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APPLICATION OF CONCEPTUAL DENSITY FUNCTIONAL THEORY IN MATERIALS SCIENCE

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Abstract

Density Functional Theory (DFT) is the most sought computational approach in recent days to understand the electronic structure of matter. In this article, we have reported application of Conceptual DFT in materials science. DFT technique play an immense importance role in predicting the structure and physico-chemical properties of materials. In recent years, transition metal clusters have fascinated a lot of attention because of their stimulating physical as well as chemical behaviour and their wide range of applications in various technological and strategic sectors. DFT studies have proven that incorporation of suitable dopant in host clusters enhances the structure, electronic, optical and magnetic properties of overall system. HOMO- LUMO energy gap shows an odd-even alteration behaviour with the cluster size, specifying that cluster with even number of atoms have large energy gap as compared to their neighbouring cluster with odd number of total atoms. HOMO-LUMO of bimetallic clusters are found in linear correlation with the chemical hardness and inverse relation with softness.

1. Introduction

Since decades various powerful computational techniques have been developed by a number of researchers to solve Schrodinger equation for many-body problems. For instance, on the basis of Feynman diagrams and Green's functions researchers have developed Diagrammatic Perturbation Theory (DPT) in physics, similarly in chemistry Configuration Interaction (CI) approach is designed on the basis of Slater determinants [1]. However, these approaches require huge computational resources and for larger systems these techniques do not provide efficient results [2]. Density Functional Theory (DFT) is an approach which provide a viable alternative, more adaptable and also offer high accuracy. The prominence to which DFT has led to the science and technology is recognized in the year 1998 Nobel prize in chemistry, which was conferred to eminent scientists Walter Kohn [3], the originator of DFT, and John Pople [4], who was able to implement DFT in computational chemistry.

DFT is the most efficient, accurate and efficacious computational approach to examine the electronic structure of many-body systems. DFT is widely used in various domains ranging from physics, chemistry, life sciences, biosciences, drug modelling, nuclear sciences, materials sciences, electronic engineering, electrical engineering, mechanical engineering to earth sciences [5]. It helps in the calculation and understanding of various physico-chemical properties of chemical species like binding energy, stability, geometry, ionization potential, electron affinity etc. DFT is categorized into three types- theoretical, conceptual and computational [6-9]. Conceptual DFT (CDFT) acts as a bridge between theoretical and computational DFT. The CDFT is highlighted following Parr's dictum "Accurate calculation is not synonymous with useful interpretation. To calculate a molecule is not to understand it" [10].

Worldwide a large number of scientists are involved in exploring suitable materials for applications in semiconductors, fabrications, photovoltaic, optoelectronic, and thermoelectric devices. In materials science, DFT has evolved as a strong approach for identifying a variety of problems for example- point defects, obtaining the ground state configuration, bandgap issue, dislocations, free energies etc.

2. Results and Discussion

Nowadays transition metal clusters especially copper, gold and silver have shown huge potential applications for semiconductors, fabrication, nanotechnology, life sciences etc. because of their distinctive physical and chemical properties [11-28]. There is a large chunk of researchers globally- experimentalists as well as theoretician are working on pure metallic clusters as well as doped clusters. Study found that doped atoms play vital role in enhancing the structure and other physico-chemical properties especially stability, electronic as well as optical properties of parent clusters [29-31]. The electronic shell structure of transition metal clusters is comparable to those of alkali-metal clusters [29-31]. The unique physical and chemical properties of copper, gold and silver clusters and their applications in various technological and strategic sectors have motivated scientists to envisage the structure, reactivity, and other physico-chemical properties [32, 33]. DFT study reveals that structural transition from 2-D to 3-D transpires at smaller size of atoms for Cu

and Ag as compared to Au clusters [34]. For Au clusters, structural transition from 2-D to 3-D occurs at n=14, whereas for cationic and anionic state of Au clusters it starts at n=8 and n=12 respectively [35, 36]. Metallic clusters are designed on the basis of alkali-metal clusters to study the jellium model and to understand the bonding behaviour among dopants atoms and parent system [29-31]. DFT studies have already been proven that impurity-doped metallic clusters offer enhanced stability, electronic and optical properties as compared to the pure metallic clusters [37, 38]. It is reported that in the case of Au_nAg (n=1-12) clusters, chemical stability of overall system is improved after incorporation of silver atom [39]. For mixed cluster Ag-Au, $Ag_n Au_{25-n}^{2+}$ ($0 \leq n \leq 13$), it is stated that photoluminescence properties of overall system is enhanced after incorporation of Ag atoms [40].

Our research group have studied various bimetallic and multi-metallic clusters for applications in optoelectronics, and photovoltaic devices [41-53]. Ranjan et al. [44] reported that inclusion of dopant atom i.e. Au enhanced the stability as well as electronic properties of $AuSi_n$ clusters. In this work, authors optimized several isomers of $AuSi_n$ and Si_{n+1} (n=1-12) nanoalloy cluster for neutral and cationic state. Relative stability in terms of binding energy, fragmentation energy, and second order difference in energy is studied. Binding energy of pure and doped clusters increases with the size of cluster. For cationic $AuSi_n$ cluster binding energy is higher than the pure Si_{n+1} cluster which shows that doping of transition metal i.e. Au improves the stability of overall cluster. HOMO (Highest Occupied Molecular orbital)- LUMO (Lowest Unoccupied Molecular orbital) energy gap shows an odd-even alteration behaviour with the cluster size, specifying that cluster with total number of even atoms have large energy gap as compared to their neighbouring cluster with odd number of total atom. Conceptual DFT based descriptors of these clusters display an interesting correlation with HOMO-LUMO energy gap.

System Au_nPt (n=1-8) is investigated by using CDFT approach in which it is stated that cluster Au_3Pt is having maximum stability [45]. In the case of Au_nPt cluster, the ground state configuration for n=3 is a rhombus like structure in which platinum is positioned at extremely coordinated sites of structure. Second order difference in energy, HOMO-Luo gap and chemical hardness display an odd-even oscillation phenomena with respect to size of cluster n. Nanoalloy cluster of $[Au_nV]$ for neutral, cationic and anionic state are studied invoking CDFT approach. There are a number of isomers are optimized in which it is found that at n=3, 5 and 3 clusters are stable for neutral, cationic and anionic state. The HOMO-LUMO energy gap fluctuates of these clusters are found in the range of 1.04 eV to 2.37 eV signifying their probable uses in optoelectronic devices and solar cells [48]. HOMO-LUMO energy gap of these clusters are found in linear correlation with the chemical hardness and inverse relation with softness.

Conclusion

Density Functional Theory (DFT) is the most efficient, accurate and computational friendly technique which helps in the prediction of structure, and physico-chemical properties of metallic clusters. In this article, we have presented the application of conceptual DFT in materials science. In the domain of cluster science, metallic clusters especially transition metal clusters have shown

large interest due to their significant physico-chemical properties and potential technological applications. Dopant atom have significant role in the enhancement of physical and chemical properties of materials. Study found that structural transition from 2-D to 3-D transpires at smaller size of atoms for Cu and Ag as compared to Au clusters. The impurity-doped metallic clusters offer enhanced stability, electronic and optical properties as compared to the pure metallic clusters. Binding energy of pure and doped clusters increases with the size of cluster. HOMO-LUMO energy gap shows an odd-even alteration behaviour with the cluster size, specifying that cluster with total number of even atoms have large energy gap as compared to their neighbouring cluster with odd number of total atom. HOMO-LUMO energy gap of these clusters are found in linear correlation with the chemical hardness and inverse relation with softness.

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References

[1] K. Capelle, "A Bird's-Eye View of Density-Functional Theory", *Braz. Braz. J. Phys*., 36, 1318-1343 **(2006)**.

[2] RG. Parr and Y Weitao, "Density-Functional Theory of Atoms and Molecules", Oxford University Press, Oxford, (1995).

[3] W. Kohn, "Electronic structure of matter-wave functions and density functional". *Rev. Mod. Phys*, 71 (5), 1253-1266, **(1999).**

[4] JA. Pople, "Nobel lecture: Quantum chemical models".*Rev. Mod. Phys*, 71, 1267, **(1999**).

[5] J. Hafner, C. Wolverton and G. Ceder, "Toward computational materials design: the impact of density functional theory on materials research", *MRS Bulletin*, 31, 659, **(2006).**

[6] RG. Parr and W. Yang ,"Density-functional theory of the electronic structure of molecules", *Annu. Rev. Phy. Chem*., 46, 701, **(1995).**

[7] W. Kohn and AD. Becke, "Density functional theory of electronic structure", *J. Phys. Chem.,* 100, 12974, **(1996).**

[8] S. Liu and RG. Parr, "Second-order density-functional description of molecules and chemical changes", *J. Chem. Phys*., 106, 5578**, (1997).**

[9] T. Ziegler, " Density functional theory study of vibrational spectra of small molecules", *Chem. Rev*., 91, 651**, (1991).**

[10] P. Geerlings and FD. Proft, "Chemical Reactivity as Described by Quantum Chemical Methods", *Int. J. Mol. Sci*., 3, 276, **(2002).**

[11] YR. Zhao, XY. Kuang, BB. Zheng, YF. Li and SJ. Wand, "The effect of intermolecular hydrogen bonding on the fluorescence of a bimetallic platinum complex". *J. Phys. Chem. A,* 115, 569, **(2010).**

[12] R. Pal, LM. Wang, W. Huang and LS. Wang, "Structural Evolution of Doped Gold Clusters: MAu_x^- (M = Si, Ge, Sn; x = 5−8)". *J. Am. Chem. Soc*., 131, 3396, **(2009).**

[13] RS. Eachus, AP. Marchetti and AA. Muenter, *Annual Review of Physical Chemistry*, 50, 117, **(1999).**

[14] M. Lu, P. Zhou, Z. Li, J. Liu, Y. Yang and K. Han , "New insights into the sensing mechanism of a phosphonate pyrene chemosensor for TNT", *Phys. Chem. Chem. Phys*., 11, 2329, **(2009).**

[15] X. Wu, Q. Li, J. Huang and J. Yang, "Nonequilibrium electronic transport of 4,4′-bipyridine molecular junction", *J. Chem. Phys*. 123, 184712, **(2005).**

[16] LB. Scaffardi, N. Pellegri, DO. Sanctis and JO. Tocho, "Sizing gold nanoparticles by optical extinction spectroscopy". *Nanotechnology,* 16 158, **(2005).**

[17] R. Fournier, "Theoretical study of the structure of silver clusters". *J. Chem. Phys*., 115, 2165, **(2001**).

[18] DW. Yuan, Y. Wang and Z. Zeng, "Geometric, electronic, and bonding properties of AuNMAuNM (N=1–7N=1–7, M=NiM=Ni, Pd, Pt)". Clusters. *J Chem. Phys*., 122, 114310, **(2005).**

[19] S. Zhao, Y. L. Ren, J. J. Wang and W. P. Yin, Density functional study of hydrogen binding on gold and silver− gold clusters, *J. Phys. Chem. A*, 114, 4917, **(2010).**

[20] MB. Torres, EM. Fernandez and LC. Balbas, "Theoretical Study of Oxygen Adsorption on Pure Au_{n+1}^+ and Doped MAu_n^+ Cationic Gold Clusters for M = Ti, Fe and n = 3−7", *J. Phys. Chem. A*, 112, 6678, **(2008).**

[21] ASK. Hashmi, A. Loos, A. Littmann, I. Braun, J. Knight, S. Doherty and F. Rominger, "Gold (I) complexes of KITPHOS monophosphines: Efficient cycloisomerisation catalysts". *Advanced Synthesis & Catalysis*, 351, 576**, (2009).**

[22] M. Neumaier, F. Weigend, O. Hamper and MM. Kappes, "Reactions of mixed silver-gold cluster cations AgmAu+nAgmAun+ (m+n=4, 5, 6) (m+n=4,5,6) with CO: Radiative association kinetics and density functional theory computations", *J. Chem. Phys.,* 125, 104308**, (2006).**

[23] J. Autschbach, B. A. Hess, M. P. Johansson, J. Neugebauer, M. Patzschke, P. Pyykkö, M. Reiher and D. Sundholm, "Properties of WAu 12", *Phys. Chem. Chem. Phys*., 6, 11, **(2004).**

[24] CJ. Ackerson, PD. Jadzinsky, GJ. Jensen and RD. Kornberg, "Rigid, specific, and discrete gold nanoparticle/antibody conjugates", *J. Am. Chem. Soc.,* 128, 2635, **(2006).**

[25] CF. Shaw III, "Gold-based medicinal agents", *Chem. Rev.,* 99, 2589**, (1999).**

[26] M. Valden, X. Lai and DW Goodman, "Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties*". Science*, 281, 1647, **(1998).**

[27] C. Fèlix, C. Sieber, W. Harbich, J. Buttet, I. Rabin, W. Schulze and G. Ertl, "Ag8 Fluorescence in Argon", *Phys. Rev. Lett*., 86, 2992**, (2001).**

[28] SH. Kim, G. Medeiros-Ribeiro, DAA. Ohlberg, RS. Williams and JR. Heath, "Individual and collective electronic properties of Ag nanocrystals*", J. Phys. Chem. B*, 103, 10341, **(1999).**

[29] J. A. Alonso, "Electronic and atomic structure, and magnetism of transition-metal clusters", *Chem. Rev*., 100, 637, **(2000).**

[30] X. Li, AE. Kuznetsov, HF. Zhang, AI. Boldyrev and LS. Wang, "Observation of all-metal aromatic molecules", *Science*, 291, 859, **(2001).**

[31] E. Janssens, S. Neukermans and P. Lievens, "Shells of electrons in metal doped simple metal clusters", *Curr. Opin Solid State Mater. Sci*., 8, 185, **(2004).**

[32] J. Ho, KM. Erwin and WC. Lineberger, "Photoelectron spectroscopy of metal cluster anions: Cu^-_n, Ag^-_n, and Au^-_n*", J. Chem. Phys*., 93, 6987, **(1990)**.

[33] L. Xiao, B. Tollberg, X. Hu and L. Wang, "Structures of undecagold clusters: Ligand effect", *J. Chem. Phys*., 124, 114309**, (2006).**

[34] HQ. Wang, XY. Wang and HF. Li, "Density functional study of structural and electronic properties of bimetallic copper–gold clusters: comparison with pure and doped gold clusters**",** *Phys. Chem. Chem. Phys.,* 12, 5156, **(2010).**

[35] F. Furche, R. Ahlrichs, P. Weis, C. Jacob, S. Gilb, T. Bierweiler and M. M. Kappes, *J. Chem. Phys.,* 117, 6982, **(2002).**

[36] S. Gilb, P. Weis, F. Furche, R. Ahrichs and MM. Kappes, **"**Structures of small gold cluster cations (Au+n,(Aun+, n<14):n<14): Ion mobility measurements versus density functional calculations**",** *J. Chem. Phys*., 116, 2002, 4094, **(2002).**

[37] D. Dong, K. Xiao-Yu, Z. Bing and G. Jian-Jun, "Geometrical, electronic, and magnetic properties of small AunSc (n= 1–8) clusters", *Phys. B*, 406, 3160, **(2011).**

[38] D. Dong, K. Xiao-Yu, G. Jian-Jun and Z. Ben-Xia, "Density functional theory study of AunMn (n= 1–8) clusters", *J. Phys. Chem. Solids*, 71, 770, (**2010**).

[39] XJ. Kuang, XQ. Wang and GB. Liu, "A density functional study on the AunAg (n= 1–12) alloy clusters*", J. Alloys. Compd*., 570, 46, **(2013).**

[40] F. Muniz-Miranda, MC. Menziani and A. Pedone, "Influence of Silver Doping on the Photoluminescence of Protected Ag_nAu_{25-n} Nanoclusters: A Time-Dependent Density Functional Theory Investigation", *J. Phys. Chem. C*, 119, 10766, **(2015).**

[41] P. Ranjan, S. Dhail, S. Venigalla, A. Kumar, L. Ledwani and T. Chakraborty, "A DFT study of vanadium doped gold nanoalloy clusters", *Mater. Sci.- Pol*., 33, 2015, 719, **(2015).**

[42] P. Ranjan, T. Chakraborty and A. Kumar, "Computational investigation of cationic, anionic and neutral Ag2AuN (N= 1–7) Nanoalloy clusters", *Phys. Sci. Rev.,* 2, 20160112, **(2017).**

[43] P. Ranjan and T. Chakraborty, "Density functional approach: to study copper sulfide nanoalloy clusters", *Acta Chim. Slov*., 66, 173, **(2019).**

[44] P. Ranjan and T. Chakraborty, "A comparative study of structure, stabilities and electronic properties of neutral and cationic [AuSin] λ and [Sin+ 1] λ (λ= 0,+ 1; n= 1–12) nanoalloy clusters",*Mater. Today Commun*., 22, 100832**, (2020).**

[45] P. Ranjan and T. Chakraborty, "Structure and electronic properties of AunPt (n= 1–8) nanoalloy clusters: The density functional theory study", *J. Nanopart. Res*., 22, 35, **(2020).**

[46] P. Ranjan and T. Chakraborty, "Structure and optical properties of (CuAg) n (n= 1–6) nanoalloy clusters within density functional theory framework", *J. Nanopart. Res*., 22, 280, **(2020).**

[47] P. Ranjan, P. Kumar, T. Chakraborty, M. Sharma and S. Sharma, "A study of structure and electronic properties of chalcopyrites semiconductor invoking Density Functional Theory", *Mater. Chem. Phys*., 241, 122346**, (2020).**

[48] P. Ranjan, S. Das, P. Yadav, H. Tandon, S. Chaudhary, B. Malik, S. K. Rajak, V. Suhag and T. Chakraborty, "Structure and electronic properties of [AunV] λ (n= 1–9; λ= 0,±1) nanoalloy clusters within density functional theory framework", *Theor. Chem. Acc*., 140, 59, **(2021).**

[49] P. Ranjan, P. Kumar, P. K. Surolia and T. Chakraborty, "Structure, electronic and optical properties of chalcopyrite semiconductor AgTiX2 (X= S, Se, Te): A density functional theory study", *Thin Solid Films*, 717, 138469**, (2021).**

[50] P. Ranjan, P. Kumar, T. Chakraborty and M. Sharma, "A study of structure and electronic properties of chalcopyrites semiconductor invoking Density Functional Theory"*, Mater. Sci.- Pol.*, 38, 97, **(2020).**

[51] P. Ranjan and T. Chakraborty, "A computational study of chalcopyrite-type nanomaterials for solar cell applications"*, Mat. Sci. Semicond. Proc*., 127, 105745, **(2021).**

[52] S. Das, P. Ranjan and T. Chakraborty, "Computational study of Cu n AgAu (n= 1–4) clusters invoking DFT based descriptors", *Phys. Sci. Rev*., 0141, **(2022).**

[53] P. Ranjan, PK. Surolia and T. Chakraborty, "Structure, electronic and optical properties of chalcopyrite-type nano-clusters XFeY2 (X= Cu, Ag, Au; Y= S, Se, Te): a density functional theory study", *Pure Appl. Chem*., 93, 591, **(2021).**