Dynamical Polarizability of Small Metal Particles: Self-Consistent Spherical Jellium Background Model

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The electronic polarizability of small metal particles is investigated within the framework of the local-density approximation applied to the spherical jellium model. Self-consistent effective potentials are used for the determination of the independent-particle susceptibility $\chi^0(\vec{r}, \vec{r}\,';\omega)$. On the basis of this χ^0 the self-consistent field response equation, determining the susceptibility $\chi(\vec{r}, \vec{r}\,';\omega)$ of the interacting electrons, is solved with the inclusion of exchange and correlation. In this way we obtain for the first time the self-consistently determined absorption spectrum of small metal clusters.

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The understanding of the dynamical screening properties of small metal particles must play an important role in the interpretation of several unique experimental observations reported in the last few years. In contrast to the predictions based on classical local electrodynamics, small metal particles show strongly enhanced photo yield,[1] enormously enhanced van der Waals interactions,[2] size-dependent frequency of collective modes,[3] and size-dependent coupling between electron-hole pairs and collective modes[4] (e.g., size-dependent Landau damping). As non-self-consistent nonlocal-response models[5-8] do not explain all the various experimental findings, we conclude that a better dielectric theory for the description of the dynamical response properties of small metal aggregates is required. Experience with both plane metal surfaces[9] and thin metal films[10] suggests that a *self-consistent* jellium model applied to a spherical particle might provide relevant information about the screening properties of, at least, the loosely bound valence electrons of a real metal cluster. Therefore, a Kohn-Sham-based calculation of both the dynamical susceptibility and the dynamical polarizability was performed in very much the same fashion as Stott and Zaremba[11] and Zangwill and Soven[12] did for the atomic case. A prerequisite for this type of calculation is a knowledge of the size-dependent self-consistent potential which determines the various single-particle states from which the susceptibility χ^0 is constructed. Such an investigation was already performed by the author,[13] and the interested reader is referred to this work.

If an angular momentum representation is used for the electronic susceptibility $\chi(\vec{r}, \vec{r}\,';\omega)$ we need to solve the following equation for the lth component of χ (Rydberg atomic units are used throughout):

$$\chi_l(r,r';\omega) = \chi_l^0(r,r';\omega) + \int_0^\infty dr''\, r''^2 \chi_l^0(r,r'';\omega)\,[dV_{xc}(r'')/d_\rho]\chi_l(r'',r';\omega)$$
$$+ \int_0^\infty dr'''\, r'''^2 \int_0^\infty dr''\, r''^2 \chi_l^0(r,r''';\omega)\,[4\pi/(2l+1)]B_l(r'',r''')\chi_l(r''',r';\omega). \tag{1}$$

In this equation $dV_{xc}/d\rho$ is the density derivative of the exchange-correlation potential in the ground state,[13] $B_l(x,y) \equiv 2x_<^l/y_>^{l+1}$, and χ_l^0 is the lth component of the independent-particle susceptibility. As was shown by Zangwill and Soven[12] (see also Ref. 11), χ_l^0 for the special case $l = 1$ (which is the only relevant angular momentum in the nonretarded limit) is obtained from the following representation[14]:

$$\chi_1^0(r,r';\omega) = \sum_{l,n_l} (1/2\pi) R_{l,n_l}(r) r_{l,n_l}(r') \{ (l+1) G_{l+1}(r,r';\epsilon_{l,n_l}+\omega) + l G_{l-1}(r,r';\epsilon_{l,n_l}+\omega)$$
$$+ (l+1) G_{l+1}^*(r,r';\epsilon_{l,n_l}-\omega) + l G_{l-1}^*(r,r';\epsilon_{l,n_l}-\omega) \}. \tag{2}$$

In Eq. (2), the sum runs over the *occupied* single-particle states R_{l,n_l} in the ground state[13] (with energy ϵ_{l,n_l}), ω is the frequency of the photon, and the Green's function $G_l(r,r';E)$ is obtained from the self-consistent ground-state potential by expressing G_l by two nonregular solutions of the respective Schrödinger-like equation as follows[12]:

$$G_l(r,r';E) = \frac{j_l(r_<;E)\,h_l(r_>;E)}{\{r^2 W(j_l,h_l)\}_{r=c}}. \tag{3}$$

Here, j_l is regular at the origin, h_l fulfills the outgoing-wave boundary condition, $W(j_l,h_l)$ is the Wronski determinant, and c is an arbitrary constant.

Having obtained $\chi_1^0(r,r';\omega)$ we may solve Eq. (1) for the dipole response.[15] Once $\chi_1(r,r';\omega)$ is known, the induced charge density $\rho_{\rm ind}(\vec{r},\omega)$ due to the external dipole potential $-E_0 z l^{-i\omega t}$ is obtained from the equation

$$\rho_{\rm ind}(\vec{r},\omega) = -(4\pi/3)^{1/2} Y_{1,0}(\theta) E_0 \times 2 \int_0^\infty dr' \, \chi_1(r,r';\omega) r'^3, \tag{4}$$

where $Y_{1,0}(\theta)$ is the normalized spherical harmonic with $l=1$ and $m=0$. Hence, the polarizability α, defined via the total dipole moment $\vec{p}$ with $\vec{p} = \int d^3r \, \vec{r} \rho_{\rm ind}(\vec{r}) = \alpha \vec{E}_0$, can be expressed with the help of χ_1 as follows:

$$\alpha(\omega) = \int_0^\infty dr \, r \{ -\tfrac{4}{3}\pi r^2 \int_0^\infty dr' \, 2\chi_1(r,r';\omega) r'^3 \} = \int_0^\infty dr \, r \alpha(r;\omega). \tag{5}$$

First, Eq. (1) was solved for the static response, $\omega = 0$, of a small particle of sodium. The result is shown in Fig. 1. In sharp contrast to the results of the infinite-barrier model or to the step-density Thomas-Fermi description,[1-3,5] the static polarizability of a small metal sphere is *not reduced but enhanced* with respect to its classical value. This behavior can be attributed to a competition of two different effects: First, as a result of the quantum size effect a reduction of the classical polarizability, R^3, is to be expected, simply because the introduction of gaps in the single-particle spectrum (with otherwise unchanged parameters) reduces the polarizability. Second, the presence of a strongly diffuse electronic charge across the surface leads to a dipole momentum density *outside* the classical surface of the particle, and this density makes the total dipole moment larger than its classical counterpart. This effect is illustrated in Fig. 2, which shows the quantity $\alpha(r;0)$ [cf. Eq. (5)], normalized to 1. As a a result of the spherical nature of the problem, this quantity may be viewed as the analog to the induced charge density at a planar jellium surface.[16] Indeed, when comparing this result to that pertaining to a *plane* surface, I find close similarities, but also some differences. The most striking similarity is the structure of the induced charge near the surface, and the most obvious dissimilarity consists of the finite number of Friedel oscillations inside the particle which, in addition, are more or less compressed.

Because the results are in sharp contrast to the non-self-consistent model calculations, an exact check of all the numerical work is highly desirable. Fortunately, this can be done with the help of the electrostatic-force sum rule recently derived by Sorbello.[17,18] Starting with Eq. (6) of Ref. 17, the following sum rule can be derived for the dipole component of the linear susceptibility of a neutral jellium particle[19] with a background radius R:

$$1 = -\tfrac{4}{3}\pi \int_0^R dr \, (r/R)^3 \int_0^\infty dr' \, 2\chi_1(r,r';0) r'^3 - \tfrac{4}{3}\pi \int_R^\infty dr \int_0^\infty dr' \, 2\chi_1(r,r';0) r'^3. \tag{6}$$

This sum rule is fulfilled by our calculated χ_1 to within a relative accuracy of 10^{-4}.

Next we come to a discussion of the dynamical response. For this purpose we have to solve Eq. (1) (for $l=1$) with a variable frequency ω. The frequency-dependent $\alpha(\omega)$ is obtained from Eq. (5) and the cross section for photon absorption, $\sigma(\omega)$, is given by $\sigma(\omega) = 4\pi(\omega/c)\,{\rm Im}\alpha(\omega)$. Again, the dynamical calcula-

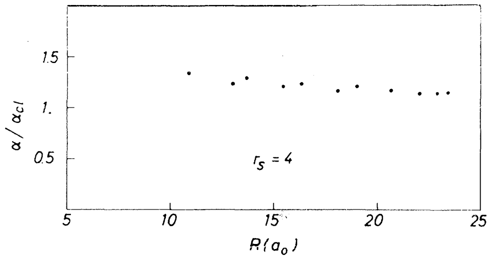

FIG. 1. Static polarizability of a small metal sphere in units of its classical value, R^3, with R the radius of the particle.

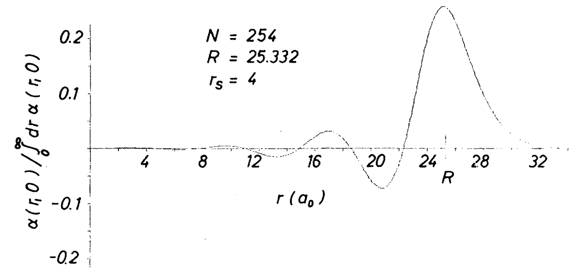

FIG. 2. Induced polarization density $\alpha(r,0)$ [see Eq. (5)], normalized to unity. $\alpha(r,0)$ near the surface looks very similar to the corresponding quantity of a plane metal surface (Ref. 16).

tions are checked with the use of a sum rule, in this case by a special Kramers-Kronig relation, namely

$$(2/\pi)\int_0^\infty d\omega\,\omega^{-1}\mathrm{Im}\alpha(\omega)=\alpha(0). \tag{7}$$

Figure 3 shows the imaginary part of $\alpha(\omega)$ for 198 valence electrons of sodium (this corresponds to an uppermost filled shell of the 4s type). Clearly, both bound-bound transitions of individual particle-hole pairs (the numerous narrow cups) and the excitation of collective modes can be observed. Furthermore, there is a broad continuum at higher frequencies resulting from single-pair bound-continuum transitions. Compared to the non-self-consistent nonlocal models,[6-8] we see that, first, the excitation of single pairs is much stronger; and, second, the shift of the peak position of the collective surface mode and of the collective volume mode, compared to their classical values $\omega_p/\sqrt{3}$ and ω_p, is in the opposite direction. Whereas the surface mode undergoes a red shift, the volume mode is slightly blue shifted. In sharp contrast, the use of the hydrodynamical model results in a blue shift of both types of collective excitation[20] (aside from being unable to describe single-pair excitation in a realistic fashion). The underlying physics of the different shift behavior of the surface and the volume modes is fairly simple to understand. As mentioned above, there are two competing effects determining the dynamical behavior of every type of mode: (1) the quantum size effect, and (2) the surface diffuseness effect. The surface mode is, of course, much more strongly influenced by the softening due to a diffuse surface charge than is the volume mode, whereas, on the contrary, the level quantization effect is more important for the volume mode.

In the numerical calculation of χ_1^0 I used a complex photon frequency $\omega+i\Delta$ with $\Delta=10$ meV$=0.000\,735$ a.u. broadening instead of the positive infinitesimal $\omega+i0^+$. This Δ, which was introduced just to save computer time, is not to be confused with a real lifetime of the single-particle states. This latter effect can be introduced in a manner as discussed in detail by Wood and Ashcroft.[8] As no detailed experimetnal information exists about this quantity in small metal clusters, the effect of a finite lifetime of the single-particle states on χ is not investigated in the present work. However, *if* this Δ is interpreted as a lifetime for use in a local dielectric constant of the Drude type, the continuous curve of Fig. 3 would give us the imaginary part of α. On comparison of these two curves, the importance of the electron-hole excitation mechanism can clearly be seen. Especially the width of the collective modes, as calculated in a self-consistent nonlocal model, is due to their decay into electron-hole pairs.

Finally I comment on the polarizability of clusters with partially filled shell. Because the present for-

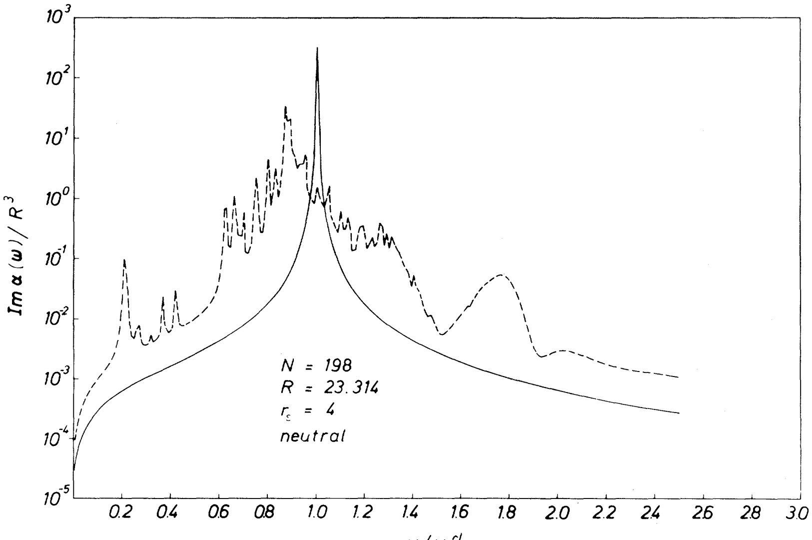

FIG. 3. Imaginary part of the complex polarizability $\alpha(\omega)$, in units of R^3. Effective single-pair excitation, surface plasmon, as well as volume plasmon excitation are clearly resolved. For comparison, the result of the local Drude theory is shown. The frequency is given in units of the classical surface-plasmon frequency, $\omega_p/\sqrt{3}=0.2497$ Ry in the case of Na.

malism is analogous to the restricted Hartree-Fock scheme there is no principal difference between, respectively, partially filled and completely filled shells. The only modification is that a fractional occupation number must be introduced for the uppermost occupied level in Eq. (2). This results in an intrashell size effect in $\alpha(\omega)$ whose magnitude, however, is small for a number of particles as large as 150.

On the other hand, real-lattice-structure–induced splittings of the various spherical l shells will modify the polarizability in a similar way as was discussed for the ground-state properties in Ref. 13: Minor changes are to be expected for a highly symmetric cluster, whereas considerable changes are to be expected for clusters of low symmetry for which a spherical model does not apply. In that case no detailed information can be obtained on the dynamical polarizability.

In summary, I have presented the first calculation of the dynamical response of small metal clusters which includes all essentials of the inhomogeneous electron gas theory. As is the case with plane metal surfaces, as a result of a fully self-consistent description the results deviate strongly from those obtained by non-self-consistent model calculations.

Presently the calculations are extended to obtain some information both on the photo yield and on the loss spectrum of fast electrons.

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