

COST WG1 meeting: **Preliminary programme & Discussion points**

July 3

9:00-10:30 XFEL and X-ray spectroscopy: experiment

Discussion leader: Jon Marangos

10:30-11:00 Coffee break

11:00-12:30 Theory of atoms and molecules under intense short wavelength radiation

Discussion leader: Peter Lambropoulos

12:30-14:00 Lunch & Posters (Posters go up and stay until 15:30 Friday)

14:00-15:30 High-harmonic spectroscopy: achievements, challenges and perspectives

Discussion leader: Yann Mairesse

15:30-16:00 Coffee break

16:00-18:00 Work in groups

Group 1: TDDFT and applications to attosecond spectroscopy

Discussion leaders: Françoise Remacle and Franck Lepine

Group2: Electron dynamics in strong IR fields

Discussion leader: Bernard Piraux

July 4

9:00-10:30 Time-dependent computational methods for multielectron systems in external fields

Discussion leader: Alejandro Saenz

10:30-11:00 Coffee break

11:00-13:00 Multielectron ionization & coupled electron-nuclear dynamics

Discussion leader: Agapi Emmanouilidou

13:00-15:30 Lunch & Posters

XFEL and X-ray spectroscopy: experiment

Discussion leader: Jon Marangos, ICL, UK

Core group: Nora Berrah (WMU, USA), Michael Meyer (European XFEL, Germany), Nina Rohringer (CFEL, Germany)

The aim of this discussion is to explore how X-ray free electron lasers (XFELs) and time resolved X-ray spectroscopy methods can be used to measure ultrafast electronic dynamics in molecules. It is apparent that by using current X-FEL technology soft- to hard-X-ray pulses of duration down to 3 fs can be produced, in the future still shorter pulses may be possible. In principle this is short enough to measure molecular dynamics, including electronic motion within the molecule, over the timescales relevant to a vast range of molecules and their reactions. Nevertheless a SASE X-ray laser is far from a perfect light source and strategies to deal with spectral and temporal jitter and intensity fluctuation must be developed to realize the full potential. Emphasis will be placed upon time resolved measurements of the native dynamics in molecules, rather than strong field driven or intense X-ray initiated dynamics but these too may be part of the developing discussion.

The session will be begun with brief overviews of the current experimental situation at LCLS and FLASH from Jon Marangos, Nora Berrah and Michael Meyer. This will introduce the present capabilities of the light sources, discuss some of the existing measurement methods, present recent experiments and suggest future directions. Immediately after this we will be opening the floor to a more general discussion with new topics brought in and presented. For instance Nina Rohringer will talk about the prospects for Raman Inelastic X-ray Scattering.

To get the ball rolling here are some of our thoughts about issues and questions we should try to address in the discussion:

- To what extent can spectral domain RIXS answer questions of attosecond electron dynamics in matter (I have in mind Abbramontes work of a few years ago)?
- What are the current limits on the pulse duration of an X-ray FEL that is (a) possible, (b) usable (given the absence of good machine diagnostics for very low bunch charge)?
- How well can the jitter between an X-ray FEL and an external laser be controlled and measured on a shot wise basis to allow sub-10 fs time sorting?
- Can we tolerate the SASE fluctuations in spectrum and time profile that beset all experiments, and what strategies do we have to deal with this?
- How can we use the recently developed schemes for self-seeding for VUV-X rays?
- What is the best way to perform X-ray pump – X-ray probe experiments?
- Is the signal in such an X-ray pump experiment meaningful given all of the ionization/Auger decay channels that are excited, to what extent is more supporting theory going to be an essential feature of experiments?
- What detection channels are available for an X-ray probe – and under which circumstances would absorption, photoelectron or Auger electrons be suitable choices?
- Can time-resolved X-ray diffraction with an X-ray FEL pick up electronic motion?
- Are other sources e.g. HHG, ever likely to be bright enough in the relevant X-ray range to be of much use?
- Will X-ray FEL pulses ever be short enough to measure correlation driven charge migration?

THEORY OF ATOMS AND MOLECULES UNDER INTENSE SHORT WAVELENGTH RADIATION

Discussion leader: P. Lambropoulos (IESL- FORTH and Dept. of Physics, Univ. of Crete, Crete, Greece)

The Free Electron Laser (FEL) is not new. It has existed in the IR for more than 40 years or so. The short wavelength FEL (VUV to X-rays), with substantial photon fluxes and pulse durations down to a few femtoseconds, is new; say, about 10 years old. Its applications and uses cover a vast range of topics, from atoms, to plasmas, to dense matter, etc. Nevertheless, energetic photons interact with individual atoms, and in fact sub-valence electrons of increasingly deeper shells, as the photon energy rises from soft to hard X-rays.

It is therefore necessary to have a quantitative understanding of the manner in which such intense, short pulse duration sources interact with atoms and molecules, irrespective of the particular application.

XUV – Soft X-rays versus Hard X-rays:

For photon energies up to, let us say 300 eV or so, the processes begin with single-photon ionization of a sub-valence shell, possibly followed by Auger, but after a few ionic stages, multiphoton processes set in (e.g. Xenon under 100 eV radiation, begins with 4d electron escape). But for photon energies of keV or more, it is mostly single-photon absorption by deep shell electrons that dominates, with Auger cascades and multiple electron escape. Multiphoton absorption is generally expected to be of negligible importance. A sharp demarcation line between the two extreme regimes does not exist, which makes the intermediate regime even more demanding.

Some basic features of the game:

- (1) Pulse durations (many field cycles) and intensities (negligible ponderomotive energy, large Keldysh parameter) are, for the time being and the foreseeable future, such that rate or density matrix equations, within LOPT (Lowest non-vanishing Order of Perturbation Theory) are valid.
- (2) No recollision dynamics, as known in the IR, is relevant. But direct (nonsequential) multielectron escape possible; under appropriate conditions of intensity and pulse duration. SAE approximation not applicable
- (3) Non-linear processes, notably multiphoton ionization of substantially high order present and in fact pronounced, especially for intermediate photon energies.

Some basic questions:

- (1)** How much ionization? Underlying mechanism; sequential, direct or both?
- (2)** Efficiency of multiple ionization in terms of photon energy and other FEL beam parameters.
- (3)** Role of the temporal (stochastic) structure of the pulse.
- (4)** Methods for the calculation of multiphoton cross sections.
- (5)** Non-linear excitation of Auger resonances.
- (6)** Double core-hole in atoms and molecules.
- (7)** Modification of core-hole dynamics via an external strong IR or optical field.

Anticipating the eventual rise in peak intensities, especially if combined with significantly shorter pulses, of the order of a few cycles, the issue of non-perturbative approaches becomes of relevance. This would require the solution of the TDSE (Time Dependent Schrodinger Equation) for a multi-electron system, in which the coupling of several shells to the field needs to be included; which is very different from the TDSE under the SAE approximation.

A first attempt and results based on TDDFT (Time Dependent Density Functional Theory) will be introduced and discussed.

Contributions to the discussion of the above, among other, issues are welcomed.

High-harmonic spectroscopy: achievements, challenges and perspectives

Discussion leader: Yann Mairesse (CELIA, U Bordeaux, France)

Even if the sensitivity of high-harmonic generation to the structure of the generating medium had been pointed out in very early studies [1], HHG really emerged as a structural probe in 2004 with the seminal work of Itatani et al [2]. The spectacular tomographic reconstruction of the highest occupied molecular orbital from N₂ triggered a lot of experiments aiming at measuring molecular structure and dynamics with HHG. What is the situation ten years after? The application of tomographic imaging stayed restricted to simple and static systems [3,4], both for fundamental reasons (structure of the recolliding electron wavepacket, requirement of a reference system, contribution from multiple molecular orbitals, possible strong-field induced dynamics) and practical reasons (difficulties in aligning complex polyatomic molecules). Nevertheless, some of the effects that prevent simple tomographic reconstruction have opened new exciting perspectives for high-harmonic spectroscopy, and the possibility to measure sub-cycle dynamics in the molecular ion, between ionization and recombination [3,5,6].

From a femtochemistry point of view, the high sensitivity of high-harmonic spectroscopy to molecular rotations [7,8], vibrations [9,10], or more general relaxation dynamics following photoexcitations [11,12,13] has been confirmed. HHS thus appears as a useful time-resolved spectroscopy, complementary to conventional femtochemistry techniques, such as photoelectron spectroscopy.

The proposed discussion points for the XLIC WG1 meeting on HHS are:

Experimental techniques: Feeding theoreticians with better data

- What new tools can be developed to fully characterize the high-harmonic emission (spectrum, polarization direction, ellipticity, phase ...)?
- Creating new observables: how can we increase the dimensionality of measurements, what parameters can we vary?
- What techniques can be developed to identify ionization channels in HHG?
- How can we measure and calibrate out the influence of the strong laser field on the measured dynamics?
- Can we measure the field-induced sub-cycle electronic dynamics occurring between ionization and recombination?
- Challenges associated with HHG by mid-IR fields: how far can we go?

Theoretical developments: how deeply should we dig into theory to understand experiments?

- What techniques should be employed to calculate strong-field ionization rates in polyatomic molecules?
- What is the role of electron correlation and multi-electron effects?
- What is the role of laser-induced coupling between channels?

- How accurately can we calculate recombination dipole moments?
- Is recombination affected by the laser field?
- What is the influence of resonances (autoionizing states, shape resonances) in the recombination process?
- Role of macroscopic propagation: what kind of artifacts can we expect?

Femtosecond dynamics in polyatomic molecules:

- How can we improve the contrast in pump-probe experiments?
- Will highly electronically excited states (with very low I_p) generate harmonics?
- Will the high-sensitivity of HHS hold for polyatomic molecules in which wavepackets can spread over several dimensions?

High harmonic spectroscopy vs other attosecond techniques: complementarity and uniqueness?

New spectroscopic schemes for HHS: HHG by XUV ionization and IR-driven recombination

- [1] C.-G. Wahlström *et al.*, Phys. Rev. A **48**, 4709 (1993).
- [2] J. Itatani *et al.*, Nature **432**, 867 (2004)
- [3] S. Haessler *et al.*, Nature Phys. **6**, 200 (2010)
- [4] C. Vozzi *et al.*, Nature Phys. **7**, 822 (2011)
- [5] S. Baker *et al.*, Science **312**, 424 (2006)
- [6] O. Smirnova *et al.*, Nature **460**, 972 (2009)
- [7] T. Kanai *et al.*, Nature **435**, 470 (2005)
- [8] C. Vozzi *et al.*, PRL **95**, 153902 (2005)
- [9] N. Wagner *et al.*, PNAS (2006)
- [10] W. Li *et al.*, Science **322**, 1207 (2008)
- [11] H.J. Woerner *et al.*, Nature **466**, 604 (2010)
- [12] H.J. Woerner *et al.*, Science **334**, 208 (2011)
- [13] H. Ruf *et al.*, JCP **137**, 224303 (2012)

Work in groups:

Group I: TDDFT and applications to attosecond spectroscopy

Discussion leaders: Françoise Remacle (University of Liège, Belgium) and Franck Lépine (Institut Lumière matière, CNRS Lyon University, France)

-Challenges, perspectives and limitations

(30')

F. Lépine & F. Remacle

Attosecond spectroscopy is offering new challenges for theoreticians as it provides observables that characterize electron and nuclear motion on time-scales and energy range where electron correlation and couplings to nuclei are crucial. The field is currently expanding to the investigation of increasingly complex species; therefore it is clear that many-body theories that are able to treat a large number of interacting electrons and nuclei become compulsory to realistically model experimental observables. TDDFT is one of the successful approaches that allow us to describe accurately complex molecular systems. In this work group discussion we will examine when TDDFT can enlighten the interpretation of experiment results. We will emphasize the current limitations of the theory in order to stimulate discussions about how these limitations can be overcome and how cross fertilization between theory and experiment can be envisioned. Questions that will be discussed include :

- Which observables to compare with experiments?
- “real time- real space” and “frequency domain” TDDFT
- Accurate description of a large number of excited electronic states and transition moments
- Treatment of electron correlation and many-electron processes
- Vibronic coupling, nuclear motion and fragmentation, Ehrenfest and beyond

-Control of electronic dynamics visualized by angularly resolved photoelectron spectra in molecules

(20' talk+10' questions)

Benoit Mignolet, Chemistry department, Liège University (Belgium)

We model realistic pump probe experiments that monitor the ultrafast electronic dynamics in PENNA ($C_{10}H_{15}N$) and LiH (Fig.1) using a coupled equation scheme that includes the ionization continua and field effects. The time-dependent wavefunction is expressed on a basis of field free stationary electronic states that are computed either in CASSCF or with the linear response implementation of TDDFT in which the states are built from an expansion of Kohn-Sham determinants. We demonstrate the control of the charge migration¹ in PENNA and its probing. A 6fs IR pump pulse photoionizes the neutral molecule

and launches the charge migration in the states of the cation. The motion of the charge is probed by a 1.5fs XUV pulse that photoionizes the molecule and is reflected in the computed time-dependent molecular frame photoelectron angular distributions. Then we show by modelling a 6fs IR pump- XUV attosecond pulse train (APT) experiment in LiH that the APT can be used to disentangle the coherent superposition of states built by the IR pump pulse.² The APT acts as a frequency filter and only probes the superposition of states with a beating frequency matching the time interval between two XUV attopulses of the train.

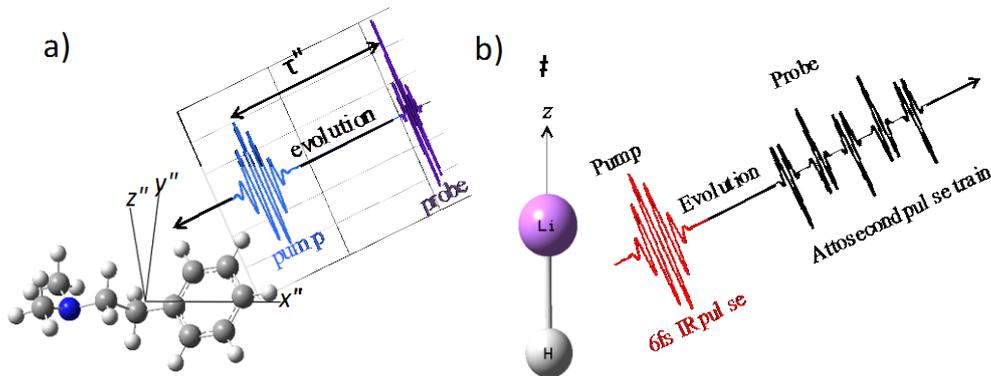


Fig 1: Schematic representation of the pump-probe experiments modelled PENNA (a) and in LiH (b).

[1]. B. Mignolet, R. D. Levine, and F. Remacle, J. Phys. B. 2014 *accepted*

[2]. B. Mignolet, R. D. Levine, and F. Remacle, Physical Review A (R) **89**, 021403 (2014)

-Modeling time-resolved spectroscopies with time-dependent density-functional theory (20' talk+ 10' questions)

Umberto De Giovannini, Nano-Bio Spectroscopy Group and ETSF Scientific Development Center, University of the Basque Country UPV/EHU, Spain

Molecular absorption and photo-electron spectra can be efficiently modeled with real-time time-dependent density-functional theory (TDDFT) [1]. We show how TDDFT can easily be extended to study time-resolved pump-probe experiments in which a system response (absorption or electron emission) to a probe pulse, is measured in an excited state [2]. This simulation tool helps in the interpretation of the fast evolving attosecond time-resolved spectroscopic experiments, where the electronic motion must be followed at its natural time-scale. We show how the extra degrees of freedom (pump pulse duration, intensity, frequency, and time-delay), which are absent in a conventional steady state experiment, provide additional information about electronic structure and dynamics that improve a system characterization. The theory is illustrated through a set of test cases ranging from atomic to molecular systems selectively including the effects of vibrations in the ionic degrees of freedom [3].

[1] U. De Giovannini, D. Varsano, M. A. L. Marques, H. Appel, E. K. U. Gross, and A. Rubio, Phys.Rev. A 85, 062515 (2012).

[2] U. De Giovannini, G. Brunetto, A. Castro, J. Walkenhorst, and A. Rubio, Chemphyschem 14, 1363 (2013).

[3] A. Crawford Uranga, U. De Giovannini, D. J. Mowbray, S. Kurth, and A. Rubio, J. Phys. B (2014), in press.

-General Discussion

(30')

Contributions are welcome!

Group2: Electron dynamics in strong IR fields

Discussion leader: Bernard Piraux (UCL, Louvain-la-Neuve, Belgium)

Electron dynamics in atoms and molecules exposed to strong infrared fields is usually understood in terms of the well established strong field model in which the main physical processes namely ionisation or high order harmonic generation proceed in three steps: a tunnelling of the electrons through the barrier formed by the Coulomb potential and the quasi-static external field followed by a field driven propagation of the electron and by a possible subsequent re-collision of the electron with the residual ion. However, recent experiments, some of them with extremely high temporal resolution, as well as various numerical simulations show clear evidences of the crucial role of the long range Coulomb potential in these processes, thereby requiring a more accurate formulation of the strong field model. The discussions will be along these lines.

Time-dependent computational methods for multi-electron systems in external fields

Discussion leader: Alejandro Saenz, Humboldt-Universität zu Berlin, Germany

Core group: Sonia Coriani (Universita di Trieste, Italy), Daniel Dundas (Queen's University, Belfast, UK), and Armin Scrinzi (LMU München, Germany)

Introduction: The quantum-mechanical description of many-electron systems, especially many-electron molecules, exposed to intense time-dependent external fields remains a formidable challenge. In fact, in view of the exponentially growing Hilbert space an exact, fully converged treatment will remain unsolvable on classical computers, if systems with really many electrons should be considered. On the other hand, quantum chemistry has a long history in showing ways to treat even very large molecules to a surprising level of accuracy. However, traditional quantum-chemical approaches are usually restricted to the electronic ground and low-lying excited states. The main focus of this discussion group will be on the question of how quantum-chemical approaches may be used for or provide insight into the challenge of treating many-electron systems exposed to time-dependent external fields, especially to ultra-short intense laser pulses. While there is natural overlap with questions discussed especially in Topics 2 and 5, the focus here will be mostly on radiation with longer wavelengths and fully quantum-mechanical approaches.

Basic challenges in intense-field theory:

- Electronic density varies strongly on very short time and space scales.
- Large spatial and momentum spread of the electronic wavepacket.
- Time-dependent populations of the initial and the different final states may differ by many orders of magnitude and changes (mostly) exponentially with laser peak intensity.
- *Many-electron systems:* exploding Hilbert space.
- *Molecules:* multi-center problem (loss of spherical-symmetry).

Solutions to the one-electron problem (many working approaches):

Wavepacket expansion (radial part):

- directly on a grid or using discrete-variable representation (DVR) or finite elements (local representations),
- in B splines (almost local representation), or
- in some "global" functions like Gaussians, hydrogenic-type functions etc. (global representation).

Note: for many-electron systems the sparseness gained by the (semi-)local methods is lost!

Multi-center problem (molecules):

- “ignoring” the multi-center problem using one-center expansions or Cartesian coordinates,
- use of special coordinate systems (like elliptical ones for diatomics), or
- local multi-center basis combined with asymptotic spherical basis.

Solution of the time-dependent Schrödinger equation:

- propagator approaches (split operator, Crank-Nicolson, etc.),
- spectral expansion (mostly in field-free eigenstates), or
- Floquet *ansatz*.

Key question:

Based on the known and working one-electron approaches, how to proceed to many-electron multi-center systems?

Many-electron approaches (partly realized, partly in progress):

1. Frozen-core one-electron calculation (“single-active-electron approximation”) where the inactive electrons are frozen in their field-free initial-state orbitals (violates gauge invariance and Pauli principle).
2. Gauge-invariant and Pauli-principle fulfilling single-determinant approximation (TD-SD).
3. Time-dependent Hartree-Fock method (TD-HF), either restricted or unrestricted Hartree Fock (known problems for multiple ionization).
4. Time-dependent density-functional theory (TD-DFT) (known problems for multiple ionization).
5. Frozen-core two-electron calculation (“two-active-electron approximation”) describing the two active electrons with, e.g., configuration interaction (CI).
6. Coupled-channel (TD-CC) approaches (usually using field-free ionic channels).
7. Time-dependent configuration interaction (TD-CI) with different variants of the selection of configurations (full CI, single-excitation CI, single- and double-excitation CI, limited active spaces like complete or restricted active spaces CAS, ...)
8. Time-dependent multi-configuration (TD-MCHF, TD-MCSCF, ...) approaches (like multi-configuration Hartree-Fock) in which also the one-electron orbitals change time-dependently.

Comments:

- Experience (mostly, but not only with small molecules) indicates that the single-active-electron (SAE) approaches seem to catch the leading-order long-wavelength strong-field response.

- One natural extension is thus the two-active-electron (TAE) approach, especially treating two electrons (with different spins) in the same orbital.
- Another natural extension is the coupled-channel (TD-CC) approach, especially for treating electrons in different orbitals like the highest-occupied orbital (HOMO) and the ones below, the HOMO-1, HOMO-2 etc.
- Especially in molecules, where ionization from an orbital may be suppressed for some orientation, the effects covered by the TD-CC seem(?) to be more important than the ones covered by TAE (with electrons in the same orbital).
- Gauge invariance and Pauli-principle violation can be an issue for both, TAE and TD-CC (assuming that in the latter case realistic calculations may be limited to a small number of (field-free) channels).
- Recent studies highlight the influence of the core polarization (field-induced time-dependent dipole moment of the core) on the strong-field behavior. This is not covered by TAE and (small channel-number) TD-CC approaches, but (partly) in the gauge-invariant single-determinant (TD-SD), the time-dependent Hartree Fock (TD-HF), or time-dependent density-functional theory (TD-DFT). It should be fully included in multi-configuration (TD-MC) or configuration-interaction (TD-CI) approaches, if a sufficient number of the relevant(!) configurations is included.
- For “larger”, chemically more relevant molecules one expects an even larger influence of the core polarization (extended system) and interfering ionization from lower-lying orbitals (energetically more densely spaced orbitals) than for most of the so far discussed small molecules.

Resulting key questions for this discussion:

- What is the current status of many-electron approaches?
- What do we know about their advantages and limitations?
- What indications do we have for the relative importance of core polarization and interfering inner-orbital ionization?
- Are there methods that treat both of these effects on similar or even equal footing?
- Can we profit even more from concepts, algorithms, and developments in quantum chemistry?
- Can we profit from the development of GPUs, i.e. graphic cards for computing, and the corresponding parallelization?

Contributions to this discussion from all participants, especially young fellows, are highly welcome!

Multielectron ionization & coupled electron-nuclear dynamics

Discussion Leader: Agapi Emmanouilidou (UCL, UK)

Core group: Jan-Michael Rost (MPIPKS, Germany), Fernando Martin (UAM, Spain), Robert Mosshamer (Max-Planck-Institut für Kernphysik, Germany)

Accounting for multi-electron dynamics as well as for the interplay of electron and nuclear motion in molecules that are strongly-driven by IR fields is a highly challenging task in the field of Attosecond and Strong-Field Science. Due to the many degrees of freedom involved, exploring multi-electron correlation and ionization in strongly-driven molecules is currently largely out of reach for quantum mechanical techniques given the computational resources available. In this session:

1) We will present results for the current status of molecular quantum mechanical techniques in the context of ionization and high harmonic generation (HHG) induced by strong IR femtosecond pulses on H_2^+ . The quantum method that will be described consists in solving the time-dependent Schrödinger equation (TDSE) in a grid for both electronic and nuclear coordinates. This method is designed to extract correlated (2D) photoelectron and proton kinetic energy spectra, as well as HHG spectra resolved in the vibrational energy of the molecular ion. It will be shown that the electron and the nucleus share the energy from the field differently depending on whether we work in the tunnel or the multi-photon regime. This suggests that correlation between electron and nuclear dynamics in strong field ionization is more complex than one would have anticipated. Moreover, it will be shown how the Coulomb explosion triggered by ionization of the molecule can be used as a clock to time-resolve the emission of near- and below-threshold harmonics.

2) We will then proceed to present alternative methods to quantum mechanical ones for describing correlated electron dynamics during the break-up of many-center strongly-driven molecules. Specifically, we will discuss recently developed classical and semiclassical techniques for strongly-driven molecules. We will describe the initial phase space distribution involved as well as the propagation technique. We will then discuss how these techniques can be used to describe different processes during the fragmentation of molecules when strongly-driven by linearly and elliptically polarized laser fields. Such a process is the formation of highly excited neutral fragments. We will also present future challenges and multi-electron ionization processes to be addressed using these classical techniques in the context of molecular systems.

3) Touching base with experimental results we will discuss whether some of the

assumptions currently used to represent the initial state in semi-classical approaches have been tested experimentally. Such an assumption is for instance the momentum distribution along and perpendicular to the laser field after an electron tunnels through the field-lowered Coulomb potential. This will be discussed in the context of Ar and H₂ for intensities in the range of 10¹⁴ W/cm². Emphasis will be given to the population of excited states or, correspondingly, to the formation of a coherent superposition of electronic states as a result of tunneling. For atoms this is probed by means of a pump-probe scheme. For H₂ it is high-resolution electron spectra for dissociating and non-dissociating molecular states that contain information about the involved states.

4) Returning to the classical description of multi-electron dynamics, we will present reasons for the increasing popularity of such techniques: (i) even multiple ionization cross sections are technically easy to formulate and compute by just counting the electron trajectories which have left the target; (ii) in particular for multiple ionization, the system has energy high above the ground state, justifying a classical approach; (iii) quantum calculations are virtually impossible for multi-electron ionization. We will then briefly introduce the classical description of ionizing quantum dynamics. That is, we will classify it according to the number of trajectories/electron from deep quantum (a single particle probability distribution described by many trajectories) over a "natural" representation (each particle has its trajectory) to the plasma regime (many body density described by a few trajectories). Open problems will be addressed, in particular, how to implement the (quantum initial) conditions in a consistent way.