Electronic and structural properties in nanocluster $\text{Al}_{n-x}\text{Ni}_x$

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Abstract. In this paper, we study electronic isosurfaces and structural properties in nanoclusters $\text{Al}_{n-x}\text{Ni}_x$ using Density Functional Theory, with the Local Density Approximation; the density of state, the highest occupied molecular orbital and lowest unoccupied molecular orbital were determined for different structures, obtaining different values of the energies. We have obtained evidence of a contribution of d orbitals for pure Ni nanoclusters and Al-Ni nanoclusters. In addition, an overlapping of the sp orbitals is evident. We also determined that the structure with the greatest binding energy corresponded to $\text{Al}_{10}$, with a $D_{2h}$ symmetry, and the structure with the minimum binding energy corresponded to $\text{Ni}_{20}$, with a $C_{2v}$ symmetry.

1. Introduction

Nanoscience and nanotechnology are important fields within scientific research mainly due to the great expectations nanoparticles in the development and creation of new materials that show increases and/or improvements in physical and chemical properties with potential applications [1]. Numerous studies on metallic, semiconductor and even insulating materials can be found in the literature. In general, it is considered that nanomaterials have to be crystalline, as well as having a size and shape as monodisperse as possible [2]. In particular, considerable effort has been put into the preparation of bimetallic AlNi nanoparticles, mainly due to recent experimental studies reporting applications in biomedical therapies, clean energy enablers and eco-friendly products [3].

Cotton [4] introduces the term cluster to designate compounds with metal-to-metal bonds and in a sufficient number of atoms to define a polyhedral structure in three dimensions. The atomic clusters are made up of groupings of atoms with well-defined compositions and only a few stable geometrical structures, which is a first difference with respect to nanoparticles and a similarity to molecules. After atoms, atomic clusters are the most elementary “atomic pieces” in nature and are distinguished by a size equivalent to the Fermi wavelength of the electron, which makes them the link between atoms and nanoparticles with ability that differ greatly between the two systems. In these molecular type structures quantum effects are the ones that cause their chemical, optical and electronic properties such as magnetism, photoluminescence, photocatalytic and electrocatalytic activities [5–8].
It is complicated to make accurate calculations of the electronic structure of metal clusters, especially for the case of larger clusters when they are in dissolution and protected by a ligand layer. In recent years, density functional theory has been used to determine structural and electronic properties of different metal clusters, but there is little information in the literature on theoretical studies with ab-initio methods of Al-Ni clusters, hence the great interest in carrying out a study using computational methods to determine different properties in nanoclusters whose compounds are Al and Ni.

The ab-initio methods provide a theoretical description of the electronic behavior by finding the kinetic and potential energy of the system represented in the Hamiltonian. In the search for the numerical solution, from the quantum point of view, the following methods have been developed: Hartree-Fock, Quantum Monte Carlo, Embedded Atom Method, Density Functional Theory, among others.

In this work, the structural and electronic properties of Al$^{n-x}$Ni$_x$ nanoclusters are studied applying Density Functional Theory in the local density approximation to evaluate the density of states, electronic density, binding energy, energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), among others.

2. Computational method

To determine the density of states, electron density and the energies of the HOMO and LUMO orbitals of the Al$^{n-x}$Ni$_x$ nanoclusters, density functional theory was used [9] with local density approximation [10] using the functional developed by Perdew-Wang was used [11].

The software used was Materials Studio 5.0 implementing the DMOL3 code. For the calculation of the energy gap (Eg), The Koopmans Theorem [12] for Hartree-Fock calculations was used [9].

There are a large number of frameworks possessing different atomic disposition in a given geometry. Typically, it is difficult to optimize all possible topological isomers for large groups and with a high doping concentration, which is why an artificial structural construction is necessary. The designed structures of the clusters can be linear, planar, Y-shaped, square pyramid, pentagonal pyramidal, tetrahedron, octahedron, hexagonal, prism configurations. For the calculations, nanoclusters were designed with a size between 10 and 20 atoms, for each structure the atoms were varied under the condition $n \geq x$.

3. Results and discussions

The Figure 1, Figure 2 and Figure 3 show the density of state for the nanocluster Al$_{10}$, Al$_5$Ni$_5$ and Ni$_{10}$ respectively. In Figure 1 it can be seen that around the Fermi level (dotted line) the highest electronic contribution is offered by the 3p orbital of aluminum, below the Fermi level (between $-0.40$ and $-0.3$ Ha) it can be observed that the contribution is represented by the 3s orbitals. The Figure 1 shows that the structure for this nanocluster is a double hexagonal ring with D$_{2h}$ symmetry.

In Figure 2, for the Al$_5$Ni$_5$ nanocluster, it is observed that around the Fermi energy the greatest electronic contribution is offered by the 3d orbitals of Ni, in the energy interval $-0.50$ and $-0.25$ Ha, it is evident that the contribution in the system is given by the 3s, 3p orbitals of aluminum and the 4s orbitals of nickel, it is also indicated that the structure for this nanocluster is a double hexagonal ring with C$_s$ symmetry.

The Figure 3 shows that the major contribution is provided by the 3d orbitals of Ni around the Fermi level, also very little contribution is observed from the 4s orbitals, also the structure for this nanocluster is double hexagonal ring with D$_{2h}$ symmetry.

The density of states of the Al$_{15}$, Al$_7$Ni$_8$ and Ni$_{15}$ nanoclusters are shown in Figure 4, Figure 5, and Figure 6, respectively. In Figure 4, is shown that around the Fermi level the major contribution is by the 3p orbitals of the Al atoms, above and below the Fermi level a
contribution from the 3p orbitals is also observed, furthermore in Figure 4 it is indicated that the structure for this nanocluster has a Cs symmetry.

For the Al$_7$Ni$_8$ nanocluster, the density of states indicates that there is a greater contribution of the 3d orbitals of nickel around the Fermi level. In addition, it is observed that there is a medium contribution from the 3p orbitals of aluminum, and very little contribution from the 3s orbitals of Al and 4s orbitals of Ni. The Figure 5, it is indicated that the structure for this nanocluster has a Cs symmetry.

The density of state of Ni$_{15}$ shows the largest contribution from the 3d orbitals around the Fermi level and very little contribution from the 3p and 4s orbitals, in Figure 6 it is observed that the structure for this nanocluster has a Cs symmetry.

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**Figure 1.** Density of states of Al$_{10}$ with double hexagonal ring structure and D$_{2h}$ symmetry.

**Figure 2.** Density of states of Al$_5$Ni$_5$ with double hexagonal ring structure and Cs symmetry.

**Figure 3.** Density of states of Ni$_{10}$ with double hexagonal ring structure and D$_{2h}$ symmetry.

**Figure 4.** Density of states of Al$_{15}$ with Cs symmetry.
The density of states for Al$_{20}$, Al$_{10}$Ni$_{10}$ and Ni$_{20}$ nanoclusters are shown in Figure 7, Figure 8 and Figure 9, respectively. Around the Fermi level in the density of states for Figure 7 shows a higher contribution from the 3p orbitals of the Al atoms, moreover it is observed that around the interval between $-0.50$ and $-0.30$ Ha there is a contribution from the 3s orbitals. The Figure 7 indicates a planar triangular structure for this nanocluster, with a $C_{2v}$ symmetry.

In Figure 8 for the Al$_{10}$Ni$_{10}$ nanocluster, the density of states indicates that there is a major contribution from the 3d orbitals of nickel around the Fermi level. In addition, it is observed that there is a medium contribution from the 3p orbitals of aluminum, and very little contribution from the 3s orbitals of Al and 4s orbitals of Ni, only a small contribution from these orbitals is observed above the 3d orbitals of Ni and 3p orbitals of Al near the energy value of $-0.50$ Ha. Also, the Figure 8 indicates a planar triangular structure for this nanocluster, with a Cs symmetry.

The density of state of Ni$_{20}$ (Figure 9) shows the major contribution from the 3d orbitals around the Fermi level and very little contribution from the 3p and 4s orbitals of Ni. Figure 9 indicates a planar triangular structure for this nanocluster, with $C_{2v}$ symmetry.
Figure 9. Density of states of Ni$_{20}$ with C$_{2v}$ symmetry.

Figure 10. Electronic isosurfaces of Al$_{10}$.

The Figure 10 and Figure 11 represent the projection in the XY plane of the electronic isosurfaces for the Al$_{10}$ and Ni$_{10}$ nanoclusters, respectively. In Figure 10, the blue colored area indicates a lower density of bonded electrons with the electrons located in the center of the Al$_{10}$ nanocluster structure, while the orange area indicates a higher density of bonded electrons, the highest electronic contribution for this nanocluster is given by the 3p orbitals.

Figure 11 also shows that the lowest density of non-bonded electrons is located in the center of the structure (blue zone), while the highest density of bonded electrons, orange zone, are located at the edge of the structure, the largest contribution for this nanocluster is provided by the 3d orbitals.

The Figure 12 shows that the lowest density of non-bonded electrons is in the blue zone, while in the orange zone where aluminum atoms are located, the highest density of bonded atoms is found, the highest electronic contribution for the Al$_7$Ni$_8$ structure is offered by the 3d orbitals of Ni with a medium contribution of the 3p orbitals of Al.

Figure 11. Electronic isosurfaces of Ni$_{10}$.

Figure 12. Electronic isosurfaces of Al$_7$Ni$_8$.

In the case of the isosurfaces presented in Figure 13, it can be seen that the blue zone, which is shared by Ni and Al atoms, has the lowest density of non-bonded electrons, while the orange zone has the highest density of bonded electrons. The largest electronic contribution in this structure is provided by the 3d orbitals of Ni.
The Figure 14 shows the average binding energy for a cluster of pure Ni n nanoclusters and doped monoatomic AlNi$_{n-1}$ nanoclusters for $n = 10 - 20$. Here a linear behavior is shown where it is observed that the average energies for the AlNi$_{n-1}$ group clusters are larger than the values of the corresponding pure Ni n clusters, indicating that when introducing an Al atom this energy presents an increase. For this case, the structure with the highest binding energy of the AlNi$_{n-1}$ group is the AlNi$_9$ nanocluster, as the cluster size increases the average binding energy decreases until reaching the nanocluster with the lowest energy AlNi$_{19}$, something similar happens with the pure Ni nanoclusters, where the Ni$_{10}$ structure is the one with the highest energy and the one with the lowest energy corresponds to the structure for Ni$_{20}$.

![Figure 13. Electronic isosurfaces of Al$_{10}$Ni$_{10}$](image)

![Figure 14. The average binding energy as a function of nanocluster size.](image)

The average binding energy, varying the concentration of Ni atoms for Al$_{n-x}$Ni$_x$ nanoclusters (for $n = 10, 15, 18, 20$ with $x \leq n$) is shown in Figure 15, for fixed values of $n$ and increasing $x$ (increasing Ni concentration) furthermore, it is observed that the average binding energy decreases linearly. On the other hand, for fixed values of $x$ and increased cluster size, the binding energies are observed to gradually decrease as $n$ increases. Generally, the structure with the highest energy is the Al$_{10}$ nanocluster and the one with the lowest binding energy is Ni$_{20}$.

Based on the results obtained from the electronic transition energies which mostly do not exceed 1 ev, the semiconducting character of the studied nanoclusters can be observed, except for the particular case of the Al$_6$Ni$_{14}$ nanocluster which has a value $E_g = 0.058$ eV tending to be more conductive than all the other structures.

![Figure 15. Average binding energy as a function of Ni atom variation for Al$_{n-x}$Ni$_x$ nanoclusters of sizes $n = 10, 15, 18, 20$ with $x \leq n$.](image)
4. Conclusions

Noble metal nanoparticles, such as Ni, have been one of the most researched nanomaterials in nanoscience and nanotechnology. Their electrical and magnetic properties make these particles a good candidate for numerous applications in the field of electronics and computer science. In this paper, we study electronic isosurfaces and structural properties in nanoclusters Al_{n-x}Ni_x using density functional theory. The main study results are summarized as follows.

(i) For the different structures studied the densities of partial and electronic states evidence a contribution of the d orbitals of the nickel atoms and an overlap of the sp orbitals when the nanoclusters are composed of Al-Ni.

(ii) The binding energy of the structure for pure nickel nanoclusters decreases as the size of the structure increases and the energy increases when an aluminum impurity atom is added to it.

(iii) It is found that the binding energy for a fixed size nanocluster decreases as the nickel concentration increases, and there is also a decrease in the binding energy in this structure when the number of nickel atoms is fixed and the number of aluminum atoms is increased.

(iv) For all the structures studied, it was determined that the nanocluster with the highest binding energy is Al_{10} and the structure with the lowest average binding energy is Ni_{20}. Based on the results obtained for the electronic transition energy (gap) for the different nanoclusters studied, these structures are semiconducting.

(v) In general the large clusters, consisting of a core of between 14 and 20 atoms and a protective layer of strong ligands, and the small clusters, consisting of a smaller number of atoms, approximately between 2 and 13, which do not need strong stabilizing ligands and have all their atoms on the surface, present discrete energy levels and a band-gap that increases with decreasing size.

(vi) It should be considered that it is interesting to establish the stability of the nanocluster structures as a function of the Gibbs free energy.

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