J. At. Mol. Sci.
doi: 10.4208/jams.012013.032213a

Vol. **4**, No. 4 , pp. 336-348
November 2013

Quantum chemical studies on NiO nanoclusters

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Received 20 January 2013; Accepted (in revised version) 22 March 2013
Published Online 30 August 2013

Abstract. The structural stability of nickel oxide $(NiO)_n$ $(n=1\sim7)$ nanoclusters were studied using Gaussian 03W program package with B3LYP/6-31G level basis set. It is observed that the ring structure is more stable in most cases compared to other structures(Linear and 3D). For $n>6$ the 3D structure is no longer stable. From the optimization results of $(NiO)_n$ clusters it is found that when the atoms in the cluster increases it leads to the increase in the stability. The dipole moment of each cluster is also studied which shows that the dipole moment depends upon the arrangement of atoms in the cluster. The HOMO LUMO gap, ionization potential, electron affinity and binding energies of Nickel Oxide clusters have been calculated and reported.

PACS: 71-10w, 71.15.Mb, 71.15.N

Key words: NiO clusters, binding energy, dipole moment, nanoclusters, ionization potential

1 Introduction

Nickel oxide (NiO) has a rock salt structure with six fold octahedral coordination. NiO is a p-type material due to its metal deficit or oxygen excess [1].The properties of nickel oxide are directly or indirectly connected to the presence of defects, in particular point defects. In previous reports the optical bandgap between the O 2p and Ni 3d bands is estimated to be 3.8 eV [2]. The electronic structure of NiO depends on its oxygen stoichiometry.

Nickel oxide has many applications such as in batteries[3], in electro chromic material [4], as an electrode in fuel cells [5] , in gas sensors [6], in thermistors [7], in optoelectronic

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devices[8], in gamma radiation sensors [9] and as catalyst [10]. Nickel oxide are good capacitors [11] and also act as a resistor [12].

Molecular modeling may be of two types, molecular dynamics or electronic structure modeling. Both the models can be used to perform the same basic type of calculations such as computing the energy of a particular molecular structure, geometry optimization for different structures with low energies. Electronic structure models utilize the laws of quantum mechanics as a basis for their computations and therefore the energy and other properties of the molecule may be obtained by solving the Schrödinger equation for that molecule. The electronic structure modeling in NiO is concentrated on many properties of NiO layers. In this work, the pseudopotentials were not used for optimization because the transition metal like Ni which is present in the fourth period, there is no need to adopt the pseudopotential approximation to optimize its structures [13] and density functional theory(DFT) is the efficient way for optimizing the structures [14]. From the literature survey much work has not been carried out in metal oxides utilizing Gaussian 03W package. We optimized the geometry of NiO nanoclusters for computation of energy, dipole moment, density of states (DOS), HOMO LUMO gap, ionization potential, electron affinity and binding energies using DFT.

2 Computational details

The clusters of nickel oxide (NiO) for $n = 1 \sim 7$ are simulated through Gaussian 03W package [15]. The energy minimization and dipole moment have been calculated by the simulation with Becke's three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional (B3LYP) method together with the 6-31G basis set [16]. Since nickel and oxygen are having charge of 28 and 8 respectively, 6-31G basis set [17-20] is used to compute the minimum energy and dipole moment and some other properties such as ionization potential, electron affinity, HOMO-LUMO gap and binding energies. GaussSum2.2[21] is used to plot DOS spectrum from the Gaussian output.

3 Results and discussion

3.1 Structures of $(NiO)_n$

The calculated energy and dipole moment values for the NiO clusters for($n = 1 \sim 7$) are shown in Table 1. The linear structure of NiO (Fig. 1(a)) is found to have a bond length of 1.8Å with optimized energy of -1583.15 Hartrees. The stability of this linear structure is low since it has only one nickel and oxygen atom. However, there is a drastic increase in the stability of linear $(NiO)_2$ structure (Fig. 2(a)) and its energy is found to be -3166.46 Hartrees. The energy of $(NiO)_2$ (Fig. 2(a)) for ring structure is also found to be -3166.53 Hartrees. Due to the increase in the nickel and oxygen atoms the energy gets decreased in $(NiO)_3$ for all linear, ring and three dimensional structures (Fig. 3(a), 3(b), 3(c)) re-

Table 1: Energy and dipole moment of $(NiO)_n$ clusters $(n=1\sim7)$.

SL No.	No. of clusters $(n=1\sim7)$ $(NiO)_n$	Model	Energy (Hartrees)	Dipole moment (debye)
1	1	Linear	- 1583.151	4.9069
2	2	Linear	-3166.466	7.4518
3	2	Ring	-3166.534	0.0000
4	3	Linear	-4749.746	9.6142
5	3	Ring	-4749.926	0.0235
6	3	3D	-4749.502	1.7995
7	4	Linear	-6331.529	7.5988
8	4	Ring	-6333.219	0.0000
9	4	3D	-6332.748	3.3222
10	5	Linear	-7916.489	0.6034
11	5	Ring	-7914.051	0.2541
12	5	3D	-7915.906	3.5175
13	6	Linear	-9499.040	11.9274
14	6	Ring	-9499.867	1.5950
15	6	3D	-9498.40 1	3.6416
16	7	Linear	-11082.502	16.1445
17	7	Ring	-11081.290	1.7009

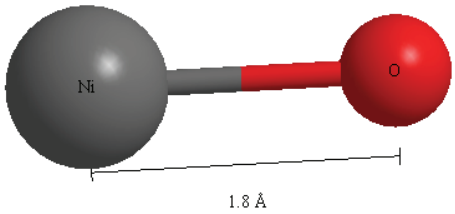
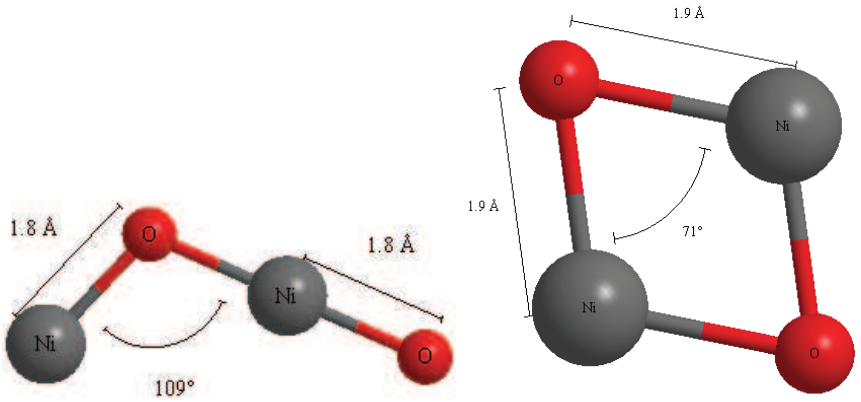


Figure 1: B3LYP/6-31G-optimized geometrical structures of $(NiO)_1$. Bond lengths are given in Å and bond angles in degrees.

spectively. Among all the structures in $(NiO)_3$ the ring structure is having an energy of -4749.92 Hartrees which is more stable because of its closed structure.

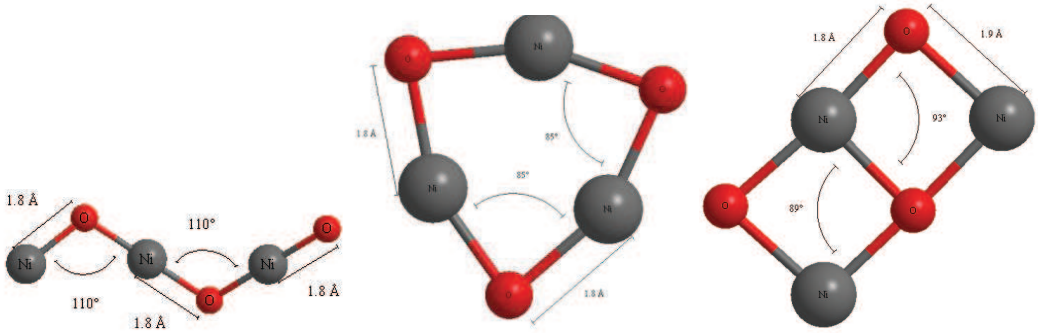
The energies of $(NiO)_4$ is found to be -6331.52, -6333.21 and -6332.74 Hartrees for linear, ring and three dimensional structures (Fig. 4(a), 4(b) and 4(c)) respectively. In the case of $(NiO)_4$ the ring structure is more stable due to its closed structure. The linear, ring and three dimensional structures of $(NiO)_5$ (Fig. 5(a), 5(b) and 5(c)) have energies of -7916.48, -7914.05 and -7915.90 Hartrees respectively. The linear structure of $(NiO)_5$ is more stable since it tries to form a closed structure.

The calculated energies of linear, ring and three dimensional structures of $(NiO)_6$ (Fig.



(a) (b)

Figure 2: B3LYP/6-31G-optimized geometrical structures of $(NiO)_2$. Bond lengths are given in Å and bond angles in degrees.



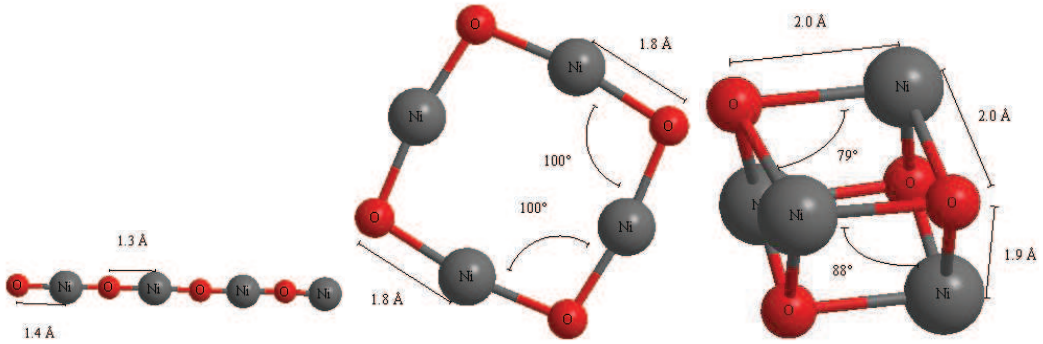
(a) (b) (c)

Figure 3: B3LYP/6-31G-optimized geometrical structures of $(NiO)_3$. Bond lengths are given in Å and bond angles in degrees.

6(a), 6(b) and 6(c)) are found to be -9499.04, -9499.86 and -9498.40 Hartrees respectively. The ring structure in this cluster is more stable. The linear and ring structure of $(NiO)_7$ is shown in the Fig. 7(a) and (b) and its energies is observed to be -11082.50 and -11081.29 Hartrees respectively. The linear structure is found to be more stable because some of the oxygen atoms projects in the ring structure which may decrease its stability.

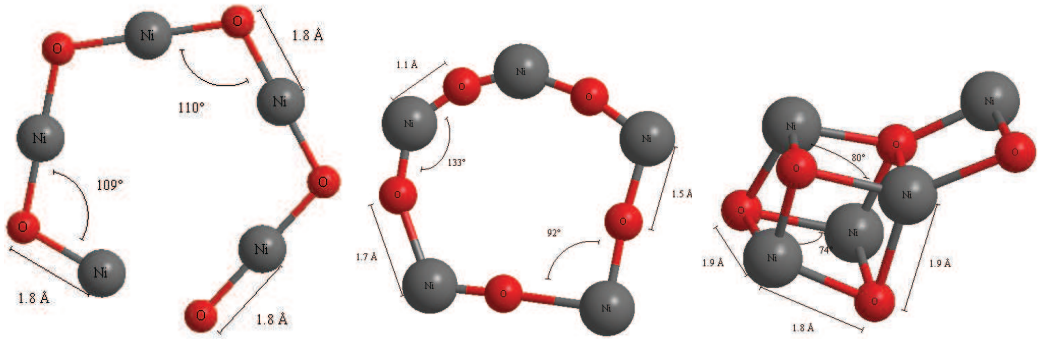
There is no dipole moment for ring structures of $(NiO)_2$ and $(NiO)_4$ due to its symmetry of nickel and oxygen atoms whereas for $(NiO)_3$ and $(NiO)_5$ it is found to be 0.023 and 0.254 Debye respectively since there is slight deviation from the symmetry among the atoms in the cluster. The dipole moment for ring structure of $(NiO)_6$ and $(NiO)_7$ are 1.59 and 1.70 Debye respectively. In both the ring structures the atoms are irregularly arranged which gives rise to dipole moment.

The dipole moment of linear structure is found to be more for all the structures except



(a) (b) (c)

Figure 4: B3LYP/6-31G-optimized geometrical structures of $(NiO)_4$. Bond lengths are given in Å and bond angles in degrees.



(a) (b) (c)

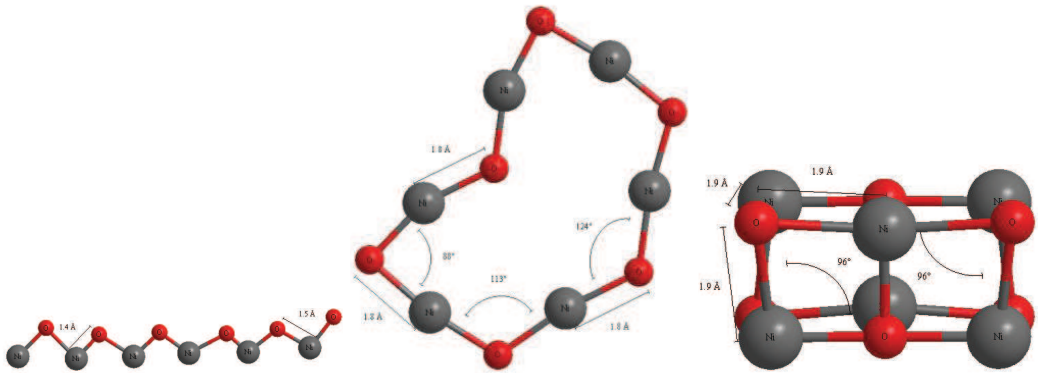
Figure 5: B3LYP/6-31G-optimized geometrical structures of $(NiO)_5$. Bond lengths are given in Å and bond angles in degrees.

$(NiO)_5$ since all the structures are not closed structure. For $(NiO)_5$ structure it tries to attain closed structure which has dipole moment of 0.603 Debye.

The dipole moment of three dimensional structures is found to be almost same for $(NiO)_4$, $(NiO)_5$ and $(NiO)_6$ since due to the resemblance of cube whereas for $(NiO)_3$ it is found to be 1.799 Debye.

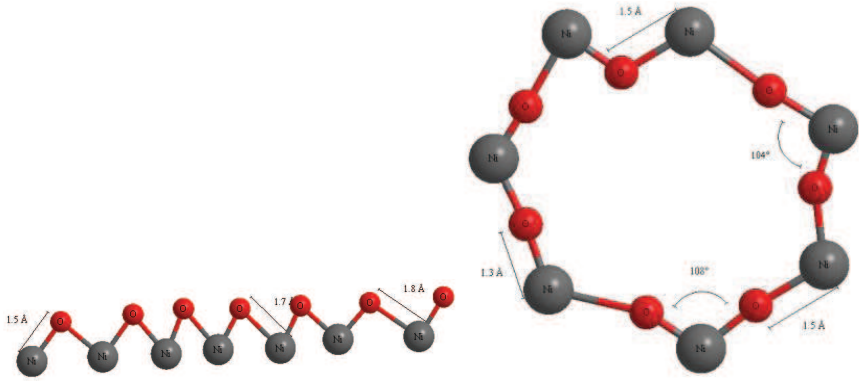
In all the linear, ring and three dimensional structures due to the addition of more number of nickel and oxygen atoms the clusters becomes more stable, from the Fig. 8 to Fig. 10, there is a linear decrease in energy for all clusters irrespective of its structures (linear, ring or three dimensional) which shows more increase in the stability.

In looking with the trend in the dipole moment, Fig. 11 to Fig. 13 ,the linear structure shows more dipole moment compared with ring and three dimensional structures because in the linear structure the nickel and oxygen atoms are in a straight line which gives rise to dipole moment. The ring structure shows no dipole moment or low dipole



(a) (b) (c)

Figure 6: B3LYP/6-31G-optimized geometrical structures of $(NiO)_6$. Bond lengths are given in Å and bond angles in degrees.



(a) (b)

Figure 7: B3LYP/6-31G-optimized geometrical structures of $(NiO)_7$. Bond lengths are given in Å and bond angles in degrees.

moment due to its closed structure symmetry. Depending upon the three dimensional structure, the dipole moment increases and for more addition of nickel and oxygen atoms it remains almost constant for increase in the cluster size.

3.2 HOMO and LUMO analysis

Electronic absorption from ground state to excited state results the highest occupied molecular orbit (HOMO) to lowest unoccupied molecular orbit (LUMO) gap. The obtained HOMO-LUMO energy values using GaussSum 2.2 with density of states(DOS) spectrum are shown in Fig. 14(a), Fig. 14(b) and Fig. 14(c). The calculated values of HOMO and LUMO energies for the linear structure of $(NiO)_n$ for $n = 1 \sim 7$ are shown in Table 2.

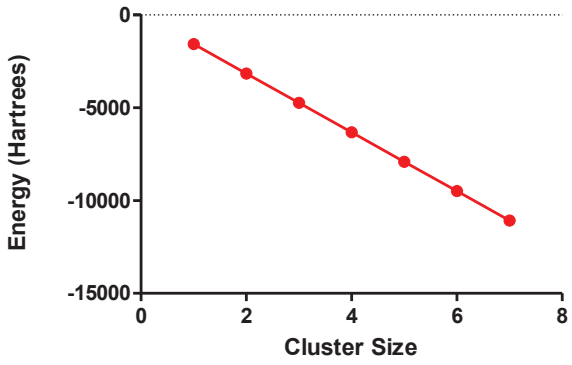


Figure 8: Linear structure (Clusters vs Energy).

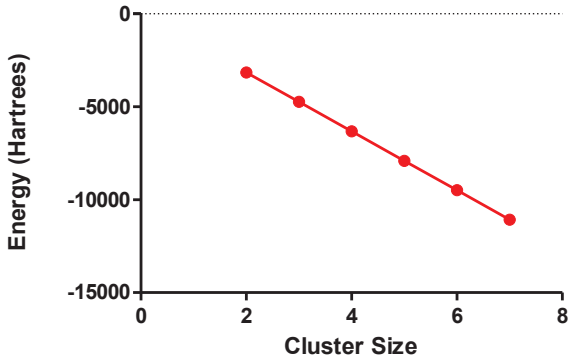


Figure 9: Ring structure (Clusters vs Energy).

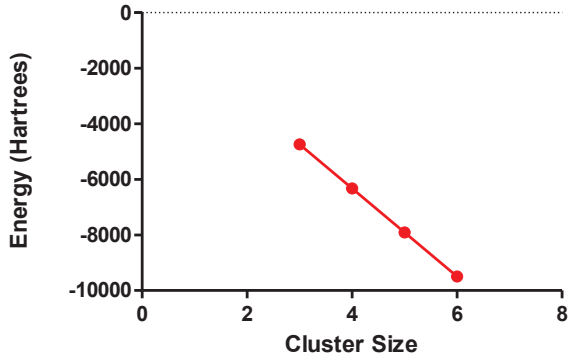


Figure 10: Three dimensional structure (Clusters vs Energy).

From the table, it is found that the energy gap of the NiO clusters purely depends on the cluster size [22]. More number of atoms results in the decrease of energy gap due to overlapping of O-2p and Ni-3d orbitals.

Due to the geometrical arrangement of Ni and O atoms in the linear structure there

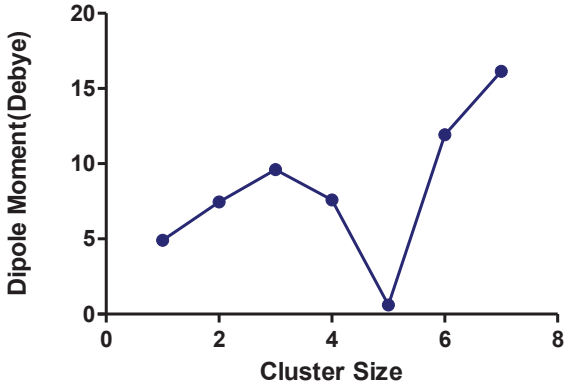


Figure 11: Linear structure (Clusters vs Dipole moment).

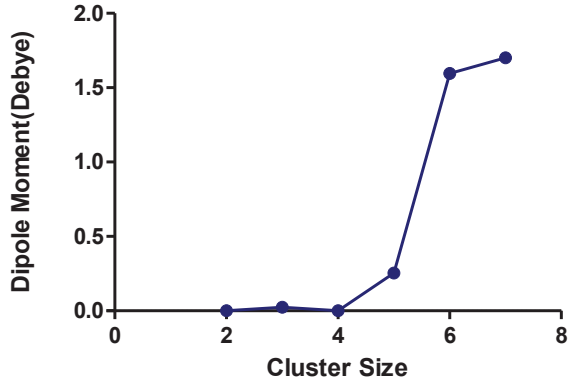


Figure 12: Ring structure (Clusters vs Dipole moment).

is slight variation in the energy gap for $n=4$ due to its structure and for all the other structure decreasing trend is seen in the energy gap. Looking at the ring structures for $n=1\sim7$ energy gap depends on the arrangement of atoms in the structure, whereas for $n=5$ the energy gap is found to be 0.77 eV. For $n=3\sim6$ (3D structure), there is no significant variation in the energy gap even the cluster size is increased. This may be due to the arrangement of cube like structure. Among all the structures the energy gap of ring structure with $n=5$ has the lowest value 0.77 eV and the maximum value 2.06 eV is seen for $n=1$ linear structure. The isosurface plot of HOMO-LUMO molecular orbitals and electron density of linear $(NiO)_1$, $(NiO)_2$ and $(NiO)_3$ structures are shown in Fig. 15(a),(b) and (c) respectively. It is seen that, the cloud density is more dense for $(NiO)_3$ than the other two. All the three isosurface plots of electronic clouds have a node between Ni and O atoms which provides a stronger interaction between the cluster atoms. From this, it is concluded that more number of atoms in a cluster have greater stability.

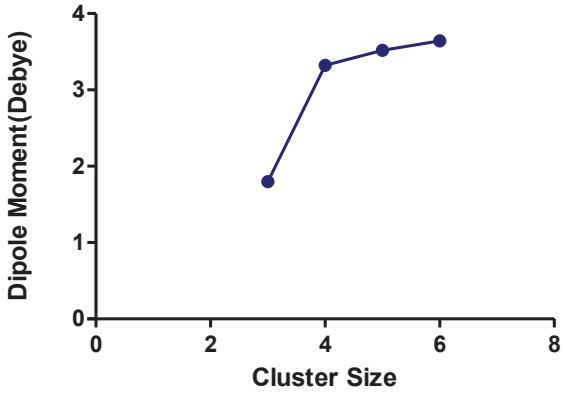


Figure 13: Three dimensional structure (Clusters vs Dipole moment).

Table 2: HOMO -LUMO values of $(NiO)_n$ clusters for $(n=1\sim7)$.

Structure	Cluster No	HOMO (eV)	LUMO (eV)	Energy gap (eV)
Linear	1	-6.18	-4.12	2.06
	2	-5.87	-4.51	1.36
	3	-6.73	-5.36	1.37
	4	-5.45	-3.71	1.74
	5	-6.46	-5.2	1.26
	6	-5.54	-4.67	0.87
	7	-5.32	-4.45	0.87
Ring	2	-5.67	-4.02	1.65
	3	-5.97	-4.78	1.19
	4	-6.58	-5.1	1.48
	5	-3.64	-2.87	0.77
	6	-6.32	-5.2	1.12
	7	-4.44	-3.35	1.09
3D	3	-4.85	-3.62	1.23
	4	-5.38	-3.91	1.47
	5	-4.79	-3.58	1.21
	6	-4.97	-3.62	1.35

3.3 Ionization potential and electron affinity of $(NiO)_n$ nano clusters

The HOMO energy (E_{HOMO}) is related to ionization potential (IP) and LUMO energy (E_{LUMO}) represent electron affinity(EA) from simple molecular orbital theory [23]. From the Table 3 the lowest ionization potential for linear structure is found to 5.32 eV for $n=7$ due to its large cluster size where the electron can be easily detached. Due to the irregular arrangement of atoms in the ring structure ($n=5$) IP is 3.64 eV which is the

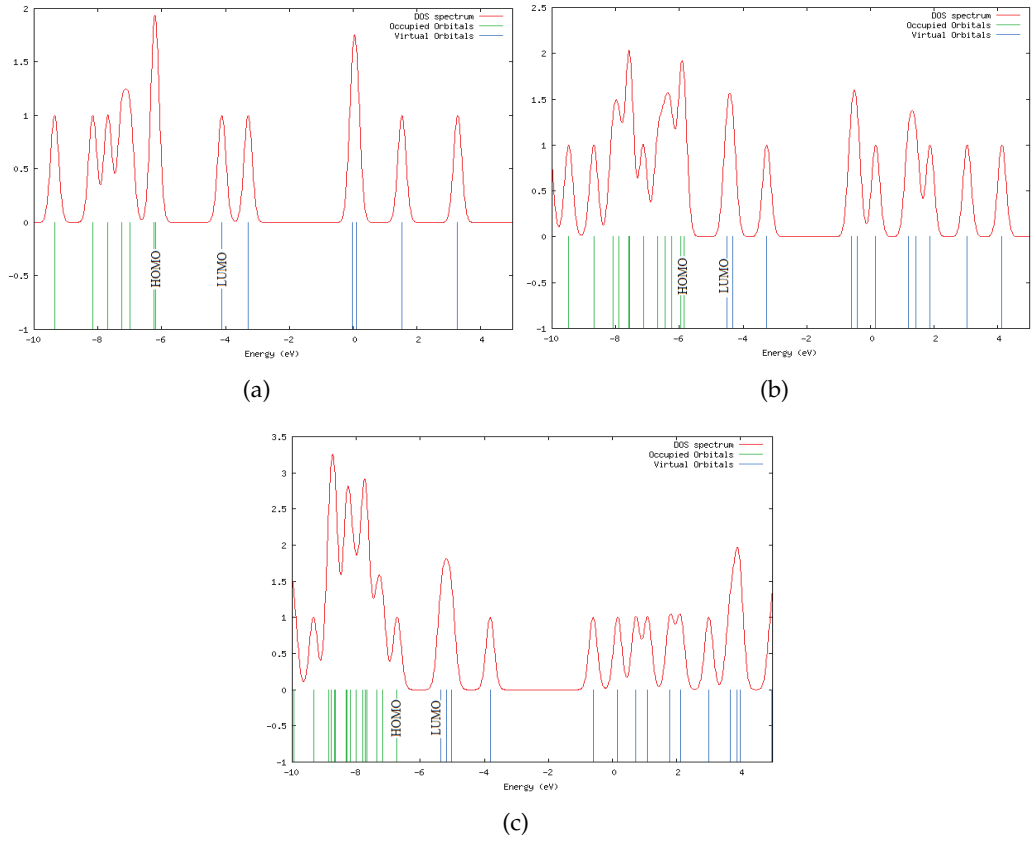


Figure 14: (a) DOS, HOMO-LUMO energy diagram of $(NiO)_1$ linear structure; (b) DOS, HOMO-LUMO energy diagram of $(NiO)_2$ linear structure; (c) DOS, HOMO-LUMO energy diagram of $(NiO)_3$ linear structure.

lowest value for ring structure. In the 3D structure IP does not varies significantly and for $n=5$ has the lowest value of 4.79 eV. The highest value of electron affinity (EA) is 5.20 eV for $n=5$ linear structure. The EA varies drastically for ring structure from 2.87 to 5.20 eV. This is due to the closed structure having different bond lengths and angles. There is no significant variation in EA for 3D structure since all the structures resembles cube form. It is observed for $(NiO)_n$ clusters, the IP and EA values depends on the number of atoms in the cluster as well as their arrangements.

3.4 Binding Energies of $(NiO)_n$ clusters

Binding energy of $(NiO)_n$ clusters for various structures is calculated using the following formula

$$E_b = (nE(\mathrm{Ni}) + nE(\mathrm{O}) - nE(\mathrm{NiO}))/n, \quad (1)$$

where E(Ni) is the energy of Ni atoms, E(O) is the energy of O atoms, E(NiO) is the energy of NiO molecule and n is the cluster size. The calculated binding energies for

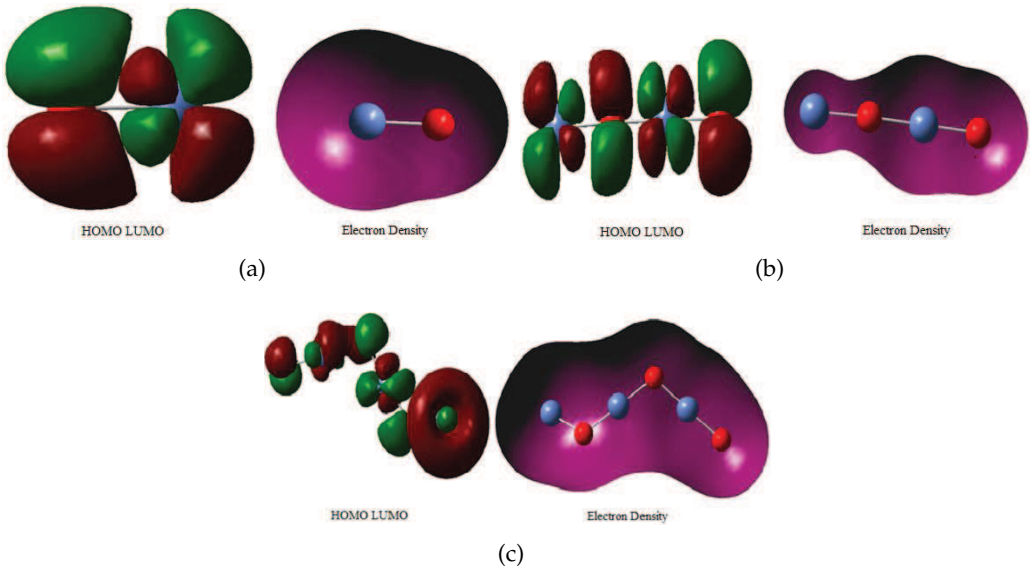


Figure 15: (a) HOMO-LUMO,Electron density Diagram of $(NiO)_1$ Linear Structure; (b) HOMO-LUMO,Electron density Diagram of $(NiO)_2$ Linear Structure; (c) HOMO-LUMO,Electron density Diagram of $(NiO)_3$ Linear Structure.

various $(NiO)_n$ structures are shown in Table 4.

From the table values it is seen that the binding energy for all the structures are varying randomly. The lowest value -0.072 eV for all the models is observed in $n=5$ ring structure. The highest value of binding energy is calculated for 0.178 eV for $n=6$ ring structure. For the 3D structures the binding energy values are consistent and it resembles the most stable structures.

4 Conclusion

Theoretical structural analysis with DFT procedure is most probable which leads to accurate prediction in the result. The visual picture of each NiO cluster gives a rough approach for its own characterization, thus the deviation of each bond length and bond angle of different possible structure are constructed and optimized. The $(NiO)_n$ clusters for $n=1$ to 7 are fully optimized with Gaussian 03W package DFT-B3LYP with 6.31G basis set. The stable structural orientation of small clusters have attracted much interest recently, the accurate orientations is a reliable approach which is the first step to investigate the minimum energy and dipole moment for such nanoclusters. The minimum energy and dipole moments for different isomers are reported in this article. Interestingly, the minimum energy for all the isomers for particular number of atoms are found to be almost same. With the increase in the atoms in the clusters, the stability of the cluster is increased. In contrast, the dipole moment of ring structured NiO clusters is zero or

Table 3: Ionization potential and electron affinity of $(NiO)_n$ clusters ($n = 1 \sim 7$).

Cluster	Size	Ionization potential IP (eV)	Electron affinity EA (eV)
Linear	1	6.18	4.12
	2	5.87	4.51
	3	6.73	5.36
	4	5.45	3.71
	5	6.46	5.20
	6	5.54	4.67
	7	5.32	4.45
Ring	2	5.67	4.02
	3	5.97	4.78
	4	6.58	5.10
	5	3.64	2.87
	6	6.32	5.20
	7	4.44	3.35
3D	3	4.85	3.62
	4	5.38	3.91
	5	4.79	3.58
	6	4.97	3.62

Table 4: Binding energies of $(NiO)_n$ clusters ($n = 1 \sim 7$).

Cluster size	Binding energy (eV)		
	Linear	Ring	3D
1	0.098	-	-
2	0.139	0.156	-
3	0.146	0.176	0.106
4	-0.036	0.174	0.116
5	0.171	-0.072	0.113
6	0.109	0.178	0.055
7	0.129	0.043	-

small value. This is due to the formation of closed structure where the center of symmetry is attained. The linear structures of NiO clusters are having high dipole moment. The dipole moment varies depending upon the atoms in the nanocluster. The HOMO-LUMO gap are also calculated which shows that increase in the cluster size results in decrease in the energy gap and have greater stability. For all the structures the ionization potential and the electron affinity values depends on the placements of atoms and size of the cluster. The calculated binding energy values confirm that 3D structure is more stable than the other two.

References

[1] M. Guziewicz1, J. Grochowski, M. Borysiewicz, E. Kaminska, J. Z. Domagala, W. Rzodkiewicz, B. S. Witkowski, K. Golaszewska, R. Kruszka, M. Ekielsk, and A. Piotrowska, Opt Appl. 41 (2011) 431.
[2] L. Ai, G. Fang,L. Yuan, N. Liu, M. Wang, C. Li, Q. Zhang, J. Li, and X. Zhao, Appl. Surf. Sci. 254 (2008) 2401.
[3] Y. Yao, J. J. Zhang, Z. Wei,and A. S. Yu , Int. J. Electrochem. Sci. 7 (2012) 1433.
[4] F. Iwata, K. Mikage, H. Sakaguchi, M. Kitaob, and A. Sasaki, Solid State Ionics 165 (2003) 7.
[5] B. Park and E. J. Cairns, Electrochem. Commun. 13 (2011) 75.
[6] I. Hotovy, J. Huran, L. Spiess, R.C apkovic, and S. Hascmk, Vacuum 58 (2000) 300.
[7] P. Umadevi and C. L. Nagendra, Sens. Actuators A 96 (2002) 11.
[8] P. Y. Yang, J. L. Wang, W. C. Tsai, S. J. Wang, J. C. Lin, I. C. Lee, C. T. Chang, H. C. Cheng, J Nanosci Nanotechnol. 11 (2011) 5737.
[9] O. Korostynska, K. Arshak, and M. Mahon, Sensors Proceedings of IEEE 1 (2003) 79.
[10] C. C. Hu and H. Teng, J. Catal. 272 (2010) 1.
[11] T. Nathan , A. Aziz , A. F. Noor, and S. R. S. Prabaharan, J. Solid State Electrochem. 12 (2008) 1003.
[12] K. Okamoto, M. Tada, K. Ito, and H. Had, Jpn. J. Appl. Phys. 50 (2011) 1.
[13] X. L. Cheng , F. Li, and Y. Y. Zhao, Theochem. 894 (2009) 121.
[14] I. Y. Kang, Y. S. Kim, Y. Chung, H. Kim, D. Kim, and J. J. Kim, J. Ceram. Proc. Res. 3 (2002) 171.
[15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, *et al.*, Gaussian 03 B01 (Gaussian, Inc., Pittsburgh PA, 1998).
[16] R. Srinivasaraghavan, R. Chandiramouli, B. G. Jeyaprakash, and S. Seshadri, Spectrochim. Acta, Part A 102 (2013) 242.
[17] M. Caus, R. Dovesi, and C. Roetti. Phys. Rev. B 43 (1991) 11937.
[18] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta 28 (1973) 213.
[19] R. C. Binning Jr. and L. A. Curtiss, J. Comp. Chem. 11 (1990) 1206.
[20] M. S. Gordon, Chem. Phys. Lett. 76 (1980) 163.
[21] N. M. O'Boyle, A. L. Tenderholt, and K. M. Langner, J. Comp. Chem. 29 (2008) 839.
[22] N. Misra, A. Dwivedi, and A. K. Pandey, J. At. Mol. Sci. 3 (2012) 187.
[23] C. G. Zhan, J. A. Nichols, and D. A. Dixon, J. Phys. Chem. A 107 (2003) 4184.