

Electronic and Magnetic Properties Of Small Nickel Clusters Ni_n ($N \leq 15$): First Principle Study

M Chibani¹, S Benamara¹, H Zitoune¹, M Lasmi², L Benchallal³, L Lamiri⁴ and Madani Samah^{4,*}

¹Department of Physics, Faculty of Sciences and Applied Sciences, University of Bouira, Bouira, Algeria

²Department of Radiological and Atomic Physics, Algiers Nuclear Research Center CRNA, Algiers, Algeria

³Department of ST, Faculty of Technology, University of A. Mira, Bejaia, Algeria

⁴Department of TCSN, Faculty of SNV, University of A. Mira, Bejaia, Algeria

***Corresponding Author:** Madani Samah, Department of TCSN, Faculty of SNV, University of A. Mira, Bejaia, Algeria, Tel.: 0657177404, E-mail: madanisamah@yahoo.fr

Citation: M Chibani, S Benamara, H Zitoune, M Lasmi, L Benchallal et al. (2024) Electronic and Magnetic Properties of Small Nickel Clusters Ni_n ($N \leq 15$): First Principle Study, J Mater Sci Nanotech nol 12(1): 104

Received Date: May 20, 2024 **Accepted Date:** June 20, 2024 **Published Date:** June 24, 2024

Abstract

We investigate structural and magnetic properties of small nickel cluster Ni_n ($n \leq 15$) by using a Density Functional Theory code. The first step consists to calculate the bond length and the binding energy in different geometries for each cluster. In the second step, after the equilibrium geometries and the binding energies have been obtained we calculate magnetic moment and the density of states.

Keywords: Nickel, cluster, DFT, magnetic, stability

Introduction

The electronic and magnetic properties of small transition metals (TM) clusters are of interest wide range of surfaces sciences, catalysis, and magnetic recording applications. They are characterized by unfilled valence d-orbitals, such as nickel. This orbital has a localized character and requires extensive compilation resources and important time. The structural evolution and magnetic properties of transition metal clusters have attracted the attention of a wide range of researchers, both from experimental and theoretical studies. The effect of geometric structure on magnetic ordering [1] is the most interesting aspect. Among transition metal (TM) clusters, nickel clusters seem to be very interesting and have potential importance in the physics and chemistry [2], and they are of special interest because of their practical applications in ferromagnetism and their superparamagnetic behaviour [3, 4]. Some experimental [4–6], and several theoretical investigations based on Density Functional Theory (DFT) are done to study the structural and electronic properties of nickel clusters [7–12].

Using the framework of Tight-binding molecular-dynamics (TB-MD) method, the magnetic and structural properties of nickel clusters of sizes from 5 to 60 atoms are investigated [13–18]. Granja et al. have used the Friedel's model to study the structural and magnetic properties of nickel clusters of sizes from 5 to 26 atoms [19]. Elsewhere, Nayak and al. used the EPEF model to investigate the structural properties of nickel clusters of sizes up to 23 atoms [20]. Rosch et al., using an all-electron spin-polarised calculations on nickel clusters with face-centered-cubic (and simple cubic) geometry, have analyzed bonding, magnetic behaviour, cohesive energy, bond distances, ionization potentials, and DOS profiles, with paying particular attention to the role of the nickel 4s and 3d electrons [21].

Small Ni_n ($n=7$ to 10) clusters are computed by a quasi-classical molecular dynamics computer simulation technique. Optimized structures of the clusters are obtained by an embedded-atom potential [22]. Structural stability and energetic of nickel clusters, Ni_n ($n=3$ to 459), have been investigated by molecular-dynamics simulations using a size-dependent empirical model potential energy function [23]. Recently, Zhou et al. [24] have explored the stable structures and energies of Ni clusters using particle swarm optimization (PSO) combined with simulated annealing. The simulation results indicated that the structures of Ni clusters are icosahedral-like and binding energy per atom tends to approach that of bulk materials when the atoms number increases. Using a newly proposed calculation scheme that combines the Hubbard approximation with the tight-binding molecular-dynamics method, Andriotis et al. obtained that the average magnetic moment per atom is significantly higher in the clusters than in the bulk, in agreement with experimental [15]. More recently, Wang et al. have, using the VASP code, explored Nickel clusters (Ni_{13} , Ni_{15} , Ni_{38} , and Ni_{55}) and their catalytic activity on Carbon adsorption [25].

Global optimization of the geometry of small nickel clusters, and their interaction with benzene were performed using the density functional theory with generalized gradient approximation for exchange and correlation [26]. Elsewhere, energetic of nickel clusters are studied using the embedded-atom method, demonstrate that geometric structural optimization of clusters are in good agreement with those of available experimental and theoretical investigations [27]. We can also cite that stabilized geometrical structures of Nickel clusters are probed via a transferable tight binding potential with a molecular-dynamics method and simulated-annealing techniques [28]. Elsewhere and beyond a variety of transition metal clusters, Nickel ones are investigated computationally using a density functional approach and the equilibrium geometries and binding energies are optimized [12]. Pablo et al. have explored the structures and energy effects of molecular nitrogen adsorbed on nickel cluster using an extended Huckel model coupled with two models of the adsorbed–nickel interaction [29]. Using first-principles calculations based on pseudo potential, Sakurai et al. examined the structural stability and magnetization for nickel clusters containing up to 500 atoms [30]. A work conducted by Chikhaoui et al. have theoretically investigated the structural, electronic, and magnetic properties of Ni_n ($n = 2-10$) clusters and the effects of the S-doping [31]. Since two years ago, Boudjahem et al. have performed a theoretical study of small nickel clusters in order to evaluate their stability, electronic and magnetic properties using density functional theory (DFT) calculations at the BLYP/Def2-TZVP level of theory [32].

This present research work is devoted to study the electronic and magnetic properties of free nickel clusters Ni_n ($n \leq 15$), that were investigated using the Density Functional Theory (DFT) and pseudo potential based on SIESTA code [33-5] as tool to predict geometrical shape, and to calculate cohesive energies and magnetic moments of this clusters.

Compilation Method

Our calculations were been performed on the Density Functional Theory (DFT) [36] by using exchange correlation functional PBE|s|r|LO [37, 38] parameterize of the Generalized Gradient Approximation (GGA). To describe the interaction between valence electrons and atomic-core, the pseudo potentials were constructed using the Troullier-Martin scheme [39] with $4s^1 3d^9 4p^0 4f^0$ as valence electronic configuration.

The atomic-orbital basis set employed was a split-valence double zeta polarized (DZP) basis for nickel atom (Ni). The cutoff-energy of 300 Ry is set to calculate a charge density in a regular real-space grid. For orbital-confining cutoff radius, a value of 0.0014 Ry is used.

To calculate properties of ground state nickel clusters Ni_n ($n \leq 15$), we investigate all possible geometric structures for each cluster. The structures of the computed ground states of Ni_n clusters for $n=2$ to 15 atoms are shown in Figure 1. The binding energies, average magnetic moments, and bond lengths are reported in the Table I.

Results and Discussion

Geometric Structure

Much possible geometric structures were examined for each nickel clusters Ni_n ($2 \leq n \leq 15$). The most stable structures obtained in our works are shown in Figure 1, and their respective energies are represented in Figure 2. The same think for magnetic moment, all possibilities were examined, and the average magnetic moment per atom is represented in Figure 3. The numerical values of bond length, binding energy, and average magnetic moment are reported in Table I.

Ni₂ and Ni₃ Clusters

In our calculations, we found the ground state of nickel's dimer Ni_2 , with a bond length value of 2.13 Å and binding energy of 1.538 eV/atom (3.076 eV).

The bond length value is in good agreement with the experimental measurement of Pinegar et al. [5] (2.1545 ± 0.0004 Å), and is slightly shorter than that of Morse et al. [40]. The binding energy of the ground state of nickel's dimer Ni_2 obtained is 3.76 eV (1.538 eV/atom). This value is considerably larger than experimental value 2.042 eV [5]. The magnetic moment obtained for the dimer of nickel is 1.00 μ_B for each atom. These results are in good agreement with those obtained by Ambrusi et al. [41]. Using the VASP package, they have obtained the respective values for inter atomic distance, bonding energy per atom and total magnetic moment as 2.10 Å, 1.44 eV/atom and 2.00 μ_B . Our values seems also to be larger than that obtained by Zhou et al. [24] using particle swarm optimization (PSO) combined with simulated annealing (SA) (they found 1.06 eV/atom as the binding energy for the Ni_2 dimer). Elsewhere, with DFT calculations at the BLYP/Def2-TZVP level of theory, Boudjahem et al. [32] have obtained 2.15 Å as the inter atomic distance for the Ni_2 cluster and binding energy per atom equal to 1.28 eV. This inter atomic distance is very close to our one and the binding energy is larger.

Equilateral triangle structure (D_{3h} point group symmetry) is the most stable structure for Ni_3 cluster. The Ni-Ni bond distances are about 2.23 Å. The average binding energy and magnetic moment obtained are respectively 1.975 eV/atom and 0.67

μ_B /atom. This inter atomic distance is very close to that reported by Nayak et al. [20]. The binding energy is in good agreement with results yielded by Reuse et al. [42]. Also, our results seem to be in good agreement with those obtained by Ambrusi et al. [41]. The triangular form of Ni_3 , was reported to be more stable elsewhere [43]. Erkoc et al. [44] have also obtained $D3h$ symmetry with 2.22 \AA as inter atomic distance whereas our results give $D3h$ and 2.23 \AA in excellent agreement. We shall note also experimental observations show that Ni_3 is triangular [45]. Michelini et al. [7] have concluded that the ground-state geometry for Ni_3 is an equilateral triangle ($D3h$ symmetry).

Ni₄, Ni₅ and Ni₆ Clusters

Erkoc et al. [44] found that the stable structures of Ni_n clusters with sizes $n = 4$ to 6 , have a regular symmetry. The corresponding point groups of these clusters are: Ni_4 (Td), Ni_5 ($D3h$) and Ni_6 (Oh) respectively. According to our findings, the tetramer Ni_4 is a distorted tetrahedron with a $D2d$ symmetry group, bond lengths ranging from 2.23 to 2.41 \AA , and an average binding energy of 2.213 eV/atom . Boudjahem et al. obtain the same space group [32]. Arzivu et al. [46] and Venkataramanan [47] have also reported the same configuration as the ground state. According to Fengyou et al. [48], a planar rhombus with $D2h$ symmetry is the lowest-energy geometry.

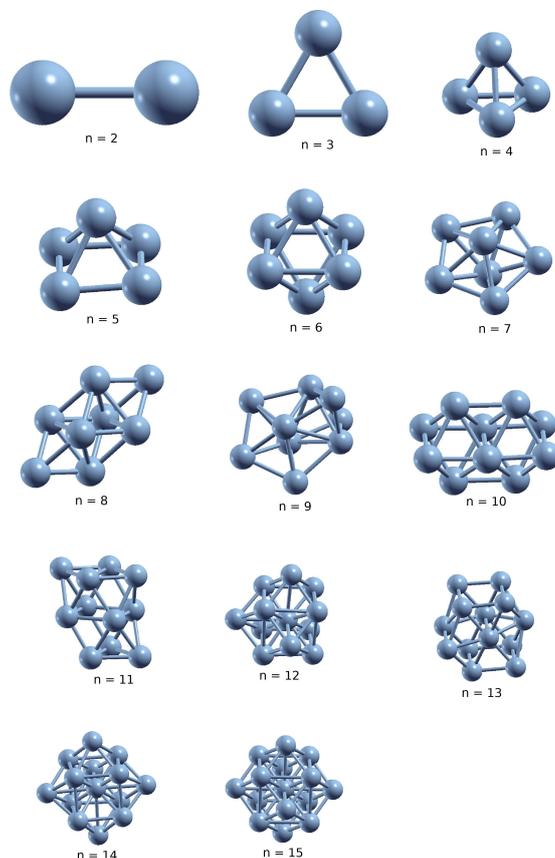


Figure 1: The most stable structures for Ni_n ($2 \leq n \leq 15$) clusters

The ground state of Ni_5 is a pyramidal structure, with a regular square base ($C4v$ symmetry group). The Ni-Ni bond length in the base is about 2.32 \AA , and the fifth atom in top of the pyramid is placed at a distances of 2.30 - 2.33 \AA . The average binding energy of Ni_5 cluster is 2.578 eV/atom . Elsewhere, it is established that a trigonal bipyramid geometry is nearly isoenergetic with the square pyramid [14, 15]. According to other studies, Ni_5 has a magnetic moment of $1.81 \mu_B$, with a trigonal bipyramid geometry [44, 45]. More recently, Boudjahem et al. found that a trigonal bipyramid geometry with $D3h$ symmetry is the most stable geometry for the Ni_5 cluster [32]. Our results are consistent with those obtained by Venkataramanan [47] as the most sta-

ble configuration, whereas Reddy et al. [49] reported the ground state to be the trigonal pyramid geometry.

Among all possible configurations of Ni_6 cluster, the most stable structure is a distorted bi pyramid (Oh symmetry). The bond lengths are 2.39 Å between atom in the base, and 2.35 Å between each atom in the top of the structure and the atoms in the base. The average binding energy equals to 2.806 eV/atom. Parks et al. have obtained experimentally that Ni_6 cluster adopts the octahedron structure [45]. Earliest works show that Ni_6 is a more tightly bound octahedron [42, 45, 50], with a smaller magnetic moment of $1.47 \mu_B$. Apsel et al. have found that Ni_6 cluster in the lowest-energy geometry is in a capped trigonal bi-pyramid structure with C_{2V} symmetry [3], and the lowest-energy geometry is a capped trigonal bi-pyramid with C_{2V} symmetry for Boudjahem et al. [32]. Moreover, using a self consistent tight-binding method, the structure of Ni_6 is an octahedron formed by atoms with coordination number $Z = 4$. In contrast, Ni_5 contains atoms with coordination $Z = 4$ and $Z = 3$ [51].

Ni7, Ni8 and Ni9 clusters

The most stable structure of Ni_7 cluster is an distorted bipyramide (D_{5h} as symmetry group) with pentagonal base. The interatomic bond lengths are between 2.38 and 2.43 Å in the base, and 2.36-2.39 Å between the atoms in top and the atoms in base. The binding energy averages 2.912 eV/atom. The total magnetic moment of Ni_7 cluster is $6.00 \mu_B$ ($0.875 \mu_B$ per atom). The same structure was obtained by Nayak et al. [20]. Recently, Boudjahem reported that the most stable configuration of the Ni_7 cluster is a bicapped trigonal bipyramid with C_{3h} symmetry [32].

An assembly of two crossed distorted tetrahedrons (D_{3d} space group) is the most stable structure for Ni_8 cluster. The total magnetic moment is equal to $8.00 \mu_B$ ($1.00 \mu_B$ per atom), the bond lengths range from 2.36 to 2.43 Å, and the binding energy obtained is equal to 2.991 eV/atom. Boudjahem et al. [32] have obtained that the bicapped octahedron geometry with C_{2V} symmetry is the most stable geometry structure for the Ni_8 cluster. The bidisphenoid (point group D_{2d}) was proposed by Zhou et al. [24] as the more stable structure of Ni_8 isomers.

The structure of Ni_9 , shown in Figure 1 is a distorted structure with bond lengths values 2.33-2.57 Å, and its binding energy is 3.101 eV/atom. This structure exhibit a total magnetic moment of $8.02 \mu_B$ ($0.89 \mu_B$ per atom). The most stable configuration of the Ni_9 cluster is a tetra-capped trigonal bi-pyramid with C_{2V} symmetry obtained by boudjahem et al. [32]. Rodriguez-Kessler et al. [52] have reported a tricapped trigonal prism geometry as the ground-state configuration. Durmus et al. suggest that Ni_9 is a capped somewhat distorted pentagonal bi-pyramid [22]. A tricapped triangular prism configuration is found to be the ground state of Ni_9 , [54]. For Ni_n , previous calculation obtained the tricapped trigonal prism as the most stable structure [28]. N_{in} ($10 \leq n \leq 15$) clusters

The most stable structures of Ni_n ($10 \leq n \leq 15$) are shown in Figure 1. The corresponding bond lengths, binding energies, and average magnetic moments are reported in the Table I.

Experimental observations [45] give for Ni_{10} a tricapped pentagonal bi-pyramid, Ni_{11} as pentagonal, Ni_{12} is in icosahedron, Ni_{13} is in icosahedron, Ni_{14} is in bi-capped hexagonal anti-prism, and finally Ni_{15} is in bicapped icosahedron form. Ni_{10} adopts a D_{2h} symmetry structure. The same results is obtained by Boudjahem et al. [32] concerning inter atomic distances and magnetic moment Durmus et al. [22] suggest for Ni_{10} the C_{3v} space group. Lu et al. [53] exploring physical properties of nickel clusters, found that the trigonal pyramid with T_d symmetry is the most stable structure of Ni_{10} and possesses a regular tetrahedral configuration. A trilayered structure with 3-5-3 stacking is found to be the ground state of Ni_{11} cluster. Ni_{12} is also three layered structures with 3-6-3 stacking. The ground state of Ni_{13} is found to be a continued layered structural pattern based on the ground states of Ni_{10} and Ni_{12} . It is also a piece of a double tetrahedron and packed with 1-3-6-3 atoms. Among all isomers, one pentagonal bi-pyramid based structure is more favorable in energy for Ni_{15} [54].

In contrast to the structure found by Boudjahem et al. [32], our results indicate that Ni₁₁ cluster crystallizes in the Cs structure, which has fewer symmetry. Their lowest-energy geometry is a combination of one square pyramid and two prisms with C2V symmetry [32]. In- teratomic distances are between 2.22 and 2.62 °A with an average binding energy of 3.21 eV per atom. According to our findings, C3v is displayed as a symmetry group for Ni₁₂ cluster. Elsewhere, other recent study [32] gives for Ni₁₂ cluster, the most stable geometry can be viewed as a combination of two prisms and two square pyra- mids with C2V symme- try. Andriotis et al. [15] find that hollow starting geometries for Ni₁₂ (icosahedral struc- ture), evolves into stable geometry with central atoms on MD relaxation, using the Hubbard approximation with the tight-binding molecular-dynamics method. The Ni₁₂ cluster with C5v symmetry has a fully occupied HOMO state with twofold degeneracy obtained by Xie et al. [55].

Our results for Ni₁₃, Ni₁₄ and Ni₁₅ evolve with these following space groups C2v, C4v and Oh respectively. Binding energies, magnetic moments and inter atomic distances can be seen in the Table I.

The Ni₁₃ cluster is one of most studied clusters because it is considered as the seed for different cluster growth patterns. For this one, Lia et al. [56] using the framework of VASP code, have obtained CCP (cubic-closed packed) structure. The total magnetic moments of Ni₁₃ cluster is 10 μ_B and a space group of C3v. Piotrowski et al. [57] indicated that Ni₁₃ has a structure much closer to the Co₁₃ hexagonal bi-layer (HBL) structure.

Song et al. [58] have investigated the magnetic properties of the nickel clusters using DFT (density functional theory)-PBE (Perdew-Burke-Ernzerhof) calculations. Their results show that the Ni₁₃ nanoclus- ters can be considered magic clusters with large chemical stability and small magnetic moments. Chaves et al. [59], based on spin-polarized symmetry-unrestricted DFT within the formulation proposed by PBE for the exchange-correlation, have obtained the icosahedral con- figuration. using Embedded-atom method (EAM), Grig- oryan et al. [27] have obtained an icosahedron as the most stable structures for Ni₁₃. Elsewhere, Lu et al. [54] have found that the ground state of Ni₁₃ is found to be a continued layered structural pattern and it is piece of a double tetrahedron and packed with 1-3-6-3 atoms. Using VASP code , the authors of reference [25] have found that Ni₁₃ adopt an icosahedral geometry. Ni₁₃ has one atom at the center and other 12 identical atoms on the spherical shell surface with a coordination number of 6. The distance between the spherical shell and the central atom is 2.32 °A. The surface Ni-Ni bond length is 2.44 °A and binding energy equals 3.22 eV per atom. Lathio- takis et al. [17] using tight-binding molecular-dy- namics scheme, obtained the icosahedral structure is the only one of the Ni₁₃. In an other work [60], using this time an other tight-binding approximations, retrieve the cuboc- tahedron structure. Luo et al. [61] have noted that Ni₁₃ about 3.04 eV and av- erage inter atomic distances aver- aging 2.52 A [60]. Song et al. proposed for Ni₁₅ cluster, the adjacently bi-capped icosahedron citeSong.

Table I: Bond length, binding energy, and average magnetic moment of Nin (10 ≤ n ≤15)

Cluster	bond length (°A)	Binding energy (eV/atom)	Average magnetic (μB)
Ni ₁₀	2.32-2.44	3.167	0.79
Ni ₁₁	2.22-2.62	3.212	0.9
Ni ₁₂	2.22-2.76	3.259	0.67
Ni ₁₃	2.28-2.47	3.285	0.75
Ni ₁₄	2.29-2.60	3.378	0.71
Ni ₁₅	2.33-2.75	3.433	0.37

The evolution of binding energy and magnetic moment with the cluster's size

The binding energy per atom E_b as function of cluster size plotted in Figure 1 was calculated according to the Equation 1.

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

where E_b is the binding energy per atom, n is the number of Ni atoms in cluster, and $E(Ni)$ is the energy of Ni atom in the most stable.

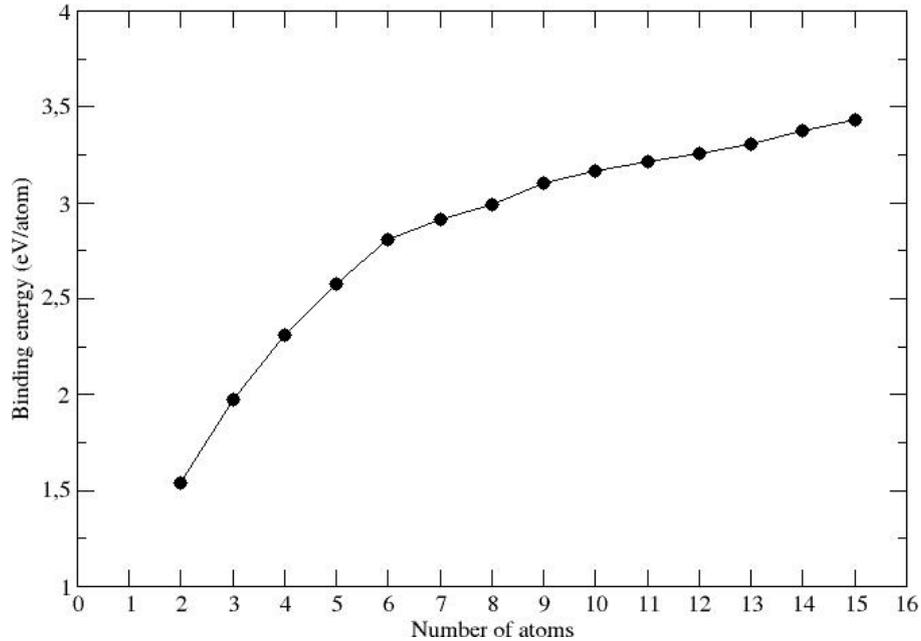


Figure 2: Binding energy of Ni_n (2 ≤ n ≤ 15) as function of cluster size (Number of atoms)

The average binding energy per atom increases as the cluster size increases, it shows an exponential like growing. We note that the variation of average binding energy with respect to the cluster size is fast from $n=2$ to $n=6$. However, this variation for $n=7$ to $n=15$ changes relatively slowly. The simulation results indicate that the binding energy per atom tends to approach that of bulk materials when the atom number increases. Lu et al. have demonstrated that binding energy increases rapidly with size n up to $n=7$, and the size dependence becomes smooth at $n=8$. It still not converges toward to the bulk value (6.38 eV/atom) [54]. The same general behavior of the binding energy of pure Ni_n clusters as function of size is observed by authors of reference [31]. Our results are also consistent with previous theoretical results [54, 62, 63].

A central issue in cluster physics is to identify particularly stable sizes using the second difference of total energies. It is also a sensitive physical parameter associated with the stability of clusters. $\Delta^2 E(n)$ is the difference of energy of two fragmentation paths Ni_{n+1} to Ni_n + Ni and Ni_n to Ni_{n-1} + Ni. If $\Delta^2 E(n) > 0$, it means that the dissociation of Ni_{n+1} into Ni_n leaving one atom free is more favorable than the dissociation of Ni_n into Ni_{n-1} and one free Ni atom. These values were calculated from the Equation 2.

$$\Delta^2 E(n) = E(Ni_{n+1}) + E(Ni_{n-1}) - 2E(Ni_n)$$

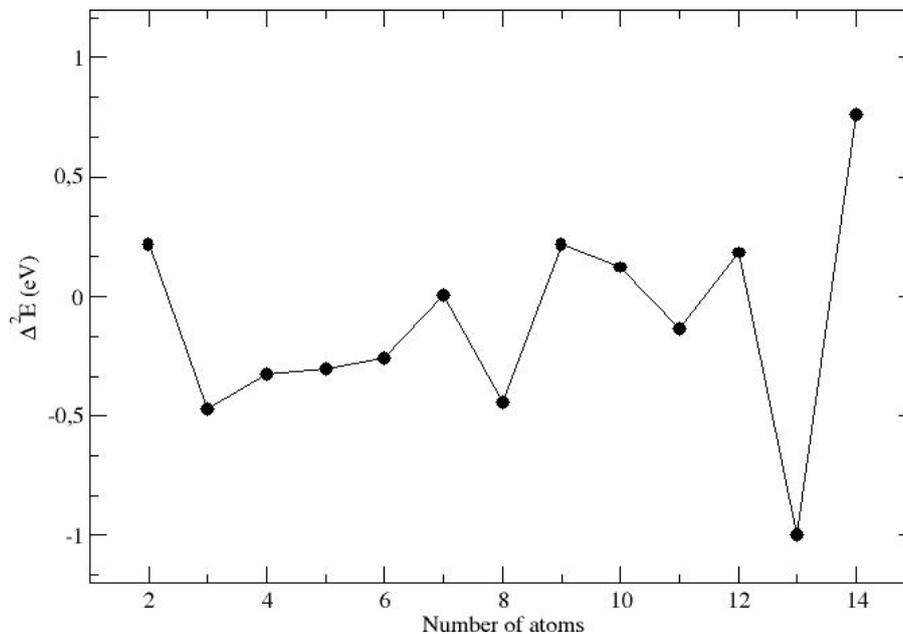


Figure 3: Second order difference in energy for Ni_n clusters ($2 \leq n \leq 14$)

As we can see in Figure 3, what shows the $\Delta^2 E$ as a function of cluster size (number of atoms), both results show the same tendency, with the exception for $n=2, 7, 9$, and 12 . For Ni_2 , Ni_7 , Ni_9 , Ni_{12} , and Ni_{14} there are pronounced peaks, these clusters are more stable than their neighboring clusters. This result confirm that in the transition metal clusters there are no magic numbers [64]. Nayak et al. [20], by using an empirical many-body potential and molecular dynamics simulation, are found that the Ni_2 cluster be most favorable channel for nickel clusters in the size range $n \leq 24$. However in the present work and as shown in Figure 3, we found that most favorable channel for nickel clusters is the Ni_{14} cluster.

Our results are different compared with those found by Erkoc et al. [44]. They access that clusters with 4, 6 and 13 atoms are the most stable. This difference is essentially due to the method used which lacks relevance and accuracy, in this case molecular dynamics simulation at constant temperature. Among other results, Zhou et al. [24] found that clusters with 13 atoms appeared to be more stable. That is to say, the stability depends on both the size and the symmetrical structure. In their stability investigation, Boudjahem et al, show that two local peaks appear at $n = 6$ and 8 , indicating that Ni_6 and Ni_8 clusters are more stable than their neighboring ones [32]. Elsewhere, Grigiryana et al. [65] demonstrate that the peaks appearing in stability curve correspond to the most stable structures (often termed magic clusters) and the minima show the most unstable. They indicate among other results that $n=13$ is magic numbers [27]. Erkoc et al. [44], and Grigoryan et al. [65] confirm that the clusters with the number of atoms $n = 4, 6, 13$, are more stable. Chaves et al. [59] investigations shown that Ni_6 and Ni_{10} are particularly more stable than their neighbours, which agree with previous results [58, 65]. However, Grigoryan et al. [65] and Nayak et al. [20] and our results do not indicate that Ni_{13} is a magic cluster as previously reported. Completely in opposite direction of our results, Luo indicates that $n=13$ is a magic number: 13, and the corresponding sizes for the most unstable clusters are: 12, 14. [61]. Same results than those Luo et al. [61] can be found in references [27, 58, 66].

The average magnetic moment per atom as a function of number of atoms in the cluster is plotted in Figure 4. The diagram shows only small variations of the average magnetic moment per atom with the clusters size. The highest value is $1.44 \mu_B/\text{atom}$ (Ni_6), and the lowest value is $0.37 \mu_B/\text{atom}$ (Ni_{15}). For Ni_2 , Ni_4 , and Ni_8 clusters, the mean magnetic moments are the same and equal to $1.00 \mu_B/\text{atom}$. For the remaining clusters the values are lower than $1.00 \mu_B/\text{atom}$. It's important to precise that clusters are ferromagnetic. The analyzed Ni_n clusters exhibited ferromagnetic behavior with a magnetic moment that depended on the size.

A recent study done by Lia et al. gives the total magnetic moments of Ni_{13} clusters the value of $10 \mu_B$ [56], being consistent with the available studies [59, 67, 68]. Our values are also lower than those of Chikhaoui et al. [31] when comparing with those obtained experimentally. It is also the case for almost all *ab initio* calculations on nickel clusters [61, 69]. These discrepancies between theory and experiment remain an open question, although the problem may arise from the additional orbital moment contributions or isomerization effects as suggested by some authors [70]. Elsewhere, other study show that the total magnetic moments of nickel clusters are in the range of 0.67 to $1.33 \mu_B/\text{atom}$. The highest magnetic moment value is obtained for the Ni_6 cluster ($1.33 \mu_B/\text{atom}$) [32]. Our magnetic moment for Ni_6 cluster is in excellent agreement with the experimental value ($1.47 \mu_B/\text{atom}$) [58].

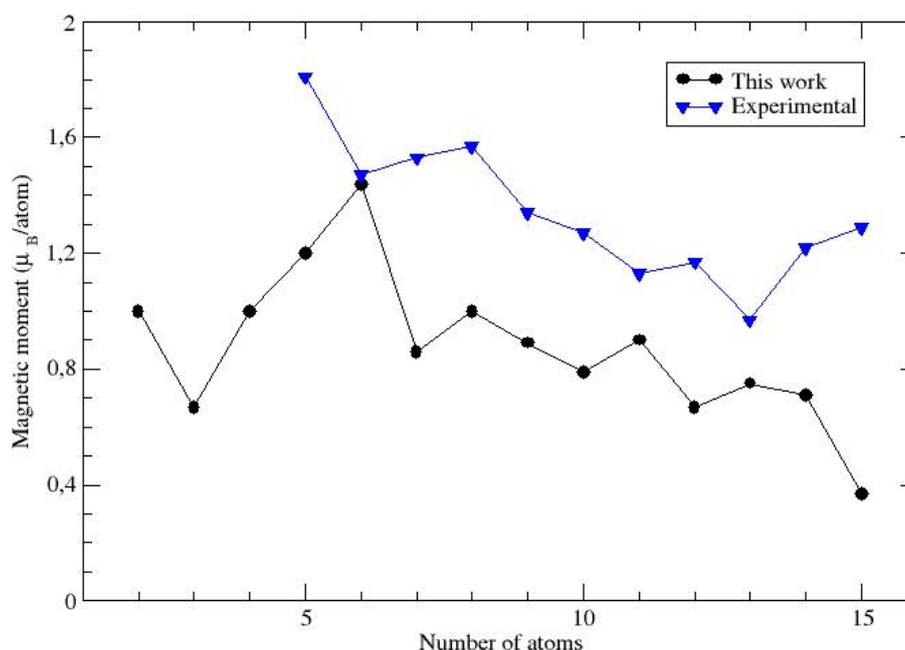


Figure 4: Evolution of average magnetic moment per atom with the number of atoms in nickel clusters Ni_n ($2 \leq n \leq 15$)

Our Ni_5 magnetic moment is much smaller than that obtained by Apsel et al., with a magnetic moment of $1.81 \mu_B$ [3]. Ni_6 is a more tightly bound octahedron [42, 45], with a magnetic moment of $1.47 \mu_B/\text{atom}$ exactly the same that our value. Our Ni_7 magnetic moment is less than $1.00 \mu_B/\text{atom}$, in opposite direction with study showing that gives a large value for this cluster [71]. Ni_{13} with closed-shell icosahedron is the first cluster with an interior atom [42, 45]. Its compact structure explains its anomalously small magnetic moment of $0.96 \mu_B/\text{atom}$ greater than our value ($0.75 \mu_B/\text{atom}$). Ni_{14} , with a magnetic moment of $0.71 \mu_B/\text{atom}$ is very less than $1.22 \mu_B/\text{atom}$ obtained by Parks et al. [45].

R.E. Ambrusi et al. and H. Xu et al., with the framework of DFT have obtained for Ni_4 a less lowest value ($0.92 \mu_B/\text{atom}$) compared to our one which equals to $1.00 \mu_B/\text{atom}$ [41, 72]. Experimentally, Apsel et al. [3] have found for Ni_n clusters for $n=5$ to $n=8$ and for $n=11$ and 12 the following magnetic moments per atom $1.65, 1.35, 1.4, 1.45, 0.93$ and $1.10 \mu_B/\text{atom}$. Our results agree perfectly with results obtained by Reddy et al. [49]. Partially, from $n=2$ to $n=8$, our variation seems to have the same tendency of variation found by Futschek et al. [73]. From $n=6$ to $n=13$, our study reproduce the same results of Duan et al. [74] and clearly differentiates before n less than 6. Guirado-Lopez et al. [75] have argued that the discrepancy between DFT and experiment is due to a large orbital moment in the clusters. Then the contribution of the orbital moment is particularly important for Ni where the difference between the orbital moment of the free atom ($L = 2 \mu_B$ for an electron configuration $4s^1 3d^9$) and in the bulk ($L = 0.05 \mu_B$) is rather dramatic.

All nickel clusters are highly magnetic [21]. As it is widely known, the bonding in nickel clusters (also in the metal) arises from the interaction of nickel atoms in a $4s^1 3d^9$ like atomic configuration. The spatial extent of the two atomic orbitals $3d$ and $4s$,

however, is very different. The radial expansion of 4s orbital is more than three times that of 3d orbital. Then, when nickel atoms combine to form a small cluster, the interaction occurs primarily between the spatially more diffuse 4s orbitals whereas the 3d-3d overlap is quite weak. Therefore the bonding originates largely from the coupling of 4s electrons resulting in a broad contribution to the DOS. However, 3d orbitals are highly localized, resulting in a much narrower DOS.

To understand the s, p, and d orbitals contribution to the magnetic moment, we examined the partial density of states (PDOS) of the Ni_6 (highest magnetic moment), and Ni_{15} (lowest magnetic moment) clusters, as shown in Figure 5. The contribution to density of states is dominated by 3d band's contribution, and the contribution of 4s and 4p bands is much less pronounced.

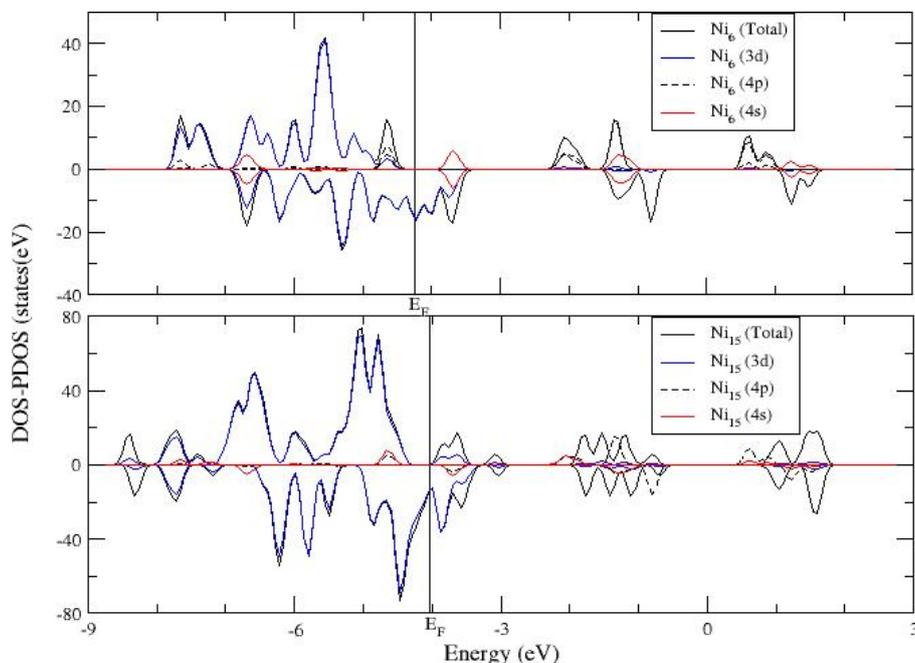


Figure 5: Partial density of States (PDOS) of Ni_n ($n=6$, and $n=15$) clusters.

As we can show in Figure 5: -The majority spin 3d band is completely filled, while the minority spin 3d band extends above E_F ; this is the origin of the ferromagnetic ordering in the clusters and shows that the unpaired electrons are localized in the 3d shell.

-The 4s band completely envelopes the 3d band in the interval of -1 to -2 eV energies and is broader. Our results are in good agreement with those Rasch et al. obtained using All-electron, spin-polarised, LCGTG-LDF calculations [21]. For the Ni_{15} cluster the majority spin 3d band is not completely filled and difference in population of electrons with minority spin 3d band is small which explains the low magnetic moment.

For all clusters calculated in our work, the majority spin 3d band are populated by electrons more than the minority spin 3d. This evidences the ferromagnetic property of the Nickel clusters Ni_n ($2 \leq n \leq 15$). experimental and theoretical. Unfortunately, in the case of nickel, experimental studies are rare, and the results of theoretical studies are not always in good agreement, and even contradictory. Through this work, we tried to shed a little more light on the electronic and structural properties of small nickel aggregates.

To investigate the geometrical, electronic structures, and magnetic properties of small nickel clusters Ni_n ($2 \leq n \leq 15$) it is very noticeable in Figure 5 that both clusters have a very low electronic density at the Fermi level. Based on this analysis, we can expect that these clusters are less chemically active. The density of states (DOS) demonstrates that the Fermi energy is located in the spin-down nickel 3d states for Ni_6 and Ni_{15} . The spin-up gap of Ni_6 is twice as wide as the spin-up gap of Ni_{15} (see Figure 5). We

note that all atoms of Ni_6 , but the majority of atoms of Ni_{15} , constitute the surface of the cluster. Our results agree with those of reference [76]. The chemical activity of some clusters is closely related to the density of electrons located near the Fermi level (E_F). The more DOS in this region, the greater the chemical activity of the cluster [77]. The PDOS spectra of Ni_6 is in quite concordance with that obtained by [31]. The hybridization is weak and involves molecular orbitals far from the Fermi level.

For all clusters calculated in our work, The majority spin 3d band are populated by electrons more than the minority spin 3d. This evidences of the ferromagnetic property for the nickel clusters Ni_n ($2 \leq n \leq 15$).

Conclusion

Several studies have been and are being devoted to the electronic properties of transition materials clusters, both $n \leq 15$). We have used the density functional theory with the generalized gradient approximation, combined to the pseudo potential Method. In a first step, we have generated, tested and optimized the pseudo potential of nickel. After in a second step, we have performed to optimize a Double Zeta basis. And finally we calculated the geometrical, electronic structures, and magnetic properties for each cluster of interest.

A great number of geometric and magnetic configurations are investigated for each size, and the ground states are depicted. For the studied clusters, the more stable structures are closed structures with inter atomic distances between 2.13 Å and 2.76 Å. Our results shown that Ni_2 , Ni_7 , Ni_9 , Ni_{12} , and Ni_{14} clusters are more stable than their neighboring clusters, and the most favorable channel for nickel clusters is the Ni_{14} cluster. This result confirm that in the transition metal clusters there are no magic numbers [64]. The average magnetic moment per atom shows only small variations with the clusters size. The highest value is $1.44 \mu_B/\text{atom}$ (Ni_6), and the lowest value is $0.37 \mu_B/\text{atom}$ (Ni_{15}). It remains in the vicinity of $1.00 \mu_B/\text{atom}$, and the electronic study shows the evidence of ferromagnetic property of the nickel clusters studied here.

Declarations

Funding Declaration

No Funding Received

Data Availability Declaration

No datasets were generated or analysed during the current study

Competing Interests Declaration

There is no competing interest

Ethical Approval Statement Declaration

Not Applicable

References

1. C. Kohl, GF Betsch (1999) *Phys Rev*, B6: 4205.
2. V Bonacic, Koustecky, P Fantucci, J Koustecky, *Chem Rev*, 91: 1035.
3. SE Apsel, JW Emmert, J Deng, LA Bloomfield (1996) *Phys. Rev. Lett*, 76: 144.
4. ML Billas, A Chatelain, WA de Heer (1994), *Science* 265: 1682.
5. CJ Pinegar, JD Langenberg, CA Arrington, EM Spain, MD Morse, *J Chem Phys*, 102: 666-74.
6. JG Louderback, AJ Cox LJ Lising, DC Douglass, LA Bloomfield (1993) *Phys D* 26: 301-3.
7. MC Michelini, R Pisdiez AH Jubert (2001) *Int J Quan-tum Chem*, 85: 22-33.
8. WJ Hu, LM Mei, H Li *Sol* (1996) *Stat Commun* 100: 129.
9. P Amerillas, I Garzon, *Phys. Rev. B* 54, 10362.
10. S Erkoç (1989) *Phys Stat Sol* (b) 152: 447.
11. S Erkoç (1990) *Phys. Stat. Sol.* (b) 161: 211.
12. T Nakazawa, T Igarashi, T Tsuru, Y Kaji (2009) *Comp Mat Sci* 46: 367.
13. FA Granja, S Bouarab, MJ Lopez, A Vega, JMM Carrizales, MP Inigues et al. (1998) *Phys Rev B*, 57: 12469.
14. N Andriotis, M Menon (1998) *Phys Rev B*, 57: 10069.
15. N Andriotis, N Lathiotakis, M Menon (1996) *Euro-phys. Lett*, 36: 37.
16. S Bouarab, A Vega, MJ Lopez, MP Inigues, JA Alonso, *Phys Rev B*, 55: 13279.
17. NN Lathiotakis, N Andriotis, M Menon, *J Con-noll* (1995), *Europhys. Lett*, 29: 135.
18. M Menon, J Connolly, N Lathiotakis, A Andriotis (1994) *Phys Rev B*, 50: 8903.
19. FA Granja, JMM Carrizales, JLM Lopez (1998) *Sol. Stat. Commun* 105: 25.
20. SK Nayak, SN Khanna, BK Rao, P Jena (1997) *J Phys Chem*, A 101: 1072.
21. N Rosch, L Ackermann, G Pacchioni (1992) *Chem Phys Let*, 199: 275.
22. P Durmus, M Boyukata, S Ozcelik, ZB Guvenc, J Jellinek (2000) *Surf. Sci*, 454: 310.
23. Gunes, P Gunes (2000) *Inter J Mod Phys C*, 11: 1013.
24. JC Zhou, WJ LI Wen, JB Zhu (2008) *Trans. Nonferrou Met. Soc. China*, 18: 410.

25. Q Wang, KH Lim, SW Yang, Y Yang, Y Chen et al. (2011) *Theor Chem Acc*, 128: 17.
26. K Rao, P Jena (2002) *J Chem Phys*, 116: 4.
27. VG Grigoryan, M Springborg (2001) *Phys Chem*, 3: 5135.
28. Luo (2000) *Modelling Simul Mater Sci Eng*, 8: 95.
29. P Nigraa, DL Freemanb, D Sabo, JD Doll (2004) *J Chem Phys*, 121.
30. M Sakurai, J Souto-Casares, JR Chelikowsky (2016), *Phys Rev B*, 94: 024437.

Submit your next manuscript to Annex Publishers and benefit from:

- ▶ Easy online submission process
- ▶ Rapid peer review process
- ▶ Online article availability soon after acceptance for Publication
- ▶ Open access: articles available free online
- ▶ More accessibility of the articles to the readers/researchers within the field
- ▶ Better discount on subsequent article submission

Submit your manuscript at

<http://www.annexpublishers.com/paper-submission.php>