Computational Study of Au\textsubscript{m}Si\textsubscript{n} (m+n=2-6) Nanoalloy Clusters Invoking Density Functional Based Descriptors

P. Ranjan \textsuperscript{1}, A. Kumar \textsuperscript{1}, T. Chakraborty \textsuperscript{2}

\textsuperscript{1} Department of Mechatronics Engineering, Manipal University Jaipur, Dehmikalan, Jaipur-303007
\textsuperscript{2} Department of Chemistry, Manipal University Jaipur, Dehmikalan, Jaipur-303007

Email: tanmoy.chakraborty@jaipur.manipal.edu, tanmoychem@gmail.com

Abstract. In this study, electronic and optical properties of Au\textsubscript{m}Si\textsubscript{n} (m+n=2-6) nanoalloy clusters are systematically investigated in terms of the Density Functional Theory (DFT) with the generalized gradient approximation (GGA). Conceptual DFT based global theoretical descriptors have been used to reveal experimental properties qualitatively. In this venture, experimental properties of Au\textsubscript{m}Si\textsubscript{n} (m+n=2-6) nanoalloy clusters are correlated in terms of DFT based descriptors viz. HOMO-LUMO gap, Global Hardness (\(\eta\)), Global Softness (S), Electronegativity (\(\chi\)) and Electrophilicity Index (\(\omega\)). Our computed bond length of this silicon-gold cluster exhibits a close agreement with experimental bond length. Regression analysis has been done in terms of correlation between our computed descriptors and their experimental counterpart.

1. Introduction

In the recent decades, nanomaterials have deeply integrated into everyday’s life. Since last few years, nanomaterials and nanotechnology have emerged as frontier research domain of science and technology [1]. The classification of nanoparticles is done in terms of 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 experimental and theoretical reports are available for describing the effects of size and structure to change the optical, electronic, magnetic, chemical and other physico-chemical 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 various 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].

Due to unique electronic, catalytic, optical and magnetic properties gold nanoclusters are very much popular and a potential candidate for fabrication, catalysis, bio-physics and medicine [12-28]. A number of 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-...
Nowadays, different compositions of nano alloys are being utilized for advancement of methodologies and characterization techniques [29-31]. 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. Silicon doped metal nanoclusters have been focus of extensive theoretical and experimental investigation due to its high importance in the field of microelectronics and semiconductor industry [28, 32]. Pal et al. [33] have reported clusters of Au_{10}M^+(M=Si, Ge, Sn) and observed that SiAu_5 cluster have a tetrahedral 3D structure but MAu_x (x=6, 7; M=Si, Ge, Sn) have quasi-planar structures. It reflects that Au-Au interactions and Au-M interactions in the MAu x clusters have a dangling unit of Au-Si, resembling that of larger Si-doped gold cluster SiAu_{16}. Majumder et al. [34] studied clusters of Au_5M (M= Na, Mg, Al, Si, P and S) and found that impurities with p electrons (Al,Si,P) exhibits nonplanar geometries while with s electrons (Na, Mg) shows planar geometries, the exception occurs for AuS. Sun et al. [35] reported the cage structure of Au_{16}Si and observed that endohedral configuration is metastable and the silicon atom prefers to be on the exterior surface of the cage. Though, a number of experimental and theoretical 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 approaches 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 [36], magnetic properties of nano alloy clusters [37, 38] quantum fluid dynamics [39], molecular dynamics [40], nuclear physics [41, 42] can be extensively studied by DFT methodology. Recently we have established the importance of DFT based descriptors in the domain of drug designing and nano-engineering materials [43-47]. The study of density functional theory is broadly classified into three sub categories viz. theoretical, conceptual, and computational [48-51]. 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” [52].

In this venture, we have studied Au_mSi_n (m+n=2-6) 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 details
In this study, we have made a computational analysis on the nano alloy clusters of Au_mSi_n; where m+n = 2-6. 3d modeling and structural optimization of all the compounds have been performed using Gaussian 03 [53] within Density Functional Theory framework. For optimization purpose, Generalized Gradient Approximation (GGA) exchange correlation with basis set LanL2dz has been adopted. Invoking Koopmans’ approximation [54], we have calculated ionization energy (I) and electron affinity (A) of all the nano alloys using the following ansatz-

\[ I = -\varepsilon_{\text{HOMO}} \]  \hspace{1cm} (1)
\[ A = -\varepsilon_{\text{LUMO}} \]  \hspace{1cm} (2)

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 computed. 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

In this study, a detailed theoretical analysis of Au\(_m\)Si\(_n\) (\(m+n=2-6\)) nanoalloy clusters has been performed using electronic structure theory. The HOMO (Highest Occupied Molecular Orbital)-LUMO (Lowest Unoccupied Molecular Orbital) energy gap is a remarkable parameter for examining the kinetic stability of nano alloy 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 electronegativity, global hardness, global softness, and electrophilicity index have been reported in the Table 1. The result from Table 1 indicates that HOMO-LUMO gap of Au\(_m\)Si\(_n\) (\(m+n=2-6\)) is maintaining a direct relationship with their evaluated global hardness values. As the frontier orbital energy gap increases, the hardness value increases. From experimental point of view, it is an expected trend. As the molecule possesses the highest HOMO-LUMO gap, it will be the least prone to response against any external perturbation. From Table 1, it is clear that Au\(_2\)Si has highest HOMO-LUMO gap which establishes magical stability in the series of nano alloy clusters. 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 Au-Si 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. There is a direct linear relationship between HOMO-LUMO gap with the difference in the energy of valence-conduction band [55]. On that basis, we may conclude that optical properties of instant nano alloy clusters increases with increase of their hardness values. Similarly, softness data exhibits an inverse relationship towards the experimental optical properties. The linear correlation between HOMO-LUMO gap along with their computed global hardness is lucidly plotted in the Figure 1. The high value of correlation coefficient (\(R^2=0.996\)) 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 (\(R^2=0.071\)) of these nano clusters.

A comparative analysis has been made between experimental bond length and our computed data of the species namely Au\(_2\), Si\(_2\) and Au-Si. The same is reported in the Table 2. An excellent agreement between our computed bond length with reported experimental values [28, 32, 56-58] established faith in the accuracy and reliability of the applied method used in this work which supports and validates our computational analysis.
Table 1. Computed DFT based descriptors of Au$_m$Si$_n$ (m+n=2-6) nanoalloy clusters

| Species | HOMO-LUMO Gap (eV) | Electronegativity (eV) | Hardness (eV) | Softness (eV) | Electrophilicity Index (eV) |
|---------|-------------------|------------------------|---------------|---------------|-----------------------------|
| AuSi    | 1.632             | 4.680                  | 0.816         | 0.612         | 13.416                      |
| AuSi$_2$| 2.748             | 4.367                  | 1.374         | 0.363         | 6.939                       |
| AuSi$_3$| 2.394             | 4.707                  | 1.197         | 0.417         | 9.254                       |
| AuSi$_4$| 2.639             | 4.748                  | 1.319         | 0.378         | 8.541                       |
| AuSi$_5$| 2.775             | 4.870                  | 1.387         | 0.360         | 8.547                       |
| Au$_2$Si| 2.911             | 5.183                  | 1.456         | 0.343         | 9.228                       |
| Au$_3$Si| 1.687             | 4.952                  | 0.843         | 0.592         | 14.537                      |
| Au$_4$Si| 3.237             | 4.897                  | 1.687         | 0.296         | 7.532                       |
| Au$_5$Si| 1.877             | 4.367                  | 0.938         | 0.532         | 10.158                      |
| Au$_2$Si$_2$| 1.714          | 4.748                  | 0.857         | 0.583         | 13.151                      |
| Au$_3$Si$_2$| 2.775          | 4.870                  | 1.387         | 0.360         | 8.547                       |
| Au$_2$Si$_3$| 2.667          | 4.680                  | 1.333         | 0.375         | 8.214                       |
| Au$_3$Si$_3$| 2.394          | 5.006                  | 1.197         | 0.417         | 10.468                      |
| Au$_2$Si$_4$| 2.557          | 4.652                  | 1.278         | 0.390         | 8.464                       |
| Au$_2$Si$_3$| 2.639          | 4.965                  | 1.319         | 0.378         | 9.342                       |

Table 2. The calculated bond length (Å) of Au$_2$, Si$_2$ and AuSi species

| Species | Computed Bond Length | Experimental Bond Length |
|---------|----------------------|--------------------------|
| Au$_2$  | 2.48                 | 2.47$^{56}$              |
| Si$_2$  | 2.36                 | 2.28$^{32}$              |
| AuSi    | 2.36                 | 2.26$^{32,33,57,58}$     |

Figure 1. A linear correlation between Global Hardness Vs HOMO-LUMO Gap

\[
y = 1.93x + 0.0771
\]

\[
R^2 = 0.9961
\]
4. Conclusion
In this report, an investigation has been done on electronic and optical properties of the mixed gold-silicon nano-alloy clusters in terms of conceptual DFT based descriptors viz. global hardness, HOMO-LUMO gap, electronegativity, softness, and electrophilicity index. Our computed result reveals that HOMO-LUMO energy gap runs hand in hand along with the molecular hardness of the compounds. Considering the direct relationship between optical properties of Au-Si nanoalloy clusters with their computed HOMO-LUMO gap, a qualitative relationship has been established between optical property of the mentioned compounds and their global hardness values. This trend is consistent with other experimental facts also. The high value of regression coefficient between HOMO-LUMO gap and hardness supports our approach pertaining to modeling. Our computed bond lengths for the species Au$_2$, Si$_2$ and Au-Si are numerically very close to the reported experimental values.

References
[1] Khosousi A Z and Dhirani A A 2008 Chem. Rev. 108 4072.
[2] Daniel M C and Astruc D 2004 Chem. Rev. 104 293.
[3] Ghosh S K and Pal T 2007 Chem. Rev. 107 4797.
[4] Chaudhuri R G and Paria S 2012 Chem. Rev. 112 2373.
[5] Alivisatos A P 1996 Science 271, 933.
[6] Kastner M A 1993 Phys. Today 46, 24.
[7] Haruta M 2002 Cattech 6 102.
[8] Ismail R 2012 Theoretical studies of free and supported nanoalloy clusters Ph.D. Thesis University of Birmingham UK.
[9] Roucoux A, Schulz J and Patin H 2002 Chem. Rev. 102, 3757.
[10] Flores B M M, Kharisov B I, Perez V M J, Martinez P E and Lopez S T 2011 Ind. Eng. Chem. Res. 50 7705.
[11] Murray R W 2008 Chem. Rev. 108 2688.
[12] Huang X, Sayed I E, Qian W and Sayed M E 2006 J. Am. Chem. Soc. 128 2115.
[13] Hainfeld J, Slatkin D and Smilowitz H 2004 Phys. Med. Biol. 49 N309.
[14] Wu D, Zhang X, Liu P, Zhang L, Fan F and Guo F M 2011 Curr. Nanosci. 7 110.
[15] Zhang X, Guo M, Wu D, Liu P, Sun Y, Zhang L, She Y, Liu Q and Fan F 2011 Int. J. Mol. Sci. 12 2972.
[16] Chen J, Wang D, Xi J, Au L, Siekkinen A, Warsen A, Li Z, Zhang H, Xia Y and Li X 2007 Nano. Lett. 7 1318.
[17] Robinson J M, Takizawa T and Vander D D 2000 J. Microsc. 199 163.
[18] Whetten R L, Khoury J T, Alvarez M M, Murthy S, Vezmar I, Wang Z L, Stephens P W, Cleveland C L, Luedtke W D and Landman U 1996 Adv. Mater 5 428.
[19] Andres R P, Bein T, Dorogi M, Feng S, Henderson J I, Kubiak C P, Mahoney W, Osifchin R G and Reifenberger R 1996 Science 272 1323.
[20] Mirkin C A, Letsinger R L, Mucic R C and Storhoff J J 1996 Nature 382 607.
[21] Alivisatos A P, Johnsson K P, Peng X G, Wilson T E, Loweth C J, Bruchez M P and Schultz P G 1996 Nature 382 609.
[22] Andres R P, Bielefeld J D, Henderson J I, Janes D B, Kolagunta V R, Kubiak C P, Mahoney W J Osifchin R G 1996 Science 272 1369.
[23] Garzon I L, Michaelian K., Beltran M R, Amarillas A P, Ordejon P, Artacho E, Portal D S, Soler J M 1998 Phys. Rev. Lett. 81 1600.
[24] Garzon I L, Rovira C, Michaelian K, Beltran M R, Ordejon P, Junquera J, Portal D S, Artacho E and Soler J M 2000 Phys. Rev. Lett. 85 5250.
[25] Michaelian K, Rendon N and Garzon I L 1999 Phys. Rev. B 60 2000.
[26] Schaff T G and Whetten R L 2000 J. Phys. Chem. B 104 2630.
[27] Priyanka and Dharamvir K 2013 J. Phys. Chem. Chem. Phys. 15 12340.
[28] Gautam S, Goel N and Dharamvir K 2014 RSC Adv. 4 13927.
[29] Ferrando R, Jellinek J and Johnston R L 2008 Chem. Rev. 108 845.
[30] Liu H B, Pal U, Medina A, Maldonado C and Ascencio J A 2005 Phys. Rev. B 71 075403.
[31] Baletto F and Ferrando R 2005 Rev. Mod. Phys. 77 371.
[32] Chuang F, Hsu C, Hsieh Y and Albao M A 2010 Chin. J. Phys. 48 82.
[33] Pal R, Wang L M, Huang W, Wang L S and Zeng X C 2009 J. Am. Chem. Soc. 131 3396.
[34] Majumder C, Kandalam A K and Jena P 2006 Phys. Rev. B 74 205437.
[35] Sun Q, Wang Q, Chen G and Jena P 2007 J. Chem. Phys. 127 214706.
[36] Wacker O J, Kümmel R and Gross E K U 1994 Phys. Rev. Lett. 73 2915.
[37] Illas F and Martin R L 1998 J. Chem. Phys. 108 2519.
[38] Johnson D D, Nicholson D M, Pinski F J, Gyorffy B L and Stocks G M 1990 Phys. Rev. B 41 9701.
[39] Kümmel S and Brack M 2001 Phys. Rev. A 64 022506.
[40] Car R and Parrinello M 1985 Phys. Rev. Lett. 55 2471.
[41] Koskinen M, Lipas P and Manninen M 1995 Nucl. Phys. A 591 421.
[42] Schmid R N, Engel E and Dreizler R M 1995 Phys. Rev. C 52 164.
[43] Ranjan P, Dhail S, Venigalla S, Kumar A, Ledwani L and Chakraborty T 2015 Mater. Sci.-Pol. 33 719.
[44] Chakraborty T and Ghosh D C 2012 Int. J. Chem. Model. 4 413.
[45] Ranjan P, Kumar A and Chakraborty T 2014 Computational Study of Nanomaterials Invoking DFT based Descriptors Environmental Sustainability: Concepts, Principles, Evidences and Innovations ed G C Mishra (New Delhi: Excellent Publishing House) chapter 33 pp 239-242.
[46] Ranjan P, Venigalla S, Kumar A and Chakraborty T 2015 A Theoretical Analysis of Bi-metallic AgAu_n, (n=1-7) Nano-alloy Clusters Invoking DFT based Descriptors Research Methodology in Chemical Sciences: Experimental and Theoretical Approaches ed T. Chakraborty and L. Ledwani (USA: Apple Academic Press & CRC Press).
[47] Ranjan P, Venigalla S, Kumar A and Chakraborty T 2014 New Front. Chem. 23 111.
[48] Parr R G and Yang W 1995 Annu. Rev. Phy. Chem. 46 701.
[49] Kohn W, Becke A D and Parr R G 1996 J. Phys. Chem. 100 12974.
[50] Liu S and Parr R G 1997 J. Chem. Phys. 106 5578.
[51] Ziegler T 1991 Chem.Rev. 91 651.
[52] Geerlings P and Prof F D 2002 Int. J. Mol. Sci. 3 276.
[53] Gaussian 03, Revision C.02, Frisch M J, Trucks G W et al., Gaussian, Inc. Wallingford CT 2004.
[54] Parr R G and Yang W 1989 Density Functional Theory of Atoms and Molecules (Oxford University Press, Oxford).
[55] Xiao H, Kheli J T and Goddard W A III 2011 J. Phys. Chem. Lett. 2 212.
[56] Huber K P and Herzberg G 1979 Constraints of Diatomic Molecules (Van Nostrand Reinhold Company New York).
[57] Schererer J J, Paul J B, Collier C P and Saykally R J 1995 J. Chem. Phys. 102, 5190.
[58] Schererer J J, Paul J B, Collier C P, O’Keefe A and Saykally R J 1995 J. Chem. Phys. 103, 9187.