CORRELATIONS, TOPOLOGY AND EFFICIENCY IN LHCII

Paolo Giorda (Institute for Scientific Interchange-ISI, Torino – Italy),
Silvano Garnerone and Paolo Zanardi (University of Southern California, Los Angeles CA -USA), Seth Lloyd(Massachusetts Institute of Technology – Cambridge – MA- USA)

I. Motivation

Quantum mechanics is the fundamental theory that rules the behaviour of atoms and molecules, and until few years ago the possibility that **biological systems** could exhibit **non-trivial quantum effects** used to be dismissed out of hand since the constituents of these systems **strongly interact** with the surrounding environment while typically coherent quantum phenomena have always been associated with **isolated quantum systems.** It was only recently that, thanks to the development of new sophisticated spectroscopic techniques, a series of experiments [1] on different **light-harvesting complexes (LH),** which are at the basis of **photosynthesis** in **bacteria, algae and plants**, have unveiled the presence of a variety of non trivial quantum coherent effects.

These findings have motivated different theoretical efforts in order to lay down a comprehensive scientific framework able to encompass the quantum phenomena exhibited by these and other biological complexes. Indeed, detailed models of the interplay between coherent exciton dynamics and decoherence and relaxation induced by the exciton's environment in Fenna-Matthew–Olson (FMO) complexes (found in green bacteria) show that the resulting energy transport is robust and efficient [2], an effect known as **environmentally assisted quantum transport** (ENAQT).

The importance of these studies is two fold.
On one hand the goal is to produce a theoretical understanding of the role of quantum phenomena, and in particular the role of **quantum correlations (entanglement)**, in biological networks. In this sense the tools developed in **quantum information theory** can provide the proper language to define a general and comprehensive framework.

On the other hand, the comprehension of how Nature has selected and optimized fundamental structures such as light-harvesting complexes, will lead to the identification of guiding principles for the design, engineering, construction and characterization of **new biologically inspired artificial devices (e.g. bio-inspired photovoltaic cells)**, able to mimic the **extremely high efficiency** with which for example light-harvesting complexes are able to convert the solar energy and use it for the metabolic activity of the organisms in which they are found.

In our work we extend and deepen the analysis of the transport properties to plants' fundamental LH complex: the LHCII. By means of a set of correlations, delocalization and efficiency measures developed in quantum information theory we analyze the different excitonic pathways and show how the environment assisted energy transport can take place in LHCII. We discuss the role of quantum correlations and we investigate the role of topology in the transport of excitons through different kind of structures.

[1] G.S. Engel, T. R. Calhoun, E. L. Read, T. K. Ahn, T. Mancal, Y. C. Cheng, R. E. Blankenship and G. R. Fleming, **Nature 446, 782 (2007);** E. Collini, C. Y.Wong, K. E.Wilk, P.M. Curmi, P. Brumer, and G. D. Scholes, **Nature 463, 644 (2010);**. G. Panitchayangkoon, D. Hayes, K. A. Fransted, J. R. Caram, E. Harel, J. Wen, Blankenship, G. S. Engel, **Proc.Nat. Acad. Sci. 107, 12766 (2010)**.
[2] M.B. Plenio and S.F. Huelga, **New J. Phys. 10, 113019 (2008)**; F. Caruso, A. W. Chin, A. Datta, S. F. Huelga, M. B. Plenio, J. Chem. Phys. 131, 105106 (2009); M. Mohseni, P. Rebentrost, S. Lloyd, and A. Aspuru-Guzik, **J. Chem. Phys. 129, 174106 (2008)**; P. Rebentrost, M. Mohseni, I. Kassal, S. Lloyd, and A. Aspuru- Guzik, **New J. Phys. 11, 033003 (2009)**.

II. Introduction: Light-Harvesting Complexes

Photosynthesis is the biological process taking places in bacteria, algae and plants that allows the capture of the energy of light and its conversion into the biochemical energy that is at basis of all the metabolic processes taking place in these organisms, and ultimately of life on earth.

Photoabsorption is the the initial step of photosynthesis. The incoming quantum of light (photons) are absorbed by a complex system of membrane associated pigment-proteins: the light harvesting antennas. These antennas consist of ordered arrays of **light-harvesting pigments**, i.e. chlorophylls (Chl) and bacteriochlorophyls (Bchl), arranged in protein scaffolds.

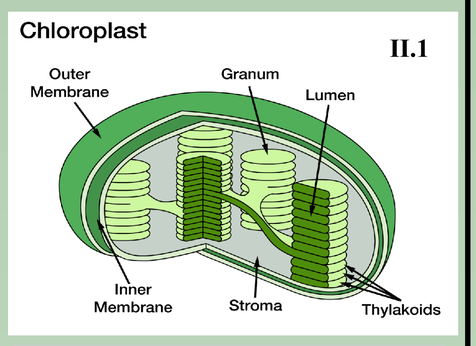
The photons impinging on the antennas are converted in electronic excited states, the **excitons**, that are transferred through the complex to a **reaction center (RC)**, where they are converted into a transmembrane electrochemical potential difference.

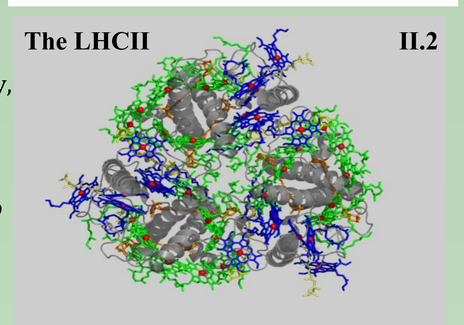
The different structures that light-harvesting complexes (LHs) can exhibit in the various living organisms have been intensively studied in the past decades. The first of such structures, the Fenna-Matthew-Olson complex, was discovered in 1975 in green bacteria. In the following years, the development of high resolution spectroscopic techniques has allowed the detailed description of the LH1 and LH2 complexes in purple bacteria, and of the LHCII complex in higher plants.

Light-Harvesting in higher plants

In higher plants photosynthesis is localized in subcellular units called **chloroplasts** (Fig. II.1). These units has the size of few micrometers and were derived from symbiotic bacteria that became integrated into the cell (an evolutionary process called endosymbiosis). The LH complexes are located in the complex membrane system found in chloroplasts:the **thylakoid** membranes. These are mainly arranged in stacks (**grana**) and are immersed in an acqueous ambient (**stroma**) that contains soluble enzimes where the carbon metabolism reactions take place and give rise to the products that can be exported out of the chloroplast and used by the plants to support cellular processes.

The **LHCII antennas** are the most important,in terms of global productivity, antenna complexes and are found in the thylakoid membrane (Fig. II.2). They are composed by three monomeric subunits each containing 14 Chls that can be distinguished on the basis of their structure and spectral absorption peaks in **Chls *a*** and **Chls *b***. In each monomer there are 8 Chls *b* and 6 Chls *a* and they are disposed in a two layers structure, the **stromal** side and the **lumenal** side, depending on their position in the thylakoid membrane (its inner side is called lumenal).





III. Model and Methods

The Hamiltonian $H_{monomer}$ of the monomeric subunit of LHCII has been determined in the past years thanks to a series of impressive experimental and theoretical efforts [3,4]. The Hamiltonian is expressed in terms of the sites basis, i.e. $|m\rangle$ is the state corresponding to the presence of an exciton on the m-th Chl. ϵ_m are the sites' energies and V_{mn} takes into account the coupling between excitons on different sites:

$$H_{monomer}=\sum_m \epsilon_m |m\rangle\langle m| + \sum_m V_{mn}(|m\rangle\langle n| + h.c)$$

As for the interaction with the environment we use a purely decohering model (Hacken-Strobl)

$$L_{deph}\rho(t)=\gamma_\phi \sum_m A_m \rho(t) A_m^+ - \frac{1}{2}\{A_m A_m^+, \rho(t)\} \qquad A_m=|m\rangle\langle m|$$

The dephasing parameter γ_ϕ is determined according an ohmic spectral distribution for the bath and can be tuned to simulate different strength of the system-environment interaction.
The dynamics of the monomer+environment can thus be described by the following Markovian master equation for the density matrix ρ of the monomer:

$$\frac{d\rho(t)}{dt}=\frac{-i}{\hbar}[H_{monomer},\rho(t)]+L_{deph}[\rho(t)]-\{H_{recomb}+H_{trapping},\rho(t)\}$$

where, besides the decoherence, we include the recombination and trapping mechanism

$$H_{recomb}=-i\,\Gamma\sum_m |m\rangle\langle m|; \qquad H_{trapping}=-i\,k_{trap}\sum_{m=a610,\,a611,612}|m\rangle\langle m|$$

where Γ is the inverse of the typical life time of the exciton and k_{trap} is the rate at which the exciton is extracted from the output sites of the complex (a610,a611,a612).

In order to study the time evolution of the system we subdivide the monomer in subsystems each composed by groups of Chls as suggested by the energy flow pathways determined in [3]: in Fig.: III.1 the exciton levels are reported together with their main site basis (Chls) contribution. The chosen subsystems correspond to the groups of sites at the bottom of the figure and are schematically reported in Fig.: III.2.

The evolution of the system can be characterized by means of correlations measures derived in quantum information theory. In particular, the **total correlations** between two subsystems A, B are measured by the **Quantum Mutual Information**:

$$I_{AB}=S(\rho_A)+S(\rho_B)-S(\rho_{AB})$$

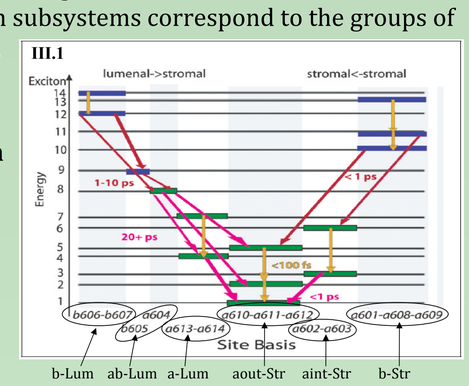
$S(\rho_A), S(\rho_B), S(\rho_{AB})$ are the vonNeumann entropies of subsystems A,B and A+B respectively.While the **quantum correlations** are measured by the **Negativity**:

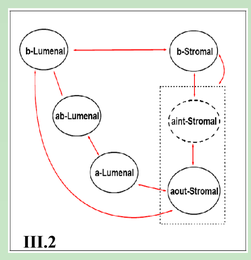
$$N_{AB}=(\|\rho_{AB}^{T_A}\|_1-1)/2$$

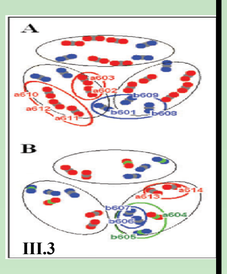
In order to describe how the exciton, once captured, is delocalized over the given structure we introduce the following **measure of delocalization**:

$$D(t)=-\sum_i \lambda_i \ln(\lambda_i) \qquad \lambda_i(t)=\langle n_i\rangle/(\sum_i \langle n_i\rangle)$$

i.e. the Shannon entropy of the nomalized populations (average occupation numbers) of the various sites.







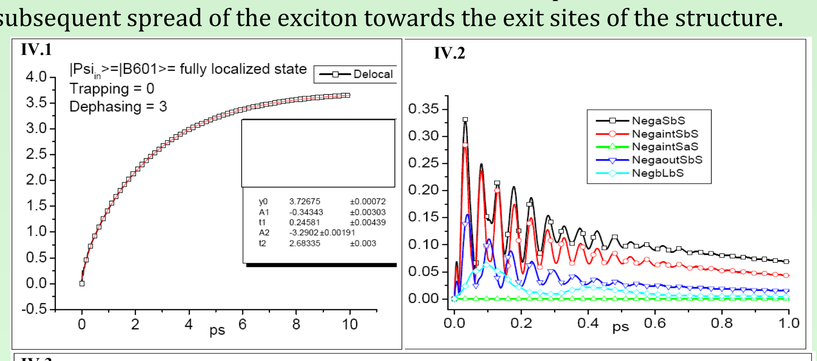
[3] G.S. Schlau-Cohen, T.R. Calhoun, N.S. Ginsberg, E.L. Read, M. Ballottari, R. Bassi, R. van Grondelle, G.R. Fleming ***J.Phys. Chem. B* 113, 1535215363 (2009).**
[4] R. van Grondelle and V. I. Novoderezhkina, ***Phys. Chem. Chem. Phys.* 8, 793807 (2006)**. T.R. Calhoun, N.S. Ginsberg, G.S. Schlau-Cohen, Y.-C. Chen, M. Ballottari, R. Bassi, G.R. Fleming, ***J. Phys. Chem. B* 2009;**

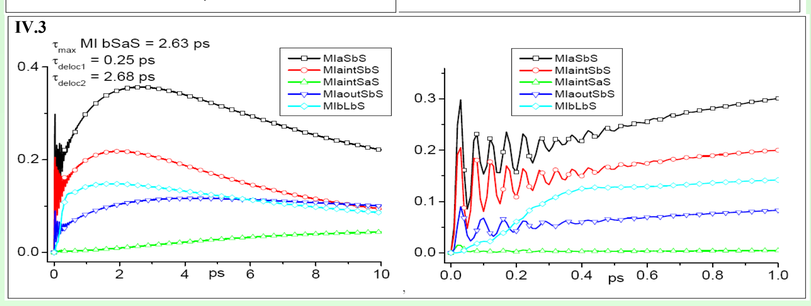
IV. Results: quantum dynamics and delocalization in the monomer

We first study the monomer dynamics in order to show how the energy flow on the stromal side can be described in term of delocalization and correlations measures. As initial state of the simulation we choose an exciton localized on the Chl b601. The value of the dephasing parameter corresponds to value of the temperature T=77 K and we suppose that no trapping sites are attached to the structure. Fig. VI.1 shows how the exciton's delocalization grows very fast at in the few picoseconds. It's behaviour can be well described by the function:

$$D(t)=y_0+A_1\exp(-t/t_1)+A_2\exp(-t/t_2)$$

There are two relevant time scales: $t_1\simeq 250\,fs$, $t_2\simeq 2.6\,ps$,
the first corresponds to the time scale over which the quantum correlations initially are activated and then suppressed (Fig. IV.2). The second corresponds to the time scale over which the total correlations reach their maximum value (Fig. IV.3).
We can therefore conclude that the **quantum correlations**, established in the first few hundreds of femtoseconds, **give their contribution for the first very rapid growth of the delocalization of the exciton over the whole structure**. This fast delocalization is therefore the precondition for the subsequent spread of the exciton towards the exit sites of the structure.





V. Results: Noise assited energy transfer and topology in LHCII

Excitonic transport through sets of coupled LHCII complexes differs in significant ways from the transport through the FMO complex of green bacteria. Notably, the LHCII can act both as an **antenna** and as a **wire**: the excitons, once captured by an LHCII or another complex, can move through a sequence of LHCII complexes, and eventually reach a RC. The excitons must move both up and down in energy, a process mediated by interactions with the environment. We have therefore analyzed the transport in LHCII in the two different configurations and for a whole range of dephasing values .

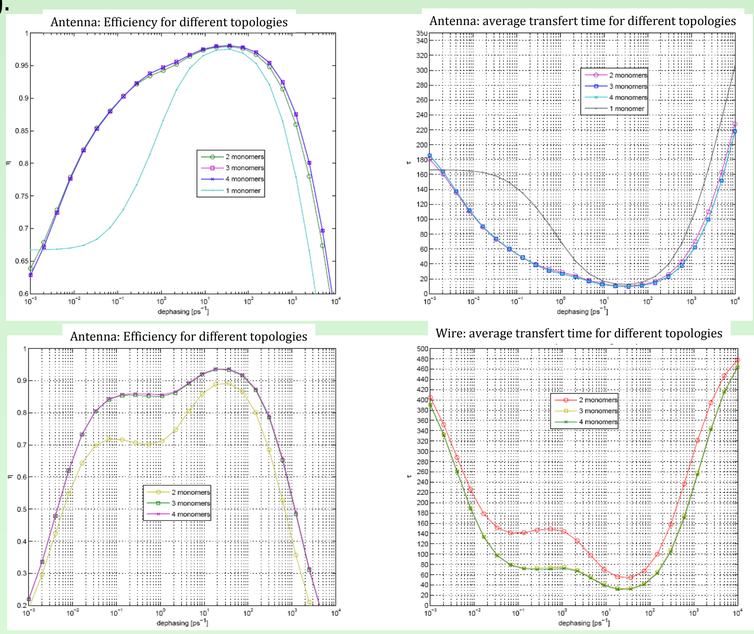
The **efficiency** of the transport can be defined in terms of the occupation probability of the output sites: $\eta=k_{trap}\sum_m \int_0^\infty \langle m|\rho(t)|m\rangle$

while the **average transfer time** to the output states is: $\tau=2\,k_{trap}\,\eta^{-1}\sum_m \int_0^\infty dt\;\; t\;\; \langle m|\rho(t)|m\rangle$

Antenna: the intial state of the simulations is the highest energy eigenstate of a given structure, which is delocalized over the b-stromal Chls (b601, b608, b609); the output sites are stromal Chls (a610, a611, a612) of the various monomers involved.
Wire: the initial state is lowest energy eigenstate, localized on the now input sites (a610, a611, a612) of a monomer of given the structure (the output sites are located on the other monomers of the structure).

Environment assisted quantum transport
Our analysis shows that an exciton initially localized on a single chromophore moves through the LCHII photocomplex in a two-step process. First, over the timescale of few femtoseconds,the exciton spreads coherently to neighboring chromophores. The coherent spreading exhibits rapid quantum oscillations and entanglement. Second, as the environment decoheres the exciton's position, the exciton diffuses semi-coherently throughout the complex.
Although the Haken-Strobl model does not include relaxation, we expect this two-step, coherent–semicoherent model to hold for more detailed models of the dynamics.

The analysis shows that even in the absence of relaxation, **pure dephasing induces effective transport in LHCII both in the antenna and the wire configuration**. The transport is **efficient** and **robust** in the presence of static disorder, and exhibits the characteristic signature of **environmentally assisted quantum transport:** low efficiency at low temperature due to transient localization, followed by a robust maximum efficiency at physiological temperature, with a falling off of efficiency at very high temperature.



Transport and topology
The comparison of different structures (monomer, dimer, trimer and tetramer) shows that the **trimeric structure is the optimal one**: for all values of dephasing, and in particular those corresponding to physiological temperatures (12 ps^-1) it exibits the highest efficiency both in the antenna and the wire configuration. This could be an **indication for a functional selection of the trimeric configuration with respect to the other ones**. The fact that the cluster with three monomers behaves as well as the cluster with four monomers could also be an indication for an **optimization with respect to the "cost" of the structure**.