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THEORETICAL STUDY OF BI-METALLIC Ag_mAu_n ; ($m+n=2-8$) NANO ALLOY CLUSTERS IN TERMS OF DFT BASED DESCRIPTORS

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ABSTRACT

Due to wide applications of bi-metallic nano alloys, the theoretical study of the same is an active field of research. A deep theoretical insight can explore vividly the physico-chemical properties of such compounds. Recently Ag-Au nano alloys have gained a considerable interest for possessing unique engineering properties. In this report, Ag_mAu_n ($m + n = 2-8$) clusters have been studied invoking DFT based descriptors. Our computed data distinctly exhibits odd-even oscillation behaviour. A successful correlation has been made between computed descriptors and their experimental counterpart. This theoretical analysis is probably the first attempt in this domain.

Keywords: Density Functional Theory, Bi-metallic Nano Alloy, Opto-electronic property.

1. INTRODUCTION

In the recent decades, nanomaterials have deeply integrated into our everyday's life. Since last few years, nanomaterials and nanotechnology have emerged as important research domains of science and technology [1]. The classification of nanoparticles is done in terms of

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size range of 1-100 nm. That particular size range exists between the levels of atomic / molecular and bulk material [1-5]. Due to existence of a large number of quantum mechanical and electronic effects, nanoparticles possess various unique physico-chemical properties [2-4]. But, there are still some instances of nonlinear transition of certain physical properties, which may vary depending on their size, shape and composition [6, 7]. A large number of scientific reports are available for describing the effects of size and structure to change the optical, electronic, magnetic, chemical and other physical properties of nanoparticles [1, 3, 4]. A deep insight into the research of nanoparticles with well –defined size and structure may lead to some other alternatives for better performance [8]. The nanoparticles, due to its vast applications in the areas of biological labeling, photochemistry, catalysis, information storage, magnetic device, optics, sensors, photonics, optoelectronics, nanoelectronics etc. have got immense importance [1, 3, 9-11].

The noble metals can be extensively applied in several technological areas due to its superior catalytic, magnetic and electronic properties [12–18]. A number of reports are available for describing the conjoint effect of two or more noble metals to enhance the above mentioned properties [13, 19-20]. Now a days, different compositions of nano alloys are being utilized for advancement of methodologies and characterization techniques [21, 13, 19]. A deep study of core-shell structure of nano compounds is very much popular as because its properties can be tuned through the proper control of other structural and chemical parameters. Group 11 metal (Cu, Ag and Au) clusters exhibit the filled inner d orbitals with having one unpaired electron in the valence s shell [22]. This electronic arrangement is responsible to reproduce the exactly similar shell effects [23-27] which are experimentally observed for the alkali metal clusters [28-30]. As a result, bimetallic noble metal clusters follow to exhibit similar physico-chemical trends with bimetallic alkali metal clusters [31-35]. Among the nano clusters of Group 11 elements, the compound formed between Ag-Au is very much popular due to its large scale applications. Fabbi et al. already reported the importance of Ag-Au dimer using dispersed fluorescence spectroscopy [36]. A number of theoretical observations have been made to explore the physico-chemical properties and importance of Ag-Au dimer [37,38]. The location of silver has a controlling effect on the optical properties of such particles as because optical properties are governed by plasmon resonance frequency of silver, which is also dependent on its structural environment [39]. It has been already established that gold-silver bi-metallic nano clusters, as catalysts can enhance the reaction efficiency and selectivity [40, 41]. Though, a number of experimental studies have been done on this particular type of compounds, a theoretical analysis invoking Density Functional Theory (DFT) is still unexplored.

DFT is one of the most successful techniques of quantum mechanics to explore the electronic properties of materials in terms of quantitative descriptors. As for the larger systems electron density is more manageable as compared to wave function, DFT is very much popular to study the many- body systems [8]. Super conductivity of metal based alloys [42], magnetic properties of nano alloy clusters [43, 44] quantum fluid dynamics [45], molecular dynamics [46], nuclear physics [47, 48] can be extensively studied by DFT methodology. Recently we have established the importance of DFT based descriptors in the domain of drug designing and engineering materials [49, 50, 51, 52].

The study of density functional theory is broadly classified into three sub categories viz. theoretical, conceptual, and computational [53-56]. The conceptual density functional theory

is highlighted following Parr's dictum "Accurate calculation is not synonymous with useful interpretation. To calculate a molecule is not to understand it" [57].

In this venture, we have studied bi-metallic Ag-Au nano-clusters in terms of DFT based conceptual descriptors. An attempt has been made to correlate the computed descriptors of the compounds with their experimental counterparts.

2. COMPUTATIONAL METHOD

In this study, we have made a computational analysis on the bi-metallic Nano Alloy clusters of Ag_mAu_n; where m + n = 2-8. 3d modeling and structural optimization of all the compounds have been performed using Gaussian 03 [58] within Density Functional Theory framework. For optimization purpose, the Hybrid functional Becke, three parameter, Lee-Yang-Parr (B3LYP) exchange correlation with basis set LanL2dz has been adopted. Energy minimization has been performed without imposing any restriction on molecular spin. We have considered Z-axis as spin polarization axis. In this process, the Symmetrized Fragment Orbitals (SFOs) are combined with auxiliary Core Functions (CFs) to ensure orthogonalization on the (frozen) Core Orbitals (COs).

Invoking Koopmans' approximation [59], we have calculated ionization energy (I) and electron affinity (A) of all the nano alloys using the following ansatz-

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

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

Thereafter, using I and A, the conceptual DFT based descriptors viz. electronegativity (χ), global hardness (η), molecular softness (S) and electrophilicity index (ω) have been computed. The equations used for such calculations are as follows:

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

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

$$S = \frac{1}{2\eta} \quad (5)$$

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

where, μ represents the chemical potential of the system.

3. APPLICATION

In this study, we have made a detail theoretical analysis of Ag-Au bi-metallic Nano clusters in terms of electronic structure theory.

3.1. Results

The orbital energies in form of HOMO (Highest Occupied Molecular Orbital)-LUMO (Lowest Unoccupied Molecular Orbital) gap along with computed DFT based descriptors viz. molecular electronegativity, global hardness, global softness, global electrophilicity index and dipole moment of instant compounds have been reported in the Table-1.

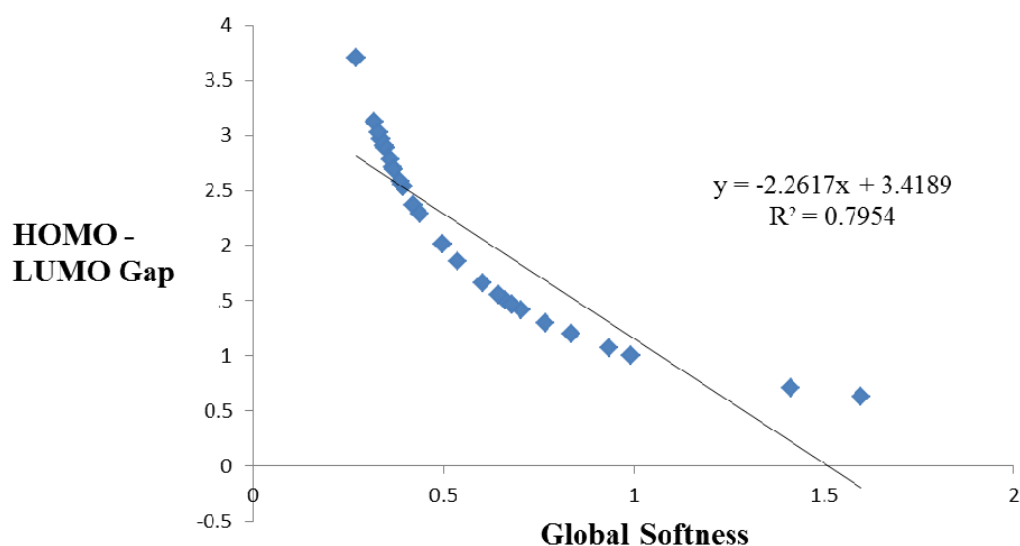
Table 1: Computed DFT based descriptors of Ag_mAu_n ; $m+n=2-8$ nano alloy clusters

Species	HOMO-LUMO Gap (eV)	Electronegativity (eV)	Hardness (eV)	Softness (eV)	Electrophilicity Index (eV)	Dipole Moment (Debye)
AgAu	3.1239	4.7553	1.5619	0.3201	2.3776	2.8191
AgAu ₂	1.3003	6.0589	0.6501	0.7690	3.0294	0.0000
AgAu ₃	2.5487	5.4973	1.2743	0.3923	2.7486	2.9422
AgAu ₄	1.5055	5.3428	0.7527	0.6642	2.6714	0.0000
AgAu ₅	2.7133	4.6948	1.3566	0.3685	2.3474	0.8952
AgAu ₆	1.0688	4.8161	0.5344	0.9356	2.4080	0.0000
AgAu ₇	1.8568	4.8784	0.9284	0.5385	2.4392	3.1101
Ag ₂ Au	1.4149	3.8366	0.7074	0.7067	1.9183	2.4083
Ag ₂ Au ₂	2.7754	4.5984	1.3877	0.3603	2.2992	0.0001
Ag ₂ Au ₃	2.3672	4.0678	1.1836	0.4224	2.0339	2.4020
Ag ₂ Au ₄	2.6937	4.6120	1.3468	0.3712	2.3060	1.9852
Ag ₂ Au ₅	1.5509	4.1767	0.7754	0.6447	2.0883	0.0150
Ag ₂ Au ₆	2.5305	4.9386	1.2652	0.3951	2.4693	2.6825
Ag ₂ Au ₇	2.0135	4.3536	1.0067	0.4966	2.1768	2.2463
Ag ₃ Au	2.5577	3.9726	1.2788	0.3909	1.9863	2.0431
Ag ₃ Au ₂	1.1972	5.1699	0.5986	0.8352	2.5849	2.0312
Ag ₃ Au ₃	3.7005	4.8978	1.8502	0.2702	2.4489	0.0031
Ag ₃ Au ₄	1.6598	4.2855	0.8299	0.6024	2.1427	0.0071
Ag ₃ Au ₅	2.8842	5.1426	1.4421	0.3467	2.5713	0.0501
Ag ₃ Au ₆	0.6258	4.5576	0.3129	1.5978	2.2788	2.2190
Ag ₄ Au	1.0067	4.4216	0.5033	0.9932	2.2108	2.3075
Ag ₄ Au ₂	2.9114	4.8569	1.4557	0.3434	2.4284	0.0000
Ag ₄ Au ₃	1.4693	4.0542	0.7346	0.6805	2.0271	2.1288

Ag_4Au_4	2.5849	4.9114	1.2924	0.3868	2.4557	0.0050
Ag_5Au	2.2856	3.8094	1.1428	0.4375	1.9047	0.6442
Ag_5Au_2	1.4693	3.8366	0.7346	0.6805	1.9183	0.0161
Ag_5Au_3	2.6937	4.7481	1.3468	0.3712	2.3740	2.6717
Ag_6Au	0.7074	3.3468	0.3537	1.4135	1.6734	0.0052
Ag_6Au_2	2.9658	4.9386	1.4829	0.3371	2.4693	2.9574
Ag_7Au	3.0203	5.0474	1.5101	0.3310	2.5237	0.7679

The linear regression analysis has been made between HOMO-LUMO energy gaps along with their computed softness in the Figure 1.

Figure 1: A linear correlation between Global Softness Vs HOMO-LUMO Gap

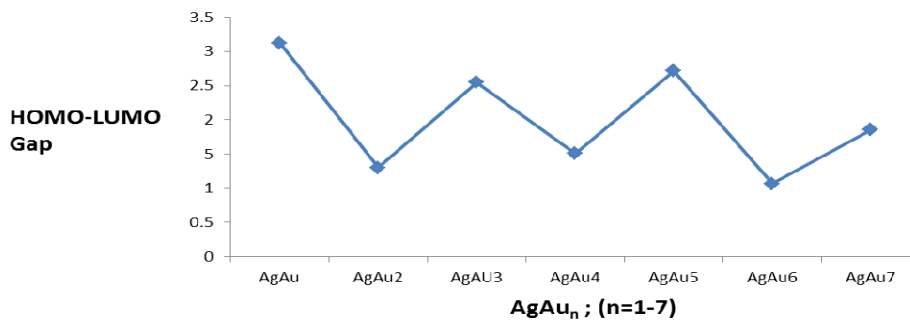
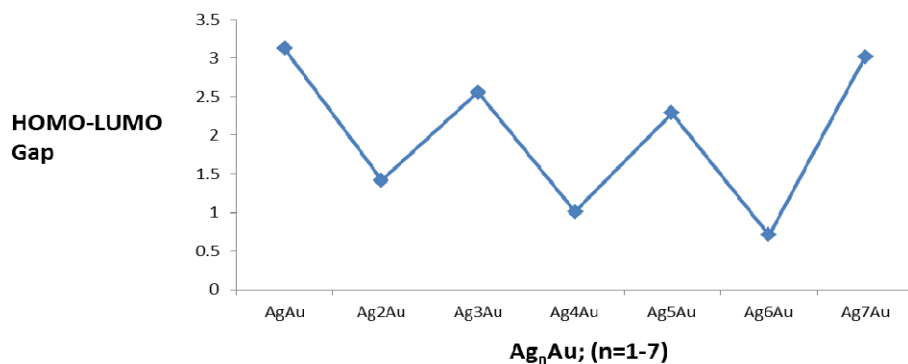
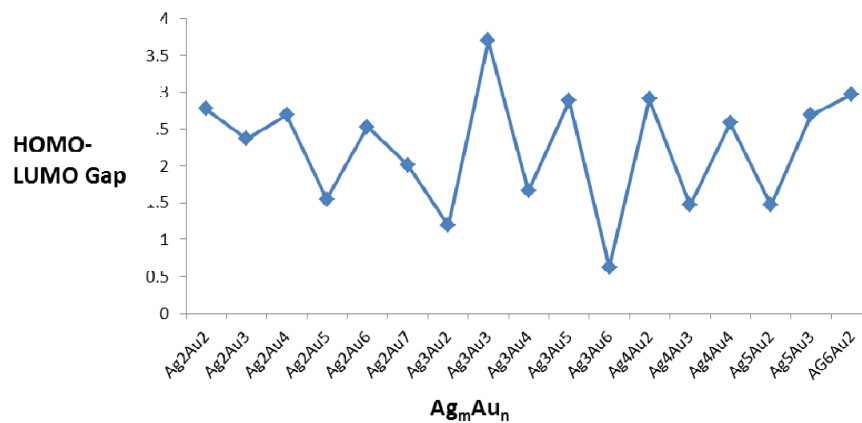


The nano alloy clusters of Ag_mAu_n ; ($m+n=2-8$) have been parted in the form of AgAu_n ($n=1-7$), Ag_nAu ($n=1-7$) and the remaining nano alloy clusters of Ag_mAu_n ($m+n=2-8$) like Ag_2Au_2 , Ag_2Au_3 , Ag_2Au_4 etc. to observe the behaviour of size dependence of the HOMO-LUMO energy gaps which are shown in the Figure -2, Figure-3 and Figure-4 respectively.

A comparative analysis of experimental and computed bond length is shown in Table 2.

Table 2: The calculated bond lengths (\AA) for the Ag_2 , Au_2 , AgAu species

Species	Theoretical Bond Length	Experimental Bond Length ^{REF}
Ag_2	2.50	2.53 ^[61]
Au_2	2.48	2.47 ^[62]
AgAu	2.50	2.50 ^[36]

Figure 2: Size dependence of HOMO -LUMO Gap and AgAu_n; (n=1-7) nano alloy clusters**Figure 3:** Size dependence of HOMO-LUMO Gap and Ag_nAu; (n=1-7) nano alloy clusters**Figure 4:** Size dependence of HOMO-LUMO Gap and Ag_mAu_n (Ag₂Au₂, Ag₂Au₃, Ag₂Au₄, Ag₂Au₅, Ag₂Au₆, Ag₂Au₇, Ag₃Au₂, Ag₃Au₃, Ag₃Au₄, Ag₃Au₅, Ag₃Au₆, Ag₄Au₂, Ag₄Au₃, Ag₄Au₄, Ag₅Au₂, Ag₅Au₃, Ag₆Au₃) nano alloy clusters

3.2. Discussion

From the Table 1, it is distinctly observed that HOMO-LUMO gaps of Ag-Au nano clusters maintain direct relationship with their computed global hardness values. As the frontier orbital energy gap increases, their hardness value increases. On experimental point of view this is expected. As the molecule possesses the highest HOMO-LUMO gap, it will be least prone to response against any external perturbation and that means it will be the least reactive. Table-1 reveals that Ag_3Au_3 is the least reactive species whereas Ag_3Au_6 will exhibit the maximum response. Though there is no such available quantitative data of optical properties of aforesaid clusters, we can assume that there must be a direct qualitative relationship between optical properties of Ag-Au nano clusters with their computed HOMO-LUMO gap. The assumption is based on the fact that optical properties of materials are interrelated with flow of electrons within the systems which in turn depend on the difference between the distance of valence and conduction band. A direct linear relationship between HOMO-LUMO gap with the difference in the energy of valence-conduction band has been already reported [60]. On the basis of above mentioned points, we may conclude that optical properties of instant bi-metallic Nano clusters increase with increase of their hardness values. Similarly softness data exhibits an inverse relationship towards the optical properties. The linear regression analysis has been made between HOMO-LUMO energy gaps along with their computed softness in the Figure – 1. The high value of regression coefficient observed in the Figure-1 ($R^2=0.7954$) validates our predicted model.

A comparative analysis has been made between experimental bond length [36, 61, 62] and our computed data of the species namely Ag_2 , Au_2 and AgAu . The same is reported in Table-2. A close agreement between experimental report and our computed bond length is reflected from the Table -2. It supports and validates our computational analysis.

We have investigated the chemical stabilities of Ag_mAu_n ; ($m+n=2-8$) in terms of energy gaps between HOMO-LUMO. It is observed that in a molecular system chemical stability is enhanced with large HOMO-LUMO energy gaps [63]. Figure-2, Figure-3 and Figure-4 reveals that the HOMO-LUMO energy gap for the nano alloy clusters exhibit remarkable odd-even oscillation behaviour, the even-number clusters show larger HOMO-LUMO energy gaps than the neighboring odd-number clusters, which is expected trend for closed/open systems [63, 64, 65, 66]. It has been already reported that the $\text{Ag}_{1,3,5,7}\text{Au}$ (even number) clusters keep higher chemical stability than their neighbor clusters (odd number). Same pattern is also visible in the Figure-2, Figure-3 and Figure-4 [63, 64, 65, 66]. The nano alloy clusters which show improved chemical stability can be used as building block of nanomaterials [63].

4. CONCLUSION

In recent day, bi-metallic nano alloy clusters have got immense importance due to its diverse nature of applications. A marked optical property is observed in case of nano cluster containing group 11 metals, namely Silver and Gold. In this paper, we have studied and analyzed for the first time about the molecular system of Ag_mAu_n ; ($m+n = 2-8$) nano clusters in terms of conceptual DFT based descriptors namely global hardness, electronegativity,

softness, electrophilicity index and dipole moment. The result of this analysis reveals that the HOMO-LUMO gap of this alloy runs hand in hand along with it evaluated global hardness. As in absence of any quantitative benchmark, the optical property of Ag-Au nano cluster has been assumed to be exactly equivalence of it HOMO-LUMO gap. Here our evaluated data reveals that optical property of these compounds maintains a direct relationship with hardness and inverse relationship with softness. Considering other experimental facts, this trend is expected. The high numerical value of regression coefficients for different models, predicted between hardness, softness and HOMO-LUMO gap successfully supports our analysis. The nano alloy clusters also exhibit interesting odd-even oscillation behaviour, by showing that even numbers of clusters are more stable in comparison to their neighbor odd number clusters. From this study, we can say that Ag_3Au_3 is the most stable cluster among Ag_mAu_n ($m+n=2-8$) nano alloy clusters. Our computed bond lengths for the species like Ag_2 , Au_2 and $AgAu$ are numerically very close to the experimental values.

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