NUMERICAL APPOACHES FOR ULTRAFAST ELECTRON-NUCLEAR DYNAMICS

January 24th-26th 2018

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1. Proposal

1.1 Introduction and motivation

Recent years have seen growing interest in ultrafast electron dynamics taking place in condensed and dilute phases. This renewed interest has been largely triggered by advances in experimental fields like the discovery of High Harmonic Generation (HHG) or XFEL (X-Free Electron Lasers) sources that have opened the possibility to probe the dynamics at the electronic pace (of the order of 1 femtosecond) and even below with the advent of ultrashort laser pulses in the attosecond domain. There are several physical chemical processes that are ruled by the ultrafast electronic motions which are themselves tightly coupled to nuclear motion. We shall mention the characterization of transitions, propagations and relaxations of spins in solids; the non-linear optical properties of solids; the electronic conductivity in metallic films; the multiscale responses of bio-molecules submitted to irradiation by light or by ionizing radiations (α, β, …); the chemical reactivity on ice coated grains in the interstellar medium, to name but a few.

In these research fields, formal developments and numerical approaches have indubitably a central role to play, either in establishing theories or in describing at a microscopic level complex dynamical processes, and thus by providing detailed mechanisms that are sometimes difficult to access experimentally. The theoretical studies of ultrafast time scales raise serious issues though, on the one hand from the diversity of particles involved (electrons, nuclei, photons, other types of particles…) and on the other hand from the complexity of the physical systems of interest which often display non-periodic or non-homogenous topologies. In most cases, the system absorbs a certain amount of energy via an external perturbation and the question is how one can describe the subsequent dynamics. For instance, these can involve continuous flows of energy among the electronic and the nuclear degrees of freedom that must be accounted for in a realistic manner. The question of dissipation and thermalisation from an out-of-equilibrium situation is by far not trivial to include in many-body quantum approaches.

In that context, it is fair to note the good position in the international competition of French laboratories. This is illustrated for example by the presence of several theoretician groups in the

GDR UP. The road towards the full understanding of the ultrafast electron-nuclear dynamics in condensed or dilute matter is however still a long and winding one. The motivation for a workshop gathering theoreticians working on ultrafast electron/nuclear dynamics emerged in September 2016 during of the first plenary conference of the GDR UP. It appeared that ***a wide array of methodologies and implementations already exist by several research groups in France, and often independently one from the other.*** This was in fact a beneficial outcome of the GDR conference to have enabled the meeting of previously disconnected communities in physics, physical-chemistry or chemistry. It appeared that a workshop would be very welcome ***to share experience on methodologies*** (formal developments, algorithmic approaches, coding aspects, …), ***to identify current locks*** and ***think together on strategies to lift them up***; ***to favor networking*** and eventually ***to initiate collaborations among these groups***. This is the purpose of the present application for a "Discussion meeting" to the Moser node of CECAM.

1.2 State-of-the-art

We here review some of the methodologies developed in France for the description of the dynamics of electronic systems, with an emphasis on the expertise of the participants of the workshop. Therefore, we do not aim at being exhaustive in this review.

Electrons are particularly important when irradiating either a molecule, a cluster, a piece of DNA or a solid, since these are the first agents to react to an external perturbation, most of cases being a laser pulse or a swift charged projectile, at the timescale of 1 femtosecond. On a later stage (tens or hundreds of femtoseconds, or even a few picoseconds), nuclei can be impacted and can themselves participate to the response of the excitation, via coupling with electrons. In the dynamical situations we aim at, quantum effects at the side of electrons are crucial to describe the response of the irradiated system in a correct way. Nuclei also certainly play a role in the sense that electronic properties, as electronic energies, symmetries, etc., are driven by nuclei. One thus faces a difficulty in the choice of the right degrees of freedom among electrons and nuclei to be treated at a quantal level, but also in the various timescales (from attoseconds up to picoseconds at worse) to cope with. Brute force numerical simulations of electronic and nuclear degrees of freedom at the quantum level are still out of reach but for rather small systems (a few electrons and a few atoms at most) and over a few femtoseconds at most. There are various quantal

approaches to attack these issues, usually bound to the system under study (molecules in isolation or in an environment, surfaces, solids, etc.) and/or to the electronic observable one wants to compute (electronic population, photoelectron spectra, high harmonic generation, …). Among the numerous dynamical scenarios one can envision, we have identified several directions to be explored in this workshop, that we now briefly describe.

From exact methods to effective approaches

Describing at a theoretical level the ultrafast chemistry or physics taking place after excitation of multielectronic systems remains a major objective and challenge in many different fields, as atomic and molecular physics, astrochemistry, biochemistry, surface sciences or material sciences. If there exist advanced wave function-based quantum-chemical methods such as complete-active space self-consistent field (CASSCF) or multi-reference configuration interaction (CI), only few have been extended in the time domain and they are generally restricted to very small systems excited over a few femtoseconds. In these approaches, electrons and nuclei are described on the same footing. Very recently, time-dependent CI (TDCI) has been successfully applied for the description of high harmonic generation in small molecules, while time-dependent CASSCF allows the study of electronic dynamics in the excited benzene.

To allow the treatment of larger electronic systems on a longer timescale, time-dependent mean-field approaches have been developed along the years, as the popular time-dependent Density Functional Theory (TDDFT) for valence electrons, while the ionic motion (by ions, we mean nuclei plus core electrons) is described by Newton's law and in practice, by Molecular Dynamics (MD). TDDFT has become over the last decades a tool of choice for the description of the dynamics of large molecular systems, at the price of an approximated exchange-correlation functional and the self-interaction error thereof. Only few tractable time-dependent self-interaction corrections (TDSIC) exist to date. One can however hope that such an elaborate approach is avoidable if the excitation energy is high enough, since the electronic response is then dominated by the Coulomb potential. For small perturbations instead, a TDSIC becomes compulsory.

A word of caution is also in place here when one talks about TDDFT. A first class of such approaches lies in the so-called "linearized TDDFT" in which a frequency dependence is accounted for but no time propagation as such is performed. Instead, "real-time" TDDFT does propagate wave functions in time, the latter being either discretized on a spatial grid or expanded on a basis set (plane waves or localized atomic orbitals). These different methodologies have their own advantages regarding computational efficiency of algorithms (e.g., efficient parallelization; Fast Fourier transforms or density fitting/Resolution of the Identity to compute Coulomb interaction, …) or the observable under study.

Electronic emission also constitutes a challenge in mean-field approaches since the latter can only provide the most probable pathway. And due to the approximate exchange-correlation functional in such methods, dynamical correlations are by essence absent and dissipation is therefore underestimated. Very recently, stochastic approaches on top of TDDFT have been developed and comparisons with more accurate methods as TDCI or TDCASSCF are highly desirable.

The dynamical cross-talk between quantal electrons and classical ions is often done within the Ehrenfest approximation. More elaborate approaches as surface hopping or exact factorization are possible alternatives, although having their own pros and cons. The TDDFT/MD approaches mentioned above are usually applied in finite electronic system. To envision the study of larger systems, one can consider the time-dependent version of time-binding DFT (TD-DFTB) or hybrid QM/MM (Quantum Mechanics/Molecular Mechanics) schemes based e.g. on the coupling of a real-time TDDFT code to a MD code or to polarization force fields. For periodic systems instead, periodic boundary conditions have been implemented in the TDDFT CP2K code for periodic systems.

Nonlinear optical response in solids

Despite the great interest in nonlinear optics, the scientific community has a poor understanding of several key aspects of the nonlinear optical response of solids. The reason is the enormous difficulty in the theoretical and numerical developments in this field. The challenge of an accurate theoretical description of the physical mechanisms behind the nonlinear optical processes is to take into account the many-body interactions among the electrons of the system.

Among these complex effects the most important are:
(i) the crystal local fields, *i.e*. the screening of the electromagnetic fields due to the microscopic nature of the material, (ii) the excitonic effects which describe the interaction between the excited electron and the remaining hole.

The macroscopic susceptibilities should include these many-body effects. In the first theoretical works on nonlinear optics, the second-harmonic susceptibility (SHG) in solids was calculated using an ab initio formalism, where crystal local-field effects (LFE) were included in the framework of the one-electron band theory. However, the inclusion of excitonic effects in $\chi^{(2)}$ is more problematic and only a few works exist on this topic, based on an effective two-particle Hamiltonian, describing the electron-hole interaction and derived from the two-particle Bethe-Salpeter equation (BSE). Recently, other approaches have been developed for the macroscopic susceptibility based on approximate exchange correlation kernels in the TDDFT framework. These approaches have been used successfully also for the third order response (THG), but the complexity of the formalism, based on perturbation theory, suggests that it would be prohibitive to extend the method to higher order. The calculation of the dynamical polarization, based on the Berry phase, replacing the calculation of response functions in the frequency domain by the evaluation of the dynamical polarization in the time domain provides a non-perturbative alternative. Note that, ab initio results for high harmonic generation in solids have been obtained recently in the framework of TDDFT, as provided in the Octopus package. However, for complex materials, it is well beyond the present state-of-the-art first-principles approaches.

1.3 Objectives

The objective of the discussion meeting is to gather researchers from the physics, chemical and physical-chemistry communities who develop numerical simulation techniques and formal approaches dedicated to ultrafast (as-fs) electronic and/or electron-nuclear dynamics. Our aim is to share experience in methodologies and numerical implementation. The workshop will gather a restricted list of participants (< 20) in order to favor constructive discussions on realistic problems. A main objective will be to identify key methodological locks and solutions that can be envisioned. For example we foresee discussions on the various approximations entering the practical definition of the TD XC potential in DFT based methods (adiabatic approximation, SIE,

asymptotic behaviors…); on the coupling between electronic and nuclear degrees of freedom and/or with an environment, or on the strategies to reach the most efficient implementations for HP architectures.

The workshop will start on January 24th (afternoon) and will end on Friday 26th. It will take place at LCP of Université Paris Sud (Salle Magat, Bâtiment 349). The timetable will be organized around long presentations of the participants (40'). We will ask the participants to emphasize the technical and, importantly, on the possible difficulties they are currently facing. Long discussion time will be possible at coffee breaks or in evenings.

1.4 Participant List (confirmed for many of them)

Name	*Methods*	*Physical objects / processes*
Federica Agostini (LCP, UPSud) federica.agostini@u-psud.fr	Exact factorization, electron-nuclear dynamics	Molecules, methodological developments
Claudio Attacalite (Cinam, Marseille) attaccalite@cinam.univ-mrs.fr	TDDFT, BSE, Berry phase	Nano objects, solids
Thierry Auguste (CEA Saclay) thierry.auguste@cea.fr	TDSE, matter-light interactions	HHG
Eric Charron (ISMO, UPSud) eric.charron@u-psud.fr	TDSE	photoelectron spectroscopy, MO tomography
Marie-Anne Hervé du Penhoat (IMPMC, UPMC) marie-anne.penhoat@impmc.upmc.fr	Ehrenfest MD, real-time TDDFT (plane waves)	Molecules of biological interest
Paul-Antoine Hervieux (IPCMS, Unistra) paul-antoine.hervieux@ipcms.unistra.fr	Semiclassical Vlasov-Poisson	Spin dynamics, metallic nanostructures
Aurélien de la Lande (LCP, UPSud) aurelien.de-la-lande@u-psud.fr	TDDFT (localized basis sets), polarizable QM/MM	radiation damages to biomolecules
Eleonora Luppi (LCT, UPMC) eleonora.luppi@upmc.fr	TDCI, TDDFT (localized basis sets)	HHG, isolated molecules
Thomas Niehaus (ILM, Lyon) thomas.niehaus@univ-lyon1.fr	TD-DFTB, MBPT	Quantum dots, molecular electronics
Phuong Mai Dinh (LPT, UP Sabatier) dinh@irsamc.ups-tlse.fr	Real-time TD-DFT (space-grid based), TDSIC, Stochastic TDHF	Ionization dynamics in finite systems; dissipation
Mathias Rapacioli (LCPQ, UP Sabatier) mathias.rapacioli@irsamc.ups-tlse.fr	TD-DFTB	Reactivity/spectroscopy for astrochemistry

André Saul (Cinam, U Aix Marseille) saul@cinam.univ-mrs.fr	DFT, DFTB, QM/MM	Surfaces, solids, magnetizations
Richard Taieb (LCMR, UPMC) richard.taieb@upmc.fr	TDSE	Electron dynamics, small molecules
Nicolas Tancogne-Dejean nicolas.tancogne-dejean@mpsd.mpg.de	TDDFT	HHG in solids
Morgane Vacher morgane.vacher@kemi.uu.se	TD-CASSCF	Electron dynamics, small molecules
Valérie Véniard (LSI, Polytechnique) valerie.veniard@polytechnique.fr	TDDFT, LFE, perturbative approaches	SHG, THG in solids

2. *Financial Support*

The budget for the workshop is indicated in the table below. Travel expenses for the members of the GDR-up will be partly covered by the GDR. Funding from the Moser node of CECAM will cover hotel expenses for 8 participants at Hôtel d'Orsay, lunches (buffet on 25th and sandwich bags on the 26th) and dinner (25th). Lunches will be purchased at CESFO (Orsay). Coffee breaks will be taken in charge by LCP. The budget is based on the enclosed invoice.

The room "Magat" of LCP where the workshop will take place will be put at our disposal at no fees.

Expenses	***estimated cost (TTC)***	***funding source***
Hotel	1300	CFCAM
Travel	1600	GDR-UP & CFCAM
coffee break/breakfast/printings	100	LCP
Lunch (25th, 26th)	373 (invoice joint, CESFO)	CFCAM
Dinner (25th)	680	CFCAM
TOTAL	4053	