

## Dynamic polarizability of small simple metal clusters in dielectric media

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The dipole dynamic polarizability of small sodium and aluminum jelliumlike clusters embedded in different dielectric media has been calculated using the time-dependent density-functional method with the frequency-dependent local exchange-correlation potential. The matrix has been taken into account through a static dielectric constant  $\epsilon$ . Photoabsorption resonances obtained within the density-functional theory are redshifted with respect to the position of the classical surface plasmon for a metal sphere of the same size within the same matrix. As  $\epsilon$  increases, photoabsorption resonances shift to lower energies. We have discovered that the peaks caused by one-electron transitions and by collective excitations move to lower energies at different rates. For sodium clusters, the surface plasmon shifts more slowly than one-electron resonances; for aluminumlike clusters, the reverse is observed. In the case of sodium, this leads to the displacement of the surface plasmon from the region below the continuum threshold (when the cluster is in vacuum) to the continuum of states (for the cluster embedded in a dielectric). [S0163-1829(96)07343-2]

### I. INTRODUCTION

In recent years, considerable progress has been made in the theoretical and experimental study of free small metal clusters.<sup>1</sup> Particular attention has been given to their electromagnetic response properties. Much of the work on response properties has focused on the collective plasma excitations and the importance of quantum-size effects. Now, it is well known that the classical electrodynamics does not adequately describe the polarizability and photoabsorption of free clusters consisting of a few tens or hundreds of atoms. Specifically, the observed surface-plasma resonance frequency<sup>2-7</sup> is redshifted with respect to the predicted classical value and depends on cluster size. The quantum calculations<sup>8-14</sup> yield the results conforming far better to experiments. These calculations were performed within the time-dependent density-functional method or the random-phase approximation applied to the jellium or to the pseudopotential models.

In parallel with free clusters, of scientific and practical interest are small metal clusters deposited on a surface or embedded in a dielectric matrix. According to the classical electrodynamics, the surface-plasma resonance frequency for a metal sphere surrounded by a medium with a dielectric constant  $\epsilon$  follows the law

$$\omega_s = \omega_{s1} \left[ \frac{3}{1+2\epsilon} \right]^{1/2},$$

where  $\omega_{s1}$  is the surface-plasmon frequency for the metal sphere in vacuum ( $\epsilon=1$ ). The quantum-mechanical calculations carried out by Serra and Rubio<sup>15</sup> with the time-dependent local-density approximation (TDLDA) for potassium clusters in different dielectrics have given the surface-plasmon position as slightly redshifted with respect to the corresponding classical values. The surface-plasmon frequency for  $K_{92}$  embedded in a matrix of MgO is in good agreement with electron-energy-loss spectroscopy experiments.<sup>16</sup>

In the present work, we compare the TDLDA and classical description of the dynamic response properties of small simple metal clusters in different dielectric matrices. In the TDLDA calculations, the metal clusters are simulated by jellium spheres. The polarization of the medium is described in terms of a static dielectric constant. This is not a bad approximation for matrices with a wide energy gap, when electron transitions in the matrix occur at higher energies than electronic excitations in the metal cluster. The positive background of jellium spheres is assumed to be rigid (its dielectric constant was taken equal to 1). The dynamic polarizability of sodium and aluminumlike jellium clusters placed in vacuum and in media with  $\epsilon=2, 3$ , and 5 is considered. Note that in an earlier paper<sup>17</sup> we have studied, within the TDLDA, the static polarizability for small jellium clusters of Al, Li, Na, K, Rb, and Cs in dielectric media with  $\epsilon=1-25$ .

### II. FORMALISM

When a metal cluster is placed in a dielectric medium, polarization charges  $n_{\text{pol}}(\mathbf{r})$  are induced on the cluster surface. The polarization charges produce a potential (Hartree atomic units are used in this paper)

$$V_{\text{pol}}(\mathbf{r}) = \int \frac{n_{\text{pol}}(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}.$$

In Ref. 17, we have shown that the ground state of a metal cluster embedded in a dielectric medium can be described by the self-consistent Kohn-Sham equations<sup>18,19</sup> with the effective potential

$$V^\epsilon(\mathbf{r}) = V(\mathbf{r}) + V_{\text{pol}}(\mathbf{r}),$$

where  $V(\mathbf{r})$  has the same form as the effective potential for the cluster in vacuum (the reader interested in details of the ground-state calculation should consult Ref. 17).

If a cluster is subjected to a weak external field, its linear response to the applied perturbation can be obtained within

the TDLDA.<sup>20,8</sup> According to the approach, the change in the electronic density of the cluster under an external field is given by the equation

$$\delta n(\mathbf{r}, \omega) = \int \chi_0(\mathbf{r}, \mathbf{r}', \omega) \delta V^e(\mathbf{r}', \omega) d\mathbf{r}'. \quad (1)$$

Here  $\chi_0(\mathbf{r}, \mathbf{r}', \omega)$  is the susceptibility function in the independent-particle approximation. Within the TDLDA, it is constructed via the retarded one-electron Green function, eigenvalues and wave functions of the ground-state Kohn-Sham equation.<sup>20,8</sup>  $\delta V^e$  is the self-consistent potential that involves the external potential  $V_{\text{ext}}(\mathbf{r}, \omega) = r^{l'} P_{l'}(\cos \theta)$  [ $P_{l'}(\cos \theta)$  denotes the Legendre polynomial] and the induced potential arising from the induced electronic density. For a cluster embedded in a dielectric host,

$$\delta V^e(\mathbf{r}, \omega) = \delta V(\mathbf{r}, \omega) + \delta V_{\text{pol}}(\mathbf{r}, \omega), \quad (2)$$

where  $\delta V(\mathbf{r}, \omega)$  has the same form as the TDLDA potential for the cluster in vacuum:

$$\begin{aligned} \delta V(\mathbf{r}, \omega) = & V_{\text{ext}}(\mathbf{r}, \omega) + \int \frac{\delta n(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ & + \frac{\partial V_{\text{xc}}(\mathbf{r}, \omega)}{\partial n(\mathbf{r})} \delta n(\mathbf{r}, \omega). \end{aligned} \quad (3)$$

In Eq. (3),  $n(\mathbf{r})$  is the ground-state electronic density and  $V_{\text{xc}}(\mathbf{r}, \omega)$  is the frequency-dependent local exchange-correlation potential. We computed  $V_{\text{xc}}(\mathbf{r}, \omega)$  as proposed by Gross and Kohn.<sup>21</sup> For  $V_{\text{xc}}(\mathbf{r}, \omega)$  at  $\omega=0$ , the parametrization of Vosko, Wilk, and Nusair<sup>22</sup> was employed. Note that the use of the frequency-dependent exchange-correlation potential makes it possible to study excitations with energies below the continuum threshold of the cluster. Within the familiar TDLDA method, using for  $V_{\text{xc}}(\mathbf{r}, \omega)$  at all  $\omega$  its value at  $\omega=0$ , the induced electronic density  $\delta n(\mathbf{r}, \omega)$  below the continuum threshold is real.

The potential  $\delta V_{\text{pol}}(\mathbf{r}, \omega)$  results from the change in the density of the polarization charges under the external field:

$$\delta V_{\text{pol}}(\mathbf{r}, \omega) = \int \frac{\delta n_{\text{pol}}(\mathbf{r}', \omega) d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \quad (4)$$

$\delta n_{\text{pol}}(\mathbf{r}, \omega)$  is related to the polarization vector, which, in turn, can be expressed in terms of  $\delta V^e(\mathbf{r}, \omega)$ .<sup>23</sup> For a spherical jellium cluster with a rigid positive background, we have

$$\delta n_{\text{pol}}(\mathbf{r}, \omega) = \frac{\varepsilon - 1}{4\pi} \text{div}[\theta(r-R) \nabla \delta V^e(\mathbf{r}, \omega)], \quad (5)$$

where  $\varepsilon$  is the static dielectric constant of the medium surrounding the cluster,  $\theta(r-R)$  denotes the Heaviside unit step function,  $R$  is the cluster radius ( $R = N^{1/3} r_s$  for a jellium sphere containing  $N$  valence electrons,  $r_s$  being the radius per valence electron of the corresponding bulk metal).

We shall restrict our consideration to the dipole response ( $l'=1$ ). In this case

$$\delta V^e(\mathbf{r}, \omega) = \delta V^e(r, \omega) P_1(\cos \theta). \quad (6)$$

Substituting Eqs. (4) and (5) into Eq. (2) and taking into account the angular dependence of  $\delta V^e(\mathbf{r}, \omega)$ , one can obtain the following expression for  $\delta V^e(r, \omega)$  (see the Appendix):

$$\delta V^e(r, \omega) = \begin{cases} \delta V(r, \omega) + \frac{1-\varepsilon}{1+2\varepsilon} \frac{2r}{R} \delta V(R, \omega), & r \leq R, \\ \frac{1}{\varepsilon} \left( \delta V(r, \omega) - \frac{1-\varepsilon}{1+2\varepsilon} \frac{R^2}{r^2} \delta V(R, \omega) \right), & r \geq R. \end{cases} \quad (7)$$

The self-consistent equations (1), (3), and (7) describe the dipole dynamic response of a small jellium sphere embedded in a dielectric medium. Using  $\delta n(r, \omega)$ , one can calculate the dipole dynamic polarizability of a metal sphere within a dielectric:

$$\alpha(\omega) = -\frac{4\pi}{3} \int_0^\infty \delta n(r, \omega) r^3 dr. \quad (8)$$

### III. RESULTS

Figures 1 and 2 present the imaginary part of the dynamic polarizability,  $\text{Im} \alpha(\omega)$ , of individual jellium spheres containing 8, 18, and 20 valence electrons with the same mean density as in bulk sodium ( $r_s = 3.98$  a.u.) and aluminum ( $r_s = 2.07$  a.u.). The spheres are placed in vacuum ( $\varepsilon=1$ ) and in dielectric media with  $\varepsilon=2, 3$ , and 5. The mesh width used by us for energy is 0.1 eV. The solid curves are the TDLDA results, the dashed curves are the predictions of the classical electrodynamic formula,

$$\alpha_{\text{cl}}(\omega) = \frac{\xi(\omega) - \varepsilon}{\xi(\omega) + 2\varepsilon} R^3, \quad (9)$$

in which the dielectric function of the metal sphere  $\xi(\omega)$  is described by the Drude expression for a free-electron-like bulk metal:

$$\xi(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}. \quad (10)$$

Here,  $\omega_p = (3/r_s^3)^{1/2}$  is the bulk plasma frequency (in atomic units). The phenomenological damping rate  $\gamma$  represents electron scattering in the metal sphere. This process is characterized by a size-dependent scattering time  $\tau \sim R/v_F$ , where  $v_F$  denotes the Fermi velocity for the corresponding bulk metal. To fit the Drude and our TDLDA results, we used  $\gamma = v_F/5R$ . Substituting Eq. (10) into Eq. (9) gives, for  $\text{Im} \alpha_{\text{cl}}(\omega)$ ,

$$\text{Im} \alpha_{\text{cl}}(\omega) = \frac{3\varepsilon \omega \omega_s^2 \gamma}{(1+2\varepsilon)[(\omega^2 - \omega_s^2)^2 + \omega^2 \gamma^2]} R^3,$$

where

$$\omega_s = \frac{\omega_p}{(1+2\varepsilon)^{1/2}}. \quad (11)$$

At  $\omega = \omega_s$ , the imaginary part of the Drude polarizability has a peak associated with the excitation of the collective surface mode. Unlike the classical predictions, the dynamic polarizability within the TDLDA has a complicated shape that de-

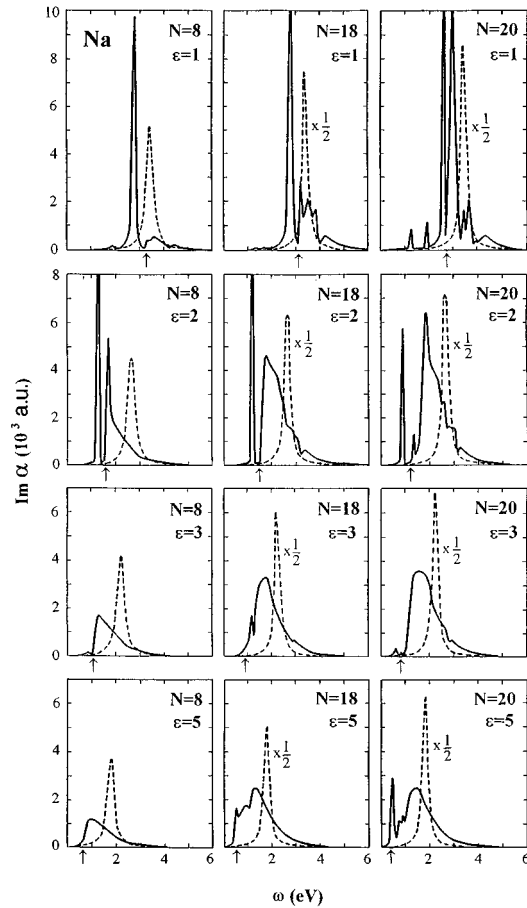


FIG. 1. Imaginary part of the dynamic polarizability for spherical jellium clusters with  $r_s = 3.98$  a.u. (sodiumlike) and  $N = 8, 18,$  and  $20$ . The results are presented for the clusters in vacuum ( $\epsilon = 1$ ) and in dielectric matrices with  $\epsilon = 2, 3,$  and  $5$ . Solid lines, TDLDA calculation; dashed lines, classical Drude theory with  $\gamma = v_F / (5R)$ . The Drude resonances for clusters with  $N = 18$  and  $20$  are depicted on a reduced scale. The upward-pointing arrows mark the continuum thresholds that follow from the ground-state Kohn-Sham energy spectra. For comparison, calculations performed by Beck (Ref. 9) within the TDLDA for free jellium spheres with  $r_s = 4.0$  a.u. have given the surface-plasma resonance at  $2.75$  eV for  $N = 8$ , at  $2.80$  eV for  $N = 18$ , and at  $2.69$  eV for  $N = 20$ . Experiments (Ref. 3) have shown resonances in photoabsorption spectra at  $2.52$  eV for free  $\text{Na}_8$ , at  $2.44$  and  $2.63$  eV for free  $\text{Na}_{18}$ , and at  $2.46$  and  $2.76$  eV for free  $\text{Na}_{20}$ .

pends strongly on the metal sphere size. The complicated structure of  $\text{Im } \alpha(\omega)$  is caused by one-electron (bound-bound and bound-continuum) excitations coupling with collective modes. The energies of some discrete one-electron transitions and the continuum thresholds, which follow from the Kohn-Sham ground-state energy spectrum of the clusters, are indicated in the figures. For jellium spherical clusters with  $N = 8, 18,$  and  $20$ , the ground-state electronic configurations are  $1s^2 1p^6$ ,  $1s^2 1p^6 1d^{10}$ , and  $1s^2 1p^6 1d^{10} 2s^2$ , respectively. The continuum thresholds correspond to energies of highest occupied levels.

For sodium clusters in vacuum, the surface plasmon lies immediately below the continuum threshold and is easily identified. Experiments<sup>3</sup> show resonances in photoabsorption spectra at  $2.52$  eV for  $\text{Na}_8$ , at  $2.44$  and  $2.63$  eV for  $\text{Na}_{18}$ , and

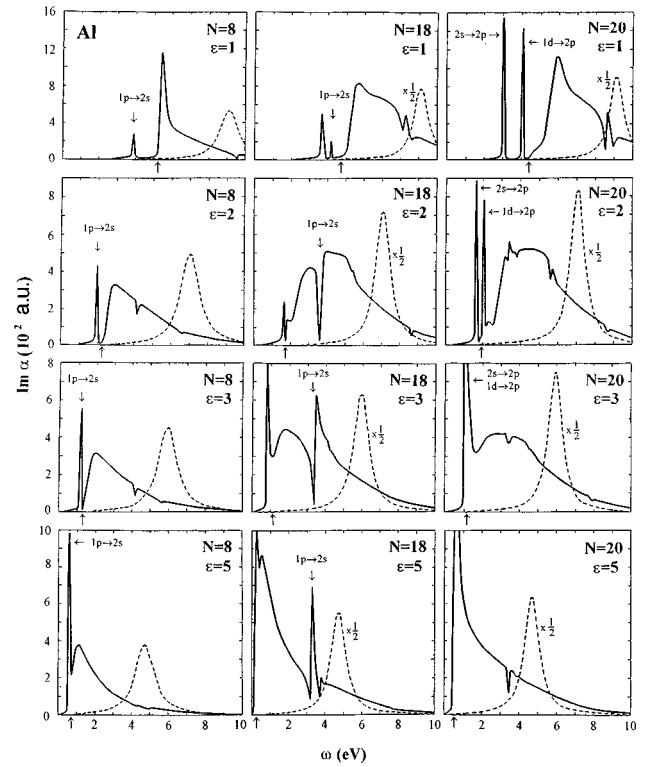


FIG. 2. Same as Fig. 1, but for aluminumlike jellium spheres ( $r_s = 2.07$  a.u.). For comparison, the surface-plasma resonance energies for free jellium spheres with  $r_s = 2.0$  a.u. from Ref. 9 are  $5.49$  eV for  $N = 8$ ,  $6.28$  eV for  $N = 18$ , and  $6.58$  eV for  $N = 20$ .

at  $2.46$  and  $2.76$  eV for  $\text{Na}_{20}$ . The classical formula (11) predicts  $\omega_s = 3.4$  eV. The TDLDA gives resonance frequencies that are redshifted with respect to Eq. (11), but are blue-shifted with respect to experiments. Our results for free sodium clusters coincide with those of previous calculations by the familiar TDLDA method applied to a spherical jellium model.<sup>8-10,14</sup> The use of the nonlocal description of exchange-correlation effects within the framework of the density-functional theory and refinements of the jellium model<sup>10,12-14</sup> improves the agreement between the calculated and observed response properties of metal clusters.

For sodium clusters in dielectric media, the surface plasmon is displaced beyond the continuum threshold; the peaks before the threshold are due to discrete electron transitions from occupied to unoccupied energy levels (see Fig. 1).

In spectra of  $\text{Im } \alpha(\omega)$  for aluminumlike clusters both in vacuum and in dielectrics, we have obtained strong wide resonances above the continuum threshold (see Fig. 2). Apparently, these resonances may be caused by surface plasmons coupling with one-electron excitations. The proximity of the one-electron and collective excitations leads to the attenuation and broadening of both resonances (the so-called Landau damping), which makes the identification of plasmon lines difficult. For comparison, in the captions for Figs. 1 and 2 we have cited the energies of surface plasmons for free jellium spheres with  $r_s = 4.0$  and  $2.0$  a.u., calculated with the TDLDA by Beck.<sup>9</sup>

With increasing  $\epsilon$ , the Drude and TDLDA resonances move to lower energies. For all considered clusters and hosts, the TDLDA yields the resonance region in  $\text{Im } \alpha(\omega)$

which is redshifted with respect to the corresponding classical predictions. For aluminumlike clusters, this shift is much greater. We have disclosed that peaks caused by collective and by one-electron excitations move to lower energies at different rates. In sodium clusters, the one-electron resonances move faster to the low-energy region than the surface plasmon. As a consequence, when sodium clusters are placed in dielectric media, the surface plasmon lies above the continuum threshold, whereas for the clusters in vacuum it lies before the threshold. For aluminumlike clusters, on the other hand, the surface-plasma resonance moves to the left more rapidly than the peaks caused by one-electron transitions. Consider, for instance, the aluminumlike jellium sphere with  $N=18$ . As seen in Fig. 2, at  $\varepsilon=1$  the discrete excitation  $1p \rightarrow 2s$  lies to the left of the plasmon; at  $\varepsilon=2$  and 3 the excitation  $1p \rightarrow 2s$  is superimposed on the plasmon and breaks it; at  $\varepsilon=5$  the one-electron transition  $1p \rightarrow 2s$  is to the right of the plasmon. In the figures for aluminumlike clusters with  $N=8$  and 20, it can be seen that with increasing  $\varepsilon$  the surface plasmon approaches the one-electron resonances located before the continuum threshold.

Note that according to the classical formula (11), the plasma-resonance frequency is higher for clusters with the higher electronic density (at identical dielectric surroundings). Within the TDLDA and the jellium model this rule breaks down. For example, at  $\varepsilon=5$  the resonances in aluminumlike jellium spheres are located at lower energies than in sodium clusters. Attention is drawn to the fact that at large  $\varepsilon$  the peaks in TDLDA spectra of  $\text{Im } \alpha(\omega)$  for aluminumlike clusters are so redshifted that they land in the near-infrared region (see the results for  $\varepsilon=5$  in Fig. 2). It has long been known<sup>24-27</sup> that the observed far-infrared absorption coefficient of small aluminum particles is some orders of magnitude larger than the classical theory predicts. The classical surface plasmon lies within the ultraviolet region and its far-infrared tail is too small to explain the measured absorption. The experimental investigations were carried out on aluminum particles embedded in dielectric hosts [e.g., in Refs. 26,27 the particles were in KCl ( $\varepsilon=4.84$ )] or on aluminum particles surrounded by an inert-gas atmosphere with addition of  $\text{O}_2$  and having the oxide coating<sup>24,25</sup> (for  $\text{Al}_2\text{O}_3$ ,  $\varepsilon=10$ ). For such systems, the TDLDA predicts the occurrence of strong photoabsorption resonances within the near-infrared region. Unfortunately, we are unaware of any experimental studies of near-infrared absorption of aluminum particles. Because of this, it is hard to judge whether the results obtained for jellium spheres can be extended to real aluminum clusters. However, it should be remarked that the far-infrared absorption of aluminumlike jellium spheres will be far greater than that of the classical Drude particles.

We emphasize once again that the discrepancy between the TDLDA and classical results decreases with the decrease of the electronic density in the cluster. So, in the similar calculations of Serra and Rubio<sup>15</sup> for  $\text{K}_{92}$  ( $r_s=4.86$  a.u.) in different dielectric matrices, the surface-plasmon energy is very close to the classical value and at  $\varepsilon=3$  it is in good agreement with experiment for potassium clusters in  $\text{MgO}$ .<sup>16</sup> In Ref. 15, the effect of dielectric surroundings was included in the Coulomb potential but not in the exchange-correlation one.

#### IV. CONCLUSION

The dipole dynamic polarizability of small aluminumlike and sodium jellium spheres embedded in different dielectric media has been calculated using the TDLDA method with the frequency-dependent local exchange-correlation potential. The polarization of a dielectric medium near the metal cluster surface was described in terms of a macroscopic dielectric constant of the medium. The positive background of the jellium cluster was assumed to be uniform and rigid.

As expected, the position of resonances caused both by one-electron transitions and by collective excitations shifts to lower energies with increasing dielectric constant of the medium surrounding the cluster. It is of interest that for aluminumlike clusters the surface plasmon moves to the left faster than one-electron resonances, while for sodium clusters the reverse is observed. In the case of sodium clusters, this leads to the displacement of the surface plasmon from the region below the continuum threshold (when the cluster is in vacuum) to the region above the continuum threshold (when the cluster is surrounded by a dielectric medium).

For all considered metal clusters and dielectric hosts, the TDLDA gives surface-plasma resonances (coupling with one-electron excitations) located at lower energies in relation to the position of the classical surface plasmons. The difference between the quantum and classical results is greater for clusters with high electronic density. For instance, under the classical theory, the surface plasmon in aluminumlike clusters embedded in a dielectric medium with  $\varepsilon=5$  lies in the near-ultraviolet region; from the TDLDA calculations, it follows that these clusters strongly absorb the near-infrared radiation. In light of the long discussion about the nature of the anomalously large far-infrared absorption by aluminum particles (in comparison with the classical predictions), it should be noted that according to the calculations reported here the dielectric surroundings of the metal particle (host or oxide coating) may lead to so large a redshift of the surface plasmon that the plasmon tail will give the observed value of the far-infrared absorption coefficient.

#### APPENDIX: TDLDA POTENTIAL $\delta V^\varepsilon(r, \omega)$

The change in the polarization potential under an external field is given by

$$\delta V_{\text{pol}}(\mathbf{r}, \omega) = \frac{\varepsilon - 1}{4\pi} \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \times \text{div}[\theta(r' - R)\nabla \delta V^\varepsilon(\mathbf{r}', \omega)] d\mathbf{r}'. \quad (\text{A1})$$

Integrating Eq. (A1) twice by parts, one obtains<sup>28</sup>

$$\delta V_{\text{pol}}(\mathbf{r}, \omega) = -(\varepsilon - 1)\theta(r - R)\delta V^\varepsilon(\mathbf{r}, \omega) + \frac{\varepsilon - 1}{4\pi} \int \delta V^\varepsilon(\mathbf{r}', \omega)\nabla_{r'} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \times \nabla_{r'}\theta(r' - R)d\mathbf{r}'.$$

Take into account the angular dependence of the potential for the dipole response [Eq. (6)] and use for  $1/|\mathbf{r} - \mathbf{r}'|$  the expansion in spherical harmonics,

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = 4\pi \sum_{lm} \frac{1}{2l+1} Y_{lm}(\hat{\mathbf{r}}) Y_{lm}^*(\hat{\mathbf{r}}') \frac{r_{<}^l}{r_{>}^{l+1}},$$

where  $r_{<}$  and  $r_{>}$  are the lesser and the greater of  $r$  and  $r'$ .  
Then

$$\delta V_{\text{pol}}(r, \omega) = -(\varepsilon - 1) \theta(r - R) \delta V^e(r, \omega) + \frac{\varepsilon - 1}{3} \delta V^e(R, \omega) \times \left[ \frac{R^2}{r^2} \theta(r - R) - \frac{2r}{R} \theta(R - r) \right]. \quad (\text{A2})$$

Substitution of Eq. (A2) into Eq. (2) yields

$$\delta V^e(r, \omega) = \begin{cases} \delta V(r, \omega) + \frac{1 - \varepsilon}{3} \frac{2r}{R} \delta V^e(R, \omega), & r \leq R, \\ \frac{1}{\varepsilon} \left[ \delta V(r, \omega) - \frac{1 - \varepsilon}{3} \frac{R^2}{r^2} \delta V^e(R, \omega) \right], & r \geq R. \end{cases} \quad (\text{A3})$$

$\delta V^e(R, \omega)$  is easily found from Eq. (A3) at  $r = R$ :

$$\delta V^e(R, \omega) = \frac{3 \delta V(R, \omega)}{1 + 2\varepsilon}. \quad (\text{A4})$$

Rewriting Eq. (A3) in terms of Eq. (A4), we obtain Eq. (7).

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<sup>1</sup>H. Haberland, *Clusters of Atoms and Molecules* (Springer, Berlin, 1994).

<sup>2</sup>K. Selby, M. Vollmer, J. Masui, V. Kresin, W. A. de Heer, and W. D. Knight, *Phys. Rev. B* **40**, 5417 (1989).

<sup>3</sup>K. Selby, V. Kresin, J. Masui, M. Vollmer, W. A. de Heer, A. Scheidemann, and W. D. Knight, *Phys. Rev. B* **43**, 4565 (1991).

<sup>4</sup>C. Bréchnignac, Ph. Cahuzac, F. Carlier, and J. Leygnier, *Chem. Phys. Lett.* **164**, 433 (1989).

<sup>5</sup>J. H. Parks and S. A. McDonald, *Phys. Rev. Lett.* **62**, 2301 (1989).

<sup>6</sup>C. R. C. Wang, S. Pollack, D. Cameron, and M. M. Kappes, *J. Chem. Phys.* **93**, 3787 (1990).

<sup>7</sup>S. Pollack, C. R. C. Wang, and M. M. Kappes, *J. Chem. Phys.* **94**, 2496 (1991).

<sup>8</sup>W. Ekardt, *Phys. Rev. Lett.* **52**, 1925 (1984); *Phys. Rev. B* **31**, 6360 (1985).

<sup>9</sup>D. E. Beck, *Phys. Rev. B* **35**, 7325 (1987); **43**, 7301 (1991).

<sup>10</sup>A. Rubio, L. C. Balbás, and J. A. Alonso, *Z. Phys. D* **19**, 93 (1991); *Phys. Rev. B* **45**, 13 657 (1992); **46**, 4891 (1992).

<sup>11</sup>C. Yannouleas and R. Broglia, *Phys. Rev. A* **44**, 5793 (1991); *Europhys. Lett.* **15**, 843 (1991).

<sup>12</sup>S. Saito, G. F. Bertsch, and D. Tománek, *Phys. Rev. B* **43**, 6804 (1991).

<sup>13</sup>J. M. Pacheco and W. Ekardt, *Ann. Phys. (Leipzig)* **B 1**, 254 (1992).

<sup>14</sup>W.-D. Schöne, W. Ekardt, and J. M. Pacheco, *Phys. Rev. B* **50**, 11 079 (1994).

<sup>15</sup>Ll. Serra and A. Rubio, *Z. Phys. D* **26**, S122 (1993); *Phys. Rev. B* **48**, 18 222 (1993).

<sup>16</sup>A. von Felde, J. Fink, and W. Ekardt, *Phys. Rev. Lett.* **61**, 2249 (1988).

<sup>17</sup>L. I. Kurkina and O. V. Farberovich, *Z. Phys. D* **37**, 359 (1996).

<sup>18</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

<sup>19</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

<sup>20</sup>A. Zangwill and P. Soven, *Phys. Rev. A* **21**, 1561 (1980).

<sup>21</sup>E. K. U. Gross and W. Kohn, *Phys. Rev. Lett.* **55**, 2850 (1985).

<sup>22</sup>S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).

<sup>23</sup>L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, New York, 1960).

<sup>24</sup>D. B. Tanner, A. J. Sievers, and R. A. Buhrman, *Phys. Rev. B* **11**, 1330 (1975).

<sup>25</sup>C. G. Granqvist, R. A. Buhrman, J. Wyns, and A. J. Sievers, *Phys. Rev. Lett.* **37**, 625 (1976).

<sup>26</sup>G. L. Carr, R. L. Henry, N. E. Russell, J. C. Carland, and D. B. Tanner, *Phys. Rev. B* **24**, 777 (1981).

<sup>27</sup>Y. H. Kim and D. B. Tanner, *Phys. Rev. B* **39**, 3585 (1989).

<sup>28</sup>A. A. Lushnikov, A. J. Simonov *Z. Phys.* **270**, 17 (1974).