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Density of states of helically symmetric boron carbon nitride nanotubes

A C M Carvalho¹,², C G Bezerra²,³, J A Lawlor² and M S Ferreira²

¹ GDENB, Instituto de Física e Química, ICE, Universidade Federal de Itajubá, Avenida BPS 1303, Itajubá, MG, Brazil
² School of Physics, Trinity College Dublin, Dublin 2, Ireland
³ Departamento de Física, Universidade Federal do Rio Grande do Norte, Natal, RN 59078-900, Brazil

E-mail: cbezerra@dfte.ufrn.br

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Abstract
Motivated by the existence of helical wrapping patterns in composite nanotube systems, in this work we study the effects of the helical incorporation of carbon atoms in boron nitride nanotubes. We consider the substitutional carbon atoms distributed in stripes forming helical patterns along the nanotube axis. The density of states and energy band gap were calculated adopting Green function formalism by using the Rubio-Sancho technique in order to solve the matrix Dyson equation. We report the effects of the helical atomic distribution of carbon atoms on the behaviour of the density of states and the energy band gap. In particular, we show that the electronic energy band gap displays a non-monotonical dependence on the helical pattern, oscillating as a function of the helical angle $\theta$.

(Some figures may appear in colour only in the online journal)

1. Introduction

Boron carbon nitride (BCN) nanostructures were first theoretically reported in 1994 [1]. This new kind of hybrid nanostructure has attracted considerable attention in past years, from both the theoretical and experimental perspectives, because results from the literature have shown that BCN tubular structures display electronic properties intermediate between metallic carbon nanotubes and dielectric boron nitride (BN) nanotubes [1–6]. From the experimental perspective, many different methods, such as laser ablation [7], pyrolysis [8, 9], bias-assisted hot-filament chemical vapour deposition (CVD) [10–12], aerosol-assisted CVD with a laser vaporization process [13], and DC arc discharge [14], have been reported for the synthesis of BCN nanotubes with different stoichiometries (BC$_2$N, BC$_4$N, BCN, B$_5$C$_2$N$_3$, and B$_5$C$_2$N$_5$) [15]. Furthermore, different forms of BCN nanostructures, for example Y-shaped BCN nanojunctions [16] and BCN hexagonal nanocages [17], have also been reported. All of these possibilities have shown that BCN nanotubes could be quite promising in applications for nanoscale electronic devices, such as electron field emitters [12], rectifying diodes [18] and super-capacitors [19]. From the theoretical perspective, it has been suggested that different distributions of boron (B), nitrogen (N), and carbon (C) atoms, for distinct stoichiometries, can change the electronic properties of BCN nanotubes, meaning it might be possible to engineer the physical properties of such tubes by an adequate control of the atomic distribution. Although the general chemical characterization of BCN materials is well established, the real spatial distribution of B, N, and C atoms in BCN nanotubes, and the relation of this atomic distribution with the electronic properties, are still objects of discussion.

In addition to the doping processes we can consider some hybrid systems combining nanotubes and charged one-dimensional-like structures, such as polymers and DNA molecules, in order to modify the electronic properties of nanotubes. It is known that polymers can interact with nanotubes resulting in different mechanical [20], thermal [21, 22] and electronic [23] properties for the nanotube–polymer composite, and as a result of this interaction these molecules can sometimes coat the walls of a nanotube. Regarding the coating morphology, there is evidence indicating that these long molecules tend to wrap around the tubular structures in a helical fashion [24–26]. Theoretical calculations have investigated the interaction effects between polymers and nanotubes showing that, depending on the polymer wrapping angle, a helically symmetric potential is formed in the hybrid system, resulting in a non-monotonic behaviour of the nanotube–polymer composite total energy [27–29].
Figure 1. Ball-and-stick schematic representation of the BCN nanotubes considered in this work. Pink balls correspond to B atoms, grey balls correspond to C atoms and blue balls correspond to N atoms. (a) The C atom stripes follow a helical path along the nanotube axis, characterized by the helical angle $\theta$. (b) In the two-dimensional depiction, the unwrapped tube is represented by a stripe of width $2\pi R$ and the helical angle $\theta$ defines a unit cell of length $2\pi R / \tan(\theta)$, where $R$ is the nanotube radius. $D$ is defined in the picture as the distance between equivalent atoms of neighbouring stripes.

On the other hand, regarding atomic distribution, DFT calculations have also shown that BN and C stripes, stacked in parallel, perpendicular, and forming helical patterns along the nanotube axis, are energetically favourable in the case of BC$_2$N stoichiometry [30].

Considering that the electronic properties of nanotubes can be modified by atomic substitution and that composite nanotube systems display helical patterns, in this work we investigate the effects of atomic substitution of B and N atoms by C atoms in BN nanotubes, leading to BCN nanotubes. We consider the substitutional C atoms distributed in stripes forming helical patterns along the nanotube axis and address how this geometry can affect the electronic structure of the system. This paper is organized as follows. In section 2 we describe the theoretical model and the method of calculation which is based on the Green function formalism. The density of states and the energy band gap of the tubes are calculated in section 3. Finally, our findings are summarized in section 4.

2. Theoretical framework

In the present work six BCN nanotubes with armchair symmetry, a diameter of 10 Å and chirality $(8,8)$ were considered. Based on the geometry of a pristine boron nitride nanotube (BNNT), we design the BCN nanotubes by substituting C atoms into BNNTs. The atomic distribution of C atoms is chosen in such way that it creates a helical stripe of C atoms in the BNNT network, with an associated helical angle $\theta$ which defines the helical path of the C atom stripe. The helical angle $\theta$ is defined so that $\theta = 0^\circ$ corresponds to the stripe of C atoms parallel to the nanotube axis and $\theta = 90^\circ$ corresponds to the stripe of C atoms in the transversal direction (see figure 1). The BCN nanotubes considered here are named BCN00, BCN30, BCN45, BCN60, BCN70 and BCN90, corresponding to the following helical angles $\theta = 0^\circ$, $30^\circ$, $45^\circ$, $60^\circ$, $70^\circ$, and $90^\circ$, respectively.

Prior to calculating the electronic properties of the BCN nanotubes, we should analyse the structural stability of these physical systems. In order to address this issue, we considered systems with 1360 atoms with terminal bonds at the nanotube ends, saturated with hydrogen atoms. Among the various thermodynamic parameters, enthalpy of formation ($\Delta_f H^0$) is a key indicator for the prediction of the structural stability and it is also instructive for the synthesis of new compounds. Therefore, we calculated the enthalpies of formation of the BN and BCN nanotubes considered here. From the enthalpy of formation, we obtain the relative enthalpy of formation per atom, or energy of incorporation ($E_I$), to verify the stability of the structures. The geometries of these tubular structures were fully optimized using the semi-empirical Austin Method 1 (AM1) quantum chemical technique [31], which is based on the Hartree–Fock theory. All geometry calculations were carried out with the GAMESS programme package [32].

As regards the electronic properties, the BCN nanotubes were described within the framework of the $\pi$-band tight-binding model. The density of states (DOS) and energy band gaps were then numerically calculated adopting the Green functions formalism, by using the Rubio-Sancho technique [33]. In our numerical calculations, we use physical parameters reported in the literature [34] as follows: the on-site energies for B atoms and N atoms are $\epsilon_B = +2.33$ eV and $\epsilon_N = -2.50$ eV, respectively, in relation to the C on-site energy ($\epsilon_C = 0.0$ eV). The values for the hopping integrals are $t_{C-C} = -3.0$ eV, $t_{B-C} = -2.7$ eV, $t_{C-N} = -3.14$ eV and $t_{B-N} = -2.81$ eV.
3. Numerical results

It has been reported in the literature that the substitution of B and N atoms by C atoms in some specific directions produces distortions in the tube walls [30]. In figure 2 we show the resulting geometry of BCN nanotubes considered in this work, obtained by replacing B and N atoms with C atoms, with helical angles \( \theta = 30^\circ, \theta = 70^\circ \) and \( \theta = 90^\circ \). We can observe that, in all three configurations, the BCN nanotube presents a very subtle wave-like profile along the axial direction, mainly around the carbon stripes. Similar results, albeit more pronounced, are reported by Machado et al [30], where wave-like profiles occur due to the nanotube wall distortions, which are related to the difference between the C–N and C–B bond distances along the nanotube axis at the interfaces between the carbon stripe and the BNNT hexagonal network. In their structures, CN and CB bonds form diametrically opposite pairs at the interfaces, leading to contractions and expansions of the wall at each side of the carbon stripe. In our structures, CN and CB bonds do not form diametrically opposite pairs at the interfaces. The absence of opposite pairs along the tube axis reduces the contractions, and as a consequence we can observe only a mild wave-like profile in our structures. Such a subtle wave-like profile was also observed in all BCN structures considered in this work.

The structural stability of the BCN nanotubes was analysed considering the energy of incorporation, \( E_1 \), which is calculated from the enthalpy of formation, \( E_1 \) is defined as the relative enthalpy of formation per atom, i.e.,

\[
E_1 = \frac{\Delta_f H^0(\text{BCN}) - \Delta_f H^0(\text{BN})}{n}.
\]  

Here \( \Delta_f H^0(\text{BCN}) \) is the enthalpy of formation of helical BCN nanotube, \( \Delta_f H^0(\text{BN}) \) is the enthalpy of formation of pristine BN nanotube and \( n \) is the total number of atoms in the tube. All enthalpies of formation were obtained from AM1 calculations. Table 1 shows a summary of the energy of incorporation of the helical BCN nanotubes considered here, and we can infer from table 1 that \( E_1 \) is dependent on the helical angle \( \theta \). Bearing in mind that all helical structures considered here present the same number of atoms, the same symmetry (armchair) and the same chirality (8, 8), any difference in the energy of incorporation should be attributed to the helical angle \( \theta \) through the number of C–C, B–N, C–B and C–N chemical bonds in the tubes. Regarding the chemical bonds, we will use the same nomenclature as [31], i.e. C–C and B–N are named regular bonds while C–B and C–N are named wrong bonds. Thus, the total number of chemical bonds is simply the number of regular bonds plus the number of wrong bonds. The ratio between the total number of chemical bonds (\( T_b \)) and the number of wrong bonds (\( W_b \)) is also shown in table 1. We can observe from table 1 that there is a general tendency to decrease the energy of incorporation \( E_1 \) as the relative number of wrong bonds decreases, i.e. as the ratio \( T_b/W_b \) increases. Therefore, the ratio \( T_b/W_b \) is proportional to the reciprocal of the energy of incorporation \( E_1 \) (i.e. \( T_b/W_b \propto 1/E_1 \)). Thus we can consider \( T_b/W_b \) as a measure of the stability of the tube: the greater \( T_b/W_b \), the greater the tube stability. Our numerical results agree qualitatively with the results of Machado et al [30].

<table>
<thead>
<tr>
<th>Structure</th>
<th>( \theta ) (deg)</th>
<th>( E_1 ) (eV/atom)</th>
<th>( T_b/W_b )</th>
<th>( E_1 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCN00</td>
<td>0</td>
<td>0.25</td>
<td>47.43</td>
<td>2.55</td>
</tr>
<tr>
<td>BCN30</td>
<td>30</td>
<td>0.34</td>
<td>35.57</td>
<td>1.63</td>
</tr>
<tr>
<td>BCN45</td>
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<td>0.38</td>
<td>34.95</td>
<td>2.18</td>
</tr>
<tr>
<td>BCN60</td>
<td>60</td>
<td>0.44</td>
<td>26.56</td>
<td>2.61</td>
</tr>
<tr>
<td>BCN70</td>
<td>70</td>
<td>0.71</td>
<td>17.17</td>
<td>2.29</td>
</tr>
<tr>
<td>BCN90</td>
<td>90</td>
<td>0.08</td>
<td>124.50</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Figure 2. Axial and lateral illustrations of the BCN nanotubes with helical angles as follows: (a) \( \theta = 30^\circ \), (b) \( \theta = 70^\circ \), and (c) \( \theta = 90^\circ \). We can observe the subtle distortion of the walls due to the C atom stripes.

Table 1. Energy of incorporation \( E_1 \) measured in eV/atom. \( T_b/W_b \) is the ratio between the total number of chemical bonds (\( T_b \)) and the number of wrong bonds (\( W_b \)).
Let us now consider the density of states of the helical BCN nanotubes. Figure 3 shows numerical results for the density of states (DOS) for pristine BN nanotube (figure 3(a)) and helical BCN nanotube (figure 3(b)). One can observe, by comparing figures 3(a) and (b), that the introduction of the carbon stripe results in a decrease of the electronic band gap ($E_g$). This is a consequence of the generation of new electronic states in the band gap region, due to the introduction of carbon atoms in the pristine BN nanotube, which contributes to narrowing of the energy band gap. We should remark that, despite narrowing the energy band gap, the incorporation of C atoms is not enough to change the conduction profile of the BCN nanotubes. Indeed, pure BN nanotubes are wide band gap semiconductors with a band gap of nearly 5 eV, therefore the introduction of the carbon stripe is not enough to change the system behaviour from insulator to metallic. However, the incorporation of the helical carbon stripe induces interesting modifications in the band gap of the helical BCN nanotubes, which are illustrated in figure 4, showing numerical results for the band gap of the six nanotubes considered in this work (see also table 1). The energy band gap is plotted as a function of the helical angle $\theta$. We can clearly observe that the electronic energy band gap has a non-monotonic behaviour as a function of the stripe direction (i.e. the helical angle $\theta$), which can be explained qualitatively as follows. Bearing in mind the unwrapped representation of figure 1(b), we can consider the carbon stripes as linear scatterers separated by a distance $D = 2\pi R \cos(\theta)$. This situation is analogous to the Kronig–Penney model in which equidistant linear scatterers generate an interference pattern, which may be constructive or destructive depending on the distance $D$ between the scatterers. This interference pattern appears in the electronic wavefunctions of the underlying nanotube and consequently in its electronic properties. As $D$ is a function of the helical angle $\theta$, the interference pattern is also dependent on the helical angle $\theta$. Therefore, we can conclude that such an interference pattern is responsible for the occurrence of the size-dependent oscillations of the energy band gap as a function of the helical angle $\theta$ of the carbon stripe. Before concluding, we should remark that a prerequisite for future technological applications of semiconductor nanotubes is the ability to fine-tune the energy band gap, and our results suggest that an appropriate choice of the helical angle $\theta$ may lead to a tunable band gap of the helical BCN nanotubes. This opens new perspectives in technological applications due to the feasibility of tunable nanodevices.

4. Conclusions

To summarize, in this work we have investigated the effects of the atomic substitution of B and N atoms in armchair BN nanotubes by C atoms, leading to BCN nanotubes, with the substitutional C atoms distributed in stripes forming helical patterns along the nanotube axis (as illustrated in figures 1 and 2). The structural stability of the helical nanotubes was analysed via calculation of the enthalpy of formation, and the corresponding energy of incorporation $E_{I}$, by using the semi-empirical Austin Method 1 (AM1) quantum chemical technique. As illustrated in table 1, our results show that the energy of incorporation depends on the helical angle $\theta$ through the number of C–C, B–N, C–B and C–N chemical bonds in the tubes. The ratio $T_b/W_b$ between the total number of chemical bonds $T_b$ and the number of wrong bonds $W_b$ is a measure of the stability of the tube. Our results in table 1 show that there is a general tendency to decrease the energy of incorporation $E_I$ as the relative number of
wrong bonds decreases, i.e. as the ratio $T_b/W_b$ increases. As regards the electronic properties, we investigated the density of states (DOS) and energy band gaps employing a $\pi$-band tight-binding model and the Green functions formalism, combined with the Rubio-Sancho technique, in order to solve the matrix Dyson equation. Our numerical results show that the incorporation of the carbon stripes does not change the system behaviour from insulator to metallic, although it narrows the energy band gap as shown in figure 3. Much more interesting behaviour is observed where the helical carbon stripe induces a new feature in the energy band gap: it is a non-monotonic function of the helical angle $\theta$. This non-monotonic behaviour of the band gap energy may be useful in technological applications due to the feasibility of tuning the band gap through an appropriate choice of the helical angle $\theta$ of the carbon stripe. We hope that our model stimulates experimental investigations on BCN nanostructures with helical symmetry and that our theoretical results can be tested.

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