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Density Functional Study of Structural and Electronic Properties of Free Gold and Silver Clusters

BENKRIMA YAMINA[1,*] and OUAHAB ABDELOUAHAB[2]

[1]Laboratoire des Énergies Nouvelles et Renouvelables Dans les Zones Arides LENREZA, University of Ouargla, Ouargla 30000, Algeria
[2]University of Biskra, Biskra 07000, Algeria

*Corresponding author: E-mail: b-amina1@hotmail.fr

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Structural and electronic properties of gold and silver clusters with number of atoms "n" varying from 3 to 10 are investigated by the density functional theory (DFT) with generalized gradient approximation implemented in the SIESTA method. In the optimized lowest energy structures of gold and silver clusters, new lowest energy structures are reported. For each size, the Average bond lengths, binding energies, HOMO-LUMO gap, second-order difference of energy, ionization potential and the density of states were calculated. The lowest energy structures for ($n \leq 5$) clusters are planar where the stability showed that the highest value in the binding energy is present in gold. Vertical ionization potential and HOMO-LUMO gap show obvious odd-even oscillations, indicating that $Ag_{4,6,8,10}$, $Au_{4,6,8,10}$, clusters keep high stabilities in comparison with their neighboring clusters. The variation of second-order difference of energy shows stabilities of gold and silver clusters. Analyzing the density of states, it is found that the gold is higher density of states near Fermi level than silver.

Keywords: Density functional theory, Cluster, Atomic structure, Electronic structure, Density of states.

INTRODUCTION

Clusters can be formed by most of the elements in the periodic table. Gold and silver have similar valence configuration $5d^{10}6s^1$ and $4d^{10}5s^1$ respectively. From the theoretical these coinage metals offer the important advantage of a completely filled *d* shell. The determination of the electronic structure and properties of clusters, in particular metal clusters, is still in the focus of active research. Noble metal nano clusters exhibit lower toxicity, they stretches the gap between the microscopic and macroscopic materials [1,2]. Properties of clusters strongly depend on size. The study of structure of metal clusters is very important because the problems in investigation of metal clusters are the limited data on their geometry, although its bulk material is chemically inert. In recent years, the study of clusters has become an increasingly interesting topic of research in both physics and chemistry, due to their interesting structural and electronic properties and promising technological applications in catalysis [3-5], nanotechnology [6-8]. Gold and silver clusters have been investigated experimentally and theoretically [9-17]. In this paper, geometrical and electronic structures of Ag_n, Au_n clusters up to ten atoms are systematically investigated using density functional theory (DFT). We find that the geometrical structures of gold and silver clusters show interesting trends.

COMPUTATIONAL METHODS

The total energy calculations in this study were based on the density functional theory [18,19], within the generalized gradient approximation (GGA) [20] parameterized by Perdew, Burke and Ernzerhof (PBE) [21] using the plan-wave pseudo potential method. All the calculations were performed with the SIESTA *ab initio* simulation package [22,23]. The Kohn-Sham orbitals were expanded in numerical pseudo atomic double zeta polarized basis sets (DZP) and electron-ion interaction was included by employing norm-conserving pseudo-potentials [24]. The pseudo potentials were generated using the ATOM code [25] within the Troullier-Martins scheme [24].

A cubic super cell of 20 Å length was used in the calculation to ensure negligible interactions between image clusters. Due to the large cell used in the calculated, the Brillouin zone integration was approximated by a single point. The cut-off energy was set to 200 Ry. Our self consist-field (SCF) calculations in total energy were carried out with convergence criteria of 5×10^{-4} eV and the maximum ionic displacement tolerance within the cluster was set to 0.05 Å. The optimized structures were obtained when the atomic forces were smaller than 0.005 eV/Å. All the clusters Ag_n and Au_n considered in this study were subject to simulated annealing

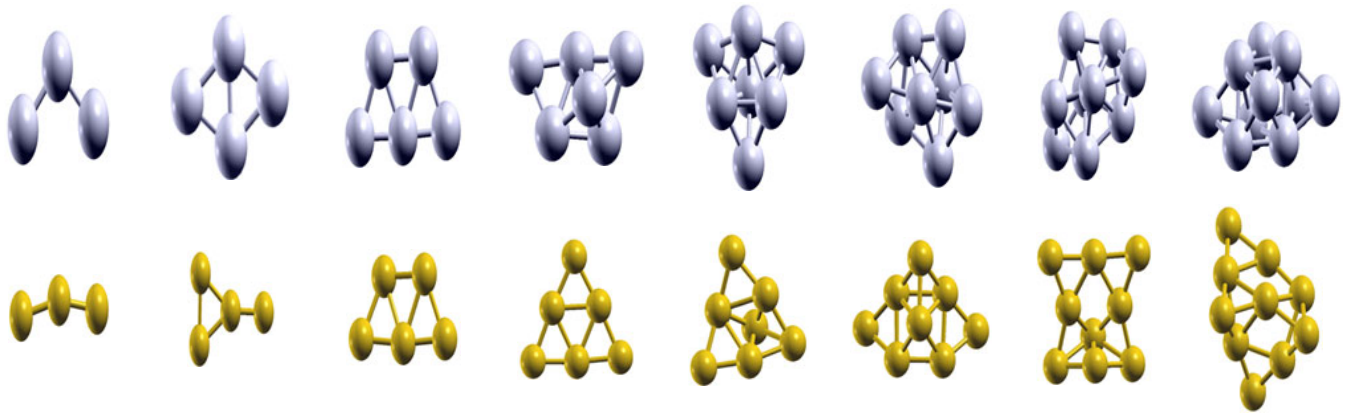

Fig. 1. Lowest energy structures of 3 to 10 atoms silver, gold clusters

process. They were heated to high temperatures around 1000 K in 1000 steps. Then, they were equilibrated at this temperature in 1000 steps and slowly cooled until 0 K in 500 steps. Finally, the clusters were allowed to conduct a relaxation process at 0 K.

RESULTS AND DISCUSSION

Geometrical structures: The optimized geometric structures for silver, gold clusters are plotted in Fig. 1. The bond length and the binding energy of Ag_2, Au_2 are listed in Table-1.

The Ag_2 dimer is calculated to have a bond length of 2.56 Å. This value agree well with Hakkinen *et al.* [26] and is close to the experimental bond length value of 2.53 Å [27]. For the Au_2 dimer's bond length (2.66 Å) is close to both theoretical and the experimental studies [26,28]. The variation of average Ag–Ag, Au–Au bond length of all the lowest energy structures as a function of cluster size is shown in Fig. 2. For Ag_3, Au_3 the lowest energy structures are linear chains with bond length 2.52 Å and 2.48 Å, respectively. The lowest energy structures of clusters with 4-5 atoms are found to adopt planar forms. Ag_4 is a planar rhombus with 2.63 Å bond length. For Au_4, the bond lengths are 2.56 Å. Generally, for each metal, it is observed that the bond length value increases as the cluster size evolves from 3 to 10 atoms. The average bond length decreases for Ag_5, Ag_{10}, Au_6, Au_8 Au_{10} in an exception of the general trend. The calculated average bond length of the silver, gold clusters are in well agreement with the measured data [10,29].

Binding energy: The binding energy per atom was calculated for each metal cluster size n as:

$$E_B = \frac{E_T - nE_{atom}}{n} \quad (1)$$

where E_T is the total electronic energy of a cluster and E_{atom} is the total electronic energy for one isolated atom.

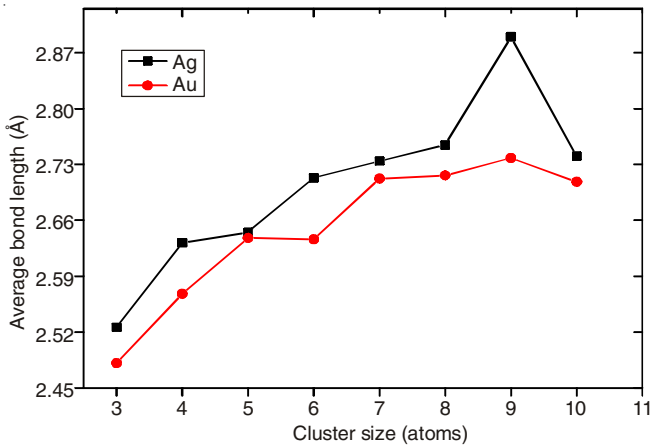

Fig. 2. Average bond lengths in Ag_n, Au_n as a function of cluster size

The calculated binding energies of Ag_2, Au_2 are 1.59 eV and 1.86 eV, respectively. They approach the results of other theoretical [26,29] and experimental works [27,28] as shown in Fig. 3. As seen in the plot, the binding energy per atom increases with the cluster size for each metal. This trend is due to the increase of the number of nearest-neighbours with increasing size, thus encouraging more average number of interactions per atom. The systems usually tend to gain stability; the larger clusters are thus more stabilized.

HOMO-LUMO gap (HLG): The HOMO-LUMO gap is the energy between the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) for the calculated lowest energy structures for each cluster size. Transition from the atomic scale to bulk metallic behaviour is accompanied by a closure of the HOMO-LUMO gap and development of collective electronic excitations [30].

Fig. 4 shows the variation of the HOMO-LUMO gap with increasing cluster size. For silver, gold clusters, there is clear odd-even oscillation. This oscillation can be understood by

TABLE-1
CALCULATED BOND LENGTH (Å), BINDING ENERGY (eV) OF Ag_2, Au_2 DIMERS COMPARED WITH EXPERIMENTAL AND THEORETICAL DATA IN LITERATURE

Work	Dimer	Present work	Other works	Experimental values
Bond length (Å)	Ag_2	2.56	2.56 [Ref. 26]	2.53 [Ref. 27]
		1.59	1.80 [Ref. 26]	1.65 [Ref. 27]
Binding energy (eV)	Au_2	2.66	2.52 [Ref. 26]	2.47 [Ref. 28]
		1.86	2.33 [Ref. 26]	2.29 [Ref. 28]

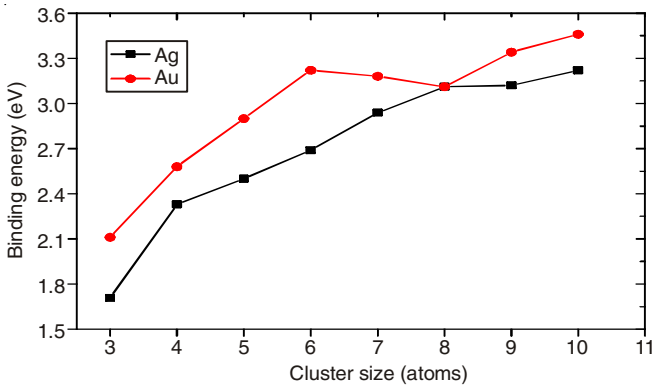

Fig. 3. Binding energies per atom of Ag_n, Au_n as a function of cluster size

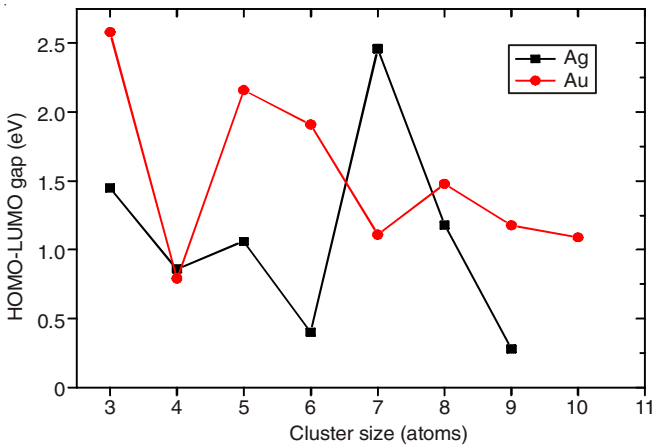

Fig. 4. HOMO-LUMO gap for different clusters sizes

the electron pairing effect. The Ag, Au 5*s* electrons are delocalized around the whole cluster. Larger HOMO-LUMO gap (HLG) is needed to excite the electrons from the valence band to conduction band.

Second differences total energies: The variation of second differences of clusters total energies $\Delta_2E(n)$ as a function of clusters size is represented in Fig. 5.

$$\Delta_2E(n) = E(n + 1) + E(n - 1) - 2E(n) \quad (2)$$

As we have seen previously in HOMO-LUMO gap, we calculate $\Delta_2E(n)$ for metal clusters (Fig. 5). The second differences energies show dramatic odd-even oscillations.

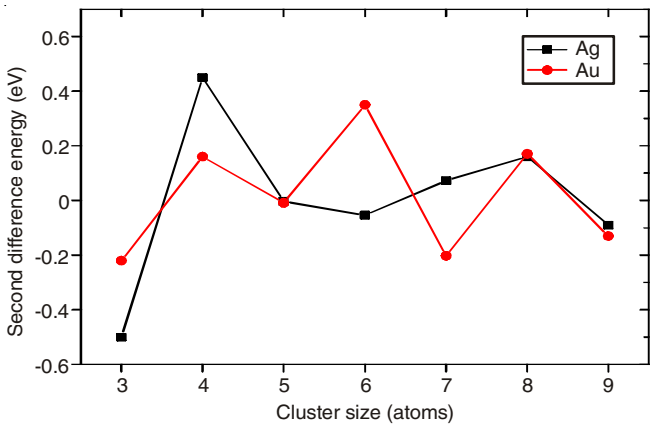

Fig. 5. Size dependences of the second-order difference of energy $\Delta_2E(n)$ for metals clusters

The even-numbered Ag_n, Au_n clusters are relatively more stable than the neighboring odd-sized and have also larger HOMO-LUMO gap values. Commonly the value of $\Delta_2E(n)$ is known to represent the relative stability of a cluster of size n atoms with respect to its neighbouring clusters of (n-1) and (n+1) atoms. Results related to silver, gold are close to [10,26]. The noticeable peaks at n = 4, 6 and 8 indicate that these clusters should be more stable than their neighbours this means that they are the most stable. It indicates that these clusters possess dramatically enhanced chemical stability and may be selected as the building block of novel nano-materials [31].

Vertical ionization potential: Vertical ionization potential (VIP) is used to investigate the chemical stability of small clusters. The larger the vertical ionization potential the less reactive or higher chemically stable the cluster. In Fig. 6 the size variation of ionization potential is plotted for the studied clusters. For linear chain trimer, Au_3 and Ag_3 our results are similar to experimental values (7.47, 5.42, 7.50 and 6.2 eV respectively) [32,33]. Computations indicate that the vertical ionization potential of small Ag, Au clusters generally decreases with the cluster size.

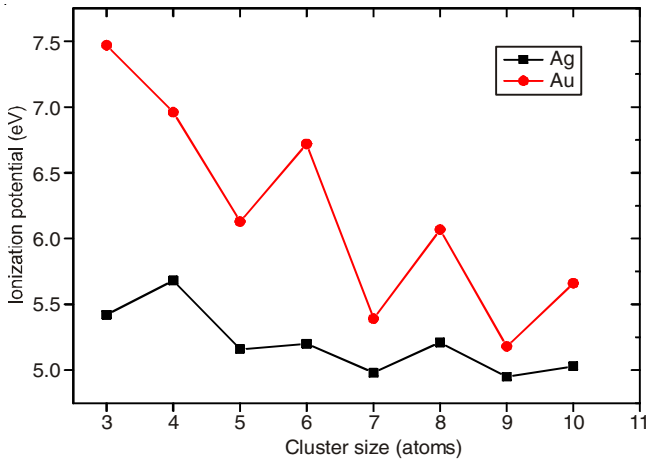

Fig. 6. Ionization potential for silver, gold clusters for different cluster size

Density of states: The density of states gives important information about the 'available' charge (electron or fraction of it) for a given energy. It is known that chemical activity of a cluster is proportional to the electron density near Fermi level [34], the high the density in this region the more chemically active the cluster. In Fig. 7, we present the plot of the variation of density of states for the studied clusters. As we can see, the highest density of states near Fermi level is present for Au clusters, while Ag clusters have little density of states in this region. Generally, the density of states peaks near Fermi level are located at energies in the range of 1.75-3 eV for Ag clusters, while for Au clusters the density of states peaks locate at energies ranging approximately from 0.25 to 1.75 eV. From this analysis, it is predicted that the gold clusters can be the most chemically active with a 'selective' activation energy due to the energy distance variation from Fermi level with changing size, which is a very important property for catalysis for example. These results are in good concordance with the ionization potential.

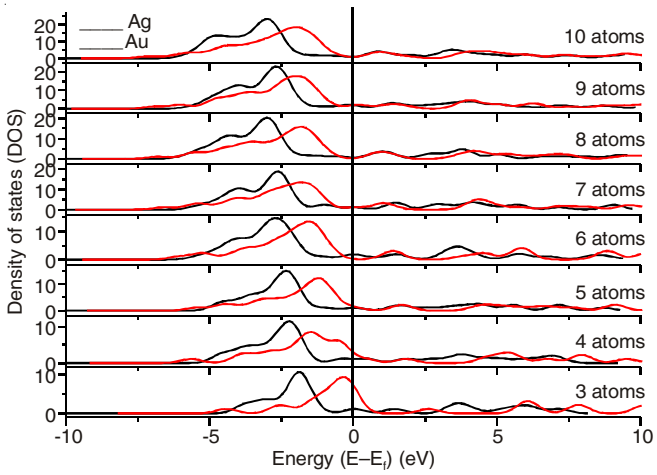

Fig. 7. Density of states for silver and gold clusters for different cluster size

Conclusion

In present work, the structural and electronic properties of Ag_n, Au_n clusters with n = 3-10 are investigated by density functional calculations with generalized gradient approximation. Clusters with total number of atoms up to five were found to have planar structures. The results show that new structures are obtained for each cluster size comparatively for those reported in the literature. The second differences energies of clusters show that the lowest energy Ag_n, Au_n with even numbers (n = 4, 6, 8) are more stable than neighboring clusters. The binding energies generally increase while the ionization potential generally decreases with the increase of clusters size, vertical ionization potential and HOMO–LUMO gap show obvious odd-even oscillations consistent with the Ag and Au clusters. We found that the highest density of states near Fermi level is present for Au, a more investigation in the partial and projected density of states for these clusters may led to control the cluster electronic properties by adjusting its size.

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