

Proposal for a PhD Thesis

Ecole doctorale Sciences Chimiques : Molécules, Matériaux, Instrumentation et Biosystèmes

Université Paris-Saclay

Quantum control of the coupled motion of electrons and nuclei in chemical processes

(Theoretical Chemistry)

Fabien Gatti, Eric Charron and Osman Atabek

Institut des Sciences Moléculaires d'Orsay

Our ability to manipulate quantum effects in customized systems and materials is now paving the way for *a second quantum revolution*, which takes quantum theory to its technological consequences. It should lead to devices with far superior performance and capabilities: for instance quantum computers that exploit the superposition principle of quantum mechanics and thus quantum coherence. In this context, a systematic use of quantum effects in molecular systems could have an enormous future potential since molecules are the building blocks of every-day life. There is indeed growing evidence that *a significant number of chemical reactions are impacted by strong quantum-mechanical effects involving both the electrons and the nuclei*. The advent of femtochemistry allows scientists to follow in real time the motion of nuclei in molecular processes. 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 thus becomes 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.

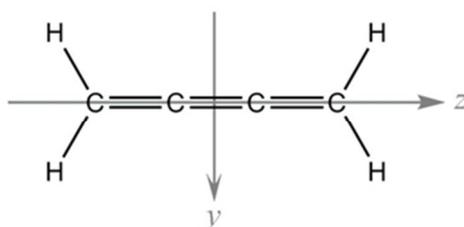


Figure 1: Molecule of butatriene

The main 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*. We will consider the following cases:

- I. Photons in the ultraviolet-visible region can promote molecules to highly excited electronic states (see Figure 2). 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. *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 and photosynthesis. The presence of conical intersections gives rise to new effects that cannot be described classically. First, the fact that a system can be transferred from one quantized state to another is per se a quantum effect. Second, the electronic states can remain coherent with respect to each other during a non-negligible period of time, leading to new quantum interference effects (for instance the appearance of the so-called geometric phase or Berry phase effect). When the system is excited by a laser pulse, which is a source of coherent light, the quantum coherence is drastically enhanced and the induced quantum interferences can be manipulated. This has already been observed experimentally in very complex systems. Indeed, recent experiments provided observation of long-lived electronic quantum coherence, after excitation by laser pulses, in energy transfer processes in light-harvesting complexes of biological systems such as photosynthetic systems at ambient temperature and in the condensed phase. Even more interesting is the fact that these interference effects have also been manipulated experimentally (by shaping the laser pulses) to change the yield of the electronic transition in retinal isomerization in bacteriorhodopsin. The goal of the PhD will be to study theoretically *the control by laser pulses of the interference effects around conical intersections* for small isolated systems for which realistic and accurate Hamiltonian operators are available. We will consider for instance the molecule of butatriene (illustrated in Figure 1). We will start with low-dimensional models and add appropriately shaped laser pulses to see how they change the interference effects and try to highlight strategies of control of these interferences.

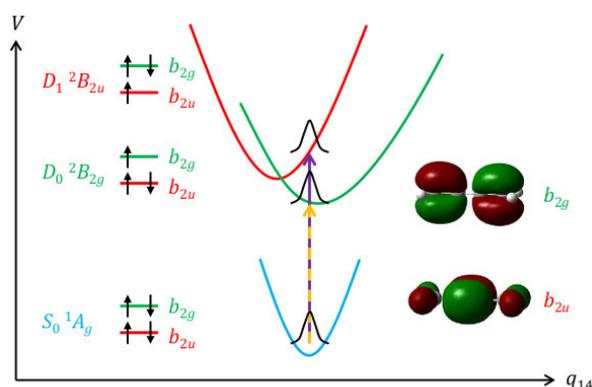


Figure 2: Excitation by a photon in the UV domain of an electronic state coupled with a second one through a conical intersection. Example of the butatriene molecule.

- II. As aforementioned since the advent of femtochemistry that allows scientists to follow in real time the motion of nuclei in molecular processes, tremendous progress has been achieved experimentally with the possibility to produce even shorter laser pulses at the attosecond time scale. The 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 the most elementary aspects of a chemical act at a quantum mechanical level. One challenge is to control the quantum coherence created by the laser pulses to guide these processes. Simulations in collaboration with experimentalists were already performed on the ozone molecule, O_3 . A quantum superposition of two electronic states, the ground state and the B state (Figure 3) was created (the transition from the ground state to the B state is responsible for the famous ozone layer effect in the upper atmosphere) using a laser pulse of 3 fs.

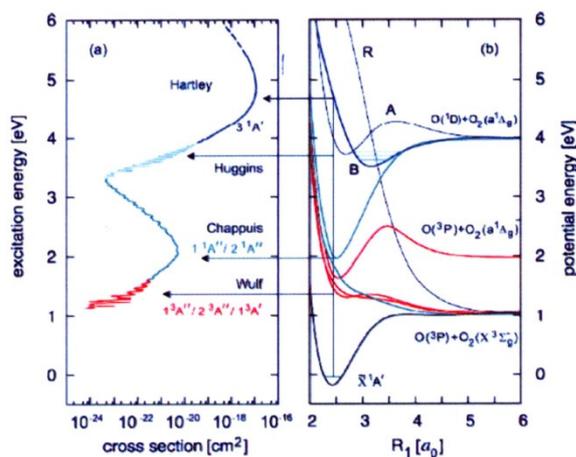


Figure 3: A laser pulse creates a superposition of the electronic ground state and the B state.

The electronic wave packet leads the system to dissociation but one part of the wave packet is trapped in the potential well of the B state. Figure 4 presents *the electronic quantum coherence* between the two electronic states. When the nuclei move the coherence decreases. The “revival” of the quantum coherence observed around 17 fs is a proof that the part of the wave packet that is trapped in the potential well keeps periodically the quantum coherence. Many important questions remain open: how is it possible to change these electronic/vibrational quantum interferences to change the process? How can we measure these quantum interferences experimentally?

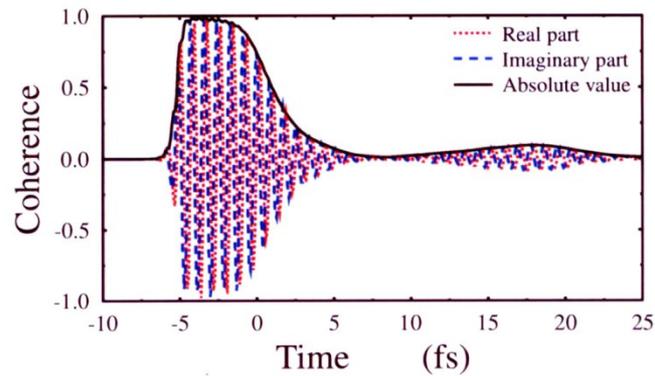


Figure 4: Quantum coherence between the ground state and the B electronic state in ozone created by a very short laser pulse.

We will use the *Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) package*. 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.

This PhD will be done in collaboration with Hans-Dieter Meyer from Heidelberg who is the main developer of the MCTDH package, Stéphane Guérin from Dijon who is an expert of quantum control and with experimentalists in the Institut des Sciences Moléculaires d'Orsay.

Contact: Fabien Gatti, fabien.gatti@u-psud.fr, Institut des Sciences Moléculaires d'Orsay, Bâtiment 350, Université Paris-Sud, 2^{ème} étage, bureau 261. Tel : 01 6915 8283.