Review:

Application of Bloch's theorem:

\[ \psi_k(r) = e^{i\mathbf{k} \cdot \mathbf{r}} \psi(r) \]

\[ \psi_k(x) = e^{i\hbar k_x} \left( A \sin(k_0 x) + B \cos(k_0 x) \right) \]

\[ x \in [-\pi, \pi] \]

\[ V(x) = \sum_j S(x-ja) \]

\[ \psi_k(x) = e^{i\hbar k(x-a)} \left( A \sin(k_0 (x+q)) + B \cos(k_0 (x+q)) \right) \]

\[ x \in [-\pi, \pi] \]

c) \[ \cos(k_0 a) = \cos(k_0 q) + \frac{\sin(k_0 q)}{k_0 a} \]

Diagram:

- Bands with states
- Band gap
- Energy levels
Energy Bands in 1D

Electric Current
in Metals: Odd # e^-'s permitted

Conduction Band

Valence Band

Band Insulator

Even # e^-'s go out cell

Thermally activated charge carrier

=) Some charge carriers!!

Band overlap

=) Charge carriers

The case of band overlap can be quite common in real materials because they live in 3D.
Energy Bands in 2D and 3D

Monovalent atom

\[ c^- \]

Con sit half of the 1st BZ

\[ \beta \text{ shown} \]

\[ 2 \pi a \]

What is the radius of the disk?

Radius of disk:

\[ \pi R^2 = \frac{1}{2} \left( \frac{2\pi a}{a} \right)^2 \]

\[ \frac{2\pi R^2}{a^2} \]

\[ R = \frac{\sqrt{2\pi}}{a} \times \frac{2.5}{a} < \frac{\pi}{a} \]

Fermi sea forms a disk: area = \[ \frac{1}{2} \left( \frac{2\pi}{a} \right)^2 \approx \frac{1}{2} \text{ PBZ} \]

Adding a periodic potential:

1. States close to zone boundary get moved down in energy (from opening of band gap.)
2. Electrons preferentially fill states near BZ edge.

Fermi surface

Fermi sea still fill \( \frac{1}{2} \) PBZ.

1. Increasing strength of \( V(\mathbf{r}) \rightarrow 10\text{eV} \) get larger BZ bands gap grows so electronic energy state @ boundary get smaller.

\[ E = E_o - 3t \cos(h_xa) - 2t \cos(h_ya) \]
An illustration of band topology at the B2 edge:

There states get filled

Draw red first!!
The shape of the Fermi sea is obtained via tight-binding:

\[
\phi(\vec{r} - \vec{r}_j) \quad \text{is a bound s-orbital (spherically symmetric)}
\]

\[
s^\text{form}
\]

\[
\psi_h(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j \exp(i\vec{R}_j \cdot \vec{r}) \phi(\vec{r} - \vec{R}_j) = |\vec{R}_j\rangle
\]

labeled with \( \vec{R}_j \) since it is a Bloch function:

\[
\psi^R(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j \exp(i\vec{R}_j \cdot \vec{r}) \phi(\vec{r} + \vec{R} - \vec{R}_j)
\]

\[
= e^{i\vec{R} \cdot \vec{R}} \frac{1}{\sqrt{N}} \sum_j \exp(i\vec{R}_j \cdot (\vec{R} - \vec{R}_j)) \phi(\vec{r} - (\vec{R}_j - \vec{R})) = e^{i\vec{R} \cdot \vec{R}} \psi_h(\vec{r}) \quad \vec{R} = \text{Lattice Vector}
\]

Thus we can calculate the energy directly:

\[
E^R = \langle \psi^R | H | \psi^R \rangle = \frac{1}{N} \sum_j \sum_m \int e^{i\vec{R}_j \cdot \vec{R}_m} \phi^*(\vec{r} - \vec{R}_m) H \phi(\vec{r} + \vec{R}_j) d\vec{r}
\]

\[
= \frac{1}{N} \sum_j \sum_m \int e^{i\vec{R}_j \cdot (\vec{R}_m - \vec{R}_j)} \phi^*(\vec{r} - \vec{R}_m) H \phi(\vec{r} - (\vec{R}_j - \vec{R}_j)) d\vec{r}
\]

\[
= \frac{1}{N} \sum_j \sum_m e^{i\vec{R}_j \cdot \vec{R}_m} \int \phi^*(\vec{r} - \vec{R}_m) H \phi(\vec{r} - \vec{R}_j) d\vec{r}
\]
There are $N$ copies of the Pauli $\sigma_z$ sum, so,

$$\langle \Phi | H | \Phi \rangle = \sum_m \sum e^{-i \frac{\pi}{3} \cdot \frac{3_m}{3} \cdot \frac{3}{3} \cdot \frac{3}{3} \cdot \frac{3}{3}} \int \phi^* (\vec{r} - \frac{\vec{3}_m}{3}) H \phi (\vec{r}) d^3 r$$

We only keep $\frac{3_m}{3} = \sum \pm \frac{3}{3}$ nearest neighbors.

$$\phi(x+\frac{3}{3}) \phi(x) \phi(x-\frac{3}{3})$$

So,

$$E_R = \langle \Phi | H | \Phi \rangle = \int \phi^* (\vec{r}) H \phi (\vec{r}) d^3 r + \sum_m \sum e^{-i \frac{\pi}{3} \cdot \frac{3_m}{3} \cdot \frac{3}{3} \cdot \frac{3}{3} \cdot \frac{3}{3}} \int \phi^* (\vec{r} - \frac{\vec{3}_m}{3}) H \phi (\vec{r}) d^3 r$$

Main tight-binding result.

$$E_R = -\alpha - \chi \sum e^{-i \frac{\pi}{3} \cdot \frac{3_m}{3} \cdot \frac{3}{3} \cdot \frac{3}{3} \cdot \frac{3}{3}} \frac{1}{R \in l'' \bar{B}Z}$$

The factor $\chi$ is what opens up the band bands!! For hydrogen 1100 states as $\phi (\vec{r})$:

$$\gamma \propto \epsilon$$

$$\frac{1}{\gamma} \propto 10$$

$$\gamma \approx 0, \quad \text{as} \quad \gamma \approx 0.5 \delta$$

Band gets wider with longer $\gamma$. 
Back to the 2D square example:

\[
\frac{1}{2} \mathbf{q}_m = (\pm q, 0), (0, \pm q)
\]

\[
E(k) = -\alpha - k \left( e^{i k_x a} + e^{-i k_x a} + e^{i k_y a} + e^{-i k_y a} \right)
\]

Show plot:

\[
= -\alpha - 2k \left[ \cos(k_x a) + \cos(k_y a) \right]
\]

These electrons move to fill lower energy states.

Show plot of SC Fermi surface:
Review:

\[ \psi_n(k) = \frac{1}{\sqrt{N}} \sum_j \exp(i\mathbf{R}_n \cdot \mathbf{R}_j) \phi(k \mathbf{R}_j - \mathbf{R}_j) \]

Tight-binding Bloch Function

\[ E(k) = -\alpha - \delta \sum_m e^{i\mathbf{k} \cdot \mathbf{S}_m} \]

Example: 2D square lattice of nonoverlapped atoms

\[ E(k) = -\alpha - 2\delta \left[ \cos(k_x a) + \cos(k_y a) \right] \]

\[ \Rightarrow \]

Fermi surface

In 3D,

Fermi surface
2D Square Lattice w/ Divalent Atoms:

- Free
- Extended

\[ \pi K_F^2 = \left( \frac{17\pi}{a} \right)^2 \]

\[ K_F = \frac{2}{a} \sqrt{\pi} \]

\[ \approx 3.55 \frac{\pi}{a} \]

Reduced

1° BZ

2° BZ

N.B. Top of section b will take up such as center of 1° BZ for neighbor cell.

Nearly Free:

Applying a potential will lower energy here & raise it here, so for a weak potential we have:
- Lower band
- Upper band

Weak

Metal →

Strong

Insulator

A Show II of divalent calcium free electron Fermi surface.
Take-home: A weak potential can allow for band overlap even when the $e^-$ is even.

Other places where Band Theory (as we've presented it) fails in predicting metal-insulator states:

- **Magnetic**: spin-spin interaction strong $\Rightarrow$ filling $N_f$ doesn't work.
- **Mott Insulator**: $(NiO, Co)$
  - strong $e^- - e^-$ interaction, so even with non-valent atoms, only 1 $e^-$ sits at each atom (no $N_f$) & the system is insulating!!

**Optical Properties & Band structure:**

- **Insulator & Semiconductor**

Bond insulators cannot absorb photons of energy less than their band gap:

$\hbar \nu = E_g \quad \nu = \frac{E_g}{\hbar}$

[Graph showing the relationship between $E(k)$ and $k$.]

- Show PBS of light absorption spectra. There is a strong drop in the absorption for wavelengths greater than bandgap wavelength.
  - If $E_g > 3.2 \text{ eV}$, the crystal will be optically transparent.
A Show Part of Semiconductors

- ColS have $E_g > 2.6$ eV so blue & violet opt absorbed & red & green

- Small band gap semiconductor such as Si, Ge, GaAs have $E_g < 1.5$ eV, so the absorb most visible light block.

- Quartz, diamond, aluminum oxide, BN have $E_g > 3.2$ eV so they are transparent.

The onset for absorption of photons can be sharp or gradual. This has to do with the indirect or direct bandgap nature.

- **Conduction**
- Direct
- **Indirect**

May involve lower energy transition.
Direct: $A \vec{k} \neq 0$

Indirect: $A \vec{k} \neq 0$

Indirect processes involve a non-zero $\vec{k}$, but the $\vec{k}$ of a photon is small:

$$\frac{\hbar}{\vec{k} \cdot \vec{c}} = \frac{E}{\vec{p} \cdot \vec{c}}$$

$$\Rightarrow 1 \frac{\hbar}{\vec{k}} \frac{E}{\hbar} \cdot \frac{1}{c} = \frac{1.6 \text{ eV}}{\frac{4 \times 10^{-19} \text{ eV} \cdot \text{s}}{3 \times 10^8}} \frac{1}{3 \times 10^5} = 10^6 \text{ cm}^{-1}$$

Compared to phonons:

$$|\vec{k}| = \frac{E}{\hbar} \cdot \frac{1}{V_s}$$

$C \gg V_s$  \[ \Rightarrow \frac{1}{a} = 10^{10} \text{ m}^{-1} \]

$$\Rightarrow |\vec{k}|_{\text{phonon}} < |\vec{k}|_{\text{photon}}$$

Because energy & momentum must be conserved, indirect transitions often involve complicated phonon absorption/emission processes that are not efficient:

Indirect absorption can still occur & does occur, just much less efficiently.
Optical Properties of Metals

What gives metals their color?

Intraband transitions dominate.

Metals absorb & reemit light very efficiently, which is why they are shiny. The re-emission process occurs very quickly.

Metals that do not form oxides look shinier, such as Ag, Au, Pt.

Color of metal:

Intraband Transitions

ΔE_{Ag} > ΔE_{Cu}, so Ag can absorb & reemit higher energy photons, as well as have very photonic, so Ag looks more mirror-like. Cu only absorbs re-emits Red-Green & looks copper.
Impurities:

Small levels of impurity can transform optical & electronic properties.

Show that $B$ in Diamond.

Semiconductor Physics:

Consider a filled valence band & excite a single electron from the valence to the conduction band.

An absence of an electron from the valence band is called a "hole".

We keep track of holes & treat them as individual elementary particles.

The charge of an electron: $-e$

The charge of a hole is: $+e$

Energy of a hole?

To move electron down, take negative energy (phonon)

To move a hole from $k_x$ to $k'_x$, take positive energy (work),

Like pushing balloon under water!!