

Proposal for a PhD Thesis

Université Paris-Saclay

Quantum Dynamics in condensed phase:

Charge transfer in biological systems and organic photovoltaics

(Theory)

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Introduction

Industrial processes involving chemical reactions are typically controlled by macroscopic parameters, such as temperature or pressure. This often results in a huge waste of energy and the massive production of unwanted by-products. These drawbacks play a major role in two of the major societal issues we are currently facing: non-renewable energy consumption and pollution. For instance, most energy production nowadays relies on fossil fuels, which are limited resources that generate CO₂, a greenhouse-effect gas thus inducing relevant perturbations on Earth's climate [1]¹. To tackle these issues, a major breakthrough would be the development of a new chemistry based on a much higher level of selectivity, a chemistry that would work **at an elementary microscopic level** and would be based on the systematic exploitation of **quantum phenomena**, such as **quantum coherence** [2]. In this context, **Nature can serve as a source of inspiration**. As pointed out by the American Office of Science of the Department of Energy [3] “*elements of quantum control are exhibited in nature in various physical processes, including the harvesting of light during photosynthesis*” and further, one should try to “*achieve quantum-level control in human technologies [...] in ways that are environmentally benign*”. **The control of quantum coherence, in particular in the context of artificial photosynthesis**, is one of the grand challenges in basic energy sciences for the future [3]. Such a “green” and highly selective chemistry, applied to artificial photosynthesis, would allow for a **clean and virtually unlimited source of energy**. It is well-known that photosynthetic organisms absorb solar photons, the energy of which they employ to live and multiply. In order to harvest and utilize efficiently this energy, photosynthetic organisms have developed a sophisticated apparatus. The absorption of an incoming solar photon by light-

¹ [1] J. Rosckstrom et al., *Nature* **461** (2009) 472. [2] F. Gatti, *Nature, News and Views* **557** (2018) 641; F. Gatti, *Molecular Quantum Dynamics*. Springer, Heidelberg, 2014. [3] G. R. Fleming and M. A. Ratner, Grand challenges in basic energy sciences. *Phys. Today* **61** (2008) 28. [4] R. Croce and H. van Amerongen, *Nature Chemical Biology* **10** (2014) 492. [5] E. Romero et al. *Nature* **543** (2017) 355. G. D. Scholes et al., *Nature* **543** (2017) 647. [6] E. A. Arsenault et al. *Nat. Comm.* **11** (2020) 1460. J. Cao et al. *Sciences Advances* **6** (2020) 4888. T. Mančal, *Chem. Phys.* **532** (2020) 110663. [7] F. D. Fuller et al., *Nature Chemistry* **6** (2014) 706.

harvesting pigments is followed by a rapid transfer of the resulting excitation energy to the reaction centres, in which photo-initiated electron transfer reactions and proton transfers achieve the ultimate transduction of the solar energy into chemical potential energy (See Fig. 1). A fascinating property of these **natural systems** is that they **perform this task with a high efficiency, even with defects and energy traps due to static and dynamic disorder, a property, which has not yet been achieved in artificial systems**. The success rate of the process is amazing.

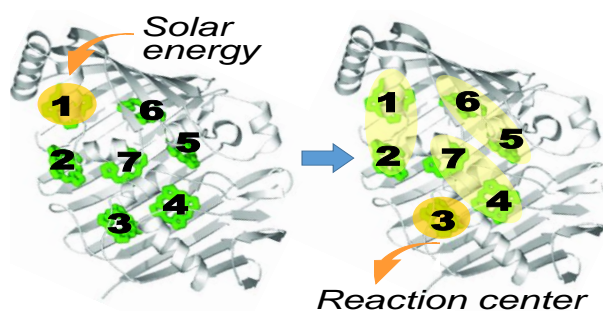


Figure 1 : Excitation Energy Transport in Photosynthesis.

Typically, in light-limiting conditions, 90% or more of the absorbed photons can be used to drive one charge separation [4]: the quantum yield of the transformation to charge separation may be over 99 % in optimal conditions (low-irradiation). In contrast, current solar cells suffer from too low efficiency. For instance, 30 % maximum of solar cell efficiency (not the quantum yield) is achieved for a single n-p junction solar cell (Shockley-Queisser limit), which collapses rapidly in the presence of any defect or impurity. There is clearly a need for a radically new technology inspired by photosynthesis. However, despite the promising advances made in several laboratories, the implementation of artificial photosynthetic systems at the industrial level is non-existent. One of the main drawbacks is that, up to now, the development of artificial photosynthetic systems has been based on the optimization of the energy and charge transfer on the basis of classical principles. However, as Nature teaches to us, it is necessary to design structures that are precisely organized to optimally exploit **quantum mechanical effects** in such processes [5]. Indeed, it has already been proven that quantum interference phenomena can have dramatic consequences for the yield of chemical processes, with differences by several orders of magnitude depending on whether the interferences are constructive or destructive. The exact nature of such quantum effects and the ability to exploit them efficiently are being the target of extensive debate in various scientific communities [6,7].

Objectives

This PhD proposes to study several molecular systems composed of donor-acceptor (D-A) dyads and triads that have been carefully selected to study the excitation energy transfer (EET) and charge transfer (CT) processes involved in artificial photosynthesis. In particular, we will study molecules where one or two light absorbing units transfer their excitation to either one or two acceptor groups in a molecule. We will start with different structures composed of the structure shown on Fig. 2.

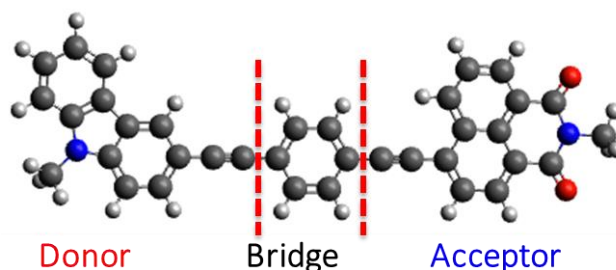


Figure 2: Donor-Acceptor Dyad with a Bridge.

We will try to establish a link between quantum coherence and chemical structure-function, i.e. to formulate general principles that govern the efficiency on the basis of quantum interference in artificial photosynthesis. For this purpose, we aim at deciphering the role of the interplay among the electronic and vibrational motions in sustaining quantum coherences. Molecules are made of electrons and nuclei, and the quantum mechanical role of the vibrations is not only to dissipate the electronic coherence. The wave nature of the nuclear wavefunction has important effects in chemistry [8]² and the interplay among electronic and nuclear motions can lead to complex quantum dynamics [9]. The challenge is to discriminate the vibrational from the electronic or “vibronic” (i.e. the mixing of the two) coherences in EET and CT, which are important for the efficiency of artificial photosynthesis. *We thus aim to deliver basic design principles that govern the efficiency of quantum interferences including coupled electronic and nuclear motions in EET and CT.* These design principles will be applied and tested in large organic systems with actual potential as artificial light-harvesting units: see Figs. 3 and 4.

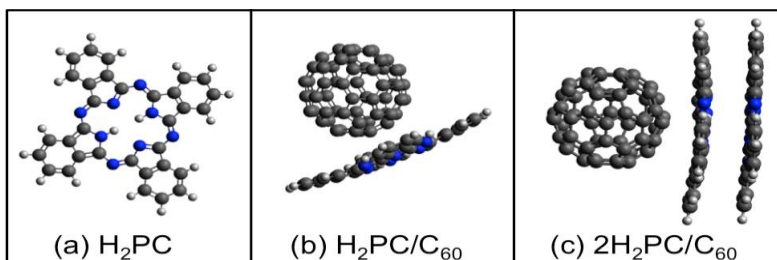


Figure 3: Possible units to design the organic photovoltaics: (a) porphyrines, (b) and (c) C₆₀ and carotenoids.

² [8] F. Gatti, B. Lasorne, H.-D. Meyer and A. Nauts, Springer, Heidelberg. [9] H. Köppel, W. Domcke and L. Cederbaum, *Adv. Chem. Phys.* **57** (1984) 59. [10] H.-D. Meyer, F. Gatti, and G. Worth, Eds. Wiley-VCH, Weinheim, 2009. H.-D. Meyer, U. Manthe, and L. Cederbaum, *Chem. Phys. Lett.* **165** (1990), 73. [11] A. Marciniak *et al.*, *Nat. Comm.* **10** (2019) 337. [12] F. Gatti *et al.*, *Physics Reports* **484** (2009) 1.

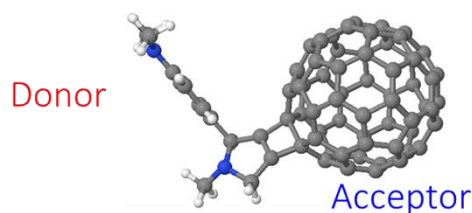


Figure 4: possible organic photovoltaics involving a charge transfer.

More precisely, we will then consider analogous structures in larger and more complex aggregates, reaching out to the scale of large biomimetic molecules in solvent. Many systems can be envisioned such as the organic photovoltaic carotenoid–porphyrin–C₆₀ molecular triad (Fig. 5) dissolved in explicit tetrahydrofuran solvent at 300 K³.

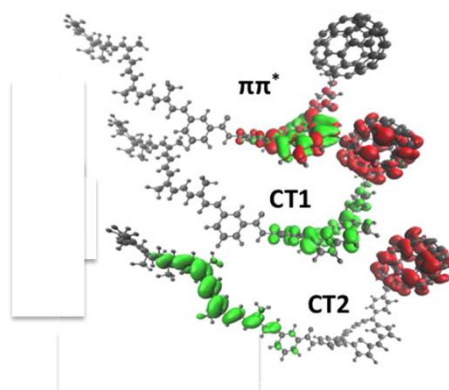


Figure 5 : Photoinduced charge transfer in Carotenoid-Porphyrin-C₆₀

The difficulty consists in describing quantum effects in biomimetic systems is to propagate high-dimensional nuclear wave-packets (up to thousands of degrees of freedom) with ab initio calculations that treat the correlated motion of both the electrons and the nuclei of the molecule on equal footing. For this, we will use propagations of high-dimensional nuclear wave-packets with the Multi-Configuration Time-Dependent Hartree (MCTDH) approach [10] on coupled electronic potential energy surfaces (PESs) based on ab initio calculations [11]. MCTDH, invented in the Theoretical Chemistry group of Heidelberg and in continuous development since more than 30 years, is nowadays one of the most powerful methods for quantum-dynamical treatment of multidimensional problems⁴. The Multi-Layer MCTDH approach [14], implemented in the Heidelberg code [15], will allow us to go much beyond and treat quantum mechanically up to a few thousands of degrees of

³ Z Hu, D Brian, X Sun, *The Journal of Chemical Physics* **155** (2021) 124105.

⁴ [13] A. Palacios and F. Martin, *Wiley Interdisciplinary Reviews: Computational Molecular Science* **10** (2020) 1430. [14] H. Wang and M. Thoss, *J. Chem. Phys.* **119** (2003), 1289. [15] O. Vendrell and H.-D. Meyer, *J. Chem. Phys.* **134** (2011) 044135. [16] R Tatabosian et al., *Nature Comm.* **9** (2018) 1. R Tatabosian et al., *J. Biol. Chem.* **294** (2019) 1451. D Mendive-Tapia et al., *J. Phys. Chem. B* **122** (2018) 126. [17] A. Dreuw and M. Wormit, *Wiley Interdisciplinary Reviews: Computational Molecular Science* **5** (2015) 82. [18] M. Drescher et al., *Nature* **419** (2002) 803. [19] F. Calegari et al., *Science* **346** (2014) 336. M. Lara-Astiaso et al., *J. Phys. Chem. Lett.* **9** (2018) 16. [20] M. Galli et al. *Opt. Lett.* **44** (2019) 1308. A. Gollinelli et al., *Opt. Exp.* **10** (2019) 13624. [21] A. Gelzinis et al., *Biochim. Biophys. Acta, Bioenerg.* **1860** (2018) 271. [22] A. Gall et al., *Biochim. Biophys. Acta, Bioenerg.* **1847** (2015) 12.

freedom. (ML)-MCTDH code will be used and further developed. ML-MCTDH makes realistic time-dependent quantum mechanical simulations for very large organic systems of biological relevance possible, including proteins (often based on Spin-Boson (SB) models including huge harmonic baths) [16]. This dynamical approach, together with a TDDFT [17] description of the electrons, will allow us to simulate the population transfer and the electronic and/or vibrational quantum coherence even in large organic molecules.

The goal of the PhD will be, in collaboration with Prof. Xiang Sun who will provide the Hamiltonian models, to simulate the quantum dynamics of the charge transfer in several organic and biological systems in solvent⁵. We will use the ML-MCTDH (Heidelberg package) to perform, for the first time, converged quantum simulation of these systems in full. We will make a link between quantum coherence and chemical structure-function (relative positions of the electronic states, strength of coupling), i.e. to formulate general principles that govern the efficiency on the basis of quantum interference in artificial photosynthesis. We could then propose to chemists to synthesize new systems that could optimize the transfers.

Collaborations:

Experimentalists:

- L. Barreau and L. Poisson, ISMO, Paris-Saclay (France).
- Manuel Llansola-Portoles and Bruno Robert, SB2SM/I2BC CEA, Paris-Saclay (France).

Theoreticians:

- H.-D. Meyer and O. Vendrell, group of Theoretical Chemistry, University of Heidelberg, (Germany).
- Xiang Sun, New York University, Shanghai (China).

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⁵ J Tinnin, S Bhandari, P Zhang, E Geva, BD Dunietz, X Sun, MS Cheung, *The Journal of Physical Chemistry Letters* **13** (2022) 763-769.