RESEARCH ARTICLE

MODELING OF THE GEOMETRY AND ELECTRONIC BANDGAP STRUCTURE OF CHIRAL SINGLE WALLED CARBON NANOTUBES

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Abstract

Carbon Nanotubes (CNTs) are one-dimensional nanostructured materials that will play a key role in future electronics. All properties of the carbon nanotubes are determined by its electronic structure. The main focus of this study has been to investigate the basic electronic bandgap structure of the chiral single walled carbon nanotubes (SWCNTs). A simple algorithm is presented in order to model the geometry of the chiral single-walled CNTs with any desired structure. The electronic bandgap structure of the chiral single-walled carbon nanotubes has been studied by employing an extended tight binding model (TBM). The changes in the energy band gap due to the chirality effect in case of metallic (6, 3) SWCNT and in the semiconducting (12, 7) SWCNT are discussed here. The value of the SWCNTs diameter is calculated also. The computed results indicates that the bandgap depends inversely on the diameter of the tube. The present results were found to be in consistent with those reported in the literature and indicated the correctness of the process of simulation technique process.

Keywords: Chiral Single walled carbon nanotubes, Tight Binding Method (TBM), Brillouin zone, Band gap structure.

1. Introduction

Carbon nanotubes (CNTs) are unique nanostructured materials which possess extraordinary physical and mechanical properties [1] making them suitable for interesting applications such as transistors, storage devices, field emission [2], and nanoscale machines [3]. The chirality of the nanotube has a significant impact on the resultant material properties, such as electronic and thermo-physical properties. Since all of the possible configurations (i.e., the chirality) of a nanotube can be specified by the chiral vector (n, m), the material properties can be segmented based on the specified by the chirality of each individual carbon nanotube [4]. A SWCNT is a hollow cylinder made up of covalently bonded carbon atoms arranged in a hexagonal pattern [5]. The SWCNT is an armchair when the chiral indices, n and m, are equal. On the other hand, the SWCNT is zigzag when either n or m is =0. Moreover, the SWCNT is chiral when their chiral indices are neither of these two [6].

Chiral tubes with chiral angle which is mid-way between zigzag and armchair tubes are found to have most prominent effects of chirality [7]. Carbon nanotube is said to be a chiral if its mirror image is identical and carbon nanotubes are chiral if its mirror image has spiral symmetry i.e., mirror image can't be superimposed. Achiral nanotube is either zigzag or armchair [8]. The diameter and the helical arrangement are the two important factors that decide whether SWCNTs will be metal or semiconductor [9]. The chirality of the tube can be expressed with the help of a role-up vector i.e $C_h=na+mb$ where both a and b indicate unit vectors of hexagonal lattice structure and both m, n are integral numbers [10]. For a two dimensional graphene layer, the bonding and anti-bonding states become degenerate at the K-points of the brillouin zone and consequently band gap of the graphene layer goes to zero. But in case of carbon nanotube, the wave function quantization along the circumference of the tube limits the permitted wave vectors to specific direction of the brillouin zone which follows the equation C.K=2j (j is an integral number). If one of the wave vector crosses the K-point, the CNT will

behave as metallic. But if none of the wave vector crosses the K-point then it will turn into a finite band gap semiconductor[11]. Carbon nanotubes are much lighter than steel making them a true material for reinforcements in polymer matrix composites [12]. Over the past 20 years, many techniques have been developed to characterize the chiral indices of SWCNTs, including imaging techniques and spectroscopy techniques [13].

The present work aims to illustrate how an appropriate geometrical model can be used to obtain chiral single-walled carbon nanotubes with different chirality, (i.e., chirality= m / n). A brief overview on geometrical models that suggested for graphitic Carbon Nanotubes geometry is reported. Then, we carried out a detailed computation procedure of the energy bandgaps for the study of the electronic bandgaps structure of chiral SWCNTs with different chirality.

2. Computational Methodology

2.1. Conventional Rolled-up Model for Graphitic Nanotubular Structures

There are few ways to view SWCNT, and the most used is by rolling up graphene sheet to construct a hollow cylinder with end caps. The cylindrical wall is made of hexagonal carbon rings, and the end caps are of pentagonal rings. This unit cell that is a hexagonal ring is repeated sequentially by the virtue of covalent bonds with neighboring carbon atoms. The covalent bond between these carbon atoms is an exceptionally strong chemical bond that has an important role for exceptional mechanical properties of the graphite structure. In the sense that all bond lengths and all bond angles are assumed to be identical [14].

The atomic structure of CNTs depends on the chirality of tube structure. This chirality is defined by two parameters that are chiral vector C_h and the chiral angle Θ. The chiral vector C_h is indicated by the lattice translational indices (n, m) and two basis vectors a_1 and a_2. A SWNT is formed by joining the parallel lines which are defined by the starting and ending point of the chiral vector [15].

$$C_h = na_1 + ma_2 \qquad (1)$$

where the indices (n, m) are integer values called the chiral index of nanotube, and **a1**, **a2** are unit vectors of the lattice. The chiral angle (θ) determines the amount of twist of CNTs, where values of θ are in the range of 0 ≤θ≤ 30 [16].

The fundamental property of an infinitely long SWNT is its translational periodicity and it is described by translation vector $\vec{T}$. Fig.(1) shows the translation vector defines the length of the nanotube unit cell. In a plain graphene sheet, $\vec{T}$ vector which along the axial direction

of the SWNT and is the orthogonal to the chiral vector [17].

$$\vec{T} = t_1 a_1 + t_2 a_2 \qquad (2)$$

where t_1 and t_2 are components of the translational vectors $\vec{T}$.
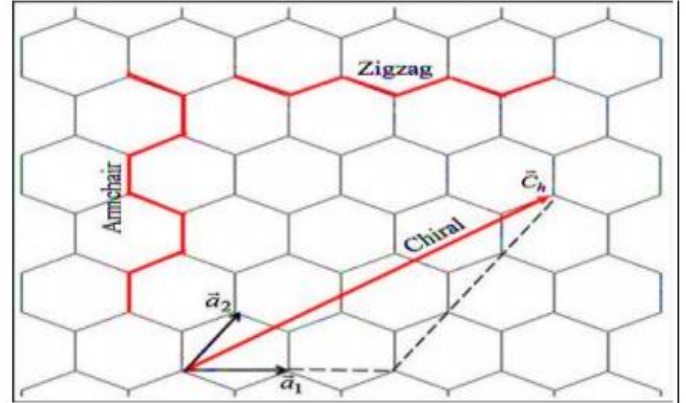

Fig. 1: Schematic view of single-walled zigzag, armchair and chiral nanotube.

The conventional rolled-up model implies that the nanotube diameter $d(n, m)$ is assumed to be given by the expression[18]:

$$d(n,m) = \frac{|C_h|}{\pi} \qquad (3)$$

and

$$|C_h| = a\sqrt{n^2 + m^2 + nm} \ (4) \qquad (4)$$

2.2. Band Structure of Carbon Nanotubes

From the electronic structure of graphene the electronic structure of carbon nanotube (CNT) can be found by imposing the geometrical constrains from the nanotube on the band structure of graphene. As shown in fig. (1), geometrically nanotubes are separated into three categories; armchair, zigzag and chiral tubes [18]. The chirality of a CNT can also define its electrical property. If (n - m) is a multiple of 3, the CNT is said to be metallic, otherwise it is semiconducting. If n is a multiple of 3, an armchair nanotube (having m = n) would always be metallic, and the same is true in the case of zigzag nanotubes because the value of m is 0[19]. Zigzag and chiral nanotubes can be either metallic or semiconducting depending on the geometry [18].

A popular and widely applied method for simulating single-wall carbon nanotubes electronic structure is the Tight Binding Method (TBM) [20]. Generally, the electronic band structure of graphene can be calculated by using the tight binding approximation. But in this study, the band structure of graphene is obtained from the tight binding approximation including only first-nearest-neighbor carbon-carbon interactions of π-orbits of a single graphite sheet and then, the band structure of graphene was plotted by solving eq.5, 6 and 7[21].

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$$E_v(k_x, k_y) = \frac{\epsilon + \gamma_o.w(k_x,k_y)}{1 + s.w(k_x,k_y)} \quad (5)$$

$$E_c(k_x, k_y) = \frac{\epsilon - \gamma_o.w(k_x,k_y)}{1 - s.w(k_x,k_y)} \quad (6)$$

$$w(k_x, k_y) = \sqrt{1 + 4.\cos\left(\frac{\sqrt{3}k_x a}{2}\right).\cos\left(\frac{k_y a}{2}\right) + 4.\cos^2\left(\frac{k_y a}{2}\right)} \quad (7)$$

where γ_o = 2.5 eV is the energy overlap integral (tight binding hopping parameter) between the nearest neighbors, ε is the on-site energy parameter in electron volt (eV), *s* is the overlap parameter is given in non-dimensional units, *a* is the lattice parameter of graphene, the *v* and *c* indices stand for valence and conduction bands, respectively, and *k* = (kx, ky) represents the 2D wave-vector components along the x and y directions in the 2D Brillouin zone (BZ) of graphene. Conduction and valence bands are the consequence of two carbon atoms per unit cell. Fig. (2a) shows the conduction band and the valence band meet at six distinct points corresponding to the corners of the first BZ and these points are referred to as K-points. Out of the six K-points are equivalent due to the spatial symmetry of the hexagonal lattice, thus two distinguishable points remain called K and K'. At the special points K and K' of the graphene BZs the valence and conduction bands cross each other at the Fermi level (energy at 0 eV). Because of the same number of states in the first BZ as in real space and two carbon atoms per unit cell, at T =0K only the valence band states are occupied, with a Fermi energy level lying exactly at the position where the two bands crosses each other [22].

The reciprocal lattice of SWNT is obtained by folding the reciprocal lattice of the graphene sheet. This is known as zone-folding approximation. The zone-folding approximation is that the electronic band structure of a nanotube is given by the superposition of the graphene electronic energy bands along the corresponding allowed k lines[23].

Fig. (2b) shows, the upper half of the energy dispersion relation curves is called π* or the antibonding band and

π is the bonding band. It is seen that the two bands are degenerated at the K and Ḱ points where they attain the same value. This is also the energy of the Fermi energy EF. There are two atoms per unit cell and therefore two π electrons per unit cell, so the electrons fully occupy the lower π-band leaving the π* antibonding band empty. The density of states (DOS) calculation shows that the density of states at the Fermi surface is zero making graphene as zero-gap semiconductor or a semi-metal [18]. The one dimensional (1D) energy dispersion relations for n- bands of SWNTs, E_{1D} is given by[21]:

$$E_{1D} = \gamma_o\sqrt{1 + 4.\cos\left(\frac{\mu\pi}{n}\right).\cos\left(\frac{k_y a}{2}\right) + 4.\cos^2\left(\frac{k_y a}{2}\right)} \quad (8)$$

where μ is the angular momentum of a standing wave in the SWCNTs corresponds to the linear momentum k of a plane wave of graphene sheet such that:

$$\vec{k}.\vec{C} = 2\pi\mu \quad (9)$$

For discrete values of μ, the above expression generates a set of equidistant parallel lines. These lines are known as cutting lines. The cutting lines must be arranged into a rectangle with a side parallel to the reciprocal lattice vectors. The dimensions of the rectangular BZ are determined by the choice of the reduced unit cell [17].

2.2.1. Effect of Nanotube Diameter on Electronic Band Structure in Chiral SWCNTS

The bandgap of the SWCNTs vary with the diameter and chiral vector. For a SWCNT having a semiconductor behaviour, the band gap E_{gap} is expressed by the following relation [24]

$$E_{gap} = \frac{2\gamma_o a_{c-c}}{d(n,m)} \quad (10)$$

Where, acc is the carbon-carbon distance (0.142nm), γ_o is the CNT tight binding parameter, and $d(n,m)$ is the diameter of CNT given by eq (3).
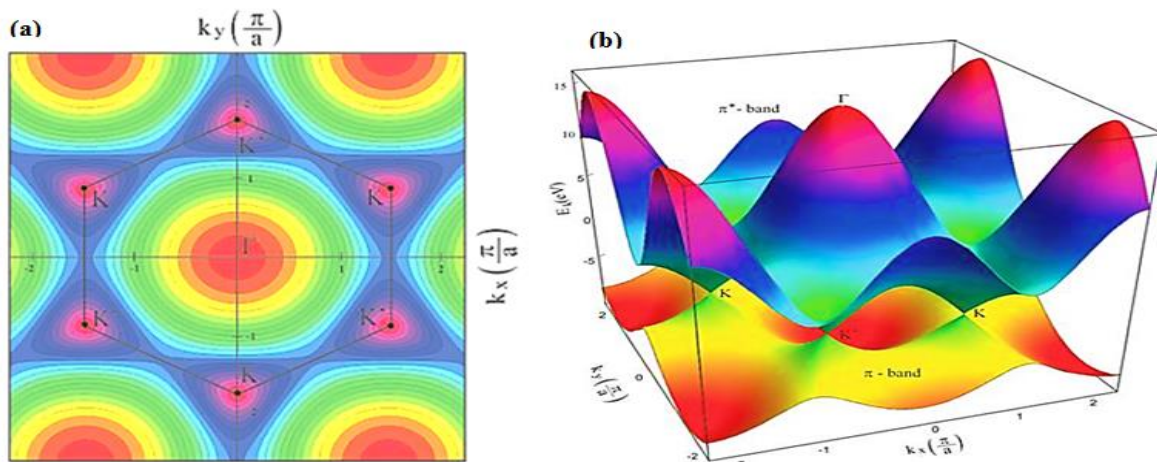

Fig. 2: shows (a) the 2D electronic band structure, (b) the 3D electronic band structure of a SWNT for any chirality (n, m) vector.

3. Results and Discussion

The first computational step is started by using MATLAB codes for generating a carbon sheet after rolling it in the basis on chiral coordination. The code inputs are the chiral coordinates, length of the nanotube, and the bond length. Different Chiral CNTs' shapes were plotted.

The SWCNTs are formed by joining the parallel lines which are defined by the starting and ending points of the chiral vector[21]. Due to the hexagonal symmetry, we need to consider chiral nanotubes with $0 < m < n$ only.

The geometrical parameters of chiral nanotubes were obtained according to the default chirality (n, m) values. Four chiral models with chirality values of (6, 3), (12, 6), (12, 7) and (15, 13), shown in Fig.(3), where the bond length for all chirality values is 2.3382 nm and the length of the graphene sheets is 100 nm.
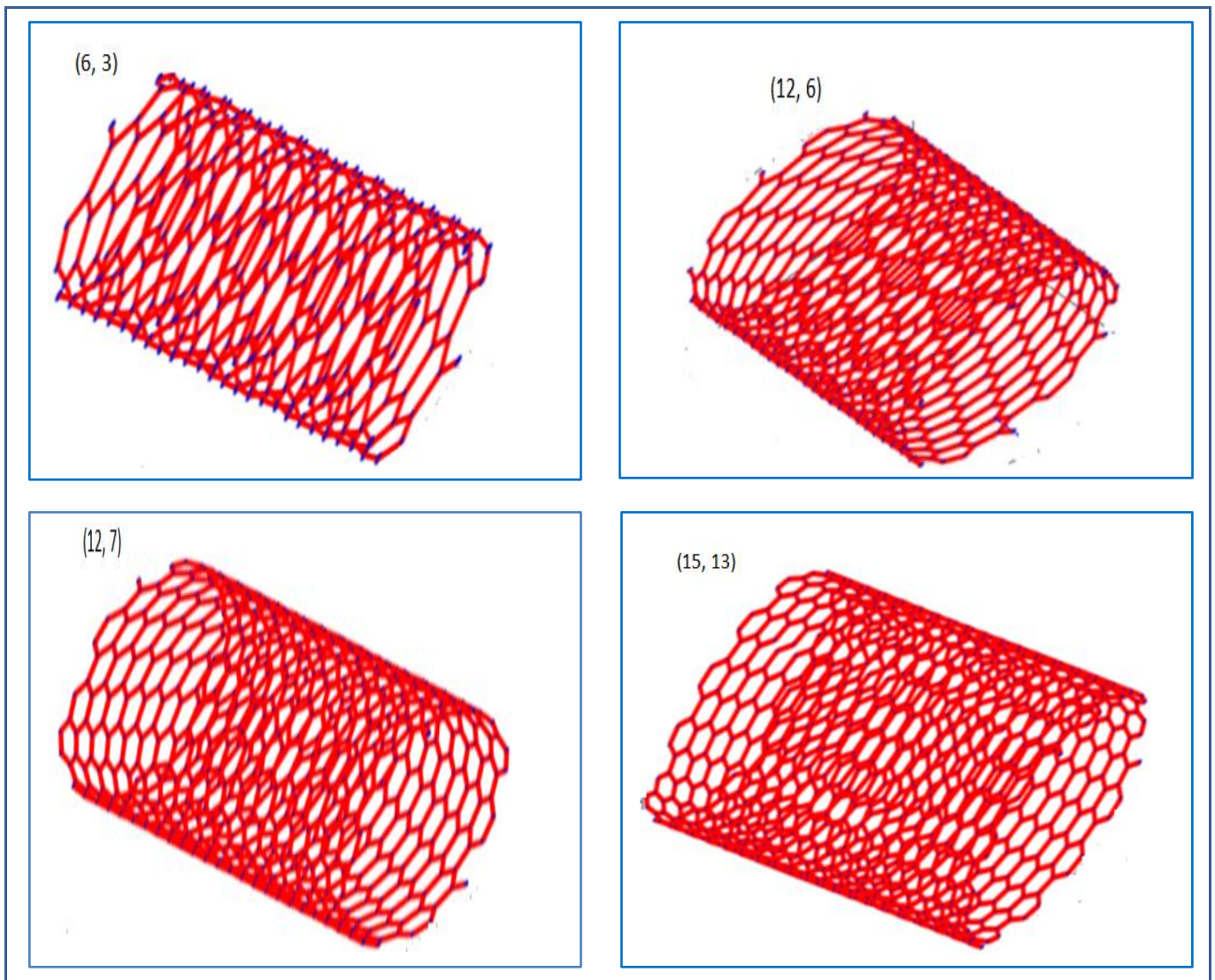

Fig. 3: Modeling of the geometry CNTs for chirality values (6, 3), (12, 6), (12, 7) and (15, 13).
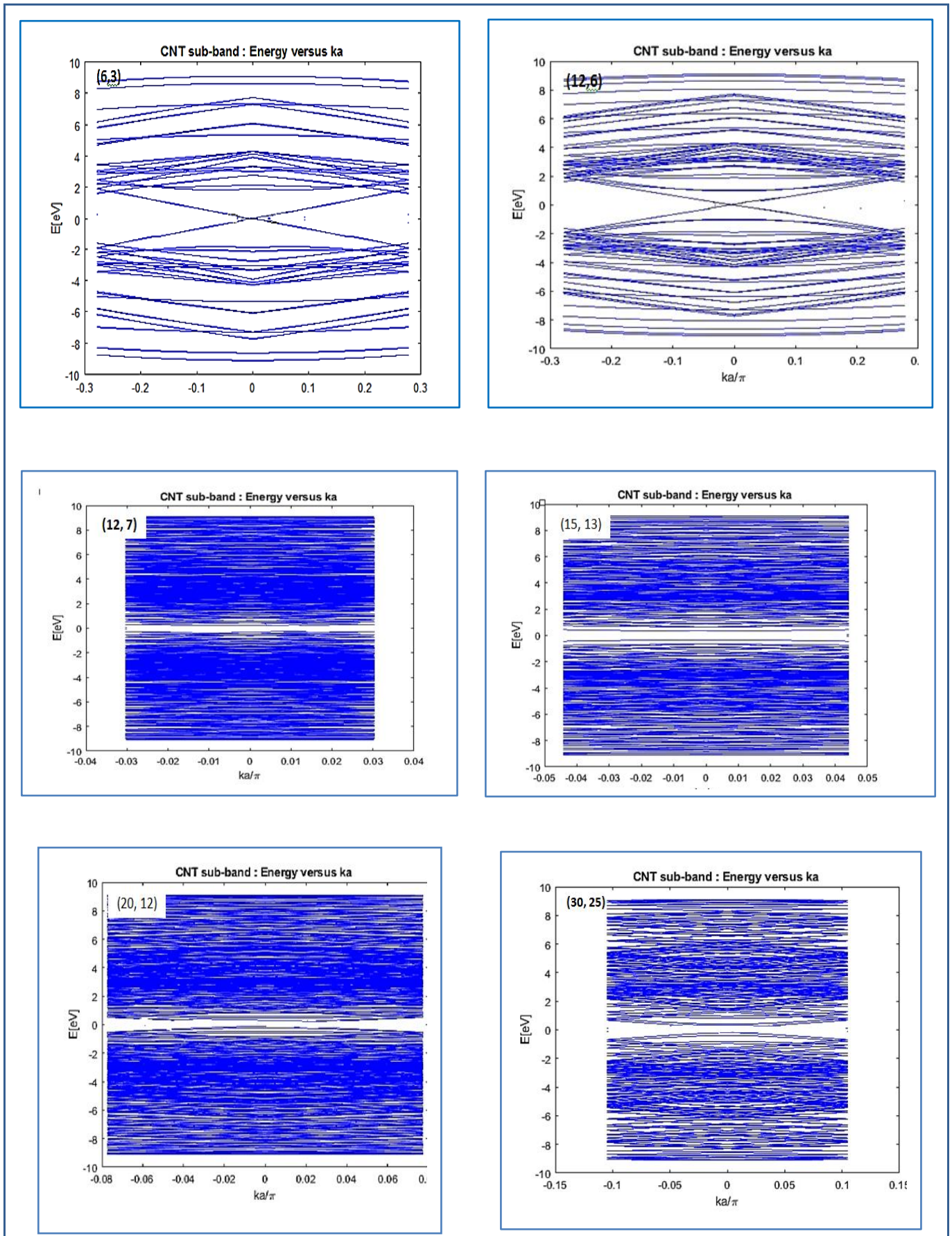
Fig. 4: Electronic band structures of chiral SWCNTs for different chirality values.

The electronic bandgap structure of Chiral SWCNTs is modeled traditionally by the simple TBM. Fig.4 shows the electronic band structure of Chiral SWNTs which calculated and plotted with different chirality values. The computed result of the band structure of (6, 3) and (12, 6) nanotubes reveals that these materials are in fact metallic tubes, where the upper valance bands and lower conduction bands are cross each other at Fermi energy level (E = 0), while the electronic band structures chiral SWCNTs with chirality values of (12, 7), (15, 13), (20, 12), and(30, 25), reveals the existence of a gap between the upper valance and lower conduction bands; i.e the upper valance and the lower conduction bands aren't cross to each other at Fermi energy (E = 0). This result was attributed to the semiconducting behavior of the present SWCNTs. Chiral nanotubes are metallic if the allowed k-lines do crosses the K points; otherwise they are semiconducting otherwise [21]. Our computed results are in agreement with the experimental results [24].
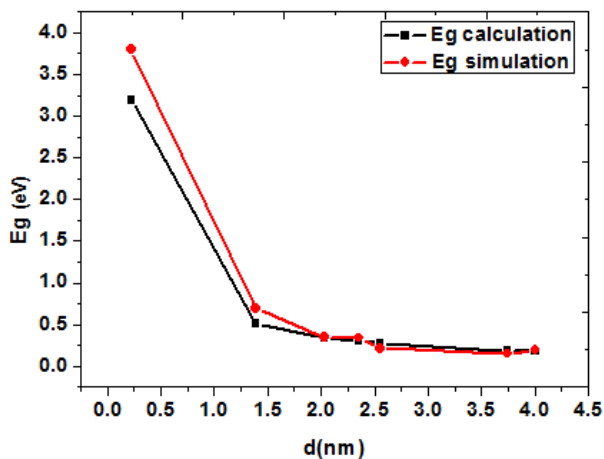

Fig. 5: Variation of chiral SWCNTs band gaps vs. diameters for both Calculated & Simulated values.

Fig. (5) shows the variation of the bandgap of the semiconducting chiral SWCNTs as a function of their diameter. It is clear that the (30, 25) chiral nanotube, which has the largest diameter and the smallest bandgap among all investigated nanotubes, while the (2, 1) chiral nanotube has the smallest diameter and largest bandgap. This result was attributed to the quantum confinement. It is obvious that the values of the band gap of the chiral nanotubes are dependent on the nanotube diameter, i.e the band gap of the chiral nanotubes is decrease due to the increasing in nanotube diameter, it [25]. This implies to that small diameter SWCNTs are always poor conductors, as they have large bandgaps [26]. Table (1) shows the values of simulated bandgap of seven chiral SWCNTs which are in consistent with calculated values. Chirality values those not found in Fig.(3) for more clearity of bandgap-diameter relation . The above results are in agreement with experimental results [24]

We found that with the decrease of the SWCNT diameter a large downshift of conduction band edge occurs due to the large curvature which induces an enormous increase of the electron density inside the SWCNTs [27].

Table (1): Comparison between calculated and Simulated band gaps values of Chiral SWNTs.

(n, m)	Diameter (nm)	Calculated Gap (ev)	Simulated Gap (ev)
(30, 25)	4.005	0.1772	0.1912
(40, 8)	3.741	0.1897	0.1491
(20, 15)	2.554	0.2779	0.2158
(20, 12)	2.352	0.3018	0.3398
(15, 13)	2.029	0.3433	0.3494
(12, 7)	1.39	0.5107	0.6906
(2, 1)	0.2222	3.1953	3.802

Conclusion

In this paper, chiral SWNTs with different structures and constant length were simulated using a simple algorithm by changing the chiral angle from 0 to 30 degrees. The geometry, as well as the electronic properties of the chiral SWCNTs were described by a chiral vector. We performed a calculation of the SWNTs band structure by using a simple tight-binding model for 1D CNTs. The tube diameter and the value of band gap were also calculated. We found that the energy bangap of semiconducting chiral-tubes is inversely proportional to their diameter. The results show a decrease in the band gap from 3.1953 eV to 0.1772eV while the diameter increases from 0.2222 nm to 4.005 nm. As a results the diameter of the nanotubes increases, the band gap decreases and the DOS increases around the Fermi level, which means that the electrons needs less energy for the transition from the valence band to the conduction band.

From the present work and our previous work on armchair and zigzag single-walled carbon nanotubes [14] reveals the difference between the structures of three types of single-walled carbon nanotubes, we can easily distinguish between these three types of SWNTs. In future, we hope to cover a complete picture of SWNTs depending on the behavior of their structural parameters at both ambient pressure and under hydrostatic pressure.

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مقالة بحثية

نمذجة البنية الهندسية والتركيب الالكتروني لفجوة الطاقة للانابيب النانونية اللاتناظرية احادية الجدار

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المُلخّص

أنابيب الكربون النانوية عبارة عن مواد ذات بنية نانوية أحادية البعد ستلعب دورًا رئيسيًا في الإلكترونيات المستقبلية. يتم تحديد جميع خصائص أنابيب الكربون النانوية من خلال تركيبها الإلكتروني. كان التركيز الرئيسي لهذه الدراسة هو دراسة بنية النطاق الإلكتروني الأساسية لأنابيب الكربون النانوية اللاتناظرية أحادية الجدار (SWCNTs). تم تقديم خوارزمية بسيطة قادرة على نمذجة هندسة الأنابيب النانوية الكربونية أحادية الجدار مع أي بنية مرغوبة. تمت دراسة بنية فجوة النطاق الإلكترونية للأنابيب النانوية الكربونية أحادية الجدار من خلال استخدام نموذج الربط الضيق الممتد (TBM). تمت هنا مناقشة التغيرات في فجوة نطاق الطاقة بسبب تأثير عدم التناظر في حالة الأنابيب المعدنية الأحادية (3،6) وفي أشباه الموصلات (7،12) SWCNTs. تم حساب قيمة قطر الأنابيب SWCNTs ايضا. وتشير النتائج المحسوبة إلى أن فجوة النطاق تعتمد عكسيا على قطر الأنبوب. وقد تبين أن النتائج تتفق مع تلك الموجودة في الأدبيات مما يشير إلى صحة عملية تقنية المحاكاة.

الكلمات المفتاحية: أنابيب الكربون النانوية اللاتناظرية أحادية الجدار، نموذج الربط المحكم (TBM)، منطقة بريليون، فجوة النطاق.