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Tight Binding Study of Armchair CNTs (14, 14) Geometrical Parameters and Energy Sub-Bands

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Abstract

Investigating the physical properties of carbon nanotubes is a useful method to recognize their nature and clarify the operation of these nanostructures in nanotechnology market. In this work we have used the tight binding method to simulate the geometrical parameters, the effect of chirality on the number of non-degenerate and degenerate sub-bands, and the sub-bands of armchair (14, 14) carbon nanotubes. The results show that the C–C bond lengths and diameter of CNTs (14, 14) are 1.39 Å and 18.53 Å, respectively. The other calculated parameters haven't been reported yet to assess the accuracy of the data. The symmetry operations of the infinitely long CNTs (14, 14) can be described via the symmetry groups D_{14d}. The crossing sub-bands at Fermi level suggest that CNTs (14, 14) has metallic behavior. The origin of energy was arbitrarily set to be at the maximum valence band. The band structure shows 56 sub-bands and it is clear that 13 conduction (valence) sub-bands are doubly degenerate, and 2 conductions and 2 valence sub-bands are non-degenerate sub-bands.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 [1], due to their special cylinder structure consisting of a graphene layer, their physical and chemical properties have attracted the scientists' attentions [2-5]. The use of carbon nanotubes (CNTs) in nanotechnology industry demands the comprehension of their geometry and electronic properties. Computer simulation is a powerful method to explore the behavior of nanomaterials and has an important place in the course of basic study of nano materials properties. The physical and chemical characteristics of CNTs are notably dependent on the nanotube geometry. As a result, studying the structural properties of CNTs is particularly a useful key to discover their essence. Translational symmetry with a screw axis in one-dimensional systems influences their electronic and structural properties [6, 7]. For the single walled

nanotubes, covalent functionalization breaks some of the carbon-carbon double bonds. Consequently, leaving holes in the structure of the carbon nanotube will alter their physical properties [8]. This research, including promising results, gives some hints to peruse the geometrical parameters and electronic band structure of armchair (14, 14) carbon nanotubes to discuss the effect of chirality and geometry on their geometric parameters and electronic sub-bands.

2. Materials and Methods

2.1 *Computational details*

A carbon nanotube is constructed from a wrapped graphene sheet. See Figure 1. The chirality of carbon nanotubes can be described via a pair of integer indices, n and m, depending on the direction the graphene sheet is rolled. There are three types of CNTs: armchair carbon nanotubes (n=m>0), zigzag carbon nanotubes (n>0, m=0), and chiral carbon nanotubes (n, m>0 and m ≠ n). Carbon nanotubes can be single-walled (SWCNT), or multi-walled (MWCNT), consisting of several concentrically interlinked nanotubes. Their length can be several micrometers or even millimeters.

The calculations have been done using the SIESTA code (https://departments.icmab.es/leem/siesta/). SIESTA is both a method and its computer program implementation, to perform efficient electronic structure calculations and ab initio molecular dynamics simulations of molecules and solids. SIESTA's efficiency stems from the use of a basis set of strictly-localized atomic orbitals. A very important feature of the code is that its accuracy and cost can be tuned in a wide range, from quick exploratory calculations to highly accurate simulations matching the quality of other approaches, such as plane-wave methods.

We have chosen an armchair (14, 14) CNT in this research. As mentioned in the "Introduction", we intend to investigate the geometrical parameters and electronic sub-bands of CNTs (14, 14). The screw symmetry of the nanotubes allows for the construction of a tight-binding model that is based on a two atom unit cell rather than on the translational unit cell with NC two-atom unit cells [9, 10]. This tight binding model has advantages regarding the computational time and the accuracy of the outputs. Our model parameters are given by $V_{ss\sigma}$= 4.76 eV, $V_{sp\sigma}$=4.33 eV, $V_{pp\pi}$=−2.77 eV, $V_{pp}\sigma$= 4.37 eV [11]. The other two parameters, $V_{s*p\sigma}$, $V_{s*s*\sigma}$, can be obtained from table 1 in reference [12].

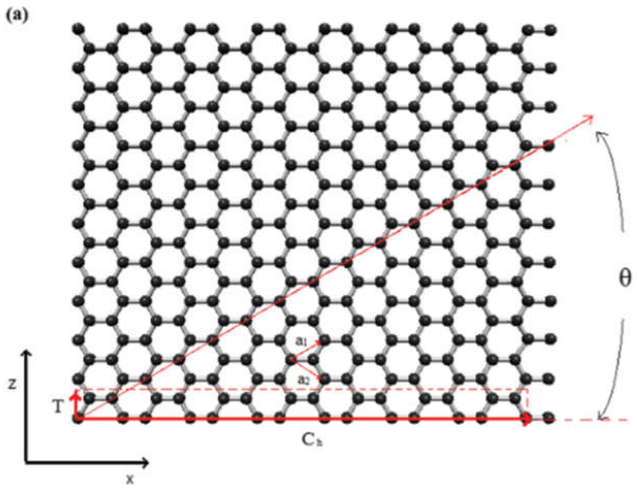

Figure 1. 2D graphene sheet. The chiral vector, $\vec{a}_1$ and $\vec{a}_2$ are represented in XZ plane

3. Results and Discussion

3.1 *Geometrical parameters*

Similar to their building block graphene, carbon nanotubes are chemically bonded with sp2 bonds, a highly strong form of molecular interaction. This feature combined with carbon nanotubes' natural inclination to rope together via van der Waals forces, supplies the probability to develop low-weight and ultra-high strength materials with highly conductive thermal and electrical properties. This makes them highly attractive for numerous applications. Carbon nanotubes literatures, for example reported results by Mori et al. [13], Movlarooy [14], Bertoni [2], have proved that the physical properties of CNTs depend on the geometrical parameters and chirality of the nanotube. Since any carbon nanotube has its particular geometry, in this study CNTs (14, 14) have been considered for simulation. Based on Ref [15], the rotation operation, ψ, of armchair ACNTs (14, 14) is $\pi/14$ radians.

The geometrical parameters of CNTs (14, 14) exploiting fundamental relations governing the geometrical parameters of CNTs are summarized in Table 1. It is worth mentioning that the results noted in Table 1 have been calculated using fundamental relations governing the geometry of carbon nanotubes and the electrons in which the wave functions in the tight binding approximation don't influence the obtained parameter. Therefore, it is essential to include the effects of electrons on the computed geometry of these nanotube structures.

The calculated geometrical parameters of armchair (14, 14) carbon nanotubes are presented in Table 3. The results show that the C–C bond lengths and diameter of CNTs (14, 14) are 1.39 Å and 18.53 Å, respectively. The other calculated parameters haven't been reported yet to assess the accuracy of the data.

The symmetry operations of the infinitely long CNTs (14, 14) can be described via the symmetry groups D_{14d} (the symmetry operations of the infinitely long armchair carbon nanotubes by odd n are the D_{nd} symmetry groups) [17]. Character table for the D_{nd} groups (n = 14) is given in Table 2 in which j is equal to 13/2.

Table 1. Geometrical parameters of ACNT (14, 14) utilizing fundamental relations

Symbol	Name	Formula [6]	ACNTs (14, 14)	ACNTs (7, 7) [16]
a_{C-C}	Carbon–Carbon distance	-	1.42 Å (graphite)	1.42 Å (graphite)
a	Length of unit vector	$\sqrt{3}a_{C-C}$	2.46 Å (graphite)	2.46 Å (graphite)
C_h	Chiral vector	$n\vec{a}_1 + m\vec{a}_2$ (n, m: integers)	$14\vec{a}_1 + 14\vec{a}_2$	$7\vec{a}_1 + 7\vec{a}_2$
L	Circumference of CNT	$a\sqrt{n2 + m2 + nm}$	59.65 Å	29.83
d_R	Diameter of CNT	L/π	18.99 Å	9.49
T	Length of T	$\lvert\vec{T}\rvert=\sqrt{3}L/d_R$	5.44 Å	2.46
$\boldsymbol{\theta}$	Chiral angle	$\mathrm{Tan}\theta = \sqrt{3}m/2n+m$	30°	30°
N	Number of hexagons per 1D unit cell	$2(n^2+ m^2+nm)/d_R$	62	14
-	Number of atoms per 1D unit cell	2N	124	28

Table 2. Character table of group D_{14d}

R	E	$2C^{1}_{\emptyset_{13/2}}$	$2C^{2}_{\emptyset_{13/2}} \dots 2C^{13}_{\emptyset_{13/2}}$	$14C'_{13/2}$
A_1	1	1	1… 1	1
A_2	1	1	1… 1	-1
E_1	2	$2\cos\emptyset_{13/2}$	$2\cos2\emptyset_{13/2}\dots 2\cos\frac{13}{2}\emptyset_{13/2}$	0
E_2	2	$2\cos2\emptyset_{13/2}$	$2\cos4\emptyset_{13/2}\dots 2\cos13\emptyset_{13/2}$	0
…	…	…	…	…
$E_{13/2}$	2	$2\cos\frac{13}{2}\emptyset_{13/2}$	$2\cos13\emptyset_{13/2}\dots 2\cos(\frac{13}{2})^2\emptyset_{13/2}$	0

Table 3. calculated geometrical parameters of ACNTs (14, 14) exploiting tight binding method

Symbol	Name	ACNTs (14, 14)	ACNTs (7, 7) [17]	Experiment results (Å)
$a_{C\text{-}C}$	Carbon–Carbon distance	1.39 Å	1.40 Å	1.42 [18]
a	Length of unit vector	2.40 Å	2.44 Å	-
L	Circumference of CNT	58.19 Å	29.39 Å	-
d_R	Diameter of CNT	18.53 Å	9.35 Å	-
T	Length of T	5.43 Å	2.44 Å	-
$\boldsymbol{\theta}$	Chiral angle	30°	30°	-
N	Number of hexagons per 1D unit cell	62	14	-
-	Number of atoms per 1D unit cell	124	28	-

Our results are in agreement with the theoretical and experimental data [16, 19-22]. From Table 1 and Table 3 it is clear that the geometrical parameters of ACNTs (14, 14) are larger than that of ACNTs (7, 7).

3.2 *Electronic sub-bands*

The geometry of a CNTs affects their electronic band structure as a result of the electronic structure and symmetry of graphene is the main reason [2, 14, 18]. The sub-bands of nanotubes arise from the periodicity along the circumference of CNTs [23]. The electronic band structures of armchair CNTs consist of 4n energy sub-bands including 2n conduction and 2n valence sub-bands, regardless of the nanotube chirality. The 2n valence (or conduction) sub-bands involve two non-degenerate valences (or conduction) sub-bands and n−1 doubly degenerate valence (or conduction)) sub-bands [16]. The simulated band structure of armchair CNTs (14, 14) is represented in Figure 2. The crossing sub-bands at Fermi level suggest that CNTs (14, 14) have metallic behavior. The origin of energy was arbitrarily set to be at the maximum valence band. The band structure shows 56 sub-bands and it is clear that 13 conduction (valence) sub-bands are doubly degenerate, and 2 conductions and 2 valence sub-bands are non-degenerate sub-bands.

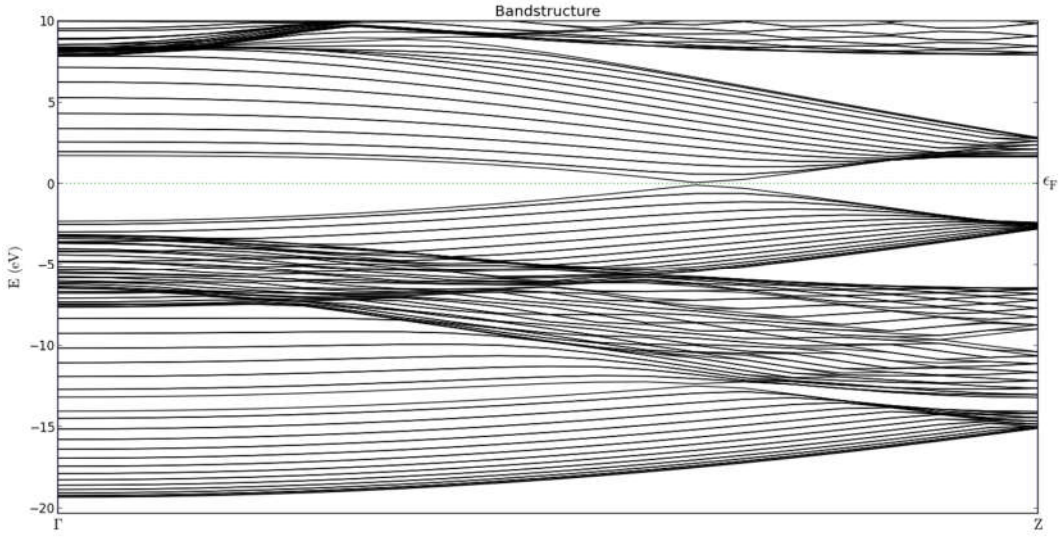

Figure 2. Electronic band structure of CNTs (14, 14)

4. Conclusions

The tight binding approach has been used to compute the geometrical parameters and electronic sub-bands of armchair (14, 14) carbon nanotubes. The data indicates that the armchair CNTs (14, 14) have metallic behavior with zero bandgap. The electronic band structures of armchair CNTs consist of 4n energy sub-bands including 2n conduction and 2n valence sub-bands, regardless of the nanotube chirality. The 2n valence (or conduction) sub-bands involve two non-degenerate valences (or conduction) sub-bands and n−1 doubly degenerate valence (or conduction)) sub-bands. The band structure shows 56 sub-bands and it is clear that 13 conduction (valence) sub-bands are doubly degenerate, and 2 conductions and 2 valence sub-bands are non-degenerate sub-bands. Our results are in agreement with the theoretical and experimental data. Last but not least, the geometrical parameters of ACNTs (14, 14) are larger than that of ACNTs (7, 7).

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding this article.

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