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First-principle Calculations of Electronic Structure of the (3,3), (4,4), (5,0) and (6,0) Single-Wall Carbon Nanotubes

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ABSTRACT

On the basis of density functional theory, we study the electronic structures of (3,3), (4,4), (5, 0) and (6, 0) SWCNTs. The results show that the cohesive energy of armchair tubes are larger than those of zigzag ones. The calculated band gap of (4,4) is smaller than those of other tubes. Moreover, the band gap for armchair tubes are smaller than those of zigzag. The variation of ionization potential, electron affinity, and Fermi energy level as the number of atoms in the tube grows up. This curve fluctuates strongly because of the change in size that produce different surfaces with different properties. The IP is larger than the EA, as is the normal situation for molecules. The highest number of degenerate states in the conduction and valence bands are about as follow: 7, 9, 9, and 7 for (3,3), (4,4), (5,0) and (6,0) CNTs, respectively.

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INTRODUCTION

A single-wall carbon nanotube (SWCNT) is a graphene sheet rolled into a cylindrical shape so that the structure is one-dimensional with axial symmetry [1]. Also, it is known that a nanotube can be metallic or semiconducting depending on their diameter and chirality [2, 3]. The extraordinary mechanical properties and unique electrical properties of carbon nanotubes (CNTs) have stimulated extensive research activities across the world since their discovery by Iijima in the early 1990s [4]. In recent years, CNTs has attracted great attention in many fields of technology and science and because it the most exciting quasi-1-D solids that exhibit fascinating electronic, structural, electrical, optical, and mechanical properties [5, 6]. Investigation into their properties has become one of the most active fields of modern research, these interesting properties have led to an increase in the number of investigations focused on application development in the past 5 years. The breadth of applications for carbon nanotubes is indeed wide ranging: biosensors, detectors, nanoelectronics, quantum wire interconnects, field emission devices, composites, chemical sensors, etc. [7-9]. It is possible nowadays to study the structural and electronic properties of nanostructures in general, and carbon nanotubes in particular as well as the energetics of many-electron systems by performing fully ab initio computations The first theoretical calculation of SWCNTs electronic structure was carried out using zone folding scheme [10,11].

In this paper, we performed density functional theory (DFT) calculation to investigate the electronic structure of (3,3), (4,4), (5, 0) and (6, 0) SWCNTs. The DFT calculations are performed using the Gaussian 09 program [12]. Becke three parameter Lee–Yang–Parr (B3LYP) functional [13, 14] using 6-31G basis set, which has been commonly used for nanotube structures have been applied in the calculations

2 Computational details:

All the computational studies were carried out using DFT implemented in the Gaussian 09 package running and visualized by GaussView5.08 program. All the structures generated by TubeGen 3.4 [15], which is available as source code.

The molecular properties of the compounds have been computed by DFT using the standard 6-31G basis sets calculations in DFT were carried out with the B3LYP hybrid functional. B3LYP is one of the often-employed hybrid functional used in theoretical studies of nanotubes. The geometry optimization of the molecule is the structure at which the molecule has the minimum energy; it is performed by finding the first derivative of the energy with respect to the distance between different atoms, known as the gradient.

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We considered (3,3), (4,4), (5,0), and (6,0) SWCNTs with an open edge. The diameters of the nanotubes are 4.07, 5.43, 3.92 and 4.70Å, respectively. The length of the optimized SWCNTs are computed to be about 15Å, and the optimized bond length is found as 1.411Å, and is in close agreement with experimental value of 1.421Å [16]. The number of atoms per tube is assumed to be 78, 104, 75, and 90 for (3,3), (4,4), (5,0), and (6,0) nanotubes, respectively.

RESULTS AND DISCUSSION

3.1 Electronic Properties:

Table 1 gives the data for all the nanotubes. The natural bond orbital calculations were performed to derive the highest occupied and the lowest unoccupied molecular orbital, the total energy (E_{Tot}), cohesive energy (E_{coh}), energy gaps (E_g), ionization potential (IP), electron affinity (EA) and Fermi level (E_F).

Table 1: Structural and electronic properties of selected SWCNTs obtained from DFT calculations.

SWCNTs	E_{Tot} (eV)	E_{coh} (eV)	E_g(eV)	IP (eV)	EA (eV)	E_F (eV)
(3,3)	-80810.01	-8.157	0.292	4.739	4.446	-4.592
(4,4)	-107771.81	-8.399	0.201	5.126	4.925	-5.026
(5,0)	-77688.93	-7.972	0.374	5.607	5.232	-5.419
(6,0)	-93239.34	-8.122	0.554	5.708	5.154	-5.431

It should be noted from Table 1 that the total energy increases with increasing the number of atoms. The cohesive energy is an important quantity to understand the trends in the formation of nanotube and study the thermodynamic stabilities of CNTs. The computed cohesive energy data suggests that it increases (in magnitude) significantly with increase in the number of atoms for both zigzag ((5,0) and (6,0)) and armchair ((3,3) and (4,4)) tubes. Here the system with larger E_{coh} is more stable. Thus, the larger CNTs are energetically more stable. According to our results E_{coh} of (n, n) armchair tubes are larger than those of (n, 0) zigzag ones because of their relatively larger radius at a given n.

Both the thermodynamic stability and kinetic stability have crucial influence on the relative abundances of different carbon nanostructures. It has been pointed out that higher kinetic stability is usually related with a larger E_g [17] because exciting electrons from low HOMO to a high LUMO is energetically unfavorable, which would be necessary to activate a reaction. As can be seen from Table 1, the calculated E_g of (4,4) is much smaller than those of other tubes. Moreover, the E_g for (n, n) armchair tubes are smaller than those of (n, 0) zigzag. The computed energy gap of (3,3) (4,4) and (6,0) CNTs is slightly larger than experimental and other theoretical results [18], while the calculated E_g for (5,0) is smaller than the semiempirical results [19]. Such a modulation of band gap can be engineered into processing nanotube devices.

The variation of IP, EA, and E_F as the number of atoms in the tube grows up is shown in Table 1. This curve fluctuates strongly because of the change in size that produce different surfaces with different properties. Each of the developed surfaces has different properties such as the upper mentioned IP and EA, therefore, these fluctuations start at the nano-scale, continue to the micro, and bulk scale. The IP is larger than the EA, as is the normal situation for molecules.

3.2 HOMO and LUMO energies:

It is well known that the frontier molecular orbitals (FMO), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), play an important role in chemical reactions for the reactant molecules, making the frontier orbital analysis of the doped CNTs necessary. We summarize the HOMO and LUMO energy levels of the (n,n) and (n,0) CNTs in Table 2 and Figure 1. As seen from the figure, the FMO of the tubes present obvious localization at the edge regions. This fact agrees with the former DFT calculations [20].

Table 2: The calculated HOMO and LUMO energies for SWNTs.

SWCNT (n, m)	E_{HOMO} (eV)	E_{LUMO} (eV)
(3,3)	-4.739	-4.446
(4,4)	-5.126	-4.925
(5,0)	-5.607	-5.232
(6,0)	-5.708	-5.154

It is clear from Table 2 the variation of HOMO and LUMO as the number of atoms of tube grows up in size. This curve fluctuates strongly because of the change in size that produce different surfaces with different properties. Not all quantities have definite convergence behavior similar to the upper investigated quantities. According to the FMO theory, the chemical reactivity is a function of interaction between HOMO and LUMO levels of the reacting species.

High value of E_{HOMO} is likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy. Therefore, the energy of E_{LUMO}, indicates the ability

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of the molecule to accept electrons. So, the lower the value of E_{LUMO}, the more probable the molecule would accept electrons. Thus, the binding ability of the inhibitor to the semiconductor surface increases with increasing of the HOMO and decreasing of the LUMO energy values. Furthermore, it can be concluded that less negative E_{coh} value for CNTs might be related to its higher LUMO energy level. The results presented in Figure 1 indicate that the calculated E_{coh} and LUMO energy were similar for the (6,0) zigzag BNNT models [21].

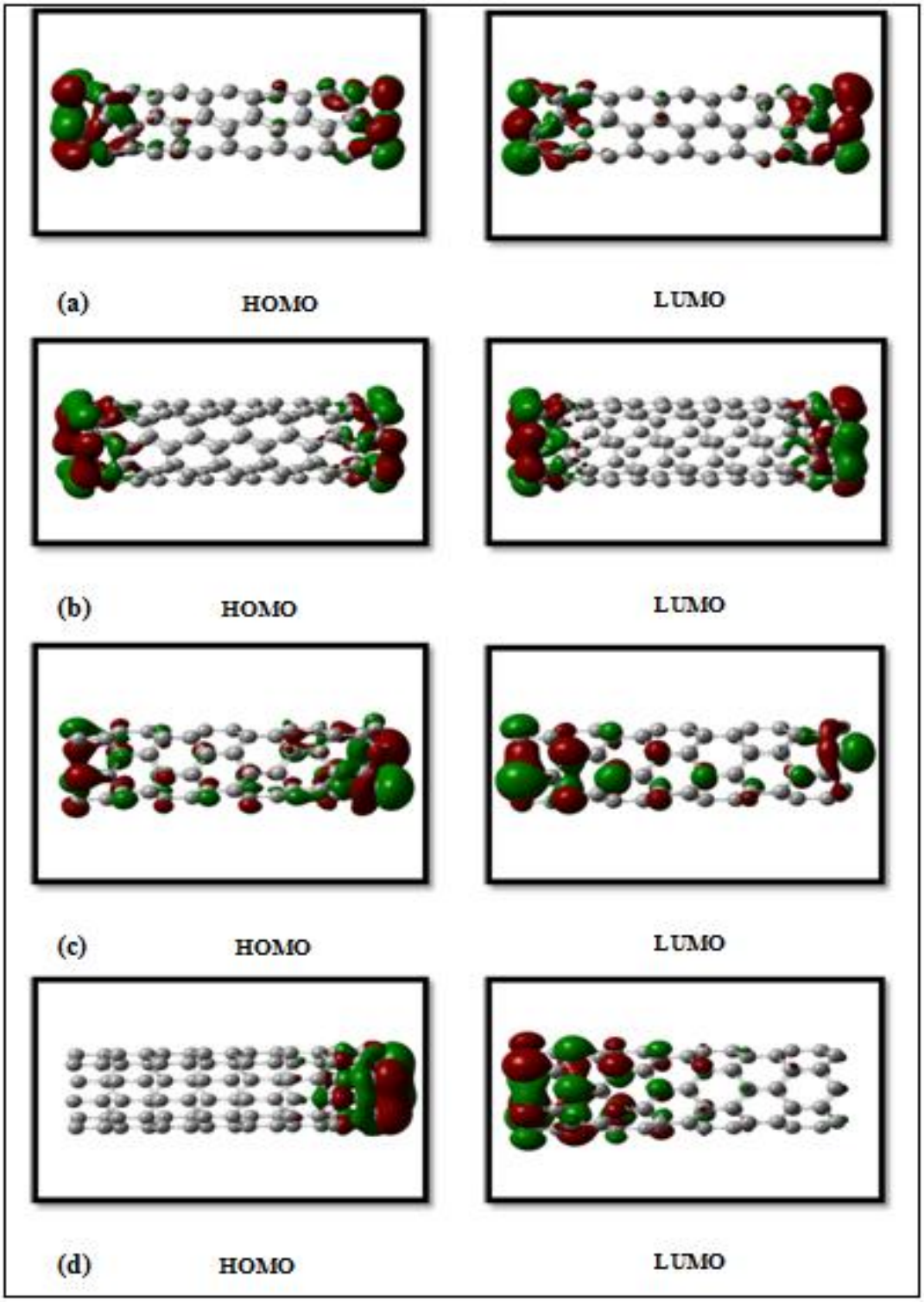

Fig. 1: Frontier molecule orbital density distributions of: **a.** (3,3), **b.** (4,4), **c.** (5,0), **d.** (6,0) SWCNTs.

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3.3 The density of states:

Density of states of (3,3), (4,4), (5,0) and (6,0) CNTs as a function of energy level is shown in Figures 2, DOS of the optimized tube indicating that the CNTs is semiconductor with E_g ranging from 0.2 to 0.55 eV. The highest number of degenerate states in the conduction and valence bands are about as follow: 7, 9, 9, and 7 for (3,3), (4,4), (5,0) and (6,0) CNTs, respectively. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level.

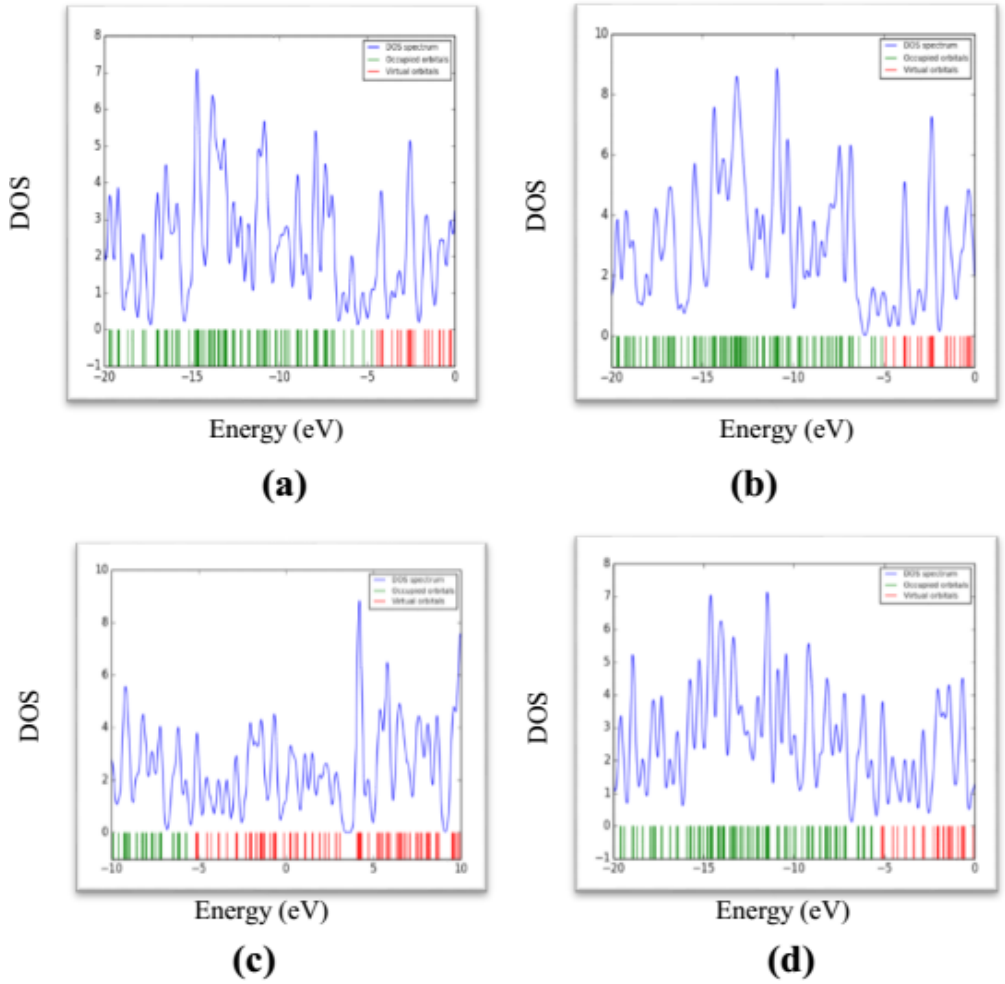

Fig. 2: Density of states of: **a.**(3,3),**b.** (4,4), **c.** (5,0) and **d.** (6,0) CNTs.

4 Conclusions:

In this paper, the electronic structure of (3,3), (4,4), (5,0) and (6,0) SWCNTs have been studied using DFT. It is found that the total energy increases with increasing the number of atoms. The computed E_g of (3,3) (4,4) and (6,0) CNTs is slightly larger than experimental and other theoretical results, while the calculated E_g for (5,0) is smaller than the semiempirical results. The B3LYP is known to overestimate the size of band gap of semiconductors but still describes quite accurately the trend in band gap. Such a modulation of band gap can be engineered into processing nanotube devices. The computed E_{coh} suggest that it increases significantly with increase in the number of atoms for both zigzag and armchair tubes. The FMO of the CNTs present obvious localization at the edge regions. This fact agrees with the former DFT calculations.

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