DFT STUDIES ON FUNCTIONAL MATERIALS FOR ADVANCED APPLICATIONS

SUMMARY OF THE THESIS

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Present thesis mainly aimed at study of the some metallic and semiconducting clusters, such as cadmium sulphide (CdS), zinc oxide (ZnO), cobalt oxide (CoO) and aluminium doped gallium nitride (Al-GaN) based on first principle calculations within the density functional theory (DFT). Study of structure and properties of nanoclusters is very important, because the properties of nanoclusters have been found to exhibit a strong size and geometry dependence at the nano and sub nanoscales, and are clearly very different from those of their atomic and bulk counterparts. This may offer new possibilities for the development of highly functional structures with desirable physicochemical properties by a bottom up approach with clusters serving as building blocks. The primary objectives of the thesis are to construct molecular clusters of some semiconductors and transition metals using different possible geometry and understanding of their structural, electronic and vibrational properties etc. The attempt has been made to extract worthwhile information as much as possible from our study which may open up new avenues for the new experimental and theoretical studies on various cluster systems. The entire thesis work has been divided into seven chapters and summary of each chapter is given in the following.

Chapter 1: Introduction

Materials have the ability to offer structure and strengths that clamp the development and advancement of society together. These materials are more deep-seated in our culture, due to this our daily life are influenced and dependent on materials in myriad ways. With the evolution of time, new techniques have been discovered for the manufacturing and analyzing novel materials. These materials have unique properties which make them superior from the ordinary

natural materials. The properties of materials could be changed by various parameters (like cooling, heating etc.) and the addition of materials or substances which was an evolution in the field of materials science and opened the door for new kinds of materials with various interesting properties. Currently, the research communities are closely focused on the development of functional materials which will lead to modern science and technology towards the development of a smart system and community for the comfort of human life. Functional materials are those materials which have the capability to execute the certain function, and their properties (i.e. chemical and physical) are very sensitive to a change in surrounding like temperature, pressure, magnetic field, electric field, optical wavelength. Functional materials can be classified on the basis of properties (electrical, optical and magnetic) of the materials and its applications in the area of information technology (IT), electrical energy conversion (EEC), biologic applications, space technology, sensing. The group of functional materials primarily includes dielectrics, pyroelectrics, piezoelectric, ferroelectrics, ferroelectric relaxors, semiconductors, clusters, ionic conductors, superconductors, electro-optics, and magnetic materials. In recent years, nanoscale materials, particularly nanoparticles and nanoclusters have gained enormous attraction of the researchers due to its inimitable properties and promising applications. Clusters are combinations of atoms or molecules, typically composed of two to ten lakhs of atoms that are controlled by some forces like metallic, covalent, Van der Waal and ionic. They signify the intermediate phase between atom and bulk systems and are potentially applicable in various fields of science (astrophysics, physics, and chemistry) and technology. Two decades ago there was no technique available to determine the properties of clusters. But nowadays, it can be investigated by both the way theoretically as well as experimentally. Clusters are not only the mediator between the atomic or molecular and bulk system, but they also support to know about the bulk behaviour of matters. Clusters may provide new ways to

build and understand the properties of novel materials. One of the reasons behind the unique properties of clusters is the variance between the structure and structural size of small clusters and bulk systems. It is found that there are many types of small clusters which prefer their stability based on structures like cubic, the octahedron, and polyhedron etc. Various functional materials can be formed by building units of clusters with precise compositions. The C_{60} Buckminster fullerene structure is the combination of twelve 5-membered rings and twenty 6-membered rings built from sixty carbon atoms at every corner. C_{60} is helpful to form salt-like compounds. K_3C_{60} is the compound which can be obtained with the help of C_{60} molecule. Properties of atomic and molecular clusters are directly related to shape, size and geometry of these clusters. Clusters may be classified on basis of atoms used in their formation and nature of bond present in clusters, such as metal cluster, semiconductor cluster, molecular cluster, rare gas cluster, ionic cluster etc. Advancement of computational power provided very efficient and accurate methodology to study the different properties of the functional materials in form of clusters. DFT is one of the most efficient, accurate and cost-effective methods for the theoretical study of the clusters for the understanding of new properties and phenomena at the atomic and molecular level.

Chapter 2: Methodology

The theoretical methods used are based on first principle calculations within the density functional theory (DFT). DFT is one of the promising and efficient methods to investigate electronic, optical properties and structural stability of nanostructures. It is a quantum mechanical theory of correlated many-body systems, which has a tremendous impact on the calculation of the electronic structure of atoms, molecules, solids and nanomaterials in the ground states. Clusters of molecules using different geometries are made by Gauss View

software. Further, the geometry optimization of these clusters has been carried out by applying the density functional theory using Gaussian 09 at B3LYP/LANL2DZ level. The structural, electronic and vibrational properties of these clusters have been studied with the help of output file of Gaussian 09. LANL2DZ incorporating effective core potential (ECP) has been used as the basic basis set in the study of these clusters for the most precise calculation. Minimum energy for each structure is achieved by relaxing the atomic positions. We have used GaussSum 3.0 for the evaluation of the density of states (DOS) spectrum. For the visualization of molecular orbitals, Chemcraft software was used. Stability of clusters is defined in terms of binding energy. We term it as the binding energy (BE) per atom. For a more accurate calculation of binding energy of a system, the zero point vibrational energy is subtracted from the previously calculated BE value which is termed as final binding energy (FBE). The harmonic vibrational frequencies of each optimized structures are evaluated by analytical differentiation of gradients.

Chapter 3: Size Dependent Structural, Electronic and Vibrational Properties of Cd_mS_n (m+n = 2–6) Nanoclusters: A DFT Study

In this chapter, first-principle calculations on the possible structures of cadmium sulphide Cd_mS_n (m+n = 2–6) clusters have been performed; and equilibrium geometries, stabilities and electronic properties have been systematically investigated by density functional theory. Binding energy (BE), highest-occupied and lowest-unoccupied molecular orbital (HOMO-LUMO) gap, density of states (DOS) have also been computed for Cd_mS_n nanoclusters. For the most stable structures, vibrational frequencies, infrared intensities (IR Int.), relative infrared intensities (Rel. IR Int.) and Raman scattering activities have been computed and analysed.

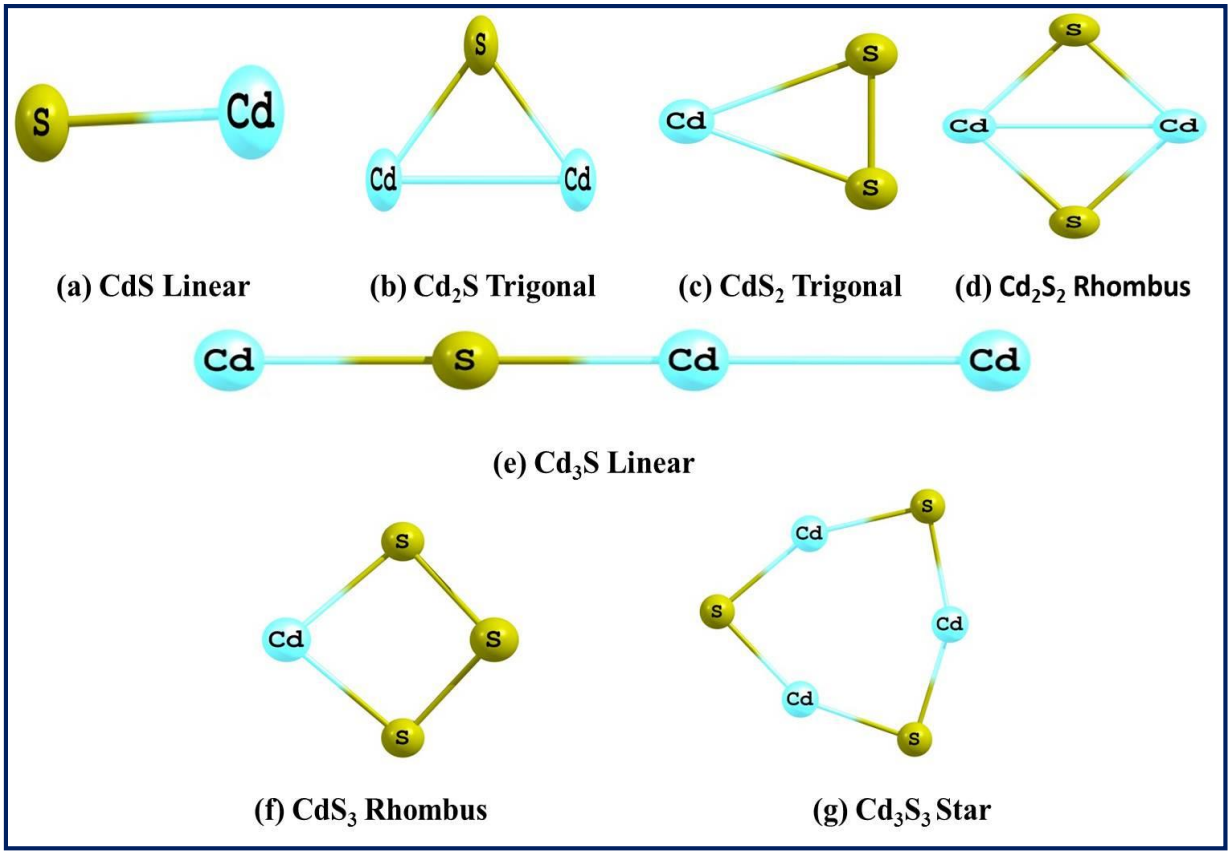


Figure 1: Most stable structures of Cd_mS_n (m+n = 2-6) nanoclusters.

Moreover, bond lengths, adiabatic, vertical ionization potentials, and electron affinity charge on atoms and dipole moments for the Cd_mS_n nanoclusters were also calculated. Results reveal that the nonlinear structured nanoclusters are most stable in comparison with linear depending on FBE. Cd_2S trigonal structure was found to be most stable structured among all the considered nanoclusters. In general, nanoclusters with high FBEs have a large number of S atoms and the HOMO-LUMO gap decreases with the number of S atoms. Further, the IP and EA both show zigzag behaviour with the clusters size. Vibrational properties are studied only for the most stable structured in which, except Cd_2S_2 and Cd_3S_3 all are IR active at the vibrational frequencies. For the most stable structure, the calculated lowest and highest frequencies are 102.56 cm^{-1}, and 397.18 cm^{-1} are infrared active.

Table 1: Symmetry, multiplicity of the ground state (GS), binding energy per atom (BE), zero point energy (ZPE), final binding energy (FBE) and HOMO-LUMO gap for all the configuration for the Cd_mS_n (m+n = 2-6) nanocluster.

Nanocluster	Configuration	Symmetry	GS Multiplicity	BE (eV)	ZPE (eV)	FBE (eV)	HOMO-LUMO (eV)
CdS	Linear Cd-S	C_{*v}	3	2.39	0.01	2.38	α =4.69 β=3.00
Cd_2S	Linear Cd-S-Cd	C_{*v}	1	1.09	0.03	1.06	α =1.99
	Trigonal	C_S	3	3.08	0.03	3.05	α =3.90 β=2.36
CdS_2	Linear S-Cd-S	D_{*h}	3	2.21	0.05	2.16	α =5.53 β=0.98
	Trigonal	C_S	3	2.26	0.04	2.22	α =3.94 β=1.89
Cd_2S_2	Bent Cd-S-Cd-S	C_1	1	1.63	0.07	1.56	α =0.65
	Linear Cd-S-S-Cd	C_1	1	1.57	0.06	1.51	α =0.90
	Linear S-Cd-Cd-S	C_1	1	1.60	0.05	1.55	α =1.99
	Bent Cd-S-S-Cd	C_1	1	1.57	0.06	1.51	α =1.28
	Rhombus	C_1	1	1.97	0.08	1.88	α =2.23
Cd_3S	Linear Cd-Cd-S-Cd	C_1	1	0.86	0.04	0.82	α =1.73
	Rhombus	C_1	1	0.75	0.0	0.75	α =1.19
CdS_3	Bent S-S-Cd-S	C_1	3	2.23	0.08	2.15	α =4.33 β=2.05
	Rhombus	C_1	1	3.33	0.09	3.24	α =1.82 β=1.82
Cd_3S_3	Hexagon (Caze)	C_1	1	1.55	0.09	1.46	α =2.40
	Hexagon (Star)	C_1	1	2.34	0.14	2.20	α =3.33

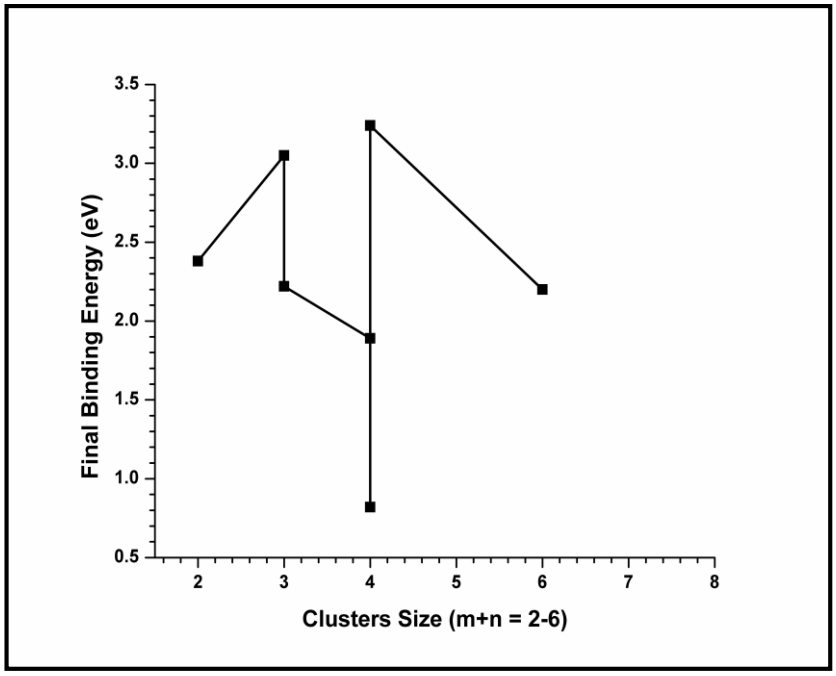


Figure 2: Final binding energy vs cluster size of Cd_mS_n (m+n = 2-6) nanoclusters.

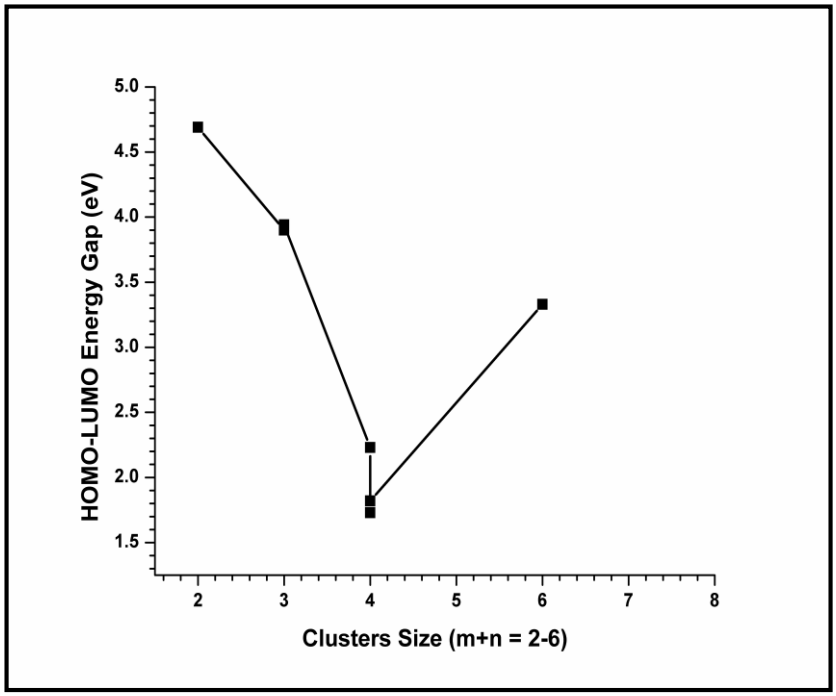
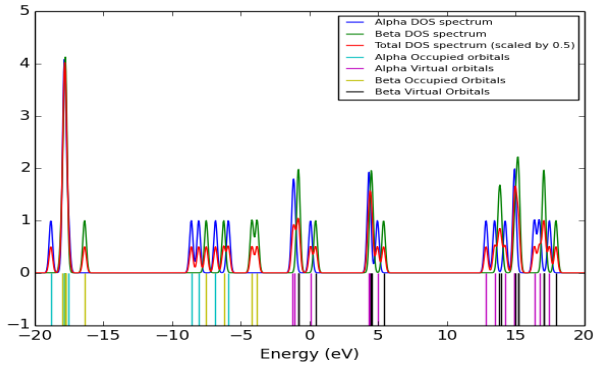
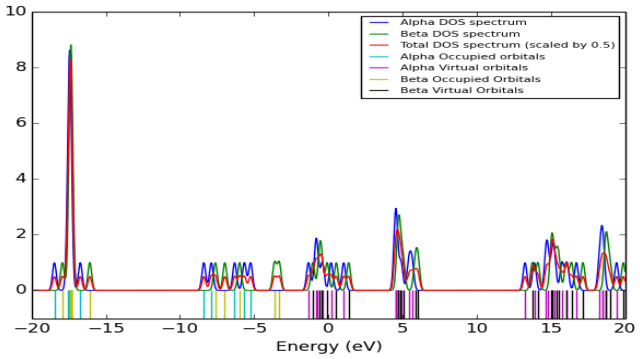


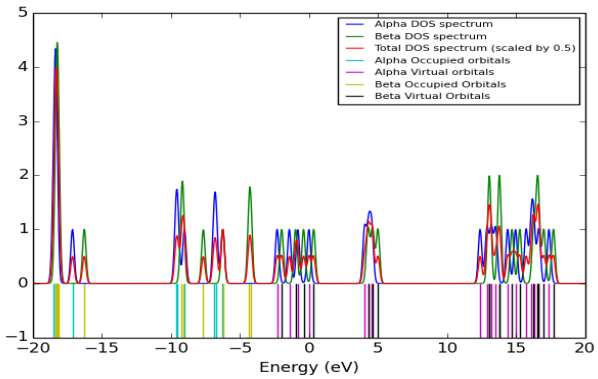
Figure 3: HOMO-LUMO Gap vs cluster size of Cd_mS_n (m+n = 2-6) nanoclusters.



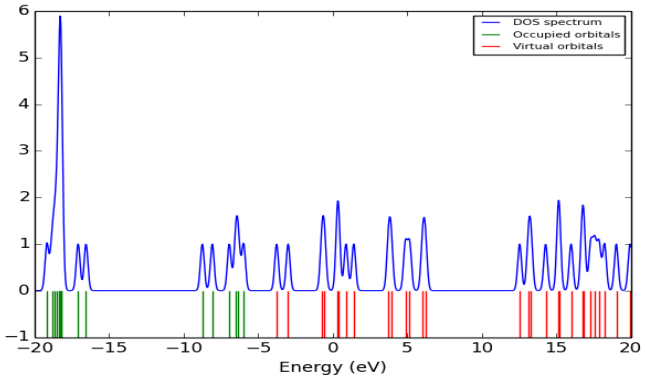
(a) CdS Linear



(b) Cd_2S Trigonal



(C) CdS_2 Trigonal



(d) Cd_2S_2 Rhombus

Figure 4: DOS, HOMO-LUMO energy diagram for all the most stable configuration of the Cd_mS_n (m+n = 2-6) nanoclusters.

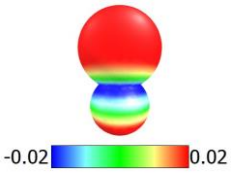
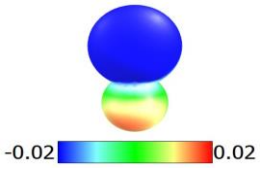
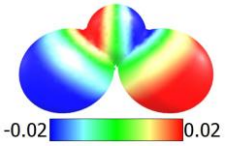
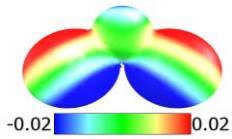
Nanocluster	**Configuration**	**HOMO**	**LUMO**
CdS	Linear (Cd-S)		
Cd_2S	Trigonal (Cd-S-Cd)		
CdS_2	Trigonal (S-Cd-S)		

Figure 5: HOMO-LUMO energy visualization for some stable configuration of the Cd_mS_n (m+n = 2-6) nanoclusters.

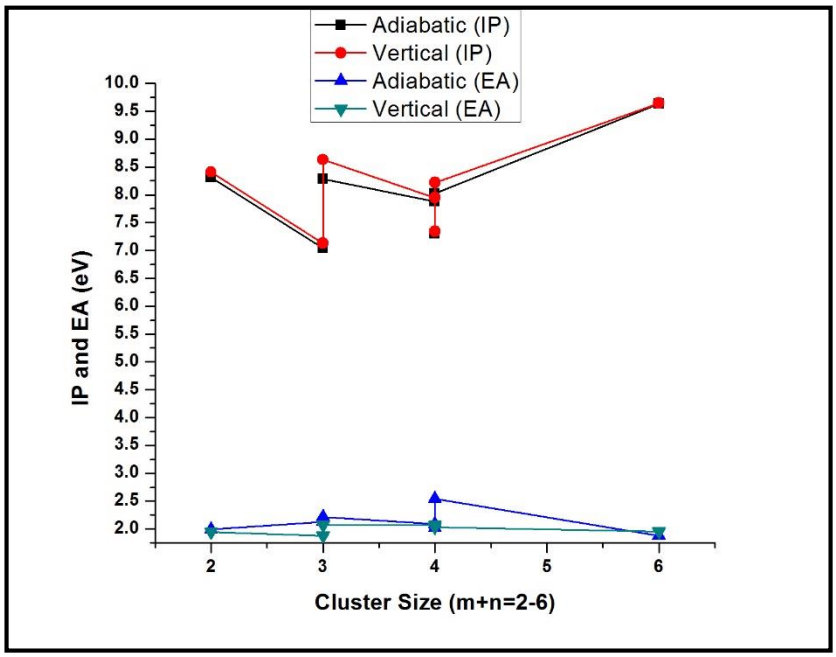


Figure 6: Ionization potential and electron affinity vs cluster size of Cd_mS_n (m+n = 2-6) nanoclusters.

The results of the present systematic study should be useful in modelling and understanding the growth of Cadmium-based clusters at the nanoscale. Our findings should also motivate new experimental studies on this important class of clusters.

Chapter 4: Quantum Chemical Studies on Zn_mO_n (m+n=2–8) Even Nanocluster's Stability

In the present chapter, the study of Zn_mO_n nanoclusters shows a simple approach for constructing small computationally reasonable clusters and provides a better understanding of structural motifs that stabilize the electronic structure of Zn_mO_n. The structural isomers of Zn_mO_n for (m+n = 2-8), only even number, are optimized using the Gaussian 09 program

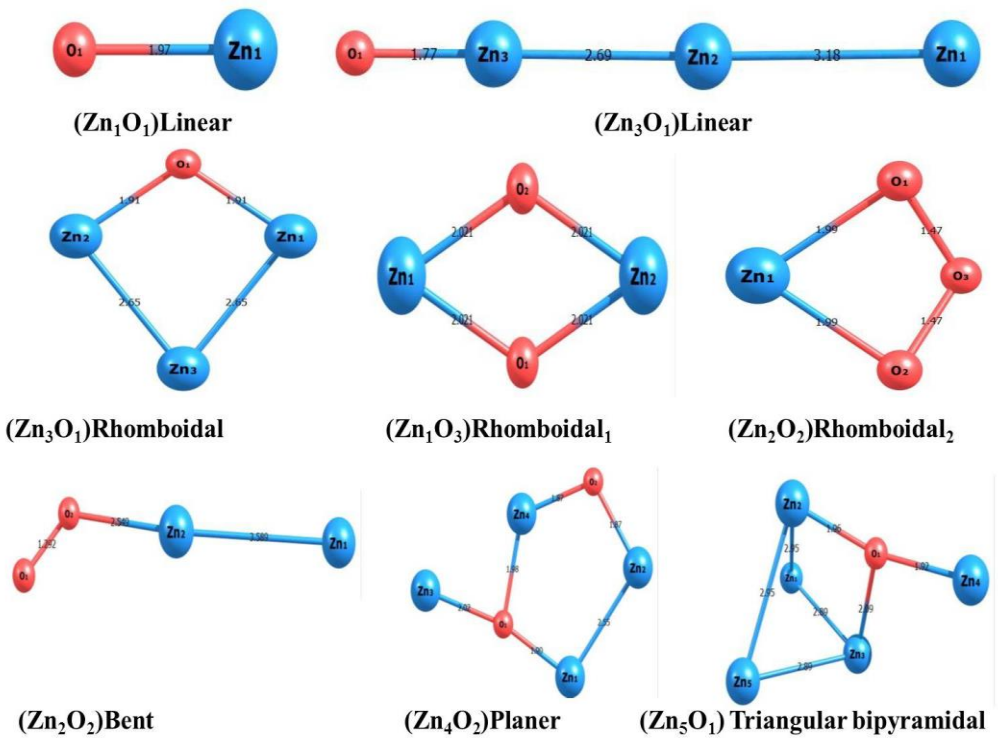


Figure 7: Some optimized structures of Zn_mO_n (m+n = 2-8) nanoclusters.

package with a B3LYP/LANL2DZ level basis set. In addition to this, other properties such as equilibrium geometry, point group symmetry, binding energy (BE), highest-occupied and lowest-unoccupied molecular orbital (HOMO-LUMO) gap, density of states (DOS), vibrational frequencies, infrared intensities (IR Int.) and Raman scattering activities, dipole moments, Ionization potential and Electron Affinity have also been computed using density functional theory. Our results reveal that the existence of the most stable configurations of various Zn_mO_n nanoclusters depends on final binding energy and the nanocluster Zn_5O_3 (m+n = 8) with linear structure is most stable among all considered nanoclusters. In general, nanoclusters with high BEs have a large number of Zn atoms. It was observed that the value of HOMO-LUMO gap decreases with the increase of cluster size. FBE is increasing with the increasing number of atoms i.e. the size of the cluster.

Table 2: The symmetry, multiplicity of the ground state (GS), binding energy (BE), HOMO-LUMO gap and dipole moment for Zn_mO_n (m+n = 2-8) nanoclusters.

Nanocluster (No. of atoms)	**Configuration**	**Symmetry**	**Multiplicity**	**FBE (E_h)**	**HOMO-LUMO Gap (E_h)**	**Dipole Moment (D)**
ZnO_ (2)	**Linear**	**C*V**	**Singlet**	**0.10**	**0.09**	**2.71**
Zn_3O_ (4)	Linear	CS	Singlet	0.04	0.07	11.94
Zn_2O_2	Bent	C_1	Triplet	0.11	0.07	1.64
Zn_3O	Rhomboidal	C_1	Singlet	0.05	0.04	2.62
ZnO_3	**$Rhomboidal_1$**	**CS**	**Singlet**	**0.13**	**0.08**	**5.84**
Zn_2O_2	$Rhomboidal_2$	C2V	Triplet	0.12	0.05	0.29
Zn_4O_2 (6)	**Planer**	**C_1**	**Singlet**	**0.50**	**0.07**	**3.87**
Zn_5O	Triangular Bipyramidal	C_1	Singlet	0.15	0.07	0.60
Zn_4O_2	Triangular $Bipyramidal_1$	C_1	Singlet	0.06	0.07	3.03
Zn_3O_3	Triangular $Bipyramidal_2$	C_1	Singlet	0.04	0.07	1.84
Zn_5O	Hexagon	C_1	Singlet	0.01	0.01	2.31
Zn_4O_2	$Hexagon_1$	C_1	Triplet	0.12	0.01	3.96
Zn_5O	Linear	CS	Singlet	0.02	0.07	14.74
Zn_4O_2	$Linear_1$	CS	Triplet	0.12	0.05	0.14
Zn_3O_3	$Linear_2$	C_1	Triplet	0.10	0.08	2.04
Zn_4O_4 (8)	Ring	C_1	Singlet	1.08	0.15	0.00
Zn_4O_4	Cube	C_2H	Singlet	1.06	0.11	0.00
Zn_5O_3	**Linear**	**C_1**	**Triplet**	**1.24**	**0.03**	**2.08**

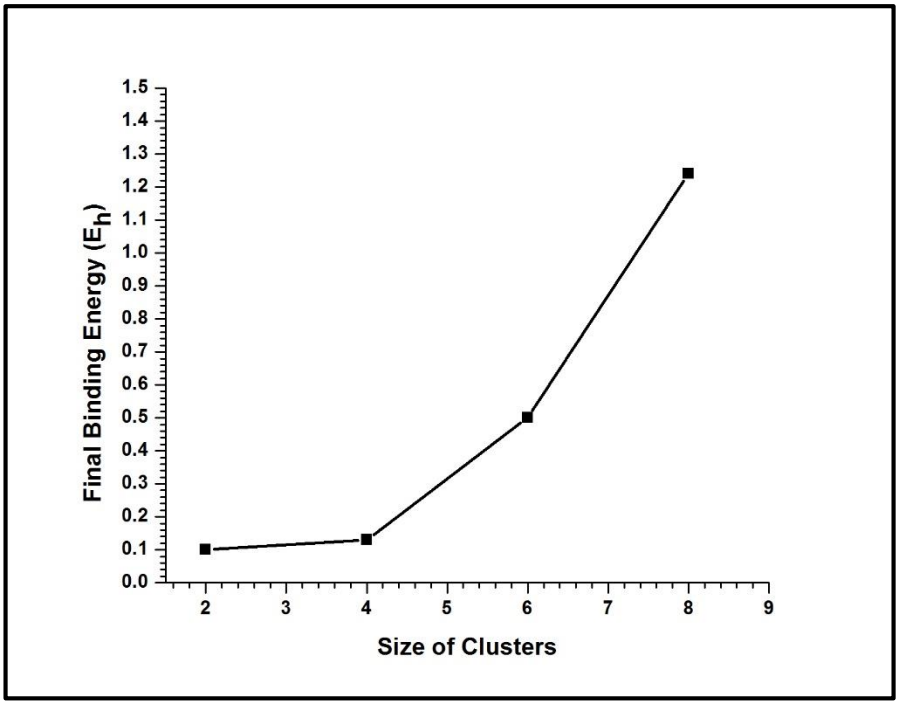


Figure 8: Final binding energy vs cluster size of Zn_mO_n (m+n = 2-8) nanoclusters.

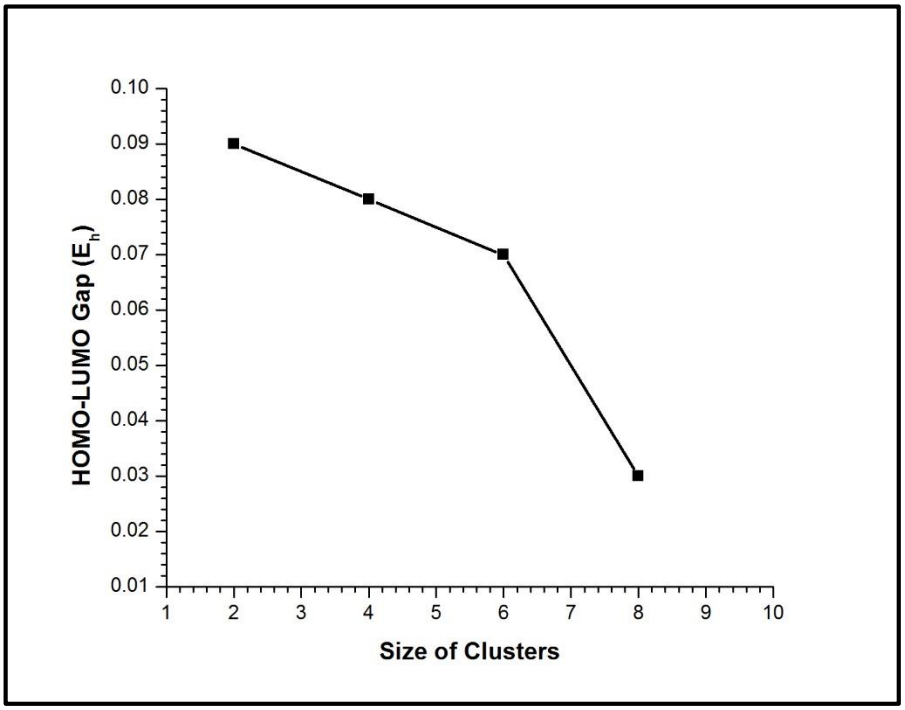


Figure 9: HOMO-LUMO gap vs cluster size of Zn_mO_n (m+n = 2-8) nanoclusters.

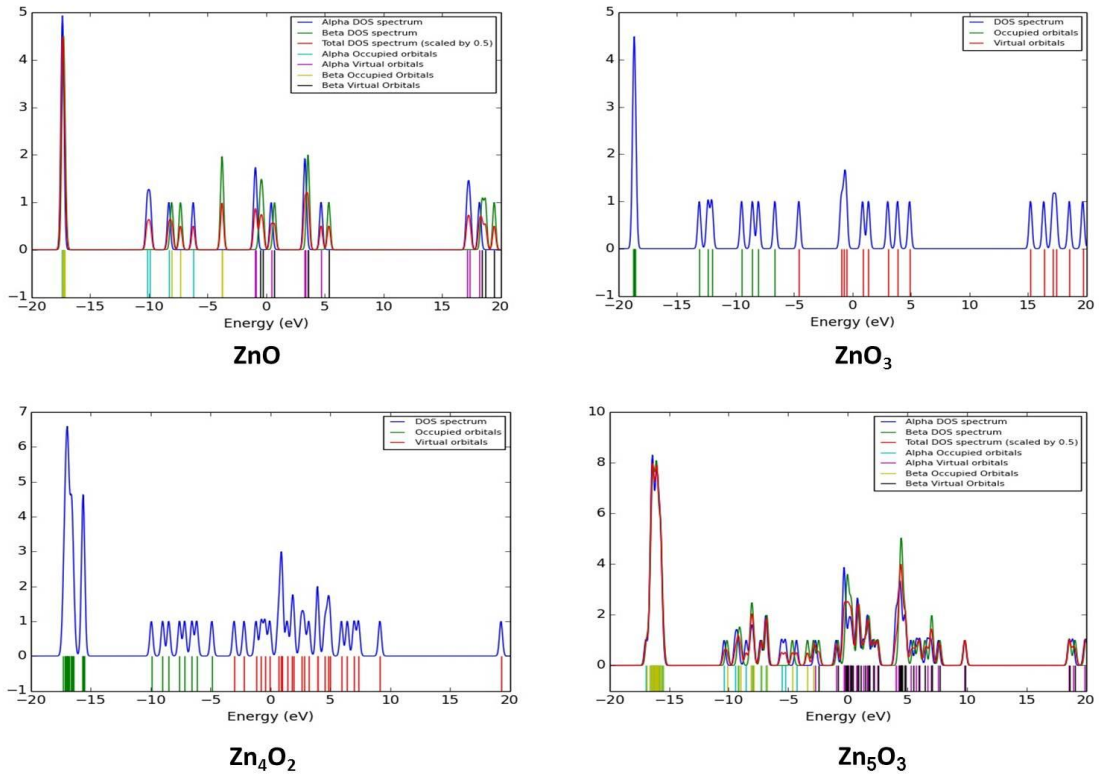


Figure 10: DOS, HOMO-LUMO energy diagram of most stable Zn_mO_n (m+n = 2-8) nanoclusters.

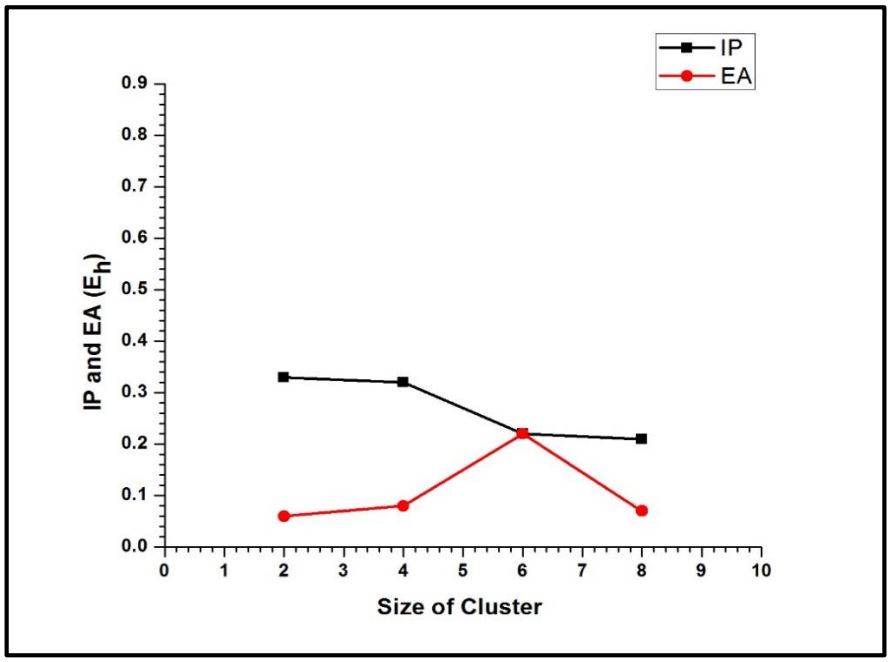


Figure 11: Ionization potential and electron affinity gap vs cluster size of most stable Zn_mO_n (m+n = 2-8) nanoclusters**.**

Value of ionization potential is greater than the electron affinity. The results of the present study should be useful in modelling and understanding the growth of Zinc-based clusters at the nanoscale. The results should also motivate new experimental studies on this important discussion of clusters.

Chapter 5: A Density Functional Theory Study on Structural Stability and Electronic Properties of Co_xO_y (x +y = 4−12) Nanoclusters

In this chapter, the structural and electronic properties of cobalt oxide (x+y = 4-12) nanoclusters have been studied using first-principles calculations within the density functional theory (DFT). The effect of size, shape, and composition on properties has been also investigated. DFT is one of the extensively employed methods for computing the structural and electronic properties of materials from the first principle. Transition metals in contact with oxygen atoms have been topic to intensive research in the scientific realm due to their special physical, chemical, electronic, magnetic properties and wide applicability. Among these, cobalt oxide (CoO) has attracted special attention owing to its enormous potential for application in sensing, catalysis, electronics, electrode materials, and magnetic materials. The oxidation states of CoO and nanoscale cobalt systems have attracted substantial attention due to their versatile properties which are most used in gas sensors, electrochromic devices, chemical and ceramic industries, and coloring glass etc. In the work presented, we have calculated the properties of cobalt oxide nanoclusters such as the bond lengths, spin multiplicity, point group symmetry, binding energy, dipole moments and HOMO-LUMO energy gap. It is observed that different configurations of cobalt oxide nanoclusters exhibit important chemical, physical and electronic properties which are very useful in the field of material science, nanotechnology etc.

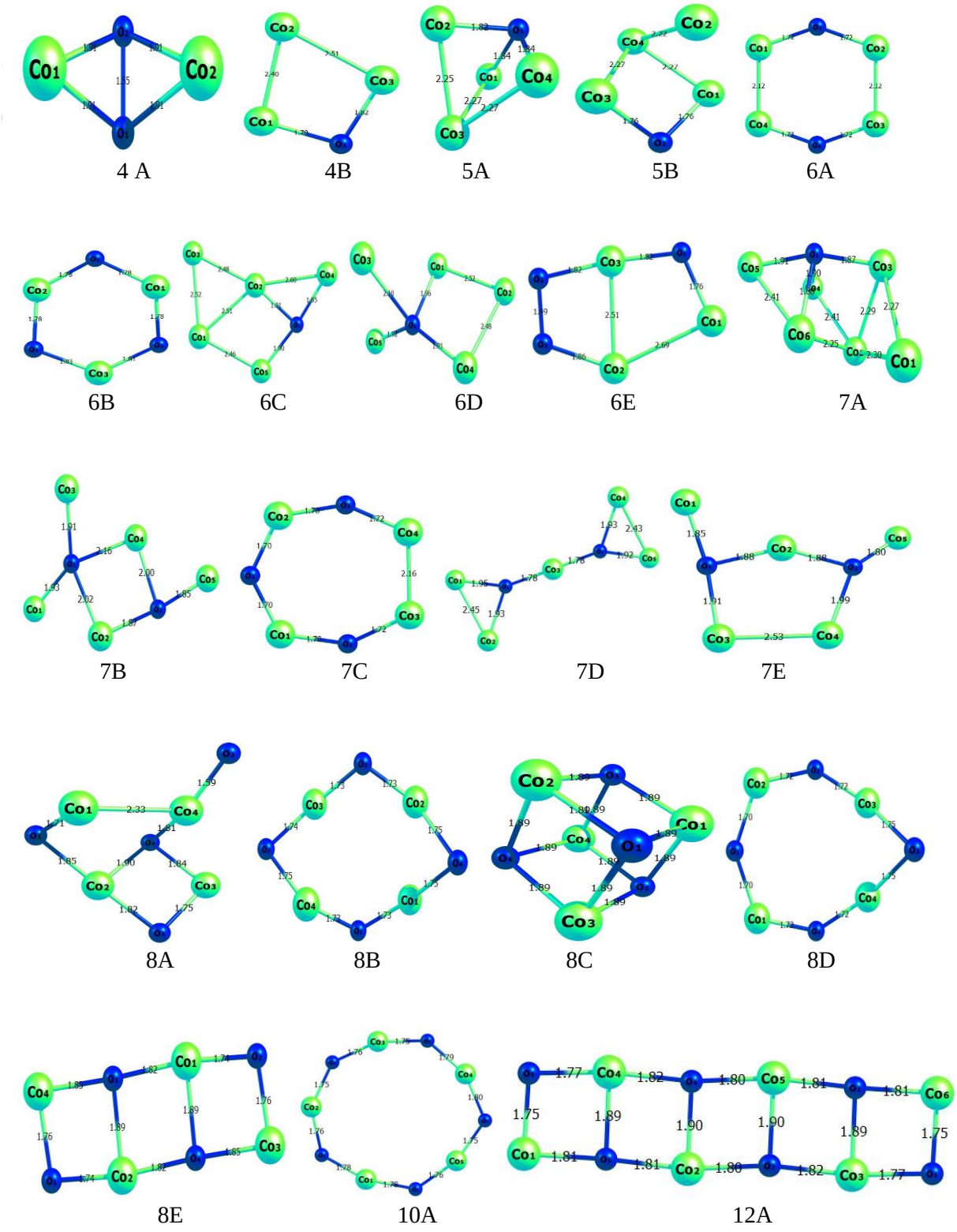


Figure 12: B3LYP/LANL2DZ geometrically optimized structures of Co_xO_y (x+y = 4-12) nanoclusters.

Table 3: Point group symmetry, spin multiplicity, final binding energy per atom (FBE), zero point energy (ZPE), dipole moment and HOMO-LUMO energy gap for all the configuration of Co_xO_y (x+y = 4-12) nanoclusters.

S.No.	Structure	Spin Multiplicity	Point Group	FBE per atom (eV)	HOMO-LUMO energy Gap (eV)	Dipole Moment (Debye)	Zero Point Energy (a.u.)
1.	CoO(4A)	Singlet	C_1	2.91	1.86	3.85	0.005
2.	**CoO(4B)**	**Doublet**	C_1	**3.09**	**2.43**	**3.78**	**0.004**
3.	CoO(5A)	Singlet	C_1	2.13	1.77	2.16	0.006
4.	**CoO(5B)**	**Singlet**	C_1	**2.21**	**2.58**	**3.62**	**0.006**
5.	CoO(6A)	Singlet	C1	2.81	2.25	0.005	0.009
6.	**CoO(6B)**	**Doublet**	C_1	**4.74**	**3.60**	**0.39**	**0.010**
7.	CoO(6C)	Doublet	C_1	2.98	1.83	0.61	0.005
8.	CoO(6D)	Doublet	C_1	2.94	1.85	0.71	0.005
9.	CoO(6E)	Doublet	C_1	4.17	2.35	6.47	0.008
10.	CoO(7A)	Singlet	C_1	1.79	1.65	0.62	0.008
11.	CoO(7B)	Doublet	C_1	3.70	2.08	0.76	0.008
12.	CoO(7C)	Singlet	C_1	3.57	2.11	1.31	0.012
13.	CoO(7D)	Doublet	C_1	3.60	2.06	0.51	0.008
14.	**CoO(7E)**	**Doublet**	C_1	**3.81**	**1.89**	**2.87**	**0.008**
15.	CoO(8A)	Singlet	C_1	4.18	2.57	2.28	0.015
16.	CoO(8B)	Singlet	C_1	3.92	2.13	2.48	0.015
17.	**CoO(8C)**	**Singlet**	C_1	**4.24**	**2.04**	**0.006**	**0.015**
18.	CoO (8D)	Singlet	C_1	4.19	2.18	2.77	0.015
19.	CoO(8E)	Singlet	C_1	4.14	1.73	0.03	0.016
20.	**CoO(10A)**	**Singlet**	C_1	**4.85**	**2.69**	**0.46**	**0.018**
21.	**CoO(12A)**	**Singlet**	C_1	**4.31**	**1.32**	**0.001**	**0.025**

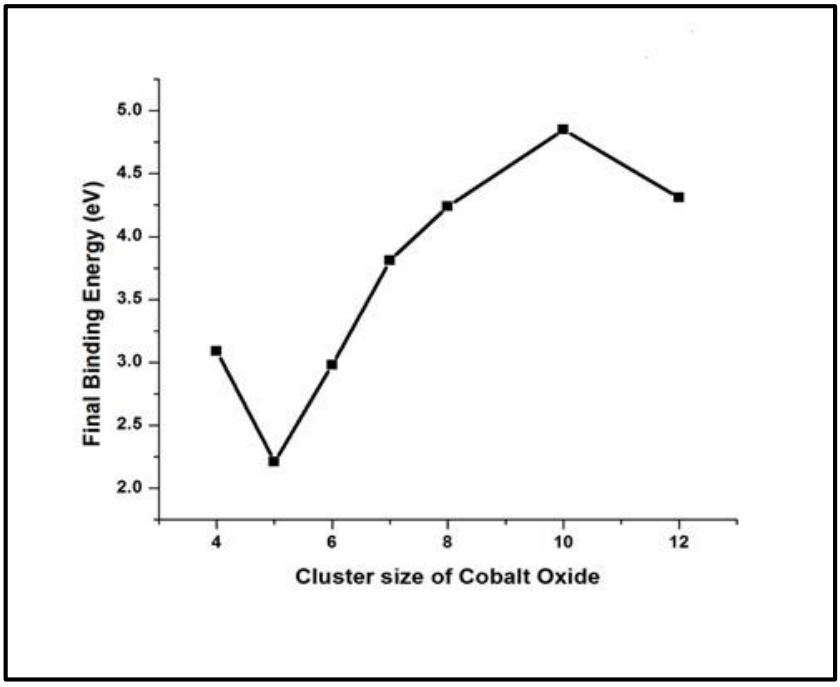


Figure 13: Graph between final binding energy and clusters size of Co_xO_y (x+y = 4-12) nanoclusters.

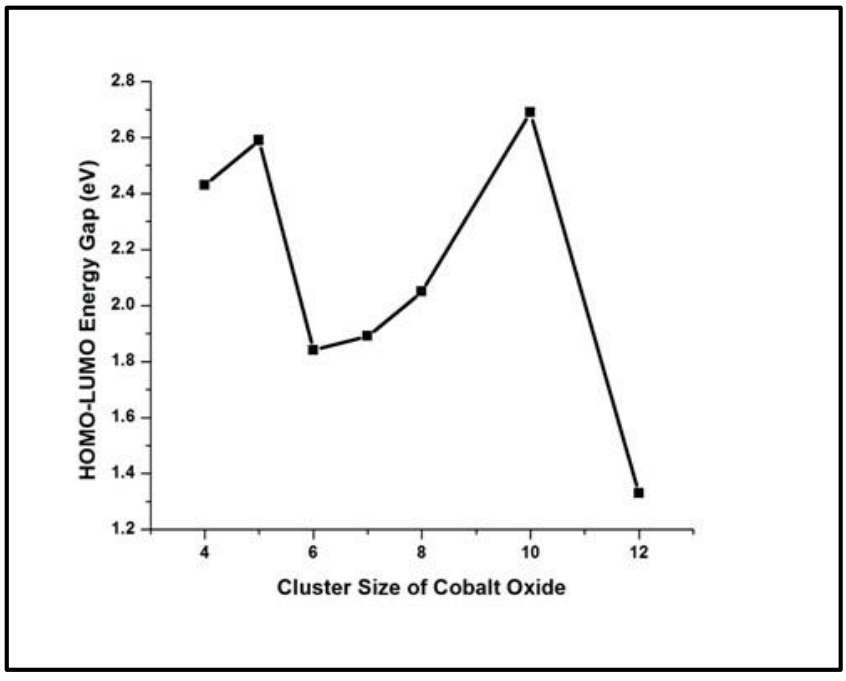


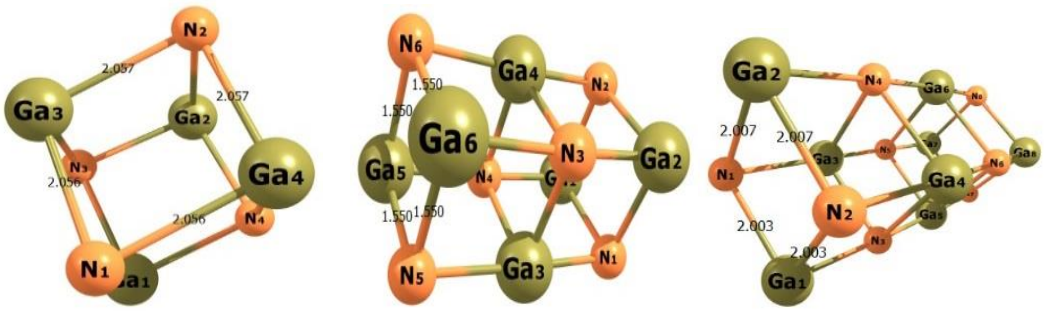
Figure 14: Graph between HOMO–LUMO energy gap and clusters size of Co_xO_y (x+y = 4-12) nanoclusters.

Our obtained results demonstrate that the presence of the best stable formations of different Co_xO_y nanoclusters depends on FBE and cluster morphology. The HOMO-LUMO energy

gaps, as well as binding energy, are highest for CoO (10A). The smallest value of HOMO-LUMO energy band gap was obtained for CoO (12A) configuration which reveals that this structure having large band gap and FBE is more stable and requires sufficiently high energy for breaking it into their components. Moreover, the HOMO-LUMO energy band gap increases by adding the more number of atoms in the clusters. We expect that our investigation on these properties will be helpful for the further study of such types of nanoclusters and also would aid the experimentalist for designing materials with new or improved applications.

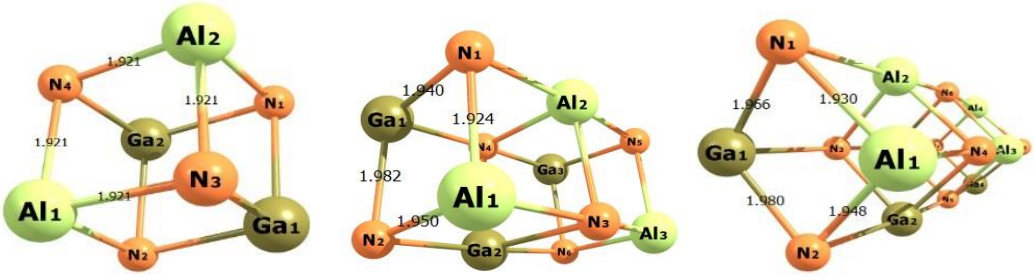
Chapter 6: A Comparative Ab Initio Study on Structural Evolution, Stability and Electronic Properties of Undoped and Al-doped Ga_xN_y (x+y = 4–25) Clusters

In this chapter, a comparative study on structure evolution, binding energies, relative stabilities, electronic and vibrational properties of size-selected GaN and Al-doped GaN clusters by employing B3LYP exchange-correlation function with double-ξ basis set LANL2DZ via the density functional theory (DFT) method. Other parameters, such as HOMO-LUMO gap, ionization potential (IP), electron affinity (EA), dipole moment (DM), the chemical potential (CP), chemical hardness (CH), and results were compared and critically discussed for interpretation of the enhanced stability and to extract useful information for their applications. The structures yield some interesting trends, and a strong size, shape and doping dependence of properties has been observed. The optimization results suggest that the evolution of basic structural entities of different morphologies from planer rings to nanotubes may be realized by taking into account the stacking mode of stable clusters. The geometry of each Al-substituted GaN cluster keeps structure similar to that of the corresponding pure GaN clusters. An analysis of binding energies shows that final binding energy, even the numbers of



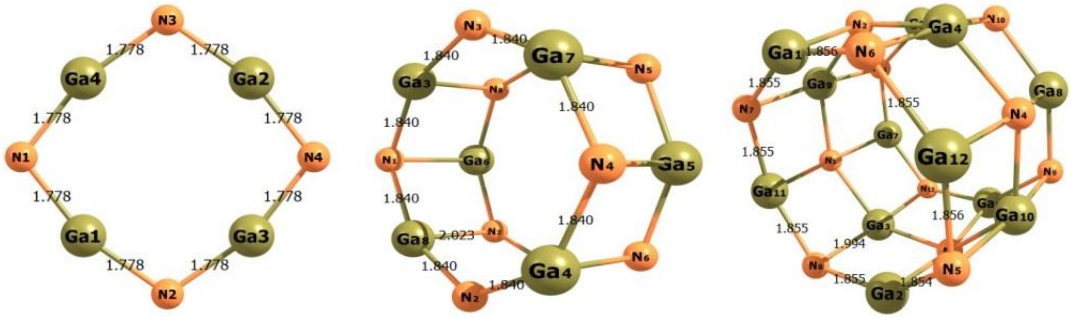
Cube I Cube II Cube III

(a) Structural pattern of cubic GaN clusters.



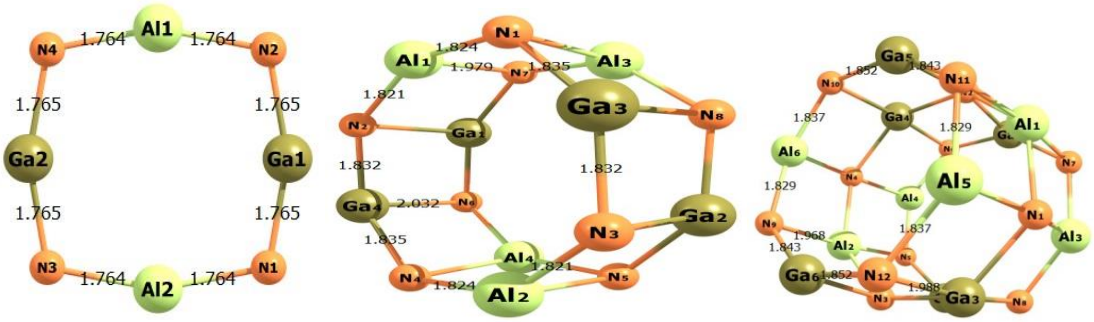
Al-Cube I Al-Cube II Al-Cube III

(b) Structural pattern of cubic Al-doped GaN clusters.



Ring I Ring II Ring III

(c) Structural pattern of ring GaN clusters.



Al-Ring I Al-Ring II Al-Ring III

(d) Structural pattern of ring Al-doped GaN clusters.

Figure 15: B3LYP/LANL2DZ Geometrically optimized structures of GaN and Al-substituted GaN clusters.

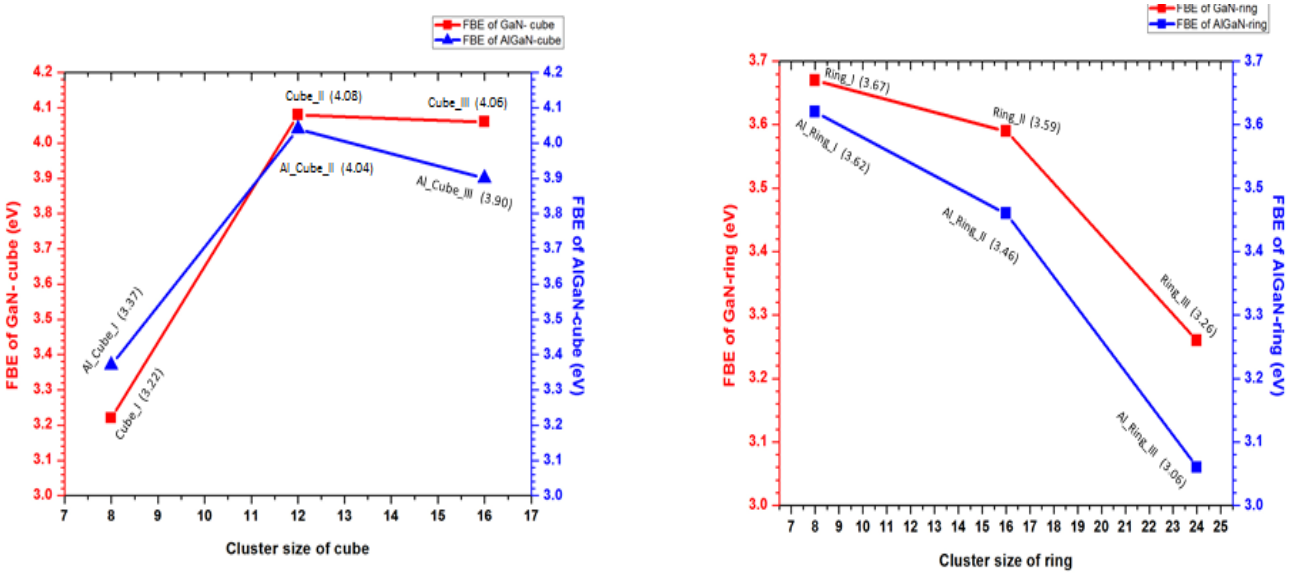


Figure 16: Variation of final binding energy (FBE) per atom with cluster size of cube and ring of GaN and Al-GaN.

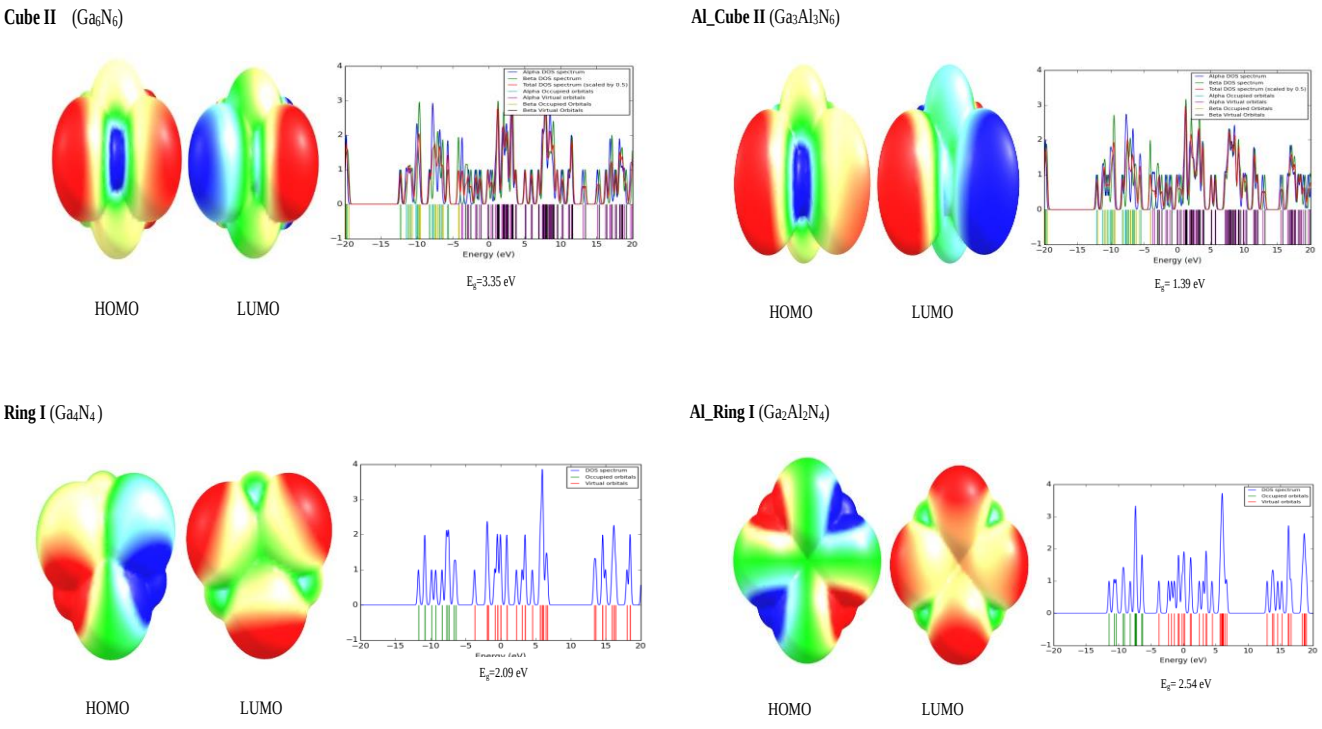


Figure 17: DOS, HOMO-LUMO energy diagram for most stable configurations of the cube of GaN and Al-GaN clusters.

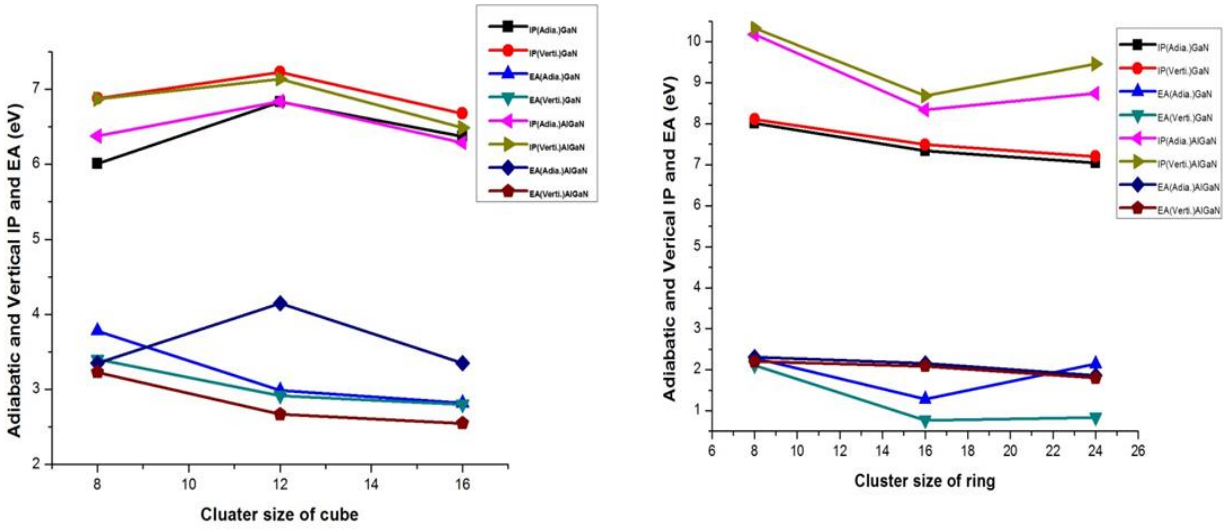


Figure 18: Variation of adiabatic, vertical IP and EA with cluster size of GaN and Al-GaN clusters.

atoms are same; varies with stacking mode or with an increase in the Al atoms. The energetic analysis shows that for all compositions and size of clusters, the cube type (GaN-cube-II) structure is found as the most stable structure. A major variation in electronic properties is observed in different structures, few of them exhibit large band gaps and ionization potentials. Dopant Al considerably modifies the HOMO-LUMO energy gap of cubes and sheets. We observed that values of dipole moment are zero in the case of Al-GaN ring, whereas in different configurations, fluctuates randomly with either increasing the number of atoms or substitution of Al atom. A comparison of ionization potential and electron affinity reveals that Al-doped cube-II cluster is most suitable for chemical sensors due to its high value of EA (4.15eV). The doping modifies remarkably the vibrational spectra of nanoclusters. The stability, IR and Raman activity vary with the growth of units and the stacking mode. A blue shift in the vibrational frequency of the most intense Raman activity has been observed with variation in size and structure. An important finding of the present study is that the linear stacking of stable

units of the ring may undergo to GaN nanowires. Similarly, sideways stacking of several units of rhombus structure results in nanotube formation. Thus, using the coalescence of GaN nanocluster building blocks, nanomaterials with different dimensionalities can be constructed whose properties may be tailored through the choice of size, composition, and doping, thereby providing a viable alternative pathway of creating materials using nanoclusters as building blocks instead of atomic elements.

Chapter 7: Conclusions

Studies of CdS, ZnO, CoO and Al-doped GaN clusters and their structural, electronic and vibrational properties applying DFT method are summarized in this chapter. This chapter also provides the strategies for further research work in the field of nanoscale materials in form of small clusters. Key conclusions are outlined as follows:

1. Density functional theory (DFT) is one of the accurate methods for theoretical studies of advanced materials in form of small clusters and provide good results very quickly, which are very helpful to understand and explain the new phenomenon. The properties of materials in form of clusters are very significant for the development of new science.
2. The properties of small clusters are the function of their size. As the size of clusters is changed, properties of the clusters change significantly. The nonlinear structures of Cd_mS_n nanoclusters are more stable in comparison with linear depending on final binding energy (FBE). In general, nanoclusters with high FBEs have the large number of S atoms. It was observed that the value of the HOMO–LUMO gap decreases with the number of S atoms.
3. Our results reveal that the existence of the most stable configurations of various Zn_mO_n and Co_xO_y nanoclusters depend on final FBEs. In general, nanoclusters with

high BEs have a large number of Zn atoms. Moreover, value of HOMO–LUMO gap decreases with the increase of cluster size. FBE is increasing with the increasing number of atoms i.e. the size of the cluster.

4. An analysis of binding energies shows that final binding energy, even the numbers of atoms are same; varies with stacking mode or with an increase in the Al-doped atoms. A major variation in electronic properties is observed in different structures, few of them exhibit large band gaps and ionization potentials.
5. The doping modifies remarkably the vibrational spectra of nanoclusters. Dopant Al considerably modifies the HOMO-LUMO energy gap of cubes and sheets. We observed that values of dipole moment are zero in the case of Al-GaN ring, whereas in different configurations, fluctuates randomly with either increasing the number of atoms or substitution of Al atom. A comparison of ionization potential and electron affinity reveals that Al-doped cube-II cluster is most suitable for chemical sensors due to its high value of electron affinity.
6. An important finding of the present study is that the linear stacking of stable units of the ring may undergo to GaN nanowires. Similarly, sideways stacking of several units of rhombus structure results in nanotube formation.
7. Variation in HOMO-LUMO gap in different sized clusters considered in the thesis could be useful for devise applications.

The overall studies on functional materials in form of small clusters obtained new properties, which are significantly associated with clusters size and very useful to understand and explain new phenomenon from the experimental point of view.