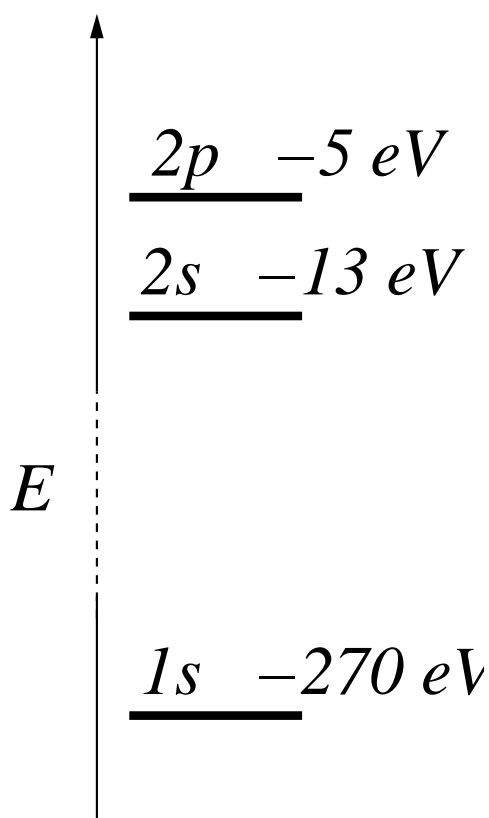


PY4T01 Condensed Matter Theory: Lecture 11

The Band Structure of Graphene

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

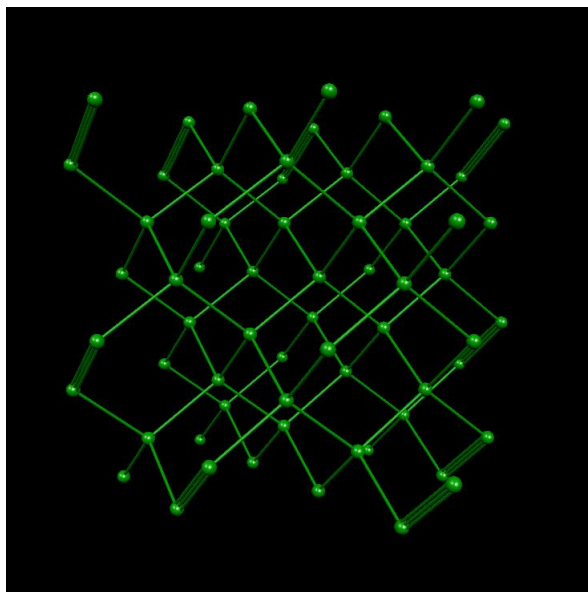


- Atomic Carbon: $1s^2 2s^2 2p^2$
- Solid State: $1s^2 2s^1 2p^3$

In solid state C appears in two different states:

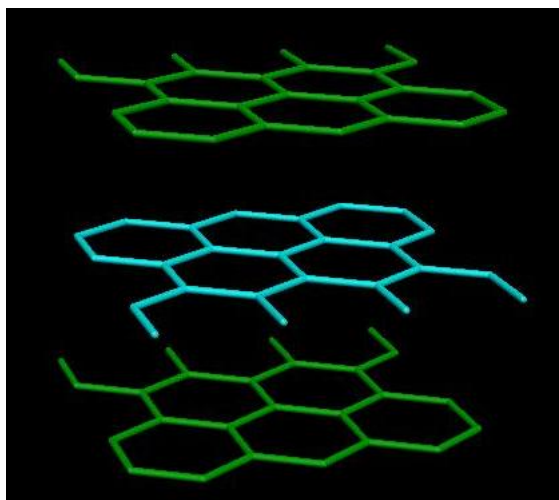
Diamond:

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:

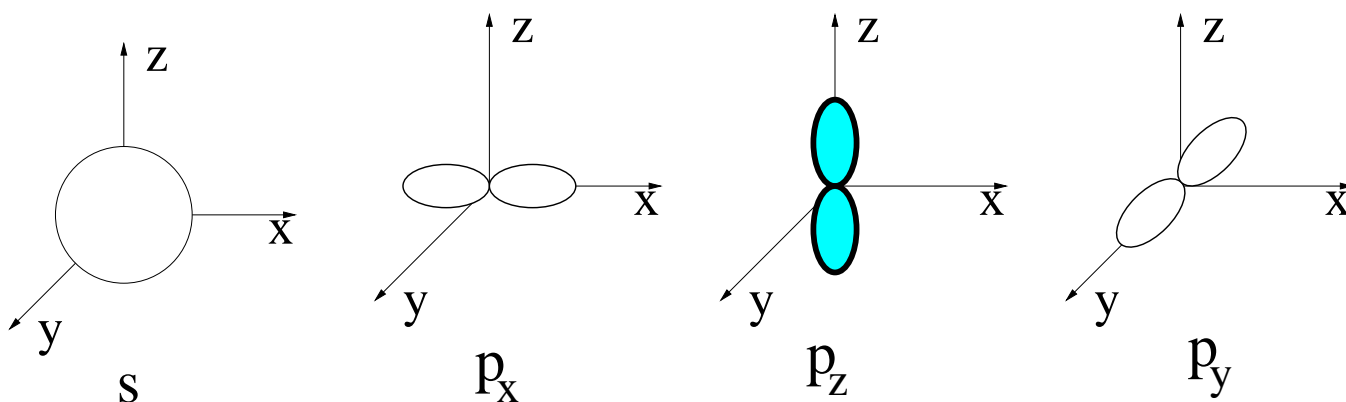
Each Carbon atom has 3 nearest neighbors in the x - y plane forming a 120° angle.



Note that in graphite:

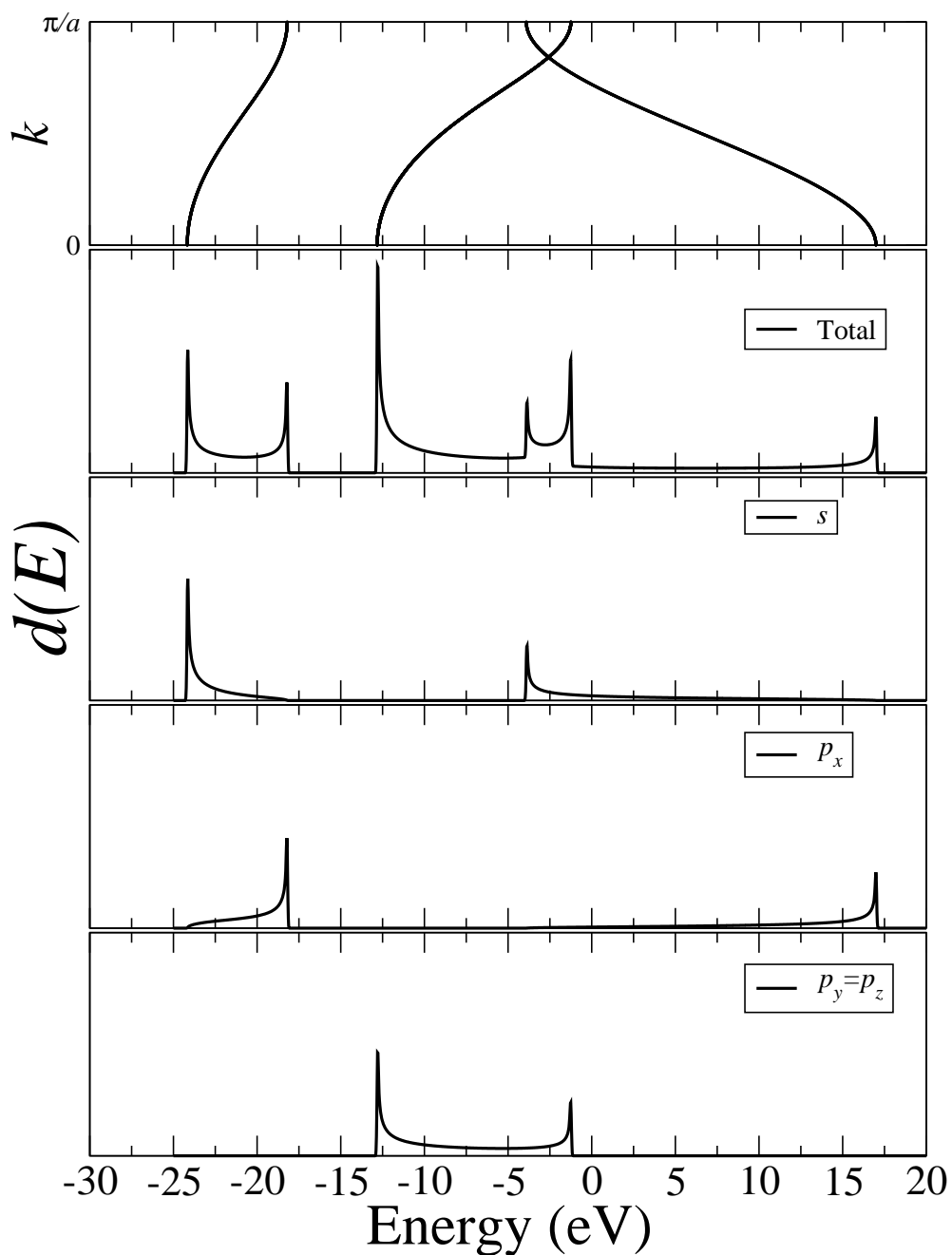
- The C-C separation is 1.42 Å
- The inter-plane separation is 3.37 Å

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



Note:

We had already one example of identical atomic orbitals that contribute in a different way in solid state: the C chain



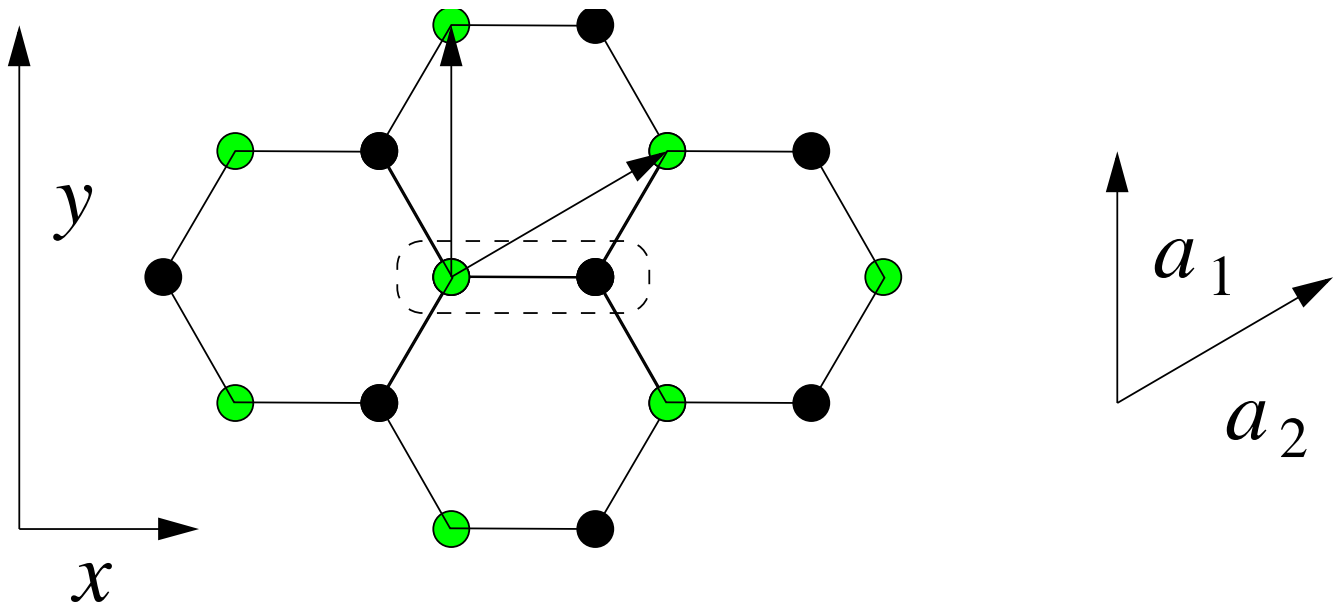
Graphene

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.

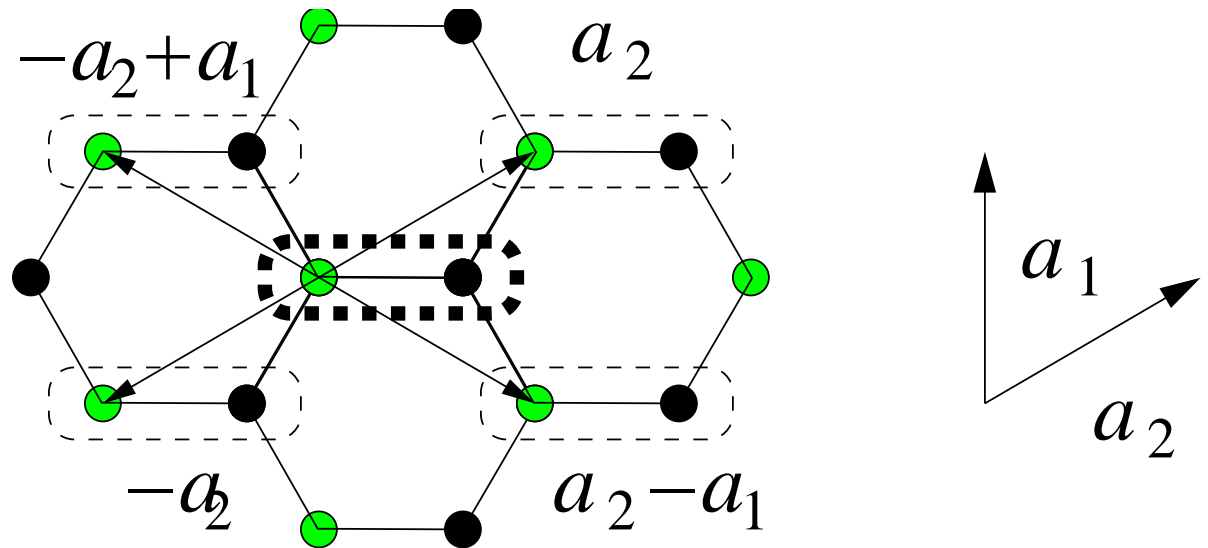
On-site energy: coupling with the primitive cell

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

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:

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

$$f(\vec{k}) = 1 + e^{-i\vec{k} \cdot \vec{a}_2} + e^{-i\vec{k} \cdot (\vec{a}_2 - \vec{a}_1)} =$$

$$= 1 + 2 e^{-ik_x \frac{\sqrt{3}}{2} a_0} \cos\left(\frac{k_y}{2} a_0\right)$$

The eigenvalues are then given by

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

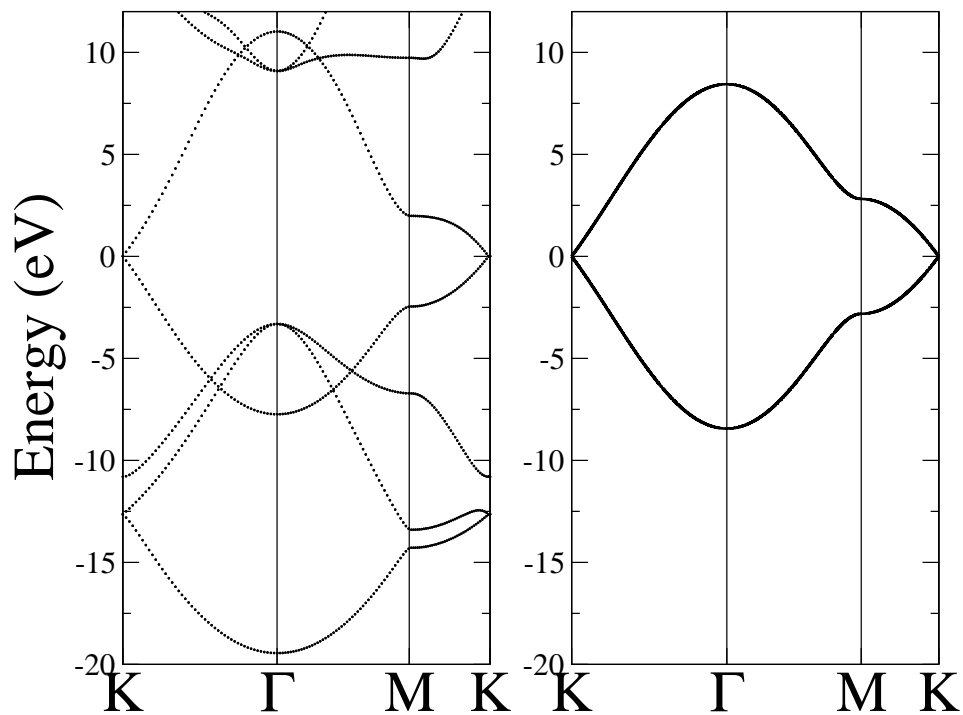
which has solutions:

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

or explicitly

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

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