Solid State Physics — Dynamics of Bloch electrons

free electron

1D $\psi = e^{ikx}$

3D $\psi = e^{i\underline{k}\underline{r}}$

Both

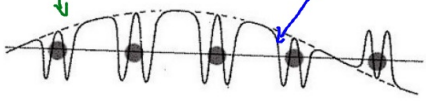
$$p = \langle \psi | \hat{p} | \psi \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi \, dx = \int_{-\infty}^{\infty} \psi^*(\underline{r}) \frac{\hbar}{i} \frac{\partial}{\partial \underline{r}} \psi(\underline{r}) \, d^3\underline{r}$$

$$p = \hbar k$$

$$E = \frac{\hbar^2 k^2}{2 m_e}$$

Bloch electron

1D $\varphi = u(x)\, e^{ikx}$ $\quad u(x + n\cdot a) = u(x)$



3D $\varphi = u_k(\underline{r})\, e^{i\underline{k}\underline{r}}$ $\quad u_k(\underline{r} + \underline{R}) = u_k(\underline{r})$

periodic boundary condition

$$p_k = \hbar \underline{k} + \frac{\hbar}{i} \int \left(u_k^*(x) \frac{d u_k(x)}{dx} \right) dx$$

$\hbar\underline{k}$: crystal momentum of Bloch-electron

$\frac{\hbar}{i} \int \left(u_k^*(x) \frac{d u_k(x)}{dx} \right) dx$: momentum of whole crystal

if $\underline{k}' = \underline{k} + \underline{K}$ (outside, inside) $\Rightarrow$ 1st Brillouin zone

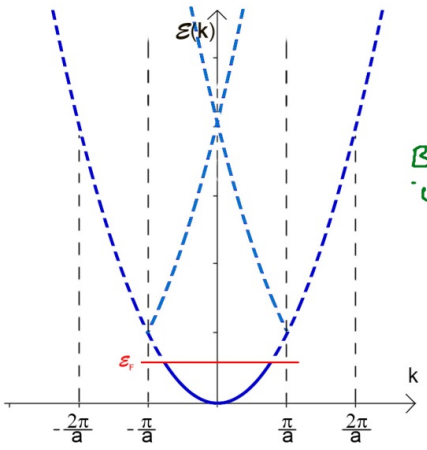
$$\psi_{k'}(\underline{r}) = u_{k'}(\underline{r})\, e^{i\underline{k}'\underline{r}} = u_{k'}(\underline{r})\, e^{i\underline{k}\underline{r}} \cdot \underbrace{e^{i\underline{K}\underline{r}}}_{=1}$$

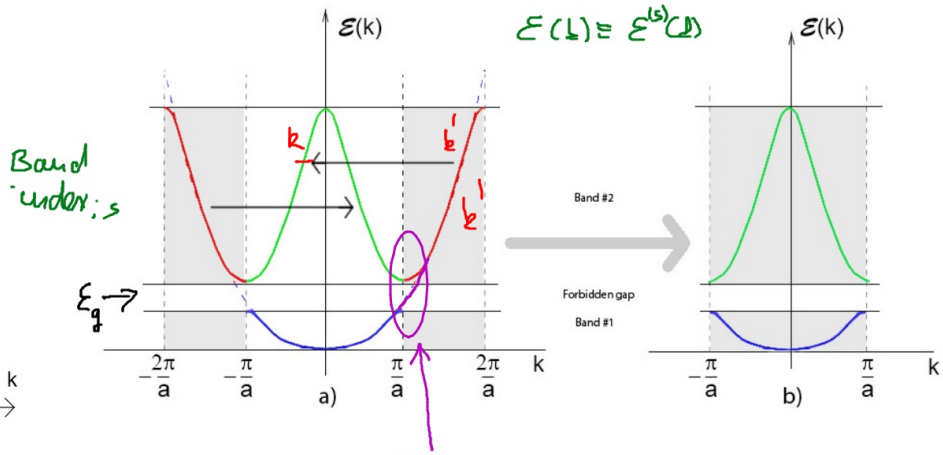
$u_{k'}(\underline{r}) \neq u_k(\underline{r}) \Rightarrow \psi_{k'}(\underline{r}) \neq \psi_k(\underline{r})$

and $p_{k'} \neq p_k$, $E(k')$ may or may not equal to $E(k)$

but the crystal momentums are equal !

$$E = \frac{\hbar^2 \underline{k}^2}{m_{eff}} + E_{crystal}(\underline{k})$$





horizontal at zone boundary

1D $\varepsilon = \frac{\hbar k}{m_e} \Rightarrow \frac{d^2\varepsilon}{dk^2} = \frac{\hbar^2}{m_e}$

$m_e = \hbar^2 \frac{1}{\left(\frac{d^2\varepsilon}{dk^2}\right)}$

$m_{eff} := \hbar^2 \frac{1}{\frac{d^2\varepsilon}{dk^2}}$

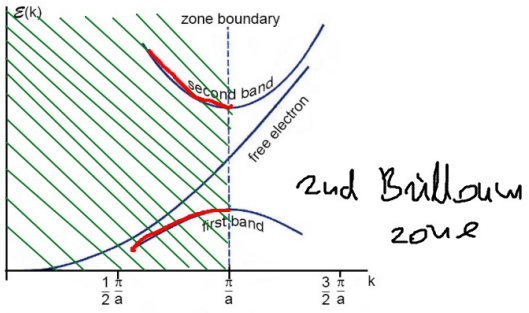
3D $\frac{1}{\hbar^2} \frac{\partial \varepsilon}{\partial k_l \partial k_m} = m_{eff\,l,m}$

$m_{eff} = \begin{pmatrix} m_{11} & m_{12} & m_{13} \\ m_{12} & m_{22} & m_{23} \\ m_{13} & m_{23} & m_{33} \end{pmatrix}$ tensor (matrix)

$m_{21} = m_{12}$ because $\frac{\partial^2 \varepsilon}{\partial k_2 \partial k_1} = \frac{\partial^2 \varepsilon}{\partial k_1 \partial k_2}$

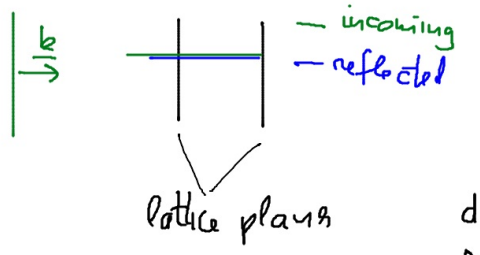
Why is $\varepsilon^{(s)}(k)$ horizontal at $\pm \frac{\pi}{a}$?

1st Brillouin zone



2nd Brillouin zone

Consider an electron wave total reflection at some k value:



Bragg: $2d \underbrace{\sin\alpha}_{1} = n \cdot \lambda$

$2d = n\lambda$

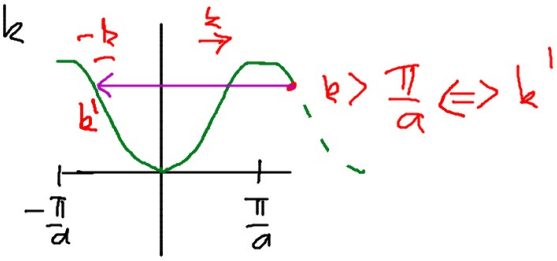
$d \equiv a$

$\lambda = \frac{2\pi}{k} \Rightarrow 2a = n \frac{2\pi}{k}$

$\boxed{k = n \cdot \frac{\pi}{a}}$

when $k = \frac{\pi}{a}$ $(\cdot n)$

total reflection: $k \to -k$



$\mathcal{E}(k)$

$\underline{p} = \underline{p}_k + \underline{p}_{crystal}$

crystal momentum $\underline{p}_k = \hbar \cdot \underline{k}$

maximum $m_{eff} < 0$! $p_k < 0$

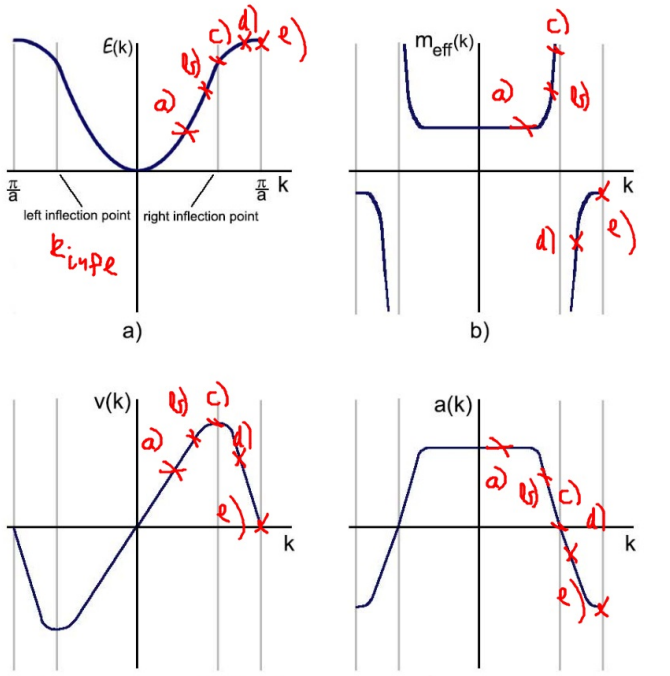
inflection point $m_{eff} = \infty$! $p_k = 0$

minimum $m_{eff} > 0$ $p_k \geq 0$

$$\underline{F} = -e\underline{E}, \quad F = m_{eff}\frac{dp}{dt} = m_{eff}\frac{dp_k}{dt} + m_{eff}\frac{dp_{crystal}}{dt}$$

Let $F > 0$

$F > 0$	0	$+$	> 0
$F > 0$	< 0		> 0



Bloch-oscillations when $F = const$

$F = -eE = const$

$t = 0 \quad k = 0, \; v = 0$

$a = \frac{F}{m_{eff}} = const$

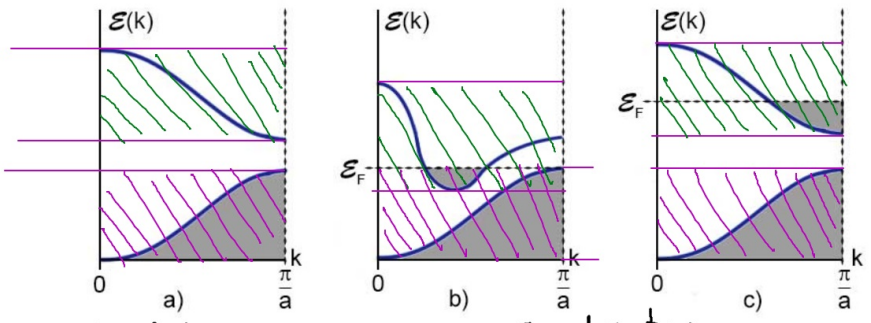
$t > 0 \quad k < \frac{\pi}{a}$ ↑ increases

	k	m_{eff}	v	a
a)	$k < k_{infl}$	> 0	↑	const
b)	$k \approx k_{infl}$	> 0	↑	↓
c)	$k = k_{infl}$	∞	const	0
d)	$k < \frac{\pi}{a}$	< 0	↓	< 0, ↓
e)	$k(t+\Delta t) = -\frac{\pi}{a}$	< 0	< 0	< 0, ↑

... (figure it out!)

starts again

Simplified band diagrams



conduction band

valence band

insulator

conductors

overlapping bands

partially empty cond. band

Bloch oscillations ⇒ if $\underline{F}$ (or $\underline{E}$) constant electrons can never leave the first Brillouin zone / band!

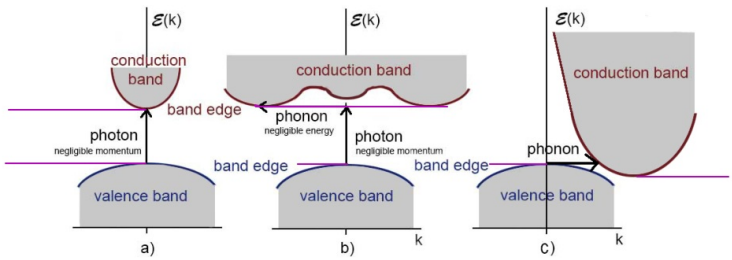
What happens in photon – electron and phonon – electron collisions?

photon – electron	phonon – electron
$\mathcal{E} = \hbar\omega$	$\mathcal{E} = \hbar\omega(k) \ll \frac{\hbar^2}{2m_{eff}}$
$p = \frac{\mathcal{E}}{c} \ll \hbar k$	$p = \sqrt{2m\mathcal{E}}$
can change: energy	momentum
cannot change: momentum	energy

— band edge

$m_{eff} > 0 \rightarrow$

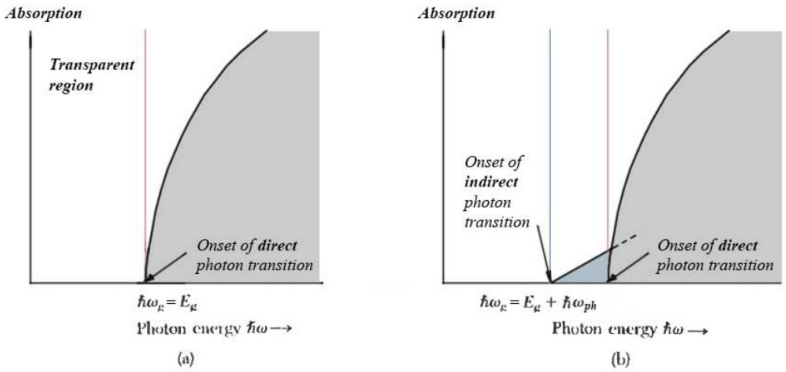
$m_{eff} < 0 \rightarrow$



direct band | indirect band | overlapping band

Experiment:

optical absorption:



Width of energy bands

Hartree – Fock : free electrons → Bloch electrons

$\psi_F = e^{ikx}$ $\quad$ $\psi_B = e^{ikx} u(x)$

Try to create Bloch-functions from atomic orbitals

Tight binding approximation

Assumption : each electron is tightly bound to the atom ⇒ each has the same $\phi(x)$ orbital. Atomic distance is a

let $\psi(x) = \sum_{n=1}^{N} C_n \phi(x - na)$

if $C_n = e^{ik \cdot na} \Rightarrow \psi(x) = \sum_{n=1}^{N} e^{ikna} \phi(x - na)$

$$\psi(x) = \sum_{n=1}^{N} \underbrace{e^{ikx} \cdot e^{-ikx}}_{1} e^{ikna} \phi(x - na)$$

$$\psi(x) = \sum_{n=1}^{N} e^{ikx} e^{-ik(x-na)} \phi(x - na)$$

$$= \underbrace{\left(\sum_{n=1}^{N} e^{-ik(x-na)} \phi(x - na) \right)}_{u(x-na)} \cdot e^{ikx}$$

and $e^{-ik(x-na)} = e^{ikx}$

$\phi(x - na) = \phi(x)$

$\Rightarrow u(x - na) = u(x)$

$\psi(x) = u(x) e^{ikx}$ → Bloch-function!

$$\langle \varepsilon(k) \rangle = \frac{\int \psi^* \hat{H} \psi \, dx}{\int \psi^* \psi \, dx} = \quad \text{where } \hat{H} = \sum_{n=1}^{N} \hat{H}(na)$$

$$= \sum_{n=1}^{N} \frac{\int e^{-ikna}\, \phi^*(x-na)\, \hat{H}\, e^{ikna}\, \phi(x-na)\, dx}{\sum_{n=1}^{N} \int \phi^*(x-na)\, \phi(x-na)\, dx}$$

here $\hat{H} \leftarrow \hat{H}(na)$ as $\phi(x-na) \approx 0$ x not around $n\cdot a$

and $\int \phi^* \phi\, dx = 1$

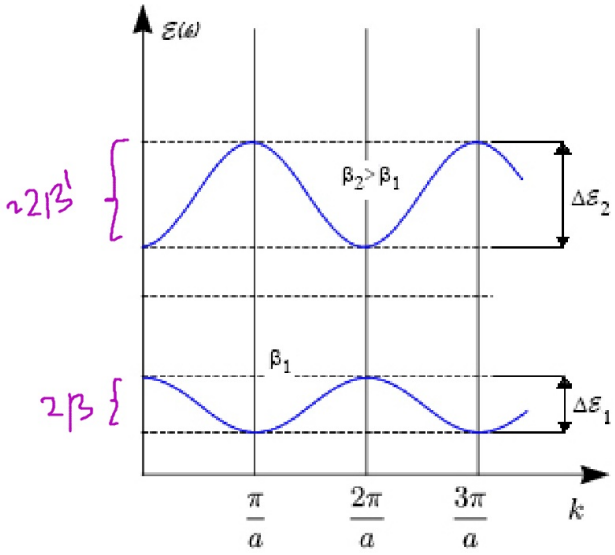
See the Book for Calculation

Result: $\langle E(k) \rangle = E_{atomic} - \alpha - 2\beta \cos ka$

$$\beta \approx \sum_{n,l=1}^{N} \int \psi^*(x-la)\, \hat{V}(x)\, \psi(x-na)\, dx$$

if $l \neq n \pm 1 \rightarrow \int \approx 0$ $\Rightarrow$ narrow d-band
wide s-band

or bond energy integral
two center integral



← larger overlap of wave f.
larger contributions
from $l \neq n \pm 1$

Holes

$\underline{j} = -n \cdot e \cdot \underline{v}$ or $\underline{v} \equiv \underline{v}(\underline{k})$, $n = n(\underline{k})$

for one Bloch-electron $\underline{j}_k = -e\,\underline{v}(\underline{k})$

$$\underline{j} = -\sum_{\substack{\text{occupied}\\ \text{levels}\\ \text{in band}}} e \cdot \underline{v}(\underline{k}) = -\frac{e}{8\pi^3} \int_{\substack{\text{occ.}\\ \text{levels}}} \underline{v}(\underline{k})\, d^3k$$

if all levels were occupied by 2 electrons

$$j_{\text{full band}} = 0 \quad \Leftarrow \text{Pauli principle}$$

if empty levels were occupied : $\underline{j}_{\text{empty}} = -\sum_{\substack{\text{empty}\\ \text{levels}\\ \text{in band}}} e\,\underline{v}(\underline{k}) = -\frac{e}{8\pi^3} \int_{\substack{\text{empty}\\ \text{levels}}} \underline{v}(\underline{k})\, d^3k$

$$\underline{j} = \underbrace{\underline{j}_{\text{occupied}}}_{j_{\text{full band}} = 0} + \underbrace{\underline{j}_{\text{empty}} - \underline{j}_{\text{empty}}}_{0}$$

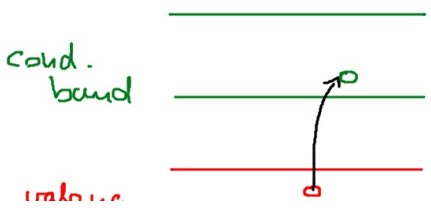
$$\underline{j} = -\underline{j}_{\text{empty}} = +\frac{e}{8\pi^3} \int_{\text{empty}} \underline{v}(\underline{k})\, d^3k$$

but $\underline{j} = \underline{j}_{\text{occupied}} \Rightarrow \underline{j}_{\text{empty}} = -\underline{j}_{\text{occupied}}$

The same current can be described as current of occupied OR current of empty levels.

But not using both!

$\underline{j}_{\text{occupied}}$ has $(-e)$ charges ↑ electrons | $\underline{j}_{\text{empty}}$ $(+e)$ charges ↑ holes



use $\underline{j}_{\text{occupied}}$ — 1 electron / majority charge carriers

band — use j_{empty} — 1 hole

$j = j_{(conduction\ band)} + j_{(valence\ band)}$

$j_{occupied}$ $\quad$ j_{empty}

But

in valence band $\quad$ $j_{valence} \neq j_{(valence)} + j_{(valence)}$

$j_{occupied} + j_{empty} = 0$

if there are both holes and electrons, which ones to use?

mobility $\quad \mu = \frac{e\tau}{m_{eff}}$

Example: Mg ... $3s^2$, Cd ... $5s^2$ > completely full, but metal $\Rightarrow \exists$ overlapping conduction band

In both

$|m_{eff}(\text{holes in valence band})| < |m_{eff}(\text{electrons in conduction band})|$

$\Rightarrow \quad \mu_h(\text{val}) > \mu_e(\text{cond}) \Rightarrow$ majority charge carriers are <u>holes</u>!