

Proposal for a PhD Thesis

Université Paris-Saclay

Quantum control of molecular processes:
Towards quantum technologies in Chemistry
(Theory)

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Nota Bene: this thesis is particularly focused at students passionate about the in-depth understanding of quantum phenomena and their concrete realizations on realistic systems.

Introduction

Our ability to manipulate quantum effects in customized systems and materials is now paving the way for *a second quantum revolution*, which is taking quantum theory towards its ultimate technological consequences. As a result, devices with a far superior performance and capabilities will be generated. An example of this are quantum computers which exploit the superposition principle of quantum mechanics and, thus, quantum coherence. In this context, the systematic control of quantum effects in molecular systems will have an enormous potential since *molecules are the building blocks of every-day life* [1]. There is indeed growing evidence that *a significant number of chemical reactions are impacted by strong quantum-mechanical effects involving simultaneously electrons and nuclei* [2,3]. The advent of femtochemistry allowed scientists to follow in real time the motion of nuclei in molecular processes. Now, tremendous progress has also been achieved experimentally with the possibility to produce even shorter laser pulses, at the attosecond (10^{-18} s) time-scale. It has become thus possible to follow and guide the motion of electrons and, in particular, to image the transfer of one electron from one molecular orbital to another. Attosecond pulses generate electronic wavepackets that could induce, in a second step, a specific motion of the nuclei leading to the field of *"attochemistry"* where it will be possible to control all the most elementary aspects of a chemical act at a quantum mechanical level.

All these quantum simulations will be performed with *the Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) package* [4-7]. MCTDH can be seen as an algorithm to solve *the time-dependent Schrödinger equation (i.e. to propagate wave packets)* for multidimensional dynamical systems consisting of distinguishable particles. The MCTDH package is probably the most general software for time-dependent quantum simulations. The PhD supervisors are official contributors of the MCTDH package and have a long-standing and continuous collaboration with the group of Heidelberg.

(i) Quantum control with lasers of non-adiabatic processes

The first goal of this PhD thesis will be *the study and the control of the quantum mechanical behavior of molecular systems*, with special emphasis put on the *processes where both electrons and nuclei are strongly coupled through a so-called “conical intersection”*. In particular, in collaboration with experimentalists (Lou Barreau and Lionel Poisson, ISMO), we will consider the case of the photodissociation of NO_2 around 400 nm (Figure 1) for which many important experimental results are available [8] but still unexplained.

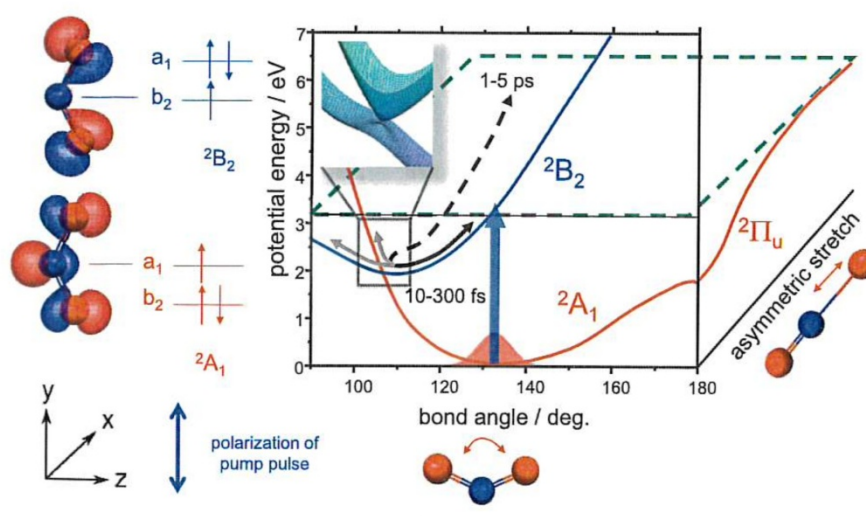


Figure 1 After excitation of UV light, NO_2 dissociates through a conical intersection (Ref. [8]).

Photons in the ultraviolet-visible region can promote molecules to highly excited electronic states. If no photodissociation occurs, an excited molecule can release its excess energy and return to the electronic ground state through spontaneous light emission: fluorescence from a singlet state or phosphorescence from a triplet state if the ground state is a singlet. However, in many cases, light emission is quenched by a much faster radiationless process that is due to the presence of *non-adiabatic couplings between electronic states*. In polyatomic molecules, *non-Born-Oppenheimer processes* occur mainly around topographical features known as conical intersections [9]. A *conical intersection induces strong couplings between electrons and nuclei*. It acts as a funnel through which a new chemical reaction can occur and enables rapid conversion of the excess electronic energy into

nuclear motion. Since conical intersections lead to very fast and efficient transfers, it is suspected that they have been selected by evolution in **important biological processes such as vision, photosynthesis or DNA stability [10]: understanding these quantum effects could lead to much more efficient solar cells for photovoltaic systems.**

The goal of the PhD will be to understand for the first time in detail the quantum behavior around 400 nm for which new experiments will be performed by Lionel Poisson and Lou Barreau, members of the same team at ISMO. The goal of the PhD fellow will be to analyze the existing and planned experiments and to devise strategies of control of the process by exploiting quantum interferences.

Very recently, new potential energy surfaces by our colleagues Richard Dawes (Missouri, USA) and Gabriel Vasquez (Mexico) have been produced that allow one to reproduce with an excellent agreement the photoabsorption spectrum of NO₂ between 300 and 600 nm. We will use these potential energy surfaces for the simulations.

(ii) Coherent excitation of molecules on surfaces for quantum computing

Another aspect of the PhD work will be the creation of quantum superposition of vibrational states for quantum computing. The possibilities offered through **quantum computation** have been well known for many years now [11,12]. A quantum computer is a computation device that makes direct use of quantum-mechanical phenomena, mainly the fact that the system can be in a coherent superposition of different eigenstates. In quantum computers, in particular, the unit of information is a “qubit”, in other words, a coherent superposition of two quantum states denoted 0 and 1. **The main challenges in quantum computing is controlling quantum decoherence** since the latter destroys the properties that are exploited in quantum computing. In addition to the superposition principle, quantum computers may also exploit other quantum properties such as entanglement (for quantum teleportation, i.e., to transmit quantum information from one location to another) or collapse of the wave function (for cryptography [13]). In the context of molecular quantum dynamics, it has been proposed that **vibrational states of molecules could be used for quantum computation processes** [14]. Vibrationally excited molecules in the gas phase could be possible candidates to encode qubits **since decoherence could be controlled more easily** [14]. As aforementioned, the key issue in molecular quantum dynamics is the creation of a coherent superposition of quantum states and its conservation over time since quantum decoherence can occur very fast upon interaction with the environment.

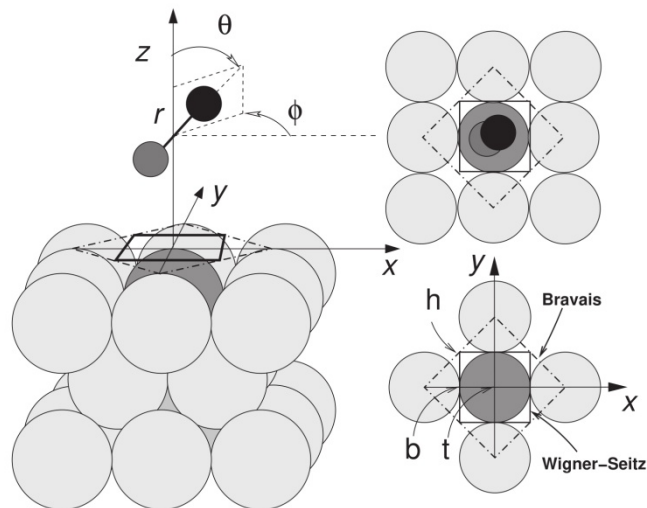


Figure 2 Co on a Copper cell: a laser pulse will create a coherent superposition of states, the interaction with the surface leads to decoherence [15].

Recently, potential and dipole moment surfaces for CO on a surface of Copper have been developed by our colleagues R. Marquardt (Strasbourg) and J.-C. Tremblay (Metz): see Figure 2. *The PhD fellow will use them and include explicitly the quantum decoherence in the simulations by means of a “Lindblad operator”. The goal of the PhD will be to devise laser pulses to create efficiently a quantum superposition of vibrational states of the molecule of CO, special emphasis will be placed on the description of the molecule “dressed by the photons” (adiabatic Floquet theory) in order to choose the parameters of the exciting pulse and on the observation of the process of decoherence in order to minimize it.*

Collaborations:

Experimentalists:

- L. Barreau and L. Poisson, ISMO, Paris-Saclay (France).

Theoreticians:

- H.-D. Meyer and O. Vendrell, group of Theoretical Chemistry, University of Heidelberg, (Germany).
- Richard Dawes, theoretical and computational chemistry, in Missouri University of Science and Technology (USA).
- Gabriel Vazquez, Institute of Physics, Mexico.
- Roberto Marquardt, Laboratory of Quantum Chemistry, University of Strasbourg, (France).
- Jean-Christophe Tremblay, Laboratory of theoretical physics and chemistry, University of Lorraine (France).
- Osman Atabek, ISMO, Paris-Saclay (France).

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References :

[1] F. Gatti, Nature, « News and Views », **557** (2018) 641.

[2] “Applications of Quantum Dynamics to Chemistry”, F. Gatti, B. Lasorne, H.-D. Meyer and A. Nauts, Springer (2017) Heidelberg.

[3] “Molecular Quantum Dynamics”, Editor: F. Gatti, Springer (2014) Heidelberg.

[4] H.-D. Meyer, U. Manthe, and L.S. Cederbaum, *Chem .Phys. Lett.* **165** (1990) 73.

[5] U. Manthe, H.-D. Meyer, and L.S. Cederbaum, *J. Chem. Phys.* **97** (1992) 3199.

[6] M. H. Beck, A. Jäckle, G. A. Worth and H.-D. Meyer, *Physics Reports* **324** (2000) 1.

[7] H.-D. Meyer, F. Gatti, and G. A. Worth, *Multidimensional Quantum Dynamics: MCTDH Theory and Applications* 2009 Wiley-VCH.

- [8] H. J. Wörmer *et al.*, *Science*, **334** (2011) 208.
- [9] C.Lévêque, D. Peláez, H.Köppel, R.Taïeb (2014), "Direct observation of spin-forbidden transitions through the use of suitably polarized light", *Nature Comm.* 5:**4126**.
- [10] M. Merchán, R. González-Luque, T. Climent, L. Serrano-Andrés, E. Rodríguez, M. Reguero, D. Peláez (2006), "Unified Model for the Ultrafast Decay of Pyrimidine Nucleobases", *J. Phys. Chem. B*, 110:**26471**.
- [11] R. P. Feynman (1982), "Simulating physics with computers", *Int. J. Theo. Phys.* 467:**258**.
- [12] D. Deutsch (1985) "Quantum theory, the church-Turing principle and the universal quantum computer", *Proc. Nat. Acad. Sci. USA*, 400:**97**
- [13] S. Barz , E. Kashefi , A. Broadbent, J.-F. Fitzsimons, A. Zeilinger, P. Walther (2012) "Demonstration of blind quantum computing", *Science*, 335:**303**.
- [14] C. M. Tesch, R. de Vivie-Riedle R (2002) "Quantum computation with vibrationally excited molecules", *Phys. Rev. Lett.*, 89:57901 **261**.