Dynamics of irradiation: from molecules to nano-objects and from material science to biology

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Abstract. We give a brief review of theoretical and computational tools developed for the description and analysis of irradiation dynamics of cluster and molecules. We illustrate the capabilities of the method on the demanding example of C$_{60}$ irradiated by various laser fields.

1. Introduction
Irradiation of matter constitutes a key tool in physics, chemistry, and biology, for analyzing structural and dynamical properties of atoms, molecules, clusters and bulk material. Lasers offer here an especially flexible and powerful instrument [1] with enormous technological progress reached in the manipulation of laser light. Collisions with charged projectiles are also used as sources of short electromagnetic pulses but require access to dedicated facilities. Generally speaking radiation damage [2] is of high current interest for example in connection with biological tissues ("human controlled" as in a medical context or "natural" when referring to earth or space radiations). In all cases, the immediate electronic response of the irradiated system plays a key role as the doorway to all subsequent dynamical scenarios. The basic optical response corresponding to electronic oscillations, defines the coupling between irradiation and matter from gentle to strong perturbations [3]. Equally important in energetic cases is electron transport, particularly electron emission. As important examples one can cite the many studies on irradiation of clusters by short and intense laser pulses [3], especially through energy (Photo Electron Spectra, PES [4]) and, more recently, angle-resolved [5] distributions of emitted electrons (Photo Angular Distributions, PAD). Secondary electrons in DNA damage [6] also provide a remarkable example. The long term societal importance of the latter studies is obvious, especially in relation to oncology. The microscopic understanding of underlying mechanisms is still in its infancy and requires dedicated efforts, particularly from a modeling point of view in order to better understand dedicated ongoing experiments.

The analysis of electronic emission from a finite system is thus a key issue in a wide range of physical, chemical and biological processes. Electrons are usually the first constituents to respond to an electromagnetic pulse. Strong excitations lead to immediate ionization of the system, often with dramatic long-time effects (dissociation, Coulomb explosion, ...). It implies electronic transport and possible indirect effects on neighboring species. Dissociative Electron Attachment (DEA) provides a typical example in biological systems where primarily emitted
electrons are attached to target biological molecules which finally leads to the break up of the latter. Emitted electrons may also ultimately provide a valuable insight into reaction pathways, for example in terms of PES and PAD. Electrons thus provide the first response at short time scales, which is more or less quickly coupled to other degrees of freedom. They are finally useful probes along the whole dynamical process, especially when emitted and properly recorded. We shall illustrate the capabilities of our approach on such typical electronic signals.

The theoretical description of irradiation scenarios with electronic emission has made remarkable progress in the past [3] and, at the same time raises challenging questions for further developments. Electron response was analyzed since long [3, 7, 8] especially in the linear domain, leading to a large corpus of theoretical investigations of the optical response of clusters and molecules [3, 8, 9]. But only very few of these go as far as to consider in a routine way non-linear excitations leading to electronic emission [7]. We have developed over the last 15 years elaborate dynamical tools to simulate such non-linear situations in simple metal clusters [7], in metal clusters in contact with an environment [10] and in organic systems [11].

2. Formal and computational framework

The formal framework is Time Dependent Density Functional Theory (TDDFT, [12]) in real time, for the description of electronic dynamics, coupled to classical Molecular Dynamics (MD) for ionic degrees of freedom. The TDDFT is used at the level of the Time-Dependent Local-Density Approximation (TDLDA), augmented with an averaged self-interaction correction (SIC) and absorbing boundary conditions. Coupling to ions is mediated by local pseudo-potentials following standard parametrizations thereof [7]. Laser excitation is described by an external classical laser field with a finite temporal envelope. We can also consider collisions with bypassing highly charged ions. The latter are then described as classical particles (when highly charged) or dressed with quantum electrons when one considers neutral or little charged projectiles [11]. We use standard coordinate-space techniques as outlined in detail in [7, 8] to represent electronic wave functions. Ions are treated as classical particles following standard MD propagation.

In order to illustrate the capabilities of this method we consider examples of electronic signals. The analysis of electron emission requires absorbing boundary conditions, as indicated in Figure 1. Absorption is performed after each time step. After having performed a standard time step from \( t \) to \( t + \delta t \) we apply a mask function \( M \) (active in an absorbing margin \( R_{\text{in}} < |r| < R_{\text{out}} \)) to the preliminary single electron wavefunctions \( \phi_\alpha \), which removes gradually any flow outwards, see [14] for details. The PES delivers the kinetic energies of emitted electrons and can be evaluated.
Figure 2. Example of application for the analysis of PES and PAD in C$_{60}$. An example of experimental PESPAD spectrum is shown in the middle panel, data taken from [17]. A typical PES is shown in upper right panel and a PAD is shown in upper left panel with a small scheme detailing the orientation problem (left lower panel).

for each state separately from the phase oscillations of the single-electron wavefunction at an analyzing point $\mathbf{r}_{\text{meas}}$ near the absorbing bounds, see Figure 1 and [15]. The protocol $\phi_\alpha(\mathbf{r}_{\text{meas}}, t)$ is then Fourier transformed to $\tilde{\phi}_\alpha(\mathbf{r}_{\text{meas}}, \omega)$ and the spectrum $\mathcal{P}(\omega) \propto |\tilde{\phi}_\alpha(\mathbf{r}_{\text{meas}}, \omega)|^2$ is translated to a kinetic-energy spectrum of emitted electrons by identifying $\hbar \omega = \varepsilon_{\text{kin}}$, thanks to the absorbing bounds which leave only outgoing waves in its vicinity. The angular distributions (PAD) are evaluated in angular bins (Figure 1) by collecting all probability removed by the absorption step and accumulating it in the bin to which $\mathbf{r}$ belongs. Again that can be done for each wavefunction separately, which finally delivers an energy and angular resolved analysis of electronic emission. Note that the calculation of PAD requires extra caution due to the compulsory angular averaging (orientation of cluster/molecule with respect to laser polarization), but this can be handled rather efficiently [16].

3. Example of application

We illustrate our approach on the case of C$_{60}$, which consists of 60 C atoms arranged in a highly symmetric configuration (fullerene, [18]) as illustrated in lower left panel of Figure 2. The Carbon 1$s$ electrons are considered as core electrons and accounted for by the pseudopotential. The four 1$p$ electronsshell of each C atom provide the 240 dynamically active electrons of C$_{60}$, with a high ionization potential (IP) of 7.58 eV. The spectral span of the occupied valence states is also rather large ranging over about 20 eV from -27 eV up to the IP [17]. To resolve the s.p. spectrum by a one-photon process, one takes a photon with frequency just above the lowest bound state at $\omega_{\text{las}} = 33$ eV. The associated PAD is shown in the upper left panel of Figure 2. The PES is illustrated in the upper right panel, this time for a photon frequency of 1.55 eV, deeply inside the multi-photon regime of emission. Comparison with experimental data, are extremely encouraging, leading to qualitative and even quantitative general agreement.

Computations of PES and PAD on such a large system as C$_{60}$ represent an enormous task requiring a sizable computational effort. These computations are feasible as the underlying developed code package is highly parallelized, each processor accounting for a small number
of single electron wave functions. Most of the electronic time propagation can be indeed performed processor per processor, the major communication consisting in exchanging the electron density which is computed as a sum over the wave function norms, thus implying full exchange between processors. Still, there remains some space for improvement in terms of computational performance. First attempts in that direction concern the use of more efficient FFT packages such as FFTW. The use of GPU at some places also provides interesting possibilities of speedup. A concerted program of optimization of our code package is underway implying several universities in Europe and China. After less than one year the first results (FFT, GPU) have already allowed significant gain in computational cost, still without exploiting all possible applications of GPU.

4. Conclusions
We have briefly reviewed the theoretical description of irradiation dynamics focusing on PES and PAD. Numerics is based on a Cartesian coordinate-space grids with absorbing boundary. PAD are simply computed from gathering the lost particles in angular segments while PES are obtained from recording the time evolution of each single electron wavefunction at a few selected measuring points near the absorbing bounds. We have been able to perform calculations on the large \( C_{60} \) cluster. The results for \( C_{60} \) are particularly interesting as several measurements on this large cluster are available and even more are to be expected in near future. Accordingly, more calculations for \( C_{60} \) are underway. We can cite as example the impact of plasmon frequency on PAD and PES characteristics, following either laser irradiation or collisions by a highly charged ion. Improving computational performances is also an important aspect which gathers joined efforts from several groups. The next envisioned step is to couple the fully microscopic (quantum) description (as discussed here) to large scale MD descriptions of an environment thus providing an original multi-scale description of irradiation dynamics and of its impact on environment.

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