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

$$\langle \varphi_A | H | \psi_k \rangle = \langle \varphi_A | Hat + \Delta U | \psi_k \rangle$$

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

(E ↑ energy of atomic p_z orbital)

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

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

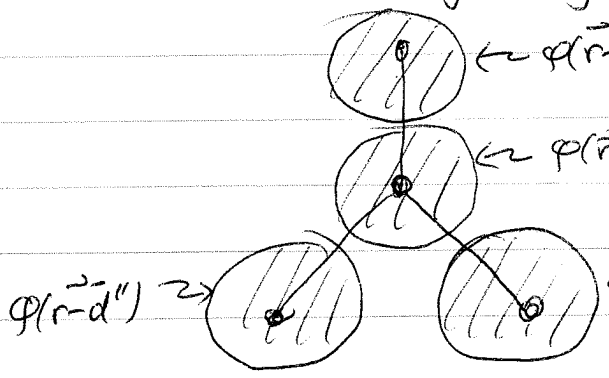
We will assume that all overlaps are negligible except for nearest neighbors - recall that the nearest neighbors of A sites are B sites and vice versa.

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,

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

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

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

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 $\langle \varphi_B | H | \psi_k \rangle$

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

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 $\vec{k}$ 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

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

So bands no not overlap, ie $\min_k \varepsilon_+(\vec{k}) \geq \max_k \varepsilon_-(\vec{k})$

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

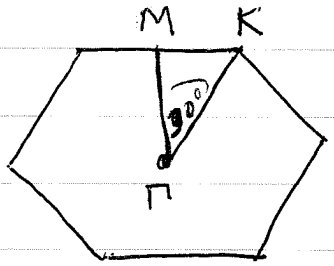
$|f(\vec{k})|$ is largest when $k_x = k_y = 0$

$\Rightarrow$ $\min \varepsilon_-(\vec{k})$ 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 $k_x = \frac{k}{2} = k\cos 60°$

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

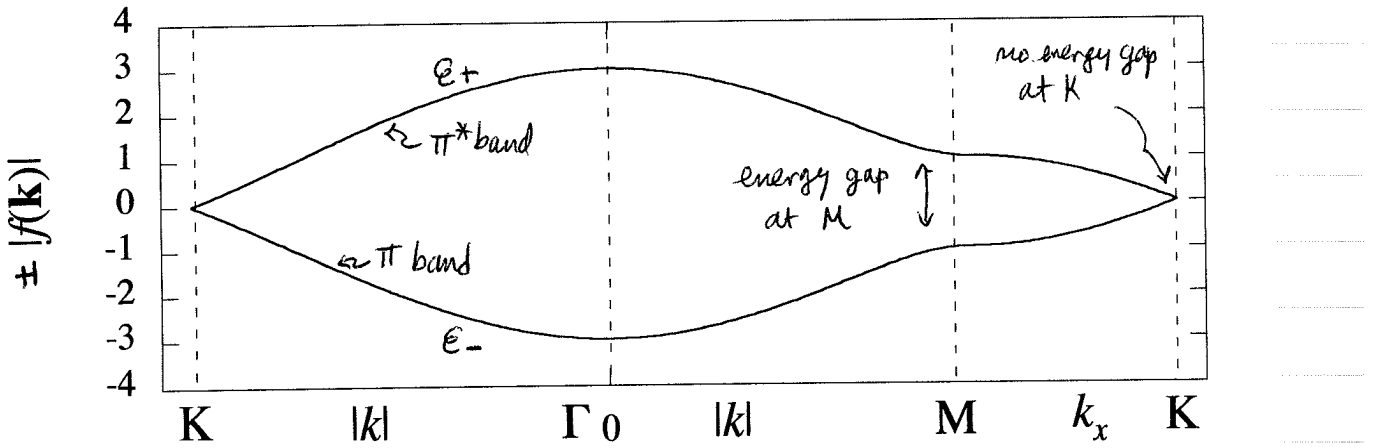
$$|f(\vec{k}_M)| = 1, \qquad |f(\vec{k}_K)| = 2\cos\frac{\pi}{3} - 1 = 0$$

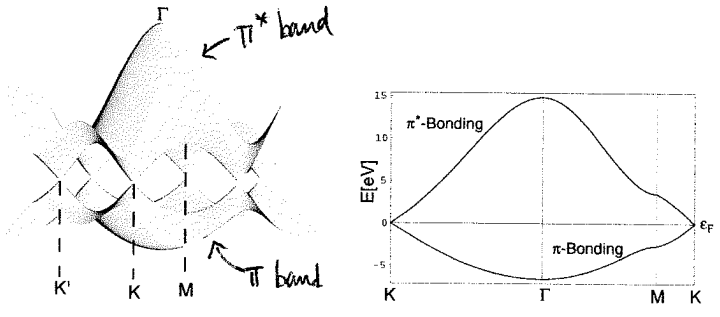
So there is an energy gap

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

along the BZ edge from M to K that 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)

Eigenvectors coefficients b_A, b_B determined by

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

Now $\varepsilon_\pm = E - \beta \pm |\gamma||f|$ so above is

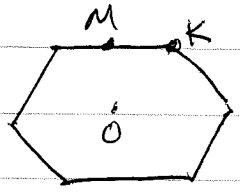
$$\begin{pmatrix} \pm|\gamma||f| & \gamma f \\ \gamma f^* & \pm|\gamma||f| \end{pmatrix}\begin{pmatrix} b_A \\ b_B \end{pmatrix} = 0$$

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 ad 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

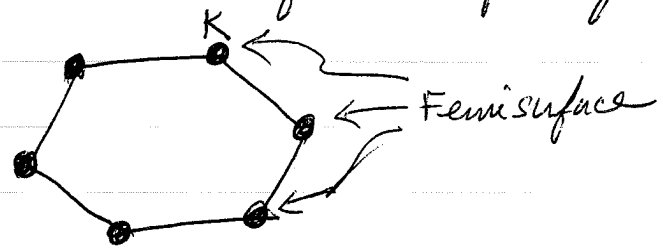
(recall, 6 electrons per atom go into the $3sp^2$ σ-bands so the remaining 2 electrons per atom now fill the π-band)

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)

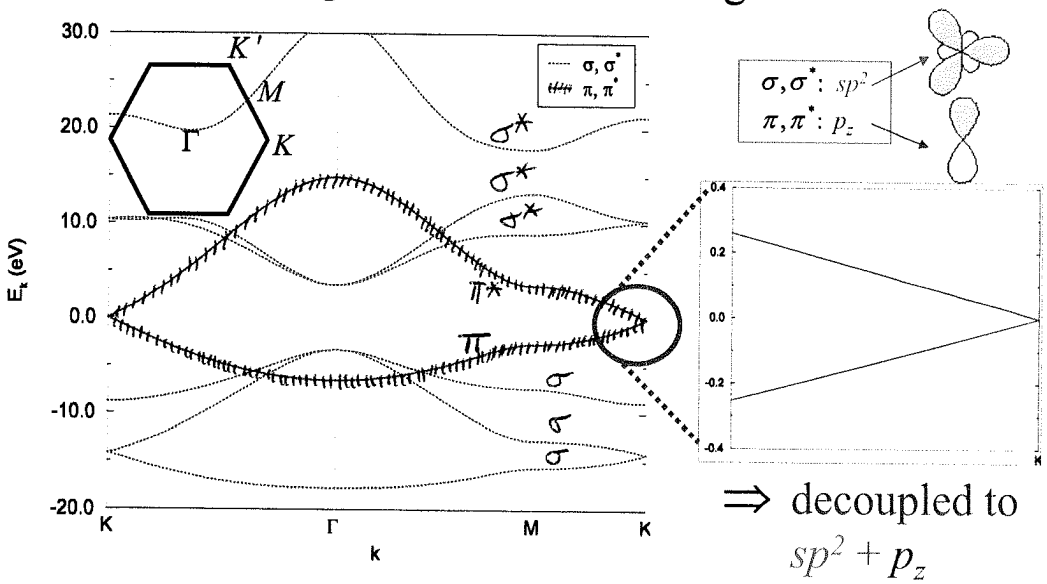
1) near $\vec{k}=0$, constant energy surfaces are circles
2) near $\vec{k}_K$, constant energy surfaces are circles centered on $\vec{k}_K$
3) near $\vec{k}_K$, $\varepsilon_\pm(\vec{k}) \sim |\vec{k}-\vec{k}_K|$ linear in k
4) density of states $g(\varepsilon)$ vanishes at ε_F

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

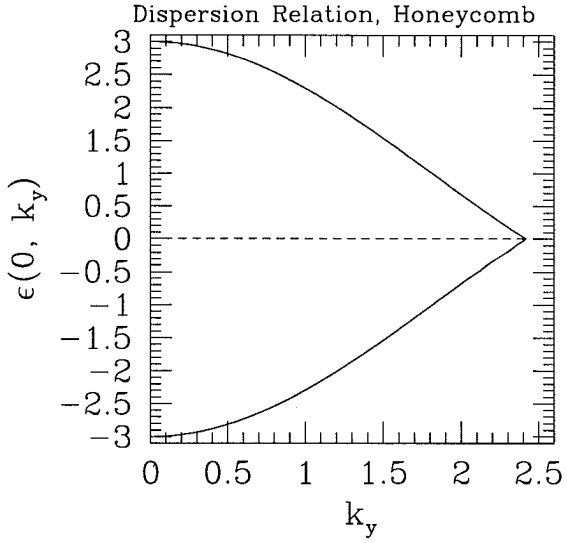
- Tight-binding model with nonorthogonal orbitals

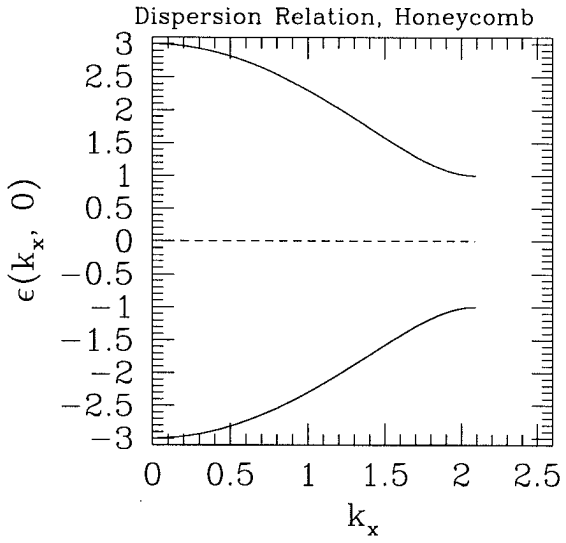


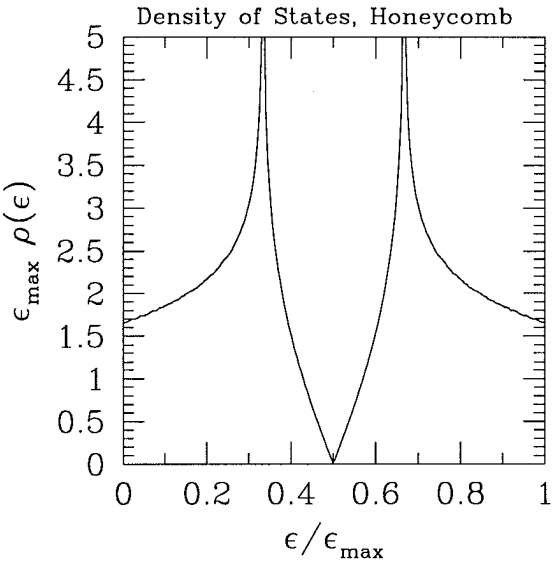
$\Rightarrow$ decoupled to $sp^2 + p_z$

(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.







Why tight binding works

In tight binding one approximates the Block wavefunction as

$$\psi_k = \sum_R e^{i\vec{k}\cdot\vec{R}} \left(\sum_n b_n \varphi_n(\vec{r}-\vec{R}) \right)$$

↑ atomic orbitals

One can show (see A+M chpt 10 pgs 187-188) that the exact Block eigenstate can always be written in the form

$$\psi_k(\vec{r}) = \sum_R e^{i\vec{k}\cdot\vec{R}} \phi(\vec{r}-\vec{R})$$

for some suitable function $\phi(\vec{r})$. This $\phi(\vec{r})$ is called the Wannier function

The tight binding approximation is then built on the assumption that the Wannier function $\phi(\vec{r})$ can be well approximated by a linear combination of atomic orbitals.

In principle the complete set of eigenfunctions of the atomic Hamiltonian H_{at} form a complete basis set of functions such that any function (and so in particular the Wannier function) can be written as a linear combination of these atomic eigenfunctions. But for this to be a complete basis we need to include the continuum of ionized atomic eigenstates as well as the

discrete bound atomic orbitals $\varphi_n(\vec{r})$.

The tight binding approximation thus consists of neglecting the ionized atomic eigenstates when trying to expand the Wannier function $\phi(\vec{r})$. It works well when $\phi(\vec{r})$ is well localized i.e. when $\phi(\vec{r})$ decays quickly to zero as $|\vec{r}| \to \infty$.