Core Polarization in the Optical Response of Metal Clusters: Generalized Time-Dependent Density-Functional Theory

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We present a generalized time-dependent density-functional theory (TDDFT) for the optical response of metal clusters where both core polarization and valence responses are treated microscopically. It is shown that the valence electrons response is described by an effective external field and residual interaction that are those of the standard TDDFT modified by the self-consistent contributions of the array of polarizable ionic cores. As an application the equations are solved within the adiabatic local-density approximation for silver clusters, where core $4d$ electrons greatly influence the optical response. The experimental data are well reproduced by the present theory. [S0031-9007(97)02517-9]

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The optical properties of simple metal clusters reflect the structure and dynamics of their set of delocalized electrons. This set is formed by the loosely bound *valence* electrons that each atom gives to the aggregate. The rest, composed of the more tightly bound electrons and atomic nuclei, constitutes the array of ionic cores. This array forms a positive charge background responsible for most of the binding forces on valence electrons. In addition to this *static*-binding effect the ionic cores may influence directly the optical response of the cluster when the energy of a core-level excitation is comparable to the energy for the collective motion of delocalized electrons. When this occurs the valence collective states are greatly influenced by the dynamic polarization of the array of ionic cores. In the present Letter we address the consistent microscopic treatment of these core-valence interactions.

In alkali metal clusters such as those of Na and K the core response is at energies much higher than the collective surface oscillation or plasmon resonance. Thus, in these clusters the main effect of the ionic cores is just as a confining background, which in first approximation may be modeled by a uniform *jellium* charge distribution or by using pseudopotentials; while the plasmon energy is almost totally controlled by the valence electron interactions that are well described within the adiabatic time-dependent local-density approximation (TDLDA) [1,2]. A different situation is found in transition and noble metal clusters [3]. For instance, in Ag clusters the core $4d$ electrons form a size-dependent polarizable background that strongly screens the valence electron interactions. These core polarization effects are also critical for materials with shallow cores (as II-VI and III-V semiconductors) [4].

The optical response of Ag clusters has recently drawn much interest because of the observed deviation from the behavior of alkali clusters. The most clear manifestation observed for isolated Ag_N^+ clusters [5] is the blueshift of the plasmon energy as the size of the cluster decreases. A similar deviation was observed in the wave-vector plasmon dispersion of an infinite planar Ag surface. In this context Liebsch has proposed a semiempirical model [6] which includes effects associated to the polarization of the core $4d$ electrons of Ag by means of the experimental effective dielectric function $\epsilon_d(\omega)$ of the bulk metal. This $\epsilon_d(\omega)$ is used in the Poisson equation to obtain the effective potential for valence electrons. The model, by ending the dielectric volume at a distance d from the surface, takes into account that the metallic layer close to the surface is actually less polarizable than the inner part. As shown in Refs. [5–8] this *dielectric model* is able to reproduce qualitatively the basic new features of the response of Ag clusters. However, from the theoretical point of view, a major drawback of the model lies on the different treatment given to core and valence responses. In fact, while valence response is treated microscopically within the TDLDA theory, core response is only considered in a macroscopic approach by means of the input function $\epsilon_d(\omega)$. Here a microscopical formalism including core-polarization effects for the optical response of finite systems like clusters, nanostructures, and quantum dots is developed. Our method is similar to the one in Ref. [3] for bulk metals but, by working in real space, we are able to obtain the general set of equations governing the cluster response. The theory can be applied to all metal and semiconductor clusters and keeps the great advantage of working only with the set of valence electrons for the ground state and optical response.

In time-dependent density-functional theory (TDDFT) the relation between the total effective potential ϕ^{tot} and the induced density $\delta\rho$ is given by the independent density-density correlation function χ^0 [9]

$$\delta\rho(\mathbf{r}) = \int d^3r'\, \chi^0(\mathbf{r},\mathbf{r}',\omega)\phi^{\mathrm{tot}}(\mathbf{r}'), \qquad (1)$$

where the time variation is given by an additional phase $e^{-i\omega t}$ in both potential field and induced density. χ^0 is

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expressed in terms of the occupied states and the single-particle Green's function $g(\mathbf{r},\mathbf{r}',\omega) = \langle \mathbf{r}|\frac{1}{H_{\rm sp}-\omega}|\mathbf{r}'\rangle$ (where $H_{\rm sp}$ is the single-particle Hamiltonian) as

$$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_h \varphi_h(\mathbf{r})\varphi_h^*(\mathbf{r}') \times [g(\mathbf{r},\mathbf{r}',\varepsilon_h - \omega - i\eta) - g(\mathbf{r},\mathbf{r}',\varepsilon_h + \omega + i\eta)]. \quad (2)$$

The sum in (2) usually includes only the valence states of the cluster [9]. In order to explicitly include the core states we separate valence and core contributions to χ^0 by restricting the sum in (2) to each subset of states. This amounts to separate the induced density $\delta\rho$ in valence $\delta\rho_v$ and core $\delta\rho_c$ contributions, each one related to the total field by the correlation functions χ_v^0 and χ_c^0, respectively. The core states will remain localized, up to some extent, around the positions of the atomic nuclei $\mathbf{R}_i$. This allows us to write χ_c^0 as a sum of atomiclike correlation functions χ_a^0 on each site i or, equivalently, the induced core density as a sum of induced core densities $\delta\rho_i$

$$\delta\rho_c(\mathbf{r}) = \sum_i \int d^3r'\, \chi_a^0(\mathbf{r} - \mathbf{R}_i, \mathbf{r}' - \mathbf{R}_i, \omega)\, \phi^{\rm tot}(\mathbf{r}') \equiv \sum_i \delta\rho_i(\mathbf{r} - \mathbf{R}_i). \quad (3)$$

Based on the localized nature of the core wave functions, and consequently of χ_a^0, we expand $\phi^{\rm tot}$ around each atomic position as

$$\phi^{\rm tot}(\mathbf{r}) = \text{const} - (\mathbf{r} - \mathbf{R}_i)\cdot\mathbf{E}_i + \int d^3r' \frac{\delta\rho_i(\mathbf{r}' - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{r}'|}, \quad (4)$$

where $\mathbf{E}_i$ is the local field at site i due to the external potential $\phi^{\rm ext}(\mathbf{r})$, the valence electrons, and the rest of ionic cores. Now the induced core density $\delta\rho_i$ is given by

$$\delta\rho_i(\mathbf{r} - \mathbf{R}_i) = \int d^3r'\, \chi_a^0(\mathbf{r} - \mathbf{R}_i, \mathbf{r}' - \mathbf{R}_i, \omega) \times [-(\mathbf{r}' - \mathbf{R}_i)\cdot\mathbf{E}_i + \textstyle\int d^3r'' \frac{\delta\rho_i(\mathbf{r}''-\mathbf{R}_i)}{|\mathbf{r}''-\mathbf{r}'|}]. \quad (5)$$

This equation clearly shows that each core responds to its local field $\mathbf{E}_i$. In other words, the core response is controlled by the dipole core polarizability $\alpha_i(\omega)$ that creates an induced dipole moment at site i of

$$\mathbf{p}_i = \alpha_i(\omega)\mathbf{E}_i. \quad (6)$$

The scenario that emerges for the cluster response corresponds to an array of polarizable dipoles embedded in the charge cloud of the valence electrons. Both the array of dipoles and the induced valence density oscillate with the frequency of the external field and are coupled to each other, since $\mathbf{p}_i$ depends on the electric field created by the valence electrons and these are influenced by the electric field of the array of dipoles. We end up in a new core-valence self-consistency problem that can be analytically solved for clusters (see below).

Because of the reduced dimension of the cluster in comparison with the wavelength of the electromagnetic radiation we can apply the dipole approximation and assume as external field $\phi^{\rm ext}(\mathbf{r}) = \lambda z$. The induced valence density, for a closed shell cluster, will be also dipolar,

$$\delta\rho_v(\mathbf{r}) = \delta\rho_v(r)Y_{10}(\Omega), \quad (7)$$

since the valence response equations decouple for different multipoles. Thus, only the dipolar component of the core potential couples to the valence induced density. This dipolar component is

$$\phi^{\rm dip}(r) = -\sum_i \alpha_i(\omega)\int d\Omega \frac{\mathbf{E}_i\cdot(\mathbf{r} - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{R}_i|^3} Y_{10}(\Omega) \equiv \sum_i \alpha_i(\omega)\mathbf{E}_i\cdot\mathbf{C}_i(r), \quad (8)$$

where the last term constitutes the definition of the vectors $\mathbf{C}_i(r)$. To simplify the vector notation in Eq. (8) we assign a greek letter ($\eta = 1,\ldots,3N_i$) to each pair vector component given by site i ($i = 1,\ldots,N_i$) and Cartesian coordinate a ($a = 1,2,3$ for x,y,z, respectively). Thus Eq. (8) reads as a simple scalar multiplication

$$\phi^{\rm dip}(r) = \sum_\eta \alpha_\eta(\omega)E_\eta C_\eta(r). \quad (9)$$

Now, the local electric field $\mathbf{E}_i$ is given by the relation

$$\mathbf{E}_i = \mathbf{E}_i^{\rm e.v.} + \sum_{k\neq i} -\frac{\mathbf{p}_k}{R_{ik}^3} + \frac{3(\mathbf{p}_k\cdot\mathbf{R}_{ik})\mathbf{R}_{ik}}{R_{ik}^5}, \quad (10)$$

where $\mathbf{E}_i^{\rm e.v.}$ is the sum of the external applied electric field and that created by the induced valence density. Using Eq. (6), we can write (10) in matrix notation as

$$\mathcal{M}_{\eta\delta}E_\delta = E_\eta^{\rm e.v.}, \quad (11)$$

where the matrix $\mathcal{M}$ depends only on the cluster geometry and it is very easily computed. We note that the external-valence field $\mathbf{E}_i^{\rm e.v.}$ satisfies the usual relation

$$\mathbf{E}_i^{\rm e.v.} = -\nabla\left(-\phi^{\rm ext}(\mathbf{r}) - \int d^3r' \frac{\delta\rho_v(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\right)\Big|_{\mathbf{r}=\mathbf{R}_i}, \quad (12)$$

which, defining a vector potential $\mathbf{B}_i(r)$ and external applied electric field in the z direction $\mathbf{D}_i = \lambda\mathbf{u}_z$, is written

$$E_\eta^{\rm e.v.} = \int B_\eta(r')\delta\rho_v(r')\, r'^2\, dr' + D_\eta. \quad (13)$$

With these relations we can now derive the equations governing the dipole response of the cluster. The total effective potential felt by the valence electrons consists of the external, induced valence, and core-polarization potentials, and its radial part is given by

$$\phi^{\rm tot}(r) = \phi^{\rm ext}(r) + \int dr' r'^2 K(r,r')\delta\rho_v(r') + \phi^{\rm dip}(r), \tag{14}$$

where $K(r,r')$ is the usual dipolar residual interaction within TDDFT, i.e., due to the bare Coulomb and residual exchange-correlation contribution [9]. From Eqs. (1) and (14), the induced valence density is written as

$$\begin{aligned}\delta\rho_v(r_1) = &\int dr_2\, r_2^2\, \chi_v^0(r_1,r_2,\omega)\, T(r_2) \\ &+ \int dr_2 dr_3\, r_2^2 r_3^2\, \chi_v^0(r_1,r_2,\omega) \\ &\times \tilde{K}(r_2,r_3)\,\delta\rho_v(r_3), \end{aligned}\tag{15}$$

where

$$T(r) = \phi^{\rm ext}(r) + \sum_{\eta\delta} \alpha_\eta(\omega) C_\eta(r) \mathcal{M}^{-1}_{\eta\delta} D_\delta, \tag{16}$$

$$\tilde{K}(r_1,r_2) = K(r_1,r_2) + \sum_{\eta\delta} \alpha_\eta(\omega) C_\eta(r_1) \mathcal{M}^{-1}_{\eta\delta} B_\delta(r_2). \tag{17}$$

Equations (15)–(17) constitute the main result of this Letter [10]. They prove that the response equations for the induced valence density are the standard TDDFT ones, but with an external field $T(r)$ and residual interaction $\tilde{K}(r_1,r_2)$ which are modified by the effect of the array of polarizable cores. In fact, $\alpha_\eta(\omega) = 0$ leads to the usual TDDFT response function [9]. All core polarization effects are included in the second terms of Eqs. (16) and (17) by means of the matrix $\mathcal{M}$ and the potential vectors **B** and **C**. We use matrix techniques to solve Eq. (15) and to obtain $\delta\rho_v$ in terms of which the dynamical valence polarizability $\alpha_v(\omega)$ is computed as

$$\alpha_v(\omega) = \int dr\, r^2\, \delta\rho_v(r)\phi^{\rm ext}(r), \tag{18}$$

and the cross section is $\sigma(\omega) = (4\pi\omega/c)\mathrm{Im}\{\alpha_v(\omega)\}$.

A necessary ingredient of Eqs. (15)–(17) is the core polarizability α_i that is computed in an embedded atom approximation assuming that the core response only depends on the valence-electron density at site i [11]. This local approximation is justified when the core-core overlap is very small and the core-shell radius is smaller than the spatial variation size of the electronic density, as is the case for the calculations presented below. Thus the dynamical polarizability of the cores in a cluster will vary from the value of a fully embedded core, for cores close to the cluster center, to a value similar to the free ion polarizability, for cores sitting near the cluster surface (the surface profile of the valence electron density makes the cores lying at the cluster surface *see* a much reduced valence density). Once this scheme is performed for all the atoms in the cluster the spatial dependence of the core polarizability is obtained as part of the microscopic time-dependent density functional calculation. The computed fully embedded core and free ion polarizabilities were presented in Ref. [8]. In the following, we solve the new generalized TDDFT equations within the adiabatic local-density approximation for exchange and correlation effects [12].

In order to better understand the core-polarization effects we consider as a test case the closed shell aggregate Ag^+_{139} and describe the valence states within the well known jellium model. The core array is approximated by the bulk fcc (or bcc) geometry, with an ion sitting at the cluster center and filling the subsequent equidistant atomic shells, as already used in Ref. [13] for the cluster geometry. The free ion polarizability is assigned to those cores in the outermost closed shell while the rest are described using the fully embedded core polarizability, i.e., with embedding density equal to that of bulk Ag. Figure 1 summarizes the results obtained for the fcc structure. In Fig. 1(a) we show the effective potential field $T(r)$ at $\omega = 0$ compared to the external one. The valence electron density and the different atomic shells are also indicated. Figure 1(b) shows the corresponding imaginary part of the valence polarizability (continuous line). Three main effects can be extracted from Fig. 1: (i) The core polarization screens the valence electron interaction by a reduction of the external field acting on the valence electrons [see Fig. 1(a)] and by reducing the valence residual interaction [because of the second term in Eq. (17)]. Comparing the jellium and core-polarization results in Fig. 1(b) we see that this screening shifts to lower frequencies the surface plasmon energy. (ii) The plasmon energy is sensitive to the core polarizability form used. The larger embedded core polarizability value, as compared to the free ion one, produces a larger screening and a shift to lower energy of the resonance frequency [see dotted and dashed lines in Fig. 1(b)]. This indicates that the decrease of plasmon energy with increasing size can be assigned to the evolution of the core polarizability from the free ion in small clusters to the fully embedded core in larger ones. (iii) The absorption shoulder at the right of the plasmon peak is not present when the free ion polarizability is used for all the atoms and, consequently, it is a signature for the presence of atoms with bulk behavior.

Figure 2 shows the calculated cross section for Ag^+_{59} in comparison with the experimental data of Ref. [5]. The free ion polarizability has been used for all the atoms because of the reduced dimension of this cluster. Our core-polarization results agree reasonably well with the measured data and correct the large discrepancy found when these effects are not included. From Fig. 2 we can also see the minor differences in the optical spectra when the bcc (continuous line) or fcc (short-dashed line) geometric structures are used, i.e., the specific structure is not as relevant for the plasmon resonance as the core-polarization effects. Also a slight redshift of plasmon

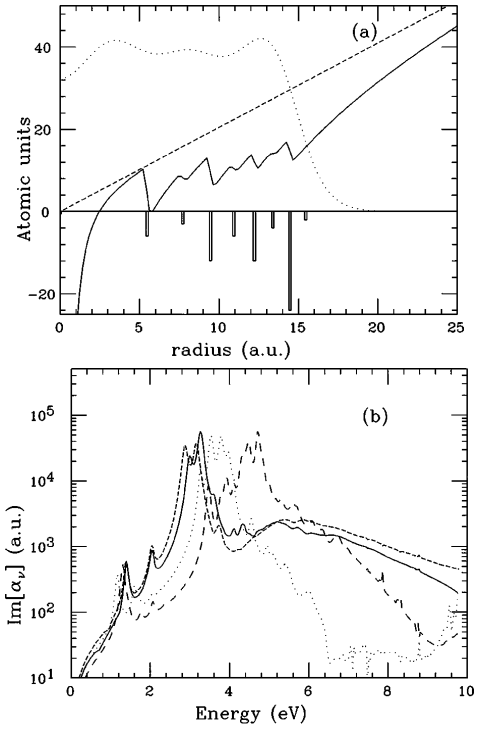

FIG. 1. For the Ag_{139}^{+} cluster in panel (a) is displayed the effective potential $T(r)$ in the static limit ($\omega = 0$) (continuous line), the external applied potential $\phi^{\text{ext}}(r)$ (dashed line), the valence density in arbitrary units (dotted line), and a histogram with the radial positions for the fcc-atomic shells. The number of atoms in each shell, with increasing r, is 1 ($r = 0$), 12, 6, 24, 12, 24, 8, 48, 4. In panel (b) the imaginary part of the valence polarizability is shown: continuous line, the result using the embedded core polarizability for atoms with $R < 14a_0$ and the free ion value for the rest. Short dashed and dotted lines correspond to calculations using for all atoms the embedded core and free ion polarizabilities, respectively. The long-dashed line corresponds to the plain jellium result.

energy with increasing size is observed when comparing the peak position in the continuous lines of Figs. 1 and 2. This behavior contrasts with the blueshift obtained in the jellium results (long-dashed line) and it is in agreement with experiments [5]. Our theory can also be applied to smaller clusters by finding first the precise ground-state geometry including polarization effects. We plan to present these calculations in the near future. Here we have focused on the theoretical model and test it for big sizes, where the jellium wave functions and bulk geometric structures are reasonable approximations.

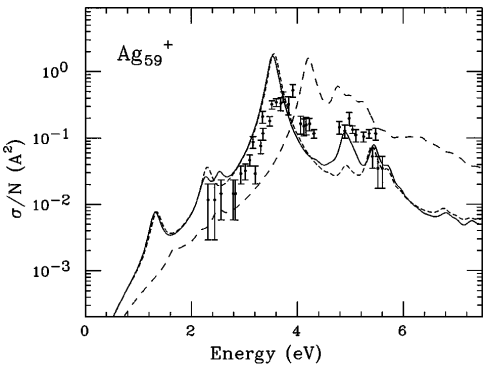

FIG. 2. Photoabsorption cross section per electron for the Ag_{59}^{+} cluster. The free ion polarizability is used for all atoms. Continuous and short-dashed lines correspond to bcc and fcc geometries, respectively. The long-dashed line shows the result without core-polarization effects. The experimental points are from Ref. [5].

In conclusion, the time-dependent density-functional theory for the optical response of metal clusters has been extended to treat both valence and core responses microscopically. New general response equations have been found and solved for the case of big Ag clusters. Good agreement with experiment has been found for the Ag_{59}^{+} cross section. The decrease of plasmon energy with increasing size has been explained by the evolution of the core polarizability in the cluster interior from the free ion in small clusters to the embedded core value in larger ones.

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[10] We note that even if the present derivation is particularized for dipolar interactions in closed-shell systems, a similar set of equations will hold in the general case of higher order electromagnetic interactions and open-shell systems. These equations can be written up easily by taking the complete expression for the potential field and induced density instead of its dipolar component.
[11] In practice the embedded core polarizability is obtained by solving the TDDFT equations for a large jellium sphere with density n (the valence density at the core site) and with a central hole of radius $r_s = (\frac{3}{4\pi n})^{1/3}$ that includes the bare atom nuclear potential [3]. This restricts the allowed transitions from core levels to unoccupied valence levels
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