
Good Afternoon

Current Trends in Condensed Matter Physics
@ NISER, Bhubaneswar

Coherences, Photosynthesis and Quantum Biology?

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Ψ?

Do biological systems use Quantum Coherences?

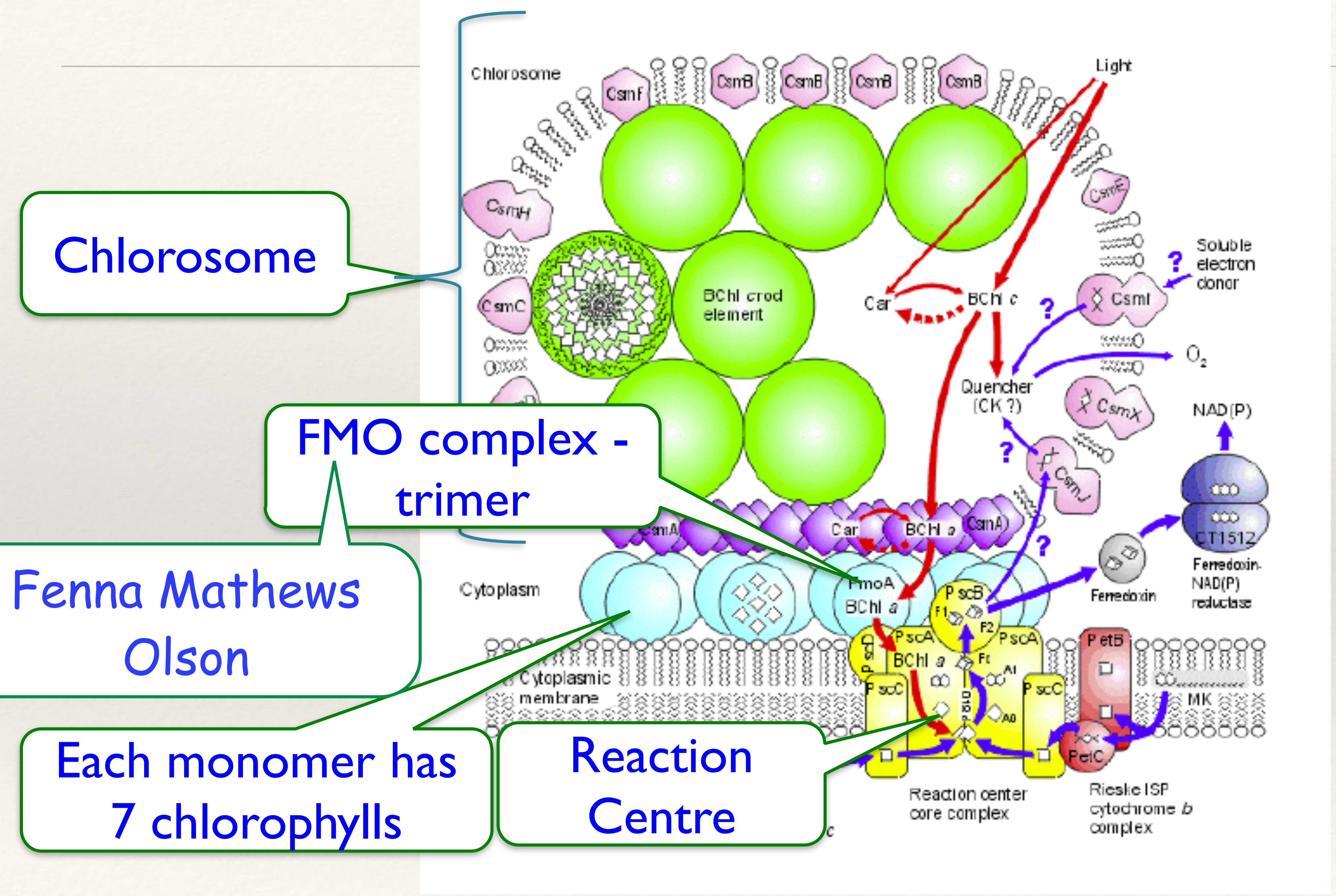

Green sulphur bacteria
at least these do!

Outline

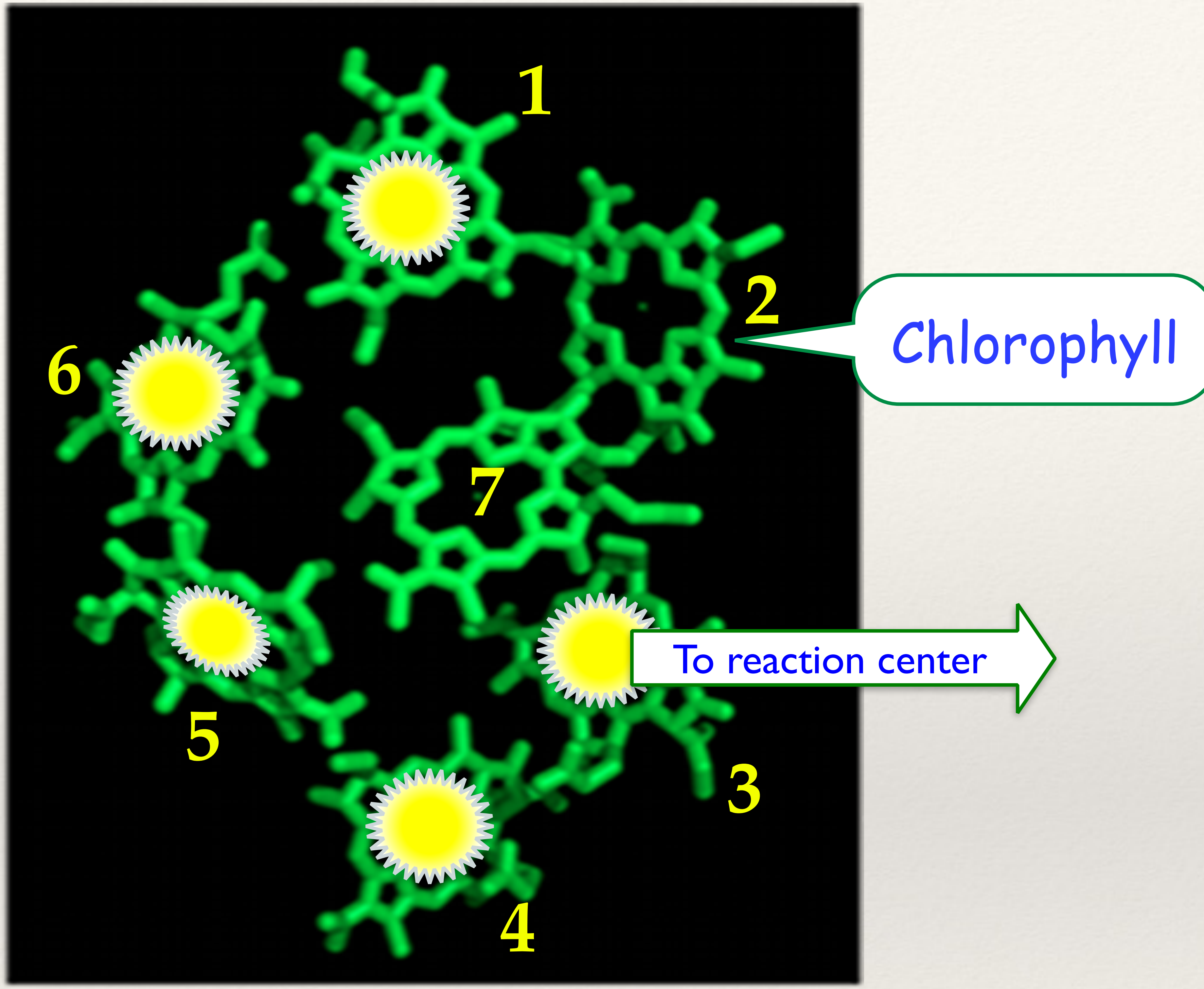
1. The Problem
2. Coherences
3. Environment – decoherence
4. The FMO Photosystem
5. Coherences – experimental observations
6. The Hamiltonian
7. The time evolution
8. Approach based on adiabatic basis
9. Decoherence and population relaxation
10. Summary and Conclusions

The problem

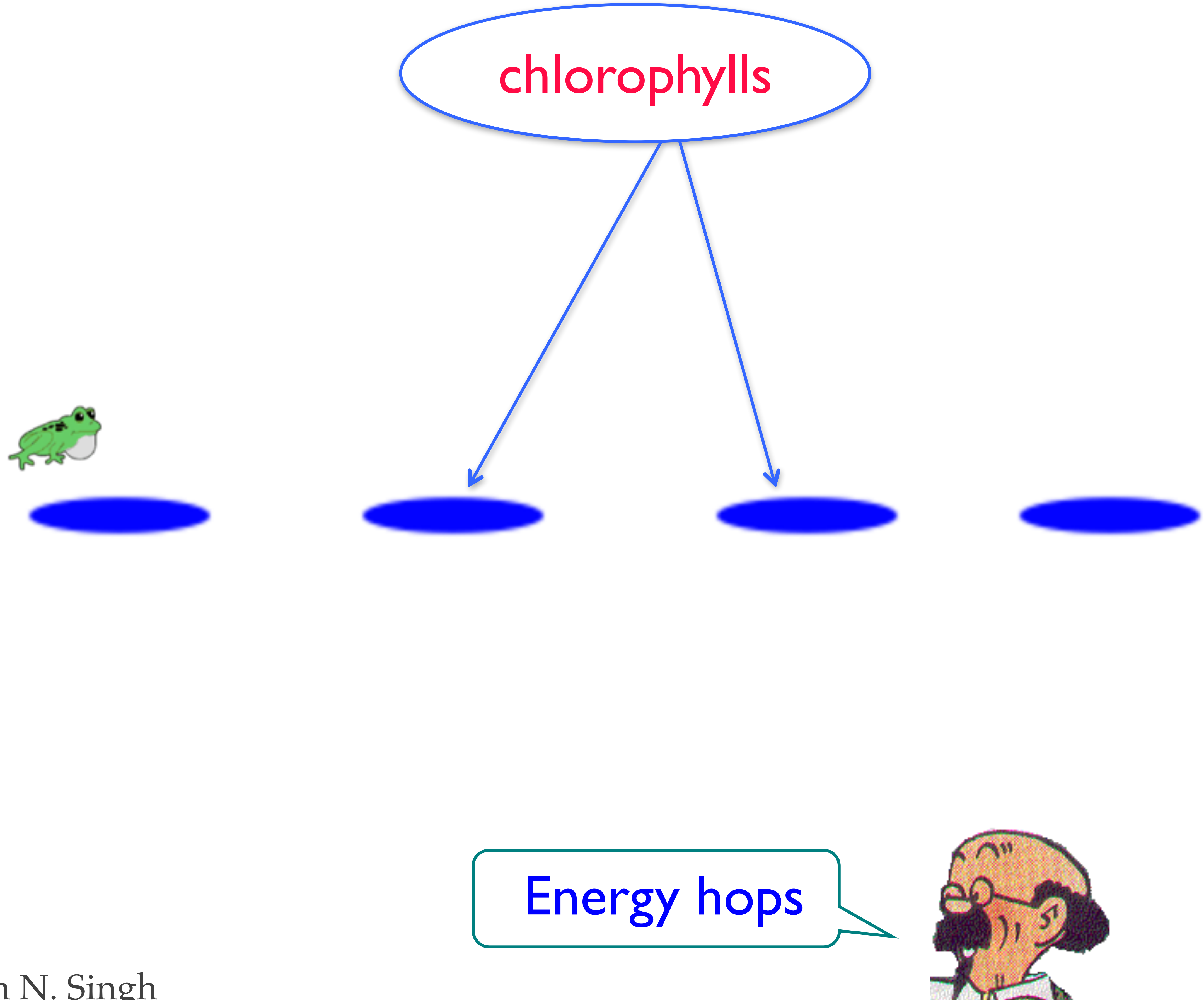
Photosystem of Green Sulfur Bacteria



http://www.bio.ku.dk/nuf/research/chlorosome.htm



The FMO Complex
(green sulphur bacteria)



Idea from N. Singh

Coherences important!

Coherences

Coherences are responsible for wave like motion!

Thundering typhoons!

$$\psi_{12} = \psi_1 + \psi_2$$

Superposition

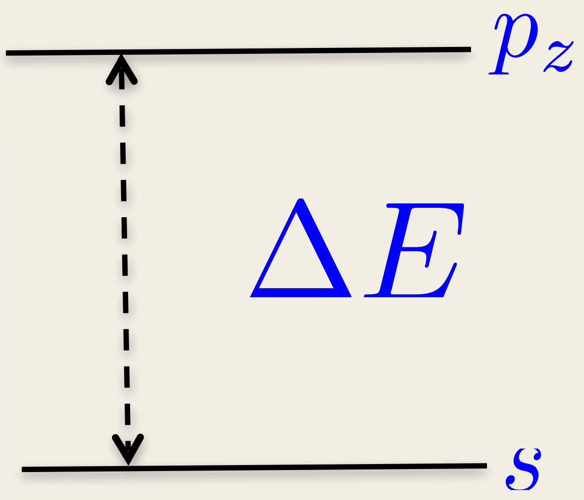
$$|\psi_{12}|^2 = |\psi_1|^2 + |\psi_2|^2 + \psi_1^* \psi_2 + \psi_1 \psi_2^*$$

Coherence

Superposing two electronic states

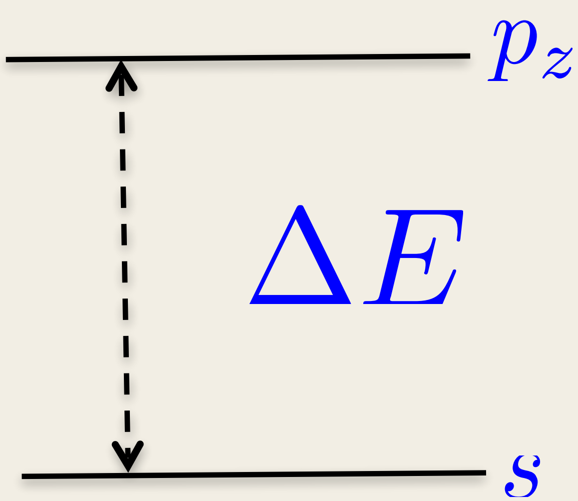
s

p_z



$$\psi = \frac{1}{\sqrt{2}}(s + p_z)$$

Electronic Coherence



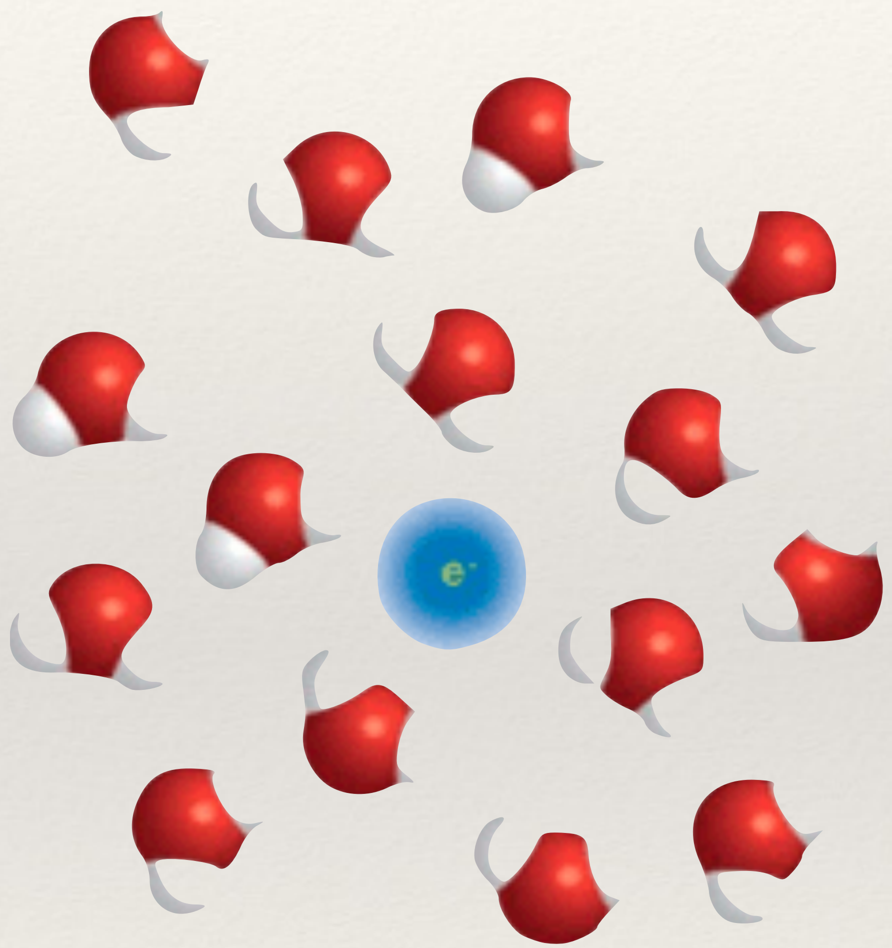
Coherent oscillations with frequency = $\Delta E/h$

Effect of environment

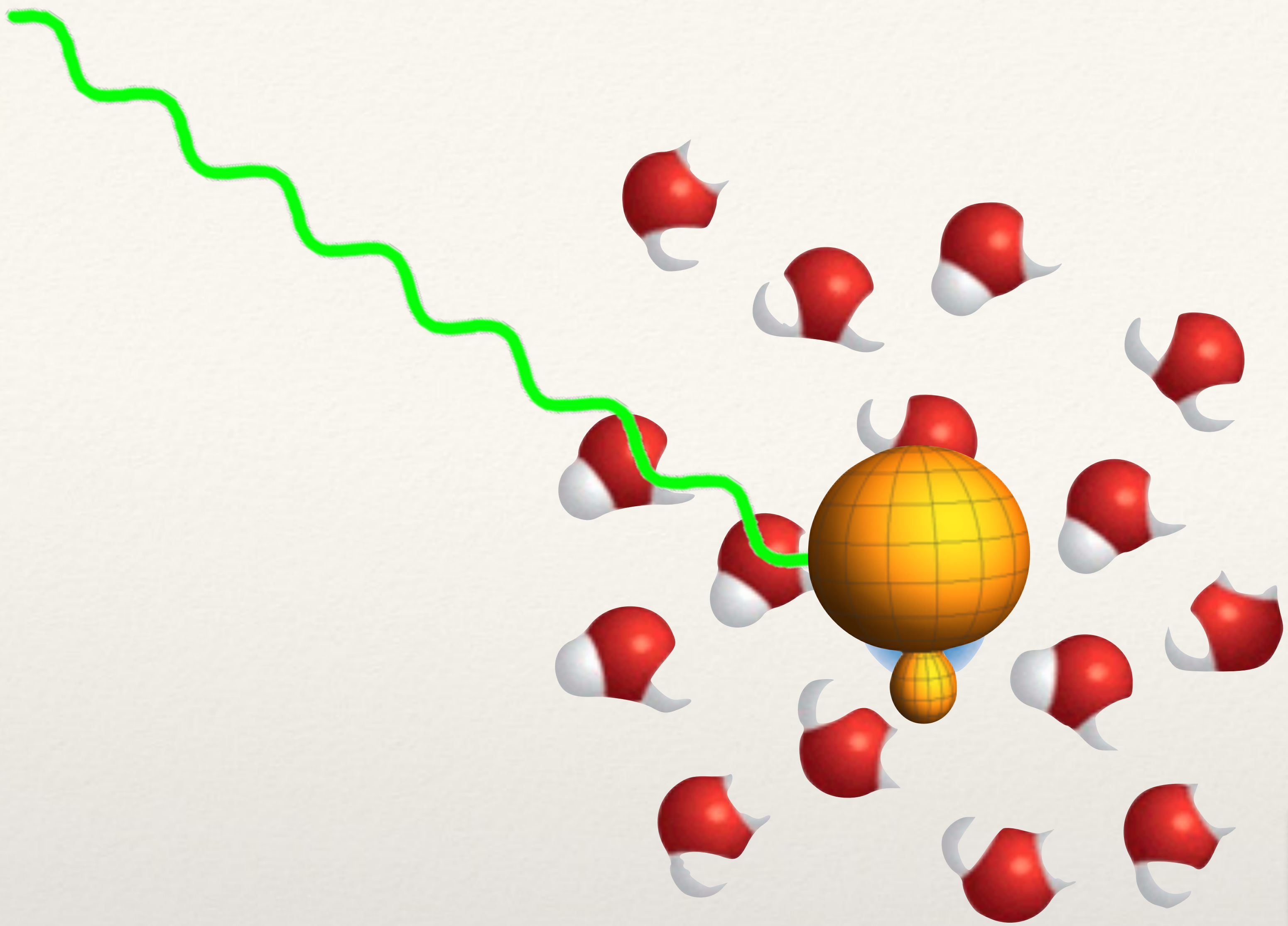
Environment causes
DECOHERENCE!

DECOHERENCE!!!??
Blistering Barnacles!!

Hydrated Electron



http://www.nature.com/nchem/journal/v2/n4/fig_tab/nchem.604_F1.html

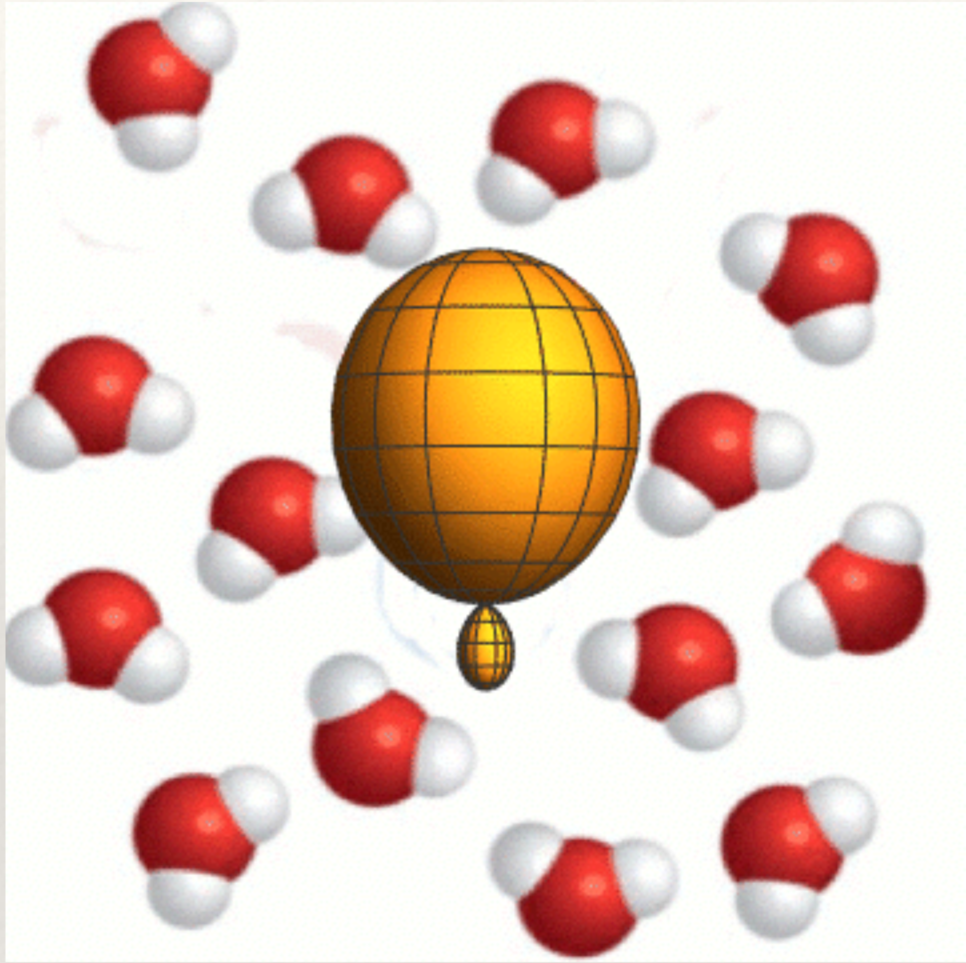


Environment

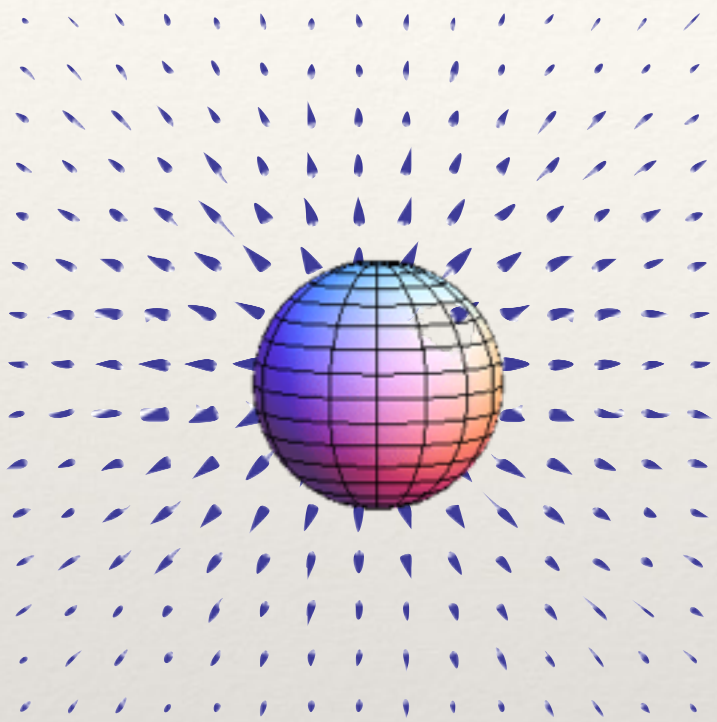
$$\Psi = \frac{1}{\sqrt{2}}(s + p_z)\psi_{Env}$$

The description is inaccurate!

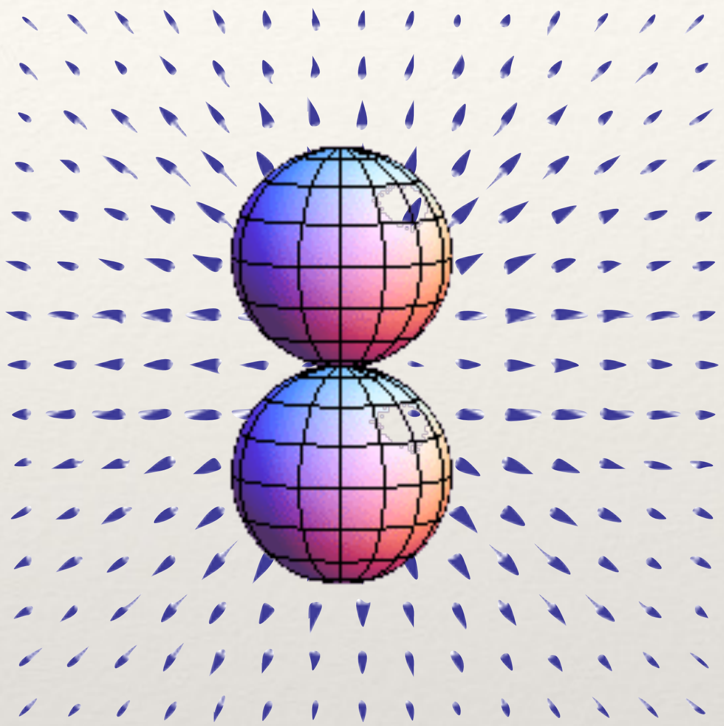
Oscillations die down
- effect of the environment



Interaction with the environment



Spherically symmetric

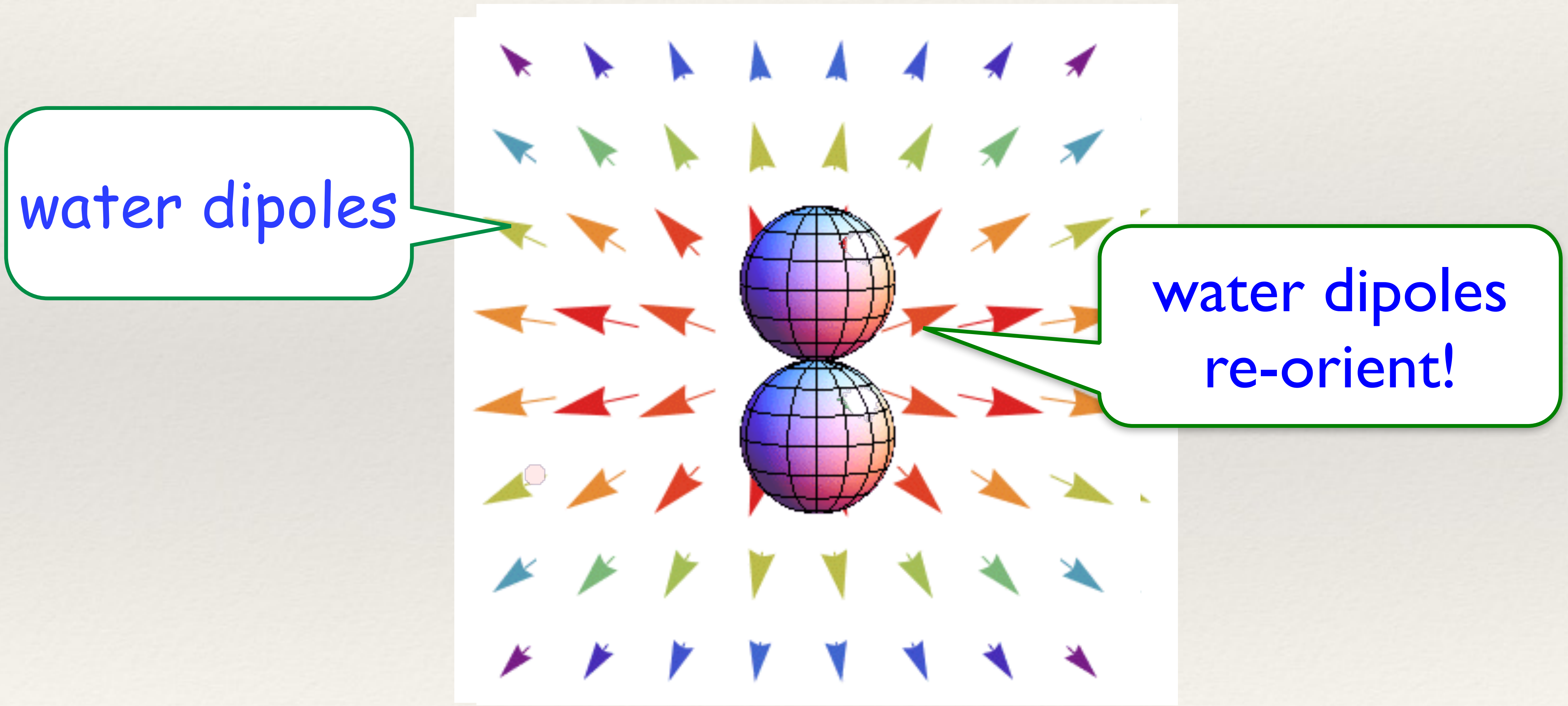


non-spherical

Electric field in the environment

$$\Psi = \frac{1}{\sqrt{2}}(s + p_z)\psi_{Env}$$

$$\Psi(t) = \frac{1}{\sqrt{2}}(s\ \psi_{Env,s} + p_z\ \psi_{Env,p_z} e^{-it\frac{\Delta E_{sys+Env}}{\hbar}})$$



Causes DECOHERENCE!

$$\int d(Env)\ \Psi^*\Psi = \frac{1}{2}(s^2 + p_z^2 + 2\ s\ p_z| < \psi_{Env,s}|\psi_{Env,p_z} > |\cos(\frac{\Delta E t}{\hbar}))$$

Has large number of particles.
Vanishes very rapidly

$$\int d(Env)\ \Psi^*\Psi = \frac{1}{2}(s^2 + p_z^2)$$

How much time does it take?

Decoherence and Relaxation

Decoherence is different from relaxation!

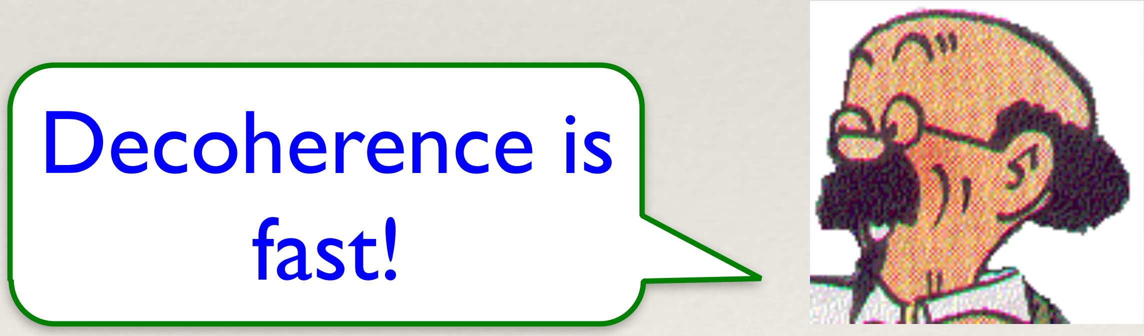
$$\left[\frac{\tau_D}{\tau_g}\right]^2 = \frac{6k_BT}{\lambda}$$

Solvent relaxation

Stokes shift

Decoherence times

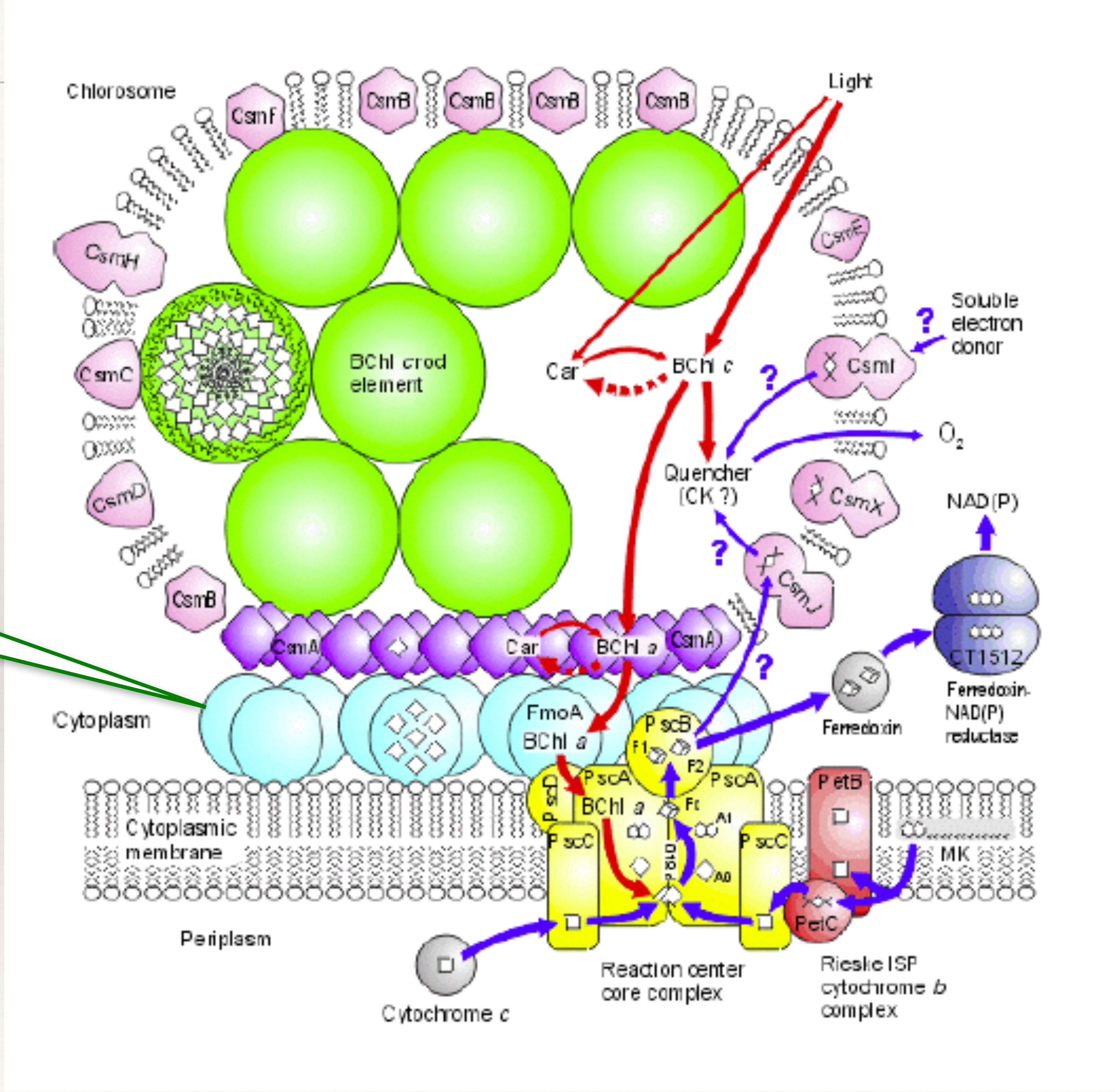
Species	Decoherence time
Hydrated electron	*4.5 fs*
Styryl dye in methanol	*6.8 fs*
Betaine-30 in acetonitrile	*49 fs*



Prezhdo and Rossky:
PHYSICAL REVIEW LETTERS, 81, 5294 (1998)

The Photosystem

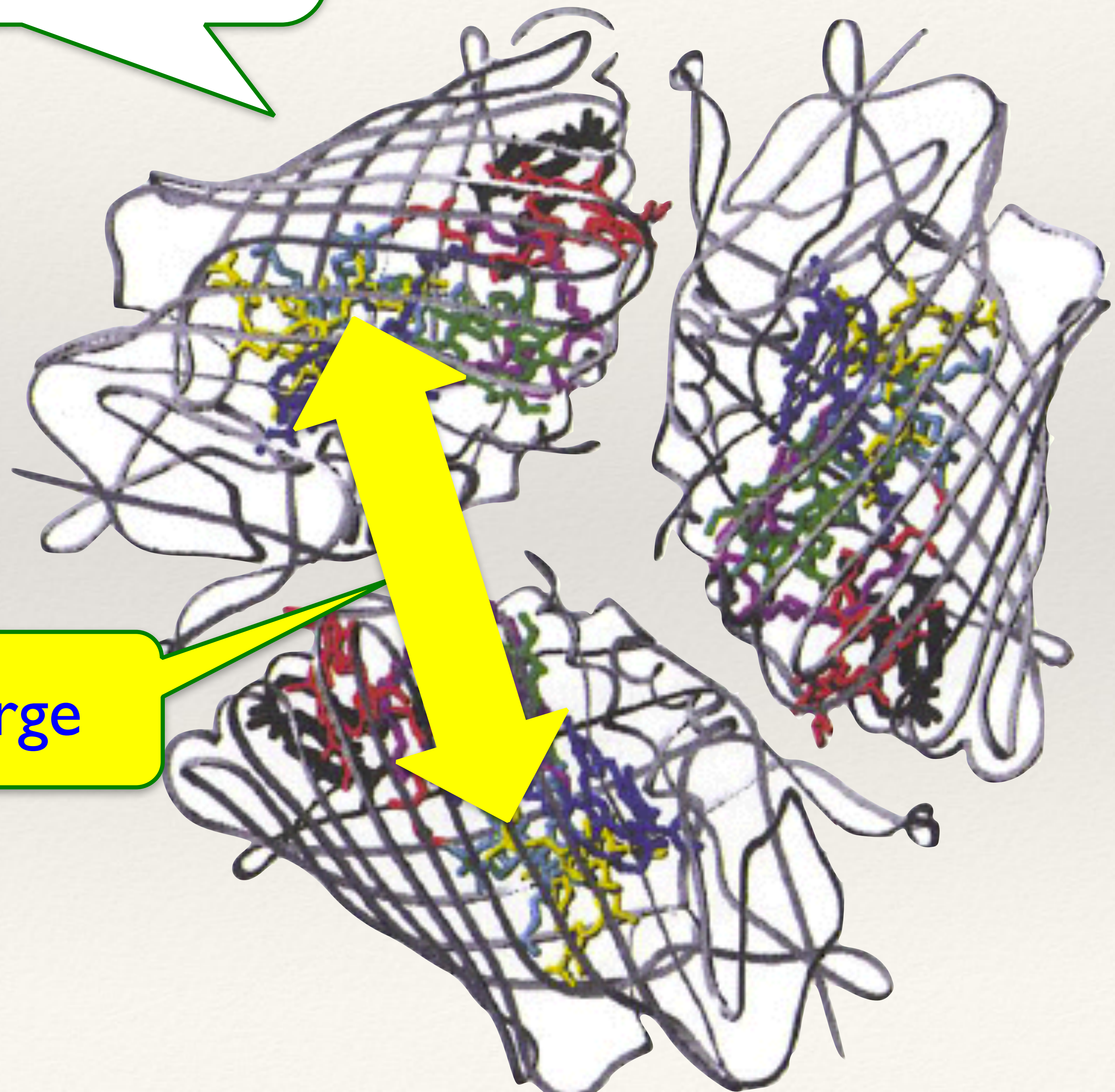
The FMO Complex



TRIMER

http://www.bio.ku.dk/nuf/research/chlorosome.htm

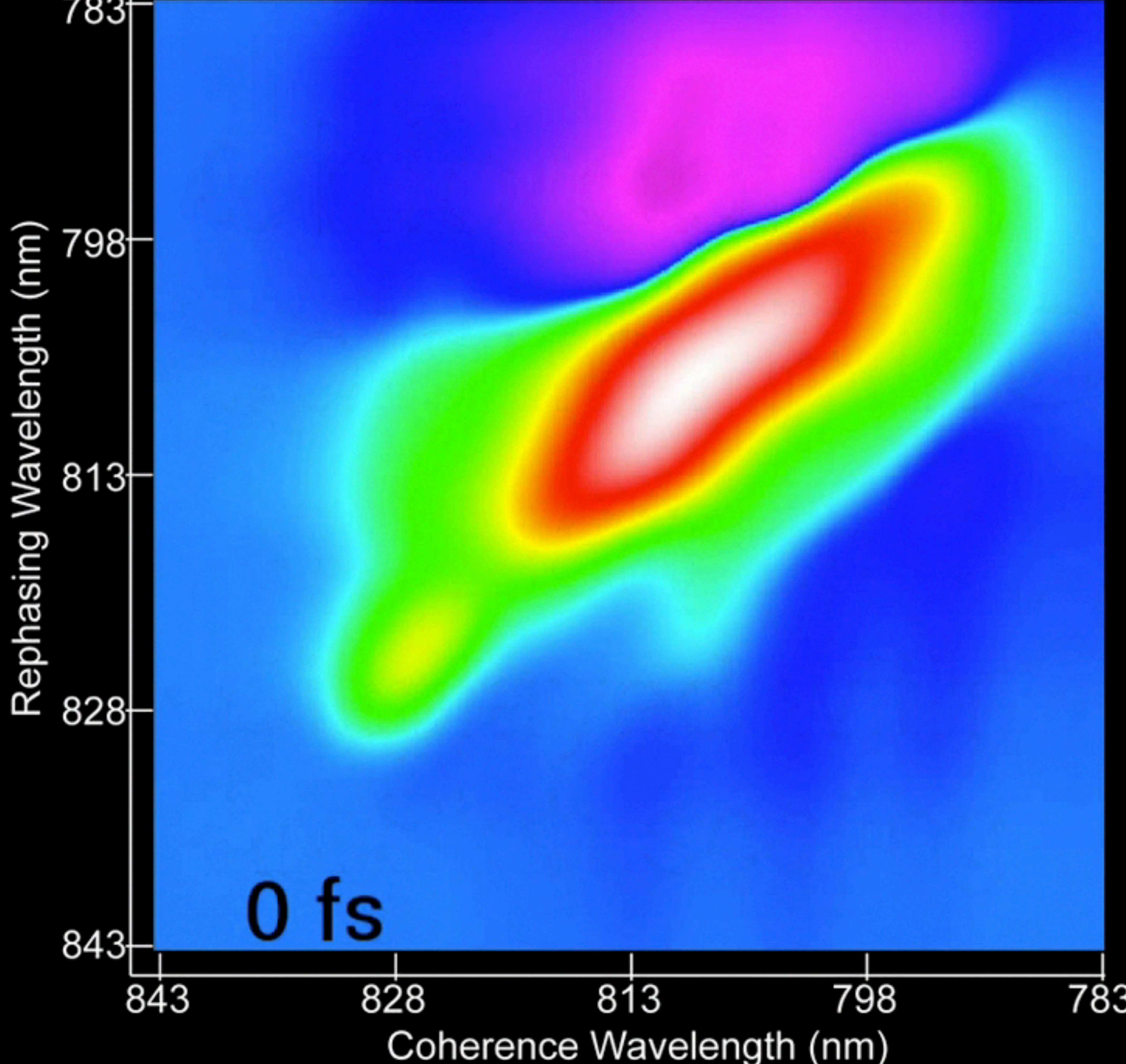
Closely packed BChls
Environment
Hydrophobic

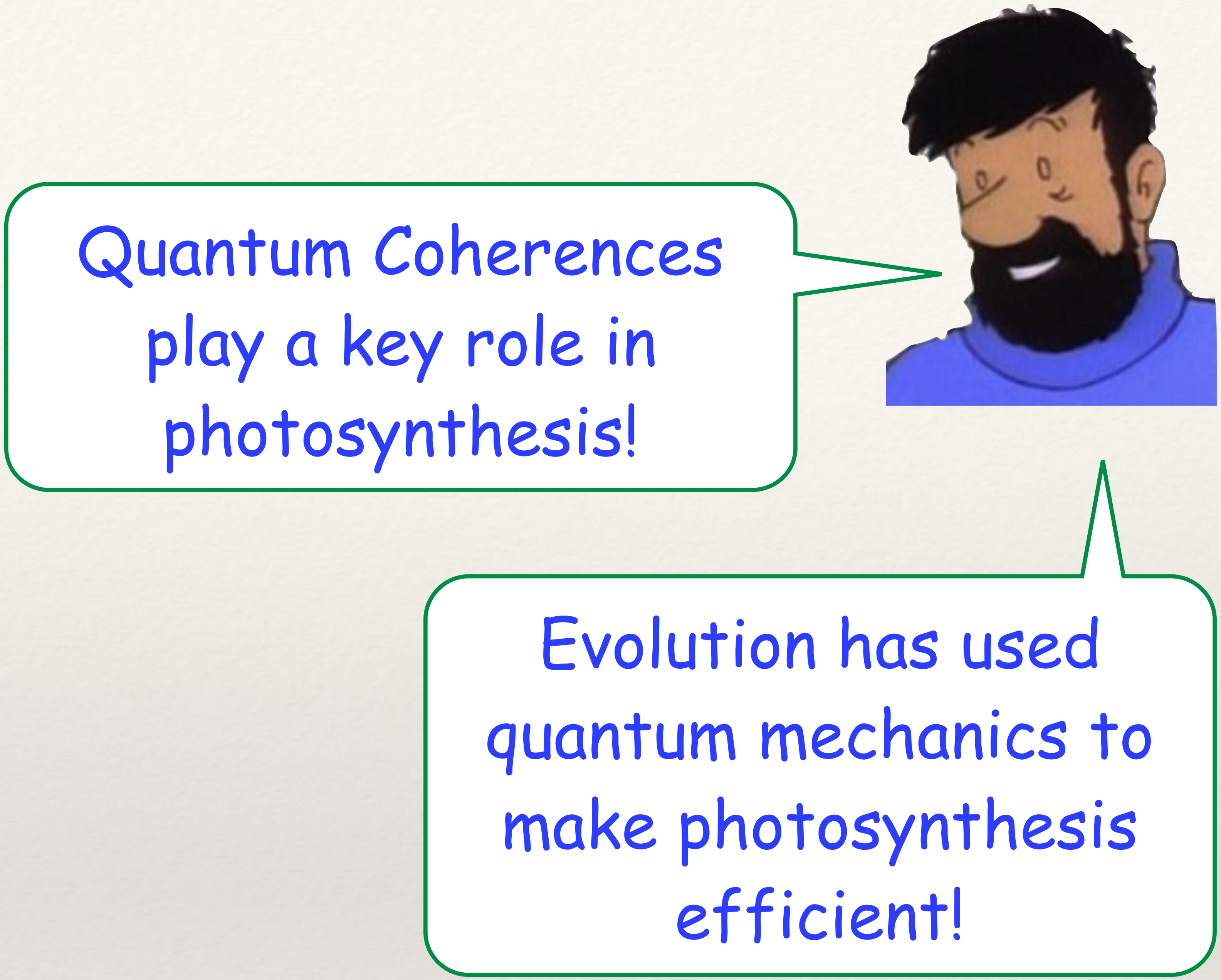


Separation large

Experimental results

G. Fleming et. al. Nature, 2007


783
798
813
828
843
Rephasing Wavelength (nm)
0 fs
843
828
813
798
783
Coherence Wavelength (nm)


Quantum Coherences play a key role in photosynthesis!
Evolution has used quantum mechanics to make photosynthesis efficient!

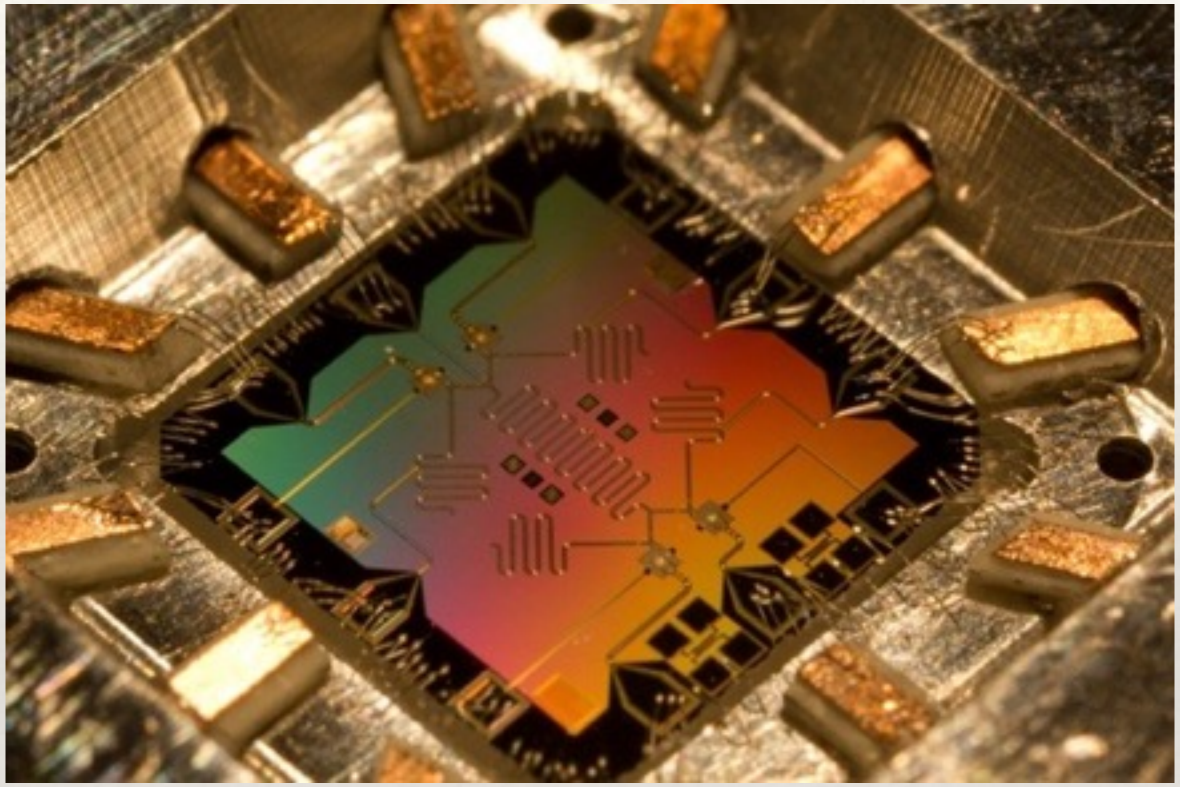
Bacteria have been quantum computing for hundreds of millions of years!

Non-trivial quantum effects seen in biology!

Dawn of QUANTUM BIOLOGY!

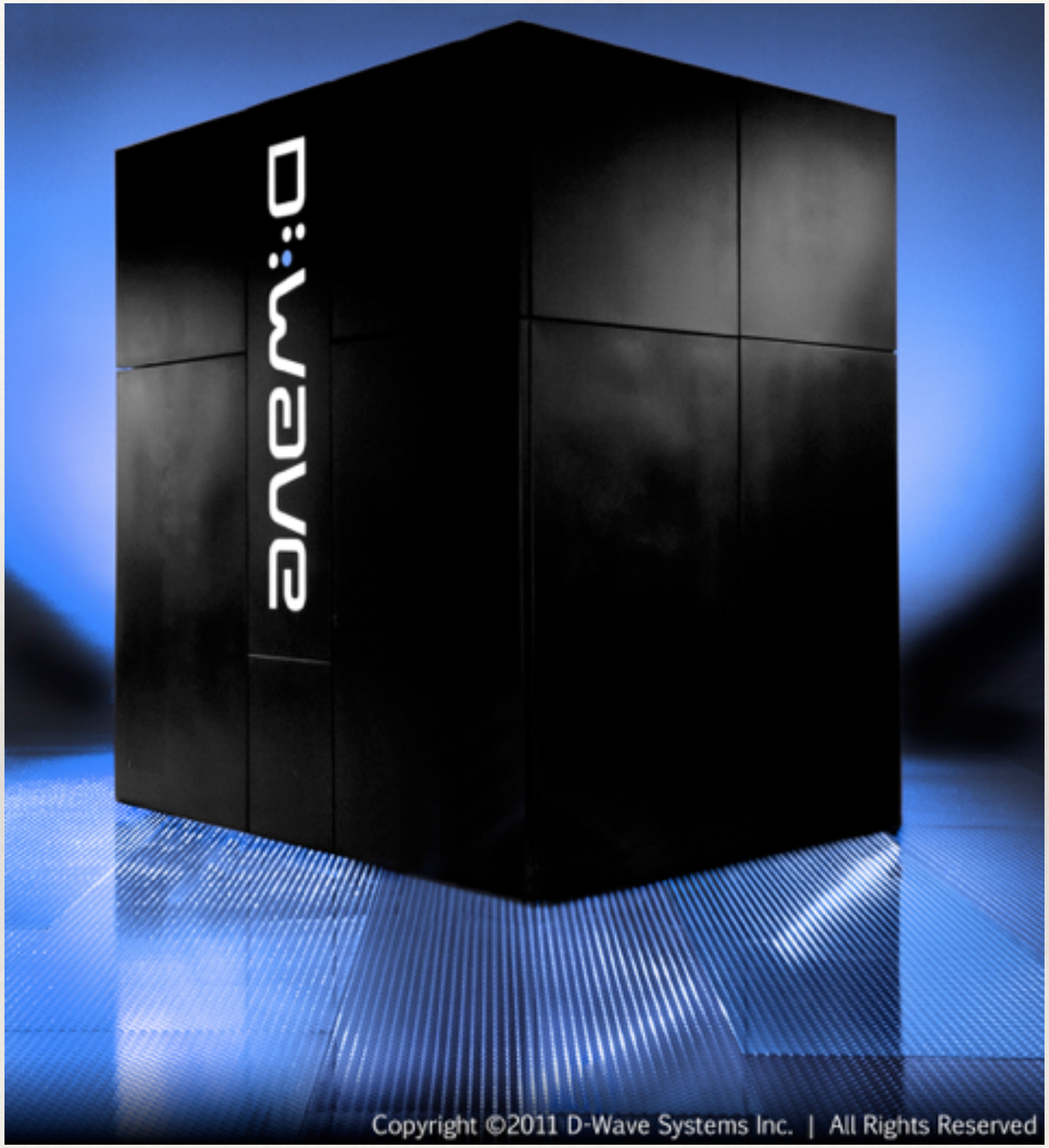
I would like to believe this!
But is this true?

D-Wave - Quantum Chip



Size of a thumbnail

Quantum Computer?

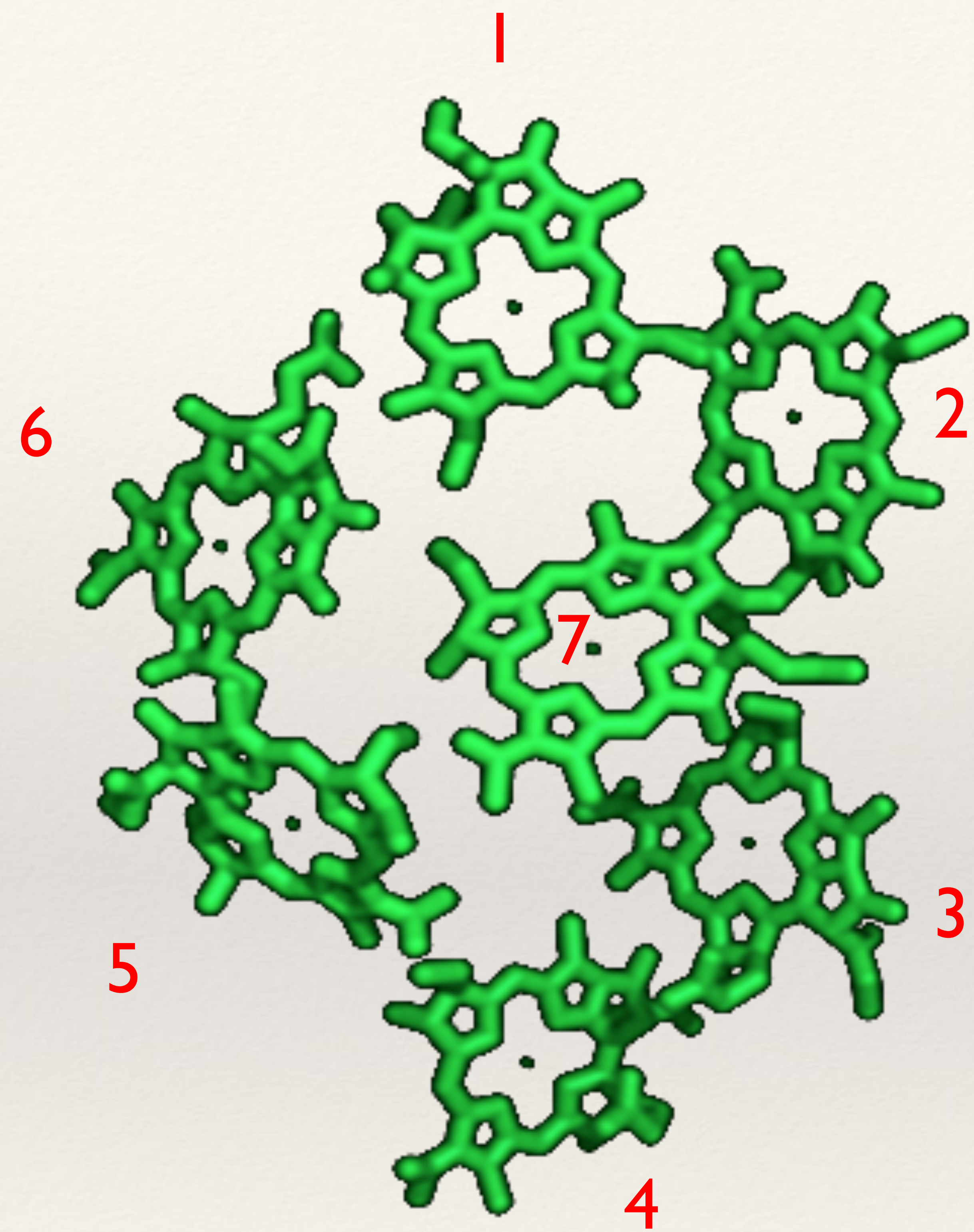


10ft x 10 ft x 12 ft

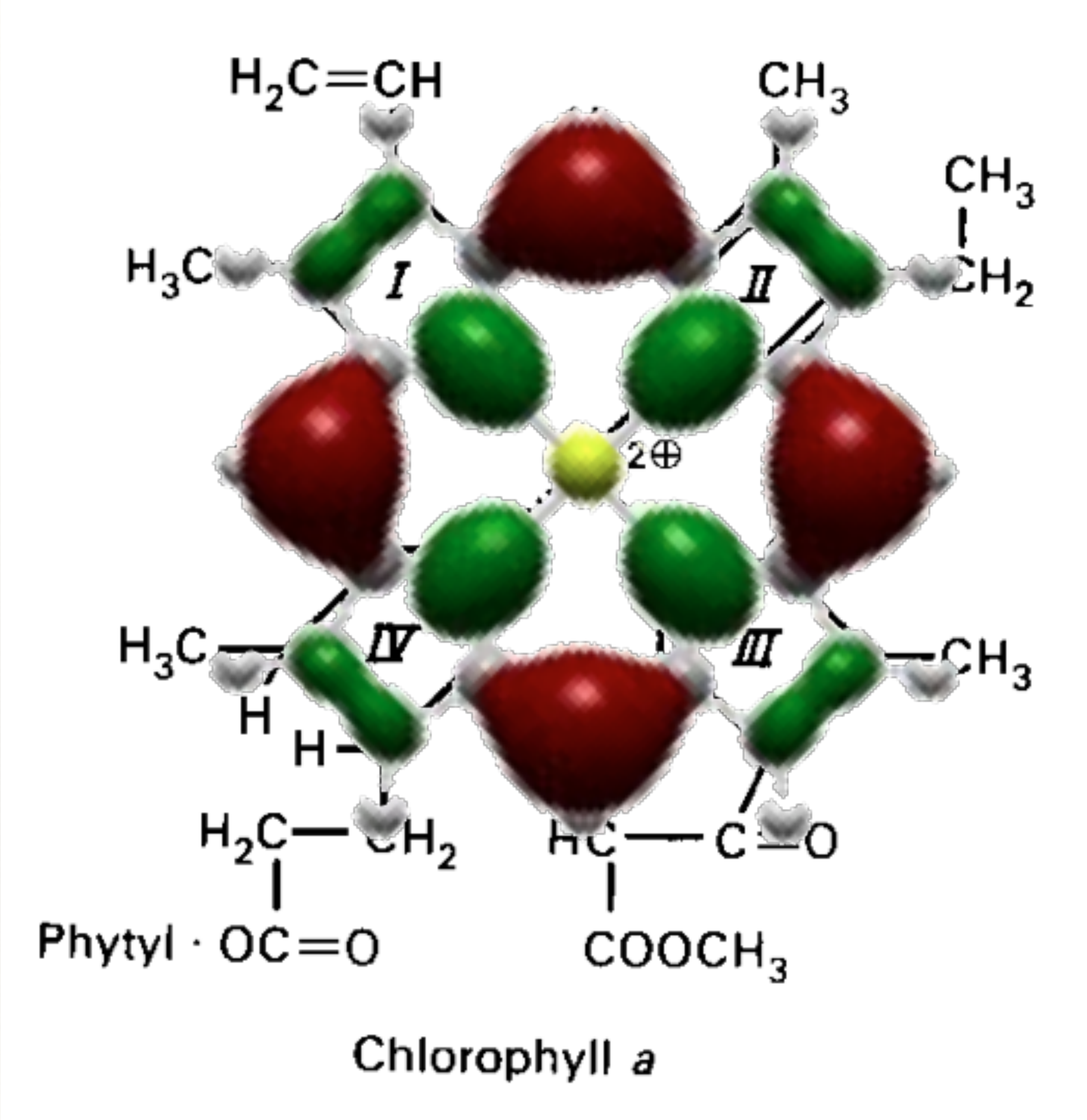
Cost: $10 million

Near ZERO Kelvin

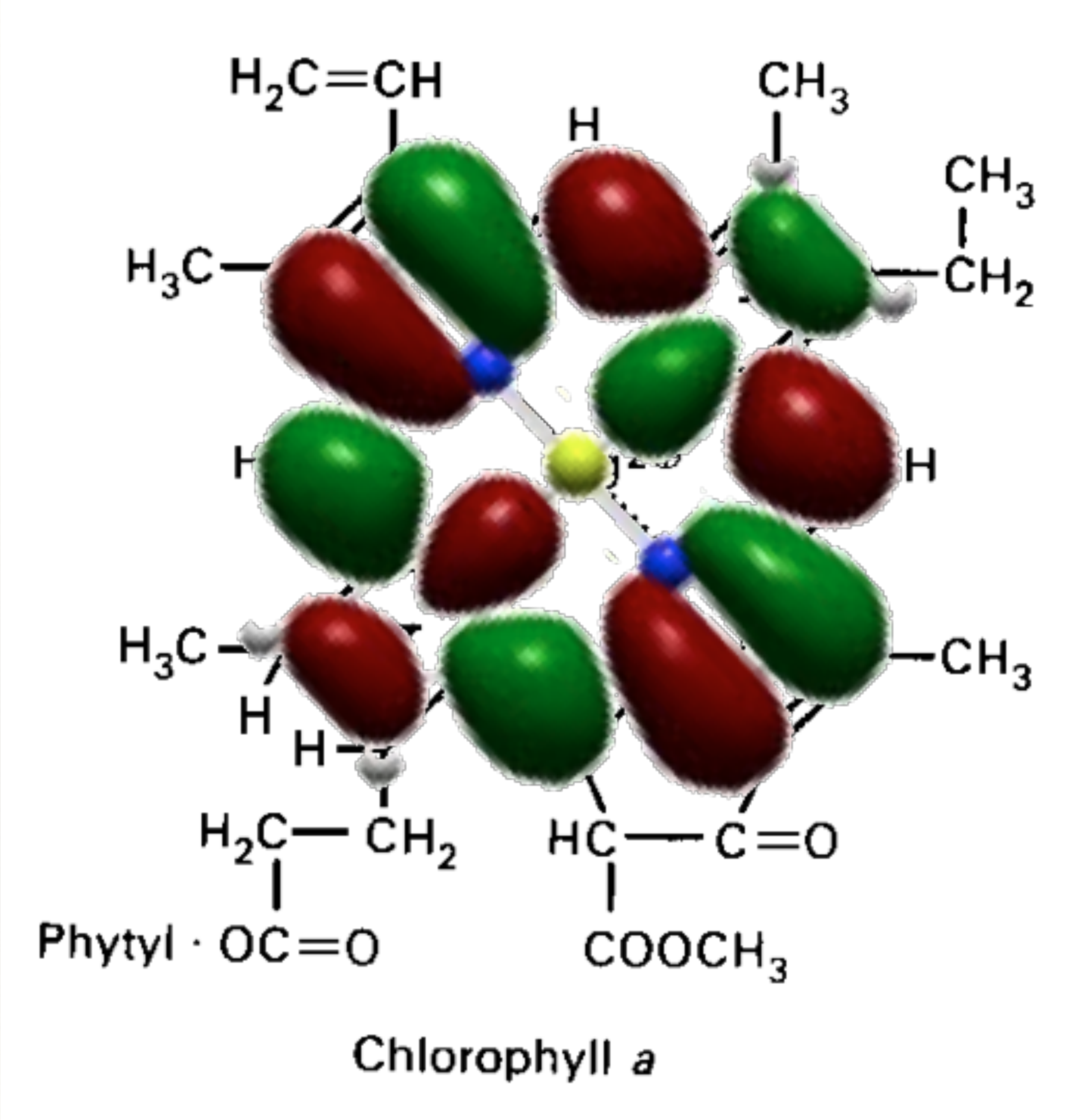
The molecules, energy levels and couplings


1
2
3
4
5
6
7

$\approx 11\ \mathring{A}$

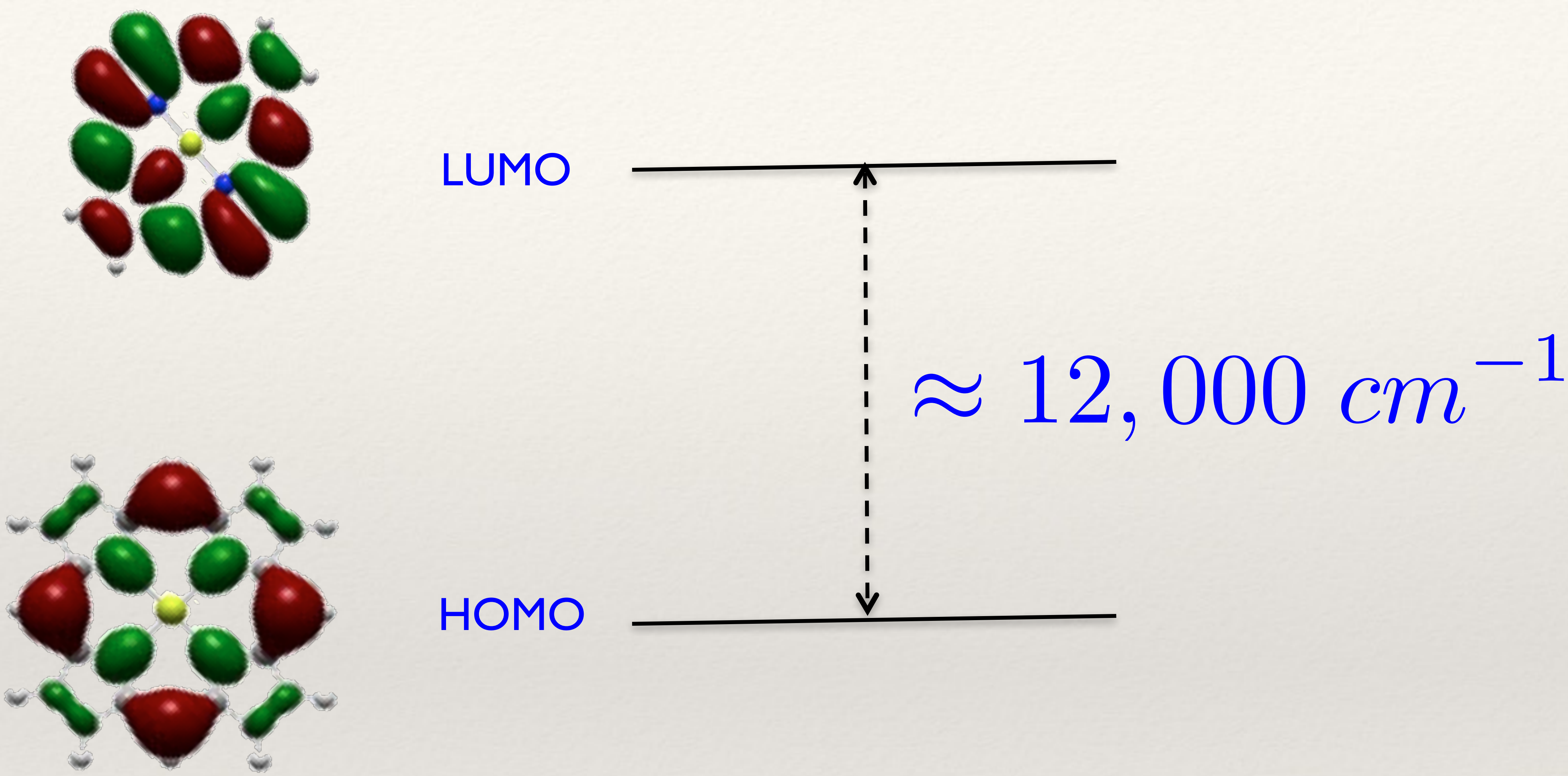


HOMO



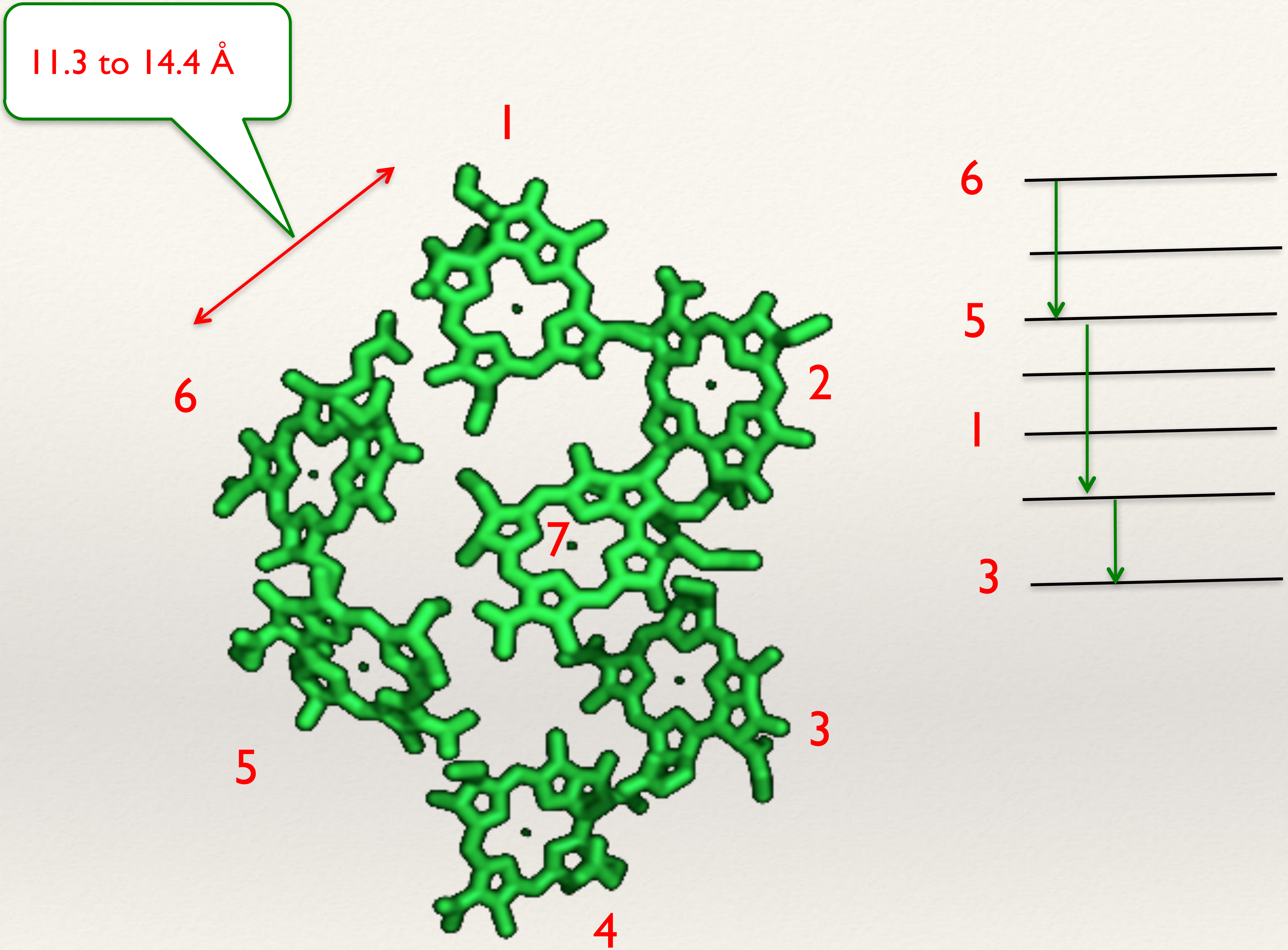
LUMO

(from the internet)

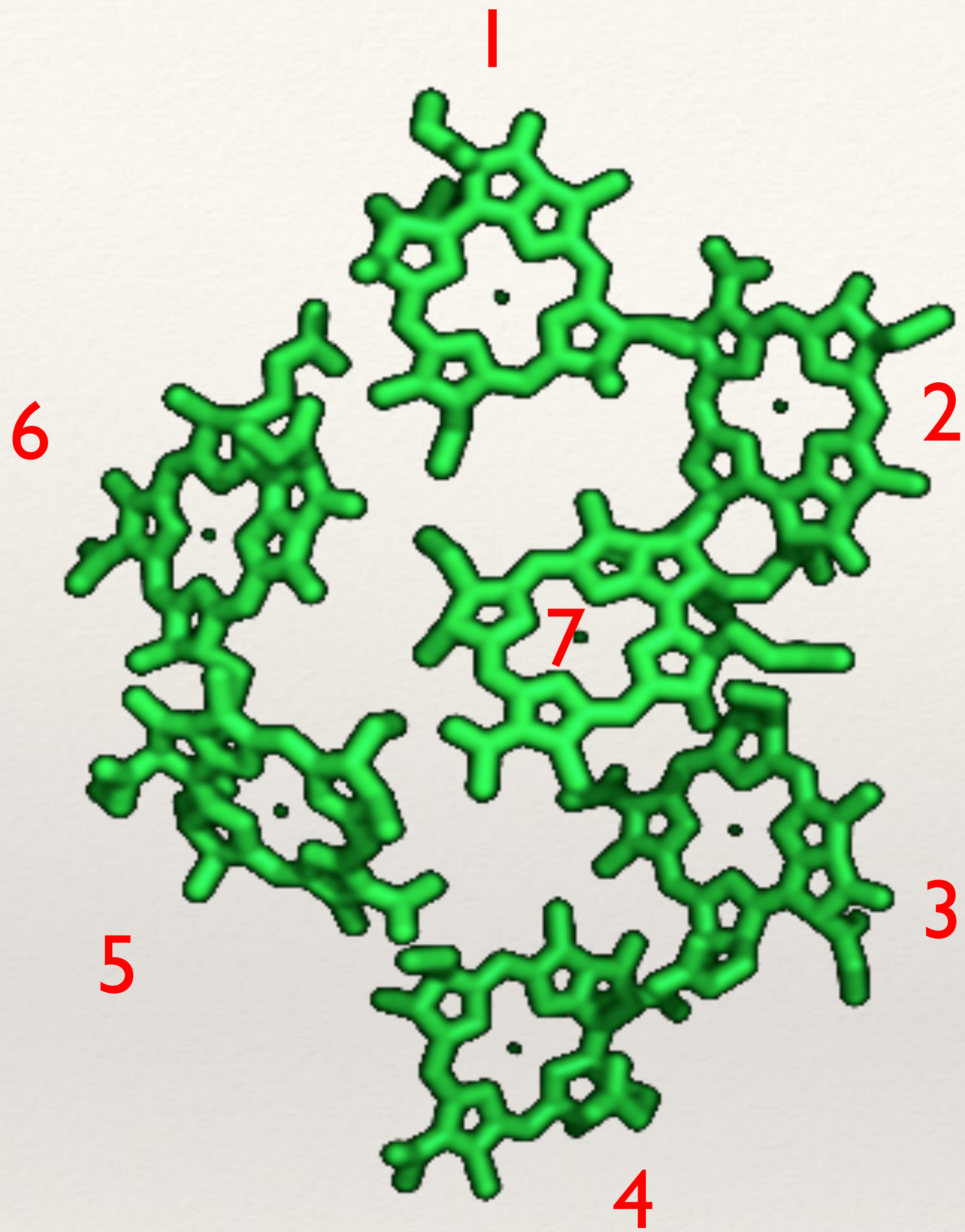


LUMO
HOMO
$\approx 12,000\ cm^{-1}$

The Hamiltonian



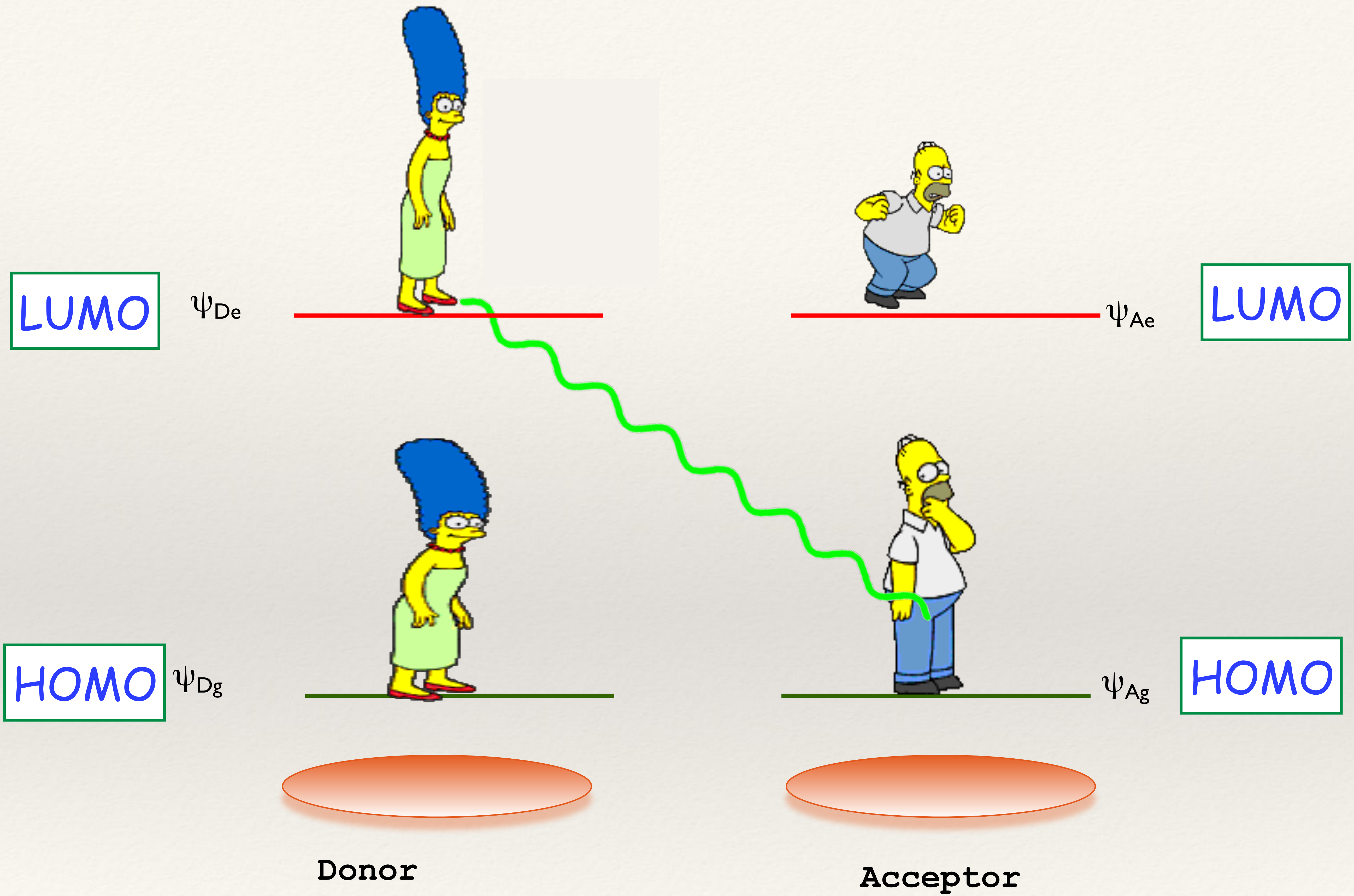
11.3 to 14.4 Å
1
6
2
7
5
3
4
6
2
5
7
1
4
3



$$\frac{H_{closed}}{cm^{-1}} = \begin{bmatrix} 240 & -87.7 & 5.5 & -5.9 & 6.7 & -13.7 & -9.9 \\ & 315 & 30.8 & 8.2 & 0.7 & 11.8 & 4.3 \\ & & 0 & -53.5 & -2.2 & -9.6 & 6.0 \\ & & & 130 & -70.7 & -17.0 & -63.3 \\ & & & & 285 & 81.1 & -1.3 \\ & & & & & 435 & 39.7 \\ & & & & & & 245 \end{bmatrix}$$

$(distance)^{-3}$

Why $(\text{distance})^{-3}$?


LUMO
ψ_{De}
ψ_{Ae}
LUMO
HOMO
ψ_{Dg}
ψ_{Ag}
HOMO
Donor
Acceptor

Matrix element =

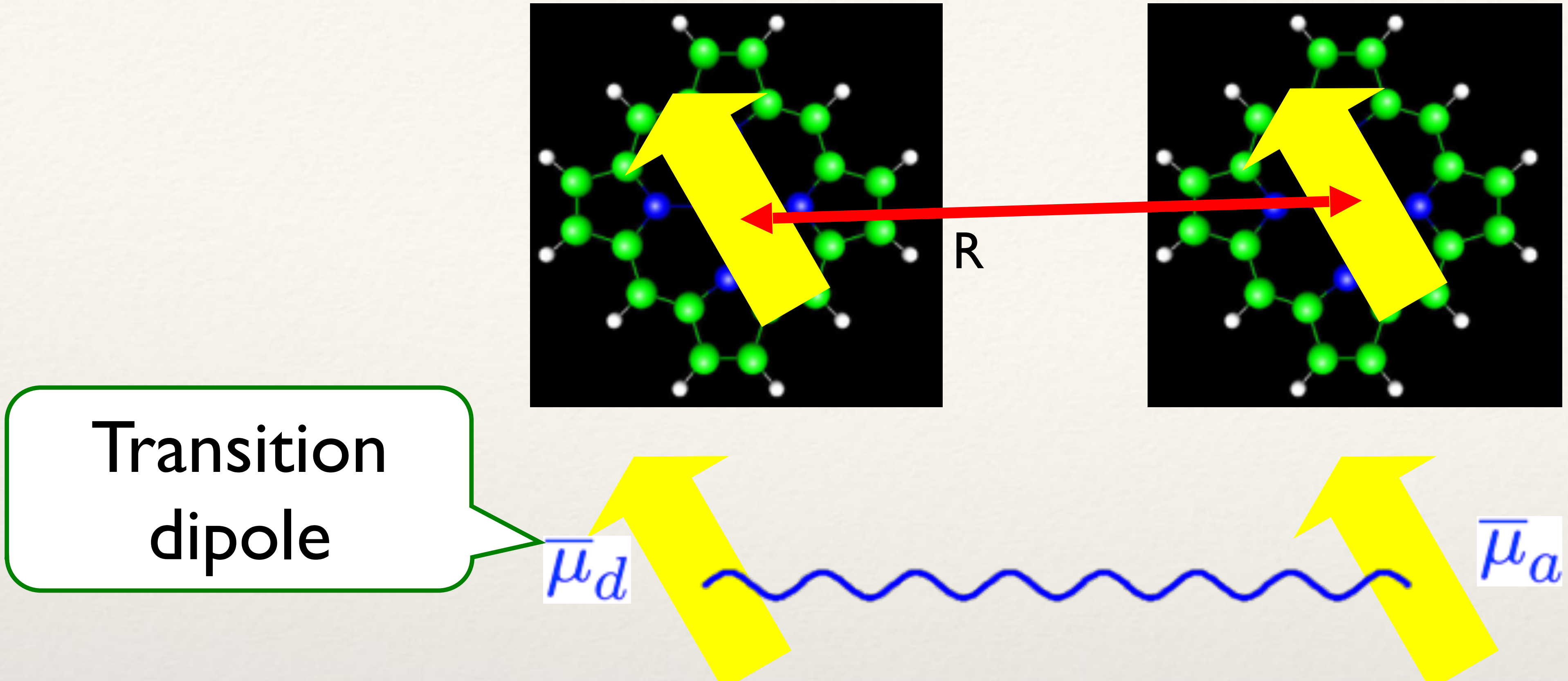
Transition density of donor!

Transition density of acceptor

$$\int d\mathbf{r}_1 \int d\mathbf{r}_2 \, \frac{\psi^*_{De}(\mathbf{r}_1)\psi_{Dg}(\mathbf{r}_1)\psi^*_{Ag}(\mathbf{r}_2)\psi_{Ae}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}$$

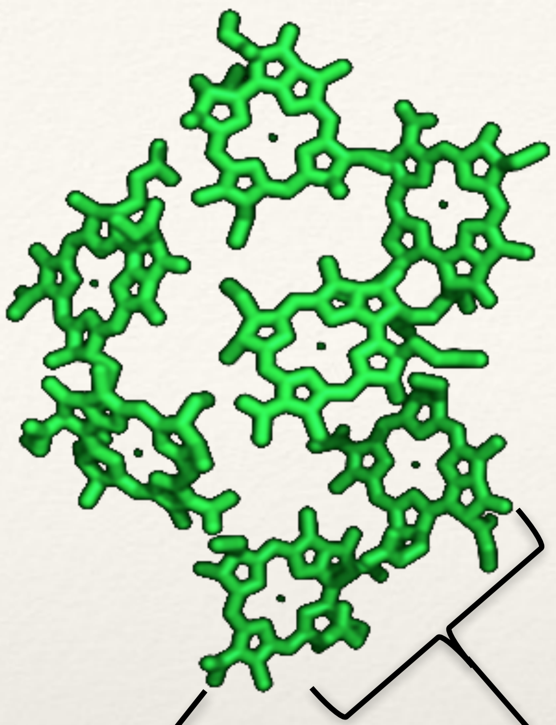
$$\psi^*_{De}(\mathbf{r}_1)\psi_{Dg}(\mathbf{r}_1) \Longleftrightarrow \psi^*_{Ag}(\mathbf{r}_2)\psi_{Ae}(\mathbf{r}_2)$$

Electrostatic interaction



$$H_{da} \propto \frac{1}{R^3}$$

$$Rate \;\propto\; H_{da}^2 \;\propto\; \frac{1}{R^6}$$



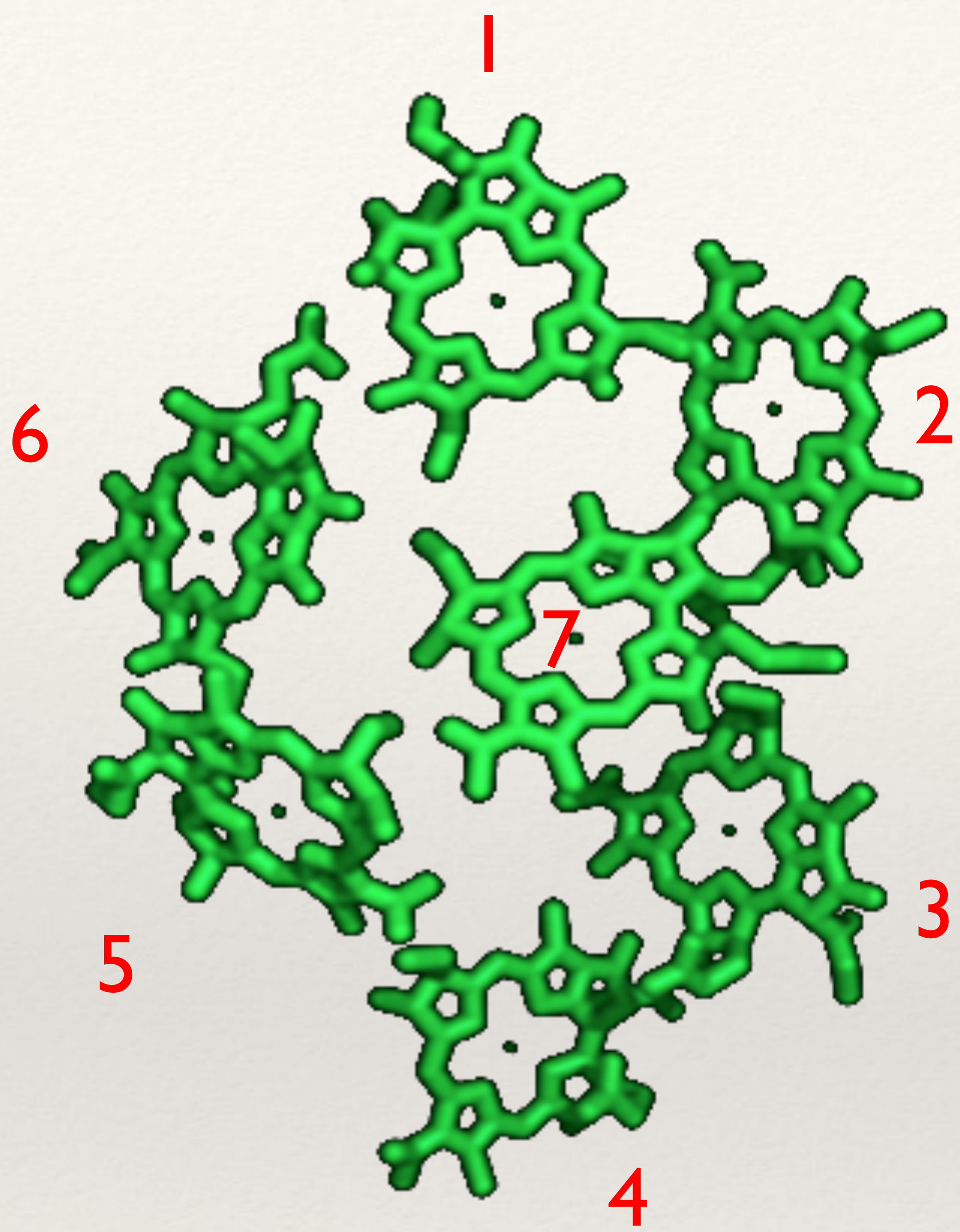
Exciton energy on j^th site

Hopping between j and i

$$H_{el} = \sum_{j} \epsilon_j |j\rangle\langle j| + \sum_{i,j} (V_{ij}|i\rangle\langle j| + V_{ji}|j\rangle\langle i|)$$

$j = 1, \ldots 7$

$V_{ij} \sim \frac{1}{R^3}$



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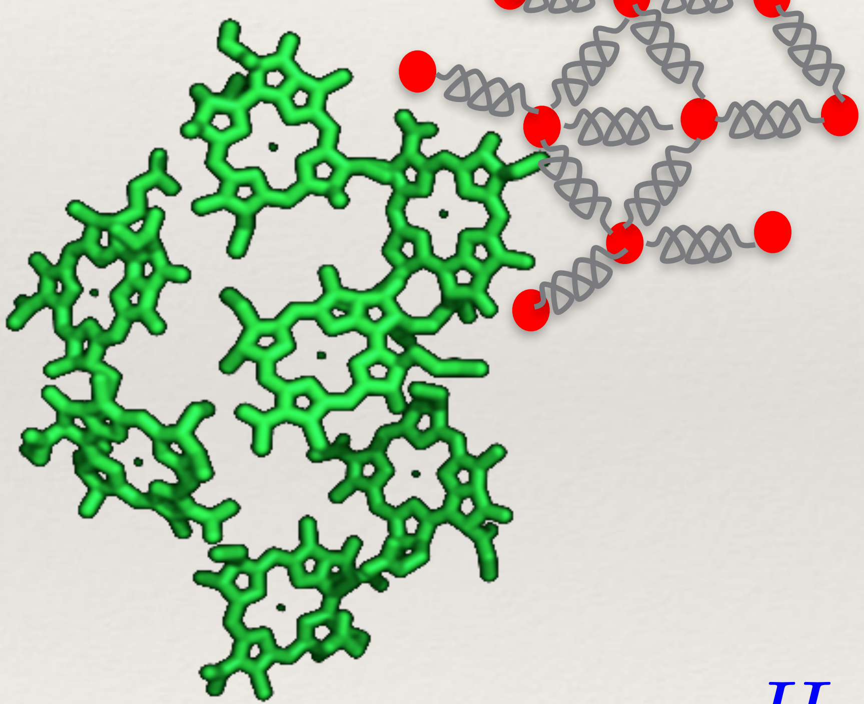
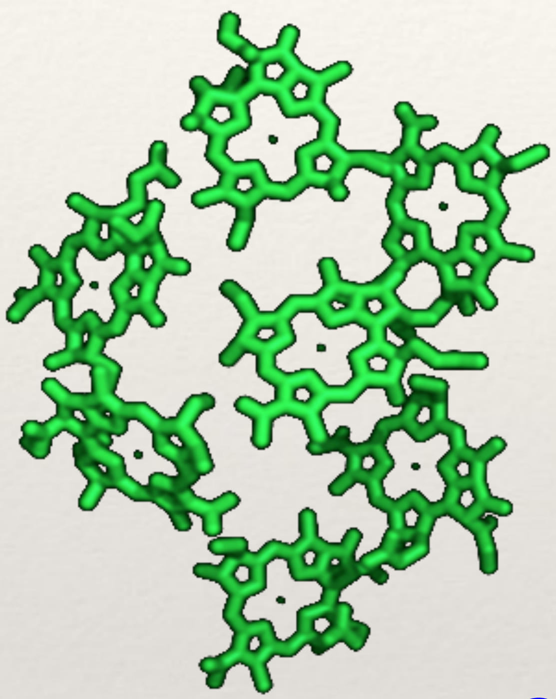
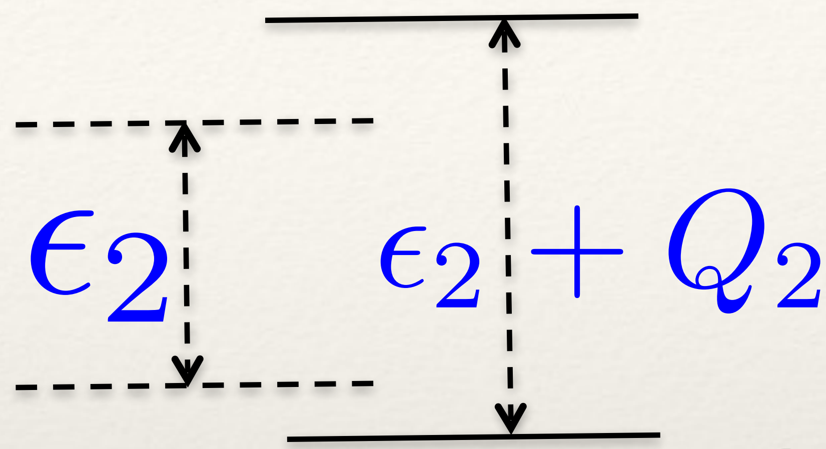
The Environment

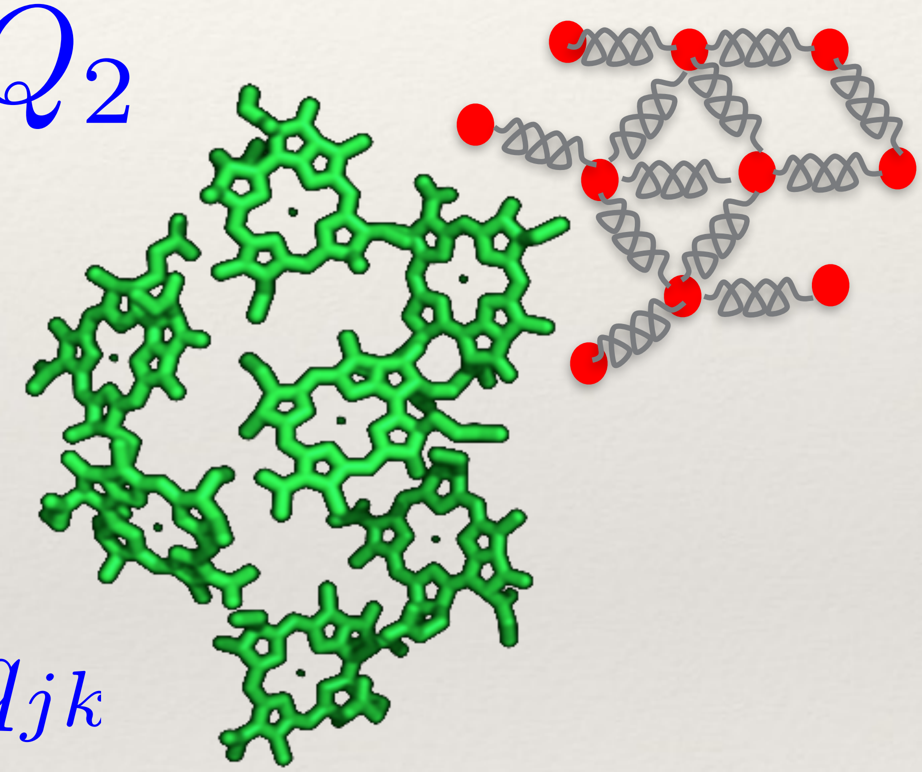


$$H_{ph,j} = \frac{1}{2}\sum_k \left(\frac{\hat{p}_{jk}^2}{m_{jk}} + m_{jk}\omega_{jk}^2 q_{jk}^2\right)$$

Coupling with environment



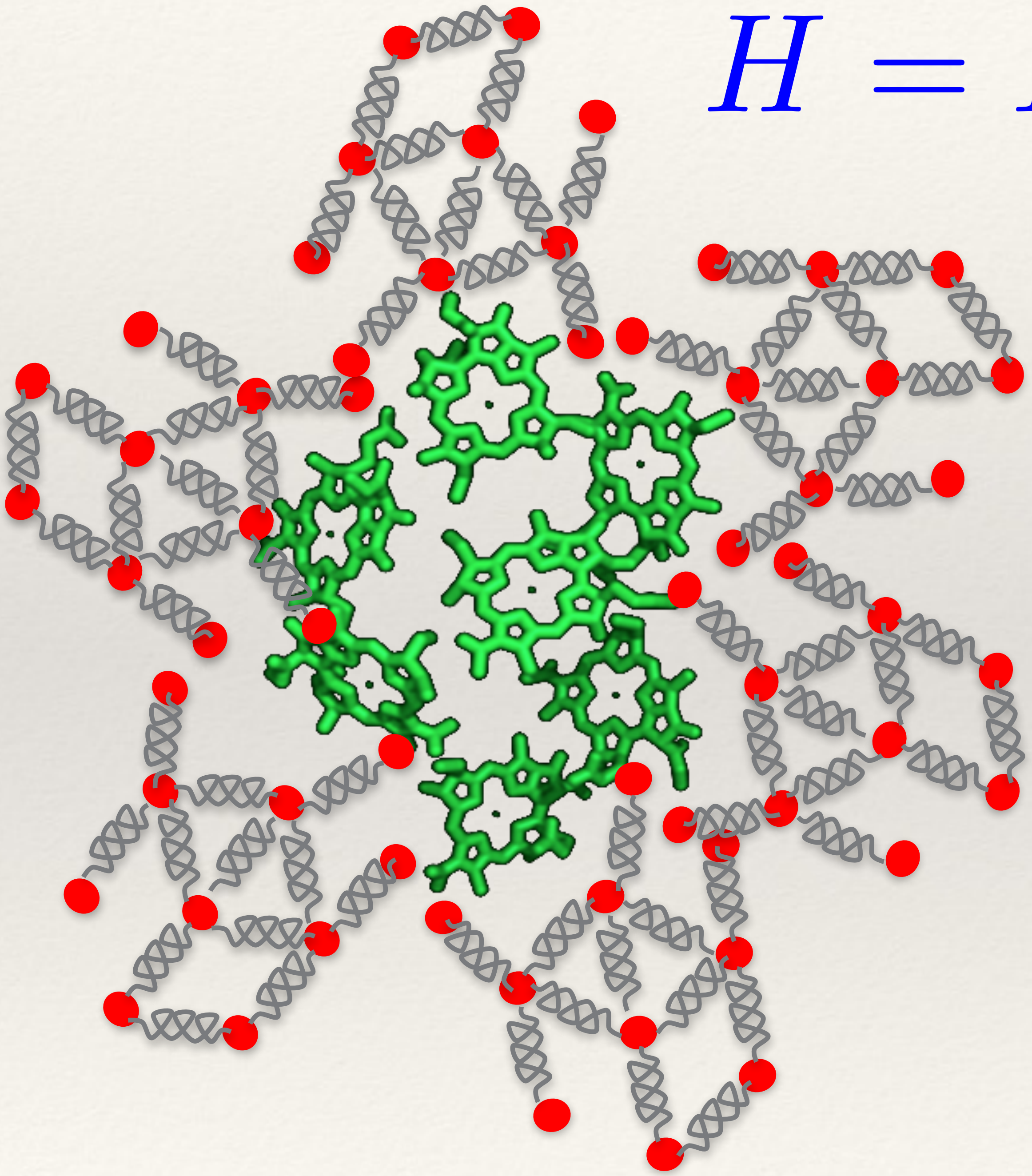




$$Q_j = \sum_k m_{jk} \nu_{jk} q_{jk}$$

$$\mathbf{Q} = (Q_1, Q_2, \ldots . Q_7)$$

$$H_{el-ph}(\mathbf{Q}) = \sum_j Q_j |j\rangle\langle j|$$



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

Initial Conditions

Initially excitation on a particular site, say, site 1

Calculate the time evolution!

The time evolution

Previous Work ($\rightarrow \infty$)

$$H_{el-ph}(\mathbf{Q}) = \sum_j Q_j |j\rangle\langle j|$$

Decoherence and population relaxation caused by the this term - NO small parameter!

$$\lambda, \ V_{ij} \ and \ \Delta\epsilon : \ comparable$$

Ishizaki and Fleming, PNAS
(eq. for density matrix, trunated)

Nalbach et al Physical Review E (2011)
(numerical, exact)

The adiabatic basis

Pallavi Bhattacharyya and KLS: PHYSICAL REVIEW E 87, 062712 (2013)

P. Bhattacharyya and KLS: J. Phys. Chem. A   (2013)

Hamiltonian in the adiabatic basis

Interaction

$$H_{ad}(\mathbf{Q})$$
$$= \sum_j (\epsilon_j + Q_j)|j\rangle\langle j| + \sum_{i,j} V_{ij}|i >< j| + h.c.$$

$$H_{ad}(\mathbf{Q})|m(\mathbf{Q})\rangle = \varepsilon_m(\mathbf{Q})|m(\mathbf{Q})\rangle.$$

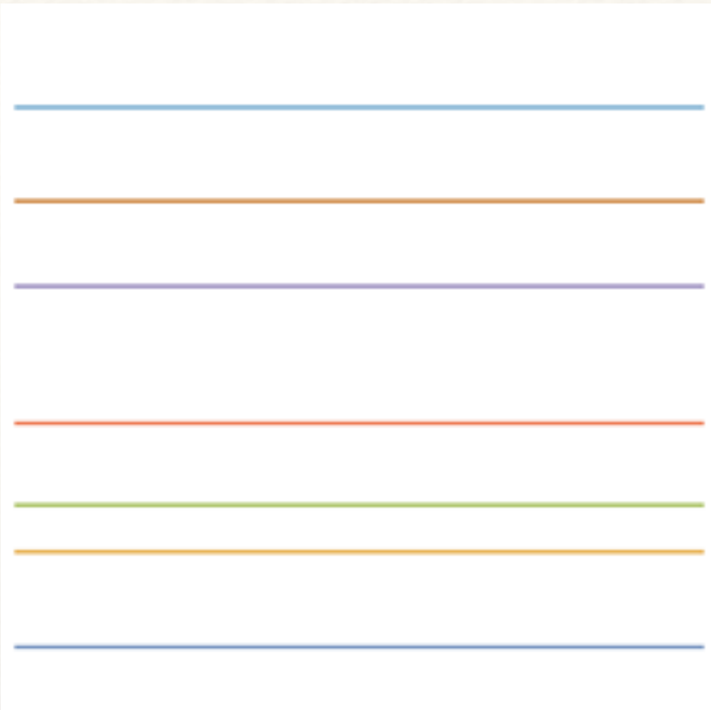
$$H = \sum_m \varepsilon_m(\mathbf{Q})|m(\mathbf{Q})><m(\mathbf{Q})| + H_{ph}$$

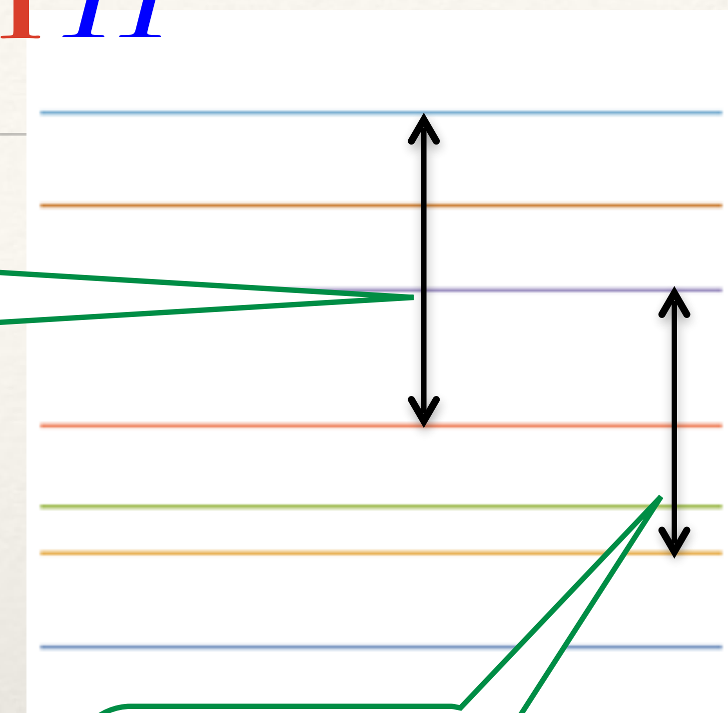
$$T|m(\mathbf{Q})>=|m(\mathbf{0})>$$

Work with

$$\tilde{H} = THT^{\dagger}$$

Different terms in $\tilde{H}$





Transitions between levels

$$\tilde{H} = \sum_m \varepsilon_m(\mathbf{Q}) |m><m| + H_{na}$$

Levels fluctuate

Causes decoherence

$$+H_{ph}$$

Time Evolution

$$\left|\frac{\partial \varepsilon_m(\mathbf{Q})}{\partial Q_i}\right| \ll 1$$

$$< \ 0.01$$

Expand $\epsilon_m(\mathbf{Q})$ and keep terms linear in $\mathbf{Q}$

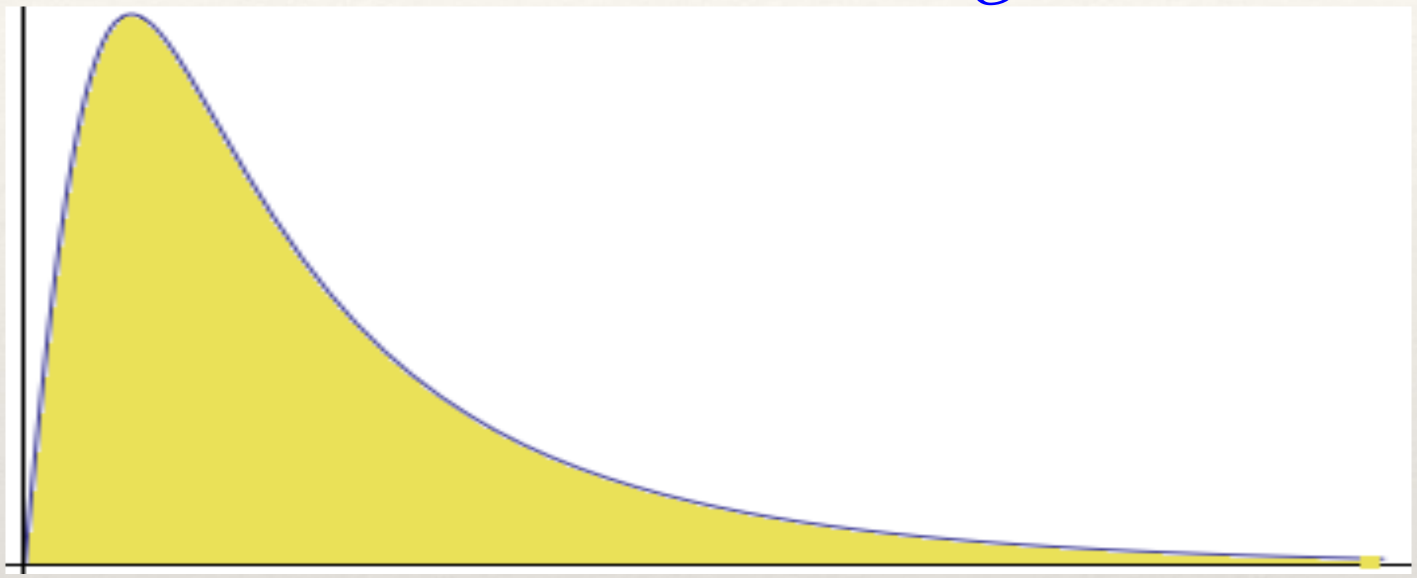
$$\tilde{H} = \sum_m \varepsilon_m(\mathbf{Q})|m><m| + H_{ph} + H_{na}$$

Accounted for by a Markovian Master equation

$$J_j(\omega) = \sum_k \frac{m_{jk}\nu_{jk}^2}{2\omega_{jk}} \delta(\omega - \omega_{jk}).$$

Spectral density

$$J(\omega) = \frac{2\lambda}{\pi} \frac{\omega\omega_c}{\omega^2 + \omega_c^2},$$



$$\lambda = \int_0^\infty d\omega J(\omega)/\omega.$$

Reorganization energy

$$\lambda = 35\ cm^{-1}\ and\ \omega_c^{-1} = 50\ fs$$

From Fleming et al.

Results

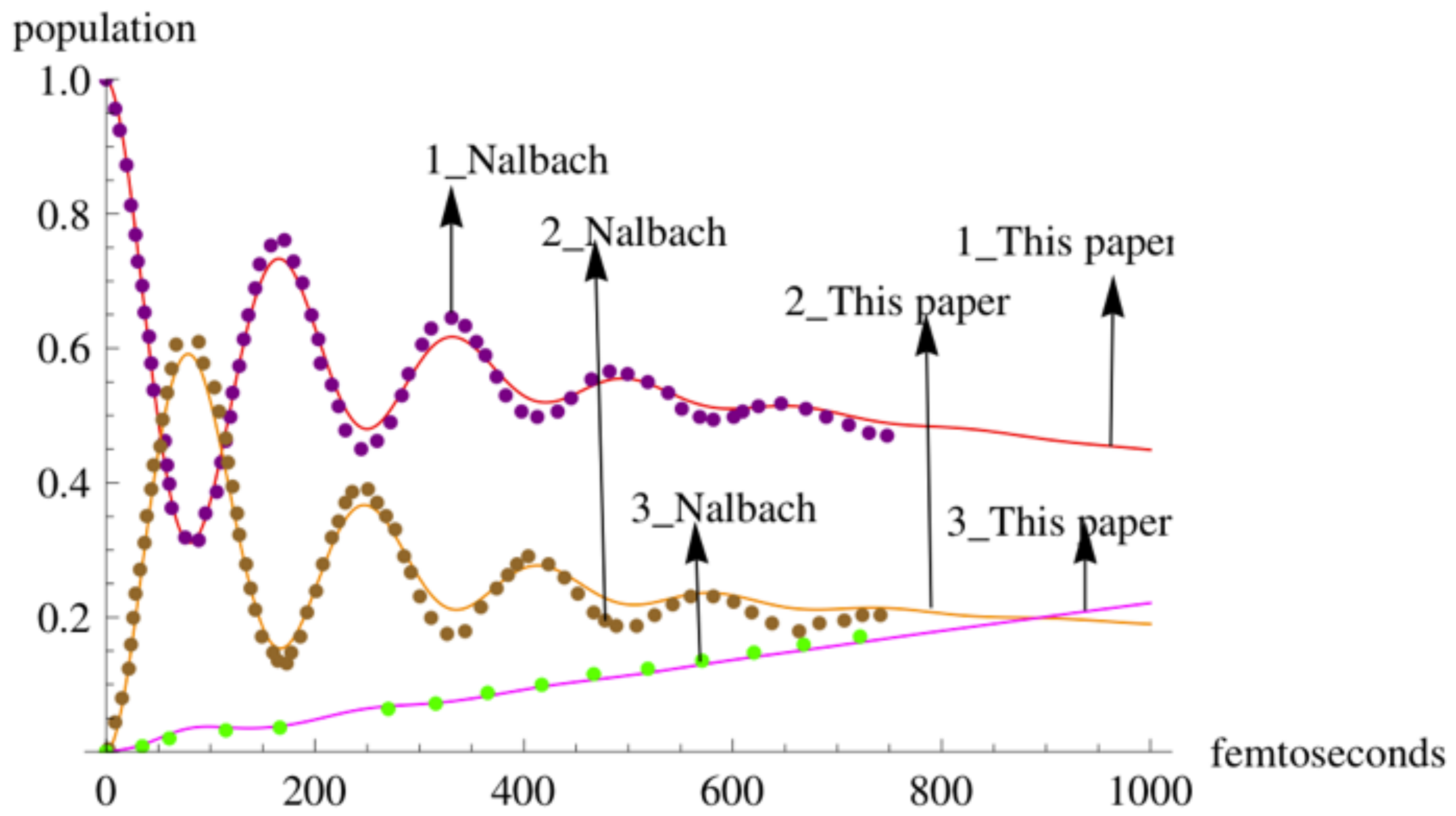
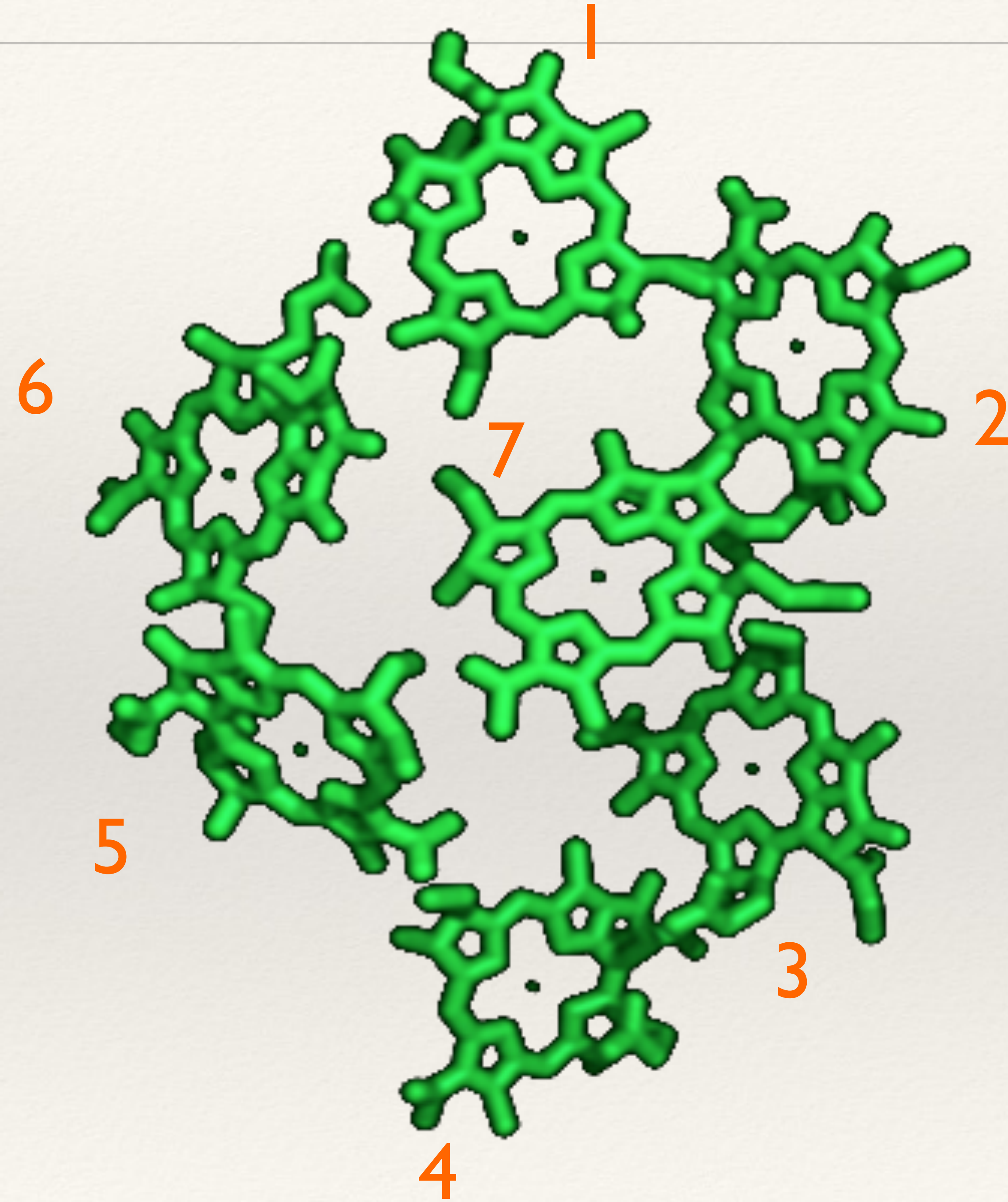
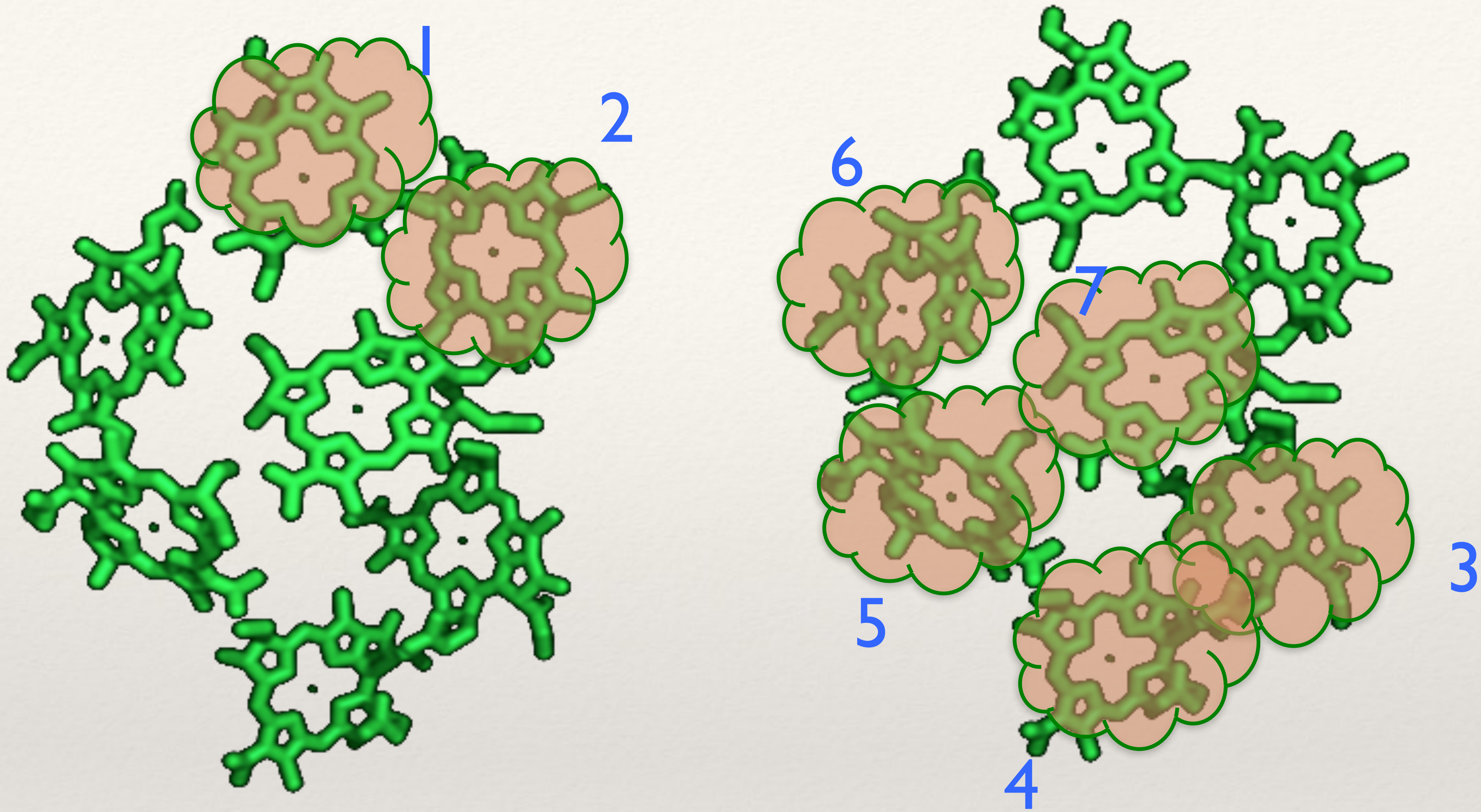


FIG. 1: Initial excitation on site 1 at 77 K; Comparison of our results with those of Nalbach *et al.* for chromophores 1,2 and 3.

Good agreement with exact results of Nalbach et al.

No Environment




1
2
6
7
3
5
4

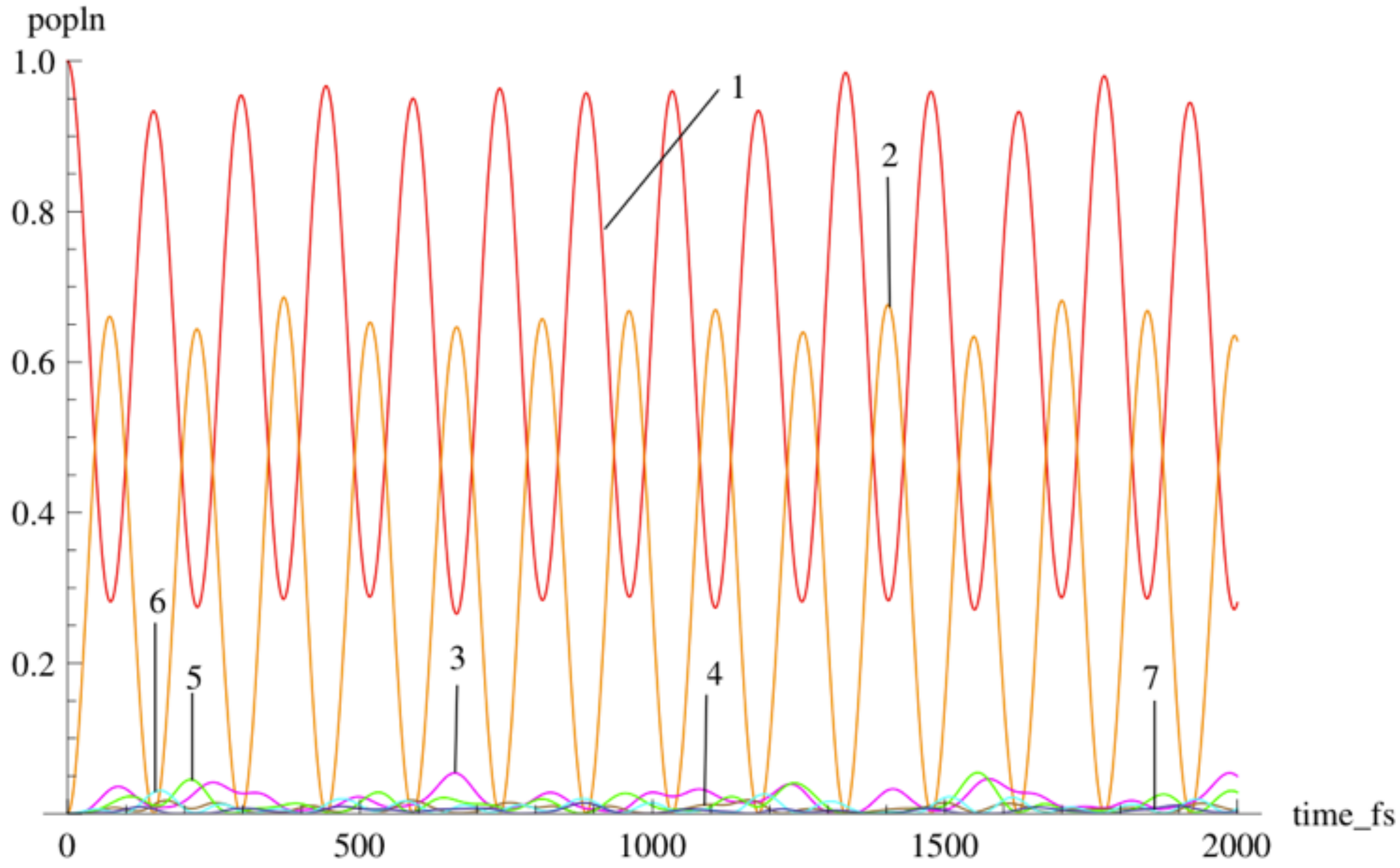
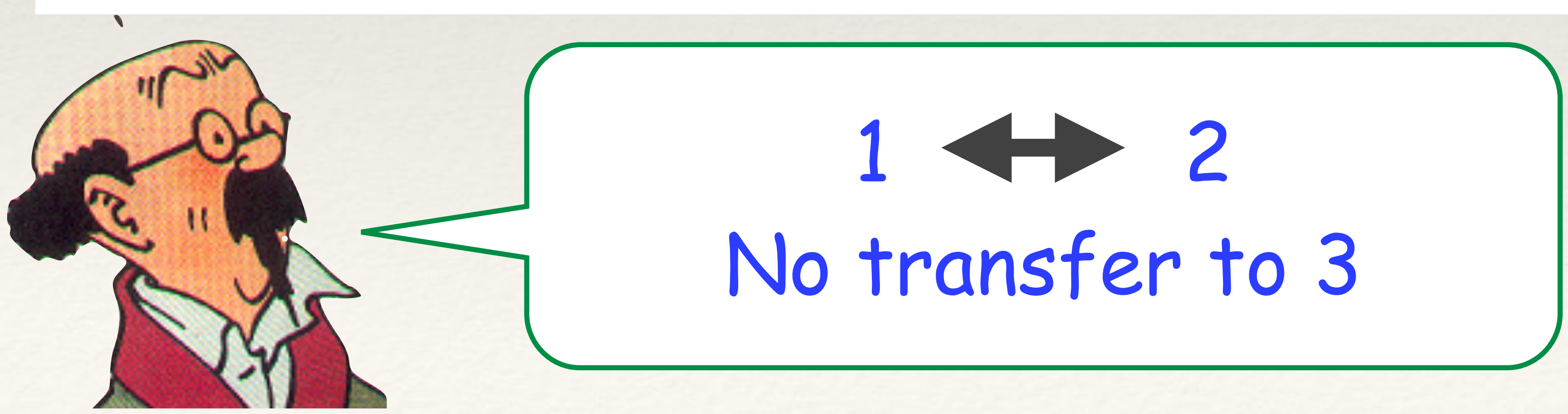


FIG. 1: Initial excitation on site 1; No Environment



With Environment

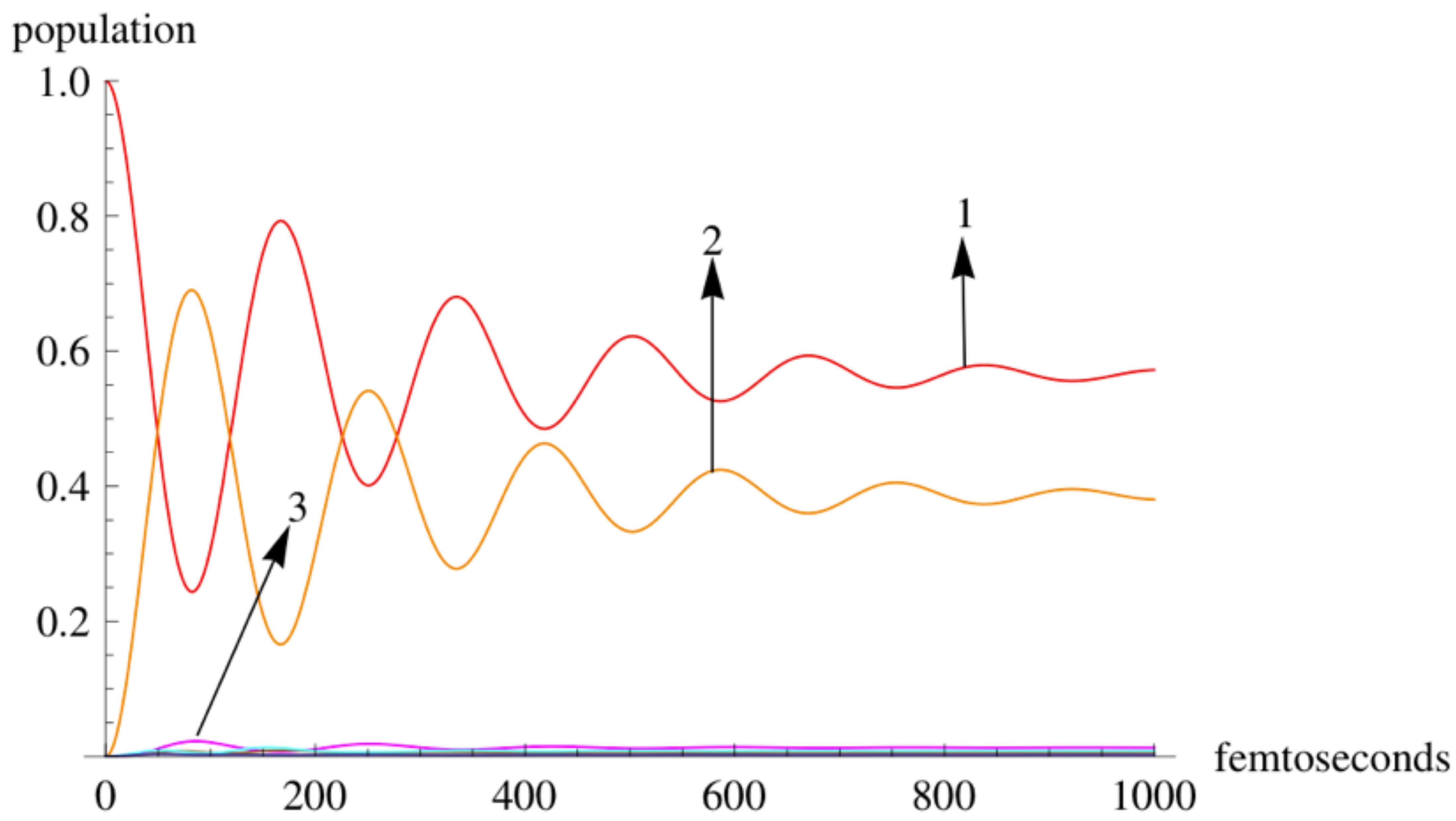
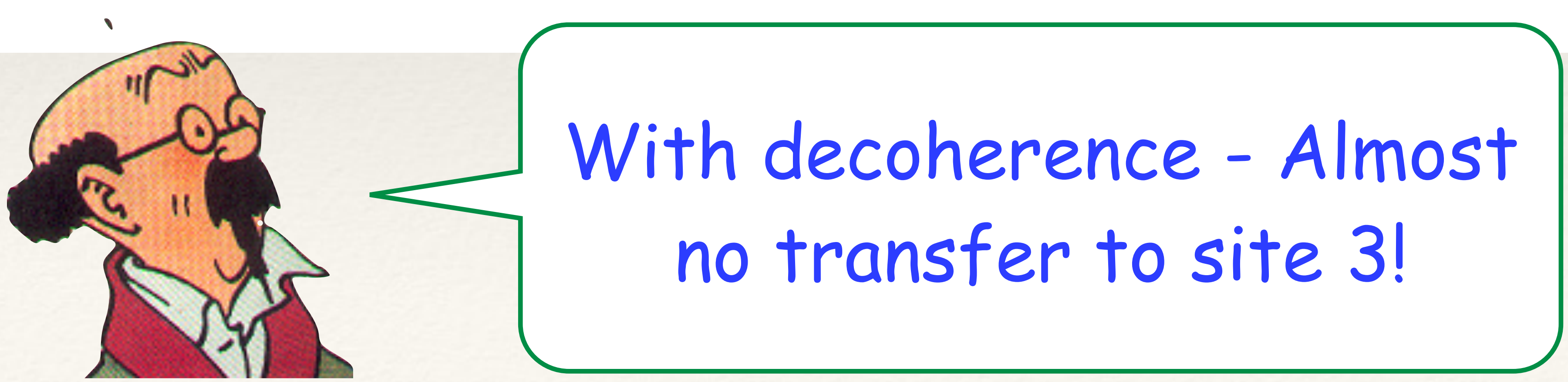
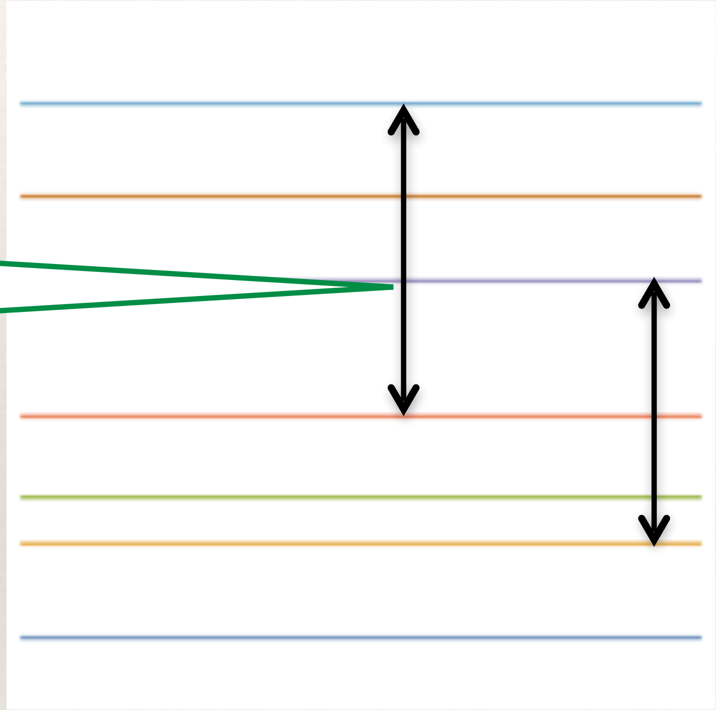


FIG. 2: Initial excitation on 1 at 77 K; Decoherence due to environment



Transitions between levels



Include H_{na}

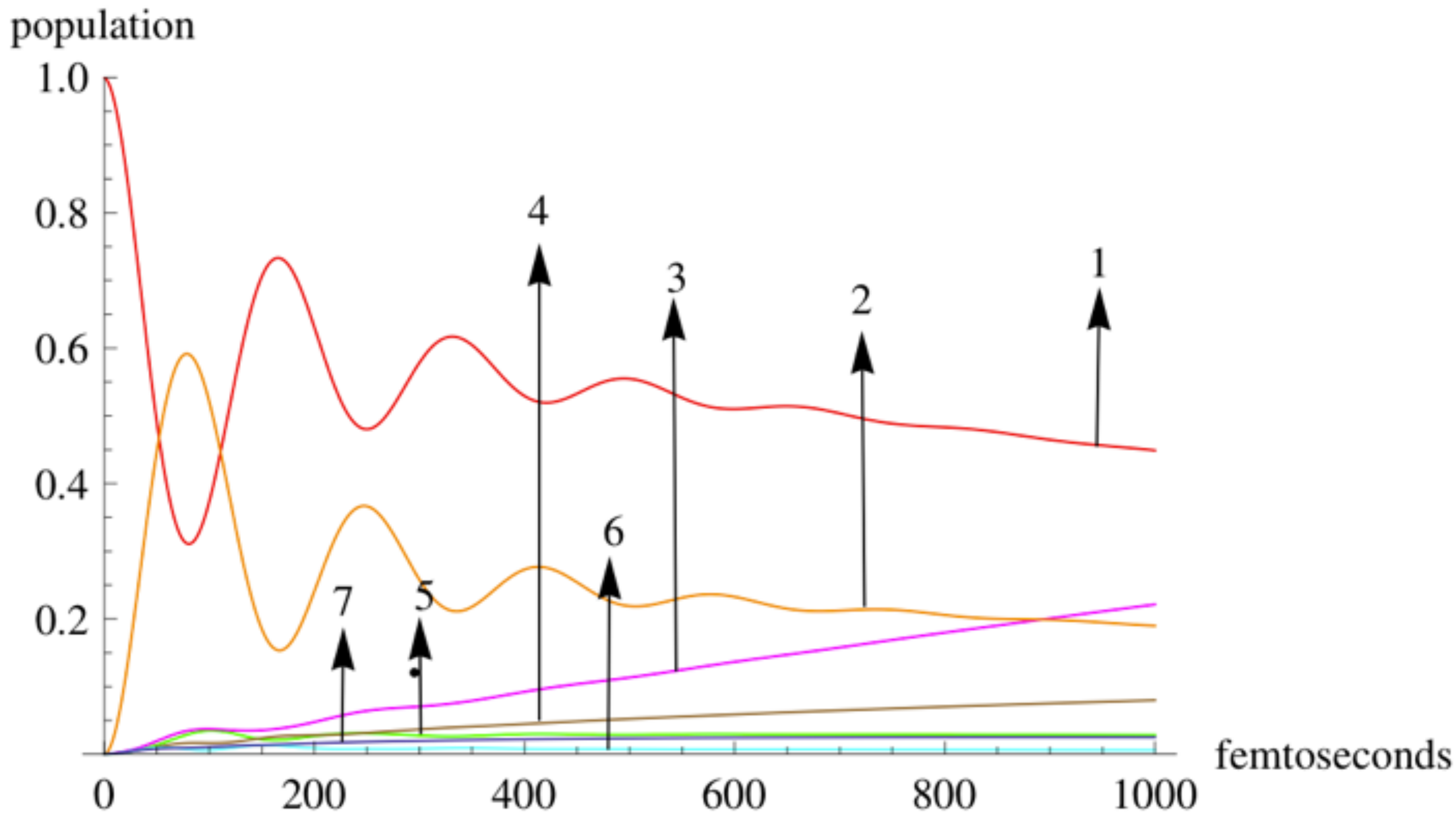


FIG. 3: Initial excitation on site 1 at 77 K; Decoherence and population relaxation due to environment

Population relaxation causes transfer to site 3

Environment ASSISTS!

300K: Results similar to 77K, but decay faster

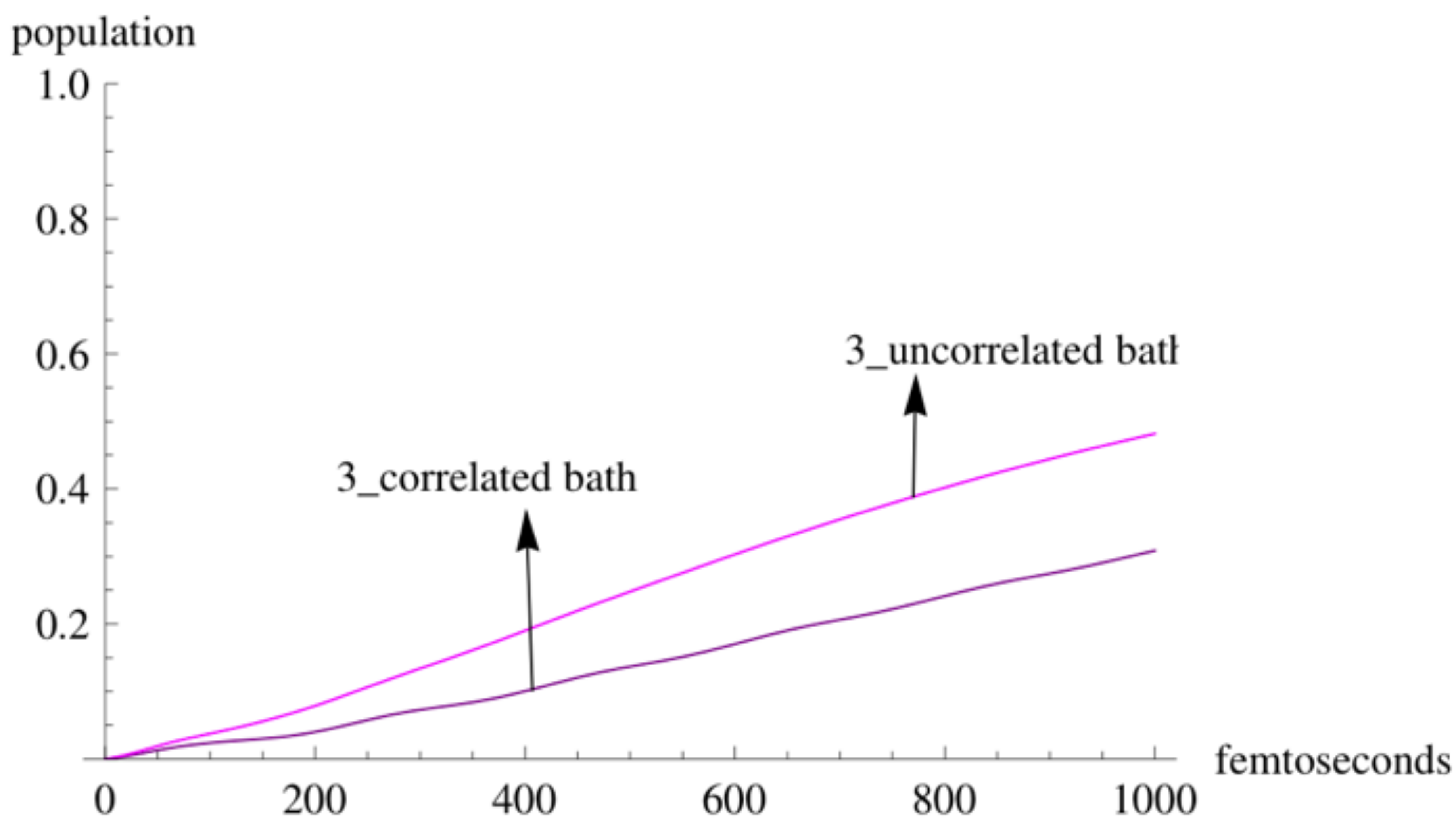
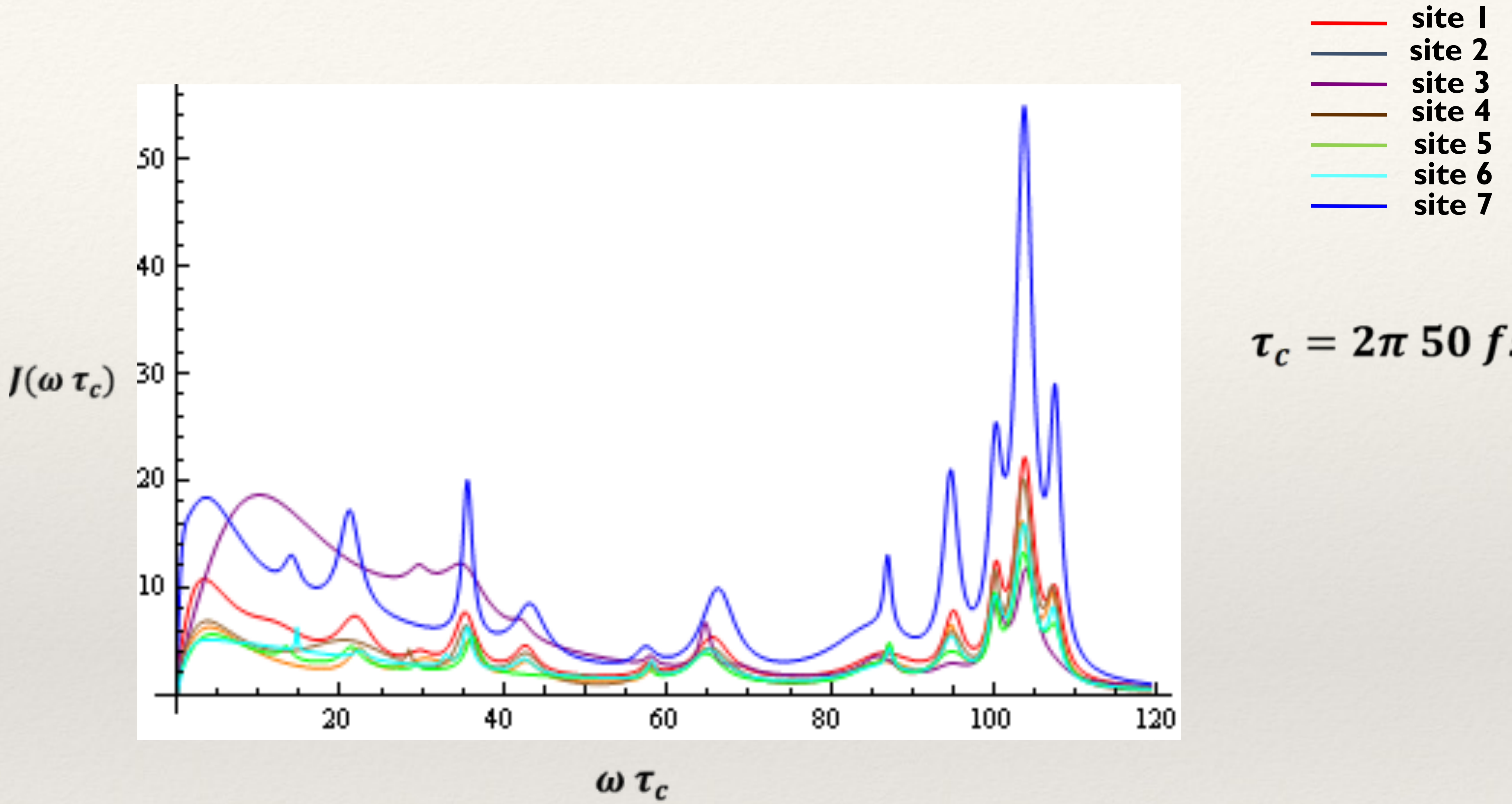


FIG. 11: Initial excitation on site 6 at 77 K; Decoherence and population relaxation due to environment; comparison of population evolution on site 3 for correlated and uncorrelated bath

Correlation between baths for different sites makes transfer less efficient!

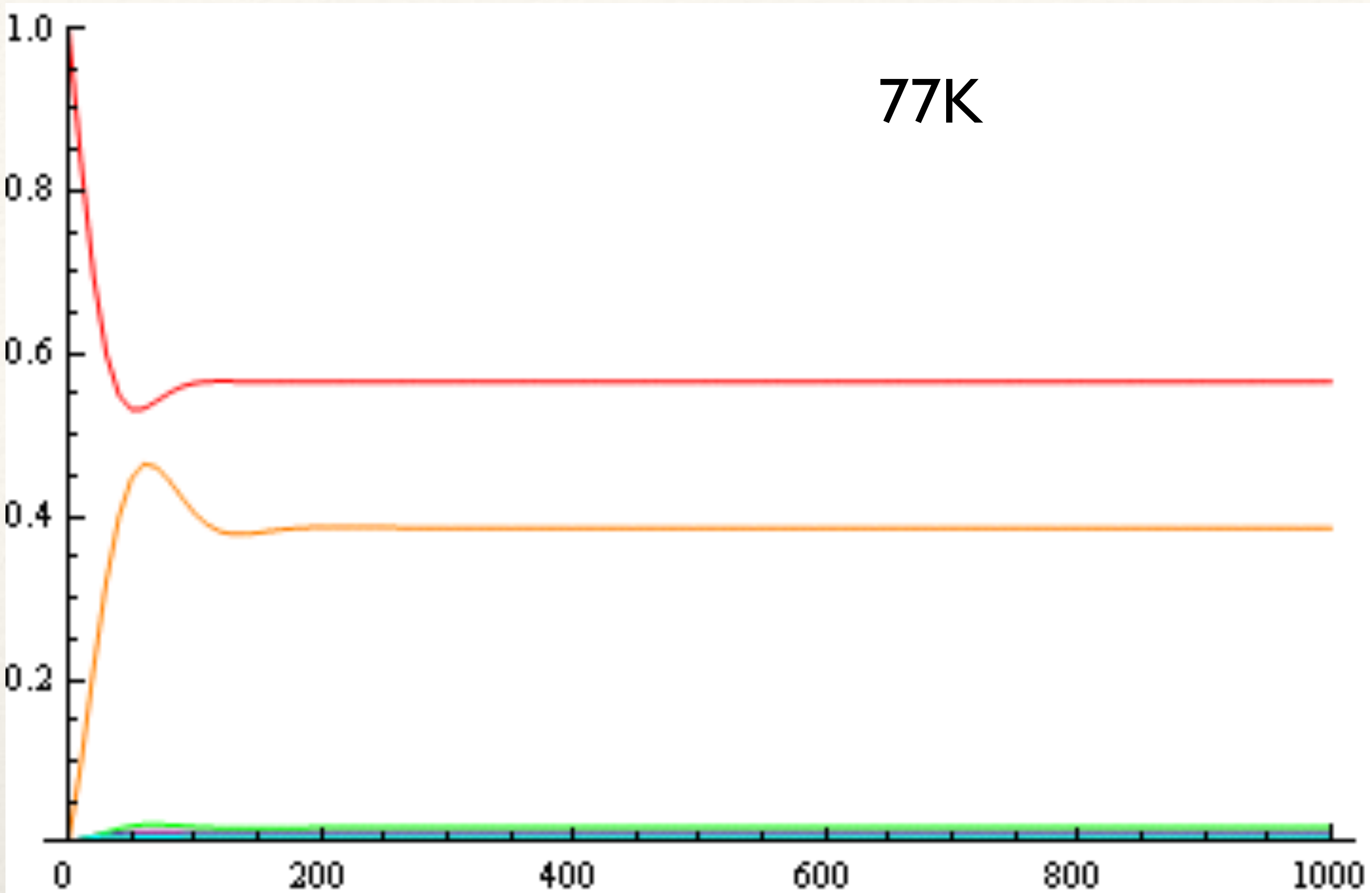
With spectral density from simulations

Spectral density by Olbrich and Kleinekathofer
(from MD simulations)



$\tau_c = 2\pi\ 50\ fs$

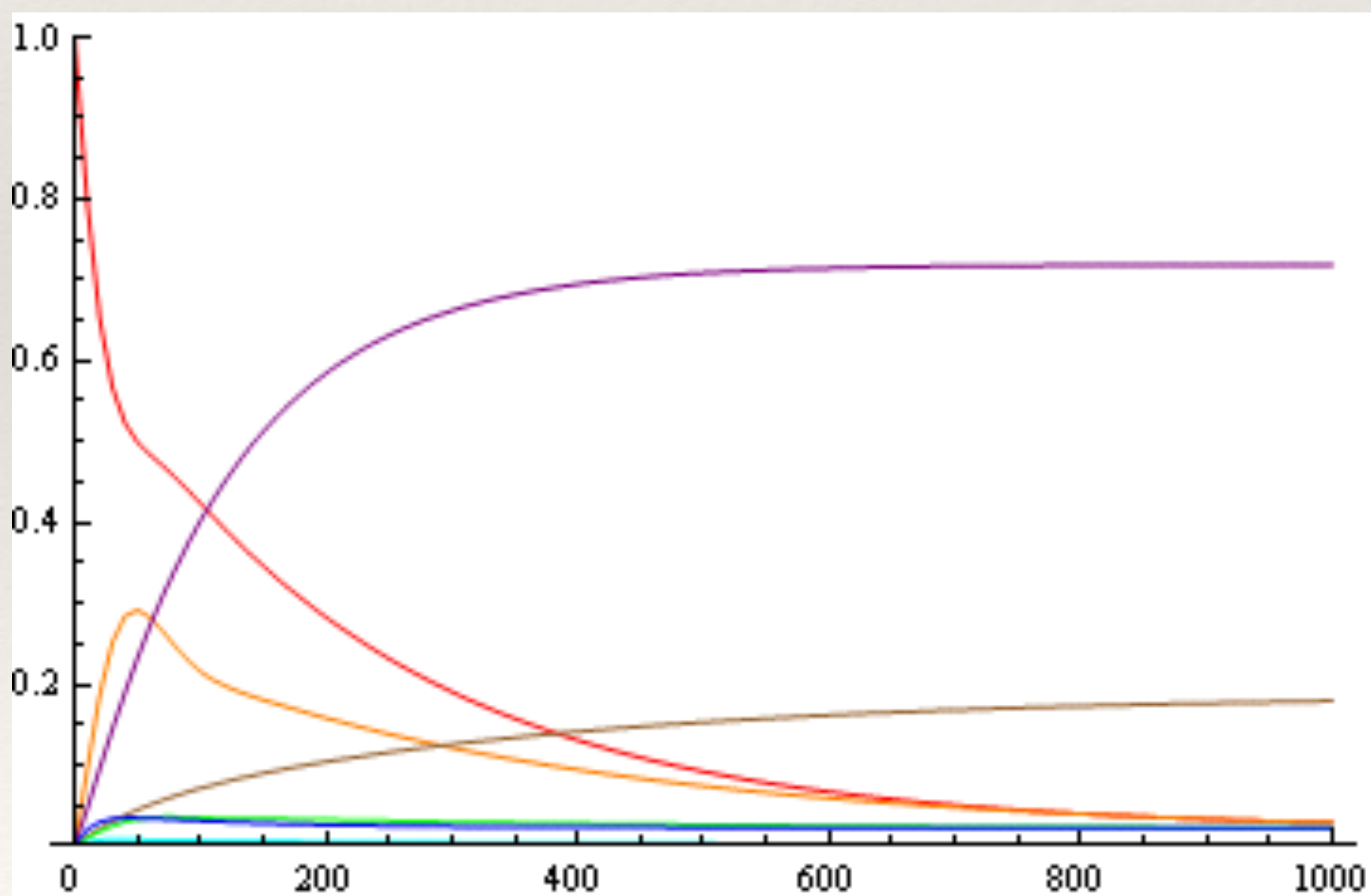
$$J_j(\omega) = \frac{2}{\pi}\tanh\left(\frac{\beta\hbar\omega}{2}\right) \times \left[\sum_{i=1}^{N_e} \frac{\eta_{ji}\gamma_{ji}}{\gamma_{ji}^2 + \omega^2} + \frac{1}{2}\sum_{i=1}^{N_o} \frac{\tilde{\eta}_{ji}\tilde{\gamma}_{ji}}{\tilde{\gamma}_{ji}^2 + (\omega - \tilde{\omega}_{ji})^2}\right]$$



population

femtoseconds

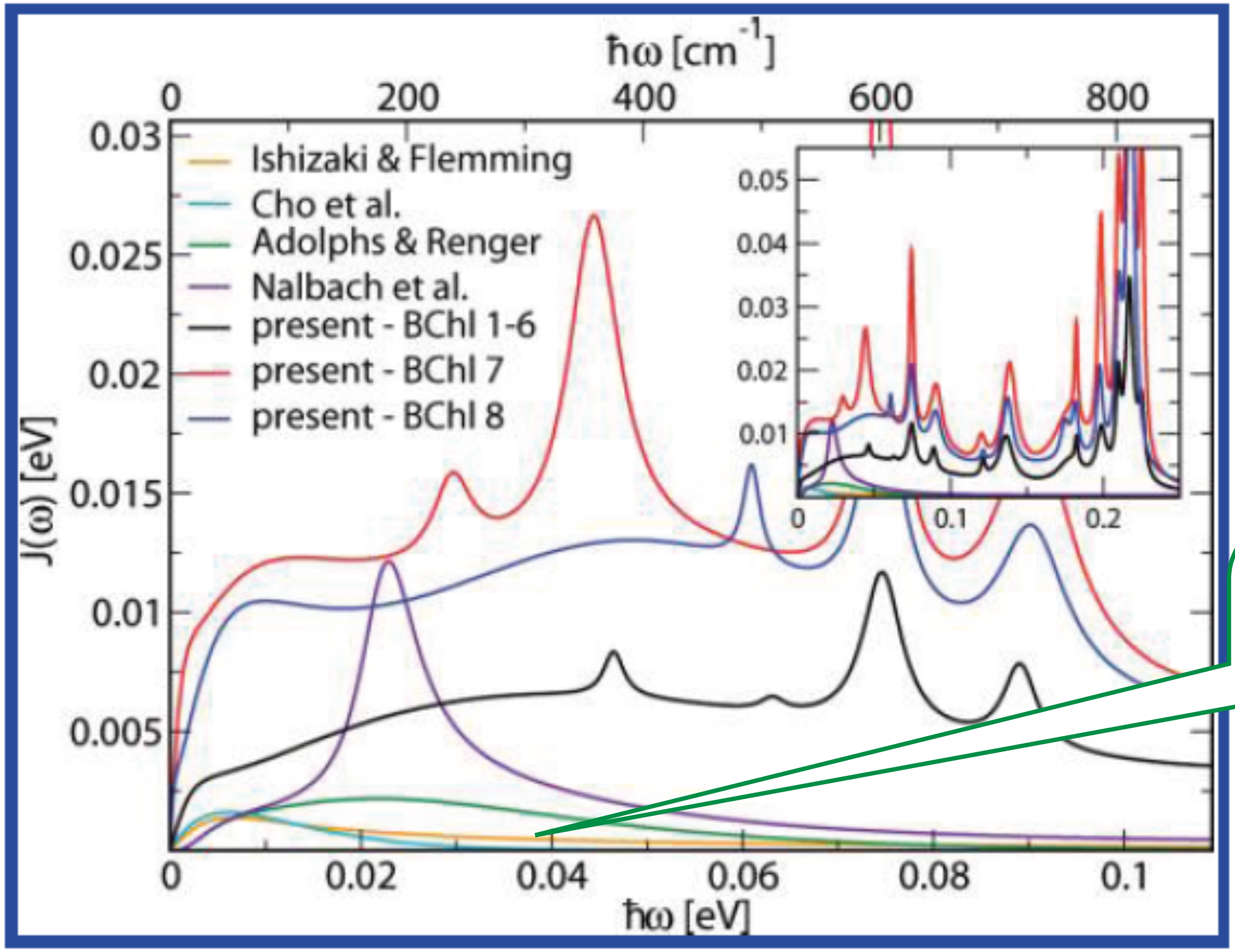
site 1
site 2
site 3
site 4
site 5
site 6
site 7



population

femtoseconds

Why this difference?



Spectral density of Fleming et al

Figure 6. Spectral densities for the FMO trimer determined in the present study compared to those of previous studies by Ishizaki and Fleming,[11] Cho et al.,[34] Adolphs and Renger,[33] as well as Nalbach et al.[19] The inset shows an enlarged energy and spectral density range.

Summary

Analytic approach

Adiabatic basis, Decoherence and relaxation separated

Excellent agreement with exact results

Easily extended to larger systems

Environment enhances the transfer to reaction site!

Coherence short-lived for realistic couplings!

Correlated bath makes transfer less efficient

OUR BIASED VIEW! There are other papers that differ!

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Thank you!