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Field amplification in Na clusters

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Abstract. We study the amplification of an incoming fs laser pulse through the resonant plasmon response in a metal cluster taking Na clusters as test case and using density-functional theory for the description of the electronic dynamics. We find large amplification factors for moderate laser intensities. The effect shrinks for higher intensities because the binding forces of the electron cloud set a limit for the effective fields. The response shows resonant behaviour much similar to an harmonic oscillator. It is found to be independent of cluster size.

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The enormous progress in the development of intense laser sources has inseminated increasing interest in the interaction of photon fields with matter. The interplay with metals is particularly interesting due to the strong coupling of photons to plasmons which leads into the domain of multiplasmon excitation and nonlinear response. One prominent effect in the plasmon response is the amplification of the incoming electro-magnetic field which can become particularly pronounced at small corners of metal particles. This has been studied with a stationary flow picture for the case of metallic tips in [1]. Another sort of small metal particles are clusters and the effect of strong fs laser fields on those is a topic of current interest [2–5]. It is the aim of this paper to investigate field amplification for Na clusters as test case. Thereby we employ a thoroughly dynamical picture trying to reproduce in detail the temporal profile of an excitation by a fs laser pulse. The theoretical tool for the investigation is density-functional theory for the electrons in the time-dependent local-density approximation (TDLDA) as we have applied it successfully in many previous investigations of nonlinear electron dynamics of metal clusters, see *e.g.* [6] for a study of spectral properties or [7,8] for the interface with laser beams. The outline of the paper is as follows. We first introduce quickly the basic tools of the dynamical description and the modelling of the laser profile. Then we explain how we extract field amplification factors quantitively. And finally, we evaluate the trends with laser intensity, frequency, and cluster size.

The dynamics of the electrons is described within the TDLDA where the occupied single-electron wavefunctions φ_α obey the time dependent Kohn-Sham equations [9]

$$i\partial_t\varphi_\alpha = (\frac{p^2}{2m} + U_{Coul} - U_{xc} + U_{ext})\varphi_\alpha \quad . \tag{1}$$

The U_{Coul} stands for the full Coulomb potential of electrons and ions, the U_{xc} is the exchange-correlation functional from LDA for which we employ here the functional of [10]. The external laser field is modelled as

$$U_{ext} = E_0 z \cos(\omega t) f(t) \tag{2}$$

$$f(t) = \cos\left(\frac{(t-0.5\ T)\pi}{T}\right)^4 \tag{3}$$

where z is the spatial dependence standing for a dipole in z direction and the forefactor E_0 is the field strength. It is related to the intensity I of the laser field as $I\ \mathrm{W/cm^2} = (E_0\, 1.07\times 10^8 \mathrm{a_0/Ry})^2$. The time dependent parts separate into the cos factor which carries the frequency of the pulse and into the profile of the laser pulse $f(t)$ for which we take here a switching much similar to a Gaussian pulse but with a very smooth start and end. The pulse length parameter was chosen as $T = 58$ fs which corresponds to a FWHM of 21 fs. We follow the dynamical evolution a bit longer than the pulse length until about 80 fs to collect all relevant electronic processes after laser excitation. This time is still short compared to typical ionic time scales, *e.g.*, we find that significant ionic motion starts up after 100 fs for a triply charged Na cluster [11]. It may show up earlier for higher charge states. But for simplicity and to concentrate on purely electronic effects, we keep the ionic

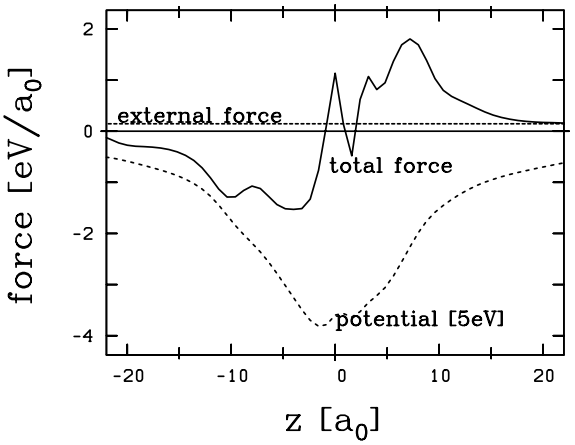

Fig. 1. Force along the z-axis for spherical $Na_9{}^+$ in jellium approximation. The cluster was irradiated with a laser beam of intensity $I = 10^{12}$ W/cm^2 for a frequency near resonance with $\omega = 2.58\,\mathrm{eV}$ and a $\cos^4$ profile with FWHM of 21 fs. The full line shows the force $-\partial_z U$ from the dynamical LDA field at a time $t = 25\,\mathrm{fs}$ near the peak of the pulse. The dashed line indicates the maximum force of the external field. The dotted line shows the Kohn-Sham potential U from which the force is derived (in units 5 eV).

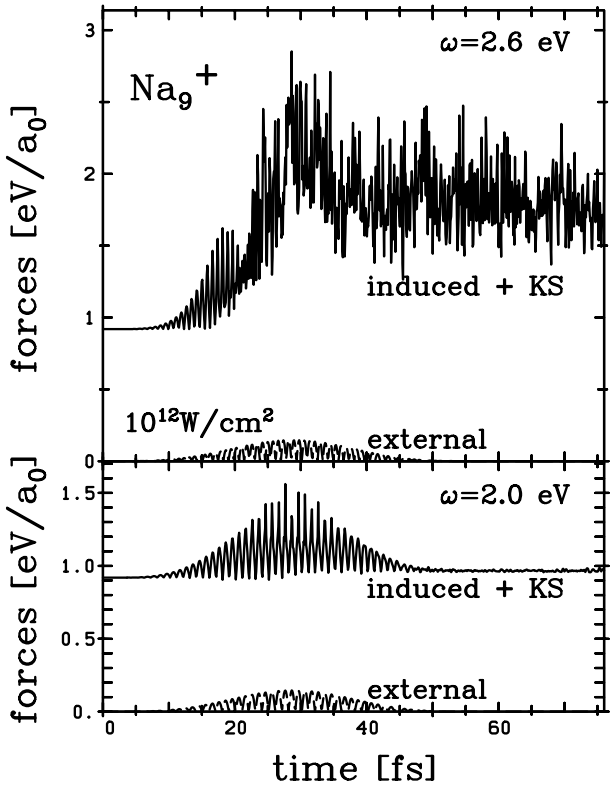

Fig. 2. Time evolution of the maximum force in a $Na_9{}^+$ cluster irradiated with a laser beam of intensity $I = 10^{12}$ W/cm^2 and for two frequencies, near resonance with $\omega = 2.58\,\mathrm{eV}$ and below resonance with $\omega = 2.04\,\mathrm{eV}$. The field strength of the external laser field is also shown for comparison. The laser pulse has a $\cos^4$ profile with FWHM of 21 fs.

background frozen during the present studies. Details of ionic structure are also expected to be less important for the present nonlinear processes [6]. We thus employ the soft jellium model with a Woods-Saxon profile of radius $R = r_s N_{ion}^{1/3}$ and surface width of $1\,a_0$ [6], which provides the proper plasmon frequencies [12]. We consider Na clusters throughout and use $r_s = 4\,a_0$. A TDLDA calculation starts from the ground state configuration and is driven away from it in the course of the time evolution by the external laser field U_{ext}. The dynamics is analyzed here with particular emphasis on the forces developing underway. As complementing information, we look also at the number of emitted electrons $N_{esc}(t) = N(t{=}0) - \int_{box} d^3r\,\rho_{el}(\mathbf{r},t)$, where "box" stands for an analyzing box covering a $2r_s$ neighbourhood of the cluster (for experiences with that definition see [7,13]), ρ_e denoting the electronic density.

In a first round, we need to look at the spatial distribution of forces. Thereby we can concentrate on the forces in z-direction because the laser field acts in that direction and will produce the strongest gradients there. Figure 1 shows results for a typical test case excited in resonance. The dotted line shows the full Kohn-Sham potential. One still recognizes the binding potential well as dominating part. Consequently, the corresponding force has its peaks in the surface regions where binding drops quickly. The dashed line indicates the maximum force from the external laser field. It is small compared to the binding forces such that it seems as if we were still in a regime of weak perturbation. But the strong coupling to the surface plasmon resonance accumulates so much energy in the course of time that actual TDLDA fields are much perturbed and show strong oscillations overlayed to the overall binding force. Similar oscillations appear when watching the force as a function of time as we will see next.

In order to study the time evolution of the forces, we have to quantify it in one number, and for this we choose the maximum absolute value of the force along the z-axis, $F_{max} = \max_{\mathbf{r}}\{-\partial_z U_{C+xc}\}$. The definition of F_{max} may seem arbitrary. The reason for this definition is that we are searching for response effects which arise on short length and time scales which requires a local and instantaneous indicator. The peak force as extracted with F_{max} is clearly a local criterion. The reduction to the amplification effects on a short time scale (of order plasmon cycle) comes a snext step. To that end, Figure 2 shows the time evolution of the maximum force for $Na_9{}^+$ excited at two different frequencies. The amplitude of the exciting pulse stays all times well below the binding forces (which can be read off from the initial value of the "induced + KS" forces). Nonetheless, the changes in the TDLDA forces are dramatic. In the resonant case ($\omega = 2.6\,\mathrm{eV}$), we observe a global increase of the force. This is due to the fact that the strong excitation leads to substantial electron emission which, in turn, leaves the residual cluster in a higher charge state, which enhances the binding force. Here we lose about 2 electrons which complies nicely with the shift of $2e^2/R^2 \sim 0.8\,\mathrm{eV}$ as seen in the figure. The global trend represents an indirect and slowly accumulating effect from the absorbed energy. Besides the global trend, there are

strong oscillations at the frequency of the exciting field. The amplitude of these oscillations is due to a resonant enhancement of the incoming force oscillations. It represents the field amplification in a genuine sense. This amplification is strongest around 20 fs and graphical evaluation yields a factor 8 as compared to the amplitude of the incoming field. The off-resonant case ($\omega = 2.0\,\mathrm{eV}$) in Figure 2 shows negligible electron emission such that the asymptotic force is nearly identical to the original binding force. Moreover, the force above the binding background follows nicely the pattern of the external force, but visibly amplified. We come here to an amplification factor of 5, smaller than in the resonant case but still pretty large. Altogether we learn from Figure 2 that there are two basically different contributions to the force: The global binding force and an oscillating force. The global binding exists already in the ground state and it becomes slowly time-dependent due to electron loss and subsequent charging of the system. The oscillating force is associated with the immediate response to the laser excitation. Its amplitude is a measure for the field amplification due to the cluster's plasmon response.

In order to investigate general trends with intensity and frequency, we take the maximum oscillation amplitude as reference value from which we read off the field amplification. The lower part of Figure 3 shows a summary of results for $Na_9{}^+$ drawn *versus* laser intensity. Three different frequencies have been used, one at resonance ($\omega = 2.58\,\mathrm{eV}$), one below and another one above. The emerging maximum force amplitudes are compared with several other crucial force values in the system. The force from external field is $\propto \sqrt{I}$ and thus seen as a straight line with slope 1/2 in this doubly logarithmic plot. The horizontal dash-dotted lines represent fixed reference values. The "g.s. binding" indicates the binding force in the ground state of $Na_9{}^+$. The "max. bind." stands for the maximum force in a cluster where all electrons are stripped (while keeping the ionic background still fixed). And the line denoted by "core f." indicates the binding force for the $2s$ and $2p$ core electrons in the Na ions. For low intensities, $I \lesssim 10^{12}$ W/cm^2, we see that the emerging forces are much larger than the external force. This is the searched field amplification. It comes out particularly large for the frequency near resonance. With further increasing intensity, however, the field amplification shrinks quickly and disappears at about $I = 10^{14}$ W/cm^2 where the resulting field merges with the external force. It is obvious that the binding forces play a limiting role here. As soon as the effective forces override the binding, electrons are quickly emitted which, in turn, suppresses any resonant response. This view is supported by the upper part of Figure 3 which shows the fraction of emitted electrons for the various cases. There is a steep increase just in that range where the field amplification is cut off, particularly for the off resonant cases. The excitation near resonance gives more field amplification for small intensities which, in turn, distributes the increase in electron emission over a broader range of intensities. In fact, there seems to be a correlation between the effective total force building up

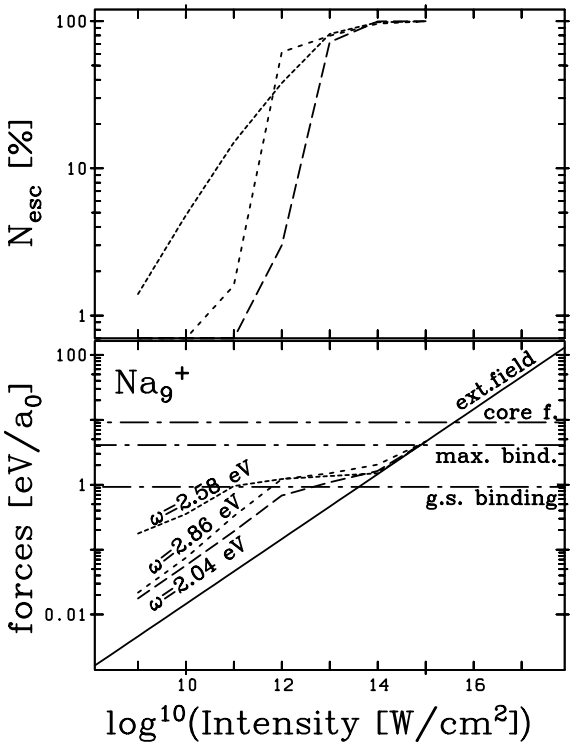

Fig. 3. Lower panel: Maximum amplitude of oscillations of the maximum local force F_{max} in a $Na_9{}^+$ cluster irradiated with a laser beam of various intensities and for three frequencies as indicated. For comparison we also provide the maximum field strength of the external laser field, the maximum Kohn-Sham field of the stationary state (characterizing the binding forces), and the typical force binding the $2s$- and $2p$-core state. Upper panel: Number of emitted electrons (in percent from the initial 8 electrons) *versus* intensity of the laser beam for the three frequencies.

and N_{esc} rather independent from the external force. We see from Figure 3 that the largest gains in resonant coupling are found for moderate laser intensities safely below 10^{12} W/cm^2 and that very intense laser beams would be counterproductive for this kind of effects. Of course, one might question, here beyond about 10^{12} W/cm^2, the relevance of restricting valence electrons to the mere $3s$ electrons of sodium. And a more elaborate calculation should indeed include $2s$ and $2p$ electrons in the valence shell. Still, below 10^{12} W/cm^2, the values of the forces attained are so small as compared to the binding forces of $2s$ and $2p$ electrons (see "core f." in Fig. 3) that such a refinement should presumably not significantly alter this calculation. The case of Na clusters is particularly robust in that respect as the maximum force for fully stripped valence electrons lies still safely below the line for emission from the core. This relation becomes more critical for other materials, as *e.g.* noble metals with their loosely bound d states in the core.

In order to see more clearly the resonant behaviour of the field amplification for moderate laser intensities, we draw in Figure 4 the maximum oscillating forces *versus* frequency. The dotted line represents the results from the

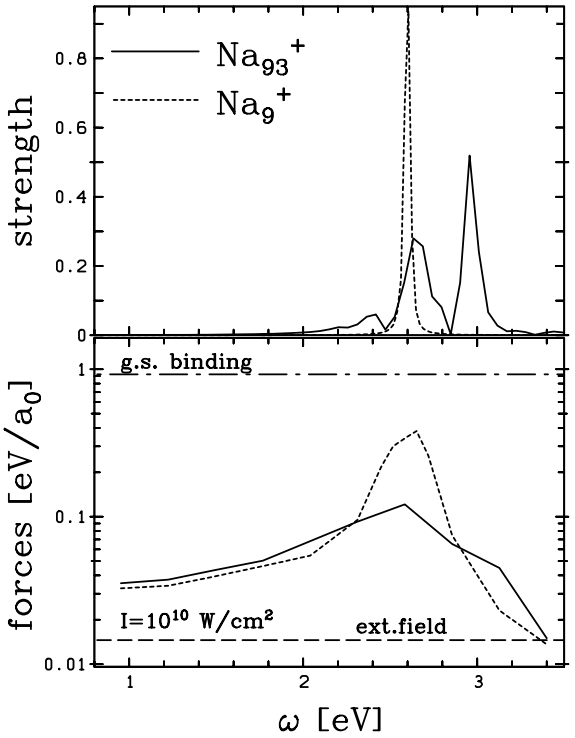

Fig. 4. Lower panel: Maximum field strength in the clusters Na_9^+ (dotted line) and Na_{93}^+ (full line) irradiated with a laser beam of intensity $I = 10^{10}$ W/cm^2 and for varying frequencies. For comparison we also provide the maximum field strength of the external laser field and the binding force of the stationary state (characterizing the binding forces). Upper panel: The power spectrum of dipole resonances for the two clusters under consideration.

previous test case Na_9^+. The amplitude of the external force is given as dashed line for comparison. We see clearly a resonant behaviour of the field amplification. The upper part of Figure 4 shows the corresponding spectral strength distribution (for its definition and details of the evaluation see [6]). The resonance peak agrees exactly with the peak of field amplification. The amplification peak, however, is much broader, delivering substantial field amplification still at much smaller frequencies and stretching out also, but not as far, towards higher frequencies. The pattern look much similar to the response function of a simple harmonic oscillator.

It remains the question of how the response develops if we proceed to larger clusters. Information on that is also provided in Figure 4 with the results for Na_{93}^+ (see the full lines). It is well known that the surface plasmon peaks in larger clusters are strongly Landau fragmented due to interference with $1ph$ states in the resonance region (see [14] and references cited therein). This is also seen from the strength distribution in the upper panel of the figure. The resonance groups into two broad peaks where each one covers several detailed levels. The broader resonance structure lets us expect a less pronounced resonant response in the forces. And that is indeed what comes out, as seen in the lower panel. There is still convincing resonant behaviour, but dampened and broadened. A most interesting result is that the overall size of the resulting forces is the same as for Na_9^+. We have checked that for various other cluster sizes in between and find it very well confirmed: field amplification is independent of the cluster size, only the resonant behaviour is smoothened with increasing Landau damping. It should be noted that we observe here, again, a resonance between maximum field amplification and the Mie plasmon, comparable to the resonance observed with electronic emission [7].

We have analyzed here field amplification effects in sodium clusters irradiated by short (about 60 fs) and intense ($10^9 \leq I \leq 10^{15}$ W/cm^2) laser pulses, using the TDLDA for describing the electronic response in real time. Our results show that at moderate intensities ($I \leq 10^{12}$ W/cm^2) one observes sizable field amplification, in particular when the laser is tuned to the Mie plasmon frequency. The field amplification pattern is roughly in resonance with the plasmon. This once again emphasizes the overall dominance of the collective Mie plasmon in the electronic response of metal clusters, as already noted for example in terms of ionization through laser excitation.

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