We know we have to use Schrödinger eqn. with \( \{ \mathbf{r}_1, \ldots, \mathbf{r}_N \} \) lattice sites. Let's ignore spin.

\[
\hat{H} \phi_n (\mathbf{r}_1, \ldots, \mathbf{r}_N) = E_n \phi_n (\mathbf{r}_1, \ldots, \mathbf{r}_N)
\]

\[
H = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{j \neq i}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right) + \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{(|\mathbf{r}_i - \mathbf{r}_j|)}
\]

But often:

\[
H = \sum_{i=1}^{N} H_i = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 + \sigma_{\text{eff}} (\mathbf{r}_i) \right)
\]

I effective potential represents interaction on of the electrons will all other e-.

1. We can start with \( \sigma_{\text{eff}} = \text{const} \Rightarrow \text{zero approx.} \)

then the single particles are plane waves:

\[
\psi_k (\mathbf{r}) = \sqrt{\frac{1}{N}} e^{i \mathbf{k} \cdot \mathbf{r}} \quad \text{with} \quad \epsilon_k = \frac{\hbar^2 \mathbf{k}^2}{2m}
\]

and are eigenstates for velocity:

\[
\frac{\hbar}{i} \frac{\partial}{\partial t} \psi_k (\mathbf{r}) = \frac{\hbar}{i} [H, \psi_k] = \frac{\hbar}{2m} \left[ \mathbf{p} \cdot \mathbf{r}, \psi_k \right] = \frac{\hbar}{m} \mathbf{p} (-i \hbar \frac{\partial}{\partial \mathbf{r}}) = \frac{\mathbf{p}}{m c} = -i \hbar \nabla
\]

with eigenvalue \( \frac{\hbar k}{m} \).

By velocity is a constant of motion the electrical
resistance = 0 and current doesn't decay in this model.

Next approx: \( V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}_i) \)

**Bloch's Theorem**

is very important to describe the motion of independent electrons in a periodic potential.

Recall from x-ray \( \Delta \mathbf{k} = \mathbf{G} \equiv \text{Bragg scattering} \)
we cannot apply Born approx. to e\(^-\) scattering
b/c ionic core potentials are very strong:

For a single particle in the periodic potential:
\[
\hat{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \quad , \quad V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}_i)
\]

if we have atomic potentials:
\[
V(\mathbf{r}) = \sum_{j} V(\mathbf{r} - \mathbf{R}_j) \quad , \quad \text{b/c of chemical bonding they are not atomic potentials.}
\]

\( \Psi \) e\(^-\) inside a solid?

**Symmetry Consideration:**

Let's start with \( V(\mathbf{r}) = \text{Const} \Rightarrow \hat{H} \) is translation...
invariant \[ [\hat{H}, \hat{T}_c] = 0 \] for any vector \( \mathbf{e} \)

The lattice translation satisfy \([\hat{T}_c, \hat{T}_c] = 0 \)
and with \([\hat{H}, \hat{T}_c] = 0 \), i.e.

\[
\hat{T}_c \hat{H}(r) \psi(r) = \hat{H}(r + \mathbf{R}_c) \psi(r + \mathbf{R}_c) = \hat{H}(r) \hat{T}_c \psi(r) \Rightarrow \\
\Rightarrow [\hat{H}, \hat{T}_c] = 0
\]

This also imply that \( \hat{T}_c \) and \( \hat{H} \) share the same eigenstates:

\[
\hat{H} \psi(r) = \epsilon \psi(r) \\
\hat{T}_c \psi(r) = C(\mathbf{R}_c) \psi(r)
\]

Since charge density is periodic

\[
|\psi(r)|^2 = |\hat{T}_c \psi(r)|^2 = C(\mathbf{R}_c)^2 |\psi(r)|^2 \\
\Rightarrow C(\mathbf{R}_c)^2 = 1 \Rightarrow C(\mathbf{R}_c) = e^{i\kappa \cdot \mathbf{R}_c}
\]

\( \kappa \) is \( \mathbf{R}_c \cdot \mathbf{R}_c \)

Thus:

\[
\hat{T}_c \psi(r) = \psi(r + \mathbf{R}_c) = e^{i\kappa \cdot \mathbf{R}_c} \psi(r)
\]

This equation expresses the Bloch theorem.

The phase accumulated by the w.f after translation by \( \mathbf{R}_c \) is just \( \mathbf{R}_c \cdot \mathbf{R}_c \)!
However, from \( T_e \psi(r) = \psi(r + R_e) \) we can conclude \( T_e \cdot T_e' \psi(r) = \psi(r + R_e + R_{e'}) = T_{e + e'} \psi \). Hence for this case \( (R_{e + e'}) = e \).

\[ \text{What if } K \text{ is imaginary } \Rightarrow \]

Charge density \( \sim |\psi(r)|^2 \) would exponentially increase, while moving from site to site or decrease.

But this is not possible b/c of the translational invariance.

In other words: if translational invar. is broken (defects) \( K \) complex is allowed, which represent the localized wave-function otherwise in a perfect crystal \( K \) is real.

In practice, this means we need to determine the w.f. behaviour only inside the primitive u.c.

\[
\begin{align*}
\left. -i\left( r + R_e \right) \right| e^{-iK_eR_e} \psi(r + R_e) &= e^{iK_eR_e} \psi(r) \Rightarrow \\
\left. -i\left( r + R_e \right) \right| e^{-iK_eR_e} \psi(r + R_e) &= e^{iK_eR_e} \psi(r) = U_{K_e} \psi(r) \\
\text{with } U_{K_e} \psi(r) &= U_{K_e} \psi(r + R_e) \\
\text{Hence the w.f. of an } e^- \text{ inside xtal is } &
\end{align*}
\]
\[ \psi_k(r) = U_k(r) e^{i k \cdot r} \]

where \( U_k(r) = \psi_k(r + r_0) \)

It states that it's just plane wave with periodically modulated amplitude \( U_k(r) \).

For computations, we started with

\[
\begin{align*}
\text{i} k r \\
\int U_k(r) \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{\hbar^2}{2m} k_0 \nabla + \frac{\hbar^2 k^2}{2m} \right) U_k(r) + \frac{V(r)}{\hbar^2} U_k(r) &= E U_k(r) \\
V(r) U_k(r) &= E U_k(r)
\end{align*}
\]

to be solved inside a p.u. cell, independent on the # of unit cells, with the periodic boundary condition \( \psi(r) = \psi(r + \text{ne}) \).

Reminder: Recall we discussed that \( k \) is not conserved but \( \hbar k \) is conserved quantity.

Note: \( \hbar k \) is not electron momentum, but we can move a wave packet out of s.waves, and their group velocity is: \( \overrightarrow{V_k} = \frac{i}{\hbar} \nabla_k \in \mathbb{C}^2 \)

This packet travels coherently throughout the cell, and M.F. \( \rightarrow \infty \). But in Drake, m.f.p. is very short.

Let's restrict ourselves to \( kBZ \), \( \Rightarrow \)

\[ \psi_k(r) = \sum_G b_G(k) e^{i (k + G + G')} \]

\[ = \sum_{\alpha+\epsilon} c_{\alpha+\epsilon}(k) \]
We can always use \( G' \) which bring \( k' = k + e' \) back to \( BZ = \)

\[
\psi_{nk'}(r) = e^{i\vec{k}' \cdot \vec{r}} \psi_{nk}(r)
\]

when \( k' \in \text{BZ} \)

\( n \equiv \) Band index to make up for this restriction

This is similar to Hydrogen atom

\[ \psi_{n} \text{ (rotational symmetry)} \]

Solid

\[ k, \text{ symmetry} \]

\[ \uparrow \text{ Lattice translation} \]

EMPTY LATTICE MODEL

In 1D with Lattice constant \( a \) \( V(r) = 0 \Rightarrow \)

\[
\psi_{k}(x) = e^{ikx} \quad \text{and} \quad \varepsilon_{k} = \frac{\hbar^{2} k^{2}}{2m}
\]

Extended zone scheme

But we can map all wave vectors back to \( BZ \) by shifting them by \( G = \frac{2\pi}{a} \)

Reduced zone scheme
The band energies are:

\[
\begin{align*}
\epsilon_{0,k} &= \frac{\hbar^2}{2m} k^2 \\
\epsilon_{1,k} &= \frac{\hbar^2}{2m} \left( k - \frac{a}{6} \right) \left( k - \frac{a}{6} \right) \frac{2\Gamma}{a} = E_1 \\
\epsilon_{n,k} &= \frac{\hbar^2}{2m} \left( k - n \frac{a}{6} \right)^2
\end{align*}
\]

- Looks like phonons but no ending for \( n \).
- Also there is band degeneracy at \( k = 0 \) but for phonons if mass is different or springs are diff. this degeneracy removed. What about for electrons? in periodic potential?

From B. theorem, the S. equ:

\[
V \frac{\hbar^2}{2m} \begin{pmatrix} u_n k \end{pmatrix} = \epsilon_{u_k} \begin{pmatrix} u_n k \end{pmatrix}, \quad U_{u_k}(r) = U_{u_k}(r+K)
\]

\[
\begin{align*}
\begin{pmatrix} u_n k \end{pmatrix} &= \begin{pmatrix} (p + h\pi)^2 \end{pmatrix} + V(r) = V(r + K) \\
\end{align*}
\]

Because of the periodicity we need to solve the eqn. only for 1st \( \mathbb{Z} \).

\( \Rightarrow \) Think of a particle in a box now!

**e.g.** 1D empty lattice: \( \Sigma = 0 \)

\[
\frac{\hbar^2}{2m} (p + h\pi)^2 \begin{pmatrix} u_n k \end{pmatrix} = \epsilon_{u_k} \begin{pmatrix} u_n k \end{pmatrix}
\]

With the bound Cond:

\[
U_{u_k}(r - \frac{a}{2}) = U_{u_k}(r + \frac{a}{2})
\]
We can choose:
\[ \Psi_{n=0} \quad \Psi_{n=1} \]

From periodic b.c.,
\[ U_{n=0} (x) = \frac{1}{\sqrt{a}} e^{-i \pi n x} \quad U_{n=1} (x) = \frac{1}{\sqrt{a}} e^{-\frac{i \pi}{a} x} \]

From periodic b.c.

Now we turn on a weak potential \( V(r) \):
\[ V(x) = V_0 \cos \left( \frac{G_1 x}{a} \right) = \frac{V_0}{2} \left( e^{i \frac{G_1 x}{a}} + e^{-i \frac{G_1 x}{a}} \right) \]

\[ n = \text{lattice site} \]

This potential scatters electrons from \( \mathbf{k} \) to \( \mathbf{k} \pm \mathbf{G}_1 \).

At the zone boundary \( \mathbf{k}_ \pm = \pm \frac{1}{2} \mathbf{G}_1 \), the states \( \Psi_{k^+} \) and \( \Psi_{k^-} \) are degenerate but mixed by \( V(r) \).

Show this:
\[ \langle \Psi_{k^+} | V | \Psi_{k^-} \rangle \neq 0 \]

If you look at the reduced zone you see that:
\[ \Psi_{k^+} = \Psi_{n=0}, \quad k = + \frac{G_1}{2} \quad \Rightarrow \text{mixing happens at the same } k \]
\[ \Psi_{k^-} = \Psi_{n=1}, \quad k = + \frac{G_1}{2} \]

\( \text{For } n=2 \text{ it's too high in energy:} \quad \text{Band, } n=2 \text{ is diff.} \)

From degenerate part. theory, we need to diagonalize:
\[ \left( \begin{array}{cc}
0 & 1 + 10 \frac{G_1}{2} \\
1 \frac{G_1}{2} & 1 + 10 \frac{G_1}{2}
\end{array} \right)\]
\[ \left( \begin{array}{cc}
\Psi_{n=0} & \Psi_{n=1} \\
\Psi_{n=1} & \Psi_{n=1}
\end{array} \right) \]
\[ \Rightarrow \Psi_{n=0} \quad \Psi_{n=1} \]

\[ \text{at } k = \frac{G_1}{2} \]

\[ \left( \begin{array}{c}
0 \\
1 \frac{G_1}{2}
\end{array} \right) \quad \left( \begin{array}{c}
1 \frac{G_1}{2} \\
1 \frac{G_1}{2}
\end{array} \right) \]
the eigenstates are at $2B$

\[ E_{\pm} = \frac{\hbar^2}{8m} \frac{G_1}{2} \pm \frac{\nu_0}{2} \]

and at \( B = \left( \frac{G_1}{2} \frac{\pi}{a} \right) \)

\[ E_+ - \varepsilon_0 = \frac{\nu_0}{2} \]

Eigen-vectors \( \Psi_{\pm} = \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ \pm 1 \end{array} \right) \)

and the states are

\[ \Psi_{\pm} > = \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ \pm 1 \end{array} \right) \]

or

\[ \Psi_{\pm} > = \frac{1}{\sqrt{2}} e^{-iG_1x} \]

at $2B$

\[
\begin{align*}
\Psi_+ (x) &= \sqrt{\frac{2}{a}} \cos \frac{G_1x}{2} \\
\Psi_- (x) &= i \sqrt{\frac{2}{a}} \sin \frac{G_1x}{2}
\end{align*}
\]

at the zone boundary

STANDING WAVES

"anti-bonding"

$\Psi_+$ are at the peaks of $V_0 = \text{higher energy}$

$\Psi_-$ are in the valley of $V_0 = \text{lower energy}$

"bonding"
So at the B.Z. the degeneracy is lifted!

Let's examine it slightly away from \( \pm \pi a \)

E.g. \( k = \frac{1}{2} \Gamma_1 - \delta k \)

The unperturbed states are not degenerate but very close in energy:

\[
\Lambda = \begin{pmatrix}
\frac{t^2}{2n} \left( \psi_{\Gamma_1/2} - \delta k \right)^2 & \frac{U_0}{4} \\
\delta_0/2 & \frac{t^2}{2n} \left( \psi_{\Gamma_1/2} - \delta k \right)^2
\end{pmatrix}
\]

\( \Rightarrow \) degenerate and get dispersion near the B.Z.

The band gap has strong impact on transport, e.g. if the chemical potential is inside the gap \( \Rightarrow \) insulator and filled band called the VALENCE BANDS and non-filled ones CONDUCTION BANDS.
Band gap & Bragg reflections

in 1D: scattering between 2 degenerate states by $V(r)$ opens a gap.

Consider a general case:

$$V(r) = \sum_{\mathbf{l} \in \mathbf{l}} V_{\mathbf{l}} \cdot e^{-i \mathbf{G} \cdot \mathbf{r}}$$

This potential scatters states from $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{G}$.

These 2 unperturbed states are degenerate:

$$\frac{\hbar^2}{2m_e} |k|^2 = \frac{\hbar^2}{2m} |k + \mathbf{G}|^2$$

Consider now the Ewald construction:

Bragg plane a bisect of $\mathbf{G}$
Any point on this dashed line satisfies the Bragg condition.

Thus a contour map of \( E(k) \) in the extended picture looks like this.

\[ \text{Discontinuity at the } E_B = \text{Bragg plane} \]

is the origin of a gap.

In the degenerate perturbation theory

\[ \psi_k = a e^{i k r} + b e^{i k + \sigma} \]

The 2x2 matrix of the Sch. eqn:

\[
\begin{pmatrix}
    a \\
    b
\end{pmatrix}
= E
\begin{pmatrix}
    a \\
    b
\end{pmatrix}
\]

where

\[
\begin{pmatrix}
    E_k & U_k^* \\
    U_k & E_{k+\sigma}
\end{pmatrix} \Rightarrow \text{eigenvalues } E_{\pm} = E_0 \pm \sqrt{E_0^2 + |U_k|^2}
\]

\[ E_{\pm} = \frac{1}{2} \left( E_k + E_{k+\sigma} \right) \]

The gradient of energy eigenvalues:

\[ \nabla_k E_+ = \nabla_k E_+ \pm \left( \nabla_k E_- \right) \frac{E_-}{\sqrt{E_0^2 + |U_k|^2}} \]

but \( \nabla_k E_+ = \frac{k^2}{m} (k + \sigma G) \) and \( E_0 \rightarrow 0 \) at \( \frac{G}{\Sigma} \) (on the Bragg plane).
we obtain

\[ \nabla_k E_\pm = \frac{\hbar^2}{m} \left( k + \frac{1}{2} \vec{a} \right) \]

but this vector is \( \perp \) to the Bragg plane \( \Rightarrow \)

Thus constant energy lines must enter the zone boundary at the right angle,

\[ \theta = 90^\circ \]
How many $\epsilon^-$ takes to fill up a band?

\[ N_{\text{states}} = \int_{-\frac{G_{1/2}}{2 \pi}}^{G_{1/2}} \frac{1}{2 \pi} \, d\epsilon = \frac{1}{2 \pi} G_1 = \frac{L}{a} = N_{\text{cells}} \]

\[ N_{\text{states}} = \left( \frac{L}{2 \pi} \right) d \int_{\frac{2 \pi}{a}} d\epsilon = N_{\text{cells}} \]

\[ \Rightarrow \text{density of states is one per cell/band/spin} \]

Recall from phonons: # of phonons per polarization = $N_{\text{cells}}$

but the number of modes: dimensionality x atoms per u.c.

In Bravais lattice one atom/cell and taking into account spin: $2N_{\text{cells}}$ atoms to fill one band.

\[ \Rightarrow \text{prediction: even # of } \epsilon^- \Rightarrow \text{insulator} \]
\[ \text{odd # } \Rightarrow \text{metal} \]

\[ \text{e.g. Al, Cu: metals odd valence } \Rightarrow \text{metal} \]
\[ \text{Si, C: even } \Rightarrow \text{insulator} \]

But sometimes $n^\text{th}$ is higher than $n^\text{th}$ charge transfer into $n+1$, leaving 2 bands partially occupied => metal

\[ n \rightarrow \text{different bands cross } \]

\[ \Rightarrow \text{metal} \]
Spin - Orbit Coupling and Band Structure

So far we ignored spin; in the spin-independent hamiltonian, spin is conserved:

So the ground state is:

\[ \Psi_{\text{}^1}\text{S}(r) \quad (\uparrow) \quad \text{and} \quad \Psi_{\text{}^3\text{S}}(r) \quad (\downarrow) \]

Two - fold degeneracy for a Bloch states:
we can say that we describe two different bands with spin \( \uparrow \) (Majority band)
and \( \downarrow \) (Minority band)

For spin-dependent hamiltonian we have

SO Coupling:

\[ H_{SO} = \frac{\hbar}{2m^2c^2} \left( \nabla V(r) \times p \right) \cdot S \]

Physically = Zeeman coupling between magnetic moment of the \( e^- \) \( \vec{\mu} = (-\gamma/e) \vec{p} \) and the magnetic field in the rest frame of the \( e^- \).

Recall in solid spherical symmetry is broken, and electrons cannot be classified by simple:

\( \lambda \neq S \) or \( J = L \pm S \)

Because \( [S_z, H] \neq 0 \)

\[ \Psi_{\text{kn}}(r, \vec{\mu}) = |k.r| \left( \begin{array}{c} \Psi_{\text{kn}}(r) \\ \text{up or down} \end{array} \right) \]
in non-spin dependent case it also carries 5, and as such bands always has a degenerate pair

with 5 so the degeneracy is lifted.

But: degeneracy still preserved for SOC if and only if

\[ \text{Spatial inversion symmetry} \]
\[ \text{Time inversion symmetry} \]

are simultaneously present.

Few symmetry points:

Spin-orbit breaks spin rotation but preserves time-reversal

i.e. 
\[ r \rightarrow \theta \, r \, \theta^{-1} = \tilde{r} \]
\[ p \rightarrow -p \]
\[ s \rightarrow -s \]

\[ \Rightarrow H_{SO} \rightarrow \Theta H \Theta^{-1} \text{ or } [\Theta, H] = 0 \]

As the result we have Kramers degeneracy = all energy levels come in pairs.

i.e. 
\[ H |\psi\rangle = \epsilon |\psi\rangle \]
\[ H \Theta |\psi\rangle = \epsilon |\psi\rangle \]

For \[ \text{Spin } \frac{1}{2} \]
\[ \hat{\Theta} = \hat{\sigma}_y \hat{K} \]

Complex conjugation operator

\[ \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \text{ purely imaginary} \]
Let's apply $\Theta$ to the $\Psi_{nk}$

$$\Theta \Psi_{nk}(r, \sigma) = (\delta_{y, k}) \begin{pmatrix} u_{nk}^\dagger(r) \\ u_{nk}(r) \end{pmatrix}$$

$$= t \imath e^{-ikr} \begin{pmatrix} -u_{nk}^\dagger(r) \\ +u_{nk}(r) \end{pmatrix} = \Psi_{n-k}(r, \sigma)$$

Thus we have a Kramers pair:

$$\begin{cases} \Psi_{n, k}(r, \sigma) \\ \Psi_{n-k}(r, \sigma) \end{cases}$$

with $\varepsilon_n(k) = \varepsilon_n(-k)$

But this does not mean that 2 dispersions are identical.

Note in the presence of parity or inversion symmetry

$r \rightarrow p \rightarrow -r$

$p \rightarrow p$

$s \rightarrow s$

If there is a center of inversion such that $v(r) = v(-r)$, parity is a symmetry of Hamiltonian $H$. By $\varepsilon_n(k) \rightarrow -\varepsilon_n(-k)$

$$\Rightarrow \varepsilon_n(k) = \varepsilon_n(-k)$$

and if $\Theta P : \varepsilon_n(k) = \varepsilon_n(-k)$

Lack of any of $\Theta$ and $P$ there will be no degeneracy.

{In materials terms: non-centrosymmetric crystals and magnetic long-range ordered}
**BAND STRUCTURE METHODS**

**CAN WE CUGH ELECTRONIC STRUCTURE OF A SOLID?**

Exactly we cannot do this as after 10 electrons we hit the exponential well.

DFT fails at about 10^7 electrons and we have to use empirical semi methods.

Enter LCAO method = Linear combination of atomic orbitals

1) We start with

\[ H = H_{\text{single atom}} + A U \]

all differences between "real" crystal potential and isolated atom at the atom position \( A U \rightarrow 0 \)

2) Single particle states are given by

\[ H \Psi_{nk}(r) = E_{nk} \Psi_{nk}(r) \]

Band index is \( n \) and \( k \) is the vector wave in the 1

- Atomic w.f. \( \Phi_i(r) \)

they are eigenstates of

\[ H_{\text{el}} \Phi_i(r) = E_i \Phi_i(r) \]

where \( \langle \Phi_i | \Phi_j (r+\mathbf{r}) \rangle = \begin{cases} 1 & i=j \text{ and } r=0 \\ 0 & \text{otherwise} \end{cases} \)

\( E_i \) is the energy of an isolated atom, they decay rapidly away from 0.
for each specific $R$, $R'-R''$ is another helium atom.

Here we have only one bond.

Let's calculate $E(c) = \langle \psi(x) | H | \psi(x) \rangle$. The separation between $x$ and $r$ is

$$E(c) = \int \int \phi(x) \phi(r) \psi_2(x) \psi_2(r) \text{d}x \text{d}r$$

where $\psi_2(x)$ and $\psi_2(r)$ are the second wavefunctions.

Proof that $\psi_2(x)$ is an eigenfunction of $H$.

$\psi_2(x)$ is a chain of hydrogen atoms.

Clearly, $\psi_2(x)$ are not good enough for what about $\psi_2(x)$ in the x-growing.

Now recall the Bloch Theorem demands that $\psi_2(x)$ must be:

$$\psi_2(x) = e^{i\kappa x} \phi_2(x)$$

So the overlap integral $\langle \phi_2(r) | \phi_2(x) \rangle$ is:

$$\int \phi_2(r) \phi_2(x) \text{d}r$$
\[ E(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{R}} \int \sum_{\mathbf{R}''} e^{i \mathbf{K} \cdot \mathbf{R}''} \int dx \psi_{\mathbf{s}}^* (\mathbf{x}) \psi_{\mathbf{s}} (\mathbf{x} - \mathbf{R}'') \]

Since each term is the same: \[ \frac{1}{N} \sum_{\mathbf{R}} \]

\[ E(\mathbf{r}) = \sum_{\mathbf{R}''} i e^{i \mathbf{K} \cdot \mathbf{R}''} \int \psi_{\mathbf{s}}^* (\mathbf{x}) \psi_{\mathbf{s}} (\mathbf{x} - \mathbf{R}'') \, dx \]

Now the wave function rapidly decays: \[ \int \psi_{\mathbf{s}}^* (\mathbf{x}) \psi_{\mathbf{s}} (\mathbf{x} - \mathbf{R}'') \, dx = \varepsilon_s \]

if \( |\mathbf{R}''| \) large \[ \int \psi_{\mathbf{s}}^* \psi_{\mathbf{s}} (\mathbf{x} - \mathbf{R}'') \, dx \approx 0 \]

So we need to include only terms where \( \mathbf{R}'' \) is small \( \approx \) \( r \). For TB we only consider terms where \( |\mathbf{R}''| \approx \text{small} \) \( r \)

\[ \text{Thus we have} \]

\[ E(\mathbf{r}) = \varepsilon_s + \sum_{\mathbf{R}''} e^{i \mathbf{K} \cdot \mathbf{R}''} \int \psi_{\mathbf{s}}^* \psi_{\mathbf{s}} (\mathbf{x} - \mathbf{R}'') \, dx \]

\[ = \varepsilon_s + \sum_{\mathbf{R}''} e^{i \mathbf{K} \cdot \mathbf{R}''} \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) \]

\[ \text{where } \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) = \int \psi_{\mathbf{s}}^* \psi_{\mathbf{s}} (\mathbf{x} - \mathbf{R}'') \, dx \]

\[ \text{Example 1: 1D crystal} \]

\[ 1D \quad x = x_1 \quad \mathbf{R} = \pm a_0 \mathbf{e}_1 \quad \mathbf{e}_1 = \mathbf{e}_z = -a_0 \mathbf{i} \]

\[ \text{just two translation vectors} \]

\[ (\mathbf{r}) \tilde{e} = \varepsilon_s + \sum_{\mathbf{R}''} e^{i \mathbf{K} \cdot \mathbf{R}''} \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) = \]

\[ = \varepsilon_s + e^{i \mathbf{K} \cdot \mathbf{R}''} \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) + e^{-i \mathbf{K} \cdot \mathbf{R}''} \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) = \]

\[ = \varepsilon_s + e^{i \mathbf{K} a_0} \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) + e^{-i \mathbf{K} a_0} \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) = \]

\[ = \varepsilon_s + \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) + \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) = \]

\[ = \varepsilon_s + \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) \left( e^{ix_2} + e^{-ix_2} \right) \]

\[ = \varepsilon_s + \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) \frac{2 \cos (x_2)}{2 \cos (x_0)} \]

Your 1st band structure for 1D solid! \[ \text{E} = \tilde{\gamma} (\mathbf{R}'' \mathbf{l}) \]
Exercise: Calculate $E(k)$ for 2D

Plot 2D case:

For $a = \AA$, $3 \text{ eV} < 1 \text{ eV} < 10 \text{ eV}$

The same for 3D face centered cubic unit cell of size $a$ with 12 nn.

**Origin of the Bands**

Before we explain why atoms condense in solids, let's try to understand why molecules exist.

$\text{H} + \text{H} \rightarrow \text{H}_2$

Once we understand this we can think of a solid line as a giant molecule.

Here we closely follow W. A. Harrison "Electronic structure and the properties of solids" pp. 16 - 22 Ch. 3

For a hydrogen molecule we have 2 orbitals:

\[ n = 1 \]
\[ l = 0 \]
\[ s = 1s \]
To determine the energy and eigenstates of the molecule we must solve the secular eqn.

\[ \sum_{\phi} \langle \phi | H | \phi \rangle \psi_{\phi} - E \psi_{\phi} = 0 \]

where \( \langle \phi | \phi \rangle = 1 \), \( \langle \phi | \psi \rangle = 0 \).

\[ E = \langle \phi | H | \phi \rangle / \langle \phi | \phi \rangle \]

\[ E_s = \langle 11111 \rangle = \langle 11112 \rangle \]

\[ E_{\phi} = -V_2 \]

\[ \left( \begin{array}{cc}
E_s & E_s \\
E_s & E_s
\end{array} \right) \left( \begin{array}{c}
\psi_1 \\
\psi_2
\end{array} \right) = 0
\]

\[ \left( E_s - E \right) \psi_1 - V_2 \psi_2 = 0 \]

\[ -V_2 \psi_1 + \left( E_s - E \right) \psi_2 = 0 \]

We can easily solve these and find

\[ E_b = E_s - V_2 \]

\[ E_a = E_s + V_2 \]

\[ \psi_1 = \psi_2 = \sqrt{2} \]

\[ \psi_1 = -\psi_2 = \frac{1}{\sqrt{2}} \]

Next we describe the case of a polar bond in heteropolar solids, e.g., \( \text{Li}^+ \text{H}^- \) or \( \text{Na}^+ \text{Cl}^- \) etc.
of $\varepsilon^1_s - \varepsilon^1_a = 0$

$\varepsilon^2_s - \varepsilon^2_a$ so we end up

$$\begin{pmatrix} \varepsilon^1_s - V_2 \\ -V_2 \\ \varepsilon^2_s \end{pmatrix} \begin{pmatrix} V_1 \\ U_1 \\ U_2 \end{pmatrix} - E \begin{pmatrix} V_1 \\ U_1 \\ U_2 \end{pmatrix} = 0$$

Let introduce a new important parameter

$$V_3 = \frac{\varepsilon^2_s - \varepsilon^1_s}{2} \Rightarrow \text{POLAR ENERGY}$$

and also define the average of the cation-anion energy

$$\overline{\varepsilon} = \frac{\varepsilon^1_s + \varepsilon^2_s}{2}$$

Then our equation becomes

$$\begin{pmatrix} \varepsilon^1_s - V_3 \\ -V_2 \\ \varepsilon^2_s + V_3 \end{pmatrix} \begin{pmatrix} V_1 \\ U_1 \\ U_2 \end{pmatrix} - E \begin{pmatrix} V_1 \\ U_1 \\ U_2 \end{pmatrix} = 0$$

$$\begin{cases} \varepsilon_b = \varepsilon - (V_2^2 + V_3)^{1/2} \\ \varepsilon_a = \varepsilon + (V_2^2 + V_3)^{1/2} \end{cases}$$

Notice how electronic charge distributes in the bonds!

This means the molecule is polar!

To describe the polarity mathematically we find $v_1$ and $v_2$, e.g., first put $\varepsilon_b$ into

$$v_1 = \frac{V_2}{\sqrt{V_2^2 + V_3}} - V_3$$

$$v_2 \equiv \alpha \varepsilon U_2 \quad v_1^2 - v_2^2 = \varepsilon_p$$

$\varepsilon_p \equiv \text{POLARITY}$
Another useful concept is **covalency** of the bond.

\[
\alpha_c = \frac{V_2}{\sqrt{V_1^2 + V_2^2}}
\]

Back to our solids.

As overlap integral \( V \) (or \( V_2 \) for the molecule) increases, the \( N \) atoms which form \( N \) degenerate states overlap and create bonding and antibonding states which called **occupied** and **unoccupied states** or **valency** and **conduction bands**.

Each band contains \( N \) allowed values of \( \pi \).

Let's describe our first real solid (though fict.) **trans-polyacetylene**.

\[
R_{AB} = \left( \frac{a}{2}, \frac{a}{2\sqrt{3}} \right)
\]

In the crystal with \( N \) atoms basis and assuming that each atom contributes only 1 orbital for bonding, we can move \( N \) linear combinations of atomic orbitals that satisfy Bloch theorem:
\[ \Psi_{i,k}(r) = \frac{1}{\sqrt{N}} \sum_{R_i} e^{i \mathbf{k} \cdot \mathbf{R}_i} \phi(r-R_i) \]

\[ i = 1, 2, \ldots, N_b \] label different atoms in basis

and \( \mathbf{R}_i \) are the translation vectors that connect different

atoms \( i \).

E.g., for our polymer: \( \mathbf{R}_0 = \mathbf{R}_{AB} \pm a \mathbf{i} \),

\( \mathbf{R}_{AB} \pm 2a \mathbf{i} \), etc.

where \( \mathbf{R}_{AB} \) is the vector

between \( A \) and \( B \).

Then the crystal is defined as:

\[ \Psi_{k,x} = \sum_i c_{i,k} \Psi_{i,k}(r) = \frac{1}{\sqrt{N}} \sum_{R_i} c_{i,k} \sum_{R_i} e^{i \mathbf{k} \cdot \mathbf{R}_i} \phi(r-R_i) \]

As for the molecule we use the variational

theorem to find a set of \( \Psi_{k,x} \) which

are determined by minimizing the expectation

of \( H \) w.r.t. \( c_{i,k} \)

\[ \sum_i (H_{ij} - \delta_{ij} E(x)) c_{i,k} = 0 \]

where \( H_{ij} = \langle \psi_{i,k} | H | \psi_{j,k} \rangle \)

Back to our polymer:

\[ N_b = 2 \]

\[ \begin{array}{c|c|c}
H_{AA} & H_{AB} & H_{AB} \\
H_{AB} & H_{BB} & -E \\
\end{array} \]

where \( H_{AB} = H_{BA}^* \Rightarrow \)

\[ E(x) = -\frac{1}{2} (H_{AA} + H_{BB}) + \sqrt{\frac{1}{4} (H_{AA} - H_{BB})^2 + H_{AB}^2} \]

2 branches for each \( k \). \( \Rightarrow \) 2 BANDS

(\text{Note: 2 atoms per basis,}

\( = 2 \text{ bands} \))

Let's calculate \( H_{AA} \) and \( H_{BB} \) for \( 1p \) orbital contribution
Let's calculate $H_{AA}$ and $H_{BB}$ for $1p$-orbital contribution to atom.

\[
H_{AA} = \frac{1}{N} \sum_{kA} e^{i(k \cdot k_A \cdot r)} \int \psi_k^* (r - k_A) \psi_k (r - k_A) \, dr
\]

\[
= \sum_{kA} e^{i(k \cdot k_A \cdot r)} \int \psi_k^* (x) \psi_k (x - k_A) \, dx
\]

\[
= \varepsilon_p + \sum_{m \neq 0} e^{imkA \cdot \gamma(1m)} \, m \text{ is } > 0 \text{ integer}
\]

The same for $H_{BB}$.

Next we restrict our overlap integral only to $\pm \hbar \cdot \hbar$ meaning $\gamma(1m) = 0$ if $|m| > 1$. So $m = \pm 1$

Thus we end up with:

\[
H_{AA} = H_{BB} = \varepsilon_p + 2\gamma(0,0) \cos(kA)
\]

Following the same logic for $H_{AB}$

\[
H_{AB} = \frac{1}{N} \sum_{kA} e^{i(k \cdot k_A \cdot r)} \int \psi_k^* (r - k_A) \psi_k (r - k_B) \, dr
\]

\[
= \sum_{kA} e^{i(k \cdot k_A \cdot r)} \int \psi_k^* (x) \psi_k (x - (k_A + k')) \, dx
\]

Again include only $\pm \hbar \cdot \hbar$ $k_A = 0$ and $k_A = -\hbar \cdot \hbar$

\[
H_{AB} = \sum_{kA} e^{i(k \cdot \mathbf{t}) \cdot \gamma(12)}
\]

$t$ are the $\pm \hbar \cdot \hbar$ vectors $t = \mathbf{k}_{AB} = (\frac{\hbar}{2}, \frac{\hbar}{2})$

and $\mathbf{t} = \mathbf{k}_{AB} - \mathbf{e}_1 = (-\frac{\hbar}{2}, \frac{\hbar}{2})$

Then

\[
H_{AB} = \left( e^{(ka/2 - ike/2)} \right) \gamma(12) = 2 \cos(kA/2) \gamma(12)
\]

Combining all the $H_{AA}$, $H_{BB}$ and $H_{AB}$ we finally get
\[ E(k) = E_p + 2 \gamma(a) \cos(ka) \pm 2 \cos(\frac{ka}{2}) \gamma(1/1) \]

1st BZ of Transpolyacetylene

\[ \gamma(a) = 0.1 eV \]
\[ \gamma(1/1) = 0.5 eV \]

Band with: \( 4 \gamma(\tau) = 2 eV \)

What about more than one orbital?

In graphene, the lowest bands are made of s/p/x/y orbitals \( \rightarrow \) sp^{2} bonding.

So let's generalize the tight binding approach.

Imagine we have now \( N_b = 2 \) s, p\(_x\), p\(_y\) orbitals.

We expect 2 \( \times \) 4 bands to develop.

Thus we will get \( (8 \times 8) \) matrix for each \( \tau \).

E.g. In this case \( i = 1 \) \( \rightarrow \) s-orbital on A

\( j = 5 \) \( \rightarrow \) p\(_x\)-orb on B

The Hamiltonian matrix element will be:

\[ H_{ij} = \frac{1}{N} \sum_{\alpha} \sum_{\beta} e^{ik(V_{\alpha} - V_{\beta})} \int \psi^*_{\alpha}(r - r_{\alpha}) \psi_{\beta}(r - r_{\beta}) dr \]

The rest are similar:

Consider the band structure of graphene.

Graphene
As you can see, there are clearly 8 bands. Mostly $p_z$ orbitals (π-bonds) form the conduction band.

Next we will apply these ideas to tight binding on graphene.
Recall that graphene spans a 2D hexagonal lattice
with electrons doing $sp^2$ hybridization.

The 2D hexagonal lattice of graphene is shown below
where $\vec{a}_1 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{pmatrix}$, $\vec{a}_2 = a \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, where $a$ is the lattice constant.

The rhombic unit cell contains 2 carbons at the positions
$\vec{r}_1 = a \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}$ and $\vec{r}_2 = a \begin{pmatrix} \frac{1}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix}$.

The position of the rest of atoms can be generated by
$\vec{r}_1 + \vec{R}$, $\vec{r}_2 + \vec{R}$ where $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2$, $n_1$ and $n_2 = 0, \pm 1, \pm 2, \ldots$ etc.

But as usual you can select a different unit cell.

BTW. if you want the unit cell which reflects clear hexagonal symmetry use WIGNER–SEITZ cell

Few notes:

1. $\vec{a}_1$ and $\vec{a}_2$ are not orthogonal.
   and this is a problem b/c
   we will need many terms like $i \vec{R}$.
Suppose we write
\[ \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \quad \text{and} \quad \mathbf{b}_1, \mathbf{b}_2 \]
\[ \mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 \]
this can be simple only if
\[ \mathbf{k} \cdot \mathbf{k} = \sum_{i,j=1}^{2} k_i n_i \mathbf{b}_i \cdot \mathbf{a}_j \]
\[ \text{Such as } \mathbf{b}_j \cdot \mathbf{a}_i = 2\pi \delta_{ji} \]
Then the phase factor
\[ e^{i\mathbf{k} \cdot \mathbf{R}} = e^{i2\pi (n_1 k_1 + n_2 k_2)} \]
\[ \text{Inverse such } \mathbf{k} \text{ lattice vectors are of course the reciprocal lattice } \]
\[ \mathbf{b}_1 \text{ and } \mathbf{b}_2 \]
\[ \text{such that } \mathbf{k} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 \]
This reciprocal lattice is shown below

To construct a Bloch wave we can take any \( \mathbf{k} \)
but if \( \mathbf{k} \) is outside of the cell span by \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \)
we always can \( \mathbf{k}' = \mathbf{k} + \mathbf{K} \)
\[ e^{i\mathbf{k} \cdot \mathbf{R}} = e^{i2\pi (m_1 k_1 + m_2 k_2)} = 1 \quad \Rightarrow \]
\[ e^{i\mathbf{k}' \cdot \mathbf{R}} = e^{i\mathbf{k}} \text{ so the } \mathbf{k}s \text{ inside the 1st } \]
\[ \text{BZ cover all the values of } \mathbf{k} \]
So let calculate \( \mathbf{b}_i = (b_{i1}, b_{i2}) \)
demanding \( \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \)
\[ b_{11} a_{11} + b_{12} a_{12} = \frac{2\pi}{a} = b_{11} \frac{\sqrt{3}}{2} - b_{12} \frac{1}{2} \]
\[ b_{11} a_{21} + b_{12} a_{22} = 0 = b_{12} \]
\[ b_{21} a_{11} + b_{22} a_{12} = 0 = b_{21} \frac{\sqrt{3}}{2} - b_{22} \frac{1}{2} \]
\[
\begin{align*}
\begin{pmatrix}
 b_{21} \ a_{11} + b_{12} \ a_{12} = 0 = b_{21} \frac{V_3}{2} - b_{12} = \frac{1}{c} \\
 b_{21} \ a_{21} + b_{12} \ a_{22} = \frac{2\pi}{a} = b_{22}
\end{pmatrix}
\end{align*}
\]

\[
\begin{align*}
\bar{b}_1 &= \frac{2\pi}{a} \left( \frac{2}{\sqrt{3}}, 0 \right) \\
\bar{b}_2 &= \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}}, 1 \right)
\end{align*}
\]

Labels or special points in \( \mathbb{B}^2 \):
\[
\begin{align*}
\Gamma &= \frac{2\pi}{a} \left( 0, 0 \right) & M &= \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}}, 0 \right) & K &= \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}}, \frac{1}{3} \right) \\
\Gamma &= \frac{1}{2} b_1 + \frac{1}{2} b_2 & M &= \frac{1}{2} b_1 + \frac{1}{2} b_2 & K &= \frac{2}{3} b_1 + \frac{1}{3} b_2
\end{align*}
\]

**NN Tight Binding Model**

We need to calculate the matrix elements like
\[
\begin{align*}
H_{11, \ k} &= \sum_R e^{i\mathbf{k} \cdot \mathbf{R}} \langle \chi_1 | H | \chi_1 \rangle = \langle \chi_1 | H | \chi_1 \rangle = E_0 \\
H_{22, \ k} &= \sum_R e^{i\mathbf{k} \cdot \mathbf{R}} \langle \chi_2 | H | \chi_2 \rangle = \langle \chi_2 | H | \chi_2 \rangle = E_0
\end{align*}
\]

Since only \( \mathbf{R} = 0 \) contributes and both sites in the sublattices 1 and 2 are equivalent.

**OFF-Diagonal**:
\[
\begin{align*}
H_{12, \ k} &= \sum_R e^{i\mathbf{k} \cdot \mathbf{R}} \langle \chi_1 | H | \chi_2 \rangle = \langle \chi_1 | H | \chi_2 \rangle \left( 1 + e^{i\mathbf{q}_1} + e^{-i\mathbf{q}_3} \right) \\
H_{21, \ k} &= \sum_R e^{i\mathbf{k} \cdot \mathbf{R}} \langle \chi_2 | H | \chi_1 \rangle = \langle \chi_2 | H | \chi_1 \rangle \left( 1 + e^{-i\mathbf{q}_1} + e^{i\mathbf{q}_3} \right)
\end{align*}
\]

\( t \) is a hoppings parameter.
Thus
\[ H_{\ell', k} = t \left( 1 + e^{i2\pi k_1} + e^{i2\pi k_2} \right) = t \left( 1 + e^{i2\pi k_1} + e^{i2\pi k_2} \right) = \pm t_k \]

Finally:
\[
\begin{pmatrix}
E_p & t_k \\
\bar{t}_k & E_p
\end{pmatrix}
\begin{pmatrix}
c_{1, k} \\
c_{2, k}
\end{pmatrix} - E(k)
\begin{pmatrix}
c_{1, k} \\
c_{2, k}
\end{pmatrix} = 0
\]

\[
E_{\pm}(k) = E_p \pm \sqrt{t_k^2} = E_p \pm \sqrt{t_k^2} =
\]

\[
\frac{E_p \pm \sqrt{3 + 2 \cos(2\pi k_1) + 2 \cos(2\pi k_2)}}{2 \cos(2\pi \frac{k_1 + k_2}{2})}
\]

and
\[
\psi^+_k = \begin{pmatrix} c_{1, k} \\ c_{2, k} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix},
\psi^- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}
\]

So here is the 2D plot (try thin in Mathematica)

Consider now what happens in high symmetry points? The coordinates in the BZ are given above.

\[ \Gamma: E_p \pm 3t_b \quad \frac{1}{\sqrt{2}} (1) \quad \text{and} \quad \frac{1}{\sqrt{2}} (-1) \]
\[
\begin{align*}
\Gamma: & \quad E_p \pm \frac{1}{2} (1) \quad \text{and} \quad \frac{1}{2} (1) \\
M: & \quad E_p \pm \frac{1}{2} (1) \quad \text{and} \quad \frac{1}{2} (-1) \\
K: & \quad E_p \quad (1) \quad \text{and} \quad (0) \\
K': & \quad E_p \quad (0) \quad \text{and} \quad (1)
\end{align*}
\]

\[\text{those are } \text{doubly degenerate!}\]

So far nothing too exciting, just another exercise in LCAO method 101.

But wait! Let's move to the long-wave length.

- Each carbon has one electron in \( p_z \) state, assuming spin degeneracy we have the band \( \frac{1}{2} \) filled.

- It means the \( E_F \) right at \( K \) and \( K' \) points (also I used the fact that bond structure is symmetric)

\[ E_F \text{ is here!} \]

- As we know the only interesting states are near the Fermi edge, so let's study those in detail.

Consider \( \bar{K} = \bar{K} + q \) we consider only states \( K' = K' + q \) with \( |q| \ll K \)

\[ \text{or } K \sim \frac{1}{a} \Rightarrow q \ll 1 \text{ or } \lambda \ll a \]

\[ \text{and } q \ll a \ll 1 \]

Love wave limit

What about Bloch wave phases?
\[ a_1 = a \left( \frac{\sqrt{3}}{2} - \frac{1}{2} \right) \]

\[ K = \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}} \frac{1}{3} \right) \]

\[ e^{iKz} = e^{iKz} (1 + i\eta z) \approx e^{i\frac{2\pi}{a} \left( \frac{1}{\sqrt{3}} \frac{1}{3} \right)} + i\varphi a \sqrt{3} \]

in the same way

\[ e^{iK_2} = e^{iK_2} (1 - i\eta z) \approx e^{-i\frac{2\pi}{a} \left( \frac{1}{\sqrt{3}} \frac{1}{3} \right)} - i\varphi a \sqrt{3} \]

Recall

\[ H_{12} = \tau \cdot (1 + e^{iK_1} + e^{iK_2}) = \frac{3a}{2} t (a_x - i a_y) \]

Similarly for \( K' \)

\[ t_{K'} = \frac{3a}{2} t (a' x + i a'y) \]

Let's define a new parameter = Fermi velocity

\[ \frac{\hbar v_F}{a} = -\frac{3}{2} a \text{ and since } t < 0 \]

Since for graphene \( t = -3 \text{ eV} \)

\[ v_F \sim 10^6 \text{ m/sec} \]

Next if we select our zero at \( E_F = \text{ the atomic value of } p - \text{orb.} \)

\[ \begin{pmatrix} E_F + t_k \\ t_k E_F \end{pmatrix} \approx \begin{pmatrix} 0 & a_x - i a_y \\ a_x + i a_y & 0 \end{pmatrix} \cdot \frac{3}{2} a t = \]

\[ = \frac{\hbar v_F}{a} \begin{pmatrix} 0 & a_x - i a_y \\ a_x + i a_y & 0 \end{pmatrix} = \frac{\hbar v_F}{a} q_y \begin{pmatrix} a_x & 0 \\ 0 & a_y \end{pmatrix} + \frac{\hbar v_F}{a} q_y \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \]

\[ \approx \begin{pmatrix} \frac{\hbar v_F}{a} q_y \\ \frac{\hbar v_F}{a} q_y \end{pmatrix} \]
So formally we have:

\[ \mp \hbar v_\text{F} \vec{q}_x \vec{\sigma}_x + \mp \hbar v_\text{F} \vec{q}_y \vec{\sigma}_y = \mp \hbar v_\text{F} \vec{q} \cdot \vec{\sigma} = v_\text{F} \vec{p} \cdot \vec{\sigma} \]

Since \( \hbar \frac{1}{2} = \vec{p} \rightarrow \) projection of momentum on spin

The eigenvalue problem now can be written as:

\[
\begin{pmatrix}
E_p & t_k & \\
-t_k & E_p & \\
       &       & \\
\end{pmatrix} \begin{pmatrix}
C_{1k} \\
C_{2k} & \\
\end{pmatrix} = E_k \begin{pmatrix}
C_{1k} \\
C_{2k} & \\
\end{pmatrix} \Rightarrow \begin{pmatrix}
0 & v_\text{F} \vec{p} \cdot \vec{\sigma} & \\
& & \\
\end{pmatrix} \psi_p = E_p \psi_p
\]

where \( \psi_p = \begin{pmatrix}
C_{1p} \\
C_{2p} & \\
\end{pmatrix} \) spinor

Note: The component of \( \psi \) are NOT referring to spin up down, but to the amplitudes of \( \psi \) on sublattice 1 and 2 of graphene

Let's solve the equation

\[
\begin{pmatrix}
0 & v_\text{F} \vec{p} \cdot \vec{\sigma} & \\
& & \\
\end{pmatrix} \psi_p = E_p \psi_p \Rightarrow \begin{pmatrix}
0 & v_\text{F} (p_x i p_y) & \\
p_x i p_y & 0 & \\
\end{pmatrix} \begin{pmatrix}
C_{1p} \\
C_{2p} & \\
\end{pmatrix} = \begin{pmatrix}
C_{1p} \\
C_{2p} & \\
\end{pmatrix} E_p
\]

\[ E_p^\pm = \pm v_\text{F} \sqrt{p_x^2 + p_y^2} = \pm \sqrt{\gamma p} \]

In undoped graphene

\[ E_\text{F} \text{ only one } k \text{ point is occupied} \rightarrow 0 \]

By gating or chemical doping we can fill up states with \( p > 0 \)

or do the same for hole

So this is unique b/c of the complete symmetry
In majority conventional materials electrons and holes are very different.

Put back $E_F^\pm$ we get the eigenvalues

$$\Psi_F^\pm = \begin{pmatrix} c_1p \\ c_2p \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & \mp i \end{pmatrix} \Phi_p$$

where $\Phi_p$ is the phase angle $p_x + ip_y = e^{i\Phi_p}$

But: If we move away from the long wave length say $> \pm 0.5$ eV the dispersion is not linear anymore.

We will return to graphene when I will introduce electrons in magnetic field, topology and quantum hole effect.

THE END OF THE e-STRUCTURE MODULE.