

Superradiance Transition in Photosynthetic Light-Harvesting Complexes

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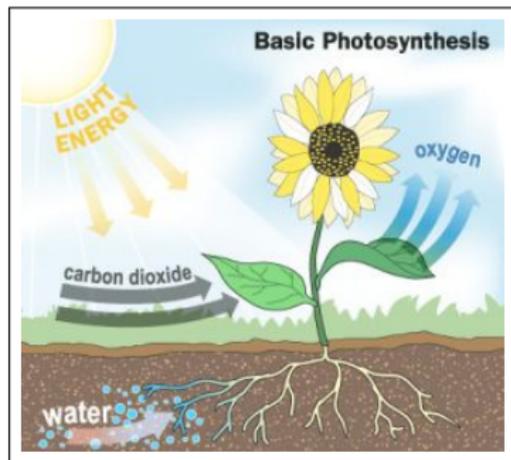
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Benasque, 8th International Workshop on Disordered
Systems



MOTIVATIONS : Evidence for Quantum Coherence in Photosynthesis



Evidence for wavelike energy transfer through quantum coherence in photosynthetic complexes,

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

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

E. Collini et al., Nature **463**, 644 (2009).

Long-Lived Quantum Coherence in Photosynthetic Complexes at Physiological Temperature,

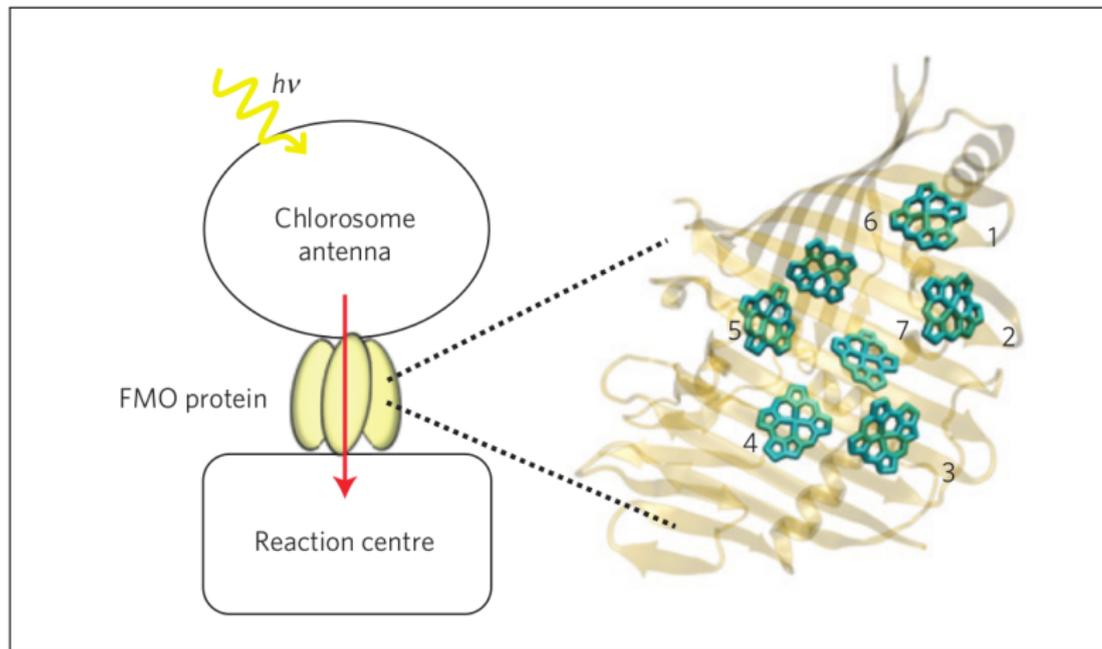
G. Panitchayakoon et al., PNAS, **107**, 12766 (2010).

ANTENNA (capture the photon) → Creation and Transport of excitons (pair electron-hole) → Reaction Center (Charge Separation)

Fundamental Questions

- 1 Transport efficiency can be up to 99%
- 2 **HOW** coherence is maintained ?
M. Sarovar, A. Ishizaki, G.R.Fleming and K.B.Whaley,
Nature Physics **6**, 462 (2010).
- 3 **WHY** quantum coherence ? (**SUPERRADIANCE ?**)
S. Lloyd and M. Mohseni, New J. Phys. **12**, 075020 (2010);
G.D. Scholes, Chem. Phys. **275**, 373 (2002).

The light-harvesting apparatus of green sulphur bacteria and the FMO protein.



Relevant Time scales

- Exciton recombination time (number of excitons conservation) ~ 1 ns
- Energy relaxation of an excitation at ambient temperature ~ 1 ps
- Exciton dephasing ~ 100 fs
- Phonon correlation time ~ 50 fs

Rebentrost et al. New J. Phys. (2009)

MODELLING THE FMO COMPLEX

Single exciton approximation:

$|i\rangle$ denote the excitations at site i . E_m are the site energies and J_{mn} , are the Coulomb couplings of the transition densities of the chromophores, often taken to be of the (Forster) dipole-dipole form:

Tight Binding Hamiltonian:

$$H_0 = \sum_{i=1}^7 E_i |i\rangle \langle i| + \sum_{i,j} (J_{i,j} |i\rangle \langle j| + h.c.)$$

Typically $|E_i - E_j| \sim J_{ij} \sim 100 \text{ cm}^{-1}$

$$J_{i,j} = \frac{C}{R_{i,j}^3} \left(\vec{\mu}_i \vec{\mu}_j - \frac{3}{R_{i,j}^2} (\vec{\mu}_i \vec{R}_{i,j})(\vec{\mu}_j \vec{R}_{i,j}) \right), \quad C|\mu|^2 = 134000 \text{ cm}^{-1} (A^0)^3$$

Disordered system : Exciton States are localized



- PHOTON ENVIRONMENT: DISSIPATION
- REACTION CENTER: DISSIPATION
- PHONON ENVIRONMENT 1 Dephasing due to classical noise
- PHONON THERMAL BATH 2 (with Gibbs relaxation)

While the latter two points have been studied within the standard master equation approach (Haken-Strobl Master equation and Lindblad under Born-Markov approximation), for the first two points we use the **Effective non-Hermitian Hamiltonian**.

ID for non HERMITIAN HAMILTONIAN

- 1 When it can be applied ? N intrinsic states, $|i\rangle$, coupled to M open channels, $|c, E\rangle$ with transition amplitude $A_i^c(E)$
- 2 Advantages : it is non-Perturbative and ideal to study Superradiance
- 3 Where it has been applied? Nuclear Physics, cold atoms, quantum transport in Mesoscopic electron system.
- 4 To quote, but a few, FESHBACH, WEIDENMULLER, ZELEVINSKY, ROTTER and collaborators.

Effective Hamiltonian and Superradiance

The effective Hamiltonian is:

$$H_{\text{eff}} = H_0 + \Delta - \frac{i}{2}W$$

with

$$W_{i,j} = 2\pi \sum_c A_i^c A_j^c$$

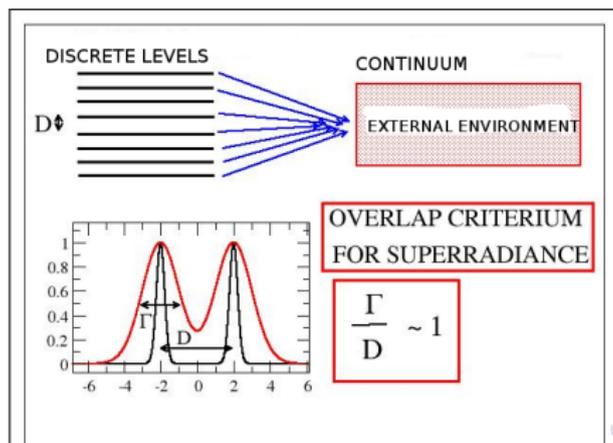
and complex energies

$$\mathcal{E}_k = E_k - \frac{i}{2}\Gamma_k$$

where Γ_k are the decay widths and c are the decay channels.

What is Superradiance?

- Discrete quantum systems coupled with environment described by a continuum of states.
- Effect of opening: Energy Shift and Finite Lifetime.
- At weak coupling, all internal states are similarly affected by the opening: lifetime decreases as the coupling increases.
- Beyond some critical value, a few states become short-lived states, leaving all other (long-lived) states effectively decoupled from the environment.



Effective Hamiltonian without Phonon Bath

- PHOTON ENVIRONMENT: DISSIPATION
- REACTION CENTER: DISSIPATION

$$H_{\text{eff}} = H_0 - iW, \text{ with } W_{i,j} = \sum_c A_i^c A_j^c$$

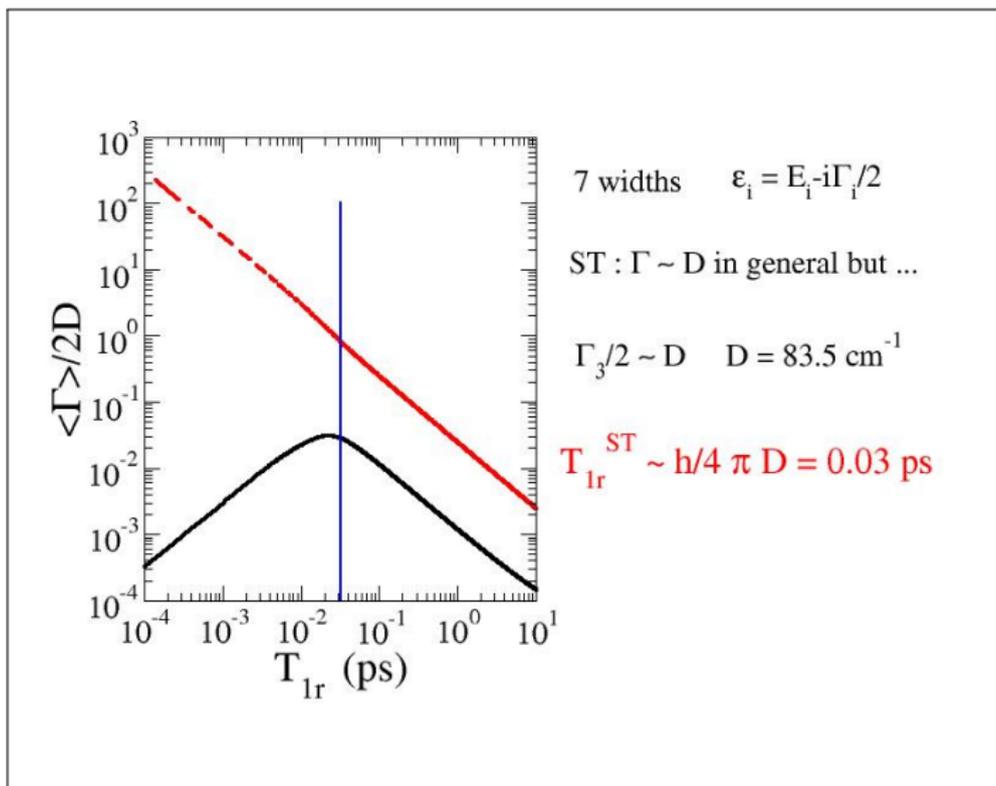
Phonon Bath: $A_i^j = \sqrt{\frac{\hbar}{2T_1}}$ with $T_1 = 1$ ns.

Reaction center: $A_3^8 = \sqrt{\frac{\hbar}{2T_{1r}}}$, 1 fs $< T_{1r} < 1$ ps.

SUPERRADIANCE:

$$\Gamma_3/2 \approx D \quad T_{1r}^{ST} \approx 0.03\text{ps}$$

Decay Widths and the Superradiant Transition



HAKEN-STROBL MASTER EQUATION:

$$\frac{d\rho_{i,j}}{dt} = -\frac{i}{\hbar}[H_0, \rho]_{i,j} - \frac{1}{\hbar}\{W, \rho\}_{i,j} - c\gamma_\phi(1 - \delta_{i,j})\rho$$

- First term : Coherent Evolution
- Second term : Dissipation due to recombination and loss (reaction center)
- Third term : Dephasing due to phonon bath

More on Dephasing

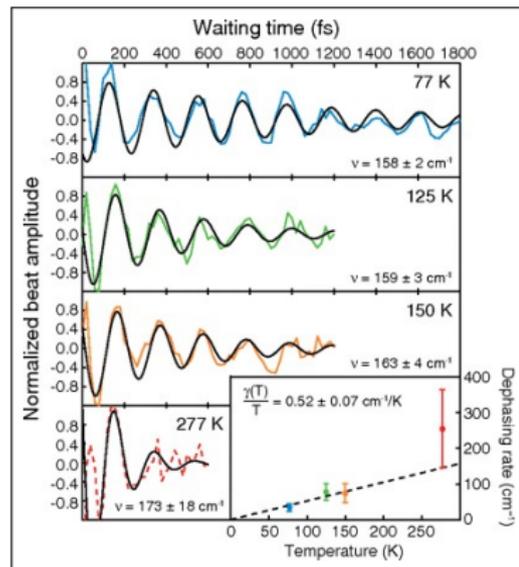
$$H_{SB} = \sum_i q_i(t) |i\rangle \langle i|$$

$$\langle q_i(t) q_j(t) \rangle = \hbar^2 \delta_{ij} \delta(t) \gamma_\phi$$

dephasing time:

$$T_d = (c\gamma_\phi)^{-1}$$

$$\gamma_\phi = 0.52 T \text{ (cmK)}^{-1}$$



“Long-lived quantum coherence in

photosynthetic complexes at

physiological temperature”, G.

Panitchayangkoona et al., PNAS, **107**,

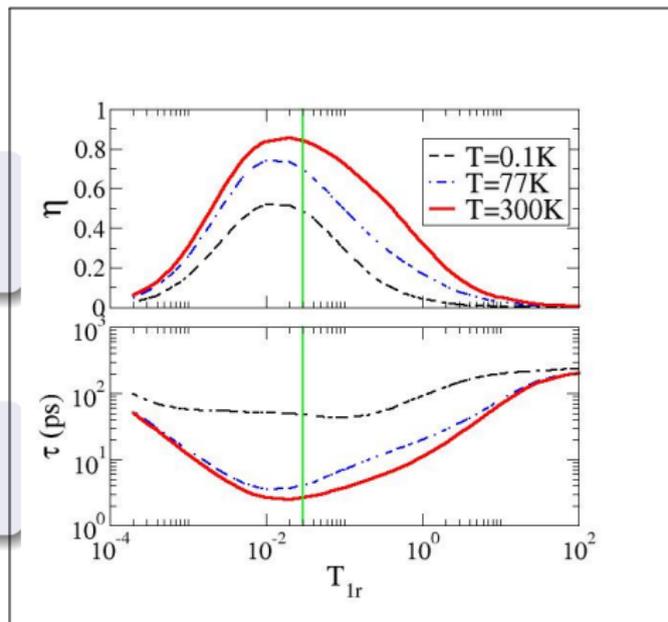
12766 (2010).

Efficiency of Energy Transport

$$\rho(t=0) = \frac{1}{2}(|1\rangle\langle 1| + |6\rangle\langle 6|)$$

$$\eta(t_{max}) = \frac{1}{T_{1r}} \int_0^{t_{max}} dt \rho_{33}(t),$$

$$\tau = \frac{1}{T_{1r}} \int_0^{\infty} dt t \rho_{33}(t) / \eta(\infty).$$



Phonon Bath 2 : Gibbs relaxation

Lindblad master equation in the Born-Markov and secular approximations:

$$\frac{d\rho_{i,j}}{dt} = -\frac{i}{\hbar}[H_0, \rho]_{i,j} - \frac{1}{\hbar}\{W, \rho\}_{i,j} + L(\rho)$$

where

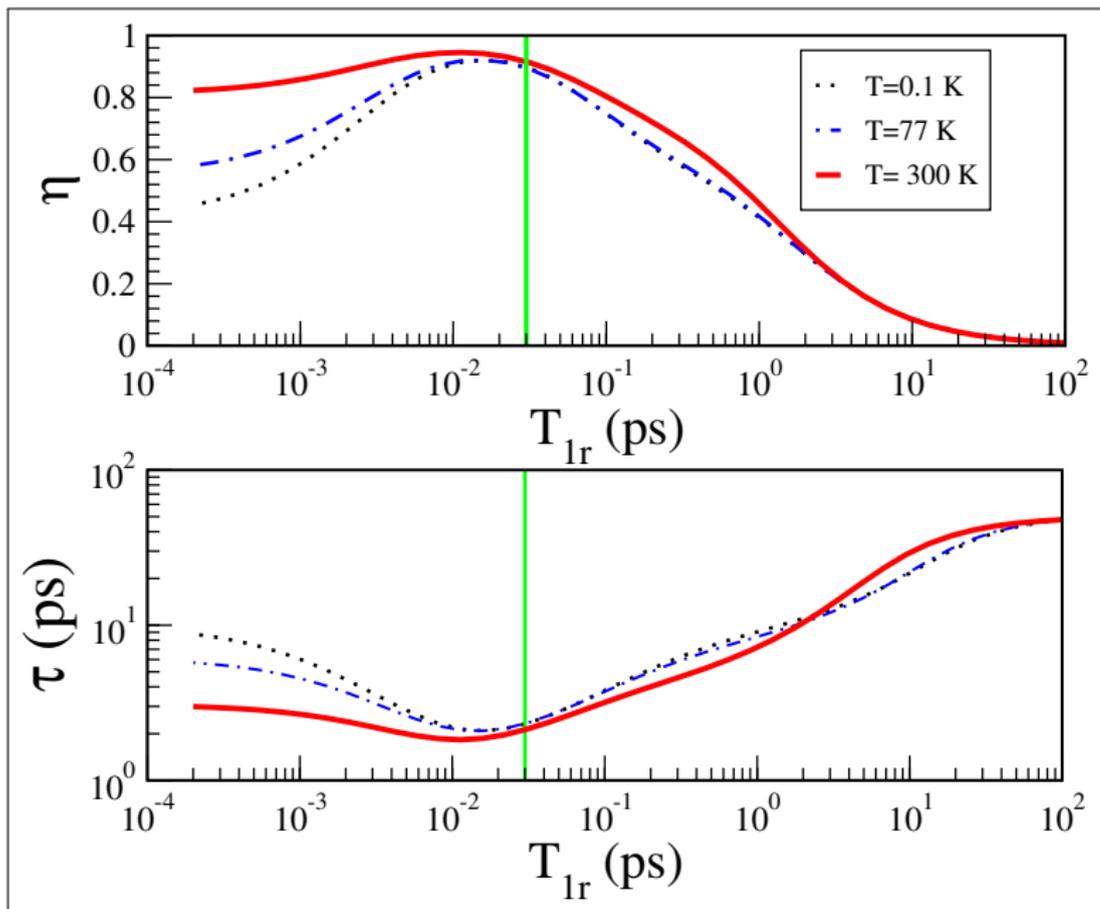
$$L(\rho) = \sum_{\omega} \sum_m \gamma(\omega) A_m^\dagger(\omega) \rho A_m(\omega) - \frac{1}{2} \rho A_m^\dagger(\omega) A_m(\omega) - \frac{1}{2} A_m^\dagger(\omega) A_m(\omega) \rho$$

$$A_m(\omega) = \sum_{\Omega' - \Omega = \omega} c_m^*(\Omega) c_m(\Omega) |\Omega\rangle \langle \Omega'| \quad |\Omega\rangle = \sum_m c_m(\Omega) |m\rangle$$

$$\gamma(\omega) = 2\pi J(\omega) [1 + n(\omega)] + J(-\omega) n(-\omega) \quad n(\omega) = 1/[e^{\beta\hbar\omega} - 1]$$

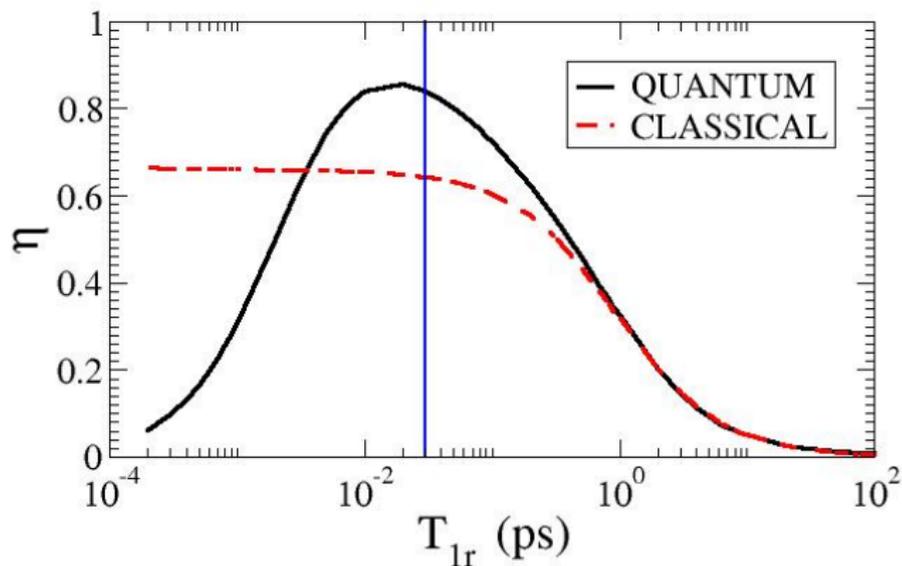
$$J(\omega) = \theta(\omega) E_R / \omega_c (\omega / \omega_c) \exp(-\omega / \omega_c)$$

M. Mohseni, P. Reberstrost, S. Lloyd and A. Aspuru- Guzik, J. Chem. Phys. 129, 174106 (2008).



QUANTUM vs CLASSICAL

$$dP_i/dt = \sum_k (T_{i,k}P_k - T_{i,k}P_i) - P_i/T_1 - \delta_{i,3}P_i/T_{1r},$$



Efficiency versus the Distance site 3-Reaction Center

$$\rho(t=0) = (1/2)(|1\rangle\langle 1| + |6\rangle\langle 6|)$$

$$\Gamma_3/2 = \frac{2\pi\rho_{RC}|V_3^{RC}|^2}{\hbar}, \Gamma_3/2 = D$$

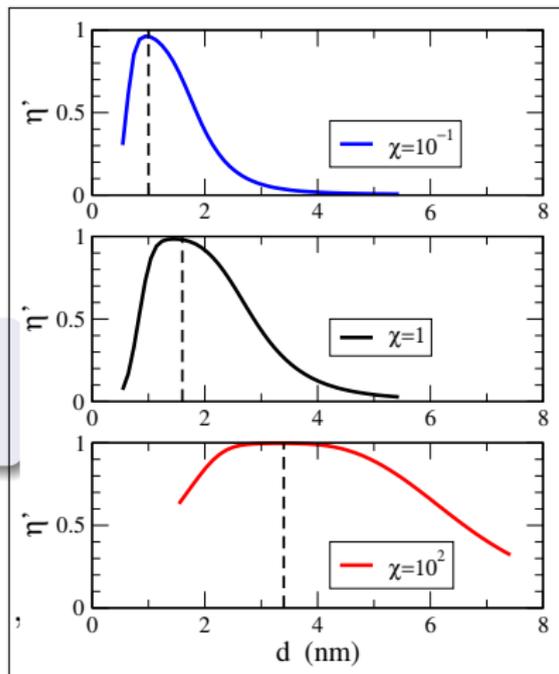
$$V_i^{RC} = \frac{C}{R_{i,RC}^3} [\vec{\mu}_i \cdot \vec{\mu}_{RC} - 3(\vec{\mu}_i \cdot \hat{R}_{i,RC})(\vec{\mu}_{RC} \cdot \hat{R}_{i,RC})]$$

$$d_{optimal} = (2\pi B^2)^{1/6} (\rho_{RC} \rho_{FMO})^{1/6}$$

where

$$B = C \left[\vec{\mu}_i \cdot \vec{\mu}_{RC} - 3(\vec{\mu}_i \cdot \hat{R}_{i,RC})(\vec{\mu}_{RC} \cdot \hat{R}_{i,RC}) \right],$$

$$\chi = \rho_{RC} / \rho_{FMO}$$



Why efficiency is maximal at the Superradiance Transition?

We may observe the following

- 1 At small coupling time T_{1r} , namely strong coupling to RC, all states are strongly localized and the only state which can decay fast is localized far from the sites where the excitation starts, e.g. 1 and/or 6. Efficiency of exciton transport can NOT be optimal.
- 2 At large coupling time, namely small coupling to RC, the states have a small decay width, they can hardly decay, and in any case exciton performs a kind of classical random walk. No quantum coherence can be exploited and efficiency can NOT be optimal too.

Therefore one can expect that at the Superradiance Transition both effects are mitigated since localization increases (w.r.t. 1) and decay increases (w.r.t. 2) and maximum can appear.

Conclusions and Perspectives

- SR strongly affects transport: non classical behavior.
- SR survives at room temperature!
- SR allows to find optimal parameters: distance from Reaction Center: **from 1 nm to 3 nm. These distances are consistent with available structural data about the RC-FMO complex**
- SR is another quantum feature which can be exploited in ingeneering efficient devices for energy transport.
- Perspective: short term: interplay of SR and Disorder (static and dynamical)
- long term: many body problem.

Thank You for Your Attention

[arXiv:1111.5443](https://arxiv.org/abs/1111.5443), submitted to Journal of Physical Chemistry
(2012)

As is common in quantum optics, we describe the dissipative system with at most one excitation by states

$$|\psi\rangle = \sum_{i=1}^7 a_i |0\rangle \otimes |i\rangle + \sum_c \int dE b_c(E) |c, E\rangle \otimes |gs\rangle, \quad (1)$$

where $|0\rangle$ is the vacuum state of the environment and $|c, E\rangle \otimes |gs\rangle$ is the state with one excitation in the environment and none on the sites. Here, c , is the quantum number labelling channels (at energies E) in the environments. The reduced density matrix is obtained by tracing over the states $|0\rangle$ and $|c, E\rangle$,

$$\rho = \sum_{i,j} a_i a_j^* |i\rangle \langle j| + (1 - \sum_i |a_i|^2) |gs\rangle \langle gs|, \quad (2)$$

which is of size 8×8 . However, $\langle gs | \rho | i \rangle = 0$ since with the choice (1), we neglect any transitions $|i\rangle \rightarrow |gs\rangle$. Moreover, $\langle gs | \rho | gs \rangle$ is just the loss of probability of excitation of the seven sites. Therefore, we restrict our considerations to the 7×7 matrix $\langle i | \rho | j \rangle$, which does not have constant trace.