

# A Rigorous Analysis of the Structural Configurations and Binding Energies of $Au_{n+1}$ and $PtAu_n$ ( $n = 1-9$ ) Clusters

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## Abstract

In the current paper, we present a systematic calculation based on the Density functional theory (DFT), which aims to highlight the potential effects of doping platinum Pt clusters and the new electronic and light structural characteristics of platinum-infused gold clusters  $Au_n$  ( $n=1-9$ ), so that less energy clusters are selected from the rest of the isomers per cluster size.

The most stable structures with the lowest 3D structures starting from  $n=6$ . The average length of the bonds between the atoms of each cluster and the binding energy of these clusters is calculated relative to their size. Structural characteristics were studied, discussed and compared with all calculated properties by Gradient Density Approximation (GGA) with the Local Density Approximation (LDA), also highlighted the intensity of calculated cases and comparison of  $Au_2$  cluster with  $PtAu$  that the grafting of  $Au_n$  clusters platinum Pt, makes them have characteristics that distinguish them to be qualified in their use of chemical stimulation.

**Key Words:** Density Functional Theory,  $PtAu_n$  and  $Au_n$  Clusters, Binding Energy, Stability Structure, Chemical Catalysis.

## 1. Introduction

The science of nanocluster physics and chemistry has become a focus of great interest for researchers over the past two decades, as researchers have gone into research into the unique characteristics of these clusters, and their unique structure between molecule and size (bulk) has been the main reason for the theoretical researcher to delve into the understanding of the transition from atom to clusters, molecule and finally to solid state. In recent years, emphasis has been placed on the structural, electronic and optical properties of mixed clusters of two minerals. This type of cluster is of great importance thanks to the possibility of using them according to special requests.

Nano-sized bimetal-metal clusters have received great attention due to their promising applications in optics, magnetism and catalysis [1,2], because they have physical and chemical properties that change in size as a result of surface change in size, nano clusters made of noble metals, particularly  $PtAu_n$  nano clusters, are attractive catalysts [3,4]. The physical and chemical properties of bimetal clusters depend not only on size and shape, but also on the atomic composition of the two metal elements [5]. The new structural and electronic variables that clusters have become enjoying due to their new size are therefore being studied [6-7].

Both gold and platinum particles have wide uses in organic chemistry, as they play an important role in protein delivery [8], as well as an important role in cancer treatment [9], and they also have a great ability to resist fungi [10]. They are optical sensors that contribute to photodynamic therapy and generally play a broad role in sensor synthesis and biomedicine [11-13]. Platinum particles are also included in the catalytic oxidation of blue carbon and in the general electrochemical behaviours of safe compounds and generally in many applications in other fields [14-16].

### **Detail of Calculations**

The electronic structure calculations of PtAu<sub>n</sub> (n = 1–9) clusters were performed using the density functional theory (DFT) [17], as implemented in the SIESTA program [18]. This code uses norm-conserving Troullier-Martins nonlocal Pseudopotentials [19], and employs flexible basis sets of localized Gaussian-type atomic orbitals. The exchange correlation energy was evaluated using the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernserh of (PBE) [20], and local density approximation LDA [21]. The self-consistent field (SCF) calculations were carried out with convergence criterion of  $1 \times 10^{-4}$  a.u. for total energy; we used a double  $\zeta$  (DZ) basis with polarization function for Pt and Au atoms. With energy shift parameter of 50 meV, the charge density was calculated in regular real-space grid with cut-off energy of 170 Ry. The simulated clusters were placed in a big cubic supercell with a parameter of 30 Å, including enough vacuums between neighboring clusters and periodic boundary conditions were imposed. To sample the Brillouin zone, only a single k-point centred at  $\Gamma$  was used because of the extended size of the super cell. The conjugated gradient method within Hellmann-Feynman forces was used and all the forces after structural relaxation were less than  $10^{-3}$  eV/Å.

We first searched for the lowest-energy structures of pure Au<sub>n</sub> clusters in the (2–10) atoms. Secondly, the most stable ground state structures obtained for Au<sub>n</sub> clusters were doped through substitution with one Pt atom. Then, the obtained Pt-Au<sub>n</sub> clusters were optimized until reaching their ground states. In order to get lowest-energy structures of the PtAu<sub>n</sub> clusters, several initial isomeric structures, including some high and low symmetries, were optimized by placing one Pt atom in substitution in different possible sites of the pure corresponding Au<sub>n</sub> in order to get as close as possible to the low energy structure. Then, we cannot be sure that a more stable structure than those found in our calculations does not exist. We aim of our study is to highlight the variation of the properties of gold cage clusters due to the Pt doping atom. We hope that this work would be useful to understand the influence of the Pt atom on the properties of gold clusters and provide some guidelines for the probable future experimental studies. Our calculated results were found to be in line with the literature, confirming the reliability of our protocol to simulate small Au clusters.

## **2. Results and Discussion**

### **1. Structural Properties of Clusters Au<sub>n+1</sub> and PtAu<sub>n</sub> (n=1-9)**

#### **1.1. Structural Characteristics**

The structural characteristics of the free gold metal clusters and platinum-doped gold depend on the structure of clusters, the locations of atoms and the average bond length between them, the DFT was chosen and using Gradient Density Approximation (GGA) and the Local Density Approximation (LDA) to reach the more stable and lower power consumption, in this work we have come up with the electronic structures of the clusters using the application of annealing simulation (SA), which is carried out through the following stages:

Phase 1: We placed a random group of atoms in the cluster simulation box.

Stage 2: The temperature of the system is raised to about 1000 K in a total of 1000 iterations.

Stage 3: The temperature of the system is stable at T = 1000 K for about 500 iterations.

Phase 4: We gradually reduce the temperature of the system to t = 0 K in 1000 iterations.

Figures 1 and 2 represent the most stable pure gold and platinum doped gold clusters, respectively.

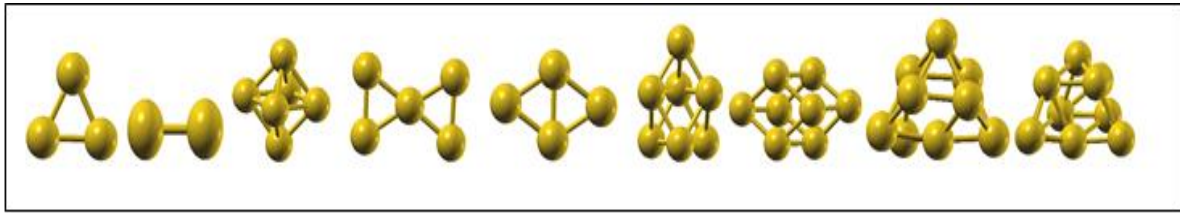


Figure 1. The most stable  $Au_n$  ( $n=2-10$ ) clusters.

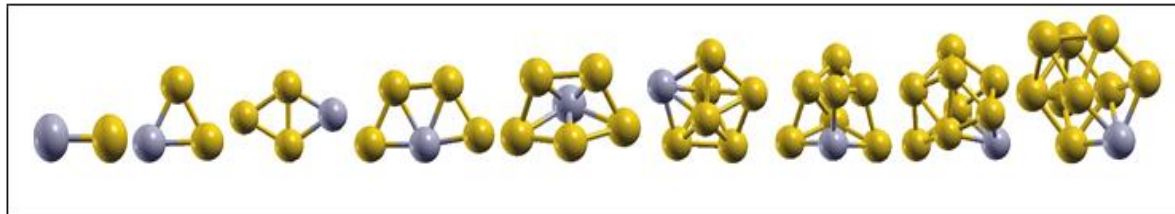


Figure 2. The most stable  $PtAu_n$  ( $n=1-9$ ) clusters.

### 1.2. Average Bond length

The average bond length of free gold clusters has been calculated in relation to:

$$R_{Au} = \frac{\sum R_{Au-Au}}{n} \quad (1)$$

Where:  $R_{Au-Au}$  it is the length of the bond between two atoms of gold,  $n$  is number of links in the cluster

And for gold infused with platinum corn in relation:

$$R_{PtAu} = \frac{\sum R_{Au-Au} + \sum R_{Pt-Au}}{n} \quad (2)$$

Where:  $R_{Pt-Au}$  is the bond length between gold atoms and platinum atom.

The length of the bond between gold and gold cluster atoms doped with platinum seed has been calculated with the XCRYSDEN program [22].

Figure3 represents the graph of the average bond length between atoms rather than the size of the cluster.

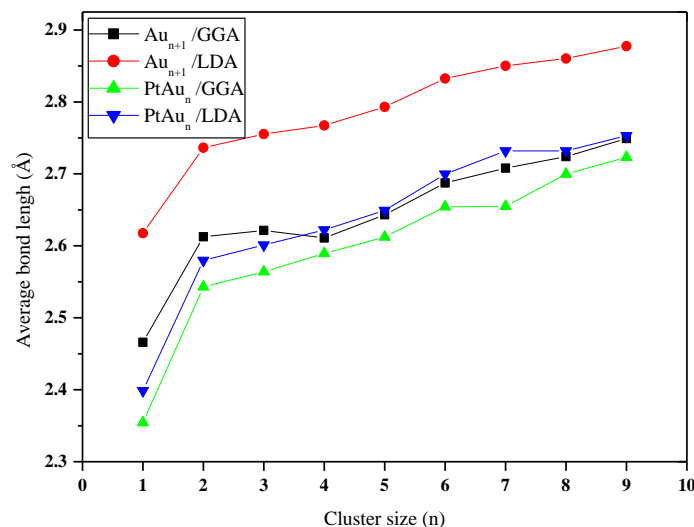


Figure 3. Average bond length for  $Au_{n+1}$  and  $PtAu_n$  ( $n=1-9$ ) clusters.

According to the curve as shown in figure 3, it is clear that the average bond length increases as the size of the cluster increases whatever rounding used, as we note that clusters Au<sub>2</sub>, Au<sub>6</sub> and Au<sub>10</sub> characterized by an average bond length estimated at 2.62 Å, 2.77 Å and 2.86 Å by approximation (LDA) and, at 2.46 Å, 2.63 Å, 2.70 Å by approximation (GGA) respectively, While the PtAu, PtAu<sub>5</sub>, and PtAu<sub>9</sub> clusters have an average bond length approximation (LDA) of 2.40 Å, 2.64 Å, and 2.73 Å and in approximation (GGA) of 2.35 Å, 2.58 Å and 2.70 Å, comparing the above, we note a slight difference in the average values of bond length for the same cluster size from the previous clusters in the two different approximations (LDA) and (GGA).

We also recorded the average bond length for Au<sub>2</sub>, Au<sub>6</sub> and Au<sub>8</sub> clusters by approximation (LDA) with the values 2.62 Å, 2.77 Å, 2.85 Å, and by approximation (GGA) the values were recorded 2.46 Å, 2.63 Å, 2.71 Å, respectively, While PtAu, PtAu<sub>5</sub>, PtAu<sub>7</sub> clusters, the average bond length values for them in (LDA) approximation are estimated at: 2.40 Å, 2.64 Å and 2.72 Å, and in (GGA) approximation they are estimated at: 2.35 Å, 2.58 Å, 2.65 Å, respectively.

For example, we notice that the average bond length of clusters Au<sub>2</sub>, Au<sub>6</sub> and Au<sub>8</sub> if we graft them with platinum atom decreases in the value of the average bond length, and this is through the use of both approaches (LDA) and (GGA).

We note that the largest value of the average bond length at cluster Au<sub>10</sub> is estimated at 2.46 Å by approximation (LDA) and this value decreases to 2.73 Å by approximation (GGA).

For the grafted gold clusters, we recorded the largest value at PtAu<sub>9</sub> with a length of 2.73 Å in (LDA) and as low as 2.70 Å in (GGA).

From the two readings we note:

The average bond length for Au<sub>10</sub> in (GGA) is the same as for PtAu<sub>9</sub> in (LDA) and is estimated at 2.73 Å.

As a result of the analysis of the four curves, and in general, there has been an increase in the average bond length of the Au<sub>n+1</sub> and PtAu<sub>n</sub> clusters by an increase in cluster size from two to 10 atoms, with the exception of the Au<sub>5</sub> and PtAu<sub>7</sub> cluster, where there has been a decrease in the mean bond length value, so the Au<sub>n+1</sub> metal cluster is the most stable than PtAu<sub>n</sub> in both LDA and GGA approximation.

### 1.3. Binding Energy

Binding energy is defined as the amount of energy stored to create an interconnected cluster [23], so if the structure has high binding energy (a significant correlation between its atoms), the structure is more stable.

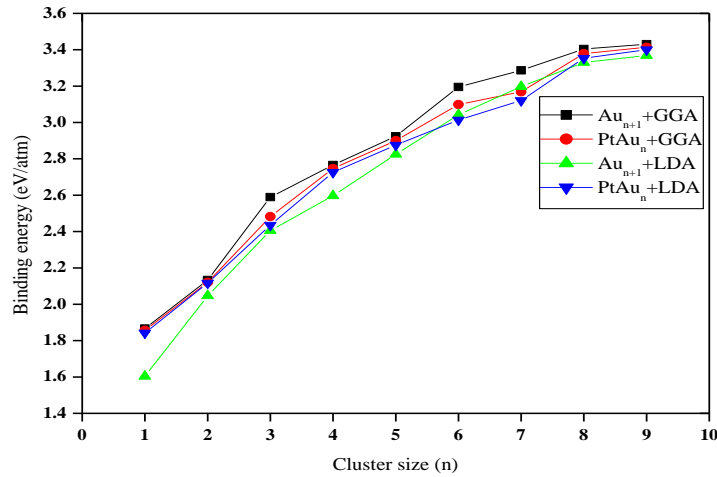
In order to calculate the energy of linking the atoms of gold metal clusters with platinum seed gold, you should know the total energy of the cluster and the energy of the single atom, depending on the relationship:

$$E_{bin}(Kn) = E_{tot}(Kn) - nE_{at}(Kn)/n \quad (3)$$

Where:

**E<sub>tot</sub>**: Total energy of the cluster, **E<sub>at</sub>** is the energy of one atom, n is number of cluster atoms, **kn** is cluster symbol.

Figure4 represents the value of the binding energy for the clusters Au<sub>n+1</sub> and PtAu<sub>n</sub> in terms of the size cluster.



**Figure 4. Binding energy of  $Au_{n+1}$  and  $PtAu_n$  ( $n=1-9$ ) clusters.**

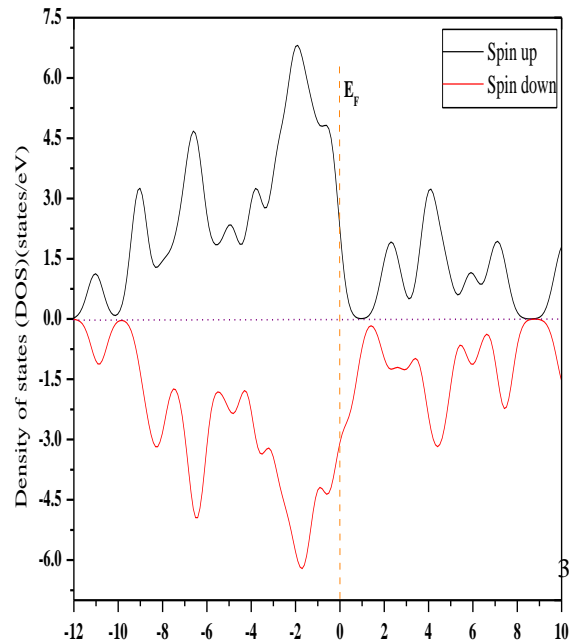
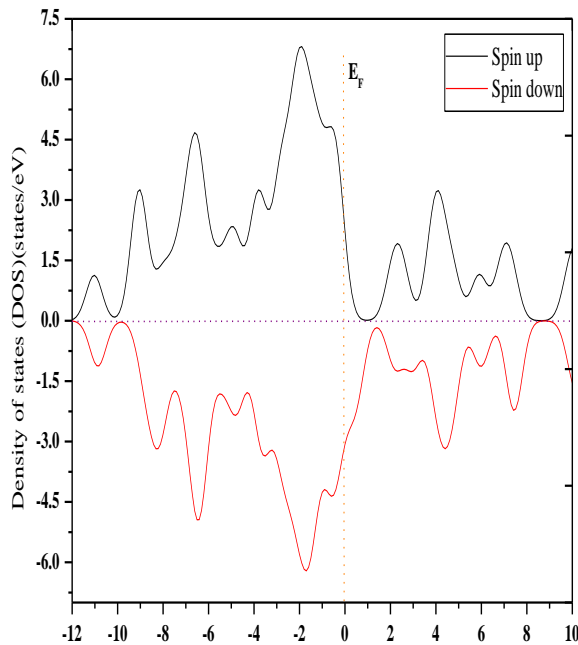
Through figure 4, which represents the binding energy of the cluster size, we observe an ejection relationship between the binding energies of clusters and their size, so that the larger the cluster size, the greater the bonding energy between atoms, The highest values of the binding energy at the clusters  $Au_2$ ,  $Au_6$  and  $Au_9$  respectively, is approximately (LDA) 1.6, 2.7, 3.28 (eV/atom) and in GGA are 1.82, 2.88, 3.38 eV/atom, for clusters PtAu, PtAu<sub>5</sub> and PtAu<sub>8</sub> they have binding energy by approximation (LDA) estimated at (1.82, 2.78, 3.28) (eV/atom) and rounded (GGA) are 1.83, 2.79, 3.29 (eV/atom), we note that these clusters have approximately the same binding energy value as LDA and GGA.

In GGA approximation, we recorded the same binding energy for  $Au_{n+1}$  and  $PtAu_n$  clusters, with the exception of three clusters, they are  $Au_4$ ,  $Au_7$  and  $Au_8$  different from PtAu<sub>3</sub>, PtAu<sub>6</sub> and PtAu<sub>7</sub> which respectively have the following energies: (eV/atom) 2.58, 3.18, 3.3, 2.46, 3.08, 3.1. It is also for rounding (LDA) with the exception of  $Au_2$  and  $Au_5$  clusters where energy is different from PtAu and PtAu<sub>4</sub> taking values: 1.6, 2.6, 1.82, 2.7 (eV/atom) respectively.

In general, we note that clusters  $Au_{n+1}$  and  $PtAu_n$  converge in terms of binding energies except for some exceptional cases mentioned earlier using GGA and LDA, which confirms the very high stability of clusters  $Au_n$  by bringing GGA closer to clusters ( $n=2-10$ ). By comparing our results for gold clusters, we find them approximately compatible with the results [24].

## 2. Density of States

Figures (5a) and (5b) represent the intensity of the density of states of clusters in terms energy, taken in order to determine the effect of introducing a platinum atom on the gold clusters and to extract the contribution made by this atom to the catalytic field.



(b)

(a)

**Figure 5. Density of States of Au<sub>2</sub> and PtAu clusters.**

Through the curve shown in figure (5-a), the density of states of Au<sub>2</sub> cluster is found to be high in the parity ring area, where it reaches the value of 7 States/eV while the value of 7.2 States/eV for the cluster is recorded, according to PtAu as confirmed by figure (5-b) This is with the energy limit -1.7eV as the area at 0 eV, i.e. at the Fermi level, has a remarkable presence of the density of the cases estimated at -1.6 States/eV, This will make the cluster vulnerable to the transfer of electrons from the valence band to the incoming transport band, that is, the block tends to have the properties of metals, and from it we find that the PtAu cluster has become more chemically active and will be able to enter strongly into the field of catalytic chemical activities.

### 3. Conclusion

The structural and electronic properties of PtAu<sub>n</sub> clusters with (n=1-9) are investigated by applying the density functional calculation with Generalized Gradient Approximation(GGA) and Local Density Approximation (LDA). Clusters with a total number of atoms up to five were found to have planar structures. To this end, the findings illustrate that new structures are attained for each cluster size comparatively for those reported in the literature. The results of binding energy clearly show that gold clusters Au<sub>n+1</sub> are more stable than PtAu<sub>n</sub> clusters at the same size of atoms. We found that the highest density of states is near the Fermi level where it is present at the Au cluster, which is likely to have an active role in the field of chemical catalysis.

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