
Research Note

Abstract

Graphene is one of the most important two-dimensional materials in modern physics. This note reports the electron properties of graphene based on the tight binding models, including the Dirac point, density of state and some existed experimental evidence of these properties.

The Tight-Binding Model

When we apply tight binding model to a physics state, we have potentially considered that the many-electrons problem can be reduced to a one-electron problem by Hartree-Fock Theory or by the density functional theory[3]. We skip these theories and naively write down a simple one-electron Hamiltonian.

$$\left[\frac{p^2}{2m} + V(\mathbf{r}) \right] \Psi = E\Psi \quad (1)$$

, where V has periodic crystalline potential.

According to the Bloch Theory, the eigenfunctions associated with eigenvalue E of equation (1) take this form:

$$\Psi(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{k}, \mathbf{r}) \quad (2)$$

We apply the Fourier inverse transform on equation (2) and easily derive a new function.

$$W(\mathbf{t}_n, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{t}_n} \Psi(\mathbf{k}, \mathbf{r}) \quad (3)$$

$$\Psi(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{t}_n} e^{i\mathbf{k} \cdot \mathbf{t}_n} W(\mathbf{t}_n, \mathbf{r}) \quad (4)$$

known as Wannier Functions. It is not hard to check that

$$W(\mathbf{t}_n + \mathbf{t}_m, \mathbf{r} + \mathbf{t}_m) = W(\mathbf{t}_n, \mathbf{r}) \quad (5)$$

That is to say:

$$W(\mathbf{t}_n, \mathbf{r}) = W(\mathbf{r} - \mathbf{t}_n) \quad (6)$$

, which implies that the Wannier function locates at \mathbf{t}_n is the translation of the one

locates at referential point.

We want to ask: Are Wannier functions localized?

It is not clear from the definition. But the tight binding model assume that the Wannier functions is the *linear combine of atomic orbital*. Apparently, it is localized and only depends on the distance from t_n . To make it easy to calculate, we define the Bloch sum as:

$$\Phi_i(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{t_n} e^{i\mathbf{k} \cdot \mathbf{t}_n} \phi_i(\mathbf{r} - \mathbf{t}_n) \quad (7)$$

And the Bloch wave functions take this form:

$$\Psi(\mathbf{k}, \mathbf{r}) = \sum_i c_i(\mathbf{k}) \Phi_i(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{t_n} e^{i\mathbf{k} \cdot \mathbf{t}_n} \sum_i c_i(\mathbf{k}) \phi_i(\mathbf{r} - \mathbf{t}_n) \quad (8)$$

To solve the eigen problem, we expand H under the base of $\Phi_i(\mathbf{k}, \mathbf{r})$. There existing a non-zero parameter c if and only if[3]:

$$\| \langle \Phi_j(\mathbf{k}, \mathbf{r}) | H | \Phi_i(\mathbf{k}, \mathbf{r}) \rangle - E \langle \Phi_j(\mathbf{k}, \mathbf{r}) | \Phi_i(\mathbf{k}, \mathbf{r}) \rangle \| = 0 \quad (9)$$

This equation can be solved by modern computational technique; frequently, however, the tight-binding method is used in a semi-empirical way. The semi-empirical tight-binding model adopt some drastic assumptions, but meaningful since it corresponds to experiment.

Assumptions[3]:

1. Crystal potential can be expressed as a sum of atomic-like potentials $H = \frac{p^2}{2m} + \sum_{t_n} V_a(r - t_n)$.
2. Atomic orbit is the eigenfunctions of $H = \frac{p^2}{2m} + V_a(r - t_n)$ associated with eigenvalues E_i .
3. Only the nearest overlaps and interactions are token account.
4. Integrals involving three different centers (Like the interaction between Position 1 and Position 2 due to the potential at Position 3) are considered negligible.

Finally, we deduce a simple expression

$$M_{ij} = E_i \delta_{ij} + \sum_{t_l} e^{i\mathbf{k} \cdot \mathbf{t}_l} \int \phi_i^*(r) V_a(r - t_l) \phi_j^*(r - t_l) \quad (10)$$

The integration has been calculated by J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498(1954), which express equation (10) in a set of independent parameters. If the integration is not independent of lattices vector, we can separate it into geometric term $F(k)$ and a constant t .

Electron properties of graphene

Here we calculate the electron properties of graphene.

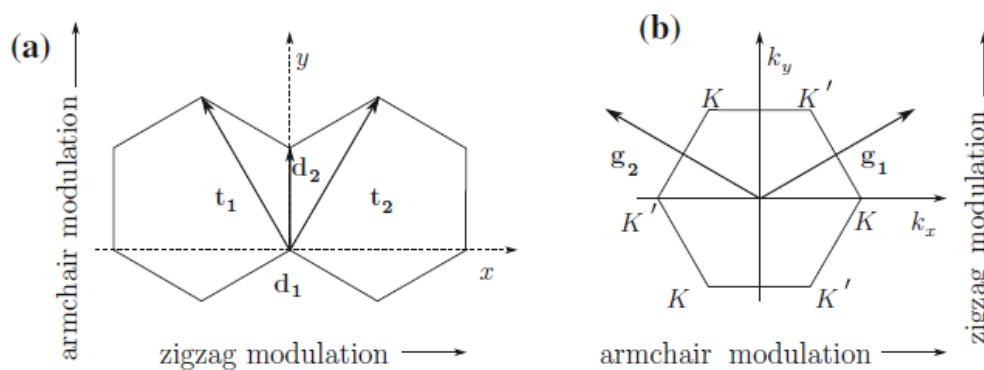


Figure 1 Geometric Structure of Graphene[3]

Graphene is one of the most important 2-D materials. It is worthwhile to study it carefully.

There are two different carbon atoms in per unit cells, so the geometric description of graphene is shown in Figure 1

$$\begin{cases} t_1 = a \left(-\frac{1}{2}, \frac{\sqrt{3}}{2} \right) \\ t_2 = a \left(\frac{1}{2}, \frac{\sqrt{3}}{2} \right) \\ d_1 = 0 \\ d_2 = a \left(0, \frac{\sqrt{3}}{3} \right) \end{cases} \quad (11)$$

And vectors in reciprocal space is $K, K' = \frac{2\pi}{a} \left(\pm \frac{2}{3}, 0 \right)$

The electronic configuration of the carbon atom is $1s^2 2s^2 2p^2$. It seems that we must handle a 12×12 determinate which is a terrible work. We use some chemical and physics to simplify our works.

Since the $1s$ orbit is highly localized near the nuclear, so the interactions of $1s$ and other orbits are neglectable. The question is quickly separated into a 4×4 and an 8×8 . As for four valence electrons, the s , p_x , and p_y orbitals of carbon atoms form the

graphene sheet by sp^2 hybridization and connected by co-planar bond rather than interacted by p_z electron[2][3], so the question separates again. They do not take part in conductivity. Only when we are interested in the forming of graphene sheet will we discuss this 6×6 determinate.

For π -bands, we start from the two basis Bloch sums[3]

$$\Phi_{1,2}(k, r) = \sum_{t_n} e^{ikt_n} \phi_{p_z}(r - d_{1,2} - t_n) \quad (12)$$

And we neglected the overlap of wave functions centered on different atoms, that is[2]

$$\int \phi_{p_z}(r - d_1 - t_n) \phi_{p_z}(r - d_2) dr = 0 \quad (13)$$

Applying the equation (10) and equation (9) and notice that the integration is not independent of lattices vector since the high symmetry, we have[3]:

$$\begin{vmatrix} E_p - E & tF(k) \\ tF^*(k) & E_p - E \end{vmatrix} = 0 \quad (14)$$

Where $F(k) = \sum_{t_l} e^{ikt_l}$ and $t_l = 0, -t_1, -t_2$

$$\begin{aligned} F(k) &= 1 + e^{-ia\left(\frac{k_x}{2} + \frac{\sqrt{3}k_y}{2}\right)} + e^{-ia\left(-\frac{k_x}{2} + \frac{\sqrt{3}k_y}{2}\right)} \\ &= 1 + 2 \cos \frac{k_x a}{2} \left(\cos \frac{\sqrt{3}k_y a}{2} + i \sin \frac{\sqrt{3}k_y a}{2} \right) \end{aligned}$$

So,

$$(E_p - E)^2 = t^2 |F(k)|$$

Usually, we set $E_p = 0$.

So, it comes to

$$E = \pm t \sqrt{1 + 4 \cos^2 \frac{k_x a}{2} + 4 \cos \frac{k_x a}{2} \cos \frac{\sqrt{3}k_y a}{2}} \quad (16)$$

We plot it by MATLAB. In Figure 1, the blue hexagon represents the first Brillouin zone, and the energy is in unit of t . We can notice that near the boundary of first Brillouin zone (K, K'), the two energy levels degenerate.

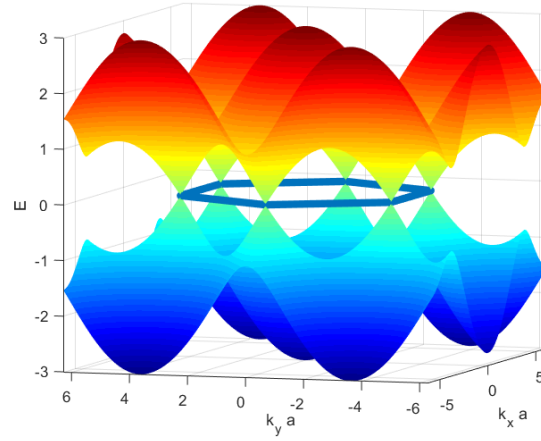


Figure 2 Energy Band of Graphene

Here we calculate this property shown in Figure 3, known as Dirac Point that the energy is linear dependent of k .

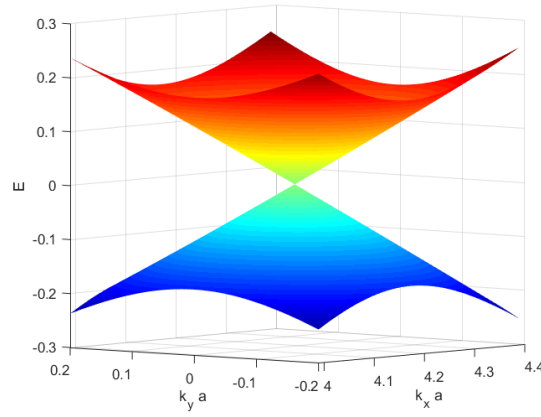


Figure 3 The Dirac Cone of Graphene

At the Dirac Point $K = \frac{2\pi}{a} \left(\frac{2}{3}, 0 \right)$, expand the $F(k)$ in Taylor series and neglect the 2-order terms.

$$F(k) = 1 + \left(-1 - \frac{\sqrt{3}}{2} a k_x \right) \left(1 - i \frac{\sqrt{3}}{2} a k_y \right) = -\frac{\sqrt{3}}{2} a (k_x - i k_y) \quad (17)$$

From Equation (14), we got

$$E(k) = \pm t \frac{\sqrt{3}}{2} a (k_x^2 + k_y^2) = \pm t \frac{\sqrt{3}}{2} a |k| \quad (18)$$

Define Fermi velocity as $v_F = \frac{\sqrt{3}}{2\hbar} a t$, we have $E(k) = \pm v_F \hbar |k|$. This name origin

from the definition of electron velocity $v(k) = \frac{1}{\hbar} \frac{\partial E}{\partial k}$, which is a constant number about 10^6m/s in graphene. Meanwhile, according to definition of electron's effective mass[3] $\frac{1}{m^*} = \frac{1}{\hbar} \frac{\partial^2 E}{\partial k^2}$, the mass of electron in graphene at the Dirac Point is massless. *Carriers are massless, and its velocity is near the lightspeed at the Dirac point.*

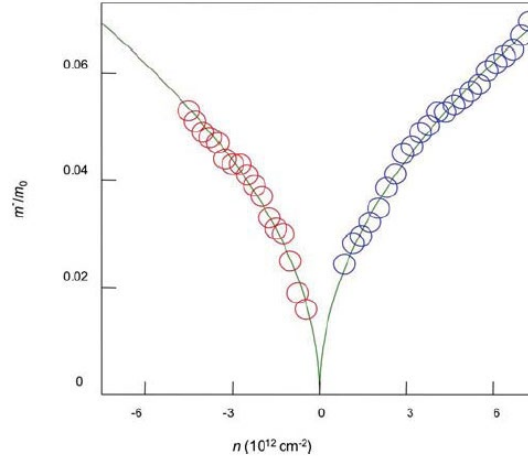


Figure 4 Experimental result of DOS of graphene[1]

Figure 4 shows the result of DOS of graphene. Fitting the experimental point with theoretic prediction, we can determine the Fermi velocity and parameter t .

Reference

- [1] Neto, A. C., Guinea, F., Peres, N. M., Novoselov, K. S., & Geim, A. K. (2009). The electronic properties of graphene. *Reviews of modern physics*, 81(1), 109.
- [2] Wallace, P. R. (1947). The band theory of graphite. *Physical Review*, 71(9), 622.
- [3] Grosso, G., & Parravicini, G. P. (2014). *Solid State Physics (Second Edition)*.