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Large amplitude femtosecond electron dynamics in metal clusters

J Daligault¹ and C Guet²

¹ Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

² Département de Physique Théorique et Appliquée, CEA-DAM Ile de France, BP 12, 91680 Bruyeres-le-Châtel, France

E-mail: daligault@lanl.gov

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Abstract

We present a theoretical model that allows us to study linear and non-linear aspects of the femtosecond electron dynamics in metal clusters. The theoretical approach consists in the classical limit of the time-dependent Kohn–Sham equations. The electrons are described by a phase-space distribution function which satisfies a Vlasov-like equation while the ions are treated classically. This allows simulations for clusters containing several hundreds of atoms and extending up to several hundreds of femtoseconds during which the description conserves the fermionic character of the electron distribution. This semi-quantal approach compares very well with the purely quantal treatment. As an application of this approach, we show the prominent role of the electron dynamics during and after the interaction with an intense femtosecond laser pulse.

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1. Introduction

Investigations of the physical properties of metal clusters, in particular their optical, magnetic and thermal properties, have been pursued rather intensively for over the last two decades (for review see for instance [1, 2]). Thorough studies of the linear optical response of clusters has provided invaluable insights into the electronic structure, ionic configurations, thermal processes and collective electron dynamics, as well as about the size-dependent evolution of these properties. Note however that, despite these efforts, a number of questions are still open and under investigation. For example, a detailed understanding of the decay mechanisms of the collective surface plasmon excitation is still lacking. This is already the case for sodium, the simplest metal.

This work has been motivated by recent experiments where metal clusters experience excitations in the non-linear domain. Current studies include ultrafast optical spectroscopy, which monitors the dynamics of excited states directly in the time domain, as well as the response of metal clusters to strong external fields (intense laser pulses, collisions with highly charged ions). At high excitation levels, delocalized electrons in metal clusters experience large amplitude dynamics on a femtosecond time scale in such physical processes as either irradiation by an intense ultrashort laser pulse or the passage of a highly charged ion. Collisions between low energy multiple charged ions and neutral metal clusters have been shown to be an efficient way to form low excited multiple charged clusters and to study the onset of charge instabilities in finite systems [3, 4]. During a collision, the electrons suffer the strong transient electric field associated with the passing charge. After collision, that is after a few femtoseconds, a highly charged and electronically excited cluster has been formed. In experiments with ultrashort intense laser pulses [5, 6], a nanoscale charged plasma is formed and explodes energetically.

These important experimental achievements appeal for reliable descriptions of the electron dynamics in metal clusters. Thus far, models have been mainly designed to cope with their linear response properties. The linear response theory has been used within the framework of the time-dependent density functional theory (TDDFT) and mostly in conjunction either with jellium-type models, where delocalized electrons are confined by a constant positively charged background, or with quantum chemical calculations, which lead to the best results for very small clusters ($N \leq 10$).

Beyond linear response the situation becomes much more complicated. A promising method is TDDFT [7]. We have developed a model that allows the description of the real-time dynamics of sodium clusters Na_N containing between 10 and 1000 atoms on a time scale of several hundreds of femtoseconds (fs) for linear and nonlinear interactions [8]. For the description of the coupled electronic and ionic dynamics, we rely on the limit $\hbar \rightarrow 0$ of the time-dependent Kohn–Sham (TDKS) equations. This results in a Vlasov-like equation for the delocalized electrons coupled with the classical evolution of the ions. The model is described in section 2. In section 3, an application is given in which we investigate the coupled dynamics of electrons and ions during and after the irradiation of metal clusters by an intense femtosecond laser pulse.

2. The model

A Na_N cluster is described as an ensemble of N ions linked by N delocalized electrons. The interaction between delocalized electrons and ions is treated in terms of a local pseudopotential (see below). As the ions are allowed to move, the ionic motion couples dynamically to the electronic motion and TDDFT has to be applied to the whole system of electrons and ions.

A cluster, initially in its ground state at times $t < 0$, is supposed to be under the influence of the external time-dependent potential $v_{\text{ext}}(t)$ at times $t \geq 0$. Within TDDFT for a two-component system, the one-to-one correspondence between time-dependent (TD) densities and TD potentials for a given initial state leads to two sets of TDKS equations, one that yields the electron density $n_e(\mathbf{r}, t)$ and the other the ionic density $n_i(\mathbf{r}, t)$. For instance, the TD electron density $n_e(\mathbf{r}, t)$ can in principle be obtained through a set of N single-electron wavefunctions $\psi_i(\mathbf{r}, t)$ that satisfy the TDKS equations (here written in terms of the Kohn–Sham density operator $\hat{n}_{\text{KS}} = \sum_{i=1}^{N_e} |\psi_i\rangle\langle\psi_i|$)

$$i\hbar \frac{d}{dt} \hat{n}_{\text{KS}} = \left[\frac{\hat{\mathbf{P}}^2}{2m} + \hat{v}_{\text{KS}}(t), \hat{n}_{\text{KS}} \right] \quad (1)$$

such that $n_e(\mathbf{r}, t) = \langle \mathbf{r} | \hat{n}_{\text{KS}}(t) | \mathbf{r} \rangle$. The self-consistent TDKS potential v_{KS} is the sum of the TD external potential $v_{\text{ext}}(\mathbf{r}, t)$, the electron–ion potential $v_{\text{ei}}(\mathbf{r}, t)$, the direct electronic Coulomb potential (Hartree part) and of the exchange–correlation potential $v_{\text{xc}}(\mathbf{r}, t)$:

$$v_{\text{KS}}[n_e](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_{\text{ei}}(\mathbf{r}, t) + \int \frac{n_e(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[n](\mathbf{r}, t). \quad (2)$$

In the following calculations, the exchange–correlation part of the self-consistent potential is taken from [9] (local density approximation). Our numerical implementation summarized below allows us to use different descriptions of the electron–ion interaction potential v_{pp} , such that

$$v_{\text{ei}}(\mathbf{r}, t) = \sum_{I=1}^N v_{\text{pp}}(\mathbf{r} - \mathbf{R}_I(t)). \quad (3)$$

For the calculations presented in the next section, we have used the realistic pseudopotential developed in [10].

A complete numerical solution of the two sets of TDKS equations for clusters containing several tens or hundreds of atoms will be rather involved and simplifications must be undertaken. First, further simplification can be achieved by treating the nuclear motion classically [7]. One obtains a set of TDKS equations (1) for the electrons coupled to a set of classical Newton equations describing the nuclear motions. If the ionic positions at time t are given by $\{\mathbf{R}_I(t)\}$, the latter can be written as (M is the ion mass)

$$M \frac{d\mathbf{R}_I(t)}{dt} = \mathbf{F}[n_e, \{\mathbf{R}_J\}](\mathbf{R}_I, t) \quad (4)$$

where $\mathbf{F}_I(t)$ is the total force acting on the I th ion

$$\mathbf{F}_I(t) = -\nabla_{\mathbf{R}_I} \left[v_{\text{ext}}(\mathbf{R}_I, t) - \int d\mathbf{r} n_e(\mathbf{r}, t) v_{\text{pp}}(\mathbf{R}_I - \mathbf{r}) + \sum_{\substack{J=1 \\ J \neq I}}^N \frac{1}{|\mathbf{R}_I - \mathbf{R}_J|} \right]. \quad (5)$$

It is important to emphasize that these equations allow for TD, excited electronic states and for transitions between these states. Thus, the electronic system is not tied to a ground state corresponding to the instantaneous ion positions, as would be required in the Born–Oppenheimer approximation. This classical treatment of nuclear motion is justified only if the probability densities of the Kohn–Sham ions remain narrow distributions during the whole process considered [7].

As stated in the introduction, a second simplification consists in taking the limit $\hbar \rightarrow 0$ of the Kohn–Sham equations (1). The latter can be formally obtained through a Wigner phase-space representation of equation (1). Then, the electron dynamics is described through the evolution of a phase-space distribution function $f(\mathbf{r}, \mathbf{p}, t)$, which evolves according to the Vlasov-like equation

$$\frac{\partial f}{\partial t} = \left\{ \frac{\mathbf{p}^2}{2m} + v_{\text{KS}}[n_e](\mathbf{r}, t), f \right\}. \quad (6)$$

The initial density, $f(\mathbf{r}, \mathbf{p}, t = 0)$, is obtained by taking the limit $\hbar \rightarrow 0$ of the Kohn–Sham ground state density operator $\hat{n}_{\text{KS}}(t = 0)$, which yields to the Thomas–Fermi distribution

$$f(\mathbf{r}, \mathbf{p}, t = 0) = \frac{2}{(2\pi\hbar)^3} \theta \left(E_{\text{F}} - v_{\text{KS}}[n_e] - \frac{\mathbf{p}^2}{2m} \right) \quad (7)$$

where E_{F} is the Fermi energy.

In the spirit of TDDFT, the only utility of the above equation is to yield an approximation for the TD electron density through

$$n_e(\mathbf{r}, t) = \int d\mathbf{p} f(\mathbf{r}, \mathbf{p}, t). \quad (8)$$

We have proved in [11] the reliability of the present approach in a direct comparison to results obtained from the resolution of the TDKS equations (within the jellium model) in the specific case of highly charged ions–metal clusters collisions. In particular, such observables as the rate of transferred electrons from the cluster to the projectile or to the continuum, the final charge and final excitation of the cluster, as well as the electron distribution in the highly excited projectile are in excellent agreement with each other.

Some special care must be paid to efficiently solve the coupled sets of equations of motion given by equations (6) and (4). In particular, the equation of motion (6) is a mean-field equation that requires the evaluation of the Coulomb potential and exchange–correlation potentials corresponding to the electronic density $n_e(\mathbf{r}, t)$ at each time step t . Moreover, due to its large variation over a small length scale compared to the cluster size, the use of a realistic pseudopotential complicates strongly the numerics in the calculation of the electron–ion forces. In order to cope with these difficulties, we have used and developed some specific computational techniques [8]. The numerical integration uses a pseudo-particle method. The one-body distribution $f(\mathbf{r}, \mathbf{p}, t)$ is approximated by the sum of a large number N_{pp} of products of the Gaussian function $g_r(\mathbf{r})$ (standard deviation σ_r) and the delta function $\delta(\mathbf{p})$, centred at $\mathbf{r}_k(t)$ and $\mathbf{p}_k(t)$:

$$f(\mathbf{r}, \mathbf{p}, t) \approx \frac{N}{N_{pp}} \sum_{k=1}^{N_{pp}} g_r(\mathbf{r} - \mathbf{r}_k(t)) \delta_{\mathbf{p}}(\mathbf{p} - \mathbf{p}_k(t)). \quad (9)$$

The equations of motion of each pseudo-particle ($\mathbf{r}_k(t)$, $\mathbf{p}_k(t)$) are obtained from a variational principle [12], and yield

$$\begin{cases} \frac{d\mathbf{r}_k}{dt} = \frac{\mathbf{p}_k}{m} \\ \frac{d\mathbf{p}_k}{dt} = - \int \vec{\nabla}_r v_{KS}[n](\mathbf{r}, t) g_r(\mathbf{r} - \mathbf{r}_k(t)) d\mathbf{r} \end{cases} \quad (10)$$

In order to cope with the Coulomb part of v_{KS} , the above scheme is coupled to a grid-based method to solve the 3D Poisson equation. Its integration is worked out on a B-Spline basis set. As to the difficulty arising from the ionic part in v_{KS} , it is overcome through an analytical evaluation of the particle–ion forces ($N \times N_{tp}$ pairs) by taking most advantage of the Gaussian shape of the test particles.

This numerical procedure, which has been fully parallelized, allows us to safely rely on simulations extending up to several hundreds of femtoseconds. To reach such a high level of stability requires using a large number of test particles (in section 3, $N_{tp} = 1.3 \times 10^6$ and $\sigma_r = 0.8$ a.u.). They are initially distributed inside a cubic grid to simulate the initial phase-space density (7) [8]. Being a stationary solution of equation (6), it is obtained by solving the test particle dynamics with a small friction term added. The time evolution of both test particles and ions are computed using the Verlet method with a time step of ≈ 0.024 fs.

3. Application: interaction with an intense laser pulse

We investigate the coupled dynamics of electrons and ions when a metal cluster is irradiated by an intense femtosecond laser pulse [12]. More precisely, we show that dynamical effects such as the electron heating and the electron pressure, which our approach treats explicitly, should not be discarded when discussing the complex features of ionization, excitation and explosion of clusters in strong laser field. We first describe the typical response of a metal cluster to a strong laser pulse.

3.1. General evolution

We consider an icosahedron Na_{147} cluster with an effective Wigner–Seitz radius $r_s = 4$ a.u. and an initial temperature $T = 300$ K. Its dipole plasmon frequency is $\omega_p = 3.0$ eV in our model. It is irradiated with a 200 fs laser pulse of peak intensity $I = 10^{11}$ W cm $^{-2}$ (figure 1(a)) and frequency at the plasmon frequency (3.0 eV). We define here relevant observables. By selecting electrons which at time t are located inside the sphere of radius twice the initial cluster one, we construct the dipole moment $D_x(t)$ in the polarization direction, the residual cluster charge $Q(t)$ and the total electronic kinetic energy $E_K^e(t)$. The observable for ions is the total ionic kinetic energy $E_K^i(t)$. The key quantities for the present discussion are $E_K^e(t)$ and $E_K^i(t)$.

When irradiated by the laser pulse, the electrons immediately respond. The dipole moment (figure 1(b)) follows the pulse profile (figure 1(a)) and the major part of ionization occurs during the constant stage when the laser field reaches the maximum peak intensities (figure 1(c)). Meanwhile, the kinetic energy of the residual electrons strongly increases (figure 1(d)) and ions begin to store kinetic energy (figure 1(e)). As the laser pulse goes down and after the pulse is switched off, $Q(t)$ grows further but much more slowly (about two electrons between $t = 150$ and $t = 250$ fs). During that time interval, the change in E_K^e is more drastic: it falls steadily from 640 eV at $t = 150$ down to 460 eV at $t = 250$ fs. Out of the 180 eV loss in E_K^e only a small fraction (about 11 eV) is taken away by the last two ionized electrons. During that time interval, a large fraction of the $180 - 11 = 169$ eV loss could have been transferred to the ionic system through electron–ion scattering. Indeed during the same time interval the total ionic energy E_K^i has increased by about 153 eV. Eventually, the overall interaction leads to the non-uniform layer by layer explosion of Na_{147} as indicated in figure 1(f) which shows the histograms of the radial positions of the sodium ions at initial time and at $t = 250$ fs.

3.2. Competition between Coulombic and kinetic effects

In order to explore the role of the laser heated electrons in the cluster dissociation, we perform different types of simulation. We first consider two types of simulation, namely, either with full ionic motion or with a rigidly fixed ionic structure. The results are presented in figure 2. A Na_{196} cluster is irradiated with a 100 fs laser pulse of peak intensity $I = 10^{12}$ W cm $^{-2}$ and frequency $\omega_l = 3.0$ eV. A first observation is that the cluster charge at the turn-off of the laser field ($Q = 46+$, not shown in figure 2) and the maximum electronic kinetic energy that are reached during the pulse are about the same whether the ions move or not. However, the subsequent relaxation of E_K^e shows very distinct trends. The loss of kinetic energy E_K^e is insignificant when ions are fixed whereas the coupling to ionic motion leads to an important transfer of energy on a short time scale of a few hundred femtoseconds from the electron system to the ionic one. This is corroborated by the

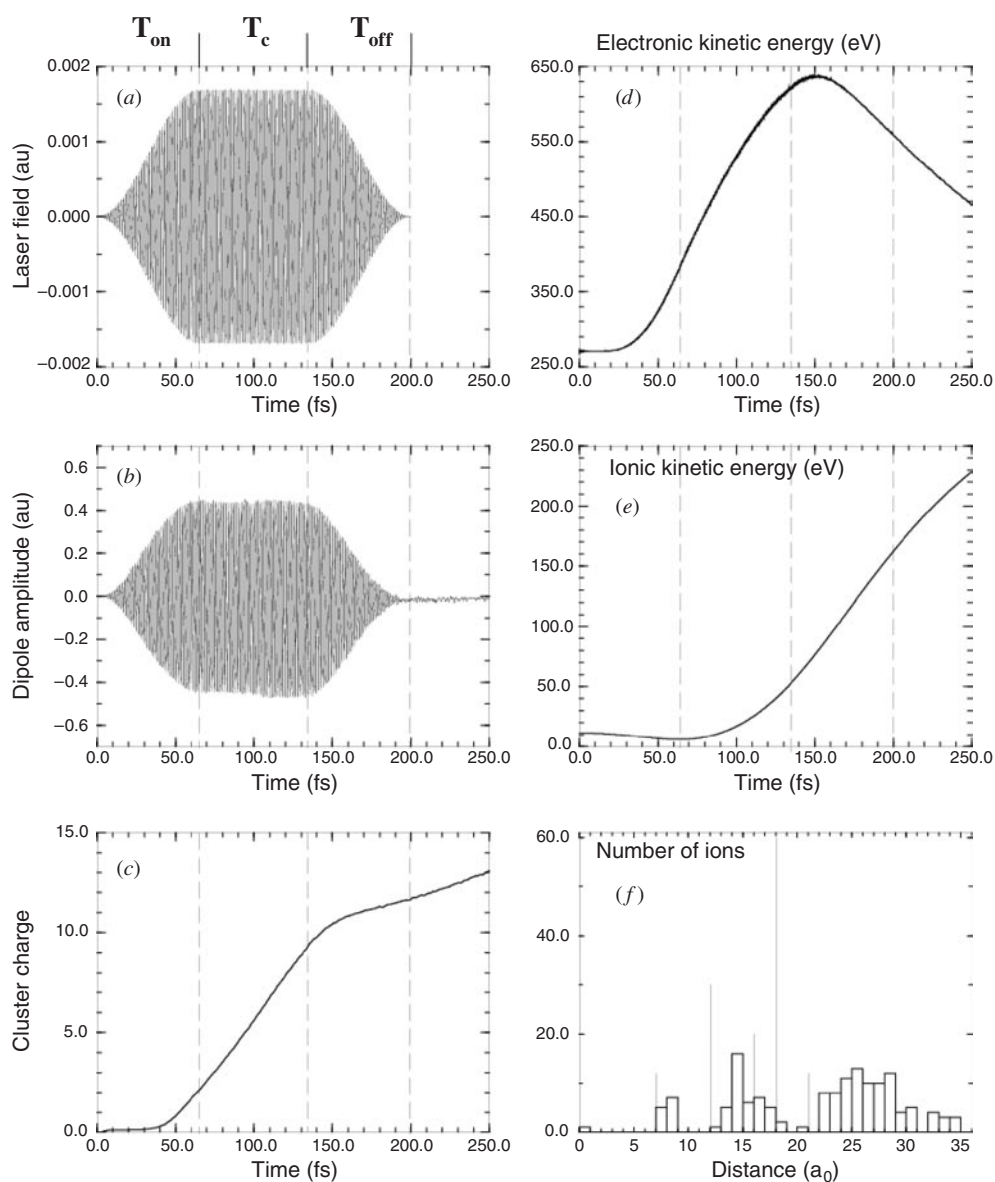


Figure 1. Electronic and ionic responses of an icosahedron Na_{147} cluster to a 200 fs laser pulse (peak intensity $10^{11} \text{ W cm}^{-2}$ and photon energy $\hbar\omega = 3.0 \text{ eV}$. Vertical dashed lines limit the laser stage T_{on} , T_{c} and T_{off} ; (b) electron dipole amplitude along the axis of laser polarization; (c) cluster charge; (d) total electronic kinetic energy as defined in the text; (f) radial distribution of the ions at the initial time $t = 0 \text{ fs}$ (vertical thin lines) and at $t = 250 \text{ fs}$ (histogram).

one-to-one correspondence between the onset of the steady increase of E_{K}^{i} and that of the fall of E_{K}^{e} .

Because of the high charge state reached ($Q = 46+$), the Coulomb forces also play a significant role in the dissociative process. In other words, the total kinetic energy E_{K}^{i} of the ions originates both from the pressure of the laser heated electrons and from the

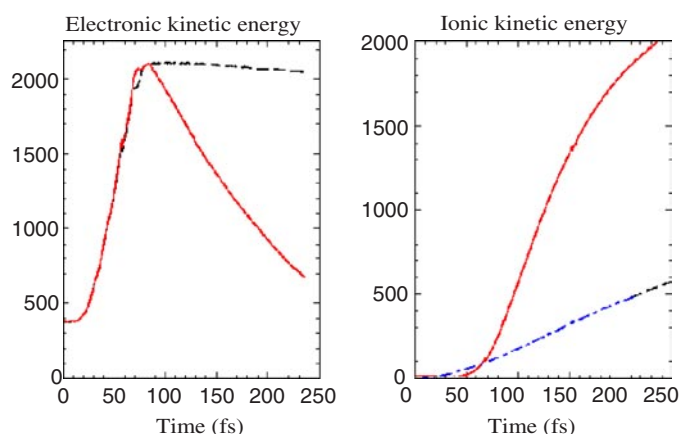


Figure 2. Kinetic energy transfer from electrons to ions in a Na_{196} cluster irradiated by a 100 fs laser pulse at the plasmon frequency $\hbar\omega = 3.0$ eV and peak intensity 10^{12} W cm^{-2} . Left-hand side: inner electronic kinetic energy when ions are moving (full line) or are rigidly fixed (dashed line). Right-hand side: corresponding total kinetic energies of the ions. The dot-dashed line corresponds to a ‘cold’ Coulomb explosion of a Na_{196}^{46+} cluster.

Coulomb energy of the charged cluster. In order to separate these two components, we have performed a calculation in which an initial Na_{196}^{46+} cluster is not exposed to an external perturbation and let to evolve freely. The time evolution of the ionic kinetic energy of this cluster is shown in figure 2 (dot-dashed line) together with that obtained in the laser experiment. It appears that despite the strong ionization state reached, the kinetic energy transfer from electrons to ions play a noticeable role in the explosion dynamics. More quantitatively, the sum of the two contributions that drive the cluster expansion, namely the pure Coulomb energy (at $t = 240$ fs, $E \approx 530$ eV) and the electronic kinetic energy (the loss in E_K^e from its maximum value (≈ 2105 eV) to its value at $t = 240$ eV (≈ 678 eV) is 1427 eV), is 1957 eV, i.e. about 98% of the total kinetic energy E_K^i of the 196 ions.

The role of the laser heated electrons has been investigated by considering an alternative approach to highly charge a cluster. We prepare a cluster of a given final residual charge with two distinct experiments, namely a collision with a highly charged ion and the interaction with a laser pulse. In the collision experiment, the projectile Xe^{25+} ion moves at a velocity of (0.2 a.u.) along the x -direction and the impact parameter is $y = 50$ a.u. The evolution of the components $D_x(t)$ and $D_y(t)$ of the electronic dipole is plotted in figure 3(a) (thin and bold dashed lines, respectively). In the laser experiment the pulse is characterized by a duration of 29 fs, a peak intensity of 0.7×10^{12} W cm^{-2} , and a frequency of 3.0 eV. Note that the laser duration corresponds roughly to the collision time, during which there is a noticeable displacement of the electrons. One observes a very large difference in the amount of kinetic energy transferred to the ions. The heating of the ions is much slower in the collision simulation contrary to the laser one. The rapid electronic oscillations in the laser field (figure 3(a)) across the ionic background heat the electron cloud much more than the passing projectile, which appears to the cluster as an equivalent single broad pulse. The laser induced ‘hot electrons’ boost strongly the kinetic ionic energy as seen in figure 3(c). This results in a much faster explosion as shown by the comparison of the cluster radius in figure 3(d).

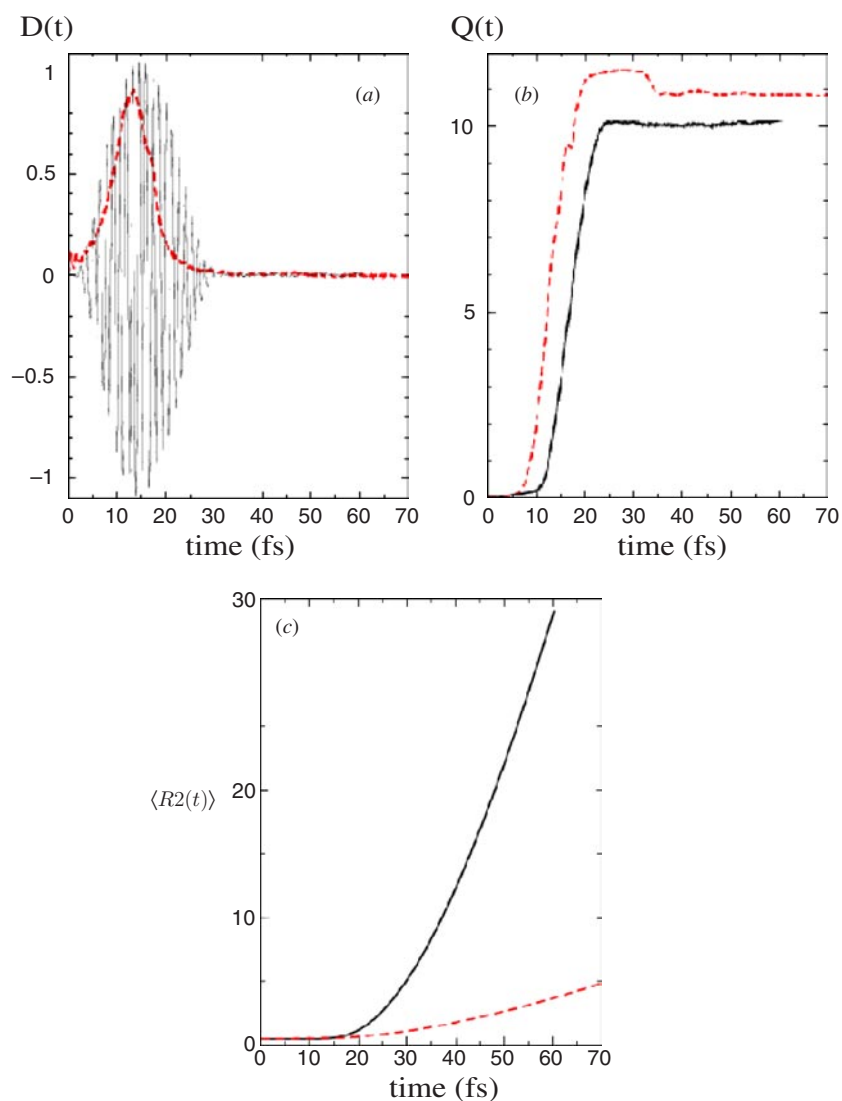


Figure 3. Comparison between an excitation process of a Na_{196} cluster by an energetic ion (dashed lines) and a laser pulse (full lines) leading to almost the same charge state (see the text for details). (a) Electronic dipole amplitude in the axis of the laser polarization (full line) and in the collision plane along (thin line) and perpendicular (dashed line) to the projectile trajectory direction; (b) cluster charge state; (c) root mean square radius of the cluster.

4. Conclusion

We have presented a model that allows the description of the real-time dynamics and in the non-linear domain of metal clusters containing between 10 and 1000 atoms on a time scale of several hundreds of femtoseconds. The Vlasov-like equation equation (6), limit $\hbar \rightarrow 0$ of the time-dependent Kohn–Sham equations, provides the time evolution of the electron density while the ions evolve classically. The model does not rely on the Born–Oppenheimer approximation. As an application, we have shown that the femtosecond electron dynamics

play a prominent role in the interaction of a metal cluster with a strong fs laser pulse. During the pulse, the response is dominated by the electron heating and ionization. When the laser field is too weak, the electronic energy is released very quickly in the ionic system.

References

- [1] Guet C (ed) 2002 *Atomic Clusters and Nanoparticles* (Berlin: Springer)
- [2] Ekardt W (ed) 1999 *Metal Clusters* (New York: Wiley)
- [3] Chandezon F *et al* 1995 *Phys. Rev. Lett.* **74** 3784
- [4] Daligault J, Chandezon F, Guet C, Huber B A and Tomita S 2002 *Phys. Rev. A* **66** 033205
- [5] Ditmire T *et al* 1997 *Nature* **386** 54
- [6] Krainov V P and Smirnov M B 2002 *Phys. Rep.* **370** 237
- [7] Gross E K U, Dobson J F and Petersilka M 1996 *Density Functional Theory of Time-Dependent Phenomena (Topics in Current Chemistry vol 181)* (Berlin: Springer) p 81
- [8] Daligault J 2001 Dynamique électronique femtoseconde dans les agrégats métalliques, Université Lyon 1 (www-drfmc.cea.fr/theses)
- [9] Perdew J and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [10] Kümmel S, Brack M and Reinhard P-G 2000 *Phys. Rev. B* **62** 7602
- [11] Plagne L, Daligault J, Yabana K, Tazawa T, Abe Y and Guet C 2000 *Phys. Rev. A* **61** 033201
- [12] Daligault J and Guet C 2001 *Phys. Rev. A* **64** 043203