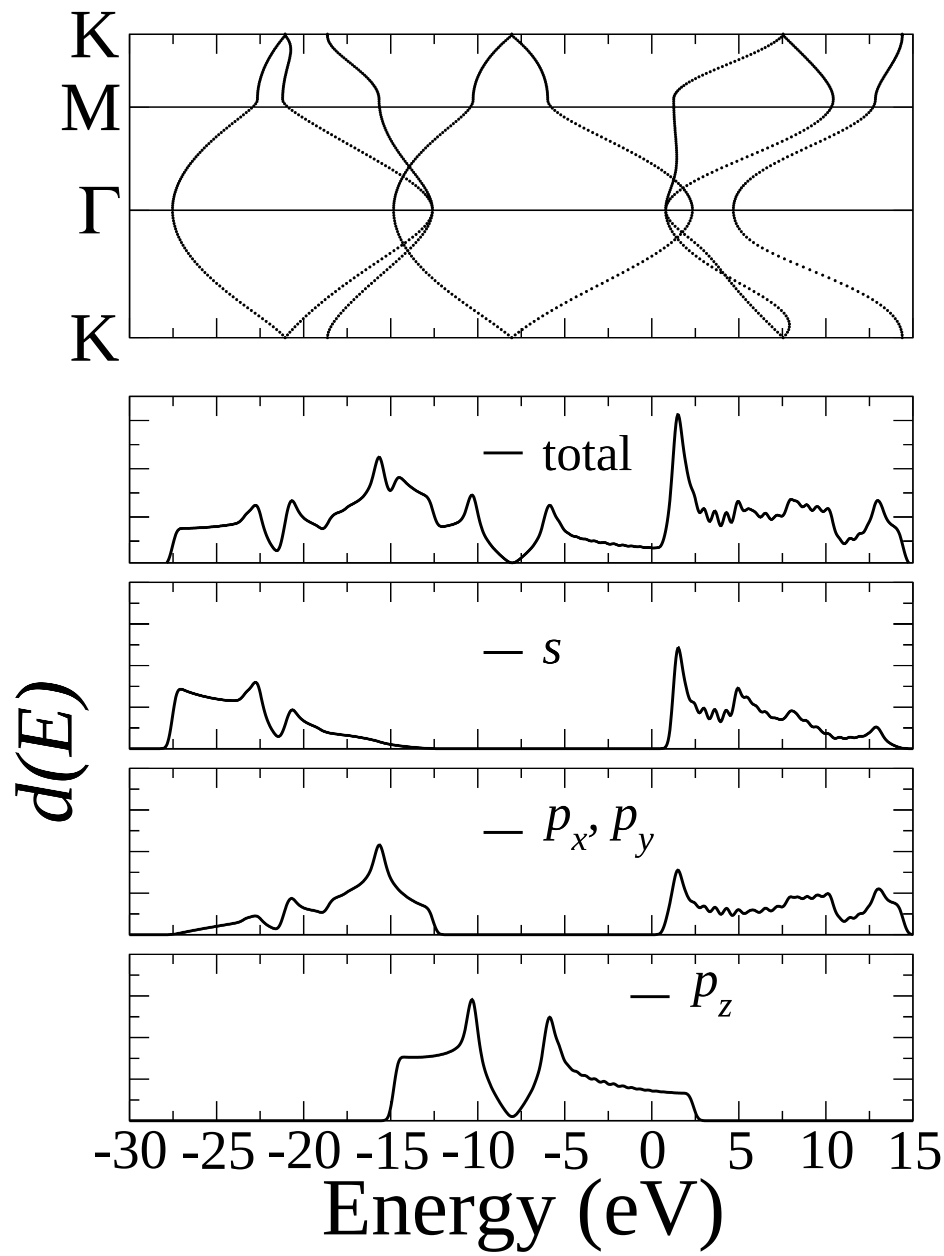
PY4T01 Condensed Matter Theory: Lecture 14

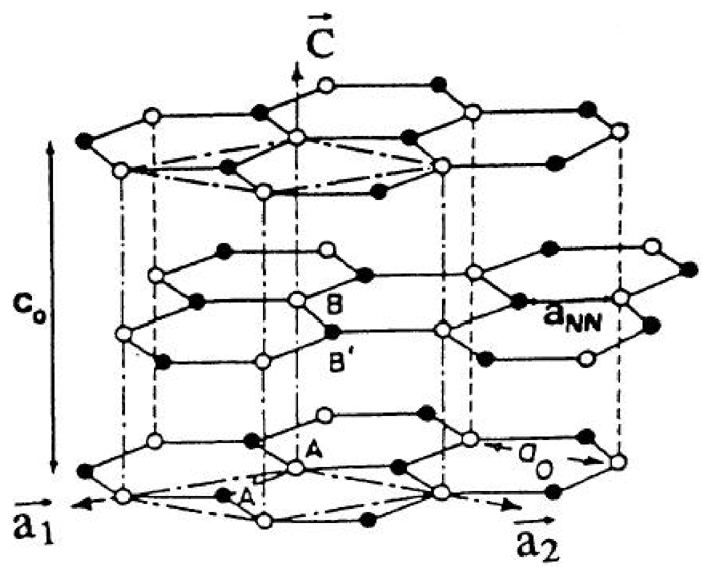
Final remarks on graphine

Graphine is a *zero-gap semiconductor*

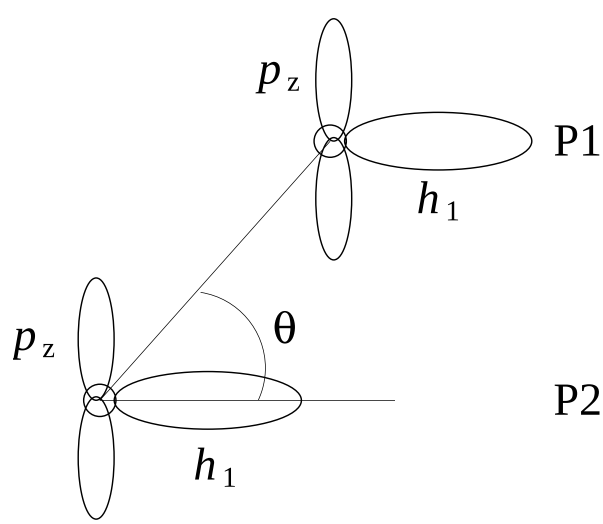


From graphine to graphite

Graphite is obtained by stacking graphine planes



In absence of interaction between planes ($\langle \mathrm{P}\ 1|H|\mathrm{P}\ 2\rangle = 0$), the band structure of graphite will be identical to that of graphine. However:

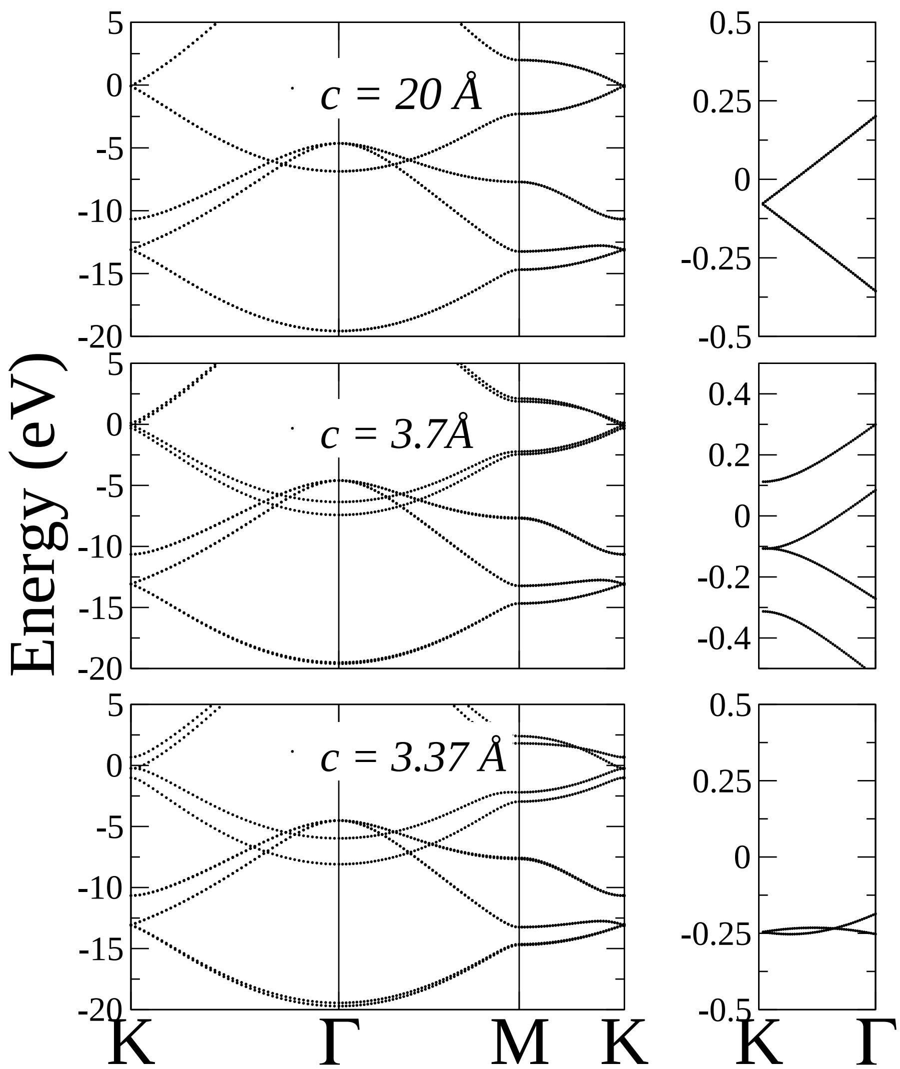


The coupling between plane is driven by:

$$ss\sigma \quad sp\sigma \quad \underline{pp\sigma}$$

This coupling elements are small, therefore the changes in the bands are small. However they are qualitatively important at E_F:

Graphite is a *semimetals*

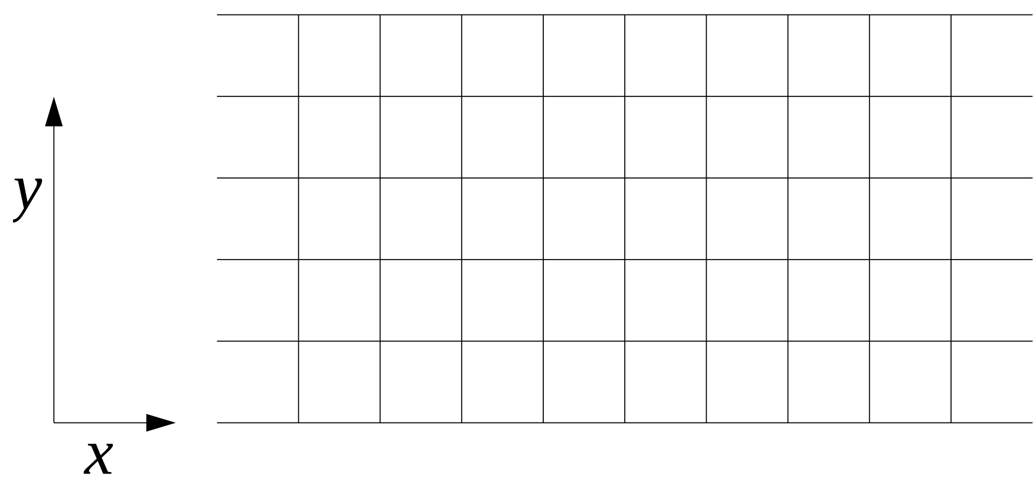


Quantization: Nanotubes

Let us start from a 2D simple cubic lattice. The band equation is:

$$E = \epsilon_0 + 2\gamma[\cos(k_x a_0) + \cos(k_y a_0)]$$

Suppose now to cut a slab along x and roll it up along $y \rightarrow$ this is a square lattice nanotube



The band for the nanotube is obtained by "quantizing" the momentum along y. It is identical to the case of a finite 2D square lattice, although now we have *periodic boundary conditions*:

$$k_y \quad \longrightarrow \quad k_y^m = \frac{2\pi m}{N_y a_0} \ \text{ with } \ m = 0, 1, ..., (N_y - 1)$$

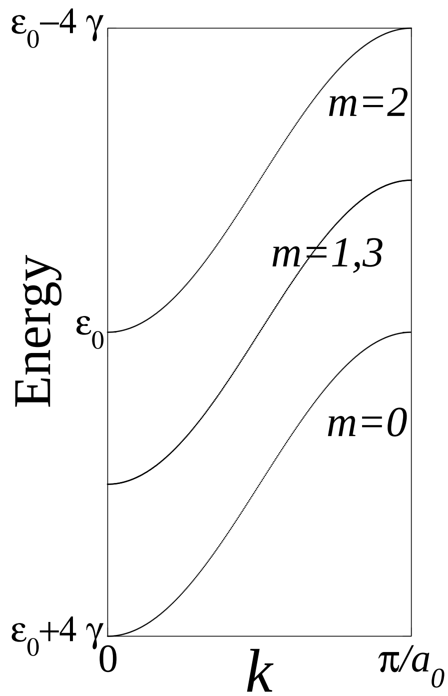
Therefore the band equation now is:

$$E(k) = \epsilon_0 + 2\gamma \left[\cos(k_x a_0) + \cos\left(\frac{2\pi m}{N_y}\right) \right]$$

and the molecular state:

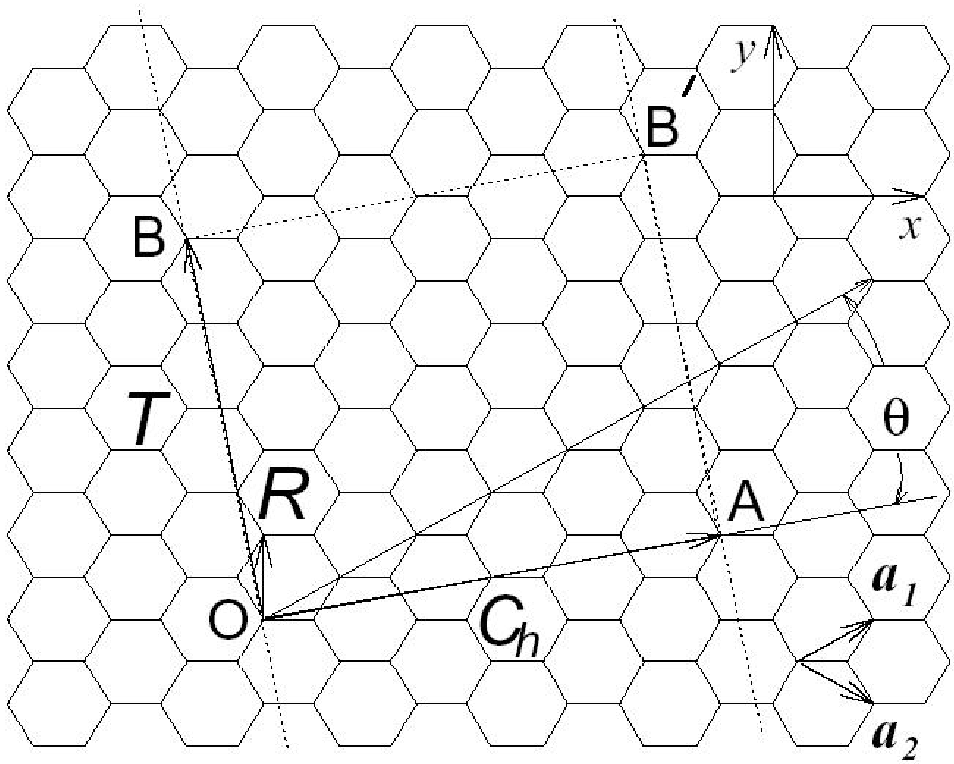
$$|\psi_{\vec{k}}^m\rangle = \sum_{jl}^{N_x N_y} \left(\frac{1}{N_x N_y}\right)^{1/2} \mathrm{e}^{ik_x a_0 j} \sin\left(\frac{2\pi m}{N_y} l\right) |jl\rangle$$

Only one component of $\vec{k}$ is continuous $\longrightarrow$ this is a **1D system**



Carbon Nanotubes: Single wall

These are obtained by rolling up a graphine sheet. We have several options:



1. Roll in such a way that $O = A$ and $B = B'$
2. $\vec{C}_h = \vec{a}_1 n + \vec{a}_2 m$ is the chiral vector
3. The indexes n, m identify uniquely the nanotube
4. $\vec{T}$ is the translational vector (primitive lattice vector for the nanotube)

5. O, A, B, B' define the unit cell

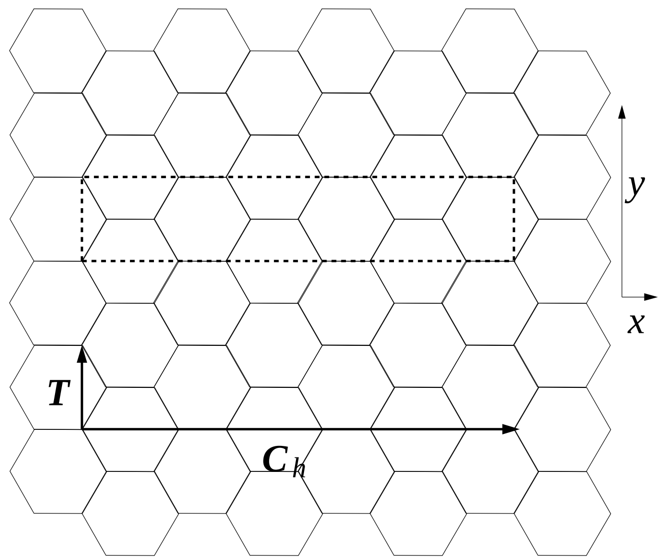
The tube circumference L is

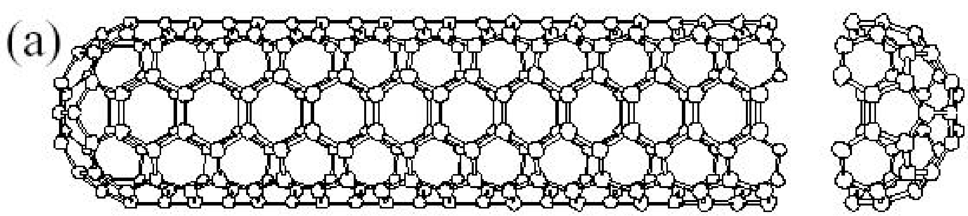
$$L = |\vec{C}_h| = \sqrt{\vec{C}_h \cdot \vec{C}_h} = a_0\sqrt{n^2 + m^2 + nm}$$

Since one dimension is finite $\rightarrow$ one component of the k-vector becomes discrete.

(n,n) Armchair Nanotubes

In this case the tube axis is along y.





The band equation is obtained from that of graphine.

Since we are interested in what happens close to E_F we consider only the π and π^* bands. For an orthogonal tight-binding we have (I take $\epsilon_p = 0$):

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

We have to impose the quantization of k_x. The condition is:

$$Lk_x^q = 2\pi q \qquad q \;\; \text{integer}$$

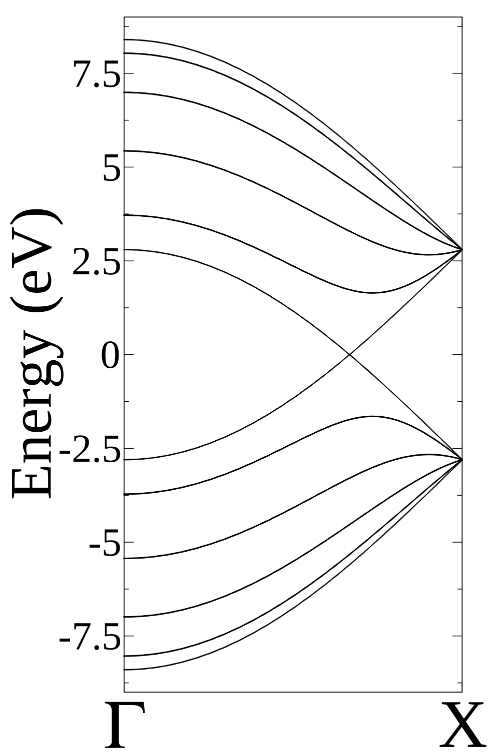
$$k_x^q = \frac{2\pi q}{n\sqrt{3}a_0} \qquad q \;\; \text{integer}$$

q assume $2n$ integer values $q = 1, ..., 2n$

Than the dispersion relation becomes:

$$E^q(k) = \pm\sqrt{1 + 4\cos^2\left(\frac{ka_0}{2}\right) + 4\cos\left(\frac{ka_0}{2}\right)\cos\left(\frac{q\pi}{n}\right)}$$

It is the usual idea of minibands: a 1D band for every q.

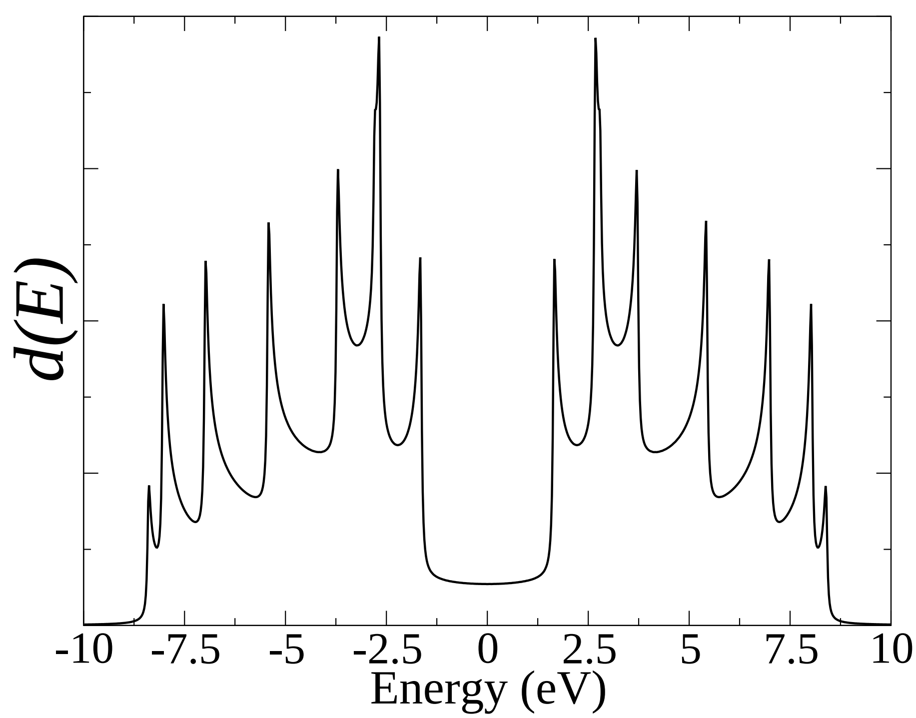


Note that there are bands crossing the Fermi level ($E_F = 0$). This is valid for any armchair nanotube. In fact

$$1 + 4\cos^2\left(\frac{ka_0}{2}\right) + 4\cos\left(\frac{ka_0}{2}\right)\cos\left(\frac{q\pi}{n}\right) = 0$$

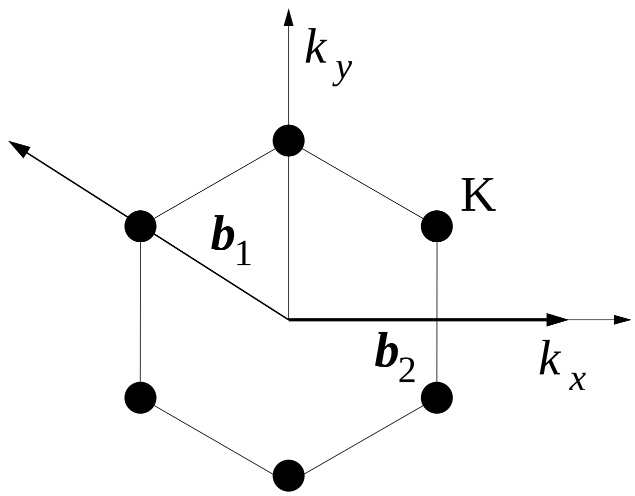
for $q = n$ and $k = \pm\frac{2\pi}{3a_0}$

Armchair nanotubes are always metallic



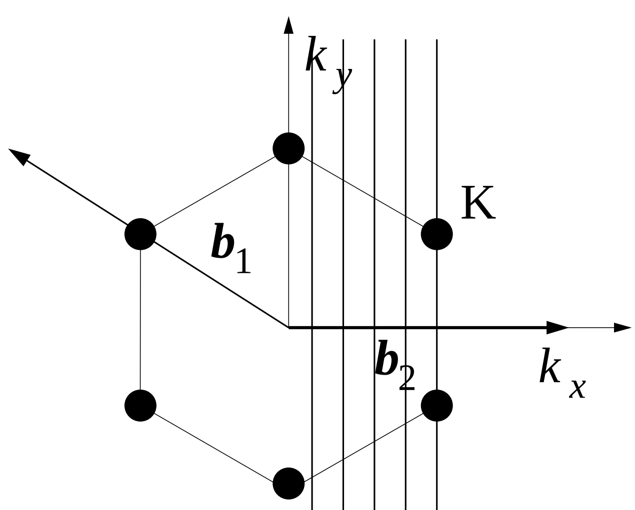
The metallicity can be understood from a simple geometrical argument. Consider the graphine Brillouin zone

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



and superimpose the quantization condition:

$$Lk_x^q = 2\pi q \qquad q \ \text{integer}$$

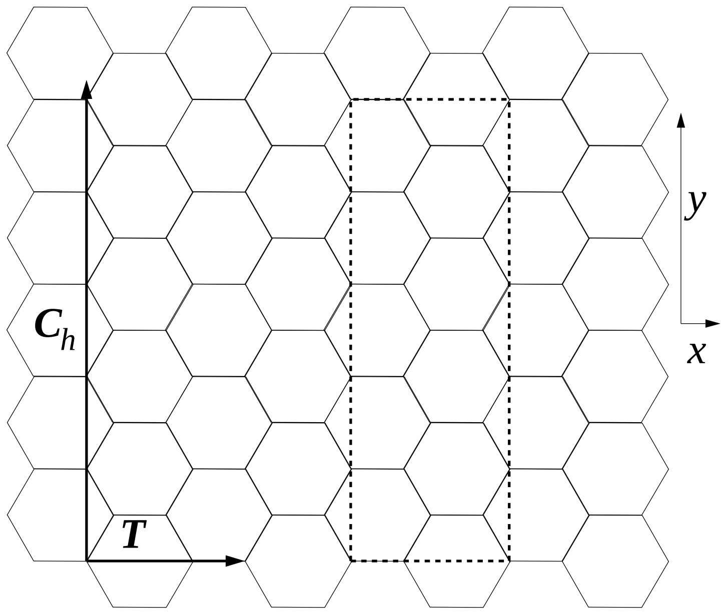


> If one of the “quantization” lines crosses the 2D graphine Fermi surface, then the nanotube will be a metal, otherwise it will be an insulator.

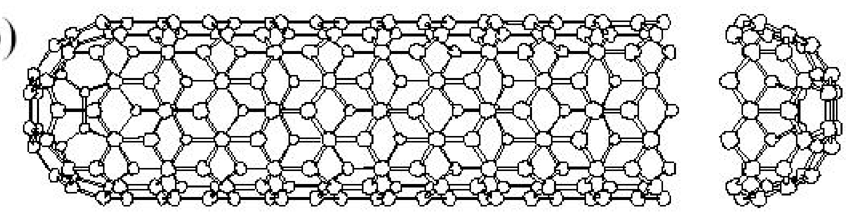
For an armchair nanotube $q = n$ passes for the K point for every n.

(n,0) Zig-Zag Nanotubes

In this case the tube axis is along x.



(b)



The quantization condition is now on k_y

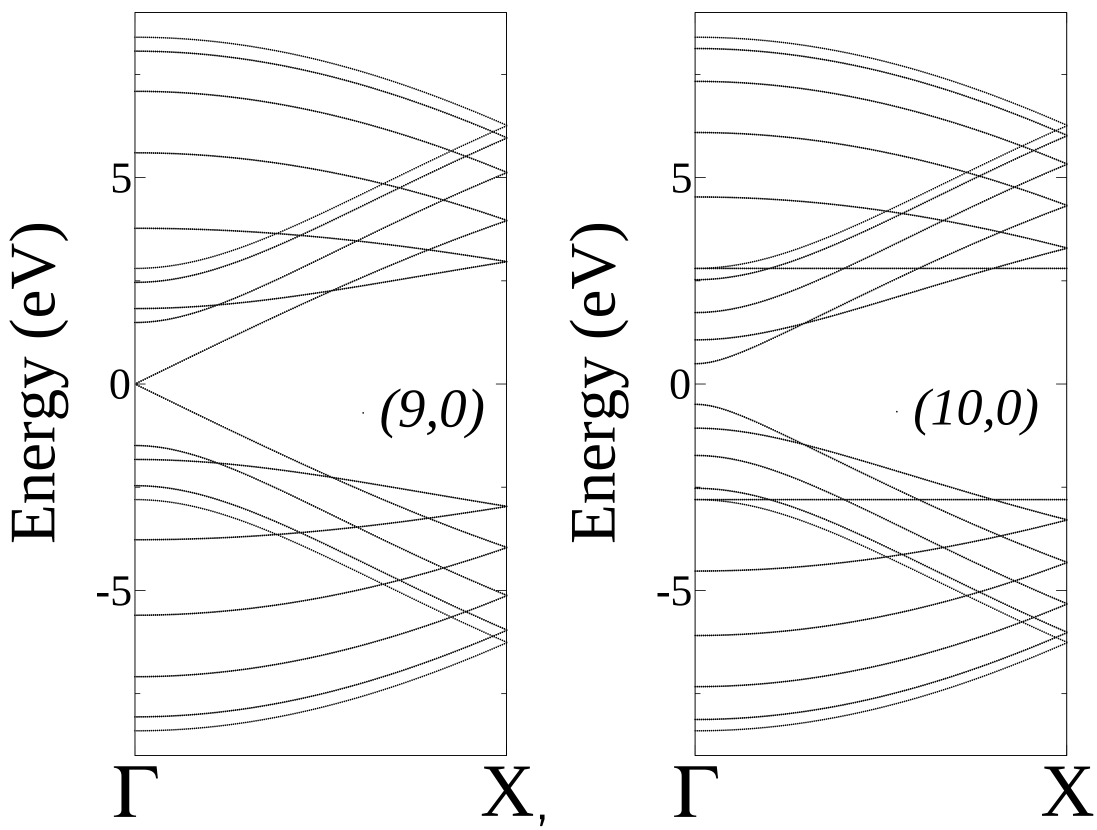
$$Lk_y^q = 2\pi q \quad q \text{ integer}$$

$$k_y^q = \frac{2\pi q}{na_0} \quad q \text{ integer}$$

Then the dispersion relation:

$$E^q(k) = \pm\sqrt{1 + 4\cos^2\left(\frac{q\pi}{n}\right) + 4\cos\left(\frac{q\pi}{n}\right)\cos\left(\frac{\sqrt{3}ka_0}{2}\right)}$$

In this case not all the zig-zag nanotubes are metallic.



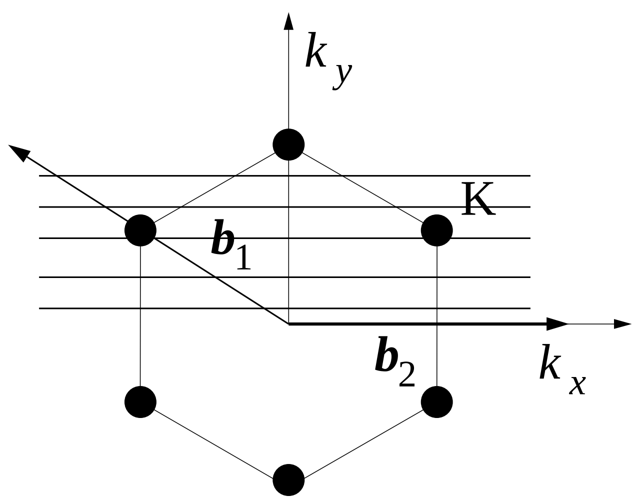
In fact one can show that:

- If $n = 3d$, with d integer $\longrightarrow$ the (n,0) nanotube is metallic
- If $n \neq 3d$, with d integer $\longrightarrow$ the (n,0) nanotube is insulating

For zig-zag nanotube the band-crossing (or the bandgap) is always at $k = 0$.

Again the metallicity can be understood by looking at the graphine Brillouin zone and superimposing the quantization lines

$$k_y^q = \frac{2\pi q}{n a_0} \qquad q = 1, ..., 2n$$



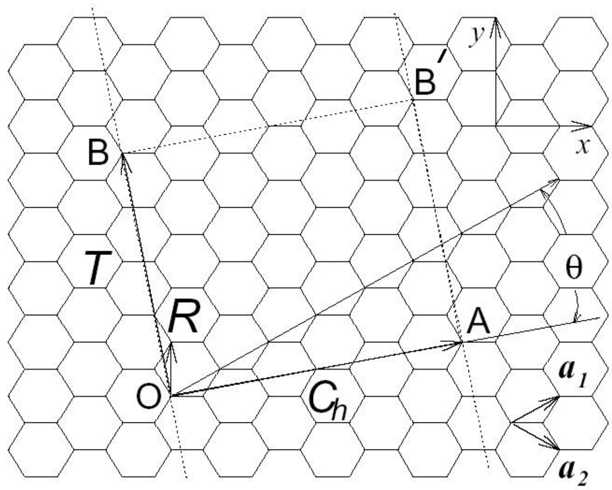
Note that

$$K = (\frac{2\pi}{\sqrt{3}a_0}, \frac{4\pi}{3a_0})$$

The metallicity is for $n = 3d$ and the metallic miniband is for $p = 2d$

General case (n,m)

The tube axis is along $\vec{T}$ and the quantization axis is $\vec{C}_h$



One needs to construct the Brillouin zone associated with the unit cell $OAB'B$. The reciprocal lattice vectors $\vec{K}_1$ and $\vec{K}_2$ can be obtained from:

$$\vec{C}_h \cdot \vec{K}_1 = 2\pi, \qquad \vec{T} \cdot \vec{K}_1 = 0$$

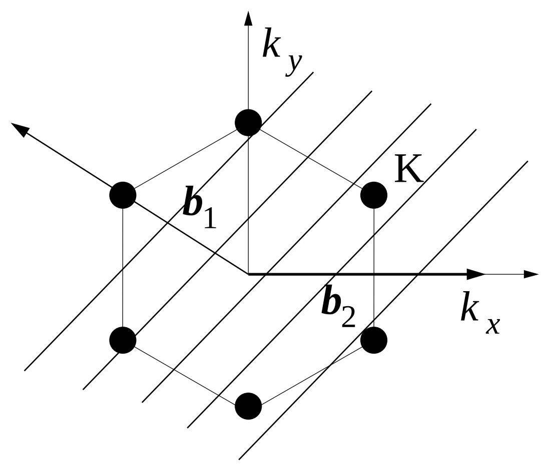
$$\vec{C}_h \cdot \vec{K}_2 = 0, \qquad \vec{T} \cdot \vec{K}_2 = 2\pi$$

$\vec{K}_2$ is continuous and $\vec{K}_1$ needs to be quantized

$$L|\vec{K}_1| = 2\pi q$$

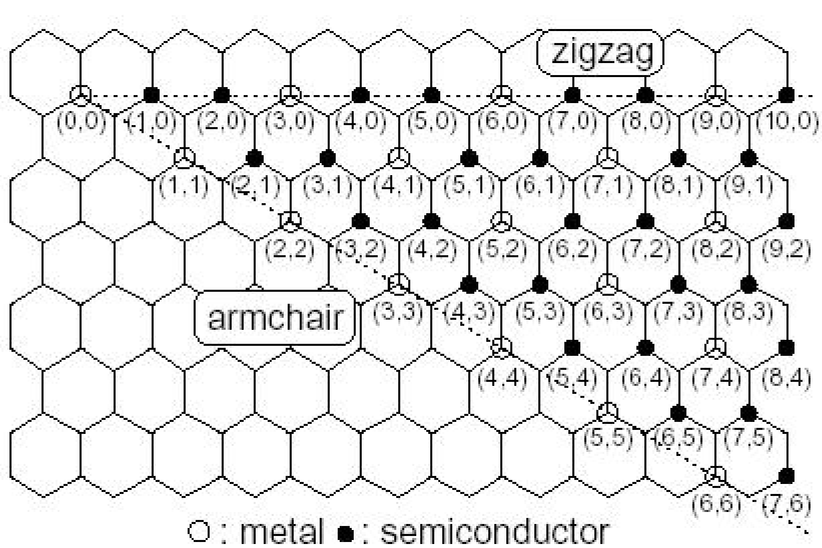
This gives a relation

$$k_y = \alpha(n,m)k_x + \beta(n,m)q$$



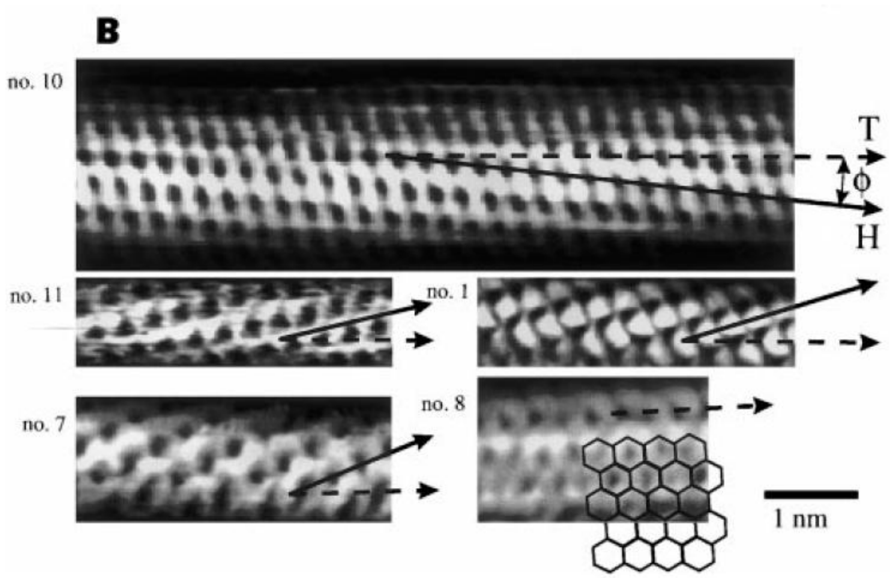
If one of the quantization lines crosses $K \longrightarrow$ metallic nanotube.

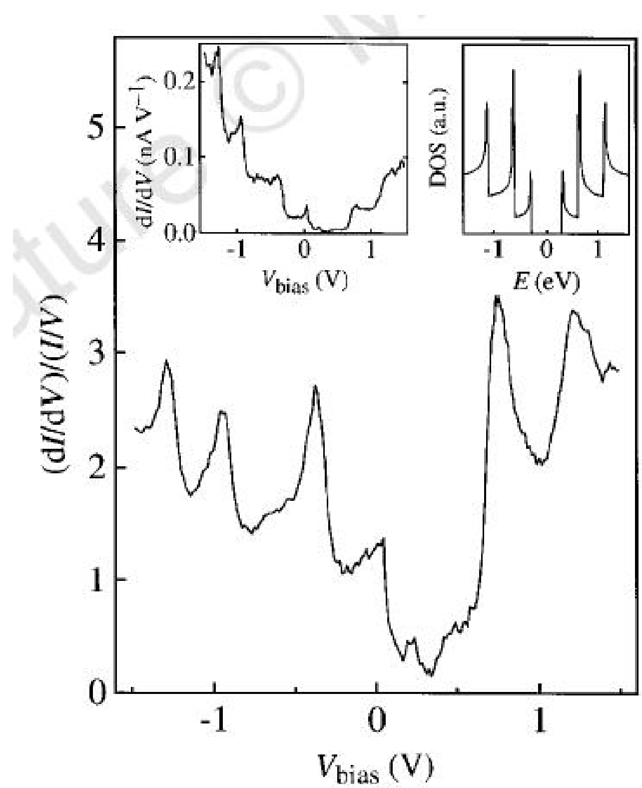
It is then possible to construct the Carbon “nanotube map”



Is all this true ?

J.W.G. Wildöer, L.C. Venema, A.G. Rinzler , R.E. Smalley and C. Dekker, Nature **391**, 59 (1999)

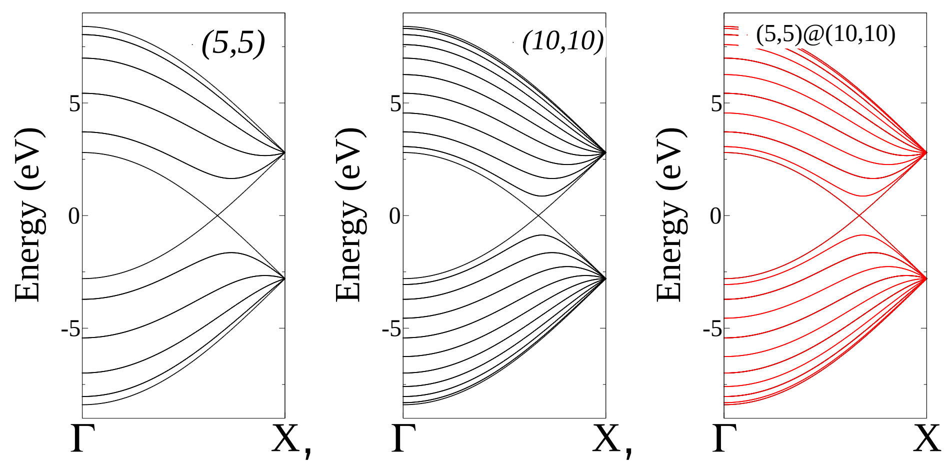




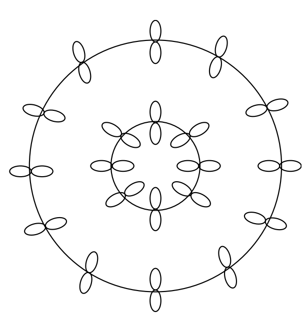
Multiwall nanotubes: $(n, m)@(n', m')$

What happens when a tube is made from more than one shell ?

If there is NOT inter-tube interaction: the band of a multiwall nanotube is the sum of the bands of the individual tubes.



However this is not the case. p_z orbitals from different tubes interact !! This is the same interaction between the graphite planes.



The details of the interaction depends on the tube type. However one can open pseudo-gaps at the Fermi level.

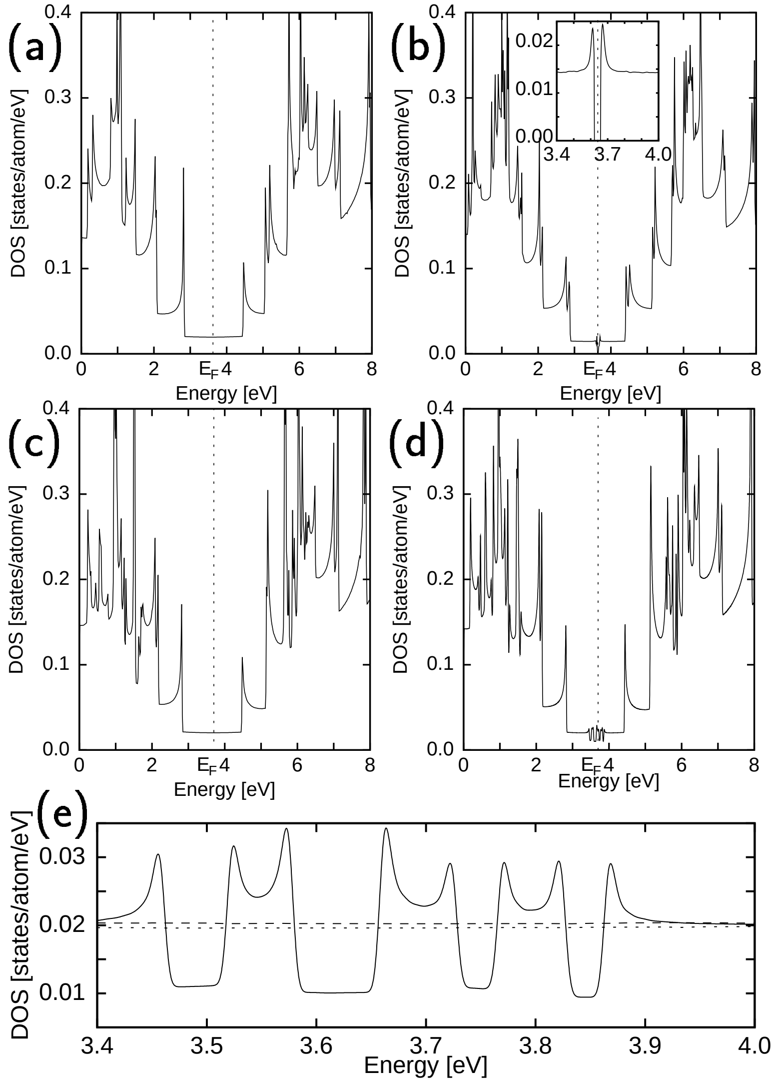


Figure 3

(Young-Kyun Kwon and David Tománek,
"Electronic and Structural Properties of Multi-Wall Carbon Nanotubes")