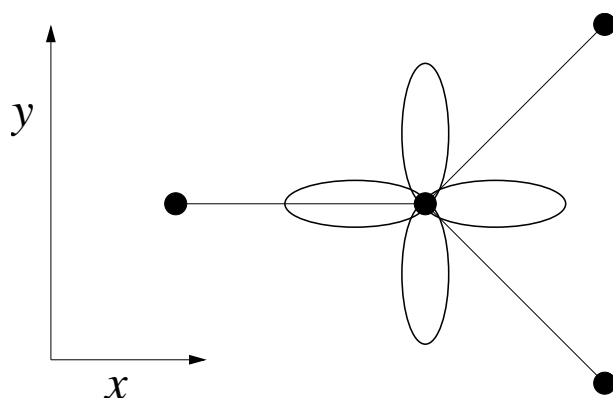


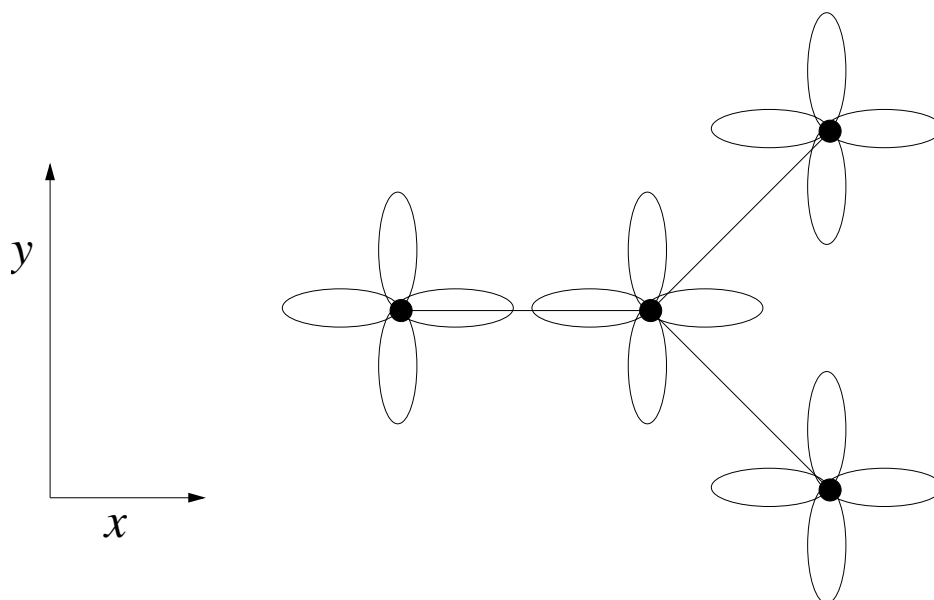
PY4T01 Condensed Matter Theory: Lecture 13

Fixing the Graphene band structure: The σ band

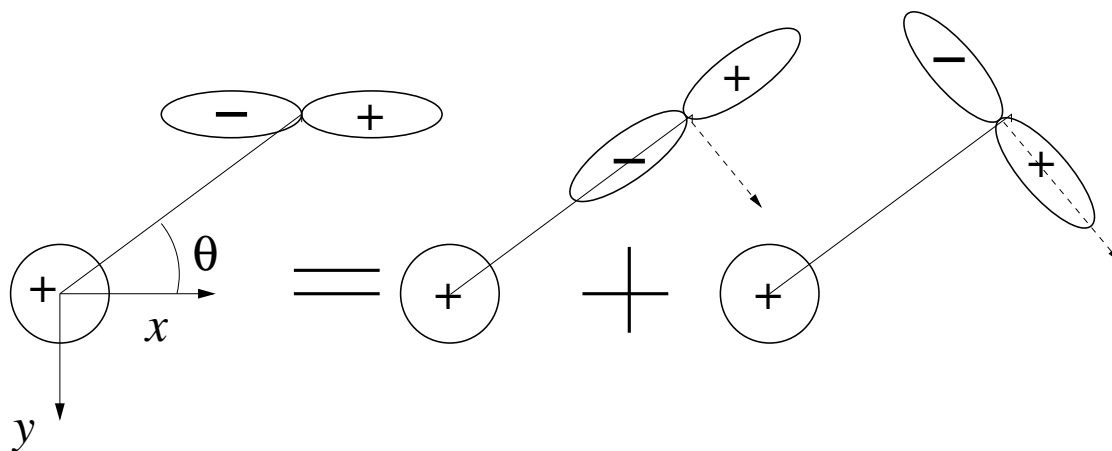
We have to consider the forgotten s , p_x and p_y orbitals. However using those orbitals is not terribly convenient for our problem !!



The problem is that the orbitals are not oriented along the bond axis

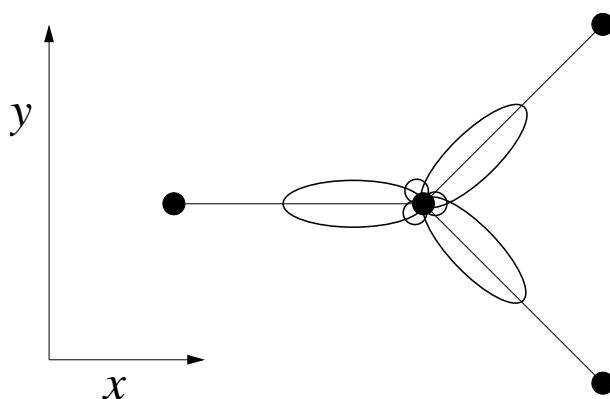


Consider for example the case of s and p orbitals



$$\gamma = (sp\sigma) \cos \theta$$

We want to get rid of the explicit angular dependence \longrightarrow we use orbitals that are oriented along the bonds.



These are called *hybrid orbitals*.

sp hybrids

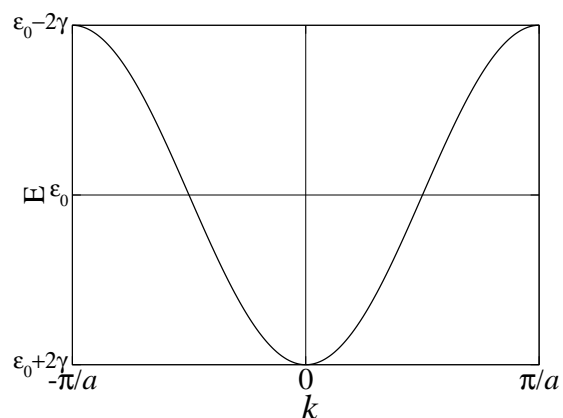
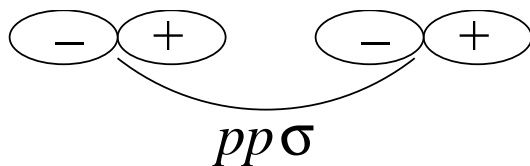
The idea is to construct a new state from a linear combination of atomic states **ON THE SAME ATOM**.

$$|\alpha\rangle = \sum_n a_n |\beta_n\rangle$$

In our case (graphene) we can use s , p_x and $p_y \rightarrow$ we form an sp hybrid.

The construction of hybrid orbitals is based on two rules:

1. *Principle of maximum overlap*: Bonding is maximized when the extent to which orbitals on adjacent sites overlap spatially is maximized.



2. *Principle of orthogonality*: The hybrid orbitals at a given atomic center should be orthogonal.

This is not a physical requirement but makes the contribution to the charge density separable.

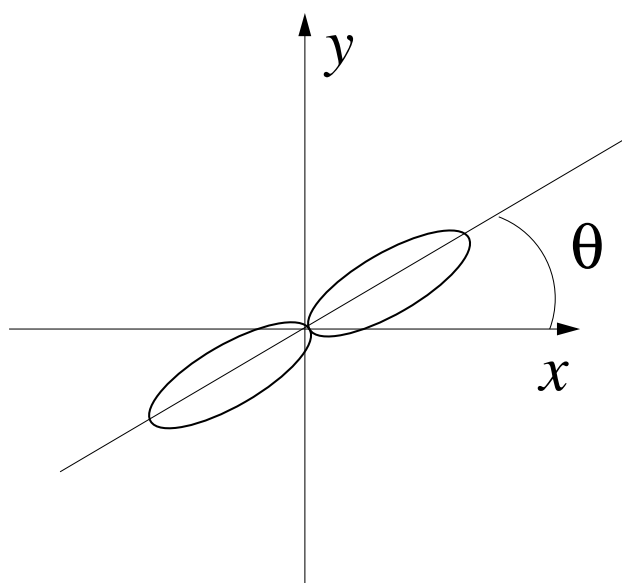
Suppose $\psi(\vec{r}) = c_1 h_1(\vec{r}) + c_2 h_2(\vec{r})$, then the total charge:

$$\int \psi^*(\vec{r})\psi(\vec{r})d\vec{r} = |c_1|^2 \int |h_1(\vec{r})|^2 d\vec{r} + |c_2|^2 \int |h_2(\vec{r})|^2 d\vec{r} + c_1^* c_2 \int h_1^*(\vec{r})h_2(\vec{r})d\vec{r} + c_2^* c_1 \int h_2^*(\vec{r})h_1(\vec{r})d\vec{r}$$

If the hybrid orbitals are orthonormal this reduces simply to $|c_1|^2 + |c_2|^2$.

Construct hybrid orbitals

Example: Suppose I want a p orbital in the $z = 0$ plane at an angle θ to the x -axis



This is simply

$$|h\rangle = \cos\theta|p_x\rangle + \sin\theta|p_y\rangle$$

sp^2 hybrid orbitals

These are obtained by mixing $|s\rangle$, $|p_x\rangle$ and $|p_y\rangle$

$$|h_1\rangle = \frac{1}{\sqrt{3}} (|s\rangle + \sqrt{2}|p_x\rangle)$$

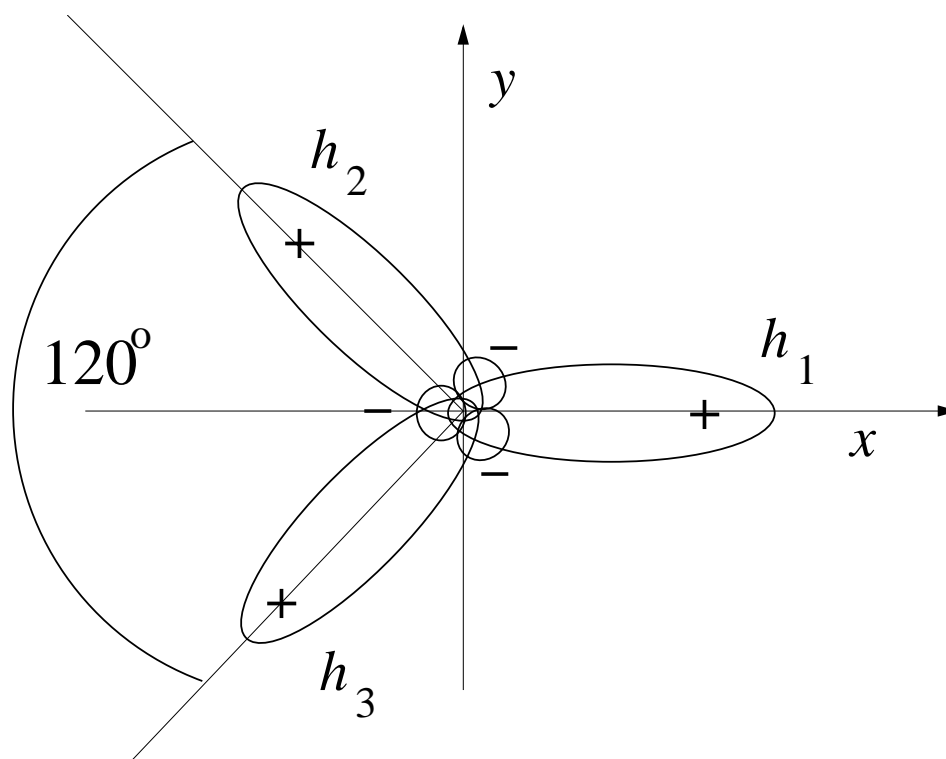
$$|h_2\rangle = \frac{1}{\sqrt{3}} \left(|s\rangle - \frac{1}{\sqrt{2}}|p_x\rangle + \sqrt{\frac{3}{2}}|p_y\rangle \right)$$

$$|h_3\rangle = \frac{1}{\sqrt{3}} \left(|s\rangle - \frac{1}{\sqrt{2}}|p_x\rangle - \sqrt{\frac{3}{2}}|p_y\rangle \right)$$

Note that for orbitals on the same atom:

$$\langle h_i|h_j\rangle = \delta_{ij}$$

The sp^2 orbitals are at 120° to each other.



It is energetically convenient to form these hybrids ?

The energy of one of the sp^2 hybrid is:

$$\epsilon_h = \langle h_i | H | h_i \rangle = (\epsilon_s + 2\epsilon_p)/3$$

I want to populate these three orbitals with 3 electrons:

$$E_{\text{tot}} = 3\epsilon_h = \epsilon_s + 2\epsilon_p$$

However in atomic carbon is $2s^2 2p^1 + 2p_z^1$

$$E_{\text{tot}} = 2\epsilon_s + \epsilon_p$$

This means that to populate the sp^2 orbital I have to spend a *promotion energy*:

$$E_{\text{pro}} = \epsilon_p - \epsilon_s$$

This is going to happen only if we gain energy in forming the bond:

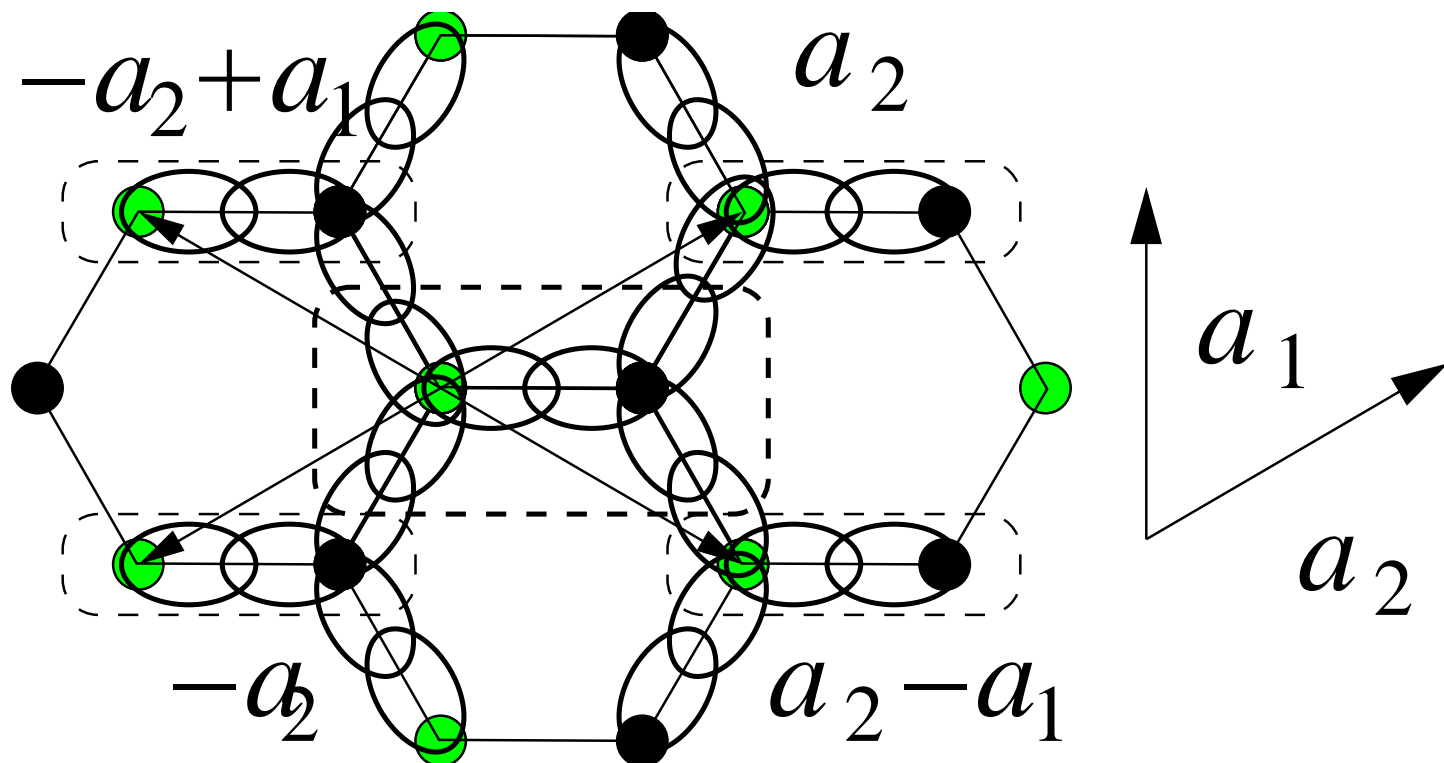
$$E_{\text{bond}} < E_{\text{pro}}$$

Calculate now the remaining bands

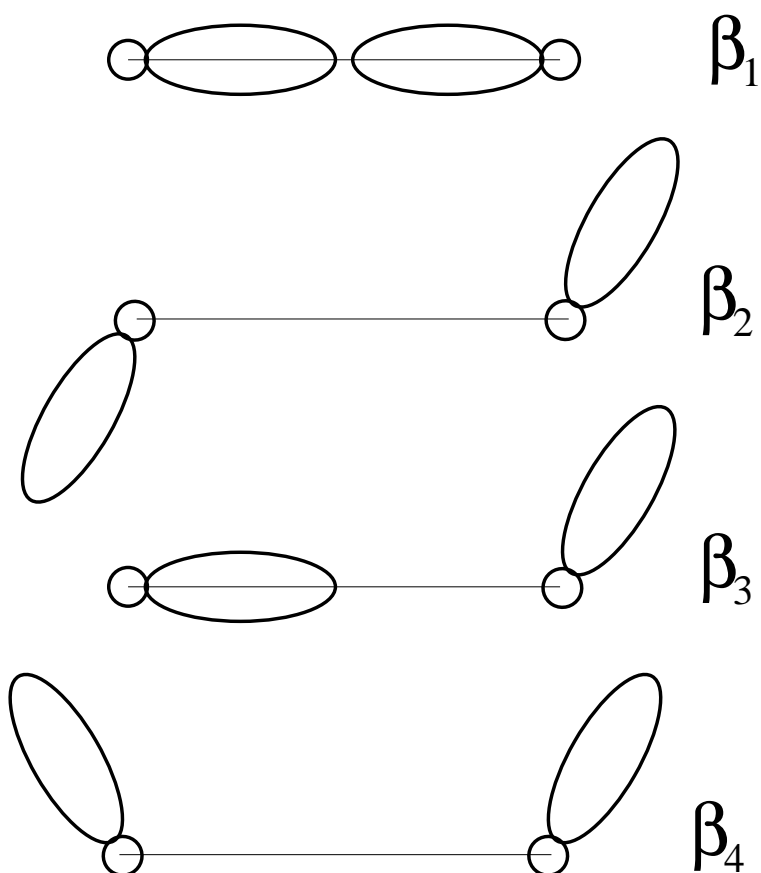
The band equation is always the same:

$$E(\vec{k})A_{n'}^{\vec{k}} = \sum_{\vec{R}} \sum_{n=1}^6 e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} A_n^{\vec{k}} \langle \vec{R}' n' | H | \vec{R} n \rangle$$

but now we have 6 degrees of freedom in the cell !!!



Note however that there are only four type of bond.



Are the respective matrix elements all large ?

Consider for instance β_1 . This is simply:

$$\begin{aligned} \beta_1 &= \langle h_1 | H | h_1 \rangle = \frac{1}{3} \left[\langle s | + \sqrt{2} \langle p_x | \right] | H | \left[| s \rangle - \sqrt{2} | p_x \rangle \right] = \\ &= \frac{1}{3} \left[s s \sigma - 2\sqrt{2} s p \sigma - 2 p p \sigma \right] \end{aligned}$$

In the same way one can show:

$$\beta_2 = \frac{1}{3} \left[ss\sigma + \sqrt{2} sp\sigma - \frac{1}{2} pp\sigma - \frac{3}{2} pp\pi \right]$$

$$\beta_3 = \frac{1}{3} \left[ss\sigma - \left(\frac{\sqrt{2}}{2} + \sqrt{2} \right) sp\sigma - pp\sigma \right]$$

$$\beta_4 = \frac{1}{3} \left[ss\sigma + \sqrt{2} sp\sigma - \frac{1}{2} pp\sigma + \frac{3}{2} pp\pi \right]$$

The point is that the integral $ss\sigma$, $sp\sigma$... are known. In particular we have the ratios (Harrison)

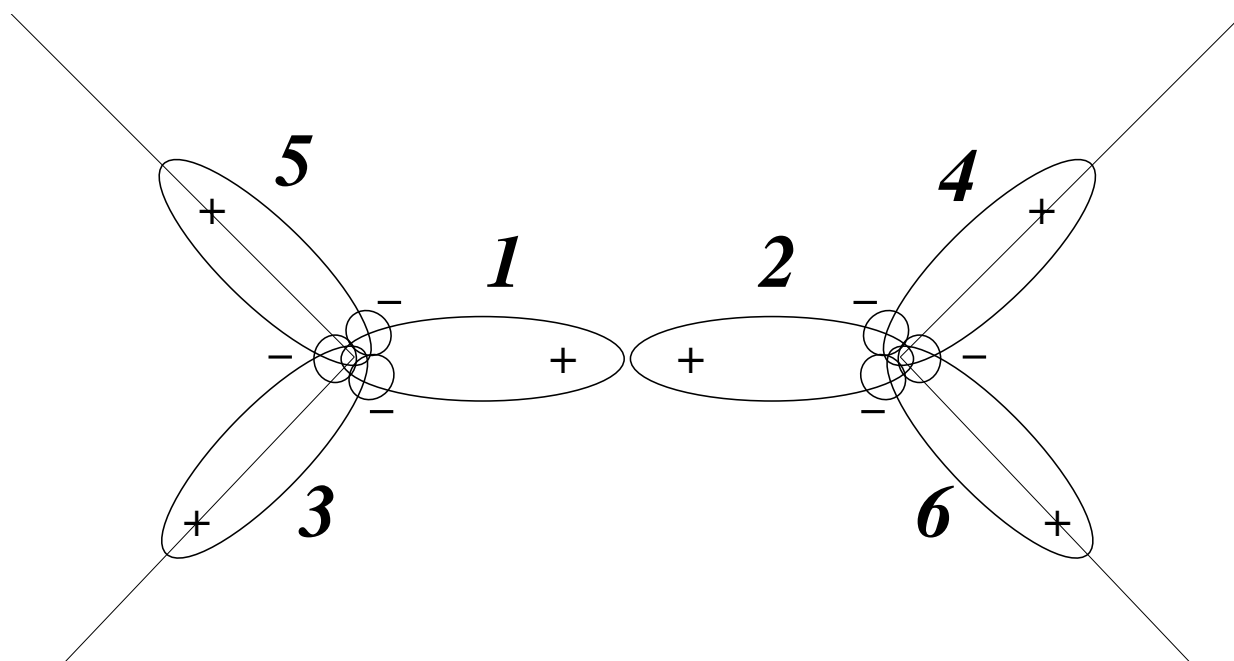
$$(ss\sigma) : (sp\sigma) : (pp\sigma) : (pp\pi) = -1.4 : 1.27 : 1.28 : -0.67$$

This means that for graphine:

$$|\beta_1| > |\beta_3| \gg |\beta_2| \sim |\beta_4|$$

Construct now the band equation:

On-site matrix:



$$\mathcal{H}_0 = \begin{pmatrix} \epsilon_h & \beta_1 & 0 & \beta_3 & 0 & \beta_3 \\ \beta_1 & \epsilon_h & \beta_3 & 0 & \beta_3 & 0 \\ 0 & \beta_3 & \epsilon_h & \beta_2 & 0 & \beta_4 \\ \beta_3 & 0 & \beta_2 & \epsilon_h & \beta_4 & 0 \\ 0 & \beta_3 & 0 & \beta_4 & \epsilon_h & \beta_2 \\ \beta_3 & 0 & \beta_4 & 0 & \beta_2 & \epsilon_h \end{pmatrix}$$

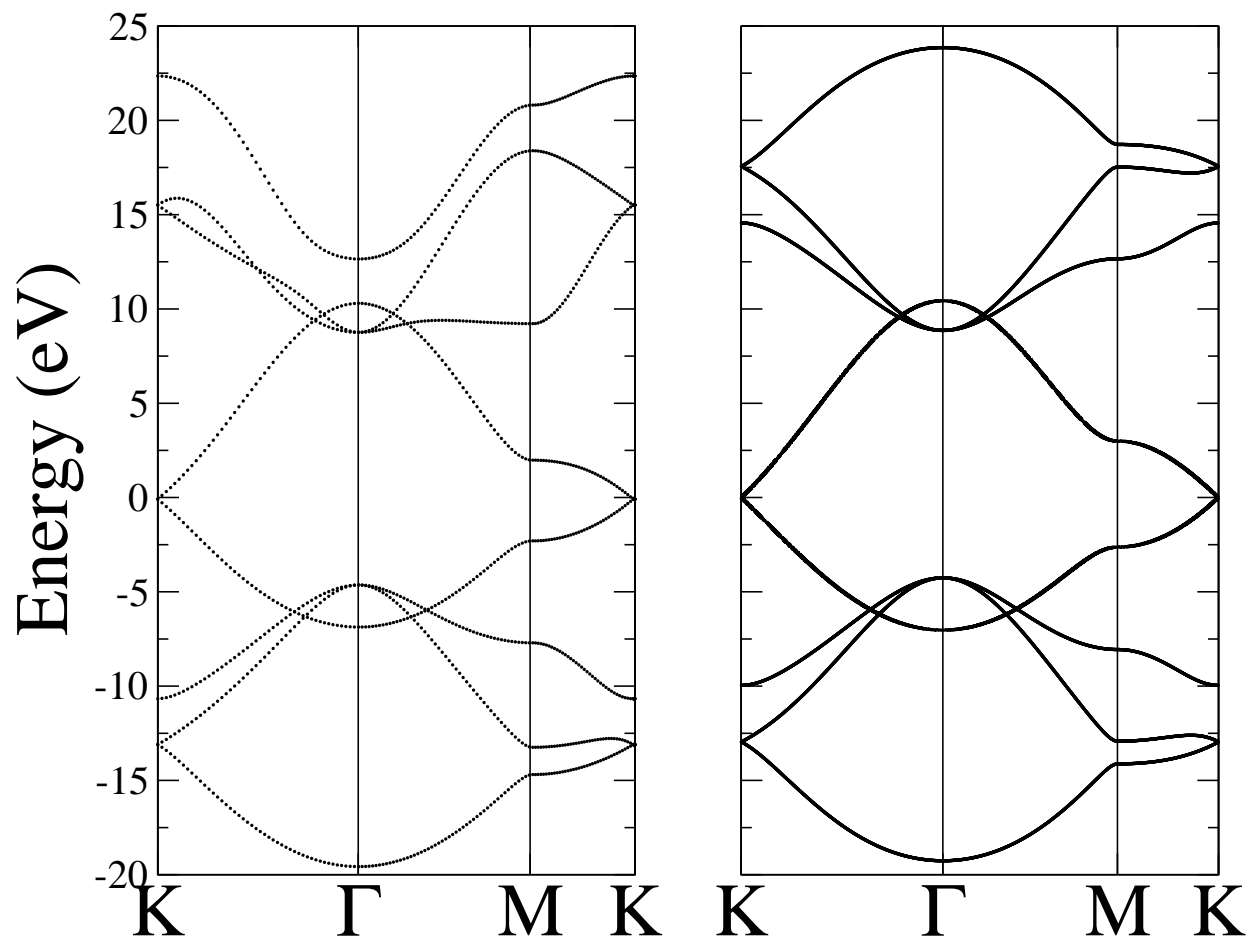
In a similar way one can construct the matrices that connect the unit cell with the other cells.

$$\mathcal{H}_1(\vec{k}) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_2 & 0 & \beta_3 & 0 & \beta_4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_3 & 0 & \beta_1 & 0 & \beta_3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_4 & 0 & \beta_3 & 0 & \beta_2 & 0 \end{pmatrix} e^{i\vec{k}\cdot\vec{a}_2}$$

$$\mathcal{H}_2(\vec{k}) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_2 & 0 & \beta_4 & 0 & \beta_3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_4 & 0 & \beta_2 & 0 & \beta_3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_3 & 0 & \beta_3 & 0 & \beta_1 & 0 \end{pmatrix} e^{i\vec{k}\cdot(\vec{a}_2-\vec{a}_1)}$$

Finally one diagonalize the resulting 6×6 matrix to find $E(\vec{K})$

$$\mathcal{H}_0 + \mathcal{H}_1(\vec{k}) + \mathcal{H}_2(\vec{k}) + \mathcal{H}_1^\dagger(\vec{k}) + \mathcal{H}_2^\dagger(\vec{k}) = E(\vec{k})\mathcal{I}$$



The Fermi Surface of graphine

First construct the reciprocal lattice. This is given by the relation

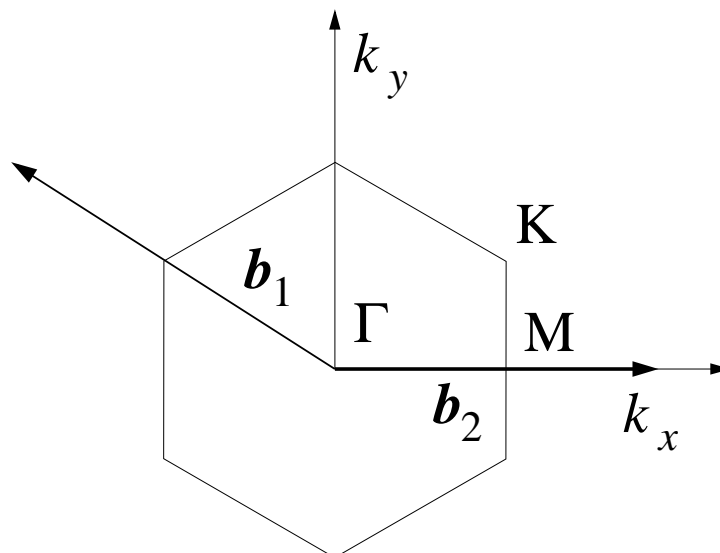
$$e^{i\vec{G}\cdot\vec{T}}$$

where \vec{T} is the translation vector of the lattice. In this case:

$$\vec{T} \rightarrow \begin{cases} \vec{a}_1 = a_0 \hat{y} \\ \vec{a}_2 = a_0 \left(\frac{\sqrt{3}}{2} \hat{x} + \frac{1}{2} \hat{y} \right) \end{cases}$$

$$\vec{G} \rightarrow \begin{cases} \vec{b}_1 = \frac{2\pi}{a_0} \left(\hat{k}_y - \frac{1}{\sqrt{3}} \hat{k}_x \right) \\ \vec{b}_2 = \frac{2\pi}{a_0} \left(\frac{2}{\sqrt{3}} \hat{k}_x \right) \end{cases}$$

The Brillouin zone is then



And the Fermi surface is simply 6 points !!!

