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Dynamics of sodium clusters in a nonadiabatic electron–ion model

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Abstract. We discuss the impact of ionic motion on the electronic response of metal clusters subject to a violent excitation. We consider in particular the coupling between electronic and ionic degrees of freedom in the course of the irradiation of a cluster by an intense laser beam. Our results hint at a quick coupling between ions and electrons, in the 100 fs range or even faster for very high excitations.

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The study of the electronic response of a metal cluster has lately motivated numerous investigations both in the linear and nonlinear regimes. Conventional optical response studies have been pursued for a long time (for reviews, see [1, 2]). The study of the nonlinear response following violent excitations, such as irradiation by intense lasers [3] and collision with an energetic ion [4], is more recent and promises to unravel a wealth of interesting phenomena at both the electronic and ionic levels [3, 5]. While for low-energy excitations it is likely that electrons stay safely on, or close to, their ground-state Born–Oppenheimer surface, this is no more the case in the nonlinear regime, and a proper theoretical description of such situations clearly requires one to account for the coupled dynamics of both electronic and ionic degrees of freedom. In a first stage of the cluster's response, it is of course the electronic cloud which stores the energy delivered by the electromagnetic pulse, as issued by the laser or the by-passing ion. The electron response is in this case characterized by prompt electron emission, electron heating, and a collective excitation of the Mie plasmon [6–8]. The further evolution of the cluster depends on its net charge and the amount of deposited energy. Electronic dynamics proceeds here far above the ground-state Born–Oppenheimer surface, and it is by no means clear how far and how fast the cluster will (or will not) come back down to this surface. To answer such questions, one has to develop a nonadiabatic molecular dynamics for the ions with an explicit treatment of electron dynamics, thus allowing for any dynamical state of the electrons. In this paper, we investigate this question in a simplified version of our full 3D nonadiabatic molecular dynamics [9, 10], allowing systematic yet tractable calculations. We want to mention that coupled electronic and ionic dynamics have been studied previously by the use of an LCAO representation of the electronic degrees of freedom [11]. This approach, however, is bound to moderately excited electronic states so that the LCAO basis may be kept manageable. We use here a representation of each electronic wave function on a full coordinate- space grid. This is well suited for large excitations, and particularly for the many continuum electrons arising in violent excitation processes.

Our starting point is a density functional theory (DFT) [12] description of the electronic degrees of freedom in the time-dependent local density approximation (TDLDA). We describe each electron by a single-particle wave function ϕ_i obeying the nonlinear time-dependent Kohn–Sham equation [13]. This TDLDA framework has been extensively discussed in a series of papers; we refer the reader to a few typical references for details and examples of applications [6, 7, 14–17]. Here we aim at studying the coupling of electronic to ionic degrees of freedom. We hence describe ion–electron interactions by means of a simple pseudopotential [9, 17]. For our exploratory study, we confine our investigations to the case of sodium clusters, for which accurate, still local, pseudopotentials can be used. Our pseudopotential is formulated in terms of error functions, which are particularly friendly for numerical purposes. It reads

$$V_{\mathrm{Ps}}(\mathbf{r}-\mathbf{R}) = e^2 \sum_{i=1,2} v_i \frac{\mathrm{erf}\left((\mathbf{r}-\mathbf{R})/\sigma_i\right)}{|\mathbf{r}-\mathbf{R}|} \qquad (1)$$

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with

$$\mathrm{erf}(r) = \int_0^r \mathrm{d}r' \exp\left(-\frac{r'^2}{2\sigma_i^2}\right) \tag{2}$$

where $\sigma_2 = 1.71\sigma_1$, $\sigma_1 = 0.8\mathrm{a}_0/(2\sqrt{\ln 2})$, $v_1 = 2.292$, and $v_2 = -3.292$. It should be noted that the parameters of this pseudopotential slightly differ from the ones previously used [9]. We have adjusted this new set of parameters to provide a proper account of the optical response in sodium clusters, in addition to standard constraints used to build pseudopotentials [18]. Structures obtained with this new pseudopotential are comparable to the ones previously optimized, although they may differ by some details. These details may nevertheless show up in the secondary fine structures exhibited, for example, by the optical response (see Fig. 1).

With the pseudopotential as given in (1) and (2), the nonadiabatic molecular dynamics equations of motion of ions finally reduce to:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}_I &= 1 - \nabla_{\mathbf{R}_I}\Bigg[V_{\mathrm{ext}}(\mathbf{R}_I, t) - \int \mathrm{d}\mathbf{r}\, n(\mathbf{r}, t) V_{\mathrm{ps}}(|\mathbf{R}_I - \mathbf{r}|) \\ &\qquad + e^2 \sum_{J \neq I} \frac{1}{|\mathbf{R}_I - \mathbf{R}_J|}\Bigg] \qquad (3) \\ \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{R}_I &= \mathbf{P}_I/M_{\mathrm{ion}} \qquad (4) \end{aligned}$$

where $n(\mathbf{r}, t)$ is the electronic density and $V_{\mathrm{ext}}(\mathbf{R}_I, t)$ the external potential acting on the system (for example the laser field). These equations are solved with the standard and robust leap-frog algorithm [19]. Such a fully nonadiabatic model has been investigated in [9] in the case of irradiation of sodium clusters by an intense laser. The full 3D calculations of [9] are still very formidable, and thus do not allow systematic studies. In order to overcome this difficulty, we propose here an approximate scheme in which we restrict electronic wave functions to axial symmetry, while keeping full 3D motion for ions. This in fact represents the dynamical extension of the Cylindrically Averaged Pseudopotential Scheme (CAPS) model, which has been shown to provide, in its static version, a fair account of ground-state properties of simple metal clusters [20]. The computational simplification is enormous, and the resulting model thus allows more systematic and exploratory investigations. One has to keep in mind, however, that the restriction to axially symmetric electronic wave functions may, in some cases, impose strong constraints on the electronic degrees of freedom. This is presumably the case when one is interested, for example, in fragmentation patterns of a highly charged cluster. In such cases, the enforced symmetry is likely to stabilize the cluster beyond what a realistic symmetry-free approach would lead to. But this does not completely inhibit the study of such situations, as long as one understands it as exploratory, and keeps in mind that the 2D approach implies an overestimate of stability or an underestimate of the fragmentation threshold. On the other hand, more gentle situations (singly or doubly charged clusters, electron and ion heating, etc.) and dynamics on shorter time scales are likely to be described qualitatively, and probably even quantitatively. We shall focus on such cases here.

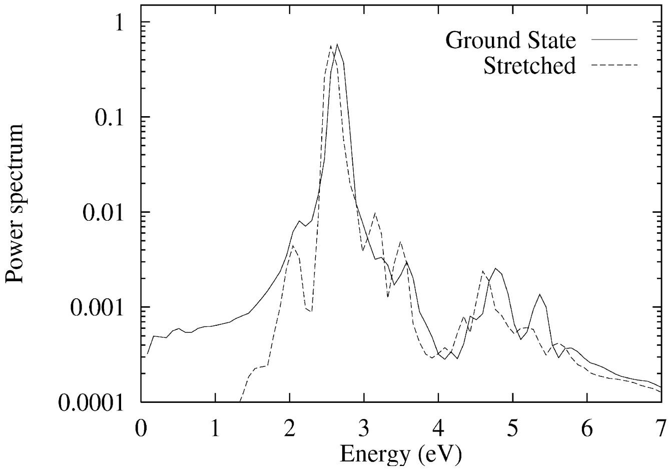

Fig. 1. Comparison of electronic power spectra for $\mathrm{Na}_9{}^+$ in a ground-state and stretched configuration.

As a first consistency check we consider the simple Na_2 cluster and compute the force between the two ions. It vanishes for an interionic distance of $5.8\, a_0$; this is in agreement with the expected bond length of this molecule. The next, dynamical check is to consider a stretching of Na_2 along the molecule axis. We record in time the ionic positions and deduce from that the frequency of vibration. We find a wavenumber of $\lambda = 142\,\mathrm{cm}^{-1}$ again in reasonable agreement with experimental data. Note that this check could have been done directly from the potential curve in the spirit of a Born–Oppenheimer approach. Performing the test dynamically allows us to further ascertain the numerical stability of our calculations, as a large number of time steps are computed in order to extract this frequency.

The comparison between present 2D calculations and the 3D results of [9] is also enlightening. But the available test case Na_{12} analyzed in [9] represents a truly triaxial cluster for which the 2D CAPS approach is inappropriate. We have to resort to more axially symmetric clusters [21]. Comparisons have thus been performed for Na_4^{2+}, which was the test case already studied in the Born–Oppenheimer calculations of [22]. This cluster is obtained by an instantaneous ionization of Na_4 in its ground-state geometry. Although such a system undergoes a Coulomb explosion, the symmetry of the problem should allow a correct 2D treatment. The first comparisons performed up to now indicate that the Coulomb explosions proceed in a similar way in the three calculations, namely with the same characteristic time scales for the emission of the outer ions. Slight differences show up, in particular, in the vibrational motion of the two ions that remain bound. This may reflect the rigidity of the imposed symmetry. But one should also keep in mind the extreme sensitivity of such calculations to the details of the initial condition [22].

We now turn to the bigger cluster, $\mathrm{Na}_9{}^+$, whose ground state is a 144 configuration in the CAPS model [20]. The cluster consists of two subsequent rings, each covering four ions and topped by one single ion. For the electronic excitation, we consider a small displacement of the electron cloud with respect to the ionic center of mass. This schematic excitation, which actually simulates quite well a fast, sub-femtosecond excitation [16], excites exclusively the Mie plasmon. The electron cloud thus starts to oscillate with respect to the ionic center of mass. As we aim here at studying ionic effects, we further excite the ionic configuration by a deliberate stretching. In order to do so, we displace the outermost ion (the top ion of the 144 configuration) along the z axis by $0.7\,\mathrm{a}_0$. This creates an ionic configuration with a large octupole moment, delivering usually a fragmented optical response [23]. As soon as time evolution starts, the displaced ion drifts back towards the rest of the ions, the positions of which essentially remain constant. The ionic motion is thus mainly confined to the initially excited ion, while the other ions are less affected by the initial ionic perturbation. The ionic drift takes place with a time scale typical of ionic motion, namely about 100 fs. In the meantime, the initially shifted electron cloud (with respect to the initial ionic configuration) oscillates with the Mie frequency. We record in time the dipole moment $D(t)$ (of electrons with respect to ions) along the excitation axis, Fourier-transform it in the frequency domain $\tilde{D}(\omega)$, and compute the power spectrum as $\mathcal{P}(\omega) = |D(\omega)|^2$. The $\mathcal{P}$ is plotted in Fig. 1 for the case of the initially perturbed ionic configuration and, for comparison, for a case where the ground- state ionic configuration is kept frozen. The two spectra are very similar; this hints that small ionic vibrations do not perturb the electronic degrees of freedom. There is a bit more substructure in the case with ionic motion; this is probably due to the initially larger (than in the ground state) octupole deformation of the stretched 144 configuration [23].

As a next, more realistic, and less linear test case, we consider the irradiation of $\mathrm{Na_9}^+$ by a laser beam at a frequency close to the Mie plasmon resonance. We know that in such a case one observes resonant emission [6]. Still, emission can be controlled by the tuning of the intensity and/or the duration of the pulse. We have tuned here the laser parameter to have a fast initial electronic emission of one unit. This requires a very short pulse of about 10 fs. The initial $\mathrm{Na_9}^+$ is thus turned, almost instantaneously, into an $\mathrm{Na_9}^{++}$, and we follow over about 1.5 ps the further evolution of the system. In this example, it turns out that direct electron emission takes place only during the laser pulse, while no further electron emission can be seen during the subsequent 1.5 ps calculated here. The dipole signal (electrons versus ions), which persists after the laser has been switched off, has an amplitude that stays almost constant up to about 500 fs and is then reduced by a factor of 2 with some (Langevin) fluctuations of the amplitude. The most interesting aspect lies in the ionic degrees of freedom. Figure 2 shows the ionic positions as a function of time, along the polarization axis of the laser and along an axis perpendicular to it. The transverse motion is essentially of vibrational nature with occasional amplitudes of order $1\,\mathrm{a}_0$. More interesting is the motion along the laser polarization axis. The $\mathrm{Na_9}^+$ cluster in the 144 CAPS configuration has been initially aligned along the laser polarization, so that one ion is, again, pointing outside the cluster. It is striking that, again, this outer ion is the most affected one, the amplitude of its motion reaching up to more than $2.5\,\mathrm{a}_0$. Altogether, ionic motion indicates that the system has been significantly perturbed, even if, at least over the 1.5 ps computed here, we do not observe a Coulomb explosion, nor a precursor of ion evaporation. The restriction to axial symmetry is probably not a basic hindrance here, because we expect evaporation predominantly along the z axis. So we can conclude that this 10 fs laser excitation is gentle enough to deliver a rather stable $\mathrm{Na_9}^{++}$ (in contrast to ns lasers, which deposit much more heat in the cluster). Finally, a remark concerning time and length scales needs mention. From Fig. 2 we see that ionic motion starts very early. Actually, the first marked turnover of the outer ion takes place at about 200 fs, which is a typical time scale for ionic motion. But it should be noted that at that time, this ion has traveled more than $2\,\mathrm{a}_0$, which is large as compared to typical bond lengths.

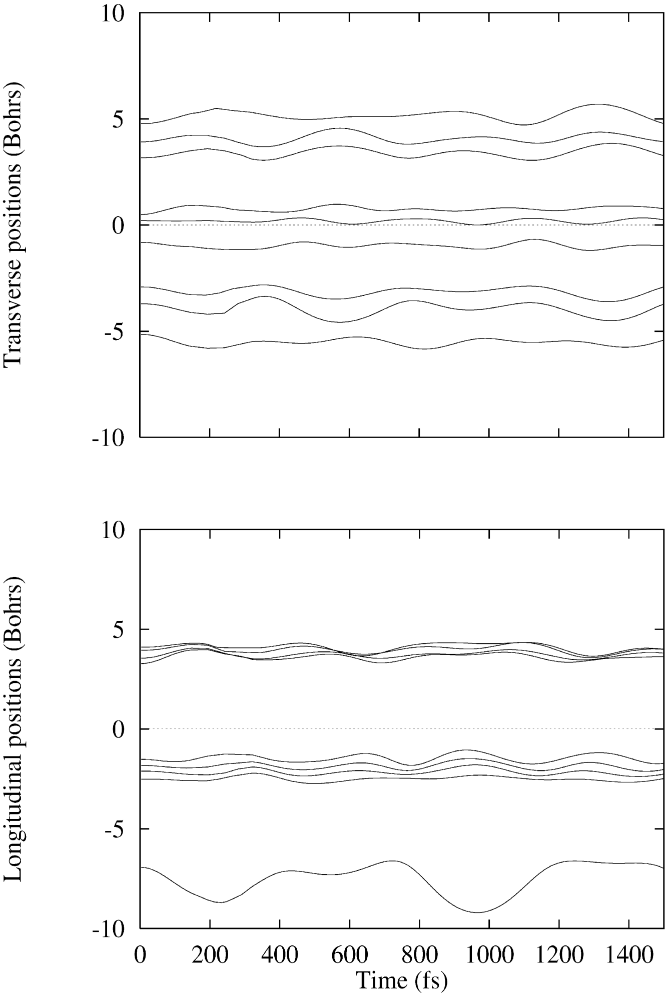

Fig. 2. Ionic positions as a function of time after an irradiation by a short laser pulse. Bottom panel: positions along polarization axis of the laser. Upper panel: positions along an axis perpendicular to the polarization axis.

It is interesting to further quantify the dynamical and (possibly) thermodynamical properties of the excited ${\rm Na_9}^{++}$ we have just created. An estimate of the ionic kinetic energy provides a first guess of the cluster temperature. One obtains a value of order 1000 K. It should be noted that we are using here a microcanonical description of the system. Our estimate of the temperature is hence mostly qualitative, as we are considering only one typical case. We have furthermore analyzed the vibration pattern of the various ions. The typical vibration wavelengths of the ions belonging to the two rings are of order $100\,{\rm cm}^{-1}$ and above, while the most outer ion displays a softer component around $40\,{\rm cm}^{-1}$ and a harder one around $200\,{\rm cm}^{-1}$. These values are in qualitative agreement with estimated cold and hot eigenfrequencies of comparable clusters [24].

In conclusion, we have shown that electronic and ionic degrees of freedom may be strongly coupled in the course of strong excitations. Sizeable effects appear already at less than 100 fs. In the rather gentle cases considered here, we have not yet observed cluster fragmentation within the time scale computed, namely 1.5 ps. Beyond such long times, it is likely that the cluster will start to evaporate thermal electrons even if the electronic temperature is not extremely large. This would speed up the fragmentation process. The model with restriction to axial symmetry that we have introduced here requires a comparatively moderate numerical effort. It thus will allow one to study these effects more systematically and at longer time scales. Work in this direction is in progress.

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