Optimal energy transfer in disordered quantum networks with application to light-harvesting complexes

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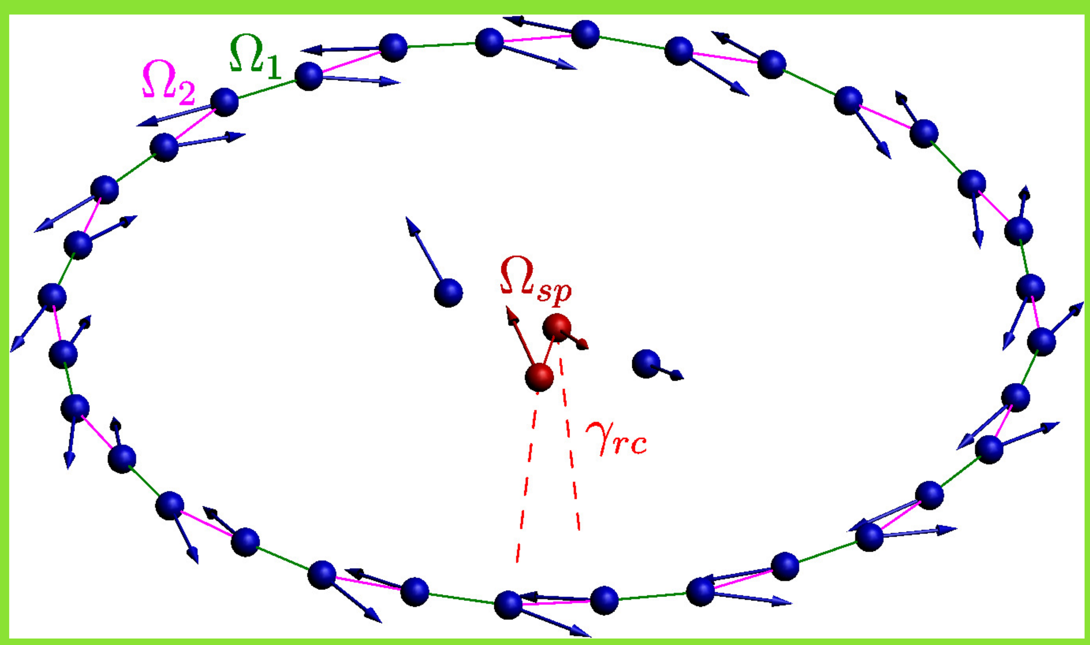
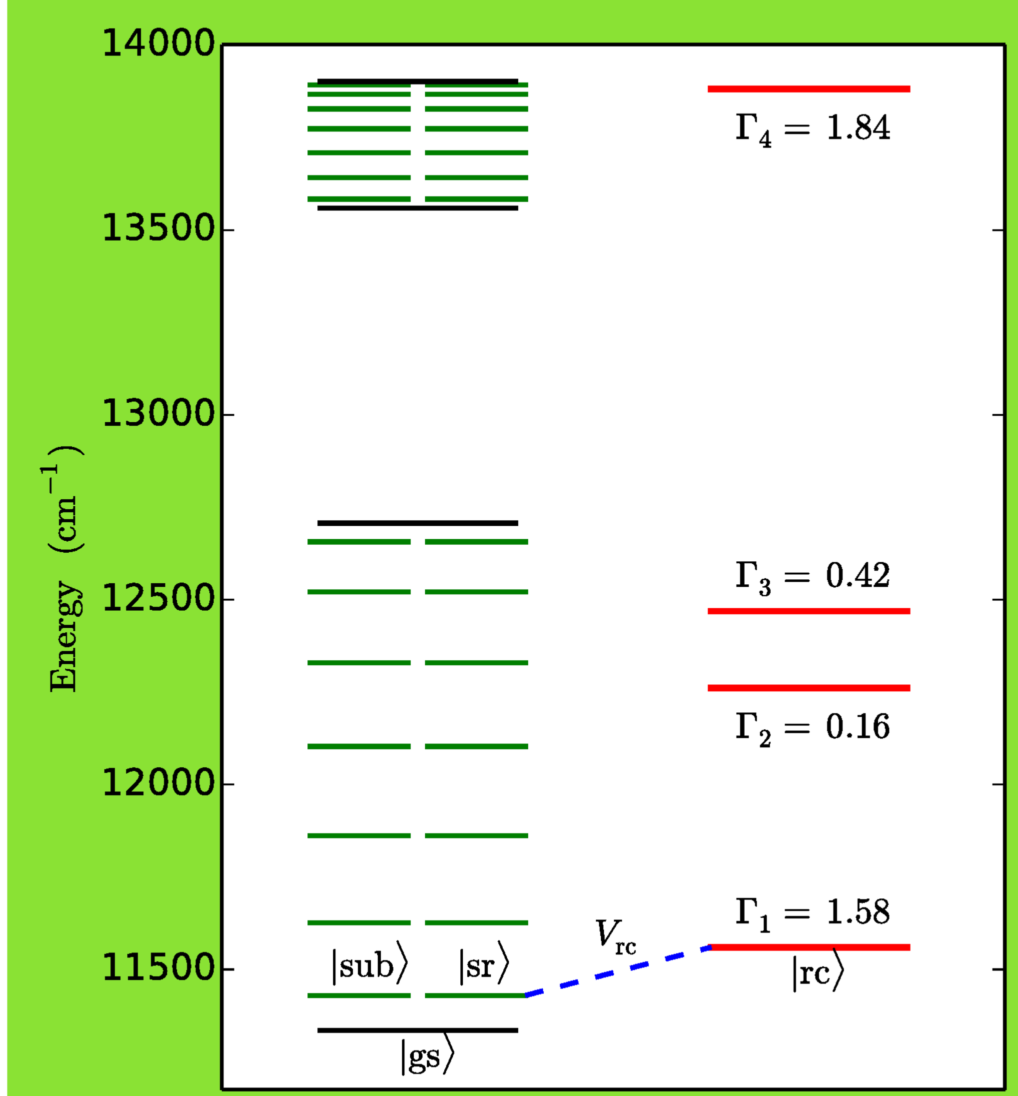
LHI-RC complex of Rhodobacter Sphaeroides

Geometry and interactions

- *$N = 32$ peripheral chromophores on LHI and 4 in RC*
- nearest-neighbor (Ω_1, Ω_2, Ω_{sp}) and dipole interaction
- *decay width γ_{rc} from the RC special pair (red)*
- dissipation via fluorescence



Energy spectra at zero disorder



Left: energies of the peripheral LHI complex, two bands of 16 levels with 7 pairs of degenerate levels enclosed by 2 non-degenerate levels

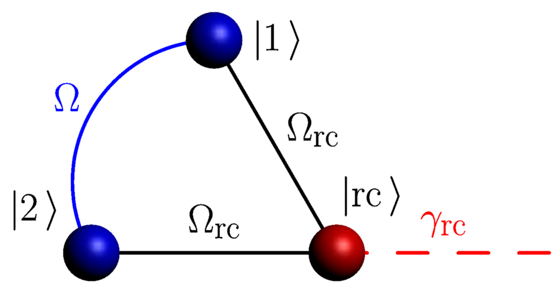
Right: energies of the RC structure, the opening γ_{rc} induces the reported decay widths Γ_k (cm^{-1})

Abstract

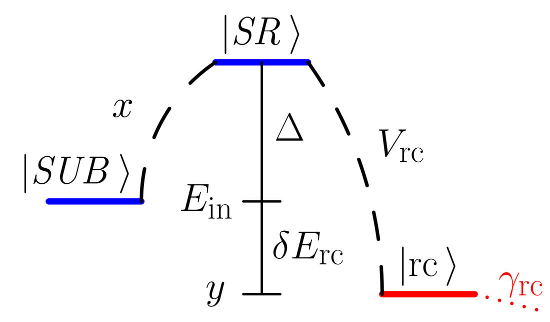
We study the interplay of cooperativity (super/sub-radiant transfer) and static disorder in the Light Harvesting complex I (LHI) of purple bacteria, a ring-like structure of $N = 32$ sites surrounding the Reaction Center (RC). At zero disorder the LHI eigenstates separate into a superradiant (small) and a subradiant (much larger) subspace of the single-excitation Hilbert space. As the static diagonal disorder increases, superradiance is destroyed, and subradiant states display a maximum in the energy transfer efficiency. The optimal transfer condition as a function of RC energy and disorder is obtained when an RC state is at resonance with the initial subradiant state and the effective disorder on that state ($\propto 1/\sqrt{N}$) equals the superradiant coupling ($\propto \sqrt{N}$) between LHI states and RC states.

The building block: a trimer model

Many important features regarding the efficiency of energy transfer from subradiant states in systems displaying the **Ring-RC structure** can be understood from the analysis of the simplest ring, i.e. two sites, connected with a central site representing the RC with equal coupling $\Omega_{\rm rc}$ and between them with coupling Ω. The excitation can escape the system from the RC with decay width $\gamma_{\rm rc}$. The site energies E_1 and E_2 are Gaussian random numbers with mean zero and variance W^2, thus introducing disorder in the system.



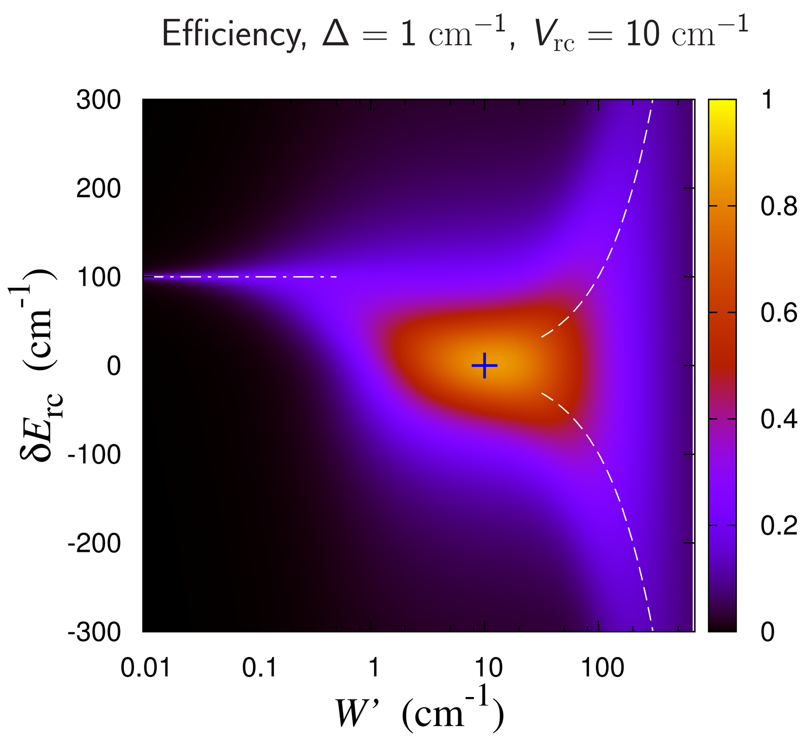
We introduce the new basis formed by $|\mathrm{rc}\rangle$ and the subradiant and superradiant states $|SUB\rangle = (|1\rangle - |2\rangle)/\sqrt{2}$ and $|SR\rangle = (|1\rangle + |2\rangle)/\sqrt{2}$, and the trimer can be viewed as a **three-site chain**.



$V_{\rm rc} = \sqrt{2}\Omega_{\rm rc}$ is the **superradiant coupling**, x has mean zero, y has mean $E_{\rm rc}$ and both have variance $W^2/2$.

Energy transfer optimization from the subradiant state of the trimer

The behavior of a disordered trimer (left) is captured by a model with deterministic coupling X (right).



Optimal conditions

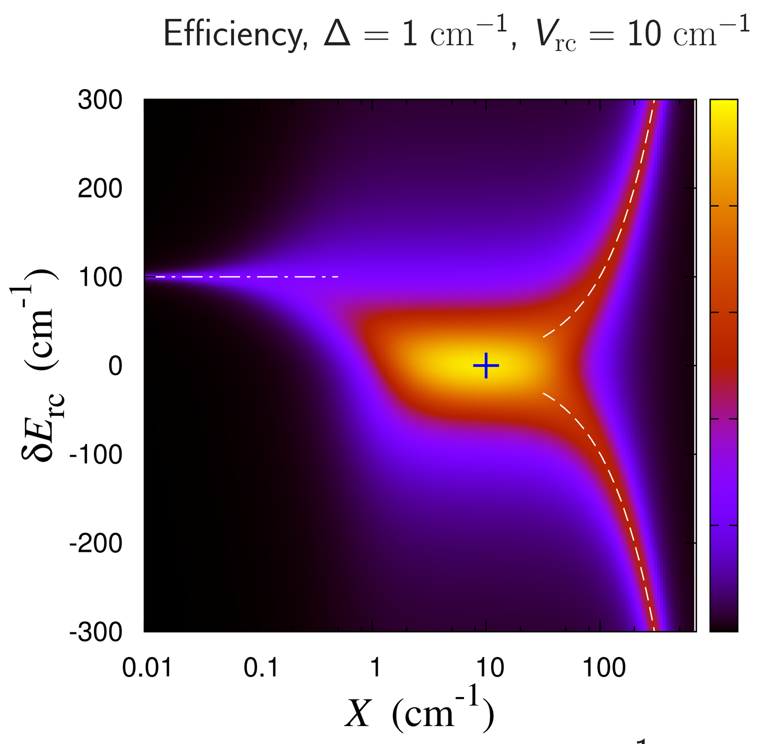
Resonance:

$$\delta E_{\rm rc} = E_{\rm rc} - E_{\rm in} = 0$$

Disorder comparable to superradiant coupling:

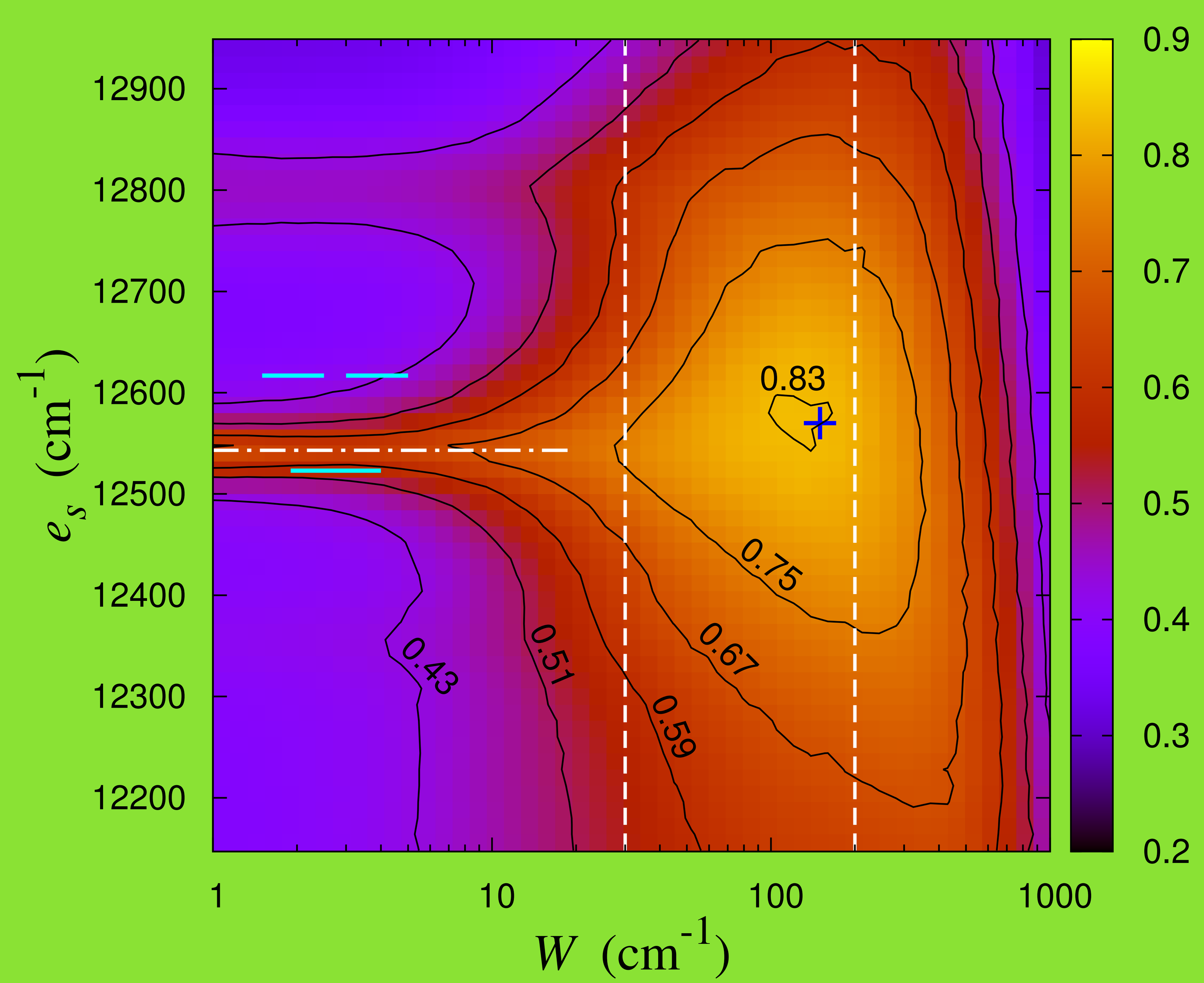
$$W' = W/\sqrt{2} = V_{\rm rc}$$

Note the width ($\sim V_{\rm rc}$) of the high-efficiency region.



In the regions where disorder is small or large if compared to the superradiant coupling $V_{\rm rc} = 10\ \mathrm{cm}^{-1}$, we can apply perturbation theory to predict the relevant resonances (white curves).

Energy transfer optimization in the LHI-RC complex



Energy transfer efficiency of the LHI-RC complex obtained starting from a **room-temperature** Gibbs' distribution of LHI states. By varying the strength W of static diagonal disorder and the energy e_s of the RC sites, the efficiency is optimized in accordance with our theoretic estimate (blue cross) and within the range of disorder strength (30–200 cm^{-1}, dashed lines) which is estimated to characterize the LHI-RC complex **in physiological situations**.

Also the prediction for the low-disorder resonance (dot-dashed line) is very good and it does not simply correspond to the resonance with LHI energy levels (cyan bars).

Reduction to independent trimers and optimal conditions

Due to the thermal environment, the **most likely populated** ring eigenstates are the three lowest-energy levels: ground state $|\mathrm{gs}\rangle$, subradiant $|\mathrm{sub}\rangle$ and superradiant $|\mathrm{sr}\rangle$. This fact makes it possible a **simultaneous optimization** of transfer from those states to the lowest RC level $|\mathrm{rc}\rangle$, since the gap between $|\mathrm{sr}\rangle$ and $|\mathrm{gs}\rangle$ is of the order of the **superradiant coupling** $V_{\rm rc} \approx 40\ \mathrm{cm}^{-1}$ with $|\mathrm{rc}\rangle$.

Due to the **direct coupling** with $|\mathrm{rc}\rangle$, transfer from $|\mathrm{sr}\rangle$ is very efficient up to $W \approx 100\ \mathrm{cm}^{-1}$, when disorder localizes edge states, hindering superradiance.

Applying the results for **suitable trimer models**, transfer from $|\mathrm{gs}\rangle$ and $|\mathrm{sub}\rangle$ would be optimal at the respective resonant energies, and at $W \approx 200\ \mathrm{cm}^{-1}$, when the effective disorder strength $W/\sqrt{N}$ equals the superradiant coupling $V_{\rm rc}$.

Since efficiency remains very high within a region **of the order of the superradiant coupling** $V_{\rm rc}$ about the foregoing estimates, we can predict a global optimization at $e_s \approx 12570\ \mathrm{cm}^{-1}$ and $W \approx 150\ \mathrm{cm}^{-1}$.

Related ongoing research

Interplay of superradiance and dirsorder or dephasing:
G. L. Celardo, G. G. Giusteri, F. Borgonovi. Phys. Rev. B, 90, 075113 (2014).
G. L. Celardo, P. Poli, L. Lussardi, and F. Borgonovi. Phys. Rev. B 90, 085142 (2014).

Effectiveness of non-Hermitian terms in modeling probability loss:
G. G. Giusteri, F. Mattiotti, G. L. Celardo. Phys. Rev. B, 91, 094301 (2015).

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