The collective excitations and static dipole polarizability in small nanoparticles

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Abstract. Collective dipole excitations for small clusters have been considered in the energy range close to the visible light. The absorption energies and static dipole polarizabilities are estimated. In the case of Ag_8, Na_{18}, Na_{20}, Cs_{40}, Mg_{10}, Ba_{20}, Ag_9^+, Na_{21}^+ and Mg_{11}^{++} clusters a semi-classical density functional method with the Thomas Fermi approximation have been used. Also, applications in Al_6, Al_7, $(ZnS)_3$ and $(ZnSe)_4$ will be discussed. The results are compared with the available data.

1. Introduction

It is quite well known that the excitation energies of small metal clusters depend on the size of these nano-particles [1]. These features have important applications in nano-electronics [2, 3] and medicine [4], for instance. In the case of solar energy equipments, Ag clusters play an important role, because they are able to absorb energy very efficiently in the desired wavelengths. By adjusting the size of the clusters, the effect of absorption is possible to optimize in order to further improve the energy efficiency. The typical size dependent optical energies are between 1.8 and 3.0 eV [5] corresponding the wavelengths of about 689 and 413 nm, respectively. These wavelengths of visible light are much larger than the diameter of small nanoclusters, which have a size of the order of one nm. This property allows the static approximation in estimating the energies of the collective excitations of small clusters [6].

In the case of small nanoparticles, the collective electron excitations have been recently interpreted as being due to the quantum electron transitions from the occupied energy levels to the empty ones [7]. For larger clusters this would mean intra band transitions [8]. Also the lifetime of these excitations is decreasing for smaller clusters (<10 nm), since the larger separations of the discrete valence energy levels make the frequency determination more uncertain [7]. Nowadays, also the size of the nanoclusters can be observed using electron spectroscopic methods, for instance by transmission electron microscopy (TEM) [1]. For larger clusters (~10^3 atoms) surface plasmons have been observed as well as longitudinal bulk plasmons using photoelectron spectroscopy [9].

The collective electron oscillations and static polarizabilities of small clusters have been estimated by a double-jellium model [10, 11], in which the static density functional (DFT) method can be used with the Thomas-Fermi approximation. The valence electrons of these free clusters are assumed to be s-like in order to avoid extra assumptions concerning the shape of the particles. The electronic shell structure and the wave functions have been omitted. Mostly, close shell clusters having a magic

number of valence electrons are considered. In this work new results are obtained, especially for charged clusters.

1. Methods

The important question is how to estimate the ground state jellium density of charges in small clusters. Although the metallic clusters are rather sophisticated ones, some approximations can be made to obtain reasonable solutions. In this case the ionic background charge is assumed to be frozen in the sense that that the kinetic energy of the ions is neglected. Only the ion-ion interactions have been retained. The total kinetic energy of valence electrons is described by the Thomas-Fermi approximation. There is a distinction between the more localized inner electrons and delocalized valence electrons which allows to treat the latter ones to be free-electron like. The former ones are assumed to belong to the background ions. The effect of ions and valence electrons will be described by different charge densities in the spheres of radii R_C and R, respectively.

To calculate the static polarization of the cluster in the case of two sharp edged jellium spheres, the Hamiltonian will be needed. In our case it is given by [12].

$$(1) \quad H = \sum_{i=1}^{N} p_i^2/2m_e - \sum_{j=1}^{Nc}\sum_{i=1}^{N} Ze^2/|\mathbf{r_i}-\mathbf{R_j}| + \tfrac{1}{2}\sum_{i=1}^{N}\sum_{j(\neq i)=1}^{N} e^2/|\mathbf{r_i}-\mathbf{r_j}| + \tfrac{1}{2}\sum_{i=1}^{Nc}\sum_{j(\neq i)=1}^{Nc}(Ze)^2/|\mathbf{R_i}-\mathbf{R_j}|$$
$$= E$$

in which E is the energy and the first term on the right hand side describes the total kinetic energy of valence electrons in the cluster. According to the Thomas-Fermi approximation, it is of the form [13, 10], in which the accuracy increases for larger number of electrons

$$(2) \quad \sum_{i=1}^{N} p_i^2/2m_e \cong 1.1N^{5/3}(\hbar^2/m_e)1/R^2, \text{ where}$$

R is the electronic radius and N denotes the total number of valence electrons of the cluster, respectively. In the Hamiltonian above, Z is the valence of the atom, N_C is the total number of ions in the cluster, r_i and R_j are the coordinates of electrons and ions, respectively.

The second term is the sum of the electron-ion interactions, which can be written by changing the double summations in (1) to integrals and Gauss´s Theorem gives [14]

$$(3) \quad -\sum_{j=1}^{Nc}\sum_{i=1}^{N} Ze^2/|\mathbf{r_i}-\mathbf{R_j}| = -\sum_{j=1}^{Nc} Ze^2\int \rho_c(r_j)\rho_e/|\mathbf{r'}-r_j|d^3r' = -4\pi Ze\int_0^{Rc} V(r)r^2\rho_c dr, \text{ where}$$

ρ_c is the constant number density of ions and ρ_e for electrons, respectively. R_C is the ionic radius of the cluster. The electrostatic potential, which is spherical in (3), takes the form inside the cluster [14]

$$(4) \quad V(r) = (eN/2R)(3-r^2/R^2).$$

The third sum in (1) consisting of electron-electron interactions can be described using

$$(5) \quad \tfrac{1}{2}\sum_{i=1}^{N}\sum_{j(\neq i)=1}^{N} e^2/|\mathbf{r_i}-\mathbf{r_j}| = e^2/3\int_0^{R}(4\pi\rho)^2r^4dr, \text{ where}$$

R is the electronic radius of the cluster and $\rho = 3[N(N-1)]^{\frac{1}{2}}/(4\pi R^3)$ is the corresponding number density of valence electrons, in which the omission of the self-interaction of electrons ($r_i \neq r_j$) has been

taken into account [10]. This means that the specific electron in (5) is screened only by other electrons. This effect is not important only for electrons but also for ions. Therefore, the last term in (1) has been treated the same way. Similarly, only the other ions screen the effect of the ion in this term, which is significant for the spherical jellium background of small clusters.

It is important to achieve the minimum energy of (1). This value can be obtained as a function of R_C/R using

(6) $(\partial/\partial R_C + \partial/\partial R)E = 0.$

The energy behavior of (1) can be found as a function of R_C/R, when the expression for $1/R$, obtained from (6), has been substituted into the Hamiltonian. The similar, but narrower minimum can be seen in Fig. 1. in the case of

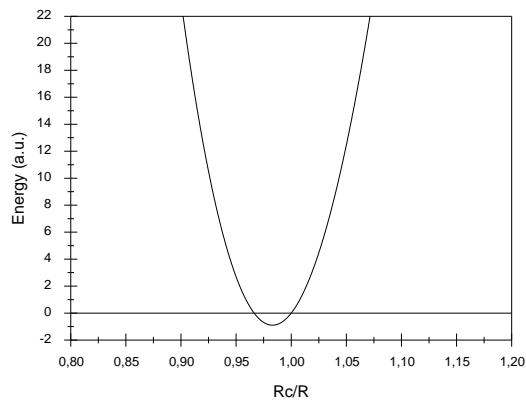(7) $(\partial/\partial R_C)E = (\partial/\partial R)E$.
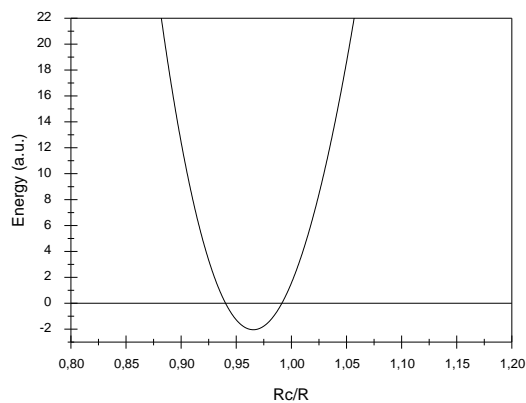

Fig.1a

Fig.1b

Fig.1. a) The energy of Hamiltonian (1) (in Hartree units) as a function of R_C/R, when the number of atoms N_c of the cluster is 20 and the valence of the atom is one (Z=1). It should be noted, that the minimum gives only the R_C/R ratio. b) Otherwise the same but now N_C=10 and Z=2. The minimum is somewhat deeper and it is shifted to lower values of R_C/R.

Combining derivatives (6) and (7) one finds

(8) $(\partial/\partial R)E=0$

and the inverse electronic radius of the cluster is of the form

(9) $1/R=e^2[1.5N(ZN_C)-0.6N(N-1)-0.9N(ZN_C)(R_C/R)^2]/(2.2N^{5/3}a_O)$, where

a_O is the Bohr radius and $R_C/R \leq 1$.

As it is well known the surface to volume ratio increases when the size of the cluster decreases [15]. In our case the number of cluster atoms N_C should be consistent with the real size of the cluster, which must be close to $2R_C$ in order to have a reasonable physical solution.

2. Results and discussion

2.1. Static dipole polarizability

For Ag_8 clusters, the ab initio calculations indicate that the d-character of valence electrons is less than 10 percent for low excitation energies and the s-like electrons dominate [16]. For instance, it is well known that for metallic silver the d-like density of states is about four electron volts lower than the Fermi level, which means that the inter band d-s transition energies must be larger than 4 eV [15]. The d-like electrons screen the effect of the s-electrons [17]. Omitting the d-like valence electron contribution to the Ag_8 cluster, one finds for the static dipole polarizability divided by the number of atoms $\alpha/N_C=R^3/N_C=7.05$ Å^3 according to (9) for N_C=8. This result is slightly larger than those obtained with ab initio methods [17].

In the case of nearly free electron like metals the situation is favorable, because it is often enough to consider only the s-like valence electrons. This approximation will be also assumed for our clusters. For the Mg_{10} cluster consisting of 10 atoms one finds $\alpha/N_C=10.44$ Å^3 and for Ba_{20} the corresponding value is 21.26 Å^3. In the case of Na_{18} the static dipole polarizability divided by the number of atoms is 16.19 Å^3, which is in good agreement with the experimental result 16.3±0.6 Å^3 of Tikhonov et al. [18] but larger than the static polarizability per atom in Ref. [19] at a low temperature of 20 K. The Cs_{40} cluster gives a value of 35.41 Å^3 being much larger than the other ones. The results indicate that the cluster size is important when considering the static dipole polarizability [20].

So far we have assumed a spherical distribution of s- valence electrons. For an Al atom, however, one has one p- and two s- electrons. This means that in order to consider the corresponding clusters we should treat the p-electrons as they would be s-like. In this case the static dipole polarizability/atom for Al_6 is 5.75 Å^3 according to (9) being smaller than 6.740 Å^3, which has been

calculated with the DFT method in Ref. [21]. The explanation is that the jellium model favors magic numbers giving lower values. This becomes evident for Al_7, in which the previous calculated value is 6.364 $Å^3$, which is the minimum in Ref. [21], indicating a stable structure, whereas our estimate with (9) gives R^3/N_C=6.78 $Å^3$.

A selenium atom contains two s- and four p-electrons. Zn has two s-valence electrons. In addition, zinc possesses 10d-electrons, which we assume to belong to the background ion, because they have larger binding energies. Using (9) for $(ZnSe)_4$ the static dipole polarizability/molecule will be 8.21 $Å^3$. The corresponding result has been calculated with the DFT method [22]. The average value for this case was $<\alpha>_{av}/n$=7.975 $Å^3$ concerning the small $(ZnS)_n$ quantum dots, when n=4 [22]. Interestingly, there is a reasonable agreement between these estimates, although the shape of the cluster is not spherical, but having a ring like structure in accordance with Euler´s Theorem [22]. However, the valence electrons are delocalized, which may in part explain the agreement between these results.

Similarly, $(ZnS)_3$ gives the static dipole polarizability/molecule of 6.06 $Å^3$ using (9). This value can be compared with $<\alpha>_{av}/3$=6.578 $Å^3$ calculated in Ref. [23], which is the local minimum suggesting a stable structure [23] in the case of the DFT method. Higher static dipole polarizability indicates easier fragmentation of the cluster.

2.2. The collective excitation of electrons

Using the atomic units ($\hbar$=e=m_e=1) the collective excitation energy in the harmonic approximation can be written as [12, 24, 10]

$$(10) \qquad \omega_e=(4\pi/(3N)\int \rho_e\rho_C d^3r)^{1/2}=((4\pi)^2/(3N)\int_0^{R_C} \rho_e (3ZN_C/4\pi R_C^3)r^2 dr)^{1/2}$$

$$=(ZN_C)^{1/2}/R^{3/2}, \text{ where}$$

ρ_e is the electronic and ρ_C the ionic density of the cluster, respectively. Z is the valence of the atom and N_C the number of ions.

In Table 1 dipole plasmon like collective excitation energies have been summarized for some of the uncharged Ag, Na, Mg, Ba and Cs clusters with diameter $2R_C$ of the corresponding particles. One could draw some general conclusions concerning the results above. It is interesting to note that the size of the Ag_8 and Mg_{10} clusters should be smaller than 1 nm. The diameters of Na_{20} and Ba_{20} do not differ much. The excitation energy values of Na_{20} and Mg_{10} are in line with the previous experimental [25] and theoretical [26] estimates, respectively. The time-dependent density functional method with self-interaction correction (SIC) results in 2.53 eV for Na_{18} Ref. [27] which is in good agreement with our value 2.57 eV. However, the time-dependent local-density approximation (TDLDA) shows a peak at 2.78 eV Ref. [27] indicating that the self-interaction correction is important. In the case of Na_{20} the experimental value is 2.46 eV [25], which is almost the same as the calculated one 2.47 eV in Table 1. The large $2R_C$ values also are in line with the argument that Mg_{10} and Ba_{20} would have a non-metallic bonding.

	$\hbar\omega_e$ [eV]		$2R_C$ [nm]	$2(N_C)^{1/3}r_s$ [nm]
Ag_8	3.94		0.73	0.635
Na_{18}	2.57	2.53[a]	1.31	1.090
Na_{20}	2.47	2.46[b]	1.40	1.129
Mg_{10}	4.58	4-5[c]	0.94	0.604
Ba_{20}	3.21		1.49	1.063
Cs_{40}	1.76		2.25	2.035
Ag_9^+	4.11	4.02[d]	0.78	
Na_{21}^+	2.51		1.43	
Mg_{11}^{++}	4.72		0.95	

Table 1. Estimated collective dipole excitations energies $\hbar\omega_e$ [eV] and sizes $2R_C$ [nm] of small neutral and charged clusters. The third column gives the size in the case of Mie resonance, in which the electronic charge density of solid has been used [34]. r_s is the volume of the sphere containing one electron.

[a]Ref.[27]

[b]Ref.[25]

[c]Ref.[26]

[d]Ref.[36]

The neutral Ag clusters are often in the matrix of adsorbates such as Ne, Ar, Kr, Xe, N_2, O_2, C_2H_4 and CO [28]. This property usually makes the comparison with experiments difficult. An analytic expression of the energy [eV] for the surface plasmon absorption band of Ag clusters in the Ar matrix, using a linear regression analysis, has been obtained [29]

(11) $\hbar\omega = 3.21 + 0.58/D$, where

the average diameter of the colloidal particle is $D \geq 1$ nm due to the limited resolution of the electron microscopy. As can be seen, $\hbar\omega$ in (11) is increasing when the size of the noble metal cluster decreases [30, 31]. Substituting the value D=0.73 nm (see Table 1.) into (11) one finds $\hbar\omega$=4.00 eV. Also, the measured optical absorption spectrum of the Ag_8 cluster in the solid matrix at 10 K temperature reveals an energy of 3.89 eV for the main peak [32] being quite consistent with the result of formula (11). It should be noted that the redshift caused by the Ar matrix has been estimated to lower the energy to 3.21 eV for $D \rightarrow \infty$ instead of 3.50 eV for pure solid Ag [33, 34]. Also, there will be smoothing of the spectra [35]. On the other hand, charged clusters can be found by using the sputtering method [36] in vacuum conditions and no matrix effect will appear.

In the case of charged clusters the obtained energy $\hbar\omega_e$ for Ag_9^+, having eight valence electrons, is equal to 4.11 eV, which is slightly larger than that of the neutral one in Table 1. The experimental

optical absorption spectrum has given a value of 4.02 eV for this charged cluster [36]. For Mg_{11}^{++} the excitation energy is 4.72 eV and for Na_{21}^{+} one has 2.51 eV, which is close to the experimental and theoretical result in Ref. [37].

Very often the shape of the cluster deviates from the spherical one [27]. In order to circumvent this problem, it has previously been assumed that the volume of the non-spherical particle can be calculated and then use this result to estimate the volume of the sphere having the R radius [25, 33].

It has been observed that the spheroid shape approximation can be used for many open shell clusters [27]. In that case two different features would be observed instead of one. The oscillation along the short axes of the spheroid would be blue shifted, whereas along the long axes it should be red shifted relative to the spherical cluster peak [38, 39]. Often classical methods have been used to consider the large metallic clusters [6, 40]. In the Mie model the plasmon energy is size independent and constant being suitable for studies concerning the effect of the cluster shape [41]. Even, if the plasmon like excitations are not observed but the energies are close to the single particle excitation the enhancement for the latter can result [42].

Conclusions.

The jellium model can be extended from the small alkaline and noble metal clusters to earth-alkaline ones. The spherical distribution of the valence electrons and ions has been assumed. At the moment, the experimental data would be useful to investigate this matter in more detail. It is possible to obtain reasonable results with the minimum number of adjustable parameters.

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