

Controlling electron trajectories to access attosecond molecular dynamics

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Charge migration underpins chemical reactions and structural changes in systems ranging from atoms and molecules to biological samples. Accessing information carried by electron/nuclei dynamics is the key to understand how photo-initiated phenomena occur. This includes photo-ionisation in physics, photo-dissociation and electron rearrangement in chemistry, photo-induced biological processes as well as current and voltages switching in solid state material. These ultra-fast dynamics remain extremely challenging to capture directly because they take place on a sub-femtosecond ($<1\text{fs}=10^{-15}\text{sec}$) timescale and there is no existing detector with a fast enough response. Therefore it is crucial to find innovative methods to access this transient information. We propose to develop and exploit such methods allowing the observation in real time of attosecond to femtosecond dynamics which are universally present in physical, chemical and biological photo-induced processes.

High order harmonic generation (HHG) is a nonlinear process that we use as an observable for capturing these ultra-fast charge migrations. The HHG consists in the up-conversion of a strong laser field frequency into its harmonics by its interaction with an atom or a molecule. The semi classical description of such process has been developed by P.B. Corkum and K. Kulander [1, 2]. In this picture the process consists of a succession of three steps within an optical cycle: (i) whilst the strong oscillating laser field is near maximum (every half optical cycle), it distorts the coulomb potential of the atom or the molecule so that a valence electron can tunnel ionise through the remaining potential barrier into the continuum; (ii) in the continuum, the freed electron can follow classical trajectories define by Newton's equations of a free charged particle in a laser field and therefore acquiring kinetic energy. Considering linearly polarised laser, the electron may return to the cation; (iii) it can then recombine with the core and the accumulated kinetic energy plus the binding energy of the electron is released as the coherent emission of an XUV photon. The quantum mechanical story of the process consists of a dipole interaction of the returning electronic wave packet with an incomplete orbital (orbital which presents a hole due to ionisation of the electron wave packet). The electronic wave packet has properties inerrant to the process itself: its duration is related to instants of ionisation and recombination that are all within half of the optical cycle so has an attosecond duration and thus the (iii) step results in the emission of attosecond bursts of XUV photons; since this process is repeated every half-cycle (at every maxima of the laser field) a train of attosecond pulses is emitted which corresponds spectrally to a comb of harmonics of the laser frequency (up-conversion); it has a de Broglie wavelength of few Angstroms (comparable to molecular internuclear distances for instance). Therefore the electron wave packet can be used as a probe for the cation dynamics (nuclear and electronic motions, electronic rearrangements, conformation changes etc...) during a time window defined by the ionisation and recombination instants. The internal dynamics of the cation which affect the dipole interaction will be encoded in the harmonic emission (self-probing approach). Studying the properties of the harmonic field emitted such as intensity, phase and ellipticity, will give key diagnostics of the attosecond dynamics of the core. Controlling the trajectories by using synthesis of the laser field interaction with the target allow the control/measure of the dynamics involved.

Experimentally the encoded information is not as easily accessible: In a gas jet, all molecules in the volume of interaction are randomly oriented. The measured harmonic signal results from an average

over all possible orientations so that any information about the molecule is lost. Therefore the molecular sample must be aligned before the interaction with the laser pulse. This can be achieved by impulsively aligning the sample using a weak pre-pulse [3]. The electric field of the pre-pulse interacts with the molecular anisotropic polarisability. It induces a torque on the molecule depending on the angle between the main molecular axis and the laser polarisation direction. A rotational wave packet is formed that evolves producing revivals of the alignment with a periodicity typically of a few picoseconds. The structural information on the intramolecular dynamics is accessible and can be studied by HHG and rotating the molecules alignment (changing pre-pulse polarisation orientation) with respect to the laser polarisation. This type of alignment is valid for symmetric molecules such as N_2 or CO_2 . For asymmetric molecules as N_2O , they should be pre-aligned but also oriented (dipolar moment in same direction). It is achievable by combining a hexapole and additional dc-fields in the interaction region to select specific rotational states [4].

The first scheme of “self-probing” ultra-fast nuclear motion using HHG has been successfully demonstrated at Imperial College London [5] on deuterated partners (D_2/H_2 then (CD_4/CH_4)), technique known as PACER (Probing attosecond dynamics using chirped electron recollision). The PACER technique has opened the route to such “self-probing” approaches. In parallel to this study, orbital tomographic reconstruction to access electronic dynamical information was first proposed by Paul Corkum and David Villeneuve [6]. The first experimental demonstration in N_2 molecule was obtained by measuring the amplitude of the harmonics emitted and assuming the value for their phase from theoretical assumptions. Recently, the group of Pascal Salières in CEA Saclay and Richard Taieb at LCPMR measured this spectral phase with their RABITT technique (reconstruction of attosecond beating by interference of two-photon transitions) [7] reducing the assumptions of such a technique. They managed to reconstruct the highest occupied molecular orbital (HOMO) and its second one (HOMO-1) of N_2 [8]. In addition other techniques based on two-sources interferometry and or alignment control has successfully allow the observation of electronic hole migration within the attosecond scale [9; 10]. All these techniques are revolutionary but most of the time relied on the comparison of the HHG emission from molecules compared to the emission from atomic or molecular partners. An alternative strategy to access the intra-molecular dynamical information is to control the electron trajectories.

We will address this point in the presentation detailing two techniques we currently use in our labs: the QPI technique and the multi-colour field synthesis.

These electron trajectories can be categorised in three families over an optical cycle with the cut-off trajectory leading to the highest photon energy. For emission of all lower energy photons (referred to as the plateau region in the high harmonic spectra), two families exist, one with duration shorter than the cut-off one known as the “short trajectory” and one with duration longer than the cut-off one known as the “long trajectory”. In the quantum picture, this corresponds to developing the interaction dipole in a Fourier sum, each complex element of the sum being a trajectory family named a “quantum path” with its amplitude and its phase. Therefore the short and the long trajectories, responsible for the same photon energy can be seen as the two arms of an interferometer with a specific weight (the amplitude) and a phase or they can be seen as two paths to probe the core dynamical process over a window ranging from few hundreds of attosecond to few femtoseconds. The difference of phase between the two arms scales as the product of the trajectories duration difference τ and the ponderomotive energy of the laser field U_p . This product is proportional to the laser intensity profile I and scales quadratically with the laser wavelength λ . Therefore experimentally two parameters can lead to trajectory interferences or trajectory control which are the laser peak intensity I and λ or a combination of wavelength (multi-colour laser field synthesis). The first calculations on the intensity dependent harmonic dipole strength, has revealed the trajectory interference signature reported by Maciej Lewenstein in the well-known saddle point model [11] and recently using the wavelength dependence of the harmonic dipole strength, these interferences have been calculated by [12], the experimental study being difficult because it requires a wavelength tunable laser system. However controlling the phase difference by I is easier and this has been our approach for re-

solving the interferences of quantum paths [13]. This approach has revealed in particular that since the phase difference is dependent on the intensity profile in time (leading to modulation of the harmonic spectral amplitude) and in space (leading to spatial rings in the far field), it is important to resolve spectrally and spatially the harmonic emission in order to resolve the quantum-path interferences known now as the QPI technique. Recently we have extended the QPI technique to the case of more complex systems such as molecules [14] and have demonstrated an accuracy of quantum path control of ~ 10 's of asec sufficient to resolve intra-molecular dynamics. Toward controlling these paths we have implemented as well synthesis of laser field using multiple colours. We manage to demonstrate that such synthesis allow the control of the quantum paths contribution to the HHG process [15] which open new degree of freedom to explore the QPI and the PACER techniques towards bigger molecular systems as ring molecules and in condensate phase.

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