Comparison between Monolayer and Bilayer Graphene energy bands using the Tight Binding model

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Abstract. The Tight Binding model is used to describe the electronic energy band structures of the monolayer and bilayer graphene. The “creation” and “annihilation” quantum operators are employed to compute the respective Hamiltonians. From this, two and four energy bands were respectively obtained. These computations are an attempt to show a unifying approach representing both cases.

1. Introduction

Many special properties of Graphene (both monolayer and bilayer) have their origins in their regular hexagonal lattice structure [1]. Their band structure is also discussed in this article. Monolayer and bilayer graphene have the same generating base vectors and also the same reciprocal lattice. Monolayer graphene has no gap between the conduction and valence band. While, in the case of bilayer graphene, it has 2 equivalent planes in its lattice structure. Furthermore, electron band structure can be analysed following the plane symmetry of the bilayers, as it is made in the analysis of graphite (i.e. over 10 graphene layers) [1].

Both, the monolayer and bilayer electronic band structures have been worked out using the Tight Binding model by different authors [2,3,5,6 and 9]. This model assumes that particles are strongly bounded to the lattice. When an electron is captured by an ion during its motion through the lattice, the electron remains there for a long time, before leaking or tunnelling to the next ion [3,4]. It is well known, in the case of graphene, that relatively strong bindings are maintained for a few layers, which is consistent with the chosen model. Evidently for graphite, such model is not applicable [2].

2. Theoretical background: Tight Binding Model

The Tight Binding model is employed to compute the electronic band structure using the basis wave functions and the linear combination of these [4,5,6]. Considering that strong potential crystal, $\Phi_v$ as an atomic orbital, is characterized by subindices $v$.

$$
\Psi_k(x) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{ikX_j} \Phi_v(x - X_j)
$$

In this equation, the coordinate $X_j$ specifies the i-th atom position. The function $\Phi_v(x - X_j)$ tells us the orbital is centred around the j-th atom. On the other hand, as it is a crystal structure $X_j = ja$, where $a$ is the crystal lattice constant, the Bloch function can be expressed as:

$$
\psi_k(x) = \frac{1}{\sqrt{N}} e^{ikx} \sum_{j=1}^{N} e^{-ik(x - X_j)} \Phi_v(x - X_j)
$$

In general, an electronic function can be obtained as a superposition of n different Bloch functions:
The energy \( E_j(k) \) of the j-th band is given as follows:

\[
E_j(k) = \frac{\langle \Psi_j | H | \Psi_j \rangle}{\langle \Psi_j | \Psi_j \rangle} \tag{4}
\]

Where \( H \) is the Hamiltonian. Replacing (3) in (4):

\[
E_j(k) = \frac{\sum_{i,l}^n H_{i,l} c_{j,i}^* c_{j,l}}{\sum_{i,l}^n S_{i,l} c_{j,i}^* c_{j,l}} \tag{5}
\]

Where:

\[
H_{i,l} = \langle \Psi_i | H | \Psi_l \rangle \quad \text{and} \quad S_{i,l} = \langle \Psi_i | \Psi_l \rangle
\]

The Energy \( E_j \) is minimized with respect to \( c_{jm}^* \), deriving and setting to zero, where is obtained:

\[
\sum_{l=1}^n H_{m,l} c_{j,l} = E_j \sum_{l=1}^n S_{m,l} c_{j,l} \tag{6}
\]

From this new equation we can find the energy as follows:

\[
det(H - E_j S) = 0 \tag{7}
\]

3. Method
In this section, calculations are presented of the energy bands following the Tight Binding model for monolayer and bilayer graphene.

3.1 Tight Binding model applied to monolayer Graphene

In the monolayer graphene (Figure 1), which has two carbon atoms in its unit cell (A and B), the bond angle between these atoms is \( 2 \pi / 3 \) or 120° [6], therefore, for each triangle sublattice, it can be written as vectors of the generating base:

\[
a_1 = \frac{3}{2} a \left( \frac{1}{\sqrt{3}} \right), \quad a_2 = \frac{3}{2} a \left( \frac{1}{-\sqrt{3}} \right) \tag{8}
\]

Where \( a \approx 1.42 \text{Å} \) is the lattice constant. Around of each atom of the sublattice A, there are three atoms of the sub lattice B. They are connected by the following vectors (first neighbors):

\[
\delta_1 = \frac{a}{2} \left( \frac{1}{\sqrt{3}} \right), \quad \delta_2 = \frac{a}{2} \left( \frac{1}{-\sqrt{3}} \right), \quad \delta_3 = a \left( \frac{1}{0} \right) \tag{9}
\]
Hence, the basis in the reciprocal lattice is:

\[ b_1 = \frac{2\pi}{3\alpha} \left( \frac{1}{\sqrt{3}} \right), \quad b_2 = \frac{2\pi}{3\alpha} \left( \frac{1}{-\sqrt{3}} \right) \]  

(10)

We form a Hamiltonian based on the “creation” and “annihilation” operators of particles in each one site of sublattices, as follows:

\[ H = -t \sum_{\langle i,j \rangle} \sum_{s = \pm 1} (a_{j,s}^\dagger b_{j,s} + c.h.) - t' \sum_{\langle i,j \rangle} \sum_{s = \pm 1} (a_{i,s}^\dagger a_{j,s} + b_{i,s}^\dagger b_{j,s} + c.h.) \]  

(11)

Where the term “c.h.”, the hermitic conjugate. Parameters \( t \) and \( t' \) are related to the probability amplitude of the electrons to effect transitions between the first and second neighbors, respectively, \( a_{i,s}^\dagger \) and \( a_{i,s} \) are “creation” and “annihilation” electron operators, in each one site \( i \) with spin \( s \) belonging to triangle sublattice A of the hexagonal lattice, similarly to the sublattice B.

By writing down the “creation” and “annihilation” operators in terms of its Fourier transform and diagonalizing it, the bands structure of the system is obtained. Boundary conditions are imposed on the Hamiltonian’s auto vectors, in such a way that \( \psi(x + a_i) = \psi(x), \ i = 1,2 \).

\[ a_{i}^\dagger = \frac{1}{N} \sum_k e^{-i\mathbf{k} \cdot \mathbf{x}_i} A_k^\dagger \]  

(12)

\[ a_{i} = \frac{1}{N} \sum_k e^{-i\mathbf{k} \cdot \mathbf{x}_i} A_k \]  

(13)

\[ b_{i}^\dagger = \frac{1}{N} \sum_k e^{i\mathbf{k} \cdot (\mathbf{x}_i + \mathbf{c}_s)} B_k \]  

(14)

\[ b_{i} = \frac{1}{N} \sum_k e^{-i\mathbf{k} \cdot (\mathbf{x}_i + \mathbf{c}_s)} B_k \]  

(15)

Since the spin does not play an important role, the subindex will be omitted and the sum over \( s = \pm 1 \), only the contribution of the first Hamiltonian neighbors are considered. Then, it is obtained:
From here, performing a suitable computation, we get:

$$\sum_{\langle i,j \rangle} a_j^\dagger b_j = \sum_k \frac{1}{N} \sum_i e^{-ik \cdot x_i} A_k^\dagger \frac{1}{N} \sum_{k'} e^{ik' \cdot (x_j + c_3)} B_{k'}^\dagger$$  \hspace{1cm} (16)

Now, we obtained the contributions of the second neighbour, where its first term is:

$$\sum_{\langle i,j \rangle} a_j^\dagger a_j = \sum_k (e^{ik \cdot a_1} + e^{ik \cdot a_2} + e^{ik \cdot (a_1 - a_2)}) A_k^\dagger A_j$$  \hspace{1cm} (17)

And the second term of the contribution of the second neighbour is:

$$\sum_{\langle i,j \rangle} b_j^\dagger b_j = \sum_k (e^{ik \cdot a_1} + e^{ik \cdot a_2} + e^{ik \cdot (a_1 - a_2)}) B_k^\dagger B_j$$  \hspace{1cm} (18)

Actually, the Hamiltonian in the Tight Binding approach can be expressed as follows:

$$H = -t \sum_k ((1 + e^{ik \cdot a_1} + e^{ik \cdot a_2}) e^{ik \cdot c_3} A_k^\dagger B_k + h.c.)$$

$$-t' \sum_k ((e^{ik \cdot a_1} + e^{ik \cdot a_2} + e^{ik \cdot (a_1 - a_2)}) (A_k^\dagger A_k + B_k^\dagger B_k) + c.h.)$$  \hspace{1cm} (20)

This Hamiltonian can be written in the matrix way as follows:

$$H = \sum_k \begin{pmatrix} A_k^\dagger & B_k^\dagger \end{pmatrix} \begin{pmatrix} C & D \\ D^* & C \end{pmatrix} \begin{pmatrix} A_k \\ B_k \end{pmatrix}$$  \hspace{1cm} (21)

Where C and D are defined as follows:

$$C = -t' ((e^{i \cdot a_1} + e^{-i \cdot a_1}) + (e^{i \cdot a_2} + e^{-i \cdot a_2})$$

$$+ (e^{i \cdot (a_1 - a_2)} + e^{-i \cdot (a_1 - a_2)})$$

$$D = -t (1 + e^{i \cdot a_1} + e^{-i \cdot a_2})$$

Diagonalizing this new Hamiltonian, the energy bands turn out to be:

$$E(k) = C \pm D$$  \hspace{1cm} (22)

If we define the following function \(f(k)\) as:

$$f(k) = 3 + 4 \cos\left(\frac{3k_1 a}{2}\right) \cos\left(\frac{\sqrt{3} k_2 a}{2}\right) + 2 \cos(\sqrt{3} k_2 a)$$

The energy is expressed as follows:

$$E_{\pm}(k) = \pm t \sqrt{f(k)} - t' [f(k) - 3]$$  \hspace{1cm} (23)
3.2 Tight Binding model applied to bilayer Graphene

The graphene bilayer consists of 2 parallel graphene monolayers [7,8,9,10]. In this case there are 4 atoms in the unit cell with unequivalent sites A1, B1 and A2, B2 on the bottom and top graphene sheets, respectively [2] as shown in Figure 2. Each site B1 of the lower layer is directly below A2 [2]. The unit vectors are the same for bilayer and monolayer graphene.

![Figure 2. Structure bilayer graphene. The orange shown path goes from A1 to B2 giving the weak coupling $\gamma_{A1B2}$ and is defined as $\gamma_3$.](image)

The Tight Binding model of the graph was used adapting the parametrization of Slonczewski-Weiss-McClure [2,9,10] of relevant couplings in order to model the graphene bilayers. The jump in the plane is parametrized by the coupling $\gamma_{A1B1} \equiv \gamma_{A2B2} \equiv \gamma_0$, with a velocity $v = (\sqrt{3}/2)a\gamma_0/h$, where $a$ is the constant parameter. Additionally, we take into account the strong coupling between layers $\gamma_{A2B1} \equiv \gamma_1$, within between the pairs of A2B1 orbitals that are directly below and above the other. As the strong coupling produces dimmers of those pairs of orbitals A2B1 leaving the formation of high band energies. In addition, the weak coupling A1-B2, $\gamma_{A1B2} \equiv \gamma_3$, was included, which leads to an effective velocity $v_3 = (\sqrt{3}/2)a\gamma_3/h$, where $v_3 \ll v$.

The Hamiltonian is written near the centres of the valleys in a base corresponding to the wave functions:

$$
\Psi = (\psi_{A1}, \psi_{B2}, \psi_{A2}, \psi_{B1}) \quad \text{en el valle } k \quad \text{(24)}
$$

$$
\tilde{\Psi} = (\psi_{B2}, \psi_{A1}, \psi_{B1}, \psi_{A2}) \quad \text{en el valle } \tilde{k} \quad \text{(25)}
$$

$$
H = \xi \begin{pmatrix}
-\frac{1}{2} \Delta & v_{3\pi} & 0 & v_{7\gamma} \\
& v_{3\pi} & -\frac{1}{2} \Delta & v_{7\gamma} \\
& v_{7\gamma} & -\frac{1}{2} \Delta & 0 \\
v_{7\gamma} & 0 & \xi_{7\gamma} & -\frac{1}{2} \Delta
\end{pmatrix}
$$

Where $\pi^- = p_x + ip_y$, $\pi^+ = p_x - ip_y$, $P = (p_x, p_y)$ is the momentum measured with respect to $k$ point. When the magnetic field is zero, $H$ has four degenerate bands valley $\epsilon^{(x\alpha)}_\pm(P)$, $\alpha=1,2$

$$
\epsilon^{(x\alpha)} = \frac{\gamma^2}{2} + \frac{\Delta^2}{4} + (v^2 + \frac{v_3^2}{2})p^2 +
$$

$$
(-1)^2 \left[ \frac{(\gamma^2 - v_3^2p^2)^2}{4} + v^2p^2(\gamma^2 + \Delta^2 + v_3^2p^2) + 2\xi v_3v^2p^3\cos 3\phi \right]^{\frac{1}{2}} \quad \text{(26)}
$$
The dispersion $\varepsilon^{(\chi2)}_\pm$ shows that there are 2 bands with energies greater than $\gamma_1$ and 2 bands with energies less than $\gamma_1$, these do not touch the point k. These bands are the result of the strong pairing $\gamma_1$ between the upper and lower layers.

4. Conclusions

- The Tight Binding model was applied to the monolayer and bilayer graphene, obtaining the energies of the band structure. The results show a low energy electronic band structure in the case of bilayer graphene.
- In the case of monolayer graphene, it has 2 electronic bands, while the graphene bilayer has 4 electronic bands of which 2 are conduction and 2 are valence.
- Both, the monolayer and the bilayer graphene, have electronic bands with a gap equivalent to zero.

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