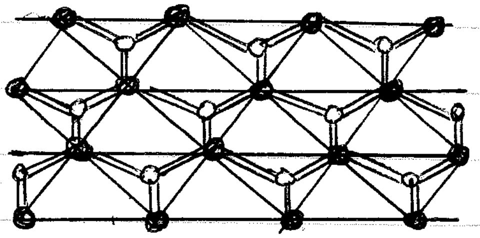
Band Structure of Graphene

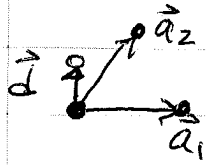
Graphene is a single 2D layer of graphite, consisting of carbon atoms arranged in a honeycomb structure.

honeycomb structure : underlying triangular BL with two point basis

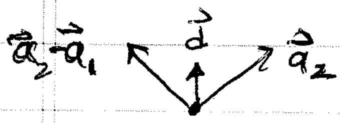


Denote {● as "A" sites
{○ as "B" sites

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

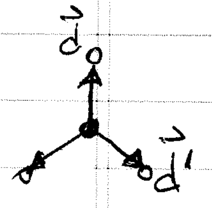


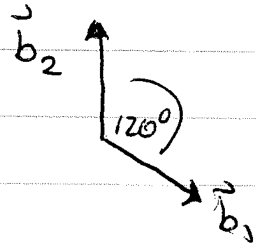
primitive vectors of the BL
$$\begin{cases} \vec{a}_1 = a\hat{x} \\ \vec{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y} \end{cases}$$



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

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
$\vec{d}$, $\vec{d}' = (\vec{a}_1-\vec{a}_2)+\vec{d} = \frac{a}{2}\hat{x} - \frac{a}{2\sqrt{3}}\hat{y}$, $\vec{d}'' = -\vec{a}_2+\vec{d} = -\frac{a}{2}\hat{x} - \frac{a}{2\sqrt{3}}\hat{y}$

<u>Atomic</u> Carbon has electron structure

$$\begin{array}{ccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow\ \uparrow \\ 1s^2 & 2s^2 & 2p^2 \end{array}$$

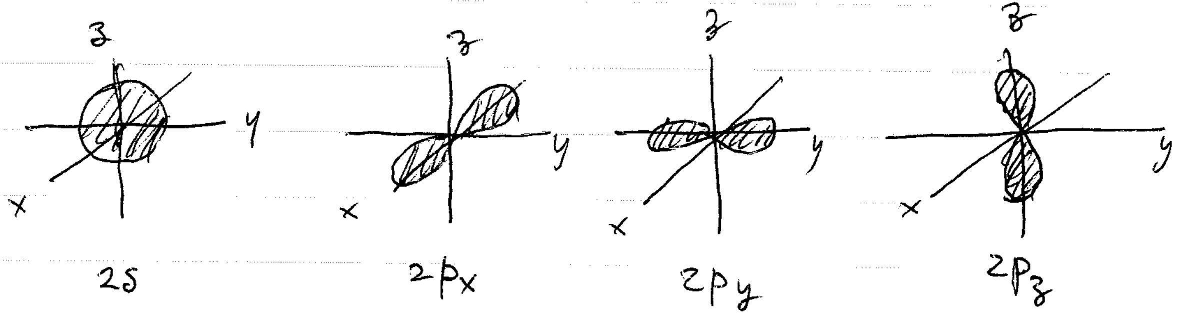
6 electrons

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 $2s^2$ ad $2p^2$ 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 $\hat{x}$, $\hat{y}$, ad $\hat{z}$ 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.

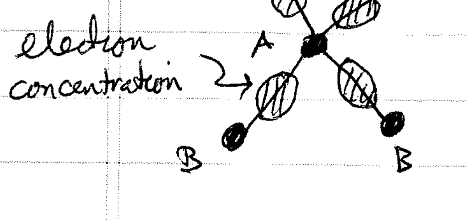
Since there are two atoms per primitive cell of the BL (since it is BL with two-point basis) and there are four atomic orbitals to consider, the Bloch wavefunction is a mixture of 8 terms:

$$\psi_k = \sum_R e^{i\vec{k}\cdot\vec{R}} \Big\{ b_{As}\varphi_{As} + b_{Ap_x}\varphi_{Ap_x} + b_{Ap_y}\varphi_{Ap_y} + b_{Ap_z}\varphi_{Ap_z} + b_{Bs}\varphi_{Bs} + b_{Bp_x}\varphi_{Bp_x} + b_{Bp_y}\varphi_{Bp_y} + b_{Bp_z}\varphi_{Bp_z} \Big\}$$

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 $\varepsilon_n(\vec{k})$, ie 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 four 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 ~~ion~~ of the two ions 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 ion – since each $\vec{k}$ can have spin $\uparrow$ and 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 <u>insulator</u>



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 neighbors

Covalent Bonding: Hybrid Orbitals

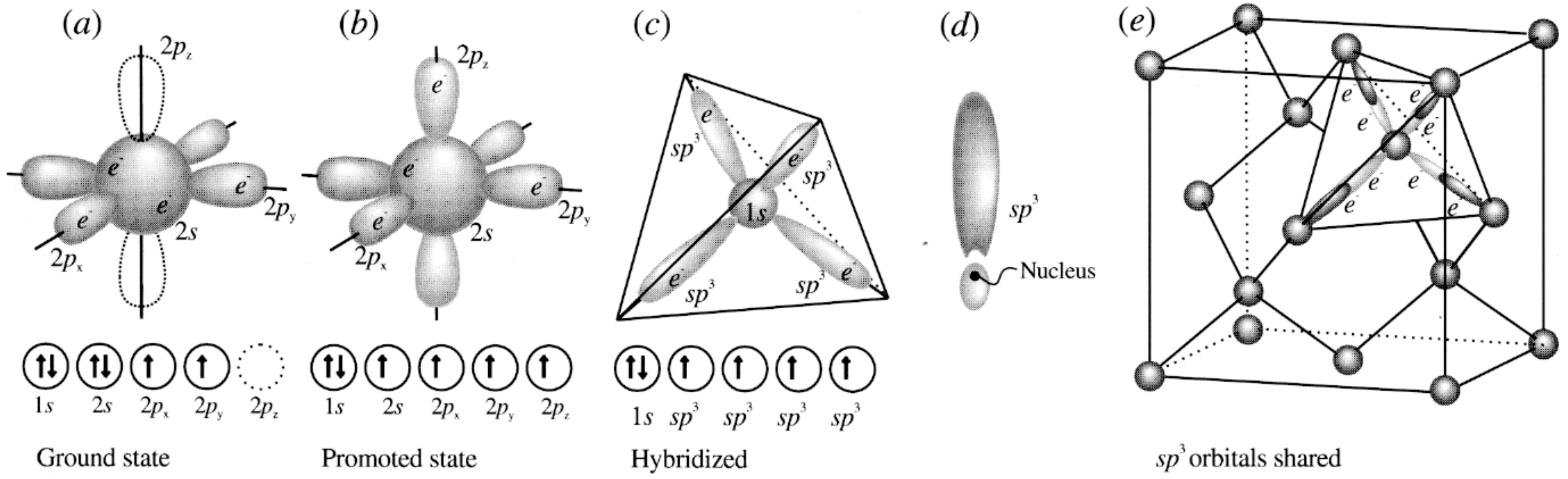


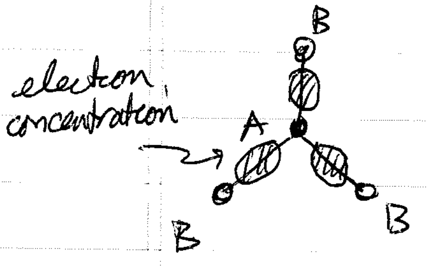
Figure 3.5 Formation of covalent sigma (σ) bonds with carbon in diamond. (*a*) Ground-state electron configuration of carbon. The 2*s* orbital contains two electrons, the $2p_x$ and $2p_y$ orbitals each contain one electron, and the $2p_z$ orbital is vacant. (*b*) One electron from the 2*s* orbital is promoted to the $2p_z$ orbital so that four orbitals are partially filled. (*c*) Hybridization of the half-filled orbitals into four identical sp^3 orbitals arrays to point to the corners of a tetrahedron. (*d*) Each sp^3 orbital consists of a large lobe and a small lobe on the opposite sides of the nucleus. The small lobes are not shown in (*c*). (*e*) Bonding of carbon atoms in diamond by sharing electrons between hybridized $2sp^3$ orgitals on adjacent atoms. Four pairs of overlapping sp^3 orbitals reaching a carbon atom are shown; similar bonds occur along each of the solid lines. The small lobes are omitted for clarity.

Diamond Example - Pure Carbon in complex 3D network

Graphene: For C in a 2D honeycomb structure one finds that the s, p_x, ad 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" hybridization as one s mixes with two p orbitals.

The sp^2 states give rise do 3 σ-bonding bands ad 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 tree nearest neighbor bonds between A ad B sites in the xy plane. These are the covalent bonds that hold the honeycomb structure together.



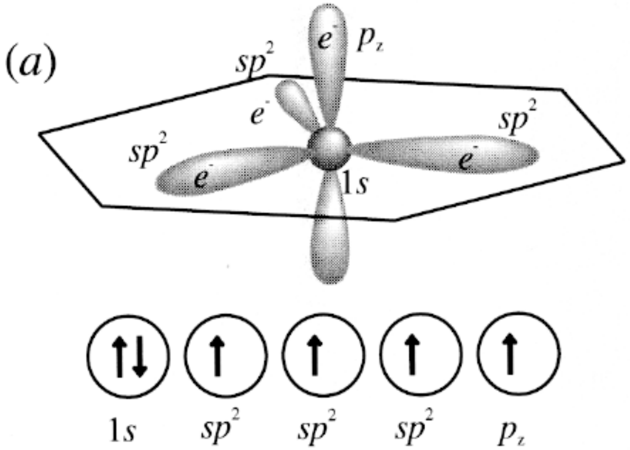
The σ-bonding bands have the lowest energy and all lie ~~before~~ below the Fermi energy. In the ground state they are completely filled taking 6 of the 8 electrons per BZ cell. Since these bands are filled, they play no role in electric conduction in graphene.

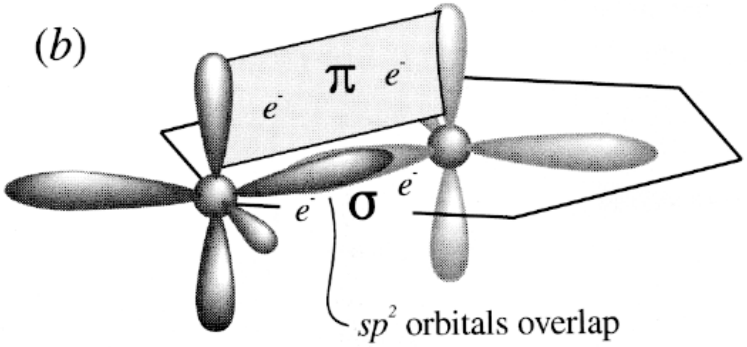
The σ^*-antibonding bands all lie above the Fermi energy. In the ground state they are completely empty, hence we ignore them. (there is a finite energy gap between the min energy of the σ^* bands and the Fermi energy)

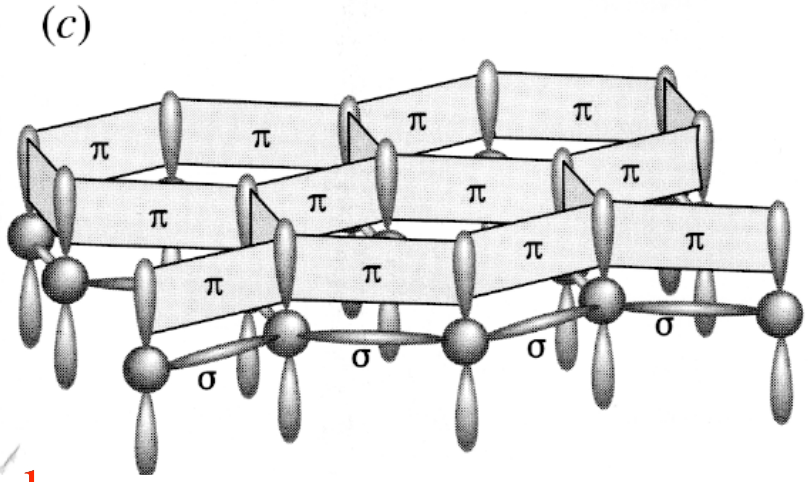
All the interesting effects concerning conduction therefore lie with the π and π^* bands. These lie essentially between the σ and σ^* bands (though actually the σ band near its max overlaps some with the min of the π band, and the max of the π^* band overlaps somewhat with the min of the σ^* band. But 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

Covalent Bonding: Sigma vs. Pi bonds







Note the hexagonal symmetry and that graphite tends to form in layered sheets

pi bonds are weaker than sigma bonds

Graphite Example - Pure Carbon in layered 3D network 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.

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:

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

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

Consider

$$\underset{\mathcal{E}_k \langle \varphi_A | \psi_k \rangle}{\underset{\parallel}{\langle \varphi_A | H | \psi_k \rangle}} = \langle \varphi_A | H_{at} + \Delta U | \psi_k \rangle$$

$$\mathcal{E}_k \langle \varphi_A | \psi_k \rangle = \underset{\substack{\uparrow \\ \text{energy of atomic } p_z \text{ orbital}}}{E} \langle \varphi_A | \psi_k \rangle + \langle \varphi_A | \Delta U | \psi_k \rangle$$

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

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

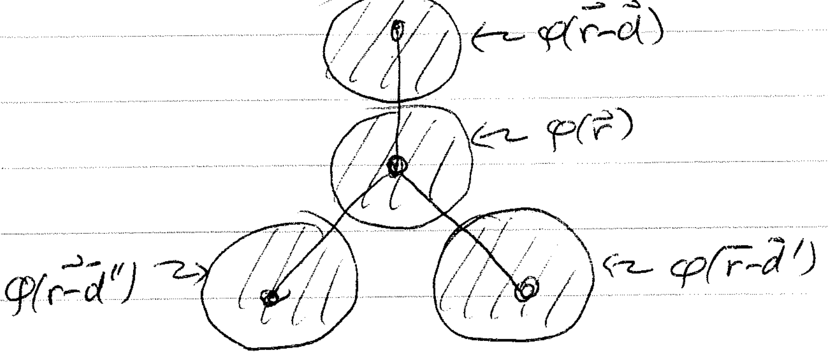
We will assume that all overlaps are negligible *except* for *nearest* *neighbors* - recall that the nearest neighbors of A sites are B sites and vice versa.

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 $\vec{R}+\vec{d} = \vec{d}, \vec{d}', \vec{d}''$ the vectors to the nearest neighbors ie $\vec{R}=0$, $\vec{R}=\vec{a}_1-\vec{a}_2$, and $R = -\vec{a}_2$

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

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

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



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

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

Then $\langle \varphi_A | \psi_k \rangle = b_A + b_B \alpha \left[1 + e^{i\vec k\cdot\vec a_1} e^{-i\vec k\cdot\vec a_2} + e^{-i\vec k\cdot\vec a_2} \right]$

$$= b_A + b_B \alpha \left[1 + e^{-i\vec k\cdot\vec a_2} e^{i\vec k\cdot\frac{\vec a_1}{2}} \left(e^{i\vec k\cdot\frac{\vec a_1}{2}} + e^{-i\vec k\cdot\frac{\vec a_1}{2}} \right) \right]$$

$$= b_A + b_B \alpha \left[1 + e^{i\vec k\cdot\left(\frac{\vec a_1}{2} - \vec a_2\right)}\, 2\cos\left(\vec k\cdot\frac{\vec a_1}{2}\right) \right]$$

Use $\vec a_1 = a\hat x$, $\vec a_2 = \frac{a}{2}\hat x + \frac{\sqrt{3}\,a}{2}\hat y$

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

Similarly,

$$\langle \varphi_A | \Delta U | \varphi_B \rangle = \sum_{\vec R} e^{i\vec k\cdot\vec R} \Big\{ b_A \int d^3r\, \varphi^*(\vec r)\Delta U(\vec r)\, \varphi(\vec r - \vec R) + b_B \int d^3r\, \varphi^*(\vec r)\Delta U(\vec r)\, \varphi(\vec r - \vec R - \vec d\,) \Big\}$$

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

$$\int d^3r\, \varphi^*(\vec r)\Delta U(\vec r)\, \varphi(\vec r - \vec d\,) = \int d^3r\, \varphi^*(\vec r)\Delta U(\vec r)\, \varphi(\vec r - \vec d\,') = \int d^3r\, \varphi^*(\vec r)\Delta U(\vec r)\, \varphi(\vec r - \vec d\,'')$$

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 $\vec d \to \vec d\,' \to \vec d\,'' \to \vec d$)

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

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

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

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

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

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

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

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

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

Repeating all the above steps, one arrives at:

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

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

f^* is complex conjugate of f.

Eqns (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:

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

where $\mathbb{M}$ is the 2×2 matrix

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

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

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

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

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

with $\alpha = 0$ we have

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

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

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

Solve for ε_k

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

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

$$\varepsilon_+(\vec{k}) \geqslant E - \beta$$
$$\varepsilon_-(\vec{k}) \leqslant E - \beta$$

So bands no not overlap, ie $\min\limits_k \varepsilon_+(\vec{k}) \geqslant \max\limits_k \varepsilon_-(\vec{k})$

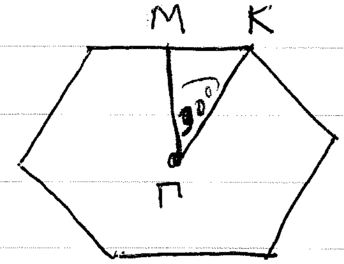
$$|f(\vec{k})| = \left[1 + 4\cos^2\left(\frac{k_x a}{2}\right) + 4\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{\sqrt{3}}{2} k_y a\right)\right]^{1/2}$$

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

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

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

$\varepsilon_+(\vec{k})$ decreases as $\vec{k}$ increases towards surface of 1st BZ we can plot $\varepsilon_\pm(\vec{k})$ 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 $k_x = 0$

$k_y = k$ 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 $\frac{2\pi}{a}\sqrt{\frac{1}{9} + \frac{1}{3}} = \frac{4\pi}{3a}$

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

$k_y = \frac{\sqrt{3}}{2}k = k\sin 60^\circ$ 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:

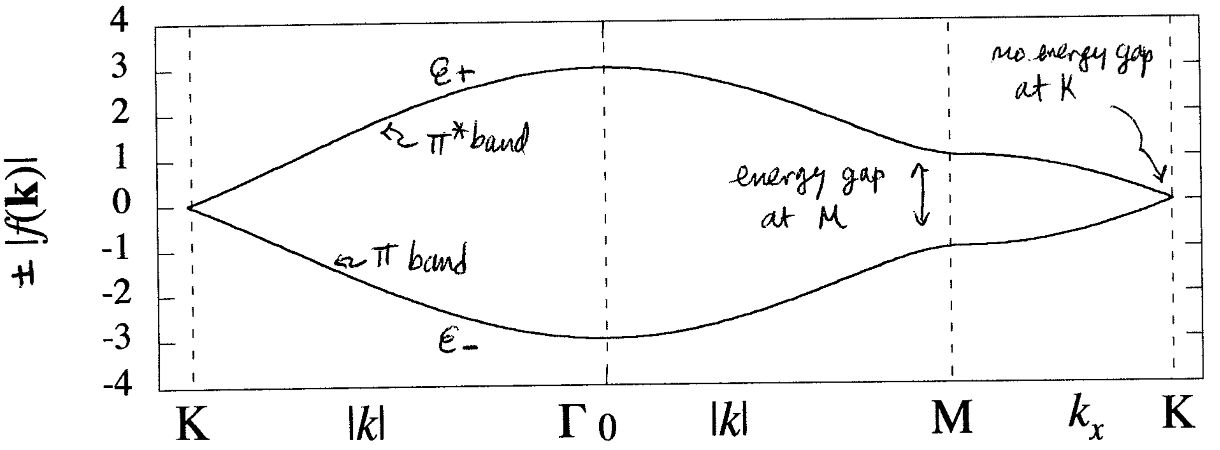
$$|f(\vec{k}_M)| = 1, \qquad |f(\vec{k}_K)| = 2\cos\frac{\pi}{3} - 1 \quad = 0$$

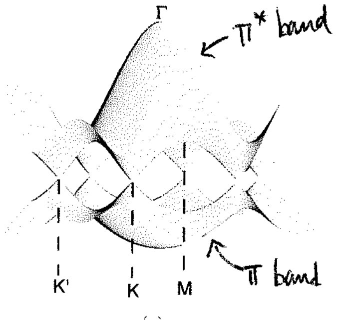
So there is an energy gap

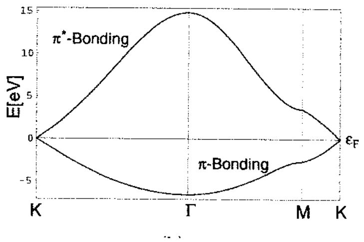
$$\Delta\varepsilon = \varepsilon_+ - \varepsilon_- = 2\gamma|f(\vec{k})| = 2\gamma\left[2\cos\frac{ka}{2} - 1\right]$$

along the BZ edge from M to K that <u>vanishes at K</u>.

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

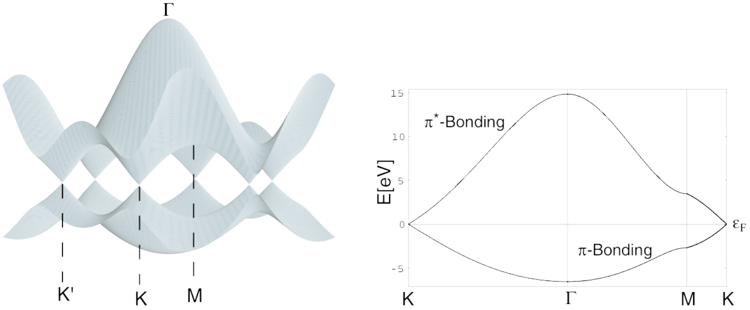






↑

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



(a) (b)

Figure 2.4: (a) shows the dispersion relation for graphene, called the tent dispersion. The points Γ, K, K' and M is high symmetry points and their placement in the Brillouin zone can be seen in Figure 2.3. (b) is appeared by cutting (a) in straight lines between the points $K \rightarrow \Gamma \rightarrow M \rightarrow K$. The two plots are drawn in mathematica by the programs seen in Appendix C.1 and Appendix C.2 respectively.

Eigen vectors coeffecients b_A, b_B determined by

$$\overleftrightarrow{M}\cdot\begin{pmatrix}b_A\\ b_B\end{pmatrix} = \begin{pmatrix}\mathcal{E}_\pm - E+\beta & \gamma f\\ \gamma f^* & \mathcal{E}_\pm - E+\beta\end{pmatrix}\begin{pmatrix}b_A\\ b_B\end{pmatrix}=0$$

Now $\mathcal{E}_\pm = E-\beta \pm |\gamma||f|$ so above is

$$\begin{pmatrix}\pm|\gamma||f| & \gamma f\\ \gamma f^* & \pm|\gamma||f|\end{pmatrix}\begin{pmatrix}b_A\\ b_B\end{pmatrix}=0$$

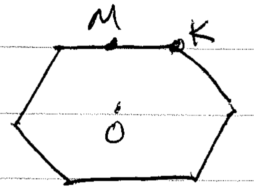
let $f=|f|e^{i\theta}$ then above is

$\gamma>0$ real

$$|\gamma||f|\begin{pmatrix}\pm 1 & e^{i\theta}\\ e^{-i\theta} & \pm 1\end{pmatrix}\begin{pmatrix}b_A\\ b_B\end{pmatrix}=0$$

$$\pm b_A + b_B e^{i\theta} = 0 \Rightarrow \boxed{b_B = \mp b_A e^{-i\theta}}$$

$$f(\vec{k}) = 1+e^{-i\frac{\sqrt{3}}{2}k_y a}\, 2\cos\left(\frac{k_x a}{2}\right)$$



all along MK, $k_y = \frac{2\pi}{\sqrt{3}a}$, so f is real and $\theta = 0$ or π

So along MK, $b_B = \mp b_A$

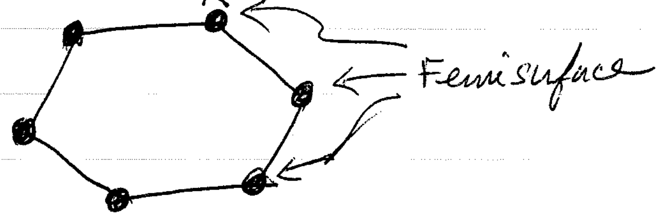
→ wave functions along BZ edge MK are symmetric and antisymmetric combinations of φ_A and φ_B!

Since π band lies below π^* band, ie 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

$$\varepsilon_F = E - \beta$$

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)

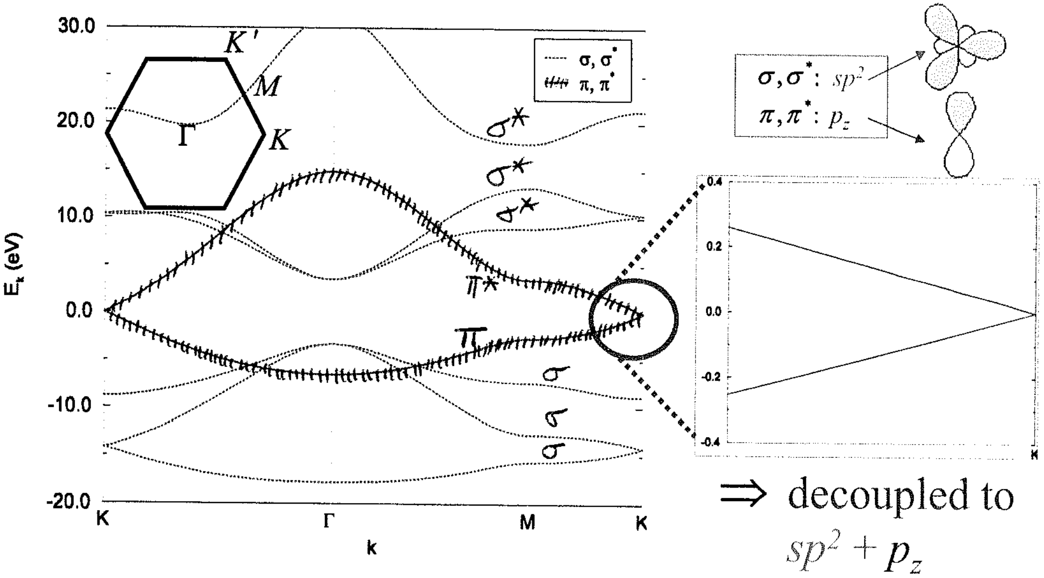
1) near $\vec{k}=0$, constant energy surfaces are circles
2) near $\vec{k}_K$, constant energy surfaces are circles centered on $\vec{k}_K$
3) near $\vec{k}_K$, $\varepsilon_\pm(\vec{k}) \sim |\vec{k}-\vec{k}_K|$ linear in k
4) density of states $g(\varepsilon)$ vanishes at ε_F

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 $g(\varepsilon_F)=0$, there are not so many electrons easily excited to conduction band. ~~Because there is no energy gap~~

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

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

- Tight-binding model with nonorthogonal orbitals



σ, σ^*: sp^2

π, π^*: p_z

⇒ decoupled to $sp^2 + p_z$

(from online talk by Hongki Min)

Also shown is the dispersion relation in some directions for the honeycomb lattice, along with the density of states. The honeycomb lattice has two bands (because there are two atoms in the unit cell) and is unusual in that the band gap goes to zero at the corners of the Brillouin zone.