Dirac electron in graphene

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Graphene is a single sheet of carbon atoms arranged in the well known honeycomb structure. Carbon has four valence electrons, of which three are used for the sp^2 bonds. We are concerned with the band structure of the fourth electrons. Chemists refer to this band as the π band. Thinking in terms of atomic orbitals this fourth electron is in a p_z orbital. Note that there are two such electrons. Thus there will be two π bands (the π and π^+ bands). There are two electrons per unit cell consisting the carbon atoms in the sublattice A and B.

1. Crystal structure of graphene

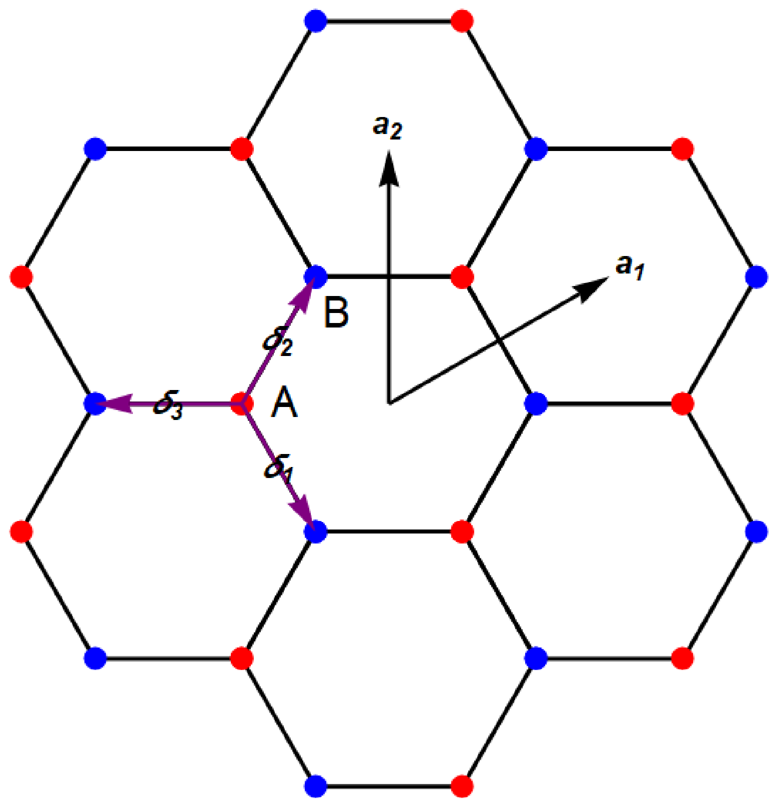


Fig. Carbon atoms on the graphene.

First we discuss the structure of graphene. The nearest neighbor distance:

$$a_0 = 1.42 \text{ Å}.$$

The lattice constant:

$$a = \sqrt{3}a_0 = 2.46\,\text{Å}$$

$$\boldsymbol{\delta}_1 = a_0(\cos\frac{\pi}{3}, -\sin\frac{\pi}{3}) = a_0(\frac{1}{2}, -\frac{\sqrt{3}}{2}),$$

$$\boldsymbol{\delta}_2 = a_0(\cos\frac{\pi}{3}, \sin\frac{\pi}{3}) = a_0(\frac{1}{2}, \frac{\sqrt{3}}{2})$$

$$\boldsymbol{\delta}_3 = a_0(\cos\pi, \sin\pi) = a_0(-1, 0)$$

Primitive lattice

$$\boldsymbol{a}_1 = \boldsymbol{\delta}_2 - \boldsymbol{\delta}_3 = a_0(\frac{3}{2}, \frac{\sqrt{3}}{2}) = \sqrt{3}a_0(\frac{\sqrt{3}}{2}, \frac{1}{2}) = \frac{a_0}{2}(3, \sqrt{3})$$

$$\boldsymbol{a}_2 = \boldsymbol{\delta}_2 - \boldsymbol{\delta}_1 = \sqrt{3}a_0(0, 1)$$

2. Reciprocal lattice and the first Brillouin zone

Reciprocal lattice

$$\boldsymbol{a}_1 \cdot \boldsymbol{b}_1 = \boldsymbol{a}_2 \cdot \boldsymbol{b}_2 = 2\pi$$

or

$$a_1 b_1 \cos\frac{\pi}{6} = 2\pi, \qquad a_2 b_2 \cos\frac{\pi}{6} = 2\pi$$

$$\boldsymbol{a}_1 \cdot \boldsymbol{b}_2 = \boldsymbol{a}_2 \cdot \boldsymbol{b}_1 = 0$$

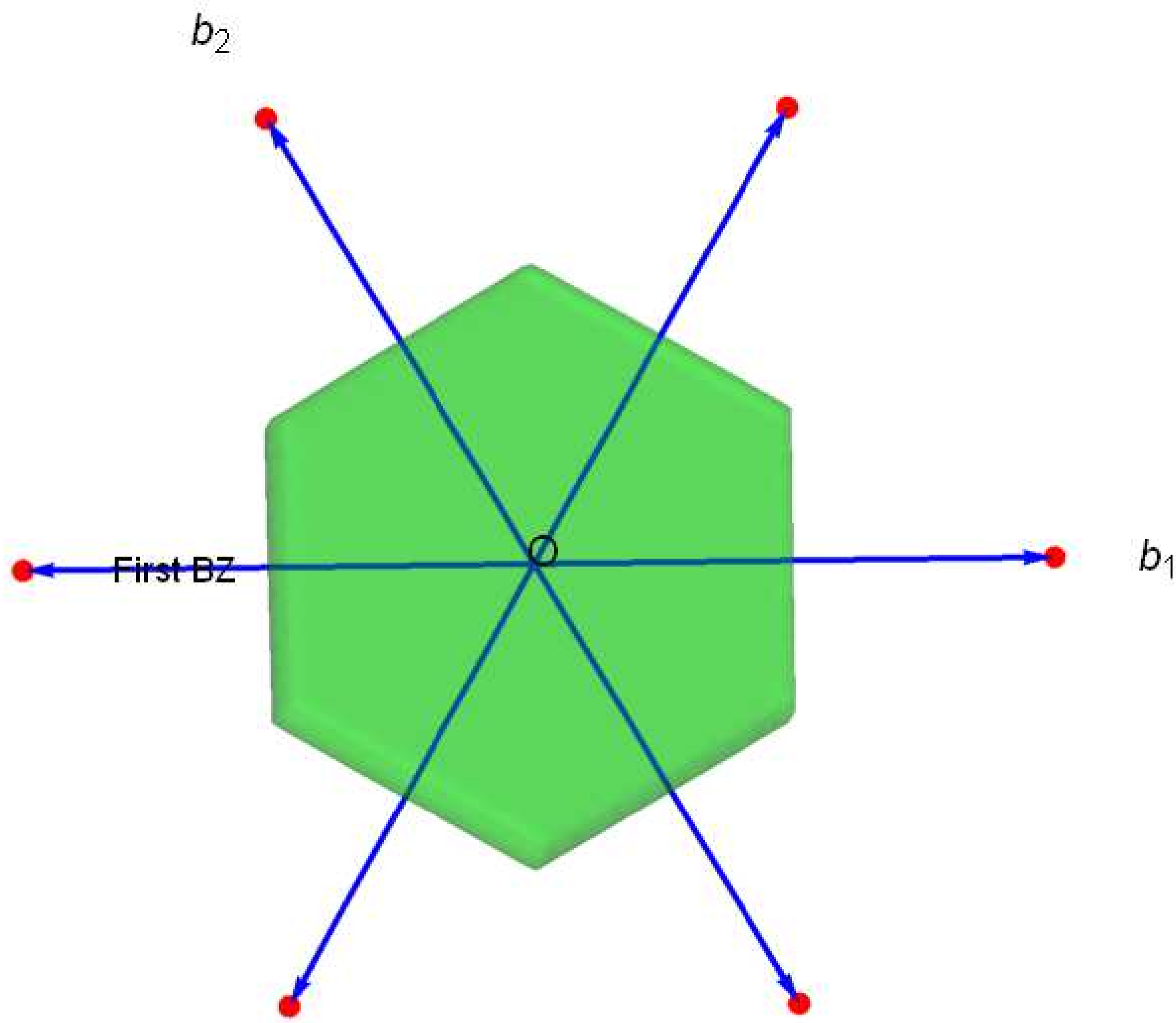
leading to

$$|\boldsymbol{b}_1| = |\boldsymbol{b}_2| = \frac{2\pi}{a_1 \cos\frac{\pi}{6}} = \frac{4\pi}{\sqrt{3}a_1} = \frac{4\pi}{3a_0} = 2.95\,\text{Å}^{-1}.$$

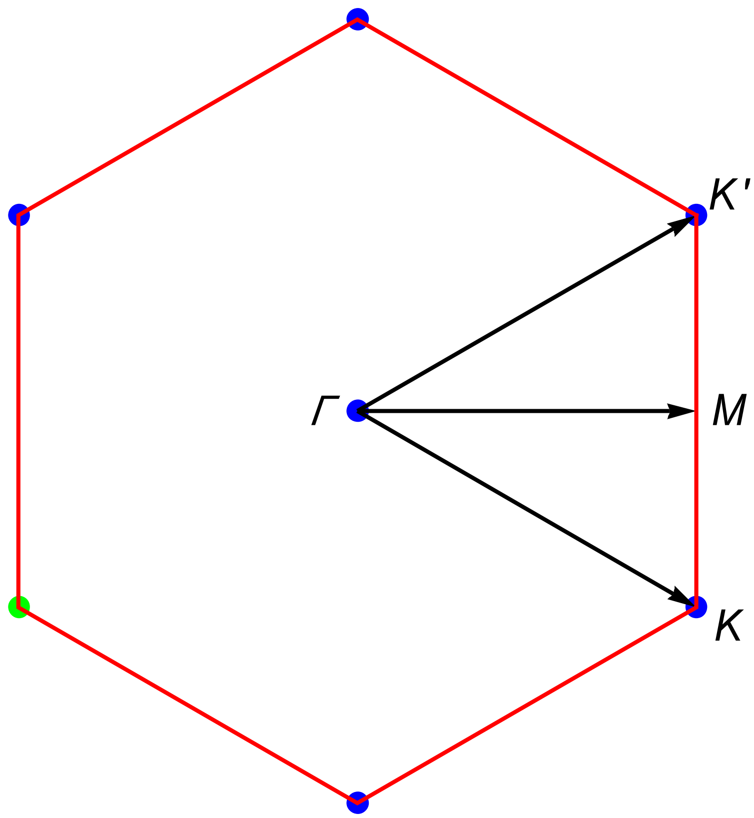
$$\boldsymbol{b}_1 = b_1(1,0) = \frac{4\pi}{3a_0}(1,0)$$

$$\boldsymbol{b}_2 = b_1(\cos\frac{2\pi}{3}, \sin\frac{2\pi}{3}) = \frac{4\pi}{3a_0}(-\cos\frac{\pi}{3}, \sin\frac{\pi}{3}) = \frac{4\pi}{3a_0}(-\frac{1}{2}, \frac{\sqrt{3}}{2}) = \frac{2\pi}{3a_0}(-1, \sqrt{3})$$

$$\boldsymbol{b}_1 + \boldsymbol{b}_2 = \frac{2\pi}{3a_0}(1, \sqrt{3})$$



The first Brillouin zone



$$\boldsymbol{K} = \frac{1}{3}(\boldsymbol{b}_1 - \boldsymbol{b}_2) = \frac{2\pi}{3a_0}(1, -\frac{1}{\sqrt{3}})$$

$$\boldsymbol{K}' = \frac{1}{3}(2\boldsymbol{b}_1 + \boldsymbol{b}_2) = \frac{2\pi}{3a_0}(1, \frac{1}{\sqrt{3}})$$

$$\boldsymbol{M} = \frac{\boldsymbol{K} + \boldsymbol{K}'}{2} = \frac{\boldsymbol{b}_1}{2} = \frac{2\pi}{3a_0}(1, 0)$$

3. Tight binding approximation

We define the Bloch sums of p_z atomic orbitals ϕ

$$\psi_{\boldsymbol{q}}{}^{A}(\boldsymbol{r}) = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}} e^{i\boldsymbol{q}\cdot(\boldsymbol{R}+\boldsymbol{\tau}_A)}\phi(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{\tau}_A) \qquad \text{for the site A}$$

$$\psi_{\boldsymbol{q}}{}^{B}(\boldsymbol{r}) = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}} e^{i\boldsymbol{q}\cdot(\boldsymbol{R}+\boldsymbol{\tau}_B)}\phi(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{\tau}_B) \qquad \text{for the site B}$$

The wavefunction of the electron in this tight-binding basis may be expanded as a superposition

$$\psi_{\boldsymbol{q}}(\boldsymbol{r}) = C_A \psi_{\boldsymbol{q}}^{\;A}(\boldsymbol{r}) + C_A \psi_{\boldsymbol{q}}^{\;B}(\boldsymbol{r}).$$

We solve the 2x2 Hamiltonian matrix eigenvalue problem

$$\begin{pmatrix} H_{AA}(\boldsymbol{q}) & H_{AB}(\boldsymbol{q}) \\ H_{BA}(\boldsymbol{q}) & H_{BB}(\boldsymbol{q}) \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = E \begin{pmatrix} C_A \\ C_B \end{pmatrix}$$

where the matrix is given by

$$H(\boldsymbol{q}) = \begin{pmatrix} H_{AA}(\boldsymbol{q}) & H_{AB}(\boldsymbol{q}) \\ H_{BA}(\boldsymbol{q}) & H_{BB}(\boldsymbol{q}) \end{pmatrix}$$

with

$$H_{ij}(\boldsymbol{q}) = \left\langle \psi_{\boldsymbol{q}}^{\;i} \middle| H \middle| \psi_{\boldsymbol{q}}^{\;j} \right\rangle$$

Since the environments around atoms A and B are identical, by symmetry, $H_{AB}(\boldsymbol{q}) = H_{BA}(\boldsymbol{q})$. Within the nearest-neighbor interaction assumption, $H_{AA}(\boldsymbol{q})$ is a constant, independent of $\boldsymbol{q}$, which we may set to be zero, and $H_{AB}(\boldsymbol{q})$ may be simplified to

$$H_{AB}(\boldsymbol{q}) = \left\langle \phi(\boldsymbol{r} - \boldsymbol{\tau}_A) \middle| H \middle| \phi(\boldsymbol{r} - \boldsymbol{\tau}_B) \right\rangle (e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}_1} + e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}_2} + e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}_3})$$

where $\boldsymbol{\delta}_1$, $\boldsymbol{\delta}_2$, and $\boldsymbol{\delta}_3$ are the vectors pointing from a given *A* atom to its three nearest neighbors. Defining the nearest-neighbor hopping integral as

$$\gamma = \left\langle \phi(\boldsymbol{r} - \boldsymbol{\tau}_A) \middle| H \middle| \phi(\boldsymbol{r} - \boldsymbol{\tau}_B) \right\rangle$$

we have

$$H_{AB}(\boldsymbol{q}) = H_{BA}^{\;*}(\boldsymbol{q}) = \Gamma(\boldsymbol{q})$$

where

$$\Gamma(\boldsymbol{q}) = \sum_{i=1}^{3} e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}_i}$$
$$= e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}_1} + e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}_2} + e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}_3}$$
$$= \exp[ia_0(\frac{1}{2}q_x - \frac{\sqrt{3}}{2}q_y)] + \exp[ia_0(\frac{1}{2}q_x + \frac{\sqrt{3}}{2}q_y)] + \exp(-ia_0 q_x)$$
$$= \exp(-ia_0 q_x)\{\exp[ia_0(\frac{3}{2}q_x - \frac{\sqrt{3}}{2}q_y)] + \exp[ia_0(\frac{3}{2}q_x + \frac{\sqrt{3}}{2}q_y)] + 1\}$$
$$= \exp(-ia_0 q_x)\{1 + 2\exp[i(\frac{3}{2}q_x a_0)\cos(\frac{\sqrt{3}}{2}q_y a_0)$$

$$\left|\Gamma(\boldsymbol{q})\right|^2 = \{1 + 2\exp[i(\frac{3}{2}q_x a_0)\cos(\frac{\sqrt{3}}{2}q_y a_0)\}\{1 + 2\exp[i(-\frac{3}{2}q_x a_0)\cos(\frac{\sqrt{3}}{2}q_y a_0)\}$$
$$= 1 + 4\cos(\frac{3}{2}q_x a_0)\cos(\frac{\sqrt{3}}{2}q_y a_0) + 4\cos^2(\frac{\sqrt{3}}{2}q_y a_0)$$

((**ContourPlot**))

$$\left|\Gamma(\boldsymbol{q})\right|^2 = 1 + 4\cos\left(\frac{3q_x a_0}{2}\right)\cos\left(\frac{\sqrt{3}}{2}q_y a_0\right) + 4\cos^2\left(\frac{\sqrt{3}}{2}q_y a_0\right)$$

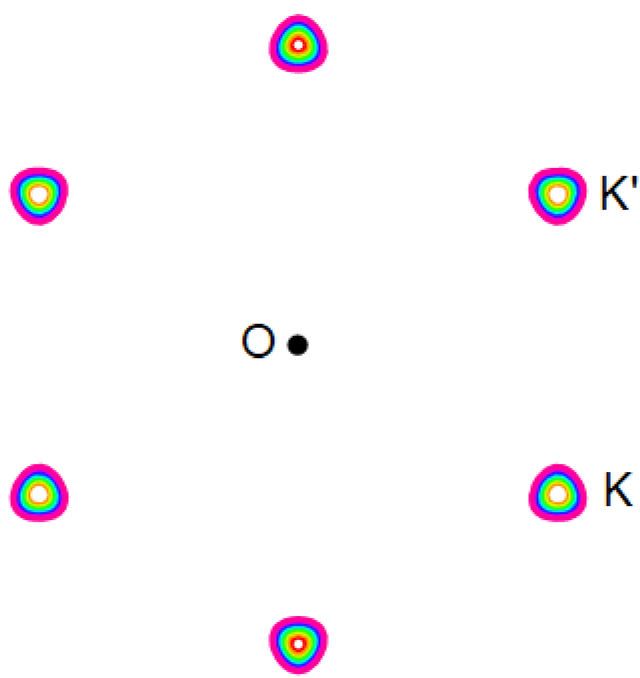


Fig. ContourPlot of $|\Gamma(\boldsymbol{q})|^2 \approx 0$ in the reciprocal lattice plane. $|\Gamma(\boldsymbol{q})|^2 = 0$ at the Dirac points K and K'.

The Hamiltonian for graphene takes on the simple form

$$H(\boldsymbol{q}) = \begin{pmatrix} 0 & \Gamma(\boldsymbol{q}) \\ \Gamma^*(\boldsymbol{q}) & 0 \end{pmatrix}$$

and the two solutions to $H(\boldsymbol{q})$,

$$E_\pm(q) = \pm|\Gamma(\boldsymbol{q})|$$

where γ ≈2.7 eV.

For the graphene, there are two π electrons per unit cell. The lower π band is occupied and the upper π band is empty, thus ε_F is at $\varepsilon = 0$. This occurs at the $\boldsymbol{q} = \boldsymbol{K}$ or $\boldsymbol{q} = \boldsymbol{K}'$ point in the Brillouin zone. We note that $\boldsymbol{q} = \boldsymbol{K}$ or $\boldsymbol{q} = \boldsymbol{K}'$ are not the same point in general. It shows the bands linearly dispersing from the $\boldsymbol{q} = \boldsymbol{K}$ or $\boldsymbol{q} = \boldsymbol{K}'$ point. Thus, the low-energy carriers in graphene behave like massless relativistic particles in 2D with the velocity given by the band velocity. These are known as 2D massless Dirac fermions. The energy surface for the electronic states corresponds to two cones, one inverted, which touch each other at two points (called Dirac points) in the Brillouin zone.

$$\boldsymbol{K} = \frac{2\pi}{3a_0}(1, -\frac{1}{\sqrt{3}})$$

$$\boldsymbol{K}' = \frac{2\pi}{3a_0}(1, \frac{1}{\sqrt{3}})$$

$$\boldsymbol{M} = \frac{\boldsymbol{K} + \boldsymbol{K}'}{2} = \frac{2\pi}{3a_0}(1, 0)$$

We note that $\Gamma(\boldsymbol{K}) = 0$. In the limit of $|\boldsymbol{k}| \ll |\boldsymbol{K}|$, $\Gamma(\boldsymbol{q})$ can be expanded by using the Taylor expansion.

(a) The case of $\boldsymbol{q} = \boldsymbol{K} + \boldsymbol{k}$ around the K point.

We have

$$
\begin{aligned}
\Gamma(\boldsymbol{K}+\boldsymbol{k}) &= e^{i\frac{2\pi}{3}} e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_2} + e^{-i\frac{2\pi}{3}} e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_3} \\
&= e^{i\frac{2\pi}{3}} \exp[ia_0(\frac{1}{2}k_x - \frac{\sqrt{3}}{2}k_y)] + \exp[ia_0(\frac{1}{2}k_x + \frac{\sqrt{3}}{2}k_y)] + e^{-i\frac{2\pi}{3}} \exp(-ia_0 k_x) \\
&= e^{i\frac{2\pi}{3}} [1 + ia_0(\frac{1}{2}k_x - \frac{\sqrt{3}}{2}k_y)] + 1 + ia_0(\frac{1}{2}k_x + \frac{\sqrt{3}}{2}k_y) + e^{-i\frac{2\pi}{3}} (1 - ia_0 k_x) \\
&= ia_0[e^{i\frac{2\pi}{3}} (\frac{1}{2}k_x - \frac{\sqrt{3}}{2}k_y) + (\frac{1}{2}k_x + \frac{\sqrt{3}}{2}k_y) - e^{-i\frac{2\pi}{3}} k_x] \\
&= \frac{3}{2} ia_0 e^{i\frac{\pi}{3}} (k_x - ik_y)
\end{aligned}
$$

Neglecting the extra phase factor ($ie^{i\pi/3}$), the Hamiltonian near K takes on the form

$$
H_K(\boldsymbol{k}) = \frac{3}{2}\gamma a_0 \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_0 \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix}
$$

where

$$
\frac{3}{2}\gamma a_0 = \hbar v_0
$$

v_0 is the band velocity of the π states near the K point (the Dirac point).

We solve the eigenvalue problem

$$
\begin{aligned}
H_K(\boldsymbol{k}) &= \hbar v_0 (k_x \sigma_x + k_y \sigma_y) \\
&= \hbar v_0 |\boldsymbol{k}| (\frac{k_x}{|\boldsymbol{k}|}\sigma_x + \frac{k_y}{|\boldsymbol{k}|}\sigma_y) \\
&= \hbar v_0 |\boldsymbol{k}| (\cos\theta \sigma_x + \sin\theta \sigma_y)
\end{aligned}
$$

where

$$
\tan\theta = \frac{k_y}{k_x}
$$

$$|+\boldsymbol{n}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix}, \qquad |-\boldsymbol{n}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -e^{i\theta} \end{pmatrix}$$

$$H_{\boldsymbol{K}}(\boldsymbol{k})|+\boldsymbol{n}\rangle = \hbar v_0 |\boldsymbol{k}||+\boldsymbol{n}\rangle, \qquad H_{\boldsymbol{K}}(\boldsymbol{k})|-\boldsymbol{n}\rangle = -\hbar v_0 |\boldsymbol{k}||-\boldsymbol{n}\rangle$$

where $\boldsymbol{n}$ is parallel to $\boldsymbol{k}$. Note that $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ are two-component spinors representing the function $\psi_{\boldsymbol{K}}{}^{A}(\boldsymbol{r})$ and $\psi_{\boldsymbol{K}}{}^{B}(\boldsymbol{r})$.

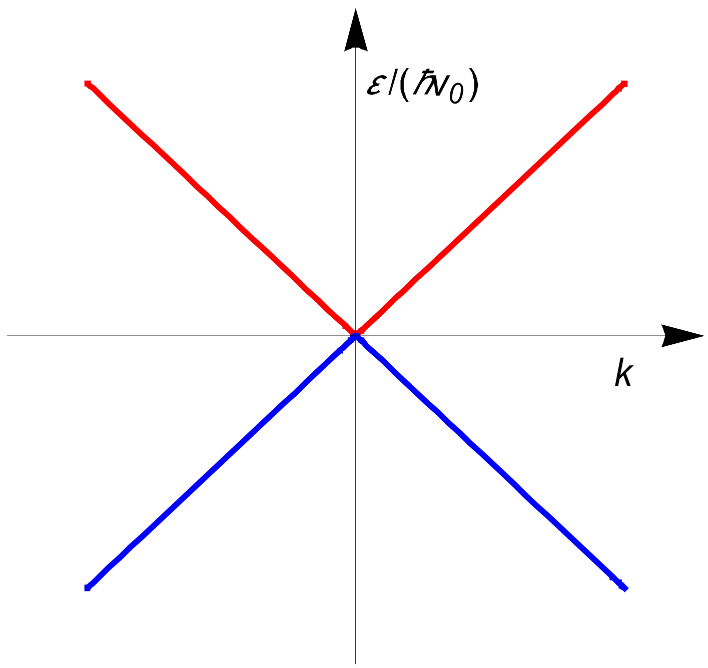


Fig. Energy dispersion at the Dirac points. The effective mass is zero at the Dirac points.

(b) The case of $\boldsymbol{q} = \boldsymbol{K}' + \boldsymbol{k}$ around the K' point

We have

$$\begin{aligned}\Gamma(\boldsymbol{K}'+\boldsymbol{k}) &= e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_1} + e^{i\frac{2\pi}{3}} e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_2} + e^{-i\frac{2\pi}{3}} e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_3} \\ &= \exp[ia_0(\frac{1}{2}k_x - \frac{\sqrt{3}}{2}k_y)] + e^{i\frac{2\pi}{3}} \exp[ia_0(\frac{1}{2}k_x + \frac{\sqrt{3}}{2}k_y)] + e^{-i\frac{2\pi}{3}} \exp(-ia_0 k_x) \\ &= 1 + ia_0(\frac{1}{2}k_x - \frac{\sqrt{3}}{2}k_y) + e^{i\frac{2\pi}{3}}[1 + ia_0(\frac{1}{2}k_x + \frac{\sqrt{3}}{2}k_y)] + e^{-i\frac{2\pi}{3}}(1 - ia_0 k_x) \\ &= ia_0[(\frac{1}{2}k_x - \frac{\sqrt{3}}{2}k_y) + e^{i\frac{2\pi}{3}}(\frac{1}{2}k_x + \frac{\sqrt{3}}{2}k_y) - e^{-i\frac{2\pi}{3}}k_x] \\ &= ia_0\frac{3}{2}e^{i\pi/3}(k_x + ik_y)\end{aligned}$$

Neglecting the extra phase factor ($ie^{i\pi/3}$) the Hamiltonian near K takes on the form

$$H_{K'}(\boldsymbol{k}) = \frac{3}{2}\gamma a_0 \begin{pmatrix} 0 & k_x + ik_y \\ k_x - ik_y & 0 \end{pmatrix} = \hbar v_0 \begin{pmatrix} 0 & k_x + ik_y \\ k_x - ik_y & 0 \end{pmatrix}$$

where

$$\frac{3}{2}\gamma a_0 = \hbar v_0$$

We solve the eigenvalue problem

$$\begin{aligned}H_{K'}(\boldsymbol{k}) &= \hbar v_0 (k_x\sigma_x - k_y\sigma_y) \\ &= \hbar v_0 |\boldsymbol{k}| (\frac{k_x}{|\boldsymbol{k}|}\sigma_x - \frac{k_y}{|\boldsymbol{k}|}\sigma_y) \\ &= \hbar v_0 |\boldsymbol{k}| (\cos\theta\sigma_x - \sin\theta\sigma_y)\end{aligned}$$

where

$$\tan\theta = \frac{k_y}{k_x}$$

$$|+\boldsymbol{n}'\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{-i\theta} \end{pmatrix}, \qquad |-\boldsymbol{n}'\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -e^{-i\theta} \end{pmatrix}$$

$$H_{\boldsymbol{K}'}(\boldsymbol{k})|+\boldsymbol{n}\rangle = \hbar v_0 |\boldsymbol{k}||+\boldsymbol{n}\rangle, \qquad H_{\boldsymbol{K}'}(\boldsymbol{k})|-\boldsymbol{n}\rangle = -\hbar v_0 |\boldsymbol{k}||-\boldsymbol{n}\rangle$$

The wavefunction of the electron can be thought of as having a pseudospin associated with it. This pseudospin is pointed either parallel or antiparallel to $\boldsymbol{k}$, depending on whether the state is in the

$$|+\boldsymbol{n}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix} \qquad \text{for the energy } \varepsilon = \hbar v_0 |\boldsymbol{k}|$$

$$|-\boldsymbol{n}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -e^{i\theta} \end{pmatrix} \qquad \text{for the energy } \varepsilon = -\hbar v_0 |\boldsymbol{k}|$$

In fact, the form $|\pm\boldsymbol{n}\rangle$ explicitly shows that the wavefunction is a linear combination of Bloch sums of π orbitals on the two sublattices with a relative amplitude of 1 to $se^{i\theta}$ ($s = \pm 1$). The orientation of the pseudo-spinor thus gives the bonding character of the state with respect to the neighboring atoms. It is in this sense that the carriers in graphene have chiral character, in analogy with the 2D massless neutrinos. We note here that the pseudospin has nothing to do with the real spin of electrons. The states at $\varepsilon = 0$ are, in fact, eightfold degenerate since there are two valleys, ***K*** and ***K***', and the real spin of the electron introduces two more degree of freedom.

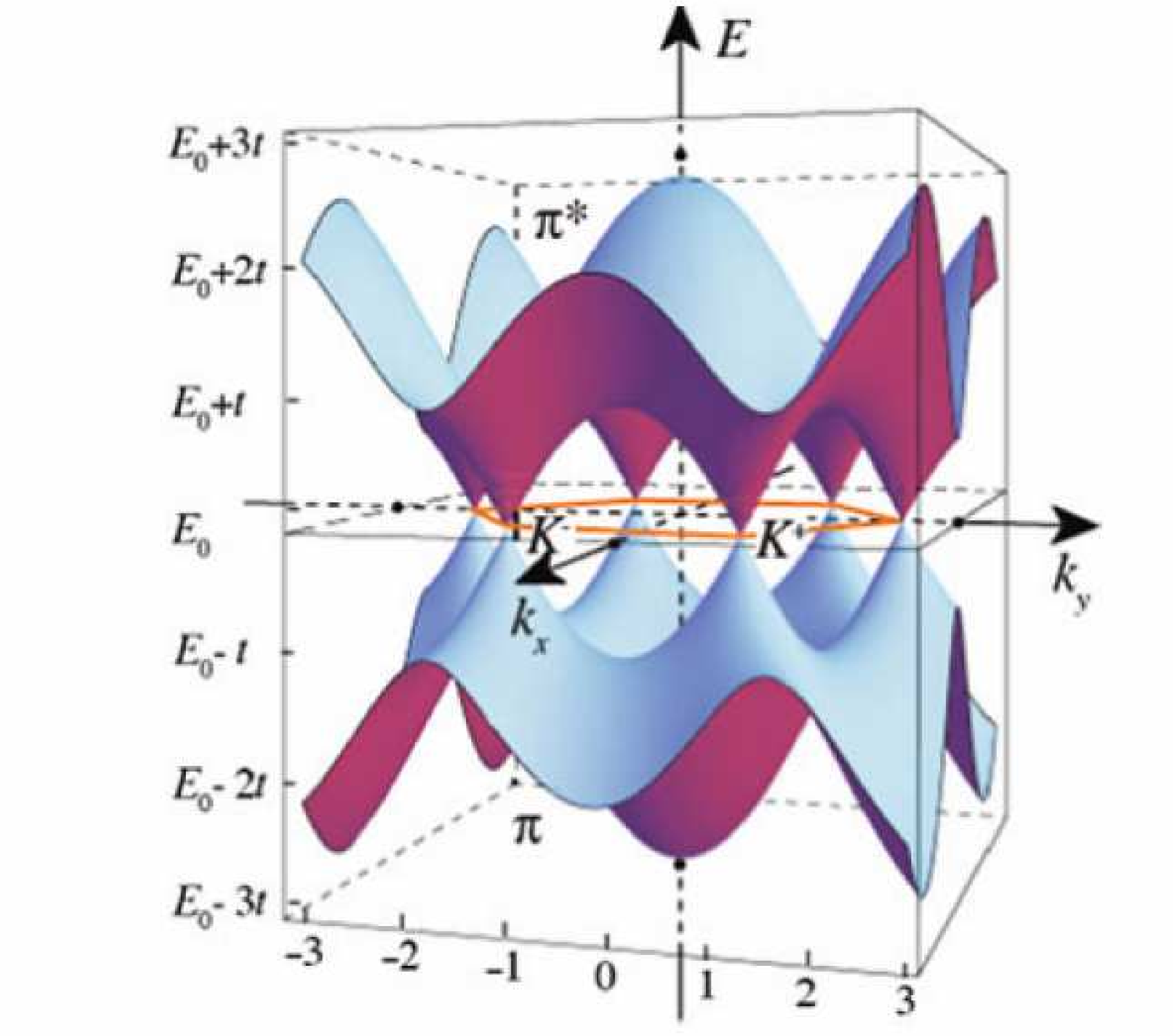


Fig. Figure from the book of Alloul.

4. Density of states

We find that the energy dispersion at the Dirac points is given by

$$\varepsilon = \pm \hbar v_F \left| \boldsymbol{k} \right|$$

The density of states:

$$
\begin{aligned}
D(\varepsilon)d\varepsilon &= \frac{2A}{(2\pi)^2} 2\pi k dk \\
&= \frac{2A}{(2\pi)^2} 2\pi \frac{\varepsilon}{\hbar v_F} d\frac{\varepsilon}{\hbar v_F} \\
&= \frac{A}{\pi \hbar^2 {v_F}^2} \varepsilon d\varepsilon
\end{aligned}
$$

$$
D(\varepsilon) = \frac{A}{\pi \hbar^2 {v_F}^2} \varepsilon
$$

It is proportional to the energy ε.

REFERENCES

H. Alloul, Introduction to the Physics of Electrons in Solids (Springer, 2007).
M.L. Cohen and S.G. Louie, Fundamentals of Condensed Matter Physics (Cambridge, 2016).