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Stability of metallic hollow cluster systems: Jellium model approach

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It is discussed that the quantum stability of a metallic cluster system with respect to the variation in the cluster shape transforms a spherical volume distribution of ionic charge core of the cluster into a spherical hollow configuration. Calculations are performed within the jellium model approach based on the Hartree-Fock theory and also within the local-density approximation. It is demonstrated that for such spherical cluster systems, there are two stable states characterized by the different distribution of the positive charge of the ionic core. One of the states corresponds to a spherical charge distribution of the ionic core uniform over the entire cluster volume. The second fullerenelike stable state arises when positive charge is uniformly distributed over a spherical shell of a certain width.

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I. INTRODUCTION

During the last decades investigations, both experimental and theoretical, of small cluster systems achieved a significant progress. This is a result of development of modern experimental techniques allowing one to deal with beams of clusters of a certain content, mass and charge, as well as to perform experiments just with single clusters placed in Penning traps. Thus, there were investigated clusters of the very different content ranging from simple metals being homogeneous in structure to the ones that are built of complex multiatomic molecules [1–7].

From the physical point of view, cluster systems are of significant interest because clusters differ in properties from both single atoms and the solid state acquiring some properties being typical to both of the systems. The physical characteristics of clusters depend significantly on the type of constituent atoms and their number N, i.e., are driven by the quantum finite-size effects. The understanding of principles of variation in the cluster properties deepens our fundamental knowledge about the matter organization at the nanoscale and, at the same time, it opens new ways for the utilization of this fundamental knowledge in various applications [2,3,6].

A special attention in the investigation of small atomic complexes is devoted to metal clusters. This happens because (i) metallic clusters are of great importance for numerous applications, (ii) the electronic structure of metallic clusters can be theoretically understood and described relatively easily (see, e.g., [2,7–13]), and also it can be studied experimentally. Experimental investigations of the electronic structure, optical properties, intercluster interactions and interactions with other particles, fusion and fission processes have been complimented by the development of novel theoretical models [2,7–27] as well as by the application of existing methods of the many-body theory. The modern quantum chemistry methods allow one to describe with a sufficient accuracy the systems consisting of relatively small number of atoms [13–16]. The use of model approaches allows one to understand properties of a system of much bigger size [24,28]. Solutions of numerous problems in the atomic cluster physics are based on the so-called jellium model [1–8,10,12,21] assuming that the delocalized valence electrons move within the cluster in a collective field created by themselves and by the jellium distribution of the ionic charge. In the simplest case, the distribution of the ionic charge is considered in a form of the uniformly charged volume sphere.

The investigation of stability and electronic structure of hollow atomic cluster systems is also of a significant interest. In recent years, the main focus in this direction was placed on the investigation of fullerenes with different number of carbon atoms (C_{20}, C_{60}, C_{70}, and etc.) [6,7]. There were also observed experimentally other hollow cluster systems, e.g., Au_{16-18} [29]. For larger gold clusters, the icosahedral structure of Au_{32} was theoretically predicted [30]. The molecule C_{60} is probably the most famous example of a hollow highly symmetrical icosahedral structure being close to spherical. It was shown that the fullerene C_{60} can be treated as a spherical shell with the thickness of a few Å [31]. For the calculation of the fullerene electronic structure, the jellium model has also been used [32–35]. In this case, the ionic core of the fullerene is treated as a uniformly charged spherical shell of a finite width. The investigation of stability of such hollow cluster systems and comparison of their properties with those for the corresponding volume-filled clusters is of a significant interest because the abundance of the hollow cluster structures is a general phenomenon being observed for different types of constituent cluster atoms or molecules (carbon, gold, water, etc.). So the understanding of the origin of the stability of such quantum systems is a multifaceted problem of general interest and importance.

The aim of this work is to investigate the stability of cluster systems with respect to the variation in their geometry resulting in the transformation of a spherical volume cluster into a spherical cluster shell.

For this purpose, we apply the jellium model for neutral spherically symmetric clusters. The delocalized valence electrons are treated in the single-particle Hartree-Fock (HF) approximation and also within the local-density theory ac-

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counting for many-electron correlations. The atomic systems of units $m=e=\hbar=1$ is used.

II. THEORETICAL MODEL

A. Jellium model

The jellium model treats a metal cluster as a sum of the two interacting subsystems: the valence electron subsystem and the subsystem of positively charged ionic core. The valence electrons move in the field created by all the cluster ions. Within the ordinary jellium model, the detailed ionic structure of the cluster is smeared out and substituted by the uniform spherically symmetric distribution of the positive charge. The potential generated by the uniform spherical distribution of the ionic core of the radius R_0 reads as

$$U_{core}(r)=\begin{cases}-\dfrac{Z}{2R_0}\left[3-\left(\dfrac{r}{R_0}\right)^2\right], & r\le R_0\\ -\dfrac{Z}{r}, & r>R_0,\end{cases} \tag{1}$$

where Z is the charge of the core (for neutral cluster Z is equal to the number of delocalized valence electrons N, coinciding with the number of atoms for clusters of monovalent elements), the core radius R_0 depends on the number of atoms in the cluster as $R_0=r_sN^{1/3}$, where r_s is the average distance between atoms in the bulk material $r_s=(\frac{3}{4\pi\rho})^{1/3}$, ρ is the density of the positive charge distribution.

The potential of a uniformly charged spherical shell with the external radius $R_{\max}$ and the internal radius $R_{\min}$ has the following form:

$$U_{core}(r)=\begin{cases}-\dfrac{Z}{r}, & r>R_{\max}\\ -\dfrac{Z}{2(R_{\max}^3-R_{\min}^3)}\left[3R_{\max}^2-r^2\left(1+\dfrac{2R_{\min}^3}{r^3}\right)\right], & R_{\min}<r<R_{\max}\\ -\dfrac{3Z(R_{\max}^2-R_{\min}^2)}{2(R_{\max}^3-R_{\min}^3)}, & r<R_{\min}.\end{cases} \tag{2}$$

At a given constant density ρ and fixed number of atoms in the cluster, the internal radius $R_{\min}$ and the thickness of the cluster shell ΔR are coupled via the following relationship:

$$\Delta R=R_{\max}-R_{\min}. \tag{3}$$

$$\frac{4}{3}\pi R_0^3\rho=\frac{4}{3}\pi\rho(R_{\max}^3-R_{\min}^3), \tag{4}$$

At $R_{\min}=0$, one obtains from Eq. (2) the potential of uniformly charged volume sphere. Below the electron structure and the binding energy of the cluster are studied as a function of $R_{\min}$ or ΔR. The core density ρ or r_s is the additional parameter of the theory.

The cluster stability is defined by its total energy, being the sum of the energy of the positively charged ionic core and the energy of the electron subsystem,

$$E_{tot}=E_{core}+E_{el}, \tag{5}$$

where the electrostatic energy of the ionic core is equal to

$$E_{core}=\frac{1}{2}\int\rho_{core}(\vec{r})U_{core}(\vec{r})d\vec{r}. \tag{6}$$

For the uniformly charged volume sphere, one obtains from Eq. (6)

$$E_{core}=\frac{6}{5}\frac{Z^2}{R_0}, \tag{7}$$

and for a charged spherical shell E_{core} reads as

$$E_{core}=\frac{2Z^2}{5}\frac{[160(R_{\min}+\Delta R/2)^4\Delta R+80(R_{\min}+\Delta R/2)^2(\Delta R)^3+2(\Delta R)^5]}{[2(R_{\min}+\Delta R/2)+\Delta R]^6}+\frac{2Z^2}{2(R_{\min}+\Delta R/2)+\Delta R}. \tag{8}$$

The energy of the ionic core decreases monotoniously with the growth of the shell size. In the limit $\Delta R\to 0$ and $R_{\min}\to r_{\max}\to R_{sphere}\to\infty$, one derives

$$E_{core}\approx\frac{Z^2}{R_{sphere}}\left(1+\frac{\Delta R}{R_{sphere}}\right).$$

The electronic subsystem is treated quantum mechanically within both the Hartree-Fock approximation [17–22] and the density-functional theory [2,15,16]. The wave function of a single electron moving in a spherically symmetric field is characterized by the ordinary set of quantum numbers: the radial quantum number n_r, the orbital momentum l, its projection m, and the spin σ. For volume-filled clusters ($R_{\min}=0$) of monovalent elements, the sequence of the so-called magic numbers characterizing the sizes of clusters possessing the higher stability is as follows: $N=2$, 8, 18, 20, 34, 40, 58, 68, 70, 92, etc. These numbers correspond to the electronic shell closures in the cluster,

$$1s^2,\ 1p^6,\ 1d^{10},\ 2s^2,\ 1f^{14},\ 2p^6, 1g^{18},\ 2d^{10},\ 3s^2,\ 1h^{22}, \ldots .$$

Note that many characteristics and quantum properties of metallic clusters can be treated quite satisfactorily on the basis of the jellium model. Accounting for the cluster deformations are shown to be also very important for the clusters with the open electronic shells. In this paper, our analysis is restricted to the spherical cluster systems possessing only the closed shells of delocalized valence electrons.

B. Hartree-Fock approximation

The total HF wave function Ψ of an electronic subsystem can be represented in a form of the Slater determinant composed of single-electron wave functions $\varphi_i(x)$ being the solutions of the system of the following integral-differential equations:

$$-\frac{\Delta}{2}\varphi_i(x) + U_{core}(r)\varphi_i(x) + \sum_{j=1}^{N_e}\int \varphi_j^*(x')V_{el}(|\vec{r}\,' - \vec{r}|) \times[\varphi_j(x')\varphi_i(x) - \varphi_i(x')\varphi_j(x)]dx' = \varepsilon_i\varphi_i(x), \qquad (9)$$

where ε_i is the single-electron energy, $x=(\vec{r},\sigma)$. In a spherically symmetric field, the electron wave functions $\varphi_i(x)$ are written as a product of radial, angular-, and spin-wave functions,

$$\varphi_{nlm\sigma}(x) = \frac{1}{r}P_{nl}(r)Y_{lm}(\theta,\varphi)X_\sigma. \qquad (10)$$

The energy of electronic subsystem E_{el} is calculated using the well-known formula,

$$E_{el}^{HF} = \sum_i \varepsilon_i - \frac{1}{2}\sum_{i,j}(\langle ij|V_{el}(\vec{r},\vec{r}\,')|ij\rangle - \langle ij|V_{el}(\vec{r},\vec{r}\,')|ji\rangle), \qquad (11)$$

where $|i\rangle, |j\rangle \equiv \varphi_i, \varphi_j$ correspondingly.

C. Local-density approximation

Within the local-density approximation (LDA), the single-electron wave functions $\varphi_i(\vec{r})$ and the energies ε_i are determined from the Kohn-Sham equations [36],

$$\left[-\frac{1}{2}\Delta + V_{eff}(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r}),$$

$$V_{eff}(\vec{r}) = U_{core}(\vec{r}) + \int\frac{n(\vec{r}\,')d\vec{r}\,'}{|\vec{r} - \vec{r}\,'|} + V_{xc}^{LDA}(\vec{r}),$$

$$n(\vec{r}) = \sum_{i=1}^{N}|\varphi_i(\vec{r})|^2. \qquad (12)$$

Here $U_{core}(\vec{r})$ is the potential of the ionic core and $V_{xc}^{LDA}(\vec{r})$ is the exchange-correlation potential. The latter is represented by a sum of the exchange Dirac term and the correlation part,

$$V_{xc}^{LDA}(r) = V_x + V_{corr} = -\left(\frac{9}{4\pi^2}\right)^{1/3}\frac{1}{r_{se}(\vec{r})} + V_{corr}, \qquad (13)$$

where $r_{se}(\vec{r})=(\frac{3}{4\pi n(\vec{r})})^{1/3}$ is the local Wigner-Seitz radius for electronic subsystem. In the calculations, we have used parametrization V_{corr} that was given by Perdew and Wang in [37],

$$V_{corr}(r_s) = \varepsilon_{corr}(r_{se})\frac{1 + \frac{7}{6}1.158\,1\sqrt{r_{se}} + \frac{4}{3}0.344\,6r_{se}}{1 + 1.158\,1\sqrt{r_{se}} + 0.344\,6r_{se}}, \qquad (14)$$

$$\varepsilon_{corr}(r_{se}) = -\frac{0.147\,1}{1 = 1.158\,1\sqrt{r_{se}} + 0.344\,6r_{se}}. \qquad (15)$$

This parametrization was used in this work for the calculations within the LDA. The obtained HF and LDA wave functions were then utilized for the calculations of the total energy of the electronic subsystem.

III. RESULTS OF CALCULATIONS

For metallic clusters with the number of electrons $N=2-92$, we have calculated the electronic structure and the total cluster energy as a function of the hole radius $R_{\min}$ and the thickness of spherical layer ΔR. The results are presented in Figs. 1–5.

The dependences of the total energies per one electron on $R_{\min}$ and ΔR obtained within the HF and LDA for different clusters are shown to possess the two minima. The deepest one corresponds to the ordinary volume-filled cluster ($R_{\min}=0, \Delta R=R_{\max}$). With the growth of the cavity size, the energy of the system initially grows. However, it passes the maximum value and then goes down again as shown in Fig. 1(a). This means that with increasing $R_{\min}$, the system overcomes the potential barrier and it reaches the second energy minimum corresponding to the second stable state of the system, in which a hollow cluster is formed. The existence of the second minimum is better seen in Fig. 1(b). Here, the dependence of the total energy versus the shell thickness ΔR is shown. These calculations lead to the conclusion that within the HF approximation, a fullerenelike form of metallic clusters should possess sufficient stability.

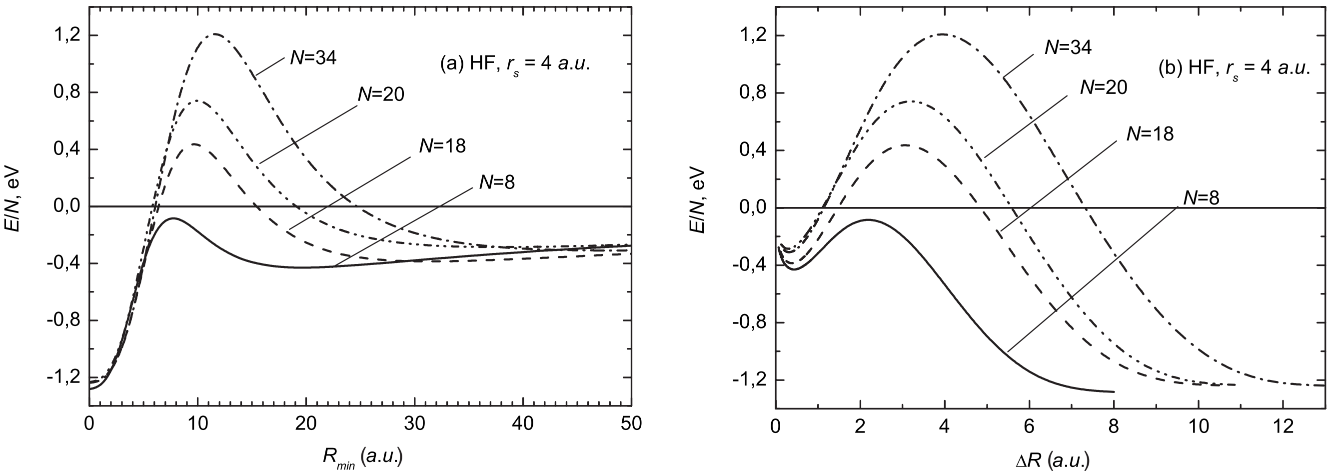

FIG. 1. Total cluster energy per atom as a function of the (a) radius R_{min} and the (b) thickness ΔR of the positively charged shell calculated within the HF approximation for different cluster sizes.

Figure 1 demonstrates that the overall behavior of the energy dependence on the shell parameters does not qualitatively change with the variation in the cluster size N. With the increase in N, the potential barrier becomes higher, and the second minimum shifts toward the larger values of R_{min} and becomes less expressed. Note that for the same density of the positive charge distribution, the second minimum arises approximately at the same shell thickness ΔR for the hollow clusters of different size.

The LDA calculations lead to a similar behavior of the total cluster energy versus the radius R_{min}. Figure 2 shows the comparison of the HF with the LDA results for clusters with $N=8$, 40, and 92. The barrier between the two minima is lower within the LDA; the minima are much deeper than those obtained from the HF calculations. This means that the many-electron correlations play the important role in the stabilization of the cluster system. Within both approximations, the second minimum arises at the same thickness of the shell independently of the cluster size: the HF value $\Delta R \sim 0.35$ a.u., LDA-$\Delta R \sim 0.5$ a.u. However, the second minimum obtained in the LDA is two times deeper than it is in the HF as seen from Fig. 2.

In the above reported calculations, we did not change the electronic configuration and kept the filling order of the single-electron energy levels the same as it is obtained for the volume-filled metal clusters,

$$1s^2 \to 1p^6 \to 1d^{10} \to 2s^2 \to 1f^{14} \to 2p^6 \to 1g^{18} \to 2d^{10} \to 3s^2 \to 1h^{22} \to \ldots .$$

With the growth of the cluster size ($N > 18$), the electron wave functions acquire one or more nodes.

For the hollow clusters, the rearrangement of electronic shell structure takes place for the cluster sizes with $N > 18$. The single-electron states without nodes become energetically more favorable than the states with one and more nodes. This can be seen from the behavior of the single-electron energies as a function of the radius R_{min}. Figure 3 shows dependences of the HF single-electron energies on R_{min} for the clusters with $N=40$ and $N=92$. The crossings of

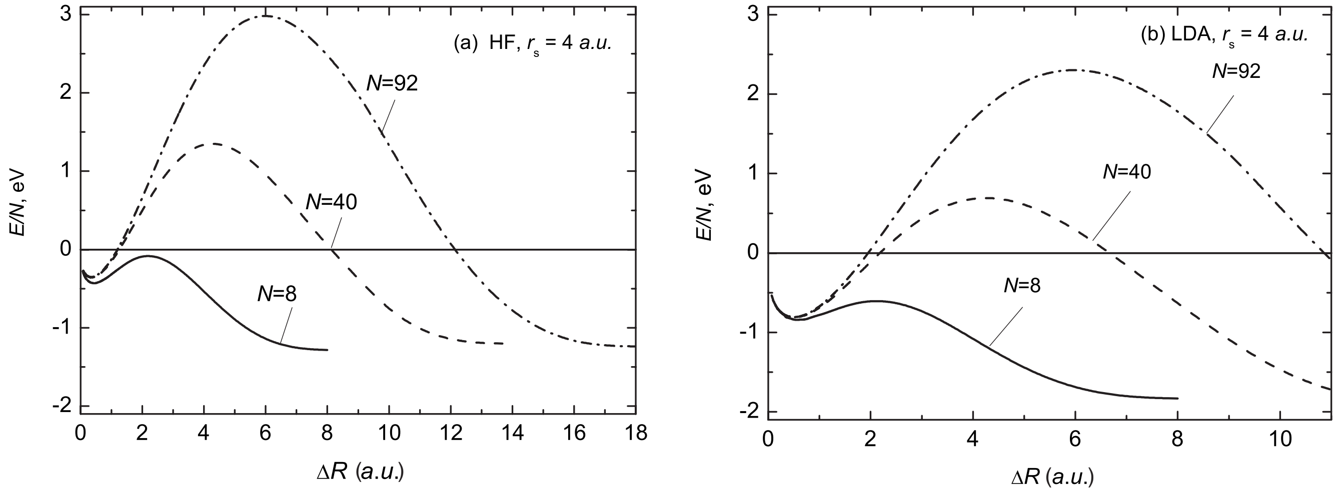

FIG. 2. Total cluster energy per atom calculated within the (a) HF and the (b) LDA for different cluster sizes at $r_s=4$ a.u.

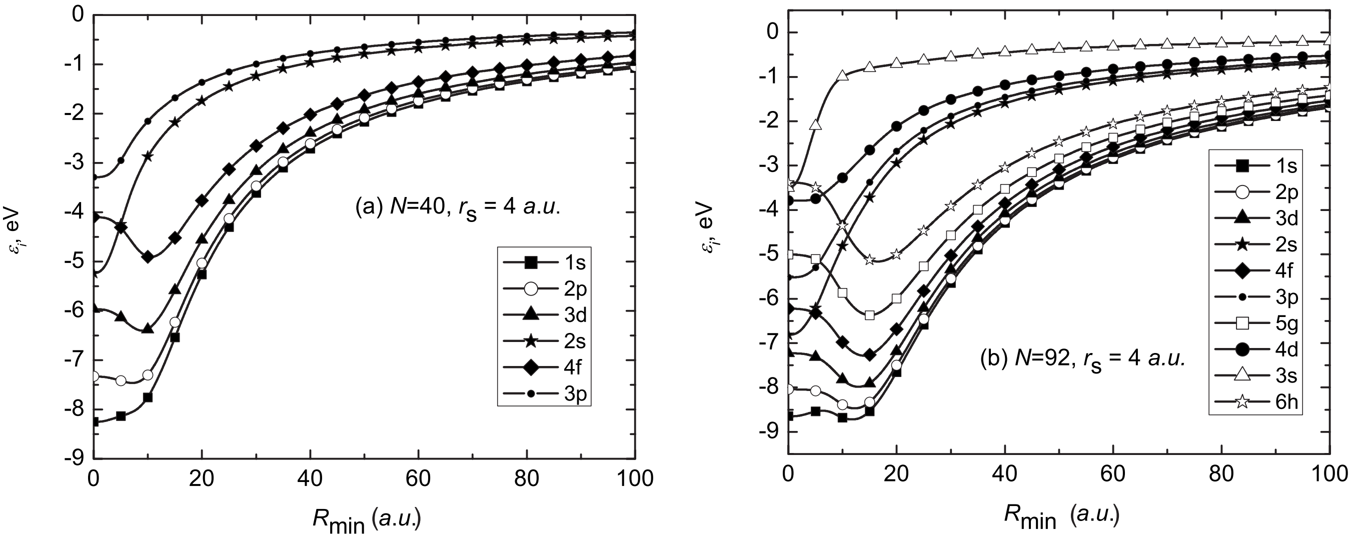

FIG. 3. HF single-electron energies as a function of R_{min} for clusters (a) $N=40$ and (b) $N=92$.

the energy levels with nodes (2s, 2p, 2d, 3s) with those without nodes demonstrate that with the growth of R_{min} it becomes energetically more favorable for the electrons to occupy the states without nodes. This means that the electronic configuration of the shell should be rearranged with the growth of its size. Earlier, the destabilization of the 2s shell in the hollow jellium has already been obtained within the density-functional calculations for hollow gold cluster Au_{18}^- [38]. The authors noted that 2s state carried too much electron density in the central region of the cluster and this increased its total energy.

Thus, for the cluster with $N=40$, there is a change in the ground-state electronic configuration $1s^21p^61d^{10}2s^21f^{14}2p^6$ to $1s^21p^61d^{10}1f^{14}1g^8$ in the vicinity of $R_{min}=5$ a.u. (see Fig. 4). For the cluster with $N=92$, there is a change in its electronic configuration from $1s^21p^61d^{10}2s^21f^{14}2p^61g^{18}2d^{10}3s^2$ $1h^{22}$ to $1s^21p^61d^{10}1f^{14}1g^{18}1h^{22}1i^{20.}$ Note that this transition takes place gradually, one electron by another.

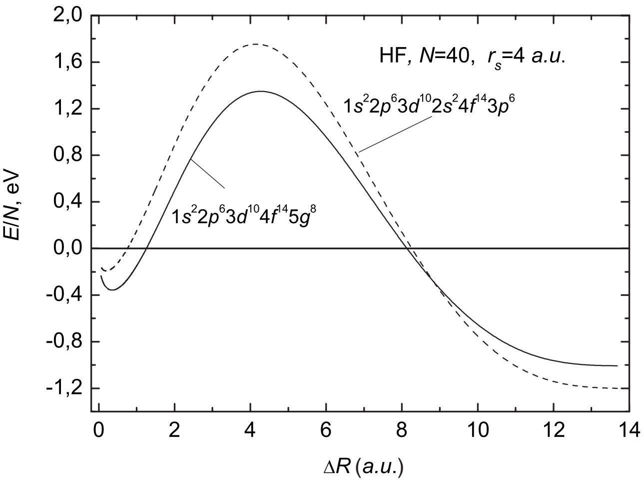

FIG. 4. Total energy per atom for the cluster with two different electronic configurations versus the spherical shell thickness: $N=40$, $r_s=4$ a.u.

Accounting for the rearrangement of the electronic structure leads to deepening of the second energy minimum, corresponding to the hollow cluster shape, and also to the shift of the minimum toward the larger values of ΔR. As seen from Fig. 4, the total energy of the cluster $N=40$ has two times deeper minimum than that calculated without accounting for the rearrangement of the electronic structure.

The above discussed results have been obtained for the constant density ρ of the positive ionic charge distribution characterized by the parameter $r_s=4$ a.u. corresponding to the average distance between atoms in the bulk sodium [2]. We have also calculated the total energies of hollow clusters with different densities, $r_s=2-6$ a.u. The results on the HF total energies obtained for the cluster with $N=40$ and different parameter r_s are presented in Fig. 5. For the volume-filled cluster ($R_{min}=0$), the total energy has a minimum at $r_s=4.5$ a.u. in the correspondence with the earlier obtained results [18]. As seen from Fig. 5, with the decrease in density ρ (increase in r_s), the potential barrier between the volume-filled cluster state and the stable state of the hollow cluster also decreases; the second minimum shifts toward larger values of ΔR and becomes deeper.

The performed LDA calculations demonstrate the essential contribution of many-electron correlations to the total energy of both the volume and the hollow cluster system. Besides that also the exchange interaction between electrons plays an important role in the stabilization of the cluster system. Calculations for the systems without the exchange interaction, for example, with the electronic configuration 1s and $1s^2$, show the absence of the potential barrier and the energy minimum corresponding to the stable hollow cluster state. Figure 6(a) shows the dependence of the HF total energy for the systems with $N=1$ and 2 with the radius of the hole R_{min}. The small nonmonotonic behavior of the total energy is related to the spill out effects. The comparison of the results of the total-energy calculations obtained within the HF and the Hartree approximations for the small cluster with $N=8$ is presented in Fig. 6(b). It is seen that without accounting for the exchange interaction, the volume cluster has only

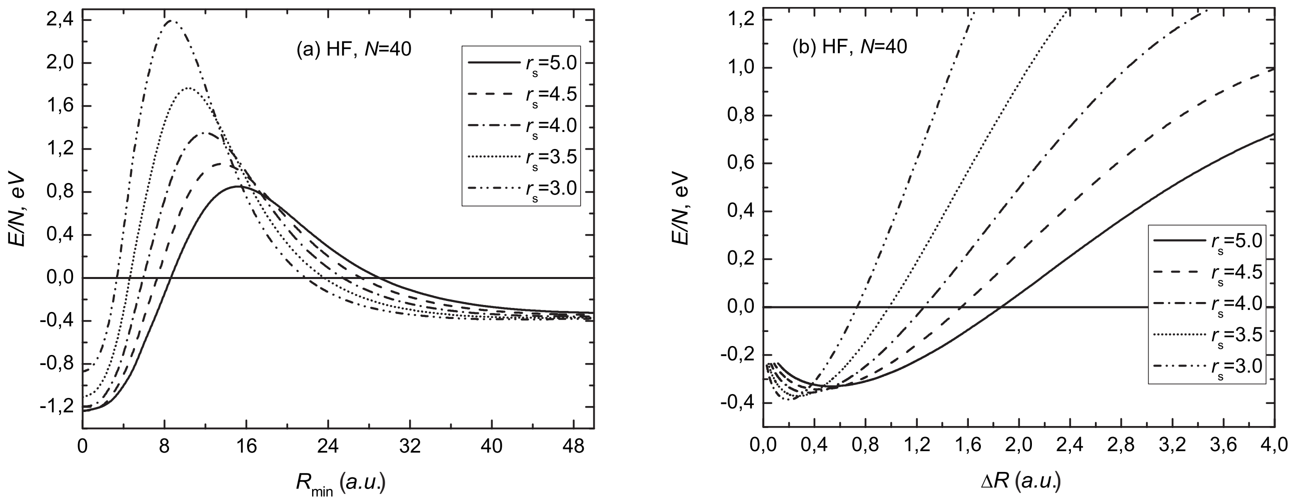

FIG. 5. HF total energy per atom as a function (a) $R_{\min}$ and (b) ΔR for the different densities of positive core r_s.

a tiny bonding energy and the stable state for the hollow cluster vanishes almost completely.

IV. CONCLUDING REMARKS

The aim of this work is to investigate the stability of the volume and the hollow metallic cluster systems within the spherical jellium model and the many-body theory accounting for the shell effects of delocalized valence electrons. The calculations performed prove that besides the ordinary volume-filled cluster, there exists an additional stable state of the system corresponding to a hollow cluster configuration. The thickness of the cluster shell practically does not depend on its size but is sensitive to the approximation in which it is calculated. The two stable states of the cluster system corresponding to the two different geometries are separated by the potential barrier which depends on the cluster size and the density of the ionic charge distribution.

The main features of the obtained total-energy dependence on $R_{\min}$ can be related to the different behavior of the energy of the ionic core and the energy of the electronic subsystem on $R_{\min}$ arising due to the spill out effect. The exchange interaction and many-electron correlations play also quite essential role in the formation of stability of a hollow metallic cluster system lowering the total energy of the system.

The analysis performed in this work can be extended in many different ways. Thus, it can be extended on the deformed jellium cluster systems. Also, it is certainly of interest to account for the details of structure of the ionic cluster core. Problems similar to those discussed in this work arise in the physics of superheavy nuclei as well as in the physics of exciton and electron-positron quantum droplets. We leave these questions open for further considerations.

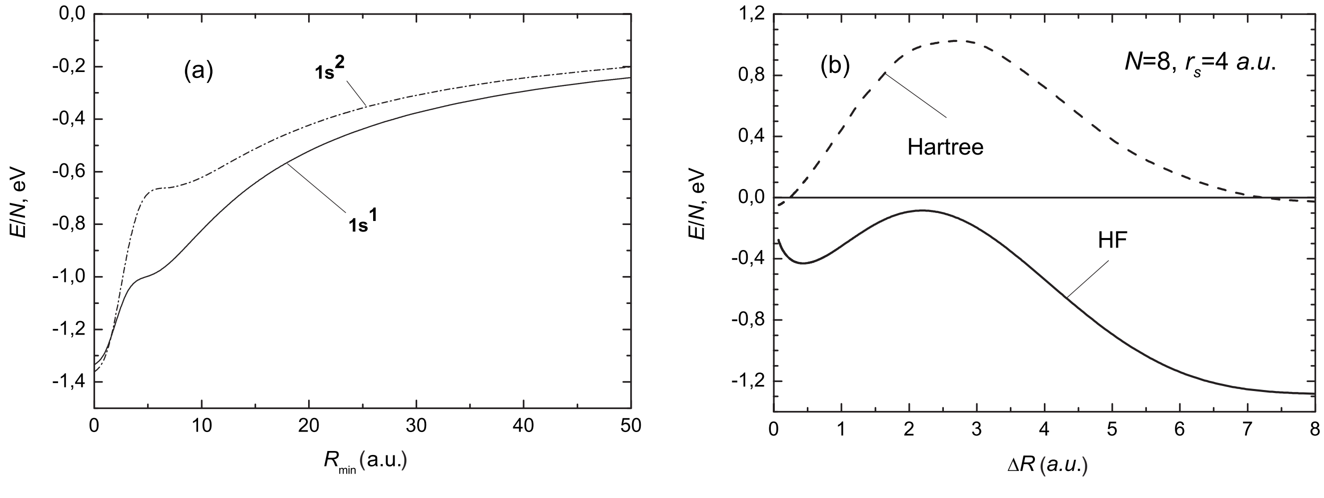

FIG. 6. Total cluster HF energy per atom for (a) $N=1$ and 2 versus the radius $R_{\min}$ and the same for (b) $N=8$ versus the shell thickness parameter ΔR obtained within the HF and Hartree approximations.

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