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 $\min_k \varepsilon_+(\vec{k}) \geqslant \max_k \varepsilon_-(\vec{k})$

$$|f(\vec{k})| = \left[1 + 4\cos^2\left(\frac{k_x a}{2}\right) + 4\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{\sqrt{3}}{2} k_y a\right) \right]^{1/2}$$
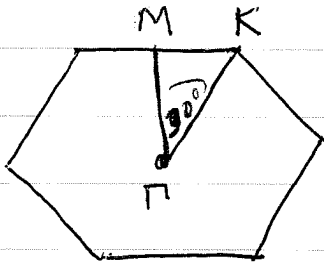
$|f(\vec{k})|$ is largest when $k_x = k_y = 0$

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

$\varepsilon_-(\vec{k})$ 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

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

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

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

So $k_x = \frac{k}{2} = k\cos 60°$
$$k_y = \frac{\sqrt{3}}{2}k = k\sin 60° \text{ with } k \in \left(0, \frac{4\pi}{3a}\right)$$

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

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

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

$$= 2\cos\left(\frac{ka}{2}\right) - 1$$
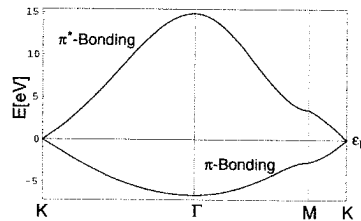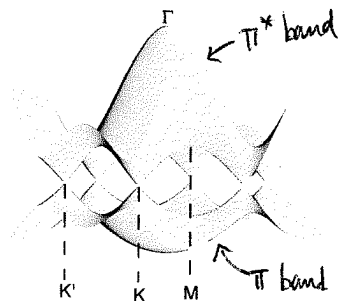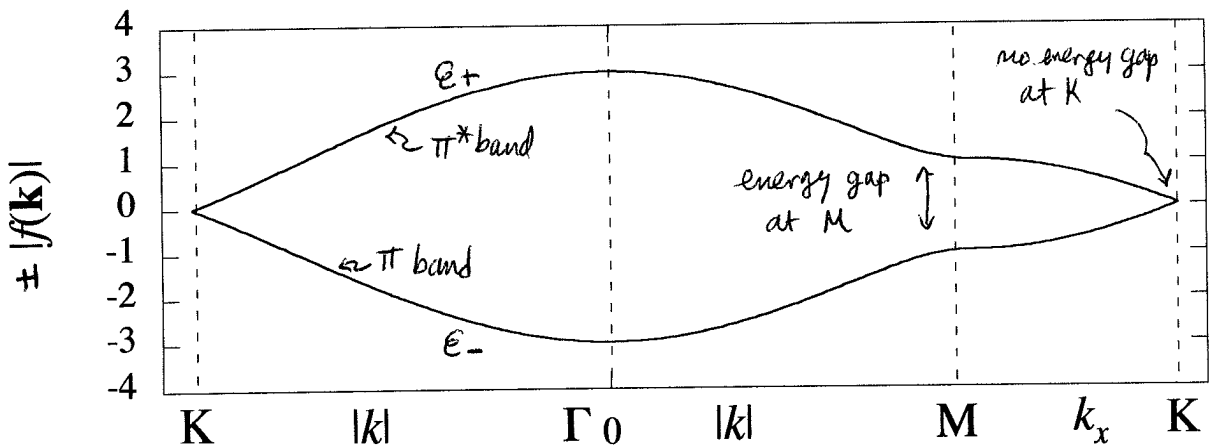
From above we have:

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

So there is an energy gap

$$\Delta\varepsilon = \varepsilon_+ - \varepsilon_- = 2\gamma|f(\vec{k})| = 2\gamma\left[2\cos\frac{ka}{2} - 1\right]$$
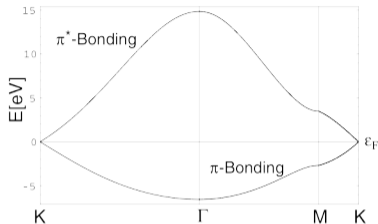
along the BZ edge from M to K that __vanishes at K__.

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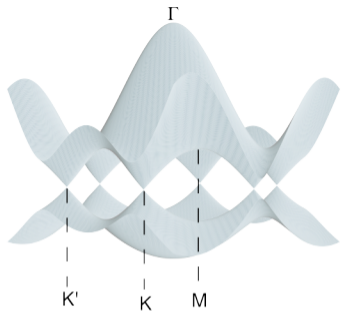
Figure 2.4: (a) shows the dispersion relation for graphene, called the tent dispersion. The points Γ, K, K' and M is high symmetry points and their placement in the Brillouin zone can be seen in Figure 2.3. (b) is appeared by cutting (a) in straight lines between the points $K \to \Gamma \to M \to K$.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

<u>Eigenvectors</u> coefficients b_A, b_B determined by

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

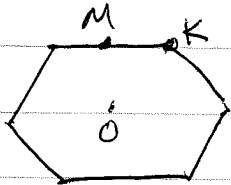Now $\varepsilon_\pm = E - \beta \pm |\gamma||f|$ so above is

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

Let $f = |f| e^{i\theta}$ then above is
$\gamma > 0$ real

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

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

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

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

So along MK, $b_B = \mp b_A$

$\implies$ 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

$$\epsilon_F = E - \beta$$

and the Fermi surface is the set of 6 discrete points
K that are the vertices of the surface of the
1st BZ
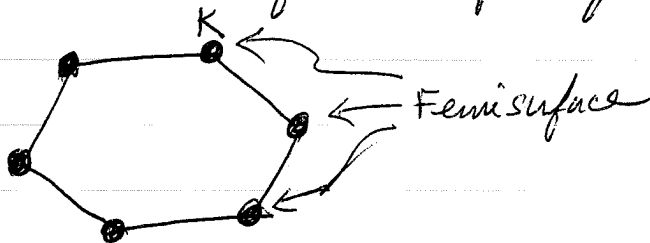
One can also show (you will do it for HW)

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 $\vec{k}_K$, $\epsilon_\pm(\vec{k}) \sim |\vec{k} - \vec{k}_K|$ linear in k
4) density of states $g(\epsilon)$ 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 $g(\epsilon_F) = 0$, there are not so many electrons easily
excited to conduction band. ~~Because there is an energy gap~~

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

$\Rightarrow$ decoupled to
$sp^2 + p_z$
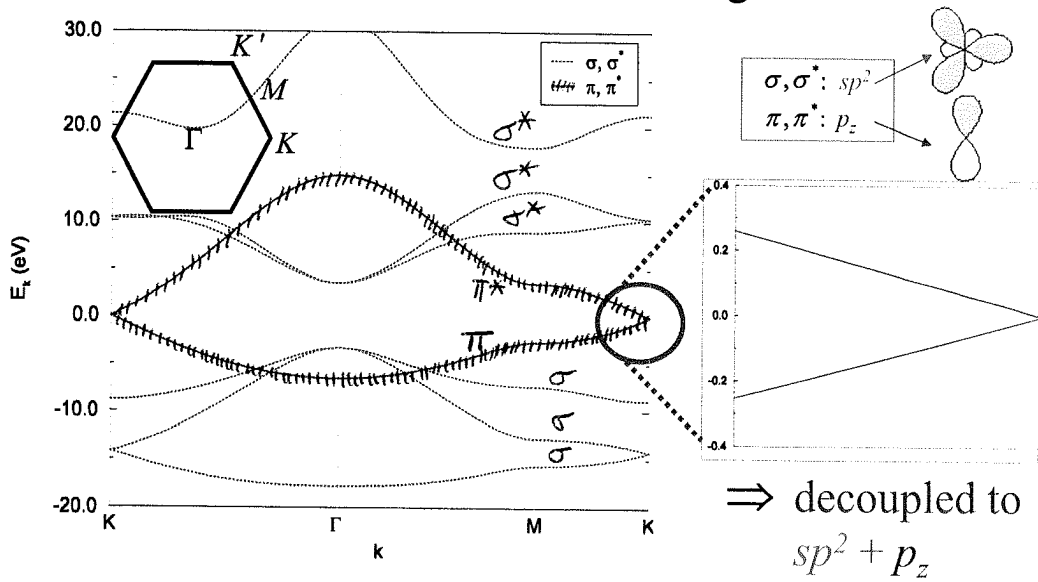
(from online talk by Hongki Min)

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.

Dispersion Relation, Honeycomb

Dispersion Relation, Honeycomb

Density of States, Honeycomb
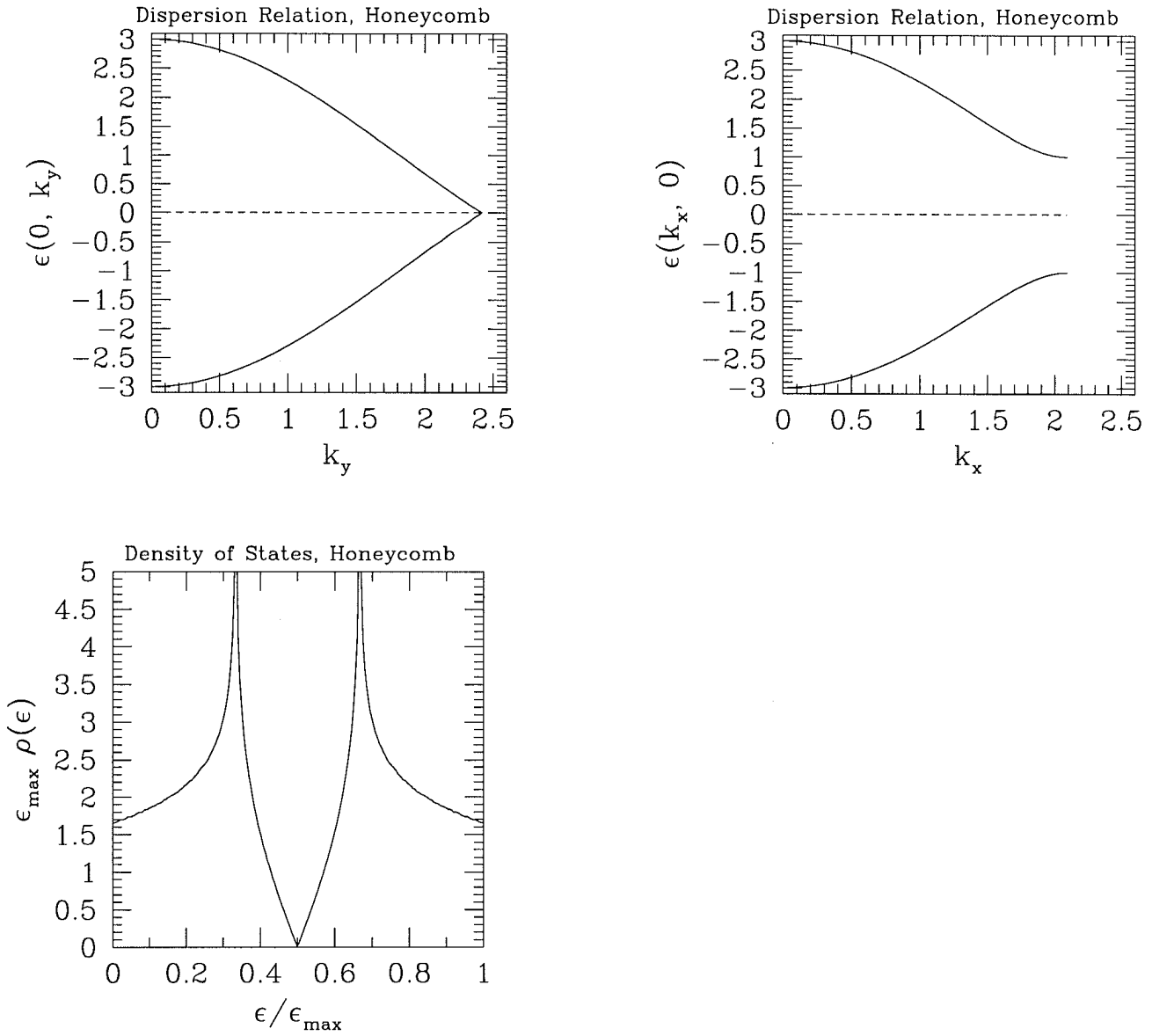
Why tight binding works

In tight binding one approximates the Bloch wavefunction as

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

$\underset{\text{atomic orbitals}}{\smile}$

One can show (see A+M chpt 10 pgs 187-188) that the exact Bloch 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 Hat form a complete basis set of functions in terms 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 then 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 $|\vec{r}| \to \infty$.

Spin - orbit interaction

We have seen in both the weak potential approx and the tight binding approx, that there may remain degeneracies in the band structure at certain points of high symmetry (for example in prob 3 of HW 4)

$S_K = 0$, no gap
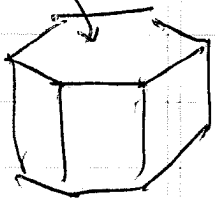
1st BZ
hcp

An example would be the absence of the expected energy gap at the top and bottom faces of the 1st BZ for hcp crystals, due to the vanishing of the geometric structure factor S_K on these faces

In such case, in the heavier elements, the degeneracy may be lifted (ie an energy gap appear) due to the effects of the spin - orbit interaction.

In principle there is always an interaction between the intrinsic electron ~~spin with interaction~~ magnetic moment $\vec{\mu}$ ~~and~~ (due to intrinsic spin) and its motion in the electric field of the ions

$$\delta H_{SO} \approx g \vec{\mu} \cdot (\underbrace{\vec{v} \times \vec{E}})$$

$\vec{B}$ in local rest frame of electron

$\vec{E}$ is from ionic potential

If one includes δH_{SO} in the single electron Hamiltonian, one can no longer ignore the coupling between electron spin state and real space wave function (as we have been doing) One needs to consider linear combinations of both different spatial orbitals and spin states, thus doubling the number of functions used in the tight binding expansion for ψ_k.

When one includes δH_{SO} one finds that symmetry induced band degeneracies can be lifted.

This effect is most noticeable in heavier elements where the ionic electric field $\vec{E}$ is stronger