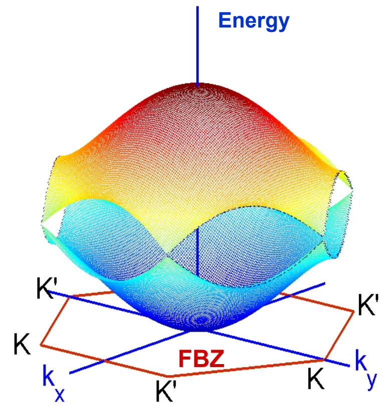
Handout 11

Energy Bands in Graphene: Tight Binding and the Nearly Free Electron Approach

In this lecture you will learn:

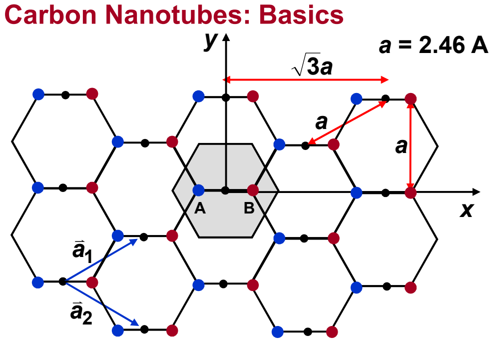
- The tight binding method (contd…)
- The π-bands in graphene



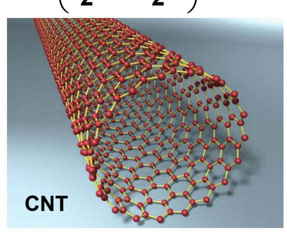
Graphene and Carbon Nanotubes: Basics

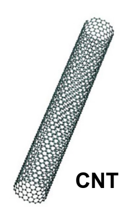
- Graphene is a two dimensional single atomic layer of carbon atoms arranged in a Honeycomb lattice (which is not a Bravais lattice)
- The underlying Bravais lattice is shown by the location of the black dots and is a hexagonal lattice
- There are two carbon atoms per primitive cell, A and B (shown in blue and red colors, respectively)
- Graphene can be rolled into tubes that are called carbon nanotubes (CNTs)

$a = 2.46$ A



$$\vec{a}_1 = \left(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}\right)a \qquad \vec{a}_2 = \left(\frac{\sqrt{3}}{2}\hat{x} - \frac{1}{2}\hat{y}\right)a$$

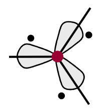


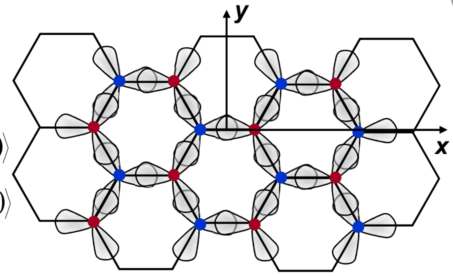


CNT

Graphene: Sp2 Hybridization

Sp2 hybridization in carbon:





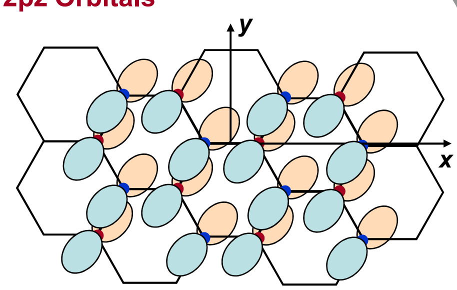
$$|\varphi_1(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle + \frac{1}{\sqrt{6}}|\phi_{2px}(\vec{r})\rangle + \frac{1}{\sqrt{2}}|\phi_{2py}(\vec{r})\rangle$$

$$|\varphi_2(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle + \frac{1}{\sqrt{6}}|\phi_{2px}(\vec{r})\rangle - \frac{1}{\sqrt{2}}|\phi_{2py}(\vec{r})\rangle$$

$$|\varphi_3(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle - \sqrt{\frac{2}{3}}|\phi_{2px}(\vec{r})\rangle$$

- All carbon atoms are all sp2 hybridized (one 2s orbital together with the $2p_x$ and the $2p_y$ orbitals generate three sp2 orbitals)
- All sp2 orbitals form σ-bonds with the sp2 orbitals of the neigboring carbon atoms
- The bonding orbital associated with each σ-bond is occupied by two electrons (spin-up and spin-down)
- There is one electron per carbon atom left in the $2p_z$ orbital

Graphene: 2pz Orbitals



π-bonding:

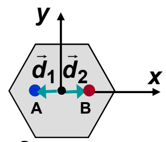
- Each carbon atom contributes one $2p_z$-orbital that participates in bonding

$\Rightarrow$ Each primitive cell contributes two $2p_z$-orbitals that participate in bonding

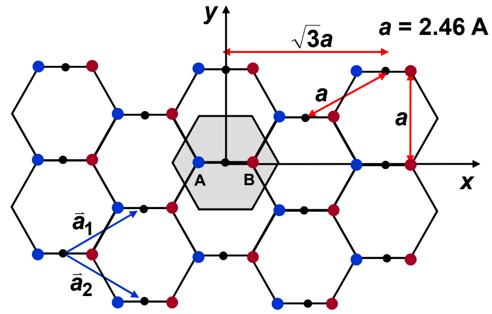
- The $2p_z$ orbital stick out of the plane of the chain and form π-bonds with neigboring $2p_z$ orbitals
- The π-bonding results in energy bands (π-bands) that we will study via tight binding

Graphene: Some Useful Vectors

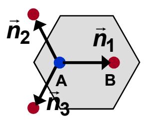
Basis vectors:



$$\vec{d}_1 = -\frac{a}{2\sqrt{3}}\hat{x} \qquad \vec{d}_2 = \frac{a}{2\sqrt{3}}\hat{x}$$



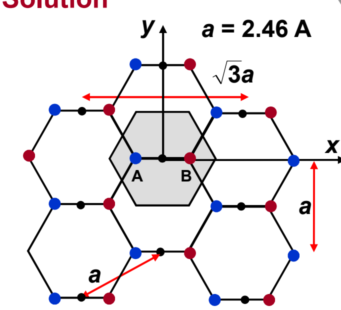
Nearest neighbor vectors:



$$\left.\begin{aligned} \vec{n}_1 &= \frac{a}{\sqrt{3}}\hat{x} \\ \vec{n}_2 &= \frac{a}{\sqrt{3}}\left(-\frac{1}{2}\hat{x} + \frac{\sqrt{3}}{2}\hat{y}\right) \\ \vec{n}_3 &= \frac{a}{\sqrt{3}}\left(-\frac{1}{2}\hat{x} - \frac{\sqrt{3}}{2}\hat{y}\right) \end{aligned}\right\}$$

These will be useful for writing the final solution in a compact form

Graphene: Tight Binding Solution



• Each basis atom contributes one $2p_z$-orbital that participates in bonding

$\Rightarrow$ Each primitive cell contributes two $2p_z$-orbitals that participate in bonding

$$\phi_{pzA}(\vec{r}) \leftrightarrow E_p \qquad \phi_{pzB}(\vec{r}) \leftrightarrow E_p$$

One can then write the trial tight-binding solution for wavevector $\vec{k}$ as:

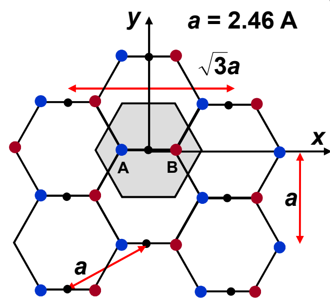
$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}}\left[c_{pzA}(\vec{k})\,e^{i\vec{k}\,.\,\vec{d}_1}\phi_{pzA}(\vec{r}-\vec{R}_m-\vec{d}_1) + c_{pzB}(\vec{k})\,e^{i\vec{k}\,.\,\vec{d}_2}\phi_{pzB}(\vec{r}-\vec{R}_m-\vec{d}_2)\right]$$

Graphene: Tight Binding Solution

Plug the solution into the Schrodinger equation:

$$\hat{H}\,|\psi_{\vec{k}}(\vec{r})\rangle = E(\vec{k})\,|\psi_{\vec{k}}(\vec{r})\rangle$$

And then, one by one, multiply by from the left by the bra's corresponding to every orbital in one primitive cell to generate as many equations as the number of orbitals per primitive cell



Step 1:

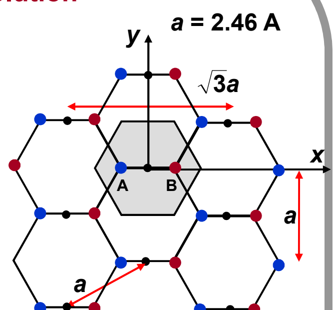
Multiply the equation with $\langle\phi_{pzA}(\vec{r}-\vec{d}_1)|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

$$E_p\, c_{pzA}(\vec{k}) - V_{pp\pi}\left(e^{i\,\vec{k}\,.\,\vec{n}_1} + e^{i\,\vec{k}\,.\,\vec{n}_2} + e^{i\,\vec{k}\,.\,\vec{n}_3}\right) c_{pzB}(\vec{k}) = E(\vec{k})\, c_{pzA}(\vec{k})$$

Notice that the final result can be written in terms of the nearest neighbor vectors

Graphene: Tight Binding Solution



Step 2:

Multiply the equation with $\langle\phi_{pzB}(\vec{r}-\vec{d}_2)|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

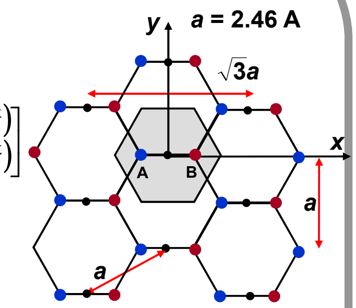
$$E_p\, c_{pzB}(\vec{k}) - V_{pp\pi}\left(e^{-i\,\vec{k}\,.\,\vec{n}_1} + e^{-i\,\vec{k}\,.\,\vec{n}_2} + e^{-i\,\vec{k}\,.\,\vec{n}_3}\right) c_{pzA}(\vec{k}) = E(\vec{k})\, c_{pzB}(\vec{k})$$

Notice that the final result can be written in terms of the nearest neighbor vectors

Graphene: Tight Binding Solution

Write the equations obtained in a matrix form:

$$\begin{bmatrix} E_p & -V_{pp\pi}\, f(\vec{k}) \\ -V_{pp\pi}\, f^*(\vec{k}) & E_p \end{bmatrix} \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}$$



Where the function $f(\vec{k})$ is:

$$f(\vec{k}) = \left(e^{i\,\vec{k}.\vec{n}_1} + e^{i\,\vec{k}.\vec{n}_2} + e^{i\,\vec{k}.\vec{n}_3} \right)$$

Solutions are:

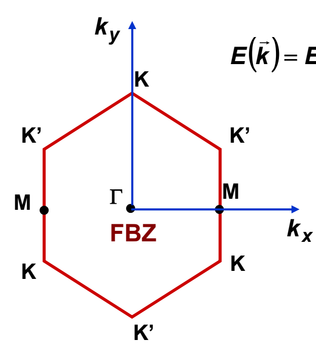
$$E(\vec{k}) = E_p \pm V_{pp\pi} \left| f(\vec{k}) \right|$$

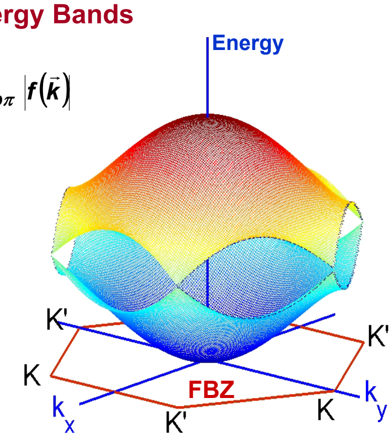
And the corresponding eigenvectors are:

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_+ = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -f^*(\vec{k}) / \left| f(\vec{k}) \right| \end{bmatrix} \qquad \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_- = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ f^*(\vec{k}) / \left| f(\vec{k}) \right| \end{bmatrix}$$

Graphene: π-Energy Bands

$$E(\vec{k}) = E_p \pm V_{pp\pi} \left| f(\vec{k}) \right|$$



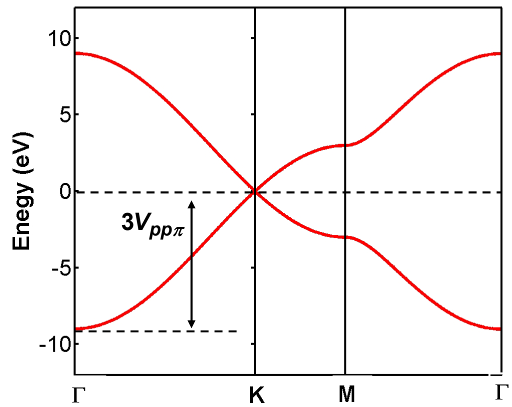


- Bandgaps open at the M-points between the first and the second bands
- No bandgaps open at the K-points and the K'-points

Graphene: π-Energy Bands

• Since graphene has two electrons per primitive cell contributing to π-bonding, the lower π-band will be completely filled at $T \approx 0$K

• The location of Fermi level near $T \approx 0$K is shown by the dashed curve



In generating the plots I chose energy zero such that:

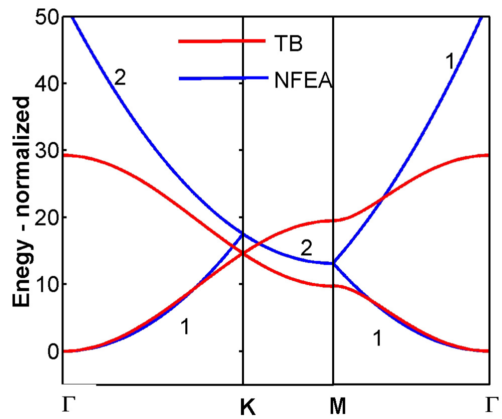
$$E_p = 0$$

And for graphene:

$$V_{pp\pi} = 3.0 \text{ eV}$$

Graphene: A Comparison of NFEA and TB

Scale normalized to: $\dfrac{\hbar^2}{2m}\left(\dfrac{1}{a}\right)^2$ and offset by V_o



To compare the nearly-free-electron approach (NFEA) to tight-binding (TB) I assumed the DC potential in NFEA to be:

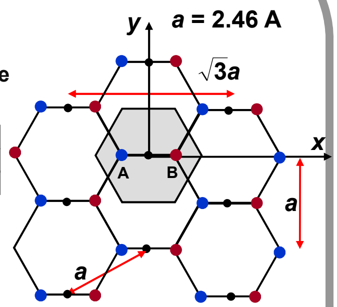
$$V_o = E_p - 3V_{pp\pi}$$

And in graphene:

$$V_{pp\pi} = 3.0 \text{ eV}$$

Why the Zero Bandgap in Graphene?

The answer from tight binding:



The two atoms in a primitive cell are identical. If they were different then there would be a non-zero bandgap:

$$\begin{bmatrix} E_{pA} & -V_{pp\pi}\, f(\vec{k}) \\ -V_{pp\pi}\, f^{*}(\vec{k}) & E_{pB} \end{bmatrix} \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}$$

$$\Rightarrow E(\vec{k}) = \frac{E_{pA}+E_{pB}}{2} \pm \sqrt{\left(\frac{E_{pA}-E_{pB}}{2}\right)^2 + V_{pp\pi}^2 \left|f(\vec{k})\right|}$$

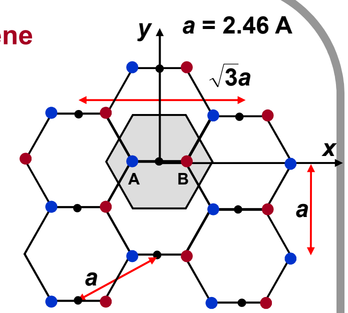
$$\Rightarrow E_g = \left|E_{pA}-E_{pB}\right| \longrightarrow \text{at the K(K')-points}$$

The answer from the nearly-free-electron approach:

As you saw in your homework, if the crystal potential lacked inversion symmetry w.r.t. the y-axis (i.e. $V(-x,y) \neq V(x,y)$) then there would be a non-zero bandgap.

Of course, if the two atoms in the primitive cell were different then the crystal would lack inversion symmetry! So both the approaches explaining the zero bandgap are consistent.

Pseudospin in Graphene



Solutions are:

$$E(\vec{k}) = E_p \pm V_{pp\pi} \left|f(\vec{k})\right|$$

$$f(\vec{k}) = \left(e^{i\,\vec{k}.\vec{n}_1} + e^{i\,\vec{k}.\vec{n}_2} + e^{i\,\vec{k}.\vec{n}_3} \right)$$

And the corresponding eigenvectors are:

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_+ = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -f^{*}(\vec{k})/\left|f(\vec{k})\right| \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ e^{i\phi(\vec{k})} \end{bmatrix}$$

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_- = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ f^{*}(\vec{k})/\left|f(\vec{k})\right| \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -e^{i\phi(\vec{k})} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ e^{i\phi(\vec{k})+i\pi} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ e^{i\theta(\vec{k})} \end{bmatrix}$$

Compare with the case of 1/2 spin particles with spins in the x-y plane:

$$\left.\begin{aligned} |x\rangle_+ &= \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix} \quad |x\rangle_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix} \\ |y\rangle_+ &= \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \end{bmatrix} \quad |y\rangle_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -i \end{bmatrix} \end{aligned}\right\} \longrightarrow |\phi\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ e^{i\phi} \end{bmatrix}$$