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Study of chromium atom adsorption on single wall carbon nanotube using first-principles density functional theory

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ABSTRACT

The effect of adsorption of Chromium (Cr) atoms on single-wall carbon nanotube (SWCNT) is studied using first-principles density-functional theory with the generalized gradient approximation. The adsorption energy, geometry, band Structure, density of states (DOS), Band gap, Charge transfer and spin of Cr atom-SWCNT system are calculated. The electronic properties like DOS, Band structure and HOMO-LUMO shows reduction in band gap of pure carbon nanotube from 0.7eV to 0.33ev due to interaction of Cr, which leads to transfer of semiconducting characteristics of SWCNT to semi metallic. The results are consistent with ionic bonding, and the adsorption is characterized by change in the electronic states and large charge transfer from Cr atom to the SWCNT. The Binding Energy and charge density analysis shows the formation of sigma bond between Carbon and chromium atom. The formation of such covalent bonding and the adsorption is characterized by strong hybridization between Cr atom-SWCNT. The molecular orbital and iso-surface charge distribution shows Cr atom is chemisorbed on carbon nanotube.

Key Words: DFT, Cr Atom, adsorption, CNT

INTRODUCTION

The design and engineering of new materials with tailor-made functionality plays an important role in materials science, and new classes of designer nanoscale materials will likely play a decisive role in the development of future technologies.

Single wall carbon nanotubes (SWCNTs) have received great interest following their discovery by Iijima in 1991 [1], owing to their excellent mechanical, thermal, and electrical properties [2-6]. In order to harness the exceptional properties of SWCNTs, one strategy is to functionalizing CNT by transition metal. Transition metal as promising functional materials have been widely used along with CNTs for catalysis applications, gas sensors, energy conversion and storage devices due to their abundance, environmental friendliness for specific physical and chemical properties [7–11]. Also carbon nanotubes can enhance the electron transport from within while the outside layer can facilitate ion transport which could bring benefits to applications in various electrochemical technologies. Therefore, SWCNTs are considered to be promising materials and building blocks for applications of future electronic devices [12, 13]. Some experimental and theoretical study of the interaction between metal and carbon nanotubes, including metal-doped, metal-cluster, and transition metal, has therefore drawn attention in the last decade. For example, the adsorption of Pt atoms on SWCNTs depends heavily on the curvature and the chirality of tube, and the diffusion barriers of the Pt atom are rather small and depend on the radii and the chirality of the supporting SWNTs [14]. Upon Pd doping, Pd4-cluster-functionalized (5, 5) and (8, 0) CNT model systems shows that the conductance of the semiconducting CNTs increases due to the narrowing band gap [15]. Study of isolated and bundled CNTs with transition-metal atom doping shows the richness of the electronic and magnetic properties [16]. However, there is little attention paid to the physical behaviour between element and CNT. In this paper, we study the interaction between the (8, 0) CNT nuclei such as Chromium. We compare their electronic characteristics by computing the band structure, density of state (DOS), Binding energy, Band Gap, HOMO-LUMO, Charge transfer and spin. With these electronic characteristic of CNT we predict the change in its semiconducting nature. As well as we found behaviour of adsorption of Chromium on CNT with the help of Binding energy, iso-surface Charge density distribution and molecular orbital. We also found the amount of charge transfer between SWCNT and Cr atom to predict type of semiconductivity of SWCNT.

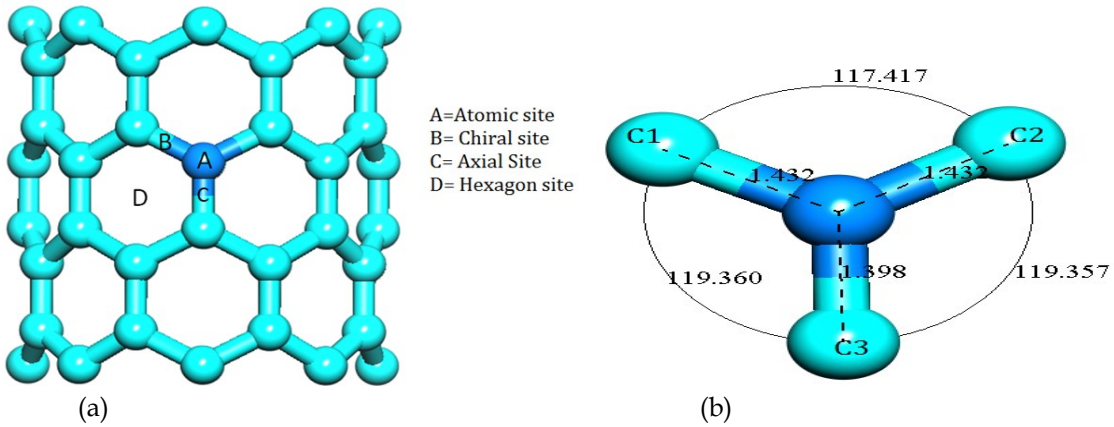
METHODOLOGY

All the calculations were carried out using first principle density functional theory (DFT), Doml[3] code. The Geometry optimizations of SWCNT with Transition metal were performed using GGA and PBE functional [17-20]. For Supercell geometries, spin unrestricted calculations were carried out with a double numeric polarised (DNP) basis set available and orbital cut-off 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 0.1eV/atom, allowing calculations without sufficient loss of accuracy. The calculations were performed to find the structural and electronic properties of optimized structures. Milliken population analysis was carried out to predict the charge transfer and spin between Cr-Atom and nanotubes.

We have selected (8, 0) zigzag CNT of diameter 6.26 Å and the length of tube is 8.52Å as a model to study the adsorption of Chromium atom. We have examined different site for adsorption of Chromium atom as shown in figure (1). 1) Carbon Atom (Site A), 2) Carbon-Carbon Axial Bond (site B), 3) Carbon-Carbon Chiral bond (site C) and 4) Hexagon (site D). In all calculations, the carbon nanotubes along with Chromium atom were first optimized to occupy their minimize energy state. For each site Cr has kept at a finite distance of 3.0 Å to optimize the system to get stable structure. The binding energy (E_b) of adsorption of Cr 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 [21].



(a) (b)

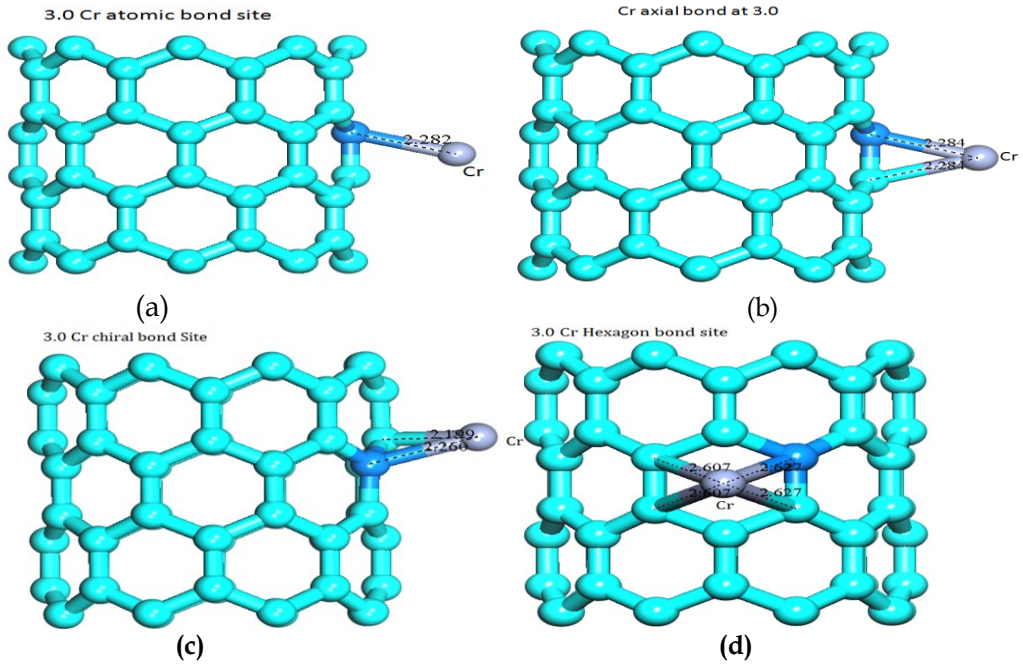
Figure1: (a) Structural model of CNT (8, 0) (b) structural parameter at target atom

RESULTS AND DISCUSSION

The Chromium atom is steely-grey, lustrous, hard and brittle metal in nature which takes a high polish, resists tarnishing, and has a high melting point. The radius of a Cr atom is 206 pm (0.206 nm) which is much greater than of a carbon atom 70 pm (0.070nm). So we studied the effect of adsorption of Cr atom on SWCNT. We are reporting here change in geometrical and electronic properties SWCNT, also adsorption nature of Cr atom.

Geometrical and Electronic properties

We have first performed geometry optimization for Cr adatom - SWCNT system and then found most stable configuration to get geometrical properties of the system. We performed first principal calculated for total energy to investigate electronic property and to observe the nature of adsorption of Cr atom on nanotube. The four different interactive sites were tested as mentioned above for the absorption of adatom. For all sites it is observed that Cr adatom get Chemisorbed with slight change bond length as in figure 2(a-d).



(a) (b)

(c) (d)

Figure (2): **(a)** Optimized structure of Cr-CNT at atomic bond position with bond length
(b) Optimized structure of Cr-CNT at axial bond position with bond length
(c) Optimized structure of Cr-CNT at Chiral bond position with bond length and
(d) Optimized structure of Cr-CNT at Hexagon bond position with bond length.

Before optimization, in the prepared model the distance of adsorption of Cr adatom is about 3.0 Å from carbon atom or carbon-carbon bond. After performing optimization Cr adatom get attached to carbon atom of nanotube by covalent bond of bond length 2.28 Å. There is minute difference in bond length of carbon - Cr atom at different sites as shown in Figure 2(a-d). Due to adsorption of Cr atom the bond lengths between C – C atom of both chiral bond at absorption site-B is changed from 1.432 A to 1.449 Å and 1.452 Å. For axial site – C the bond length of C – C atom is changed from 1.398 Å to 1.421 Å.

So slight variation in bond lengths at absorption sites were observed for chiral and axial bonds. This shows the carbon atom at adsorption sites are slightly bumped out of the cylindrical structure of nanotube and the bond angles between C - C - C bonds were ranging from115 ^{0} to 119^{0} which is less than 120^{0} indicates trigonal structure of bonding and prefers SP^2 hybridization as shown in Table 1.

Table 1: The Table shows Structural properties of adsorption of Cr atom on CNT: Bond lengths, bond angles.

Site	Distances in Å for CNT	Binding distance in Å	Angle of CNT in degree	Angle of CNT with Cr in degree
Pure (8,0) CNT	d(C-C) CH L=1.432 Å		(C-C-C)CH-CH =117.41	
	d(C-C) CH R= 1.432 Å		(C-C-C)CHAx1=119.36	
	d(C-C) Axial = 1.398 Å		(C-C-C)CHAx2=119.36	
3.0 Cr Atomic	d(C-C) CH L=1.45 Å	*l(C-Cr)*	(C-C-C)CH-CH =115.86	
	d(C-C) CH R= 1.451 Å	2.282 Å	(C-C-C)CH-Ax1=118.8	
	d(C-C) Axial = 1.421 Å		(C-C-C)CH-Ax2=118.7	
		l(C-Cr)	(C-C-C)CH-CH =115.86	<(C-Cr-C)=36.245
3.0 Cr Axial Bond	d(C-C) CH L=1.449 Å d(C-C) CH R= 1.452 Å	2.283 Å	(C-C-C)CHAx1=118.78	
	d(C-C) Axial = 1.421 Å		(C-C-C)CHAx2=118.702	
3.0 Cr Chiral Bond	d(C-C) CH L=1.454 Å	*l(C-Cr)*	(C-C-C)CH-CH =116.012	<(C-Cr-C)=39.047
	d(C-C) CH R= 1.485 Å	2.248-2.201	(C-C-C)CH-Ax1=118.46	
	d(C-C) Axial = 1.408 Å		(C-C-C)CH-Ax2=116.926	
3.0 Cr Hexagon	d(C-C) CH L =1.467 Å d(C-C) CH R =1.466 Å	*l(C-Cr)* 2.627-2.608		<(C-Cr)CH-CH=56.252 <(C-Cr-C)Axial L=30.944
	d(C-C) Axial L = 1.39 Å			<(C-Cr-C) Axial R=30.694
	d(C-C) Axial R = 1.39 Å			
	d(C-C) CH l L below=1.467 Å			
	d(C-C) CH R below=1.466 Å			

Table 2: The Table shows Electronic Properties of adsorption of Cr atom on SWCNT: Binding Energy, Band gap, Charge, Spin, HOMO and LOMO energy

	B.E (eV)	Band gap (eV)	Charge (Qt)	Spin	HOMO energy (eV)	LUMO energy (eV)
CNT (8,0)		0.701				
CNT - 3.0 Cr Atomic	-0.5822	0.3278	0.407	5.256	-3.698	-3.459
CNT - 3.0 Cr Axial Bond	-0.5822	0.3277	0.406	5.257	-3.695	-3.459
CNT - 3.0Cr Chiral Bond	-0.5632	0.3824	0.453	5.072	-3.484	-3.420
CNT - 3.0 Cr Hexagon	- 1.2545	0.3935	0.501	0	-3.363	-3.282

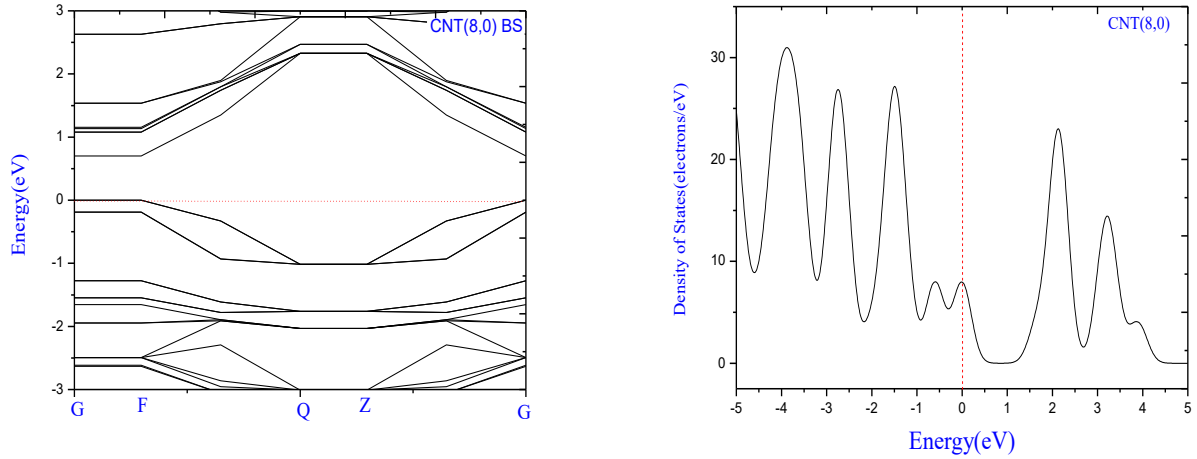


Figure 3: (a) Band structure and DOS of Pure CNT (8,0)

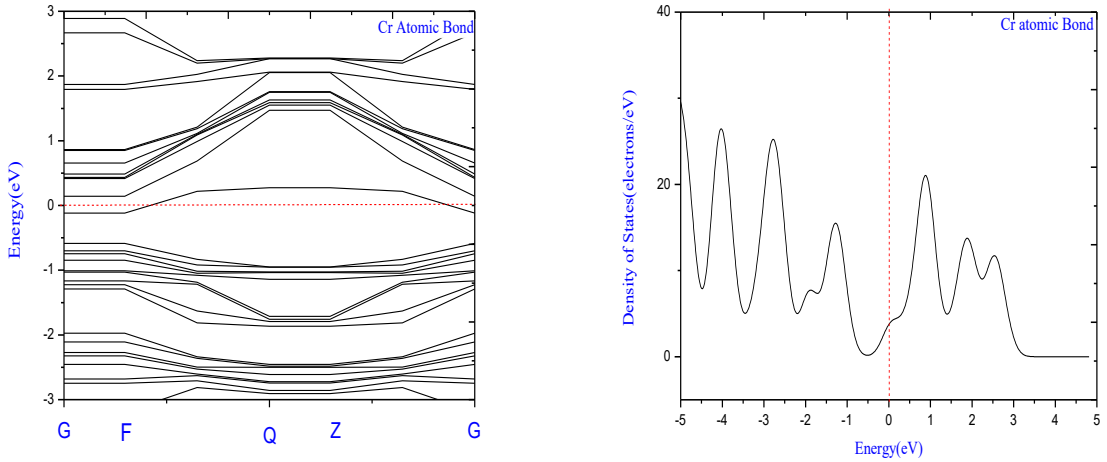


Figure 3: (b) Band structure and DOS of CNT with adatom Cr for Atomic site - A

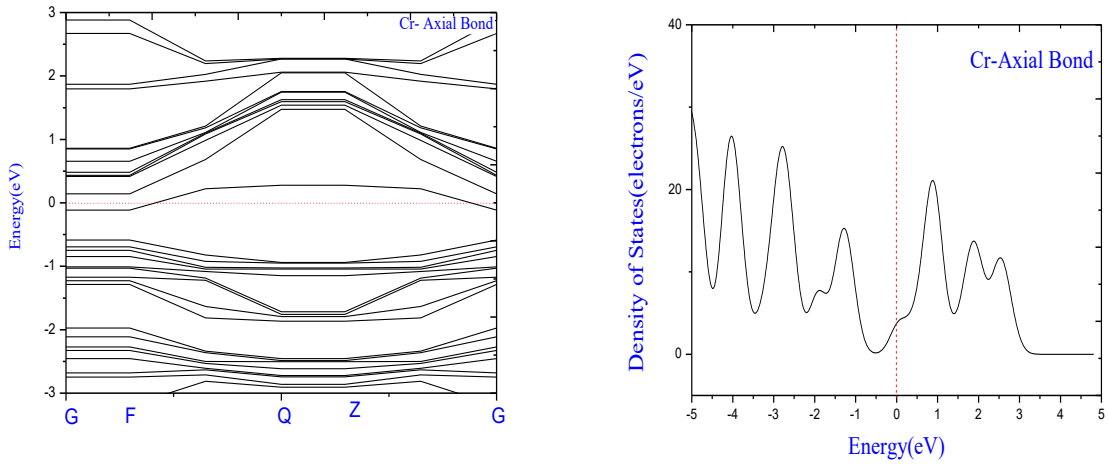


Figure 3: (c) Band structure and DOS of Cr-CNT at axial bond site - C

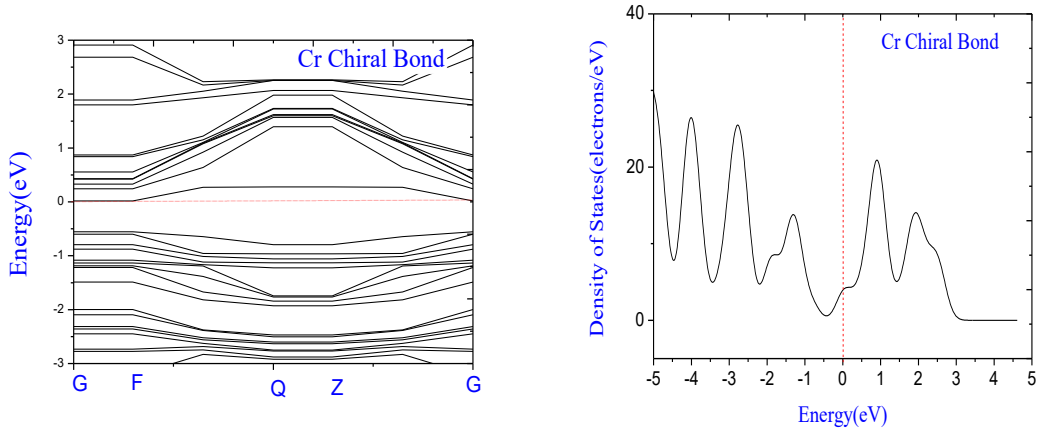


Figure 3: (d) Band structure and DOS of Cr-CNT at Chiral bond site - B

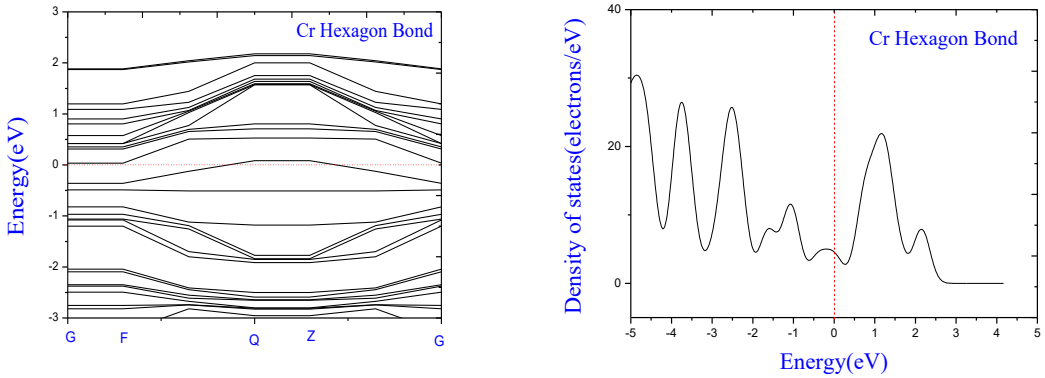
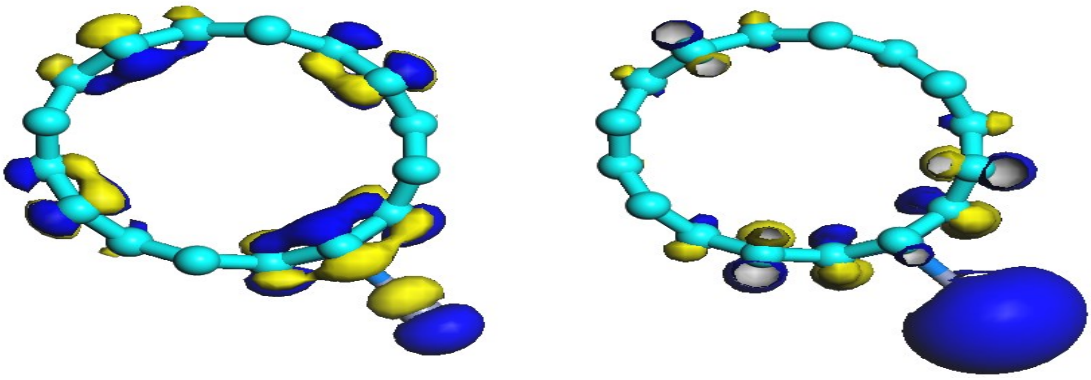


Figure 3: (e) Band structure and DOS of Cr-CNT Hexagon site - D

The binding energy of Cr adatom on SWCNT for Atomic site – A and Axial bond site – C is - 0.585eV, whereas for Chiral bond site – B is - 0.56eV and for Hexagon site – D is - 1.25eV. The binding energy for Hexagon is more. The binding energy values clearly indicate the Cr atom is chemisorbed on CNT for all four sites.

The Band Structure (BS) and Density of State (DOS) of pure SWCNT is Shown in figure 3(a). The energy band gap found from BS and DOS for pure CNT is 0.701, which is competent to theoretically and experimentally reported result. Figure 3(b-e) shows BS and DOS for interaction Cr atom with CNT at four different sites. BS and DOS for atomic site – A, axial bond site – C and chiral bond site – B shows there is an extra occupied states near Fermi energy in valance band. For hexagon site – D there is heavily occupied state near Fermi energy in valance band. The energy levels in valance band are at - 1.7068eV and - 0.479eV as compared to CNT. The newly formed extra state at 0.244eV in conduction band for interaction of Cr atom with CNT is almost reduced and shifted near to Fermi level as compared to CNT. This results in reduction of band gap of CNT from 0.7eV (of pure CNT) to 0.327eV for atomic and axial bond site. For chiral bond and Hexagon position band gap reduced to 0.382eV and 0.393 respectively as shown in Table 2. The Charge transfer between Cr atom and nanotube has been calculated by using Mulliken population analysis. The charge transferred from Cr atom to CNT therefore Cr atom occupies positive charge. The magnitude of charge donated by Cr atom to CNT at site – A is 0.407 e and at site – C is 0.406 e. The quantity of charge transfer from Cr to CNT for sit – B is 0.453 e and that of sit – D is 0.501 e. The higher values shoes sharing of charge with more carbon atom in CNT leads to form multiple covalent bonds. We have also calculated spin of electron in Cr atom which has more values for site – A, site – C and less for site – B where for site – D is almost zero because of pairing electron in four covalent bonds.



(a) HOMO (b) LUMO

Figure 4: (a) HOMO for Cr-CNT (b) LUMO for Cr-CNT

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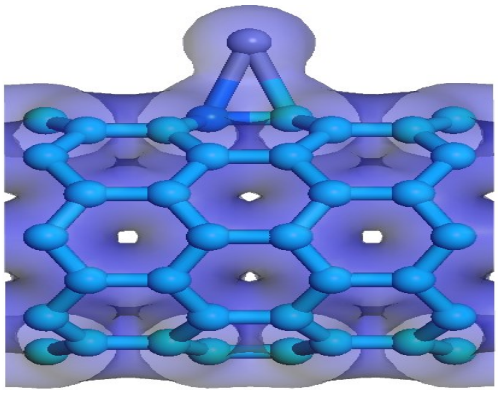

Figure 5(a) shows the iso-surface of charge density. It shows formation of sigma bond between Cr atom and carbon atoms

The Frontier molecular orbitals are important in interpreting chemical reactivity. We thus exhibits the highest occupied molecular orbitals (HOMO) and Lowest Unoccupied Molecular orbitals (LUMO) as shown in figure 4(a-b). The HOMO energy is -3.695 eV and LUMO energy is -3.458 eV for atomic bond and axial bond.

CONCLUSION

The density functional theory based on linear combination of atomic orbital is used to study the adsorption of chromium atom on CNT at various four sites. In all four adsorption site chromium atom is chemisorbed onto CNT by forming covalent bonds with carbon atom. Chromium atom creates extra states near the Fermi energy level in each case of absorption produces fictionalization in carbon nanotube. We also found that there is net charge transfer from chromium to CNT which converts semiconducting carbon nanotube into semimetal. The change electronic properties of carbon nanotube lead to use it as basic building block in nano-electronic devices and sensors. The charge density and molecular orbital clearly shows formation of sigma bond between chromium and carbon atoms.

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