Computational Investigation of Ge Doped Au Nanoalloy Clusters: A DFT Study

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Abstract. In this study, electronic and optical properties of AuₙGe (n=1-9) nanoalloy clusters are systematically investigated in terms of the Density Functional Theory (DFT) with the Becke, three parameter, Lee-Yang-Parr (B3LYP) exchange correlation functional. Conceptual DFT based global descriptors have turned to be indispensable tools for correlating the experimental properties of compounds. In this study, experimental properties of AuₙGe (n=1-9) nanoalloy clusters are correlated in terms of DFT based descriptors viz. HOMO-LUMO gap, Global Hardness (η), Global Softness (S), Electronegativity (χ) and Electrophilicity Index (ω).

Our computed bond length exhibits a close agreement with experimental data. The high value of regression coefficient between global softness and HOMO-LUMO gap supports and validates our predicted model.

1. Introduction
Since last few years, the study of nanoscale materials and nanoelectronics has been developed as real field of research in domain of science and technology [1]. The nanoparticles have been classified in terms of size, ranging between 1-100 nm. That particular size range exists between the levels of atomic / molecular and bulk material [1-5]. Nanoparticles possess several physical and chemical properties because of large number of quantum mechanical and electronic effects present in the molecular system [2-4]. However, there are still some cases of nonlinearity shift of certain physico-chemical properties, which may vary depending on their composition and molecular size [6, 7]. There are a large number of experimental and theoretical reports are available which describes the variation in electronic, mechanical, magnetic, optical and other physico-chemical behaviour due to effects of size, composition and structure of nanoparticles [1,3,4]. A thorough study of nanoparticles with well – defined size, composition and structure may lead to some other alternatives for better performance [8]. The nanoparticles have received a lot of attention, due to its various applications in the areas of life sciences, bio-medicine, photocatalysis, data storage, optoelectronics, microelectronics etc. [1,3,9-11].

Due to unique electronic, catalytic, optical and magnetic properties gold nanoclusters are very much popular and a potential candidate for catalysis, optoelectronic, bio-physics and medicine [12-28]. A number of scientific reports are available for describing that impurity atoms can enhance the above mentioned properties of doped gold clusters that are sensitive towards the nature of dopant atom [28-30]. Nowadays, a well-defined composition of nanoalloy is being utilized for the
development of methodologies and characterization techniques [29-31]. A through study of core-shell structure of nanoalloy clusters is very much popular as because its properties can be altered through the suitable control of other structural and chemical restrictions. Germanium doped metal nanoalloy clusters have been focus of research due to its magnetic and superconducting behaviours, photoelectric effect, thermodynamic properties, and reduced energy gap [32-40]. It has been already reported that metal doped Ge clusters can be used in novel cluster-assembled materials due to its small energy difference between HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) [38-39]. Julian et al. have fabricated Ge-Au nanoclusters by placing Germanium into the unannealed Gold-doped silica films. The concentration of germanium and gold in silica films have been calculated by Rutherford backscattering spectrometry (RBS) before and after the thermal annealing process. In this study, authors have observed that concentration of gold in silica decreased from 1.2 to 1.1% and gold content decreased after annealing process, after performing calibration and diffraction experiments it has been found that there is no diffraction either from Ge or Au, which shows that they are amorphous in nature. The result obtained from HAADF-STEM (high-angle annular dark-field scanning transmission electron microscopy) indicates that germanium-gold nanoclusters have a bi-lobe structure. The in-situ Raman spectroscopy experiment shows that a phase transition occurs from β Ge-Au to crystalline Ge after 80 °C [41]. Kumar et al. have studied a series of clusters of TMXn (X= Si, Ge, Sn, and Pb; TM=Ni, Pd, Pt, Zn and Cd; n=10 and 12) using DFT method and also shows that doping of Ni or Pt atom into clusters of Xn (X=Si, Ge, Sn and Pb) gives the smallest metal-encapsulated clusters [42-43]. However, a number of experimental and theoretical studies have been done on Germanium-Gold nanoalloy clusters, a computational investigation invoking density functional based descriptors is yet to explore.

Since the last couple of years Density Functional Theory (DFT) has been dominant method to explore the variety of properties of solids and molecules in terms of quantitative descriptors. DFT methods have been extensively termed as effective computational tool to study the many-body systems [8], super conductivity of metal based alloys [44], electronic, magnetic, optical, mechanical properties [45-46] quantum fluid dynamics [47], molecular dynamics [48] and nuclear physics [49-50]. Recently we have established the importance of density functional based descriptors in the area of bi-metallic and gold-silicon nanoalloy clusters [51-56]. The study of density functional theory is broadly classified into three sub categories viz. theoretical, conceptual, and computational [57-60]. 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” [61].

In this report, we have successfully investigated the electronic and optical properties of AuₙGe (n=1-9) nanoalloy clusters in terms of DFT based descriptors. An attempt has been made to compare the computed descriptors of the real compounds with their experimental counterparts.

2. Computational details

In this report, a computational analysis on the nano alloy clusters of AuₙGe; where n = 1-9 has been performed. 3-dimensional material modeling and structural optimization of all the clusters have been implemented using Gaussian 03 [62] within Density Functional Theory frame. For optimization purpose, Becke, three parameter, Lee-Yang-Parr (B3LYP) exchange correlation with basis set LanL2dz has been adopted. With the help of Koopmans’ approximation [63], we have computed ionization potential (I) and electron affinity (A) of all the nano alloys using the following ansatz-

\[ I = -\varepsilon_{HOMO} \]  
\[ A = -\varepsilon_{LUMO} \]

Thereafter, using I and A, the conceptual DFT based descriptors viz. electronegativity (\(\chi\)), global hardness (\(\eta\)), molecular softness (S) and electrophilicity index (\(\omega\)) have been calculated. The equations used for such calculations are as follows-
\[ \chi = -\mu = \frac{I + A}{2} \]  

(3)

Where, \( \mu \) represents the chemical potential of the system.

\[ \eta = \frac{I - A}{2} \]  

(4)

\[ S = \frac{1}{2\eta} \]  

(5)

\[ \omega = \frac{\mu^2}{2\eta} \]  

(6)

3. Results and discussions

3.1 HOMO-LUMO Gap

In this study, a detail computational analysis of Au\(_n\)Ge (\( n=1-9 \)) nanoalloy clusters has been performed in terms of electronic structure theory. The electronic properties of Au-Ge nanoalloy clusters have been studied by computing the energy difference between HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital). The HOMO-LUMO energy gap is a remarkable parameter for examining the kinetic stability of nanoalloy clusters. The electronic energy gap indicates the energy required for an electron to move from the HOMO to the LUMO. The orbital energies in form of HOMO -LUMO energy gap along with computed DFT based descriptors, namely molecular hardness, softness, electronegativity and electrophilicity index have been reported in the Table 1. From Table 1, it is clear that Au\(_9\)Ge has highest HOMO-LUMO gap of 2.040 eV which establishes magical stability in the series of nano alloy clusters. The computed HOMO-LUMO gaps of Au-Ge nanoalloy clusters follow the similar trend with the reported data [39].

3.2 Hardness and Softness

The hardness is an electronic parameter of clusters which characterize the stability of the molecular system. The result from Table 1 reveals that there is a direct relationship between HOMO-LUMO gaps of nanoalloy clusters with their computed hardness. From experimental point of view, frontier energy gap exhibits parallel behaviour with the evaluated hardness values. As the cluster possesses the highest HOMO-LUMO gap, it will be the least prone to response against any external perturbation. The linear correlation between HOMO-LUMO energy gap along with their computed molecular softness is lucidly plotted in the Figure 1. The high value of correlation coefficient (\( R^2=0.911 \)) observed in the Figure 1, validates our predicted model. From the obtained correlation coefficients of several DFT based descriptors and their HOMO-LUMO gaps, it can be concluded that the best linear relationship is observed in case of hardness and the least one for electronegativity (\( R^2=0.118 \)) of these nano clusters. However, due to absence of any quantitative data for optical properties of this particular compound, we can tacitly assume that there must be a direct qualitative connection between optical properties of germanium-gold nanoalloy 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 molecular systems which in turn depend on the difference between the distance of valence and conduction band. There is a direct linear relationship between HOMO-LUMO energy gap with the difference in the distance of valence and conduction band [64]. From On that basis, we may conclude...
that optical properties of Au-Ge nanoalloy clusters increase with increase of their molecular hardness values. Similarly softness data shows an inverse relationship towards the experimental optical properties.

A comparative study has been made between our computed bond length and experimental data of the species namely Au$_2$, Ge$_2$ and Au-Ge [65-67]. The same is reported in the Table 2. An excellent agreement between experimental bond length and our computed results supports and validates our computational analysis.

**Table 1.** Computed DFT based descriptors of Au$_n$Ge (n=1-9) nanoalloy clusters

| Species | HOMO-LUMO Gap (eV) | Electronegativity (eV) | Hardness (eV) | Softness (eV) | Electrophilicity Index (eV) |
|---------|-------------------|------------------------|--------------|--------------|---------------------------|
| AuGe    | 1.551             | 4.503                  | 0.775        | 0.644        | 13.075                    |
| Au$_2$Ge| 1.061             | 5.101                  | 0.530        | 0.942        | 24.528                    |
| Au$_3$Ge| 0.462             | 4.476                  | 0.231        | 2.161        | 43.312                    |
| Au$_4$Ge| 1.550             | 5.101                  | 0.775        | 0.644        | 16.782                    |
| Au$_5$Ge| 1.578             | 4.271                  | 0.789        | 0.633        | 11.563                    |
| Au$_6$Ge| 0.435             | 5.115                  | 0.217        | 2.296        | 60.106                    |
| Au$_7$Ge| 1.578             | 4.680                  | 0.789        | 0.633        | 13.878                    |
| Au$_8$Ge| 1.659             | 4.911                  | 0.829        | 0.602        | 14.532                    |
| Au$_9$Ge| 2.040             | 4.367                  | 1.020        | 0.490        | 9.345                     |

**Table 2.** The calculated bond length (Å) of Au$_2$, Ge$_2$ and Au-Ge species

| Species | Computed Bond Length | Experimental Bond Length |
|---------|----------------------|--------------------------|
| Au$_2$  | 2.48                 | 2.47$^{65}$              |
| Ge$_2$  | 2.44                 | 2.39$^{66}$              |
| AuGe    | 2.45                 | 2.56$^{67}$              |
4. Conclusion
Due to large scale of applications, Au-Ge nanoalloy clusters have gained immense importance. In this report, we have successfully investigated the electronic and optical properties of gold-germanium nanoalloy clusters in terms of conceptual DFT based descriptors viz. molecular hardness, HOMO-LUMO gap, electronegativity, softness, and electrophilicity index. The computed HOMO-LUMO gap are within the range of 2eV, indicating their potential applications in novel cluster-assembled materials. The result reveals that HOMO-LUMO energy gap have direct relationship with their hardness value. Due to unavailability of any quantitative data, optical properties of Au-Ge nanoalloy clusters have been assumed to be exactly equivalent to its HOMO-LUMO energy gap. Considering the direct relationship between optical properties of Au-Ge nanoalloy clusters with their computed HOMO-LUMO gap, a qualitative relationship has been established between optical property of the instant nanoalloy clusters and their hardness values. This trend is consistent with other experimental facts also. The high value of regression coefficient between HOMO-LUMO gap and softness supports our approach pertaining to modeling. The computed bond lengths for the species Au$_2$, Ge$_2$ and Au-Ge are in very well agreement with the experimental data which supports and validates our computational analysis.

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