Abstract. We show, with an example of Na$_{92}$, that for jellium metal clusters the interference of fast electron-waves emitted from equivalent sites on the cluster edge produces monochromatic oscillations in all photoionization observables as a function of the photoelectron momentum; the effect is equivalent to the usual dispersion phenomenon. In dealing with formalisms, a serious consequence of the inadequacy of self-interaction corrected local density-functional theory in correctly accounting for the exchange interaction is identified. We also briefly discuss the influence of the ionicity of the residual core on photospectra by considering the neutral member with $N = 58$ and and the ionic member with $N = 52$ of the Na$_{58}$ iso-jellium series, where $N$ is the number of valence electrons. A few final remarks on possible implications of these results on other quantum systems of delocalized electrons are made.

Keywords: Jellium cluster, photoionization, density-functional theory

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1 Introduction

Due to the near-Coulomb character of a typical atomic potential with its strong attractive behavior at close distances resulting electronic wavefunctions are generally compact around the nucleus. As a result, electrons in an atom are largely localized. There are two important consequences of this property. First, since the gradient of such a potential varies smoothly, electrons can receive the necessary recoil force ($-dV/dr$) to photoionize from ‘everywhere’ within the spatial extent of the system. Second, any rapid variation of the potential within a small range does not significantly affect photo-dynamical properties, because the potential with its steep slope practically overwhelms such local structures.

On the other hand, atomic clusters exhibit properties that hover across the realm between the single atom and the bulk. Contrary to the atomic context, where the nucleus is practically dimensionless, a system of positive core-ions with a certain spatial extension provides the necessary binding for valence electrons in a cluster. This background positive core can be approximated as a homogeneously smeared out charge distribution, the jellium, for a cluster of sufficiently large atoms with one or two valence electrons per atom. Consequently, the effective potential of such a system acquires, in comparison to the atomic potential, a radically different shape by having a flat interior and a sharp edge. We focus in this paper on this aspect of the cluster potential to scrutinize how does the shape influence the high energy photoionization behavior of a metal cluster and its ions. We further point out an unphysical consequence of an ad hoc correction scheme that is popularly applied to the Kohn-Sham local-density-approximation (LDA) to account for spurious self-interactions.

2 Results and discussions

Alkali-metal clusters having one valence electron per atom can be well described by a spherical jellium model which entirely disregards the structure of the ionic core [1]. The Schrödinger equation can then be approximately solved by some ground state many body theory considering Coulomb interactions among only valence electrons. As pointed out, the resulting radial potential ($V$) typically behaves flat from the origin up to almost the edge and then over a short range across the edge ($r = R_C$) produces a steep barrier. This behavior physically implies that the valence electron cloud is quasi-free over the most of the interior region of the cluster but feels a rather strong confining force in the vicinity of the surface. To understand the basic mechanism of the photoionization from such systems let us consider the dipole amplitude of a typical $nl \rightarrow l'$ transition.
The radial matrix element in the acceleration form of the dipole interaction, that is proportional to the ionization
recoil force, is then \(< \psi_{nl}|dV/dr|\psi_{n'l'}>\); of course, the
dual assumption of spherical symmetry and unpolarized
photon is implied. Now, the structure of \(V\) clearly sug-
gests that its radial derivative must show a strong peak
at the edge while is virtually vanishing elsewhere. This
means that the predominant contribution to the overlap
integral will come from the edge, which equivalently im-
plies that photoelectrons will largely emit from the sur-
face region where it receives enough recoil to eject. Strong
contribution to the amplitude from equivalent sites of the
cluster edge will, therefore, show the signature of interfer-
ence in the form of oscillations in the ensuing cross section
as well as in other physical parameters. While there has
been no experimental study on metal clusters, oscillations
in the valence photoelectron intensity are indeed observed
for \(C_{60}\) [2] and \(C_{70}\) [3] fullerine molecules, which are also
systems of quasi-free de-localized electrons confined within
a nearly spherical shell.

Situation begins to get simpler as the energy of the in-
cident photon increases. In general, the continuum radial
wavefunction \(\psi_{n'l'}\) for such potentials are very nearly the
spherical Bessel function \(j_{nl}(k_{nr})\), where \(k_{nr}\) is the photo-
electron momentum. With high photon-energy, and there-
fore fast photoelectrons, this function limits to \(\cos(k_{nr}r +
\pi/2)\), the usual first Born picture. Insertion of this high
energy form into the radial matrix element immediately
reveals that the oscillation in the dipole amplitude will
have a frequency close to the radius of the cluster. Evi-
dently, the cross section, which is the sum of the squared
modulus of amplitudes of allowed transitions, will then oscillate in a frequency approximately the diameter:

\[
\sigma_{nl} \sim \cos(2Rc k_{nl} + l' \pi) \tag{1}
\]

In fact, the oscillation in alkali-metal clusters has been
predicted earlier through a kind of semi-classical study [4]
and has later been verified by numerical calculations of the
total cross section of \(Na_{40}\) using some effective mean-field
LDA potential [5].

In this study, we calculate subshell photoionization
cross sections for \(Na_{92}\) cluster (\(1s^2 1p^6 1d^{10} 2s^2 2p^{14} 2d^{10}\)) from threshold to about 1 KeV photon-energy
in an independent particle frame. The ground state is
described by the electron self-interaction corrected local-
density approximation (LDASIC) [6], that approximately
restores the physical long range \(-1/r\) behavior of the
resulting single-electron potential. Figure 1 presents some
selected subshell cross sections from \(n = 1\) manifold. The
oscillation in cross sections is very much in evidence and
the Fourier transform (not shown) of the cross sections (as
a function of the respective \(k_{nl}\) indeed peaks at a position
which is approximately the diameter of the cluster.

An interesting physical analogy of this phenomenon
can apparently be drawn with the usual diffraction mech-
anism in optics. The light shines on a metal cluster which
is like a spherical double-slit with slit width to be the clus-
ter diameter. ‘Free’ delocalized electrons over the bulk of
the interior region are nearly insensitive to the light. Pho-
toelectron waves emanate only from the two slits, which
effectively are the diametrically opposite sites on the sur-
face of the sphere. These secondary waves with a certain
path difference, that is equal to the slit width and hence
the diameter, subsequently interfere. As a result, the cross
section oscillates in a frequency \(2Rc\), a feature equivalent
to the distance between consecutive fringes in a diffraction
pattern being \(2\pi/(2Rc)\).

For a ground state subshell of the angular momen-
tum \(l\) the two dipole-allowed free angular momenta are
\(l' = l \pm 1\). Therefore, it can be easily verified by using
equation (1) that the phase contribution to any \(\sigma_{nl}\)
from the continuum wavefunctions is always \(2\pi\) at high enough
energy. This implies that the high energy phase difference
between any two subshell cross sections will be predom-
nantly determined by the phase contribution from their
ground state angular momentum \(l\). Thus, for any two sub-
shells with the difference between their \(l\) values being an
odd integer the corresponding cross sections will show os-
cillations largely out of phase, while the difference being
even they will oscillate in phase. This behavior is clearly
evident among the cross sections in Figure 1; while a rough
phase agreement is seen between 1s and 1d cross sections,
1g and 1h are clearly out of phase.

Figure 2 shows the cross sections for 2d and 3s sub-
shells. Surprisingly, oscillations in these cross sections seem
to have more than one frequency. Indeed, the correspond-
ing Fourier spectra identify several other frequencies besides the physical one that connects to the cluster diameter. These extra frequencies can be shown to be entirely spurious and originate from the unphysical cusp that the self-interaction correction (SIC) generates in subshell-dependent radial potentials at the position where the respective single electron density attains nodal zero [7]. Figure 3 shows some of these potentials. Subshells with \( n = 1 \) are nodeless and, therefore, the 1s potential is seen to have the usual shape. This fact explains the correct behavior of the resulting cross section for \( n = 1 \) family. Subshells with \( n = 2 \), containing one node (Figure 3), yields a second frequency in the dipole amplitude that interferes with the physical frequency to contaminate the cross section with three spurious frequencies. The same mechanism works for \( n = 3 \) subshell which has two nodal points (Figure 3) to eventually produce eight unphysical frequencies in the photo cross section. The correct elimination of the self-interaction must treat fully the exchange effect which is intrinsically non-local. This answers why SIC is automatically built in the non-local Hartree-Fock formalism. The LDASIC is certainly a powerful tool to handle the low energy dynamics [6], but it is also true that the effect discussed here remains virtually recessive in this energy range for this method, because the continuum wave with the longer wavelength can hardly ‘detect’ this structure in the potential. On the other hand, at higher energies this intrinsic limitation of the formalism causes major problem, although SIC is found largely unimportant over the high energy range since with the contribution to the overlap integral predominantly coming from the edge any refinement in the long distance character of the wavefunction leaves the result practically unaltered. It is, therefore, of crucial importance to choose appropriate theoretical techniques to avoid mis-interpretation of photo-dynamical results for metal clusters.

It is often of interest to examine the influence of the initial ionization state on the photoionization dynamics. A possible approach to this direction is to look at the change in the behavior of photo cross sections as a function of the residual charge by reducing the valence electron number \( (N) \) but keeping the charge of the jellium background constant (iso-jellium series). In the atomic regime, recent investigations on isoelectronic sequences revealed a number of important effects at low photon-energies [8]. We consider here the photoionization of neutral Na_{58}(N = 58) and Na_{58}^{6+}(N = 52) ion to make a preliminary study on the effect of the residual core ionicity on the total ion-
ization cross section; a detailed study including subshell cross sections for several other ions along both iso-jellium and isoelectronic series will be considered elsewhere.

Total cross sections for both the systems calculated via LDA, but without SIC incorporated, are compared in Figure 4. Both the cross sections look qualitatively similar having the identical trend in terms of oscillations. Of course, with the increase of positive residual ionicity bound electrons find it harder to escape, which explains why the ionic cross section is lower. At this point it may be rather interesting to look at the LDA ground state radial potentials for both the systems, as are plotted in Figure 5. Clearly, the increase of the residual positive charge from +1 in the neutral to +7 in the ion only deepens the potential while the position and the softness of the edge remains largely unchanged. Although this is a direct consequence of the jellium approximation, but a proper inclusion of the ionic dynamics is not expected to change the situation significantly. It is evident that the identical frequency of the oscillation in both the cross sections is owing to the unaltered position of the cluster edge. Also, the identical softening at the edge of the potentials accounts for the similar background decay pattern of the cross sections. What is rather interesting, however, is while the depth of the potential for the ion increases greatly, by about 200% of that of its neutral partner, respective total cross sections (Figure 4) are very close to each other! In fact, over the entire high energy range they differ only by a simple energy-independent scaling factor that is roughly close to unity.

It turns out that this scaling quantity is a function of \( z \), the initial ionization of the system. Starting from the fact that the dominant contribution to the cross section comes from the cluster edge, where the derivative of the potential peaks, it immediately follows that the \( z \)-dependence of the cross section will be predominantly determined by the \( z \)-dependence of the bound state wavefunction at the edge. Therefore, cross sections must be of similar strength as the magnitude of radial waves are considerably close to each other at the edge, no matter what positive charge they experience. Thus, the situation clearly offers a possibility of generating the theoretical ionic photoionization data over the high energy range through a simple scaling of the result for respective neutral member; the formulation of a detailed scheme is on the anvil.

3 Concluding remarks

Energetic photo-spectra of metal clusters are largely dominated by oscillations from a diffraction-like mechanism through the interference of electron waves emitted by the cluster edge. This behavior is directly connected to the delocalized character of the electron charge distribution. Similar mechanism is also found operative for the valence photoionization of \( C_{60} \) molecule [9]. A unique structural feature of \( C_{60} \) is a hollow cage that can easily hold an atom inside; in fact such endohedral confinement has been made possible in the laboratory. Therefore, having understood the mechanism of oscillations in \( C_{60} \) photo-spectra it is now of considerable interest to study the influence of \( C_{60} \) cavity on the photo-response of an atom endohedrally confined into it and the associated spectroscopy. Investigations along this line is underway and will be published soon [10]. Furthermore, with the enormous advent of semiconductor technology it has been possible to prepare small electron-islands of strong quantum properties, quantum dots, within the semiconductor lattice. Understanding of the physics of quantum dots is valuable because of the potentially huge applicational importance of these objects. Electrons forming a quantum dot are certainly delocalized in nature and, therefore, their ionization by photon impact with high enough energy may show diffraction pattern providing valuable information about the hither-to-unknown geometry of the dot. A part of our current endeavor is focussed on this subject.

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