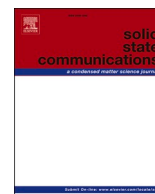




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## Solid State Communications

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# Effect of self-interaction corrections (SIC) on physical properties of small Al, Ag and Ni nanoparticles

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## ABSTRACT

The density functional method with self-interaction corrections (SIC) has been used to calculate the static dipole polarizations and surface plasmons of small metallic nanoparticles. It turns out that SIC lower the static dipole polarization per atom in the case of Al clusters when decreasing the number of atoms. In the case of silver, the dipole plasmon like excitation energies increase on going to smaller nanoparticles. The comparison with experiments has been shown to be in good agreement. Also, the static dipole polarizabilities of the Ni nanoparticles have been considered.

## 1. Introduction

The self-energy interaction correction effects have been widely used in calculations of solids in the context of the Kohn-Sham approximations [1]. Also, a time-dependent local density functional method has been useful in studies of small metallic clusters [2,3]. The problem of SIC is that the electronic wave-functions are no longer orthogonal to each other in the case of the local density approximation (LDA) [4]. Therefore, semi-classical methods are often useful since they allow the treatment of larger clusters with a static approximation. Also, a jellium model gives the average properties of static dipole polarizations and collective dipole excitation energies of nanoparticles in many cases [5].

The metallic nanoparticles have plenty of applications in medicine research [6]. Noble metal nanoparticles provide useful properties in thermal ablation therapy [6,7] and in the local surface plasmon resonance (LSPR) identifying plenty of different antibodies very efficiently at the same time. They are also useful in solar energy instruments in which the size of silver clusters determines the efficiency of the energy production [8]. Al nanoparticles have local plasmon resonances, which are sensitive to the size of clusters [9]. This feature makes possible to use Al in the wide range of wave lengths. The problem has been the oxidation of nanoparticles [10].

Previously, the free-electron metal clusters such as sodium have been studied extensively [11]. It has been found for small neutral (uncharged) nanoparticles that the surface plasmon energy decreases when the size of the cluster becomes smaller [5]. Also, the static dipole polarizability

per atom increases for smaller nanoparticles [5,11]. These effects have been explained by the quantum mechanical spill-out effect [12] which is important for small clusters.

In the nearly free atom nanoparticles of Al the spherical jellium model calculations have been shown to agree well with the experimental polarizability per atom measurements for larger than 40 atoms [13]. For smaller number of atoms there is a disagreement with theory and experiment which has been ascribed to the non-jellium effects due to the ionic background of the nanoparticles [14]. This indicates that there is a difference regarding the free-electron metal clusters which show good agreement with quantum mechanical spherical jellium calculations [13].

The Ag clusters show a strong blue shift of collective excitations on going to smaller sizes. This phenomenon has been explained to be due to the weakening of the s-d electron interaction because of the quantum mechanical spill-out effect [15,16]. The s-electrons are more delocalized than the d ones as in the solid metal surfaces of Ag. The spill-out of the s-electrons extends outside the cluster radius and the screening due to the d-like electrons becomes weaker [17]. Therefore, the surface plasmon energies increase towards the free-electron (Mie-plasmon) values since the effect in question is stronger for smaller clusters [17].

In the case of Ni clusters it will be shown that for the static dipole polarization the background of ions plays an important role due to the partially filled d-states. The self-interaction corrections of the s-like valence electrons explain the increase of this polarization per atom on going to larger clusters [18].

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## 2. The method

The calculation of metallic nanoparticles is performed using the local density method with the Thomas-Fermi-Dirac approximation. The self-interaction corrections of electron-electron and the background ion-ion interactions have been taken care by using the Fermi-Amaldi factors [19].

The total energy of the cluster can be described by the functional of electron and ion charge densities  $\rho_e$  and  $\rho_C$ , respectively.

$$E(\rho_e, \rho_C) = C_F \int \rho_e(\mathbf{r})^{5/3} d\mathbf{r} + \frac{1}{2}(1 - 1/N) \iint \rho_e(\mathbf{r})\rho_e(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d\mathbf{r}d\mathbf{r}' + A_x \int \rho_e(\mathbf{r})^{4/3} d\mathbf{r} + \int V_{ext}(\mathbf{r})\rho_e(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \left( 1 - \frac{1}{N_C} \right) \iint \rho_C(\mathbf{R})\rho_C(\mathbf{R}') / |\mathbf{R} - \mathbf{R}'| d\mathbf{R}d\mathbf{R}' \quad (1)$$

In which the atomic units have been assumed ( $e = \hbar = 1$ ) and [5].

$$V_{ext}(\mathbf{r}) = -(N / (2R_c))(3 - r^2 / R_c^2) \text{ for } r \leq R_c$$

$$= 0 \text{ when } r > R_c$$

$R_e$  and  $R_C$  is the radius of the sphere containing the valence electrons and ions of the cluster, respectively.  $N$  is the number of electrons and  $N_C$  is the number of background ions.  $C_F = (3/10)(3\pi^2)^{2/3} \approx 2,871$  and  $A_x = -(3/4)(3/\pi)^{1/3} \approx -0,738$ .

The valence electron charge density  $\rho_e(\mathbf{r})$  is described by the step function being constant inside radius  $R_e$  and zero outside. The same applies to the ionic background of the cluster with radius  $R_C$  [20].

The first term on the righthand side of (1) is the total kinetic energy of the valence electrons. The second one denotes the electron – electron contribution multiplied with the Fermi – Amaldi factor of valence electrons. The third term is the Dirac – exchange expression and the fourth one comes from the ion – valence electron interaction. The last term arises from the ion – ion interaction multiplied with the corresponding Fermi – Amaldi factor.

If the cluster consists of  $N^2$  mutual interactions then the electron – electron interactions can also be considered as a matrix of  $N^2$  elements. Then the self-interactions will be cancelled by having zero diagonal elements in the matrix.

The minimum of the total energy (1) can be obtained using

$$\frac{\partial E}{\partial R_e} = 0 \text{ and } \frac{\partial E}{\partial R_C} = 0 \quad (3)$$

Then one finds the inverse electronic radius of the cluster [21,22] added by the Dirac exchange contribution

$$\frac{1}{R_e} = \left[ 1.5N(ZN_C) - (0.6)N(N - 1) + 0.458N^{4/3} - 0.9N(ZN_C)(R_C/R_e)^2 \right] / (2.2N^{5/3}a_0) \quad (4)$$

The expression (4) is proportional to the surface area divided by the volume of the spherical nanoparticle [17].

## 3. Static polarizabilities of free Al clusters

The effect of the self-interaction corrections of valence electrons and background ions on the behavior of static dipole polarizations is considered in the case of 30–60 atoms ( $N_C$ ). It can be seen in Fig. 1 the minimum energy of (1) as a function of  $R_C/R_e$  in the case of  $N_C = 30$ . The minimum occurs when the ratio  $R_C/R_e$  is smaller than one. This is the consequence of the self-interaction corrections of the background ions because the screening of coulombic interactions of these particles has been reduced [19]. The effect is more pronounced in the case of Al clusters since for the polyvalent atom the valence is  $Z = 3$  as compared with the monovalent atom such as Na ( $Z = 1$ ). The contribution of SIC is

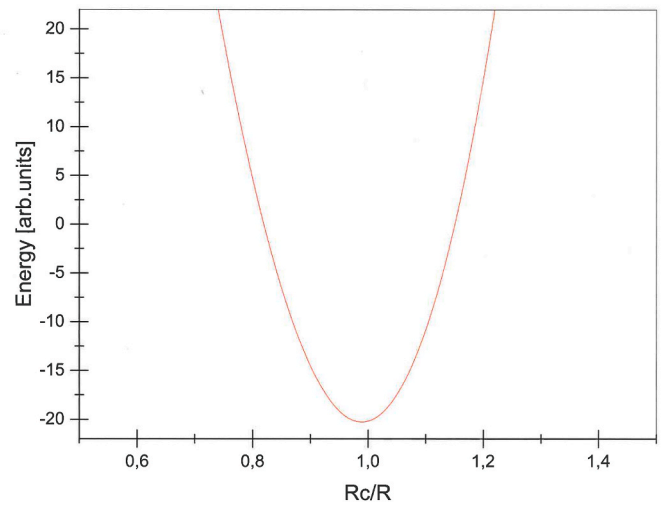


Fig. 1. Minimum of the total energy of Al<sub>30</sub> can be found when  $R_c$  is smaller than  $R_e$ .

about three times larger for the background ions than for valence-electrons of Al. Because the charge density of the valence-electrons and ions is the same one finds [21].

$$N \frac{4\pi}{3} R_c^3 = Z(N_C - 1) \frac{4\pi}{3} R_e^3 \quad (5)$$

This is caused by the minimum of the total energy in (1) which indicates that the influence of SIC is larger on the small clusters.

The static dipole polarization can be described by [12].

$$\alpha = (R_e + \delta), \text{ in which} \quad (6)$$

$\delta$  is due to the spill – out splitting of valence electrons [12], which we assume to be zero in the present case [13]. In Fig. 2 can be seen the experimental static dipole polarizations per atom of Al clusters [13]. Using the jellium radius of  $R_e$  for (6) and the metallic density the agreement between theory and experiment is excellent for  $N_C = 32$  [13]. But for larger clusters there is an increase of polarizability per atom up to 42 atoms deviating from the constant value of the metallic density case. The solid curve in Fig. 2 shows the Thomas-Fermi-Dirac calculation

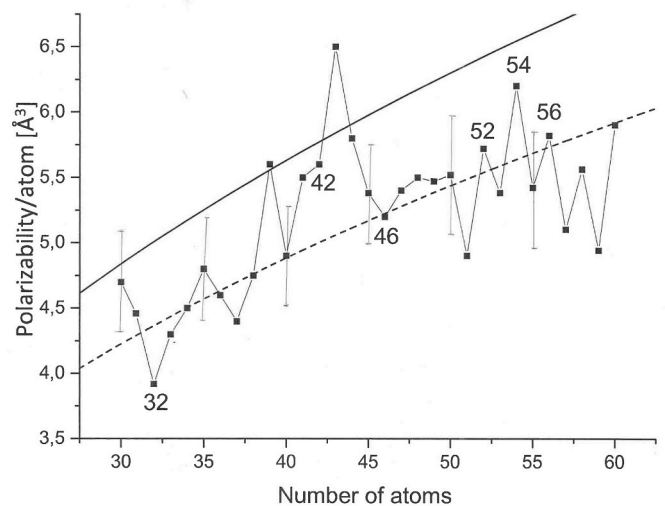


Fig. 2. Upper (solid) curve gives the static dipole polarization per atom according to the DFT calculation for  $Al_{N_C}$  clusters. The lower (dashed) one denotes the same but now in the case of  $A_x = -0.812$ . The number of atoms is indicated for closed shell structures [23].

giving the similar behavior as the experimental one. The lower curve (dashed) describes the situation, in which the parameter  $A_x$  in (1) has been modified by 10% showing the sensitivity of the static dipole polarization per atom to the Dirac exchange term.

There have also been noted the cluster sizes in which the shell structure of the jellium model is expected to be closed [23]. The  $s$ - $p$  hybridization has been shown to be valid for the case studied [23]. Fig. 2 indicates that the static dipole polarization anomalies can be largely described by SIC for the cluster sizes of  $N_C = 30$ –40. Previously, the larger clusters have been shown to be in agreement with the jellium calculations [13], whereas the deviations in the case of smaller ones have been remained unexplained. It turns out that the self-interaction corrections of the background ions give a large contribution to these anomalies.

The oscillations of the experimental data have been attributed to the geometry and shape of the clusters [24]. Nevertheless, the calculations show smaller effects than the experiment [25]. The oscillations are even stronger for smaller clusters  $N_C < 30$  [13] (not shown) in which also the spill-out effects of valence electrons may have a contribution [12] and the molecular like structure becomes more evident.

#### 4. Surface plasmons of silver nanoparticles

Recent time – dependent DFT calculations indicate from molecular to plasmon type behavior on going to larger particles [2,3]. Also, the full – potential linearized – augmented plane wave and local basis function pseudopotential methods show a transition from molecular clusters to nanoparticles at about 1.7 nm size [26]. Furthermore, higher temperatures favor collective excitations [27] and the electronic structure approximated by step like functions [26]. In our case the  $d$  – like electrons are assumed to belong to the background ions and the valence electron is  $s$  type (with  $Z = 1$ ). The dipole plasmon energies of nanoparticles have been estimated using [21].

$$\omega_{sp} = \sqrt{ZN_C} / R_c^{3/2} \quad (7)$$

This can be seen in Fig. 3 as a function of the particle diameter, in which the experimental result [28] is also included. The self-interaction corrections of valence electrons decrease  $R_e$ . The effect of SIC on the background ions is to reduce the ratio  $R_c/R_e$  to be less than one, which further reduces  $R_e$  according to (4). The increase of dipole plasmon energies for smaller nanoparticles is a consequence of decrease of the particle size when the ratio of the surface area to the volume becomes larger.

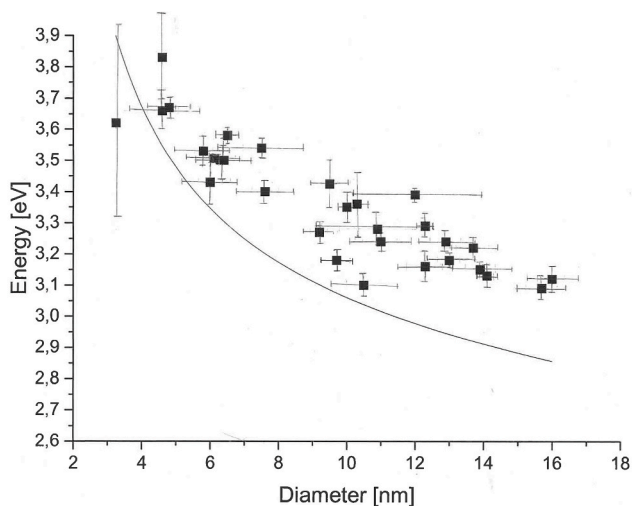


Fig. 3. Solid curve shows the dipole plasmon energies for free  $Ag_{N_C}$  spherical nanoparticles ( $A_x = -0.738$ ). The experimental results are from Ref. [28].

Regarding the structure of nanoparticles it has been shown for  $Ag_{369}$  that an almost spherical shape gives a lower ground state energy compared with the less symmetrical ones [26]. Also, recent experimental data support this conclusion [15,16,28]. For larger metallic clusters (50 nm), in which the self-interaction corrections are expected to be small according to (4) and (5), the shape of nanoparticles can be more important [6].

The experimental electron energy loss spectroscopy (EELS) results [28] are shown in Fig. 3. The nanoparticles on the  $Si_3N_4$  substrate give surface plasmon resonances with decreasing energy for larger sizes of particles. If the nanoparticle diameter exceeds 5 nm then the substrate should affect considerably on the dipole mode [28] whereas for smaller ones the effect would be not so strong.

The interesting thing is that for diameters less than 10 nm, the nanoparticles should behave quantum mechanically [29] and even smaller sizes have been proposed [30]. This conclusion is supported by the Dirac exchange - term which also contributes in this region. The agreement with theory and experiment is good for particles less than 5 nm considering the error limits of measurements.

Previously, the incomplete  $d$  – electron screening of spill – out valence electrons has been shown to give a blue shift for surface plasmons in the case of small Ag nanoparticles [17,31]. The decrease of  $d$  – electron screening resembles the effect of the self - interaction corrections of the background ions because there is less screening of ions which would affect the valence electrons. In our case the  $d$  – electrons are assumed to be implicitly included in the background ions.

#### 5. Static dipole polarizabilities of Ni clusters

In metallic Ni the valence band consists of  $4s^1$  and  $3d^9$  electrons. This means that there is a  $d$  – hole which will contribute to the electronic structure.

In Ni clusters there should be an attractive interaction between the  $d$  – hole and  $s$  – valence electron and therefore one would have  $R_c/R_e \approx 1$ . This ratio can be obtained by having only the self – interaction corrections between the  $s$  – electrons [19]. The approximation results in charge densities of the form

$$N \frac{4\pi}{3} R_c^3 = ZN_C \frac{4\pi}{3} R_C^3 \quad (8)$$

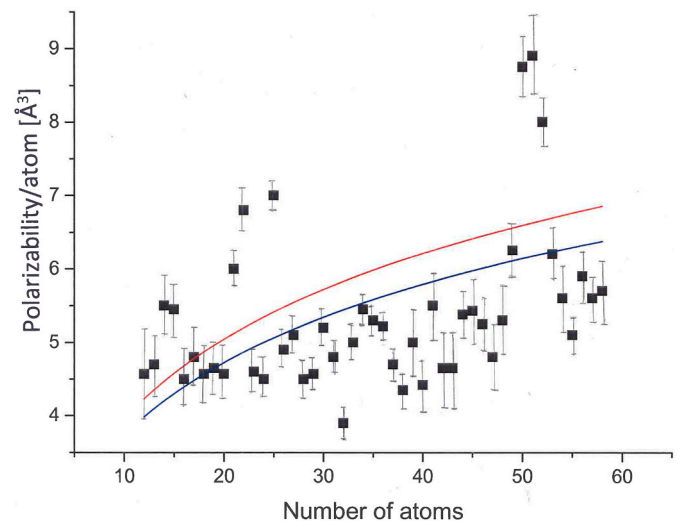


Fig. 4. Upper (red) curve of  $Ni_{N_C}$  describes the static dipole polarization per atom ( $A_x = -0.738$ ). The lower one (blue) is the corresponding result for  $A_x = -0.762$ . The experiment is from Ref. [18]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4 shows the experimental static dipole polarizabilities of Ni nanoclusters [18]. Also, the calculated spherical nanoparticles with the self - interaction corrections of valence electrons have been included. The upper curve has been obtained using the Thomas – Fermi – Dirac approximation. The lower one gives the corresponding result, when the exchange interaction has been changed 3.3%. This shows the sensitivity of the exchange term. The behavior of the calculated and experimental curves is quite similar except that the measured one shows strong peaks around  $n = 20$  and  $50$  indicating the importance of the structure [32] and shape [33] in these nanoparticles. It is evident that the effect of SIC is just the opposite regarding the valence electron spill – out phenomenon which in turn shows a decreasing static dipole polarizability per atom on going to larger particles [32].

## 6. Conclusions

The self-interaction corrections change the surface to volume ratio of the spherical metallic nanoparticles. The effect is to decrease the static dipole polarization per atom and increase the surface plasmon energies when the size of the nanoparticle has been reduced. In the case of polyvalent atoms the self-interaction corrections are larger than for monovalent ones. This is due to the influence of the background ions.

## Statement

The work has been performed at the University of Turku, Finland

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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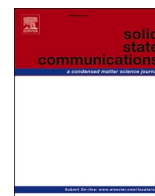
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**Update**

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## Corrigendum to “Effect of self-interaction corrections (SIC) on physical properties of small Al, Ag and Ni nanoparticles” [Solid State Commun. 371 (2023) 115278]

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The author regret that there is a misprint on the second page (middle), equation (6):  $\alpha = (R_e + \delta)$  should read  $\alpha = (R_e + \delta)^3$ . This error has

no influence on **Fig. 2** and **Fig. 4**, because the correct expression has been used.

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