Simulation of the Band Structure of Graphene and Carbon Nanotube
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Simulation technique has been performed to simulate the band structure of both graphene and carbon nanotube. Accordingly, the dispersion relations for graphene and carbon nanotube are deduced analytically, using the tight binding model & LCAO scheme. The results from the simulation of the dispersion relation of both graphene and carbon nanotube were found to be consistent with those in the literature which indicates the correctness of the process of simulation technique. The present research is very important for tailoring graphene and carbon nanotube with specific band structure, in order to satisfy the required electronic properties of them.

1. Introduction.
Graphene, which is a monolayer of carbon atoms packed into a two-dimensional honeycomb lattice, has been experimentally demonstrated to possess remarkable carrier transport properties [1–5]. The high mobility and carrier velocity of graphene promises ballistic devices and high switching speeds [6,7]. Graphene also offers ultrathin body for optimum electrostatic scaling and excellent thermal conductivity. Besides its purely fundamental importance, researchers view graphene as a promising new material for electronic [8], chemical [9], or electromechanical [10] applications, where graphene’s unique properties may be of substantial benefit. Two-dimensional graphene is a semi-metal without a band-gap [11]. A band-gap can be obtained by using a narrow graphene nanoribbon (GNR) [12]. Unlike carbon nanotubes (CNTs), which are mixtures of metallic and semiconducting materials, a recent experiment [12] demonstrated that all sub-10nm GNRs are semiconducting due to the edge effect, which make them more attractive for electronic device applications.

Different from other carbon materials, such as graphite, diamond and fullerene, CNTs are one dimensional carbon materials which can have an aspect ratio greater than 1000. They can be envisioned as cylinders composed of rolled-up graphite planes with diameters in nanometer scale [13-16]. The cylindrical nanotube usually has at least one end capped with a hemisphere of fullerene structure. Depending on the process for CNT fabrication, there are two types of CNTs [14-17]: single-walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs). SWCNTs consist of a single graphene layer rolled up into a seamless cylinder whereas MWCNTs consist of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow core with van der Waals forces between adjacent layers. According to the rolling angle of the graphene sheet, CNTs have three chiralities: armchair, zigzag and chiral one. The chirality of nanotubes has significant impact on their transport properties, particularly the electronic properties [18].

The authors [19,20] investigated the transport characteristics of carbon nanotube mesoscopic device under the influence of ac-field of wide range of frequencies. Also the authors [21] investigated the angular dependence of the chiral tunneling through bilayer graphene under the effect of the electromagnetic field of wide range of frequencies.

The purpose of the present paper is to generate a simulator in order to simulate the band structure of both graphene and carbon nanotube.

2. The Model & Its Simulation.
2.1. Band structure of Graphene. In graphene it is the electrons participating in the sp² hybridization which are responsible for the bindings to the three nearest neighbor atoms in the plane [15]. This kind of bond is called an σ-bond. The last pₓ electron then makes a π-orbital perpendicular to the plane. It is the
electron in this orbital, which is responsible for the weak binding between the planes in graphene, and which is able to move around, both in and perpendicular to the graphene plane, making it a semi-metal or a zero gap semiconductor.

The hexagonal lattice of graphene is shown in “figure 1” where there are two atoms in every unit cell. The distance between two nearest neighbor atoms is $a=1.42 \text{ Å}$ [22]. The unit cell ,“figure 1” is defined by the unit vectors $\vec{a}_1$ and $\vec{a}_2$. In x-y coordinates these are expressed as:

$$\vec{a}_1 = \left( \frac{a}{2}, \frac{\sqrt{3}}{2} a \right)$$

$$\vec{a}_2 = \left( -\frac{a}{2}, -\frac{\sqrt{3}}{2} a \right)$$

(1)

Figure 1: A hexagonal lattice with the lattice vectors $a_1$ and $a_2$, the grey area corresponds to one choice of unit cell, $r_A$ and $r_B$ points to the two atoms in the unit cell.

where $a = |\vec{a}_1| = |\vec{a}_2| = 1.42\text{Å} \times \sqrt{3} = 2.46\text{Å}^0$ is the lattice constant.

The electronic structure of graphene could be computed using the tight binding & LCAO scheme [22,23] for this purpose, we start with a Bloch function $\Phi_j(\vec{k}, \vec{r})$

$$\Phi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R} \in G} e^{i\vec{k} \cdot \vec{R}} \phi_j(\vec{r} - \vec{R})$$

(2)

In Eq.(2) $\Phi_j$ is the wave function for an electron in the atomic $j^{th}$ orbital in the unit cell, or in other words, $\Phi_j$ is the wave function for the p$_z$ orbitals which is localized at the position of the j-atom. Also, in Eq.(2) N is the number of lattice points and G is a set of vectors pointing to every lattice point in the graphene. The eigenfunctions of the electron in graphene can be written as a linear combination of the Bloch function for the two atoms in the unit cell, that is, we have
\[
\Psi_a(k, \vec{r}) = \sum_{j=1}^{2} C_{a_j}(\vec{k}) \Phi_j(\vec{k}, \vec{r})
\]  \hspace{1cm} (3)

To get an expression for the dispersion relation for graphene, we have to solve the Schrödinger equation quantum mechanically, \[22,23\], we get the following secular equation:

\[
\text{det}[\mathcal{H} - E \mathcal{S}] = 0 \hspace{1cm} (4)
\]

where \(\mathcal{H}\) and \(\mathcal{S}\) are matrices called the transfer and the integral matrix with \(\mathcal{H}_{ij}\) and \(\mathcal{S}_{ij}\) as the entries. They are given by

\[
H_{jj'}(\vec{k}) = \langle \Phi_j | H | \Phi_{j'} \rangle \hspace{1cm} \text{and} \hspace{1cm} S_{jj'}(\vec{k}) = \langle \Phi_j | \Phi_{j'} \rangle \hspace{1cm} (5)
\]

Eq. (4) is of degree \(n\) and its solution gives the \(n\)- different eigenvalues for \(E(\vec{k})\) resulting in the dispersion relation for the \(n\)-bands, where \(n\) is the number of electronic orbitals participating in the band structure in each unit cell. For the case of graphene, \(n=2\) due to two atoms participating each with one orbital. From Eq.(5) we have that:

\[
\langle \Phi_A | H | \Phi_A \rangle = \frac{1}{N} \sum_{R=K} \langle \Phi_A (r-R) | H | \Phi_A (r-R) \rangle + \frac{1}{N} \sum_{R=K} e^{i\vec{k} \cdot (\vec{R} - \vec{R'})} \langle \Phi_A (r-R') | H | \Phi_A (r-R) \rangle \hspace{1cm} (6)
\]

Now, using the tight binding approximation technique, Eq (6) can be written as \[22,23\]:

\[
\langle \Phi_A | H | \Phi_A \rangle \approx 2\varepsilon_{2p}
\]

where \(\varepsilon_{2p}\) is the orbital energy from \(2p\) level. It can be shown that the expression for the off-diagonal terms \(\mathcal{H}_{AB}\) are expressed as \[22,23\]:

\[
\mathcal{H}_{AB} = \mathcal{H}^*_A = \gamma_1 \left[ 1 + e^{i\vec{k} \cdot \vec{a}} + e^{-i\vec{k} \cdot \vec{a}} \right] = \gamma_1 g(\vec{k}) \hspace{1cm} (7)
\]

where \(\gamma_1\) is the overlap integral \[22,23\]. With the use of the unit vectors \(\vec{a}_1\) and \(\vec{a}_2\), we get:

\[
g(\vec{k}) = 1 + e^{-i\vec{k} \cdot \vec{a}_1} \frac{\sqrt{3}}{2} \cos \left( \frac{\vec{k} \cdot \vec{a}_1}{2} \right) \hspace{1cm} (8)
\]

Now, we are going to find the integral matrix \(\mathcal{S}\). We notice that

\[
S_{AA} = S_{BB} = 1,
\]
Since the wave function is normalized. For the off diagonal terms for matrix, we can write as before [22,23]:

$$S_{AB} = S_{AB}^* = \gamma_0 g(k)$$  \hspace{1cm} (9)

The transfer and integral matrices are

$$\mathbf{H} = \begin{pmatrix} \varepsilon_{2p} & \gamma_1 g(k) \\ \gamma_1 g^*(k) & \varepsilon_{2p} \end{pmatrix}$$

and

$$\mathbf{S} = \begin{pmatrix} 1 & \gamma_0 g(k) \\ \gamma_0 g^*(k) & 1 \end{pmatrix}$$

So the secular equation for graphene is given by:

$$\text{det}[\mathbf{H} - \mathbf{E} \mathbf{S}] = \text{det} \begin{pmatrix} \varepsilon_{2p} - E_i & (\gamma_1 - \gamma_0 E_i)g(k) \\ (\gamma_1 - \gamma_0 E_i)g^*(k) & \varepsilon_{2p} - E_i \end{pmatrix} = 0$$  \hspace{1cm} (10)

Solving, we get an expression for the dispersion relation, i.e.

$$E_i(k) = \frac{\varepsilon_{2p}}{1 \pm |g(k)|^2} \frac{1}{\gamma_0}$$  \hspace{1cm} (11)

where $|g(k)|$ is given by:

$$|g(k)| = \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}}{2}k \cdot a\right) \cos\left(\frac{k \cdot a}{2}\right) + 4 \cos^2\left(\frac{k \cdot a}{2}\right)}$$  \hspace{1cm} (12)

The Brillouin zone of two-dimensional graphene is shown as the shaded area in the “figure 2”, where $\Gamma$, $K$, $\tilde{K}$ and $M$ represent points of high symmetry. The reciprocal unit vectors are given by
Figure 2

“Figure 2” shows the reciprocal lattice point and the Brillouin zone for graphene, with its high symmetry points. K and K’ are the points where the $\pi$ and $\pi^*$ dispersion bands is touching each other. The three K points are equivalent since they are connected by the reciprocal lattice vectors $\vec{b}_1$ & $\vec{b}_2$. While the points K and K’ cannot be connected by the reciprocal lattice vectors, so as they are not equivalent. The simulation techniques to Eq.(11) show the dispersion relation for graphene (see “figure 3”) where $\gamma_0=0.129$ eV and $\gamma_1 = -3.033$ eV and $\varepsilon_{2p}=0$ [11,24,25].

\[
\vec{b}_1 = \left( \frac{2\pi}{a}, \frac{2\pi}{\sqrt{3}a} \right)
\]

and

\[
\vec{b}_2 = \left( -\frac{2\pi}{a}, -\frac{2\pi}{\sqrt{3}a} \right)
\]
The curve in “figure 4” is a slice of “figure 3” between the symmetry point. The upper half of the energy
dispersion relation curves is called $\pi^*$ or the antibonding band and $\pi$ is the bonding band. It is seen that the
two bands are degenerated at the K and $\bar{K}$ points where they attain the same value. This is also the energy
of the Fermi energy $E_F$. We have two atoms per unit cell and therefore two $\pi$ electrons per unit cell so the
electrons fully occupy the lower $\pi$-band leaving the $\pi^*$ antibonding band empty. A density of states
calculation shows that the density of states at the Fermi surface is zero making graphene a zero-gap
semiconductor or semi-metal [22,24,25]. When the overlapping integral $\gamma_0$ become zero and also $\varepsilon_{2p}$=0 the
dispersion (Eq.(11)) will be expressed as:

$$E(k) = \pm \gamma_1 \sqrt{1 + 4 \cos \left( \frac{\sqrt{3} k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_x a}{2} \right)}$$

The results from the simulation techniques for graphene are consistent with those in the literature for
graphene [22, 24, 25].

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.
Geometrically nanotube are separated into three categories; armchair, zigzag and chiral tubes. It will be
shown that armchair tubes are always metallic while zigzag and chiral tubes can be either metallic or
semiconducting depending on the geometry.

2.2(a)-Geometrical structure.

The structure of carbon nanotubes (CNTs) is described by circumference vector or chiral vector $\tilde{C}_h$
which represents the full circumference of the tube. It is defined by:

$$\tilde{C}_h = n \tilde{a}_1 + m \tilde{a}_2$$

where $\tilde{a}_1$ and $\tilde{a}_2$ are the unit vectors in the hexagonal lattice, and n, m are integers. $\tilde{C}_h$ “figure 5” also
defines the propagation vector $P_h$ representing the periodicity of the tube parallel to the tube axis.
Furthermore, it settles the so-called chiral angle which is the angle between $C_h$ and $a_1$. If either n or m is
zero, the chiral angle is 0° and the structure is called zigzag. If n=m, the chiral angle is 30° and the
structure is called armchair. All other nanotubes show chiral angles between 0° and 30°. They are known
as chiral nanotubes because they produce a mirror image of their structure upon an exchange of n and m
[26]. It can be seen that $|C_h|$ is equal to the circumference length of the nanotube so the diameter $d_t$ of
the tube is given by:

$$d_t = \frac{|C_h|}{\pi}$$

and

$$|C_h| = a \sqrt{n^2 + m^2 + nm}$$
In general, the table below shows the different categories of the nanotube:

**Table 1.** Types of the carbon nanotube.

| Type   | θ     | Ch   |
|--------|-------|------|
| Zigzag | 30°   | (n,0) |
| Armchair | 0°   | (n,n) |
| Chiral | 0°<|θ|<30° | (n,m) |

![Figure 5](image)

**2.3. The translation vector T.**

It describes how far we should move along the nanotube before the pattern of the carbon atoms on the nanotubes repeats itself and it therefore defines the length of the nanotube unit cell. T is defined by:

\[
\vec{T} = t_1 \vec{a}_1 + t_2 \vec{a}_2
\]  

(18)

where \( t_1 \) and \( t_2 \) are indices. Since \( \vec{C}_h \times \vec{T} \) is the size of a carbon nanotube unit cell then
where $N$ is the number of hexagons in the unit cell implying that there are $2N$ carbon atoms in the unit cell.

Now, we shall find out the dispersion relation of carbon nanotube as follows: Since there are $2N$-atoms in the unit cell this should leads to $N$-pairs of $\pi$- bonding and $\pi^*$-anti-bonding bands. The reciprocal lattice vectors $\vec{K}_1$ and $\vec{K}_2$ for a carbon nanotube are defined as:

$$\vec{C}_h \cdot \vec{K}_1 = 2\pi$$
$$\vec{T} \cdot \vec{K}_1 = 0$$
$$\vec{C}_h \cdot \vec{K}_2 = 0$$
$$\vec{T} \cdot \vec{K}_2 = 2\pi$$

(20)

It is easy to show that $\vec{K}_1$ and $\vec{K}_2$ are expressed as [22]:

$$\vec{K}_1 = \frac{1}{N} \left(-t_2 \vec{b}_1 + t_1 \vec{b}_2\right)$$
$$\vec{K}_2 = \frac{1}{N} \left(m\vec{b}_1 - n\vec{b}_2\right)$$

(21)

where $\vec{b}_1$ and $\vec{b}_2$ are the reciprocal lattice vectors for graphite. Under the periodic boundary conditions the only allowed wave vectors component in the circumferential direction are those that obey the following relation:

$$\vec{k} \cdot \vec{C}_h = 2\pi \ell$$

where $\ell$ is an integer. The allowed states [26] are defined by:

$$\vec{k} = \ell_1 \vec{K}_1 + \ell_2 \frac{\vec{K}_2}{|\vec{K}_2|}$$

$$-\frac{\pi}{|\vec{F}|} \leq \ell_2 \leq \frac{\pi}{|\vec{F}|}, \quad \ell_1 = 0,1,\ldots,N-1$$

(22)

If one of the slices happens to cut through the $\vec{K}$ point the nanotube will be metallic and if the slices do not cut through a $\vec{K}$ point it will be semiconducting [22,26].

The simulation techniques show the dispersion relation for the three different carbon nanotubes (see “figure 6a,b,c”).

(a) It is a metallic (10,10) carbon nanotube;
(b) It is a metallic (15,0) carbon nanotube;
(c) It is a semiconducting (12,8) carbon nanotube.
Figure 6a

Figure 6b
The results for the dispersion relation for different types of carbon nanotube are consistent with those in the literature [25-28], which shows the correctness of the simulation technique performed in the present paper. The present research is very important for nanofabricating graphene and carbon nanotube with specific band structure. We shall extend this research in future, taking into consideration, for example, phonons, and doped ferromagnetic nanoparticles.

3. References.

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