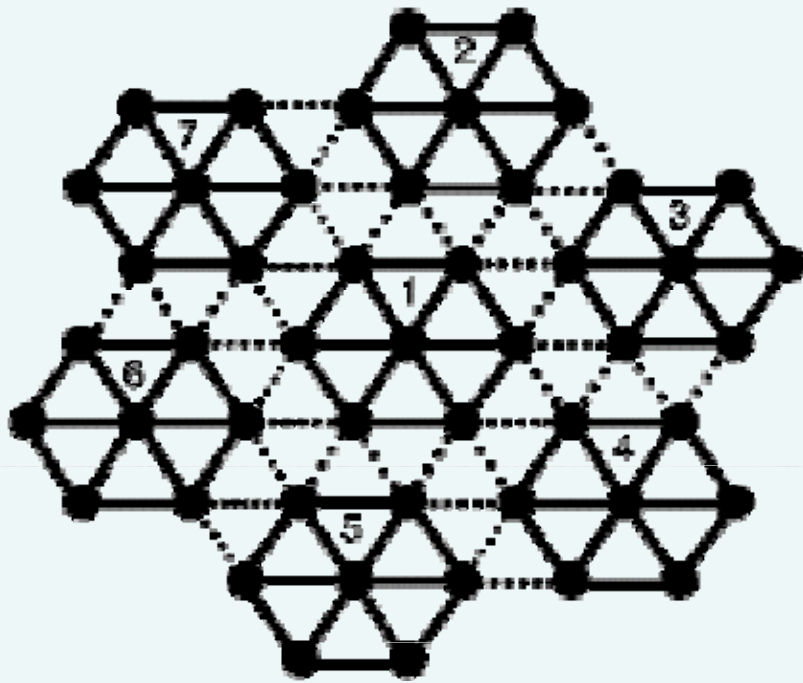
$$H = -t \sum_{\langle i,j \rangle, \sigma} [c_{i\sigma}^\dagger c_{j\sigma} + \text{H. c.}] + U \sum_i \left( \frac{1}{2} - n_{i\uparrow} \right) \left( \frac{1}{2} - n_{i\downarrow} \right)$$

- ◆ Entanglement for the ground state

$$E_j = -\text{Tr} \rho_j \ln \rho_j, \quad \rho_j = \text{Tr}_j |\psi\rangle\langle\psi|$$

$\text{Tr}_j$  denotes the trace over all but the  $j$ -th site

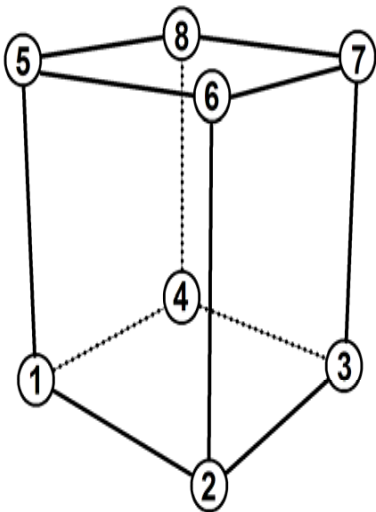
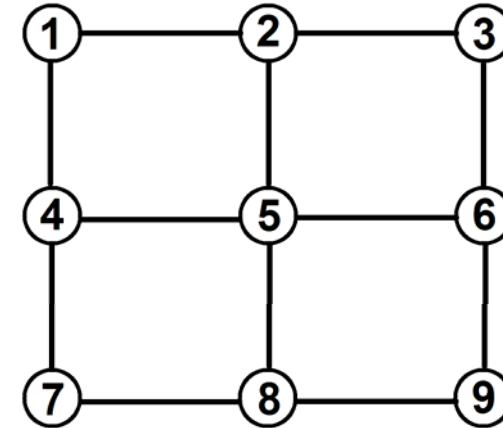
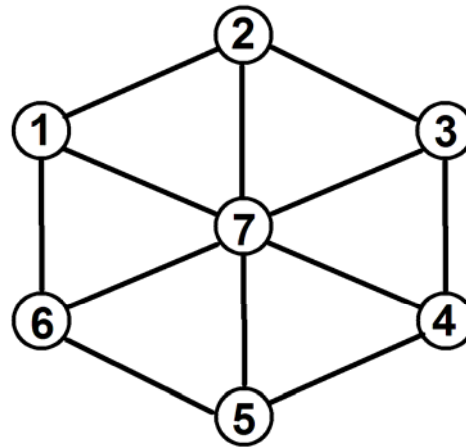
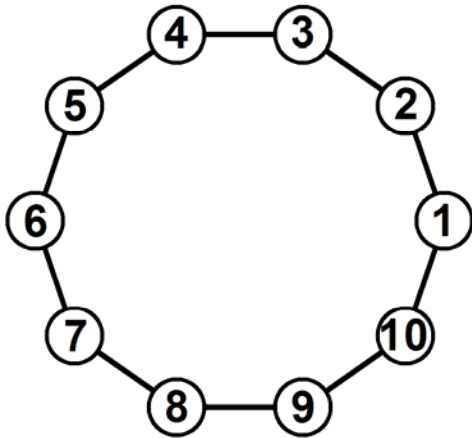
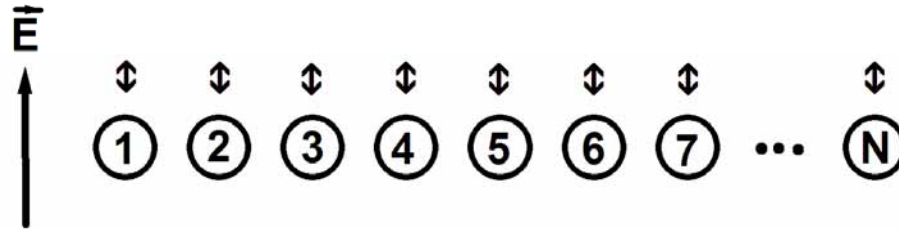
## Metallic State $\rightarrow$ Insulating State



There is an abrupt jump of the entanglement when a first-order quantum phase transition occurs.  
There is a block-block entanglement scaling

# Dipole Systems

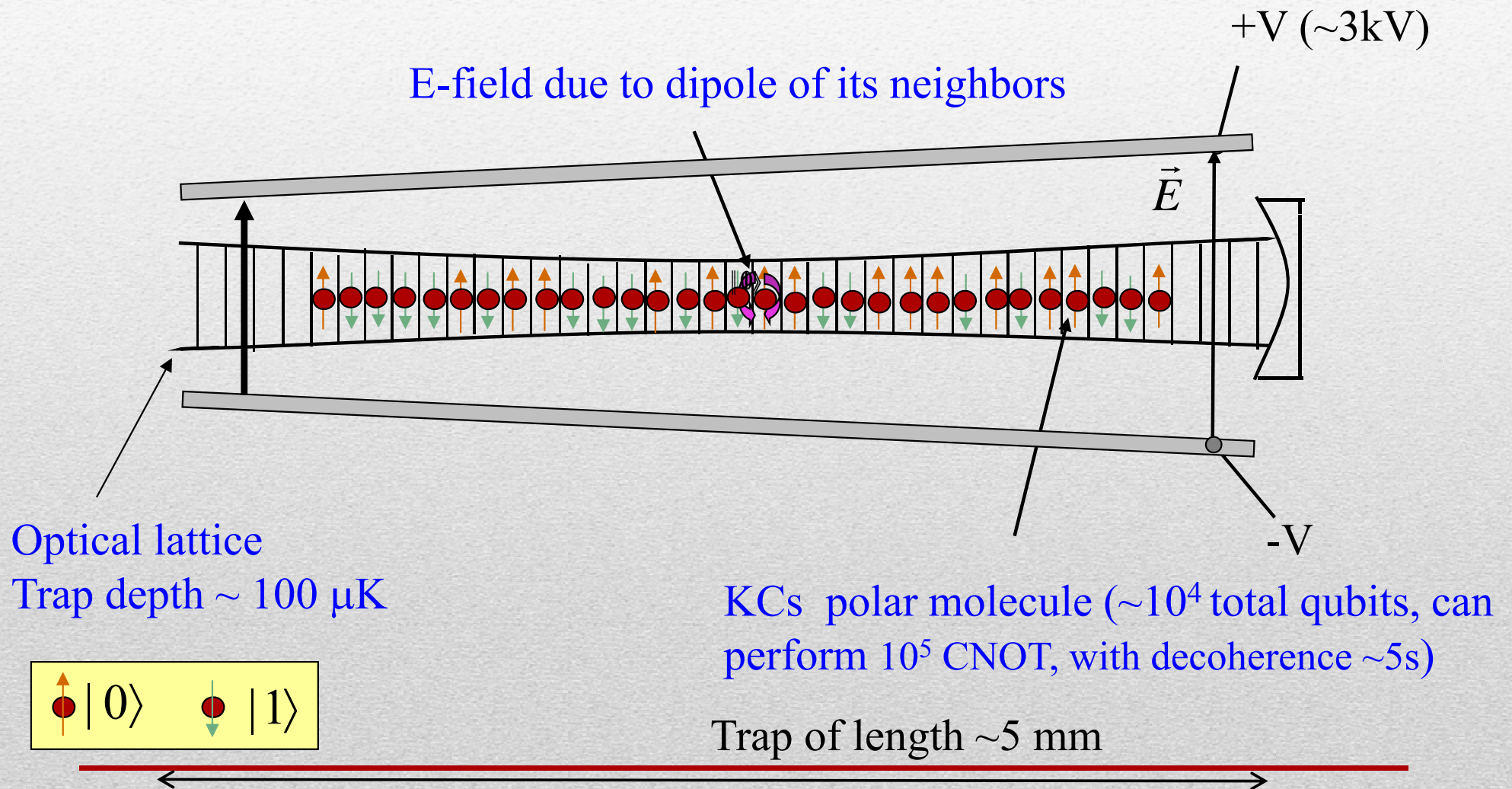
Qi Wei, Sabre Kais, Bretislav Friedrich and Dudley Herschbach



**Arrays of ultracold polar molecules as platform to implement a quantum computer**

Q. Wei, et. al. J. Chem. Phys. 134, 124107 (2011)

# Quantum Computation with Cold Polar Molecules in an Optical Lattice

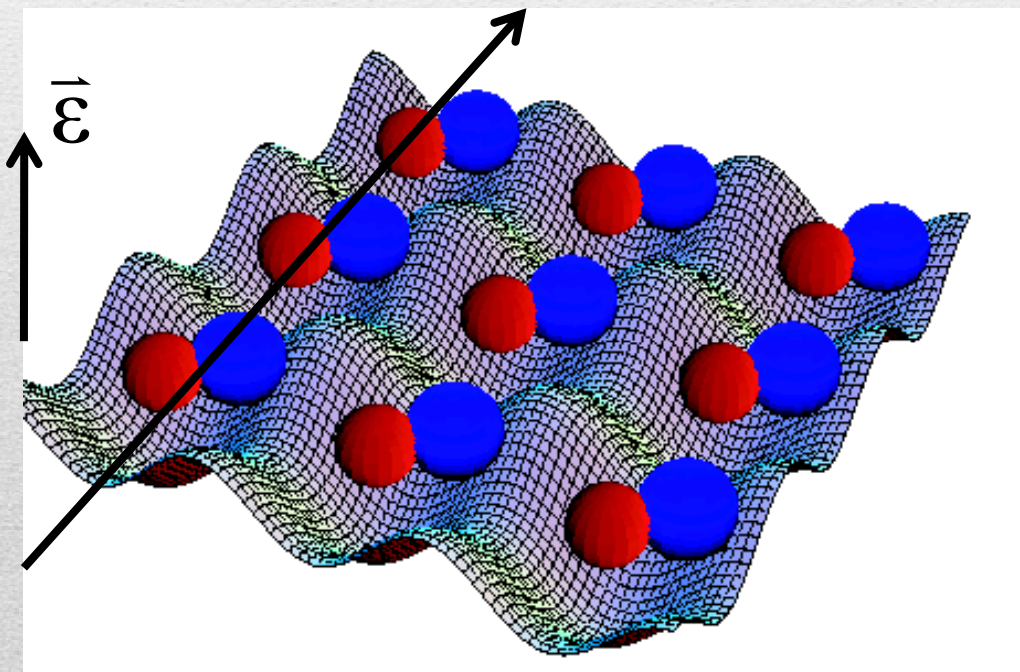


D. DeMille, PRL 88, 067901 (2002)

# Hamiltonian for a Single Molecule

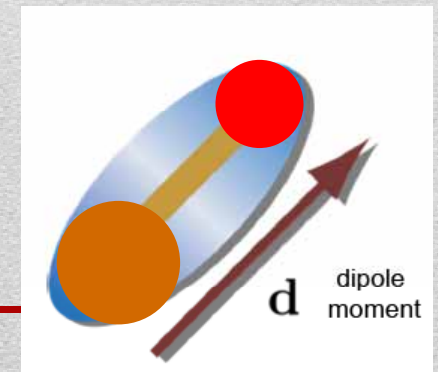
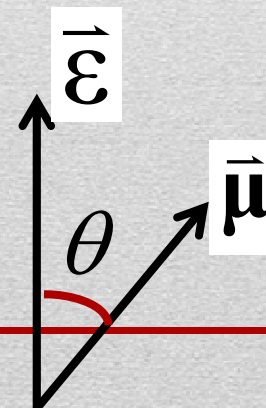
$$\hat{H} = \frac{P^2}{2m} + V_{trap}(\vec{r}) + BJ^2 - \vec{\mu} \cdot \vec{\mathcal{E}}$$

Kinetic energy	Trapping potential	Rotational energy	Electric field
└──────────┘		└──────────┘	
Assume Separable		Rotational state $H_S$	

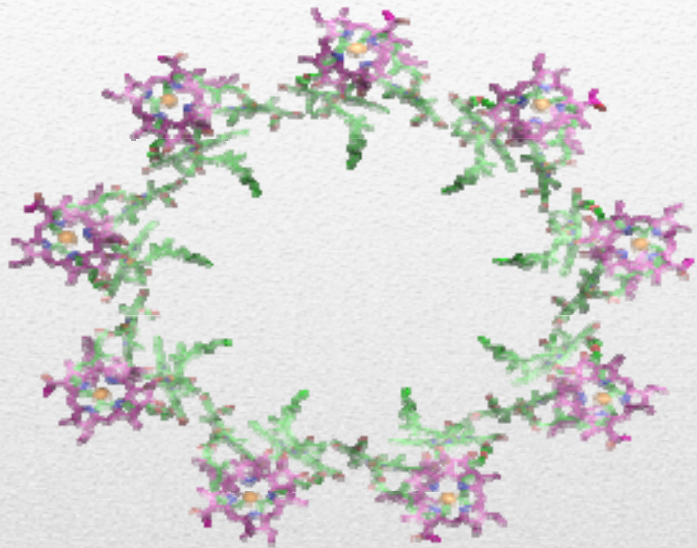


$$\hat{H}_S = BJ^2 - \mu \mathcal{E} \cos \theta$$

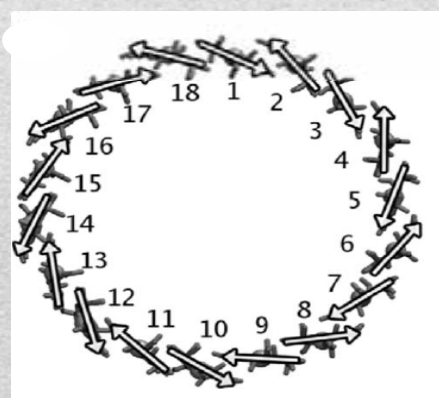
**Eigenfunctions : Pendular states**



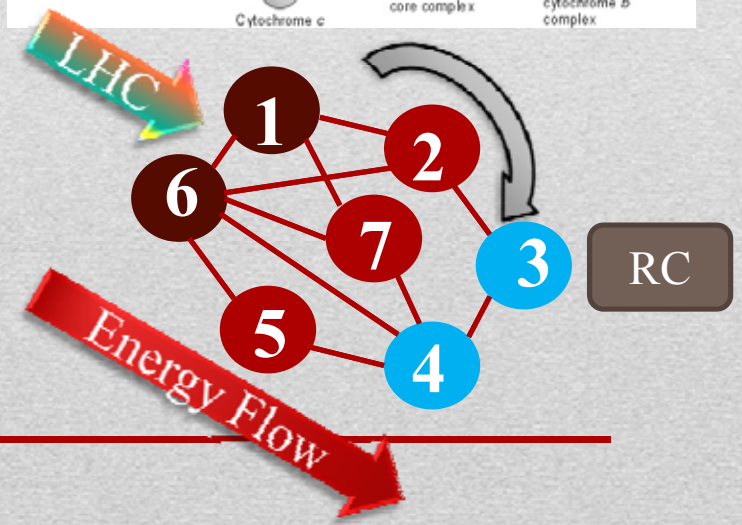
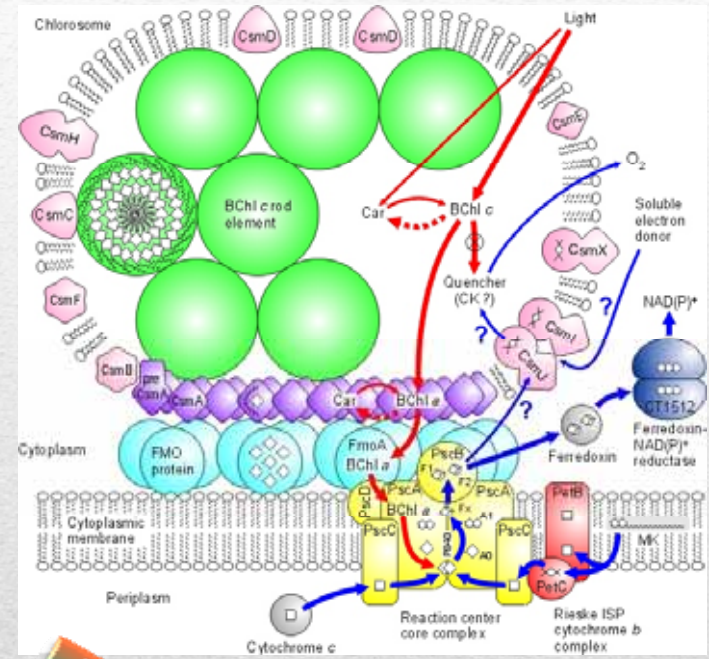
# Entanglement and Excitation Dynamics in Light Harvesting Complex



FMO Complex



LH2 Complex



**Chromophore:** Is the part of a molecule responsible for its color. The color arises when a molecule absorbs certain wavelengths of visible light and transmits or reflects others. The chromophore is a region in the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its ground state into an excited state.

**Photosynthesis:**

Is a chemical process that converts carbon dioxide into organic compounds, especially sugars, using the energy from sunlight. Photosynthesis occurs in plants, algae, and many species of bacteria.

---

**Proteins** are biochemical compounds consisting of one or more **polypeptides** typically folded into a globular form, facilitating a biological function. A **polypeptide** is a single linear polymer chain of amino acids bonded together by peptide bonds between the carboxyl and amino groups of adjacent amino acid residues.

The sequence of amino acids in a protein is defined by the sequence of a gene, which is encoded in the genetic code

---



# Objective

The existence of life on earth relies on the conversion of light energy into chemical energy by bacteria and plants. These natural organisms execute the conversion with extremely high efficiency.

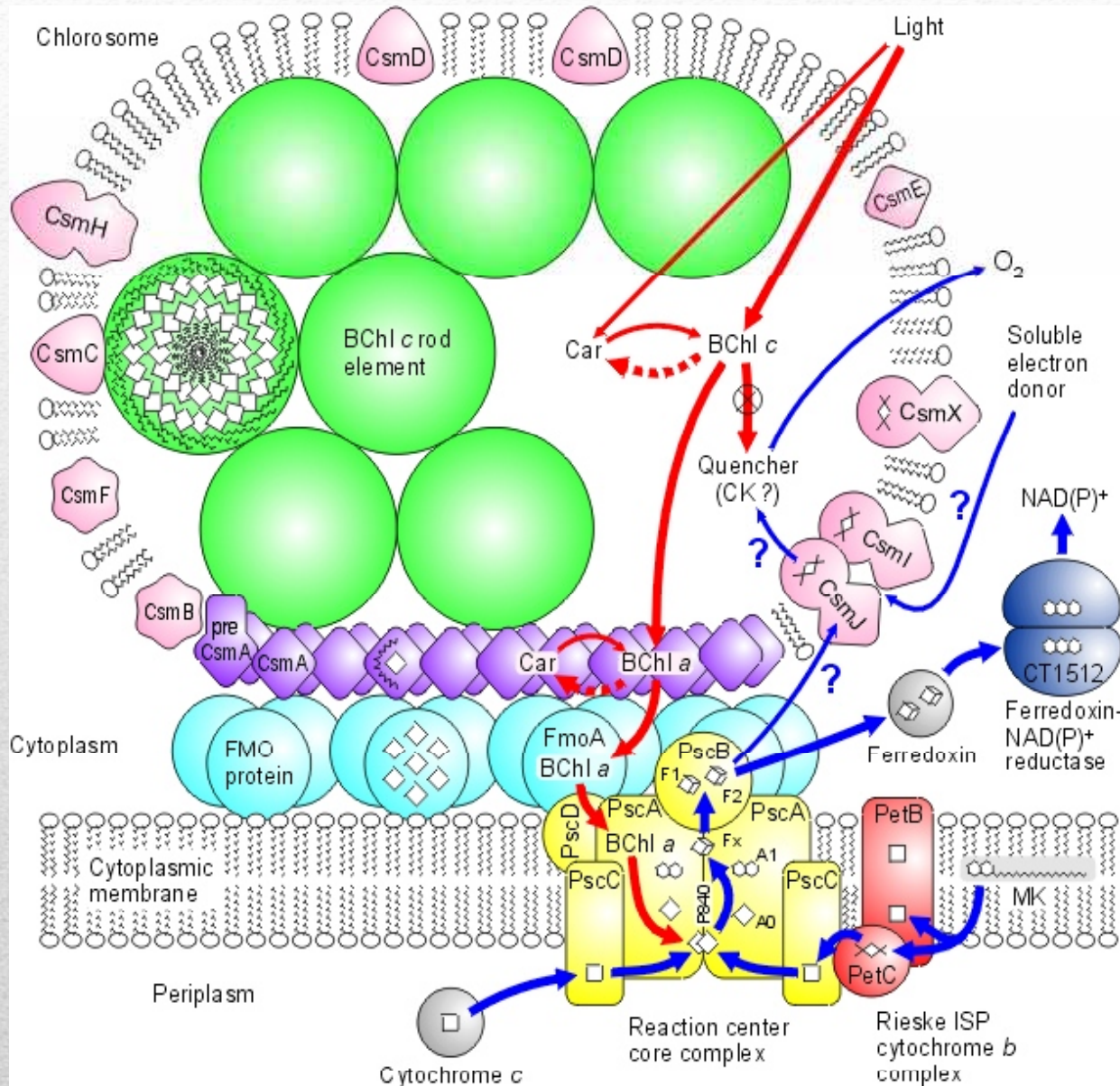
- To understand the role of quantum coherence & entanglement in complex systems such as photosynthesis
  - Photosynthesis is one of the most common phenomenon in nature, but the detailed principles of the whole process are still unclear.
  - The energy transfer from the light harvesting complex (LHC) to the reaction center (RC) is amazingly high (almost 100%)
-

**The energy transport in light-harvesting complexes is extremely efficient**

**Could it be the case that entanglement is responsible for this efficiency?**

---

# Process of Photosynthesis



- Green sulfur bacteria

- Energy flow

omit

*Light* → *LHC*

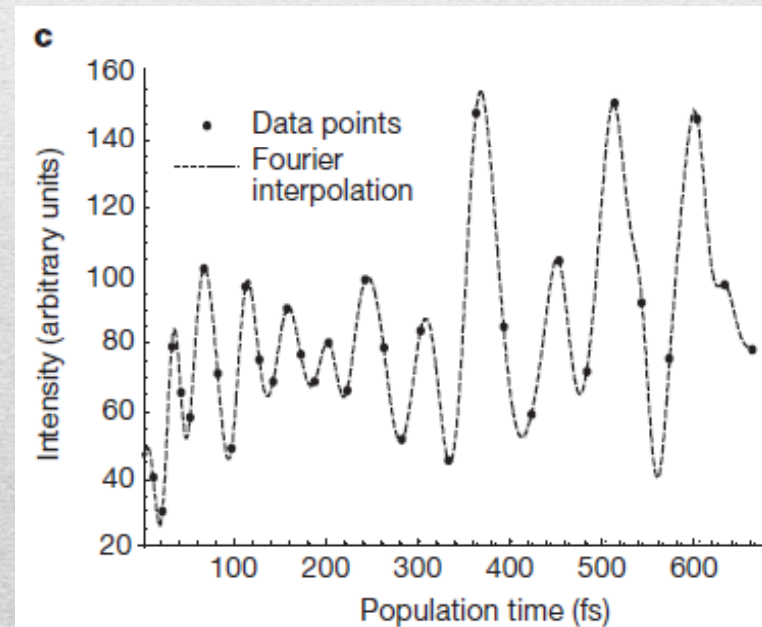
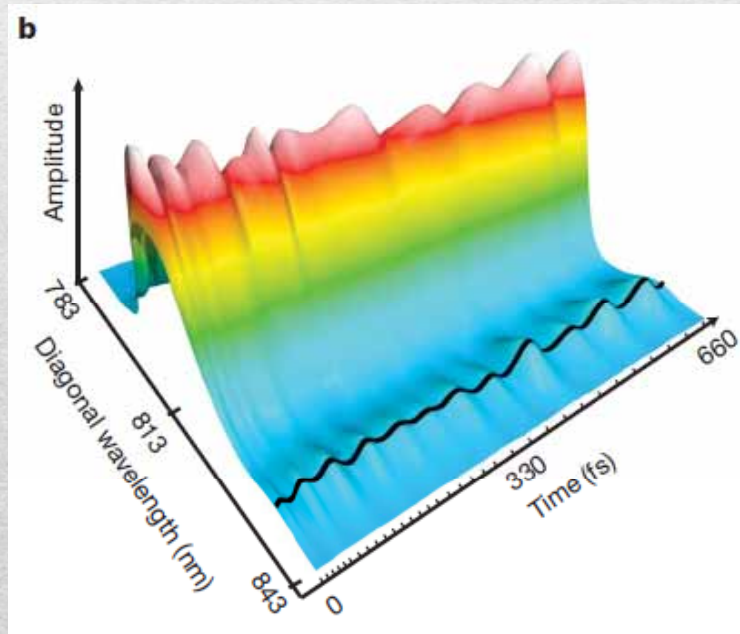
→ *FMO\** Complex

→ *RC*

\* FMO = Fenna-Matthews-Olson

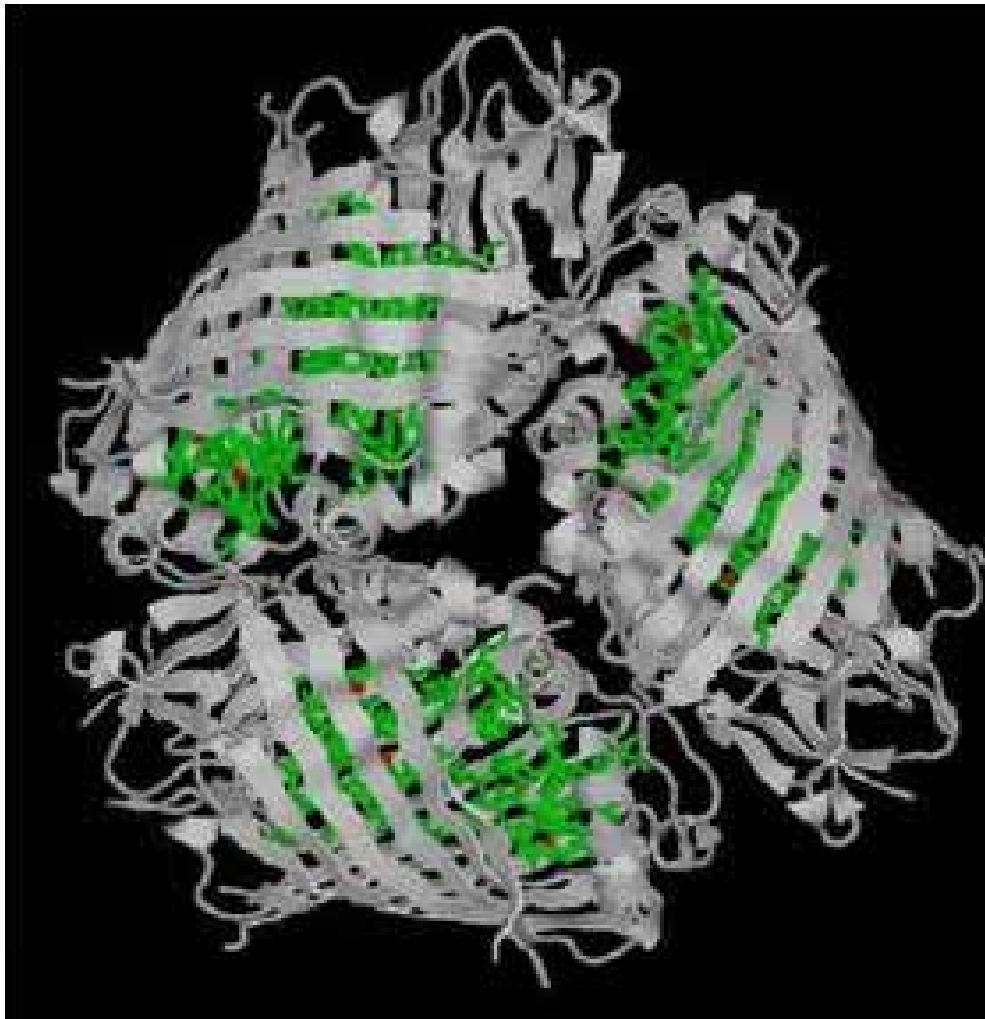
# Experimental Results

- FMO has the function of a wire in the energy transfer
- The transfer efficiency is 100%
- Direct evidence of long-lived coherence has been experimentally demonstrated during the energy transfer at  $T=77\text{K}$



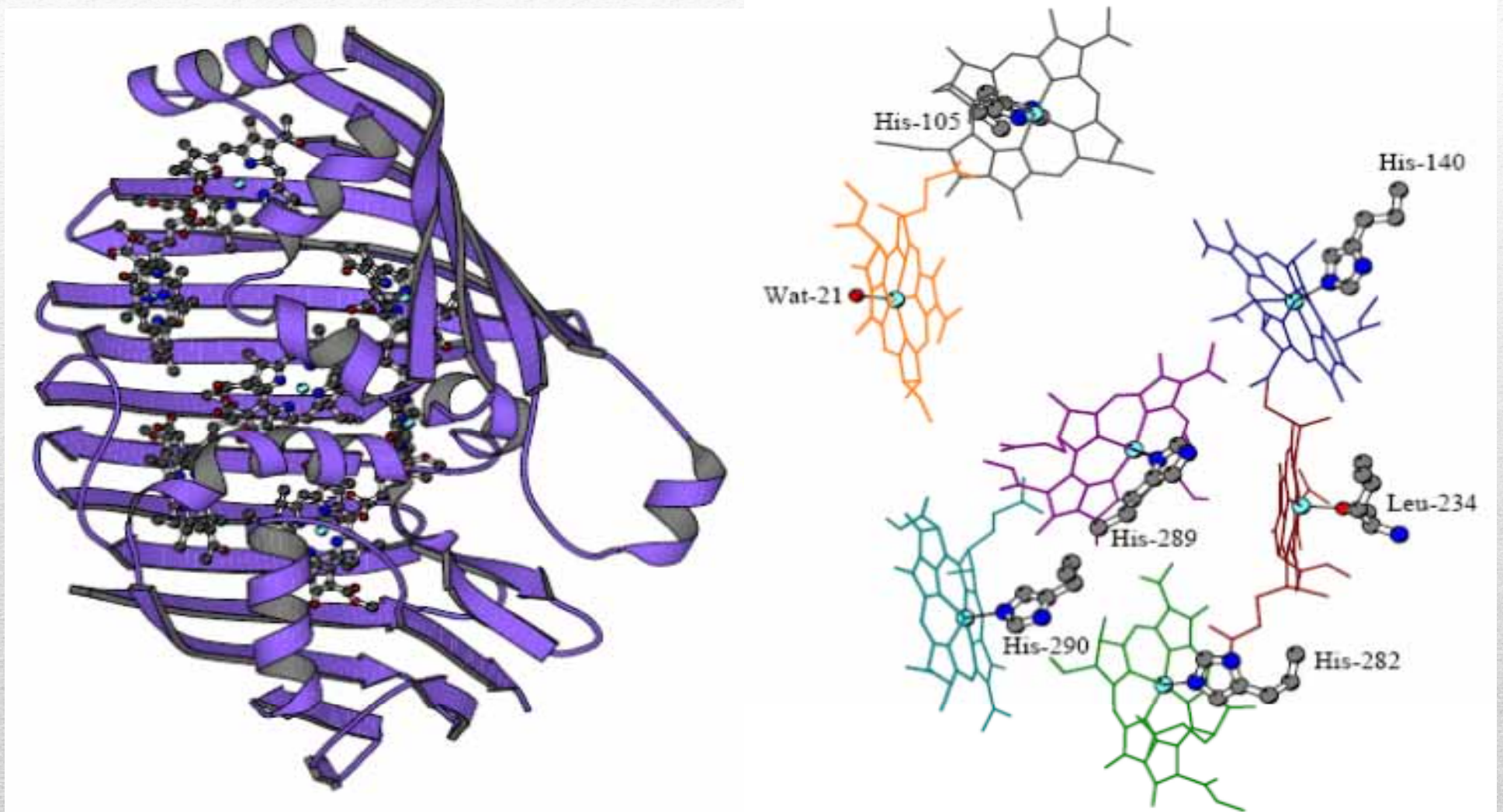
***G. Engel, et al. , Nature, 446, 782 (2007)***

# The Structure of FMO Complex

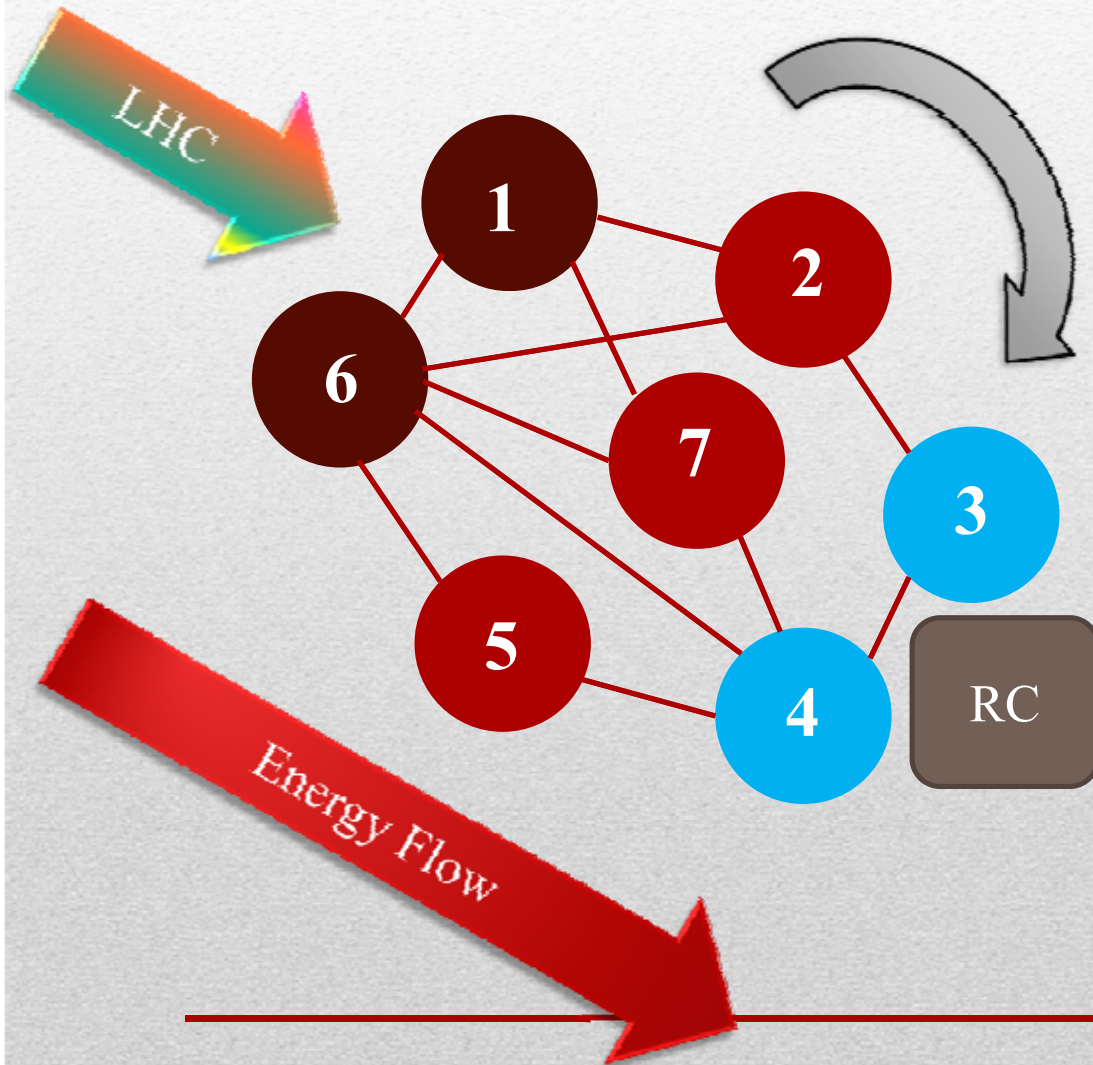


- FMO protein of green sulfur bacteria
- 3 monomers
- C3 symmetry
- Each monomer works independently
- 7 BChl molecules for each monomer

# Detailed Structure of Each Monomer



# The Organization of Each Monomer



- Site 1&6 combined with the LHC
- Site 3&4 combined with the RC
- Energy flows from site 1&6 to site 3&4

# Seeking a minimal model for this quantum system and its environment

- Must capture and give insights into essential physics.
  - Tells us which physical parameters lead to qualitative changes in quantum dynamics.
-



- Consider each site as a 2-level system

$$\mathcal{H}_S = \sum_{j=1}^N |j\rangle \varepsilon_j \langle j| + \sum_{j \neq k} (|j\rangle J_{jk} \langle k| + |k\rangle J_{kj} \langle j|)$$

- Hamiltonian for the environmental phonons

$$\mathcal{H}_B = \sum_{j=1}^N \mathcal{H}_B^j = \sum_{j=1}^N \sum_{\xi=1}^{N_{jB}} \frac{P_{j\xi}^2}{2m_{j\xi}} + \frac{1}{2} m_{j\xi} \omega_{j\xi}^2 x_{j\xi}^2$$

- The Hamiltonian of the system-environment coupling

$$\mathcal{H}_{SB} = \sum_{j=1}^N \mathcal{H}_{SB}^j = \sum_{j=1}^N |j\rangle \langle j| \cdot F_j \quad F_j = \sum_{\xi} c_{j\xi} \cdot x_{j\xi}$$

site 6  $\rightleftharpoons$  7  $\rightarrow$  3 and 4  
 6  $\rightleftharpoons$  5  $\rightarrow$  3 and 4

- Site 6 initially excited:

6  $\rightarrow$  3 and 4

12410	-87.7	5.5	-5.9	6.7	-13.7	-9.9
-87.7	12530	30.8	8.2	0.7	11.8	4.3
5.5	30.8	12210	-53.5	-2.2	-9.6	6.0
-5.9	8.2	-53.5	12320	70.7	-17	-63.3
6.7	0.7	-2.2	-70.7	12480	81.1	-1.3
-13.7	11.8	-9.6	-17	81.1	12630	39.7
-9.9	4.3	6.0	-63.3	-1.3	39.7	12440

# Several approaches for dealing with this complex Hamiltonian

- Redfield Equation
    - Assumption: the system-environment coupling is weak
  - Förster Theory
    - Assumption: the coupling within the system is weak compared to the system-environment coupling
  - Hierarchical Equation of Motion (HEOM) Approach
    - No previous assumptions
-

# Model Details

$$\rho(t) = \text{Tr}_B[\rho_{\text{tot}}(t)] = \text{Tr}_B[e^{-i\mathcal{H}t/\hbar} \rho_{\text{tot}}(0) e^{i\mathcal{H}t/\hbar}]$$

- Using the over damped Brownian oscillator model; replace the stick spectra with the Drude spectral density

$$J_j(\omega) = \sum_{\xi} \frac{c_{j\xi}^2 \cdot \hbar}{2m_{j\xi} \cdot \omega_{j\xi}} \delta(\omega - \omega_{j\xi}) \quad \Rightarrow \quad J(\omega) = \eta\gamma \frac{\omega}{\omega^2 + \gamma^2}$$

- The correlation function can be written as

$$C_j(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \cdot J_j(\omega) \cdot \frac{e^{-i\omega t}}{1 - e^{-\beta\hbar\omega}} \quad \Rightarrow \quad C_j(t > 0) = \sum_{k=0}^{\infty} c_k \cdot e^{-v_k t}$$

$$c_0 = \frac{\eta\gamma}{2} \left[ \cot\left(\frac{\beta\hbar\gamma}{2}\right) - i \right]$$

$$c_k = \frac{2\eta\gamma}{\beta\hbar} \cdot \frac{v_k}{v_k^2 - \gamma^2} \quad \text{for } k \geq 1$$

$$v_0 = \gamma$$

$$v_k = 2k\pi/\beta \quad \text{when } k \geq 1$$

# Excitation Dynamics of FMO Complex

$$\begin{aligned} \frac{d}{dt} \tilde{\rho}_{\mathbf{n}} = & - \left( i\mathcal{L}_S + \sum_{j=1}^N \sum_{k=0}^K n_{jk} v_k \right) \tilde{\rho}_{\mathbf{n}} - i \sum_{j=1}^N \sqrt{(n_{jk} + 1) |c_k|} \left[ \mathcal{V}_j, \sum_k \tilde{\rho}_{\mathbf{n}_{jk}^+} \right] \\ & - \sum_{j=1}^N \sum_{m=K+1}^{\infty} \frac{c_{jm}}{v_{jm}} \cdot [\mathcal{V}_j, [\mathcal{V}_j, \tilde{\rho}_{\mathbf{n}}]] - i \sum_{j=1}^N \sum_{k=0}^K \sqrt{n_{jk}/|c_k|} \left( c_k \mathcal{V}_j \tilde{\rho}_{\mathbf{n}_{jk}^-} - c_k^* \tilde{\rho}_{\mathbf{n}_{jk}^-} \mathcal{V}_j \right) \end{aligned}$$

$$\mathcal{V}_j = |j\rangle\langle j|$$

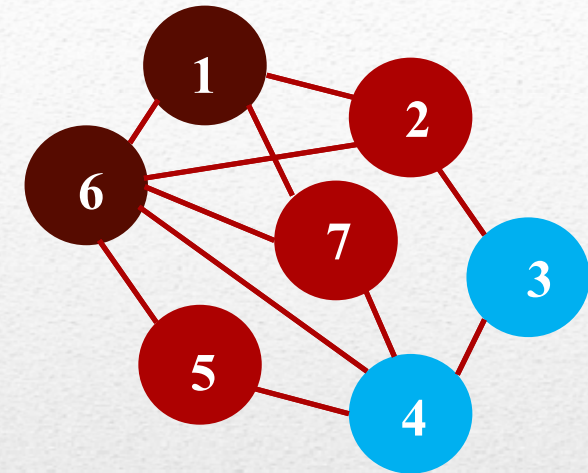
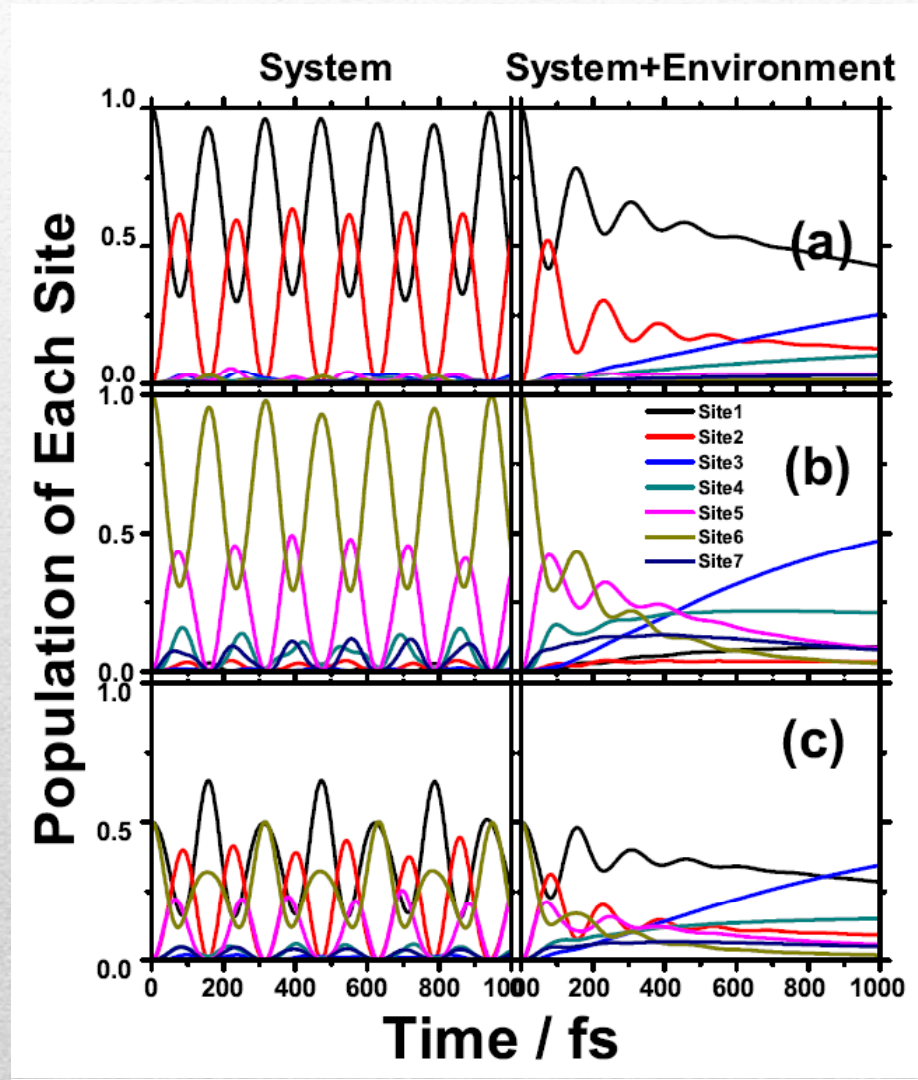
$$\mathcal{L}_S \bullet = \frac{1}{\hbar} [\mathcal{H}_S, \bullet]$$

$$\mathbf{n} \equiv \{n_1, n_2, \dots, n_N\} = \{\{n_{10}, n_{11}, \dots\} \dots \{n_{N0}, n_{N1}, \dots\}\}$$

$\mathbf{n}_{jk}^{\pm}$  refers to change the number  $n_{jk}$  to  $n_{jk} \pm 1$  in the whole index  $\mathbf{n}$

- $\rho_0 = \{\{0,0,\dots\}, \dots \{0,0,\dots\}\}$  is system reduced density operator (RDO)
- All others are considered as auxiliary density operators (ADOs)
- The truncation level
  - The truncation level of the correlation function is K
  - The cut-off level of ADOs is at  $\mathcal{N}_c$
  - In our simulation: K=0 and  $\mathcal{N}_c$

# Excitation Population During Transfer in FMO



- The coherence oscillation is due to the system rather than the environment
- The oscillation time scale is around 650fs, which is consistent with the experimental observation

# Entanglement

- Method to calculate the pairwise concurrence in FMO complex on the single excitation basis sets

$$C_{ij}(t) = 2 |\rho_{ij}(t)|, \text{ where } \rho_{ij}(t) \text{ is the density matrix.}$$

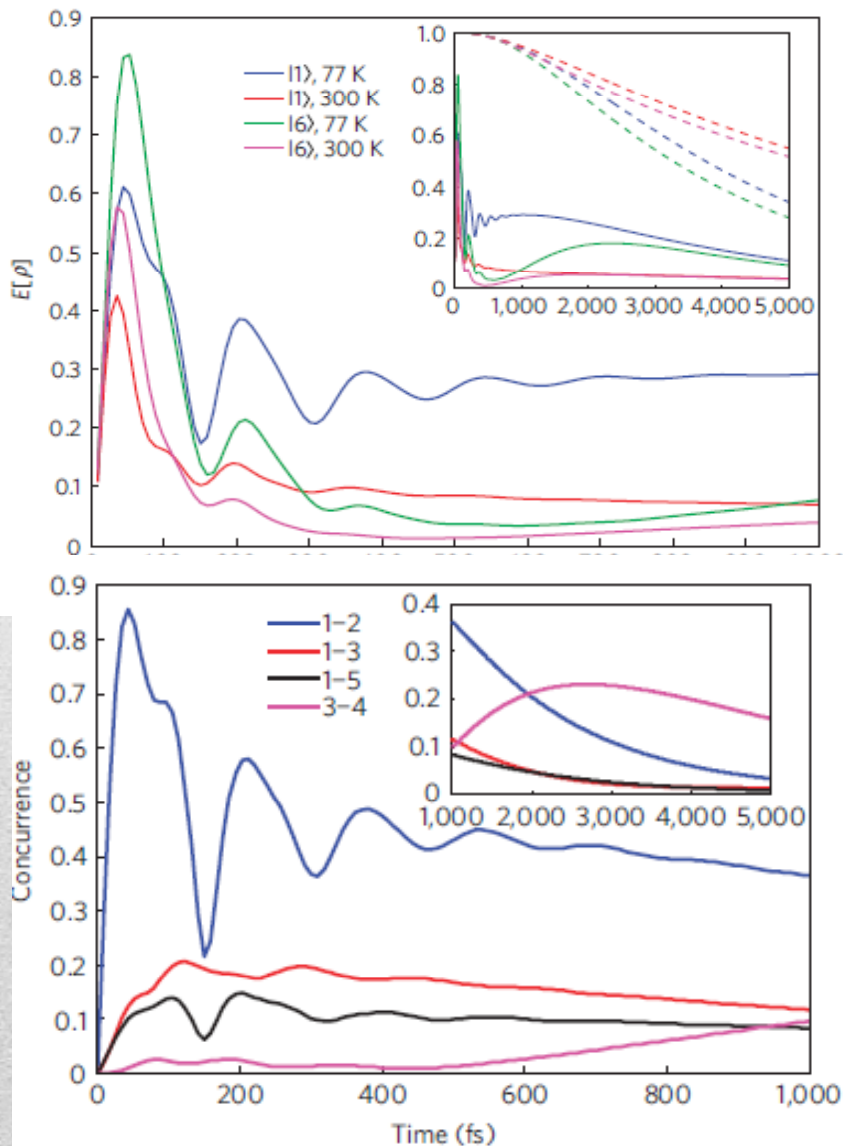
Global entanglement:

$$E_T[\rho] = - \sum_{i=1}^N \rho_{ii} \cdot \ln(\rho_{ii}) - S(\rho)$$

$S(\rho) = -\text{Tr} \rho \ln(\rho)$  is the Von Neumann entropy of state  $\rho$

---

# Pairwise Entanglement Evolution in FMO Complex



- The total entanglement and the concurrence of pair sites at 77K when site 1 is initially excited
- The coherence oscillation also exists in the entanglement evolution
- They concluded that the entanglement in FMO complex can exist at long-range and multipartite even at room temperature.



# Multipartite Entanglement

## Meyer-Wallach measure

$$Q_{MW}(|\psi\rangle) = \frac{2}{n} \sum_{i=1}^{n_q} [1 - \text{Tr}(\rho_i^2)] \quad \rho = |\psi\rangle\langle\psi|$$

$\rho_i$  is the reduced density matrix of the  $i^{\text{th}}$  qubit

## Monotone

$$\eta_S = \frac{2^{|S|}}{2^{|S|} - 1} (1 - \text{Tr}(\rho_S^2)) \quad S \text{ is a set of } k \text{ qubits} \quad |S| = k$$

$\rho_S$  is the reduced density matrix over those  $k$  qubits.

## Monogamy of entanglement

Among three qubits ABC, if A&B are maximally entangled, then C can not entangled with A&B

$$\tau_{A|B} + \tau_{A|C} \leq \tau_{A|BC}$$

$\tau_{A|B}$  is measuring the entanglement of qubit A and B

---

# Cayley map and Lie Groups

- Convex roof extension of entanglement monotones

$$E(\rho) \equiv \inf_{\mathfrak{N}} \left[ \sum_i p_i \eta(|\psi_i\rangle) \right]$$

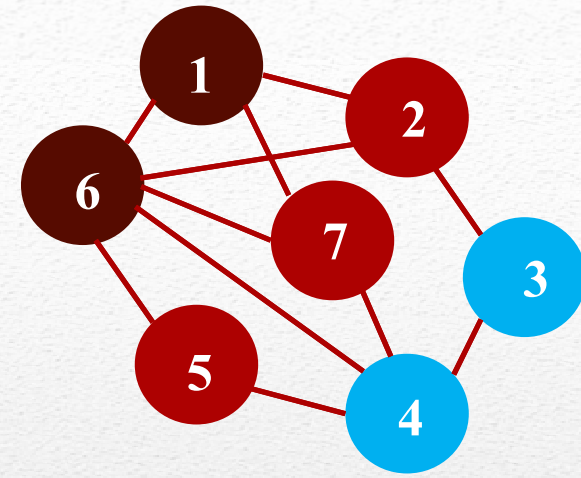
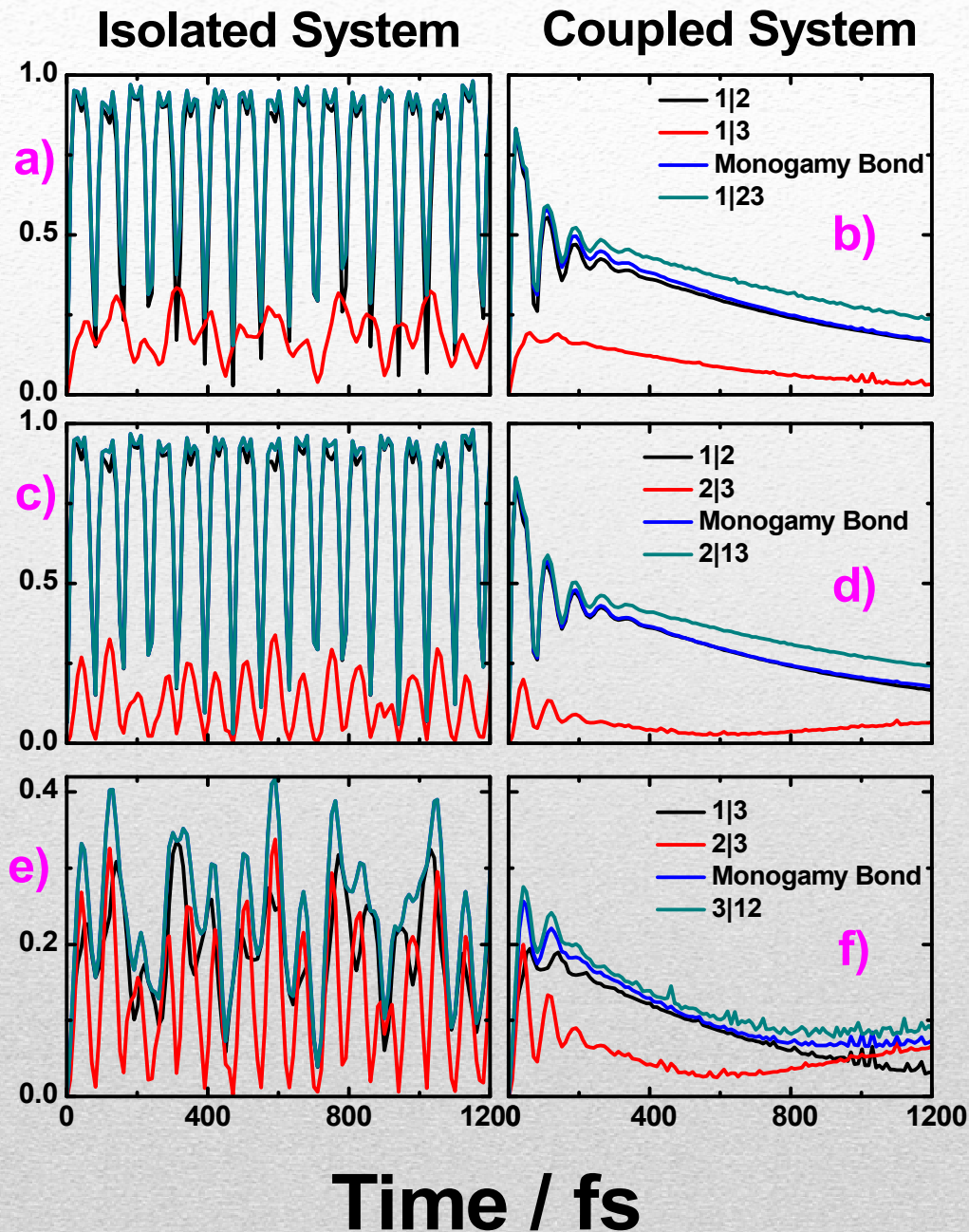
$$\mathfrak{N} \equiv \left\{ p_i, |\psi_i\rangle : \sum_i p_i |\psi_i\rangle \langle \psi_i| = \rho \right\}$$

$$\rho = V \Lambda V^\dagger \quad \rho = \sum_i \lambda_i |v_i\rangle \langle v_i| \quad \tilde{\Phi} \equiv V \Lambda^{1/2}, \text{ so that } \tilde{\Phi} \tilde{\Phi}^\dagger = \rho$$

$$\tilde{\Psi} = \tilde{\Phi} U \text{ for some unitary matrix } U, \text{ then } \tilde{\Psi} \tilde{\Psi}^\dagger = \rho.$$

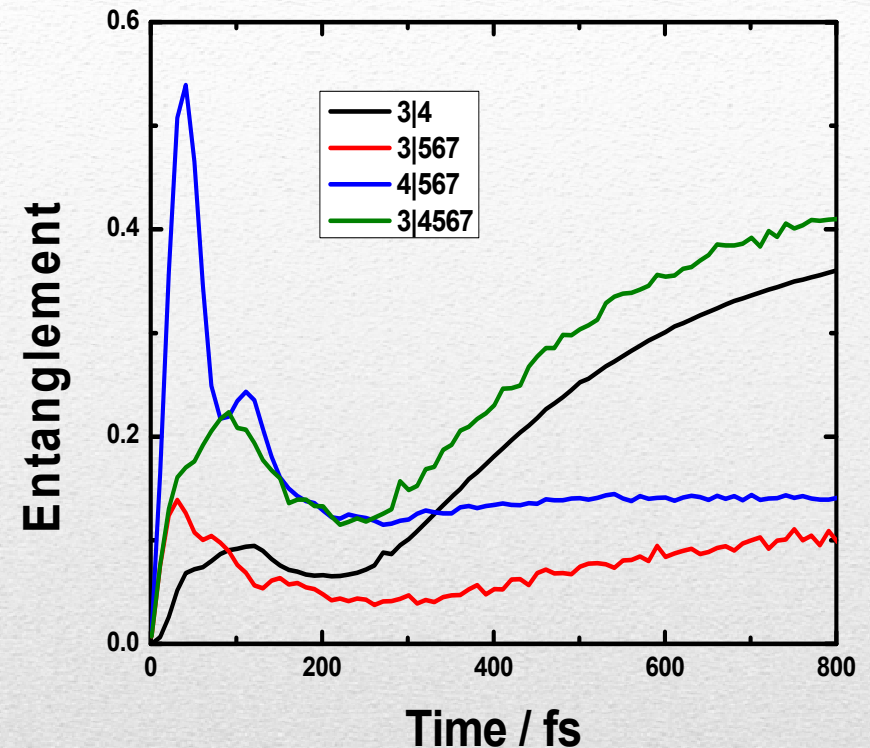
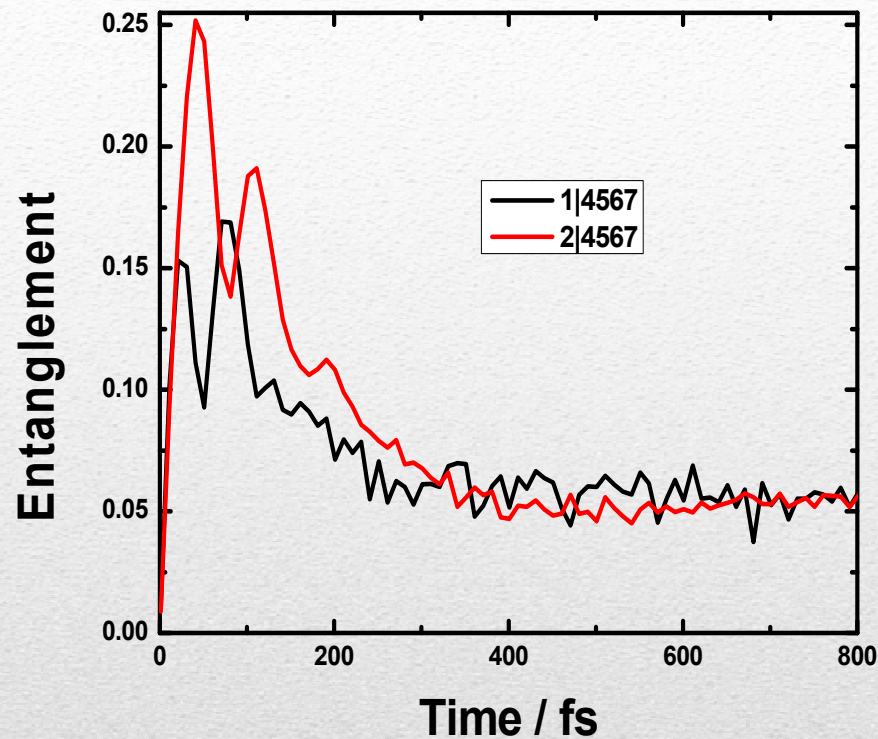
Employ the Cayley map to obtain the unitary  $U$  which minimize the  $E(\rho)$

# Entanglement



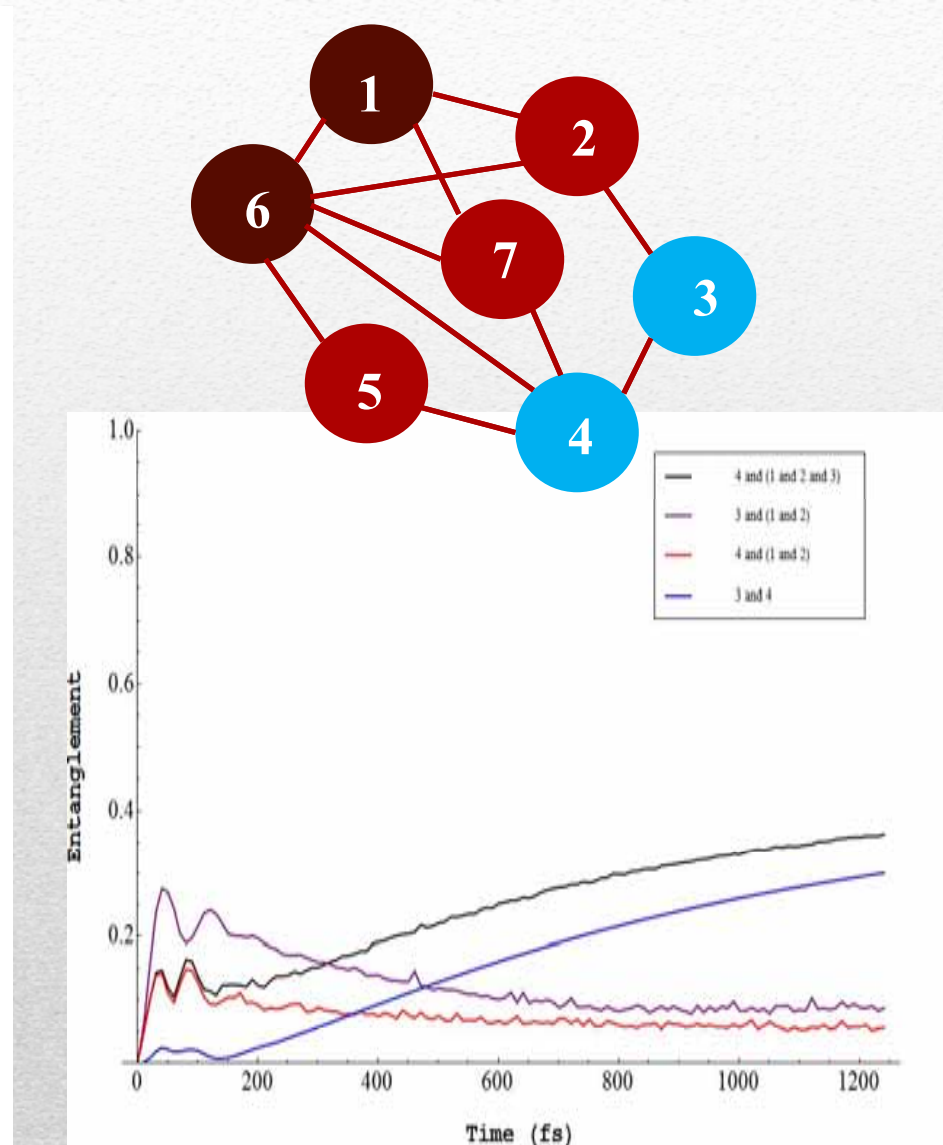
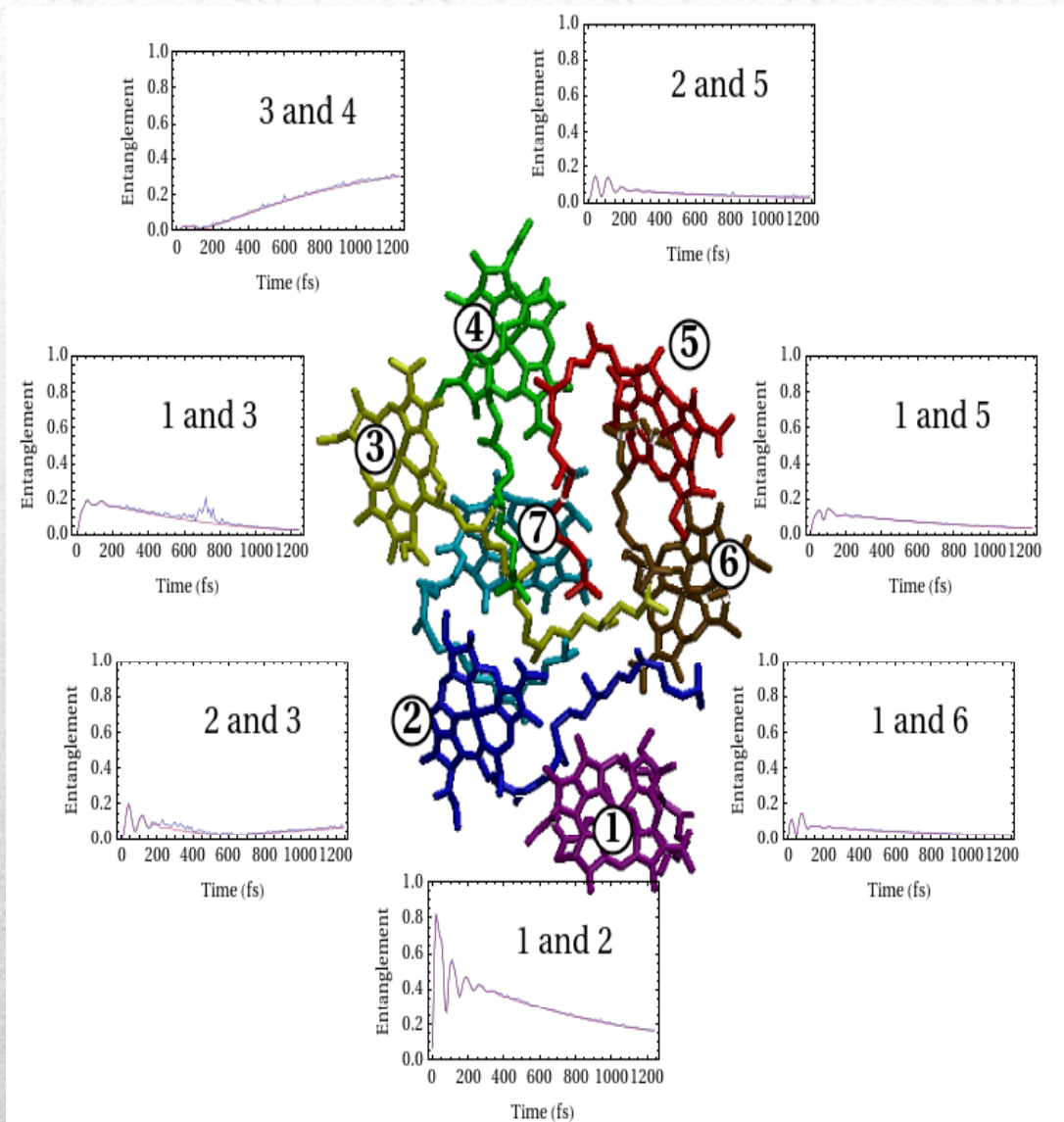
- Entanglement evolution of site 1, 2&3; Site 1 initially excited; T=77K
- 1|23 larger than monogamy bound
- 1|2 is the domain pair
- 2|3 has coherence oscillation

# Entanglement evolution for the site 6 initially excited at T=77K



- Left panel: entanglement evolution off the pathway; smaller compared with that involved in the pathway
- Right panel: entanglement evolution related to site 3&4; pair 3|4 becomes the most significant pair at the end

# Entanglement for FMO



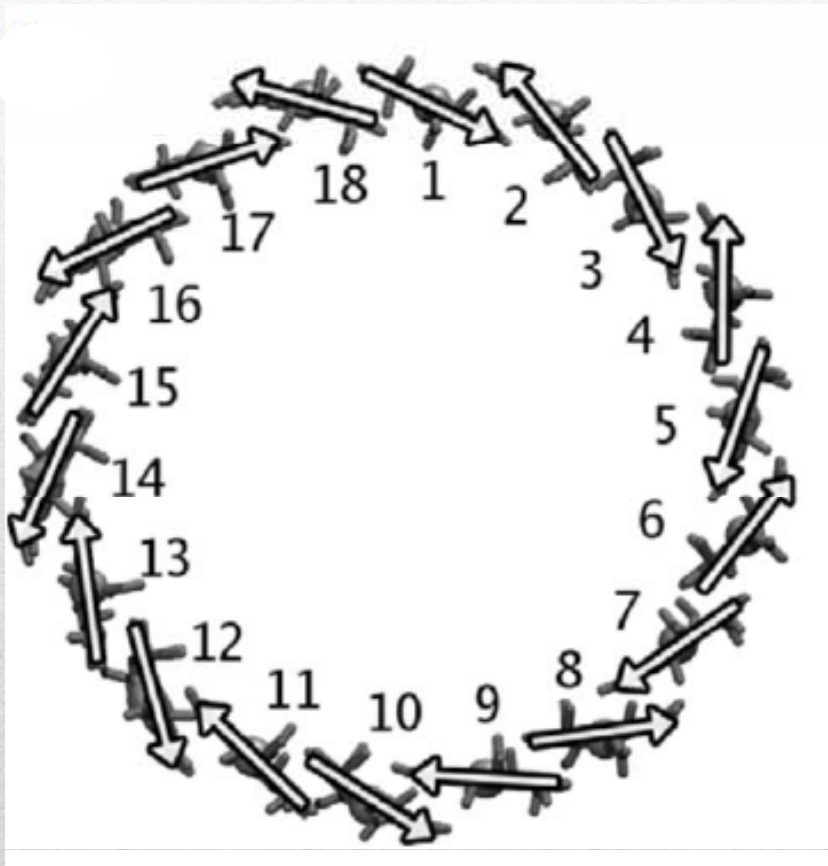
Multipartite Entanglement is Max along the excitation transfer pathway

# Population and Entanglement Dynamics in Light Harvesting Complex 2 LH2

LH2 consists of two structural units  
(named after the positions of their absorption peak)  
called **B800** with **9** bacteriochlorophylls (BChls)  
and **B850** with **18** BChls.

---

# Hamiltonian of LH2



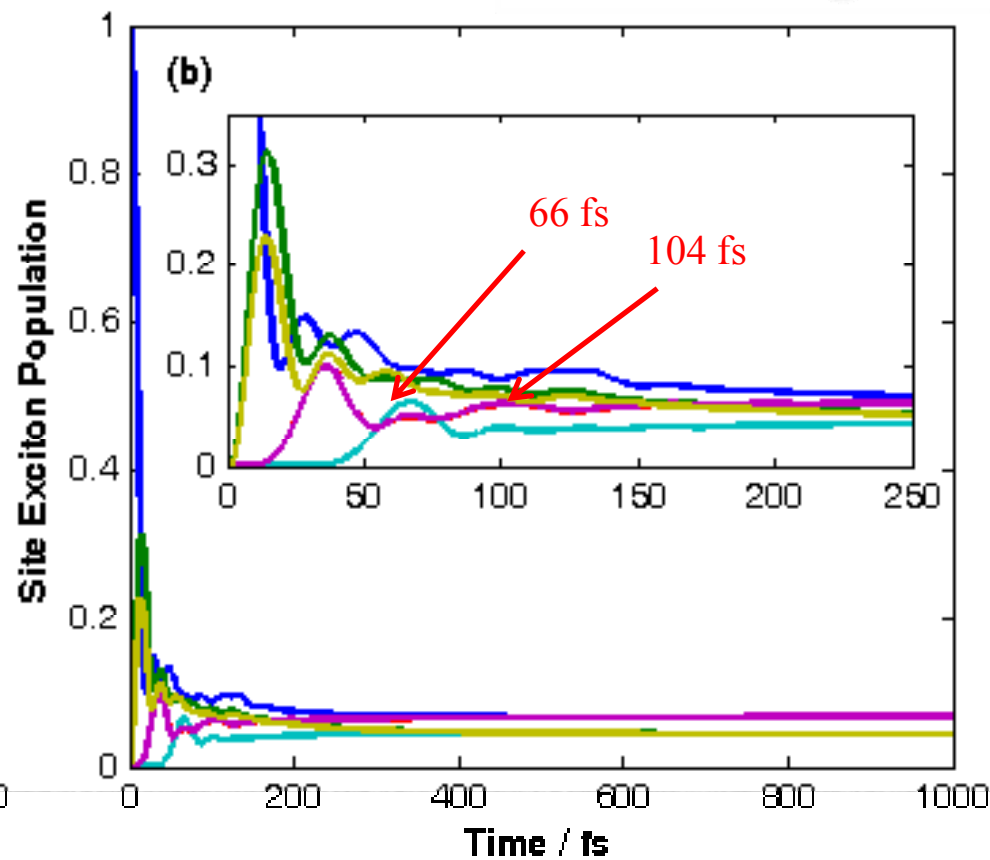
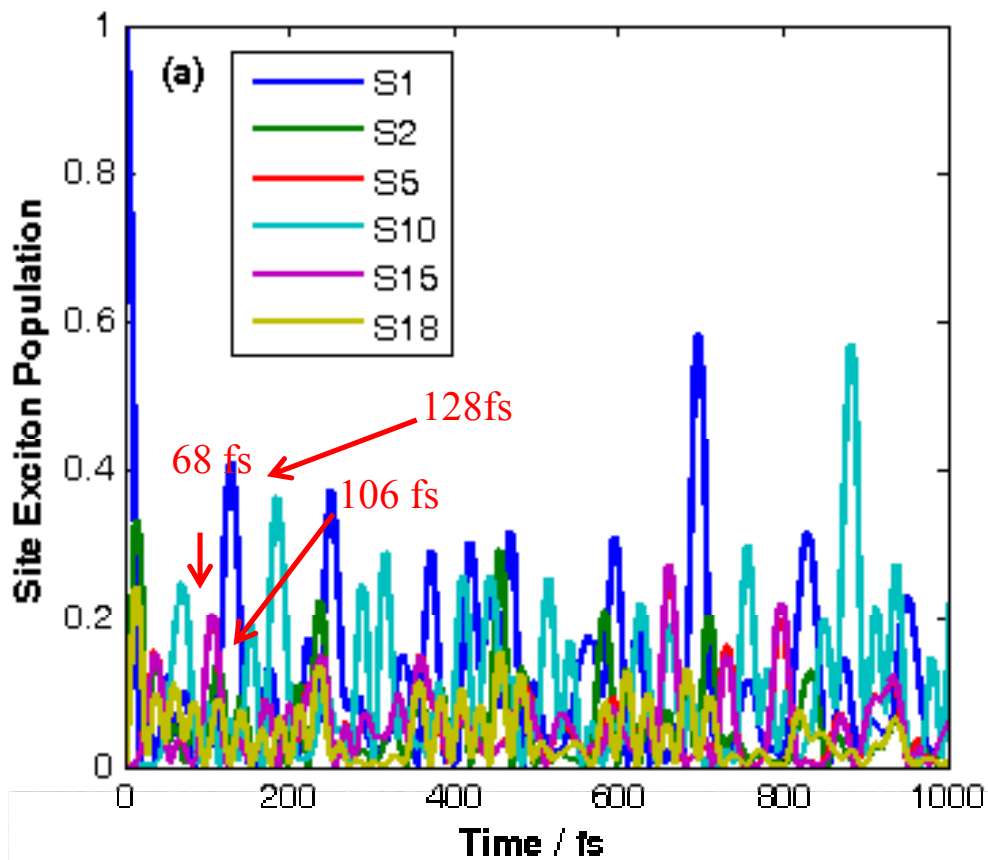
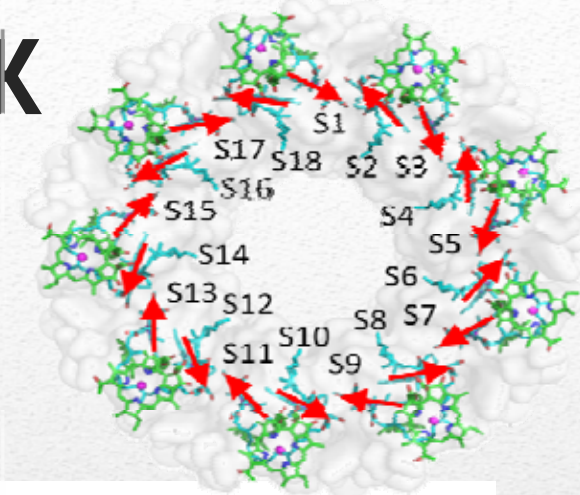
$$H_S = \sum_{i=1}^N E_i |i\rangle\langle i| + \sum_{i=1}^N \sum_{j=1}^N V_{ij} |i\rangle\langle j|$$

$$V_{ij} = C \frac{\mathbf{d}_i \cdot \mathbf{d}_j - 3(\mathbf{d}_i \cdot \mathbf{r}_{ij})(\mathbf{d}_j \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^3}$$

$E_i \sim$  site energy

$V_{ij} \sim$  induced dipole- induced dipole interaction

# Site Exciton Population at T = 300K





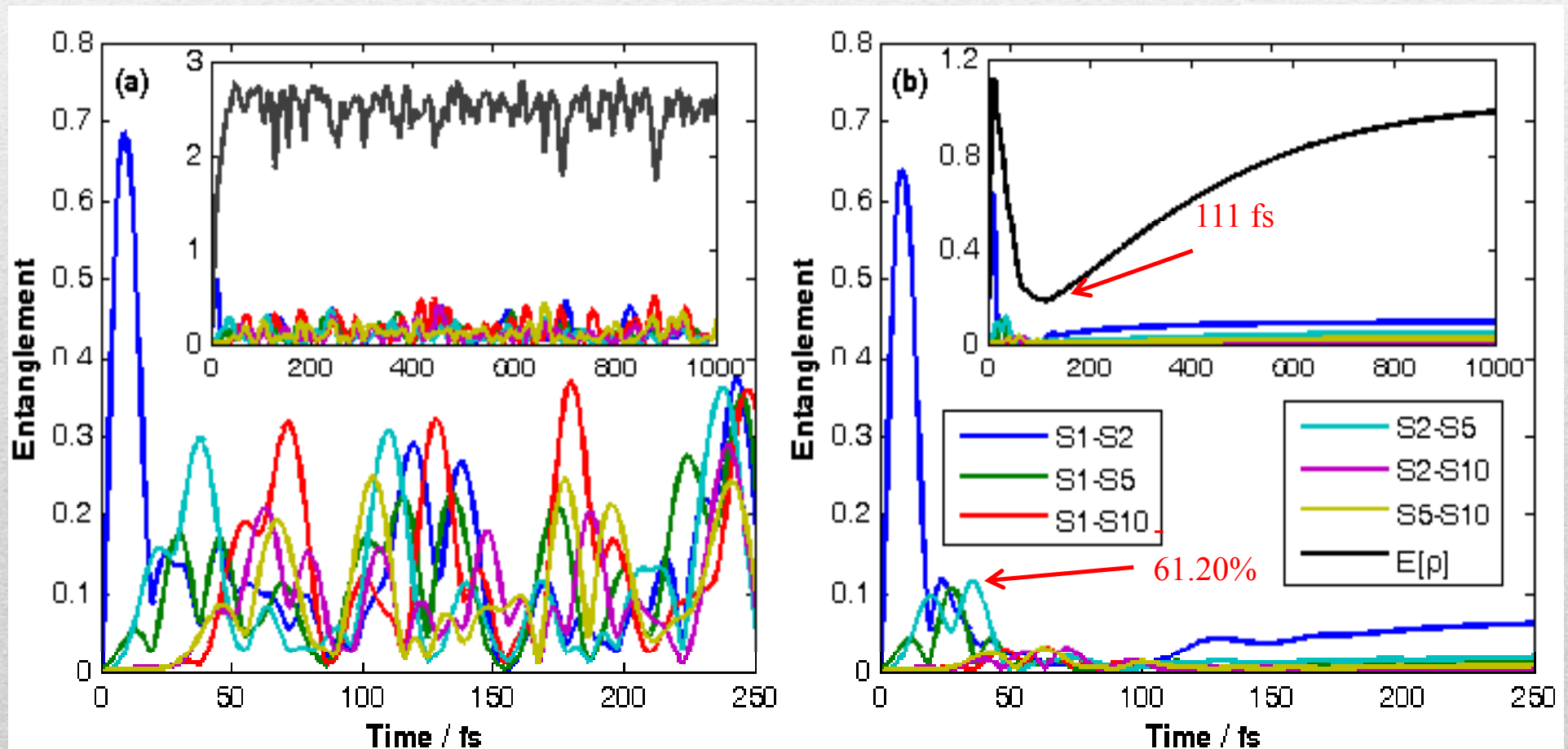
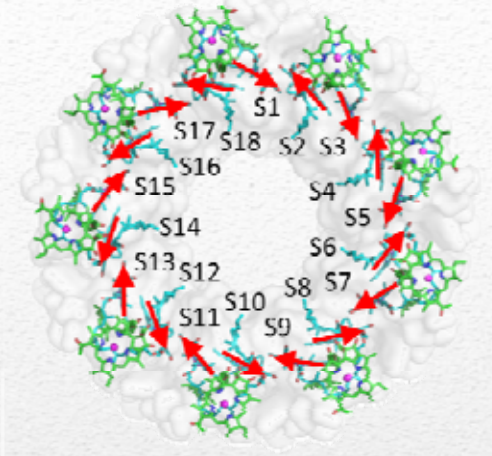
# Entanglement Dynamics at T = 300K

► Global entanglement:

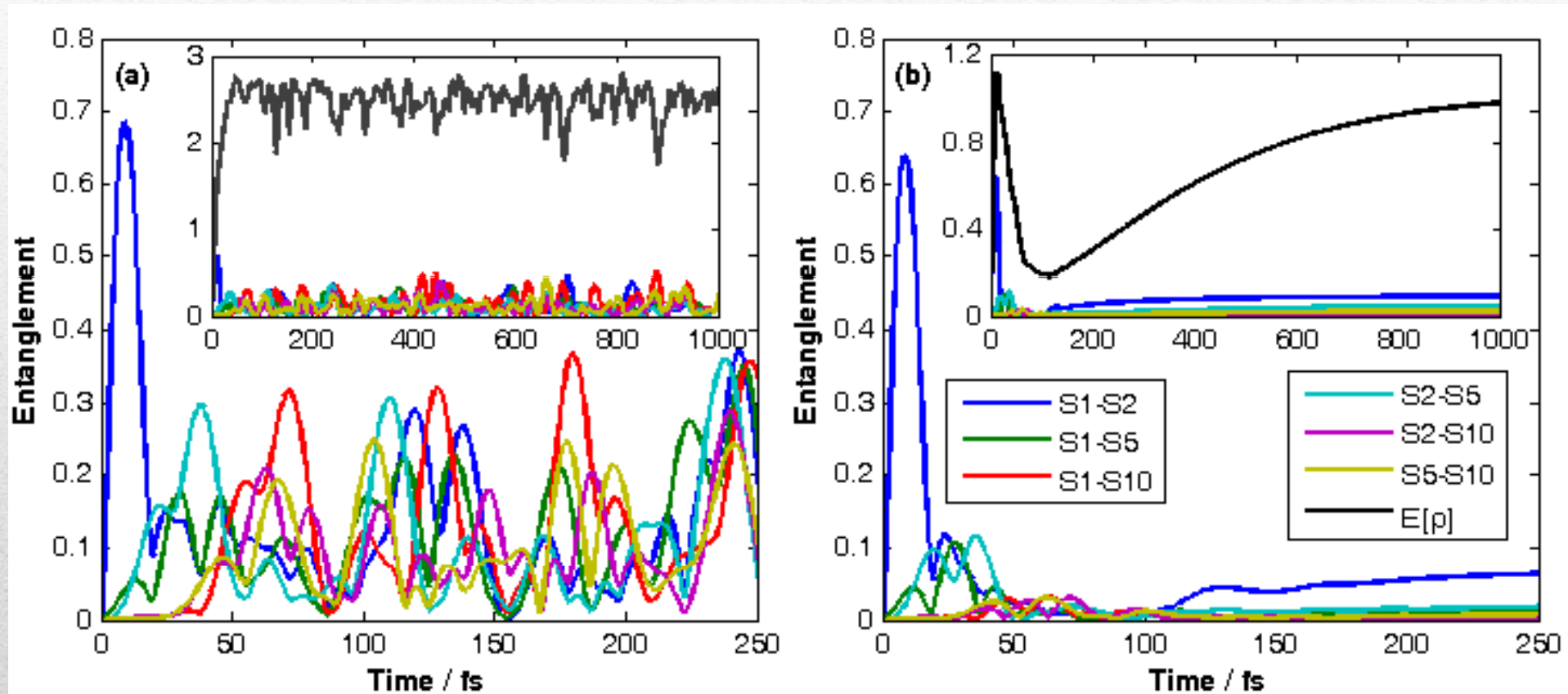
$$E[\rho] = -\sum_{i=1}^N \rho_{ii} \ln \rho_{ii} - S(\rho)$$

► 2-sites entanglement (concurrency):

$$C_{ij} = 2|\rho_{ij}|$$

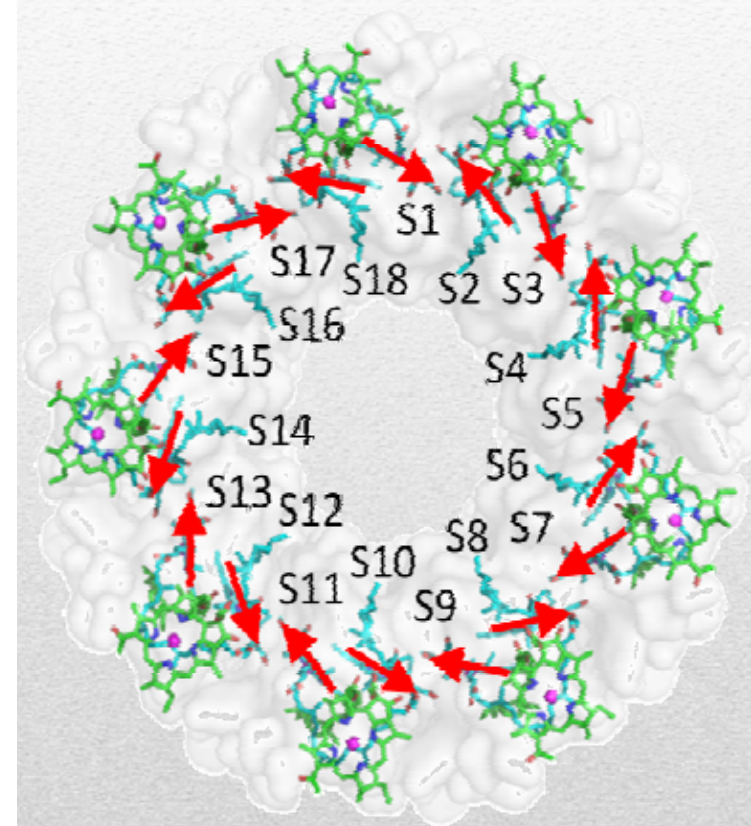
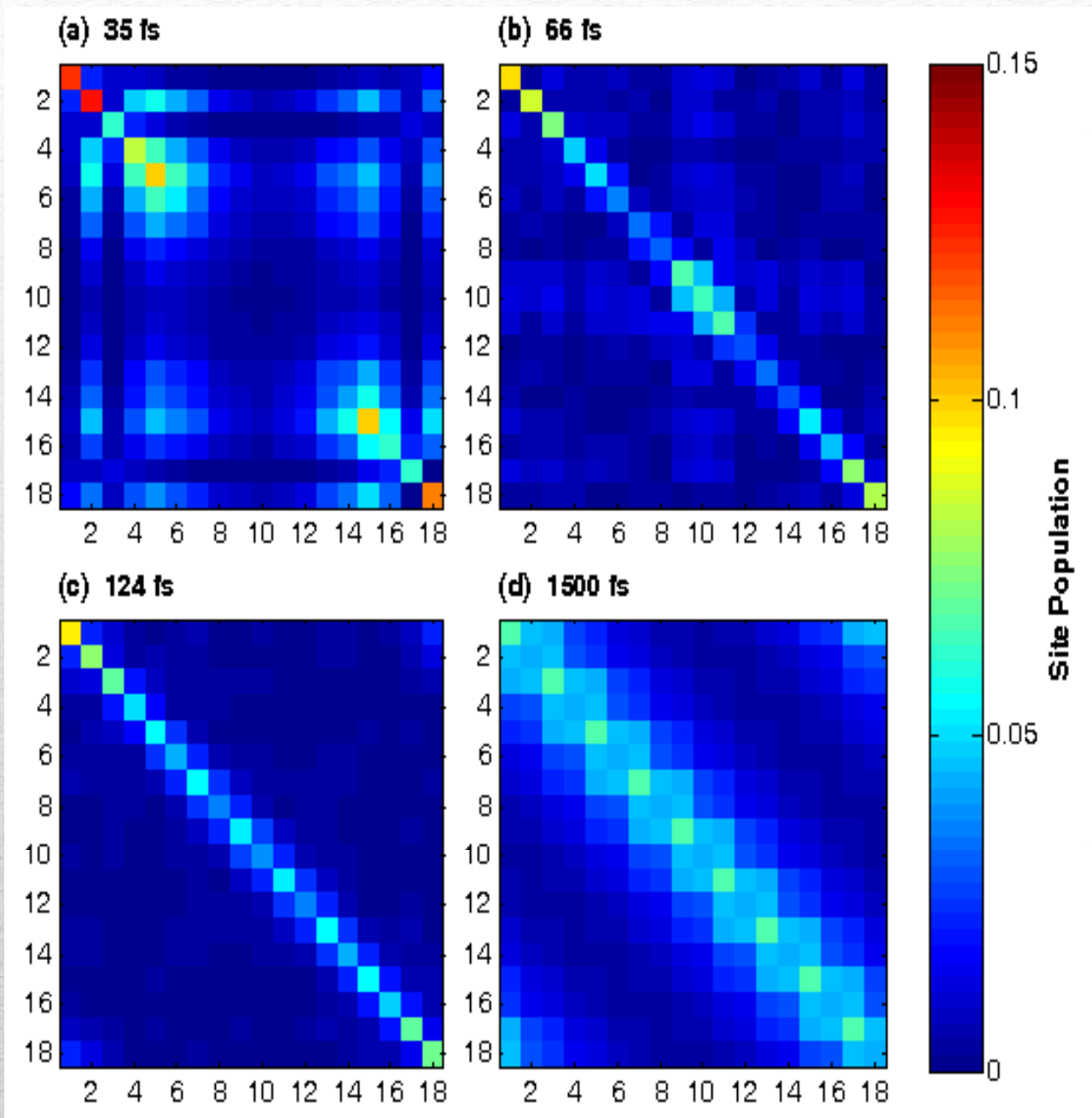


# Entanglement Dynamics of LH2

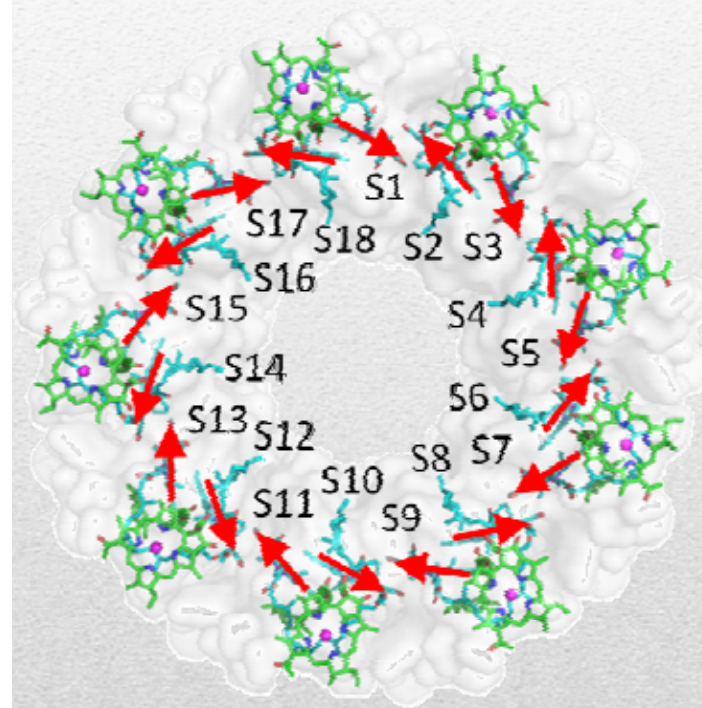
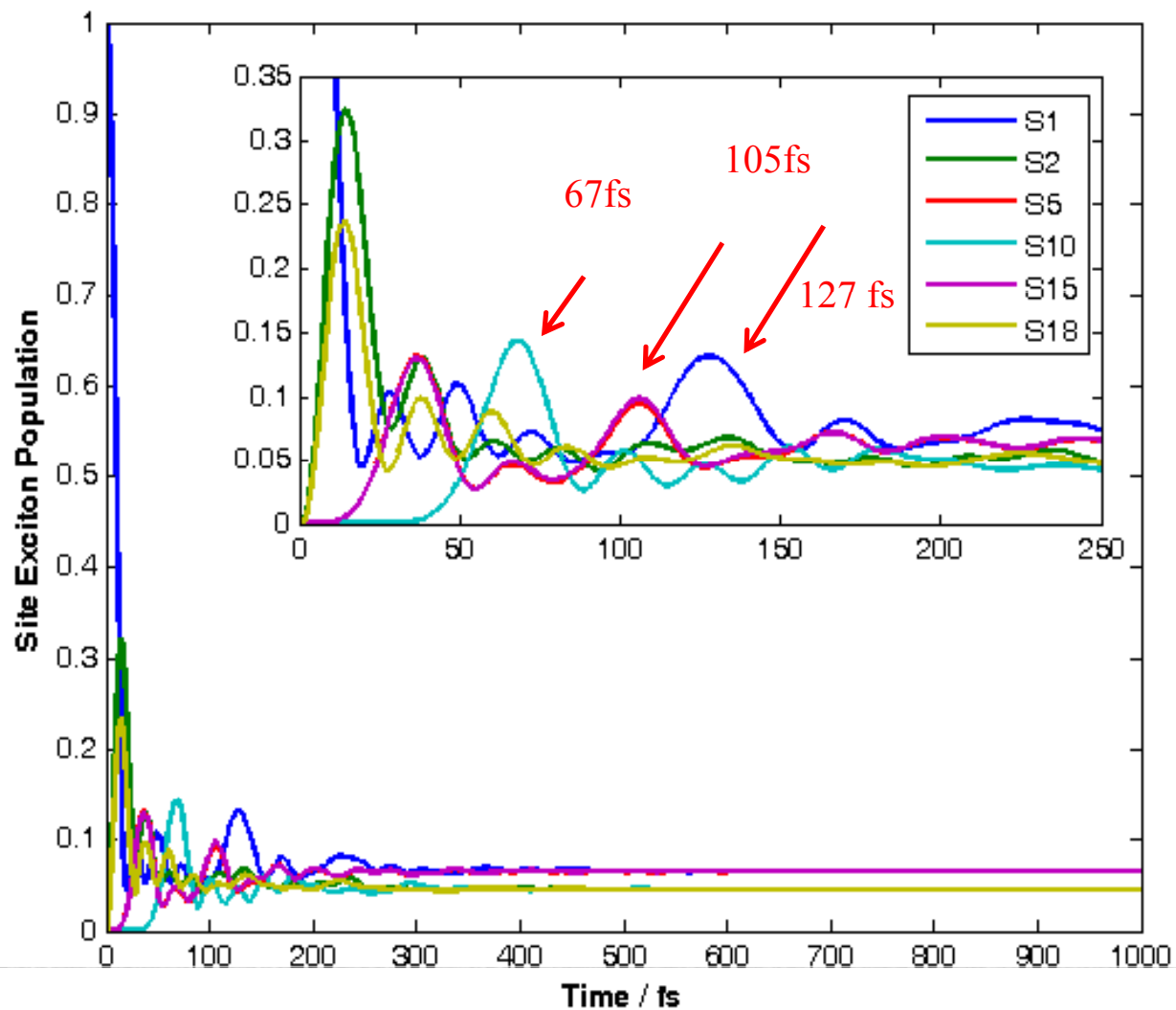


$$E[\rho] = - \sum_i \rho_{ii} \ln \rho_{ii} - S(\rho_{ii})$$

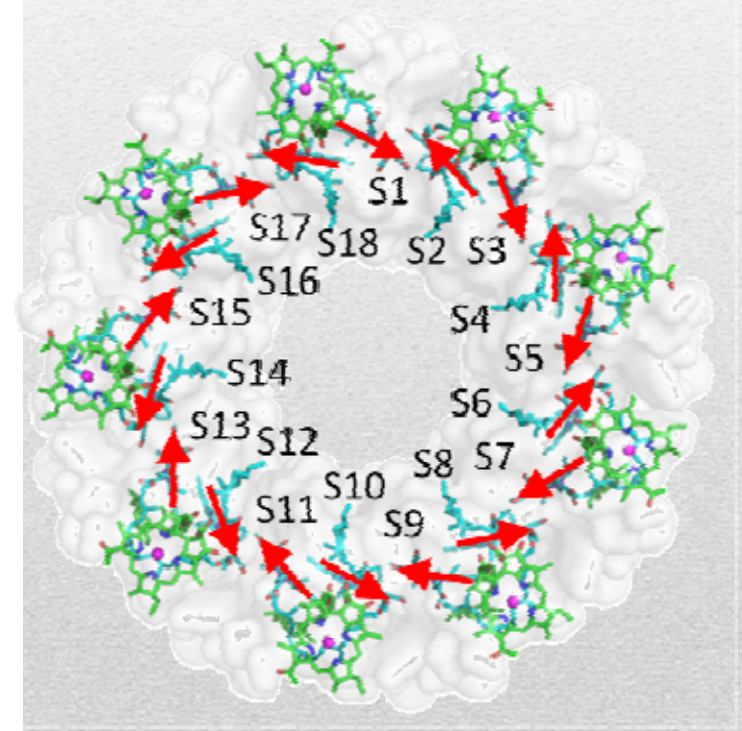
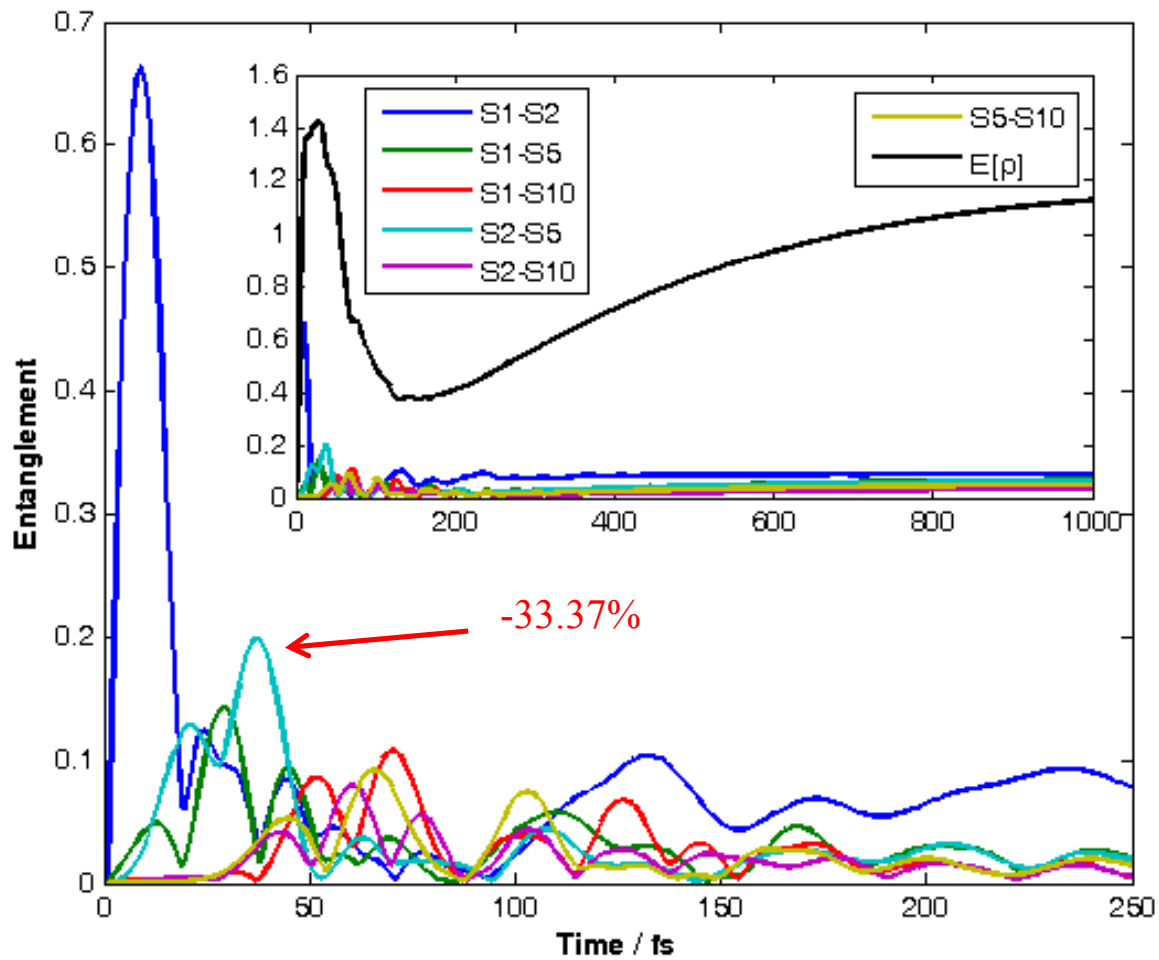
# Time Evolution of Density Matrix at T = 300K



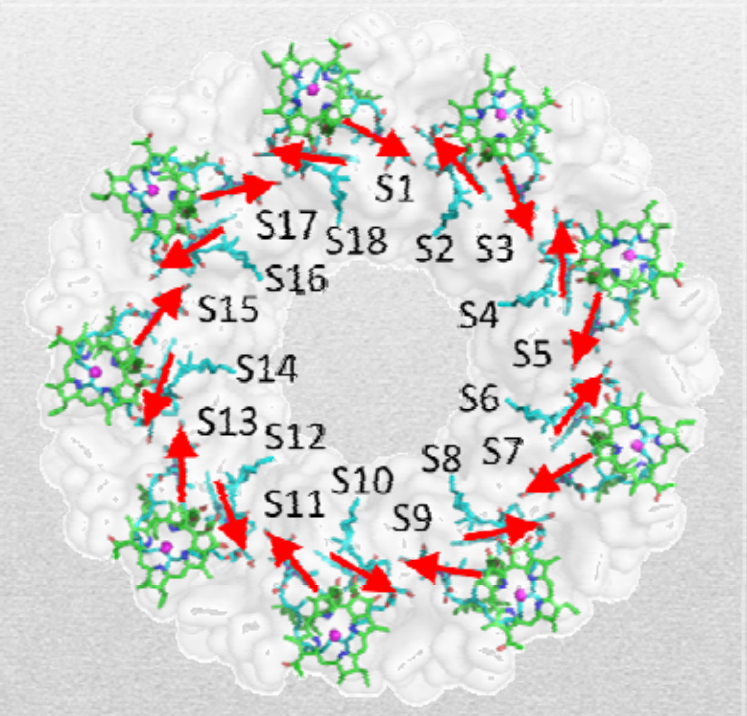
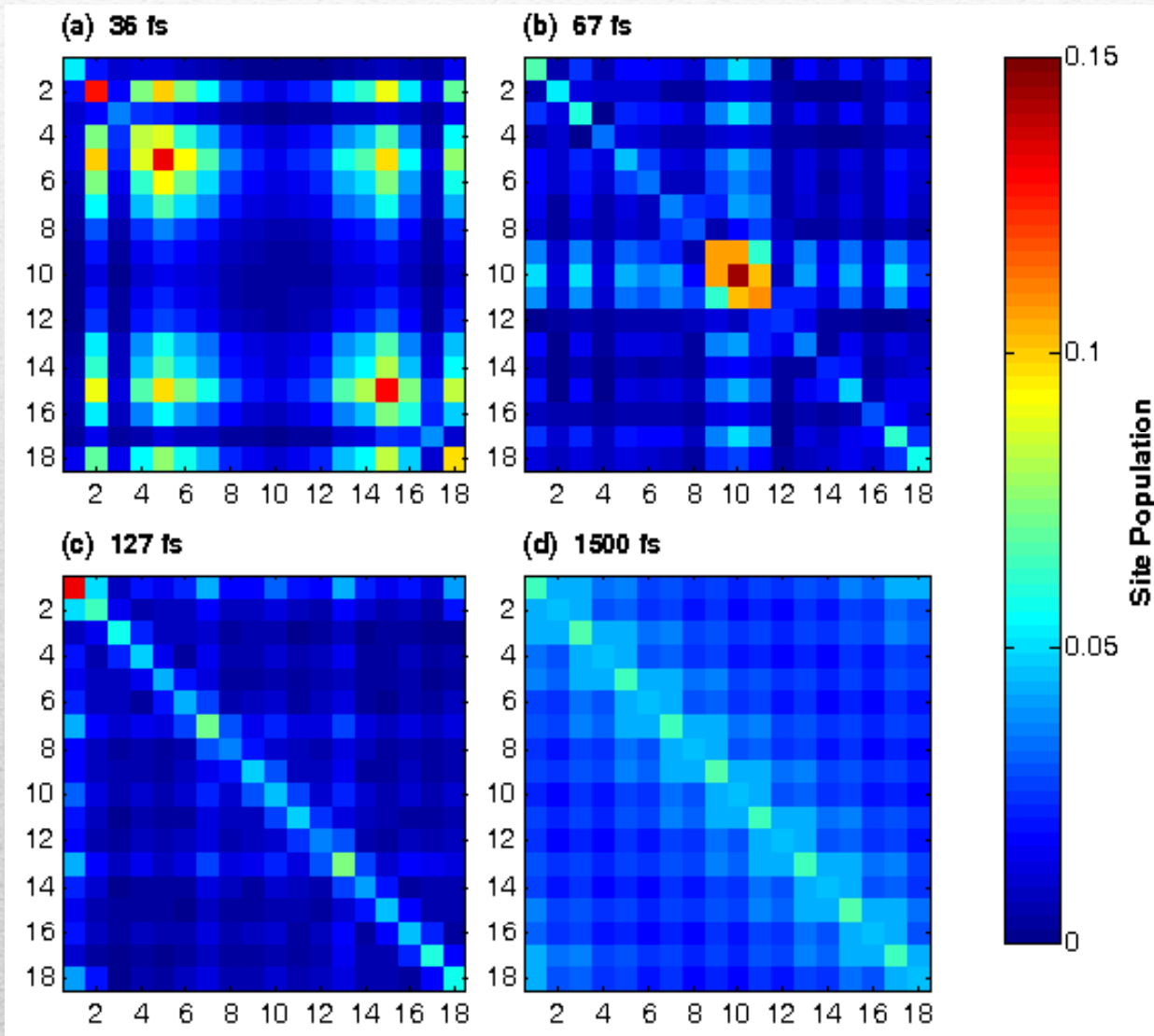
# Site Exciton Population at T = 77K



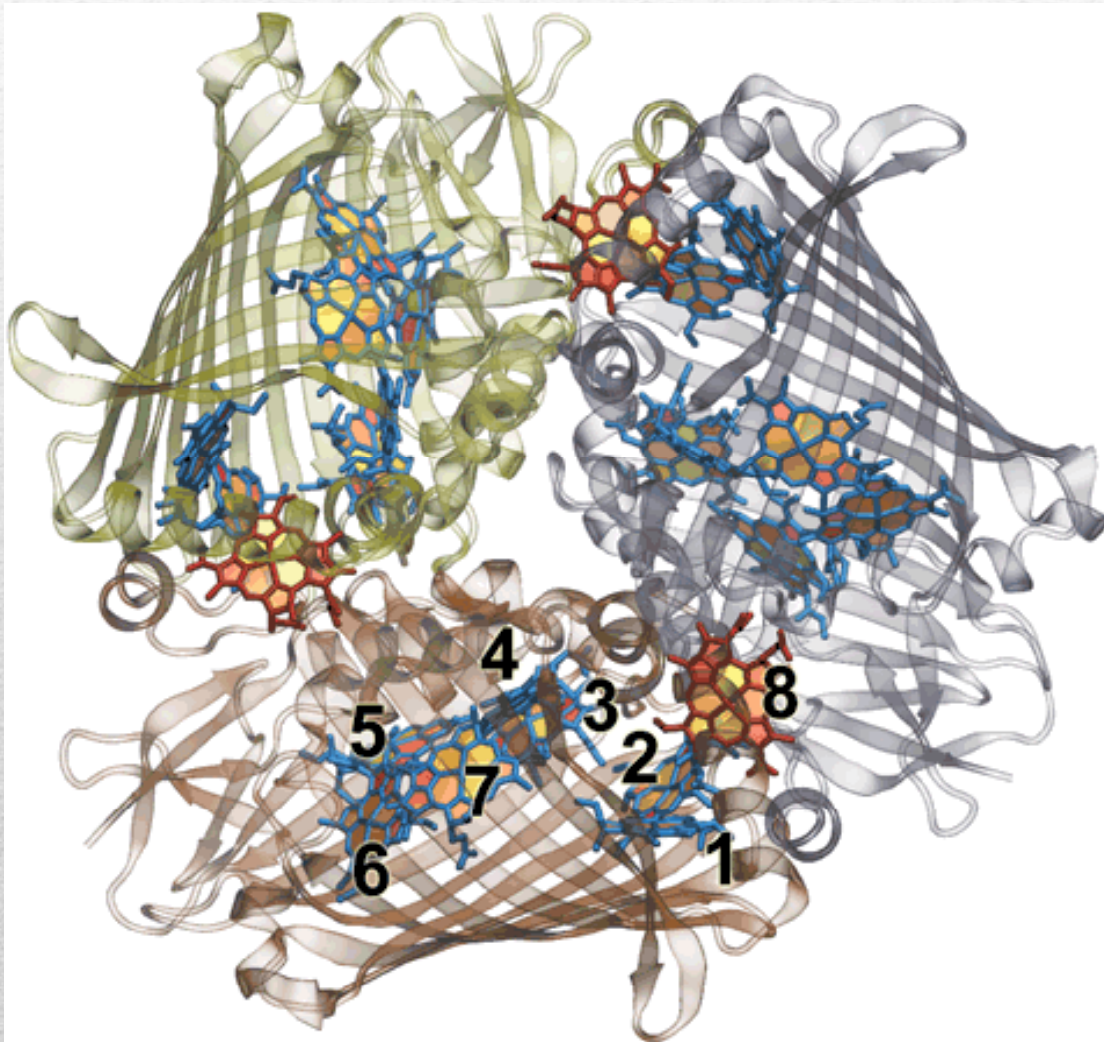
# Entanglement Dynamics at T = 77K



# Time Evolution of Density Matrix at T = 77K



# New Structure of FMO Complex



- FMO protein of green sulfur bacteria
- One additional 8<sup>th</sup> BChl between each monomer
- The 8<sup>th</sup> BChl is close to the 1<sup>st</sup> BChl

# System Hamiltonian

$$H = \sum_n^N \epsilon_n |n\rangle \langle n| + \sum_{n \neq m}^N V_{nm} |n\rangle \langle m|$$

BChl	present work	
	<i>apo</i>	<i>holo</i>
1	12490	12505
2	12445	12425
3	12205	12195
4	12380	12375
5	12570	12600
6	12535	12515
7	12495	12465
8		12700
$\epsilon_{\text{eff}}$	3.0	3.0
$E_0/\text{cm}^{-1}$	12570	12570

	2	3	4	5	6	7	8
1	94.8	5.5	-5.9	7.1	-15.1	-12.2	39.5
2		29.8	7.6	1.6	13.1	5.7	7.9
3			-58.9	-1.2	-9.3	3.4	1.4
4				-64.1	-17.4	-62.3	-1.6
5					89.5	-4.6	4.4
6						35.1	-9.1
7							-11.1

*M. Schmidt am Busch, F. Müh, M. E. Madjet, and T. Renger, J. Phys. Chem. Lett. 2, 93 (2011).*

*J. Moix, J. Wu, P. Huo, D. Coker and J. Cao, arXiv:1109.3416v1*



# Quantum Mechanism for Magnetoreception in Birds

The recent discovery that quantum coherence plays a central role in excitonic transport in photosynthesis invites us to explore other places in biological systems where quantum coherence is important.

- Understand the role of quantum coherence and entanglement in the biological compass system.
  - Explore the potential role of a quantum phase transition in the local nuclear environment.
-

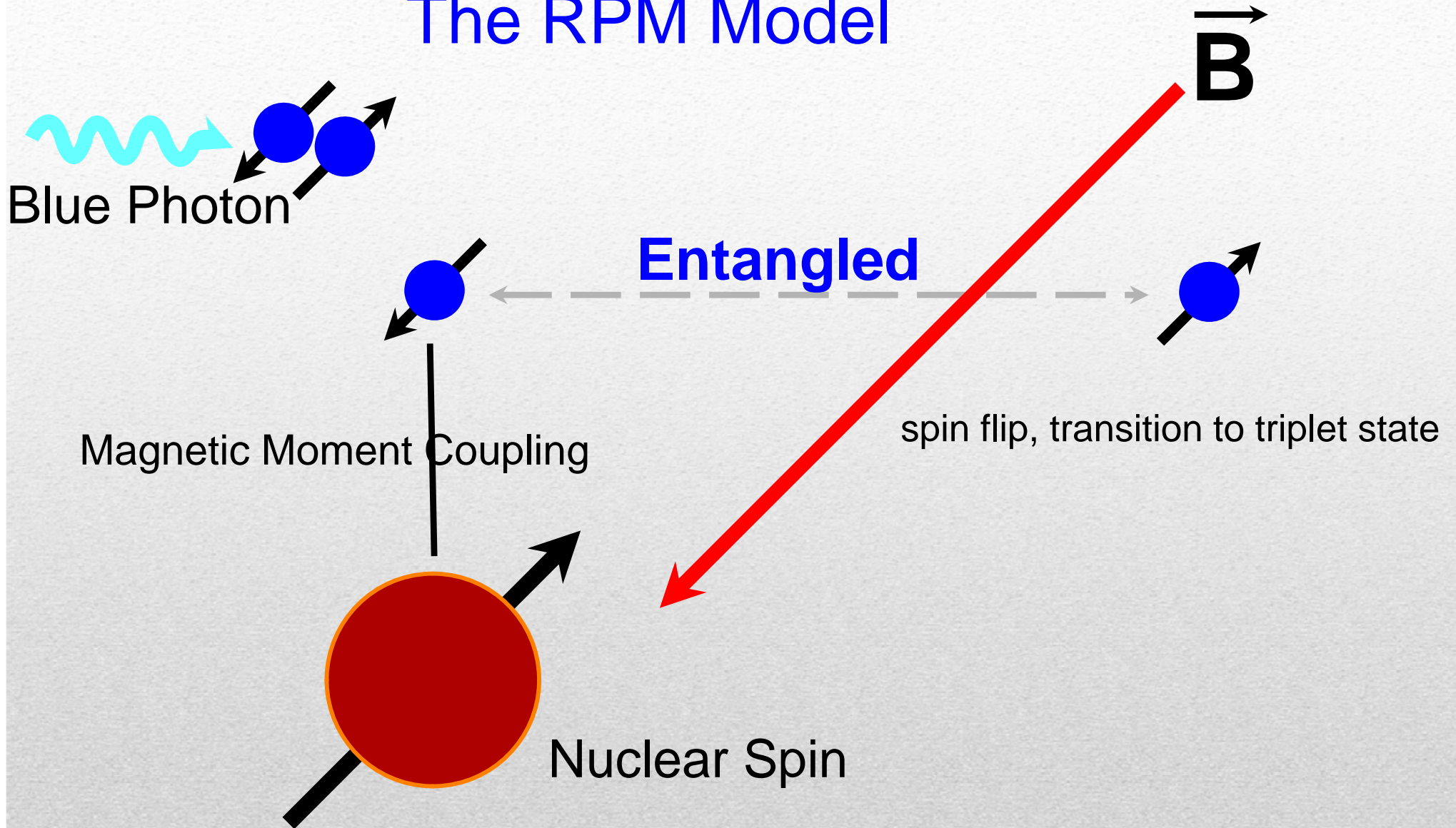
# Radical Pair Mechanism



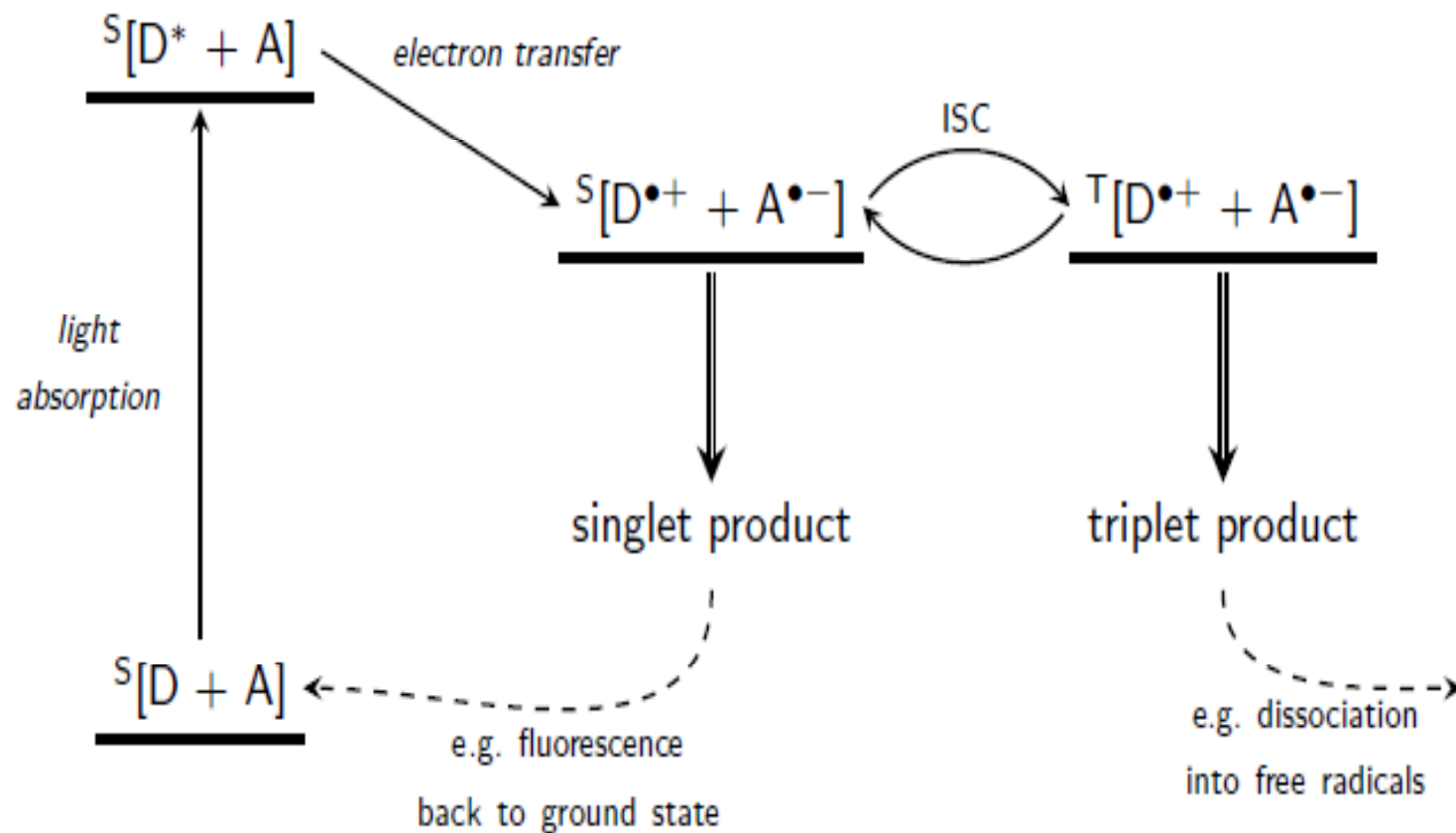
James Abraham "Abe" Pauls  
Undergraduate Student from Goshen College  
NSF REU Program

$$H = I^z \cdot A \cdot R(\theta, B) \cdot \sigma_1^z + \gamma \cdot B \cdot \begin{pmatrix} z & z \\ \sigma_1 & \sigma_2 \end{pmatrix}$$

# The RPM Model

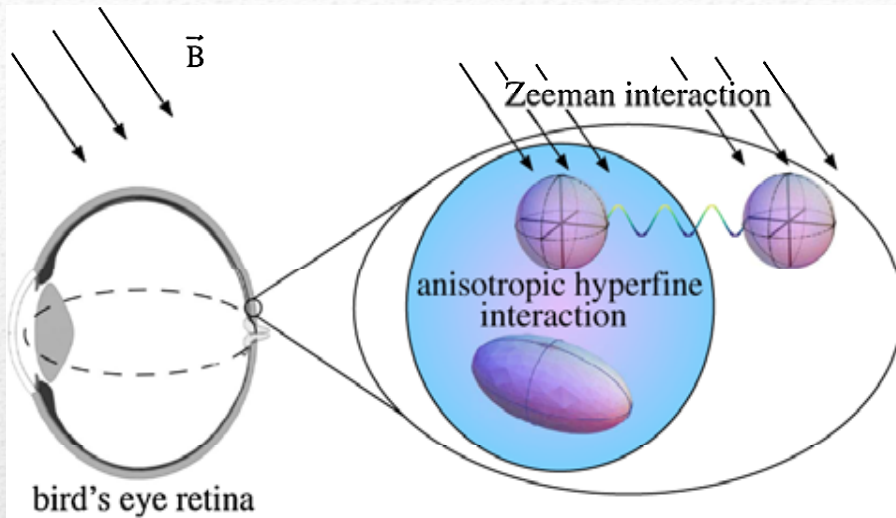


**Singlet and triplet states will have different reaction products**

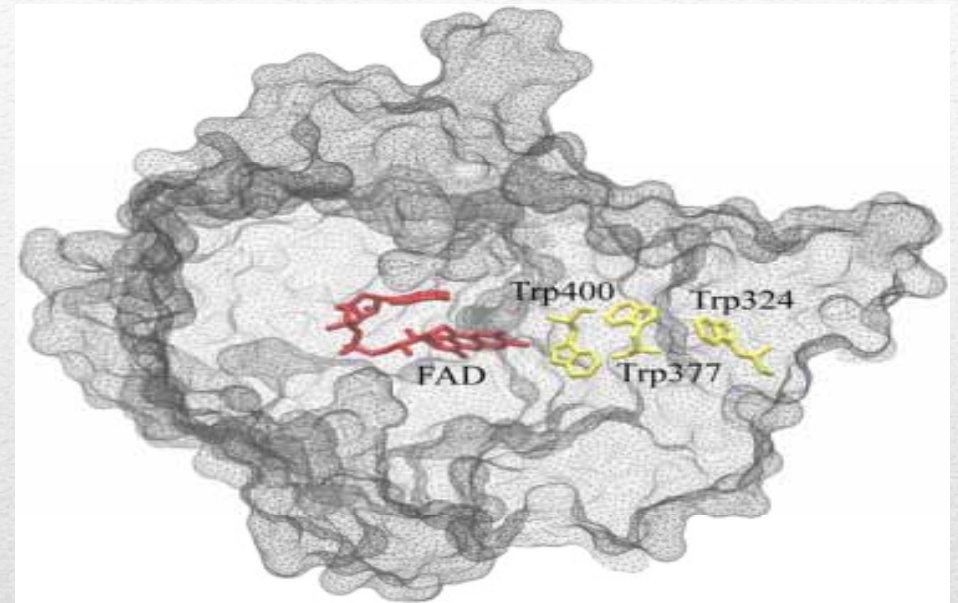


Scheme of the radical pair mechanism. Donor (D) and acceptor (A) molecules form correlated spin radical pair after a light-induced electron transfer. Due to magnetic fields the spin character of the radical spins is interconverted between singlet and triplet states, the so-called inter-system crossing (ISC).

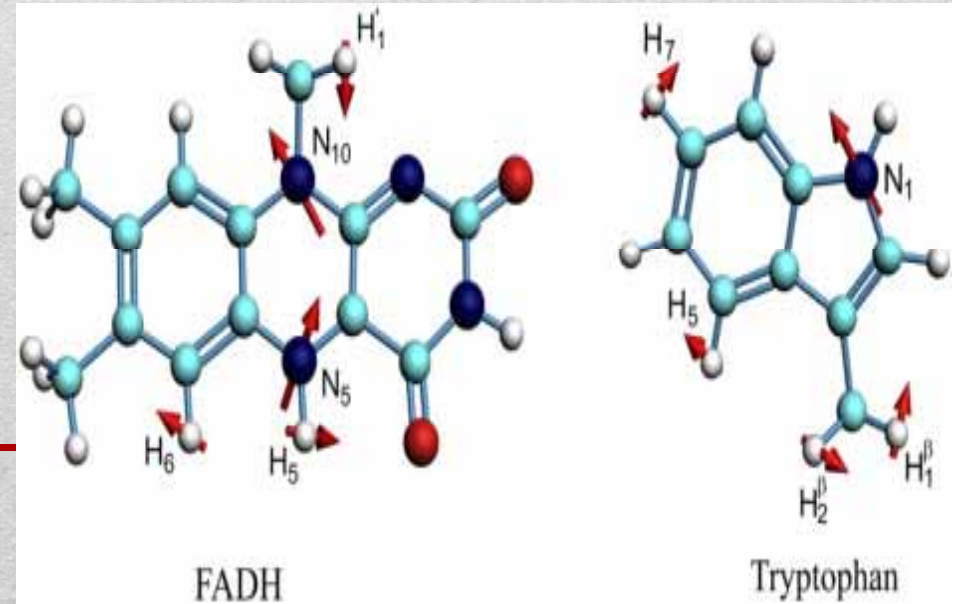
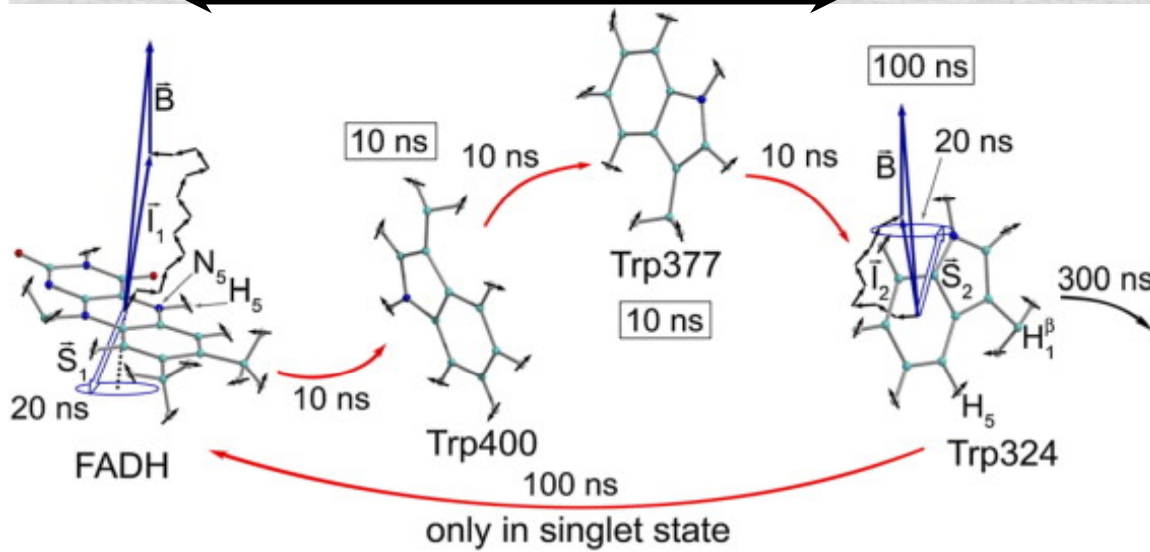
# Excitation and Electron Hole Transfer



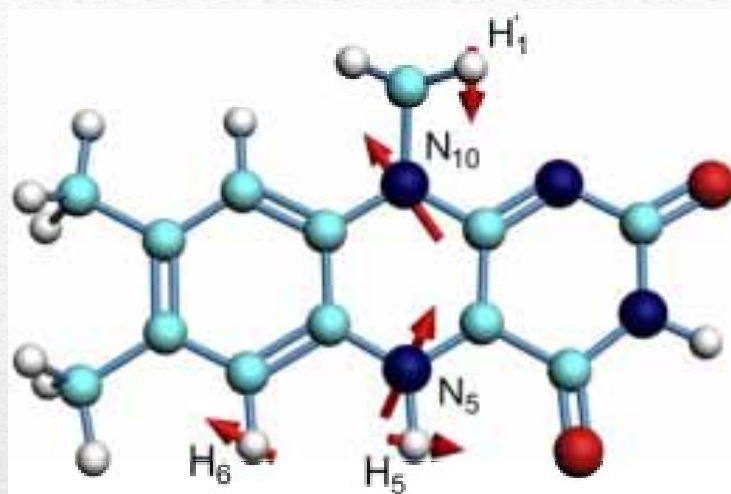
Cryptochrome Molecule



13.3 Angstroms



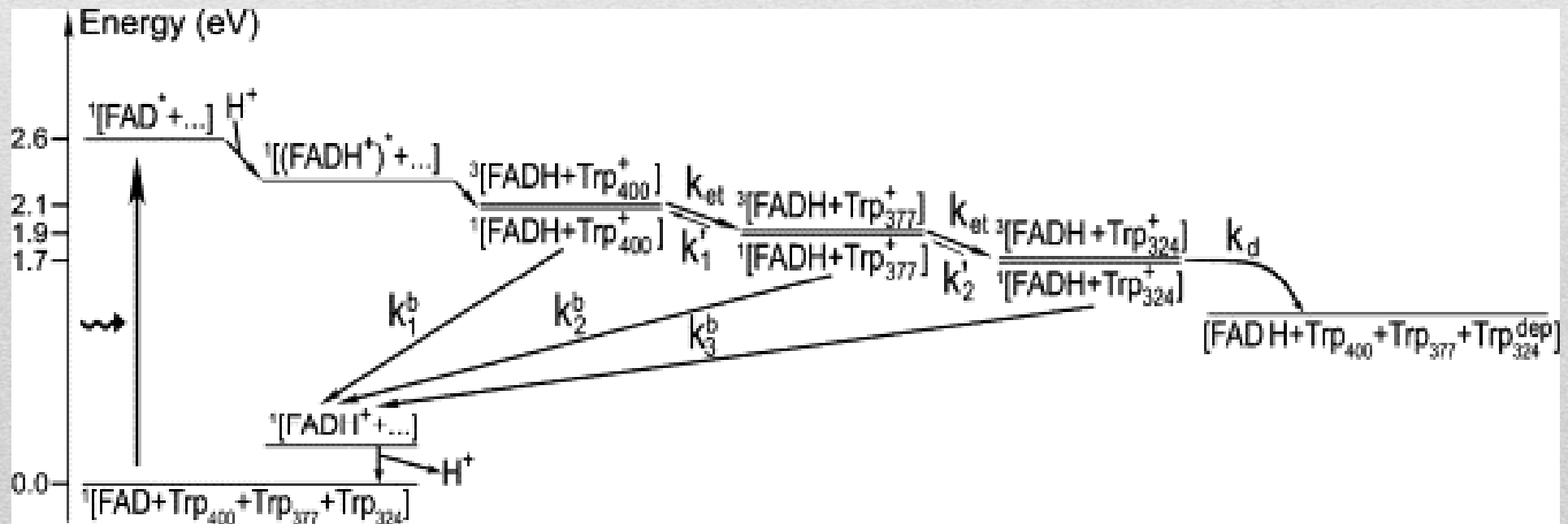
# Structure and Energy Levels



FADH



Tryptophan



**The Hamiltonian for the system is:**

$$H = g\mu_B \cdot \sum_{j=1}^2 \vec{S}_j \cdot (\vec{B} + \vec{A}_j \cdot \vec{I}_j)$$

Where  $\vec{B}$  is the Earth's (external) magnetic field,  $\vec{I}_j$  is the single spin-1/2 nucleus,  $\vec{A}_j$  denotes the hyperfine coupling tensor.

We use the numbers as:

$$\vec{B} = 0.5\text{G}$$

$$A_1 = \begin{pmatrix} 10\text{G} & 0 & 0 \\ 0 & 10\text{G} & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad A_2 = \begin{pmatrix} 5\text{G} & 0 & 0 \\ 0 & 5\text{G} & 0 \\ 0 & 0 & 5\text{G} \end{pmatrix}$$

The density matrix  $\rho(t)$  is governed by the stochastic Liouville Equation:

$$\dot{\rho}(t) = -\frac{i}{\hbar} [H, \rho(t)] - \frac{k_S}{2} \{Q^S, \rho(t)\} - \frac{k_T}{2} \{Q^T, \rho(t)\}$$

Assuming the recombination rates are spin-dependent,

$$k = k_S = k_T$$

One can express the density matrix in this form:

$$\rho(t) = \frac{1}{N} e^{-iHt/\hbar} Q^S e^{iHt/\hbar} e^{-kt}$$

With  $N$  is the number of nuclear spin states

$$\rho(0) = Q^S / \text{Tr } Q^S$$

---



The singlet yield  $\Phi^S$  is defined as the amount of products decaying via the singlet channel:

$$\Phi^S = \int_0^{\infty} k_s S(t) dt$$

Where  $S(t)$  is the fraction of the radical pairs in the singlet state:

$$S(t) = \text{Tr} \left[ Q^S \rho(t) \right]$$

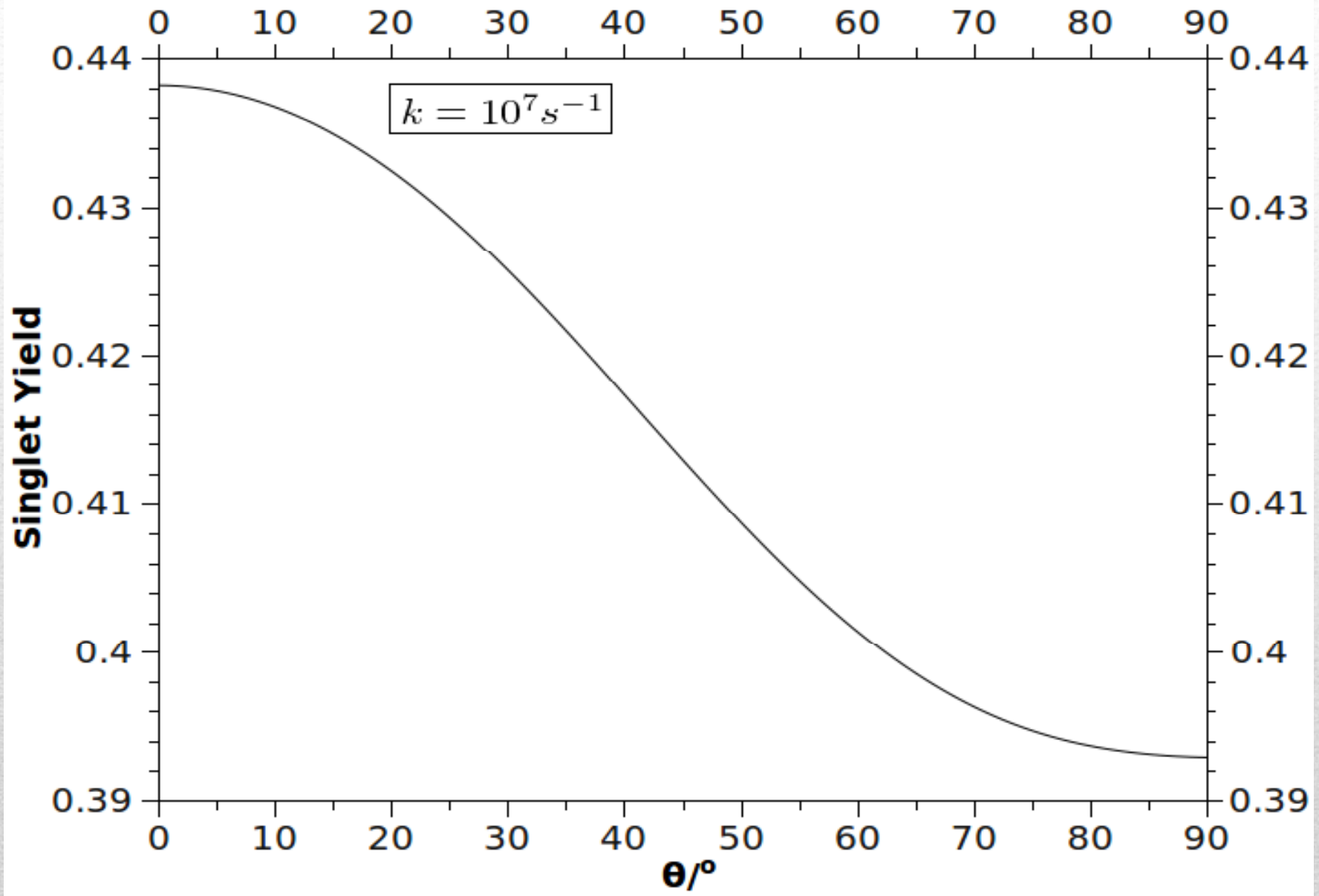
$$S(t) = \frac{1}{N} e^{-kt} \cdot \sum_{m=1}^{4N} \sum_{n=1}^{4N} Q_{mn}^S Q_{mn}^S \cos[(w_m - w_n)t]$$

Then we can get:

$$\Phi^S = \frac{1}{N} \sum_{m=1}^{4N} \sum_{n=1}^{4N} Q_{mn}^S Q_{mn}^S \frac{k^2}{k^2 + (w_m - w_n)^2}$$

---

# Singlet Yield VS Angle



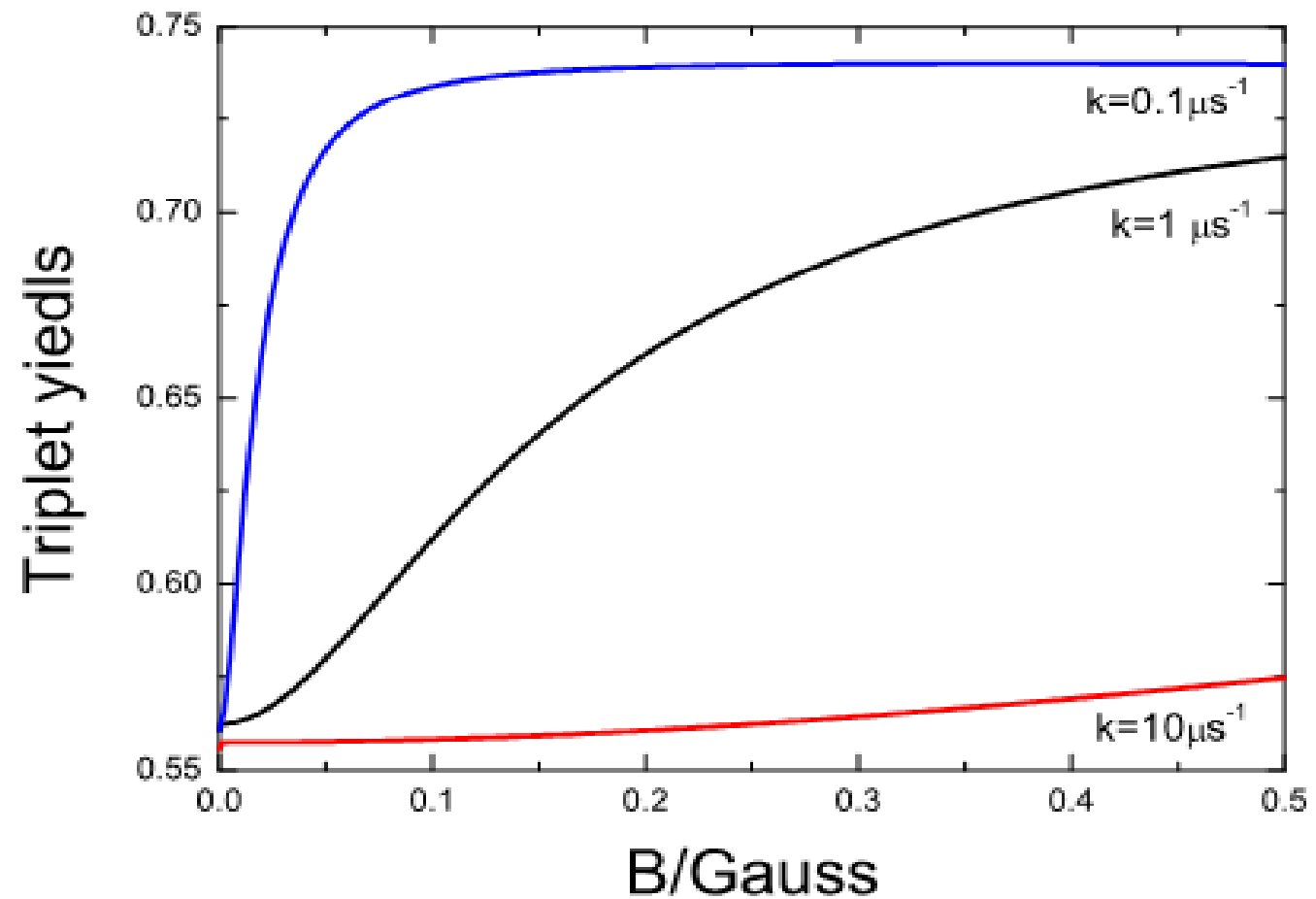
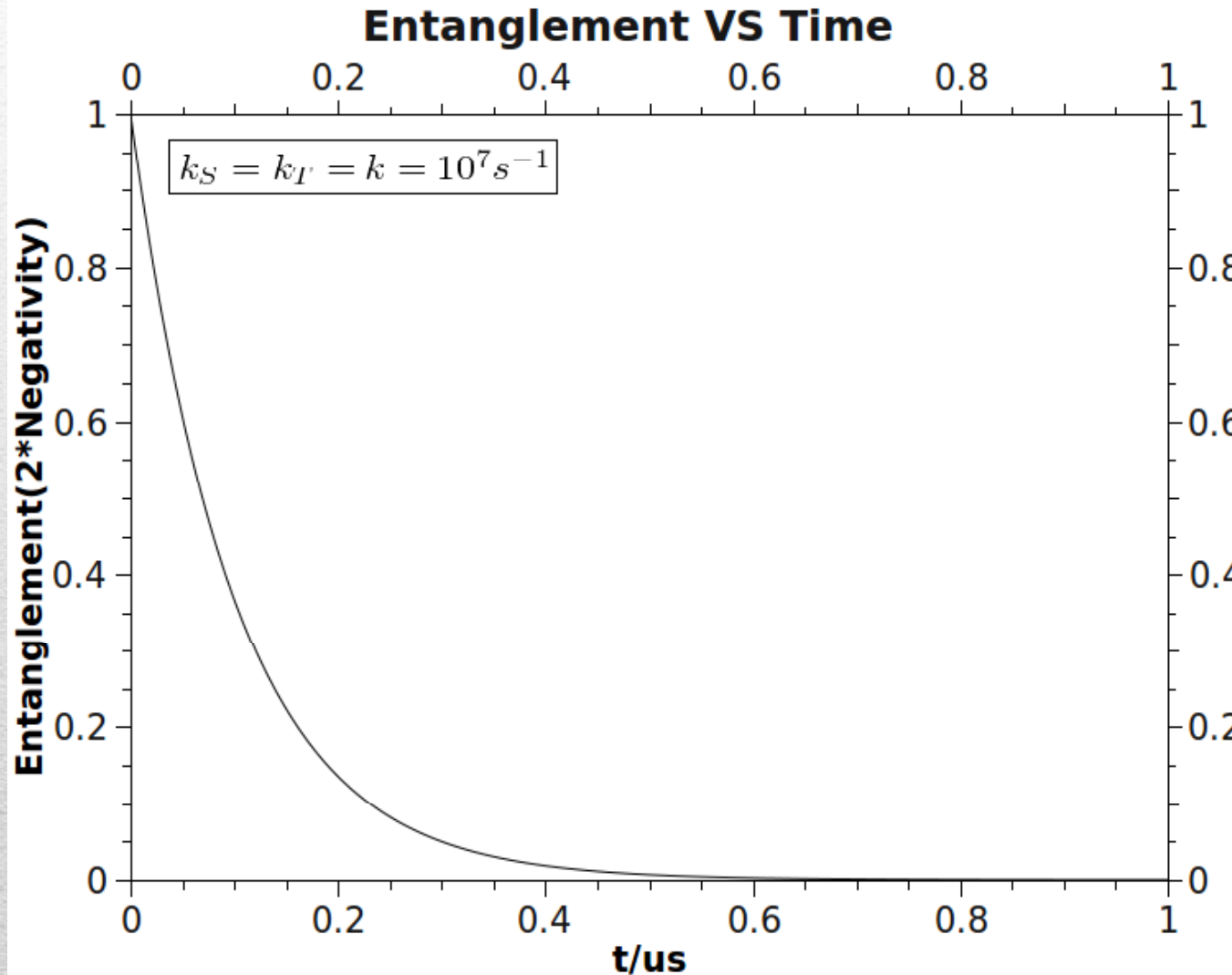


FIG. 2: The triplet yields for three different decay rates as a function of the external magnetic field magnitude. The black line, for which  $k = 1\mu\text{s}^{-1}$  seems to be a reasonable curve.

# Entanglement Dynamics of Avian Magnetic Compass

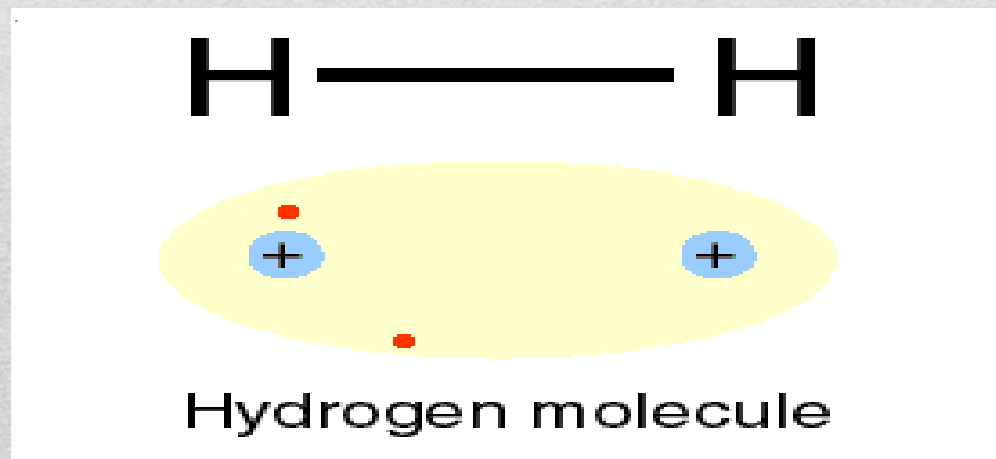


$$\text{Entanglement} = 2 \times \left\| \rho^{Tr_A} \right\| / 2$$

Where  $\rho^{Tr_A}$  is the partial trace of the density matrix

# The Simplest Double Slit

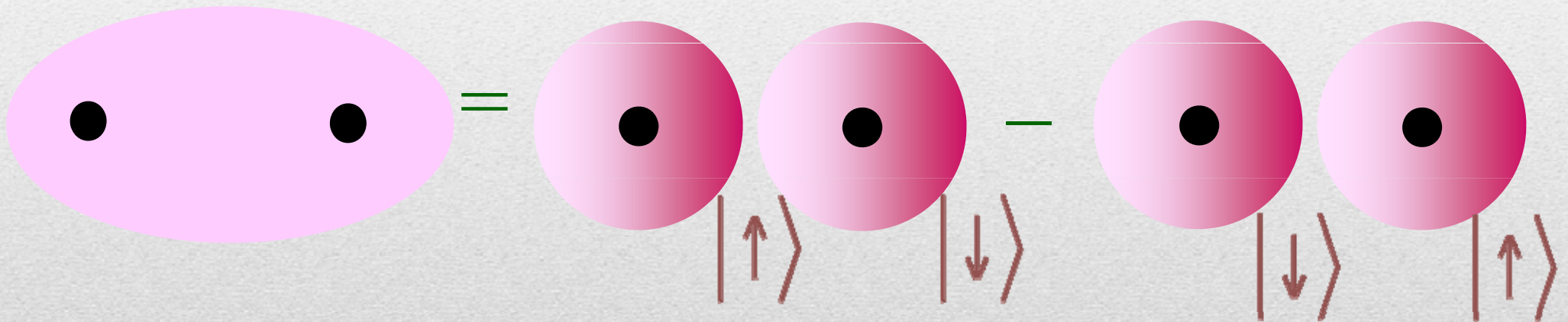
Interference and Entanglement in Double  
Photoionization  
of the Hydrogen Molecule



# Quantum Entanglement:

Hydrogen atom:   $|\uparrow\rangle$

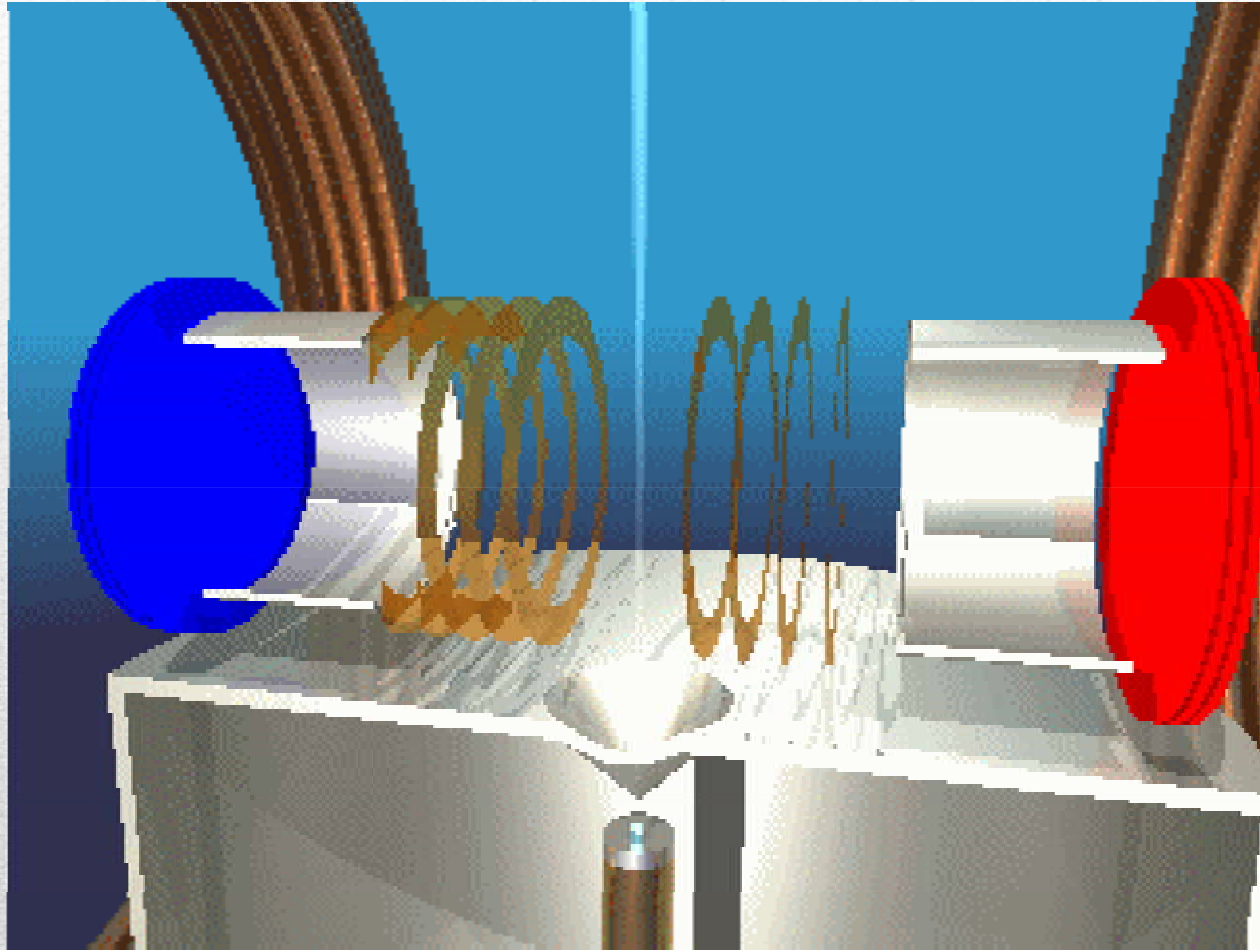
Hydrogen molecule:



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

Superposition of two electron states leads to non-local correlations between spins

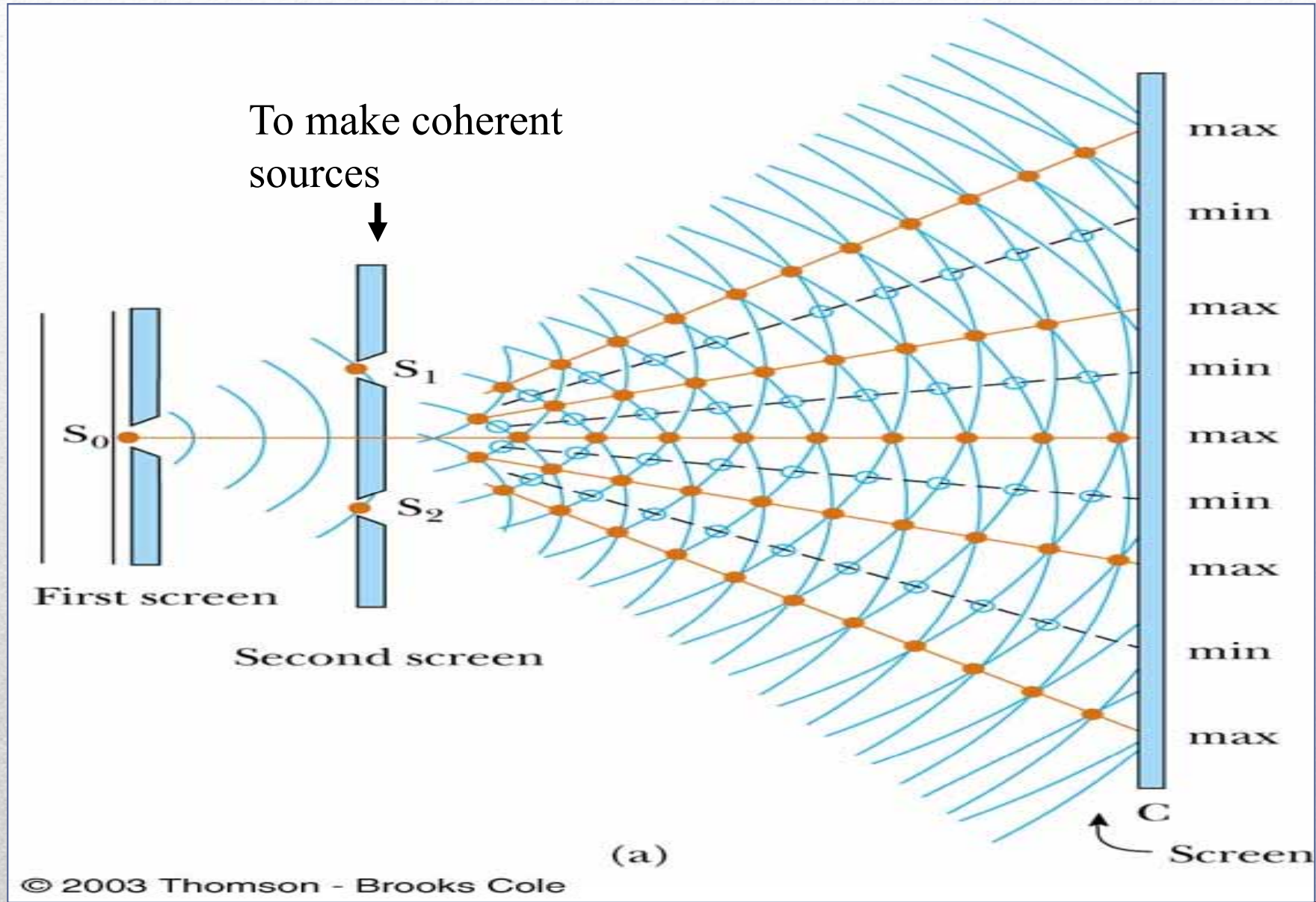
# Introduction to COLTRIMS



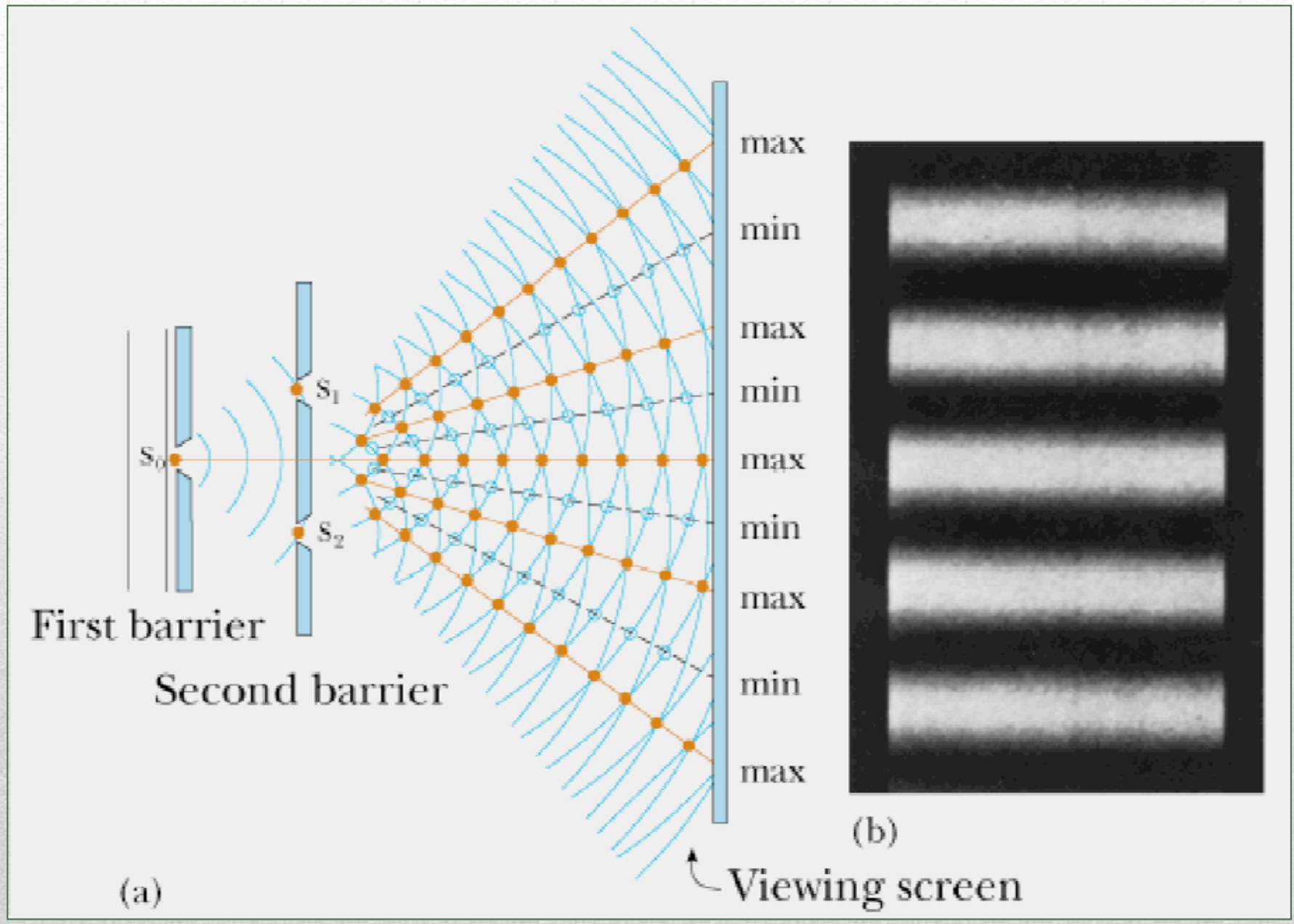
---

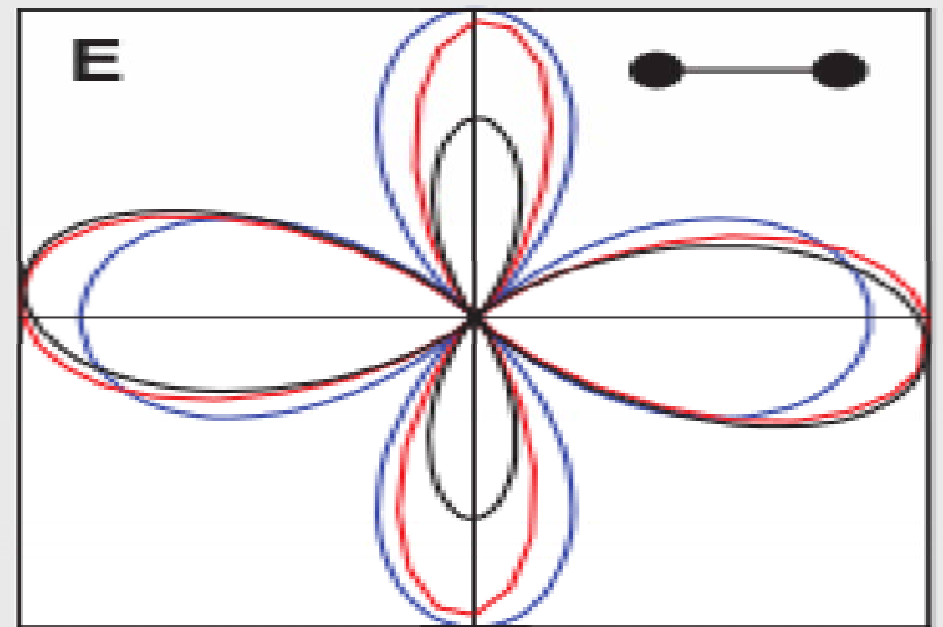
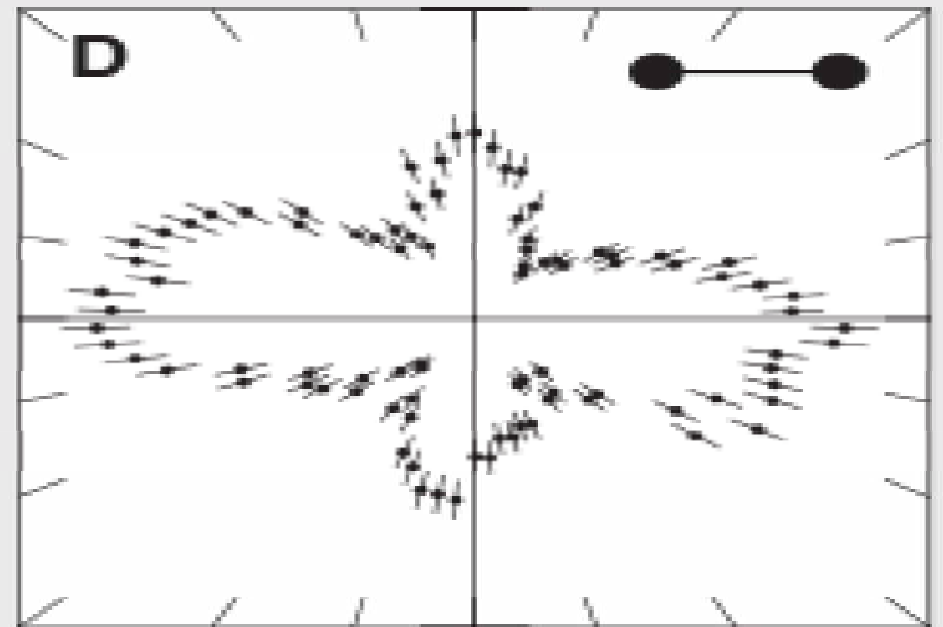
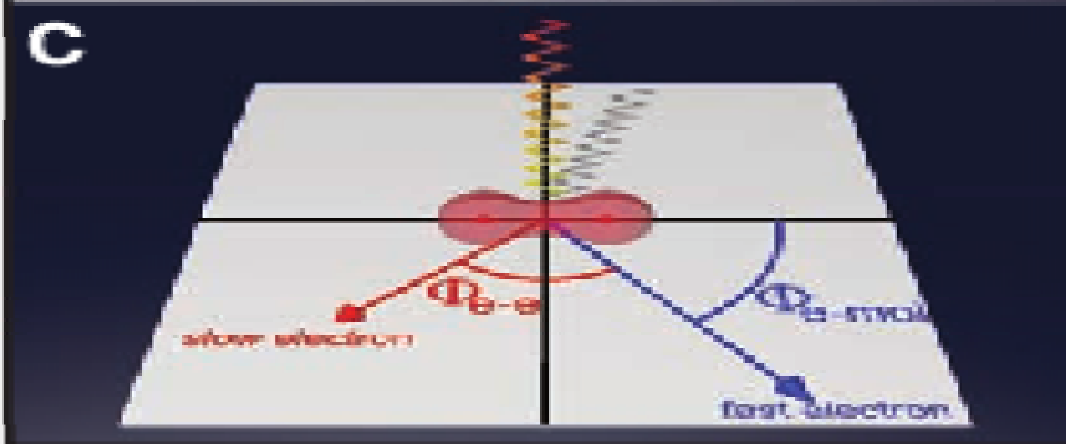
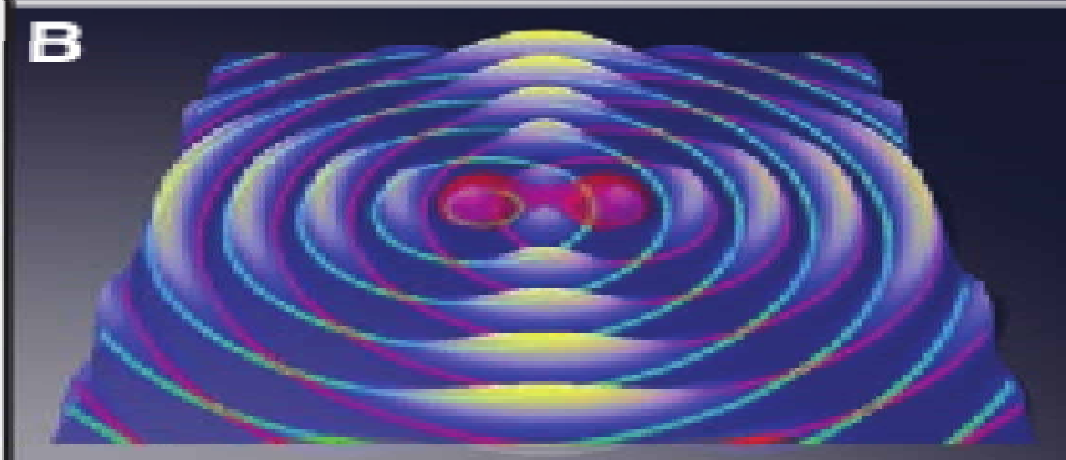
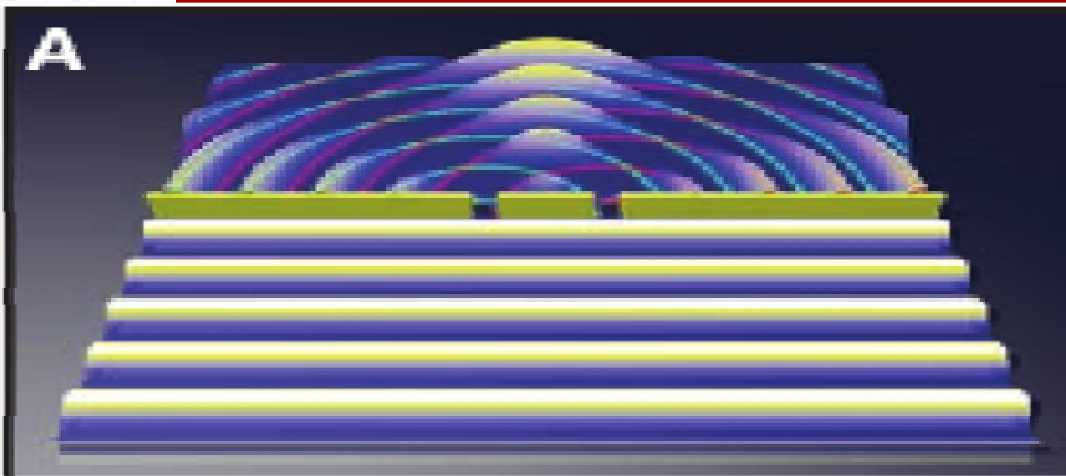
Graphic of Cold Target Recoil Ion Momentum Spectroscopy

# Young's Double Slit Experiment









**D. Akoury et. al. *Science* 318, 949 (2007)**

# Entanglement as Measure of Electron Correlation

- ◆ The correlation energy is defined as the difference between the HF limit energy and exact solution of nonrelativistic Schrodinger equation.

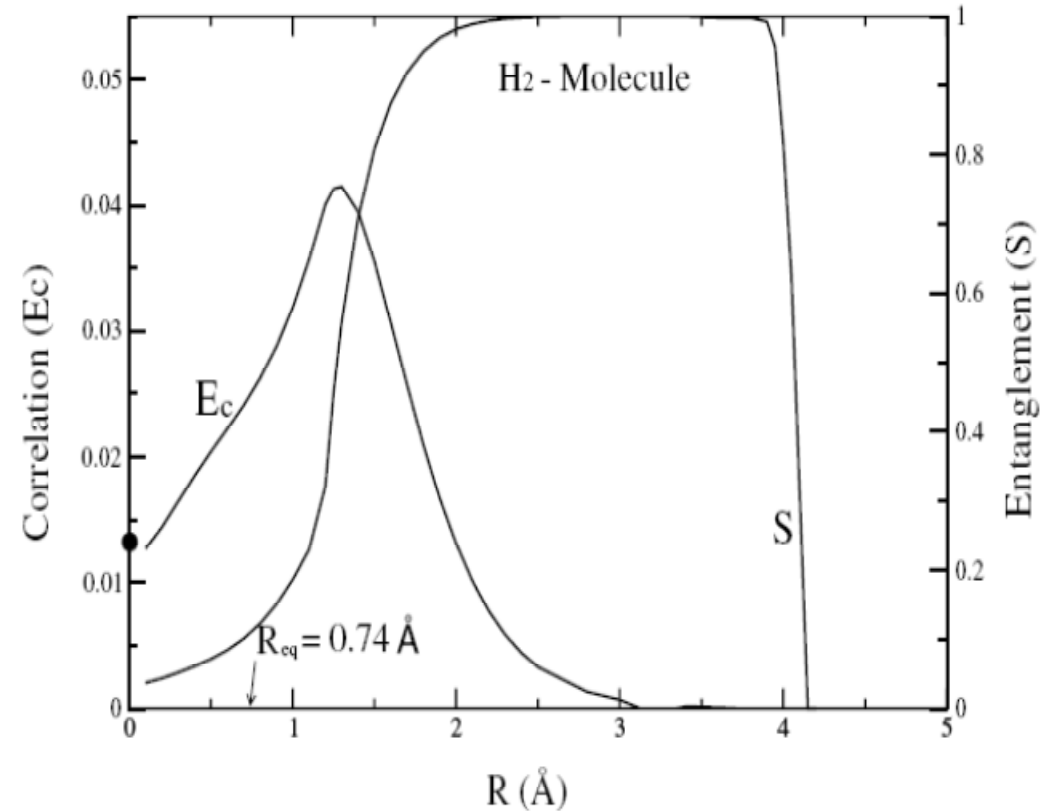
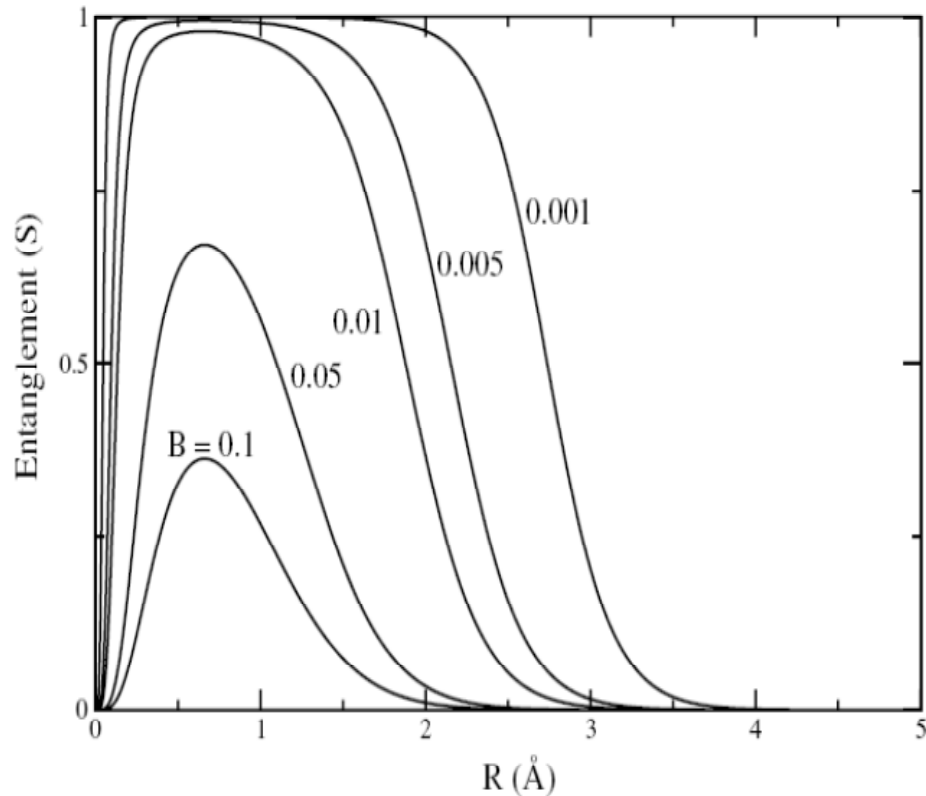
Electron correlation is not directly observable.

- ◆ Entanglement is directly observable and it is one of the most striking properties of quantum mechanics.

---

$$S(\rho_1) = -Tr(\rho_1 \log_2 \rho_1)$$

# Electron Correlation and Entanglement for $H_2$



Entanglement as a function of the distance R between two spins for different values of the magnetic field strength B

Entanglement for  $H_2$   
Huang and Kais, CPL 413, 1 (2005)

# Summary

## Entanglement can be used to:

- Characterize/classify quantum phase transitions
  - Perform quantum teleportation
  - Perform quantum computing using ultracold polar molecules
  - Understand complex processes such as photosynthesis, mechanism with which birds determine magnetic north and chemical reactions
  - Measure electron-electron correlation
-

# NSF Center for Quantum Information and Computation for Chemistry

## CCI Phase I



<http://web.ics.purdue.edu/~kais/qc/>



**Alan Aspuru-Guzik (Harvard)**  
**Kenneth R. Brown (Georgia Tech)**  
**Daniel A. Lidar (USC)**  
**Peter J. Love (Haverford)**  
**Sabre Kais (Purdue)**