Manifestation of Charge-Density Fluctuations in Metal Clusters: Suppression of the Ionization Channel

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The fluctuations in the electronic charge density of metallic clusters in response to an approaching electron suppress the single-ionization channel. This conclusion is made on the basis of numerical calculations for the total ionization cross sections using the random-phase approximation with exchange to describe the particle-hole (de)excitations. The general trends can be understood by means of the Thomas-Fermi model. The present theory explains, for the first time, the behavior of the measured total ionization cross section for C_{60}. The interplay between finite size and nonlocal screening effects is studied by tracing the changes in the ionization cross sections for Li clusters with an increasing cluster radius.

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The primary source of knowledge on the structure and the dynamics of electronic systems is provided by their characteristic response to external perturbations. For systems with a large number of active electrons, such as clusters and surfaces, the collective response is determined basically by the cooperative behavior of the system's constituents, e.g., the delocalized electrons in a metallic surface shield, by an organized rearrangement, an external electric field which might be induced by an approaching test charge. These correlated fluctuations of the electronic density, i.e., the excitation and deexcitation of electron-hole pairs, can be described by the so-called polarization operator Π (or the particle-hole propagator) [1]. On the other hand, the spin and the charge density fluctuations of the medium modify the properties of the electron-electron interaction U. How the modified potential U_{eff} emerges from the naked interaction U is determined by Π through the integral equation [1] $U_{\text{eff}} = U + U\Pi U_{\text{eff}}$. This relation can be formally written as $U_{\text{eff}} = \frac{U}{1-U\Pi}$. Thus the *screening* of U is given by $\kappa := 1/(1 - U\Pi)$ which is referred to as the generalized dielectric function [1] and plays a central role in a variety of phenomena. To name one, the frequency (ω) and wave vector ($\boldsymbol{p}$) dependent electrical conductivity $\sigma(\boldsymbol{p}, \omega)$ of a plasma is obtained from $\kappa(\boldsymbol{p}, \omega)$ as $\sigma(\boldsymbol{p}, \omega) = i\omega(1 - \kappa)$. This is just one of numerous examples for the fundamental interest in the study of the dynamical screening in electronic systems.

The determination of the renormalized interaction U_{eff} and of the dielectric function κ entails the knowledge of Π. In essence, Π is a two-point Green function that describes the particle-hole excitations. Its lowest order approximation Π_0 is provided by the so-called random phase approximation (RPA) [1]. For a homogeneous system and in the long wavelength limit ($\lambda \gg \lambda_F$, where λ_F is the Fermi wave length) one obtains $\Pi_0 \approx -2N(\mu)$. Here $N(\mu)$ is the density of states at the Fermi level μ. Hence, for $\lambda \gg \lambda_F$, the screened potential of the bare electron-electron interaction $U(\boldsymbol{q}) = 4\pi/q^2$ is readily derived as $U_{\text{TF}} = 4\pi/[q^2 + 8\pi N(\mu)]$. In configuration space we recover thus the well-known Thomas-Fermi potential $U_{\text{TF}} = e^{-r/r_0}/r$ [$r_0 = 1/\sqrt{8\pi N(\mu)}$]. This form of the interaction gives a first hint of the nature of electronic collisions in many-particle systems, such as in metallic clusters: In an isolated scattering of two charged particles, events with a small momentum transfer q (far collisions) are predominant, for the naked potential behaves as $U \propto 1/q^2$. In contrast, these events are suppressed in the presence of a polarizable medium due to the finite range of the renormalized scattering potential U_{eff} which dictates that scattering can occur only at distances close enough such that the medium is not able to screen the external field ($\lim_{q\ll 1} U_{\text{TF}}(q) \propto 1/[2N(\mu)] = \text{const}$). Hence, we conclude that the scattering probability as a function of the impact parameter saturates at a distance d determined by the extent r_0 of the scattering region ($\lim_{r_0\to\infty} d \to \infty$), these conclusions are endorsed by the full-numerical RPA calculations presented in this work.

The ideas sketched above are the key to resolving a yet open question of how metal clusters are ionized in response to an external perturbation induced by an approaching electron. In the experiments, which have been performed using free C_{60} clusters, one measures the absolute total ionization cross sections $W(\epsilon_0)$, i.e., the yield for the C_{60}^+ production, as a function of the energy (ϵ_0) of an incoming electron [2–4]. These measurements confirmed repeatedly that the cross section $W(\epsilon_0)$ possesses a plateau shape: Near the ionization threshold it rises strongly with increasing ϵ_0 and then falls off slowly at higher energies. This saturation effect is markedly different from what is known for atomic targets where $W(\epsilon_0)$ shows a pronounced peak at low ϵ_0 [cf. Fig. 1(a)].

Theoretical attempts to explain the behavior of $W(\epsilon_0)$ for C_{60} are scarce. For the energy region $\epsilon_0 < 100$ eV only semiempirical models exist [4,5], whereas for $\epsilon_0 > 100$ eV a quantum scattering approach has been proposed in Refs. [6,7]. All of these previous theories [4–7] were unable to explain the energy dependence of $W(\epsilon_0)$,

basically because the problem has been approached from an atomic scattering point of view without accounting for the influence of the fluctuating electron density on the scattering process which is of a key importance at low energies ($\epsilon_0 < 1000$ eV) , as shown here in detail: The central quantity that determines $W(\epsilon_0)$ is the transition matrix element $T(\boldsymbol{k}_0, \phi_\nu; \boldsymbol{k}_1, \boldsymbol{k}_2)$. This matrix element is a measure for the probability that an incoming electron with momentum $\boldsymbol{k}_0$ ionizes a valence electron bound to the state ϕ_ν of the cluster with a binding energy ϵ_ν, where ν stands for a collective set of quantum numbers that quantify uniquely the electronic structure of the cluster. The emitted and the scattered electrons' states are labeled by the momenta $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$. As outlined above the renormalized electron-electron interaction U_{eff} is determined by an integral equation with a kernel describing the particle-hole (de)excitation. Therefore, the evaluation of the T matrix entails a self-consistent solution of an integral equation. In the random-phase approximation with exchange (RPAE) [1] and within the *post* formulation [8] the T matrix has the form $T_{\text{RPAE}} = \langle \boldsymbol{k}_1 \boldsymbol{k}_2 | U_{\text{eff}} | \phi_\nu \boldsymbol{k_0} \rangle$, where

$$\langle \boldsymbol{k}_1 \boldsymbol{k}_2 | U_{\text{eff}} | \phi_\nu \boldsymbol{k}_0 \rangle = \langle \boldsymbol{k}_1 \boldsymbol{k}_2 | U | \phi_\nu \boldsymbol{k_0} \rangle + \sum_{\substack{\varepsilon_p \le \mu \\ \varepsilon_h > \mu}} \left(\frac{\langle \varphi_p \boldsymbol{k_2} | U_{\text{eff}} | \phi_\nu \varphi_h \rangle \langle \varphi_h \boldsymbol{k_1} | U | \boldsymbol{k_0} \varphi_p \rangle}{\epsilon_0 - (\varepsilon_p - \varepsilon_h - i\delta)} - \frac{\langle \varphi_h \boldsymbol{k_2} | U_{\text{eff}} | \phi_\nu \varphi_p \rangle \langle \varphi_p \boldsymbol{k_1} | U | \boldsymbol{k_0} \varphi_h \rangle}{\epsilon_0 + (\varepsilon_p - \varepsilon_h - i\delta)} \right). \tag{1}$$

The spin averaged cross section $W(\epsilon_0)$ is obtained from the weighted average of the singlet $\propto |T^{(S=0)}|^2$ [vanishing total spin ($S = 0$) of the electron pair] and the triplet $\propto |T^{(S=1)}|^2$ cross sections (we assume spin-flip processes to be irrelevant)

$$W(\epsilon_0) = \frac{(2\pi)^4}{k_0} \int d^3\boldsymbol{k}_1 \, d^3\boldsymbol{k}_2 \left\{ \sum_\nu \frac{1}{4} |T^{(S=0)}(\boldsymbol{k}_0, \phi_\nu; \boldsymbol{k}_1, \boldsymbol{k}_2)|^2 + \frac{3}{4} |T^{(S=1)}(\boldsymbol{k}_0, \phi_\nu; \boldsymbol{k}_1, \boldsymbol{k}_2)|^2 \delta[\epsilon_0 + \epsilon_\nu - (k_1^2/2 + k_2^2/2)] \right\}. \tag{2}$$

In Eq. (1) φ_p and φ_h are, respectively, the intermediate particle's and hole's states with the energies ε_p, ε_h, whereas δ is a small positive real number. The first line of Eq. (1) amounts to a neglect of the electron-hole (de)excitations, as done in Ref. [7]. If U_{TF} is employed as an effective potential only the first line of Eq. (1) has to be evaluated, and we obtain the much simper expression $T_{\text{TF}} = \langle \boldsymbol{k}_1 \boldsymbol{k}_2 | U_{\text{TF}} | \phi_\nu \boldsymbol{k}_0 \rangle$ from which the cross section W_{TF} follows according to Eq. (2). In contrast, as evident from Eqs. (1),(2), the numerical evaluation of $W(\epsilon_0)$ within RPAE is a challenging task. To tackle this problem we proceeded as follows: The quantum states of the metal clusters are constructed within the Hartree-Fock approximation and within the spherical jellium model [8,9]. The cluster potential which is a superposition of atomic potentials, is replaced by a shell confinement. The latter is formed by the delocalized valence electrons of carbon atoms and is modeled by the potential well: $V(r) = V_0$ within the region $R - \Delta < r < R + \Delta$, and $V = 0$ elsewhere. For C_{60} we use $R \approx 6.7 a_0$ as the radius of the fullerene. The thickness of the shell is $2\Delta \approx 2a_0$ (a_0 is the Bohr radius). The height of the well was chosen such that the experimental value of the electron affinity of C_{60} and the number of valence electrons are correctly reproduced. Alternatively, one can employ a model cluster potential as derived from the density functional theory (DFT) within the local density approximation [7]. As shown below, the DFT potential leads basically to the same conclusions as the model potential outlined above.

As remarked in Refs. [6,7], the relatively large size of the cluster leads to severe convergence problems in evaluating the transition matrix elements. To circumvent this situation we utilized the nonlocal variable phase approach [10–12] for the numerical calculation of the Hartree-Fock states. In this method the electronic eigenfunctions and eigenvalues of the cluster are provided through scattering phase functions and through the poles of the scattering amplitudes in the complex plane of the particle's wave vectors. We find that this choice for the numerical realization renders a rapid and a reliable convergence of the self-consistent calculations. Upon the numerical summation over the states ϕ_ν in Eq. (2) we carry out the six-dimensional integral over the momenta $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ using a Monte Carlo procedure.

To get an insight into the effect of the screening we calculated $W_{\text{TF}}(\epsilon_0)$ for different strengths of screening as quantified by r_0. As seen in Fig. 1(a), when approaching the unscreened limit ($r_0^{-1} = 0.01$ a.u.), the calculated $W_{\text{TF}}(\epsilon_0)$ agree well both in shape and magnitude with the finding of Ref. [5] at lower energies. At higher energies, the present model and the DFT calculations [6,7] yield basically the same results. To simulate experimentally this atomic case let us assume the C_{60} molecule to be simply an ensemble of 60 independent carbon atoms, in which case the cross section for C_{60} is a factor 60 larger than $W(\epsilon_0)$ for atomic carbon [13]. The experimental cross sections we obtain by this procedure [Fig. 1(a)] agree very well with the shape of the calculated $W_{\text{TF}}(\epsilon_0)$ at low screening. On the other hand, all of the theoretical models shown in Fig. 1(a) are clearly at variance with the measured $W(\epsilon_0)$ for C_{60} (note the measured and the calculated cross sections are on an absolute scale). Figure 1(b) sheds light on the underlying reasons for the shortcomings of the

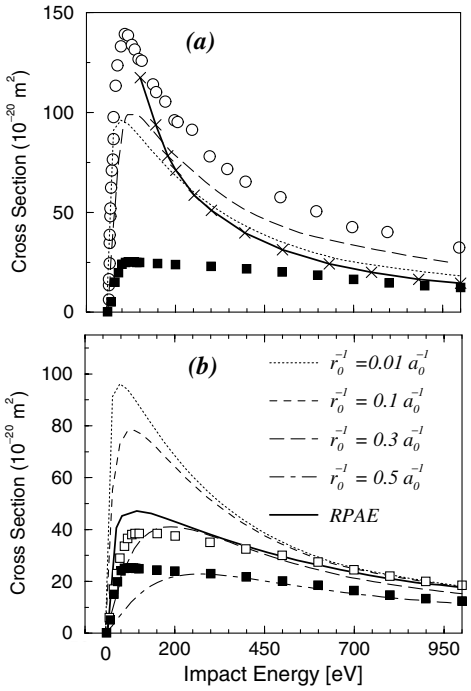

FIG. 1. (a) The total ionization cross section [Eq. (2)] for the electron impact single ionization of C_{60} as a function of projectile energy. The *absolute* experimental data (full squares) for the production of stable C_{60}^+ ions [2,3] are shown along with the experimental electron-impact total ionization cross sections for atomic carbon (open circles) [13] multiplied by a factor of 60 (cf. text). The solid line with crosses is the result of the DFT calculations [6], whereas the dashed line is due to the model of Ref. [5]. The dotted line indicates the present calculations with very small screening ($r_0^{-1} = 0.01$ a.u.). (b) The RPAE results (solid line) are shown together with calculations employing the Thomas-Fermi model of screening with varying values of the screening length, as shown in the figure. Full squares as in (a), whereas the open squares are the *absolute* experimental total counting cross section for the emission of one electron from the initially neutral cluster (cf. text for details) [2,3].

theories shown in Fig. 1(a): As alluded to in the introduction, with increasing screening the region where scattering may take place shrinks. This results in a suppression of the ionization cross section with increasing screening length, as is evident from Fig. 1(b). This effect is not a simple scaling down of $W(\epsilon_0)$, but the shape is also affected. The peak of $W(\epsilon_0)$ is shifted to higher energies and $W(\epsilon_0)$ is generally flattened. In fact, for extremely high screening the cross section is very small and shows basically very weak dependence on ϵ_0. This can be understood from the behavior of the form factor of the potential U_{TF} which for large screening is independent of ϵ_0, i.e., $U_{\mathrm{TF}}(q) \propto r_0^2 = \mathrm{const}, \forall\ \epsilon_0$ [14]. Another extreme limit that shows up in Fig. 1 (cf. also Fig. 2) is that when ϵ_0 is very large the electronic density of the cluster cannot react within the very short passage time of the electron through the interaction region and hence only small deviations between all the models are observed in the high energy regime.

The full numerical RPAE calculations for the cross section $W_{\mathrm{RPAE}}(\epsilon_0)$ confirm the trends we pointed out by means of the locally screened potential U_{TF}. In fact, by comparing the $W_{\mathrm{RPAE}}(\epsilon_0)$ and $W_{\mathrm{TF}}(\epsilon_0)$ one may deduce a rough estimate of the screening length which is of importance for the consideration of the relaxation time due to electron-electron collisions [15]. We obtain a qualitative agreement between $W_{\mathrm{RPAE}}(\epsilon_0)$ and $W_{\mathrm{TF}}(\epsilon_0)$ when $r_0^{-1} = 0.3$ a.u. is used to evaluate $W_{\mathrm{TF}}(\epsilon_0)$, however, it should be stressed that we were not able to reproduce correctly the RPAE calculations by simply adjusting r_0, as can be concluded from Fig. 1(b).

For a comparison of $W_{\mathrm{RPAE}}(\epsilon_0)$ with the experiments we recall the remarks of Ref. [5] that, experimentally the electron impact on C_{60} may lead not only to the formation of stable C_{60}^+ but also may produce unstable C_{60}^+ that within a certain lifetime, not resolved by the experiment, decay subsequently into various fragmentation channels. Therefore, we show in Fig. 1(b) the experimental total counting rates, i.e., the total electron-impact ionization cross sections for the emission of one electron from C_{60} along with the experimental total cross section for the ionization of C_{60} and for the formation of the stable C_{60}^+ ion. We regard the agreement between the parameter-free $W_{\mathrm{RPAE}}(\epsilon_0)$ and the experimental results as satisfactory, in view of the fact that the RPA is the first order approximation to the two-point particle-hole Green function, as outlined in the introduction.

To study the interplay between quantum-size effects and the nonlocal screening as described by RPAE we calculated within the spherical jellium model the cross section $W_{\mathrm{RPAE}}(\epsilon_0)$ for Li clusters with varying sizes. For a judicious conclusions we normalized the cross sections to the number of electrons in the respective cluster. Figures 2(a) and 2(b) reveal a striking influence of charge density fluctuation on $W(\epsilon_0)$, in particular at low energies: The RPAE model predicts a suppression of $W_{\mathrm{RPAE}}(\epsilon_0)$ with an increasing cluster size due the increasing phase space for the particle-hole creation [cf. inset of Fig. 2(a)]. In contrast the neglect of charge density fluctuations results in increased peak values of $W(\epsilon_0)$ for larger clusters. Furthermore, according to the RPAE, the peak in $W(\epsilon_0)$ is considerably broadened and shifted towards higher energies when the cluster size is increased (for the cluster with a radius $R_{\mathrm{Li}} = 4a_0$ the peak is at $\epsilon_0 \approx 200$ eV whereas this peak is shifted to $\epsilon_0 \approx 700$ eV for $R_{\mathrm{Li}} = 10a_0$) [cf. Fig. 2(a) and inset]. As explained above, this is consistent with the behavior of $W(\epsilon_0)$ with increased screening length [14]. In contrast, the neglect of the particle-hole (de)excitations leads to cross sections with the peak positions being shifted towards lower energies as the cluster size grows [cf. Fig. 2(b) and inset]. For small clusters or for $\epsilon_0 \gg 1$ there is hardly an influence of charge density fluctuations [cf. heavy solid lines in Figs. 2(a) and 2(b)].

Summarizing the above results, we have seen how the particle-hole (de)excitations suppress and modify the

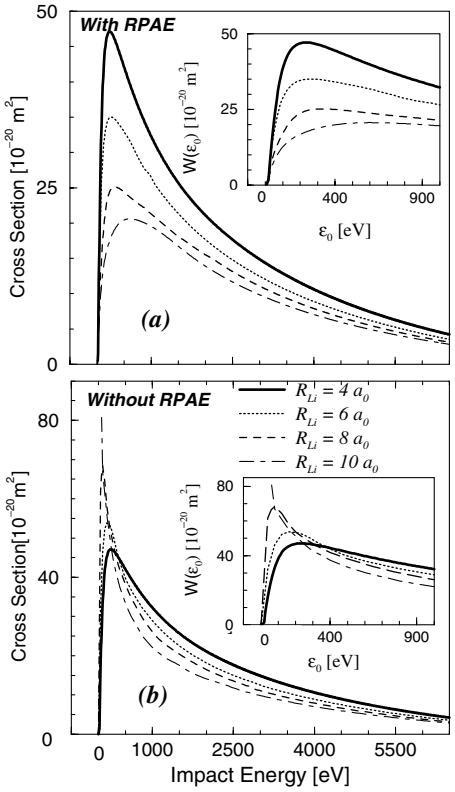

FIG. 2. The total electron-impact cross section for the ionization of spherical Li clusters with varying radius size R_{Li}. (a) shows the RPAE calculations. (b) shows the results when the particle-hole (de)excitation is neglected [the first term of Eq. (1)]. The insets in (a) and (b) highlight the low-energy region.

ionization cross sections for the electron scattering from neutral metal clusters. The simple Thomas-Fermi (TF) model of screening provided a useful tool to obtain global views on the role of delocalization of the electrons. The more elaborate random phase approximation confirmed and specified more precisely the understanding gained from the TF model. We also envisaged the interrelation between quantum-size and screening effects. From a formal point of view, we note that to treat scattering processes in isolated few charged particle systems, such as in atoms or small molecules, one has to deal with the infinite-range tail of the Coulomb interaction that precludes the use of standard methods [16] and induces multiple scattering between the collision partners up to very large distances. In contrast, the presence of the screening in systems with a large number of delocalized active electrons renders possible the use of standard scattering theory but on the considerable expense of actually calculating the nonlocal screening properties of the medium, e.g., as described by the polarization propagator Π. The crossover between the two cases is marked by a breakdown of the RPAE for dilute systems, where other methods such as the ladder approximation become more appropriate. In any case one has to bear in mind that, both from a practical and a conceptual point of view, approximate methods that perform well for few particle scattering may not be suitable for the treatment of delocalized many-particle systems (and vice versa).

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