Quantum chemical studies on NiO nanoclusters

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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.

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-