

# Theoretical Analysis of Au-Pd Nanoalloy Clusters: A DFT Study

Prabhat Ranjan<sup>a\*</sup>, Tanmoy Chakraborty<sup>b\*</sup>

<sup>a</sup>Department of Mechatronics Engineering, Manipal University Jaipur, Dehmi Kalan, Jaipur-303007, INDIA, Email: prabhat23887@gmail.com

<sup>b</sup>Department of Chemistry, Manipal University Jaipur, Dehmi Kalan, Jaipur-303007, INDIA

prabhat23887@gmail.com; tanmoychem@gmail.com

**Abstract :** The study of bimetallic nanoalloy clusters has attracted a lot of attention now a days due to its unique physico-chemical properties. Among several bimetallic clusters, the compound formed between gold and palladium is of high importance due to its interesting catalytic properties. Density Functional Theory (DFT) is highly dominating method to compute the electronic properties of materials. In this article, we have reported the physical and chemical properties of Au<sub>n</sub>Pd (n=1-6) nanoalloy clusters in terms of Conceptual Density Functional Theory (CDFT) based descriptors. The CDFT based descriptors viz. HOMO-LUMO energy gap, hardness, softness, electronegativity and electrophilicity index of Au<sub>n</sub>Pd nanoalloy clusters have been calculated. The result exhibits that energy gap of Au-Pd clusters maintain linear relationship with hardness values and inverse relationship with softness values. The HOMO-LUMO energy gap also display odd-even oscillation behavior, in which cluster containing total number of even atoms are more stable as compared to their neighbor cluster with total number of odd atoms.

**Keywords:** Density Functional Theory; Bimetallic Nanoalloy Clusters; HOMO-LUMO Energy Gap; Gold-Palladium; Odd-Even Oscillation;

## 1. Introduction

In recent years, bimetallic nanoalloy clusters have attracted a lot of attention due to their interesting electronic, optical and catalytic properties [1]. The physico-chemical properties of bimetallic nanoalloy clusters are entirely different from bulk metal [2,3], particularly their catalysis properties [4-9]. Gold nanoparticles are of immense importance, because of its significant electronic and optical properties, relativistic effects and greater stability [10,11]. There are a number of reports available in which gold is mixed with other metals to enhance the electronic and optical properties [12-15]. The cluster formed between gold and palladium is of high importance due to its importance in catalysis activity [10, 16-18].

Tran et al. studied nanosized alloy structure of Au-Pd [19]. They described that core-structure of Au<sub>2</sub>Pd<sub>41</sub> is formed after face capping with 12 additional atoms of palladium. The insight on the atomic structure, composition ratio of materials for preparation of well-ordered catalyst for bimetallic Pd<sub>core</sub>Au<sub>shell</sub> is reported by Tiruvalam et al. [20]. The study shows that Pd shell is deposited on the Au core which is having similar lattice constant as Au and with the orderly Pd/Au interface geometry [21]. Ferrer et al. [22] reported that addition of another metal enhances the catalytic properties of the gold-palladium molecular system. Paz-Barbon et al. [23] reported that when effects of charge transfer is weak, segregation depends on the surface energy and bond interactions, which reflects Pd<sub>shell</sub>Pt<sub>core</sub>, Ag<sub>shell</sub>Pt<sub>core</sub> and Pd<sub>core</sub>Au<sub>shell</sub> are the desired segregation for these molecular system. Negreiros et al. [24] studied AgPd clusters of 38 to 100 atoms using density-functional/empirical-potential approach. They found that empirical potential result follow similar trend with density functional result. We have also studied a number of bimetallic nanoalloy clusters using density functional theory, as it possess unique electronic and optical properties which are very significant when trying to identify their potential applications and physico-chemical properties [25-27].

In this report, we have studied Au<sub>n</sub>Pd (n=1-6) nanoalloy clusters by using Density Functional Theory (DFT) methodology. We have computed DFT based descriptors viz., HOMO-LUMO energy gap, molecular hardness, softness, electronegativity and electrophilicity index.



## 2. Computational Details

Density Functional Theory is one of the most successful computational technique to study the physical and chemical properties of metallic clusters. DFT techniques are being implemented to various domains in material science, solid state chemistry, semiconductor physics, nanoscience, nanoelectronics, biology, and earth sciences [28]. The geometry optimization of  $\text{Au}_n\text{Pd}$  ( $n=1-6$ ) nanoalloy clusters have been done using Gaussian 03 [29] within DFT framework. The Local Spin Density Approximation (LSDA) exchange correlation is effective for metallic clusters, which is already reported by researchers [30, 31]. The basis set LanL2dz has high accuracy for bimetallic and multi-metallic clusters [31, 32]. For computation purpose, we have adopted LSDA exchange correlation with basis set LanL2dz.

Invoking Koopmans' approximation [33], Ionization Energy (I) and Electron Affinity (A) of nanoalloy clusters of  $\text{Au}_n\text{Pd}$  ( $n=1-6$ ) have been computed. Subsequently, using I and A, the DFT based descriptors viz. electronegativity ( $\chi$ ), molecular hardness ( $\eta$ ), softness (S) and electrophilicity index ( $\omega$ ) have been calculated.

$$I = -\epsilon_{\text{HOMO}} \quad (1)$$

$$A = -\epsilon_{\text{LUMO}} \quad (2)$$

$$\chi = -\mu = \frac{I + A}{2} \quad (3)$$

Where,  $\mu$  represents the chemical potential, I- Ionization Potential and A- Electron Affinity of the system.

$$\eta = \frac{I - A}{2} \quad (4) \quad S = \frac{1}{2\eta} \quad (5)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (6)$$

## 3. Results and Discussion

Theoretical analysis of  $\text{Au}_n\text{Pd}$  ( $n=1-6$ ) nanoalloy clusters has been performed by using electronic structure calculation. The DFT based descriptors viz. HOMO-LUMO energy gap, hardness, softness, electronegativity and electrophilicity index have been computed, which is presented in Table-1. The HOMO-LUMO energy gap is an important parameter to understand the reactivity index and stability of nanoalloy clusters. It signifies the minimum energy required for an electron to move from upper layer of valence band to the lower layer of conduction band. The large value of energy gap specifies least interference from any peripheral disturbance, whereas clusters with small value of energy gap will be highly reactive. The result shows that  $\text{AuPd}$  has maximum HOMO-LUMO energy gap (2.419 eV) and  $\text{Au}_2\text{Pd}$  has lowest energy gap (0.435) in this range. There is a linear relationship observed between hardness and HOMO-LUMO energy gap of  $\text{Au}_n\text{Pd}$  nanoalloy clusters from Table-1. This concept is based on the experimental facts, as for any molecular system when the frontier orbital energy gap increases their hardness value also increases. The clusters  $\text{AuPd}$  and  $\text{Au}_2\text{Pd}$  display maximum and minimum value of molecular hardness respectively. The HOMO-LUMO energy gap have inverse relationship with computed softness values. The cluster  $\text{Au}_2\text{Pd}$  exhibits maximum value of softness, whereas cluster  $\text{AuPd}$  have least softness value. Similar relationships are observed between HOMO-LUMO energy gap and other DFT based descriptors. The linear correlation between HOMO-LUMO energy gap and electrophilicity index is presented in Figure-1 (a). The correlation coefficient,  $R^2 = 0.792$  is observed between HOMO-LUMO energy gap and electrophilicity index for  $\text{Au}_n\text{Pd}$  nanoalloy clusters, which supports our predicted model.

As per the theory of cluster science, dissociation energy and second-order difference in energy have very high impact on the stability of clusters. These two energies are very dominant quantities and they pronounced odd-even oscillation behavior, as a function of cluster size [34, 35]. The similar type of oscillation behavior is also observed by HOMO-LUMO energy gap of  $\text{Au}_n\text{Pd}$  nanoalloy clusters. The HOMO-LUMO energy gap as a function of cluster size,  $n$  is presented in the Figure-1 (b). It is noticeable from Figure-1 (b) that clusters with even number of total atoms have higher energy gap as compared to their neighbor cluster with odd number of total atoms.

Table 1. The DFT based descriptors of  $\text{Au}_n\text{Pd}$  ( $n=1-6$ ) nanoalloy clusters in eV.

Species	HOMO-LUMO Energy Gap	Electronegativity	Hardness	Softness	Electrophilicity Index
AuPd	2.419	5.427	1.209	0.413	12.176
Au <sub>2</sub> Pd	0.435	6.043	0.218	2.297	83.889
Au <sub>3</sub> Pd	1.197	6.177	0.599	0.835	31.866
Au <sub>4</sub> Pd	0.555	6.060	0.278	1.802	66.151
Au <sub>5</sub> Pd	1.565	5.609	0.782	0.639	20.111
Au <sub>6</sub> Pd	1.054	5.791	0.527	0.949	31.826

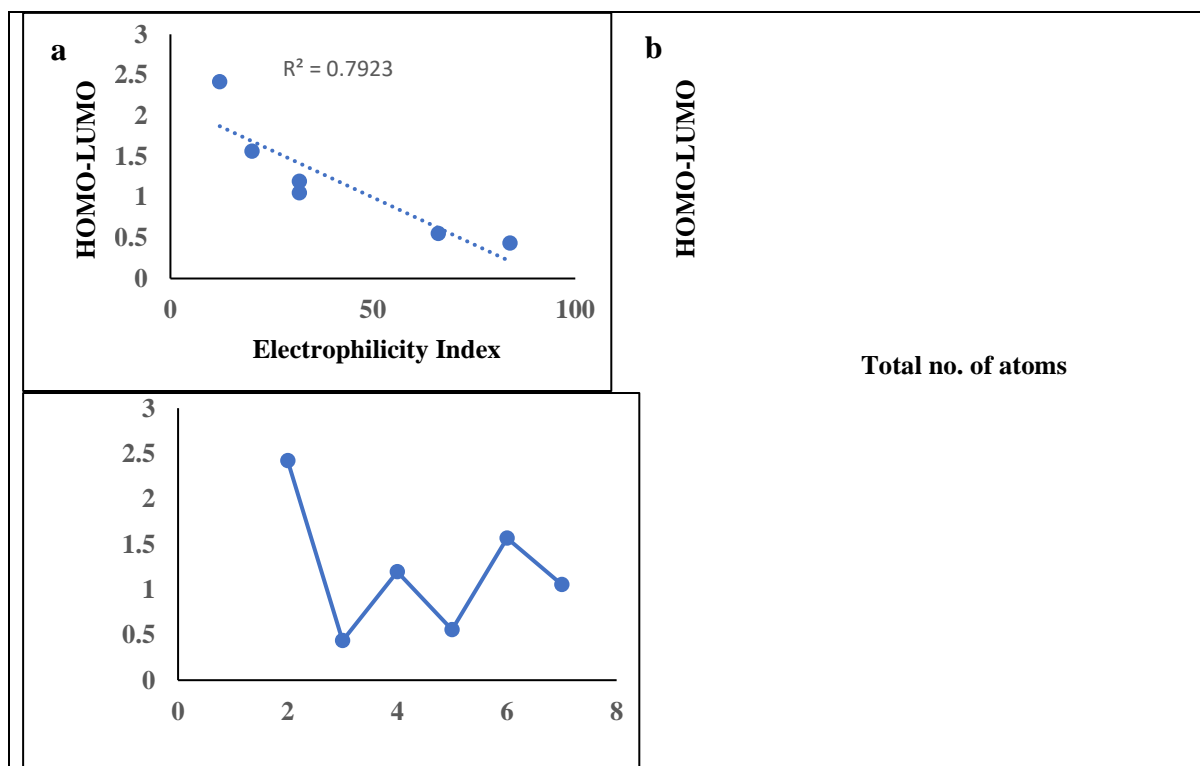


Fig. 1. (a) A linear correlation between Electrophilicity Index and HOMO-LUMO Energy gap; (b) Oscillation behavior of HOMO-LUMO Energy gap as a function of cluster size

#### 4. Conclusion

In this report, theoretical analysis of bimetallic clusters Au<sub>n</sub>Pd (n=1-6) is performed by using DFT methodology. The study of AuPd nanoalloy clusters is of considerable interest due to its interesting catalytic activity. The DFT based descriptors viz. HOMO-LUMO energy gap, electronegativity, hardness, softness and electrophilicity index of Au<sub>n</sub>Pd nanoalloy clusters are computed. The result reveals that clusters AuPd and Au<sub>2</sub>Pd have maximum and minimum values of HOMO-LUMO energy gap respectively. The HOMO-LUMO energy gap have linear relationship with molecular hardness and inverse relationship with softness values. Similar kind of relationship is observed between HOMO-LUMO gap and other DFT based descriptors. The correlation coefficient  $R^2 = 0.792$  obtained between HOMO-LUMO energy gap and electrophilicity index supports our analysis. The HOMO-LUMO energy gap also display interesting odd-even oscillation behavior, which specifies that clusters with an odd number of atoms have small energy gap as compared to their neighbor clusters with even number of atoms.

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