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Investigation of Nickle nanoclusters properties by density functional theory

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ABSTRACT

Clusters play important role for understanding and transferring microscopic to macroscopic properties.Geometric and electron properties of Small nickel clusters up to the tetramer has been investigated by Density Functional Theory (DFT). Raising the number of nickel clusters atoms were indicated decreasing the average equilibrium (Ni-Ni) distance of atoms and also the binding energy of per atom were showed increasing trend. Ni-Ni binding energy diagram shows a linear behavior in terms of ($n^{-1/3}$). It is correspond with the previous findings. During the process HOMO-LUMO gap energies reduce. The lowest HOMO-LUMO gap energy was related to Ni_8 cluster, so it proves that the cluster is more reactive and less kinetic stability. The linear relationship between size of clusters ($n^{-1/3}$) with some properties of clusters indicate that it can get these properties ($X\infty$) and extrapolated to the mass of the material.

Keywords: Ni nanocluster; DFT; Electronic properties; HOMO-LUMO gap; Binding energy

1. Introduction

For three decades, studies of transition metals clusters attract empirical and theoretical point of view. Scientists studied physical, chemical, electronic, and magnetic properties of the clusters. They develop the properties to the mass of the material.Clusters play important role to understanding the transferring microscopic to macroscopic properties [1-3]. It is possible to study geometry of nanoparticles in the gas phase. This approach gives exact information about the size of clusters and absence of any environmental interactions. Quantum mechanical calculations model of clusters properties defined species accurately [4]. Although many articles about small neutral nickel clusters exist, but there is less attention to the structure and properties of cationic and anionic systems. Many questions about these ions have not resolved yet. Recently, the compilation of Density Function Theory (DFT) provided reliable data structures [5]. Structure of a nickel crystal network which has face-centered cubic (fcc) is 3.524(Å). Also its crystal network constant is 3.524(Å) too.

This structure is the main components of many high-temperature applied alloys. It is resistant to oxidation with high flexibility. Alloy of nickel and aluminum is (Ni3Al) which used in aerospace and energy industries [6-8]. A nickel atom has an electron density of 3d94s1 and a 3d mode in the ground state. This atom has an electron configuration of 3d84s2 and a 3f mode in the first excited state [9, 10]. Structure and electronic properties of small nickel clusters (n = 2-4) investigate by the density function theory in multiplicities (M = 3, 5, 7). It provides that nickel structures are more stable in multiplication 3. In this study, the molecular orbital HOMO and LUMO was determined the lowest energies of anions, Ni^{-n} and Ni^{+n} cations. Experimental observations calculate the ionization potentials and electrons energy which match other reported theoretical results [11]. Michelin et al. (2001) examine the structure of 2 to 6 nickel clusters,

according to the results by increasing the number of atoms, its stability increases too [12]. Lopez et al., found that the trend of some properties such as ion potential energy is compatible with the previous findings [13].

2. Computational method

In this study B3LYP hybrid method [14,15] in conjunction with the exchange function B3 and LYP correlation function [16-17] also the base set of LANL2DZ for nickel atoms [18] was used [19,20]. For these clusters different structures optimized, then at the same computational level frequency calculations performed to confirm the stability of the compounds. The calculations were performed with Software Gaussian 09 [21].

3. Results and discussion

The most stable optimized structures for 2 to 10 nickel clusters were calculated (fig.1). The optimized structure of Ni2 was showed that atoms of nickel are at a distance of 2.58 Å, while in the study of M.C. Michelini and et al. [22] this distance is 2.07 Å. In the experimental study of J. C. Pinegar andet al. [23] this value report as 2.16 Å.

G. Lopez Arvizu reporte determine this distance between two atoms by TZVP-GGA / PW86 level, 2.15 Å [6]. The binding energy for this small cluster calculated as 1.52 electron volts. The most stable structure with triangular shape and internal angles for Ni_3 cluster is 59.98, 60.00 and 60.02 degrees. A twisted Tetrahedron was obtained for Ni_4 cluster, but it was consistent with previous findings [6]. The structure of Ni5 cluster was obtained as a two pyramid Triangular. For clusters with 6 to 9 atoms the irregular structures and for Ni10 cluster regular and pyramidal structure were obtained.

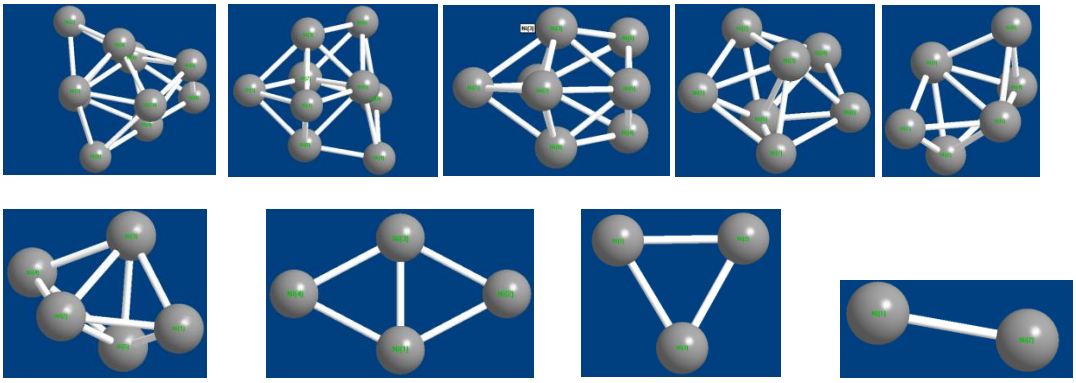

Figure 1. The structure of stable of Ni nano-clusters (2 up to 10 atoms)

Equation (1) and the computational level of B3LYP acquired the binding energy on the atom for these clusters

$$E_b = \frac{nE(Ni) - E(Ni_n)}{n} \quad (1)$$

In this equation $E(Ni_n)$ is the energy of the most stable cluster with **n** atom and $E(Ni)$ is the energy of the each atom [24-26].The binding energies range were increased from 1.52 up 2.76 electron volt by increasing the number of nickel atoms in the investigated clusters.

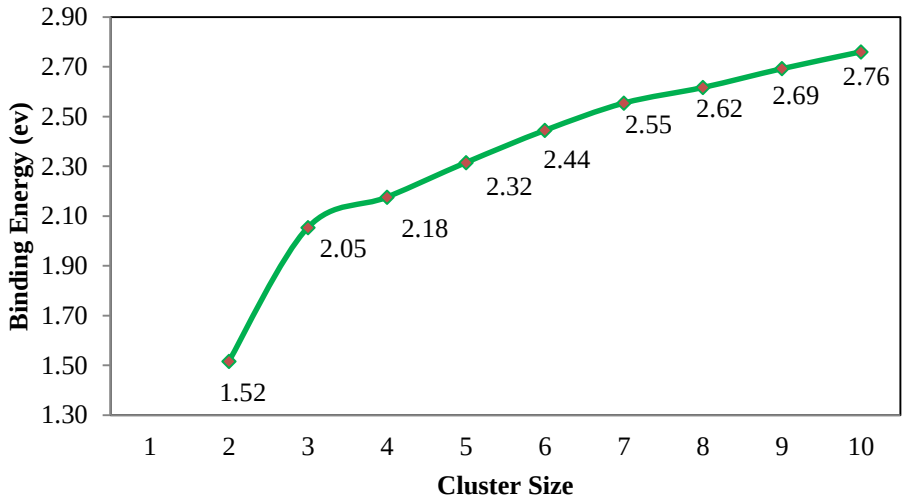

Figure 2. The binding energy of Ni nano-clusters

According to the following equation(2)the linear relationship between the size of clusters ($n^{-1/3}$) and some of the cluster properties showed that it is possible to extract these properties (X_∞) by extrapolating to the mass of the material [27-30].In this case, k_x shows the slope of the characteristic graph of the cluster (X_n) that is being studied.

$$X_n=k_x n^{-1/3}+X_\infty \quad (2)$$

Figure 3 shows the linear behavior of Ni-Ni binding energy in $n^{-1/3}$ in these clusters. The extrapolation of this diagram toward the number of many atoms (mass limits) was obtained Ni-Ni as Å 98.2.

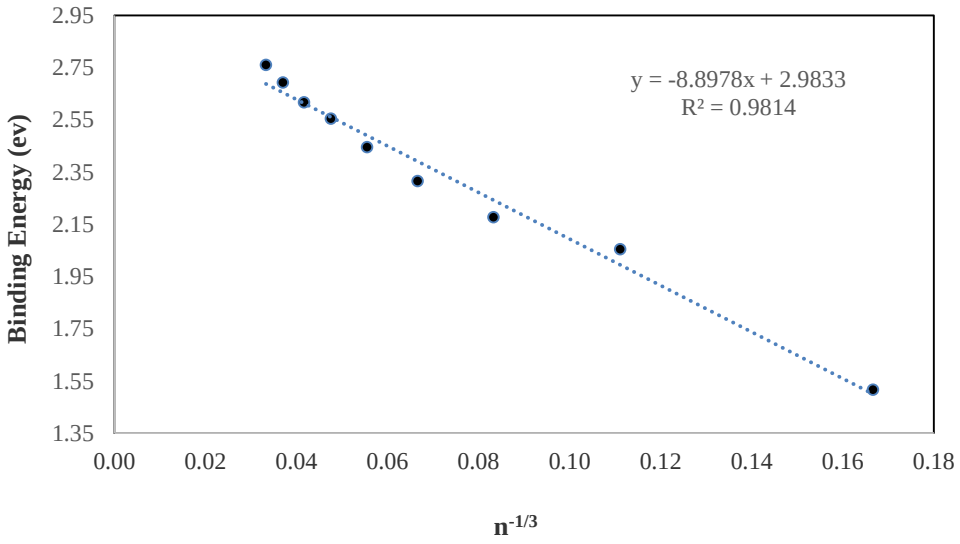

Figure 3. The binding energy of Ni nano-clusters with 2 to 10 atoms versus $n^{-1/3}$

Figure 4 illustrates the HOMO-LUMO energy Changes for these structures. This figure shows that the HOMO-LUMO energy difference decreases and reaches zero in the mass of the metal bulk by increasing the number of atoms on the structure of this sample. Ni_8 has the least amount of HOMO-LUMO energy difference among the Nano-clusters were investigated with 2-10 atoms,it indicates that the cluster is more reactive and less kinetic stability.

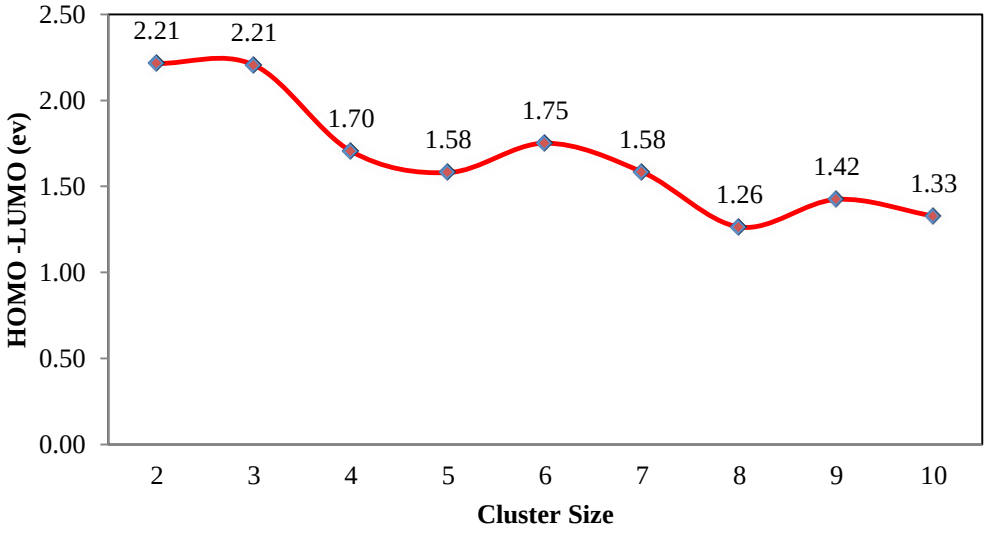

Figure 4. HOMO-LUMO gap energy

Figure 5 shows that the dipole momentum variations of 2 to 10 atomic nickel clusters. Small clusters with a low atom number (2 to 4 atoms) are symmetrical and have a dipole moment of zero.

Ni_8 cluster has the highest dipole momentum among clusters of 2 to 10 atoms, due to the fact that the dipole moment relates to the geometric structure [31-32].

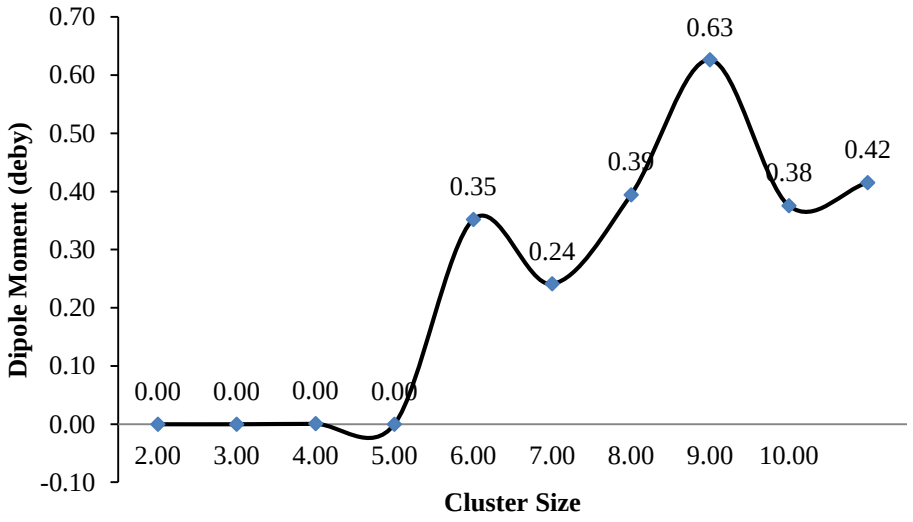

Figure 5. Dipole momentum variations

The Mulliken charges (Table 1) were determined the charge on Ni atoms up to Ni4 is zero which are measured on the most stable structures of these Nano-clusters. Dipole moment in Figure 5 illustrates these structures are non-polar, and charge distribution on clusters with more than 4atoms is asymmetric. Theatoms distribution of Mulliken charges in these clusters varies from -0.017 to 0.093.

Table 1. Mulliken charges

	Number of atoms									
	1	2	3	4	5	6	7	8	9	10
Ni5	0.088	0.089	-0.099	0.023	-0.101					
Ni6	-0.017	0.178	-0.017	-0.038	-0.038	-0.068				
Ni7	-0.251	0.092	-.095	-0.095	0.093	0.128	0.128			
Ni8	-0.088	-0.115	0.006	-0.115	-0.089	0.104	0.151	0.145		
Ni9	-0.048	-0.065	0.077	-0.158	0.407	0.110	-0.053	-0.033	0.083	
Ni10	0.081	-0.026	-0.029	0.081	-.026	0.084	0.014	-0.051	-0.063	-0.064

Each table or figure should be on main body of the text. Discussion should contain a critical review of the results of the study with the support of relevant literature.

4. Conclusion

In this paper some properties of Nano-clusters with 2 to 10 atoms of nickel and its geometric shape was investigated. By increasing the number of cluster atoms, the average equilibrium distance, and the binding energy on the atom increased, but HOMO-LUMO energy differences decreased. The linear behavior of the Ni-Ni binding energy diagram in $n^{-1/3}$ is well visible in these clusters. According to investigated clusters the lowest difference HOMO-LUMO energy is related to Ni_8, we can conclude that this cluster is more reactive and less kinetic stability. Also,Studies have shown that the Ni8 cluster has the highest dipole moment.

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