Solid State Communications 147 (2008) 323–326

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Magic number 32 and 90 of metal clusters: A shell jellium model study

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ARTICLE INFO

Article history:
Received 14 January 2008
Received in revised form
16 March 2008
Accepted 24 May 2008 by S. Scandolo
Available online 5 June 2008

PACS:
73.22.-f
71.15.Mb

Keywords:
A. Metal clusters
D. Electronic states

ABSTRACT

Motivated by the recent discovery of cage-like metal clusters, a shell jellium model is proposed to study the stability of cage-like clusters, using the density functional theory (DFT) with local density approximation (LDA). Based on the shell jellium model, it is found that certain metal clusters of a special number of electrons are even more stable than the sphere-like clusters described by the conventional spherical jellium model. The result shows two new magic numbers 32 and 90. These results provide us with a straightforward explanation for the stability of 32-electron clusters.

1. Introduction

The spherical jellium model has been greatly successful for explaining experimental abundances of simple and noble metal clusters since the pioneering work of Knight on alkali-metal clusters [1]. In the framework of a spherical jellium model, the valence electrons are assumed to be delocalized and moving freely in the background of a homogeneously distributed positive charge of ion core [1–7]. By the self-consistent solution of a Kohn–Sham equation, certain electron numbers for electronic shell closure have been found, e.g., 2, 8, 18, 20, 34, 40 …, at which the cluster shows high stability. These numbers are called magic numbers. In the past two decades, such magic numbers have been observed in various alkali and simple metal clusters, such as sodium, potassium [5] and aluminum [8]. Furthermore, they were also detected in noble metal clusters [9,10]. Succedent modification of the spherical jellium model had shown its own success. For example, some fine structures in abundance spectrums were explained by ellipsoidal deformation of the jellium sphere [11]. Besides, Reimann et al. successfully found a series of magic triangular and tetrahedral clusters and predicted some new electronic magic numbers of tetrahedral ground states [12], using an *Ultimate* Jellium Model (UJM) which allowed the jellium shape to be relaxed [13]. These results are consistent with the recent experimental discovery of tetrahedral pyramidal Au_{20} [14].

2. Computational details

Cage-like clusters composed with only Au atoms had been theoretically predicted and some of them had been experimentally observed and confirmed by further theoretical calculation [15–21]. The ground state structure of Au_{32} could be a perfect cage with I_h symmetry, which has an energy gap as wide as 1.5 eV [15,16], comparable with 1.8 eV of C_{60} [22]. Au_{16} [18], Au_{42} [19] and Au_{50} [20,21] were also found to have similar cage-like structures. The electronic properties of these cage-like structures cannot be described by the conventional jellium model [1,5–7], because the positive ions are located in a shell. In fact, it is intriguing whether the concept of the jellium model still works for cage-like metal clusters. In this paper, we propose a shell jellium model within the DFT scheme, resulting in the new magic numbers 32 and 90.

As shown in Fig. 1, our shell jellium model replaces the metal ions with a uniform positive charge background in a hollow spherical shell while the specific ionic structure is ignored. As in a conventional jellium model, only valence electrons are considered to interact with the positive background. Apparently, three independent parameters are needed to define the model, i.e., valence electron number N, electron density ρ_+ and inner radius r_{in} of the spherical shell. For the positive shell jellium charge, the classical electrostatic potential can easily be calculated. We have carried out self-consistent calculations with LDA approximation of exchange-correlation energy and the wave-function is expanded in plane waves with an energy cutoff ~250 eV, which is high enough for our local potential. The ion interaction energy is defined as the electrostatic energy of the positive charge shell.

We choose Au as the sample element to apply our shell jellium model, where the averaged valence electron density ρ_+ in Au bulk

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doi:10.1016/j.ssc.2008.05.039

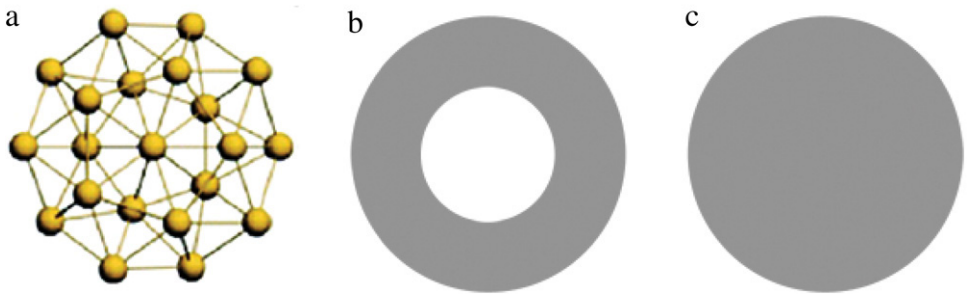

Fig. 1. (a) Au_{32} cage as representative of cage-like metal clusters. The cross sections of shell jellium model (b) and spherical jellium model (c).

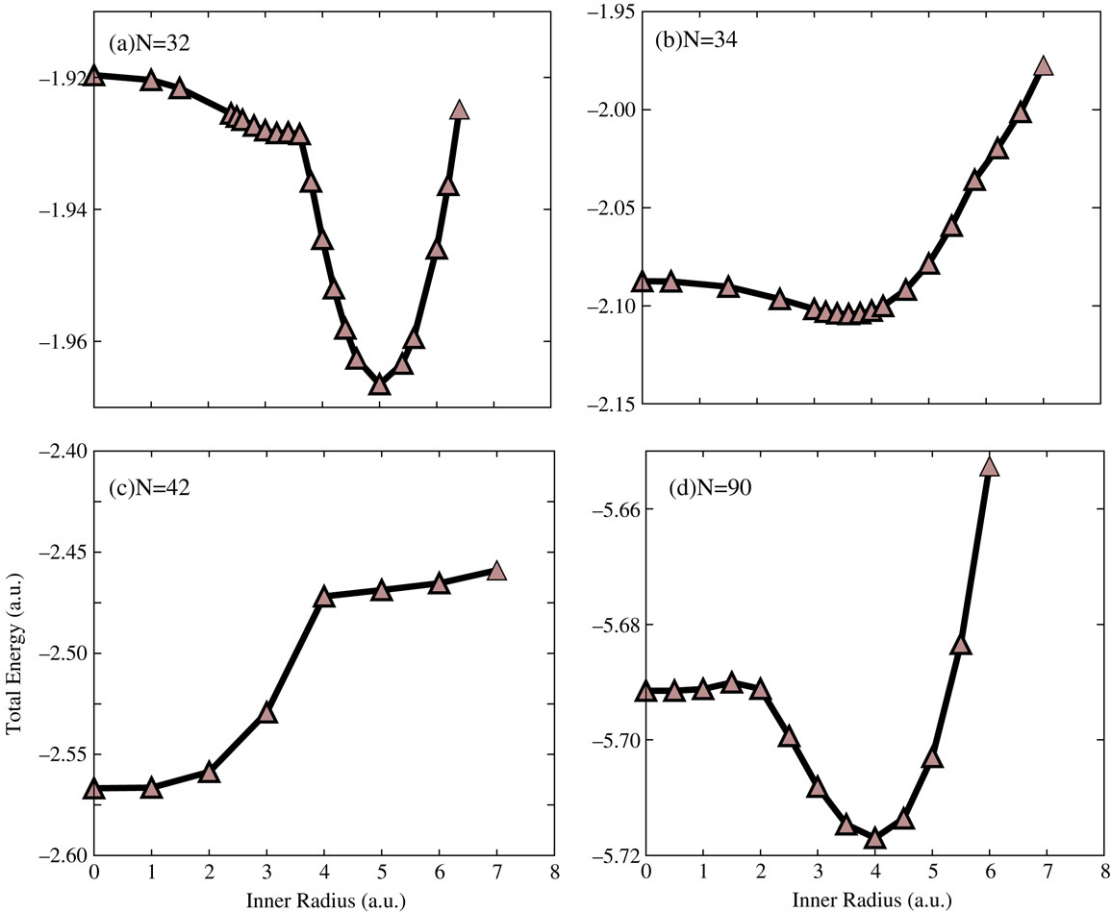

Fig. 2. Total energy of ground states of Au clusters as a function of inner radius from the shell jellium model. N is the number of electrons. The energy minimum corresponds to the ground state structure of the cluster.

is adopted. For a specific electron number N and inner radius r_{in}, the corresponding electrostatic jellium potential $V_{\text{jel}}(\rho_+, N, r_{in})$ is constructed and total energy could be expressed as

$$E[\rho_+, N, r_{in}, \rho] = T_s[\rho] + \int \rho(r) V_{\text{jel}}(\rho_+, N, r_{in}) \mathrm{d}r + \frac{1}{2} \int\int \frac{\rho(r)\rho(r')}{|r - r'|} \mathrm{d}r\mathrm{d}r' + E_{xc}[\rho] + E_{II}[\rho_+, N, r_{in}]$$

where the different terms on the right side are the kinetic energy of non-interacting electron gas, the interaction energy between valence electrons and positive charge background, the classical Coulomb energy between electrons, the exchange-correlation energy and ion interaction energy, respectively. Solving the variational equation

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{jel}}(\rho_+, N, r_{in}) + \int \frac{\rho(r)}{|r - r'|} \mathrm{d}r' + \frac{\delta E_{xc}}{\delta \rho(r)} \right] \psi_i(r) = \epsilon_i \psi_i(r)$$

with conjugate-gradient minimization optimizes the total energy with respect to r_{in} for the system with N atoms.

3. Results and discussion

Total energy dependence on the inner radii of selected electron numbers is shown in Fig. 2. It can obviously be seen that the 32-electron cluster favors a cage-like structure with an inner radius about 5 *a.u.*, in great agreement with our previous density functional calculation [15]. A similar result is obtained for $N = 90$.

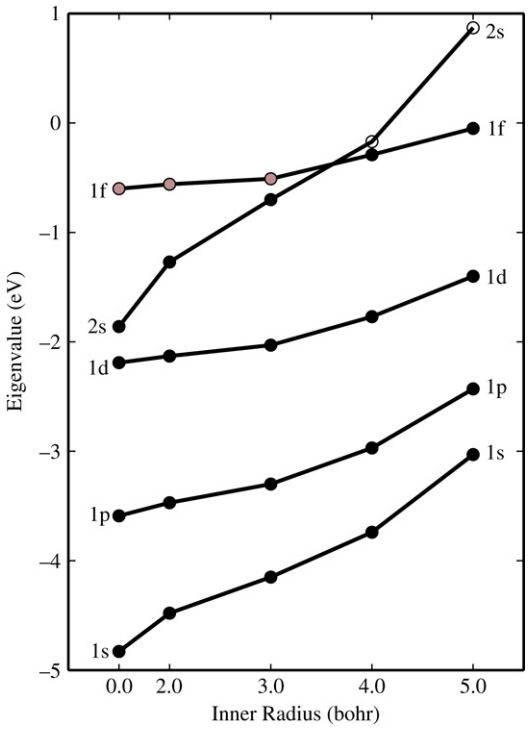

Fig. 3. Electronic energy levels of Au_{32} derived from shell jellium model from various inner radii. The solid dots show the occupied states. The empty cycles show the unoccupied states. The gray circles show partially occupied states. The crossover of 1f and 2s levels results in electron number 32 being magic.

An extensive search of electron numbers up to 110 shows the cage-like structures obviously appear when the number of electrons of the clusters equals 32 or 90. Interestingly, based on this model, a 34-electron cluster also favors a cage-like structure. However, in comparison with a 32-electron cluster, both the energy decrease related to its compact counterpart and inner radius are smaller.

It is interesting to know the reason why such numbers 32 and 90 result from the shell jellium model. In Fig. 3, we show the different electronic energy levels vary with inner radii for electron number $N = 32$. One can see that all electronic energy levels increase monotonously with inner radius r_{in}. Especially, s level varies most rapidly. However, in Fig. 2, the change of total energies with r_{in} is not monotonous for $N = 32, 42$ and 90 due to the contribution of positive charge interaction. The crossover of 2s and 1f level, which is due to the hollow cage shape of the cluster, opens a HOMO–LUMO electronic energy gap for $N = 32$. In this case, a 32-electron cluster has a mostly closed outer electronic shell, resulting in a new magic number. The case of $N = 90$ is similar, where the 3s level crosses 1h level, also resulting in a HOMO–LUMO gap.

The underlying physics for the crossover between 2s and 1f is simple. The wave-function of s electrons is exponential-like and has its maximum at the center of the clusters. In the shell jellium model, the density of positive charge near the center is small, which influences s orbital more than p, d, f orbital. In fact, electrons with lower angular momentum are more sensitive to the hollow shape, as shown in Fig. 3. In this respect, our shell jellium model is analogical to the $2(l + 1)^2$ rule of spherical aromaticity in I_h symmetrical fullerenes [23]. As an interesting issue, a class of endohedral clusters $[An@Pb_{12}]^x$(An = Pu, Am, Cm; $x = 0, +1, +2$) of I_h symmetry, with an actinide atom enclosed in plumbaspherene [24], was also reported recently [25]. These cluster compounds, pronounced as 32-electron systems, have wide energy gaps and could be potential candidates of chemical inert clusters. In such case, all 32 electrons fill up the atomic 6s, 6p, 5d, 5f shell of the center atom completely.

The new magic number $N = 32$ predicted based on the shell jellium model is in consistent with the Au_{32} cage found recently. As for $N = 90$, one could imagine a perfect Au_{92}^{2+} cage obtained by placing 32 gold atoms on 32 mini surfaces of Au_{60} cages with I_h symmetry, which contains 90 valence electrons and keeps the I_h symmetry. In our shell jellium model, this cage-like Au_{92}^{2+} with electronic shell closure and geometrical quasi-planar structure, which is favorable for Au element [15], should be geometrically stable. Density functional calculation shows that this Au_{92}^{2+} has a considerable HOMO–LUMO gap indeed. However, its total energy is higher than its space-filling counterpart [16] due to the geometrical effect. It is expected that possibly larger cage-like structures could also be unstable. Therefore, cage-like Au_{32} might be a special case, which is accidentally stable because the electronic shell is closed, while 32 atoms also form a complete atomic shell with the high symmetry of a icosahedron.

The second-order derivative of the total energy $\Delta_2(N), E(N+1) + E(N-1) - 2E(N)$ is calculated to get the abundance spectrum. Total energy per atom, $\Delta_2(N)$ and corresponding inner radii versus the number of electrons are shown in Fig. 4, together with the results of the spherical jellium model for comparison. From $\Delta_2(N)$, one can see the new magic number 32 and 90 clearly resulting from the shell jellium model. The total energy per atom shows most of the ground state structures around number of electrons 32 and 90 are also hollow cage-like from shell jellium model, but both their inner radii and energy decrease related to their compact counterparts are smaller than $N = 32$ and 90.

To confirm the validity of our results, we calculated the electronic structures of several cage-like 32-electron clusters not consisting of any Au atoms. All of our first principles calculations are based on the density functional theory with local density approximation implemented in VASP code [26]. Only the valence electrons are treated explicitly and their interaction with atomic ions are described by PAW pseudo-potentials. For a cage-like Hg_{16} cluster with the same T_d structure as Au_{16} [18], full geometrical relaxation is applied and the results shows that this Hg_{16} cage with T_d symmetry(referred as T_d–Hg_{16} in the following) is really a metastable structure with a HOMO–LUMO gap as wide as 1.8 eV. It is intriguing that similar results could also be obtained for 32-electron T_d–Mg_{16} cluster, I_h–Ag_{32} cluster and even I_h–Na_{32} cluster made of the most-metallic element sodium. All of them show the metastable structures with considerable HOMO–LUMO gaps. Meanwhile, the calculated results show that all the cage-like metal clusters with 32 electrons do indeed have HOMO–LUMO gaps, which is in consistent with the shell jellium model. However, unlike I_h–Au_{32} cluster with strong electronic relativistic effect, the cage-like metal clusters listed above are not their ground state structures due to the geometrical effect.

4. Conclusion

In summary, we have studied the stability of metal clusters by using the shell jellium model. We have found two new magic numbers $N = 32, 90$ corresponding to the cluster of hollow cage shape. These numbers are different from what is predicted by the conventional jellium model. The stability of the recently found Au_{32} cage can be quantitatively understood in the framework of the shell jellium model.

Acknowledgments

This work was supported by the National Science Foundation of China, the special funds for major state basic research and Shanghai Project. The computation is performed in the Supercomputer Center of Shanghai and Fudan supercomputer center.

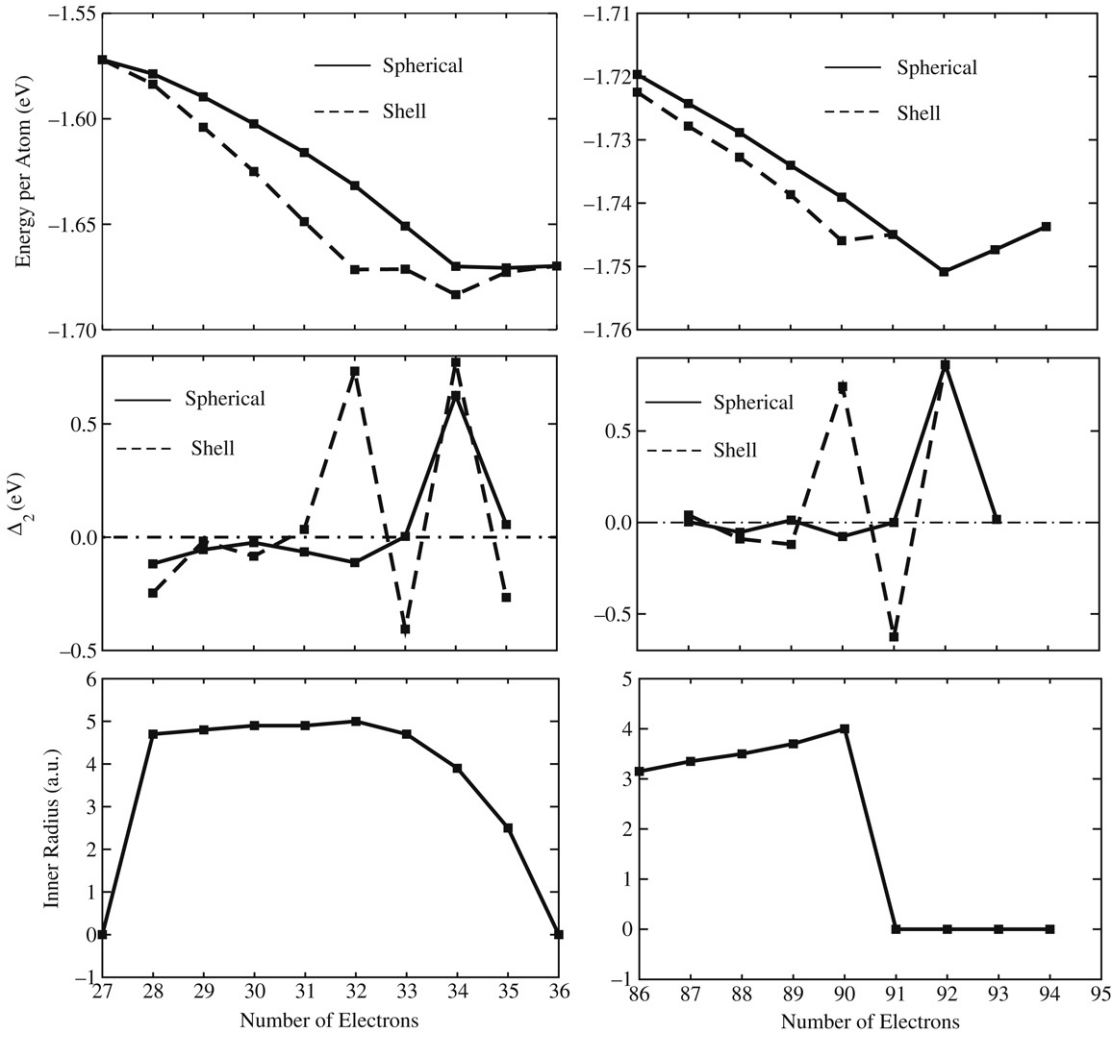

Fig. 4. Results from spherical and shell jellium model: Total energy per atom (up panel), $\Delta_2 = E(N+1) + E(N-1) - 2E(N)$ of the ground states of Au clusters (middle panel) and corresponding inner radius (lower panel). New magic numbers 32 and 90 can clearly be observed.

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