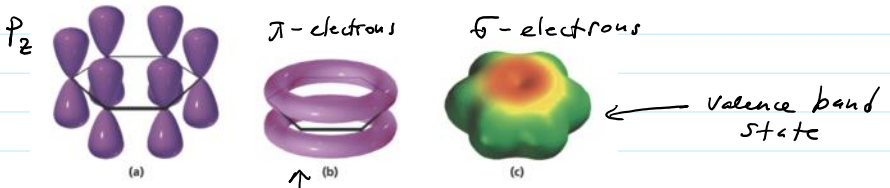
Graphene electronic structure

Friday, October 26, 2018 2:11 PM

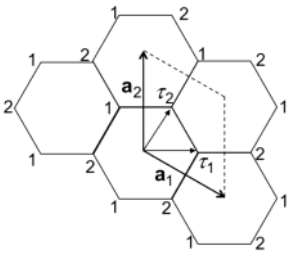
Recal that graphene spans a 2D hexagonal lattice with electrons doing sp_2 hybridization



they make up conduction band

2D hexagonal lattice of graphene is shown below

where $\bar{a}_1 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$ $\bar{a}_2 = a(0,1)$ where a is the lattice constant



The rhombic unit cell contains 2 carbons at the position

$\bar{\tau}_1 = a\left(\frac{1}{\sqrt{3}}, 0\right)$ and $\tau_2 = a\left(\frac{1}{2\sqrt{3}}, \frac{1}{2}\right)$

The position of the rest of atoms can be generated by

$\bar{\tau}_1 + \bar{R}$, $\bar{\tau}_2 + \bar{R}$ where $\bar{R} = n_1\bar{a}_1 + n_2\bar{a}_2$

n_1 and $n_2 = 0, \pm 1, \pm 2$ etc.

But as usual you can sellect a different unit cell.

BTW. if you want the unit cell which reflects clear hexagonal symmetry use WIGNER-SEITZ cell (see Simon's book)

Few notes:

1. $\bar{a}_1$ and $\bar{a}_2$ are not orthogonal and this is a problem b/c we will need many terms like $e^{ik.R}$

Suppose we write

$$\bar{R} = n_1 \bar{a}_1 + n_2 \bar{a}_2 \qquad n_1, n_2 = 0, 1, 2, \text{ etc}$$

$$\bar{k} = k_1 \bar{b}_1 + k_2 \bar{b}_2$$

this can be simple only if

$$k \cdot R = \sum_{i,j=1}^{2} k_i n_i \, b_i \cdot a_j$$

Such as $\bar{b}_j \cdot \bar{a}_i = 2\pi \delta_{ji}$

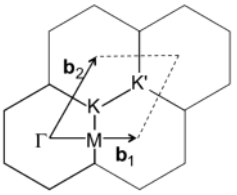
Then the phase factor

$$e^{i \bar{k} \bar{R}} = e^{i 2\pi (k_1 n_1 + k_2 n_2)}$$

such inverse lattice vectors $\bar{b}_1$ and $\bar{b}_2$ are of course the reciprocal lattice

such that $K = m_1 b_1 + m_2 b_2$

This reciprocal lattice is shown below



To construct a Bloch wave we can take any k'

but if k' is outside of the cell span by $\bar{b}_1$ and b_2

we always can $k' = k + K$

$$e^{iK \cdot R} = e^{i 2\pi (m_1 n_1 + m_2 n_2)} = 1 \Rightarrow$$

$$e^{ik'R} = e^{ikR}$$ so the ks inside the 1st BZ cover all the values of k.

So let calculate $\bar{b}_i = (b_{i1}, b_{i2})$ demanding $\bar{b}_i \cdot \bar{a}_j = 2\pi \delta_{ij}$

$$b_{11} a_{11} + b_{12} a_{12} = \frac{2\pi}{a} = b_{11} \frac{\sqrt{3}}{2} - b_{12} \frac{1}{2}$$

$$b_{11} a_{21} + b_{12} a_{22} = 0 = b_{12}$$

$$b_{21} a_{11} + b_{22} a_{12} = 0 = b_{21} \frac{\sqrt{3}}{2} - b_{22} \cdot 1/2$$

$$\frac{2\pi}{1}$$

$$\begin{cases} b_{21}\, a_{11} + b_{22}\, a_{12} = 0 = b_{21}\frac{\sqrt{3}}{2} - b_{22}\cdot \frac{1}{2} \\ b_{21}\, a_{21} + b_{22}\, a_{22} = 2\pi/a = b_{22} \end{cases}$$

$$\vec{b}_1 = \frac{2\pi}{a}\left(\frac{2}{\sqrt{3}}, 0\right) \qquad \vec{b}_2 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, 1\right)$$

Labels or special points in BZ:

$$\Gamma = \frac{2\pi}{a}(0,0) \qquad M = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, 0\right) \qquad K = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, \frac{1}{3}\right)$$

$$\Gamma = 0\,b_1 + 0\,b_2 \qquad M = \frac{1}{2}b_1 + 0\,b_2 \qquad K = \frac{1}{3}b_1 + \frac{1}{3}b_2$$

$$K' = \frac{2}{3}b_1 + \frac{2}{3}b_2$$

NN tight Binding model

We need to calculate the matrix elements like

$$H_{11,k} = \sum_R e^{ikR} \langle \chi_1 | H | \chi_{1R} \rangle = \langle \chi_1 | H | \chi_1 \rangle = E_p$$

$$H_{22,k} = \ldots\ldots\ldots = \langle \chi_2 | H | \chi_2 \rangle = E_p$$

since only $R=0$ contributes and both atoms in the sublattice 1 and two are equivalent.

OFF - Diagonal:

$$H_{12,k} = \sum_R e^{ikR} \langle \chi_1 | H | \chi_{2R} \rangle = \overbrace{\langle \chi_1 | H | \chi_2 \rangle}^{t} \left(1 + e^{ika_1} + e^{-ika_2}\right)$$

$$H_{21,k} = \sum_R e^{ikR} \langle \chi_2 | H | \chi_{1R} \rangle = H^*_{12,k} = \overbrace{\langle \chi_2 | H | \chi_1 \rangle}^{t} \left(1 + e^{-ika_1} + e^{ika_2}\right)$$

t is a hopping parameter

t is a hopping parameter

thus

$$H_{12,k} = t\left(1 + e^{ika_1} + e^{-ika_2}\right) = t\left(1 + e^{i2\pi k_1} + e^{-i2\pi k_2}\right) =$$

$$= t_k$$

Finally:

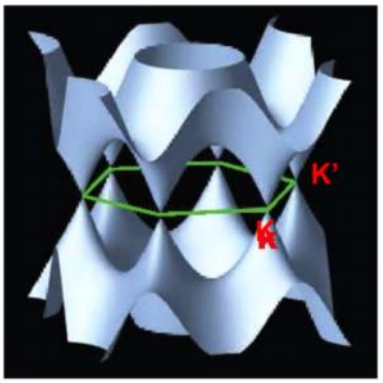
$$\begin{pmatrix} \varepsilon_p & t_k \\ t_k^* & \varepsilon_p \end{pmatrix}\begin{pmatrix} c_{1,k} \\ c_{2,k} \end{pmatrix} - E(k)\begin{pmatrix} c_{1,k} \\ c_{2,k} \end{pmatrix} = 0$$

$$E^{\pm}(k) = \varepsilon_p \pm |t_k| = \varepsilon_p \pm \sqrt{t_k^* t_k} =$$

$$= \varepsilon_p \pm t\sqrt{3 + 2\cos(2\pi k_1) + 2\cos(2\pi k_2) + 2\cos(2\pi(k_1 + k_2))}$$

and $\psi_k^{\downarrow} = \begin{pmatrix} c_{1k} \\ c_{2k} \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ $\psi^{-} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \end{pmatrix}$

So here is the 2D plot (try this in Mathematica)



Consider now what happens in high symmetry points? The coordinates in the BZ are given above.

Γ: $\varepsilon_p \pm 3t$ $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \end{pmatrix}$

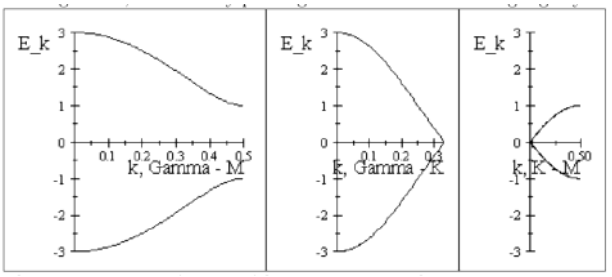
M: $\varepsilon_p \pm t$ $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \end{pmatrix}$

Γ: $\varepsilon_p \pm 3t$ $\quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$

M: $\varepsilon_p \pm t$ $\quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}-1\\1\end{pmatrix}$

K: ε_p $\quad \begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$ | those are doubly degenerate!

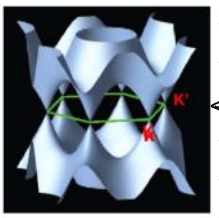
K': ε_2



So FAR nothing too exciting, just another exersise in LCAO method 101.

But wait! lets move to the long-wave length.

- Each carbon has one electron in p_z state assuming spin degeneracy we have the band 1/2 filled.
- It means the E_F right at K and K' points (also I used the fact that band structure is symmetric)



← E_F is here!

- As we know the only interesting states are near the Fermi edge, so lets study those in detail.

Consider $\bar{k} = \bar{K} + \bar{q}$

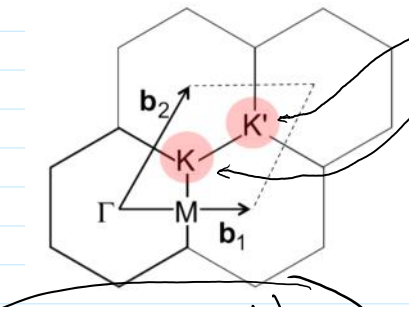
$\bar{k}' = \bar{K}' + \bar{q}$

we consider only states with $|q| \ll K$

or $K \sim \frac{1}{a} \Rightarrow qa \ll 1$, or $\lambda \gg a$

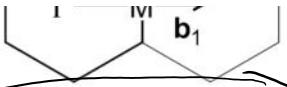
and $q'a \ll 1$

Long wave limit



What about Bloch wave phases?

$e^{ika_1} \quad e^{ika_2} \quad e^{iq\cdot a} \approx (1 + iq\cdot a_1)$ b/c $q\cdot a \ll 1$



$$a_1 = a\left(\frac{\sqrt{3}}{2} \quad -\frac{1}{2}\right)$$

$$K = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}} \quad \frac{1}{3}\right)$$

phases!

$$e^{ika_1} = e^{iKa_1} e^{iq a_1} \approx \left(1 + iq\cdot a_1\right)$$

b/c $q \cdot a \ll 1$

$$\approx e^{i\frac{2}{3}\pi}\left(1 + i\vec{q}\cdot\vec{a}_1\right) = e^{i\frac{2}{3}\pi}\left(1 + iq_x a + iq_y a\sqrt{3}\right)$$

$a_1 K = 2\pi\left(\frac{\sqrt{3}}{2}\frac{1}{\sqrt{3}} - \frac{1}{2}\frac{1}{3}\right) = \frac{2}{3}\pi$

in the same way

$$e^{ika_2} = e^{-iKa_2} e^{-iqa_2} =$$

$$\approx e^{-i\frac{2\pi}{3}}\left(1 - iqa_2\right) = e^{-i\frac{2}{3}\pi}\left(1 - iq_x a + iq_y a\sqrt{3}\right)$$

Recall $H_{12,k} \equiv t_k = t\left(1 + e^{ika_1} + e^{ika_2}\right) =$

$$\approx \frac{3a}{2} t\left(q_x - iq_y\right)$$

an similarly for k'

$$t_{k'} \cong \frac{3}{2} a t\left(q_x' + iq_y'\right)$$

Let's define a new parameter "Fermi velocity"

$$\hbar v_F \equiv -\frac{3}{2} at \qquad \text{and since } t < 0 \quad v_F > 0$$

since for graphene $t = -3\,eV$

$v_F \sim 10^6$ m/sec

– Next if we select our zero at E_p = the atomic values of p-orb.

$$\begin{pmatrix} E_p & t_k \\ t_k^* & E_p \end{pmatrix} \approx \begin{pmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{pmatrix} \cdot \left(-\frac{3}{2} at\right) =$$

$$= \hbar v_F \begin{pmatrix} \cdot & \cdot \\ \cdot & \cdot \end{pmatrix} = \hbar v_F q_x \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \hbar v_F q_y \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\equiv \vec{\sigma}_x \qquad \equiv \vec{\sigma}_y$$

$\equiv \hat{\sigma}_x$ / $= \hat{\sigma}_y$ /

the Pauli matrixes

So formaly we have:

$$\hbar v_F q_x \hat{\sigma}_x + \hbar v_F q_y \hat{\sigma}_y = \hbar v_F \bar{q}\cdot\bar{\sigma} = v_F \bar{p}\cdot\bar{\sigma}$$

Since $\hbar q \equiv p$ — projection of momentum on spin

The eigenvalue problem now can be written as:

$$\begin{pmatrix} E_p & t_k \\ t_k & E_p \end{pmatrix}\begin{pmatrix} c_{1k} \\ c_{2k} \end{pmatrix} = E_k \begin{pmatrix} c_{1k} \\ c_{2k} \end{pmatrix} \Rightarrow \boxed{\left(v_F \bar{p}\cdot\bar{\sigma}\right)\psi_p = E\psi_p}$$

where $\psi_p = \begin{pmatrix} c_{1p} \\ c_{2p} \end{pmatrix}$ spinor

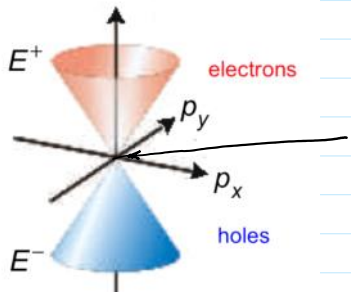
The component of Ψ are NOT referring to spin up down but to the amplitudes of Ψ on sublattice 1 and 2 of graphene

Lets solve the equation

$$\left(v_F\, p\cdot\sigma\right)\psi_p = E_p \psi \Rightarrow v_F \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix}\begin{pmatrix} c_{1p} \\ c_{2p} \end{pmatrix} =$$

$$= \begin{pmatrix} c_{1p} \\ c_{2p} \end{pmatrix} E_p$$

$$\boxed{E_p^{\pm} = \pm v_F \sqrt{p_x^2 + p_y^2} = \pm v_F |p|}$$



In undoped graphene

E_F only one k point is occupied $\simeq 0$

By gating or chemical doping we can fill up states with $p > 0$

or do the same for hole

So this is unique b/c of the complete symmetry

of the 2D lattice

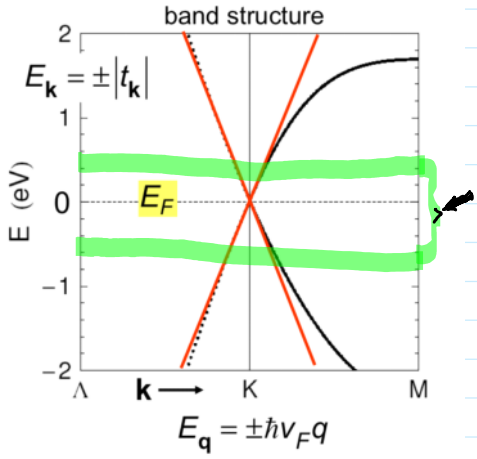
In majority conventional materials electron and hole are very different.

Put back $E_p^{\pm}$ we get the eigenvalues

$$\psi_p^{\pm} = \begin{pmatrix} c_{1p} \\ c_{2p} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} \pm 1 \\ e^{i\varphi_p} \end{pmatrix}$$

where φ_p is the phase angle $p_x + i p_y = e^{i\varphi_p} \cdot p$

IF we move away from the long-wave length say $> \pm 0.5$ eV the dispersion is not linear anylonger



We will return to graphene when I will introduce electrons in magnetic field, Topology and quantum hole effect.