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Angle-resolved photoelectron spectra of metal cluster anions within a many-body-theory approach

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A consistent many-body theory based on the jellium model is applied for the description of angular resolved photoelectron spectra of metal clusters anions. The results of calculations demonstrate the dominant role of the many-body effects in the formation of angular distributions of photoelectrons emitted from sodium clusters and are in a good agreement with recent experimental data. The concrete comparison of theory and experiment has been performed for the photoionization of Na_7^- and Na_{19}^- anions being characterized by the entirely closed shells of delocalized electrons.

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The problem of photoionization of metal clusters has been studied intensively during the last two decades, see, e.g., [1], and references therein. Within this period a number of important achievements has been made. Thus, the plasmon resonances in photoabsorption spectra of small metal clusters of nanometer size for different materials, e.g., Na, K, Mg have been observed, for references see [1]. The detail geometrical structure of mass selected clusters has been also studied by means of low temperature photoelectron spectroscopy and the density functional theory (DFT). For example, for sodium cluster anions with up to 350 atoms the geometrical structures have been determined with high accuracy from the comparison of DFT calculations results with measured photoelectron spectra [2,3].

The measurement of photoabsorption and photoionization of small mass selected clusters is not a trivial task. Until recently the measurement was fulfilled only for the total photoionization or photoabsorption cross sections of various cluster targets. In the recent work [4] the first measurement of angular resolved photoelectron spectra of sodium clusters has been reported. These experiments have been performed for negatively charged sodium ions (anions) in a broad range of cluster sizes $3 \leqslant N \leqslant 147$ [4]. These experiments allowed to probe the angular momenta of single electron orbitals in sodium metal clusters. In the work [4] it was also demonstrated that simple models based on single electron treatment of the photoionization process fail to describe the angular anisotropy of photoelectrons emitted in the process of photoionization of cluster anions. Let us note here also that the angular anisotropy of photoelectrons emitted in the process of photoionization of atomic negative ions has been investigated in sufficient detail both theoretically and experimentally (see, for example, review [5]). It was demonstrated that the parameter of angular anisotropy β [6] is very sensitive to accounting for the many-electron correlation effects. Therefore, the failure of single-particle approaches reported in [4] for the case of the photoionization of cluster targets is not a surprise.

In this Rapid Communication we apply a consistent many-body theory for the description of angular resolved photoelectron spectra of metal clusters. As a case of study sodium cluster anions have been chosen. The Hartree-Fock (HF) approximation has been used as a single particle theoretical framework. Many-electron correlations have been accounted for within the random phase approximation with exchange (RPAE), which takes into account the influence of dynamical polarizability of the many-electron system. The results of calculations allow one to conclude that many-electron correlations play the very essential role in the formation of angular distributions of photoelectrons in the process of photoionization of metal clusters. This effect is a consequence of the large dynamic polarizability of metal cluster targets, being entirely determined by many-electron correlations in the vicinity of the plasmon resonance frequencies. For the concrete analysis and illustration we have chosen the Na_7^- and Na_{19}^- magic clusters.

We consider here the simplest case of a spherically symmetric cluster target and apply the jellium model for the description of the photoionization process. The jellium model treats a metal cluster as two interacting subsystems: the valence electron subsystem and the subsystem of positively charged ionic core. The valence electrons move in the field created by all the cluster ions. Within the spherical jellium model the detailed ionic structure of the cluster is smeared out and substituted by the uniform, spherically symmetric distribution of the positive charge. This model proved to be well applicable for the description of electronic structure [7] and collision processes involving metal clusters and fullerenes [1,8]. Cross sections of the collision processes are very sensitive to the correct accounting for many-electron correlations, see [1,8], and references therein.

In a spherically symmetric field, the single electron wave functions can be presented by the radial n_r, orbital l, and magnetic m quantum numbers. This means that when neglecting the spin-orbital interaction the cluster electronic shells with quantum numbers $n_r l$ consist of $2(2l+1)$ electrons. For instance, in the case of Na_7^- and Na_{19}^- the electronic configurations of the ground state have the form: $1s^2 1p^6$ and $1s^2 1p^6 1d^{10} 2s^2$, respectively.

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The wave functions of excited states have been calculated both in the field of a "frozen" electronic cluster core with the created vacancy and with the entirely rearranged residual electronic structure of the cluster. The latter case corresponds to the situation of the so-called static rearrangement.

Within the dipole approximation the angular distribution of photoelectrons ionized from the $n_r l$ state by linearly polarized light can be written in a well-known general form [6]:

$$\frac{d\sigma_{n_r l}(\omega)}{d\Omega} = \frac{\sigma_{n_r l}(\omega)}{4\pi}[1 + \beta_{n_r l}(\omega) P_2(\cos\theta)], \tag{1}$$

where $\sigma_{n_r l}(\omega)$ is the total photoionization cross section from $n_r l$ state, ω is the photon energy, $P_2(\cos\theta)$ is the Legendre polynomial of the second order, θ is the electron emission angle with respect to the polarization of the incident light. The angular asymmetry parameter β in the single-electron approximation reads as [6]

$$\beta_{n_r l}(\omega) = \frac{1}{(2l+1)\left(d_{l-1}^2 + d_{l+1}^2\right)}[(l-1)d_{l-1}^2 + (l+2)d_{l+1}^2 - 6\sqrt{l(l+1)}\, d_{l-1} d_{l+1} \cos(\delta_{l+1} - \delta_{l-1})]. \tag{2}$$

Here $\delta_{l\pm1}$ is the phase shift of photoelectron, $d_{l\pm1}$ is the reduced dipole matrix element, which can be obtained from photoionization amplitude by the integration over angles and the summation over spin variables.

There is a certain threshold value for the angular anisotropy parameter β in the cross section of photodetachment from negative ions [5]. For $l > 1$ it is equal to

$$\beta_{n_r l} \to \frac{l-1}{2l+1}. \tag{3}$$

In the case $l = 0$ the β parameter is equal to 2.

Expression for the angular distribution of photoelectrons within consistent many-body theory accounting for many-electron correlations has been derived in [9] and reads as

$$\begin{aligned}\beta_{n_r l}(\omega) = {} & \frac{1}{(2l+1)(|D_{l-1}|^2 + |D_{l+1}|^2)} \\ & \times \{(l-1)|D_{l-1}|^2 + (l+2)|D_{l+1}|^2 \\ & + 6\sqrt{l(l+1)}[(\mathrm{Re}D_{l-1}\mathrm{Re}D_{l+1} + \mathrm{Im}D_{l-1}\mathrm{Im}D_{l+1}) \\ & \times \cos(\delta_{l+1} - \delta_{l-1}) - (\mathrm{Re}D_{l-1}\mathrm{Im}D_{l+1} \\ & - \mathrm{Re}D_{l+1}\mathrm{Im}D_{l-1})\sin(\delta_{l+1} - \delta_{l-1})]\},\end{aligned} \tag{4}$$

where $D_{l\pm1}$ are the complex reduced amplitudes obtained from the dipole matrix elements being solutions of the RPAE matrix equation (see, for example, [10]).

Using the formalism presented above we have calculated the angular anisotropy parameter β for the photoionization cross section of the magic Na_7^- and Na_{19}^- cluster anions. Calculations have been performed in the single particle HF approximation and also with accounting for many-electron correlations.

In Fig. 1 we present comparison of the experimental data from [4] with the results of our calculations of angular anisotropy parameter β for the photoionization of the $1p$ shell of the Na_7^- cluster performed in the single particle HF approximation. Different experimental dependencies A, B, C in Fig. 1 correspond to the photodetachment of p electrons from different sublevels of the $1p$ orbital arising due to its splitting by the crystalline field of the cluster. In the paper [4] the calculation of the parameter β in a single-particle approximation with the use of the self-consistent Ekardt potential and additional accounting for the image-charge and dipole potentials was also performed. Our result here is based on Eq. (2) with the amplitudes being calculated using the HF wave functions. As it follows from Eq. (3) the threshold value of β for the p photoelectrons should be equal to 0. From the results obtained it is clear that within a single-particle formalism it is neither possible to derive the overall correct behavior of $\beta(\omega)$ corresponding to the experimentally measured dependence.

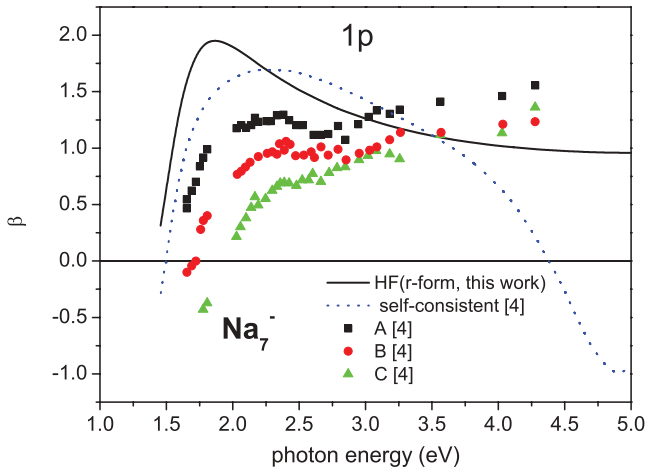

FIG. 1. (Color online) Angular anisotropy parameter β for the partial photoionization cross section of the Na_7^- cluster versus photon energy; solid line is a result of the HF approach derived in this work (length form); dotted line is a result of a single-particle approach used in [4]; A, B, C are the experimentally measured dependencies [4].

In order to elucidate the role of many-electron correlations the angular anisotropy parameter β has been calculated on the basis of the matrix RPAE approach. In Fig. 2 the results of this

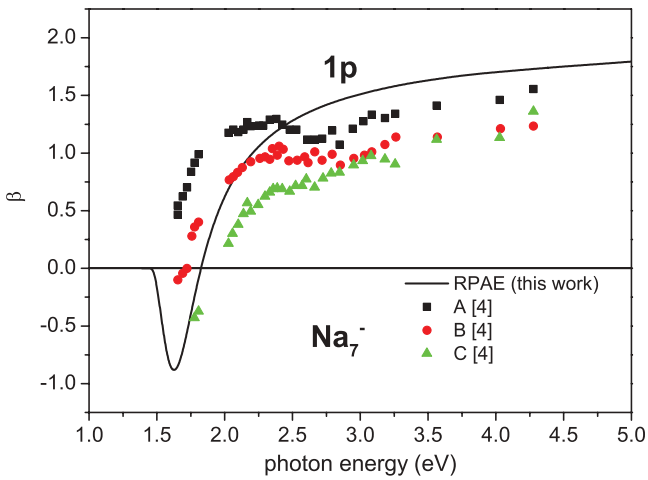

FIG. 2. (Color online) Angular anisotropy parameter β for the partial photoionization cross section of the Na_7^- cluster versus photon energy; solid line is a result of the RPAE calculation accounting for many-electron correlations (length and velocity forms are completely consisted); A,B,C are the experimentally measured dependencies from [4].

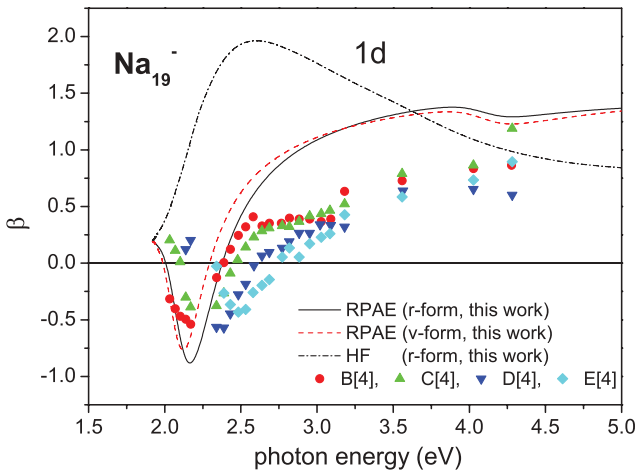

FIG. 3. (Color online) Angular anisotropy parameter β for the partial photoionization cross section of the Na_{19}^- cluster versus energy of photon; solid and dotted lines are the RPAE results, dash-dotted line presents HF results in the lengths form; dependencies B,C,D,E are the experimental data [4].

calculation of β for the photoionization of the Na_7^- cluster are presented and compared with the experimental results from [4]. A comparison of Figs. 1 and 2 demonstrates that accounting for many-electron correlations leads to a qualitative change of behavior of the calculated dependence and thus the angular distribution of photoelectrons. Figure 2 demonstrates also that the consistent many-body theory improves substantially the agreement of theoretical results with experimental data.

A similar calculation and analysis of β have been performed for the photodetachment from the Na_{19}^- cluster anion. In this case we have calculated the wave functions for outgoing photoelectrons in the entirely rearranged electronic cluster core. In Fig. 3 we compare the obtained dependence $\beta(\omega)$ for the d-shell photoionization of the Na_{19}^- cluster. As in the case of Na_7^- different experimental dependencies B,C,D,E correspond to the photoionization from the sublevels of the $1d$ orbital split by the crystalline field of the cluster. Note that the calculated dependence of $\beta(\omega)$ on ω possesses a characteristic minimum in the vicinity of the threshold, which is well seen in all experimental curves. A small deviation of the parameter β calculated using the length and the velocity form of the amplitudes $D_{l\pm1}$ arises due to accounting for the electronic cluster core rearrangement in the static approximation. A small shift in ω of the calculated curves with respect to the experimental ones is a result of some deviation of the experimental value of I_p from the one calculated within the jellium model framework.

The next logical step of these investigations could be an extension of the formalism presented in this work for clusters with partially filled shells. This treatment is to be performed within the framework of the deformed jellium model [11]. The most detailed description of the problem, of course, should take into account the detail geometrical structure of the ionic core. Also, for the accurate description of the near-threshold behavior of the photoionization cross sections of negative ions one need to account for the effect of dynamical polarization of the electronic core, i.e., for the polarization of the electronic core by the outgoing electron, as well as the relaxation processes of the electronic core. This can be achieved by the method combining the Dyson equation method and RPAE [5,12]. All these problems can be addressed for different type of metal clusters (Au, Ag, Mg, Al, K, Sr, etc.) and remain open for further investigations in this field.

In this Rapid Communication the consistent many-body theory has been applied to the calculation of the angular distributions of photoelectrons emitted the process of photoionization of metal clusters. The concrete analysis was performed for sodium cluster anions Na_7^- and Na_{19}^- possessing nearly spherical geometry arising due to the closure of all electronic shells of delocalized electrons. For these clusters we have calculated the parameter of angular anisotropy β of the photoionization cross sections. These calculations revealed the very important role of many-electron correlations in the formation of angular distributions of photoelectrons and explained the behavior of the angular anisotropy parameter $\beta(\omega)$ versus photon energy for sodium clusters recently measured in [4].

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