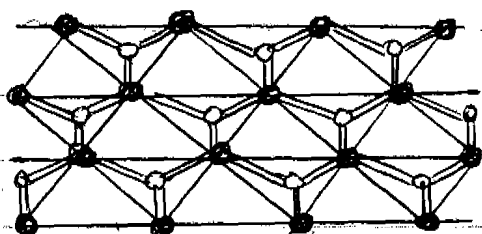


Band structure of Graphene

Graphene is a single ^{2D} layer of graphite, consisting of carbon atoms arranged in a honeycomb structure.

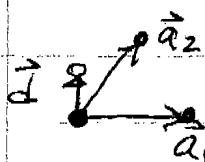
honeycomb structure : underlying triangular BL with two point basis



Denote $\bullet$ as "A" sites
 $\circ$ as "B" sites

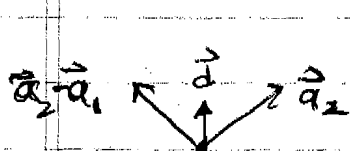
A sites sit on the sites $\vec{R}$ of the underlying triangular lattice.

B sites sit at sites $\vec{R} + \vec{d}$



primitive vectors of the BL

$$\begin{cases} \vec{a}_1 = a \hat{x} \\ \vec{a}_2 = \frac{a}{2} \hat{x} + \frac{\sqrt{3}}{2} a \hat{y} \end{cases}$$

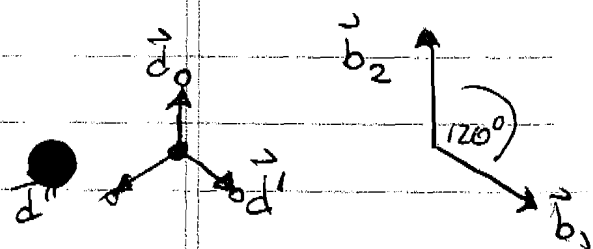


basis vectors

$$\begin{cases} \vec{0} \\ d = \frac{1}{3} (\vec{a}_2 + (\vec{a}_2 - \vec{a}_1)) \\ = \frac{a}{\sqrt{3}} \hat{y} \end{cases}$$

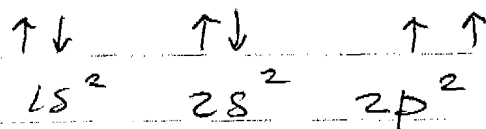
primitive vectors of R-L.

$$\begin{cases} \vec{b}_1 = \frac{2\pi}{a} \hat{x} - \frac{2\pi}{\sqrt{3}a} \hat{y} \\ \vec{b}_2 = \frac{4\pi}{\sqrt{3}a} \hat{y} \end{cases}$$



nearest neighbors of A site are displaced from A by vectors
 $\vec{d}, \vec{d}' = (\vec{a}_1 - \vec{a}_2) + \vec{d} = \frac{a}{2} \hat{x} - \frac{a}{2\sqrt{3}} \hat{y}, \vec{d}'' = -\vec{a}_2 + \vec{d} = -\frac{a}{2} \hat{x} - \frac{a}{2\sqrt{3}} \hat{y}$

Atomic Carbon has electron structure



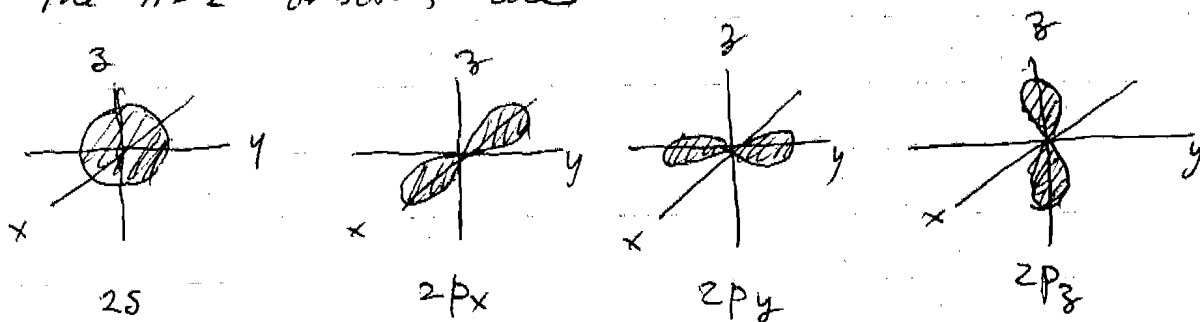
6 electrons

4 electrons in outermost $n=2$ shell.

The $1s^2$ electrons have significantly lower energy than the $n=2$ electrons. When C is in the honeycomb structure, they remain tightly bound to the C ion and do not participate in bonding or conduction. We thus forget about them!

The $2s^2$ and $2p^2$ electrons are very close in energy. When C is placed in the honeycomb structure, these atomic orbitals will mix ("hybridize").

The $n=2$ orbitals are



$2s$ is spherically symmetric

$2p$ has lobes oriented along $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes

honeycomb structure we take to be in the xy plane

If one does a tight binding calculation of the band structure from the $n=2$ shell electrons, one should mix in all $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals.

Since there are two atoms per primitive cell of the BL (since it is BL with two-point basis) and there are four atomic orbitals to consider, the Bloch wavefunction is a mixture of 8 terms:

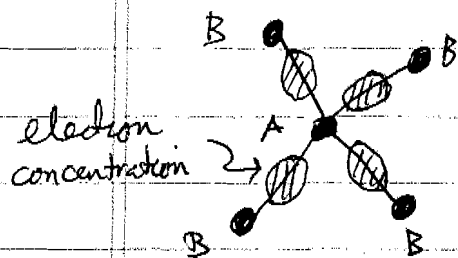
$$\psi_{\vec{k}} = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left\{ b_{AS} \varphi_{AS} + b_{AP_x} \varphi_{AP_x} + b_{AP_y} \varphi_{AP_y} + b_{AP_z} \varphi_{AP_z} + b_{BS} \varphi_{BS} + b_{BP_x} \varphi_{BP_x} + b_{BP_y} \varphi_{BP_y} + b_{BP_z} \varphi_{BP_z} \right\}$$

where φ_{AS} , φ_{AP_x} etc are the s , p_x , etc atomic orbital wavefunctions centered at sites "A", and φ_{BS} , φ_{BP_x} etc are the s , p_x , etc atomic orbital wavefunctions centered at sites "B".

For each value $\vec{k}$ in 1st BZ one then get eight energies $E_n(\vec{k})$, i.e. 8 bands,

Digression: For C in a 3D diamond structure (fcc with 2-point basis) one finds that the s , p_x , p_y , and p_z orbitals all mix together ~~to~~ roughly equally - this is called " sp^3 " hybridization since one s mixes with three p orbitals. The 8 bands separate into two distinct groups: the lowest four bands are called " σ -bonding" bands. Here the

wavefunctions from the A and B sites add roughly symmetrically so that the electron probability density is concentrated midway between A and B atoms. These form σ -bonding bands give Bloch electron wavefunctions where the electron density is concentrated on the nearest neighbor bonds of the diamond structure. These are the covalent bonds that hold the diamond structure together. The higher four bands are called " σ^* -antibonding" bands. Here the A and B site wavefunctions add roughly antisymmetrically so that the electron probability vanishes midway between A and B. The σ^* -antibonding bands lie higher in energy than the σ -bonding bands and do not overlap them. In the ground state, each ~~con~~ of the two C atoms in a primitive cell of the BL give 4 electrons, for a total of 8 electrons per BL cell. These 8 electrons fill up the 4 σ -bonding bands (each band can hold 2 electrons per C - since each C can have $\text{spin } \uparrow$ and $\text{spin } \downarrow$). Hence the 4 σ -bonding bands are completely filled and the 4 σ^* -antibonding bands are completely empty. There is a finite energy gap between the σ and σ^* bands $\Rightarrow$ diamond is an insulator.

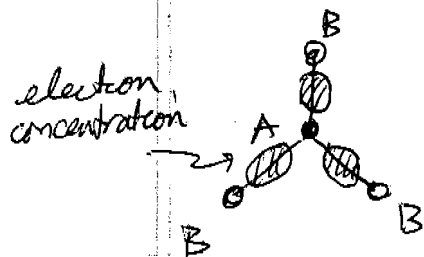


the 4 nearest neighbors of an A site are the equidistant B sites that lie at the vertices of a regular tetrahedron. The σ -bonding states concentrate electron density along bonds connecting nearest neighbor

Graphene : For C in a 2D honeycomb structure one finds that the s , p_x , and p_y orbitals all mix together roughly equally (these are the orbitals which have significant electron probability in the xy plane) - while the p_z orbital remains separated. The s - p_x - p_y mixed states are called " sp^2 " hybridized as one s mixes with two p orbitals.

The sp^2 states give rise to 3 σ -bonding bands and 3 σ^* -antibonding bands. The p_z states give rise to two bands - the π -band and the π^* -band. (so we have a total of 8 bands)

The σ -bonding bands give wavefunctions with electron concentration along the three nearest neighbor bonds between A and B sites in the xy plane. These are the covalent bonds that hold the honeycomb structure together.



The σ -bonding bands have the lowest energy and all lie ~~below~~ below the Fermi energy. In the ground state they are completely filled taking 6 of the 8 electrons per BL cell. Since these bands are filled, they play no role in electric conduction in graphene.

The σ^* -antibonding bands all lie above the Fermi energy. In the ground state they are completely empty, hence we ignore them. (There is a finite energy gap between the min energy of the σ^* bands and the Fermi energy)

All the interesting effects concerning conduction therefore lie with the π and π^* bands. These lie essentially between the σ and σ^* bands (though actually the σ band near its max overlaps some with the min of the π band, and the max of the π^* band overlaps somewhat with the min of the σ^* band. But these overlapping regions lie well below or well above, respectively, the Fermi energy and so play no role in conduction - conduction is determined by electrons in close vicinity of the Fermi energy only!)

We will soon see that the π and π^* bands do not overlap. Therefore in the ground state, with 8 electrons per BL cell, 6 electrons go to completely filling the 3 σ bands, and 2 electrons go to completely filling the π band. The π^* and σ^* bands are completely empty. This would be an insulator except we will see that the π and π^* bands

are degenerate (no energy gap) at the Fermi surface.

We therefore will do a tight binding calculation involving only the p_z orbital alone as a rough calculation for the π and π^* bands.

$$\text{let } \begin{cases} \varphi_A(\vec{r}) \equiv \varphi(\vec{r}) & p_z \text{ orbital centered at origin (site A)} \\ \varphi_B(\vec{r}) \equiv \varphi(\vec{r}-\vec{d}) & p_z \text{ orbital centered at position } \vec{d} \text{ (site B)} \end{cases}$$

Our assumed Bloch wavefunction then has

the form:

$$\psi_k(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \{ b_A \varphi_A(\vec{r}-\vec{R}) + b_B \varphi_B(\vec{r}-\vec{R}) \}$$

$\vec{k} \in 1^{st} BZ$

Consider

$$\langle \varphi_A | H | \psi_k \rangle = \langle \varphi_A | H_{\text{at}} + \Delta U | \psi_k \rangle$$

||

$$E_k \langle \varphi_A | \psi_k \rangle = E \langle \varphi_A | \psi_k \rangle + \langle \varphi_A | \Delta U | \psi_k \rangle$$

$\uparrow$
energy of atomic p_z orbital

$$\langle \varphi_A | \psi_k \rangle = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \{ b_A \langle \varphi_A(\vec{r}) | \varphi_A(\vec{r}-\vec{R}) \rangle + b_B \langle \varphi_A(\vec{r}) | \varphi_B(\vec{r}-\vec{R}) \rangle \}$$

$$= \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left\{ b_A \int d^3r \varphi^*(\vec{r}) \varphi(\vec{r}-\vec{R}) + b_B \int d^3r \varphi^*(\vec{r}) \varphi(\vec{r}-\vec{R}-\vec{d}) \right\}$$

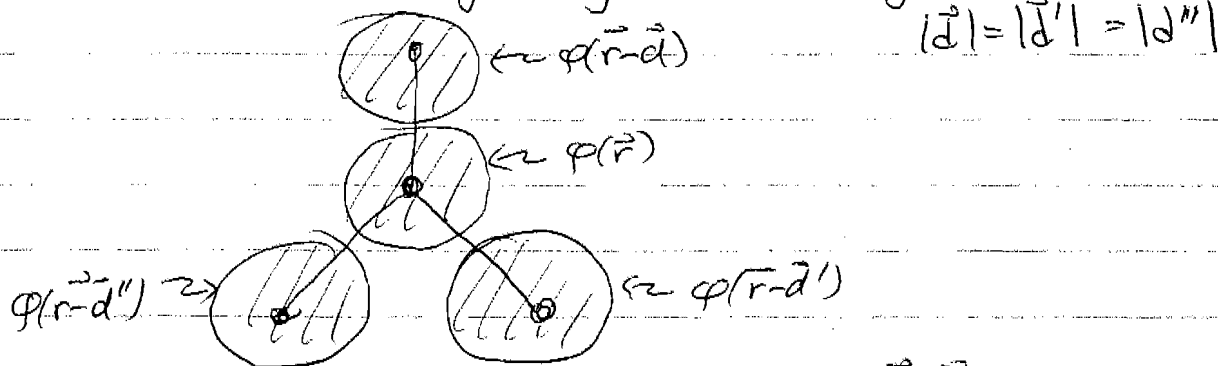
We will assume that all overlaps are negligible except for nearest neighbors - recall that the nearest neighbors of A sites are B sites and vice versa.

So in the first term the only $\vec{R}$ we consider is $\vec{R} = 0$.
In the 2nd term the only $\vec{R}$ we consider are for $\vec{R} + \vec{a} = \vec{J}, \vec{J}', \vec{J}''$ the vectors to the nearest neighbors
ie $\vec{R} = 0, \vec{R} = \vec{a}_1, -\vec{a}_2$, and $\vec{R} = -\vec{a}_2$

$$\langle \psi_A | \psi_B \rangle = b_A + b_B \int d^3r \varphi^*(\vec{r}) \varphi(\vec{r} - \vec{a}) \times \left[1 + e^{i\vec{k} \cdot (\vec{a}_1 - \vec{a}_2)} + e^{i\vec{k} \cdot (-\vec{a}_2)} \right]$$

where we used $\int d^3r \varphi^*(\vec{r}) \varphi(\vec{r}) = 1$ by normalization
and $\int d^3r \varphi^*(\vec{r}) \varphi(\vec{r} - \vec{a}) = \int d^3r \varphi^*(\vec{r}) \varphi(\vec{r} - \vec{a}')$
 $= \int d^3r \varphi^*(\vec{r}) \varphi(\vec{r} - \vec{a}'')$

where the overlap integrals are all equal since φ has rotational symmetry about the $\hat{z}$ axis and



The term in $[\dots]$ is just $\sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}}$ over the set of $\vec{R} = \{ \vec{0}, \vec{a}_1, -\vec{a}_2, -\vec{a}_2 \}$ that give the nearest neighbors $\vec{J}, \vec{J}', \vec{J}''$. The overlap integral is a common factor for all these terms.

Define $\alpha \equiv \int d^3r \varphi^*(\vec{r}) \varphi(\vec{r}-\vec{a})$

$$\begin{aligned} \text{Then } \langle \varphi_A | \varphi_k \rangle &= b_A + b_B \alpha \left[1 + e^{i\vec{k} \cdot \vec{a}_1} e^{-i\vec{k} \cdot \vec{a}_2} + e^{-i\vec{k} \cdot \vec{a}_2} \right] \\ &= b_A + b_B \alpha \left[1 + e^{-i\vec{k} \cdot \vec{a}_2} e^{i\vec{k} \cdot \frac{\vec{a}_1}{2}} \left(e^{i\vec{k} \cdot \frac{\vec{a}_1}{2}} + e^{-i\vec{k} \cdot \frac{\vec{a}_1}{2}} \right) \right] \\ &= b_A + b_B \alpha \left[1 + e^{i\vec{k} \cdot (\frac{\vec{a}_1}{2} - \vec{a}_2)} 2 \cos(\vec{k} \cdot \frac{\vec{a}_1}{2}) \right] \end{aligned}$$

Use $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y}$

$$\langle \varphi_A | \varphi_k \rangle = b_A + b_B \alpha \left[1 + e^{-i\frac{\sqrt{3}}{2}k_y a} 2 \cos(k_x \frac{a}{2}) \right]$$

Similarly,

$$\begin{aligned} \langle \varphi_A | \Delta U | \varphi_B \rangle &= \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left\{ b_A \int d^3r \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r}-\vec{R}) \right. \\ &\quad \left. + b_B \int d^3r \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r}-\vec{R}-\vec{a}) \right\} \end{aligned}$$

Again, keep only nearest neighbor overlaps, so $\vec{R}=0$ only in 1st term, and $\vec{R} = \{\vec{0}, \vec{a}_1 - \vec{a}_2, -\vec{a}_2\}$ in 2nd term.

Again, all the overlap integrals in 2nd term are equal

$$\begin{aligned} \int d^3r \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r}-\vec{a}) &= \int d^3r \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r}-\vec{a}') \\ &= \int d^3r \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r}-\vec{a}'') \end{aligned}$$

because $\varphi(\vec{r})$ has rotational symmetry about $\hat{z}$ axis
and because $\Delta U(\vec{r})$ has rotation by 120° symmetry about $\hat{z}$ axis (maps $\vec{a} \rightarrow \vec{a}' \rightarrow \vec{a}'' \rightarrow \vec{a}$)

Define $\beta \equiv - \int d^3r \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r})$

$\gamma \equiv - \int d^3r \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r}-\vec{d})$

Then

$$\langle \varphi_A | \Delta U | \psi_k \rangle = -b_A \beta - b_B \gamma \left[1 + e^{-i \frac{\sqrt{3}}{2} k_y a} 2 \cos(k_x a) \right]$$

where [...] is the same factor from $\sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}}$ that we had in $\langle \varphi_A | \psi_k \rangle$.

Define $f(\vec{k}) \equiv 1 + e^{-i \frac{\sqrt{3}}{2} k_y a} 2 \cos(k_x a)$

Our equation $E_k \langle \varphi_A | \psi_k \rangle = E \langle \varphi_A | \psi_k \rangle + \langle \varphi_A | \Delta U | \psi_k \rangle$ can now be written as:

$$0 = (E_k - E) [b_A + b_B \alpha f(\vec{k})] + b_A \beta + b_B \gamma f(\vec{k})$$

(1) or $(E_k - E + \beta) b_A + [(E_k - E) \alpha + \gamma] f(\vec{k}) b_B = 0$

We also need to consider $\langle \varphi_B | H | \psi_k \rangle$

$$\Rightarrow E_k \langle \varphi_B | \psi_k \rangle = E \langle \varphi_B | \psi_k \rangle + \langle \varphi_B | \Delta U | \psi_k \rangle$$

Repeating all the above steps, one arrives at:

(2) $(E_k - E + \beta) b_B + [(E_k - E) \alpha + \gamma] f^*(\vec{k}) b_A = 0$

Note α, β, γ are real because for the p_z orbital $\varphi^* = \varphi$ is real.

f^* is complex conjugate of f .

Eqs (1) and (2) combine to give a set of two ~~two~~ homogeneous linear equations in two unknowns b_A, b_B . We can write them as:

$$M \cdot \begin{pmatrix} b_A \\ b_B \end{pmatrix} = 0$$

where M is the 2×2 matrix

$$M = \begin{bmatrix} \epsilon_k - E + \beta & [(\epsilon_k - E)\alpha + \gamma] f(\vec{k}) \\ [(\epsilon_k - E)\alpha + \gamma] f^*(\vec{k}) & \epsilon_k - E + \beta \end{bmatrix}$$

there is a non-trivial solution for b_A, b_B only when $\det M = 0$. This condition gives a quadratic equation to solve for the two possible values of $E(\vec{k})$. Call these values $E_{\pm}(\vec{k})$. For each $\vec{k}$ there are two solutions: $E_{-}(\vec{k})$ is the π band, $E_{+}(\vec{k})$ is the π^* band.

It is straightforward to solve the above quadratic for E_k . But to make things even simpler, let us assume that $\alpha \ll \gamma$ and set the α terms to zero.

$$\text{Note: } \begin{cases} \alpha \equiv \int d^3r \phi^*(r) \phi(\vec{r}-\vec{d}) \\ \gamma \equiv -\int d^3r \phi^*(r) \Delta U(\vec{r}) \phi(\vec{r}-\vec{d}) \end{cases}$$

Since $\Delta U(\vec{r})$ is large at $\vec{r}-\vec{d}$, then roughly $\phi(\vec{r}-\vec{d}) \ll \Delta U(\vec{r}) \phi(\vec{r}-\vec{d})$, so indeed expect $\alpha \ll \gamma$

with $\alpha=0$ we have

$$M = \begin{bmatrix} \epsilon_k - E + \beta & \gamma f(\vec{k}) \\ -\gamma f^*(\vec{k}) & \epsilon_k - E + \beta \end{bmatrix}$$

and $\det M = 0$ is trivial to solve. We have

$$\det M = (\epsilon_k - E + \beta)^2 - \gamma^2 |f(\vec{k})|^2 = 0$$

Solve for ϵ_k

$$\Rightarrow \boxed{\epsilon_{\pm}(\vec{k}) \equiv E - \beta \pm |\gamma| |f(\vec{k})|}$$

Note that since $|\gamma| |f(\vec{k})| > 0$, then

$$\epsilon_+(\vec{k}) \geq E - \beta$$

$$\epsilon_-(\vec{k}) \leq E - \beta$$

So bands do not overlap, i.e. $\min_{\vec{k}} \epsilon_+(\vec{k}) \geq \max_{\vec{k}} \epsilon_-(\vec{k})$

$$|f(\vec{k})| = \left[1 + 4 \cos^2\left(\frac{k_x a}{2}\right) + 4 \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right) \right]^{1/2}$$

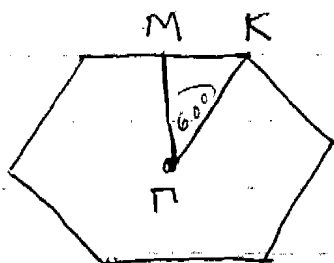
$|f(\vec{k})|$ is largest when $k_x = k_y = 0$

$\rightarrow \min \epsilon_-(\vec{k})$ and $\max \epsilon_+(\vec{k})$ are both at $\vec{k} = 0$.

$\epsilon_-(\vec{k})$ increases as $\vec{k}$ increases towards surface
of 1st BZ

$\epsilon_+(\vec{k})$ decreases as $\vec{k}$ increases towards surface
of 1st BZ

We can plot $\epsilon_{\pm}(\vec{k})$ for $\vec{k}$ along various directions in the 1st BZ



$$\vec{k}_M = \frac{1}{2} \vec{b}_2 = \left(0, \frac{2\pi}{\sqrt{3}a}\right)$$

$$\vec{k}_K = \left(\frac{2\pi}{3a}, \frac{2\pi}{\sqrt{3}a}\right)$$

along ΓM we let $k_x = 0$

$$k_y = k \quad \text{with } k \in \left(0, \frac{2\pi}{\sqrt{3}a}\right)$$

$$|f(k)| = \sqrt{1 + 4 \cos^2(0) + 4 \cos(0) \cos\left(\frac{\sqrt{3}}{2}ka\right)}$$

$$= \sqrt{5 + 4 \cos\left(\frac{\sqrt{3}}{2}ka\right)}$$

along ΓK magnitude of $\vec{k}$ goes from 0 to $\frac{2\pi}{a} \sqrt{\frac{1}{9} + \frac{1}{3}} = \frac{4\pi}{3a}$

$$\text{so } k_x = \frac{k}{2} = k \cos 60^\circ$$

$$k_y = \frac{\sqrt{3}}{2} k = k \sin 60^\circ \quad \text{with } k \in \left(0, \frac{4\pi}{3a}\right)$$

$$|f(k)| = \sqrt{1 + 4 \cos^2\left(\frac{ka}{4}\right) + 4 \cos\left(\frac{ka}{4}\right) \cos\left(\frac{3ka}{4}\right)}$$

along MK $k_y = \frac{2\pi}{\sqrt{3}a}$, $k_x = k$ with $k \in \left(0, \frac{2\pi}{3a}\right)$

$$|f(k)| = \sqrt{1 + 4 \cos^2\left(\frac{ka}{2}\right) + 4 \cos\left(\frac{ka}{2}\right) \cos \pi} = \sqrt{1 + 4 \cos^2\left(\frac{ka}{2}\right) - 4 \cos\left(\frac{ka}{2}\right)}$$

$$= 2 \cos\left(\frac{ka}{2}\right) - 1$$

From above we have:

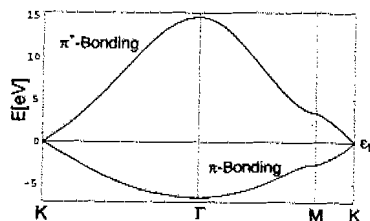
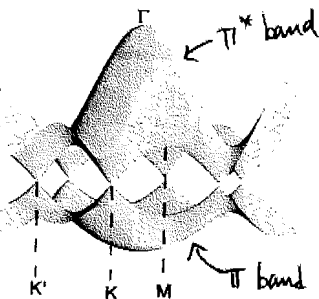
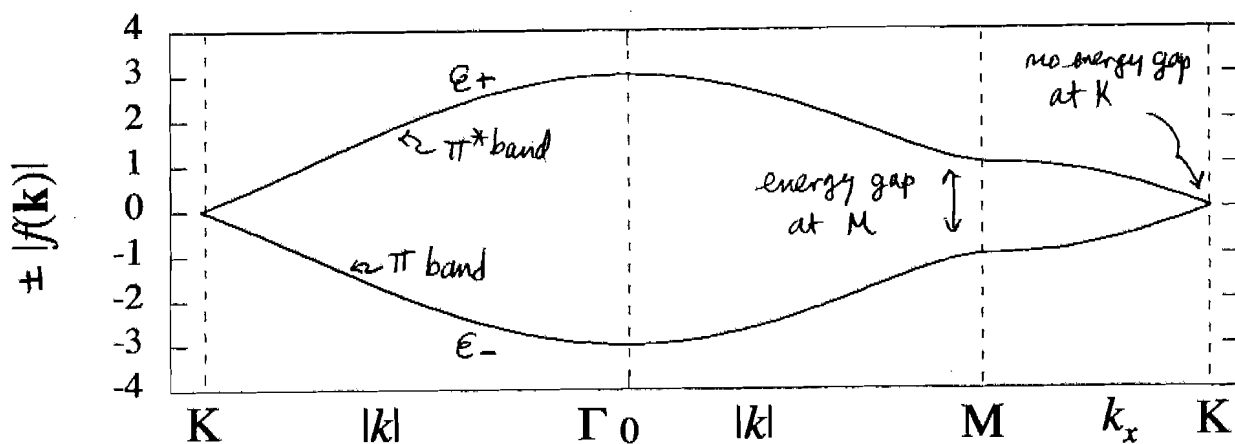
$$|f(\vec{k}_M)| = 1, \quad |f(\vec{k}_K)| = 2\cos\frac{\pi}{2} - 1 = 0$$

So there is an energy gap

$$\Delta E \equiv E_+ - E_- = 2\gamma |f(\vec{k})| = 2\gamma [2\cos\frac{k_x a}{2} - 1]$$

along the BZ edge from M to K that vanishes at K.

By symmetry, the same happens along all edges of the 1st BZ.



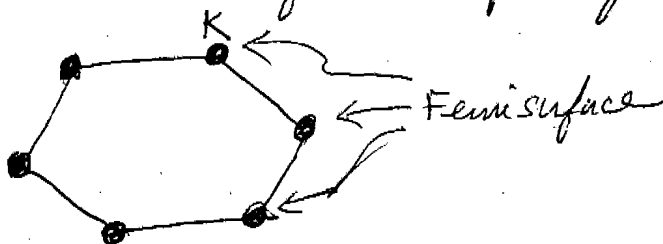
3D picture of π and π^* bands
(from Master's thesis of JR Hauptmann)

Since π band lies below π^* band, as they do not overlap, in the ground state the π band is completely filled and π^* band is completely empty.
 (recall, 6 electrons per atom go into the $3sp^2$ σ -bands
 so the remaining 2 electrons per atom now fill the π -band)

The Fermi surface consists of the points in k -space which have the maximum energy electrons in the ground state.
 Here we have

$$E_F = E_g$$

and the Fermi surface is the set of 6 discrete points K that are the vertices of the surface of the 1st BZ



One can also show (you will do it for HW)

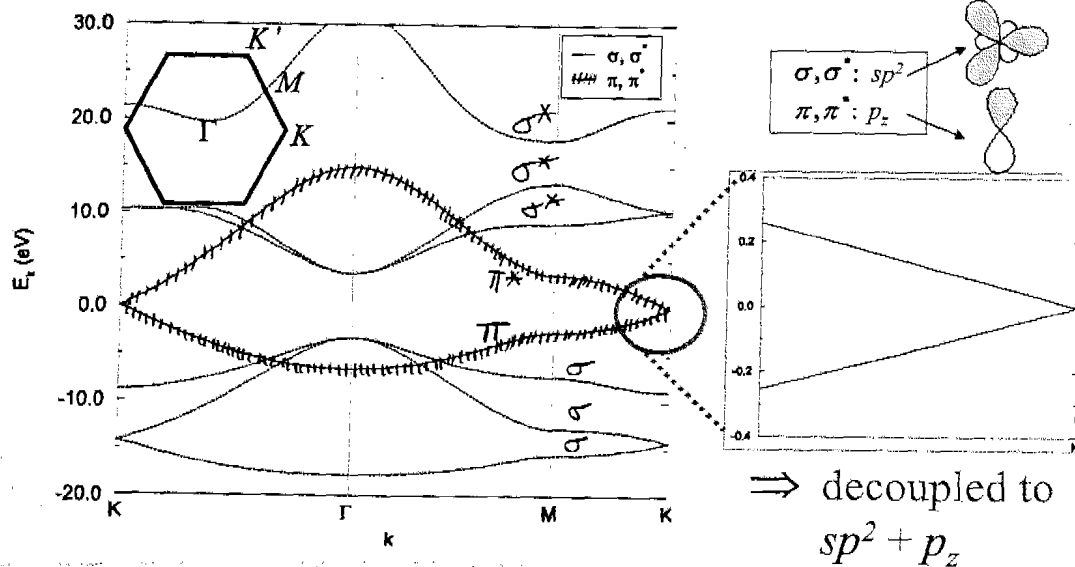
- 1) near $\vec{k}=0$, constant energy surfaces are circles
- 2) near $\vec{k}_K$, constant energy surfaces are circles centered on $\vec{k}_K$
- 3) near $\vec{k}_K$, $E_{\pm}(\vec{k}) \sim |\vec{k} - \vec{k}_K|$ linear in k
- 4) density of states $g(E)$ vanishes at E_F

Because the energy gap vanishes at the Fermi surface (the vertices K) it costs no energy to excite electrons from the π -band (valence band) into the π^* band (conduction band). Hence the electrons in the π -band allow for conductivity. But since $g(E_F)=0$, there are not so many electrons easily excited to conduction band. ~~But it is not a semiconductor~~

Because the carrier density of conduction electrons is thus small, graphene is called a semimetal.

A more complete calculation of band structure showing $\sigma, \pi, \pi^*, \sigma^*$ bands

- Tight-binding model with nonorthogonal orbitals



(From online talk by Hongki Min)