DFT Studies on HOMO-LUMO Gaps of CBNNTs

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Abstract: We have investigated the energetics and molecular orbitals of HOMO and LUMO levels for carbon boron nitride nanotubes (CBNNTs) corresponding to zigzag (5,0), (7,0) and (9,0) and armchair (4,4), (6,6) and (7,7) structures using B3LYP/6-31g(d,p). Their HOMO-LUMO gaps due to various compositions and distributions of BN atoms to C atoms within the heteronanotubes, CBNNTs(1:4) and CBNNTs(1:5) have been also studied and compared with corresponding carbon nanotubes and boron nitride nanotubes. It is found that the HOMO-LUMO gaps are dependent on the diameter of NT and on the distribution way of BN atoms to C atoms within the heteronanotubes. The important outcome of this work is that we can decrease the band gap of BNNTs (5.88 eV) by ~ 96% when heteronanotube (9,0)CBNNTs(1:5) is obtained with band gap 0.25 eV.
[A. A. El-Barbary, Kh. M. Eid, M. A. Kamel , M.M.Hassan. **DFT Studies on HOMO-LUMO gaps of CBNNTs.** *J Am Sci* 2012;8(9):146-153]. (ISSN: 1545-1003). http://www.jofamericanscience.org. 21

Keywords: CBNNTs, HOMO-LUMO gap, DFT, B3LYP.

1. Introduction

The discovery of carbon nanotubes (CNTs) by Iijima[1] in 1991, results in extensive theoretical studies on CNTs [2-3] due to their special electric conductivity, mechanical properties and potential applications in molecular device. The nearest atoms to C in the periodic table are N and B and could form hexagon boron nitride (h-BN). Nasreen *et a*l.[4] synthesized BNNTs firstly in 1995 with plasma arc discharge method, which has paved the way for further investigation into BNNTs experimentally and theoretically. CNTs and BNNTs possess different electrical behaviors. The former, CNTs are known to be intrinsically either semiconducting or metallic, depending upon the chirality of the nanotube[5] and the latter, BNNTs are electrical insulators, with a large band gap of ~ 5.5 eV, independent of their chirality[6]. Heterojunction carbon boron nitride nanotubes (CBNNTs) can be prepared experimentally by using CNTs as the base, C atoms are substituted by B and N atoms to obtain doped NTs with chemical replacement method[7].

The electronic structures of BNNTs are relatively rare, thereby much work should be done to further investigation. In this paper the HOMO-LUMO molecular structures gaps due to various compositions and distributions of BN atoms to C atoms within the heteronanotubes, CBNNTs(1:4) and CBNNTs(1:5) have been investigated by using DFT method, and the results are compared with those of CNTs and BNNTs.

2. Computational methods

All calculations were performed within the density-functional theory (DFT) as implemented within G03W package [8-9], using B3LYP exchange-functional and applying basis set 6-31g(d,p). All structures are fully optimized under spin average. Twelve different geometries of pure CNTs and pure BNNTs were considered; six structures of them to zigzag CNTs and BNNTs: (5,0)CNT, (7,0)CNT, (9,0)CNT, (5,0)BNNT, (7,0)BNNT and (9,0)BNNT. The remaining six structures are to armchair CNTs and BNNTs: (4,4)CNT, (6,6)CNT, (7,7)CNT, (4,4)BNNT, (6,6)BNNT and (7,7)BNNT, see Figure 1. For pure heteronanotubes CBNNTs, thirty-six different configurations have been investigated. Eighteen structures with ratio CBNNTs(1:4) and eighteen structures with ratio CBNNTs(1:5). The BN atoms are distributed through the CNT by three ways as explained above: BN-row, BN-random and BN-zigzag. Every distribution is applied on six CBNNTs structures; (5,0)CBNNT, (7,0)CBNNT, (9,0)CBNNT, (4,4)CBNNT, (6,6)CBNNT and (7,7)CBNNT.

3-Results

3.1-HOMO-LUMO Band Gaps

3.1.a :Pure CNTs and pure BNNTs

To understand the electrical properties of CBNNTs, different configurations of the pure CNTs and pure BNNTs should be investigated. As shown in Figure 1, there are twelve configurations have been investigated, six configurations for pure CNTs and six configurations for pure BNNTs.

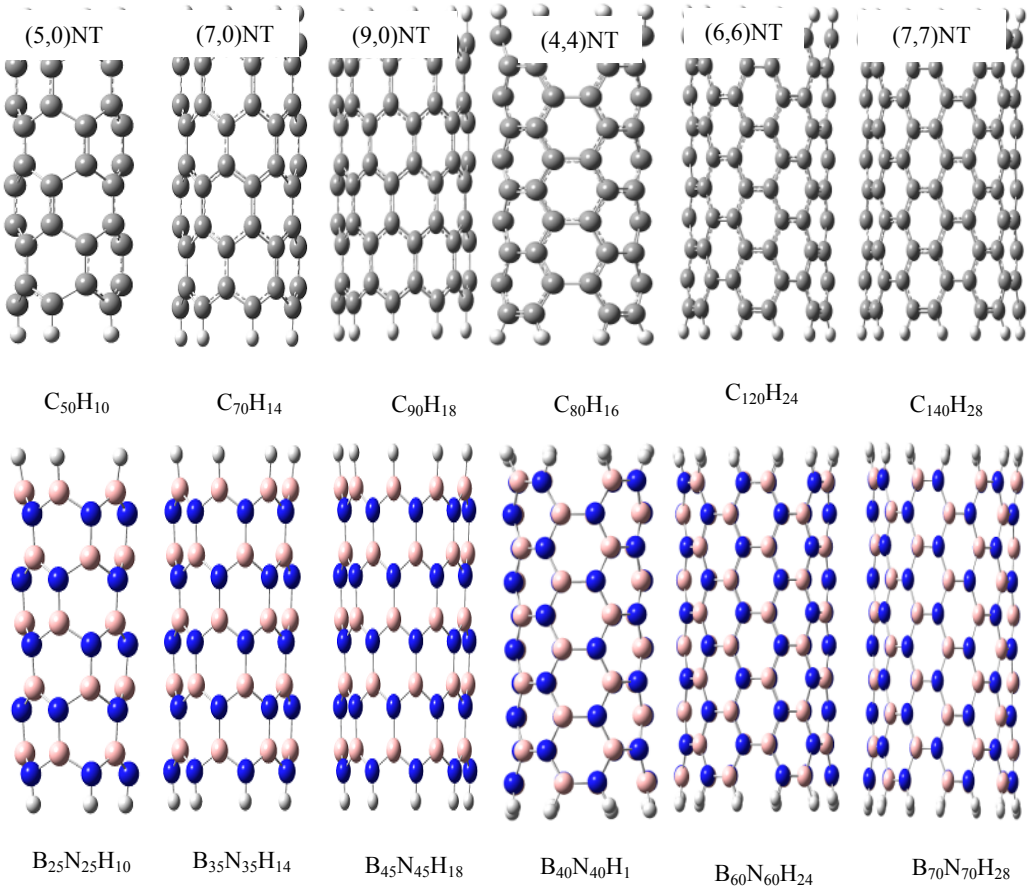


Figure 1: Twelve fully Optimized geometries of (5,0), (7,0), (9,0), (4,4), (6,6) and (7,7) for pure CNTs and pure BNNTs. Carbon atom (gray), nitrogen atom (blue) and boron atom (pink).(For interpertation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Table1: Calculated HOMO and LUMO energies for pure CNTs and BNNTs. Energy is given by eV.

System	CNTs		BNNTs	
	HOMO	LUMO	HOMO	LUMO
(5,0)	-2.91	-3.57	-2.65	-6.47
(7,0)	-3.28	-3.62	-1.39	-6.57
(9,0)	-3.40	-3.70	-0.69	-6.57
(4,4)	-2.69	-4.18	-0.15	-6.44
(6,6)	-2.60	-4.42	-0.11	-6.42
(7,7)	-2.58	-4.49	-0.12	-6.45

The band gaps for pure CNTs and BNNTs are calculated, as shown in Table 1. For pure CNTs, it is found that the band gaps for zig-zag NTs are decreased with increasing the diameter of NTs and vice versa for arm-chair CNTs. However, the band gaps of arm-chair BNNTs are independent on the diameters and are calculated to be 6.3 eV, agree with previous calculations[6]. Our calculations show that the band gaps for zig-zag BNNTs are not constant but the convergence is achieved by increasing the diameters of NTs, ~ 5.9 eV.

3.1.b: Heterojunction CBNNTs

We have investigated NTs with different number of atoms for heterojunction BNCNTs. we define three distinct structural combinations of CNTs with BNNTs to be used in our modeling investigations: (1) alternating segments of CNT and BNNT (BN-random distribution), (2) continuous segments of CNT and BNNT through the radial tube (BN-row distribution), and (3) continuous segments of CNT and BNT through the tube axis (BN-zigzag distribution). While many other arrangements can be imagined, we focus on these three well-defined geometric linkages, in order to establish well-characterized energetic and electrical behaviors of heteronanotube CBNNTs. Also, the modifications of electrical properties of CBNNTs due to effects of various ratios of number of BN atoms to number of C atoms within CBNNTs have been investigated. The studied ratios for number of BN atoms to number of C atoms were chosen to be CBNNTs (1:4) and CBNNTs (1:5). Our calculations agree with previous calculations[10-13]. For undefected heteronanotube

CBNNTs, thirty-six configurations have been investigated. Twelve structures of these configurations are for CBNNTs (1:4) and CBNNTs (1:5) and their structures are given in Table 2.

From Tables (3, 4) the calculated energy gaps for CBNNTs(1:4) and CBNNTs(1:5) indicate that the band gaps decrease with increasing the diameter of NTs. Also, the band gaps of CBNNT(1:4) are always higher than CBNNT(1:5) independent on the type of CBNNT and the type of BN-distribution. Except for BN-random distribution of zig-zag CBNNT and BN-random distribution of armchair (6,6) CBNNT and (7,7) CBNNT systems. The smallest band gap is 0.29 eV for BN-random (9,0)CBNNTs(1:4) and 0.25 eV for BN-row (9,0)CBNNTs(1:5). The largest band gap is 1.92 for BN-row (4,4) CBNNTs(1:4) and 1.90 eV for BN-row (6,6)CBNNTs(1:5).

Table2: The studied configuration of the undefected CBNNT`s.

System	**configuration Structure of CBNNT`s**	
	1:4	1:5
(5,0)	$C_{40}B_5N_5H_{10}$	$C_{50}B_5N_5H_{10}$
(7,0)	$C_{56}B_7N_7H_{14}$	$C_{70}B_7N_7H_{14}$
(9,0)	$C_{72}B_9N_9H_{18}$	$C_{90}B_9N_9H_{18}$
(4,4)	$C_{64}B_8N_8H_{16}$	$C_{80}B_8N_8H_{16}$
(6,6)	$C_{96}B_{12}N_{12}H_{24}$	$C_{120}B_{12}N_{12}H_{24}$
(7,7)	$C_{112}B_{14}N_{14}H_{28}$	$C_{140}B_{14}N_{14}H_{28}$

Table3: Calculated HOMO and LUMO energies for CBNNTs(1:4). Energy is given by eV.

System	BN-random		BN-row		BN-Zigzag	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
(5,0)	-2.91	-3.72	-3.11	-4.05	-2.88	-4.35
(7,0)	-3.45	-4.02	-3.22	-3.59	-3.08	-3.94
(9,0)	-3.33	-3.75	-3.35	-3.66	-3.38	-3.73
(4,4)	-2.71	-4.16	-2.44	-4.36	-2.75	-4.02
(6,6)	-3.04	-4.00	-2.77	-4.13	-2.94	-3.94
(7,7)	-2.97	-4.16	-2.85	-4.08	-3.24	-3.72

Table 4: Calculated HOMO and LUMO energies. Energy is given by eV.

System	BN-random		BN-row		BN-Zigzag	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
(5,0)	-3.04	-4.36	-2.92	-3.78	-3.06	-4.35
(7,0)	-3.29	-3.88	-3.21	-3.49	-3.12	-3.69
(9,0)	-3.54	-3.82	-3.32	-3.57	-3.37	-3.75
(4,4)	-2.94	-4.07	-2.56	-4.37	-2.79	-4.00
(6,6)	-3.28	-4.01	-2.56	-4.46	-3.28	-3.74
(7,7)	-3.29	-3.95	-2.58	-4.46	-3.29	-3.75

3.2 HOMO-LUMO molecular orbitals

To see in details, we have plotted the molecular orbital for pure (5,0), (6,0), (9,0), (6,6), (7,7) CNTs and BNNTs, and heterojunction (5,0), (6,0), (9,0), (6,6), (7,7), (9,9) CBNNTs(1:4) and CBNNTs(1:5).

3.2.a :zig-zag CNTs and BNNTs structures

Figure (2) is represented the molecular orbitals for pure (5,0), (6,0), (9,0) CNTs and BNNTs with two different configurations. The HOMO and LUMO levels of CNTs are found to be located between the HOMO and LUMO levels of BNNTs, except for (5,0) structures. Also, it is noticed that the molecular orbitals for CNTs are located at the terminal hexagon rings however for BNNTs are distributed over half of tube length. Results in increasing the band gaps of BNNTs, comparing with the band gaps of CNNTs.

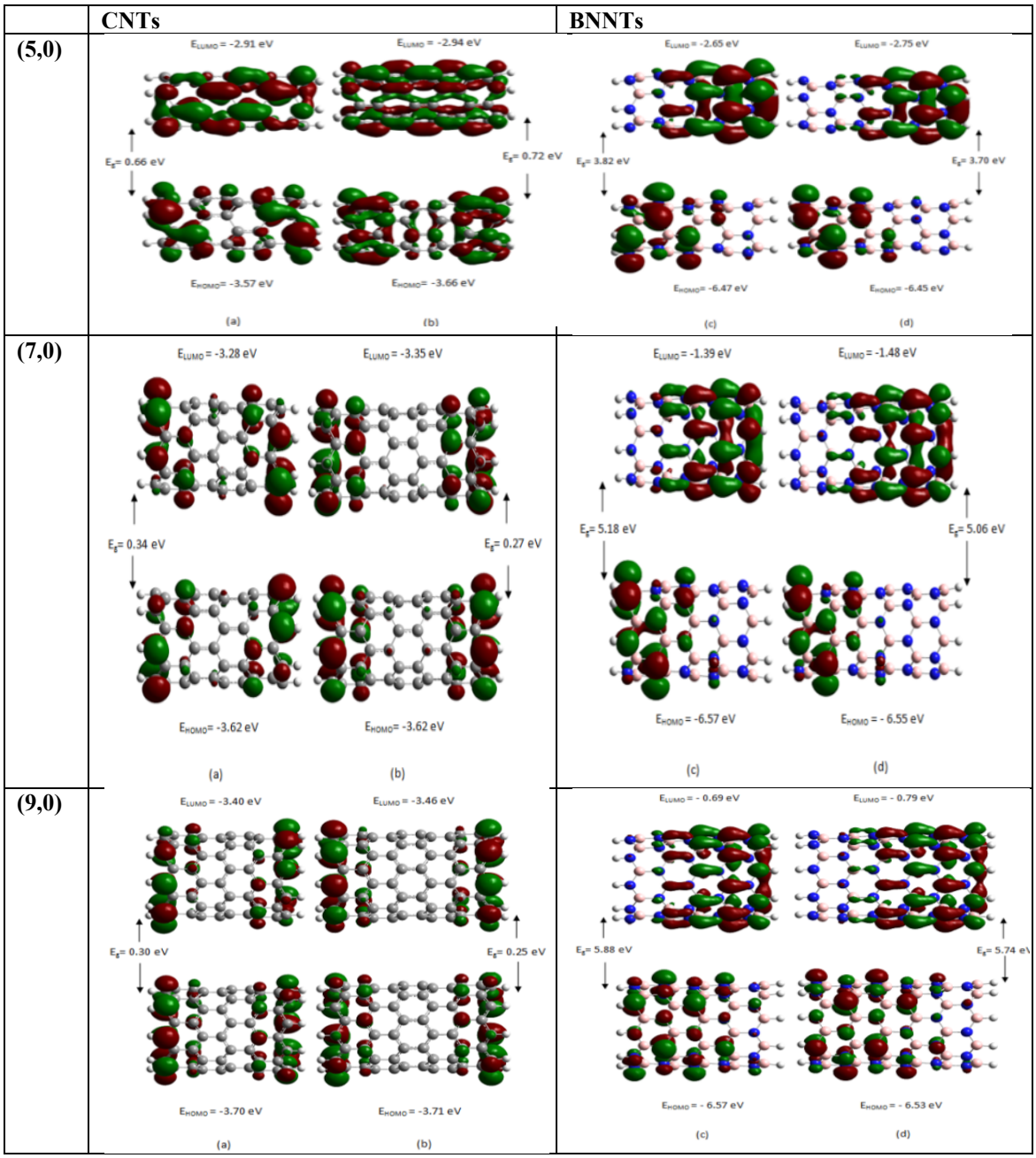


Figure 2: Molecular orbitals for HOMO and LUMO levels of a) (5,0) $C_{50}H_{10}$, (7,0) $C_{70}H_{14}$, (9,0) $C_{90}H_{18}$ CNTs b) (5,0) $C_{60}H_{10}$, (7,0) $C_{84}H_{14}$, (9,0) $C_{108}H_{18}$, c) (5,0) $B_{25}N_{25}H_{10}$, (7,0)$B_{35}N_{35}H_{14}$, (9,0) $B_{45}N_{45}H_{18}$ d) (5,0) $B_{30}N_{30}H_{10}$, (7,0) $B_{42}N_{42}H_{14}$, (9,0) $B_{54}N_{54}H_{18}$.

3.2.b :armchair CNTs and BNNTs structures

Figure (3) is represented the molecular orbitals for pure (6,6), (7,7) CNTs and BNNTs with two different configurations . The HOMO and LUMO levels of CNTs are also found to be located between the HOMO and LUMO levels of BNNTs.

However, the molecular orbitals for CNTs and BNNTs are distributed over all tubes length, the overlap are noticed only for the molecular orbitals of CNTs. Results in increasing the band gaps of BNNTs, comparing with the band gaps of CNNTs.

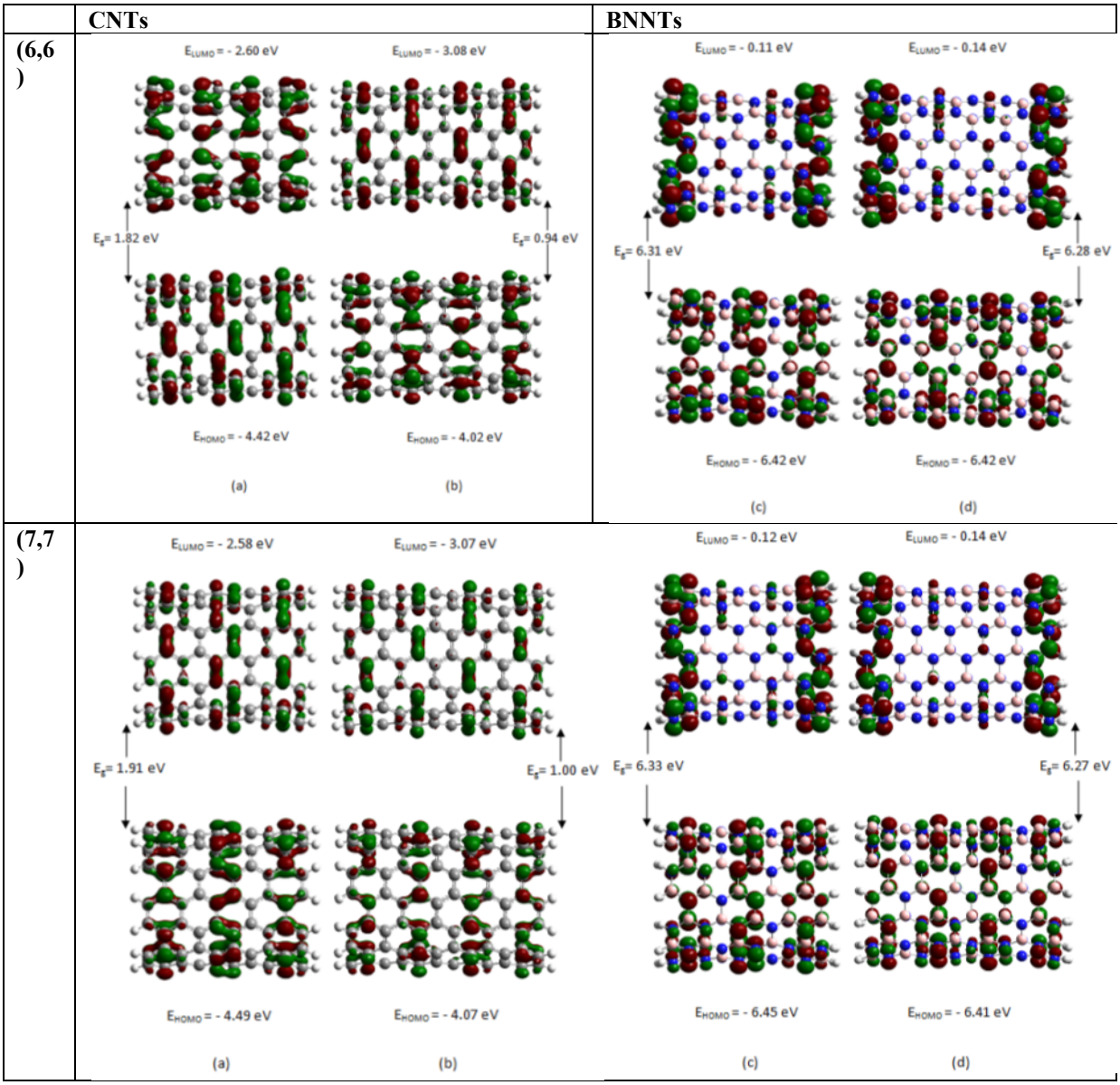


Figure 3: Molecular orbitals for HOMO and LUMO levels of a) (6,6) $C_{80}H_{16}$ (7,7)$C_{140}H_{28}$, b) (6,6)$C_{96}H_{16}$, (7,7)$C_{168}H_{28}$ c) (6,6)$B_{40}N_{40}H_{16}$, (7,7)$B_{70}N_{70}H_{28}$ d) (6,6)$B_{48}N_{48}H_{16}$, (7,7)$B_{84}N_{84}H_{28}$.

3.2.c: zig-zag CBNNTs structures

Figure (4) is represented the molecular orbitals of heterojunction (5,0)CBNNTs(1:4), (5,0)CBNNT(1:5),(7,0)CBNNTs(1:4),(7,0)CBNNT (1:5), (9,0)CBNNTs(1:4), and (9,0)CBNNT(1:5) for random-, raw-, zig-zag distributions. The HOMO and LUMO levels of CBNNTs are found to be located between the HOMO and LUMO levels of BNNTs. Also, it is noticed that the molecular orbitals for CBNNTs are distributed over the tube length, except for (9,0) CBNNTs system. Results in increasing the band gaps of CBNNTs, comparing with the band gaps of CNNTs and in decreasing the band gaps of CBNNTs, comparing with the band gaps of BNNTs. The small values for band gaps are due to (9,0)CBNNTs where the molecular orbitals are located at the terminal rings. The smallest band gap is 0.25eV.

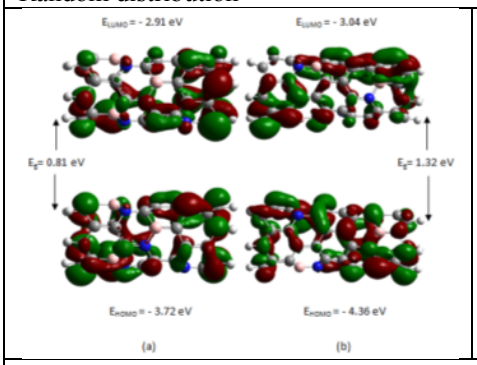
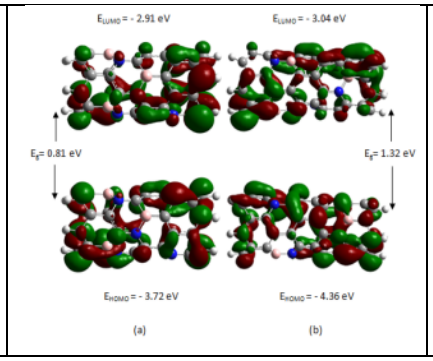
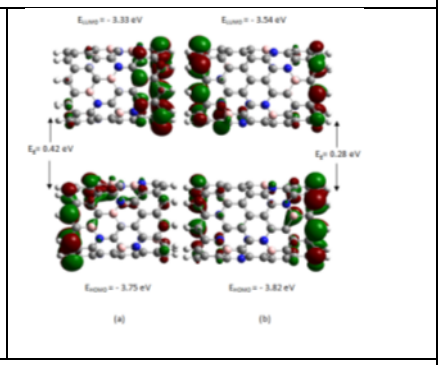
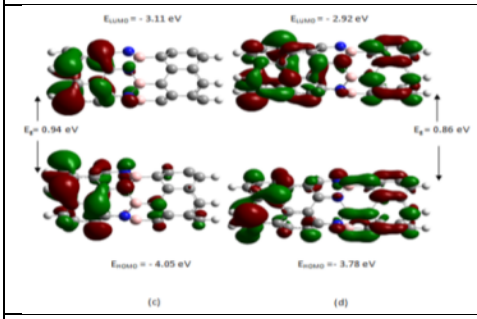
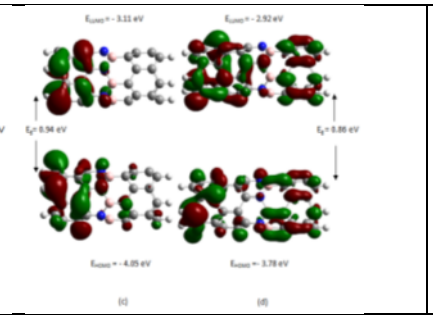
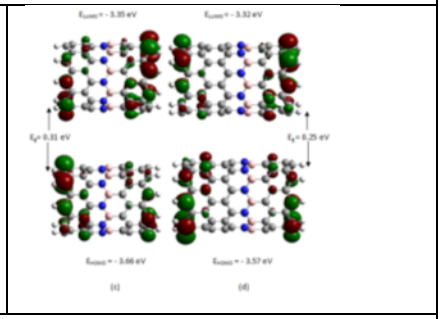
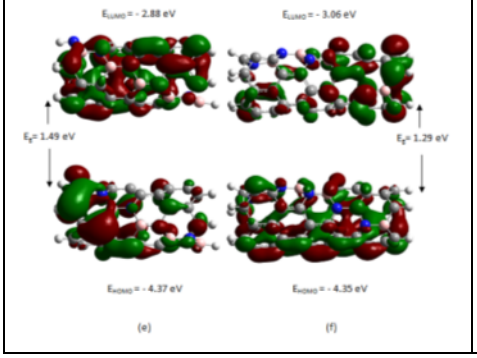
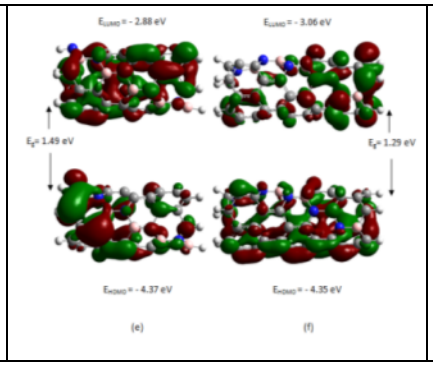
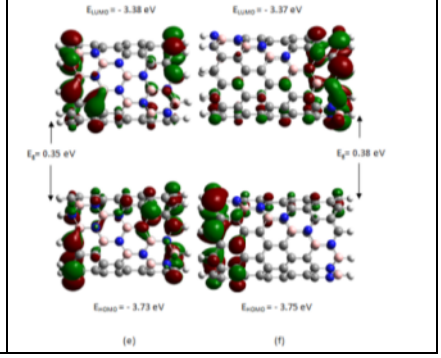
(5,0)CBNNTs	(7,0)CBNNTs	(9,0)CBNNTs
Random distribution		
		
Raw distribution		
		
Zig-zag distribution		
		

Figure 4: Molecular orbitals for HOMO and LUMO levels of a) (5,0) CBNNT(1:4), $C_{40}B_5N_5H_{10}$, b)(5,0)CBNNTs(1:5), $C_{50}B_5N_5H_{10}$, c) (7,0)CBNNTs(1:4), $C_{56}B_7N_7H_{14}$, d) (7,0)CBNNTs(1:5), $C_{70}B_7N_7H_{14}$, e)(9,0)CBNNTs(1:4), $C_{72}B_9N_9H_{18}$, f)(9,0)CBNNTs(1:5) for random-, raw- and zig-zag distributions.

3.2.d: arm-chair CBNNTs structures

Figure (5) is represented the molecular orbitals of pure (6,6)CBNNTs(1:4), (6,6)CBNNT(1:5), (7,7)CBNNTs(1:4) and (7,7)CBNNT(1:5) for random-, raw-, zig-zag distributions. The HOMO and LUMO levels of CBNNTs are found to be located between the HOMO and LUMO levels of BNNTs. Also, it is noticed that the molecular orbitals for CBNNTs are distributed over the tube. Results in increasing the band gaps of CBNNTs, comparing with the band gaps of CNNTs and in decreasing the band gaps of CBNNTs, comparing with the band gaps of BNNTs. The small values for band gaps are due to zig-zag distribution for (7,7)CBNNTs(1:5), (7,7)CBNNT(1:4), and are calculated 0.46 and 0.48 eV, respectively. The important outcome of this work is that we can decrease the band gap of BNNTs (5.88 eV) by ~ 96% when heterojunction (9,0)CBNNTs(1:5) is obtained with band gap 0.25 eV.

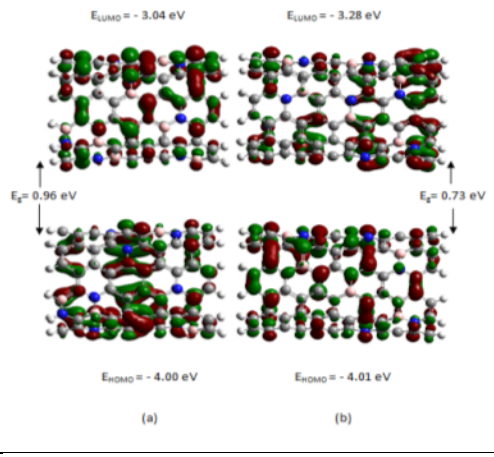
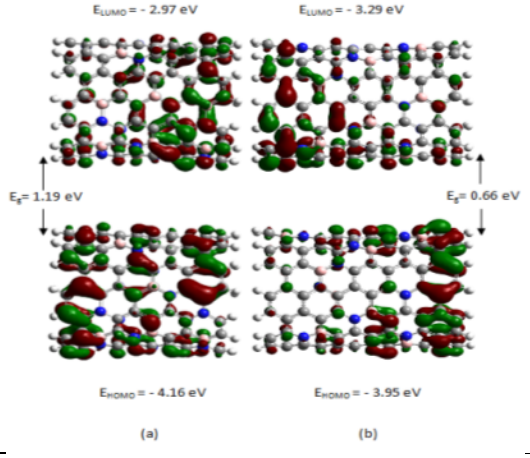
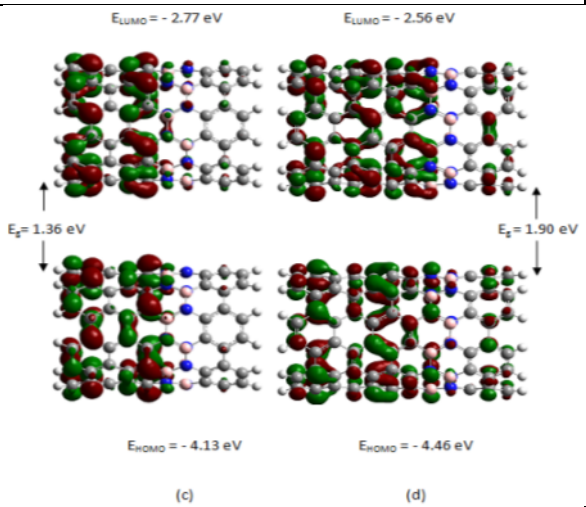
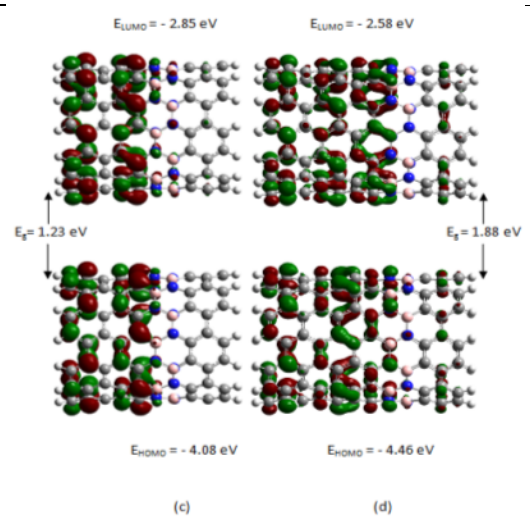
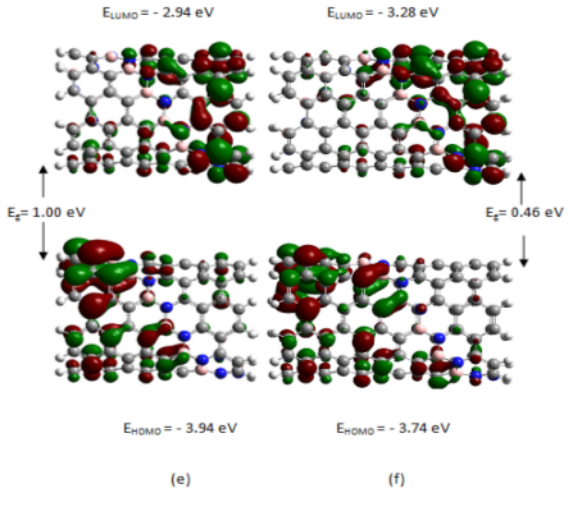
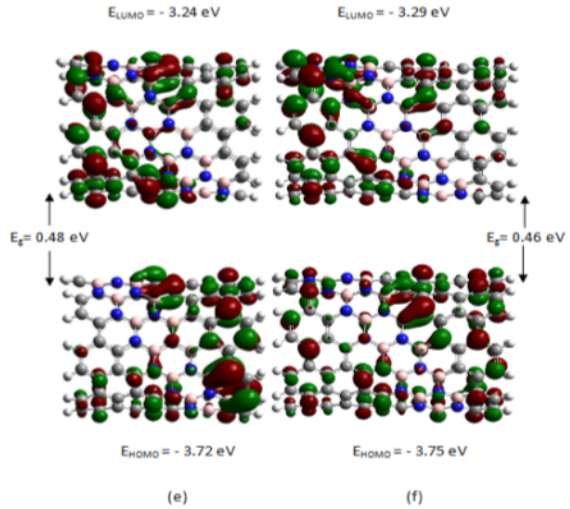
Distribution	(6,6)CBNNTs	(7,7)CBNNTs
Random		
Raw		
Zig-zag		

Figure 5: Molecular orbitals for HOMO and LUMO levels of a) (6,6)CBNNTs (1:4), $C_{96}B_{12}N_{12}H_{24}$ b) (6,6)CBNNTs (1:5), $C_{120}B_{12}N_{12}H_{24}$, c)(7,7)CBNNTs(1:4) $C_{112}B_{14}N_{14}H_{28}$, d) (7,7)CBNNTs(1:4), $C_{140}B_{14}N_{14}H_{28}$

4- Conclusion

There are three distinct structural combinations of CNTs with BNNTs have been used in our modeling investigations: (1) random segments of C and BN (BN-random distribution), (2) continuous segments of C and BN through the

radial tube (BN-row distribution), and (3) continuous segments of C and BN along the tube axis (BN-zigzag distribution). It is found that the band gaps decrease with increasing the diameter of NTs. Also, the band gaps of CBNNT(1:4) are always higher than CBNNT(1:5) independent on the type of CBNNT and the type of BN-distribution. The smallest band gap is 0.29 eV for BN-random (9,0)CBNNTs(1:4) and 0.25 eV for BN-row (9,0)CBNNTs(1:5). The largest band gap is 1.92 for BN-row (4,4) CBNNTs(1:4) and 1.90 eV for BN-row (6,6)CBNNTs(1:5). The results are explained by molecular orbitals, in terms of molecular orbitals distribution over terminal (or all) carbon and BN atoms.

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7/28/2012