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# Density Functional Study of Adsorption of Nickel Atom on Carbon Nanotube

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**ABSTRACT**

The adsorption of individual atoms on the semiconducting carbon nanotubes (CNT) has been investigated by using the first principles method within density functional theory. The stable adsorption geometries and binding energies have been determined for a Nickel (Ni) Transition Metal (TM) atom. We have found that the character of the bonding and associated physical properties strongly depends on the type of adsorbed atoms, in particular on their valence electron structure. Our results indicate that the properties of CNTs can be modified by the adsorbed Ni adatom. Owing to the curvature effect, these binding energies are larger for different sites of adsorption that we have used. We have showed that the Ni adatom can form strong and directional bonds with carbon atom of CNT. We have calculated Band Structure (BS), density of state (DOS) and charge transfer to find out the conducting nature of CNT. We have also calculated the HOMO and LUMO energy from which we can say HOMO shows the ability to donate electron and LUMO shows ability to accept the electron.

**Keywords**: DFT, Ni Atom, adsorption, CNT.

## INTRODUCTION

Carbon nanotubes (CNT) have been remarkable objects that look to revolutionize the technological landscape in the future. Tomorrow's society will be shaped by nanotube applications, just as silicon-based technologies dominate society today. [1, 2] The mechanical properties of carbon nanotubes have prominent application as they are flexible and can sustain large elastic deformations radially. At the same time CNT are very strong with high yield strength i.e. it is easy to apply elliptical de- formations but it becomes very difficult to elongate the system. Their strength exceeds far from any other fiber [3, 7]. Even more striking properties of CNT are the response of electronic structure to the radial deformation leading dramatic changes. As it has been predicted theoretically and confirmed experimentally, a semiconducting zigzag tube becomes metallic with finite state density at the Fermi level as a result of radial deformation, transforming the circular cross section into an ellipse. At the same time chemical activity of the surface of the tube undergoes into change; the interaction of adatoms with the CNT occurs differently at high and low-curvature sites. Metal-semiconductor transition induced by an elastic deformation has important implications.

The Physical properties of a CNT can also be modified by the adsorption of foreign atoms or molecules. This process is usually named as functionalization, and carries a great potential in constructing new nanostructures and to engineer them according to a desired application. For example, depending on the pattern of hydrogen atom coverage, while a metallic armchair CNT is transformed to wide-band gap semiconductor, a semiconducting zigzag tube becomes a metal with very high state density [8]. A free CNT, which is normally non-magnetic, becomes magnetic with unpaired spins upon the adsorption of oxygen molecule or specific transition metal atoms [9]. A recent study demonstrates that a semiconducting zigzag tube becomes both magnetic and high-conducting wire as a result of Ti coating. The increasing interest in the interactions between metal atoms and carbon nanotubes surface arises from the important role of CNT-metal junctions such as electronic devices, nanocomposites materials and catalysts systems. The Binding Energy between CNTs and Metals can be efficiently tuned by reactive chemical groups at the CNT surface.

The Binding between transition metals and the sidewall of carbon nanotubes plays very important role in the performance CNT-based nano devices. The Binding nature of TM can be identified by the magnitude of the binding energy and formation of bonds. The chemisorbed TM atoms can modify the electronic structure of Carbon nanotubes here have chosen Ni atom to test its interaction on side wall of CNT, and found nature of its adsorption on CNT.

## METHODOLOGY

The computing calculations were carried out using Doml3 code of Accelrys [10] based on density functional theory (DFT). Structural and electronic properties of CNT were derived to investigate the interaction of adatom Nickel on CNT. The Geometry optimizations of CNT along with Ni were performed using GGA and PBE functional [11, 14]. For Supercell geometries, spin unrestricted calculations were carried out with a double numeric polarized (DNP) basis set available and orbital cut-off was set to 4.4 Å. Scalar relativistic effects were included via a pseudo potential for all-electron calculations. 1 x 1 x 2 k-points were used for the Brillioun zone. All the calculations were performed using boundary conditions with 64 atoms within the Supercell. The tetragonal unit cell of 20 x 20 x 8.4 Å dimensions and sufficient separation between tubes is used to avoid interaction between the atoms. The chosen cut off value leads to atomic energies with an accuracy of 0.1 eV/atom, allowing calculations without sufficient loss of accuracy. Mulliken population analysis was carried out to predict the charge transfer and spin between Ni-adatom and nanotubes.

The (8, 0) zigzag CNT of diameter 6.26 Å and the length of tube is 8.52 Å as a model to study the adsorption of Nickel atom. We have examined different site for adsorption of Nickel atom as shown in figure (1). The Sites were (1) Carbon Atom (Site A), (2) Carbon-Carbon Axial Bond (site C), (3) Carbon-Carbon Chiral bond (site B) and (4) Hexagon (site D).

In all calculations, the carbon nanotubes along with Nickel atom were first optimized to occupy their ground state energy.

For each site Ni adatom has kept at a finite distance of 3.0 Å and then system is optimized to get stable structure. The binding energy ($E_b$) of adsorption of Ni atom on nanotube for all ground state structures were calculated by

$$E_b = -[E_{T\,(adsorbent + adsorbate)} - E_{T\,(adsorbent)} - E_{T\,(adsorbate)}].$$

Where $E_{T\,(adsorbent + adsorbate)}$ is the total energy of atom and CNT system, $E_{T\,(adsorbent)}$ is total energy of CNT and $E_{T\,(absorbate)}$ is the total energy of atom. To verify the computational accuracy of the structure we have calculated the binding energy of CNTs, density of state, band gap Charge Density, HOMO-LUMO, Milliken Charge and spin [15].

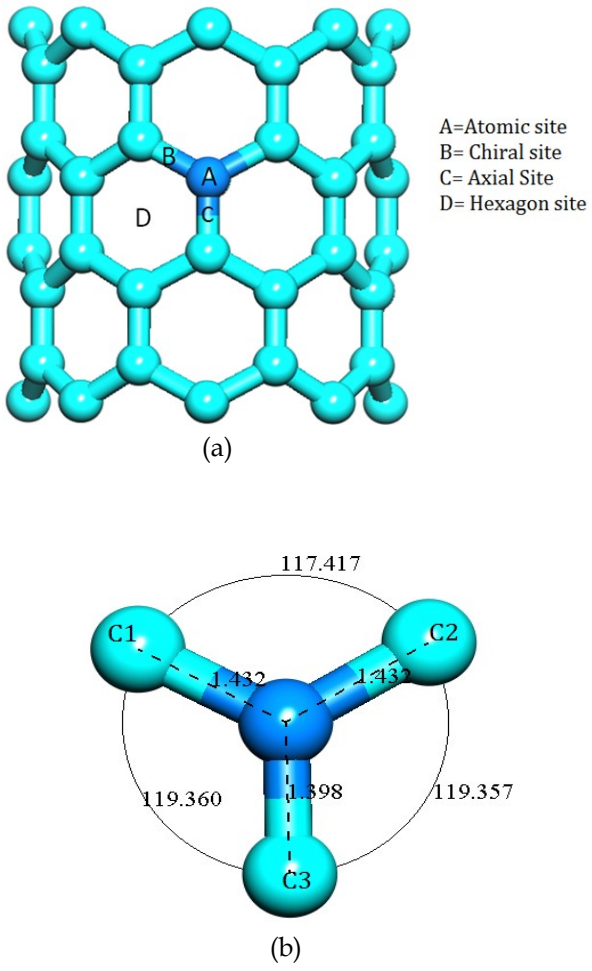



**Figure 1:** (a) Structural model of CNT (8, 0) (b) structural parameter at target atom

## RESULT AND DISCUSSION:

### 1. Geometrical properties

In order to get the accuracy of the first principles approach to the geometrical and electronic structure of the CNT, we have optimized the structure of (8, 0) CNT and then CNT along with Ni adatom. The optimized structure of (8, 0) CNT has a C - C axial bond of length 1.382 Å and C - C Chiral bond of length 1.44 Å. After performing geometry optimization CNT along with Ni adatom the bond length of C - C axial bond and C - C chiral bonds are slightly changed to 1.44 Å and 1.46 Å respectively as shown in Figure 1(a-b). The variation in bond length of C – C atom at all adsorption site is negligible therefore the change in bond angle between carbon atom of CNT is very less, this shows the SP2 hybridization of carbon atom of CNT is not changed due to interaction of Ni adatom. For all four sites the Ni atom is chemisorbed on carbon nanotube with minimum binding distance of 1.9 Å. The Ni adatom is chemisorbed on all four sites forming covalent bonds. The Bond length for C – Ni adatom for Site - A, Site - C, Site – B and Site – D is 1.9 Å as shown in figure in figure 2(a-d).

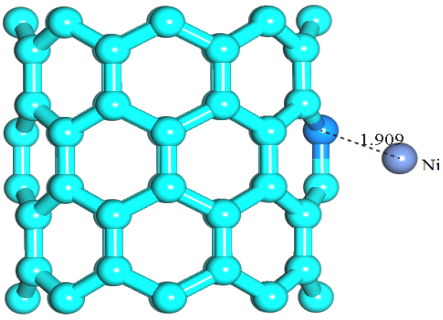



**Figure 2:** (a) Geometrically optimized structure for Ni-CNT at atom, site (A)

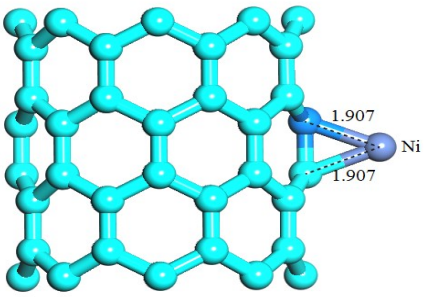



**Figure 2:** (b) Geometrically optimized structure for Ni- CNT at Axial bond position, site B

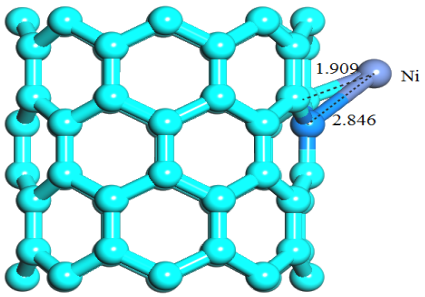



**Figure 2:** (c) Geometrically optimized structure for Ni-CNT at Chiral bond position, site C

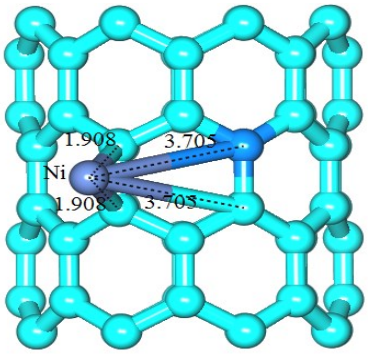



**Figure 2:** (d) Geometrically optimized structure for Ni- CNT at Hexagon position, site D

## 2. Electronic properties

The binding energies of CNT with Ni adatom were calculated for different adsorption sites. The value of binding energy determines the stability of system. The lower the binding energy is higher the stability of the system. The table 2 summarizes the calculated binding energies to the four different adsorption sites as mentioned. The binding energy of Ni adatom on CNT is - 1.8 eV. The larger value of B.E. indicates the Ni adatom is chemisorbed on CNT clearly seen in figure 2 (a – d). The band Structure and DOS Shown in figure 3 (a - d) shows that two states in valence band near fermi level merges into single highly occupied energy state at - 0.64 eV which is very close to Fermi energy. Due to adsorption of Nickel atom, highly occupied state in valance band and unoccupied states in conduction band near the Fermi energy level get closer and they reduce the bang gap of CNT from 0.701 eV to 0.46 eV for all four adsorption sites. The creation of highly occupied state at Fermi energy changes the semiconducting nature of CNT into almost metallic. We also performed Milliken population analysis to find the charge transfer between CNT and Ni adatom as shown in table 2. The Ni atom acquires positive charge of magnitude 0.364 e by donating charge to carbon atom. The isosurface electron density shows the formation of covalent bond between Nickel atom and neighboring carbon atoms as shown in figure 4.

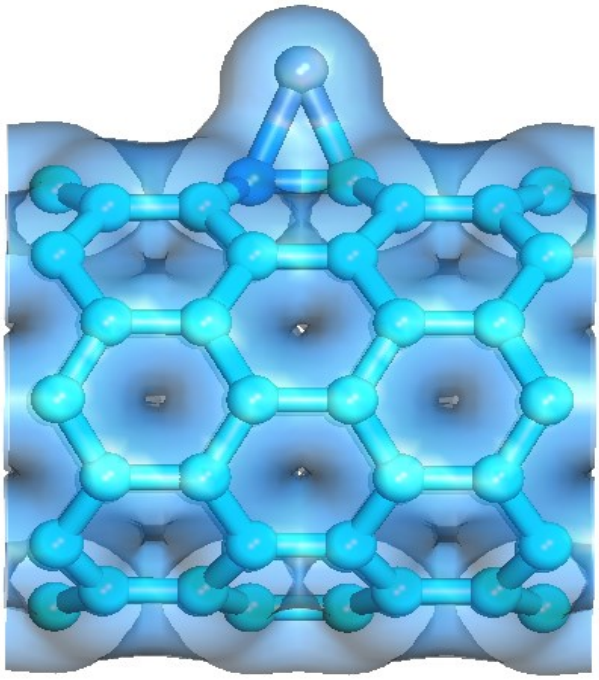
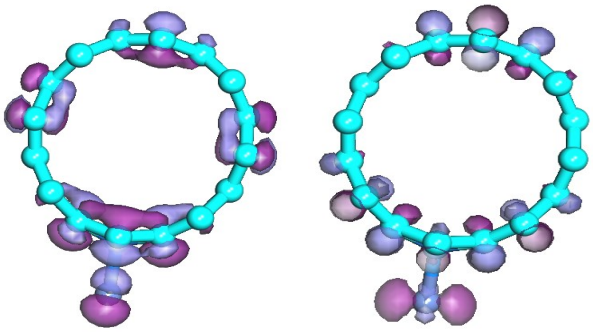


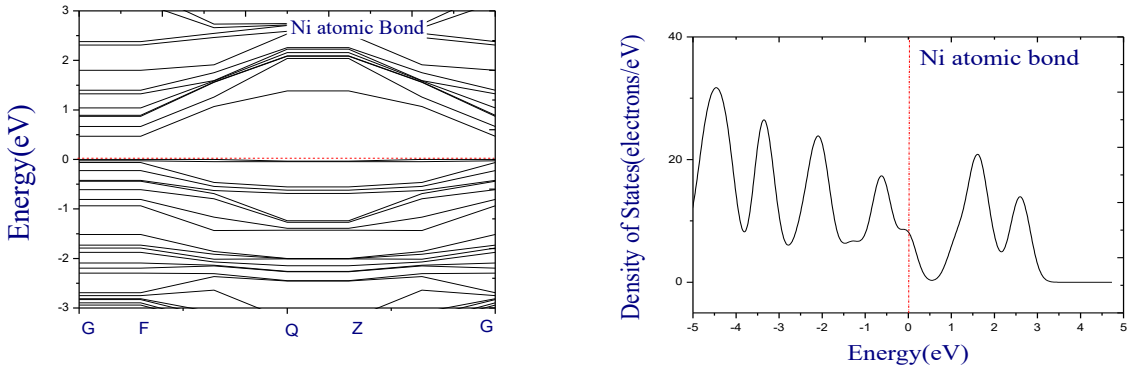
**Figure 4 :** Isosurface of Ni-CNT at Axial bond site

Figure 5(a) and (b) Shows HOMO and LUMO structure in which HOMO shows the ability to donate electron and LUMO shows ability to accept the electron. HOMO has energy - 3.804 eV and LUMO has energy - 3.510 eV.

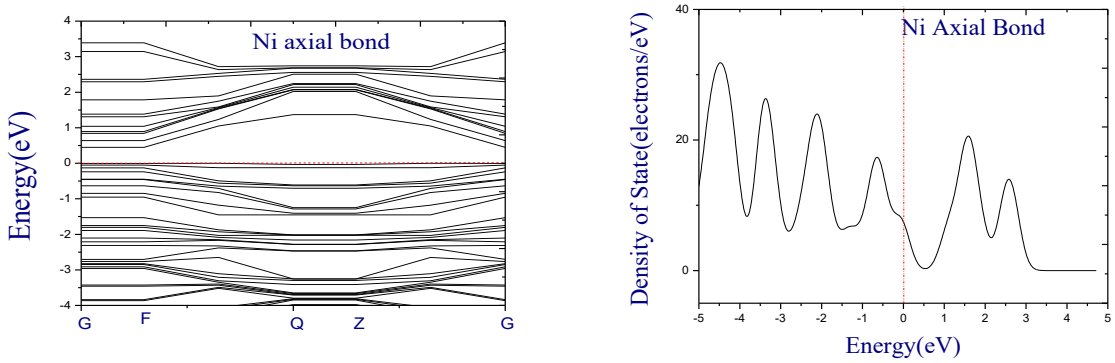


(a)HOMO (b) LUMO

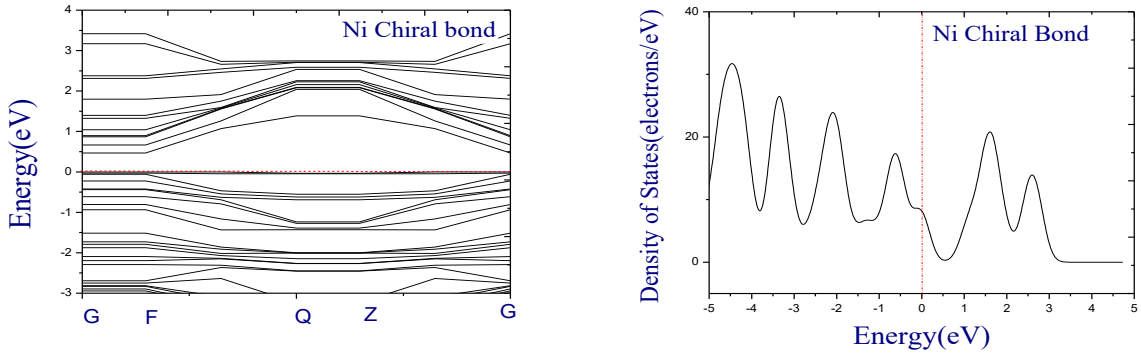
**Figure 5:** Stable structure of HOMO and LUMO



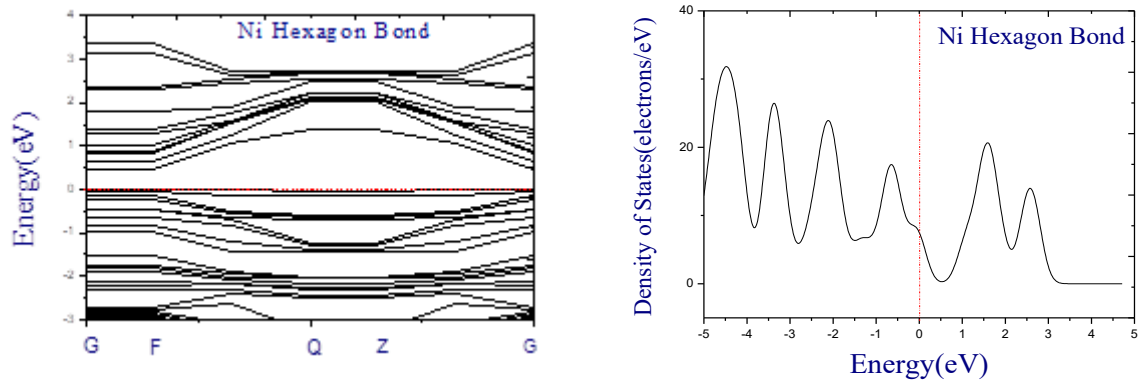

(a) Band structure and DOS of atomic (site A)




(b) Band structure and DOS of Axial Bond (site c)




(c ) Band structure and DOS of Chiral Bond (site B)




(d) Band structure and DOS of Hexagon (site D)

**Table 1:** shows structural properties i.e. binding distance and bond angles.

| Site | Binding distance in Å | Angle of CNT with Ni in degree |
|---|---|---|
| Pure (8,0) CNT | | |
| 3.0 Ni Atomic | l(C-Ni)=1.909 Å | |
| 3.0 Ni Axial Bond | l(C-Ni)=1.907 Å | <(C-Ni-C)=44.498$^0$ |
| 3.0 Ni Chiral Bond | l(C-Ni)=1.909, Å -2.846 Å | <(C-Ni-C)=28.002$^0$ |
| 3.0 Ni Hexagon | l(C-Ni)=1.909, Å -3.705 Å | <(C-Ni-C)=37.855$^0$ |
| | | <(C-Ni-C)=44.459$^0$ |

**Table 2:** Electronic properties of Ni-CNT

| | B.E (eV) | Band gap (eV) | Charge (Qt) | HOMO energy (eV) | LUMO energy (eV) |
|---|---|---|---|---|---|
| CNT (8,0) | | 0.701 | | | |
| CNT - 3.0 Cr Atomic | - 1.815 | 0.467 | 0.467 | - 3.806 | - 3.502 |
| CNT - 3.0 Cr Axial Bond | - 1.8205 | 0.449 | 0.449 | - 3.804 | - 3.510 |
| CNT - 3.0Cr Chiral Bond | - 1.815 | 0.45 | 0.45 | - 3.804 | - 3.502 |
| CNT - 3.0 Cr Hexagon | - 1.8232 | 0.468 | 0.468 | - 3.806 | - 3.510 |

## CONCLUSION

The interaction (8, 0) CNT with Nickel was investigated using DFT method. Transition metal interaction caused in the change in electronic structure of CNT and stability of the system is increased. Even though, the geometrical structure of CNT is not changed due to adsorption of Ni adatom. The Ni adatom is chemisorbed on CNT and forms covalent bonds. The band gap for CNT – Ni system is reduced and conductivity of CNT almost reached metallic. Improved conductivity of CNT can be used as fundamental tool to investigate nano electronic and sensing devisees.

**Conflicts of interest:** The authors stated that no conflicts of interest.

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