Bending Deformation on the electronic structure of the (3,3), (4,4), (5,0) and (6,0) single-wall carbon nanotubes

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ABSTRACT
In this work we investigate the effect of bending defect on the electronic and structural properties of the (3,3), (4,4), (5,0) and (6,0) single-wall carbon nanotubes (SWCNTs) using density functional theory (DFT) within Becke three parameter Lee–Yang–Parr (B3LYP) functional using 6-31 basis set. Our result revealed that as the bending angle increases, the deformation of atomic structure of the tube increases, particularly in the centralized zone of the tube. The obtained outcomes revealed that the bandgap fluctuates with the bending angle of CNTs and the cohesive energy, the highest occupied (E_{HOMO}) and the lowest unoccupied molecular orbitals energies (E_{LUMO}) decrease (in magnitude) as the CNTs bending increases. On the other hand, the electron affinity and the ionization potential increases with the bending angle of CNTs, while the Fermi energy decreases with the bending angle of CNTs, with a fluctuation of Fermi energy with the bending for (4,4) tube. Finally, in the presence of bending deformation, the highest number of density of states in the valence and conduction bands decrease with increasing the bending angle of CNTs.

KEYWORDS: Carbon Nanotubes, B3LYP, Bending, Electronic Structure.

1. INTRODUCTION
Investigation into carbon nanotubes (CNTs) properties has become one of the greatest active fields of present research. Though early research concentrated on growth and characterization, these interesting properties have led to increasing the number of investigations focused on application development in the past 5 years. The breadth of applications of CNTs is indeed wide-ranging field emission devices, nanoelectronics, composites, quantum wire interconnects, biosensors, chemical sensors, detectors, etc.
In the last decades, computer simulations have emerged as a fundamental and powerful new tool for condensed matter research. Simulations not only make
conceivable the comprehensive explanation of experimental outcomes, especially in the atomic scale, but in most cases, they provide predictions of properties and processes not yet observed in the laboratory. Various defects in CNTs are widely observed in experiments. CNTs were found to be not as perfect as it seems. Defects can be existing in as prepared CNTs. These defects can significantly change the electrical, thermal, electronic and mechanical properties of CNTs. Regardless of these extensive properties, but it is very infrequent for imperfection control to be perilous to a specific application.

Carbon nanotubes bending is a topic, that have applications in numerous ranges of the nanotechnology, as well as nanotoxicology and nanoelectromechanical systems. Atomistic simulations are essential to comprehend in detail the phenomena and the basics detected in experiments. The molecular dynamics permits the require of angular boundary situations on the atomistic systems. Naturally, bending is a significant method of mechanical deformation, as well as many studies focus on the bending actions of SWCNTs. Iijima et al. used computer simulation to model the bending behavior of SWNTs of varying diameters and helicity. The prediction shows that CNTs are extremely flexible when subjected to deformation of large strains. The hexagonal network of nanotubes can be retained by bending up to approximately 110°, despite formation of a kink. The bend permits the nanotube to relax elastically through compression. However, Falvo et al. utilized atomic force microscopy to investigate the bending responses of MWNTs under large strains. They established that MWNTs can bend recurrently through large angles by means of the atomic force microscope tip without suffering catastrophic failure—the bending is completely elastic. These studies detected nonlinear buckling behavior in the CNTs. Nano mechanical simulations are needed to understand in atomic detail the phenomena detected in experimental studies of bending behavior.

In this paper, we introduce a theoretical analysis of bending deformation on (3, 3), (4, 4), (5, 0) and (6, 0) SWCNTs based on first-principles calculations. The density functional theory (DFT) calculations are achieved by the Gaussian 09 package. Becke three parameter Lee–Yang–Parr (B3LYP) functional using 6-31G basis set, have been applied in the calculations, where B3LYP is one of the often-utilized hybrids functional that used in studies of nanotubes.
2. COMPUTATIONAL METHODS

All the computational studies were carried out using DFT implemented in the Gaussian 09 programs running and visualized by GaussView 5.08 program. The calculated properties of nanotubes have been calculated via DFT with 6-31G basis sets, the calculations in DFT were executed in the B3LYP hybrid functional. B3LYP is one of the most active hybrids functional used in studies of nanotubes. The optimized structure for a nanotube at which the nanotubes have the lowest energy; and can be achieved by discovery the first derivative of energy with respect to the distance between different atoms, known as the gradient. In Figure 1 the geometries of the bent (4,4) nanotube considered in the present study are schematically shown. We have built models with bending angles of 20°, 40°, 60° and 80° using a constant length of the tube to introduce the distortion. As the bending angle increases, the deformation of atomic structure of the tube increases, particularly in the essential zone of the tube. The 20° bend induces a compression of the C–C bonds in the inner side of the tube while the bonds on the outer side are stretched. The general tubular shape, however, remains essentially intact in both straight and bent regions. After a 20° bend, the increased compression of C–C bonds in the center of the nanotube leads to a flattening of its cross-section. Further bending increases this flattening to the point where the force between opposite nanotube walls becomes high enough to induce the formation of a kink as in the 80° model. The front views of the central sections of the bent tube models clearly show the drastic structural deformations that occur as the bending angle is increased from 60° to 80°.

![Fig. 1. The optimized structures of bent (4, 4) nanotubes studied in this work, the bending angles are: (a) 20°, (b) 40°, (c) 60° and (d) 80°.](image-url)
We considered SWCNTs (3, 3), (4, 4), (5, 0), and (6, 0) with an open edge. The diameters of the nanotubes are 4.07, 5.43, 3.92 and 4.70 Å, respectively. The length of the optimized pristine (perfect) 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\(^{11}\). 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.

3. RESULTS AND DISCUSSION

3.1. Electronic Properties:

Figure 2 shows the total energy of (3, 3), (4, 4), (5, 0) and (6, 0) under bending deformation which is calculated by DFT. The total energy of the bent nanotube shows very little change in energy under the deformation.

The most important modification of the electronic structure induced by bending a nanotube is the fluctuating of a band gap. Figure 3 shows the variation of the energy gap (\(E_g\)) as a function of the bending angle for (3, 3), (4, 4), (5, 0) and (6, 0) CNTs. We find that for (4, 4), (5, 0) and (6, 0) nanotube, the band gap decreases gradually with bending angle up to 20°, then increases gradually with bending angle up to 40° and so on at higher angles. On the other hand, for (3, 3) nanotube, the band gap decreases gradually with bending angle up to 40°, and increases with bending angle up to 60° and so on. This behavior may be attributed to the compression and dilatation of C-C bonds along the axis of the tube, brought about by bending. The band gap variation displayed in Figure 3 is consistent with the prediction based on uniform cross-sectional deformation\(^{12}\).

![Fig. 2. Calculated total energy versus bending angles in CNTs.](image-url)
The smallest value of energy gaps is 0.16, 0.075, 0.158 and 0.172 eV for (3, 3), (4, 4), (5, 0) and (6, 0) NTs, respectively. These values observed at 60°, 40°, and 20° for (6, 0), (3, 3) and both (4, 4), (5, 0), respectively. The opening of a band gap in nanotubes leads to a drastic modification of the electrical properties of nanotubes upon bending even by low angles.

**Fig. 3.** The Energy gap as a function of the bending angles in CNTs.

The results in Figure 4 show that the cohesive energy (in magnitude) slightly decreases as the CNTs bending increase for both zigzag ((5, 0) and (6, 0)) and armchair ((3, 3) and (4, 4)) tubes. The system with larger $E_{coh}$ is more stable. Thus, the pristine CNTs are energetically more stable than bending CNTs.

**Fig. 4.** The Cohesive energy as a function of bending angles in CNTs.
Figures 6 and 7 show the electron affinity (EA) and ionization potential (IP), respectively, as a function of bending angle for the selected CNTs, the EA and IP increases with bending angle. The most important observation of these figures is the fluctuating of EA and IP for (4, 4) and (6, 0) tubes with the bending angle. On the other hand, the fluctuation in (4, 4) is more than (6, 0) tube, this can be attributed to number of atoms in the tube, the number of atoms in (4, 4) tube is 104 atom which is more than the number of atoms in (6, 0) (90 atom). One can say that bending angle has significant influence on the EA and IP.

Figure 8 Shows the Fermi energy ($E_f$) for selected NTs, Fermi energy of the deformed nanotube shows little change in energy, increasing the bending angle causes decreases in Fermi energy, with fluctuation of Fermi energy with the bending for (4, 4) tube.
3.2 HOMO and LUMO energies

Figures 9 and 10 shows the highest occupied (E_{HOMO}) and the lowest unoccupied molecular orbitals energy (E_{LUMO}), respectively. One can notice from these figures that HOMO and LUMO energies show little change in energy, increasing the bending angle causes decreases in these energies, with fluctuation of HOMO and LUMO energies under the bending for (4, 4) tube. This behavior is similar to Fermi energy with bending (Figure 8).
3.3 The density of states

The Results of density of states (DOS) obtained by B3LYP functional are displayed in Figures 11 to 14 for (3, 3), (4, 4), (5, 0) and (6, 0) nanotubes, respectively. The charge density associated with conduction-band bottom is localized on atoms in the regions of maximal curvature while the charge density associated with valence-band top is uniformly distributed across the whole tube and retains its characteristic. This confirms that: (1) Most of the electronic structure change takes place in the conduction band and that (2) regions of maximal curvature are primarily responsible for the observed band gap change in deformed nanotubes. A high DOS at a specific energy level means that there are many states available for occupation. The Figures show that increasing the bending angle for all NTs, decreasing the high of peaks, i.e., the highest number of DOS in the valence and conduction bands are less\textsuperscript{13-17}. 

![Graph showing density of states](image1)

![Graph showing density of states](image2)
Fig. 11. Variation of DOS for bent (3, 3) CNT with bending degree: (a) 20°, (b) 40°, (c) 60°, (d) 80°. DOS spectrum (blue line), occupied orbitals (green line), and virtual orbitals (red line).
Fig. 12. Variation of DOS bent (4, 4) CNT with bending degree: (a) 20°, (b) 40°, (c) 60°, (d) 80°.
4. Conclusions

*Ab-initio* calculations based on density functional theory (DFT) have been performed to study the electronic structure of (3, 3), (4, 4), (5, 0) and (6, 0) single-wall carbon nanotubes. We have built models with bending angles of...
20°, 40°, 60° and 80° using a constant length of the tube to introduce the distortion. The cohesive energy, total energy, band gap, Fermi energy, ionization potential, electron affinity, highest occupied and lowest unoccupied molecular orbital, and density of state were studied in details. The results indicated that the cohesive energy and total energy increase (in magnitude) with increasing number of atoms. The bent carbon nanotubes present smaller cohesive energy than those of the pristine ones. The Fermi energy of carbon nanotubes vary when the bending is introduced into the nanotubes due to the change in size that produces different surfaces with different properties. It has been found that the bending cause significant changes in energy gap, with fluctuating of band gap according to the bending angle of carbon nanotubes. In general, ionization potential and electron affinity increase as bending defects are introduced into the nanotubes. In addition, presence of defects in nanotube causes some distribution of charge along the length of tube. It is also found that the bending defects in tubes decreasing the height of peaks; the highest number of DOS in the valence and conduction bands are less.

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