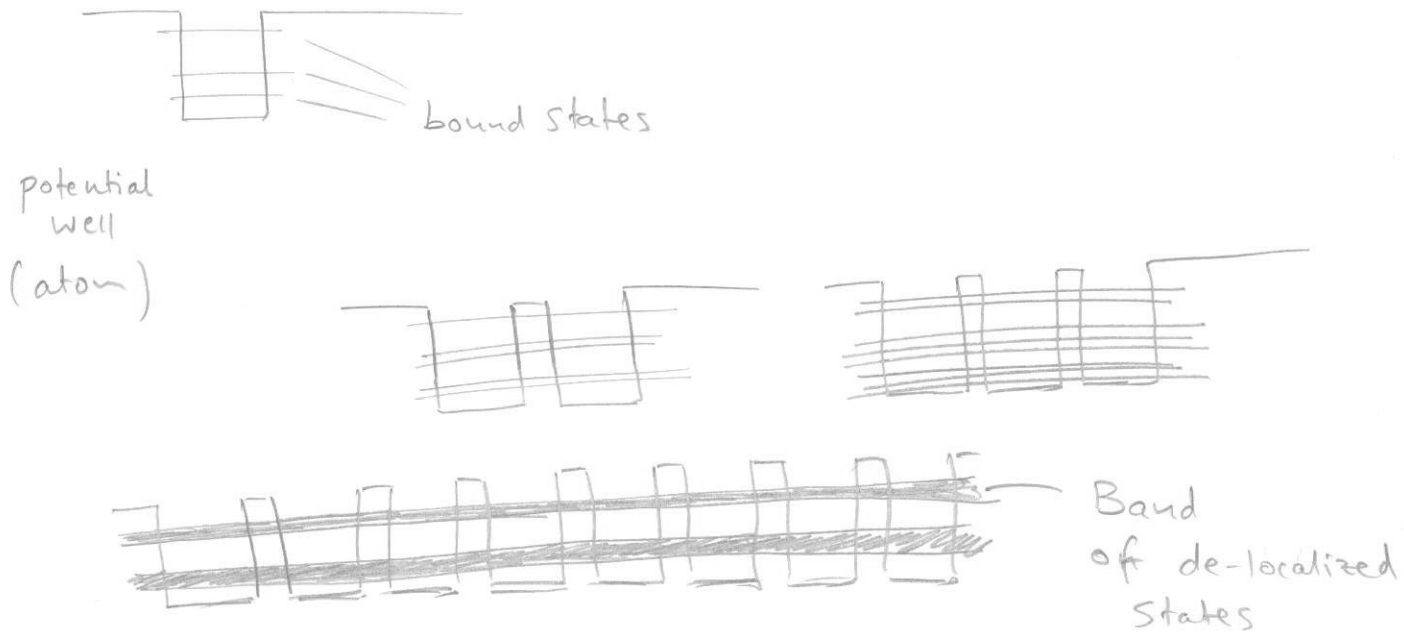
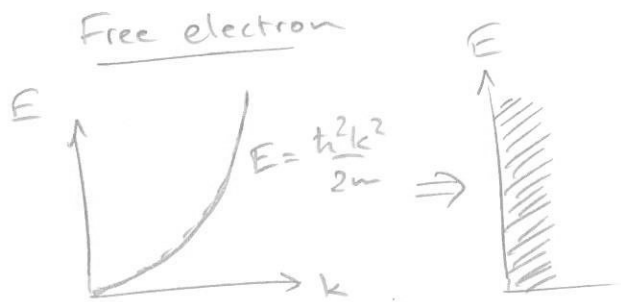


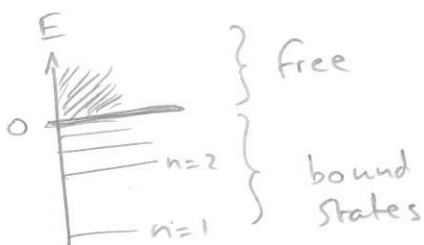
Splitting of energy levels - Effect of potential



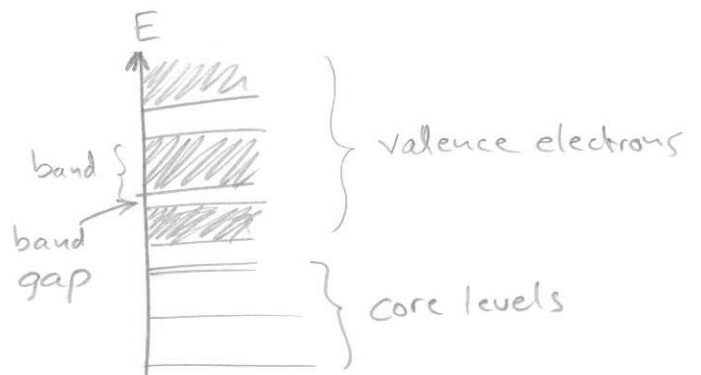
Energy levels



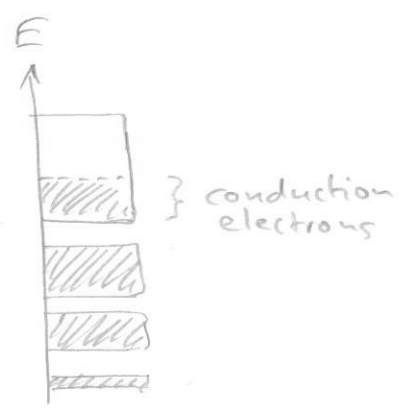
Hydrogen atom



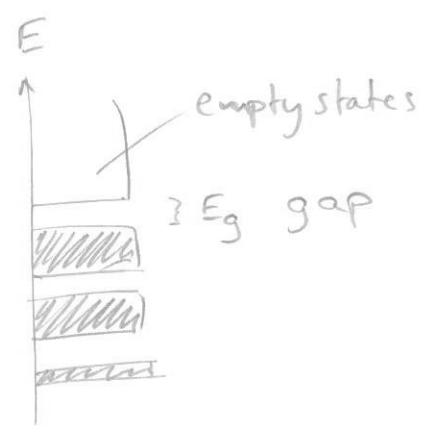
Electron in crystal



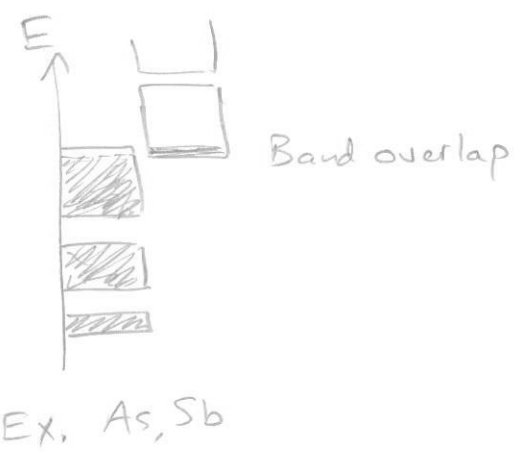
Metal



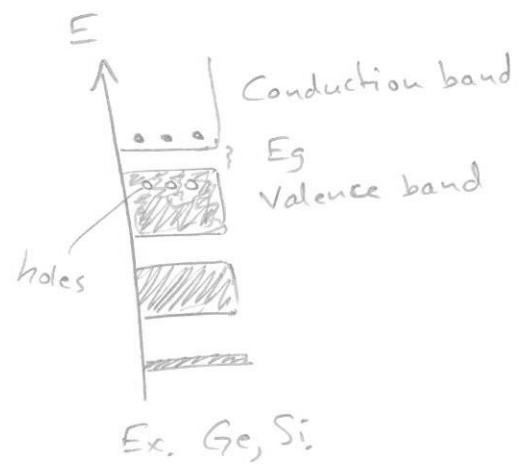
Insulator



Semi-metal



Semiconductor



One-electron approximation



Assume that every valence electron feels the same potential

$$V(\vec{r}) = V_{\text{core}}(\vec{r}) + V_{\text{val}}(\vec{r})$$

$V(\vec{r})$ periodic in the lattice

$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

average potential from all val. electrons

Solve Schrödinger

$$V_{\text{val}}(\vec{r}) \text{ from } -e \sum_j |\psi_j|^2$$

all valence electrons

Methods to study one-electron states

in periodic potentials $V(\vec{r})$

- ⊕ Nearly free electron model
- ⊕ Tight-binding model
- ⊕ Numerical models

Numerical models

Method Search for solutions to Schrödinger eq. for one electron in periodic potential $V(\vec{r})$

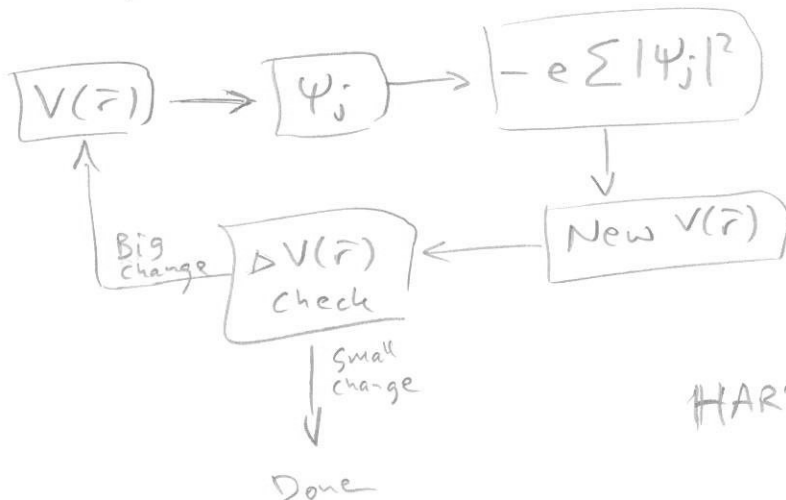
$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r})$$

$\Rightarrow \psi_1, \psi_2, \psi_3, \dots$ with E_1, E_2, E_3, \dots

Fill states with N electrons

Calculate $-e \sum_{j=1}^N |\psi_j|^2$

\Rightarrow set new $V(\vec{r}) \Rightarrow$ check if $V(\vec{r})$ is stable



HARTREE

Bloch electrons

(4)

Periodic potential $U(\vec{r} + \vec{R}) = U(\vec{r})$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r})$$

$$\hat{H} \psi = \epsilon \psi$$

No longer free electrons



Bloch electrons

(one-electron approximation)

Bloch's theorem

$$\hat{H} \psi = \epsilon \psi \quad \text{with} \quad \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r})$$

and $U(\vec{r})$ periodic in the lattice

has solutions of the form

$$\psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

$$\text{with} \quad u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r} + \vec{R})$$

Here $n = 1, 2, 3, \dots$ is the band index

Proof - Bloch's theorem

$$\text{Write } \psi(\vec{r}) = \sum_{\vec{k}} C(\vec{k}) e^{i\vec{k}\cdot\vec{r}}$$

superposition of eigenstates

$$U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

periodic potential

$$\text{Schrödinger } \hat{H}\psi = E\psi$$

Look at the different terms

$$\textcircled{1} \quad -\frac{\hbar^2}{2m} \nabla^2 \sum_{\vec{k}} C(\vec{k}) e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} C(\vec{k}) e^{i\vec{k}\cdot\vec{r}}$$

$$\textcircled{2} \quad U(\vec{r})\psi = \sum_{\vec{G}} \sum_{\vec{k}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} C(\vec{k}) e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{G}, \vec{k}} U_{\vec{G}} C(\vec{k}) e^{i(\vec{G}+\vec{k})\cdot\vec{r}}$$

$$\underbrace{\sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} C(\vec{k}) e^{i\vec{k}\cdot\vec{r}}}_{-\frac{\hbar^2}{2m} \nabla^2 \psi} + \underbrace{\sum_{\vec{G}, \vec{k}} U_{\vec{G}} C(\vec{k}) e^{i(\vec{G}+\vec{k})\cdot\vec{r}}}_{U\psi} = \underbrace{\sum_{\vec{k}} E \cdot C(\vec{k}) e^{i\vec{k}\cdot\vec{r}}}_{E\psi}$$

$e^{i\vec{k}\cdot\vec{r}}$ are orthogonal functions for different \vec{k}

\Rightarrow sum of coefficients for each term $e^{i\vec{k}\cdot\vec{r}}$ is zero.

$$e^{i\vec{k}\cdot\vec{r}} \left\{ \frac{\hbar^2 k^2}{2m} C(\vec{k}) + \sum_{\vec{G}} U_{\vec{G}} C(\vec{k}-\vec{G}) - E C(\vec{k}) \right\} = 0$$

Central equation

$$\left(\frac{\hbar^2 k^2}{2m} - E \right) C(\vec{k}) + \sum_{\vec{G}} U_{\vec{G}} C(\vec{k}-\vec{G}) = 0$$

This equation shows that $C(\vec{k})$ only depends on \vec{k} -vectors differing by reciprocal lattice vectors \vec{G}

cont. \rightarrow

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c(\vec{k}-\vec{G}) e^{i(\vec{k}-\vec{G}) \cdot \vec{r}} = \left[\sum_{\vec{G}} c(\vec{k}-\vec{G}) e^{-i\vec{G} \cdot \vec{r}} \right] e^{i\vec{k} \cdot \vec{r}}$$

(
 an eigenstate
 can be constructed
 using all related
 $c(\vec{k})$ terms

define as $f(\vec{r})$

$$f(\vec{r} + \vec{R}) = \sum_{\vec{G}} c(\vec{k}-\vec{G}) e^{-i\vec{G} \cdot (\vec{r} + \vec{R})} = \sum_{\vec{G}} c(\vec{k}-\vec{G}) e^{-i\vec{G} \cdot \vec{r}} e^{-i\vec{G} \cdot \vec{R}}$$

= $f(\vec{r})$ = 1

$$U_{\vec{k}}(\vec{r}) = f(\vec{r})$$

$$\Rightarrow \psi_{\vec{k}}(\vec{r}) = U_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad \text{Bloch's theorem}$$

$$\begin{aligned} \psi(\vec{r} + \vec{R}) &= e^{i\vec{k} \cdot (\vec{r} + \vec{R})} U_{\vec{k}}(\vec{r} + \vec{R}) = \\ &= e^{i\vec{k} \cdot \vec{R}} e^{i\vec{k} \cdot \vec{r}} U_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r}) \end{aligned}$$

$\psi(\vec{r})$

Alternative formulation
 of Bloch's theorem

$$\psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r})$$

Going backwards: Assume \nearrow and that $\psi_{\vec{k}}(\vec{r}) = f(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$

$$\Rightarrow \psi_{\vec{k}}(\vec{r} + \vec{R}) = f(\vec{r} + \vec{R}) e^{i\vec{k} \cdot (\vec{r} + \vec{R})} = e^{i\vec{k} \cdot \vec{R}} \underbrace{f(\vec{r}) e^{i\vec{k} \cdot \vec{r}}}_{\psi_{\vec{k}}(\vec{r})}$$

$$\Rightarrow f(\vec{r} + \vec{R}) = f(\vec{r})$$

Central equation: $\left(\frac{\hbar^2 k^2}{2m} - \epsilon\right) C(\bar{k}) + \sum_{\bar{G}} U_{\bar{G}} C(\bar{k} - \bar{G}) = 0$
 (write k' inst. of k)

Restatement of the Schrödinger equation with periodic potential

If we define \bar{G}' so that $\bar{k} = \bar{k}' + \bar{G}'$ is in 1st Brillouin Zone

$$\left(\frac{\hbar^2}{2m} (\bar{k} - \bar{G}')^2 - \epsilon\right) C(\bar{k} - \bar{G}') + \sum_{\bar{G}} U_{\bar{G}} C(\bar{k} - \bar{G}' - \bar{G}) = 0$$

$\bar{G} \leftrightarrow \bar{G}'$

$$\left(\frac{\hbar^2}{2m} (\bar{k} - \bar{G})^2 - \epsilon\right) C(\bar{k} - \bar{G}) + \sum_{\bar{G}'} U_{\bar{G}' - \bar{G}} C(\bar{k} - \bar{G}') = 0$$

In this equation \bar{k} is in the 1st B.Z.

⇒ We have separated problem into N independent problems, one for each value of \bar{k} in the 1st B.Z.

Each problem has solutions that consist of plane waves containing wave vectors $\bar{k} + \bar{G}$

Only \bar{k} -vectors contained to the 1st B.Z. need to be considered. No new states are found with \bar{k} outside the 1st B.Z.

The equation above has infinitely many equations for given \bar{k} in the 1st B.Z. (all different \bar{G})

⇒ Solutions with different energy ϵ

Index these by the band index n , $\epsilon \rightarrow \epsilon_n$

Crystal momentum

Since $\Psi_{\bar{k}}(\vec{r}) = \sum_{\bar{G}} c(\bar{k}-\bar{G}) e^{i(\bar{k}-\bar{G})\cdot\vec{r}}$

$\Rightarrow \hbar\bar{k}$ is not eigenvalue to momentum operator

$$\hat{p} = -i\hbar\nabla$$

$$\Psi_{\bar{k}}(\vec{r}) = e^{i\bar{k}\cdot\vec{r}} u_{\bar{k}}(\vec{r})$$

$$\hat{p}\Psi_{\bar{k}}(\vec{r}) = \hbar\bar{k} \underbrace{e^{i\bar{k}\cdot\vec{r}} u_{\bar{k}}(\vec{r})}_{\Psi_{\bar{k}}(\vec{r})} + \underbrace{e^{i\bar{k}\cdot\vec{r}} \cdot (-i\hbar)\nabla u_{\bar{k}}(\vec{r})}_{\text{additional term}}$$

$\Psi_{\bar{k}}(\vec{r})$ not momentum eigenstate

so now : $\boxed{\bar{p} \neq \hbar\bar{k}}$

$\hbar\bar{k}$ is called crystal momentum

Why do we need to consider only 1st BZ?

We had $\Psi_{\bar{k}}(\vec{r}) = \sum_{\bar{G}} c(\bar{k}-\bar{G}) e^{i(\bar{k}-\bar{G})\cdot\vec{r}}$

$$\Psi_{\bar{k}+\bar{G}'}(\vec{r}) = \sum_{\bar{G}} c(\bar{k}+\bar{G}'-\bar{G}) e^{i(\bar{k}+\bar{G}'-\bar{G})\cdot\vec{r}} \quad \bar{G}' \text{ rec. lattice vector}$$

set $\bar{G}'' = \bar{G}-\bar{G}'$

$$\Rightarrow \Psi_{\bar{k}+\bar{G}'}(\vec{r}) = \sum_{\bar{G}''} c(\bar{k}-\bar{G}'') e^{i(\bar{k}-\bar{G}'')\cdot\vec{r}} = \Psi_{\bar{k}}(\vec{r})$$

$$\boxed{\Psi_{\bar{k}+\bar{G}}(\vec{r}) = \Psi_{\bar{k}}(\vec{r})}$$

$$\boxed{E_{n,\bar{k}+\bar{G}} = E_{n,\bar{k}}}$$

Group velocity

(Velocity of particle = group velocity of wave) ⑨

$$\text{Velocity operator } \hat{v} = \frac{d\vec{r}}{dt} = \frac{1}{i\hbar} [\vec{r}, \hat{H}] = \frac{\hat{p}}{m} = -i\frac{\hbar}{m} \nabla$$

$$\text{Appendix E } \Rightarrow \boxed{\bar{v}_n(\vec{k}) = \bar{v}_{n,\vec{k}} = \frac{1}{\hbar} \frac{\partial \epsilon_{n,\vec{k}}}{\partial \vec{k}}}$$

$$\text{Free electrons: } \epsilon = \frac{\hbar^2 k^2}{2m} \quad \frac{\partial \epsilon}{\partial k} = \frac{\hbar^2 k}{m} \quad v = \frac{\hbar k}{m}$$

Forces

$$v_g = \frac{\partial \omega}{\partial k}$$

$$E = \hbar \omega$$

(time dep. Schrödinger...)

$$\Rightarrow v_g = \frac{1}{\hbar} \frac{\partial E}{\partial k}$$

Study force \vec{F} acting during time δt .

$$\text{Added energy: } \delta E = \vec{F} \cdot \underbrace{\bar{v}_g}_{\text{distance}} \delta t = \vec{F} \cdot \left(\frac{1}{\hbar} \frac{\partial E}{\partial k} \right) \delta t$$

$$\text{But } \delta E = \frac{\partial E}{\partial k} \delta k \quad \rightarrow \text{some approximations...}$$

$$\Rightarrow \frac{\delta k}{\delta t} = \frac{\vec{F}}{\hbar}$$

$$\boxed{\hbar \frac{d\vec{k}}{dt} = \vec{F}}$$

$$\text{Ex. } \vec{F} = -e\vec{E}$$

$$\frac{d\vec{k}}{dt} = -\frac{e\vec{E}}{\hbar}$$

$$\boxed{\hbar \frac{d\vec{k}}{dt} = -e(\vec{E} + \vec{v}_g \times \vec{B})}$$

equation of motion

Requirements:

- 1) well-defined \vec{k}
- 2) — " — \vec{E}, \vec{B}
($\Delta x \ll \lambda_f$)
macroscopic fields

The free electron wave function $\Psi(\vec{r}) = C \cdot e^{i\vec{k} \cdot \vec{r}}$
 with energy $E = \frac{\hbar^2 k^2}{2m}$

is a special case of Bloch functions.

$$\Psi_{\vec{k}}(\vec{r}) = U_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad \text{where } U_{\vec{k}}(\vec{r}) = \text{const.}$$

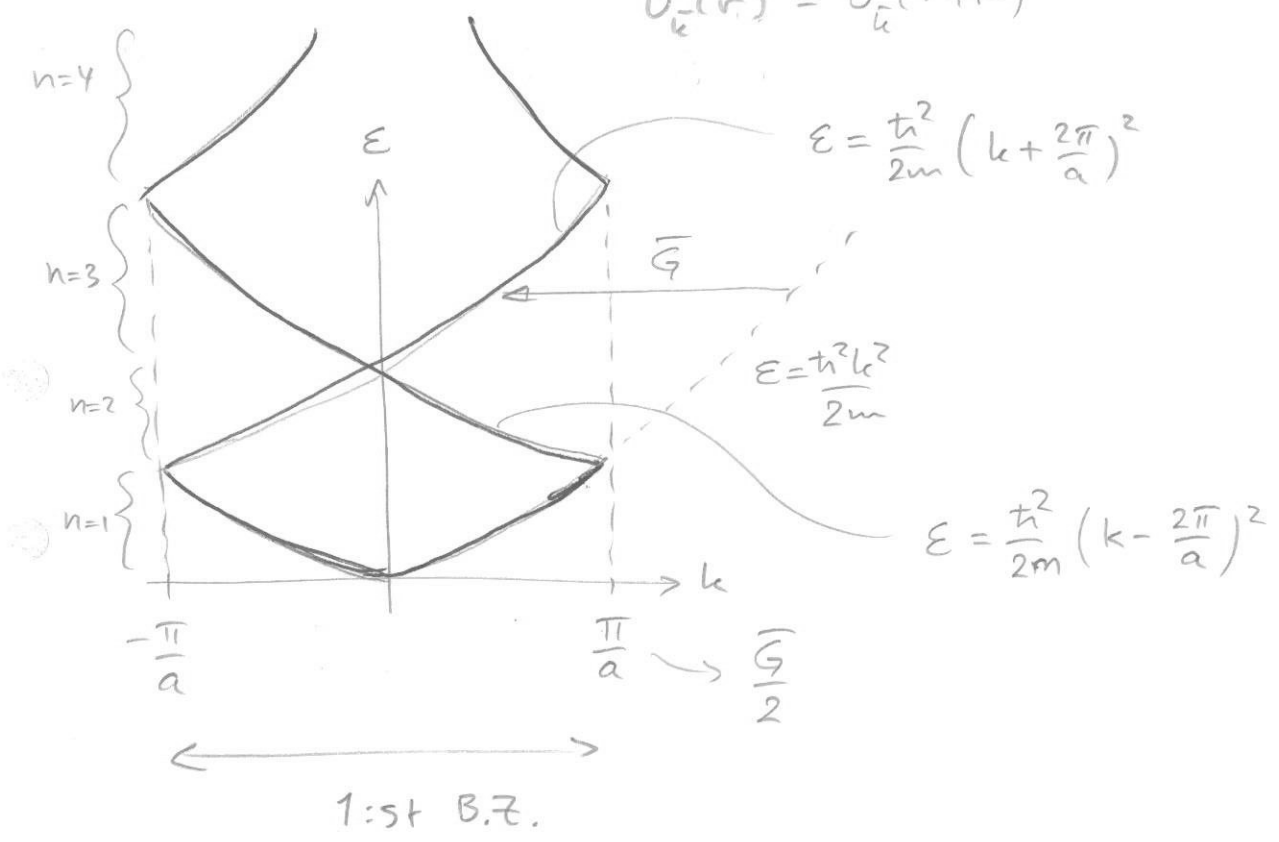
$$U_{\vec{k}}(\vec{r}) = U_{\vec{k}}(\vec{r} + \vec{R})$$

But with Bloch notation \vec{k} is limited to 1:st B.Z.

Choose \vec{G} so that \vec{k} is in the 1:st B.Z.

$$\Rightarrow \Psi_{\vec{k}}(\vec{r}) = C \cdot e^{i\vec{G} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{r}}$$

$$U_{\vec{k}}(\vec{r}) = U_{\vec{k}}(\vec{r} + \vec{R})$$



General
 The volume of the 1:st B.Z. is $\frac{8\pi^3}{V_c}$
 Volume per \vec{k} -point $\frac{8\pi^3}{V}$
 \Rightarrow Each "band" has $\frac{V}{V_c} = N$ levels \rightarrow number of cells.
 Spin $\uparrow\downarrow \Rightarrow 2N$ states/band

Adding periodic potential



Electron waves "Bragg-scatter" at B.Z. boundary

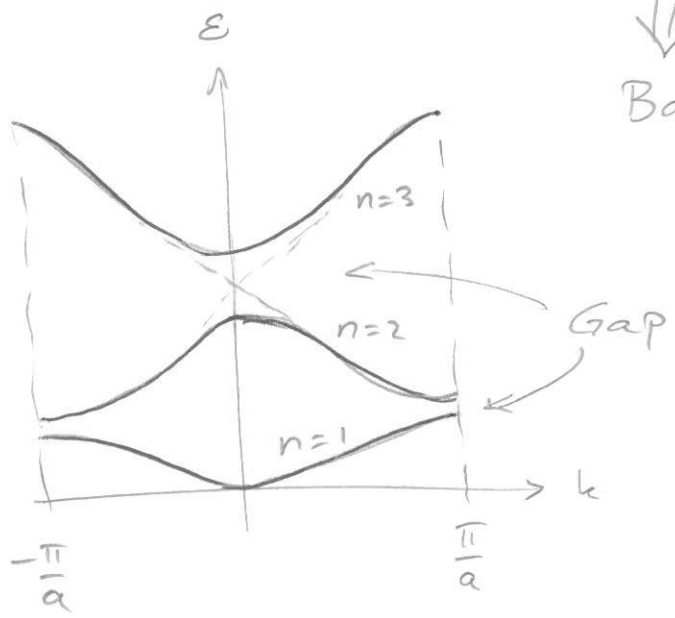
Compare Laue condition

$\vec{k} \cdot \vec{G} = \frac{1}{2}G \iff$ Scattering when \vec{k} touches B.Z. boundary



Strongest influence on $E(\vec{k})$ at B.Z. boundary.

⇓
Band gap at B.Z. boundaries.



⇓
"BANDS"
 $n = 1, 2, 3, \dots$

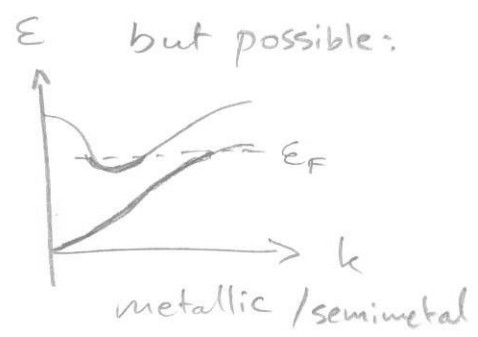
If the valence Z is even \implies band may be filled completely.

————— " ————— odd

⇓
may be isolator
but possible:

Fermi surface
 $E_F = E(\vec{k}_F)$
⇓
 \vec{k}_F ————— no longer sphere

⇓
Metal



Van Hove singularities

The density of states of the system with periodic pot.

$$g(E) = \sum_n g_n(E)$$

/
 band index

It can be shown $g_n(E) = \frac{1}{4\pi^3} \int_{S_n(E)} \frac{dS}{|\frac{\partial E_n}{\partial k}|}$

/
 constant energy surface

Ex. $g_n(E_F) = \text{integral over Fermi surface of } \frac{1}{\frac{\partial E}{\partial k}}$

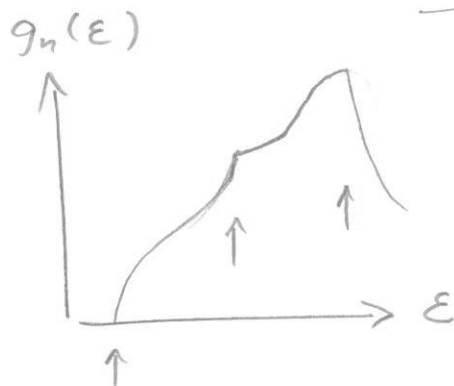
Close to the Brillouin zone boundary:

$$\hbar v_g = \frac{\partial E}{\partial k} \rightarrow 0 \implies \text{density of states integrand diverges}$$



divergence of $\frac{dg_n}{dE}$

called Van Hove Singularity



Typical $g_n(E)$ not smooth

Effective mass

$$v_g = \frac{1}{\hbar} \frac{\partial E}{\partial k} \qquad \bar{F} = \hbar \frac{d\bar{k}}{dt}$$

$$\frac{d}{dt} v_g = \frac{1}{\hbar} \frac{\partial^2 E}{\partial k^2} \frac{d\bar{k}}{dt} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \cdot \bar{F}$$

~
"a"

Define $\boxed{\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}}$

Effective mass m^*

Free electrons: $\frac{\partial^2 E}{\partial k^2} = \frac{\hbar^2}{m}$

$$\Rightarrow m^* = m = \text{const.}$$

Generally: $m^* = m^*(\bar{k})$

	<u>Free electrons</u>	<u>Bloch electrons</u>
Quantum number	\bar{k}	\bar{k}, n
Momentum	$\bar{p} = \hbar \bar{k}$	$\hbar \bar{k} \neq \bar{p}$
Energy	$E = \frac{\hbar^2 k^2}{2m}$	$E_{n,\bar{k}}$ no simple expression
Velocity	$\bar{v} = \frac{\hbar \bar{k}}{m} = \frac{1}{\hbar} \frac{\partial E}{\partial \bar{k}}$	$\bar{v}_{n,\bar{k}} = \frac{1}{\hbar} \frac{\partial E_{n,\bar{k}}}{\partial \bar{k}}$
Mass	m	$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}$
Wavefunc.	$\psi_{\bar{k}}(\bar{r}) = \left(\frac{1}{V}\right)^{1/2} e^{i\bar{k} \cdot \bar{r}}$	$\psi_{n,\bar{k}}(\bar{r}) = U_{n,\bar{k}}(\bar{r}) e^{i\bar{k} \cdot \bar{r}}$ $U_{n,\bar{k}}(\bar{r}) = U_{n,\bar{k}}(\bar{r} + \bar{R})$ no simple expression