Large scale simulations of photosynthetic antenna systems: interplay of cooperativity and disorder

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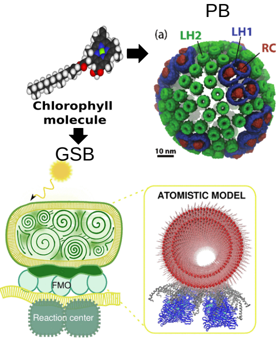
Florence Theory Group Day
March 19th 2025

Simmetry and cooperativity in Biology

QUANTUM BIOLOGY:
1. Role of quantum mechanics in biological systems
2. Applications: PHOTON SENSORS
BIO-INSPIRED SUNLIGHT PUMPED LASER
SOLAR CELLS



Light harvesting complexes:
high degree of symmetry, order and complexity

Symmetry favors the emergence of quantum cooperative properties robust to noise: **SUPERRADIANCE** and **SUPER-TRANSFER**

How does cooperativity donate robustness?
Fast time scales (faster than thermal relaxation) $\longrightarrow$ high internal efficiency

Related papers:
J. Am. Chem. Soc. 2014, 136, 5, 2048–2057
J. Phys. Chem. Lett. 2012, 3, 4, 536–542
Marco Gullì et al 2019 New J. Phys. 21 013019

MOTIVATIONS

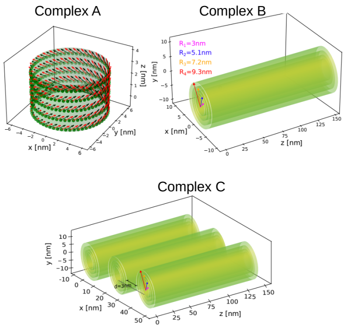
- Relationship between structure and functionality.
- Cooperativity and superradiance in GSB and PB light-harvesting systems.
- Robustness to static and thermal noise.

Ongoing collaborations:

- Study of the EET in GSB and PB antennae.
- Applications: bio-inspired sunlight pumped lasers.

1. Hierarchical organization in GSB and PB complexes

GSB complexes A,B,C



$$L_{max} = 148.57 \text{ nm}$$
$$N_{max} = 132840 \text{ Bchlc (complex C)}$$
$$e_0 = 15390 \text{ cm}^{-1}$$
$$\lambda_0 \sim 650\ nm$$
$$|\vec{\mu}| = \sqrt{30} \text{ D}$$

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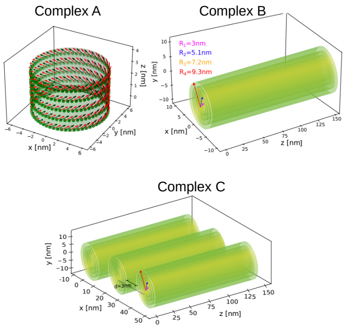

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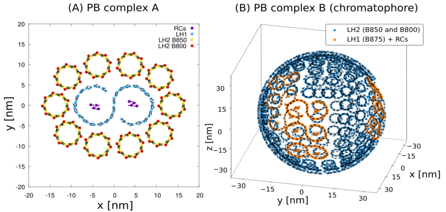
PB complexes A,B



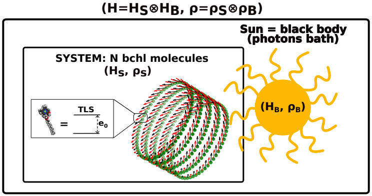
$$N = 334 \text{ Bchla}$$
$$\bar{e}_0 = 12500 \text{ cm}^{-1}$$
$$\lambda_0 \sim 800 \text{ nm}$$
$$|\vec{\mu}| = 10.157 \text{ D}$$

$$R = 30 \text{ nm}$$
$$N = 4113 \text{ Bchla}$$
$$\bar{e}_0 = 12500 \text{ cm}^{-1}$$
$$\lambda_0 \sim 800 \text{ nm}$$
$$|\vec{\mu}| = 10.157 \text{ D}$$

2. The model: why the Non-Hermitian Hamiltonian approach?

Bchl molecule = TLS ($e_0 = \hbar\omega_0$, $\vec{\mu}_0$, γ)

OPEN QUANTUM SYSTEM



$$\frac{d\rho_s}{dt} = -\frac{i}{\hbar}\left[H_0 + \Delta, \rho_s\right] + \frac{1}{\hbar}\sum_{i,j}\left(\sigma_j^- \rho_s \sigma_i^+ - \frac{1}{2}\left\{\sigma_i^+\sigma_j^-, \rho_s\right\}\right)$$

1. Born-Markov and secular approx. (Lindblad approach);
2. EMF: black body at 0 K;
3. Sunlight very dilute: single excitation manifold.

Radiative non-Hermitian Hamiltonian (NHH)

$$\hat{H}_{eff} = \sum_{j} \left(\omega_0 - i\frac{\gamma}{2}\right) |j\rangle \langle j| + \sum_{\substack{i,j \\ i \neq j}} \left(\Delta_{ij} - \frac{i}{2}\gamma_{ij}\right) |i\rangle \langle j|$$

Spontaneous emission of an ensemble of TLS and interactions mediated by the vacuum fluctuations of the EMF.

Complex eigenvalues:

$$\epsilon_n = E_n - \frac{i}{2}\Gamma_n$$

- $\Gamma_n \gg \gamma$: superradiant eigenstate
- $\Gamma_n \ll \gamma$: subradiant eigenstate

Related paper: Grad J., Hernandez G., Mukamel S., PRA 37, 3835 (1988)

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The Hermitian Hamiltonian and the Dipole stregth

HH: Hermitian Hamiltonian

Resonance overlap criterion: $\Gamma_n < \delta$

$\delta = \frac{E_{max} - E_{min}}{N}$ (average energy mean level spacing)

$$H_H = \sum_{i=1}^{N} e_0 |i\rangle\langle i| + \sum_{i \neq j} \Delta_{ij} |i\rangle\langle j|$$

Dipole strength:

$$\vec{D}_n = \sum_{i=1}^{N} \langle i|E_n\rangle \,\hat{\mu}_i.$$

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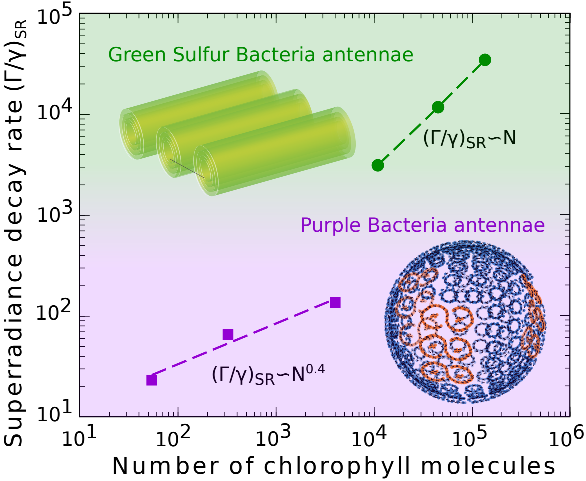
3. The emergence of Superradiance in GSB and PB



J. Phys. Chem. B 2024, 128, 9643-9655

4. Robustness to thermal noise and static disorder

THERMAL NOISE

Density matrix of a state at the canonical equilibrium:

$$\rho_{ij} = \sum_n \frac{e^{-\beta E_n}}{\mathrm{Tr}(e^{-\beta \hat{H}})} \langle i|E_n\rangle\langle E_n|j\rangle,$$

where $\beta = 1/k_B T$ at room temperature.

The **thermal coherence length** L_ρ is defined by:

$$L_\rho = \frac{1}{N} \frac{\left(\sum_{ij} |\rho_{ij}|\right)^2}{\sum_{ij} |\rho_{ij}|^2}$$

L_ρ measures how much a single excitation is spread coherently over the molecules of the aggregate: $\frac{1}{N} \leq L_\rho \leq N$

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Static and thermal noise in GSB

STATIC DISORDER W [cm^{-1}]: strength of the energy fluctuations

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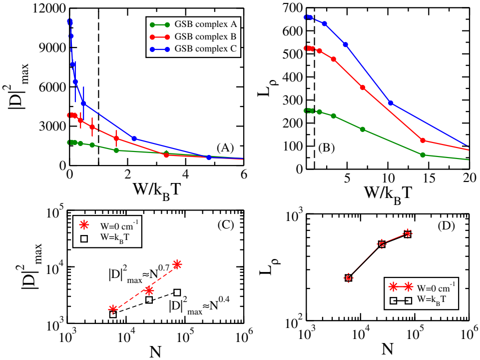
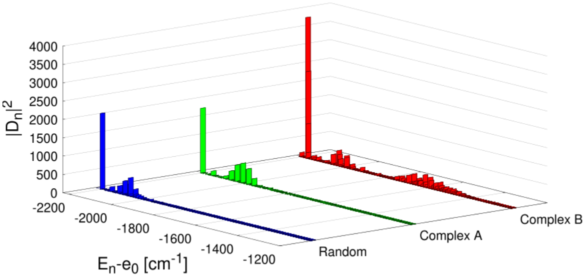


5. Robustness of Superradiance with respect to random dipole orientation in GSB



Increasing the system size by adding the molecules in the same positions but with randomized dipole directions: **no superradiant enhancement.**

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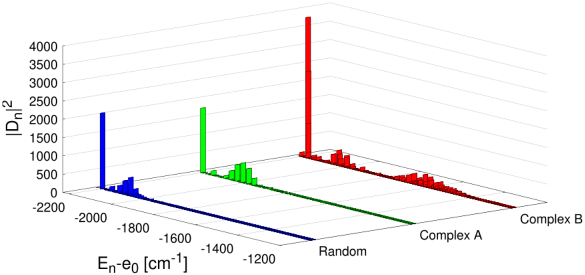

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Large Scale Simulations of Photosynthetic Antenna Systems: Interplay of Cooperativity and Disorder

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PAPER

Macroscopic coherence as an emergent property in molecular nanotubes

Marco Gulli[1], Alessia Valzelli[1], Francesco Mattiotti[1,2], Mattia Angeli[1,3], Fausto Borgonovi[1,2] and Giuseppe Luca Celardo[4]

SCAN ME

6. Conclusions and outlook

CONCLUSIONS

1. **Superradiance** in the whole antenna complexes.
2. Cooperative effects robust even with **disorder** and **noise** levels comparable with ambient conditions.
3. Cooperative effects strictly related to the **geometry of the system**.

OUTLOOK

1. Experimental validation of cooperative response in LHC.
2. Artificial devices for light-harvesting and clean energy production.

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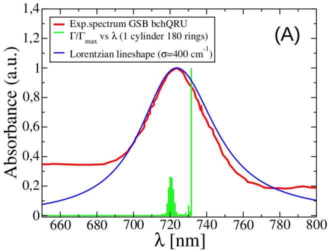

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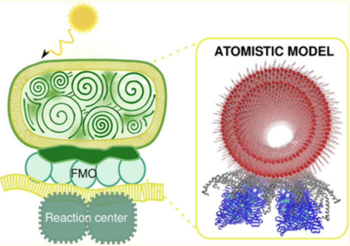
II. ONGOING COLLABORATIONS

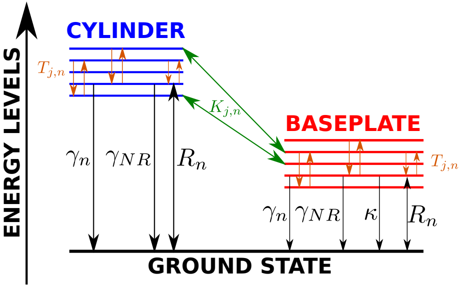
Study of EET in PB and GSB light-harvesting units

Bio-inspired sunlight pumped lasers

Optimization of EET in GSB light-harvesting complexes

- ANTENNA SYSTEM (chlorosome-baseplate-FMO trimer-RCs).
- Incoherent rate equations to model EET.
- MC-FRET: transition rate between chlorosome and baseplate
- Solar radiation: black body at Sun temperature $T = 5800$ K ($R_n =$).
- k average transfer rate from the FMO to the RC.





Related papers:
Phys. Chem. Chemical Phys. 18 7459 (2016)
J. Am. Chem. Soc. 2014, 136, 5, 2048–2057
Strong collaboration with DINFO, prof. D. Fanelli and F. Bagnoli

Bio-inspired sunlight pumped lasers: how to turn unconcentrated thermal sunlight into a coherent laser beam with LHC

TOWARDS A BIO-MIMETIC SUNLIGHT PUMPED LASER BASED ON PHOTOSYNTHETIC ANTENNA COMPLEXES

apace
solar laser with photosynthetic antenna complexes

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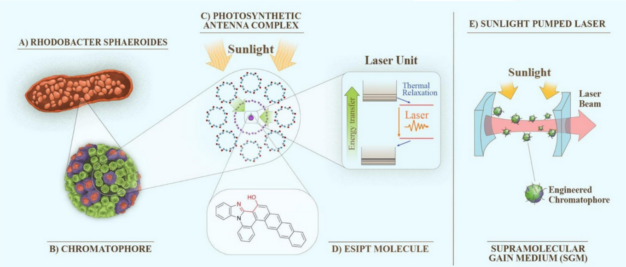

Related paper: Francesco Mattiotti et al 2021 New J. Phys. 23 103015

THANK YOU

FOR THE

ATTENTION!

Appendix 1: Radiative non-Hermitian Hamiltonian

Bchl molecule = TLS ($e_0 = \hbar\omega_0$, $\vec{\mu}$, γ)

NHH: radiative non-Hermitian-Hamiltonian

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$$\epsilon_n = E_n - \frac{i}{2}\Gamma_n$$

$$\Delta_{ij} = \frac{3\gamma}{4}\left[\left(-\frac{\cos(k_0 r_{ij})}{(k_0 r_{ij})} + \frac{\sin(k_0 r_{ij})}{(k_0 r_{ij})^2} + \frac{\cos(k_0 r_{ij})}{(k_0 r_{ij})^3}\right)\hat{\mu}_i \cdot \hat{\mu}_j + \right.$$
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$$\gamma_{ij} = \frac{3\gamma}{2}\left[\left(\frac{\sin(k_0 r_{ij})}{(k_0 r_{ij})} + \frac{\cos(k_0 r_{ij})}{(k_0 r_{ij})^2} - \frac{\sin(k_0 r_{ij})}{(k_0 r_{ij})^3}\right)\hat{\mu}_i \cdot \hat{\mu}_j + \right.$$
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Appendix 2: Radiative Hamiltonian and the Dipole Approximation

HH: Hermitian Hamiltonian

Resonance overlap criterion: $\Gamma_n < \delta$

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DH: Dipole Hamiltonian (resonance overlap criterion and $k_0 r_{ij} \ll 1$)

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Appendix 3: Dipole strength

For HH and DH models we compute the **dipole strength**:

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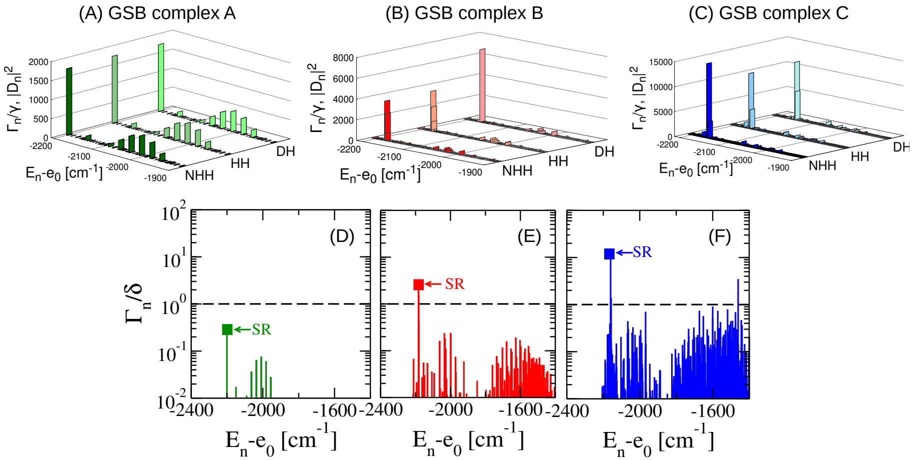
where $|E_n\rangle = \sum_{i=1}^{N} C_{ni} \, |i\rangle$

If resonances do not overlap: $|\vec{D}_n|^2 \approx \Gamma_n/\gamma$.

Appendix 4a: Results in GSB



Appendix 4b: Results in PB