

ENERGY DISPERSION OF GRAPHENE BEYOND THE NEAREST NEIGHBOR ELECTRON HOPPING

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Abstract

In this paper, we solve, by using tight binding approximation approach, the energy dispersion relation of monolayer graphene beyond the nearest neighbour electron hopping and show their contribution to the electronic properties of graphene. The first three nearest neighbours have been found and an axiom is proposed to take care of the periodicity of the lattice.

1. Introduction

Graphene is a two-dimensional (2D) crystal made out of carbon atoms arranged on a hexagonal (honeycomb) structure. Although it has been experimentally isolated only recently (2004) [1], graphene has been the object of theoretical investigations for more than 60 years, because it represents the simplest structure to understand the electronic properties of all other allotropes of carbon with sp^2 hybridization [2]. Each atom is tied to its three nearest neighbours via strong bonds that lie in the graphene plane with angles of 120° . The bond is a result of the sp^2 hybridization of the 2s, $2p_x$, and $2p_y$ orbitals for the three valence electrons. The fourth valence electron is in the $2p_z$ orbital that is orthogonal to the graphene plane. A weak bond is formed by the overlap of half-filled $2p_z$ orbitals with other $2p_z$ orbitals. The transport properties of graphene are determined by these delocalized electrons and its structural flexibility is reflected in its electronic properties [3]. The sp^2 hybridization between 1s orbital and 2p orbitals leads to a trigonal planar structure with a formation of a bond between carbon atoms that are separated by 1.42 Å. The band is responsible for the robustness of the lattice structure in all allotropes. Due to the Pauli principle, these bands have a filled shell and, hence, form a deep valence band. The unaffected p orbital, which is perpendicular to the planar structure, can bind covalently with neighbouring carbon atoms, leading to the formation of a band. Since each p orbital has one extra electron, the band is half filled [4]. The most important aspect of graphene's energy dispersion (and the one attracting most attention) is its linear energy-momentum relationship with the conduction and valence bands intersecting at the Dirac points, with no energy gap [5]. Graphene is thus a zero band-gap semiconductor with linear rather than quadratic long wavelength energy dispersion for both electrons (holes) in the conduction (valence) bands. Therefore, we would like to investigate the effect of the first, second and third nearest neighbours on the energy dispersion of graphene and consequently propose an axiom for the periodicity of the lattice.

2. Theoretical Analysis

a. Energy dispersion relation of graphene in its first nearest neighbor electron hopping

The Hamiltonian for arbitrary electron is given by

$$\hat{H} = \frac{\hbar^2}{2m} \Delta + \sum_{j=1}^N V(r - R_j) \quad (1)$$

In order to derive the band structure of graphene (E-K) relation, we solve the Schrodinger's equation as follows

$$\hat{H}\psi = E\psi \quad (2)$$

The total wave function ψ can be written as a linear combination of two Bloch functions u_A and u_B as follows [6]

$$\psi(\vec{k}, \vec{r}) = C_A u_A(\vec{k}, \vec{r}) + C_B u_B(\vec{r}) \quad (3)$$

By substituting equation (3) into equation (2), multiplying by the complex conjugate of u_A^* and u_B^* and integrating over the entire space, we can re-write the Schrodinger's equation in equation (2) as follows

$$\begin{pmatrix} E_A - E & \hat{H}_{AB} - ES_{AB} \\ \hat{H}_{BA} - ES_{BA} & E_B - E \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = 0 \quad (4)$$

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Where S_{AB} and S_{BA} are the overlapping between wave functions of atoms A and B

To get a non-trivial solution of equation (4), the determinant of the matrix must vanish, therefore

$$E = H_{AA} \pm |H_{AB}| \tag{5}$$

To evaluate the matrix elements which are given in equation (5), the assumptions from the tight binding approximation are used

$$u_{A(B)}(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{A(B)}^N e^{i\vec{k}\cdot\vec{r}} A(B) X(\vec{r} - \vec{r}_{A(B)}) \tag{6}$$

where $X(\vec{r})$ is the orbital $2p_z$ wave function for an isolated carbon atom, N is the number of the unit cell [7].

The diagonal matrix elements H_{AB} can be calculated as follows

$$H_{AB} = \frac{1}{N} \sum_i e^{-i\vec{k}\cdot\vec{R}_i} \int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) \tag{7}$$

Where \vec{R}_i are the vectors connecting atom A to its three nearest neighbour atoms B. Equation (7) becomes

$$H_{AB} = (e^{-i\vec{k}\cdot\vec{R}_1} + e^{-i\vec{k}\cdot\vec{R}_2} + e^{-i\vec{k}\cdot\vec{R}_3}) \int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) d\tau \tag{8}$$

Where $\int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) d\tau = \gamma_0$ is the transfer integral on the nearest neighbour interaction

$$H_{AB} = (e^{-i\vec{k}\cdot\vec{R}_1} + e^{-i\vec{k}\cdot\vec{R}_2} + e^{-i\vec{k}\cdot\vec{R}_3}) \gamma_0 \tag{9}$$

But $\vec{R}_1 = (\frac{a}{\sqrt{3}}, 0)$, $\vec{R}_2 = (\frac{-a}{2\sqrt{3}}, \frac{a}{2})$, $\vec{R}_3 = (\frac{-a}{2\sqrt{3}}, \frac{-a}{2})$

Substituting the coordinates into equation (8) and multiplying the result by its conjugate gives

$$H_{AB} = \gamma_0 \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}}{2} k_x a\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)} \tag{10}$$

Therefore, the energy dispersion for the first nearest neighbours in a closed form is

$$E = E_0 \pm |H_{AB}| \tag{11}$$

$$E(k) = E_0 \pm \gamma_0 \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}}{2} k_x a\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)} \tag{12}$$

$$E = E_0 \pm \gamma_0 \sqrt{1 + 4 \cos\alpha \cos\beta + 4 \cos^2\beta} \tag{13}$$

Where $\alpha = \frac{\sqrt{3}}{2} k_x a$ and $\beta = \frac{k_y a}{2}$

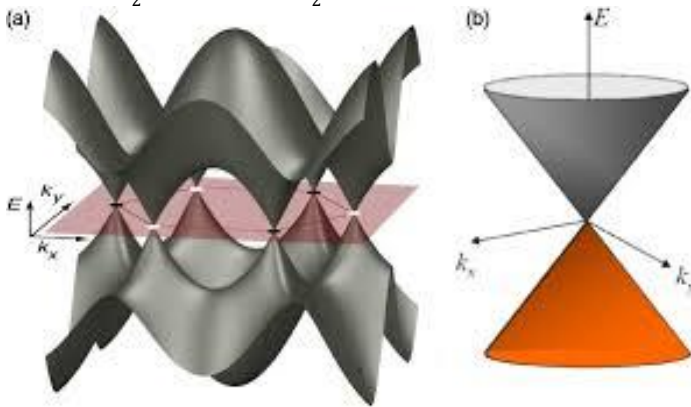


Fig. 1: The focus on the Dirac points in the dispersion relation which show a conical shape

b. Energy dispersion relation of graphene in its second nearest neighbor electron hopping

The atoms in this site are geometrically similar to atom A (the origin atom) and the Hamiltonian is represented by

$$H_{AA}$$

The diagonal matrix elements (H_{AA}) can be calculated as follows

$$H_{AA} = \frac{1}{N} \sum_A \sum_{A^*} e^{i\vec{k}\cdot(\vec{r}_A - \vec{r}_{A^*})} \int X^*(\vec{r} - \vec{r}_A) H X(\vec{r} - \vec{r}_{A^*}) d\tau \tag{14}$$

To calculate the matrix elements in equation (14), we consider the six atoms (the next nearest neighbour atoms) in this site

Equation (14) can be re-written as

$$H_{AA} = \frac{1}{N} \sum_i e^{-i\vec{k}\cdot\vec{R}_i} \int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) d\tau \tag{15}$$

$$H_{AA} = (e^{-i\vec{k}\cdot\vec{R}_1} + e^{-i\vec{k}\cdot\vec{R}_2} + e^{-i\vec{k}\cdot\vec{R}_3} + e^{-i\vec{k}\cdot\vec{R}_4} + e^{-i\vec{k}\cdot\vec{R}_5} + e^{-i\vec{k}\cdot\vec{R}_6}) \int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) d\tau \tag{16}$$

Where $\int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) d\tau = \gamma_1$ is the transfer integral on the next nearest neighbour interaction

$$H_{AA} = (e^{-i\vec{k}\cdot\vec{R}_1} + e^{-i\vec{k}\cdot\vec{R}_2} + e^{-i\vec{k}\cdot\vec{R}_3} + e^{-i\vec{k}\cdot\vec{R}_4} + e^{-i\vec{k}\cdot\vec{R}_5} + e^{-i\vec{k}\cdot\vec{R}_6}) \gamma_1 \tag{17}$$

The vector coordinates are geometrically calculated as

$$\left. \begin{aligned} \vec{R}_1 &= \left(\frac{a\sqrt{3}}{3}, \frac{a}{2}\right), \vec{R}_2 = \left(\frac{a\sqrt{3}}{2}, \frac{-a}{2}\right), \vec{R}_3 = (0, -a), \\ \vec{R}_4 &= \left(-\frac{a\sqrt{3}}{3}, \frac{a}{2}\right), \vec{R}_5 = (0, -a), \vec{R}_6 = \left(-\frac{a\sqrt{3}}{2}, \frac{-a}{2}\right) \end{aligned} \right\} \quad (18)$$

Substituting the values of all the vectors in equation (18) yields

$$H_{AA} = (e^{-ik_x \frac{a\sqrt{3}}{2}} + e^{ik_x \frac{a\sqrt{3}}{2}}) (e^{-ik_y \frac{a}{2}} + e^{ik_y \frac{a}{2}}) + e^{-ik_y a} + e^{ik_y a} \quad (19)$$

$$H_{AA} = 4 \cos k_x \frac{a\sqrt{3}}{2} \cos k_y \frac{a}{2} + 2 \cos k_y a \quad (20)$$

Therefore, the energy band derived from this Hamiltonian for the second nearest neighbor takes the form

$$E(k) = \gamma_1 (4 \cos k_x \frac{a\sqrt{3}}{2} \cos k_y \frac{a}{2} + 2 \cos k_y a) \quad (21)$$

$$E_2(\alpha, \beta) = \gamma_1 (4 \cos \alpha \cos \beta + 2 \cos 2\beta) \quad (22)$$

$$E_2(\alpha, \beta) = \gamma_1 (4 \cos \alpha \cos \beta + 4 \cos^2 \beta - 2) \quad (23)$$

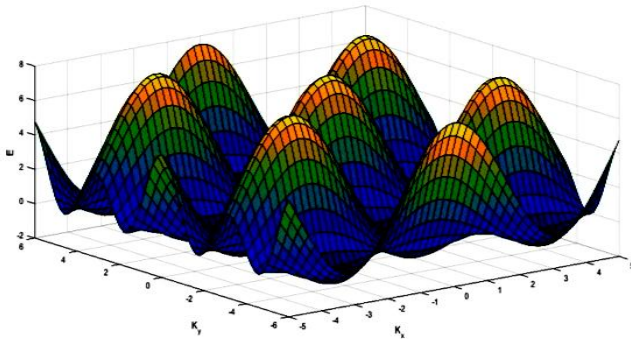


Fig.2. Band structure of graphene for the second nearest neighbor electron hopping

c. Energy Dispersion of Graphene in its Third Nearest Neighbor Hopping

The atoms in this site are geometrically similar to atoms B (the first nearest neighbour atoms) and the Hamiltonian is represented by H_{AB}

The diagonal matrix elements (H_{AB}) can be calculated as follows

$$H_{AB} = \frac{1}{N} \sum_A \sum_{B^*} e^{-i\vec{k} \cdot (\vec{r}_A - \vec{r}_{B^*})} \int X^*(\vec{r} - \vec{r}_A) H X(\vec{r} - \vec{r}_{B^*}) d\tau \quad (24)$$

To calculate the matrix elements in equation (24), we consider the nine atoms (the next nearest neighbour atoms) in this site

$$H_{AB} = \frac{1}{N} \sum_i e^{-i\vec{k} \cdot R_i} \int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) d\tau \quad (25)$$

$$\begin{aligned} H_{AB} &= (e^{-i\vec{k} \cdot R_1} + e^{-i\vec{k} \cdot R_2} + e^{-i\vec{k} \cdot R_3} + e^{-i\vec{k} \cdot R_4} + e^{-i\vec{k} \cdot R_5} \\ &+ e^{-i\vec{k} \cdot R_6} + e^{-i\vec{k} \cdot R_7} + e^{-i\vec{k} \cdot R_8} + e^{-i\vec{k} \cdot R_9}) \int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) d\tau \end{aligned} \quad (26)$$

Where $\int X^*(\vec{r}) H X(\vec{r} - \vec{R}_i) d\tau = \gamma_2$ is the transfer integral on the next next nearest neighbour interaction

The connecting vectors are calculated geometrically as

$$\left. \begin{aligned} \vec{R}_1 &= \left(\frac{5a\sqrt{3}}{6}, \frac{-a}{2}\right), \vec{R}_2 = \left(\frac{5a\sqrt{3}}{6}, \frac{a}{2}\right), \vec{R}_3 = \left(\frac{a\sqrt{3}}{3}, a\right) \\ \vec{R}_4 &= \left(-\frac{a\sqrt{3}}{6}, \frac{3a}{2}\right), \vec{R}_5 = \left(-\frac{2a\sqrt{3}}{3}, a\right), \vec{R}_6 = \left(-\frac{2a\sqrt{3}}{3}, 0\right) \\ \vec{R}_7 &= \left(-\frac{2a\sqrt{3}}{3}, 0\right), \vec{R}_8 = \left(-\frac{a\sqrt{3}}{6}, \frac{-3a}{2}\right), \vec{R}_9 = \left(\frac{a\sqrt{3}}{3}, a\right) \end{aligned} \right\} \quad (27)$$

$$\begin{aligned} H_{AB} &= e^{-ik_x \frac{5a\sqrt{3}}{6}} \left(e^{ik_y \frac{a}{2}} + e^{-ik_y \frac{a}{2}} \right) + e^{-ik_x \frac{a\sqrt{3}}{3}} (e^{-ik_y a} + e^{ik_y a}) + \\ & (e^{ik_y \frac{3a}{2}} + e^{-ik_y \frac{3a}{2}}) + e^{ik_x \frac{2a\sqrt{3}}{3}} (e^{-ik_y a} + e^{ik_y a}) + e^{-ik_x \frac{2a\sqrt{3}}{3}} \end{aligned} \quad (28)$$

$$\begin{aligned} H_{AB} &= 2e^{-ik_x \frac{5a\sqrt{3}}{6}} \cos k_y \frac{a}{2} + 2e^{ik_x \frac{a\sqrt{3}}{3}} \cos k_y a + 2e^{ik_x \frac{a\sqrt{3}}{6}} \cos k_y \frac{3a}{2} \\ & + 2e^{ik_x \frac{2a\sqrt{3}}{3}} \cos k_y a + e^{-ik_x \frac{2a\sqrt{3}}{3}} \end{aligned} \quad (29)$$

Multiplying by its conjugate H_{AB}^* and simplifying the terms yields the energy dispersion of graphene for the third nearest neighbor electron hopping in terms of α and β

$$E_3(\alpha, \beta) = E_0 \pm \gamma_2 [1 + 4\cos^2\beta + 4\cos^23\beta + 4\cos2\beta + 8\cos^22\beta + 4\cos\alpha\cos3\beta + 8\cos\alpha\cos3\beta\cos2\beta + 4\cos2\alpha\cos2 + 8\cos2\alpha\cos^22\beta + 8\cos\alpha\cos3\beta\cos2\beta + 4\cos3\alpha\cos + 8\cos3\alpha\cos\beta\cos2\beta + 8\cos2\alpha\cos\beta\cos3\beta + 8\cos\alpha\cos\beta\cos2\beta]^{\frac{1}{2}} \quad (30)$$

3. Results and discussion

Equation (12) gives the energy dispersion relation of graphene and at the Dirac points, $(\alpha, \beta) = (0, \frac{2\pi}{3}), (\pi, -\frac{\pi}{3}), (-\pi, \frac{\pi}{3})$, divided the band structure in two non-equivalent set of three points which is half filled with a filled conduction band and empty valence band as shown in fig.1. Equation (21) shows the energy dispersion relation of graphene in the second nearest neighbour electron hopping and at its Dirac points, the band structure is set to a completely filled conduction band as shown in fig.2. Finally, equation (30) presents the energy dispersion of graphene in the third nearest neighbour electron hopping and its energy band structure is predicted to be similar to that in equation (12) (nearest neighbour) due to its linearization at the Dirac points.

4. Conclusion

This paper shows that, the first and third nearest neighbour electron hopping of the dispersion relation of graphene have their conducting and valence band meet at the Dirac point while the second nearest neighbour dispersion relation only result to an energy renormalization. Therefore, we conclude that only the odd nearest neighbour electron hopping are the ones that contribute to the electronic properties of graphene.

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