Bud 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 \( R \) of the underlying triangular lattice,
B sites sit at sites \( R + \vec{d} \)

Primitive vectors of the BL
\[
\begin{align*}
\vec{a}_1 &= a \hat{x} \\
\vec{a}_2 &= \frac{a}{2} \hat{x} + \frac{\sqrt{3}}{2} a \hat{y}
\end{align*}
\]

Basis vectors
\[
\begin{align*}
\vec{d} &= \frac{1}{3} (\vec{a}_2 + (\vec{a}_2 - \vec{a}_1)) \\
&= \frac{a}{\sqrt{3}} \hat{y}
\end{align*}
\]

Primitive vectors of BL
\[
\begin{align*}
\vec{b}_1 &= \frac{2\pi}{a} \hat{x} - \frac{2\pi}{\sqrt{3}} a \hat{y} \\
\vec{b}_2 &= \frac{4\pi}{\sqrt{3}} a \hat{y}
\end{align*}
\]

Nearest neighbors of A site are displaced from A by vectors
\[
\vec{d}, \quad \vec{d}' = (\vec{a}_1 - \vec{a}_2) + \vec{d} = \frac{a}{2} \hat{x} - \frac{a}{2\sqrt{3}} \hat{y}, \quad \vec{d}'' = -\vec{a}_2 + \vec{d} = \frac{a}{2} \hat{x} - \frac{a}{2\sqrt{3}} \hat{y}
\]
Atomic Carbon has electron structure

\[ 1s^2 \quad 2s^2 \quad 2p^2 \quad 6 \text{ electrons} \]

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 atom and do not participate in bonding or conduction. We thus forget about them!

The 2s\(^2\) and 2p\(^\pm\) 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:

\[ 2s \quad 2p_x \quad 2p_y \quad 2p_z \]

2s is spherically symmetric
2p has lobes oriented along \( x, y, \) and \( z \) axes

Honeycomb structure we take to be in the \( xy \) plane.
If one does a tight binding calculation of the band structure from the 1s, 2s, 2p, 3s, 3p, 3d orbitals, one should mix in all 2s, 2p, 2p, 2p 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 wave function is a mixture of 8 terms:

\[ \Psi_k = \sum b_{\alpha} \phi_\alpha e^{-i\mathbf{k} \cdot \mathbf{R}} \]

where \( b_{\alpha} \phi_\alpha \) are the 5, 6, 7, 8 atomic orbitals and \( \phi_\alpha \) are the 2s, 2p, 2p, 2p orbitals centered at sites "A", and \( \phi_\beta \) are the 2s, 2p, 2p, 2p orbitals centered at sites "B".

For each value \( \mathbf{k} \) in 1st BZ one then get eight energies \( E_n(k) \), ie 8 bands.

**Digression:** For C in a 3D diamond structure (fcc with 2-point basis) one finds that the s, p, p, and p orbitals all mix together roughly equally - this is called "sp³" hybridization since one s mixes with three p orbitals. The 8 bands separate into two distinct groups: the lowest four bands are called "O-bonding" bands. Here the
Wave functions 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 6 bonding bands. The Bloch electron wave functions where the electron density is concentrated are the nearest neighbor bonds of the diamond structure. These are the covalent bonds that hold the diamond structure together. The lower four bands are called "$\sigma^*$ antibonding" bands. Here the A and B site wave functions add roughly antisymmetrically so that the electron probability vanishes midway between A and B. The $\sigma^*$ antibonding bands lie higher in energy than the $\sigma$ bonding bands and do not overlap them. In the ground state, each of the two ions in a primitive cell of the BZ give 4 electrons for a total of 8 electrons per BZ cell. These 8 electrons fill up the 4 $\sigma$ bonding bands (each band can hold 2 electrons per ion - since each $\mathbf{k}$ can have spin $\uparrow$ and $\downarrow$).

Hence the 4 $\sigma$ bonding bands are completely filled and the 4 $\sigma^*$ antibonding bands are completely empty. There is a finite energy gap between the $\sigma$ and $\sigma^*$ bands. 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 $\sigma$ 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 2s 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 2s 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 arrayed 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 orbitals 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 $s$, $p_x$, 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 "$sp^2"$ hybridization as one $s$ mixes with two $p$ orbitals.

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

The $\sigma$-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 $\sigma$-bonding bands have the lowest energy and all lie below the Fermi energy. In the ground state, they are completely filled, taking 6 of the 8 electrons per $B2\bar{1}$ cell. Since these bands are filled, they play no role in electric conduction in graphene.
The $\sigma^*$-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 $\sigma^*$ bands and the Fermi energy.)

All the interesting effects concerning conduction therefore lie with the $\pi$ and $\pi^*$ bands. These lie essentially between the $\sigma$ and $\sigma^*$ bands (though actually the $\sigma$ band near its max overlaps some with the min of the $\pi$ band, and the max of the $\pi^*$ band overlaps somewhat with the min of the $\sigma^*$ 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 $\pi$ and $\pi^*$ bands do not overlap. Therefore in the ground state, with 8 electrons per B1 cell, 6 electrons go to completely fill the 3 $\sigma$ bands, and 2 electrons go to completely fill the $\pi$ band. The $\pi^*$ and $\sigma^*$ bands are completely empty. This would be an insulator. Except we will see that the $\pi$ and $\pi^*$ 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 $\Pi$ and $\Pi^*$ bands.

Let
\[
\begin{align*}
\varphi_A(\mathbf{r}) &= \varphi(\mathbf{r}) & \text{$p_z$ orbital centered at origin (site A)} \\
\varphi_B(\mathbf{r}) &= \varphi(\mathbf{r}-\mathbf{d}) & \text{$p_z$ orbital centered at position $\mathbf{d}$ (site B)}
\end{align*}
\]

Our assumed Bloch wave function then has the form:
\[
\psi_k(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \left\{ b_A \varphi_A(\mathbf{R}+\mathbf{r}) + b_B \varphi_B(\mathbf{R}+\mathbf{r}) \right\}
\]

Consider $\mathbf{k} \in 1^{st} BZ$.

\[
\begin{align*}
\langle \varphi_A | H | \psi_k \rangle &= \langle \varphi_A | [H_{\text{at}} + U] | \psi_k \rangle \\
\varepsilon_k \langle \varphi_A | \psi_k \rangle &= E \langle \varphi_A | \psi_k \rangle + \langle \varphi_A | U | \psi_k \rangle
\end{align*}
\]

Energy of atomic $p_z$ orbital

\[
\begin{align*}
\langle \varphi_A | \psi_k \rangle &= \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \left\{ b_A \langle \varphi_A(\mathbf{r}) | \varphi_A(\mathbf{r}-\mathbf{d}) \rangle + b_B \langle \varphi_A(\mathbf{r}) | \varphi_B(\mathbf{r}-\mathbf{d}) \rangle \right\} \\
&= \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \left\{ b_A \int d^3r \ \varphi^*(\mathbf{r}) \varphi(\mathbf{r}-\mathbf{d}) \\
&\quad + b_B \int d^3r \ \varphi^*(\mathbf{r}) \varphi(\mathbf{r}-\mathbf{d}-\mathbf{d}) \right\}
\end{align*}
\]
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 \( \vec{R} = \vec{d} \), \( \vec{R} = \vec{d} + \vec{d}' \), \( \vec{R} = \vec{d} + \vec{d}' + \vec{d}'' \), the vectors to the nearest neighbors i.e. \( \vec{R} = 0 \), \( \vec{R} = \vec{a}_1 - \vec{a}_2 \), and \( \vec{R} = -\vec{a}_2 \).

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

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

where the overlap integrals are all equal since \( \varphi \)
has rotational symmetry about the \( \vec{a}_2 \) axis and \( |\vec{d}'| = |\vec{d}| = |\vec{d}''| \).

The term in \( [\ldots] \) is just \( \sum_R e^{i \vec{k} \cdot \vec{R}} \) over the set of \( \vec{R} = \{0, \vec{a}_1 - \vec{a}_2, -\vec{a}_2 \} \) that give the nearest neighbors \( \vec{d}, \vec{d}', \vec{d}'' \). The overlap integral is a common factor for all three terms.
Define \( \alpha = \int d^3r \ \varphi^*(\vec{r}) \varphi(\vec{r} - \vec{d}) \)

then \( \langle \varphi_A | \varphi_k \rangle = b_A + b_B \alpha \left[ 1 + e^{i\vec{k} \cdot \vec{a}_1} e^{-i\vec{k} \cdot \vec{a}_2} + e^{i\vec{k} \cdot \vec{a}_2} e^{-i\vec{k} \cdot \vec{a}_1} \right] \)

\[ = b_A + b_B \alpha \left[ 1 + e^{-i\vec{k} \cdot \vec{a}_2} e^{i\vec{k} \cdot \vec{a}_1} \left( e^{i\vec{k} \cdot \vec{a}_1} - e^{i\vec{k} \cdot \vec{a}_2} \right) \right] \]

\[ = b_A + b_B \alpha \left[ 1 + e^{i\vec{k} \cdot (\vec{a}_1 - \vec{a}_2)} 2 \cos(\vec{k} \cdot \vec{a}_1/2) \right] \]

Use \( \vec{a}_1 = \alpha \vec{x}_1 \), \( \vec{a}_2 = \frac{\alpha}{\sqrt{2}} \vec{x}_1 + \frac{\sqrt{2}}{\sqrt{2}} \vec{y} \)

\[ \langle \varphi_A | \varphi_k \rangle = b_A + b_B \alpha \left[ 1 + e^{-i \frac{\sqrt{2}}{\sqrt{2}} k \vec{y} \cdot \alpha} 2 \cos(k \alpha/2) \right] \]

Similarly,

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

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.

\[ \int d^3r \ \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r} - \vec{d}) = \int d^3r \ \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r} - \vec{d} - \vec{d}) \]

\[ = \int d^3r \ \varphi^*(\vec{r}) \Delta U(\vec{r}) \varphi(\vec{r} - \vec{d}'') \]

because \( \varphi(\vec{r}) \) has rotational symmetry about \( \vec{z} \) axis

and because \( \Delta U(\vec{r}) \) has rotation by \( 120^\circ \) symmetry about \( \vec{y} \) axis (maps \( \vec{d} \rightarrow \vec{d}' \rightarrow \vec{d}'' \rightarrow \vec{d} \))
Define \( \beta = -\int d^3r \varphi^*(\vec{r}) \Delta \varphi(\vec{r}) \varphi(\vec{r}) \)

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

Then

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

where \([---]\) is the same factor from \( \sum \frac{e^{i\vec{k} \cdot \vec{r}}}{\vec{r}} \) that we had in \( \langle \varphi_A \mid \psi_k \rangle \).

Define \( f(\vec{r}) = 1 + e^{-\frac{i\sqrt{3}kya}{2}} \cos \left( \frac{k_x a}{2} \right) \)

Our equation \( E_k \langle \varphi_A \mid \psi_k \rangle = E \langle \varphi_A \mid \psi_k \rangle + \langle \varphi_A \mid \Delta \varphi \mid \psi_k \rangle \)

can now be written as:

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

or

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

(1)

We also need to consider \( \langle \varphi_B \mid \Delta \varphi \mid \psi_k \rangle \)

\( \Rightarrow E_k \langle \varphi_B \mid \psi_k \rangle = E \langle \varphi_B \mid \psi_k \rangle + \langle \varphi_B \mid \Delta \varphi \mid \psi_k \rangle \)

Repeating all the above steps, one arrives at:

\[
(E_k - E + \beta) b_B + \left[ (E_k - E) \alpha + \gamma \right] f^*(\vec{r}) b_A = 0.
\]

(2)

Note \( \alpha, \beta, \gamma \) are real because for the \( p^2/2m \) orbitals \( \varphi^* = \varphi \) is real,

\( f^* \) is complex conjugate of \( f \),

\[
E_k = E + \langle \varphi_k \mid \Delta \varphi \mid \varphi_k \rangle
\]
Eqs. (1) and (2) combine to give a set of two homogeneous linear equations in two unknowns \( b_A \) and \( b_B \). We can write them as:

\[
\mathbf{M} \begin{pmatrix} b_A \\ b_B \end{pmatrix} = 0
\]

Where \( \mathbf{M} \) is the 2x2 matrix

\[
\mathbf{M} = \begin{bmatrix}
\varepsilon_k - \varepsilon + \beta & \left[ (\varepsilon_k - \varepsilon) \alpha + \gamma \right] f(\mathbf{r}) \\
\left[ (\varepsilon_k - \varepsilon) \alpha + \gamma \right] f^*(\mathbf{r}) & \varepsilon_k - \varepsilon + \beta
\end{bmatrix}
\]

There is a non-trivial solution for \( b_A \), \( b_B \) only when \( \det \mathbf{M} = 0 \). This condition gives a quadratic equation to solve for the two possible values of \( \varepsilon(\mathbf{r}) \). Call these values \( \varepsilon_+(\mathbf{r}) \) and \( \varepsilon_-(\mathbf{r}) \). For each \( \mathbf{r} \) there are two solutions:

- \( \varepsilon_-(\mathbf{r}) \) is the \( \Gamma \) band,
- \( \varepsilon_+(\mathbf{r}) \) is the \( \Gamma^* \) band.

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

Note:

\[
\begin{cases}
\alpha = \int d^3r \ \phi^*(r) \varphi(\mathbf{r}-\mathbf{d}) \\
\gamma = -\int d^3r \ \phi^*(r) \ \Delta \varphi(\mathbf{r}) \varphi(\mathbf{r}-\mathbf{d})
\end{cases}
\]

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