Any stationary states in a periodic crystals are called Bloch states.

Properties of Bloch states

1) $\hat{\vec{P}} = -i\hbar\vec{\nabla}$ does not commute with $\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2 + U(\vec{r})$, except when there is a free electron.

$\Downarrow$

    a) $\psi_{\vec{k}}$ are not eigenfunctions of $\hat{\vec{P}}$ (NOT PLANE WAVES)

    b) $\vec{P}$ does not have a definite value $\left(\vec{P} \neq \hbar\vec{k}\right)$ QUASI-MOMENTUM (CRYSTAL MOMENTUM)

    NOT CONSERVED

    $\hbar\vec{k} = \hbar\vec{g}$

    RECIPROCAL VECTOR

2) $\langle\vec{P}\rangle = \displaystyle\int \psi_{\vec{k}}^* \hat{\vec{P}} \psi_{\vec{k}} \, dV \implies \dfrac{\langle\hat{\vec{P}}\rangle}{m} = \langle\vec{v}\rangle = \dfrac{1}{\hbar}\dfrac{\partial\mathcal{E}(\vec{k})}{\partial\vec{k}} = \dfrac{1}{\hbar}\vec{\nabla}_{\vec{k}}\,\mathcal{E}(\vec{k})$ AVERAGE VELOCITY

Lecture #10

Periodic boundary conditions

For a non-free electron we can only know the average velocity $\langle\vec{v}\rangle$. That is similar to the group velocity of a wave packet.
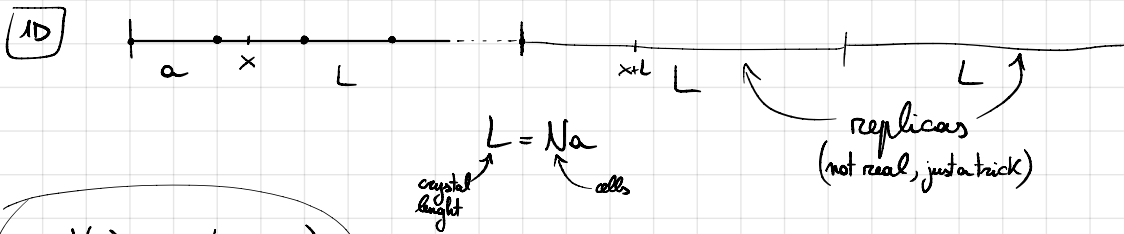
Wave packet

$\psi = \displaystyle\int_{K_0-\Delta K}^{K_0+\Delta K} A e^{i(Kx-\omega t)} dK$ Quantum particle $\mathcal{E} = \hbar\omega$ $p = \hbar K$

HEISENBERG PRINCIPLE

$\Delta x \Delta p \approx \hbar$

LOCALISED PARTICLE

$\boxed{\vec{v}_g = \dfrac{\partial\omega(K)}{\partial K}}$

$\mathcal{E} = \hbar\omega = \dfrac{\hbar^2 K^2}{2m}$

$\vec{v}_g = \dfrac{1}{\hbar}\dfrac{\partial\mathcal{E}(\vec{k})}{\partial\vec{k}}$

Similarity to average velocity

Finite crystal + translational symmetry? Periodic boundary conditions known as Born-Von Karman conditions must be applied.

1D

$L = Na$

crystal lenght

cells

replicas (not real, just a trick)

$\boxed{\psi(x) = \psi(x+Na)}$

All the macroscopic properties do not depend on boundary conditions (except for the surface)

3D

$\psi(\vec{r}) = \psi(\vec{r} + N_1\vec{a}_1)$
$\psi(\vec{r}) = \psi(\vec{r} + N_2\vec{a}_2)$
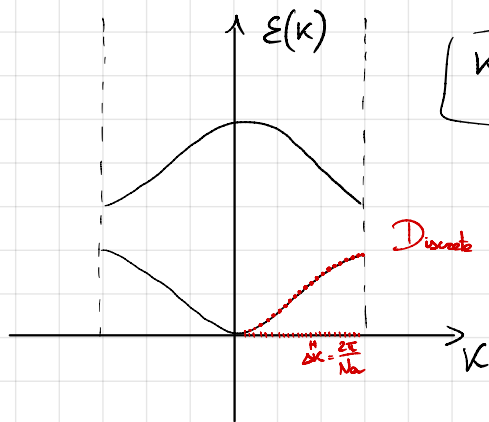$\psi(\vec{r}) = \psi(\vec{r} + N_3\vec{a}_3)$

$N_1 N_2 N_3 = N_{TOT}$ cells

Now let's consider Bloch theorem too in 1D.

$\psi_K(x) = \psi_K(x+Na) = e^{iKNa}\psi_K(x)$

REMEMBER THAT BLOCH FUNCTION IS NOT PERIODIC FOR EVERY TRANSLATION; HERE IT IS BECAUSE WE ARE TRANSLATING FOR THE CRYSTAL LENGHT.

$e^{iKNa} = 1 \iff KNa = m2\pi \rightsquigarrow K = m\dfrac{2\pi}{Na} = m\dfrac{2\pi}{L}$

$$K = m\frac{2\pi}{L}$$ allowed values of K

Discrete values of energy are allowed! (almost continue though)

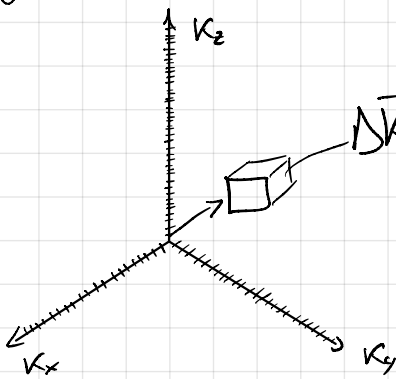$$-\frac{N}{2} < m \le \frac{N}{2} \leadsto \text{\# permitted } K \text{ in } 1^{st} BZ = N \quad (\text{as well as energy levels})$$

$\Delta K = \frac{2\pi}{Na}$

Let's extend this concept in 3D.

$$\vec{g} = 2\pi\left(h\vec{b_1} + k\vec{b_2} + \ell\vec{b_3}\right) \rightarrow \text{for PBC, permitted } \vec{K}: \quad \vec{K}_{m_1,m_2,m_3} = 2\pi\left(\frac{m_1\vec{b_1}}{N_1} + \frac{m_2\vec{b_2}}{N_2} + \frac{m_3\vec{b_3}}{N_3}\right)$$

$$-\frac{N_1}{2} < m_1 \le \frac{N_1}{2} \text{ and so on}$$

Once again # permitted $K = N_1 N_2 N_3 = N_{TOT}$.

$$\Delta\vec{K} = \frac{(2\pi)^3}{V_P N_{TOT}} = \frac{V_{P,RL}}{N_{TOT}} = \frac{(2\pi)^3}{V}$$

Density of states in the reciprocal space

$$\frac{1}{\Delta\vec{K}} = \frac{V}{(2\pi)^3}$$

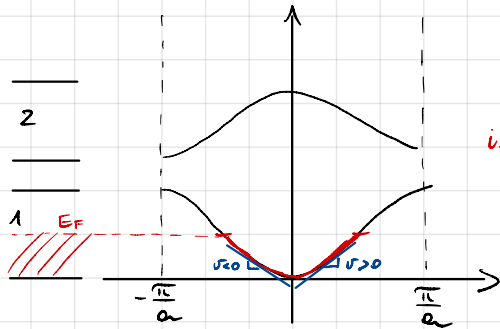Each Bloch state is univocally determined by m_1, m_2, m_3

Basis

Step back to 1D $\Longrightarrow$ N cells
s atoms in the basis
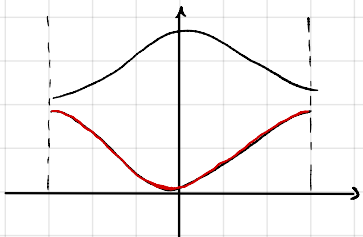m_v valence electrons

$N s m_v = \text{\# itinerant electrons}$

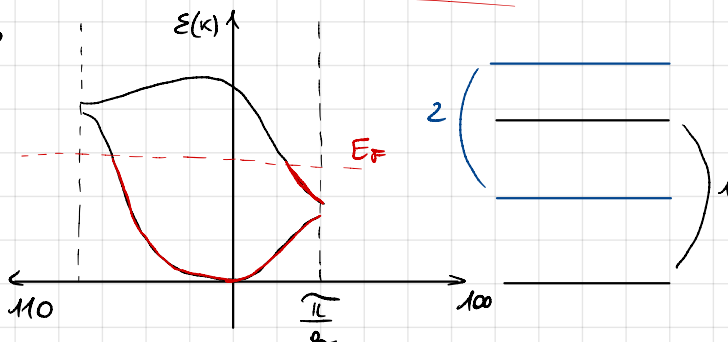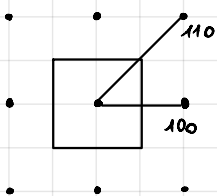$\dfrac{N s m_v}{2N} = \dfrac{s m_v}{2} = \text{\# filled bands}$

electrons in a band

i.e. $s = 1$
$m_v = 1$
$\Downarrow$
$\#f.b. = \frac{1}{2}$

2
1 E_F

$-\frac{\pi}{a}$ $\quad$ $\frac{\pi}{a}$

$v<0$ $\quad$ $v>0$

$S = 1$
$M_v = 2$
$\Downarrow$
$\#f.b. = 1$ INSULATOR? **NO** it is a metal!

1D representation is incorrect

$\mathcal{E}(K)$

110
100

E_F

110 $\quad$ $\frac{\pi}{a}$ $\quad$ 100

two bands are partially filled

2
1

$\downarrow$

CONDUCTOR
(overlapping bands)

Potential considerations

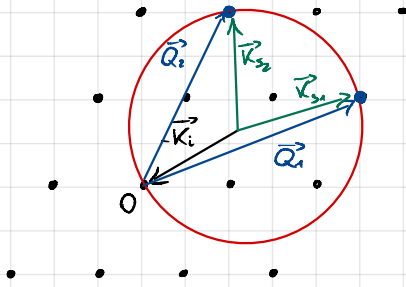$$U(\vec{r}) = U_{el-ion} + U_{MEAN}$$

— screening potential
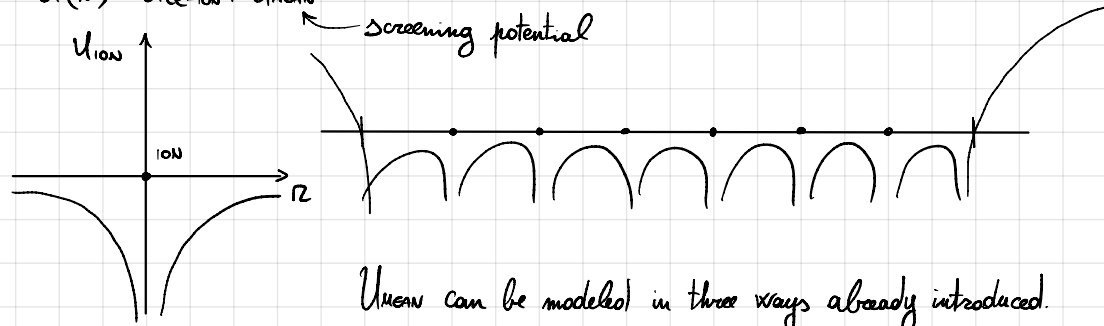
U_{MEAN} can be modeled in three ways already introduced.

1) $U = 0$ FREE e^-

2) $U \neq 0$ SMALL ⟶ PERTURBATION (NEARLY FREE e^-)

3) $U \neq 0$ STRONG ⟶ TIGHT BINDING

Tutorial #5

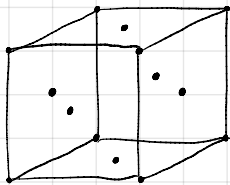Laue condition for diffraction : $\vec{Q} = \vec{K}_s - \vec{K}_i = \vec{g}_{hke}$

Ewald sphere construction (visualize diffraction)

1) Draw $-\vec{K}_i$ in RL
2) Draw a sphere of radius K_i
3) Find the RL points touched by the sphere
4) Draw $\vec{Q}$ for each point
5) Find allowed $\vec{K}_s$

Calculate diffraction peaks

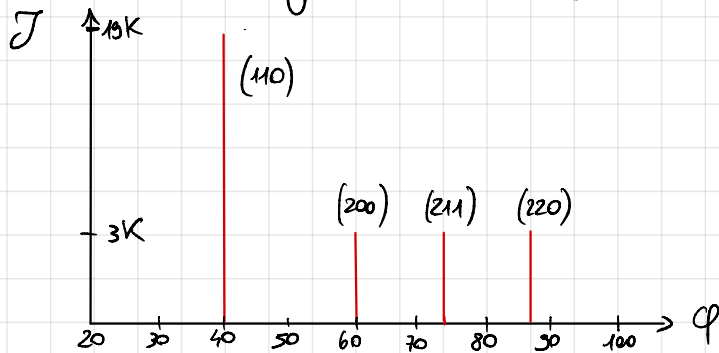Polycrystalline Ni FCC, $a = 3.52$ Å , $\lambda = 0.988$ Å

$$\vec{g}_{hke} = \frac{2\pi}{a}\left(h\vec{x} + K\vec{y} + \ell\vec{z}\right)$$

$$g_{hke} = \frac{2\pi}{a}\sqrt{h^2 + K^2 + \ell^2}$$

$$d_{hke} = \frac{2\pi}{g_{hke}} = \frac{a}{\sqrt{h^2 + K^2 + \ell^2}}$$

$2K_s \sin\vartheta = g$
$2d_{hke}\sin\vartheta = \lambda$
$\varphi = 2\vartheta = 2\arcsin\left(\frac{\lambda}{2d_{hke}}\right)$

Calculate a given the spectrum

φ	ϑ	$\sin\vartheta$
40,42	20,21	0,345
58,36	29,18	0,487
73,33	36,665	0,597
86,91	43,455	0,688

$$\begin{cases} 2d_{hke}\sin\vartheta = \lambda \\ d_{hke} = \dfrac{2\pi}{g_{hke}} = \dfrac{a}{\sqrt{h^2+K+\ell^2}} \end{cases}$$

Comment why XRD spectra of Na (BCC) and CsCl (BCC) look different
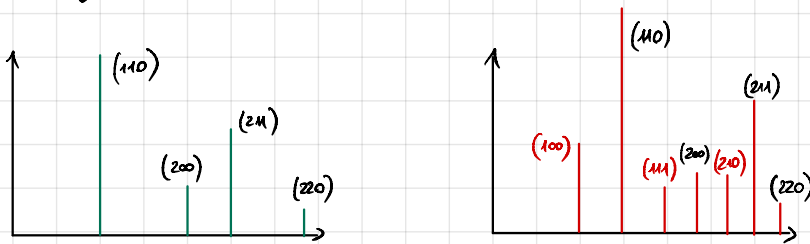
It depends on the atomic form factor $f_p(g)$.

$\boxed{Na}$ $T_{hke} = f_{Na}(g)\left[e^{-ig r_1} + e^{-ig r_2}\right] = f_{Na}(g)\left[1 + (-1)^{h+K+\ell}\right] = \begin{cases} 0 & \text{if } h+K+\ell \text{ odd} \\ 2f_{Na} & \text{if } h+K+\ell \text{ even} \end{cases}$

$\boxed{CsCl}$ $T_{hke} = f_{Cs}(g)e^{-ig r_1} + f_{ce}(g)e^{-ig r_2} = f_{Cs}(g) + f_{ce}(g)(-1)^{h+K+\ell} \neq 0 \text{ if } h+K+\ell \text{ odd}$

Lecture #11

Free electron model

__Empty lattice__
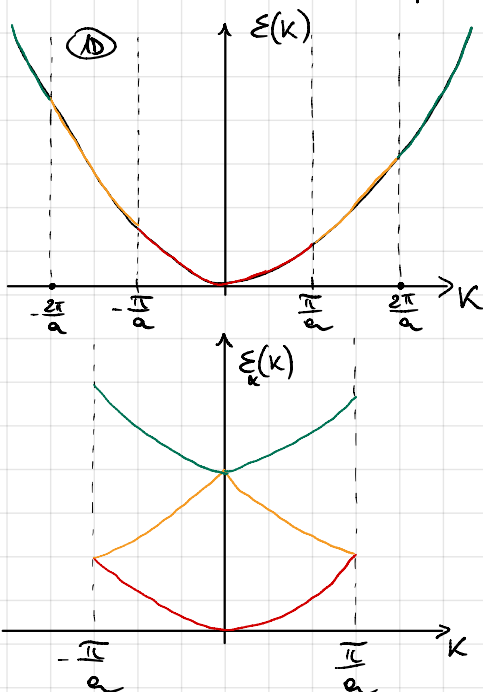
$U(\vec{r}) = 0$

$\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2$

$\hat{H}\psi = \mathcal{E}\psi \implies \psi(\vec{r}) = \dfrac{1}{\sqrt{V}}e^{i\vec{K}\cdot\vec{r}} \rightsquigarrow V = \int_V |\psi|^2 dV = 1$

$\psi_{\vec{K}} = \underbrace{U_{\vec{K}}(\vec{r})}_{\text{Constant for } U=0} e^{i\vec{K}\cdot\vec{r}}$

$?\begin{cases} \mathcal{E}(\vec{K}) = \dfrac{\hbar^2 K^2}{2m} = \dfrac{\hbar^2 |\vec{K}|^2}{2m} \\ \mathcal{E}_\alpha(\vec{K}) \end{cases}$ $\psi_{\vec{K}}(\vec{r}) = \dfrac{1}{\sqrt{V}}e^{i\vec{K}\cdot\vec{r}} \rightsquigarrow \psi_{\vec{K}}(\vec{r}+\vec{n}) = \dfrac{1}{\sqrt{V}}e^{i\vec{K}\cdot\vec{r}}e^{i\vec{K}\cdot\vec{n}}$
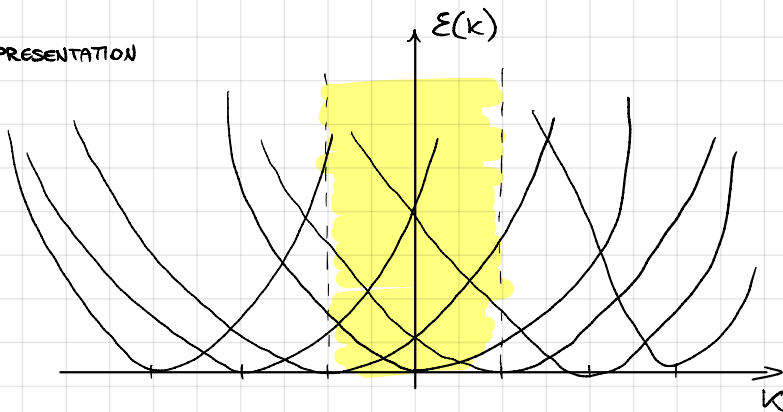
Is that the same representation?

EXTENDED ZONE REPRESENTATION

$g_n = n\dfrac{2\pi}{a}$
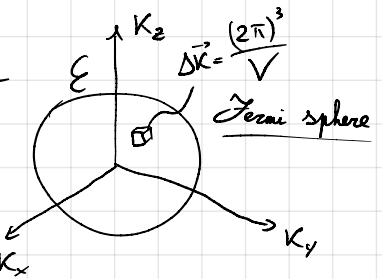
REDUCED ZONE REPRESENTATION

SAME K, DIFFERENT $\mathcal{E}$

$\mathcal{E}_{RZ}(K) = \mathcal{E}_{EZ}(K') = \dfrac{\hbar^2 K'^2}{2m} = \dfrac{\hbar^2(K+g)^2}{2m}$

if $K' = K+g$

Obviously in 2D the representation is more complicated. In 3D that would be $\mathcal{E}_{\vec{k}} = \frac{\hbar^2 (K_x^2 + K_y^2 + K_z^2)}{2m}$

Isoenergetic surfaces

Those surfaces suffice $\mathcal{E}(\vec{k}) = \mathcal{E}_F$ constant.
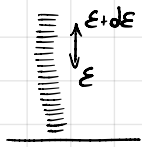We must remember that we have a discrete number of K.

$N = \int_{\mathcal{E}_1}^{\mathcal{E}_2} g(\mathcal{E}) d\mathcal{E}$

$\Delta \vec{k} = \frac{(2\pi)^3}{V}$

Fermi sphere

$dN = g(\mathcal{E}) d\mathcal{E}$

#states with energy from $\mathcal{E}$ to $\mathcal{E} + d\mathcal{E}$

Density of states in RL $\frac{1}{\Delta \vec{k}}$

Density of electronic states in energy
$g(\mathcal{E}) = \frac{dN(\mathcal{E})}{d\mathcal{E}}$

where $N(\mathcal{E})$ is the total number of states having energy from 0 to $\mathcal{E}$.

$\mathcal{E} = \frac{\hbar^2 K^2}{2m}$

$\Downarrow$

$K = \frac{\sqrt{2m\mathcal{E}}}{\hbar}$

$\longrightarrow$ $N(\mathcal{E}) = \frac{\frac{4}{3}\pi K^3(\mathcal{E})}{\frac{(2\pi)^3}{V}} \cdot 2 \overset{\text{POSSIBLE SPINS}}{} \implies g(\mathcal{E}) = \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\mathcal{E}}$

$g(\mathcal{E})$ $\sqrt{\mathcal{E}}$
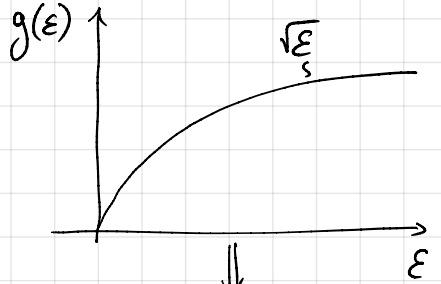
We can calculate the Fermi energy: $N(\mathcal{E}_F) = N_{TOT}$ $\left(N \sim K^3 \sim \mathcal{E}^{3/2}\right)$
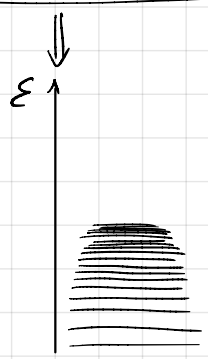
$K(\mathcal{E}_F) = (3\pi^2 n)^{1/3} = K_F$ where $n = \frac{N_{TOT}}{V}$ electron density
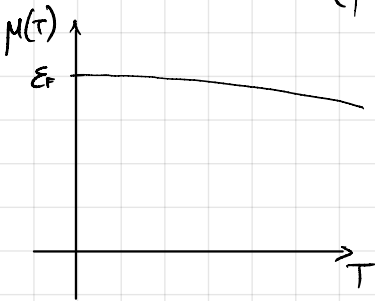
Fermi wavevector

$\mathcal{E}_F = \frac{\hbar^2 K_F^2}{2m} \sim n^{2/3} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$ This is when $T = 0$

If $T \neq 0$ we have to use the Fermi-Dirac statistics: $f(\mathcal{E}, T) = \frac{1}{e^{\frac{\mathcal{E}-\mu}{KT}} + 1}$ ← CHEMICAL POTENTIAL

$\mu(T) = \frac{U - TS - pV}{N} \rightsquigarrow \begin{cases} \mu(T=0) = \mathcal{E}_F \\ \mu(T\neq 0) \approx \mathcal{E}_F \end{cases}$

$\mu(T)$, $\mathcal{E}_F$

For us, the chemical potential will always be the Fermi energy. Now let's plot the Fermi-Dirac statistics.

$f(\mathcal{E},T)$ KT T $\frac{1}{2}$ $\mathcal{E}_F$ $\mathcal{E}$ $T = 0$
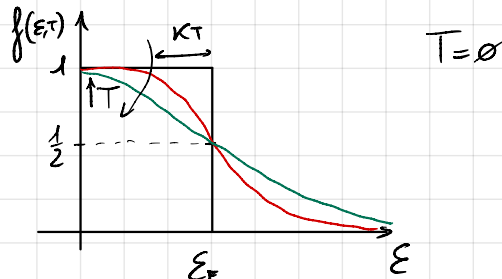
Density of occupied states $\left(g(\mathcal{E})f(\mathcal{E},T)\right)$

$N_{TOT} = \int_0^{\mathcal{E}_F} g(\mathcal{E}) d\mathcal{E} = N(\mathcal{E}_F) = \int_0^{+\infty} g(\mathcal{E}) f(\mathcal{E},T) d\mathcal{E}$

$g(\mathcal{E}) = \frac{dN(\mathcal{E})}{d\mathcal{E}}$

Total energy

$U = \int_0^{+\infty} \mathcal{E} g(\mathcal{E}) f(\mathcal{E},T) d\mathcal{E}$

Specific heat
$C_V = \frac{\partial U}{\partial T}\Big|_V$

$g(\mathcal{E}) f(\mathcal{E},T)$ $f(\mathcal{E},T)$ $g(\mathcal{E})$ $\mathcal{E}$
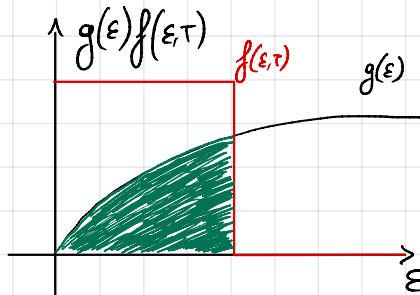
Nearly free electron model

$$g(\varepsilon) \sim \sqrt{\varepsilon} \qquad U = \int_{-\infty}^{+\infty} \varepsilon g(\varepsilon) f(\varepsilon) \, d\varepsilon \qquad U_0 = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) \, d\varepsilon \qquad \text{Energy at } T=0$$

$$C_V = \left. \frac{\partial U}{\partial T} \right|_V \qquad \longleftarrow \quad \text{We want to calculate this in a qualitative way.}$$

$$\int_{\varepsilon_1}^{\varepsilon_2} g(\varepsilon) \, d\varepsilon = \# \text{ states with } \varepsilon \in [\varepsilon_1, \varepsilon_2]$$

DIFFERENCE WHEN T CHANGES
∫ (ELECTRONS ARE EXCITED)

$$\delta N = g(\varepsilon_F) KT$$

GAINED
ENERGY
$$\delta U = \delta N KT = g(\varepsilon)(KT)^2$$
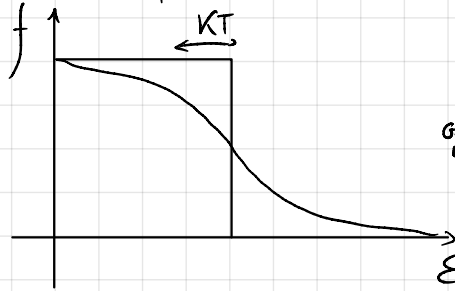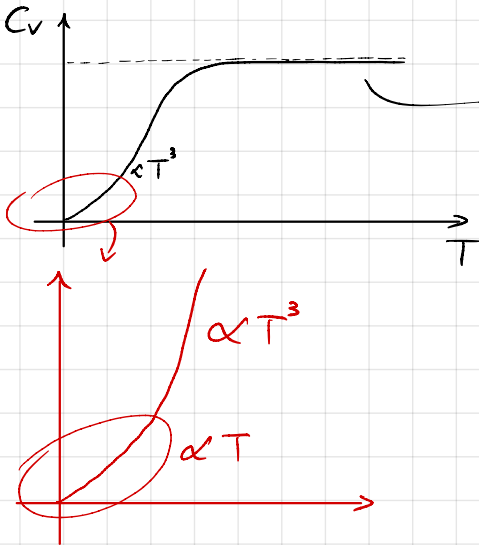
And so $C_V \approx 2 K^2 T g(\varepsilon_F)$

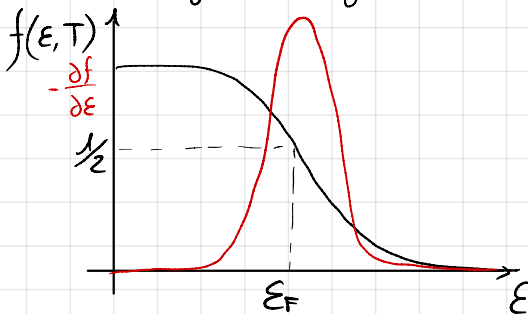$$\left(\text{Exact result: } \frac{\pi^2}{3} K^2 T g(\varepsilon_F) \right)$$

Linear dependence on T is the most important aspect.

→ Heat is absorbed by lattice (ion) vibrations; electrons do not give any contribution unless T is very small.

$\propto T^3$

αT^3

αT

Sommerfeld expansion

It is a tool to calculate integrals including Fermi-Dirac distribution.

$f(\varepsilon, T)$

$-\frac{\partial f}{\partial \varepsilon}$

$\frac{1}{2}$

ε_F

$$\int_0^{+\infty} -\frac{\partial f}{\partial \varepsilon} \, d\varepsilon = 1$$

If $T=0$, $-\frac{\partial f}{\partial \varepsilon}$ becomes a delta in ε_F.

$$\lim_{T \to 0} \left(-\frac{\partial f}{\partial \varepsilon} \right) = \delta(\varepsilon - \varepsilon_F)$$

ANY FUNCTION OF ENERGY

$$\int_0^{+\infty} H(\varepsilon) \left(-\frac{\partial f}{\partial \varepsilon} \right) d\varepsilon = H(\mu) + \frac{\pi^2}{6} \left. \frac{\partial^2 H}{\partial \varepsilon^2} \right|_\mu K^2 T^2 + \cdots \qquad \text{OR} \qquad \int_0^{+\infty} G(\varepsilon) f(\varepsilon, T) \, d\varepsilon = \int_0^\mu G(\varepsilon) \, d\varepsilon + \frac{\pi^2}{6} \left. \frac{\partial G}{\partial \varepsilon} \right|_\mu K^2 T^2 + \cdots$$

SMALL TERMS   SMALL TERMS

$$N_{TOT} = \int_0^{\varepsilon_F} g(\varepsilon) \, d\varepsilon = \int_0^{+\infty} g(\varepsilon) f(\varepsilon, T) \, d\varepsilon \longrightarrow \mu(T) = \varepsilon_F - \cdots$$

SOMETHING
VERY
SMALL

Free electron model is very rough, so when can it be applied? If we have electrons sent from outside to a periodic crystal we get diffraction, but also the inside electrons interact with one another (we have still a diffraction). That's when this model becomes uneffective.

$$\boxed{\vec{K_i} \cdot \frac{\vec{g}}{g} = \frac{g}{2}}$$ _Laue condition of diffraction_
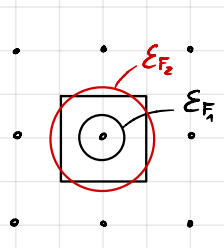
$$\mathcal{E}_F \sim m^{\frac{2}{3}}$$
$$K_F \sim m^{\frac{1}{3}}$$

For the second case, electrons generate diffraction.

Free electron model is valid until the Fermi sphere is enclosed in Bragg planes. Specifically, it is good for metals with low electronic density ($N_V - 1$).

Time independent perturbation theory

$$\hat{H}_o \quad \text{UNPERTURBED} \quad \leadsto \quad \hat{H}_o \varphi_m = \mathcal{E}_m^{(o)} \varphi_m \quad \underline{\text{we Know the solution}}$$

$$\begin{cases} \hat{H} = \hat{H}_o + \hat{V} \\ \hat{V} = \lambda \hat{W} \quad \text{a \underline{small} perturbation is added} \quad (\lambda \ll 1) \end{cases}$$
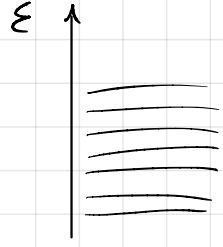
$$\hat{H} \psi_m = \mathcal{E}_m \psi_m ? \quad \text{The solution will be similar to the previous case if } \lambda \text{ is small.}$$

$$\varphi_m \longrightarrow \psi_m \; ?$$
$$\mathcal{E}_m^{(o)} \longrightarrow \mathcal{E}_m \; ?$$

HOW ????

NON DEGENERATE UNPERTURBED SPACE IF $M \neq m$, $\mathcal{E}_m^{(o)} \neq \mathcal{E}_m^{(o)}$

$\mathcal{E} \uparrow$

UNPERTURBED LEVELS

MATRIX ELEMENT $V_{Km} = \int \varphi_K^* \hat{V} \varphi_m \, dV$

$$\psi_m \approx \varphi_m + \sum_{K \neq m} \frac{V_{Km}}{\mathcal{E}_m^{(o)} - \mathcal{E}_K^{(o)}} \varphi_K + \cdots \qquad \text{STOP AT } 1^{ST} \text{ ORDER}$$

$$\mathcal{E}_m \approx \mathcal{E}_m^{(o)} + V_{mm} + \sum_{K \neq m} \frac{|V_{mm}|^2}{\mathcal{E}_m^{(o)} - \mathcal{E}_K^{(o)}} + \cdots \qquad \text{STOP AT } 2^{ND} \text{ ORDER}$$

$\alpha \lambda$ $\alpha \lambda^2$

Perturbation mixes the new state with other stationary states. If we have degenerate states (two for simplicity):

much more mixing K m

φ_1 φ_2 $\mathcal{E}^{(o)}$

$$\psi_m = a_1 \varphi_1 + a_2 \varphi_2$$
$$\mathcal{E} = \mathcal{E}^{(o)} + \Delta \mathcal{E}$$

φ_1 φ_2
$\mathcal{E}_o$ $\mathcal{E}_o$

$\mathcal{E}^+$
$2|V_{12}|$
$\mathcal{E}^-$
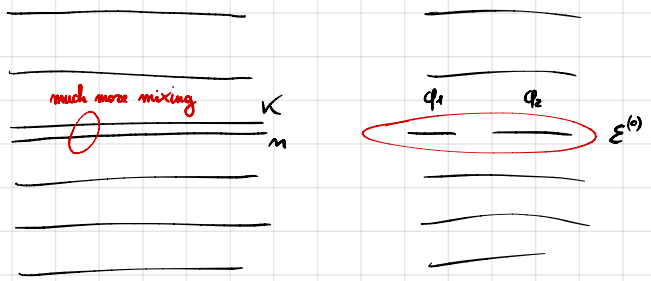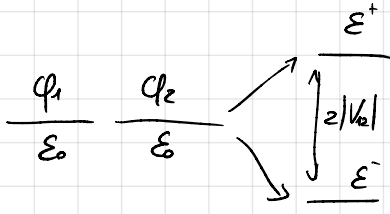
$$\mathcal{E}^{\pm} = \mathcal{E}^{(o)} \pm |V_{12}|$$

MATRIX ELEMENT $V_{12} = \int \varphi_2^* \hat{V} \varphi_1 \, dV$

$\left(\overline{\text{Perturbation removes degeneration}}\right)$

Nearly free electron model

$$\hat{V} = \mathcal{U}(\vec{r}) \; \underline{\text{SMALL}} \quad \text{(shape is not important)}$$

$$\hat{H}_o = -\frac{\hbar^2}{2m} \nabla^2 \quad \text{as expected}$$

Perturbation is actually crystal potential.

Now let's consider the perturbed energy to the 2nd order.

$$\mathcal{E}(\vec{K}) \approx \frac{\hbar^2 |\vec{K}|^2}{2m} + V_{\vec{K}\vec{K}} + \sum_{\vec{K}' \neq \vec{K}} \frac{|V_{\vec{K}\vec{K}'}|^2}{\mathcal{E}_{\vec{K}}^{(0)} - \mathcal{E}_{\vec{K}'}^{(0)}}$$

$$V_{\vec{K}\vec{K}} = \int \varphi_{\vec{K}}^* \hat{V} \varphi_{\vec{K}} \, dV = \frac{1}{V} \int e^{-i\vec{K}\cdot\vec{n}} U(\vec{n}) e^{i\vec{K}\cdot\vec{n}} \, dV = \bar{U}$$

ELECTRONS ARE STILL FREE

plane waves are normalized by $\frac{1}{\sqrt{V}}$

if V is big
$$\int e^{-i(\vec{Q}-\vec{g})\cdot\vec{n}} \, dV = \delta(\vec{Q}-\vec{g})$$

$$V_{\vec{K}'\vec{K}} = \frac{1}{V} \int e^{-i\vec{K}\cdot\vec{n}} U(\vec{n}) e^{i\vec{K}'\cdot\vec{n}} \, dV = \int e^{-i(\vec{K}-\vec{K}')\cdot\vec{n}} U(\vec{n}) \, dV = \frac{1}{V} \sum_{\vec{g}} U_{\vec{g}} \int e^{-i(\vec{K}-\vec{K}'-\vec{g})\cdot\vec{n}} \, dV$$

$$\boxed{\begin{array}{l} U(\vec{n}) = U(\vec{n}+\vec{m}) \\ U(\vec{n}) = \sum_{\vec{g}} U_{\vec{g}} e^{i\vec{g}\cdot\vec{n}} \end{array}}$$

$$\underbrace{V \delta_{\vec{K}-\vec{K}', \vec{g}}}$$
Kronecker delta

$\nearrow 1$ $0 \searrow$
if $\vec{K}-\vec{K}'=\vec{g}$ if $\vec{K}-\vec{K}'\neq\vec{g}$

$\vec{K}$ does not mix with any $\vec{K}'$, but only with the ones that satisfy $\vec{K}-\vec{K}' = \vec{g}$

negligible (not important)

$$\mathcal{E}(\vec{K}) \approx \frac{\hbar^2 |\vec{K}|^2}{2m} + \cancel{\bar{U}} + \sum_{\vec{g}\neq 0} \frac{|U_{\vec{g}}|^2}{\mathcal{E}_{\vec{K}}^{(0)} - \mathcal{E}_{\vec{K}-\vec{g}}^{(0)}} = \frac{\hbar^2 |\vec{K}|^2}{2m} + \sum_{\vec{g}\neq 0} \frac{|U_{\vec{g}}|^2}{\frac{\hbar^2 |\vec{K}|^2}{2m} - \frac{\hbar^2 |\vec{K}-\vec{g}|^2}{2m}}$$
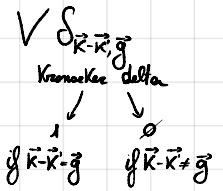
STATES MUST NOT BE DEGENERATE

We have a degenerate situation when $|\vec{K}|^2 = |\vec{K}-\vec{g}|^2 \implies \boxed{\vec{K}\cdot\frac{\vec{g}}{g} = \frac{g}{2}}$

Supporting lecture #2

Time independent perturbation theory

It is one way to solve Schrödinger equation.

$$\hat{H}\psi = \mathcal{E}\psi \qquad \hat{H} = \hat{H}_0 + \hat{V}$$

Perturbation operator

$$\boxed{\hat{V} = \lambda \hat{W} \quad \text{with} \quad \lambda \ll 1}$$

We already know the solution for $\hat{H}_0$

$$\hat{H}_0 \, \varphi_m = \mathcal{E}_m^{(0)} \varphi_m$$

$$\int \varphi_i^* \varphi_j \, dV = \delta_{ij} = \begin{cases} 1 & \text{if } i=j \\ 0 & \text{if } i\neq j \end{cases} = \langle \varphi_i | \varphi_j \rangle$$

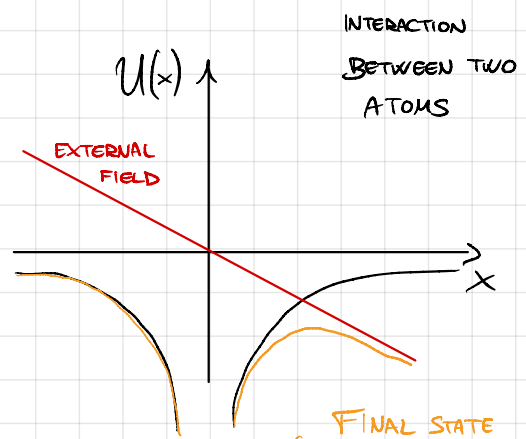1] $\mathcal{E}_m^{(0)}$ values are non degenerate (if $i\neq j$, $\mathcal{E}_i \neq \mathcal{E}_j$)

$$\psi = \sum_K \alpha_K \varphi_K \qquad \text{LINEAR COMBINATION OF UNPERTURBED STATES}$$

$$\hat{H}\psi_m = \mathcal{E}_m \psi_m \qquad \text{when is it that } \varphi_m \to \psi_m ?$$

$$\mathcal{E}_m = \mathcal{E}_m^{(0)} + \lambda \mathcal{E}_m^{(1)} + \lambda^2 \mathcal{E}_m^{(2)} + \cdots \qquad ①$$

$$\alpha_K = \underbrace{\delta_{Km}}_{\alpha_K^{(0)}} + \lambda \alpha_m^{(1)} + \lambda^2 \alpha_m^{(2)} + \cdots \qquad ②$$

just ideas

INTERACTION BETWEEN TWO ATOMS

$U(x)$

EXTERNAL FIELD

x

FINAL STATE (DUE TO PERTURBATION)

The stronger the external field, the stronger the perturbation.

$$\psi = \sum_K a_K \varphi_K \qquad \text{Solution ?}$$

$$\hat{H}_0 \psi_m + \lambda \hat{W} \psi_m = \mathcal{E}_m \psi_m$$

$$\sum_K a_K \underbrace{\hat{H}_0 \varphi_K}_{\mathcal{E}_K^{(0)} \varphi_K} + \lambda \sum_K a_K \hat{W} \varphi_K = \mathcal{E}_m \sum_K a_K \varphi_K$$

$$\sum_K a_K \mathcal{E}_K^{(0)} \int \varphi_m^* \varphi_K dV + \lambda \sum_K a_K \int \varphi_m^* \hat{W} \varphi_K dV = \mathcal{E}_m \sum_K a_K \underbrace{\int \varphi_m^* \varphi_K dV}_{\delta_{mK}}$$

$$a_m \mathcal{E}_m^{(0)} + \lambda \sum_K a_K W_{mK} = \mathcal{E}_m a_m \longrightarrow \boxed{\left(\mathcal{E}_m - \mathcal{E}_m^{(0)} \right) a_m = \lambda \sum_K a_K W_{mK}}$$

Schrödinger equation rewritten with a_m and a_K

$$W_{mK} = \int \varphi_m^* \hat{W} \varphi_K dV = <m|\hat{W}|K>$$

$$\left(\mathcal{E}_m^{(0)} + \lambda \mathcal{E}_m^{(1)} + \lambda^2 \mathcal{E}_m^{(2)} + \cdots - \mathcal{E}_m^{(0)} \right) \left(\delta_{mn} + \lambda a_m^{(1)} + \lambda^2 a_m^{(2)} + \cdots \right) = \lambda \sum_K \left(\delta_{Km} + \lambda a_K^{(1)} + \lambda^2 a_K^{(2)} + \cdots \right) W_{mK}$$

a) $\boxed{m = M}$

Now we compare terms of the same order

AVERAGE VALUE OF PERTURBATION FOR STATE m

$$\mathcal{E}_m^{(1)} = W_{mm} \qquad \text{1}^{ST}\text{ ORDER CORRECTION} \quad \mathcal{E}_m^{(1)} = W_{mm} = \int \varphi^* \hat{W} \varphi_m dV \Rightarrow \mathcal{E}_m \cong \mathcal{E}_m^{(0)} + \lambda W_{mm} = \mathcal{E}_m^{(0)} + V_{mm} = \mathcal{E}_m^{(0)} + <V>_m$$

$$\underbrace{\mathcal{E}_m^{(1)} a_m^{(1)}}_{\text{NEGLIGIBLE}} + \mathcal{E}_m^{(2)} = \sum_K a_K^{(1)} W_{mK} \qquad \text{2}^{ND}\text{ ORDER CORRECTION} \quad \mathcal{E}_m^{(2)} = \sum_{K \neq m} \frac{|V_{Km}|^2}{\mathcal{E}_m^{(0)} - \mathcal{E}_K^{(0)}}$$

b) $\boxed{m \neq m}$

$$a_m^{(1)} \left(\mathcal{E}_m^{(0)} - \mathcal{E}_m^{(0)} \right) = W_{mn}$$

$$\mathcal{E}_m^{(1)} a_m^{(1)} + \left(\mathcal{E}_m^{(0)} - \mathcal{E}_m^{(0)} \right) a_m^{(2)} = \sum_K a_K^{(1)} W_{mK}$$

$a_m^{(1)} = \dfrac{W_{mn}}{\mathcal{E}_m^{(0)} - \mathcal{E}_m^{(0)}}$

For 1st order approximation it is true that

$$\psi_m \approx \varphi_m + \sum_{K \neq m} \frac{V_{Km}}{\mathcal{E}_m^{(0)} - \mathcal{E}_K^{(0)}} \varphi_K$$

For 2nd order approximation then

$$\mathcal{E}_m \approx \mathcal{E}_m^{(0)} + V_{mm} + \sum_{K \neq m} \frac{|V_{Km}|^2}{\mathcal{E}_m^{(0)} - \mathcal{E}_K^{(0)}}$$

$$\psi \qquad\qquad\qquad \mathcal{E}$$

$$\boxed{V_{Km} = \lambda W_{Km} = \lambda \int \varphi_K^* \hat{W} \varphi_m dV} \qquad \text{If the matrix element of the perturbation } V_{Km} \text{ increases, the mixing is stronger.}$$

CONDITION: $|V_{Km}| \ll |\mathcal{E}_m^{(0)} - \mathcal{E}_K^{(0)}| \quad \forall K \neq m$

$\boxed{2}$ Degenerate levels (just two for simplicity)

IN GENERAL
$$\psi = \sum_{K=1}^S a_K \varphi_K \qquad \hat{H}_0 \varphi_K = \mathcal{E}^{(0)} \varphi_K \quad \forall K$$

HERE
$$\psi = a_1 \varphi_1 + a_2 \varphi_2$$

$$\begin{cases} \hat{H}_0 \varphi_1 = \mathcal{E}^{(0)} \varphi_1 \\ \hat{H}_0 \varphi_2 = \mathcal{E}^{(0)} \varphi_2 \end{cases}$$

$$\hat{H} = \hat{H}_0 + \hat{V}$$
$$\mathcal{E} = \mathcal{E}^{(0)} + \Delta \mathcal{E}$$

$$\longrightarrow |a_1|^2 + |a_2|^2 = 1$$
NORMALIZATION

$$\begin{cases} \int \varphi_1^* \hat{H} \psi \, dV = \int \varphi_1^* \mathcal{E} \psi \, dV \\ \int \varphi_2^* \hat{H} \psi \, dV = \int \varphi_2^* \mathcal{E} \psi \, dV \end{cases} \Longrightarrow \begin{cases} (V_{11} - \Delta\mathcal{E}) a_1 + V_{12} a_2 = 0 \\ V_{21} a_1 + (V_{22} - \Delta\mathcal{E}) a_2 = 0 \end{cases}$$

$$\underbrace{\begin{bmatrix} V_{11} - \Delta\mathcal{E} & V_{12} \\ V_{21} & V_{22} - \Delta\mathcal{E} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \underline{0}}_{\det V = 0}$$

$$\Delta\mathcal{E} = \frac{1}{2}\left[V_{11} + V_{12} \pm \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2} \right] \Longrightarrow V_{11} = \int \varphi_1^* \hat{V} \varphi_1 \, dV \quad \boxed{\text{if } V_{11} = V_{22} = 0, \ \mathcal{E} = \mathcal{E}^{(0)} \pm |V_{12}|}$$

if $V_{12} \in \mathbb{R}, \ V_{12} < 0 \Longrightarrow \begin{cases} a_1 = \pm \frac{1}{\sqrt{2}} \\ a_2 = \mp \frac{1}{\sqrt{2}} \end{cases} \qquad \mathcal{E}^{(0)} \begin{cases} \mathcal{E}^+ = \mathcal{E}^{(0)} + |V_{12}| \\ \mathcal{E}^- = \mathcal{E}^{(0)} - |V_{12}| \end{cases}$

For more than two degenerate levels

$$\begin{cases} \psi_m = \sum_{K=1}^{s} a_K \varphi_{mK} \\ \hat{H} \varphi_{mK} = \mathcal{E}_m^{(0)} \varphi_{mK} \end{cases} \Longrightarrow \sum_{K=1}^{s} \left(H_{mK} - \mathcal{E}_m \delta_{mK} \right) a_K = 0 \qquad (m = 1, \dots, s)$$

$$\begin{vmatrix} H_{11} - \mathcal{E}_m & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} - \mathcal{E}_m & & \\ H_{31} & & H_{33} - \mathcal{E}_m & \\ \vdots & & & \end{vmatrix} = 0 \qquad \underline{\text{We find } s \text{ solutions}}$$

Lecture #13

Degenerate states

Fermi velocity, Fermi energy and Fermi temperature describe the crystal.

$$v_F \triangleq \frac{P_F}{m} = \frac{\hbar K_F}{m} \qquad \lambda_F = \frac{2\pi}{K_F} \qquad \mathcal{E}_F = K T_F$$

We consider the unperturbed state as the free electron gas; the perturbation is small.

$$\mathcal{E}(\vec{K}) = \frac{\hbar^2 K^2}{2m} + \cancel{U_0} + \sum_{\vec{g} \neq 0} \frac{|U_{\vec{g}}|^2}{\frac{\hbar^2}{2m}\left(|\vec{K}|^2 - |\vec{K} - \vec{g}|^2\right)} \qquad U_{\vec{g}} = \frac{1}{V_P} \int_{V_P} U(\vec{r})\, e^{-i\vec{g}\cdot\vec{r}} \, d\vec{r}$$

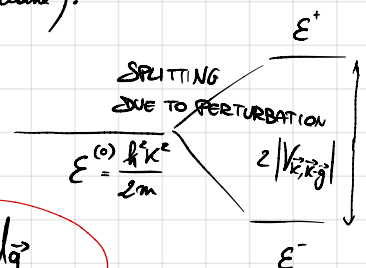CORRECTION IS BIG WHEN DENOMINATOR IS SMALL

When $\vec{K} \cdot \frac{\vec{g}}{g} = \frac{g}{2}$ we have a degenerate situation ($\vec{K}$ is on a Bragg plane).
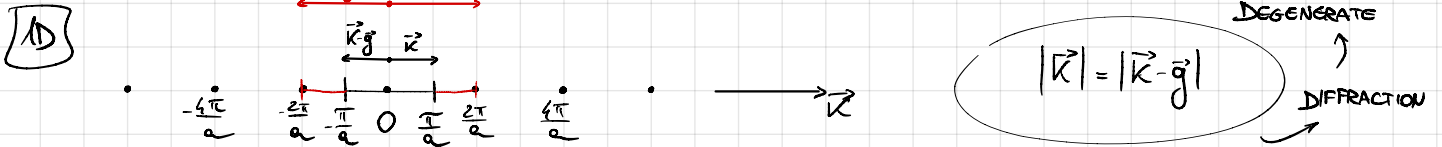
Degenerate perturbation theory

$\psi = a_1 \varphi_{\vec{K}} + a_2 \varphi_{\vec{K} - \vec{g}}$ \qquad Perturbation affects only same energy states.
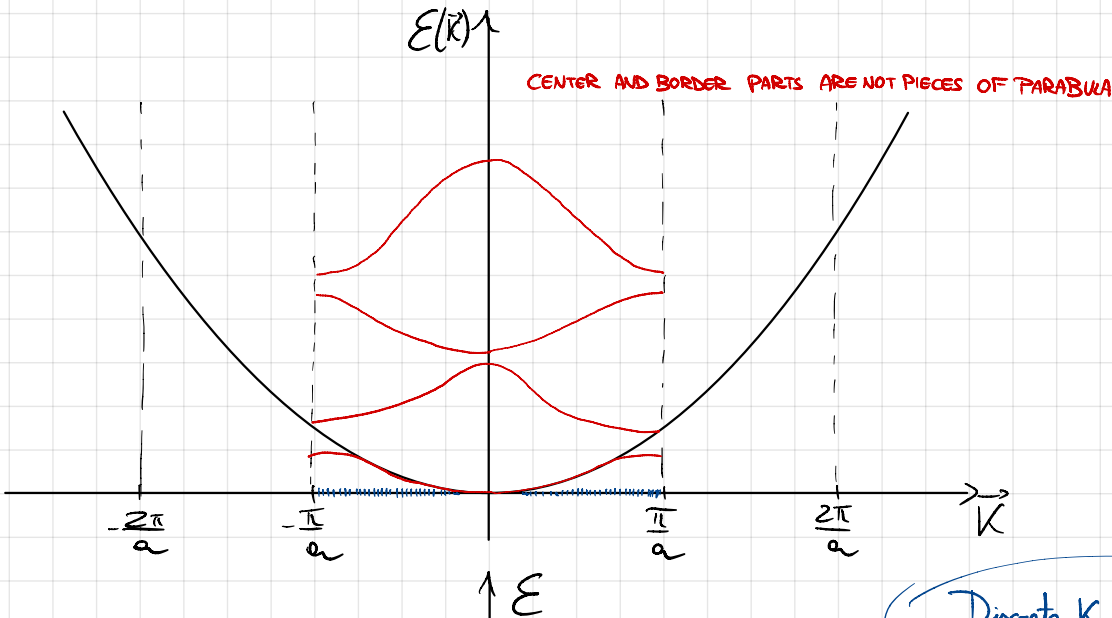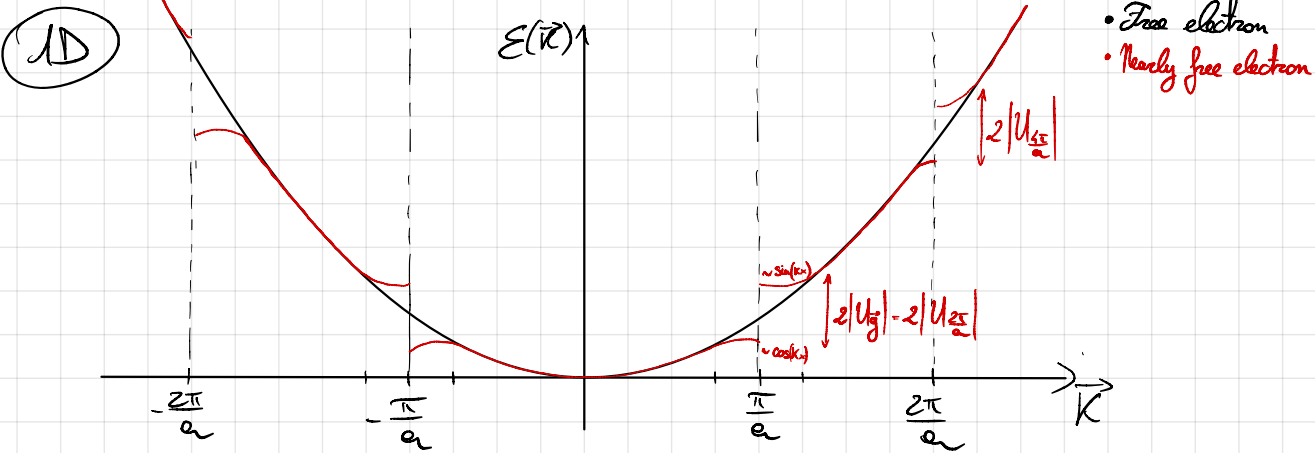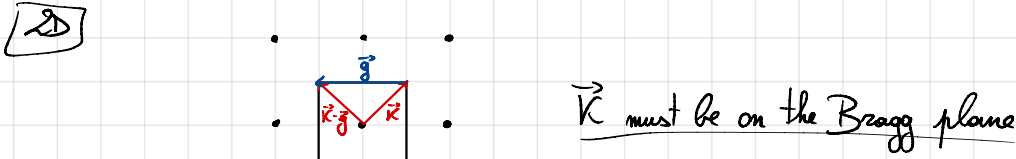
$$V_{\vec{K}, \vec{K} - \vec{g}} = \int \varphi_{\vec{K}}^* \hat{V} \varphi_{\vec{K} - \vec{g}} \, dV = \frac{1}{V} \int e^{-i\vec{K}\cdot\vec{g}} U(\vec{r}) e^{i(\vec{K} - \vec{g})\cdot\vec{r}} = \frac{1}{V} \int e^{i\vec{g}\cdot\vec{r}} U(\vec{r}) \, dV = \boxed{U_{\vec{g}}}$$

$\mathcal{E}^+$ \
SPLITTING DUE TO PERTURBATION \
$\mathcal{E}^{(0)} = \frac{\hbar^2 K^2}{2m}$ \qquad $2|V_{\vec{K}, \vec{K} - \vec{g}}|$ \
$\mathcal{E}^-$

What is like to have $\vec{K}$ and $\vec{K}-\vec{g}$ in a crystal?

①

$\vec{K}-\vec{g}$ $\vec{K}$

$\vec{K}-\vec{g}$ $\vec{K}$

$-\frac{4\pi}{a}$ $-\frac{2\pi}{a}$ $-\frac{\pi}{a}$ 0 $\frac{\pi}{a}$ $\frac{2\pi}{a}$ $\frac{4\pi}{a}$ $\longrightarrow \vec{K}$

$\boxed{|\vec{K}| = |\vec{K}-\vec{g}|}$ DEGENERATE   DIFFRACTION

Correction here is not small.

②

$\vec{g}$

$\vec{K}-\vec{g}$ $\vec{K}$

$\vec{K}$ must be on the Bragg plane

①

$\mathcal{E}(\vec{K})$

• Free electron
• Nearly free electron

$2|U_{\frac{4\pi}{a}}|$

$\sim \sin(k_x)$

$2|U_{\frac{\pi}{a}}| - 2|U_{\frac{2\pi}{a}}|$

$\sim \cos(k_x)$

$-\frac{2\pi}{a}$ $-\frac{\pi}{a}$ $\frac{\pi}{a}$ $\frac{2\pi}{a}$ $\vec{K}$

$\mathcal{E}(\vec{K})$

CENTER AND BORDER PARTS ARE NOT PIECES OF PARABOLA

$-\frac{2\pi}{a}$ $-\frac{\pi}{a}$ $\frac{\pi}{a}$ $\frac{2\pi}{a}$ $\vec{K}$

$\mathcal{E}$

For Block states, $\langle \vec{v} \rangle = \frac{1}{\hbar} \vec{\nabla} \mathcal{E}(\vec{K})$

On the Brillouin borders,   GAPS
$\langle \vec{v} \rangle = 0$

STATIONARY STATES
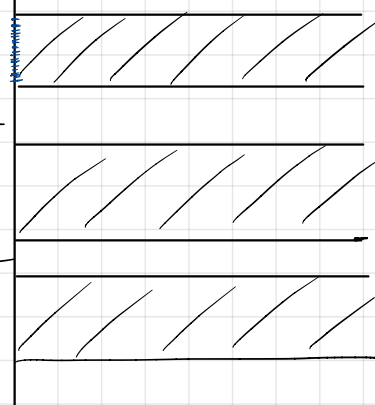
$\boxed{\text{Discrete } K, \text{ discrete } \mathcal{E}}$

Wavefunction at Bragg planes

$\psi = a_1 \varphi_{\vec{K}} + a_2 \varphi_{\vec{K}-\vec{g}}$

SPLITTING IN ENERGY $\begin{array}{c} -\sim\sin \text{ } (\mathcal{E}^-)\\ +\sim\cos \text{ } (\mathcal{E}^+)\end{array}$

① $\psi \sim e^{iKx} \mp e^{i(K-g)x} = e^{iKx} \mp e^{-iKx}$

$\underbrace{K-g=-K}$

a
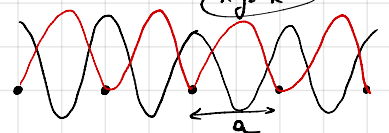
$K = \frac{\pi}{a}$

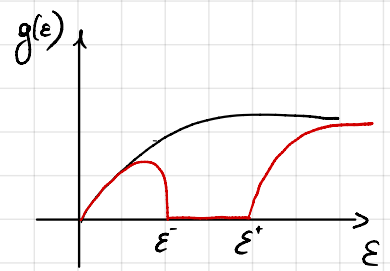In the free electron model, isoenergetic surfaces are spheres: $\mathcal{E} = \dfrac{\hbar^2 k^2}{2m}$

Mixing of degenerate states at Bragg planes can be interpreted as a diffraction by the potential. When this happens, $\vec{K}$ is diffracted into $\vec{K} \mp \vec{g}$, so $\mathcal{E}\left(\frac{\pi}{a}\right)$ is diffracted into $\mathcal{E}\left(-\frac{\pi}{a}\right)$ and vice versa.

NOT VALID

IN THE NFE MODEL
A DISTORTION BECOMES NOTICEABLE BY GETTING CLOSER TO BRAGG PLANES, UNTIL IT BECOMES A DISCONTINUITY

$\vec{K}$ representation

$\mathcal{E}$ representation

$\mathcal{E}(\vec{K})$

2

$\mathcal{E}_F$

1

110   100
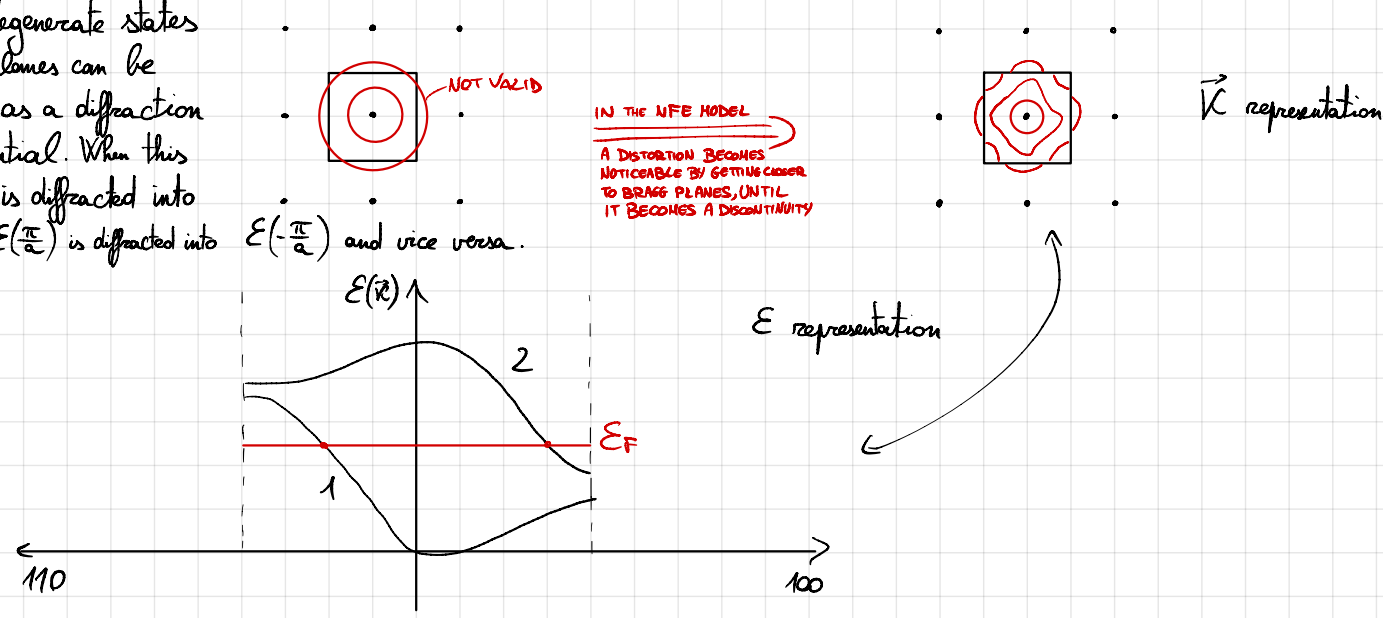
Now we compute density of states in the most generic way.

$$g(\mathcal{E}) = \frac{dN}{d\mathcal{E}} \rightsquigarrow N = \int_{\mathcal{E}_1}^{\mathcal{E}_2} g(\mathcal{E}) d\mathcal{E}$$

$g(\mathcal{E}) \sim \sqrt{\mathcal{E}}$ in FE MODEL

$g(\mathcal{E})$

$\mathcal{E}^-$ $\mathcal{E}^+$ $\mathcal{E}$

In the NFE we have gaps:

$\mathcal{E}$

$\mathcal{E}^+$

$\mathcal{E}^-$

K_z

$\vec{K}$ $dS_{\mathcal{E}}$

INFINITESIMAL ELEMENT OF ISOENERGETIC SURFACE
(SPHERE IN FE, SOMETHING ELSE IN NFE)

K_y

K_x

$dS_{\mathcal{E}}$

$\mathcal{E}+d\mathcal{E}$

$\vec{K}$

$\mathcal{E}$

$dK_\perp$
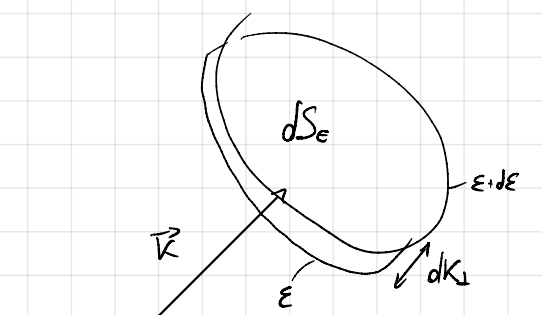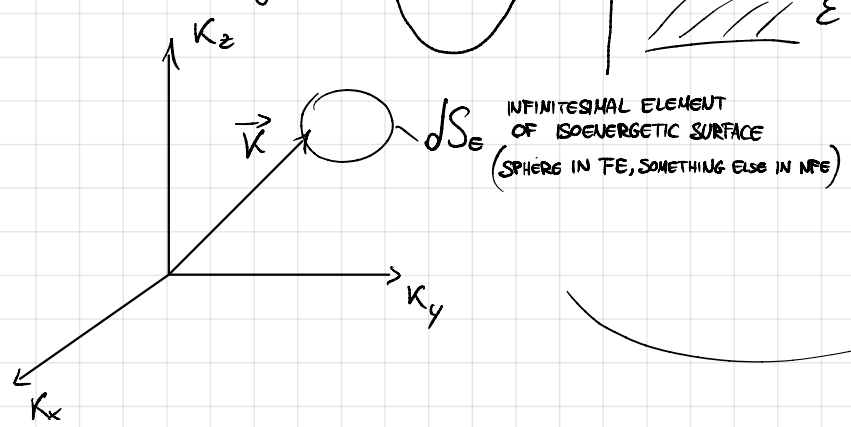
DISCRETE $\vec{K}$

$\Delta \vec{K} = \dfrac{(2\pi)^3}{V}$

$g(\vec{K}) = \dfrac{1}{\Delta K}$

STATES IN INFINITESIMAL VOLUME

$$\Delta K = dS_{\mathcal{E}} \, dK_\perp \rightsquigarrow dN = g(\vec{K}) \, dS_{\mathcal{E}} \, dK_\perp$$

How many states ($\vec{K}$) in the shell $\mathcal{E}, \mathcal{E}+d\mathcal{E}$?

$$dN_{\substack{\text{ISOEN} \\ \text{SHELL}}} = \int_{S_{\mathcal{E}}} \frac{V}{(2\pi)^3} \, dS_{\mathcal{E}} \, dK_\perp = \int_{S_{\mathcal{E}}} \frac{2V}{(2\pi)^3} dS_{\mathcal{E}} \frac{d\mathcal{E}}{|\vec{\nabla}\mathcal{E}(\vec{k})|}$$

SPIN

$$g(\mathcal{E}) = \frac{dN}{d\mathcal{E}} = \sum_{\alpha} \frac{2V}{(2\pi)^3} \int_{S_{\mathcal{E}}} \frac{dS_{\mathcal{E}}}{|\vec{\nabla}\mathcal{E}_\alpha(\vec{k})|}$$
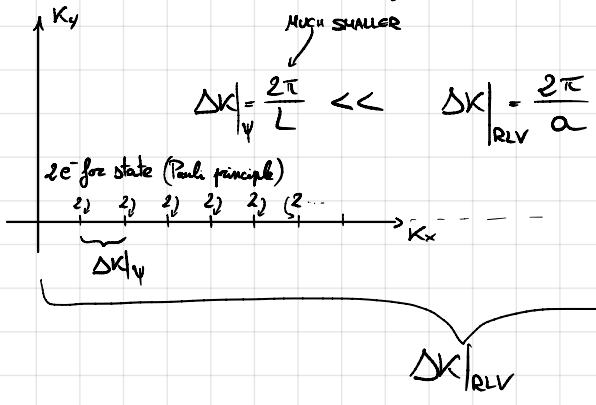
SUM OVER ALL BRANCHES

GENERAL FORMULA

$$|\vec{\nabla}\mathcal{E}(\vec{k})| = \frac{d\mathcal{E}}{dK_\perp}$$ Gradient is always perpendicular to isoenergetic surfaces.

Tutorial #6

The idea behind free electron model is to consider $\psi_{\vec{k}}(\vec{r}) = A e^{i\vec{k}\cdot\vec{r}}$ with $\vec{k} = n_x \frac{2\pi}{L_x}\hat{u}_x + n_y \frac{2\pi}{L_y}\hat{u}_y + n_z \frac{2\pi}{L_z}\hat{u}_z$

and $\varepsilon = \frac{\hbar^2 k^2}{2m}$; are those k comparable to the ones of RL?

QUANTUM NUMBERS

$\left.\Delta k\right|_\psi = \frac{2\pi}{L} << \left.\Delta k\right|_{RLV} = \frac{2\pi}{a}$

MUCH SMALLER

The granularity is much smaller than the RL one.

2 e^- for state (Pauli principle)

All states can be occupied until we run out of electrons; we call this particular border k Fermi wavevector.

$$N(k_F) = 2\frac{\frac{4}{3}\pi k_F^3}{\left.\Delta k^3\right|_\psi} = N_e \implies k_F = (3\pi^2)^{1/3}\left(\frac{N_e}{V}\right)^{1/3}$$

TOTAL NUMBER OF STATES WITHIN A SPHERE OF RADIUS k_F (FERMI SPHERE)

TOTAL NUMBER OF STATES OCCUPIED BY e^-

$\Delta k^3 = \frac{8\pi^3}{V}$

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi^2)^{2/3}\left(\frac{N_e}{V}\right)^{2/3}$$

We now want to highlight the dependence of the number of states on the energy.

$$N(\varepsilon) = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar}\right)^{3/2}$$

$$g(\varepsilon) = \frac{dN(\varepsilon)}{d\varepsilon} = \frac{3}{2}\frac{N_e}{\varepsilon_F}\sqrt{\frac{\varepsilon}{\varepsilon_F}}$$

Also we can find the electron density as

$$\frac{N_e}{V} = \frac{N_a Z e}{V} = Z_e N_{AV}\frac{m}{V} = Z_e N_{AV}\frac{\rho}{M}$$

AVOGADRO NUMBER   MOLES   ATOMIC DENSITY

MOLAR MASS (#PROTONS + #NEUTRONS)

Another rearrangement is

$$\varepsilon_F = \frac{\hbar^2 k_F^2 c^2}{2m c^2} = \frac{(\hbar c)^2}{(mc^2)} \frac{1}{2} k_F^2 = \frac{0.4\,\mu m^2 eV^2}{500\,KeV}\frac{1}{2}\left(1.75\cdot10^6\,\mu m^{-1}\right)^2 = 11.7\ eV$$

500 KeV

just to avoid mass

Doing so we can compute, i.e., $k_F(Al) = 1.75\cdot10^8\ cm^{-1}$

Then, since $k_F \propto \frac{1}{a}$, $\varepsilon_F \propto \frac{\hbar^2}{2m}\frac{1}{a^2}$

Our system can also be thought as a gas of free electron confined in a box; thermodynamic laws are useful.

$(T=0)$

$$U = \int_0^{\varepsilon_F} g(\varepsilon)\,\varepsilon\,d\varepsilon = \frac{3}{2}\frac{N_e}{\varepsilon_F^{3/2}}\left[\frac{2}{5}\varepsilon^{5/2}\right]_0^{\varepsilon_F} = \frac{3}{5}N_e\varepsilon_F$$

$$\boxed{<U> = \frac{U}{N_e} = \frac{3}{5}\varepsilon_F}$$

AVERAGE ENERGY OF THE SYSTEM

$$Q = U + \mathcal{L} \implies U = Q - \mathcal{L}$$

$$dU = TdS - PdV \rightsquigarrow P = -\frac{dU}{dV}$$

$T=0$

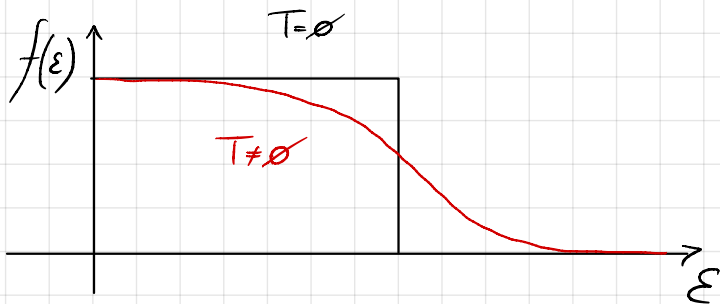$$P_F = -\frac{dU}{dV} = \frac{2}{5}\frac{N_e}{V}\varepsilon_F \quad \text{Fermi pressure} \implies PV = nRT$$

$$B = -V\frac{dP}{dV} \longrightarrow \frac{8}{3}\left|\frac{N_e}{V}\right|\varepsilon_F$$

When $T \neq 0$, situation is of course different.

$$U = \int_{-\infty}^{+\infty} \varepsilon g(\varepsilon) f(\varepsilon) d\varepsilon \qquad\qquad f(\varepsilon) = \frac{1}{1 + e^{\frac{\varepsilon - \mu}{KT}}}$$
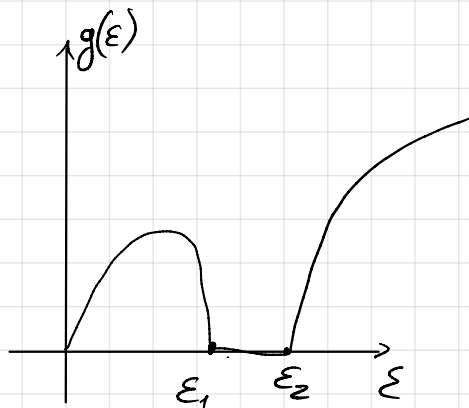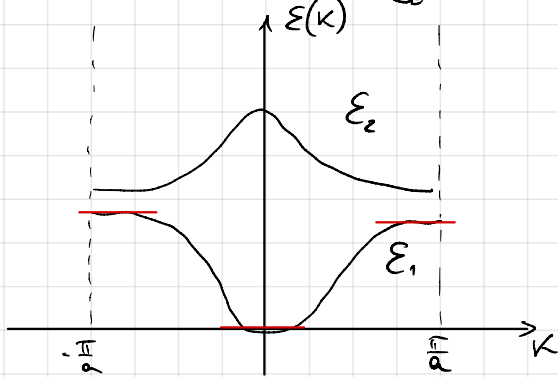

Lecture #14

$$g(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{2V}{(2\pi)^3} \sum_{\alpha} \int \frac{dS_E}{|\vec{\nabla}_{\vec{k}} \varepsilon(\vec{k})|}_{S_E}$$

Tight binding

When $\vec{\nabla} \varepsilon(\vec{k}) = 0$ we have a discontinuity.

Van Hove singularities

$$\sum_{\vec{k}} f(\vec{k}) \longrightarrow \frac{2V}{(2\pi)^3} \int_{RS} f(\vec{k}) d\vec{k}$$

with $\frac{1}{\Delta \vec{k}}$ marked.

To make calculations in the reciprocal space, we have to solve integrals and divide for the discrete volume.

Tight binding model

Potential is now not negligible, but it is still periodic.
$$U(\vec{n}) = U(\vec{n} + \vec{m})$$
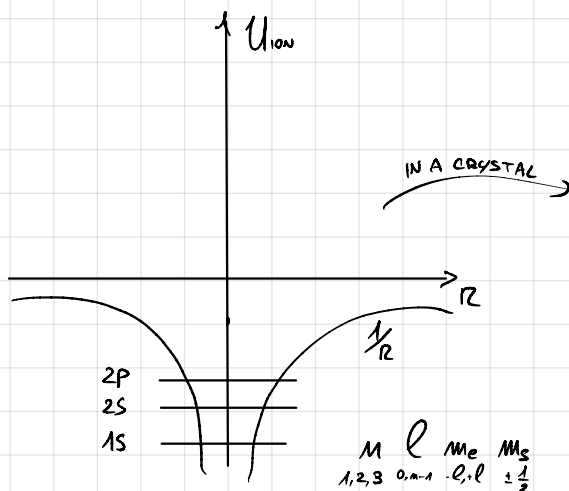
$$\varphi_A = \frac{F_{n\ell}(R)}{R} Y_{\ell m_\ell}(\vartheta, \varphi) X_{m_s}$$

this is a generic wavefunction of an atom

SIMPLE CRYSTAL

$\vec{m}$

$\varphi_A(\vec{n} - \vec{m})$
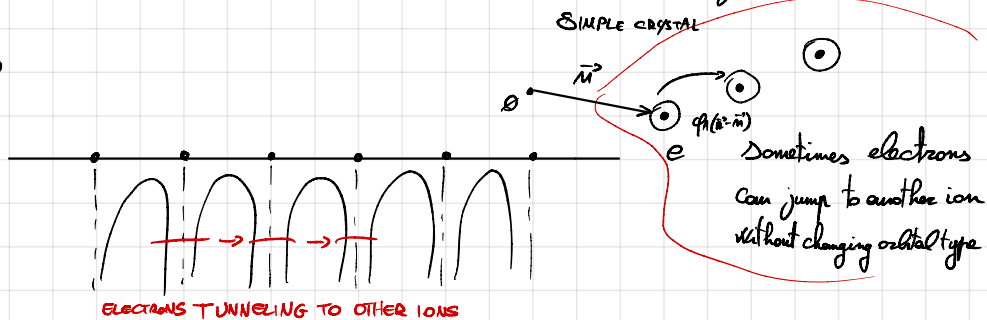
e — sometimes electrons can jump to another ion without changing orbital type

n	ℓ	m_ℓ	m_s
1,2,3	0,n-1	$-\ell, \ell$	$\pm \frac{1}{2}$

ELECTRONS TUNNELING TO OTHER IONS

When an electron is close to an atom, we can write its wavefunction as $\psi_{\vec{k}}(\vec{n}) = \frac{1}{\sqrt{N}} \sum_{\vec{m}} \varphi_A(\vec{n} - \vec{m}) e^{i \vec{k} \cdot \vec{m}}$; function must satisfy

Bloch theorem: $\psi_{\vec{k}}(\vec{n} + \vec{\ell}) = \frac{e^{i \vec{k} \cdot \vec{\ell}}}{\sqrt{N}} \sum_{\vec{m}} \varphi_A(\vec{n} - (\vec{m} - \vec{\ell})) e^{i \vec{k} \cdot (\vec{m} - \vec{\ell})} = \psi_{\vec{k}}(\vec{n}) e^{i \vec{k} \cdot \vec{\ell}}$

This function is not normalized, though.

$$\int |\psi|^2 dV = \int \psi_{\vec{k}}^* \psi_{\vec{k}} \, dV = \frac{1}{N} \sum_{\vec{m},\vec{m}'} e^{i\vec{k}\cdot(\vec{m}-\vec{m}')} \int \varphi_A^*(\vec{n}-\vec{m}') \varphi_A(\vec{n}-\vec{m}) \, dV = 1 + \frac{1}{N} \sum_{\vec{m}\neq\vec{m}'} e^{i\vec{k}\cdot(\vec{m}-\vec{m}')} \int \varphi_A^*(\vec{n}-\vec{m}') \varphi_A(\vec{n}-\vec{m}) dV$$

OVERLAP INTEGRAL
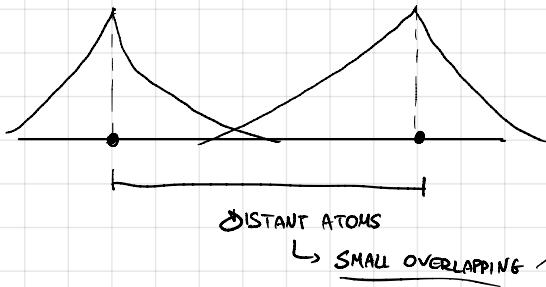
we assume that this is null

DISTANT ATOMS
↳ SMALL OVERLAPPING

$$\Delta U \triangleq U(\vec{n}) - U_0(\vec{n})$$

$$\hat{H}_0 = \hat{T} + U_0 \implies \hat{H}_0 \varphi_A = \mathcal{E}_A \varphi_A$$

U_0

$-\Delta U$

U

$$\mathcal{E}(\vec{k}) = \mathcal{E}_A + (\Delta U)_A + \sum_{\vec{h}\neq\vec{o}} \mathcal{E}_{\vec{h}} e^{i\vec{k}\cdot\vec{h}}$$

ATOMIC ORBITAL RELATED

ADDITION DUE TO BLOCH FUNCTION
(RELEVANT IN SHORT DISTANCES)

What is the energy of the tight binding function?

$$\hat{H}\psi = \mathcal{E}\psi \quad \text{not exactly}$$

We want the average $\mathcal{E}(\vec{k}) = \langle \hat{H} \rangle_{\vec{k}} = \int \psi_{\vec{k}}^* \hat{H} \psi_{\vec{k}} \, dV$

$$\hat{H} = \hat{T} + \overset{*}{\hat{U}} = \hat{T} + U_0 + \Delta U = \hat{H}_0 + \Delta U$$

Kinetic energy — crystal potential — single ion potential

atomic energy

$$\mathcal{E}(\vec{k}) = \langle \hat{H} \rangle_{\vec{k}} = \mathcal{E}_A + \sum_{\vec{h}} \mathcal{E}_{\vec{h}} e^{i\vec{k}\cdot\vec{h}}$$

HOPPING INTEGRAL

$$\boxed{\mathcal{E}_{\vec{h}} \approx \int \varphi_A^*(\vec{n}\cdot\vec{h}) \, \Delta U(\vec{n}) \, \varphi_A(\vec{n}) \, dV}$$

$\vec{h}$
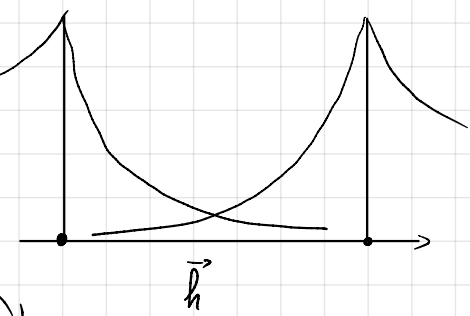
$$\mathcal{E}_{\vec{o}} = (\Delta U)_A \quad \text{AVERAGE VALUE OF } \Delta U \text{ FOR } \varphi_A \text{ (an atomic state)}$$

$$\mathcal{E}(\vec{k}) = \mathcal{E}(\vec{k}+\vec{g})$$
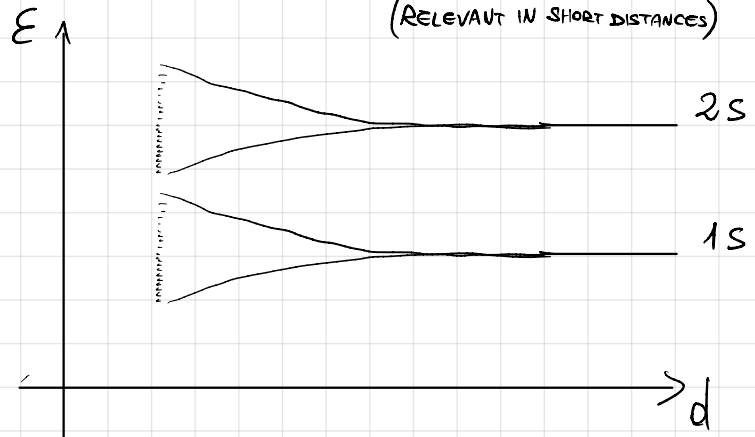
Jumping probability decreases when distance gets bigger.

$\mathcal{E}$

2S

1S

d

[1D] Tight binding between nearest neighbours

$(m-1)a \quad (ma) \quad (m+1)a \qquad x$
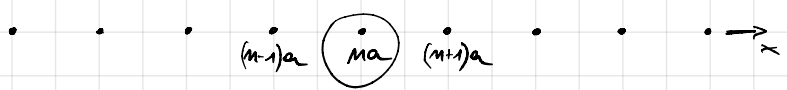
STOP AT THE NEAREST NEIGHBOURS

$$\mathcal{E}_{-1} = \int \varphi_A^*(x-(m-1)a) \, \Delta U \, \varphi_A(x-ma) \, dx = \mathcal{E}_{+1} \implies \mathcal{E}(k) = \mathcal{E}_A + (\Delta U)_A + \mathcal{E}_1\left(e^{ika} + e^{-ika}\right) =$$

$$= \mathcal{E}_A + (\Delta U)_A + 2\mathcal{E}_1 \cos(ka)$$

Hopping integral can be either positive or negative.

if $\mathcal{E}_1 < 0$ (s states)
if $\mathcal{E}_1 > 0$

$2\mathcal{E}_1$

$\mathcal{E}_A + (\Delta U)_A$
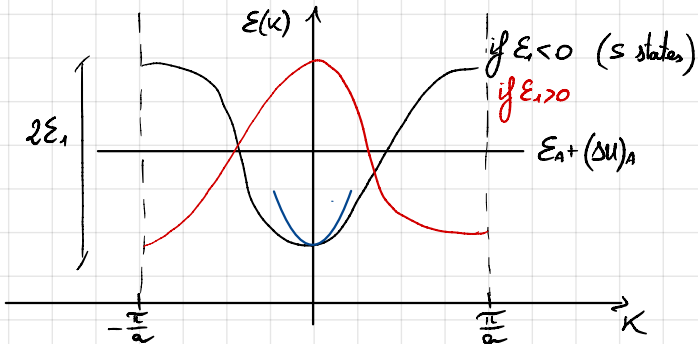
Also in 3D we have sin and cos

Now we consider an electron on the minimum ($K \to 0$):

$$\mathcal{E}(K) = \mathcal{E}_{min} + \frac{1}{2} \frac{\partial^2 \mathcal{E}}{\partial K^2}\bigg|_{K=0} K^2$$

PARABOLIC APPROXIMATION

$$m^* \triangleq \frac{\hbar^2}{\left(\frac{\partial^2 \mathcal{E}}{\partial K^2}\right)\big|_{K=0}} \implies \mathcal{E}(K) = \mathcal{E}_{min} + \frac{\hbar^2}{2m^*} K^2$$

EFFECTIVE MASS

Around maxima and minima of the band, electrons behave like they were free with a different mass.

Lecture #15

Electron dynamics

$$\psi_{\vec{K}}(\vec{n}) = \frac{1}{\sqrt{N}} \sum_{\vec{m}} \varphi_A(\vec{n} - \vec{m}) e^{i \vec{K} \cdot \vec{m}}$$

Not perfectly normalized due to hopping integral contribution.

$$\langle \hat{H} \rangle_{\vec{K}} = \mathcal{E}(\vec{K}) = \mathcal{E}_A + \sum_{\vec{h}} \mathcal{E}_B e^{i \vec{K} \cdot \vec{h}}$$

$$\int \varphi_A^*(\vec{n} + \vec{h}) \, \Delta U \, \varphi_A(\vec{n}) \, dV$$

jumping probability due to crystalline potential

POSSIBLE

$\vec{h}$

Noble metals

They have an external shell configured as $(m-1)d^{10} + ms^1$; Au, Ag, Cu are noble metals. If orbitals are close in energy, bands overlap.
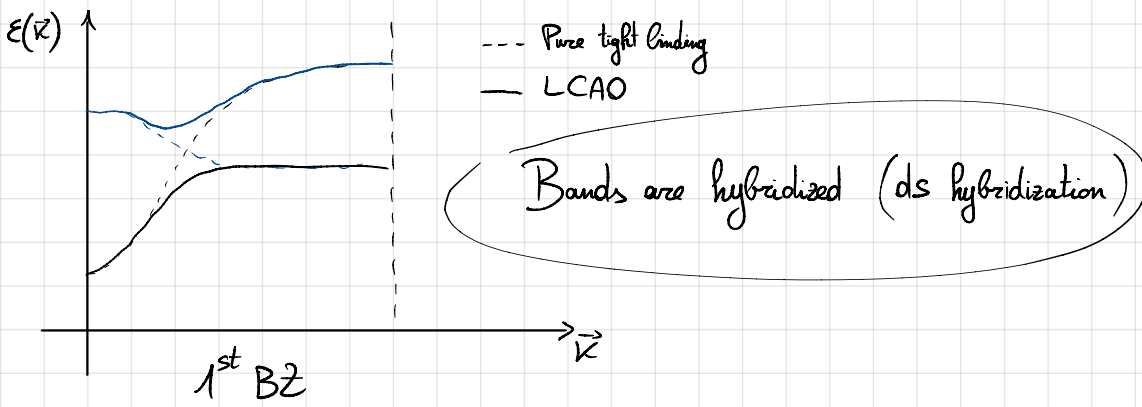

4S

3d

1st BZ

$\vec{K}$

(110)
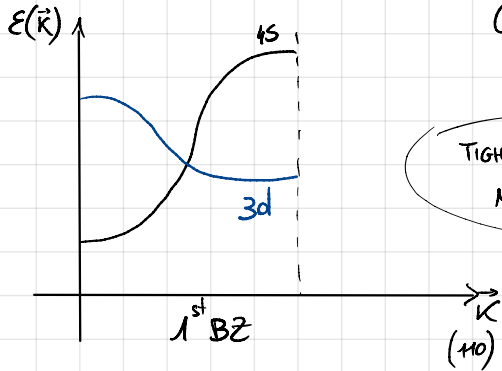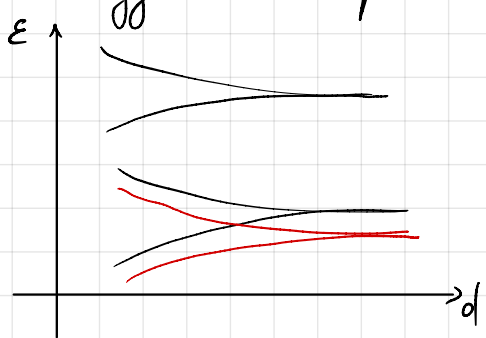
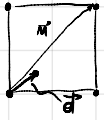Cu: $4s^1 3d^{10}$

TIGHT BINDING MODEL
MUST BE MODIFIED

We have to develop the LCAO (Linear Combination of Atomic Orbitals).

FREE PARAMETERS

$$\psi_{\vec{K}}(\vec{n}) = \frac{1}{\sqrt{N}} \sum_{\vec{m}} \sum_i B_i \varphi_{A,i}(\vec{n} - \vec{m}) e^{i \vec{K} \cdot \vec{m}} \implies \mathcal{E}(\vec{K}) = \langle \hat{H} \rangle_{\vec{K}}$$

This energy has to be minimized in respect to B_i in order to find the free parameters.

$$\int \psi_{\vec{K}}^* \hat{H} \psi_K \, dV$$

$\varepsilon(\vec{k})$

--- Pure tight binding
— LCAO

1st BZ

Bands are hybridized (ds hybridization)

Pure tight binding with a basis

$$\psi_{\vec{k}} = \frac{1}{\sqrt{N}} \sum_{\vec{n}} \left[a \, \varphi_A(\vec{r}-\vec{n}) + b \, \varphi_A(\vec{r}-\vec{n}-\vec{d}) \right] e^{i\vec{k}\cdot\vec{n}}$$

Electron dynamics

This is about the electron behaviour in an external electric field; that is also called semi-classical dynamics approach.

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r}) \longrightarrow \begin{array}{c} \psi_{\vec{k}} \\ \varepsilon(\vec{k}) \end{array} \rightarrow \hat{H}_0 \psi_{\vec{k}} = \varepsilon(\vec{k})\psi_{\vec{k}}$$

This is the situation in equilibrium, but now $\hat{H} = \hat{H}_0 + U_E(\vec{r}) \longrightarrow \hat{H}\vec{\Psi} = i\hbar\frac{\partial\Psi}{\partial t} \longrightarrow \Psi(\vec{r},t)$

TIME DEPENDENT SCHRÖDINGER EQUATION

In the semiclassical approach, electrons are represented by wave packets (localized $\Delta x \cdot \Delta p \sim \hbar$).
Classical dynamics for $<x>$ may be applied.
This is true for some hypoteses.

$|\psi|^2 \rightarrow \vec{v}_g$

$<x>$

Δx
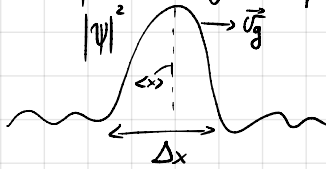
Free electron is a plane wave
$\Psi = A e^{i(\vec{k}\cdot\vec{r}-\omega t)} \xrightarrow{1D} \Psi = A e^{i(Kx-\omega t)}$
$\vec{p} = \hbar\vec{K} \quad \varepsilon = \frac{\hbar^2 K^2}{2m} = \hbar\omega \quad \omega = \frac{\hbar K^2}{2m}$

For a pack of free electron

$$\psi = \int_{K_0-\Delta K}^{K_0+\Delta K} A e^{i(Kx-\omega t)} dK \quad \rightsquigarrow \quad v_g = \left|\frac{\partial\omega}{\partial K}\right|_{K_0} = \frac{\hbar K}{m} = \frac{P_0}{m} = \frac{1}{\hbar}\frac{\partial\varepsilon(k)}{\partial K}\bigg|_{K_0}$$

In a crystal we have wavepackets of Bloch waves

PLANE WAVE

$$\overline{\Psi}(\vec{r},t) = \int a(\vec{k})\psi_{\vec{k}}(\vec{r}) e^{-i\frac{\varepsilon(k)t}{\hbar}} d\vec{k} = \int a(\vec{k}) u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}} e^{-i\frac{\varepsilon(k)t}{\hbar}} d\vec{k}$$

$$\boxed{\vec{v}_g = \frac{1}{\hbar}\vec{\nabla}_{\vec{k}}\varepsilon(\vec{k})}$$ SAME AS THE FREE ELECTRON CASE
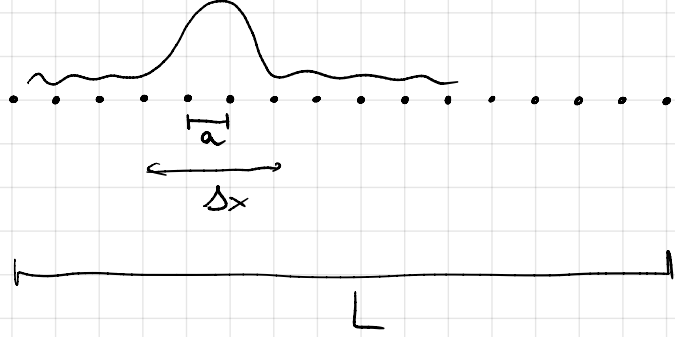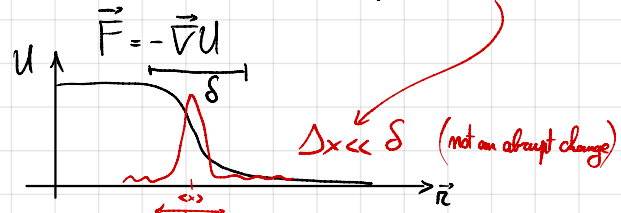
Limits

1) $\Delta x \ll L$

We can say that the electron is localized if the uncertainty of the position is lesser than the crystal lenght. Also $\vec{p} \neq \hbar K$, but $<\vec{p}> = \hbar<\vec{K}>$.
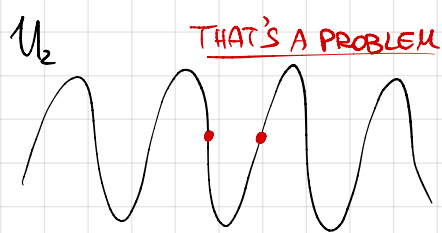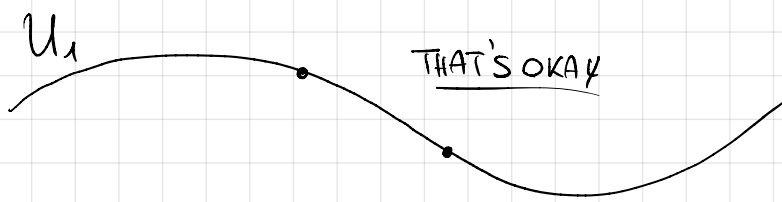
2) $\Delta K \ll \frac{\pi}{a}$

Maximum wavevector available is the one on the Bragg planes. Also, since $\Delta x \cdot \Delta p \sim \hbar$, $\Delta x \cdot \Delta K \sim 1 \Longrightarrow \boxed{\Delta x \gg a}$

a

Δx

L

We can use classical equations for Bloch wavepackets (Newton / Hamilton) if U is smooth.

U

$\vec{F} = -\vec{\nabla}U$

δ

$\Delta x \ll \delta$ (not an abrupt change)

$<x>$
Δx

$\vec{r}$

U_1

THAT'S OKAY

U_2

THAT'S A PROBLEM

This is described in the Ehrenfest theorem.

$\vec{K} = -i\vec{\nabla}$

We don't know what is the force

<u>Wannier theorem</u>

We know $\mathcal{E}(\vec{K})$; we call Wannier operator $\hat{W} \doteq \mathcal{E}(-i\vec{\nabla})$ and if we apply it to a wavefunction

$$\mathcal{E}(-i\vec{\nabla})\,\psi_{\vec{K}} = \mathcal{E}(\vec{K})\,\psi_{\vec{K}}$$

Jordan rules
$$\hat{\vec{R}} = \vec{r}$$
$$\hat{\vec{P}} = -i\hbar\vec{\nabla} = -i\hbar\frac{\partial}{\partial x}$$
$$\frac{\hat{P}^2}{2m} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$\sim \quad -i\vec{\nabla} = \frac{\hat{\vec{P}}}{\hbar}$

BLOCH FUNCTIONS
ARE EIGENFUNCTIONS OF
THE WANNIER OPERATOR

Also $\hat{H}_0\,\psi_{\vec{K}} = \mathcal{E}(\vec{K})\,\psi_{\vec{K}}$, so $\hat{W} = \hat{H}_0$.

(1D) $\quad \mathcal{E}(K) = \sum_m \mathcal{E}_m e^{iKna} \implies \hat{W} = \mathcal{E}\left(-i\frac{\partial}{\partial x}\right) = \sum_m \mathcal{E}_m e^{na\frac{\partial}{\partial x}} = \sum_m \mathcal{E}_m \hat{T}_{ma} \implies \hat{W}\psi_{\vec{K}}(x) = \sum_m \mathcal{E}_m \psi_{\vec{K}}(x+ma) = \sum_m \mathcal{E}_m e^{iKma}\psi_{\vec{K}}(x) =$

$= \mathcal{E}(K)\psi_{\vec{K}}(x)$

DL

$\xleftarrow{\quad a \quad}$

RL

$\xleftarrow{\frac{2\pi}{a}}$
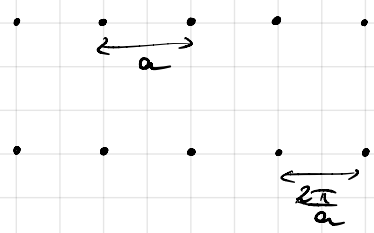
$$e^{\alpha x} = 1 + \alpha x + \frac{1}{2}\alpha^2 x^2 + \frac{1}{6}\alpha^3 x^3 + \cdots$$
$$e^{na\frac{\partial}{\partial x}} = 1 + na\frac{\partial}{\partial x} + \frac{1}{2}(na)^2\frac{\partial^2}{\partial x^2} + \cdots$$

$\longrightarrow e^{na\frac{\partial}{\partial x}}\psi_{\vec{K}}(x) = \psi + na\frac{\partial\psi}{\partial x} + \frac{1}{2}(na)^2\frac{\partial^2\psi}{\partial x^2} + \cdots = \psi_{\vec{K}}(x+na)$

THIS IS A TRANSLATION

Lecture #16

Semiclassical approach

For the Wannier theorem $\mathcal{E}(\vec{K}) \to \mathcal{E}(-i\vec{\nabla})\psi_{\vec{K}} = \mathcal{E}(\vec{K})\psi_{\vec{K}}$ and $\hat{T}_{\vec{n}} = e^{\vec{n}\cdot\vec{\nabla}}$ $\left(\hat{T}_{na} = e^{na\frac{\partial}{\partial x}}\right)$.

Effective mass theorem
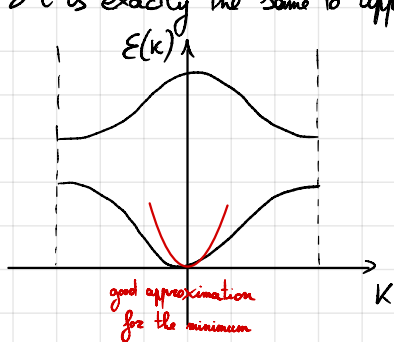
It is also known as the equivalent hamiltonian theorem. $\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})$ and $\hat{H} = \hat{H}_0 + U_E(\vec{r})$ are the starting point; let's take a Bloch wavepacket $\Psi(\vec{K},t) = \int a(\vec{K})\psi_{\vec{K}}e^{-\frac{i\mathcal{E}(\vec{K})t}{\hbar}}\,d\vec{K} = \int \tilde{a}(\vec{K},t)\psi_{\vec{K}}\,d\vec{K}$ and apply $\hat{H}_0$:

$$\hat{H}_0\Psi = \hat{H}_0\int\tilde{a}(\vec{K},t)\psi_{\vec{K}}\,d\vec{K} = \int\tilde{a}(\vec{K},t)\hat{H}_0\psi_{\vec{K}}\,d\vec{K} = \int\tilde{a}(\vec{K},t)\mathcal{E}(-i\vec{\nabla})\psi_{\vec{K}}\,d\vec{K} = \mathcal{E}(-i\vec{\nabla})\Psi$$

Now we consider an external potential too, so $\hat{H} = \hat{H}_0 + U_E(\vec{r})$

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \implies \hat{H}_0\Psi + U_E\Psi = i\hbar\frac{\partial\Psi}{\partial t} \implies \mathcal{E}(-i\vec{\nabla})\Psi + U_E\Psi = i\hbar\frac{\partial\Psi}{\partial t} \implies \left(\mathcal{E}(-i\vec{\nabla}) + U_E\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t} \implies \left(\hat{H}_0 + U_E\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

It is exactly the same to apply $\hat{W}$ or $\hat{H}$.

$\mathcal{E}(k)$

K

good approximation for the minimum

KINETIC ENERGY OPERATOR

$$\begin{cases} \mathcal{E}(k) \simeq \cancel{\mathcal{E}_{min}}^{\text{negligible}} + \frac{1}{2}\frac{\partial^2\mathcal{E}}{\partial K^2}\Big|_0 K^2 = \frac{\hbar^2 K^2}{2m^*} \implies \mathcal{E}\left(-i\frac{\partial}{\partial x}\right) = -\frac{\hbar^2}{2m^*}\frac{\partial^2}{\partial x^2} \\ m^* = \frac{\hbar^2}{\frac{\partial^2\mathcal{E}}{\partial K^2}\big|_0} \end{cases}$$
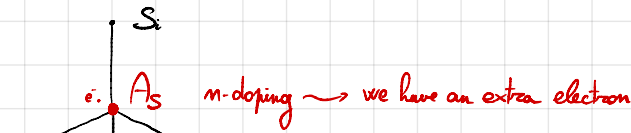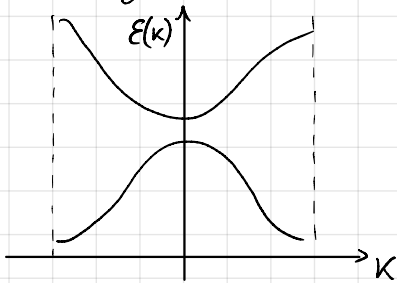
IN COMPARISON TO THE ORIGINAL SCHRÖDINGER EQUATION

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2 + U_E\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U_{CRYSTAL} + U_E\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Provided that we change the mass of the electrons, we can forget about crystal potential

$\Downarrow$

All the effect of the crystal potential goes inside the effective mass

Doping levels in a semiconductor

$\mathcal{E}(K)$
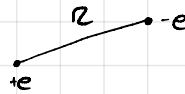
As — n-doping → we have an extra electron

Si, Si, Si, Si

How strong is the bonding with the ion?

$$\hat{H} = \hat{H}_0 + U_E = \hat{H}_0 - \frac{e^2}{4\pi \varepsilon R} = -\frac{\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{4\pi \varepsilon R}$$

just like hydrogen (proton + electron)

From those considerations we can conclude that

$$\mathcal{E}_{BINDING} = R_y \underbrace{\left(\frac{\varepsilon_0}{\varepsilon}\right)^2 \left(\frac{m^*}{m}\right)}_{\sim \frac{1}{1000}}$$

R_y is the binding energy for H

$$\boxed{R_y = \frac{e^4 m}{8 \hbar^2 \varepsilon_0^2}}$$

R •−e •+e

$$E_n = -\frac{R_y}{n^2}$$

Rydberg energy
$R_y = 13,6\ eV$

Binding energy in silicon is much weaker ($\sim$ 10 meV), even less than thermal energy. The extra electron, therefore, is free to move.
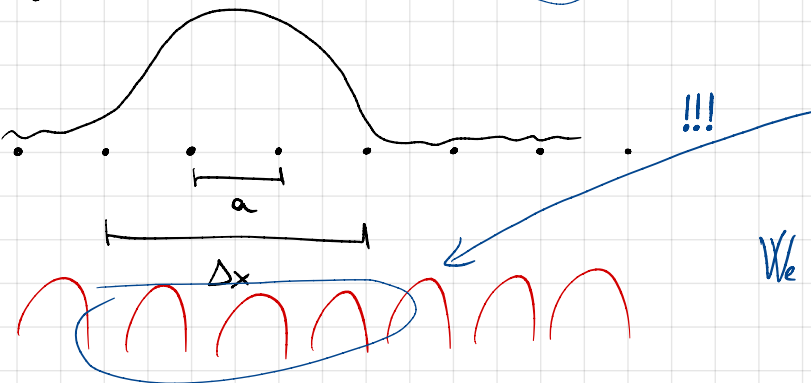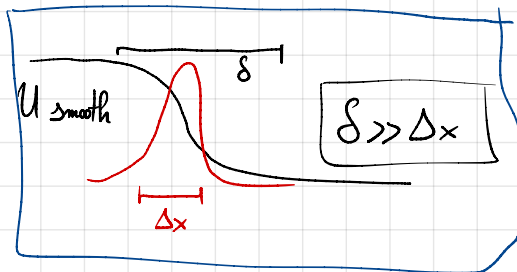

$\mathcal{E}(K)$
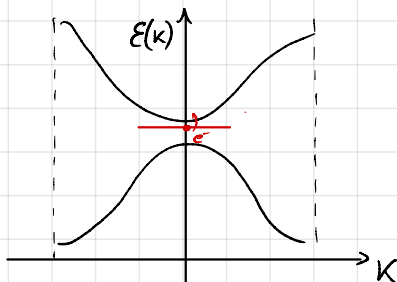
Doping increases semiconductor conductability

Potentials in the crystal

$$-\frac{\hbar^2 \nabla^2}{2m} + U_{CRYSTAL}(\vec{r}) + U_E(\vec{r}) \iff \mathcal{E}(-i\vec{\nabla}) + U_E(\vec{r})$$

We don't care anymore about $U_{CRYSTAL}$ — this must be smooth

U smooth

$\delta \gg \Delta x$

a

Δx

!!!

We cannot use semiclassical approach for the crystalline potential

Hamilton equations in classical physics

$$\mathcal{E}(\vec{r}, \vec{p}) = H_{cl}(\vec{r}, \vec{p})$$

Same name, different nature.

$$H_{cl} = \frac{P^2}{2m} + U(\vec{r})$$

$$\begin{cases} \dfrac{d\vec{p}}{dt} = -\dfrac{\partial H_{cl}}{\partial \vec{r}} \\[2mm] \dfrac{d\vec{r}}{dt} = \dfrac{\partial H_{cl}}{\partial \vec{p}} \end{cases}$$

They are completely equivalent to Newton laws

$$\frac{d\vec{p}}{dt} = -\vec{\nabla}U \implies m\frac{d\vec{v}}{dt} = -\vec{\nabla}U$$

$$\vec{K} = \frac{\vec{P}}{\hbar}$$

$$H_{cl,eq}(\vec{r}, \vec{p}) = \mathcal{E}\left(\frac{\vec{p}}{\hbar}\right) + U_E(\vec{r})$$

$?\ \Downarrow$

$$H_{cl}(\vec{r}, \vec{p}) = \frac{P^2}{2m} + U_{CRYSTAL} + U_E$$

$(\vec{p} \to -i\hbar\vec{\nabla})\ \Downarrow$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U_{CRYSTAL} + U_E$$

EMT $\Downarrow$

$$\hat{H}_{eq} = \mathcal{E}(-i\vec{\nabla}) + U_E$$

Then all becomes

$$\begin{cases} \dfrac{d\vec{P}}{dt} = -\partial H_{cl,eq} = -\dfrac{\partial U_E}{\partial \vec{n}} = \vec{F_E} \\[4mm] \dfrac{d\vec{n}}{dt} = -\dfrac{\partial H_{cl,eq}}{\partial \vec{P}} = -\dfrac{\partial \mathcal{E}\left(\frac{\vec{P}}{\hbar}\right)}{\partial \vec{P}} \end{cases} \Longrightarrow \begin{cases} \hbar \dfrac{\partial \vec{K}}{\partial t} = -\vec{\nabla} U_E = \vec{F_E} \\[4mm] \dfrac{d\vec{n}}{dt} = \vec{v} = \dfrac{1}{\hbar}\dfrac{\partial \mathcal{E}(\vec{K})}{\partial \vec{K}} = \vec{v_g} \end{cases}$$

Semiclassical dynamics equations for an e^- in a crystal

Wavevector changes in time due to an external force.

Tutorial #7

$$\hat{H}\psi_{\vec{K}} = -\dfrac{\hbar^2}{2m}\nabla^2\psi_{\vec{K}} + V(\vec{n})\psi_{\vec{K}} = \mathcal{E}_{\vec{K}}\psi_{\vec{K}}$$

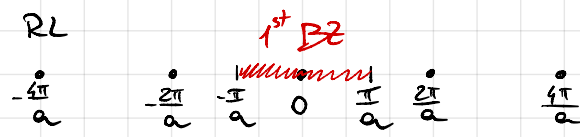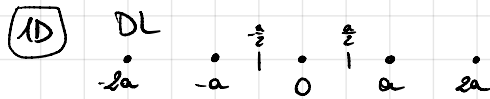$$\begin{cases} \psi_{\vec{K}} = u_{\vec{K}}(\vec{n})\,e^{i\vec{K}\cdot\vec{n}} \\ u_{\vec{K}}(\vec{n}+\vec{R}) = u_{\vec{K}}(\vec{R}) \end{cases}$$ Bloch wavefunctions: stationary states of one electron in a periodic potential $U(\vec{n}+\vec{R}) = U(\vec{n})$

$\vec{K}$ is to be intended as a quantum number of the wavefunction

For a free electron $\hat{H}_0\psi_{\vec{K}}^{(0)} = -\dfrac{\hbar^2}{2m}\nabla^2\psi_{\vec{K}}^{(0)} = \mathcal{E}_{\vec{K}}^{(0)}\psi_{\vec{K}}$, Bloch wavefunction become plane waves $\psi_{\vec{K}}^{(0)} = \dfrac{1}{\sqrt{V}}e^{i\vec{K}\cdot\vec{n}}$ and energy eigenvalues go as K^2: $\mathcal{E}_{\vec{K}} = \mathcal{E}(\vec{K}) = \dfrac{\hbar^2 K^2}{2m}$.

For a nearly free electron $\hat{H}\psi_{\vec{K}} = (\hat{H}_0 + \hat{W}(\vec{n}))\psi_{\vec{K}} = \mathcal{E}_{\vec{K}}\psi_{\vec{K}}$, where $\hat{W}(\vec{n}) = \sum_{\vec{g}} U_{\vec{g}}\,e^{-i\vec{g}\cdot\vec{n}}$. So $\mathcal{E}(\vec{K}) = \dfrac{\hbar^2 K^2}{2m} + \dfrac{2m}{\hbar^2}\sum_{K_0 \neq K_0}\dfrac{|\langle K_0|\hat{W}|K_0'\rangle|}{K_0^2 - K_0'^2}$, degenerating if $K_0 = K_0$ (zone boundary). perturbation

Band structure

(1D) DL

$$\underset{-2a}{\bullet} \quad \underset{-a}{\bullet} \quad \overset{-\frac{a}{2}}{|} \quad \underset{0}{\bullet} \quad \overset{\frac{a}{2}}{|} \quad \underset{a}{\bullet} \quad \underset{2a}{\bullet}$$

RL   1st BZ

$$\underset{-\frac{4\pi}{a}}{\bullet} \quad \underset{-\frac{2\pi}{a}}{\bullet} \quad \underset{-\frac{\pi}{a}}{\overset{\bullet}{}} \quad \underset{0}{} \quad \underset{\frac{\pi}{a}}{\overset{\bullet}{}} \quad \underset{\frac{2\pi}{a}}{\overset{\bullet}{}} \quad \underset{\frac{4\pi}{a}}{\overset{\bullet}{}}$$

$$\begin{cases} K = \dfrac{2\pi}{Na}m \\ \Delta K = \dfrac{2\pi}{Na} \end{cases}$$ N allowed K values in the 1st BZ

Repeated zone is highly redundant; extended/reduced are better representations. Structure of silicon is diamond. 2D and 3D are too complex to draw (see slides). Some values of energy do not have a corresponding K (GAPS).

Lecture #17

$$\hat{H}_0 + U_E \implies -\dfrac{\hbar^2\nabla^2}{2m} + U_{CRYSTAL} + U_E \longrightarrow$$
$$\downarrow$$
$$\mathcal{E}(-i\vec{\nabla}) + U_E$$

$$\begin{cases} \hbar\dfrac{d\vec{K}}{dt} = -\vec{\nabla}U_E = \vec{F_E} \\[4mm] \dfrac{d\vec{n}}{dt} = \dfrac{1}{\hbar}\vec{\nabla}_{\vec{K}}\mathcal{E}(\vec{K}) = \vec{v_g} \end{cases}$$

$$\leadsto \quad \dfrac{d^2\vec{n}}{dt^2} = \dfrac{d}{dt}\left(\dfrac{1}{\hbar}\dfrac{\partial\mathcal{E}}{\partial\vec{K}}\right) =$$
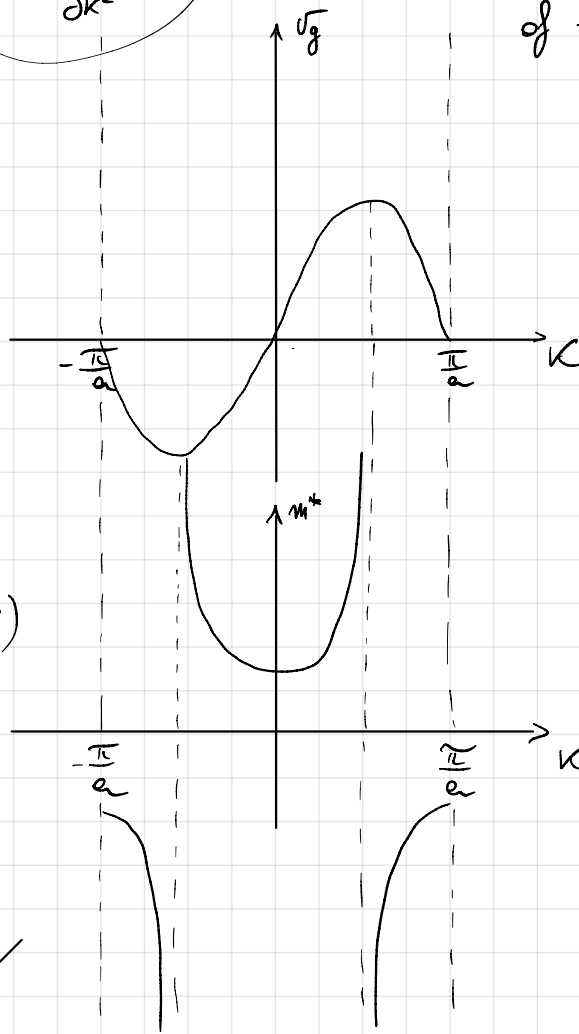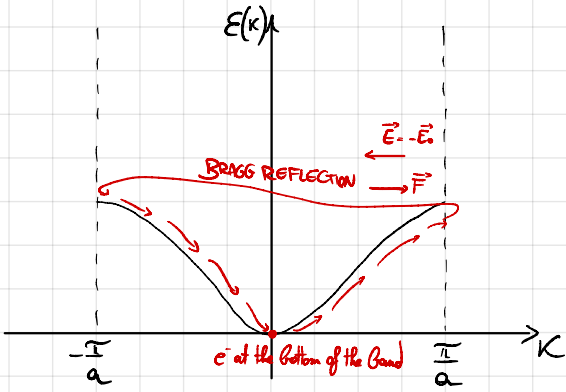$$= \dfrac{1}{\hbar}\dfrac{\partial^2\mathcal{E}}{\partial\vec{K}\partial\vec{K}}\dfrac{\partial\vec{K}}{\partial t} =$$

$$\begin{bmatrix} \partial K_x \partial K_x & \partial K_x \partial K_y \cdots \\ \partial K_y \partial K_x & \partial K_y \partial K_y \end{bmatrix} \overset{TENSOR}{\longleftarrow}$$

$$= \dfrac{1}{\hbar^2}\dfrac{\partial^2\mathcal{E}}{\partial\vec{K}\partial\vec{K}}\vec{F_E} = \dfrac{\vec{F_E}}{m^*}$$

We got that $\frac{1}{m^*} \triangleq \frac{1}{\hbar^2} \frac{\partial^2 \mathcal{E}}{\partial \vec{K} \partial \vec{K}} \xrightarrow{1D} \boxed{m^* = \frac{\hbar^2}{\frac{\partial^2 \mathcal{E}}{\partial K^2}}} \quad \ddot{\smile}$

$\mathcal{H}$ is a tensor because it depends on the direction of the application of the force.

$\mathcal{E}(K)$

BRAGG REFLECTION

$\vec{E} = -\vec{E_0}$

$\vec{F}$

e^- at the bottom of the Band

$-\frac{\pi}{a}$ $\frac{\pi}{a}$ K

v_g

$-\frac{\pi}{a}$ $\frac{\pi}{a}$ K

Effective mass is related to the curvature

m^*

$-\frac{\pi}{a}$ $\frac{\pi}{a}$ K

If $\vec{E}$ is constant and uniform $\quad (\vec{F_e} = -e\vec{E})$

1) $\hbar \frac{d\vec{K}}{dt} = -e\vec{E}$ and $\vec{K}(0) = 0$

$\vec{K}(t) = \vec{K}(0) - \frac{e\vec{E}}{\hbar}t = -\frac{e\vec{E_0}}{\hbar}t$

$\vec{K}(t)$

$\frac{\pi}{a}$

BRAGG REFLECTION

$-\frac{\pi}{a}$

t

1 ....→ ....→ ...→ ..→ .→ 2

←.. ←.. ←... ←....
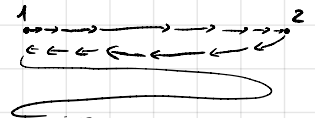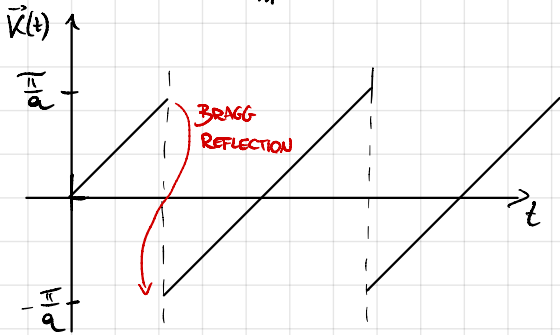
Constant force → oscillating trajectory

Bloch oscillations

If we want to know what happens in the real space we have to consider $\frac{d\vec{n}}{dt} = \frac{1}{\hbar} \vec{\nabla} \mathcal{E}(\vec{K})$

We have Bloch oscillations everytime we have a periodic potential.
We don't have oscillating current with constant $\vec{E}$ though; that's because periodicity is not perfect due to atomic vibrations (collisions) and defects.

• → ✕ → ✳
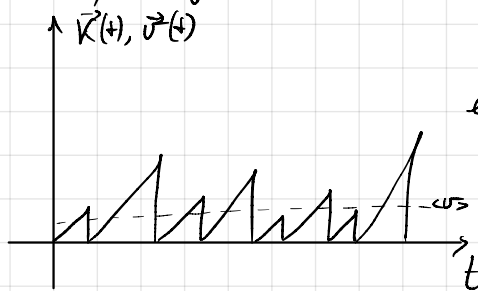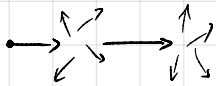
electron never arrives near to Bragg planes
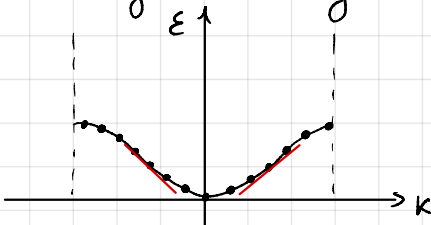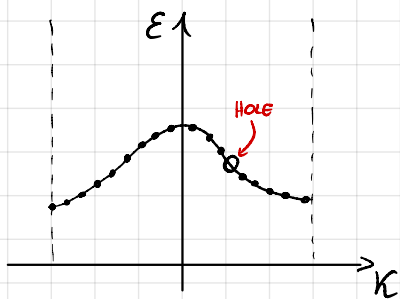
Bloch oscillations can be seen in very peculiar situations.

$\vec{K}(t), \vec{v}(t)$

$\langle v \rangle$

t

Holes
(Qualitatively, it is a missing electron.

$\mathcal{E}$

K

$\mathcal{E}(\vec{K}) = \mathcal{E}(-\vec{K}) \quad$ EVEN FUNCTION

$I_\alpha \sim \sum_{\vec{K}} (-e)\vec{v_g} = \sum_{K} (-e)\frac{\partial \mathcal{E}(\vec{K})}{\partial K} = 0$

A completely occupied band cannot carry current

$$I \sim \sum_{\vec{k} \text{ occupied}} (-e)\vec{v}_g = \sum_{\text{all } \vec{k}} (-e)\vec{v}_g - \sum_{\substack{\text{empty} \\ \vec{k}}} (-e)\vec{v}_g = \sum_{\substack{\text{empty} \\ \vec{k}}} +e\vec{v}_g$$

Hole is a fictitious positive particle

This band completely occupied except for one $-e$ behaves like a band completely empty except for one $+e$
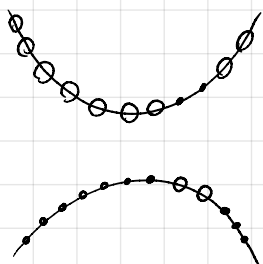

HOLE

Energy of the holes increases going downwards. Occupation probability is also the opposite:

$$f_e = \frac{1}{e^{\frac{\varepsilon - \varepsilon_F}{kT}} + 1} \implies f_h = 1 - f_e = \frac{1}{e^{\frac{\varepsilon - \varepsilon_F}{kT}} + 1}$$
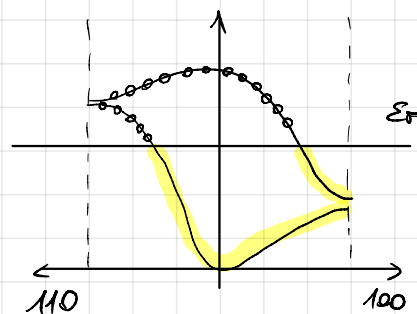
If $m_e^* < 0$, $m_h^* > 0$

Also $\vec{k}_h = \sum_{\text{all } \vec{k}} \vec{k} - \vec{k}_e$, while group velocity is still the same.
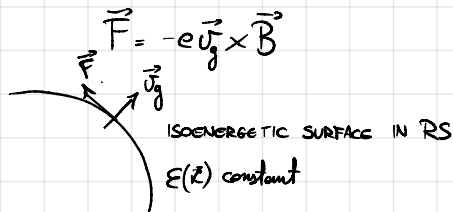
In a semiconductor


$$I = I_c + I_v$$

Holes contribution is very important

ε_F
110   100

If we apply a magnetic field, Lorentz Force occurs.

$$\vec{F} = -e\vec{v}_g \times \vec{B}$$

ISOENERGETIC SURFACE IN RS
$\varepsilon(\vec{k})$ constant

Particles doesn't change energy

Tutorial #8

In the nearly free electron model $\varepsilon_k = \frac{\hbar^2 k^2}{2m} \pm U_g$
This separation is responsible for the formation of band gaps.
In these gaps there is no energy value assigned to a k.
This model is closer to reality. Where does Fermi level lie?

gap
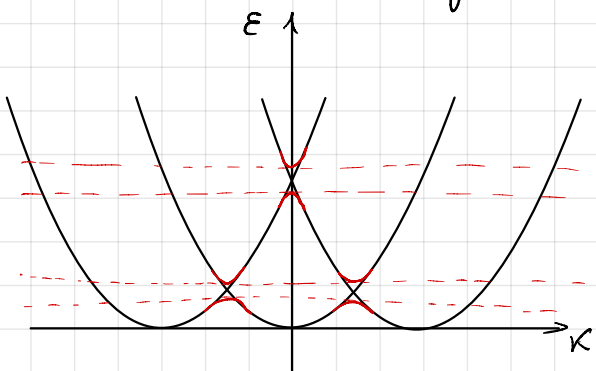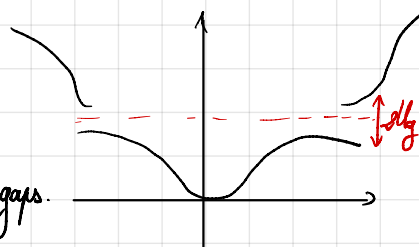
Fermi level is the chemical potential, while Fermi energy is the last electrons-filled band.

$\downarrow$

At $T = 0$, they are the same

If Fermi level is situated inside a gap, we have an insulator. If it falls within a band, we have a conductor.
Fermi level can be engineered by doping.

How can we assume if we have an insulator or a conductor? We can compare the number of electrons with the number of states, as both depend on N.

$$NK \text{ in a } BZ \implies NK \text{ in an energy band} \xRightarrow{\text{2 spins}} 2N \text{ available states}$$

If a solid has odd number of valence electron per primitive cell, band is half filled (alkali). If number is even, the situation is complicate.

Fermi surface

For practically filled bands, occupied and unoccupied levels are separated by a surface; the set of all those surfaces is the Fermi surface. $\boxed{\text{Dimensionality of the surface = Dimensionality of the lattice} - 1}$

For a solid with gaps, Fermi surface is not defined. Where there is a Fermi surface, there is the possibility of making a free transition. Far from BZ boundaries, FEM is good (we have a perfect Fermi sphere); otherwise, deformations become relevant. BZ borders reflect whatever crosses them. For Alkali (monovalent), FEM is perfect. Calcium is not a good metal (K space is reduced).

Tutorial #9

We want to build our electronic wavefunction writing in term of atomic wavefunction (for tight binding).

$$\psi_{\vec{K}}(\vec{r}) = C \sum_i \varphi\left(\vec{r} - \vec{R}_i\right) e^{i \vec{K} \cdot \vec{R}_i} \qquad \underline{\text{Bloch theorem must be fullfilled}}$$

LOCALIZED STATE   i-th LATTICE SITE

The localized state can be written as a combination of atomic states.

$$\varphi = \sum_\beta \varphi_\beta \, b_\beta \qquad \beta \text{ encloses a set of quantum numbers used to identify each specific atomic wavefunctions.}$$

COLLECTION OF STATES

We use just one kind of atomic wavefunctions for now: the S states $(\ell = 0) \implies \varphi(\vec{r}) = \varphi(r)$ just dependent on modulus

$$\mathcal{E}(K) = \mathcal{E}_0 + \sum_j e^{i\vec{K}\cdot \ell_j} \, \mathcal{E}_j \qquad \text{where } \mathcal{E}_j = \int \varphi^*(\vec{r}-\vec{R}_j)\,\Delta U(\vec{r})\, \varphi(\vec{r})\,dV \text{ is the hopping integral.}$$

ATOMIC ENERGY   JUMPING ON LATTICES   DESTINATION

SIMPLIFICATION

$\mathcal{E}_1$ CONSTANT (NEGATIVE CONTRIBUTION)

$$\mathcal{E}(K) = \mathcal{E}_0 + \sum_{\substack{\text{FIRST} \\ \text{NEIGHBOURS}}} e^{i\vec{K}\cdot\vec{R}_j} \boxed{\mathcal{E}_j} = \mathcal{E}_0 - |\mathcal{E}_1| \sum_{FN} e^{i\vec{K}\cdot\vec{R}_j}$$

VERY SMALL   REFERENCE R_j
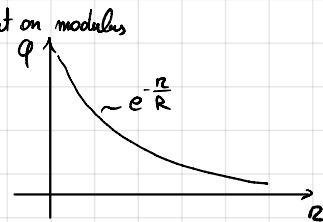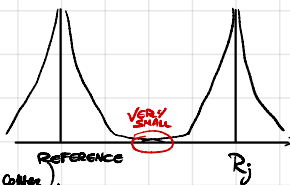
Now we apply all of this to FCC crystals (noble metals like copper).
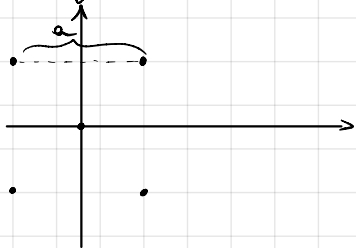
XY	YZ	XZ
$\frac{a}{2}\left(\frac{a}{2}, \frac{a}{2}, 0\right)$	$\frac{a}{2}(0, 1, 1)$	$\frac{a}{2}(\pm 1, 0, \pm 1)$
$\frac{a}{2}\left(\frac{a}{2}, -\frac{a}{2}, 0\right)$	$\frac{a}{2}(0, 1, -1)$	
$\frac{a}{2}\left(-\frac{a}{2}, -\frac{a}{2}, 0\right)$	$\frac{a}{2}(0, -1, -1)$	
$\frac{a}{2}\left(-\frac{a}{2}, \frac{a}{2}, 0\right)$	$\frac{a}{2}(0, -1, 1)$	

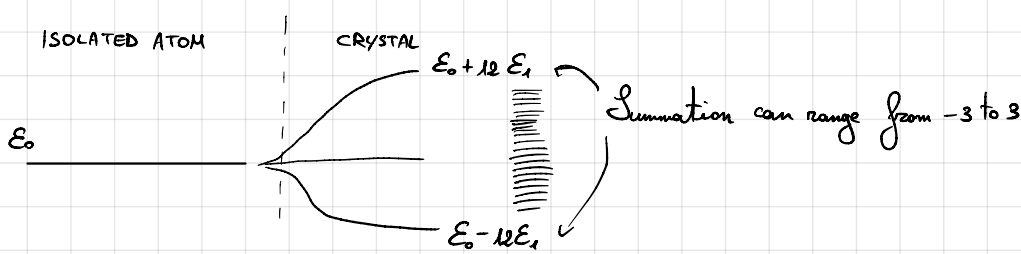We have to calculate $e^{i\vec{K}\cdot\vec{R}_j}$ for all 12 terms

$$\vec{K} = (K_x, K_y, K_z)$$

For XY, $e^{i\frac{a}{2}(K_x+K_y)} + e^{i\frac{a}{2}(K_x-K_y)} + e^{i\frac{a}{2}(-K_x+K_y)} + e^{-i\frac{a}{2}(K_x+K_y)} = e^{i\frac{a}{2}K_x}\left(e^{i\frac{a}{2}K_y} + e^{-i\frac{a}{2}K_y}\right) + e^{-i\frac{a}{2}K_x}\left(e^{i\frac{a}{2}K_y} + e^{-i\frac{a}{2}K_y}\right) = \left(e^{i\frac{a}{2}K_y} + e^{-i\frac{a}{2}K_y}\right)\left(e^{i\frac{a}{2}K_x} + e^{-i\frac{a}{2}K_x}\right) = \underline{\underline{4\cos\left(\frac{a}{2}K_x\right)\cos\left(\frac{a}{2}K_y\right)}}$

For the others, procedure is the same.

$$\mathcal{E}(K) = \mathcal{E}_0 - 4|\mathcal{E}_1|\left[\cos\left(\frac{a}{2}K_x\right)\cos\left(\frac{a}{2}K_y\right) + \cos\left(\frac{a}{2}K_y\right)\cos\left(\frac{a}{2}K_z\right) + \cos\left(\frac{a}{2}K_x\right)\cos\left(\frac{a}{2}K_z\right)\right] \qquad \underline{\text{Band structure is already known}}$$

$\mathcal{E}_0 + 12\,\mathcal{E}_1$

$\mathcal{E}_0$

$\mathcal{E}_0 - 12\,\mathcal{E}_1$

Summation can range from -3 to 3

What if $K \to 0$?

$\cos(x) \sim 1 - \dfrac{x^2}{2}$ for $x \to 0$

$\cos\left(\dfrac{a}{2}K_x\right)\cos\left(\dfrac{a}{2}K_y\right) \sim \left(1 - \dfrac{1}{2}\left(\dfrac{a}{2}K_x\right)^2\right)\left(1 - \dfrac{1}{2}\left(\dfrac{a}{2}K_y\right)^2\right) = 1 - \dfrac{a^2}{8}K_y^2 - \dfrac{a^2}{8}K_x^2 + \underbrace{K_x^2 K_y^2 \dfrac{a^2}{16}}_{\text{NEGLIGIBLE} \;\to\; 0}$

$\Longrightarrow \mathcal{E}(K) = \mathcal{E}_0 - 4|\mathcal{E}_1|\left[3 - \dfrac{a^2}{4}\left(K_x^2 + K_y^2 + K_z^2\right)\right] =$

$= \mathcal{E}_0 - 12|\mathcal{E}_1| + a^2|\vec{K}|^2 \mathcal{E}_1$ __Parabula__
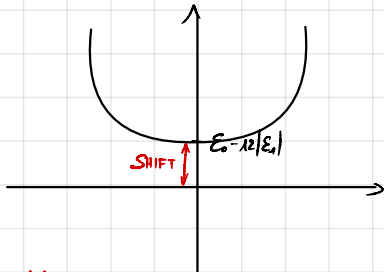
$\cancel{\mathcal{E}_{FEM} = \dfrac{\hbar^2 K^2}{2m}}$ NO SHIFT HERE

SHIFT $\mathcal{E}_0 - 12|\mathcal{E}_1|$

Is TB connectable with FE? __NO__ $\left(m^* = \dfrac{\hbar^2}{a^2 \mathcal{E}_1}\right)$

Tutorial #10

Now we focus on all types of orbitals, not just s.

$\psi_{\vec{K}}(\vec{r}) = \sum_i \varphi(\vec{r} - \vec{R}_i)\, e^{i\vec{K}\cdot\vec{R}_i}$ i runs through all the lattice

$\varphi(\vec{r}) = \sum_m b_m \varphi_m(\vec{r})$ LCAO (Linear Combination of Atomic Orbitals)   method used to build a molecule from atoms in Chemistry $\Longrightarrow$ everything is done on the same position, while in Solid State Physics we are considering a Bloch function

$\begin{cases} \hat{H}_{AT}\,\varphi_m = \mathcal{E}_m\,\varphi_m \quad \text{atomic Schrödinger equation is satisfied} \quad \left(\hat{H}_{AT} = -\dfrac{\hbar^2 \nabla^2}{2m} - \dfrac{2e^2}{4\pi\varepsilon_0|\vec{r}|}\right) \\[2mm] \left(\hat{H}_{AT} + \Delta\hat{U}\right)\psi_K = \mathcal{E}(K)\,\psi_K \end{cases}$

$H_{12} = \langle \psi_1 \hat{H} \psi_2 \rangle = \displaystyle\int \psi_1^* \hat{H} \psi_2 \, dV$

$\langle \varphi_m | \varphi_n \rangle = \displaystyle\int \varphi_m^* \varphi_n \, dV = S_{mn} \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases}$

in TB considering φ

$\langle \varphi_m(r-R_i) | \varphi_n(r-R_j) \rangle = S_{mn}\,\delta_{ij}$

__We face a 1D problem now__

$\langle \varphi_m |$ (integrate both sides multiplying by φ_m)

$\left(\hat{H}_{AT} + \Delta\hat{U}\right)\psi_K = \mathcal{E}(K)\psi_K \Longrightarrow \underbrace{\hat{H}}_{\text{(A)}}|\psi_K\rangle = \mathcal{E}(K)|\psi_K\rangle \Longrightarrow \langle \varphi_m|\hat{H}_{AT} + \Delta\hat{U}|\psi_K\rangle = \langle \varphi_m|\mathcal{E}(K)|\psi_K\rangle$ $\psi_K = \sum_i \sum_m b_m \varphi_m(r-R_j) e^{iKR_j}$

$\sum_i \sum_m \mathcal{E}(K)\langle \varphi_m|b_m \varphi_m(r-R_j)\rangle e^{iR_j K} = \mathcal{E}(K) b_m \Longrightarrow \langle \varphi_m|\hat{H}_{AT}|\psi_K\rangle + \langle \varphi_m|\Delta\hat{U}|\psi_K\rangle = \mathcal{E}(K) b_m$

only term not equal to $\varnothing$ $(m=n)$

$i=-1 \;\; i=0 \;\; i=1$ — we stop at the nearest neighbours

$\langle \varphi_m(r-R_i)|\varphi_n(r-R_j)\rangle = S_{mn}\delta_{ij}$

$\langle \varphi_m|\Delta\hat{U}|\psi_K\rangle = \langle \varphi_m|\Delta\hat{U}|\sum_i \sum_m b_m \varphi_m(r-R_i) e^{iKR_i}\rangle =$

$\langle \psi_K|\hat{H}_{AT}|\varphi_m\rangle = \langle \psi_K|\mathcal{E}_m \varphi_m\rangle = \mathcal{E}_m\langle \psi_K|\varphi_m\rangle = \mathcal{E}_m b_m$

$\hat{H}_{AT}\varphi_m = \mathcal{E}_m \varphi_m$

$= \sum_m b_m\left[e^{iKa}\mathcal{E}_{mn}^{(-1)} + e^{iK0}\mathcal{E}_{mn}^{(0)} + e^{iKa}\mathcal{E}_{mn}^{(1)}\right] = \sum_m b_m\, G_{mn}$

$\mathcal{E}_{mn}^{(i)} = \displaystyle\int \varphi_m^*(r)\Delta\hat{U}\varphi_m(r-R_j)\,dx$ HOPPING INTEGRAL

$$G_{mn}(K) = \sum_{j=-1,0,1} e^{iK(ja)} \mathcal{E}_{mn}^{(j)}$$ By defining this quantity here we can simplify the equation.

Final result: $b_m(\mathcal{E}(K) - \mathcal{E}_m) = \sum_m b_m G_{mn}$ ⤳ Since m is generic, we have a set of equations.

Our system can be rewritten
$$\underline{b}\,\mathcal{E}(K) = \underline{b}\left(G + \mathcal{E}\,I\right) \qquad \overset{\mathcal{E}<0}{}$$

MATRIX FORM

$$\begin{cases} b_1(\mathcal{E}(K) - \mathcal{E}_1) = \sum_m b_m G_{1m} \\ \vdots \\ b_{LAST}(\mathcal{E}(K) - \mathcal{E}_{LAST}) = \sum_m b_m G_{LAST,m} \end{cases} \implies \underline{b} = \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_{LAST} \end{pmatrix}$$

Weighting coefficients number is equal to the wavefunctions one.

$$G = \begin{bmatrix} G_{11} & \cdots & G_{1,LAST} \\ & \diagdown & \\ G_{LAST,1} & & G_{LAST,LAST} \end{bmatrix}$$

Now we consider just s and p states.

S (EVEN) P (ODD)

Each G depends on K (difference from Chemistry)
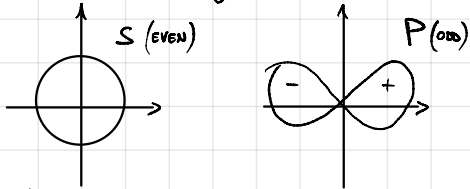
$$\mathcal{E}(K)\begin{bmatrix} b_s \\ b_p \end{bmatrix} = \begin{bmatrix} G_{SS} - \mathcal{E}_s & G_{SP} \\ G_{PS} & G_{PP} - \mathcal{E}_p \end{bmatrix}\begin{bmatrix} b_s \\ b_p \end{bmatrix}$$

Eigenvectors give weighting coefficients

$$\mathcal{E}_{ss}^{(j=0)} = \langle \varphi_s | \Delta \hat{U} | \varphi_s \rangle = -|\Delta U_s|$$

$$\mathcal{E}_{PP}^{(j=0)} = -|\Delta U_p|$$

$$\mathcal{E}_{sp}^{(j=0)} = \langle \varphi_s | \Delta \hat{U} | \varphi_p \rangle = \int \varphi_s^* \Delta U \varphi_p dx = \varnothing \quad \text{(INTEGRAL OF AN ODD QUANTITY)}$$

$$\mathcal{E}_{PS}^{(j=0)} = \varnothing$$

$$\mathcal{E}_{ss}^{(j=1)} = \int \varphi_s^*(r) \Delta\hat{U} \varphi_s(r-a)\,dx = -|V_{ss}|$$

REAL HOPPING

$$\mathcal{E}_{ss}^{(j=-1)} = -|V_{ss}|$$

$$\mathcal{E}_{sp}^{(j=-1)} = \int \varphi_s^*(r)\Delta\hat{U}\varphi_p(r-a)\,dx = +|V_{sp}|$$

$$\mathcal{E}_p^{(j=\pm 1)} = +|V_{pp}|$$

$$\mathcal{E}_{sp}^{(j=-1)} = -|V_{sp}|$$

POSITIVE ENERGY anti-binding

binding

$$G_{SS} = \overbrace{-|\Delta U_s| - |\mathcal{E}_s|}^{-|\mathcal{E}_{s,o}|} - |V_{SS}|\underbrace{\left(e^{-iKa} + e^{iKa}\right)}_{2\cos(Ka)}$$

$$G_{PP} = \overbrace{-|\Delta U_p| - |\mathcal{E}_p|}^{-|\mathcal{E}_{P,o}|} + |V_{PP}|\left(e^{-iKa} + e^{iKa}\right)$$

$$G_{SP} = |V_{SP}|\left(-e^{iKa} + e^{-iKa}\right)$$

$$G_{PS} = |V_{SP}|\left(e^{iKa} - e^{-iKa}\right)$$

$$\implies \begin{bmatrix} -|\mathcal{E}_{s,o}| - 2\cos(Ka)V_{SS} & -2i\sin(Ka)|V_{sp}| \\ \\ 2i\sin(Ka)|V_{sp}| & -|\mathcal{E}_{p,o}| + 2\cos(Ka) \end{bmatrix}\begin{bmatrix} b_s \\ \\ b_p \end{bmatrix} = \mathcal{E}(K)\begin{bmatrix} b_s \\ \\ b_p \end{bmatrix}$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{M}$$

$$[M - \mathcal{E}]\,\underline{b} = 0 \implies \det(M - \mathcal{E}) = 0$$

If M is diagonal, eigenvalues are trivial.

$$\mathcal{E}_1 = -\mathcal{E}_{s,o} - 2\cos(Ka)V_{SS} \implies \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{Pure } s$$

$$\mathcal{E}_2 = -\mathcal{E}_{P,o} + 2\cos(Ka)V_{PP} \implies \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad \text{Pure } p$$

This happens when $V_{sp} = 0$ (minimal overlapping) or when $K=0$ or $K = \frac{\pi}{a}$. Mixing terms prevent the crossing (see excel).

Tutorial #11

We find effective mass through semiclassical approach.
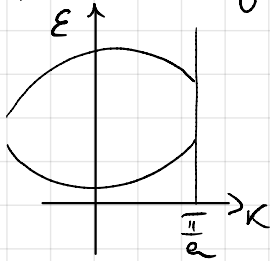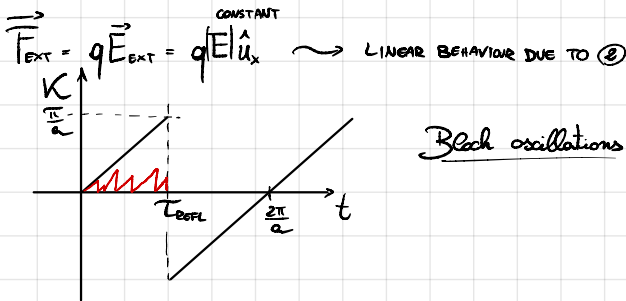

$$\mathcal{E}_\alpha(k)\,\psi = \hat{H}_{CRYSTAL}\,\psi$$

According to Wannier theorem, $\mathcal{E}_k(\vec{K}) \longleftrightarrow \mathcal{E}(-i\vec{\nabla})$

$$\psi_{\vec{K}} = U_{\vec{K}}(\vec{r})\,e^{i\vec{K}\cdot\vec{r}}$$

Bloch states are not good approximations of particle-like solutions. Wavepackets are: $\Psi(\vec{r},t) = \int \tilde{a}(\vec{K},t)\,\psi_{\vec{K}}(\vec{r})\,d\vec{K}$

At the end we have a set of semiclassical operations:

$$
\begin{cases}
① & m^*\vec{a} = \vec{F}_{EXT} = m^*\dfrac{d^2\vec{r}}{dt^2} \\[2mm]
② & \vec{F}_{EXT} = \dfrac{d\vec{p}}{dt} = \hbar\dfrac{d\vec{K}}{dt} \\[2mm]
③ & \vec{v} = \dfrac{d\vec{r}}{dt} = \vec{v}_g = \dfrac{1}{\hbar}\dfrac{\partial\mathcal{E}}{\partial K}\Big|_{K=0}
\end{cases}
\implies
m^*_{ij} = \frac{\hbar^2}{\left|\dfrac{\partial^2\mathcal{E}}{\partial K_i\,\partial K_j}\right|_{K_i=K_j=0}}
\xrightarrow{\text{1D or ISOTROPIC CRYSTAL}}
m^* = \frac{\hbar^2}{\dfrac{\partial^2\mathcal{E}}{\partial K^2}\Big|_{K=0}}
$$

What happens if we apply an external field to a crystal?

$$\vec{F}_{EXT} = q\vec{E}_{EXT} = q|E|\hat{u}_x \overset{CONSTANT}{\leadsto} \text{LINEAR BEHAVIOUR DUE TO } ②$$
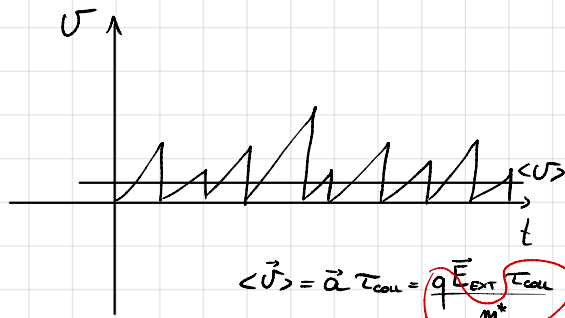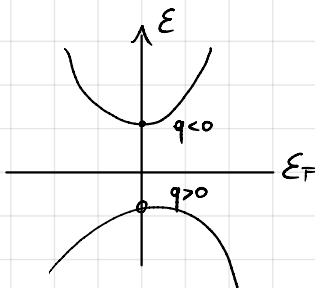

Bloch oscillations

We actually never see Bloch oscillations due to electron collisions and lattice vibrations (reset of the momentum). An average collision time τ_{coll} can be estimated.

$$
\begin{cases}
\tau_{REFL}\, qE = \hbar\dfrac{\pi}{a} \implies \tau_{REFL} = \dfrac{\hbar\dfrac{\pi}{a}}{qE} = 4\,ns \\[3mm]
\tau_{coll} \sim [ps-fs]
\end{cases}
$$

$a = 5\,\text{Å}$
$q = e$
$E = 10\,\text{V/cm}$
$\hbar = 6.6\cdot 10^{*}\,eVs$

$\underline{\tau_{coll} \ll \tau_{REFL}}$

$$\langle\vec{v}\rangle = \vec{a}\,\tau_{coll} = q\frac{\vec{E}_{EXT}}{m^*}\tau_{coll}$$

$$\mu$$

$$\vec{v}_{CB} = -\mu_e\,\vec{E}_{EXT}$$
$$\vec{v}_{VB} = \mu_h\,\vec{E}_{EXT}$$

We can associate to $\langle\vec{v}\rangle$ a current density $\vec{J} = q\,n\langle\vec{v}\rangle = \dfrac{q^2 n\,\tau_{coll}}{m^*}\vec{E}_{EXT}$.

$$\sigma$$

In a semiconductor, $\vec{J}_{TOT} = \vec{J}_{CB} + \vec{J}_{VB} = e(n_e\mu_e + n_h\mu_h)\vec{E}_{EXT}$; sign is the same for both contribution. In a typical metal $n_h \approx 0$, so $\vec{J}_{TOT} \approx \vec{J}_{CB} = \underbrace{\dfrac{e^2 n_e\,\tau_{coll}}{m^*}}_{\text{Drude's model}}\vec{E}_{EXT}$ (isotropic $\to$ no tensors).

What if we apply a magnetic field?

<u>Hall effect</u>

$\vec{F_e} = -eE_{EXT}\hat{u}_x \qquad \vec{F_m} = -qvB\hat{u}_y$

$$\begin{cases} \vec{J} = -en_e\vec{v} \\ \vec{E_H} = -vB\hat{u}_y = -R_H(\vec{J} \times \vec{B}) \end{cases} \qquad \text{where} \quad R_H = \frac{E_H}{J_{CB}B} = \frac{1}{n_e}$$
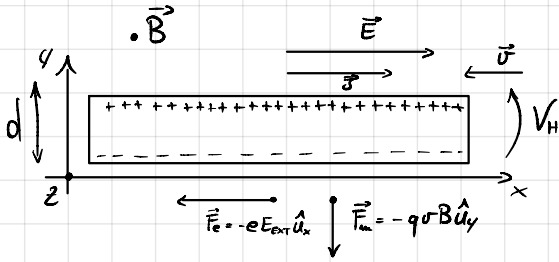
Lorentz force is $\quad \vec{F_L} = \underbrace{q\vec{E}}_{\vec{F_e}} + \underbrace{q\vec{v} \times \vec{B}}_{\vec{F_m}}$

At the equilibrium, Hall potential V_H appears.

$\vec{E_H} = -\dfrac{V_H}{d}\hat{u}_y \implies \vec{F_H} = -e\vec{E_H} \implies \vec{F_H} + \vec{F_m} = 0$

$$-evB + e\frac{V_H}{d} = 0$$

$$V_H = vBd \rightarrow E_H = vB$$