Towards Single-Particle Spectroscopy of Small Metal Clusters

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We investigate the kinetic-energy spectra of electrons emitted from a metal cluster following laser excitation. This is done in the framework of a coupled ionic and electronic dynamics. Properly chosen laser parameters, leading to gentle excitations, yield kinetic-energy spectra which nicely resolve the multiphoton processes for each occupied state separately. This gives access to the single-particle energies in clusters, provided one works at sufficiently low temperatures and low electron flow.

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The single-particle levels of a many fermion system carry important information concerning its structural and dynamical features. There exist thus many different techniques for a spectroscopy of individual levels in the various areas of physics, mostly relying on an analysis of the spectrum of emitted particles, e.g., for atoms [1], nuclei [2], solids [3], or nanoparticles [4]. In particular, atoms have been widely studied by means of high intensity lasers in the multiphoton ionization regime, leading to above threshold ionization [5–7]. There exist also several measurements of single-particle spectra for negatively charged metal clusters by means of photoelectron spectroscopy with lasers [8,9]. Neutral or even positively charged clusters are harder to access because they have a much higher ionization threshold. One can stay at the level of direct one-photon processes by going to higher frequencies from synchroton radiation [10]. Steadily improving experimental facilities allow one meanwhile to measure the kinetic-energy spectra (KES) from multiphoton processes triggered by fs laser pulses [11–13]. The experimental KES of medium size clusters ($n \sim 100$) at moderate temperatures ($T \sim 100$ K) display statistical features which are typical of an already significantly excited large system [13]. Such a behavior was actually also found in exploratory calculations [14]. Experiments on large deposited Ag clusters, on the other hand, seem to display the footprints of the single-particle spectra [12]. The topic thus calls for a deeper analysis. It is the aim of this paper to present a theoretical exploration of KES from multiphoton processes, their relations to underlying cluster properties, their trends with laser intensity or temperature, and possible limitations in experimental resolution. As a test case we chose the cluster Na_9^+ throughout.

Our theoretical description of cluster structure and dynamics is based on density functional theory for the valence electrons and classical motion for the ions. For the electrons, we employ the time-dependent local-density approximation (TDLDA) which has become meanwhile a standard tool to analyze electronic response in metal clusters [15,16]. We use here the energy functional of [17]. Only the valence electrons are treated explicitly, and are coupled to ions via a pseudopotential. We use a recently developed smooth local pseudopotential which provides a high quality description of static as well as dynamical properties of Na clusters [18]. The electronic dynamics is handled in axially symmetric approximation, the cylindrically averaged pseudopotential scheme (CAPS) [19,20], which provides a reliable approximation for structure and dynamics of our test case Na_9^+ [21]. The ionic dynamics is treated as classical motion in the force field created by the (pointlike) Coulomb repulsion among the ions and the gradient of the electron-ion pseudopotential. Both electrons and ions are propagated simultaneously [22,23]. Note that this nonadiabatic molecular dynamics allows one to accommodate simultaneously both electronic excitations and thermal ionic motion.

With KES we aim at exploring single-particle properties. Mere TDLDA is not well suited for their description. One has to add at least the self-interaction corrections (SIC) which improves the single-particle energies, e.g., by recovering Koopmann's theorem [24]. We refer here to a simple form using a globally averaged SIC potential [Eq. (7) of [25], without further approximation]. This simple approximation suffices to align the single-particle energies with Koopmann's theorem, and that is just what we need to obtain realistic KES. A more detailed investigation of the various approaches to SIC follows in a separate publication.

The external laser field, acting on both electrons and ions, reads $V_{\rm las} = E_0 \hat{z} f_{\rm las}(t) \cos(\omega_{\rm las} t)$ where $\hat{z}$ is the (local) dipole operator. The laser characteristics are amplitude $E_0 \propto \sqrt{I}$ (where I is the intensity), frequency $\omega_{\rm las}$, and temporal profile $f_{\rm las}(t)$. We consider usually a cosine profile, $f_{\rm las} = \cos^2[\pi(t - T_{\rm pulse})/2T_{\rm pulse}]$ of FHWM equal to $T_{\rm pulse}$. This profile provides very good spectral resolution for a given $T_{\rm pulse}$. In order to study deliberately less clean pulses, we also employ in one case a ramp profile where 10% of the pulse length is used for a linear switching on and off.

Concerning the observables, we keep the standard protocol of previous studies which encompasses the dipole moment $D(t) = \langle \hat{z} \rangle$ (along laser polarization), from which we deduce the spectral strength distribution $S(\omega) = |\Im\{\tilde{D}(\omega)\}|$ by Fourier transformation, and the

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number of emitted electrons $N_{\rm esc}$ [20]. Note that $D(t)$ as well as $N_{\rm esc}$ are mean values from a mean-field theory. They thus represent averages over an ensemble of measurements. More detailed quantities, as, e.g., ionization probabilities, can be derived in a second step of analysis [26,27], but this plays no role here where inclusive measurements are discussed. The KES of the emitted electrons is computed from the local frequency spectrum of the electronic wave functions at a measuring point near the boundaries of the grid. We thus record the single-electron wave functions $\varphi_\alpha(\mathbf{r}_{\rm bc}, t)$ over time at the measuring point $\mathbf{r}_{\rm bc}$. Then we Fourier transform them into the frequency domain $[\varphi_\alpha(\mathbf{r}_{\rm bc}, t) \rightarrow \tilde{\varphi}_\alpha(\mathbf{r}_{\rm bc}, \omega)]$. Note that the measuring point $\mathbf{r}_{\rm bc}$ near the (absorbing) boundary is far off the interaction zone. Moreover, the absorbing boundary conditions [20] guarantee that only outgoing waves are passing by $\mathbf{r}_{\rm bc}$. The frequency spectrum $|\tilde{\varphi}_\alpha(\mathbf{r}_{\rm bc}, \omega)|^2$ is thus also the KES of electrons emitted from state α. Altogether the total KES of the N electrons becomes

$$n(E_{\rm kin}) = \sum_{\alpha=1}^{N} |\tilde{\varphi}_\alpha(\mathbf{r}_{\rm bc}, E_{\rm kin})|^2. \qquad (1)$$

This is the quantity which will be discussed in the following. From a formal point of view, it is worth noting that (i) it is robust under unitary transformations among the occupied single-electron states; and (ii) the actual spectra will take the energy of the highest occupied electron level as ionization energy. SIC (even in approximate manner) delivers here the correct value.

A first KES is shown in the lower panel of Fig. 1. One sees pronounced structures which have clear relations to system parameters. The laser frequency is indicated by a horizontal bar, and the patterns are obviously repeated, each shifted by $\omega_{\rm laser}$. Within one block of width $\omega_{\rm laser}$ one spots two well separated peaks. Their distance of about 1.3 eV coincides with the energetic separation of the $1s$ and the $1p$ states in Na_9^+. This suggests that we resolve emission from the $1s$ *and* $1p$ states separately. We have counterchecked this interpretation by omitting the sum in Eq. (1) and computing the KES for each state α separately. Moreover, the position of the peaks is well described as a ν-photon process

$$E_{\rm kin}^{\rm peak} = \nu\omega_{\rm laser} - E_{\rm bind}\,, \qquad (2)$$

where $E_{\rm bind}$ is the binding energy of the corresponding single-electron level. Note also that the overall $n(E_{\rm kin})$ decreases with increasing $E_{\rm kin}$ because higher multiphoton processes become less and less likely.

At a second glance of Fig. 1, one realizes that there appear substantial substructures in the peaks of the KES. They carry forth the spectral features of the system and of the excitation process. The upper panel of Fig. 1 shows the spectral distribution of dipole strength $S(\omega)$. The vertical lines therein indicate the position of the laser frequency and multiples thereof. One sees that already the main peak (at laser frequency) looks fuzzy and the spectrum is stretched to the red side. This happens because we have chosen the laser frequency close to, but slightly above, the (plasmon) resonance frequency of the system [26]. And we have decided to use here the spectrally less clean ramp pulse. Both effects together lead to a substantial coexcitation of the plasmon resonance. This is seen as the side peak below the laser frequency in $S(\omega)$. The spectral stretching is repeated then in the second and third harmonic signals of $S(\omega)$. It is also copied into the peaks of the KES (lowest panel), even with amplification of the fragmentation. Altogether, we thus see that the KES carries a lot of useful information. We have an explicit picture of multiphoton processes and can map the single-electron spectrum of the cluster. The detailed shape of the peaks in the KES furthermore gives a hint on the spectral mix in the actual excitation process.

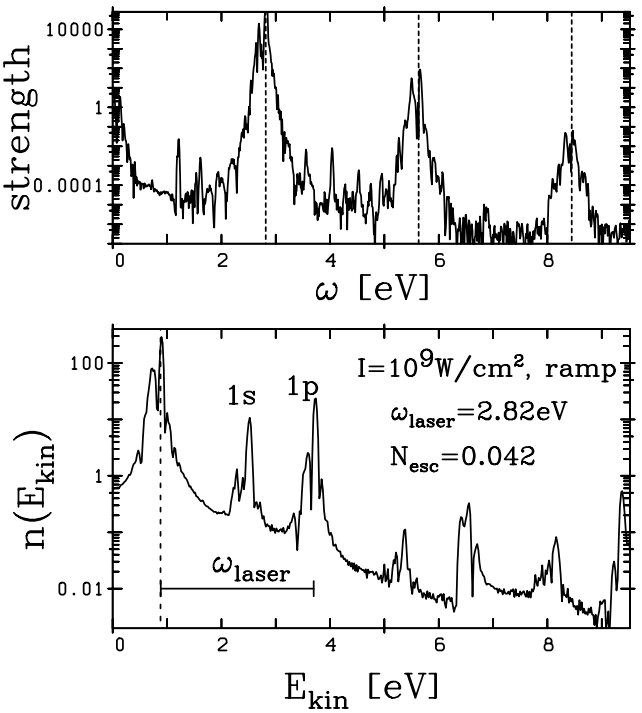

FIG. 1. Observables from excitation of Na_9^+ in the CAPS 144 ground state with a laser of frequency $\omega = 2.8$ eV, intensity $I = 10^9$ W/cm^2, and ramp pulse with 10% ramp at both ends ($T_{\rm pulse} = 180$ fs FWHM). Upper part: Dipole strength $S(\omega)$. Lower part: KES $n(E_{\rm ekin})$ of emitted electrons (arbitrary units).

Figure 2 demonstrates the change of the KES with increasing laser intensity I. We use here the cosine^2 laser profile and place the frequency at resonance to model a good spectral selectivity of the laser signal. The KES for the lowest intensity indeed displays well developed sharp peaks reproducing, of course, the general pattern of multiphoton processes from separate single electron states as discussed above. But these nice structures fade away quickly with moderate increase of intensity, which reflects the fact that the system has entered a truly nonlinear

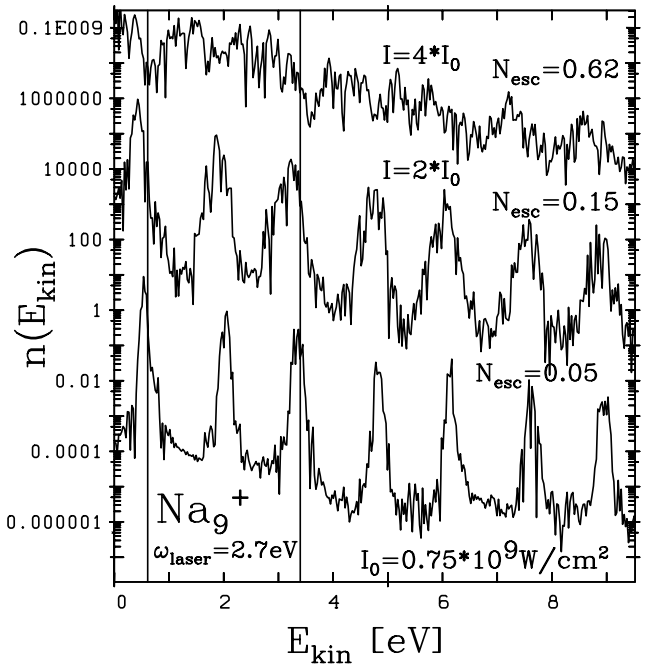

FIG. 2. KES of emitted electrons (arbitrary units) after excitation of Na_9^+ (144 CAPS ground state) with a laser of frequency $\omega = 2.7$ eV, $\cos^2$ pulse with $T_{\text{pulse}} = 100$ fs FWHM, and with varying intensity as indicated.

regime. Doubling the intensity already yields a strong broadening, and another doubling wipes out all structures. Inside our approach, this destructive trend can be understood by looking at the average number of emitted electrons N_{esc}, which dramatically grows with intensity. That is not surprising because ν-photon processes grow with I^ν [28]. The strong outflow of charge (indicated by large N_{esc}) has a large back effect on the mean field at the cluster site. It deepens the Coulomb field, and thus the average Kohn-Sham potential, by a typical amount $\delta U_{\text{KS}} = N_{\text{esc}} e^2/R$, where $R = r_s N^{1/3}$ is the cluster radius. All separation energies are hence shifted upwards by the same amount, which implies a redshift of KES peaks. But the above δU_{KS} is building up in the course of time. Thus, the electronic wave functions leaving the cluster at different times explore different separation energies, which widens the accumulated peak up to δU_{KS}. The broadening thus "continuously" stretches the strength to lower E_{kin} (curve at $2 * I_0$ in Fig. 2). With $R = 8a_0$ the above outlined picture provides a broadening of order $\delta U_{\text{KS}} \sim 0.8$ eV in accordance with the result shown in the figure. For the highest intensity we estimate a broadening of about 2.2 eV which, together with the $1p$-$1s$ splitting of 1.3 eV, spans more than the interval given by laser frequency. It is obvious that no structure can survive under these conditions. This marked evolution of total yield and emerging pattern thus sets rather strict limits on the working point. The intensity should thus be small enough to preserve spectral resolution, but a too small intensity curbs the yield down to a poor statistics.

It is to be noted that the predicted broadening with N_{esc} and its interpretation in terms of δU_{KS} relies on the underlying TDLDA description. It is an open question how correlations beyond TDLDA would influence the results. In that context, it is noteworthy that comparable peak broadening is observed in the fully correlated time-dependent configuration-interaction for two-electron systems [29]. This suggests that the mean-field approach does provide a meaningful picture, at least qualitatively. But the quantitatively correct description of the peak broadening remains an important task for future research. Even the case that one observes sizable correlations would have its positive aspect. Such an effect could be exploited to deliver hints on correlations: The quick excitations we are studying here lead to diabatic ionization, so that one should directly observe the single-particle levels of the original cluster, as seen in our calculations. And this is all the more true for the multiphoton processes in which electrons are emitted at very high kinetic energy. Peak spreading would then give information on the correlations contained in the system.

In a last step, we explore the possible impact of ionic temperature. Up to now, we let the ions move but started always at the ground state configuration, i.e., at temperature $T = 0$. The perturbation for the cases with high resolution is small, such that no effect of ionic motion can be spotted. And electron emission wipes out any detailed information in the more violent cases for which we also produce substantial ionic deviations. The situation is different in the (more realistic) case of clusters at finite temperature. Ionic motion is then an unavoidable constituent of the cluster configuration, independent from the excitation process. We have thus simulated clusters at finite T by giving the ions an initial kinetic energy of $3T$ which is the ions total share of thermal energy (in the vibrational regime). We then let the cluster evolve freely for about one ionic cycle which suffices to distribute this thermal energy over kinetic and potential energy each taking in the time average about $1.5T$ energy. The initialization was done by sampling at random a Maxwellian velocity distribution. Of course, one cluster is then to be represented by an ensemble of such calculations starting at different random choices. Observables (KES, N_{esc}, etc.) are then accumulated as ensemble averages. Results for the KES at three temperatures are shown in Fig. 3. One sees a substantial loss of resolution due to the step from $T = 0$ to 100 K. Part of the broadening comes from thermal fluctuations of the threshold energy (about 0.3 eV broadening). But the larger part of the broadening is again due to electron emission and its back effect on the mean field. The average electron yield remains at $N_{\text{esc}}(T = 100\ \text{K}) = 0.046$ as in the $T = 0$ case. But the variance grows from zero to a large $\Delta N_{\text{esc}}(T = 100\ \text{K}) = 0.043$. The members in the ensemble with the largest electron yield dominate the spectrum, and their large ionization is related, of course, to a smoother KES. Both effects together (fluctuation of

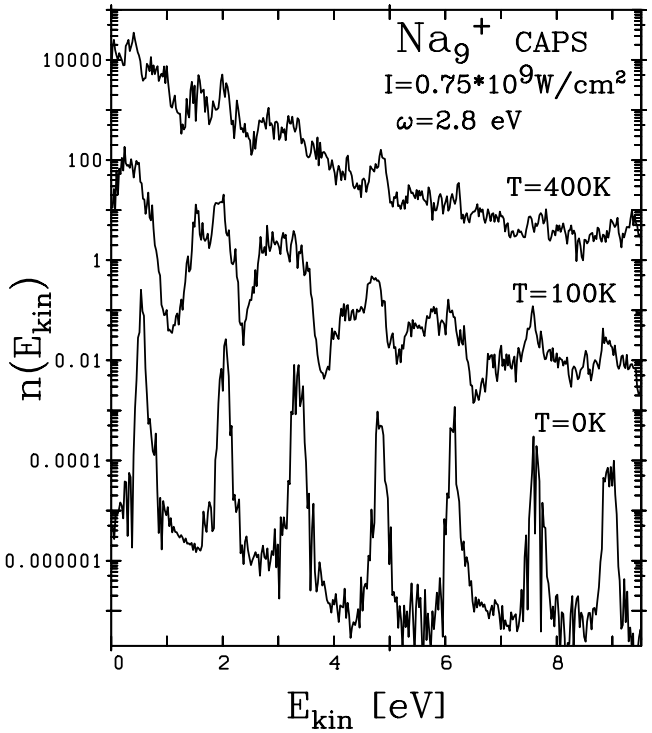

FIG. 3. KES of emitted electrons (arbitrary units) after excitation of Na_9^+ (144 CAPS ground state) with a laser of frequency $\omega = 2.7$ eV, intensity $I = 10^9$ W/cm^2, and cos^2 profile with 100 fs FWHM. Results from ensembles at three different temperatures (as indicated) are compared.

threshold and fluctuation of ionization yield in the thermal ensemble) add up to the observed 1 eV broadening. The step to the higher temperature $T = 400$ K wipes out the structures completely because the fluctuations grow, enhancing the uncertainty of the threshold as well as producing events with even larger emission. The latter fact is also seen from the enhanced average emission which is now $N_{\mathrm{esc}}(T = 400\ \mathrm{K}) = 0.078$ with a larger variance $\Delta N_{\mathrm{esc}}(T = 400\ \mathrm{K}) = 0.068$.

Altogether, we have seen that the KES of emitted electrons can carry a lot of useful information. In particular, they give access to the energies of the single-electron states occupied in the cluster. There are, however, several effects which smear out the spectral distribution and thus spoil the signal which one wants to study. One should use sufficiently low intensities to avoid too strong electron emission and clusters need to be kept at low temperature (safely below 100 K). Furthermore, a short laser pulse in the range of 50 fs is desirable in two respects. It stays safely below the time where dynamically induced ionic motion interferes [30], and it reduces competition with electronic thermalization through electron-electron collisions [31]. Small clusters are preferable because their more dilute single-electron spectrum is easier to resolve. Last but not least, one can easily suppress the background signal from thermal electron evaporation collecting the electrons only along the direction of the laser polarization where the direct emission ejects them.

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