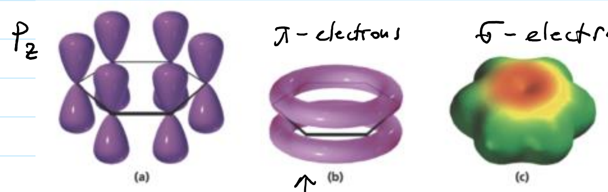
EXAMPLE OF DEGENERATE PERT. THEORY

Graphene electronic structure

Friday, October 26, 2018 2:11 PM

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

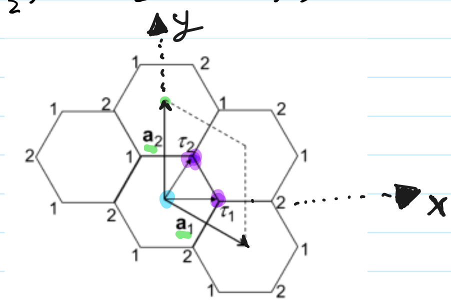


Valence band state

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



$a = 2.46\,\text{Å}$

The rhombic unit cell contains 2 carbons at the positions

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

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 $e^{ik.R}$ $\Rightarrow$

Bloch theorem: in any periodic xtal the wave function of e^- is $\Psi_k = U_k(\bar{r})\, e^{i\bar{k}\cdot\bar{r}}$, $U_k(\bar{r}) \equiv U_k(\bar{r}+\bar{R})$

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

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

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

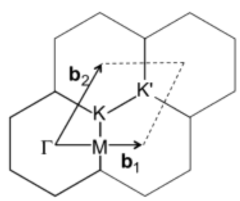
Then the phase factor

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

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

Reciprocal version of graphene lattice: $\Big\} \Rightarrow$ 

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 alwey can $\bar{k}' = \bar{k} + \bar{K}$

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

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

since the motion of electrons happens in the momentum space we transform from real space $\vec{a}_i \to \vec{b}_i$ in the momentum space

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

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

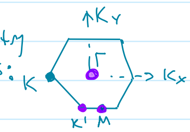
$$b_{21} a_{11} + b_{22} a_{12} = 0 = b_{21}\frac{\sqrt{3}}{2} - b_{22}\cdot \tfrac{1}{2}$$

$$b_{21} a_{21} + b_{22} a_{22} = 2\pi/a = b_{22}$$

reciprocal vectors b_i

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

High symmetry points:



Labels or special points in BZ:

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

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

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

$\langle 1|H|1\rangle$

$$\begin{pmatrix} H_{11} & & \\ & \ddots & \\ & & \ddots \end{pmatrix}$$

NN tight Binding model

We need to calculate the matrix elements like

$$\boxed{\chi_{1R} \equiv \chi_1(r-R)}$$

$$H_{11,k} = \sum_R e^{ikR} \langle \chi_1 | H | \chi_{1R} \rangle = \boxed{\langle \chi_1 | H | \chi_1 \rangle} = \boxed{E_p} \quad \text{energy of atom}$$

($R=0$)

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

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

$$\begin{pmatrix} \epsilon_a & t \\ t^* & \epsilon_b \end{pmatrix}$$

OFF - Diagonal terms:

$$t_k \equiv H_{12,k} = \sum_R e^{ikR} \langle \chi_1 | H | \chi_{2R} \rangle = \overbrace{\langle \chi_1 | H | \chi_2 \rangle}^{\simeq t} \left(1 + e^{i\bar{k}\cdot\bar{a}_1} + e^{-i\bar{k}\cdot\bar{a}_2}\right)$$

$$t_k \equiv H_{21,k} = \sum_R e^{ikR} \langle \chi_2 | H | \chi_{1R} \rangle = H^*_{12,k} = \overbrace{\langle \chi_2 | H | \chi_1 \rangle}^{\simeq t} \left(1 + e^{-i\bar{k}\bar{a}_1} + e^{i\bar{k}\cdot\bar{a}_2}\right)$$

2,1
1,2 Conjugate

t is a hopping parameter

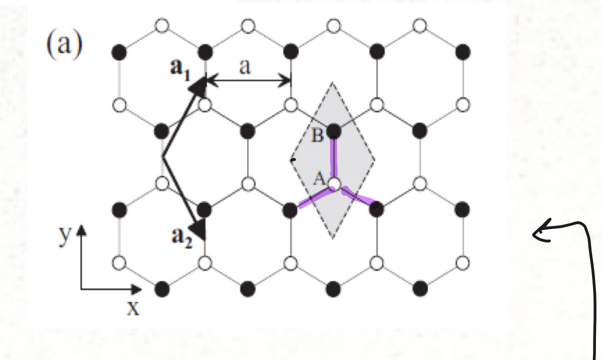
We can form n Bloch functions

$$\Phi_j(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{i\mathbf{k}.\mathbf{R}_{j,i}} \phi_j\left(\mathbf{r} - \mathbf{R}_{j,i}\right)$$

$$\left\{ \begin{array}{l} A \equiv \text{site } 1 \\ B = \text{site } 2 \\ R_{is} \text{ the location of atoms } A \text{ and } B \end{array} \right\}$$

$$H_{AA} = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{i\mathbf{k}.(\mathbf{R}_{A,j} - \mathbf{R}_{A,i})} \langle \phi_A\left(\mathbf{r} - \mathbf{R}_{A,i}\right) | \mathcal{H} | \phi_A\left(\mathbf{r} - \mathbf{R}_{A,j}\right) \rangle$$

$\mathbf{k} = (k_x, k_y)$



Look at the atom A it's surrounded by 3 atoms; with R_{AB}

$$t_k \equiv H_{AB} = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{i\mathbf{k}.(\mathbf{R}_{B,j} - \mathbf{R}_{A,i})} \langle \phi_A\left(\mathbf{r} - \mathbf{R}_{A,i}\right) | \mathcal{H} | \phi_B\left(\mathbf{r} - \mathbf{R}_{B,j}\right) \rangle$$

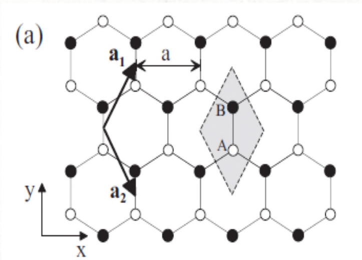
$$t_k \equiv H_{AB} = \sum_{l=1}^{3} e^{i\mathbf{k}.(\mathbf{R}_{B,l} - \mathbf{R}_{A,i})} \underbrace{\langle \phi_A\left(\mathbf{r} - \mathbf{R}_{A,i}\right) | \mathcal{H} | \phi_B\left(\mathbf{r} - \mathbf{R}_{B,l}\right) \rangle}_{t_0 \text{ hoping integral}}$$

Therefore

$$t_k \equiv H_{AB} = -t_0 \sum_{l=1}^{3} e^{i\mathbf{k}.\boldsymbol{\delta}_l} \equiv -t_0 f(\mathbf{k}) \qquad f(\mathbf{k}) = \sum_{l=1}^{3} e^{i\mathbf{k}.\boldsymbol{\delta}_l}$$

$$\boldsymbol{\delta}_l = \mathbf{R}_{B,l} - \mathbf{R}_{A,i}$$

Position of atom B relative to atom A



Positions of those 3 B atoms:

$$\boldsymbol{\delta}_1 = \left(0, \frac{a}{\sqrt{3}}\right) \qquad \boldsymbol{\delta}_2 = \left(\frac{a}{2}, -\frac{a}{2\sqrt{3}}\right)$$

$$\boldsymbol{\delta}_3 = \left(-\frac{a}{2}, -\frac{a}{2\sqrt{3}}\right)$$

$$t_k = \underset{1,2}{H_{AB}} \approx -t_0 f(\mathbf{k}) ; \quad \underset{2,1}{H_{BA}} \approx -t_0 f^*(\mathbf{k}) \equiv t_k^*$$

where $f(\mathbf{k}) = e^{ik_y a/\sqrt{3}} + 2e^{-ik_y a/2\sqrt{3}} \cos(k_x a/2)$

Finally:

Euler!

$$\cos kx = \frac{e^{ikx} + e^{-ikx}}{2}$$

$$\begin{array}{cc} AA & AB \\ \end{array}$$
$$\begin{pmatrix} \epsilon_p & t_k \\ t_k^* & \epsilon_p \end{pmatrix} \begin{pmatrix} c_{1,k} \\ c_{2,k} \end{pmatrix} - E(k) \begin{pmatrix} c_{1,k} \\ c_{2,k} \end{pmatrix} = 0$$
$$\begin{array}{cc} BA & BB \\ \end{array}$$

interaction removes degeneracy!

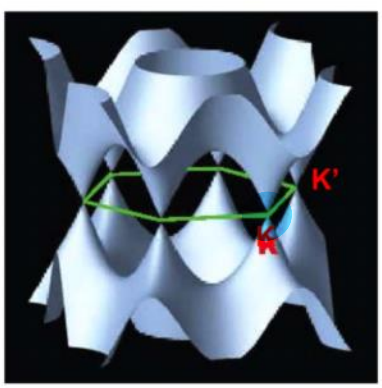
but not everywhere !!! there are special points.

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

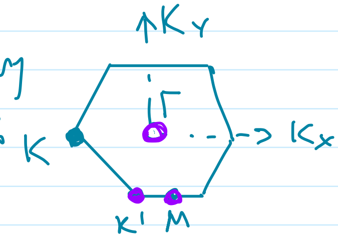
$$= \epsilon_p \pm t \sqrt{3 + 2\cos(2\pi k_1) + 2\cos(2\pi k_2) + 2\cos(2\pi(k_1 + k_2))}$$

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

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



High symmetry points:



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

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

$$K = \frac{1}{3} b_1 + \frac{1}{3} b_2$$

Recall:

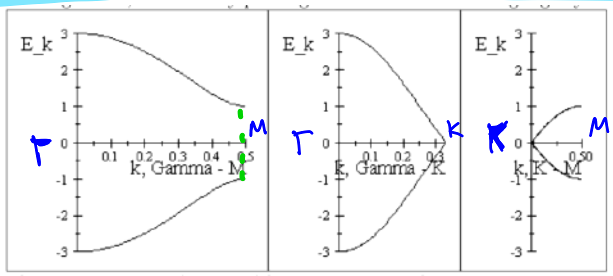
Γ: $\quad \varepsilon_p \pm 3t \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$

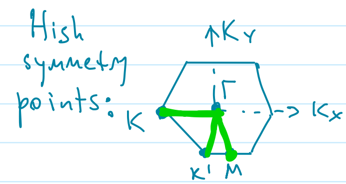
M: $\quad \varepsilon_p \pm t \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}-1\\1\end{pmatrix}$

K: $\quad \varepsilon_p \quad \begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$

K': $\quad \varepsilon_p$

those are doubly degenerate!



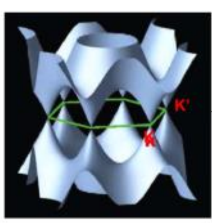


So FAR nothing too exciting, just another exersise in LCAO method 101.

But wait! lets move to the long-wave length. or k is small around K and K' points in momentum space.

- 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.

Let's first move to the point in BZ, K.

LONG WAVE-LENGTH LIMIT

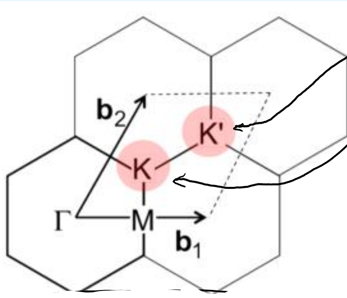
Consider $\bar{k} = \bar{K} + \bar{q}$ $\qquad$ we consider only states

$\bar{k}' = \bar{K}' + \bar{q}$ $\qquad$ with $|q| \ll K$

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

and $qa \ll 1$

Long wave limit



What about Bloch wave phases?

phases! in the Long wave-length limit

$K = K + q$; $qa \ll 1$

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

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

$$e^{i\bar{K}\cdot\bar{a}_1} = e^{i\bar{K}\cdot\bar{a}_1} e^{i\bar{q}\cdot\bar{a}_1} \approx \quad \approx(1 + iq\cdot a_1) \text{ b/c } q\cdot a \ll 1$$

$$\approx e^{i\frac{2}{3}\pi}(1 + i\bar{q}\cdot\bar{a}_1) = e^{i\frac{2}{3}\pi}(1 + iq_x a + i q_y a\sqrt{3})$$

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

in the same way $$e^{i\bar{k}\cdot\bar{a}_2} = e^{-i\bar{K}\cdot\bar{a}_2} e^{-i\bar{q}\cdot\bar{a}_2} =$$

$$\approx e^{-i\frac{2\pi}{3}}(1 - i\bar{q}\cdot\bar{a}_2) = e^{-i\frac{2}{3}\pi}(1 - iq_x a + iq_y a\sqrt{3})$$

Recall $$H_{12,k} \equiv t_k = t\,(1 + e^{i\bar{k}\cdot\bar{a}_1} + e^{i\bar{k}\cdot\bar{a}_2}) \cong$$

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

an similarly for K'

$$H_{K'} \cong \frac{3}{2}a\,t\,(q_x' + iq_y')$$

Let's define a new parameter = "Fermi velocity"

$$\alpha \equiv \hbar v_F \equiv -\frac{3}{2}at$$ and since $t < 0$, $v_F > 0$

since $\boxed{\text{for graphene } t = -3\text{ eV}, \; v_F \sim 10^6 \text{ m/sec}}$

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

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

$H_{11} = E_p = 0$, H_{12}, H_{21}, $E_p = 0$

$$= \hbar v_F\begin{pmatrix} 0 & \\ & 0 \end{pmatrix} = \hbar v_F q_x \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\equiv \vec{\sigma}_x !} + \hbar v_F q_y \underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\equiv \vec{\sigma}_y}$$

So formaly we have: the Pauli matrixes

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

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

$$H(k) \approx v_F \bar{p}\cdot\bar{\sigma}$$

The eigenvalue problem now can be written as:

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

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

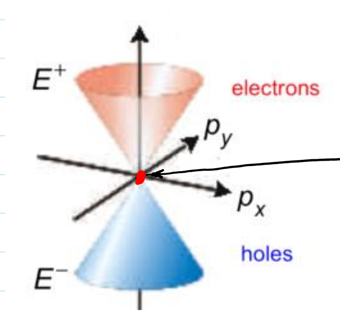
Note: The component of ψ are NOT refering to spin up down but to the amplitudes of ψ on sublattice 1 and 2 of graphene

Lets solve the equation

$$(v_F \bar{p}\cdot\bar{\sigma})\psi_p = \varepsilon_p \psi \Rightarrow v_F \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix}\begin{pmatrix} c_{1p} \\ c_{2p} \end{pmatrix} = \begin{pmatrix} c_1 p \\ c_2 p \end{pmatrix} \varepsilon_p$$

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

~~k~~ or k' when $p \ll K$ or K'



In undoped graphene

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

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

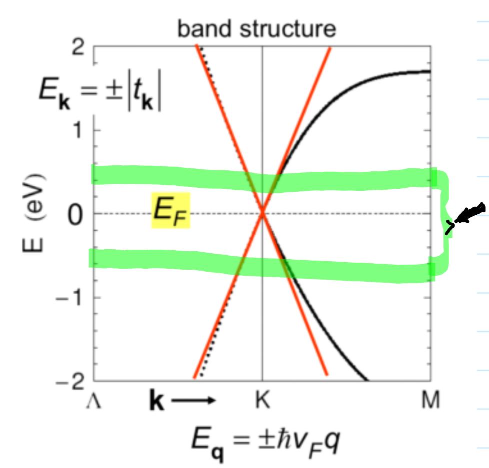
In majority conventional materials electron and holes are very different.

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

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

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

But: If we move away from the long-wave length say $> \pm 0.5\,eV$ the dispersion is not linear anylonge



linear only here

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

THE END OF THE

GRAPHENE + DEGERATE PERTURBATION THEORY