Geometries and Electronic Structures by DFT Simulated Annealing Study of Some Noble Metal Small Size Clusters

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ABSTRACT

The minimum energy geometries and the electronic structure for noble metals clusters Agn, Aun, Ptn and Cun, with number of atoms n varying from 3 to 10 atoms are obtained employin density functional theory (DFT) with generalized gradient approximation (GGA) performed in the SIESTA method. New lowest energy structures not reported previously are obtained. The lowest energy structures for (n ≤ 5) clusters are planar where the stability showed that the highest value in binding energy is present in platinum. The calculated second–order differences in energies, and the highest occupied orbital-lowest unoccupied orbital (HOMO-LUMO) energy gap, the density of state (DOS) shows peculiar odd-even oscillation behaviours, showing that Ag4,6,8,10, Au4,6,8,10, Cu4,6,8,10 and Pt3,7,9 clusters remain in highly stable in comparison with their neighboring clusters. (VIP) Vertical ionization potential is discussed then compared with other studies.

Keywords: Cluster, Noble metal, DFT, Electronic structure, Catalysts

INTRODUCTION

The study about of small clusters of group IB noble metals, e.g., gold, silver, copper and platinum have been Previously intensively studied due to their large potential applicability originating from their unique optical, electronic, catalytic and magnetic properties, biological sensing and biomedicine [1,2]. Due to their shells (3d104s1 for copper, 4d105s1 for silver, 5d104s1 for gold and 6d10 for platinum), Cu, Ag, Au and Pt clusters lie between that of alkali metals and transition metals. The presence of d-type electrons strongly affects the physical and chemical properties of clusters. Due to the quantum size effects, discrete electronic levels are indeed observed in metal clusters smaller than 2 nm in diameter [3]. Moreover, the catalytic Characteristics of metallic particles are known, in certain circumstances, to be enhanced when the cluster is reduced [4-6].

The size dependent evolution of the structural and electronic properties of small noble metal clusters has been done the subject of many experimental and theoretical studies for many years. At the atomic level, the energetic position of the nd-levels is approximately 4 eV bellow the (n+1) s levels in silver, but only about 2 eV in copper, gold and platinum.

Recently, the most and stable structures of Agn, Aun, Cun and Ptn clusters were determined n<10 calculated based on density functional theory (DFT) [7-14]. Our study successfully reproduced the result of stable geometries structures obtained in previous studies. Because considered in this work was subject to simulated annealing process.

COMPUTATIONAL DETAILS

The energy calculations in this work were based on the density functional theory (DFT) [15,16], within the generalized gradient approximation (GGA) [17], parameterized by Perdew, Burke and Ernzerhof (PBE) [18] using the plan-wave pseudo potential method. All the calculations were conducted with the SIESTA ab initio package [19,20]. and the interaction between electron and ion were included by employing norm-conserving pseudo- potentials [21]. The pseudopotentials were Created using the ATOM code [22] within the Troullier-Martins scheme [21].

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 A°. The structures were obtained when the atomic forces were smaller than 0.005 eV/A°. All the clusters Agn, Cun, Aun and Ptn considered in this work were subject to simulated annealing process. They were heated to temperatures around 1000 K in 1000 steps. Then, they were equilibrated at this temperature in 1000 steps, and very slowly cooled until 0 K in 500 steps. Finally, all the clusters were allowed to conduct a relaxation process at 0 K.

RESULTS AND DISCUSSION

Geometrical structures

The optimized geometric structures for gold, copper, silver, and platinum clusters are plotted in Figure 1. The bond length and the binding energy of Ag_2, Au_2, Cu_2 and Pt_2, are listed in Table 1.

The Ag_2 dimer is calculated to have a bond length 2.56 Å. These values close to Zhao et al. [23], and are close to the experimental bond length value of 2.53 Å [24]. For the Au_2 dimer's bond length (2.66 Å) is close to theoretical and the experimental studies [23,25,26]. For Cu_2 and Pt_2 the bond lengths are 2.17 Å, 2.55 Å, respectively, very close to other results experimental and theoretical results [27-31].

The variation of average Ag–Ag, Au–Au, Cu–Cu and Pt–Pt bond length of all the lowest energy structures as a function of cluster size is described in the Figure 2. For Ag_3, Au_3, Cu_3 and Pt_3, the lowest energy structures are linear chains with bond length 2.52 Å, 2.48 Å, 2, 20 Å, 2.30 Å, respectively. The lowest energy structures of metal 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, Cu_4, and Pt_4 the bond lengths are 2.56 Å, 2.31 Å, 2.42 Å, respectively. 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} and Pt_7 in an exception of the general trend. The calculated average bond length of the gold, copper, silver and platinum clusters are in well agreement with the measured data [11,27,32].
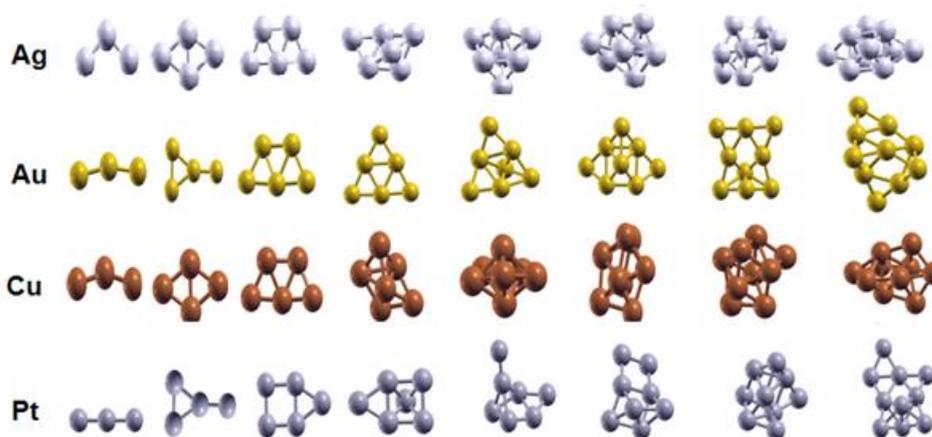

Figure 1: The lowest energy structures of 3 to 10 atoms Silver, gold, copper and platinum clusters

Table 1: Calculated bond length (A°), binding energy (eV) of Ag₂, Au₂, Cu₂ and Pt₂ dimers compared with experimental and theoretical data in literature

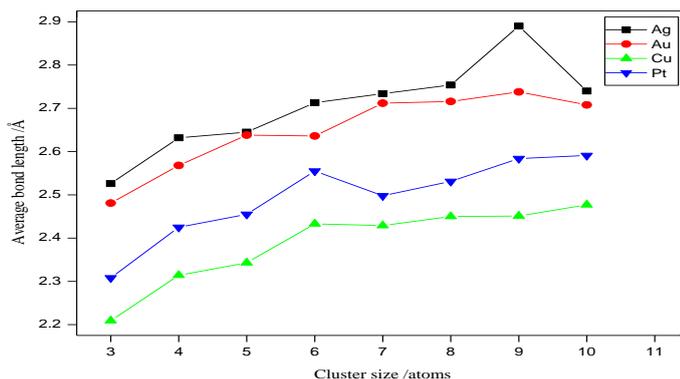| Work	Dimer	Present work	Other works	Experimental values
Bond length (Å)	Ag_2	2.56	2.56 [23,24]	2.53 [25]
		1.59	1.80 [23,24]	1.65 [25]
	Au_2	2.66	2.52 [23]	2.47 [26]
		1.86	2.33 [23]	2.29 [26]
	Cu_2	2.17	2.22 [27]	2.21 [28]
Binding energy (eV)		1.69	1.13 [27]	1.04 [33]
	Pt_2	2.55	2.39 [29]	2.34 [30,31]
		2.51	3.59 [29]	3.14 [34]

Figure 2: Average bond lengths in Ag$_n$, Au$_n$, Cu$_n$, Pt$_n$ as a function of cluster size

Binding energy

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

$$E_B = [E_T - nE_{atom}]/n \ (1)$$

Where E_T is the total electronic energy of a cluster and E_{atom} is the total electronic energy for one isolated atom. The calculated binding energies of Ag$_2$, Au$_2$, Cu$_2$ and Pt$_2$ are 1.59 eV, 1.86 eV, 1.69 eV and 2.51 eV respectively. They approach the results of other theoretical [23,27,29] and experimental works [25,26,33,34] as shown in Figure 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.
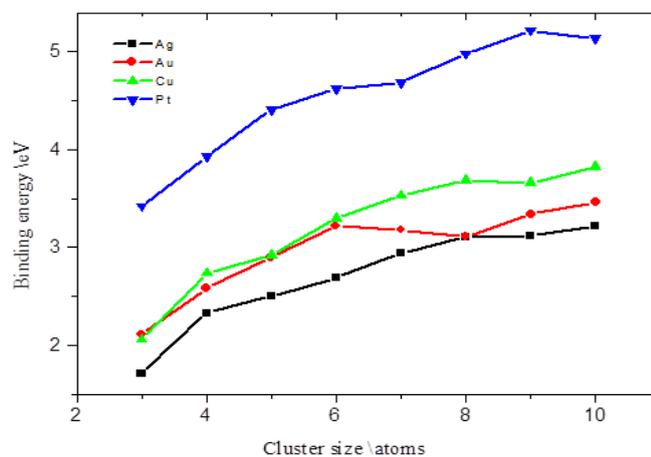

Figure 3: Binding energies per atom of Ag$_n$, Au$_n$, Cu$_n$ and Pt$_n$ as a function of cluster size

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. 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 [35].

Figure 4 shows the size difference of the HOMO-LUMO gap. For silver, gold, copper and platinum clusters, there is clear odd-even oscillation. This oscillation can be understood by the electron pairing effect. The Ag, Au, Cu 5s electrons are delocalized around the whole cluster, while this observation is not recorded in Pt clusters. This is may be due to the fact that platinum clusters have unsaturated atomic orbitals. Larger HOMO-LUMO gap (HLG) is needed to excite the electrons valence band to conduction band.
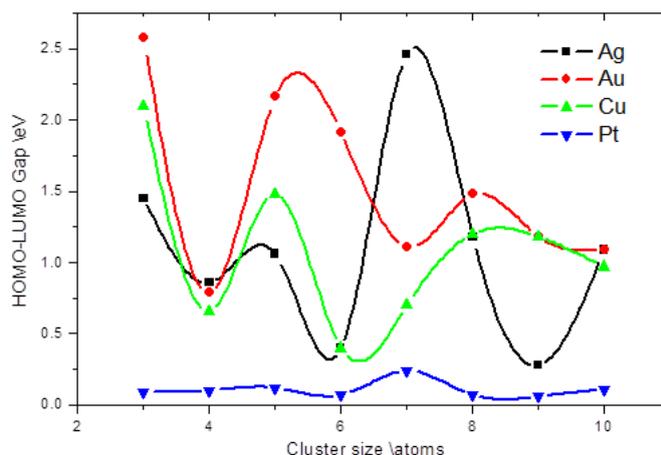
Figure 4: HOMO-LUMO gap for different clusters sizes

Second differences total energies

The variation of second differences of clusters total energies $\Delta_2 E(n)$ as a function of clusters size is represented in Figure 5.

$$\Delta_2 E(n) = E(n + 1) + E(n - 1) - 2E(n) \quad (2)$$

As we have seen previously in HOMO-LUMO gap, we calculate $\Delta_2 E$ (n) for metal clusters. As shown in Figure 5. The second differences energies show dramatic odd-even oscillations. The even numbered Ag_n, Au_n, Cu_n and Pt_n clusters are relatively more stable than the neigh boring odd-sized and have also larger HOMO-LUMO gap values. Commonly the value of $\Delta_2 E(n)$ is known to represent the relative stability of a cluster of size n, with respect to its neighbours. Results related to silver, gold, copper and platinum are close [23,32,36]. The noticeable peaks at n=4, 6, and 8 indicate that these clusters should be more stable than their neighbours. It is also noticed that the cluster Pt_3 has more stable structure compared to other clusters of Ag, Au, Cu, of the same size. Pt_3, Pt_5, Pt_9 have larger second difference energy than their neighboring clusters. This means that they are the most stable, while Ag_n, Au_n, Cu_n with (n=4, 6, 8) are the most stable clusters. It indicates that these clusters possess dramatically enhanced chemical stability and may be selected as the building block of novel nano-materials [37].
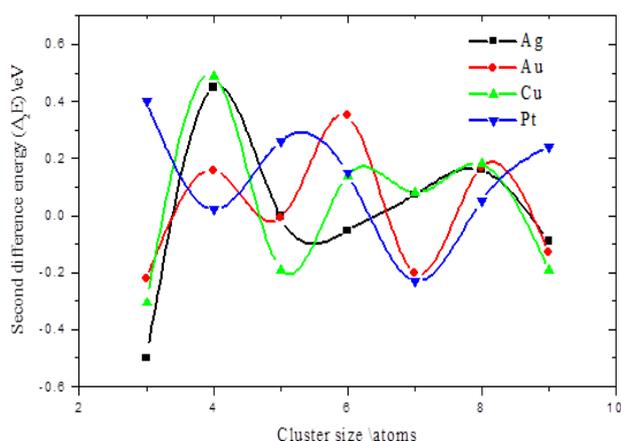

Figure 5: Second-order difference of energy $\Delta_2 E(n)$ for metals clusters

Vertical ionization potential (VIP)

Vertical ionization potential (VIP) is used to investigate the chemical stability of small clusters. The larger the VIP the less reactive or higher chemically stable the cluster.

In Figure 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 eV 5.42 eV, 7.50 eV, 6.2 eV respectively) [38,39]. For Pt_3, our result is slightly below experimental results (7.44 eV, 8.17 eV respectively) [40] whereas, for Cu_3 the obtained result is close to that reported in other results (6.53 eV, 6.00 eV respectively) [27]. Computations a statement that VIP of small Au, Cu, Ag and Pt clusters generally decreases with cluster size.
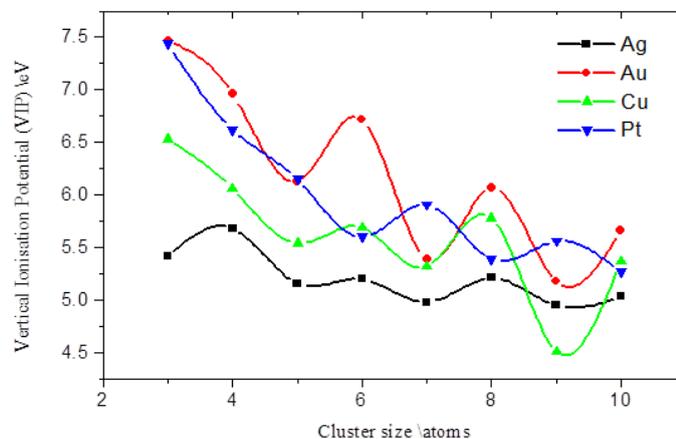
Figure 6: Ionization potential for silver, gold, copper and platinum clusters for different cluster size

Density of states

The density of states gives important information about the 'available' charge (electron or fraction of it) for a given energy. For example, chemical activity of a cluster is proportional to the electron density near Fermi level [41]; the high the density in this region the more chemically active the cluster. In Figure 7, we present the variation of DOS for the studied clusters. As we can see, the highest DOS near Fermi level is present for Cu, Au and Pt, while Ag clusters have little DOS in this region. Generally, the DOS peaks near Fermi level are located at energies in the range of 1.75 ~ 3 eV for Ag clusters, while for Cu and Au clusters the DOS peaks locate at energies ranging approximately from 0.25 to 1.75 eV. In contrast to this picture, the Pt clusters seem to have less shifting locations from Fermi level of 0.25-0.5 eV. From this analysis, we can predict that platinum and copper 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 important property for catalysis for example. In the other hand, these results are in good concordance with the ionization potential.
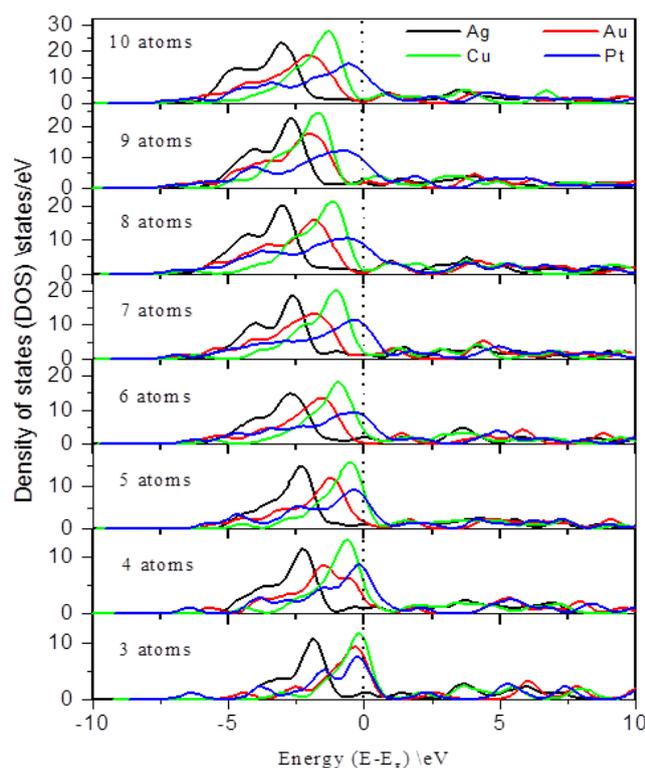
Figure 7: Density of states for silver, gold, copper and platinum clusters for different cluster siz

CONCLUSION

In this paper, we performed DFT simulating annealing calculation of geometric and electronic structure of Cu_n, Ag_n, Au_n, Pt_n clusters with n=3–10. Our results show that new structures are obtained for each cluster size comparatively for those reported in the literature. The second differences energies of cluster show that the lowest energy Ag_n, Au_n, Cu_n with even numbers (n=4, 6, 8) are more stable than neighboring clusters. Pt_n shows different behavior where the most stable is found for the odd numbers (n=3, 5, 9). The binding energies generally increase while the ionization potential generally decreases with the increase of clusters size and the HOMO–LUMO gap show clear odd-even oscillation. We found that the highest DOS near Fermi level is present for Au, Cu and Pt. A more investigation in the partial and projected DOS for these clusters may led to control the cluster electronic properties by adjusting its size.

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