

5001 Electronic Structure: Lecture 4

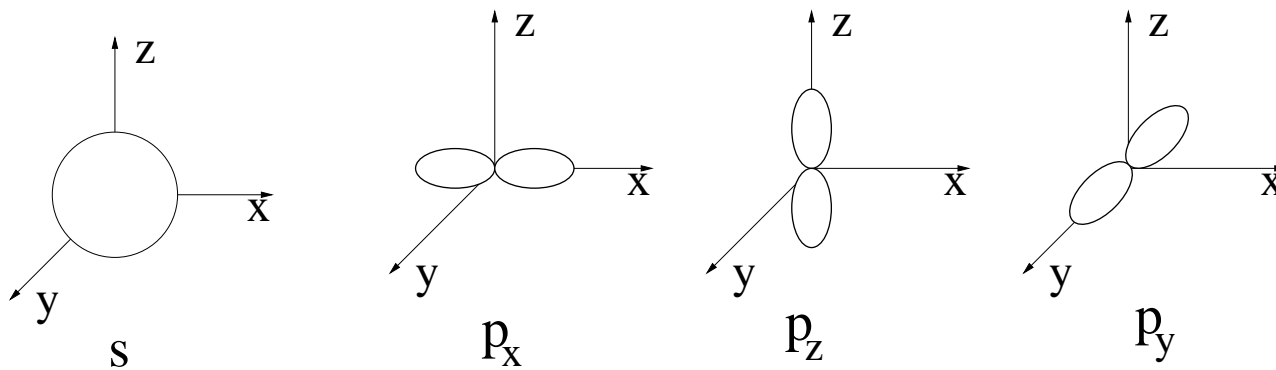
Including more molecular orbitals: Tight-binding method

Consider an infinite chain of C atoms.

Atomic C: $2s^2 2p^2$

In most solids C: $2s^1 2p^3$

It means that both the s and p states are relevant!!!



We can then expand our molecular state $|\psi\rangle$ as follows

$$|\psi\rangle = \sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha} |j\alpha\rangle$$

where $|j\alpha\rangle$ is the molecular orbital α of the atom j

So the Schrödinger equation takes the form

$$\sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha} H |j\alpha\rangle = E \sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha} |j\alpha\rangle$$

Again multiplying by $\langle l\beta|$

$$\sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha} \langle l\beta| H |j\alpha\rangle = E \sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha} \langle l\beta| j\alpha\rangle$$

Since translational symmetry, we can apply Bloch's Theorem:

$$\psi_{j\alpha} = A_{\alpha} e^{iKj}$$

So we obtain the secular equation:

$$\sum_j^N \sum_{\alpha}^{N_{\alpha}} A_{\alpha} e^{iKj} \langle l\beta | H | j\alpha \rangle = E \sum_j^N \sum_{\alpha}^{N_{\alpha}} A_{\alpha} e^{iKj} \langle l\beta | j\alpha \rangle$$

Atomic orbital with $l > 0$

The hydrogen atom wave-function are:

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

Note that:

- $R_{nl}(r)$ are real functions
- $Y_{lm}(\theta, \phi)$ may be complex

It is usually convenient to work with a linear combination of the spherical harmonics:

$$\Psi_{n1m}(r, \theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r) \begin{cases} x/r \\ y/r \\ z/r \end{cases}$$

Note that these orbitals have an odd parity (change sign under inversion)

Let us now calculate the matrix elements

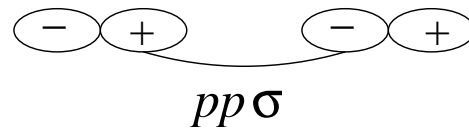
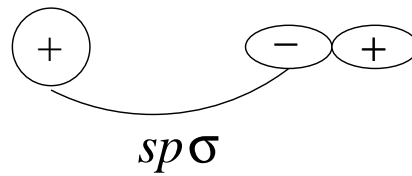
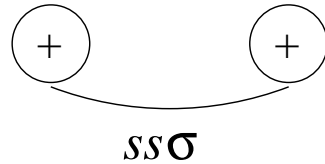
Orthogonal basis set:

$$\langle l\beta | j\alpha \rangle = \delta_{\alpha\beta} \delta_{lj}$$

Nearest-neighbors interaction

$$\langle l\beta | H | j\alpha \rangle = \begin{cases} \text{If } j = l & \begin{cases} \epsilon_{\alpha} & \text{for } \alpha = \beta \\ 0 & \text{for } \alpha \neq \beta \end{cases} \\ \text{If } j = l \pm 1 & \begin{cases} \gamma_{\alpha} & \text{for } \alpha = \beta \\ \gamma_{\alpha\beta} & \text{for } \alpha \neq \beta \end{cases} \end{cases}$$

How many orbitals shall we use?



Then $N_\alpha = 2$

$$\sum_j^N \sum_\alpha^{N_\alpha} A_\alpha e^{iK(j-l)} \langle l\beta | H | j\alpha \rangle = EA_\beta$$

Since our hypothesis on the matrix elements

$$EA_\beta = \sum_{\alpha}^{N_\alpha} A_\alpha [\langle l\beta|H|l\alpha\rangle + \\ + e^{iK}\langle l\beta|H|(l+1)\alpha\rangle + e^{-iK}\langle l\beta|H|(l-1)\alpha\rangle +]$$

This can be written in a simpler matrix form

$$E \begin{pmatrix} A_s \\ A_p \end{pmatrix} = \left[\begin{pmatrix} \epsilon_s & 0 \\ 0 & \epsilon_p \end{pmatrix} + \right. \\ \left. + \begin{pmatrix} \gamma_{ss\sigma} & \gamma_{sp\sigma} \\ -\gamma_{sp\sigma} & \gamma_{pp\sigma} \end{pmatrix} e^{iK} + \begin{pmatrix} \gamma_{ss\sigma} & -\gamma_{sp\sigma} \\ \gamma_{sp\sigma} & \gamma_{pp\sigma} \end{pmatrix} e^{-iK} \right] \begin{pmatrix} A_s \\ A_p \end{pmatrix}$$

which reduces to

$$\begin{pmatrix} \epsilon_s + 2\gamma_{ss\sigma} \cos K & 2i\gamma_{sp\sigma} \sin K \\ -2i\gamma_{sp\sigma} \sin K & \epsilon_p + 2\gamma_{pp\sigma} \cos K \end{pmatrix} \begin{pmatrix} A_s \\ A_p \end{pmatrix} = E \begin{pmatrix} A_s \\ A_p \end{pmatrix}$$

Note that:



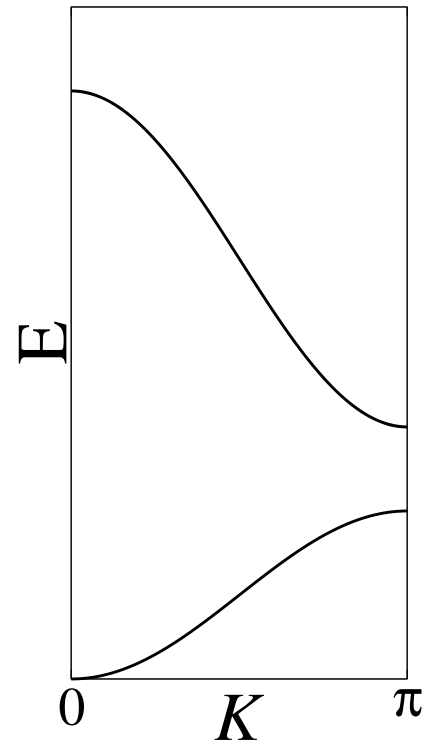
Simple solution: $\gamma_{sp\sigma} = 0$

Then

$$E = \begin{cases} \epsilon_s + 2\gamma_{ss\sigma} \cos K = \epsilon_s(K) \\ \epsilon_p + 2\gamma_{pp\sigma} \cos K = \epsilon_p(K) \end{cases}$$

This is equivalent to two independent chains one only with s electrons and one

only with p



General Case:

One must solve the eigenvalues equation:

$$\begin{pmatrix} \epsilon_s + 2\gamma_{ss\sigma} \cos K & 2i\gamma_{sp\sigma} \sin K \\ -2i\gamma_{sp\sigma} \sin K & \epsilon_p + 2\gamma_{pp\sigma} \cos K \end{pmatrix} \begin{pmatrix} A_s \\ A_p \end{pmatrix} = E \begin{pmatrix} A_s \\ A_p \end{pmatrix}$$

which has solutions

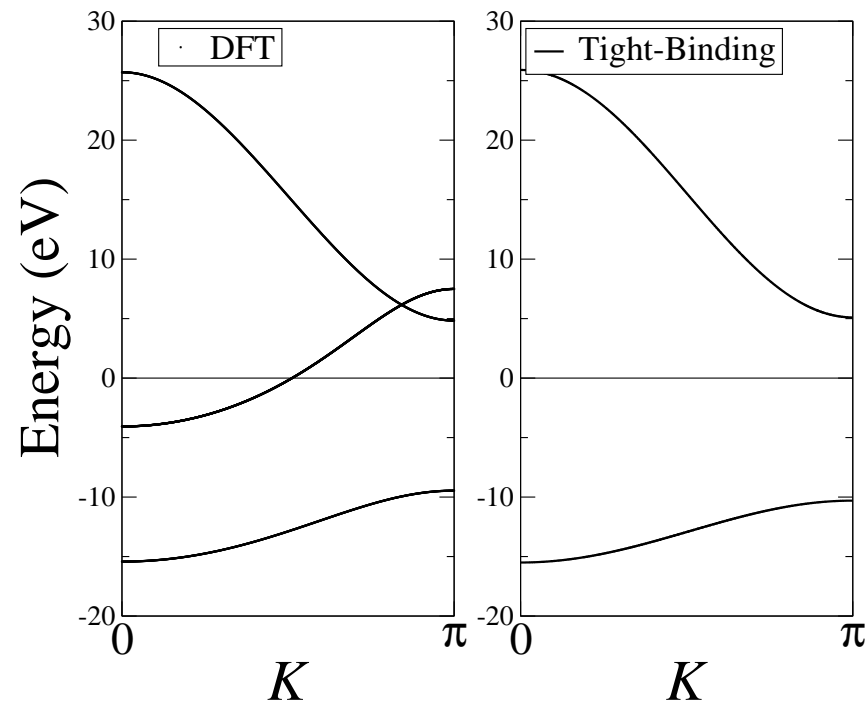
$$E = \frac{1}{2} \left[\epsilon_s(K) + \epsilon_p(K) \pm \sqrt{[\epsilon_s(K) - \epsilon_p(K)]^2 + 16\gamma_{sp\sigma}^2 \sin^2 K} \right]$$

with

$$\epsilon_s(K) = \epsilon_s + 2\gamma_{ss\sigma} \cos K \quad \text{and} \quad \epsilon_p(K) = \epsilon_p + 2\gamma_{pp\sigma} \cos K$$

Note the correct limit for $\gamma_{sp\sigma} \rightarrow 0$

This work remarkably well !!!!

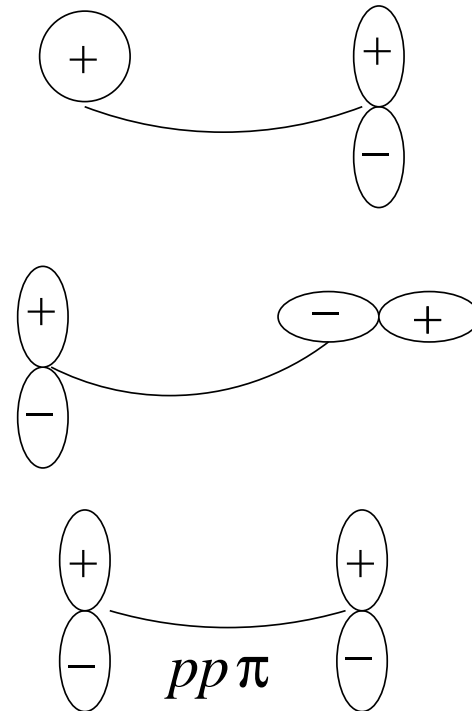


$$\epsilon_s = -12.9 \text{ eV}, \epsilon_p = 15.5 \text{ eV}, \gamma_{ss\sigma} = -1.3 \text{ eV}, \gamma_{pp\sigma} = 5.2 \text{ eV}, \gamma_{sp\sigma} = 0.5 \text{ eV}$$

What about the remaining band?

We have to include the forgotten p_y and p_z

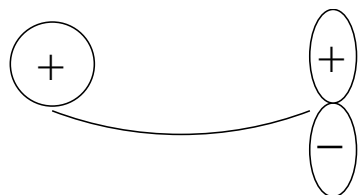
This gives us matrix elements such as: $\langle l^{p_y} | H | (l-1)^s \rangle$, $\langle l^{p_y} | H | (l-1)^{p_x} \rangle$...



However only $pp\pi$ is not zero!!!

How to assign values to matrix elements?

- The zeros are mostly given by symmetry



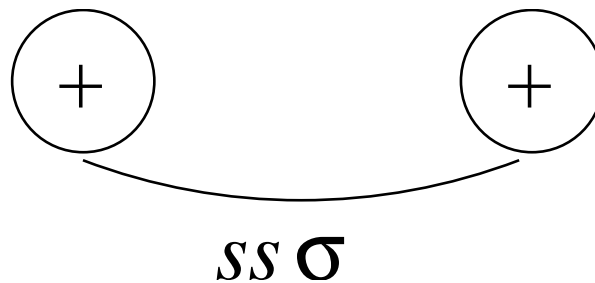
The rule is: *A matrix element $\langle l^\beta | H | (l-1)^\alpha \rangle$ is zero if the two atomic states at either end of the bond share the same angular momentum component about the bond axis*

Consider a circuit of radius r around the bond axis. The length of the circuit is the $2\pi r = \lambda n$, where λ is the wave length, and n the number of time the circuit pass through two lobes with opposite sign.

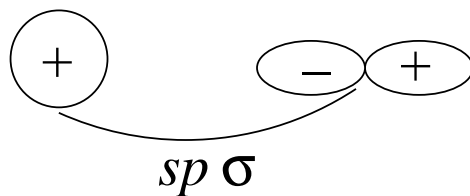
The linear momentum is $p = h/\lambda = nh/(2\pi r)$

The angular momentum is $pr = nh/2\pi \rightarrow m = n$

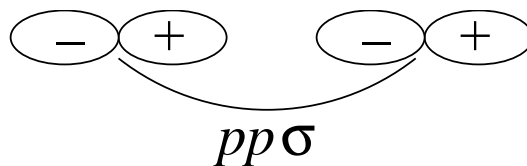
- $ss\sigma$: $\langle s|H|s\rangle < 0$



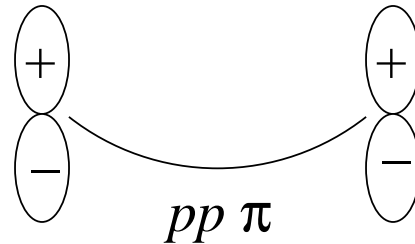
- $sp\sigma$: $\langle s|H|p_x\rangle > 0$



- $pp\sigma$: $\langle p_x|H|p_x\rangle > 0$



- $pp\pi: \langle p_y | H | p_y \rangle < 0$



- The amplitude of the matrix elements depends on the degree of overlap.

From this one can conclude:

1. The first band is mainly s and dominated by $ss\sigma$
2. The last band is mainly p and dominated by $pp\sigma$
3. The one in between must have something to do with p and $pp\pi$

Extension of the model

Include also p_y and p_z . Now $N_\alpha=4$.

$$\sum_j^N \sum_\alpha^{N_\alpha} A_\alpha e^{iK(j-l)} \langle l\beta | H | j\alpha \rangle = EA_\beta$$

Since our consideration on the overlap integrals we can write:

$$H_0 A + e^{iK} H_1 A + e^{-iK} H_1^\dagger A = AE$$

where now

$$A = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \end{pmatrix}, \quad H_0 = \begin{pmatrix} \epsilon_s & 0 & 0 & 0 \\ 0 & \epsilon_{p_x} & 0 & 0 \\ 0 & 0 & \epsilon_{p_y} & 0 \\ 0 & 0 & 0 & \epsilon_{p_z} \end{pmatrix}$$

$$H_1 = \begin{pmatrix} \gamma_{ss\sigma} & \gamma_{sp\sigma} & 0 & 0 \\ -\gamma_{sp\sigma} & \gamma_{pp\sigma} & 0 & 0 \\ 0 & 0 & \gamma_{pp\pi} & 0 \\ 0 & 0 & 0 & \gamma_{pp\pi} \end{pmatrix}$$

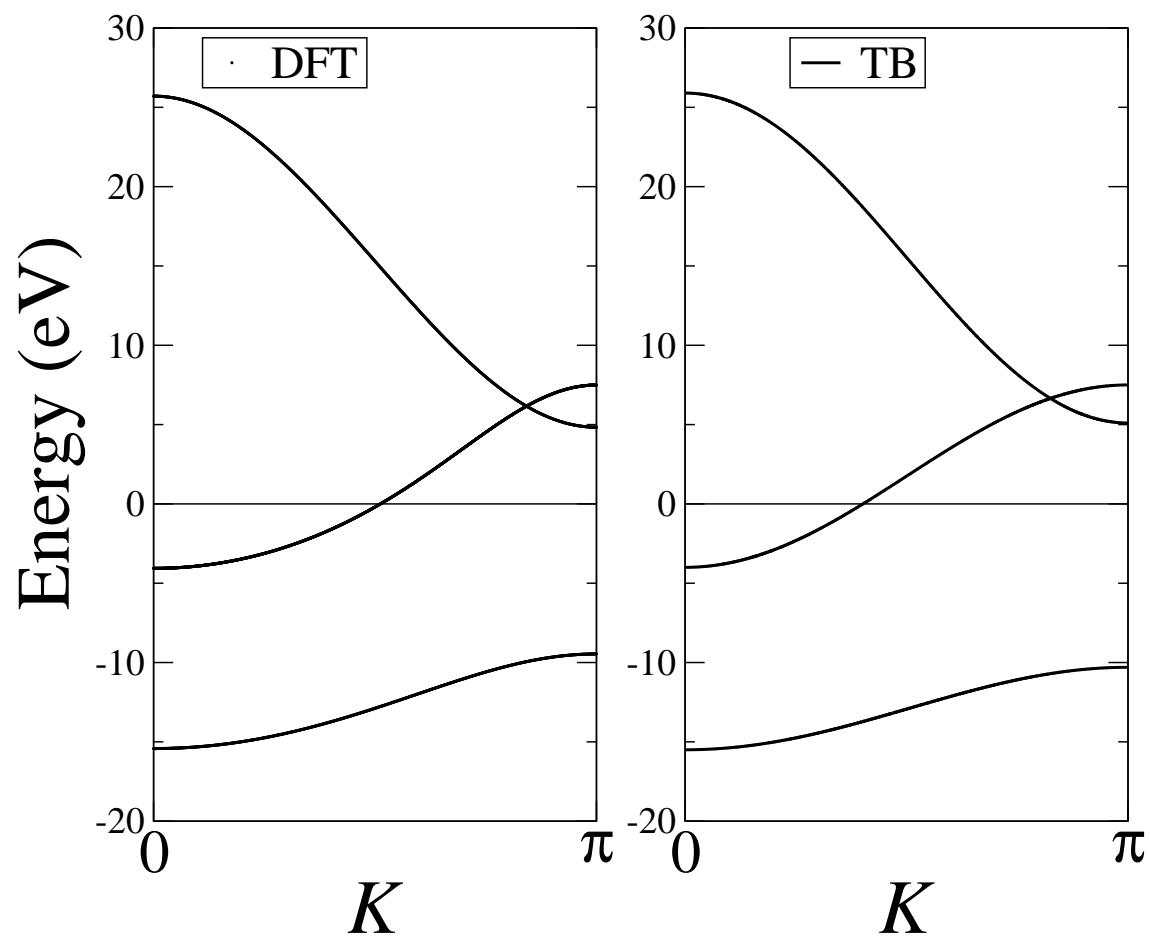
The solutions of the secular equation are:

$$E = \frac{1}{2} \left[\epsilon_s(K) + \epsilon_{p_x}(K) + \sqrt{[\epsilon_s(K) - \epsilon_{p_x}(K)]^2 + 16\gamma_{sp\sigma} \sin^2 K} \right]$$

$$E = \frac{1}{2} \left[\epsilon_s(K) + \epsilon_{p_x}(K) - \sqrt{[\epsilon_s(K) - \epsilon_{p_x}(K)]^2 + 16\gamma_{sp\sigma} \sin^2 K} \right]$$

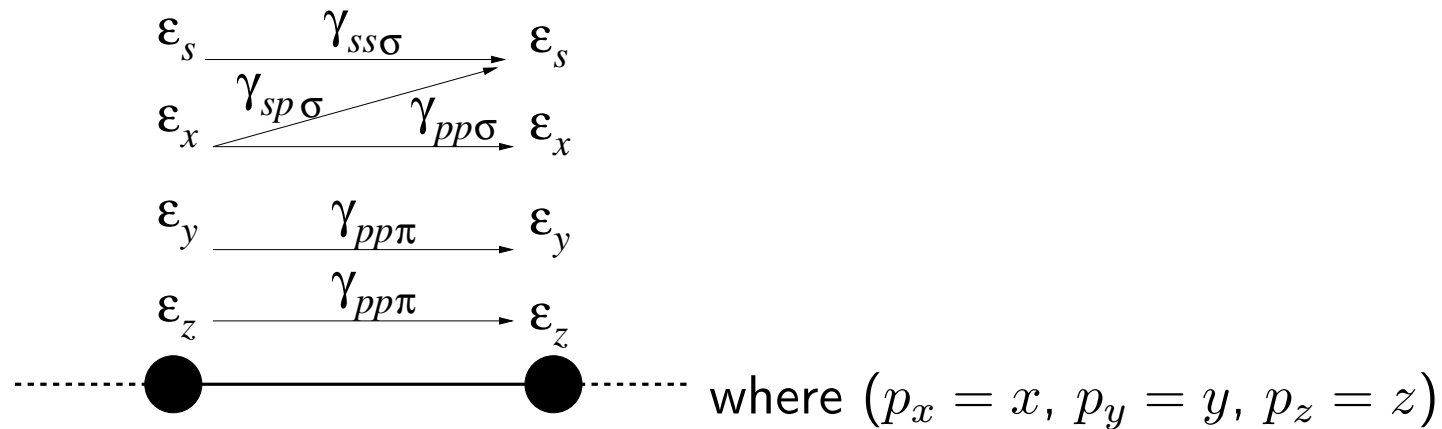
$$E = \epsilon_{p_y} + 2\gamma_{pp\pi} \cos(K)$$

$$E = \epsilon_{p_z} + 2\gamma_{pp\pi} \cos(K)$$



Constructing the secular equation

- Draw the system introducing the relevant degrees of freedom and their coupling

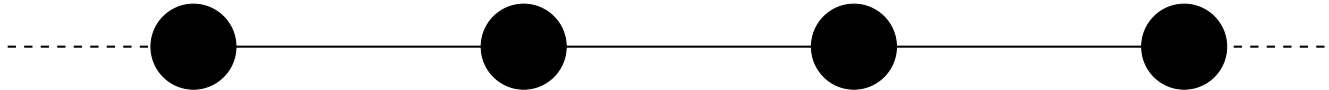


- The secular equation has the form: $[H_0 + H_1 e^{ika} + H_1^\dagger e^{-ika}] \Psi = E \Psi$

$$\Psi = \begin{pmatrix} A_s \\ A_x \\ A_y \\ A_z \end{pmatrix}, H_0 = \begin{pmatrix} \epsilon_s & 0 & 0 & 0 \\ 0 & \epsilon_x & 0 & 0 \\ 0 & 0 & \epsilon_y & 0 \\ 0 & 0 & 0 & \epsilon_z \end{pmatrix}, H_1 = \begin{pmatrix} \gamma_{ss\sigma} & \gamma_{sp\sigma} & 0 & 0 \\ -\gamma_{sp\sigma} & \gamma_{pp\sigma} & 0 & 0 \\ 0 & 0 & \gamma_{pp\pi} & 0 \\ 0 & 0 & 0 & \gamma_{pp\pi} \end{pmatrix}$$

Local Density of States (LDOS)

Consider again the infinite Carbon chain



Our basis set is as usual $|j\alpha\rangle$ (j labels the atomic position, α the orbitals).

Consider a generic eigenstates $|\psi_k\rangle$. This is written as:

$$|\psi_k\rangle = \sum_j \sum_\alpha |j\alpha\rangle \langle j\alpha | \psi_k \rangle = \sum_j \sum_\alpha \langle j\alpha | \psi_k \rangle |j\alpha\rangle$$

As usual $|\langle j\alpha | \psi_k \rangle|^2$ is the probability to find an electron in the state $|\psi_k\rangle$ at the particular basis state $|j\alpha\rangle$

The idea is then to “weight” the total DOS $D(E)$ with the $|\langle j\alpha | \psi_k \rangle|^2$. We

then define *Local Density of States* $d_{j\alpha}(E)$ as

$$d_{j\alpha}(E) = \sum_{\text{all } E_k} |\langle j\alpha | \psi_k \rangle|^2 f(E - E_k)$$

Note that from the orthonormality of $|j\alpha\rangle$ we have the important *sum rule*

$$\sum_{j\alpha} d_{j\alpha}(E) = D(E)$$

This tells us the DOS of a particular orbital sitting on a particular atom (it is not the total DOS per atom !!!).

In particular two quantities are usually interesting:

1. Atomic Density of States

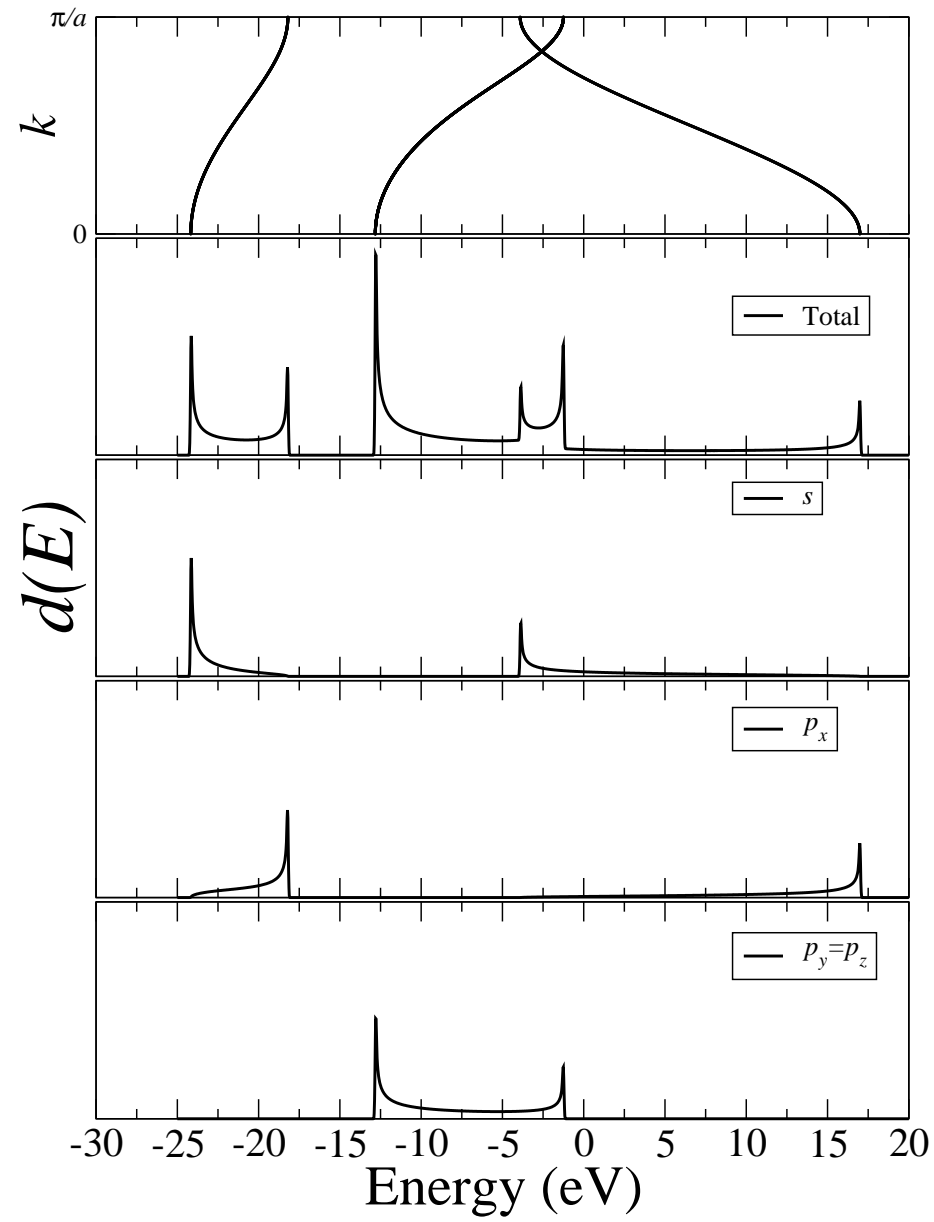
$$d_j(E) = \sum_{\alpha} d_{j\alpha}(E) = \sum_{\alpha} \sum_{\text{all } E_k} |\langle j\alpha | \psi_k \rangle|^2 f(E - E_k)$$

this is important for finite system (surfaces, dots ...)

2. Orbital resolved density of states

$$d_{\alpha}(E) = \sum_j d_{j\alpha}(E) = \sum_j \sum_{\text{all } E_k} |\langle j\alpha | \psi_k \rangle|^2 f(E - E_k)$$

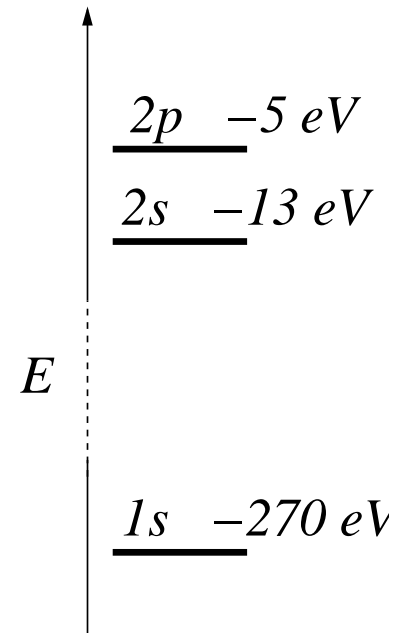
this is important for understanding how the electrons distribute over the basis orbitals



The Band Structure of Graphene

Consider again Carbon. Which atomic orbitals are appropriate to describe solid state C ?

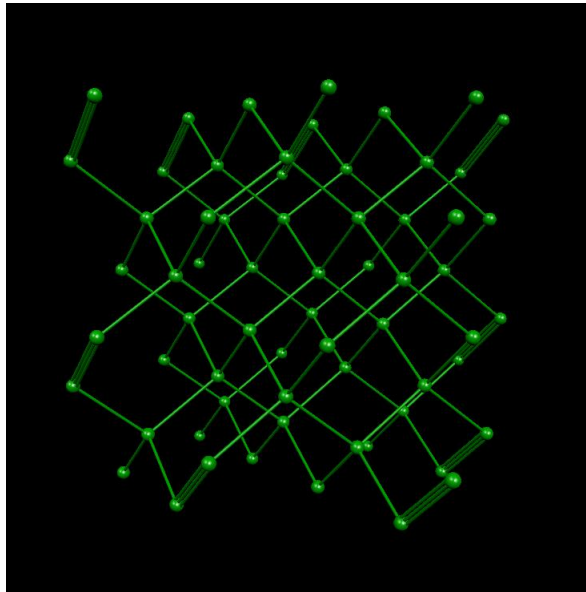
- Atomic Carbon: $1s^2 2s^2 2p^2$
- Solid State: $1s^2 2s^1 2p^3$



In solid state C appears in two different states:

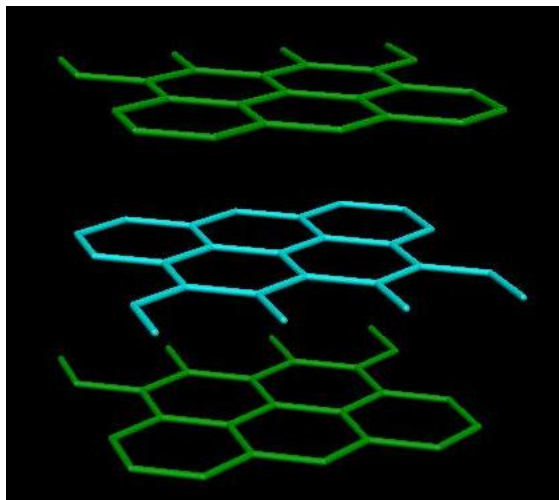
Diamond:

Each Carbon atom has 4 nearest neighbors forming a 109° angle \longrightarrow All s , p_x , p_y , and p_z must be equivalent.



Graphite:

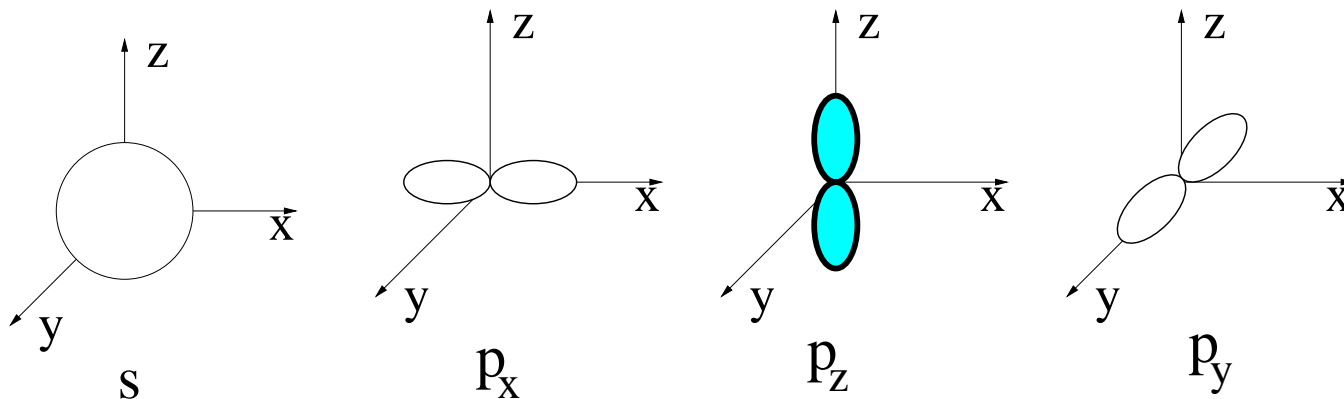
Each Carbon atom has 3 nearest neighbors in the $x-y$ plane forming a 120° angle.



Note that in graphite:

- The C-C separation is 1.42 \AA
- The inter-plane separation is 3.37 \AA

Clearly s , p_x , p_y , must be treated differently than p_z .



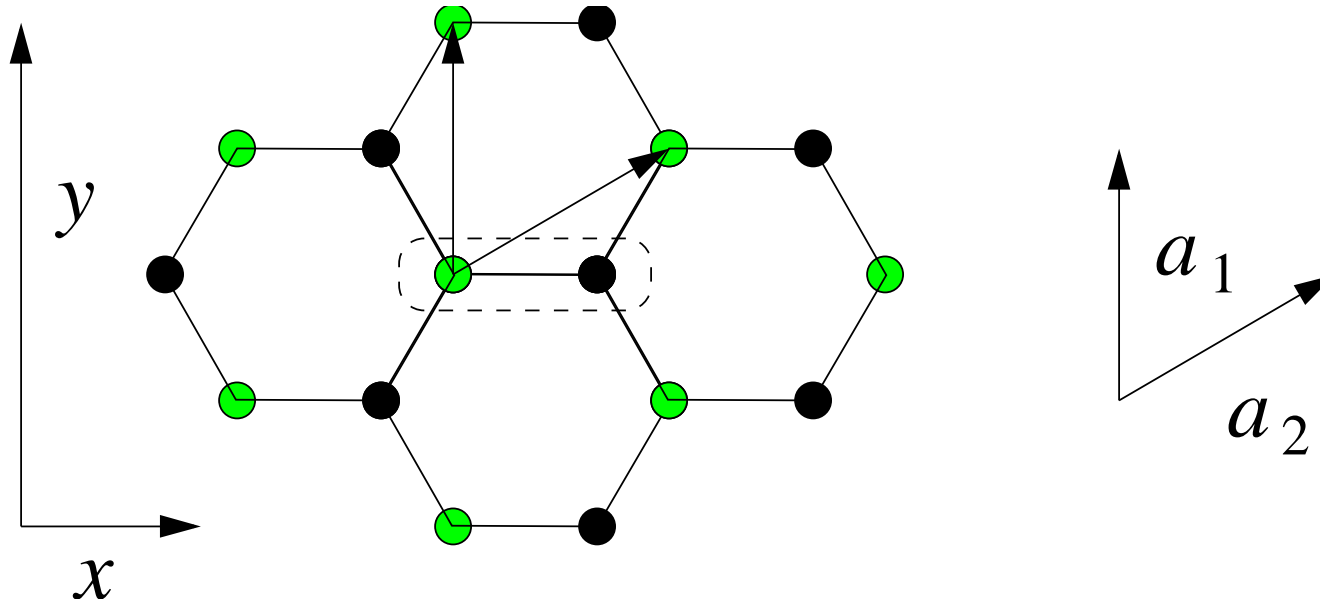
Graphene

In analogy with the linear C-chain, we guess that the relevant orbitals at the Fermi level are the p_z . This means that our “molecular state” $|\psi_{\vec{k}}\rangle$ can be written as:

$$|\psi_{\vec{k}}\rangle = \frac{1}{N^{1/2}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} |\vec{R}\rangle$$

$|\vec{R}\rangle$ represents a p_z orbital at the atomic site \vec{R} .

Let us define the geometry of the problem:



where

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

All the atoms of the crystal can be obtained as follows:

1. We need to consider two atoms in the cell (black and green). This is called the *primitive cell*
2. All the other atoms can be obtained from the primitive cell with a translation $\vec{T} = \vec{a}_1 m + \vec{a}_2 n$ (m and n are integer).
 \vec{a}_1 and \vec{a}_2 are called *primitive lattice vectors*

Since we have two atoms in the cell a better choice of basis is $|\vec{R} n\rangle$:

$$|\psi_{\vec{k}}\rangle = \frac{1}{N^{1/2}} \sum_{\vec{R}} \sum_{n=1}^2 e^{i\vec{k}\cdot\vec{R}} A_n^{\vec{k}} |\vec{R} n\rangle$$

where $|\vec{R} n\rangle$ represents an atom n ($n=1$ for green atoms, $n=2$ for black atoms) belonging to the cell located at \vec{R} . We assume an orthogonal basis set.

$|A_n^{\vec{k}}|^2$ is the probability to find an electron in the state $|\psi_{\vec{k}}\rangle$ on the atom n .

Then the energy $E(\vec{k})$ is given by (Bloch's Theorem)

$$E(\vec{k})A_{n'}^{\vec{k}} = \sum_{\vec{R}} \sum_n^2 e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} A_n^{\vec{k}} \langle \vec{R}' n' | H | \vec{R} n \rangle$$

Let us consider carefully the matrix elements:

Again we use the matrix notation for the amplitudes $A_n^{\vec{k}}$. We also consider only nearest neighbors interaction.

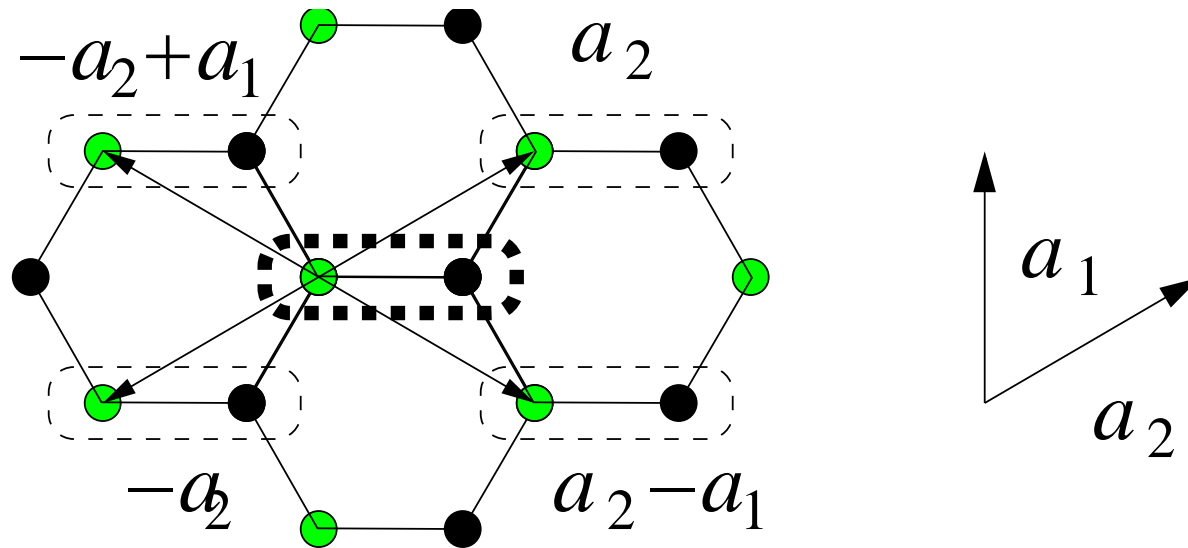
On-site energy: coupling with the primitive cell

$$\langle \vec{R}' n' | H | \vec{R}' n \rangle = \begin{pmatrix} \epsilon_p & \gamma_{pp\pi} \\ \gamma_{pp\pi} & \epsilon_p \end{pmatrix}$$

The phase factor is $e^{i\vec{k}\cdot(\vec{R}'-\vec{R}')} = 1$

Off-diagonal terms: coupling with other cells

Each cell has four nearest neighbor cells



1. Cell \vec{a}_2

$$\langle \vec{R}' n' | H | \vec{R}' + \vec{a}_2 n \rangle = \begin{pmatrix} 0 & 0 \\ \gamma_{pp\pi} & 0 \end{pmatrix}$$

The phase factor is $e^{i\vec{k}\cdot(\vec{R}' + \vec{a}_2 - \vec{R}')} = e^{i\vec{k}\cdot\vec{a}_2}$

2. Cell $\vec{a}_2 - \vec{a}_1$

$$\langle \vec{R}' n' | H | \vec{R}' + \vec{a}_2 - \vec{a}_1 n \rangle = \begin{pmatrix} 0 & 0 \\ \gamma_{pp\pi} & 0 \end{pmatrix}$$

The phase factor is $e^{i\vec{k}\cdot(\vec{R}' + \vec{a}_2 - \vec{a}_1 - \vec{R}')} = e^{i\vec{k}\cdot(\vec{a}_2 - \vec{a}_1)}$

3. Cell $-\vec{a}_2$

$$\langle \vec{R}' n' | H | \vec{R}' - \vec{a}_2 n \rangle = \begin{pmatrix} 0 & \gamma_{pp\pi} \\ 0 & 0 \end{pmatrix}$$

The phase factor is $e^{i\vec{k}\cdot(\vec{R}' - \vec{a}_2 - \vec{R}')} = e^{-i\vec{k}\cdot\vec{a}_2}$

4. Cell $-\vec{a}_2 + \vec{a}_1$

$$\langle \vec{R}' n' | H | \vec{R}' - \vec{a}_2 + \vec{a}_1 n \rangle = \begin{pmatrix} 0 & \gamma_{pp\pi} \\ 0 & 0 \end{pmatrix}$$

The phase factor is $e^{i\vec{k}\cdot(\vec{R}' - \vec{a}_2 + \vec{a}_1 - \vec{R}')} = e^{-i\vec{k}\cdot(\vec{a}_2 - \vec{a}_1)}$

Now let us put all together:

$$E(\vec{k})\Psi_{\vec{k}} = \begin{pmatrix} \epsilon_p & \gamma_{pp\pi} f(\vec{k}) \\ \gamma_{pp\pi} f(\vec{k})^* & \epsilon_p \end{pmatrix} \Psi_{\vec{k}}$$

where:

$$\Psi_{\vec{k}} = \begin{pmatrix} A_1^{\vec{k}} \\ A_2^{\vec{k}} \end{pmatrix}$$

$$\begin{aligned}
 f(\vec{k}) &= 1 + e^{-i\vec{k}\cdot\vec{a}_2} + e^{-i\vec{k}\cdot(\vec{a}_2-\vec{a}_1)} = \\
 &= 1 + 2 e^{-ik_x\frac{\sqrt{3}}{2}a_0} \cos\left(\frac{k_y}{2}a_0\right)
 \end{aligned}$$

The eigenvalues are then given by

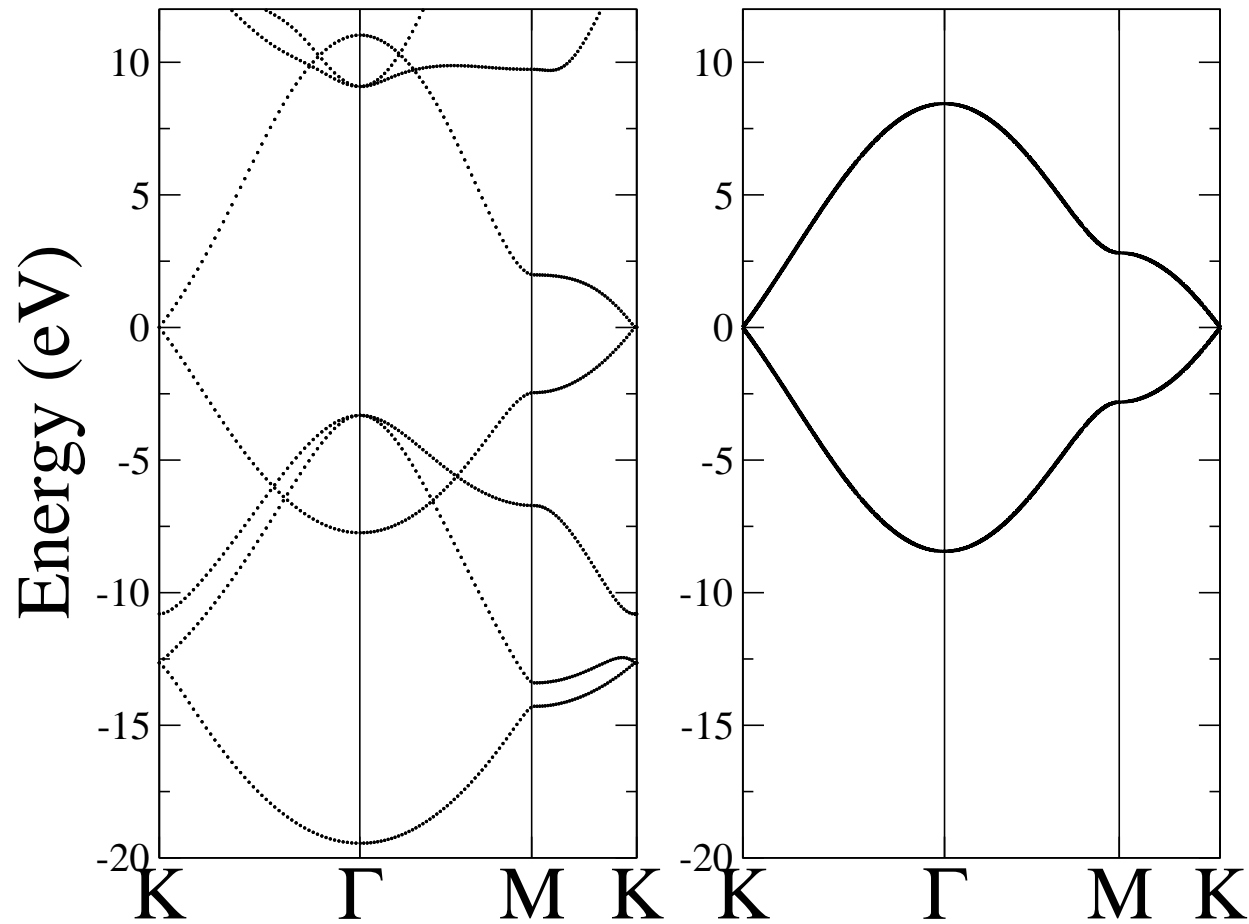
$$\det \begin{pmatrix} \epsilon_p - E(\vec{k}) & \gamma_{pp\pi} f(\vec{k}) \\ \gamma_{pp\pi} f(\vec{k})^* & \epsilon_p - E(\vec{k}) \end{pmatrix} = 0$$

which has solutions:

$$E(\vec{k}) = \epsilon_p \pm \gamma_{pp\pi} \sqrt{f(\vec{k})f(\vec{k})^*}$$

$$E(\vec{k}) = \epsilon_p \pm \gamma_{pp\pi} \sqrt{1 + 4 \cos^2\left(\frac{k_y a_0}{2}\right) + 4 \cos\left(\frac{k_y a_0}{2}\right) \cos\left(\frac{\sqrt{3}}{2} k_x a_0\right)}$$

This gives



The band just described is called the π band. Moreover:

- π band with $E(\vec{k}) < \epsilon_p$ is the bonding part of the band
→ π band
- π band with $E(\vec{k}) > \epsilon_p$ is the antibonding part of the band
→ π^* band

This is somehow unsatisfactory since:

1. The π bands are symmetric with respect to $E = \epsilon_p$
2. One band is completely missed

Fixing the π band

The approximation we have to give up in this case is that of orthogonality of the basis set:

$$\langle \vec{R}' n' | \vec{R} n \rangle = \begin{cases} 1 & \text{if } (\vec{R}' n') = (\vec{R} n) \\ S & \text{if } (\vec{R}' n'), (\vec{R} n) \text{ nn} \\ 0 & \text{elsewhere} \end{cases}$$

we can still use the “molecular state”

$$|\psi_{\vec{k}}\rangle = \frac{1}{N^{1/2}} \sum_{\vec{R}} \sum_{n=1}^2 e^{i\vec{k}\cdot\vec{R}} A_n^{\vec{k}} |\vec{R} n\rangle$$

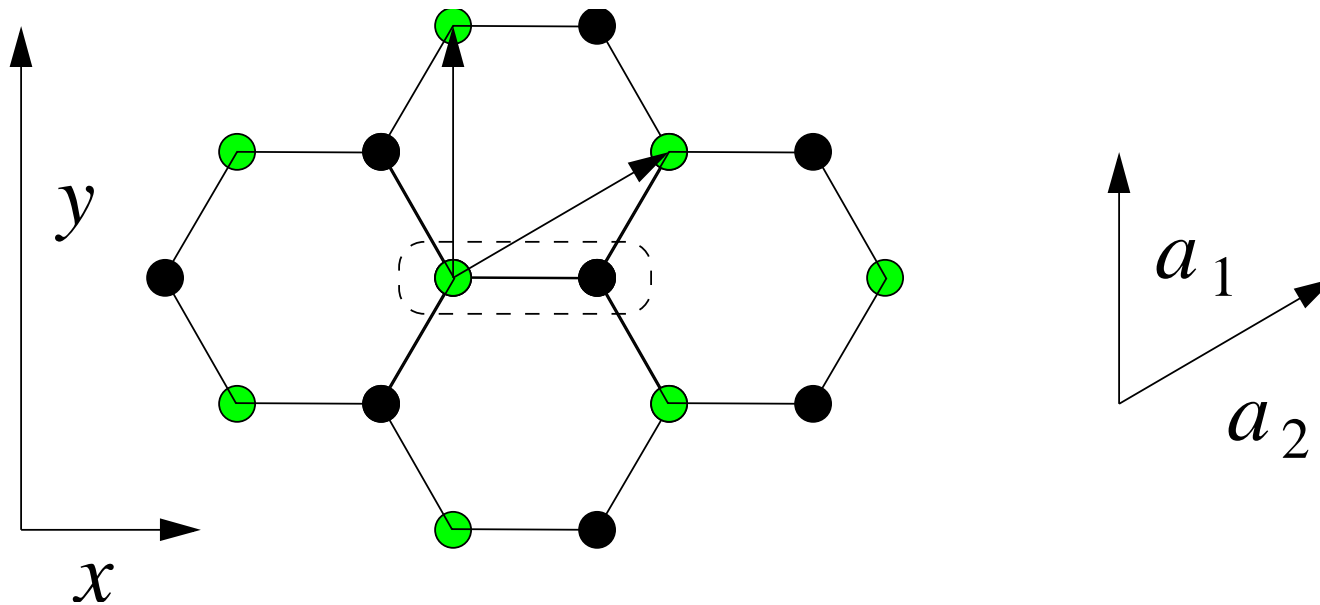
to solve the Schrödinger equation $H|\psi_{\vec{k}}\rangle = E|\psi_{\vec{k}}\rangle$

$$\sum_{\vec{R}} \sum_{n=1}^2 A_n^{\vec{k}} e^{i\vec{k}\cdot\vec{R}} H|\vec{R} n\rangle = E(\vec{k}) \sum_{\vec{R}} \sum_{n=1}^2 A_n^{\vec{k}} e^{i\vec{k}\cdot\vec{R}} |\vec{R} n\rangle$$

But now when we multiply by $\langle\vec{R}' n'|\$, we obtain

$$\sum_{\vec{R}} \sum_{n=1}^2 A_n^{\vec{k}} e^{i\vec{k}\cdot\vec{R}} \langle\vec{R}' n'|H|\vec{R} n\rangle = E(\vec{k}) \sum_{\vec{R}} \sum_{n=1}^2 A_n^{\vec{k}} e^{i\vec{k}\cdot\vec{R}} \langle\vec{R}' n'|\vec{R} n\rangle$$

This is analogous to the case of the H molecule. However the overlap matrix \mathcal{S} now has some phases (as well as the Hamiltonian matrix elements).



On-site terms: overlap within the primitive cell

$$\langle \vec{R}' n' | \vec{R}' n \rangle = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}$$

The phase factor is $e^{i\vec{k} \cdot \vec{R}'}$

Off-diagonal terms: overlap with other cells

Each cell has four nearest neighbor cells

1. Cell \vec{a}_2

$$\langle \vec{R}' n' | \vec{R}' + \vec{a}_2 n \rangle = \begin{pmatrix} 0 & 0 \\ S & 0 \end{pmatrix}$$

The phase factor is $e^{i\vec{k} \cdot (\vec{R}' + \vec{a}_2)}$

2. Cell $\vec{a}_2 - \vec{a}_1$

$$\langle \vec{R}' n' | H | \vec{R}' + \vec{a}_2 - \vec{a}_1 n \rangle = \begin{pmatrix} 0 & 0 \\ S & 0 \end{pmatrix}$$

The phase factor is $e^{i\vec{k} \cdot (\vec{R}' + \vec{a}_2 - \vec{a}_1)}$

3. Cell $-\vec{a}_2$

$$\langle \vec{R}' n' | \vec{R}' - \vec{a}_2 n \rangle = \begin{pmatrix} 0 & S \\ 0 & 0 \end{pmatrix}$$

The phase factor is $e^{i\vec{k}\cdot(\vec{R}' - \vec{a}_2)}$

4. Cell $-\vec{a}_2 + \vec{a}_1$

$$\langle \vec{R}' n' | \vec{R}' - \vec{a}_2 + \vec{a}_1 n \rangle = \begin{pmatrix} 0 & S \\ 0 & 0 \end{pmatrix}$$

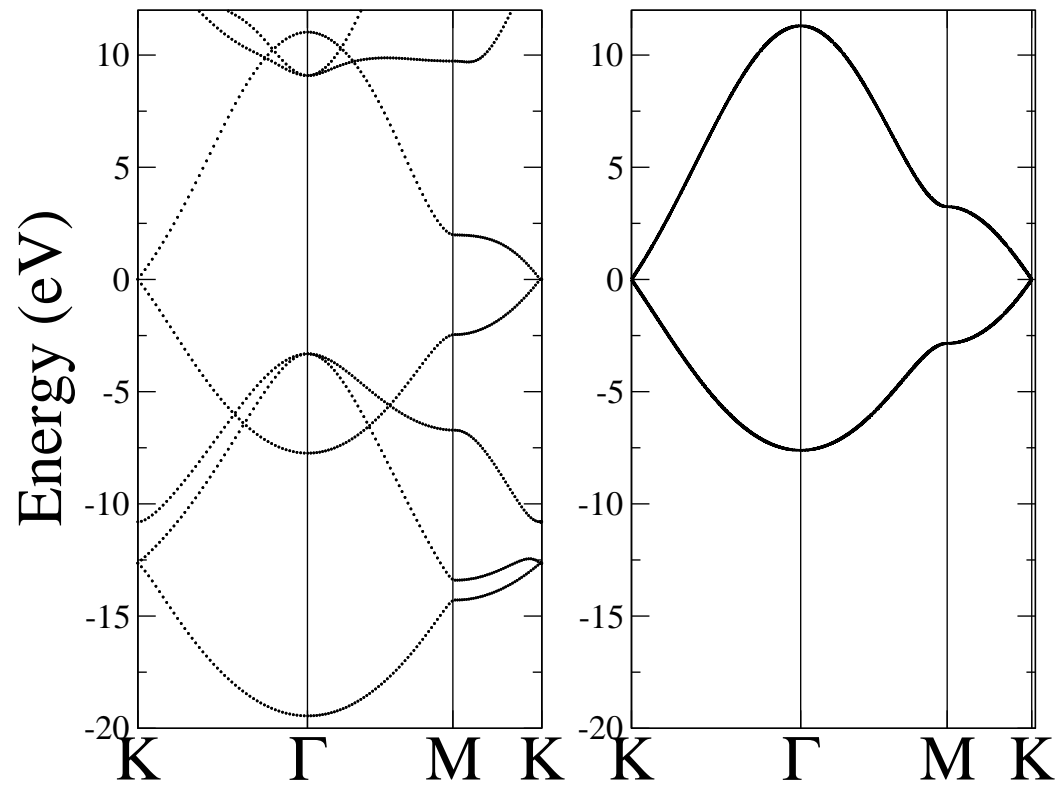
The phase factor is $e^{i\vec{k}\cdot(\vec{R}' - \vec{a}_2 + \vec{a}_1)}$

Now let us put all together $(\mathcal{H} - ES)\Psi_{\vec{k}}$:

$$\begin{pmatrix} \epsilon_p & \gamma_{pp\pi} f(\vec{k}) \\ \gamma_{pp\pi} f(\vec{k})^* & \epsilon_p \end{pmatrix} \Psi_{\vec{k}} = E(\vec{k}) \begin{pmatrix} 1 & S f(\vec{k}) \\ S f(\vec{k})^* & 1 \end{pmatrix} \Psi_{\vec{k}}$$

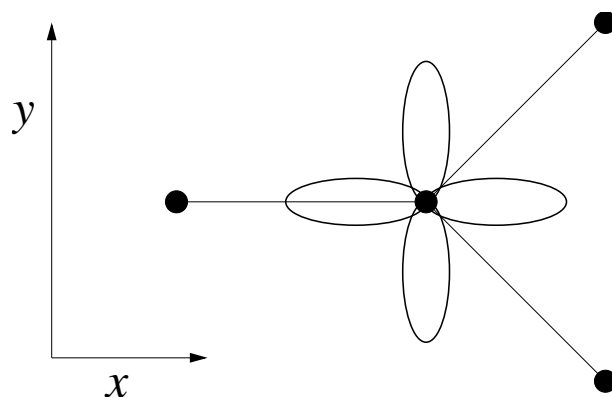
It is easy to see that the solutions are:

$$E(\vec{k}) = \frac{\epsilon_p \pm \gamma_{pp\pi} \sqrt{|f(\vec{k})|^2}}{1 \pm S \sqrt{|f(\vec{k})|^2}}$$

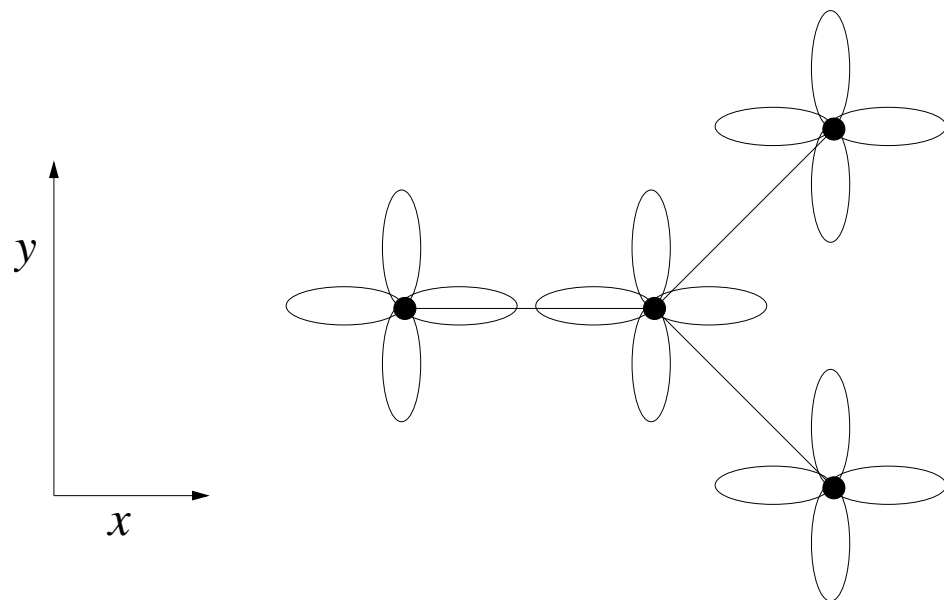


Fixing the σ band

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

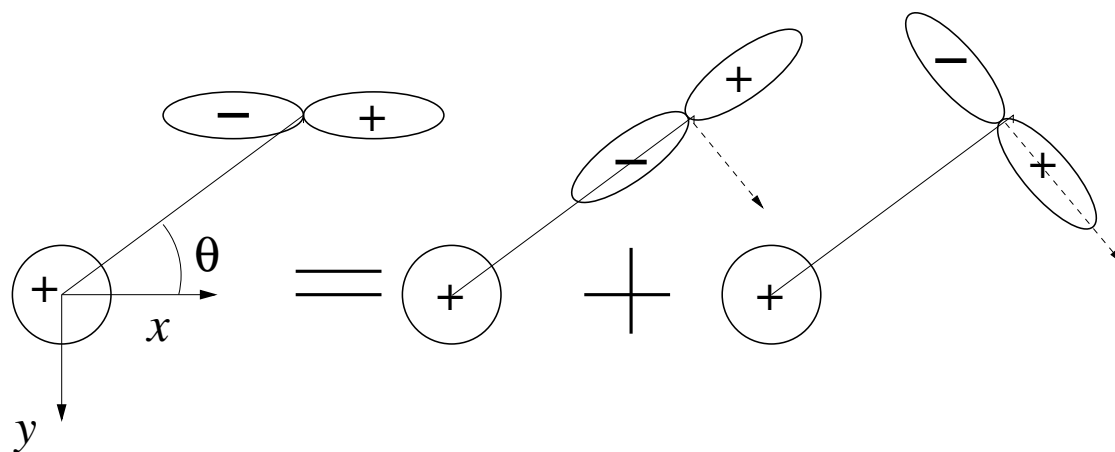


The problem is that the orbitals are not oriented along the bond axis



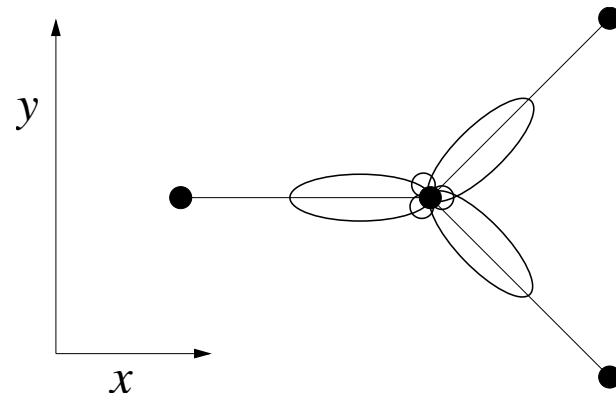
Consider for example the case of s and p orbitals

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

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 $p_y \longrightarrow$ we form an sp hybrid.

 sp^2 hybrid orbitals

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

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

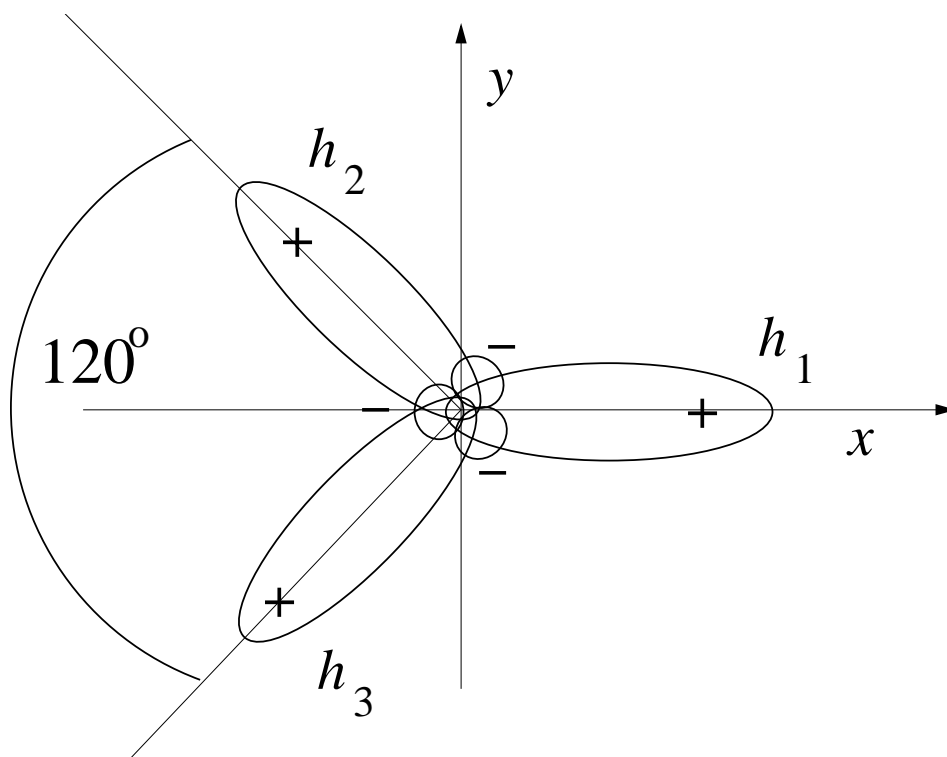
$$|h_2\rangle = \frac{1}{\sqrt{3}} \left(|s\rangle - \frac{1}{\sqrt{2}}|p_x\rangle + \sqrt{\frac{3}{2}}|p_y\rangle \right)$$

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

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.

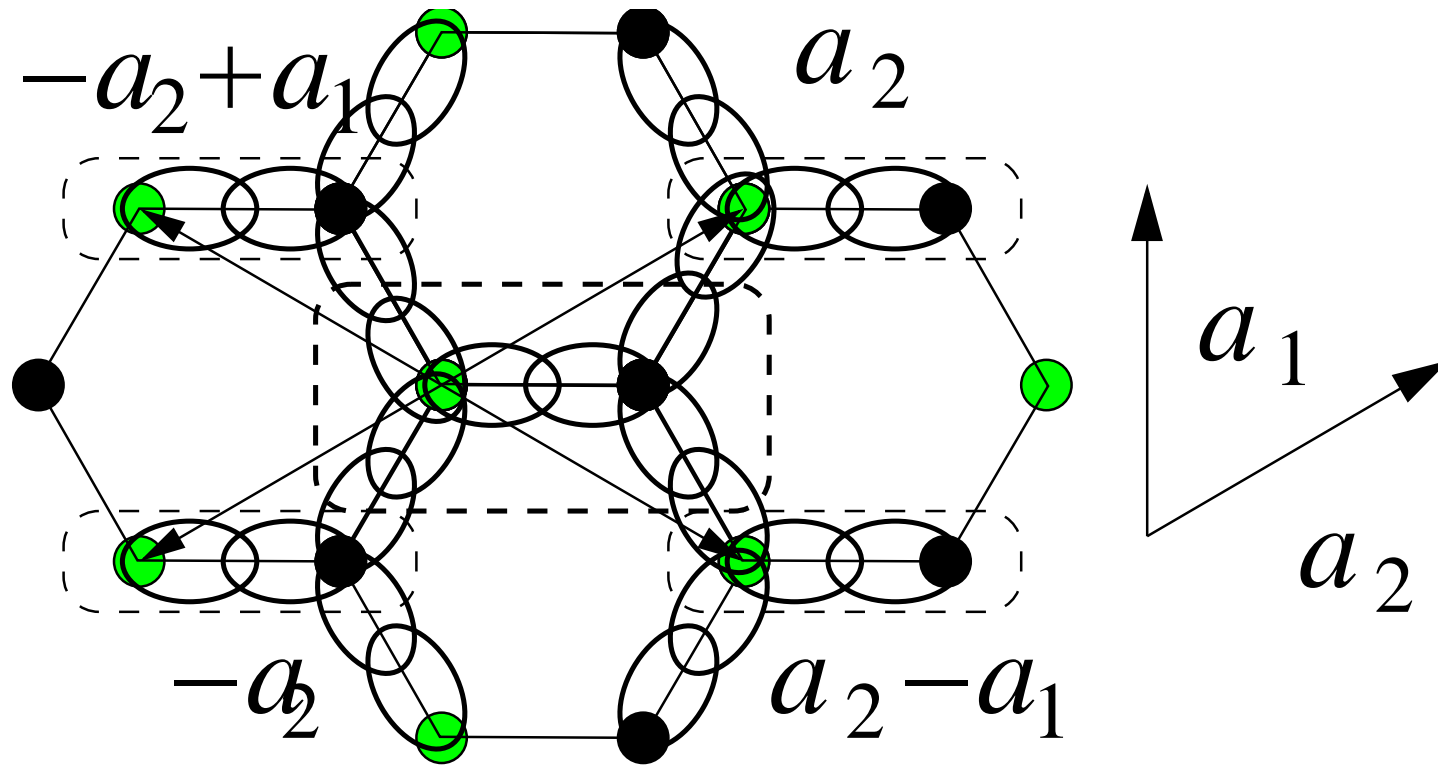


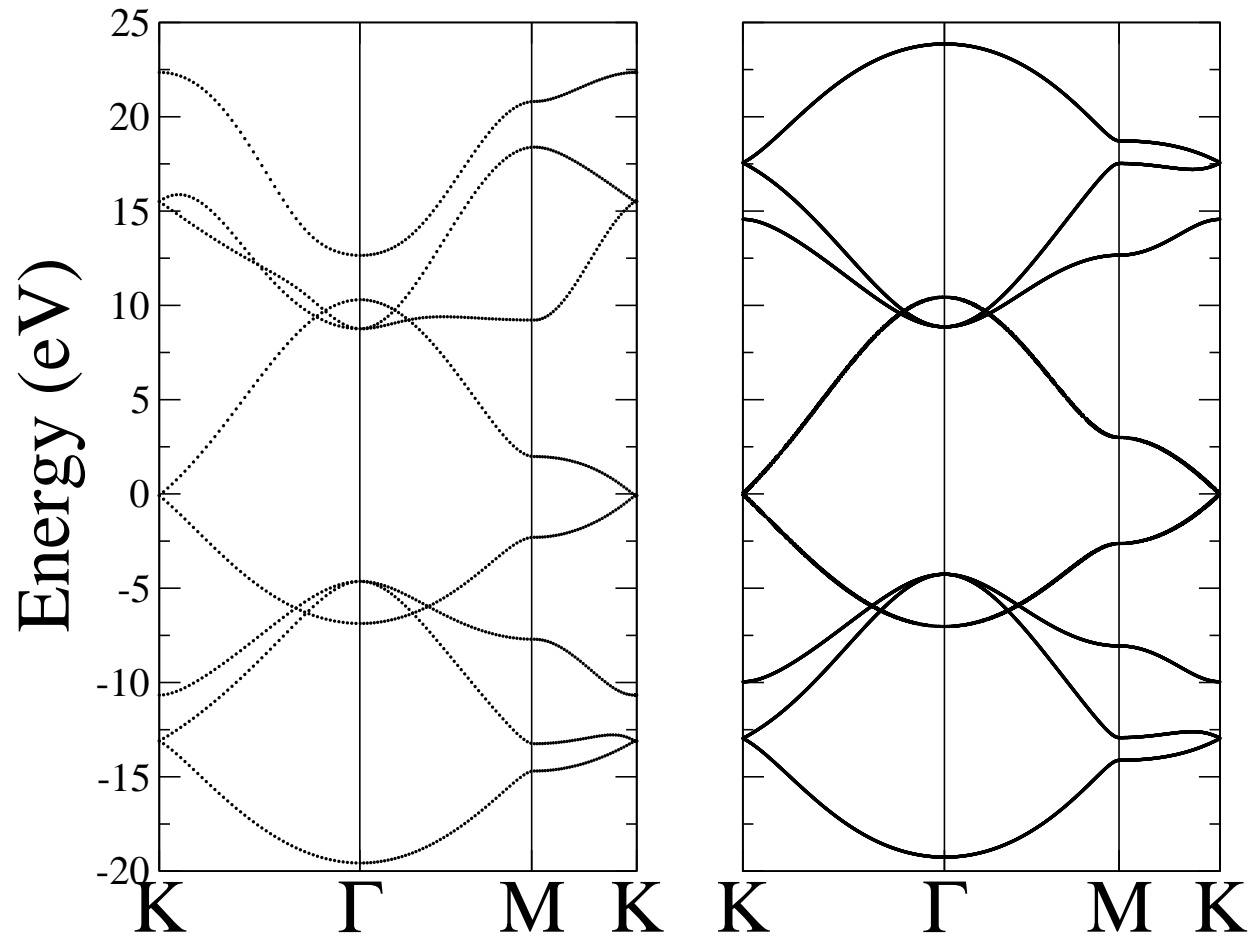
Calculate now the remaining bands

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 !!!





The Fermi Surface of graphene

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

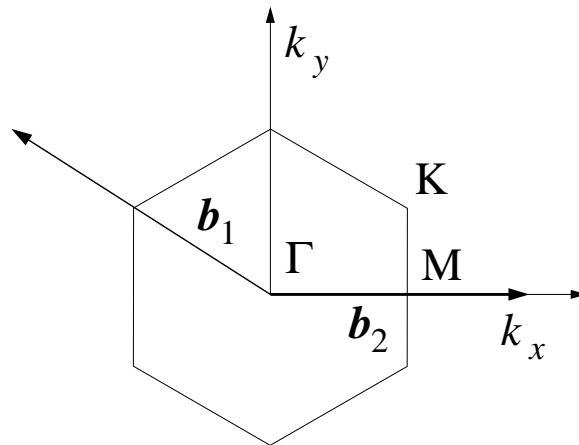
$$e^{i\vec{G}\cdot\vec{T}}$$

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 !!!

