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Shell structure of cesium layer covering the C_{60} fullerene core[*]

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Abstract. Strutinsky shell corrections for the cesium-coated fullerenes were investigated. The single particle levels of electrons are obtained using the spherical mean-field potential of a shifted Wood-Saxon type. The parameters of the potential are adjusted to reproduce the experimental ionization energies of the Cs(N) clusters and the magic numbers observed in their photo-ionization spectra of the $C_{60}Cs(N)$ aggregates.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 71.23.-k Electronic structure of disordered solids

1 Introduction

The world wide interest on metallic clusters started in the early 80's when a group of physicists from Berkeley performed the first experiments with tiny alkali clusters [1,2]. Since that time an enormous amount of work both on the experimental and theoretical side has been accomplished. Metallic clusters are the quantum many body systems built from several up to a few thousands atoms and their radii are of the order of 10 Å. It is well-known that the shell structure of electronic orbitals in the metallic cluster can be well reproduced not only by selfconsistent calculations but also within some average potential approach based on the jellium model (see *e.g.* [3]). In the jellium model one assumes, that electrons are moving in the mean field potential which is produced by the background of positive ions and by other free electrons.

In 1996 an experimental group from Stuttgart [4] succeeded in producing and the measuring optical response of cesium coated fullerenes C_{60} covered by a layer of N Cs-atoms with $N \leq 500$. The electronic shell structure of these $C_{60}Cs(N)$ agglomerates was studied in reference [5] using the local approximation to the density-functional theory. The measured abundances of metal-coated fullerenes $C_{60}Cs(N)$ were interpreted there in terms of the magic numbers corresponding to the electronic shell closures. Recently, in reference [6] the shell structure of thin spherical metallic layers was discussed using the Strutinsky shell correction method [7] and an infinite square well approximation to the mean field potential for electrons. In spite of this rather rough approxi-

mation to the average mean field potential it was shown there that for $C_{60}Cs(N)$ the minima of the shell correction as function of the atom number N in the cluster were found not far from the experimental magic numbers given in reference [5]. The agreement was better at higher mass numbers, where the jellium model is more reliable.

The aim of the present investigation is to use a similar approach as in reference [6] but with a more realistic approximation to the mean-field potential. We are going to keep the spherical symmetry of the potential because the fullerene C_{60} core is a spherical ball, what additionally stabilizes the system against deformation. We show in the following, that a shifted Saxon-Woods potential reproduces reasonably well the experimental magic numbers and the ionization energies. It will also be shown how the magic numbers of the cesium layer change with the core radius. This is not only an *academic* study since one can easily imagine an experiment in which one covers a spherical insulator with a thin metal layer.

2 Theoretical model

The valence electrons have a decisive influence on the abundance of metallic clusters. The electrons are moving in a mean field potential which is produced by the jellium, *i.e.* the positively charged ions and the rest of the electrons.

It was shown (see discussion in Ref. [3]) that the Saxon-Woods type potential

$$V_{\text{phen}}(r) = \frac{-V_0}{1 + e^{\frac{r-R_0}{a}}}, \qquad (1)$$

approximates quite well the mean field which is felt by free (valence) electrons. The radius R_0 in (1) has to be

chosen as

$$R_0 = r_0 N^{1/3}, \quad (2)$$

with

$$r_0 = r_{00}\left(1 + \frac{\alpha}{N^{1/3}}\right), \quad (3)$$

where r_{00} is the Wigner-Seitz cell radius, N the number of atoms in the cluster and α a constant originating from the so-called "spilled-out" effect [1,3]. The potential depth V_0 and the surface thickness a are usually adjusted to the experimental values of ionization energies and to some spectroscopic data (*e.g.* magic numbers) of clusters in a broad range of N. Solving the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_{\mathrm{phen}}\right)\Psi_\nu = e_\nu \Psi_\nu, \quad (4)$$

one can obtain the ionization energy by looking for the energy of the last occupied level (Fermi energy). One has to keep in mind that due to the spin of the electron one has to put two electrons on each single-particle level e_ν. In the spherical case the levels are strongly degenerated

$$\Psi_\nu = \Psi_{n\ell m m_s}, \quad \text{while} \quad e_\nu = e_{n\ell}.$$

The magic numbers can be roughly identified with the numbers of particles below energy gaps in the single-particle spectrum e_ν or more accurately as minima in the considered as function of the particle number N Strutinsky shell correction $\delta E_{\mathrm{shell}}(N)$ [7,8]

$$\delta E_{\mathrm{shell}}(N) = 2\sum_{\mathrm{occ}} e_\nu - \widetilde{E}(N), \quad (5)$$

where $\widetilde{E}$ is energy of electrons in the cluster with smeared-out shell structure. We have used here, as usually done in the Strutinsky procedure, a Gauss function with the six order correctional polynomial to washed out the shell effects. The width (γ) of the Gaussian was fixed from the plateau condition of

$$\widetilde{E}(N) = 2\sum_{\nu=1}^{\infty} e_\nu \tilde{n}_\nu(\gamma), \quad (6)$$

where $\tilde{n}_\nu$ is the average occupation number of the level e_ν.

We are going to discuss the shell structure of the electron orbitals in thin Cesium layers built on a fullerene core or another spherical ball made from insulator. A shifted Saxon-Woods potential seems to be most appropriate in this case. Such a potential, shown in Figure 1, is described by the following equation

$$V(r) = V_0\left(\frac{1}{1 + e^{\frac{r - R_2}{a_2}}} - \frac{1}{1 + e^{\frac{r - R_1}{a_1}}}\right), \quad (7)$$

where R_2 is the radius of the inner core and R_1 depends on the number of atoms in the cluster

$$R_1 = \left(r_0^3 N + R_2^3\right)^{1/3}. \quad (8)$$
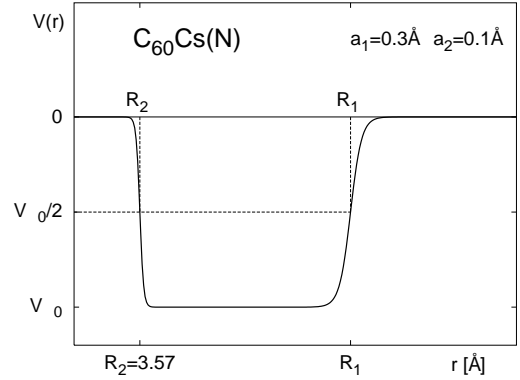
Fig. 1. The shape of the spherical average potential for electrons in the $C_{60}Cs(N)$ cluster.

The parameters a_1 and a_2 describe the diffuseness of the outer and inner potential wall at R_1 and R_2 respectively. The parameter a_1 should be essentially equal to the parameter a from equation (1) for the compacted cluster. The potential which feels the electron in the region between the core and the metallic layer of the cesium atoms is described by the parameter a_2 which will be adjusted to reproduce the observed magic numbers in the $C_{60}Cs(N)$ agglomerates as explained in the next section.

3 Results

The single-particle levels of electrons were evaluated using the Woods-Saxon potential (1) for the compact spherical clusters build from a few to 1 000 atoms. The magnitude of the ionization energy dependents on the depth V_0 of the potential, its radius R_0, and surface thickness a:

$$E_{\mathrm{io}} = e_{N/2}(V_0, R_0, a). \quad (9)$$

In order to fix the parameter set of the potential (1) we have performed a preliminary computation for sodium $Na(N)$ and potassium $K(N)$ clusters which are the best known clusters of metals with one valence electron and for which the ionization energies were measured in reference [9], in a relatively broad range of N.

We have found that using the radius shift constant $\alpha = 0.8$ and the depth of potential $V_0 = 6.0$ eV for sodium and 4.6 eV for potassium clusters, and the surface thickness $a = 0.3$ Å for both type of clusters one can reproduce quite accurately the experimental systematics of ionization energies as well as their average phenomenological dependence on N [10]:

$$E_{\mathrm{io}}^{\mathrm{phen}}(N) = \frac{3}{8}\frac{e^2}{r_0 N^{1/3}} - E_{\mathrm{io}}(\infty), \quad (10)$$

where $E_{\mathrm{io}}(\infty)$ is the ionization energy equal to 2.7 eV for sodium and 2.4 eV for potassium metals.

The comparison of the theoretical and the experimental ionization energies and their average dependences on N is presented in Figure 2 for the sodium clusters and in Figure 3 for the potassium clusters. In both cases the theoretical values of $E_{\mathrm{io}}(\infty)$ are close to the average experimental
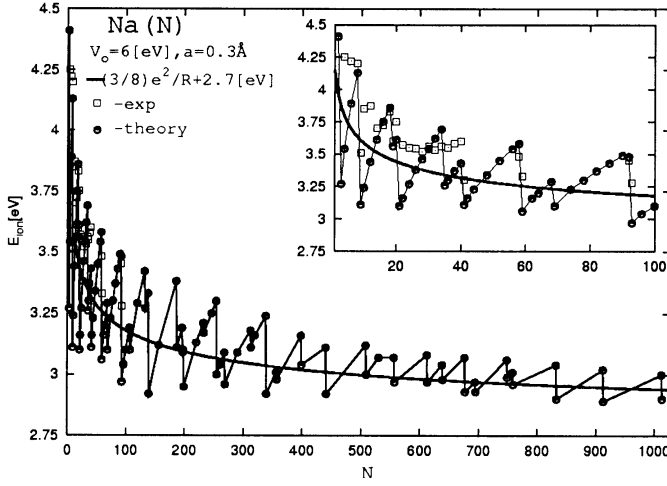
Fig. 2. The ionization energy of sodium clusters Na(N).
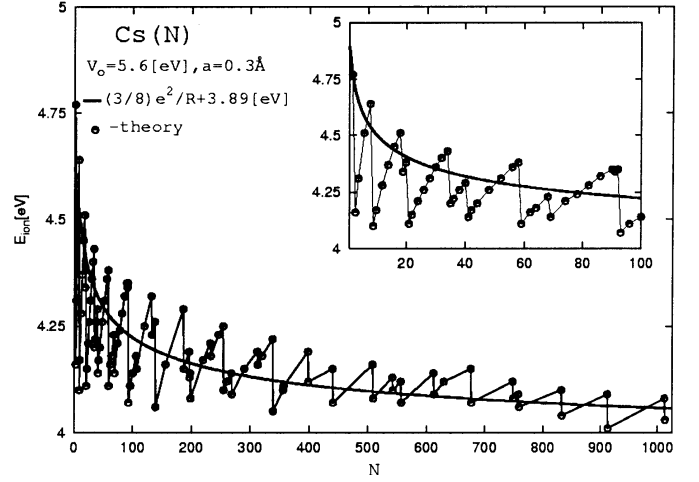
Fig. 4. The ionization energy of cesium clusters Cs(N).
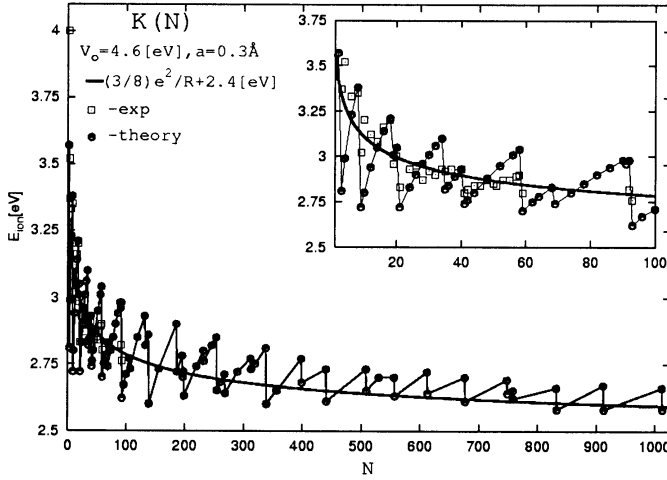
Fig. 3. The ionization energy of potassium clusters K(N).
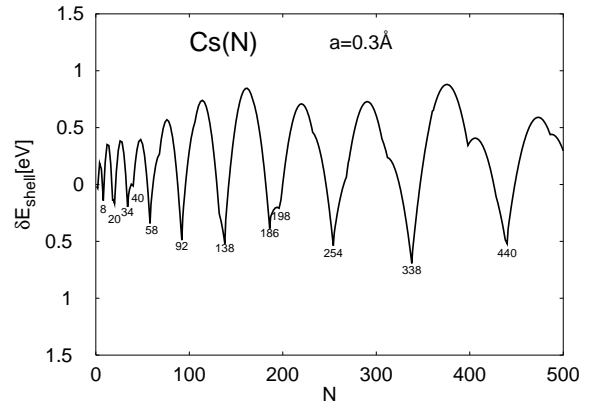
Fig. 5. The shell-correction energy and the magic numbers for the Cs(N) cluster evaluated with the surface thickness $a = 0.3$ Å.

trend, but for the variation with N of the ionization energy is significantly worse reproduced for sodium clusters than in the case of potassium ones. The experimental magic numbers for sodium and potassium as well as the other alkaline clusters are the same and equal

$$N_{\text{exp}} = 2, 8, 18, 20, 34, 40, 58, 92, 138, 198, 264, 344, 442.$$

The theoretical magic numbers closest to the experimental ones

$$N_{\text{th}} = 2, 8, 18, 20, 34, 40, 58, 92, 138, 186, 198, 254, 338, 440,$$

which are obtained with the diffuseness parameter of the Saxon-Woods potential equal to $a = 0.3$ Å.

The cesium with the ionization energy $E_{\text{io}}(\infty) = 3.89$ eV belongs also to the group of the alkaline metals, so the Cs clusters should have similar properties as the Na and K clusters. It is the main reason why we have adopted the same value of the radius shift parameter (3) $\alpha = 0.8$ performing calculations for the Cs aggregates. The theoretical systematics of the ionization energies for the Cs(N) clusters obtained with the depth of the Saxon-Woods potential equal to $V_0 = 5.6$ eV and with the surface thickness

$a = 0.3$ Å is very close to its phenomenologic estimate [10] as it can be seen in Figure 4. If the surface thickness a is larger than 0.5 Å the asymptotic behavior of the ionization energy differs significantly from the estimate made in reference [10].

In Figure 5 the Strutinsky shell correction for the compact spherical cesium clusters is plotted. The amplitude of the shell correction (5) reaches even 0.9 eV and its minima correspond to the predicted magic numbers. It is seen that the theoretical magic numbers are exactly the same as the experimental ones for $N \leq 138$ and very close to the measured ones for heavier clusters.

Varying the inner and outer surface widths of the shifted Saxon-Woods potential (1) and keeping the rest of the parameters constant we have tried to find a combination of the a_1 and a_2 widths leading to the magic numbers experimentally found in reference [4] for the C$_{60}$Cs(N) aggregates. The experimental and theoretical magic numbers from reference [5] obtained in the local density-functional theory are shown in the first two columns of Table 1. The magic numbers obtained in reference [6] for the square well potential are printed in the third column. In columns 4–6 we have displayed the magic numbers obtained with the

Table 1. Comparison between the magic numbers obtained in some theoretical models with their experimental values for $C_{60}Cs(N)$. The single particle potential thickness parameters a_1 and a_2 are in Å units.

			a_1, a_2 0.1, 1.6	a_1, a_2 1.6, 0.1	a_1, a_2 0.3, 0.1
Exp. [4]	[5]	[6]			
1	2	3	4	5	6
12 ± 0	14	14	14	14	14
27 ± 1	24	24	24	24	24
33 ± 1	38	38	38	38	38
44 ± 1					
61 ± 1	58, 64	58	56	64	64
98 ± 1	96	86, 96	86	96	96
146 ± 2	136	136	122, 136	138	136
198 ± 0	192	186, 192	184	202	192
255 ± 5	258	258	248, 258	258, 272	258
352 ± 10	338	336	336	338, 362	338, 344
445 ± 10	434	434	428	444, 466	444

potential (7) for different sets of the surface thicknesses. We begin with the outer surface thickness a_1 significantly larger than the inner one (a_2) in column 4 and we take an opposite choice of the thicknesses in column 5. It is seen that, in spite of the dramatic change of the parameters, the predicted magic numbers for the lighter clusters do not differ significantly. More pronounced differences are found for the middle mass and heavy Cs clusters. We follow the suggestion made in reference [5] when evaluating the positions of the magic numbers in $C_{60}Cs(N)$ and assume that 6 electrons are accumulated in the fullerene core.

There is no reason why the parameter a_1 in equation (7) for $C_{60}Cs(N)$ should not be equal to the parameter a in equation (1) for the compact cluster. So, in the following, we have restricted our model and we keep $a_1 = 0.3$ Å and we change only the inner surface thickness. The magic numbers closest to the experimental data obtained with the above restriction are shown in the last column of Table 1. An example of evaluated shell corrections for $C_{60}Cs(N)$ clusters is plotted in Figure 6. The minima of δE_{shell} correspond to the magic numbers predicted by our model when one take into account six electrons being inside the C_{60} core. One can observe some differences in the positions of the minima in comparison with Figure 5. This is due to the effect of the inner potential wall originating from the fullerene core. The amplitude of the shell correction for the $C_{60}Cs(N)$ aggregates exceeds even 1 eV and its average value is larger than for the compact clusters.

4 Summary

The phenomenological Woods-Saxon potential with an repulsive inner core describes relatively well the values of the magic numbers observed in the abundance of the
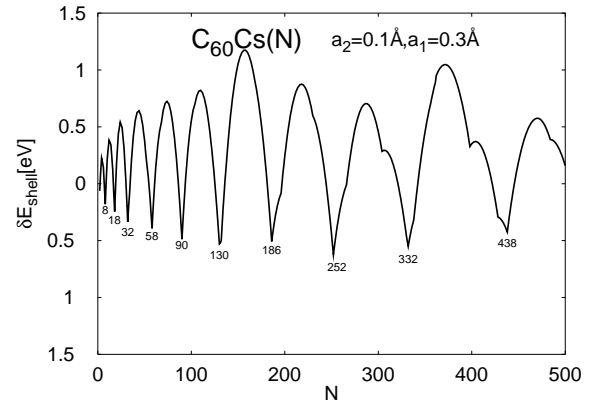
Fig. 6. Shell-correction energy and the magic numbers for the $C_{60}Cs(N)$ cluster evaluated with the surface thickness $a_1 = 0.3$ Å and $a_2 = 0.1$ Å.

$C_{60}Cs(N)$ clusters. We have shown how strongly the structure of the single-particle electron levels changes with the thickness of the metal layer covering the spherical core.

The results of our investigation could be also important for practical or even technological applications, because we indicate how one can tune in an almost continuous way the eigenenergies of electrons. In other words we give a prescription how to change the optical response of thin metallic layers covering arbitrary spherical cores made *e.g.* from insulator or other material with significantly different properties, by changing the thickness of the layer or the core size.

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