Physik-Institut

Open Day:

November 21 15:00-18:00 for Master and Bachelor students
J floor

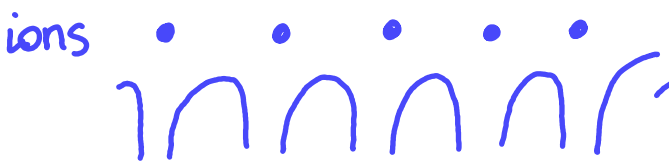
17:00 Dectris prize for best master thesis in experimental physics

Electronic Band Structure

Lecture 2

Singleton Chapter 3
(Also Kittel, and Simon)

Recap



$$V(\vec{r}) = \sum_{\vec{G}} V_G e^{i\vec{G}\vec{r}}$$

$$\psi(\vec{r}) = \sum_{\vec{K}} c_K e^{i\vec{K}\vec{r}}$$

periodic boundary conditions

$\vec{K}\vec{q} = 2\pi \frac{m_i}{N_i}$

Schrödinger equation rewritten taking into account periodic potential.

$$\left(\frac{\hbar^2 K^2}{2m} - E\right) c_{\vec{K}} + \sum_{\vec{G}} V_{\vec{G}} c_{\vec{K}-\vec{G}} = C$$

CENTRAL EQUATION

(set of linear eq for the coefficients c_K)

0) $V_G = 0$: No potential ⇒ Free e⁻ case

i) $V_G \neq 0$: For a fixed $\vec{K}$, central eq. couples only those coefficients that differ by $\vec{K}$ by a R.L. vector $\vec{G}$ (i.e. 1D $0, K \pm \frac{2\pi}{a}, K \pm \frac{4\pi}{a}$ ...)

$$\Rightarrow \psi_{\vec{q}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{q}-\vec{G}} e^{i(\vec{q}-\vec{G})\vec{r}} = \underbrace{e^{i\vec{q}\vec{r}}}_{\text{plane wave}} \underbrace{\sum_{\vec{G}} c_{\vec{q}-\vec{G}} e^{-i\vec{G}\vec{r}}}_{\text{function with periodicity of the lattice}} = \underbrace{e^{i\vec{q}\vec{r}} \cdot u_{\vec{q}}(\vec{r})}_{\text{BLOCH THEOREM}}$$

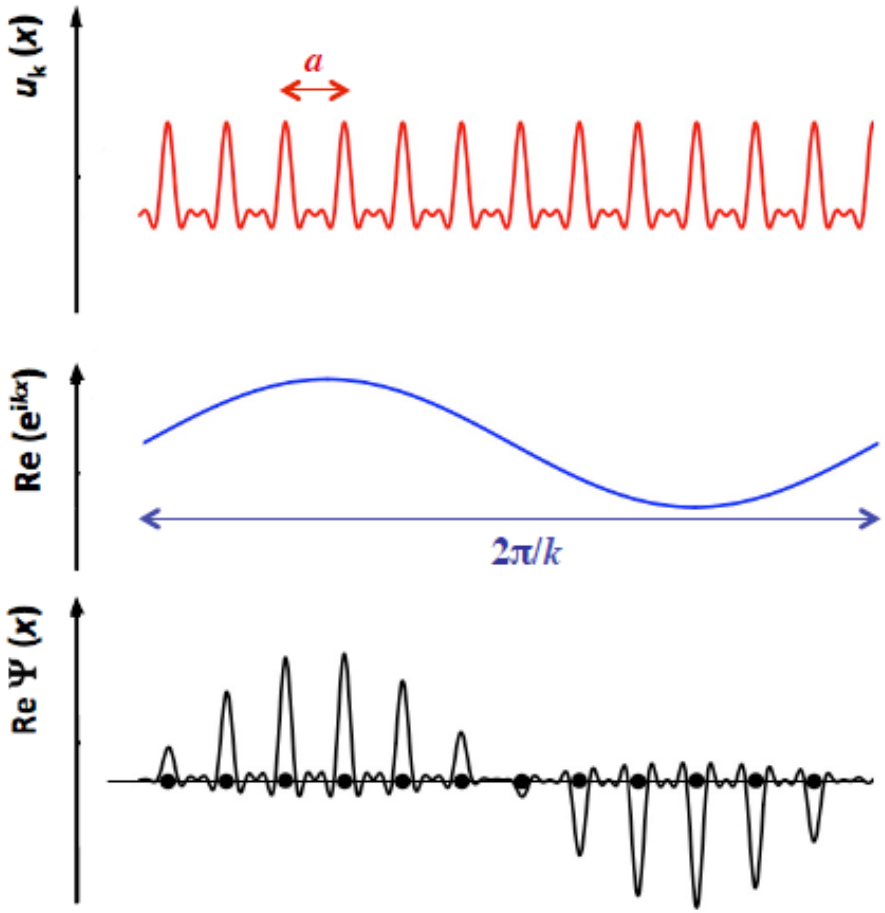
$\vec{q}$ ↑ wavevector

Bloch wavefunction

$$\psi_q(\vec{r}) = e^{i\vec{q}\vec{r}} u_{\vec{q}}(\vec{r})$$

periodic function
$u_q(\vec{r}) = u_q(\vec{r} + T)$

$\vec{q}$ crystal momentum or quasimomentum

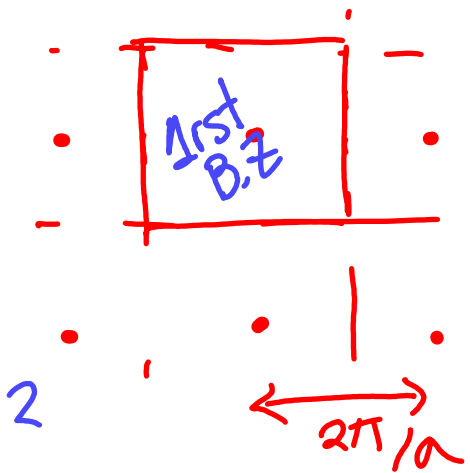


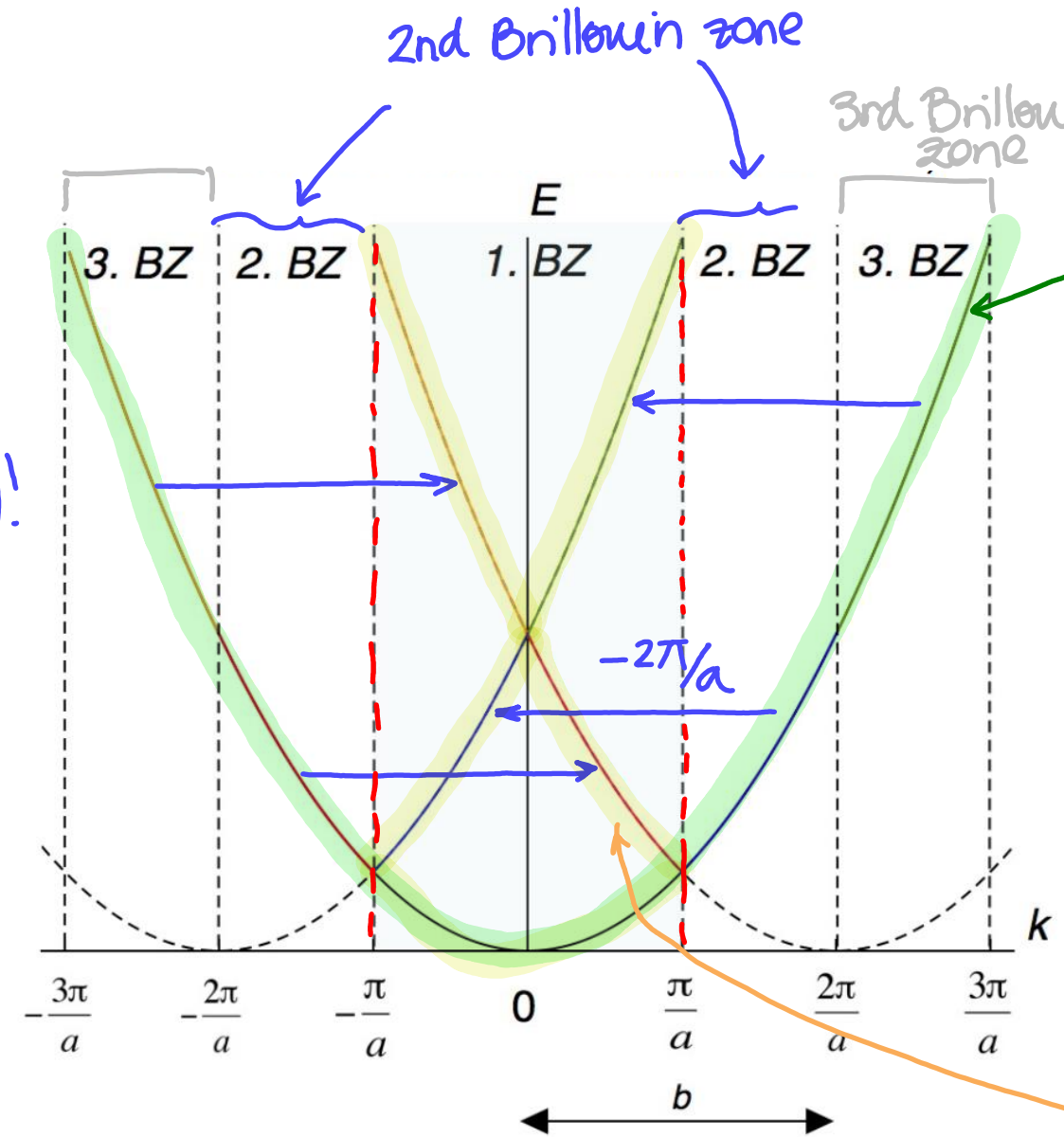
$$\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}+\vec{G}}(\vec{r})$$

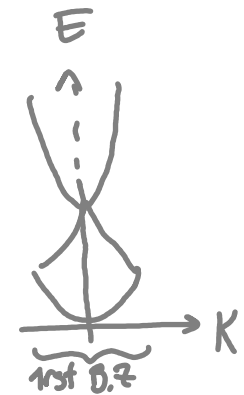
$$E(\vec{k}) = E(\vec{k}+\vec{G})$$

Dispersion relation E(k) repeats periodically!

Remember definition Brillouin zone! (how to construct it, boundaries, ...).

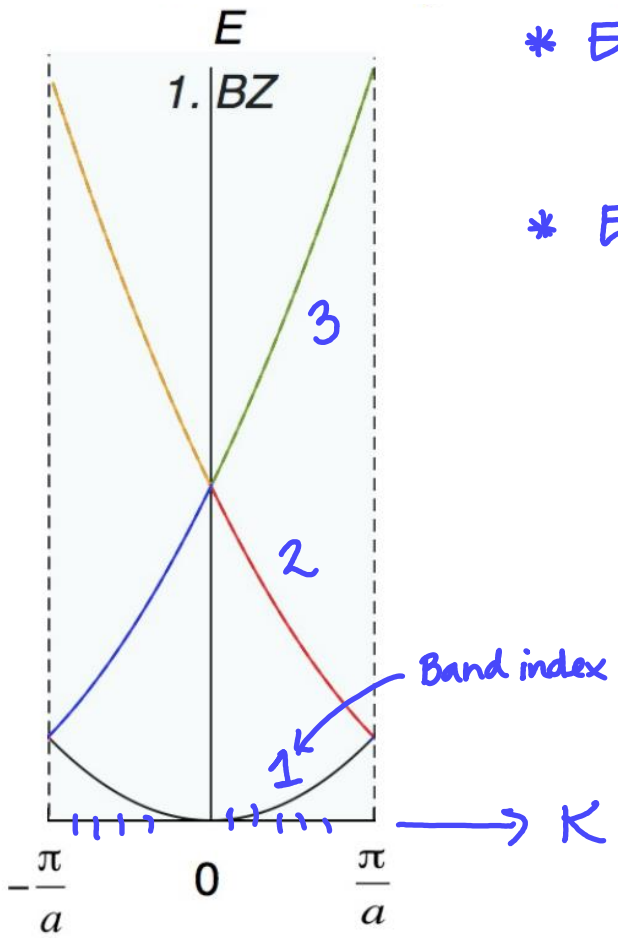






Energy bands

Reduced-zone scheme → (seen as the emergence of branches within 1st B.Z.)



$\psi_{n,\vec{q}}(\vec{r})$

n = band index

$\vec{q}$: specifies the e⁻ state

For each n, the set of electronic levels specified by $E_n(\vec{k})$ is called Energy band

Info contained in the $\neq n$ & $\vec{q}$ = Band structure of the solid

Remember! # u.c. in the crystal ↓

* Each band contains N states within 1st B.Z.

* Each state can accommodate at max 2 e⁻ (Pauli)

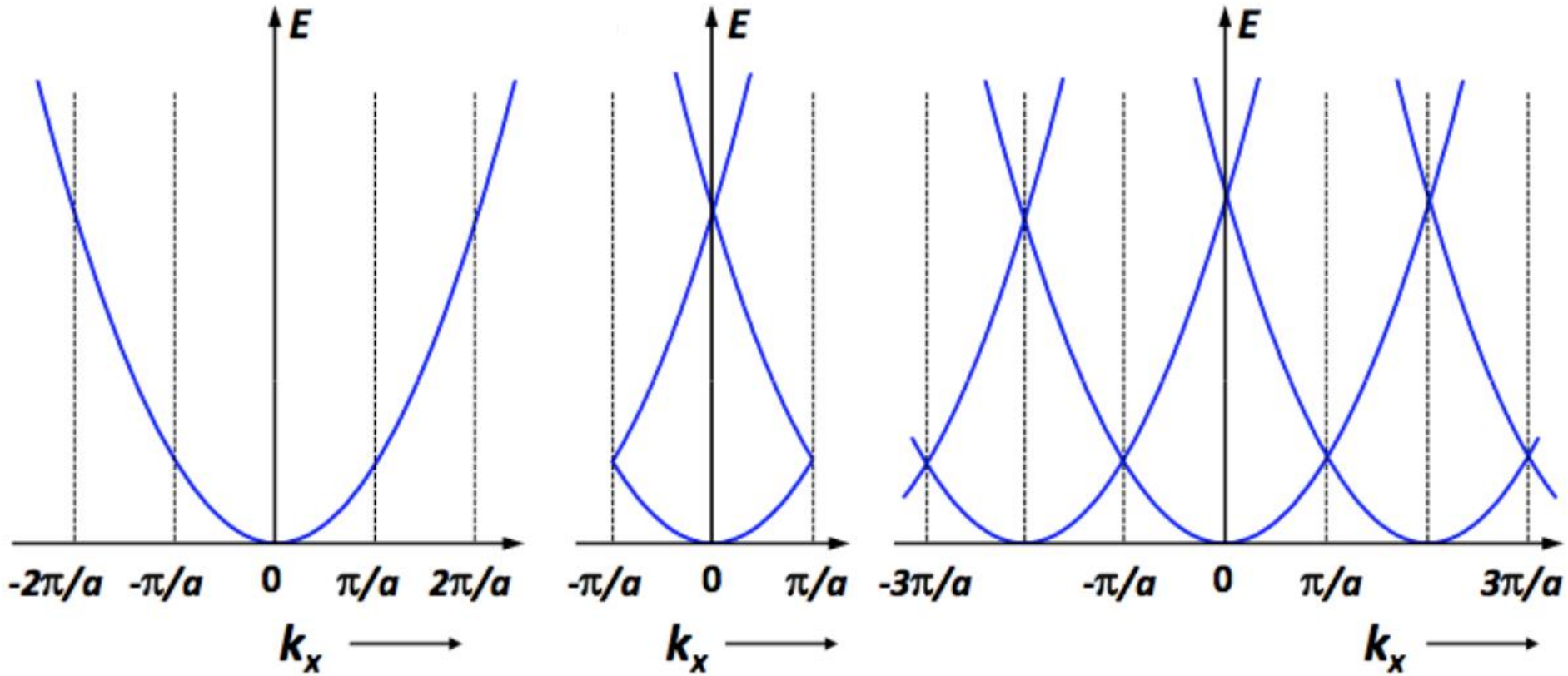
⇒ **2N e⁻ per band**

↓

Very important to decide if a material is a metal or an insulator

Goal of today!

Zonenschemata (für V=0)



Ausgedehntes Zonenschema Reduziertes Zonenschema Periodisches Zonenschema

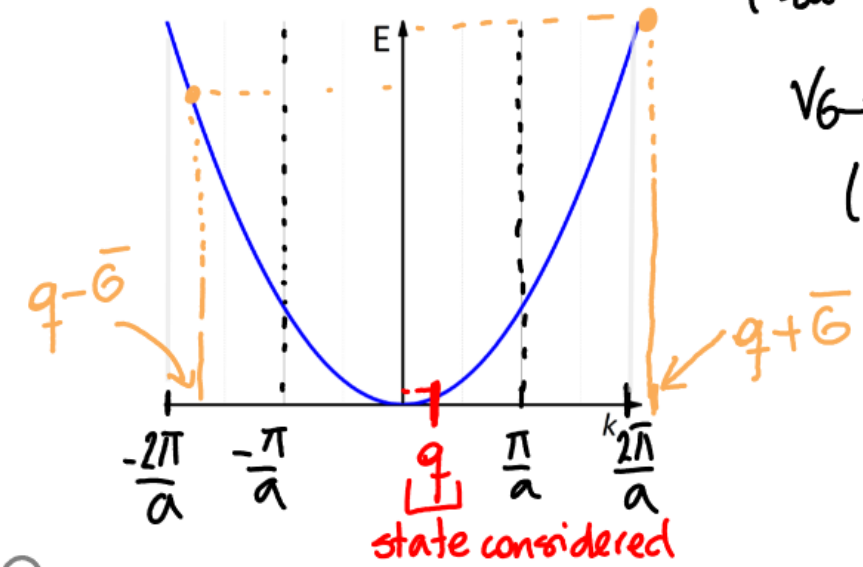
Recap

$$(E^0_{q-G'} - E)C_{q-G'} + \sum_{G''} V_{G''-G'} C_{q-G''} = 0$$

Nearly free electron model

Single electron energy state

Let's consider an e⁻ state defined by $E(\bar{q}-\bar{G})$ such as there is no other state at that point in k-space (*)



$V_G \to 0$:

$$(E^0_{\bar{q}-\bar{G}} - E)\, c_{\bar{q}-\bar{G}} = 0$$

$$c_{\bar{q}-\bar{G}} = 0$$

$$E_{\bar{q}-\bar{G}} = E = \underbrace{\frac{\hbar^2(\bar{q}-\bar{G})^2}{2m}}_{\text{energy of state considered}}$$

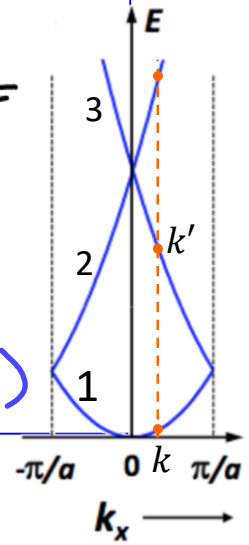
(*) Note that states $\bar{q}+\bar{G}$ and $\bar{q}-\bar{G}$ have energies very different to that of state $\bar{q}$

only one $c_{\bar{q}-\bar{G}} \neq 0$

$$\Psi = \sum_{\bar{K}} c_{\bar{K}}\, e^{i\bar{K}\cdot\bar{r}}$$

$$\Rightarrow \Psi(\bar{r}) = c_{\bar{q}-\bar{G}}\, e^{-i(\bar{q}-\bar{G})\cdot\bar{r}}$$

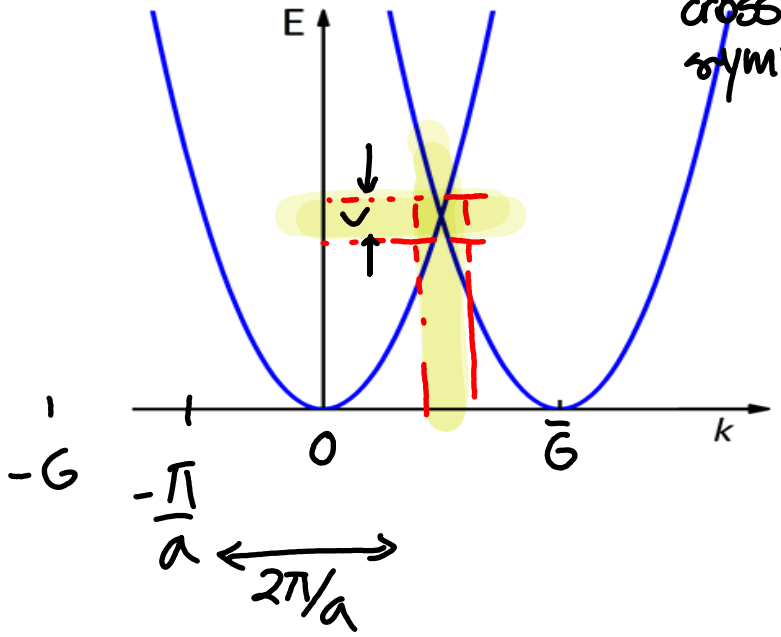
We recover case of the free e⁻ model (+ periodicity in space)



Nearly free electron model

$$(E^0_{q-G'} - E)C_{q-G'} + \sum_{G''} V_{G''-G'} C_{q-G''} = 0$$

Degenerate states



Let's look now the case where the dispersion energy curves of the free e⁻ cross (i.e. typically at boundaries by symmetry).

$$\Rightarrow \quad |E_{\bar{q}-\bar{G}_1} - E_{\bar{q}-\bar{G}_2}| \lesssim V$$

and $|E_{\bar{q}-\bar{G}_1} - E_{\bar{q}-\bar{G}|} \gg V$ for all $\bar{G} \neq \bar{G}_2$

$$(E - E^0_{q-G_1})\, C_{q-G_1} = \overbrace{V_{G_1-G_1}}^{\equiv V_0 \equiv 0} C_{q-G_1} + V_{G_2-G_1} C_{q-G_2} + \sum_{G \neq G_1, G_2} V_{G-G_1} C_{q-G}$$

$$(E - E^0_{q-G_2})\, C_{q-G_2} = \underbrace{V_{G_2-G_2}}_{\equiv V_0 \equiv 0} C_{q-G_2} + V_{G_1-G_2} C_{q-G_2} + \sum_{G \neq G_1, G_2} V_{G-G_2} C_{q-G}$$

very small corrections

$$\left.\begin{aligned} (E - E^0_{q-G_1})\, C_{q-G_1} &= V_{G_2-G_1} C_{q-G_2} \\ (E - E^0_{q-G_2})\, C_{q-G_2} &= V_{G_2-G_1} C_{q-G_1} \end{aligned}\right\}$$

2 finite coefficients $c_{\bar{q}-\bar{G}_1}$ & $c_{\bar{q}-G_2}$

Solution: superposition of two plane waves.

Let's simplify notation $\vec{K} = \vec{q} - \vec{G}_1$

$\vec{G} = \vec{G}_2 - \vec{G}_1$

$$\begin{cases} (E - E^0_K) c_K = V_G c_{K-G} \\ (E - E^0_{K-G}) c_{K-G} = V_{-\bar{G}} c_K = V^*_{\bar{G}} c_K \end{cases}$$

$V_{-G} = V^*_{\bar{G}}$ (because potential must be real)

Solution of this system of eqs.

$$E = \frac{1}{2}\left(E^0_K + E^0_{K-\bar{G}}\right) \pm \left\{ \left(\frac{E^0_K - E^0_{K-G}}{2} \right)^2 \pm |V_G|^2 \right\}$$

$$\boxed{E \simeq \frac{E^0_K + E^0_{K-G}}{2} \pm |V_{\bar{G}}|}$$

$\Rightarrow$ Symmetric splitting of the levels of the free electron energy where E^0_K and E^0_{K-G} cross

(and the split is $|2V_G|$)

$$E \simeq \frac{1}{2}(E_k^\circ + E_{k+G}^\circ) \pm |V_G|$$

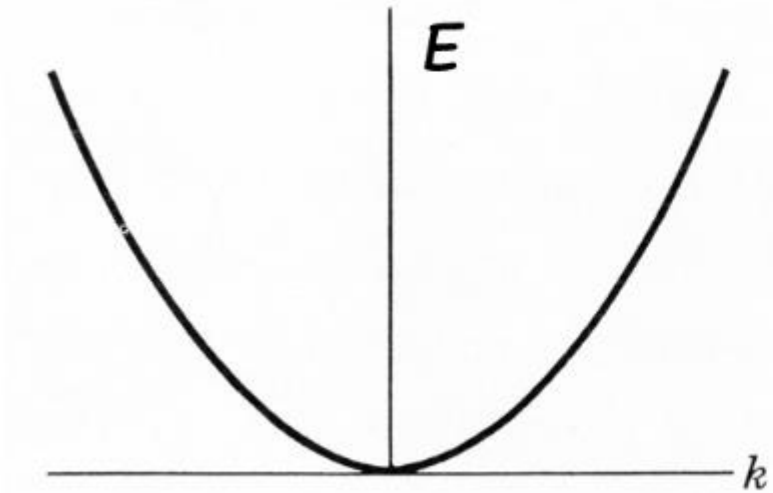
(band splitting)

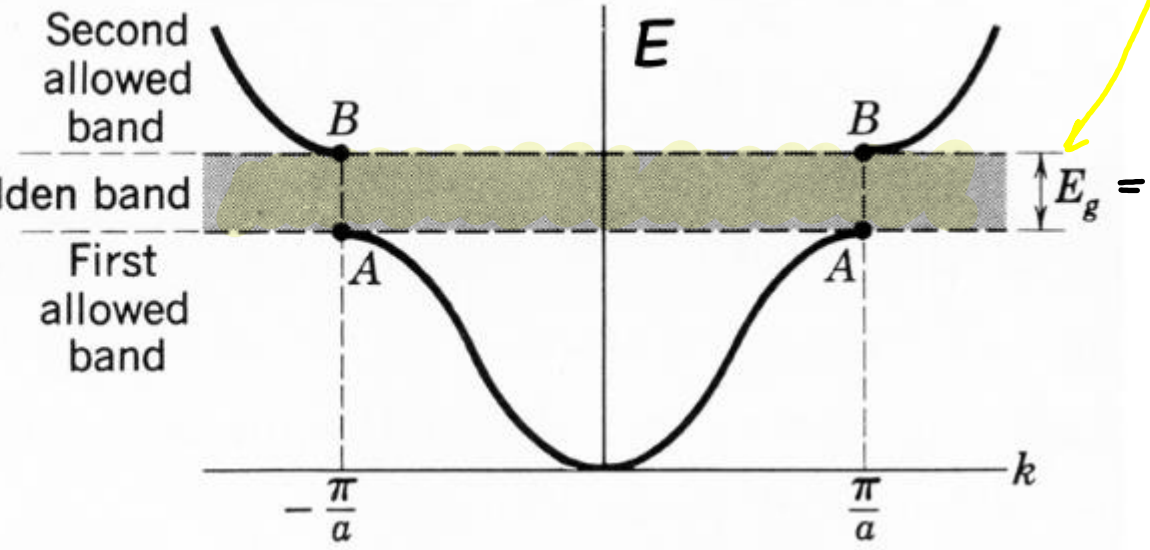
the result of adding a weak periodic potential is the opening of an energy gap

i.e. "region of forbidden energies"

"One level is raised by $|V_G|$ and the other uniformly lowered by the same amount ⇒ no states in energy in between"

Free e- model





Where do the bands $E^0_{\vec{k}}$ and $E^0_{\vec{k}-\vec{G}}$ cross?

$E^0_{\bar{K}} = E^0_{\bar{K}-\bar{G}}$ when $|\bar{K}| = |\bar{K}-\bar{G}|$

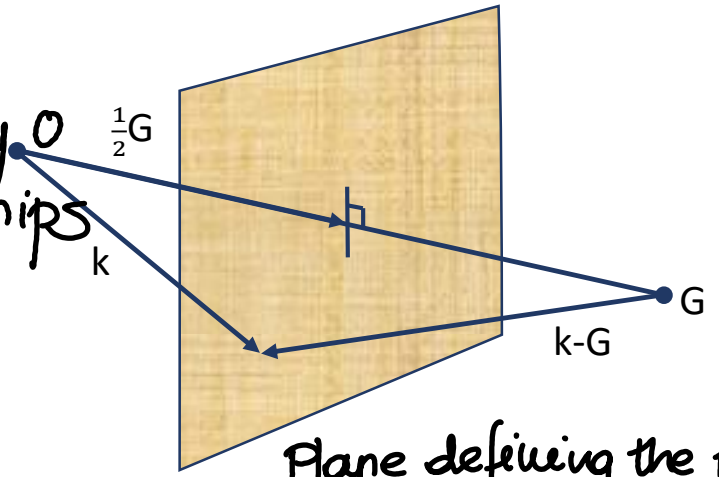
$$\frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 (K-G)^2}{2m} \Rightarrow \bar{K}^2 = K^2 + G^2 - 2\bar{K}\cdot\bar{G}$$

(Remember diffraction condition!)

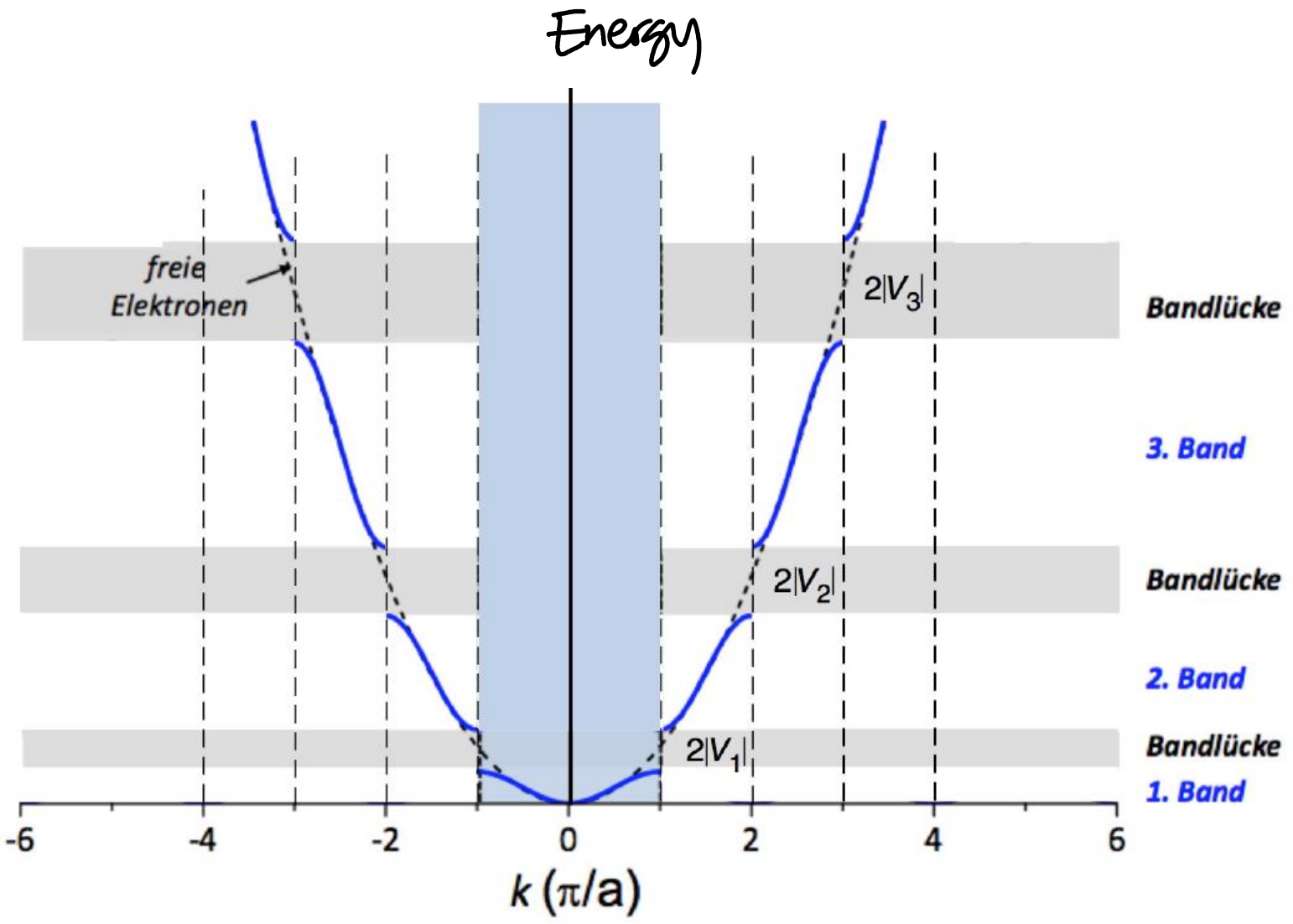
$$\Rightarrow \boxed{2\bar{K}\cdot\bar{G} = G^2}$$

$\Rightarrow$ A weak periodic potential has its strongest effects at the zone boundaries

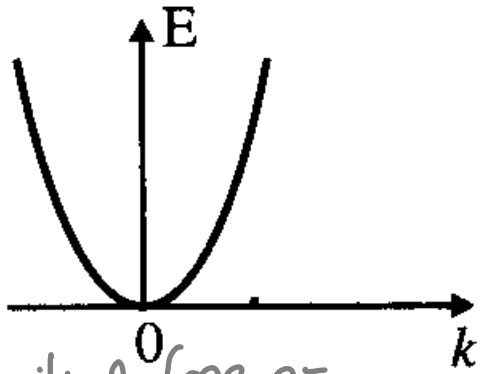
At these points, a band gap opens symmetrically around the free-electron dispersion relationships



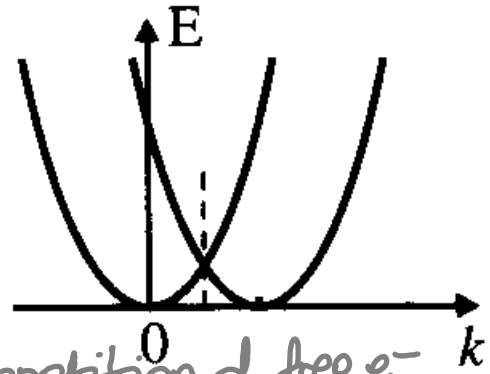
Plane defining the points at which $E^0_{\bar{K}} = E^0_{\bar{K}-\bar{G}}$


Energy
freie Elektronen
$2|V_3|$
$2|V_2|$
$2|V_1|$
Bandlücke
3. Band
Bandlücke
2. Band
Bandlücke
1. Band
-6
-4
-2
0
2
4
6
k (π/a)

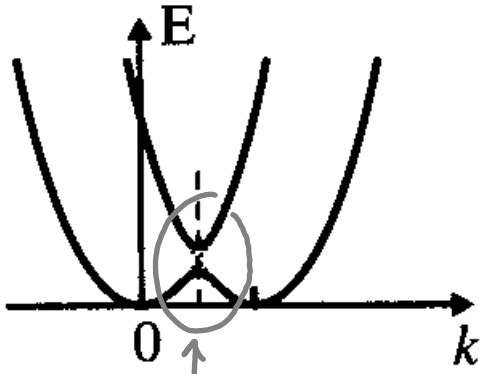
Effect of gap opening in a band



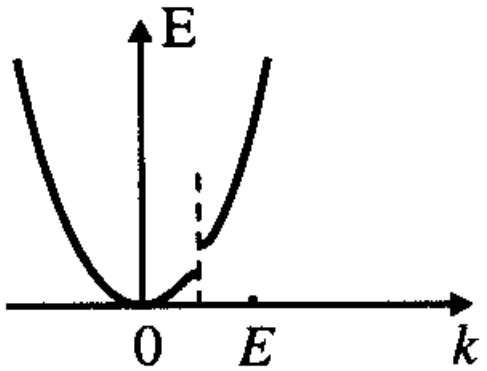
Initial free e⁻ model



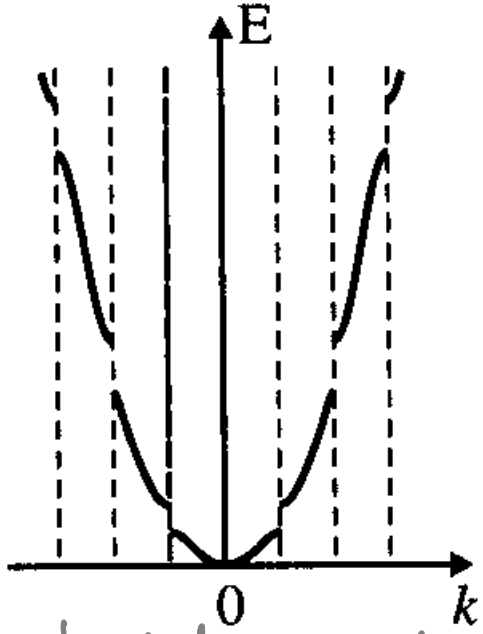
Repetition of free e⁻ due to periodicity of K-space



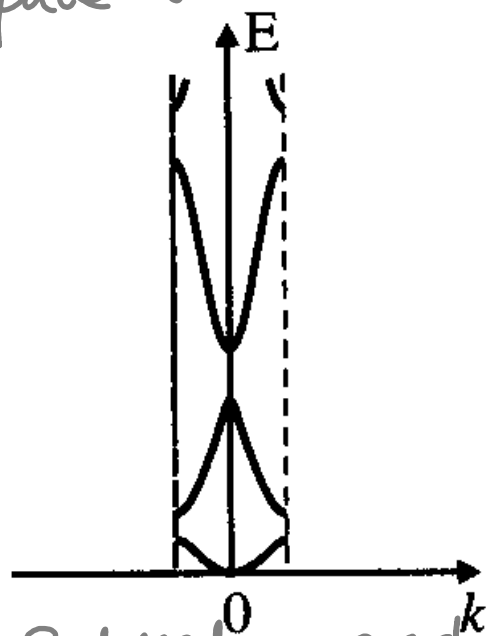
opening of the gap at zone boundary where the 2 curves cross



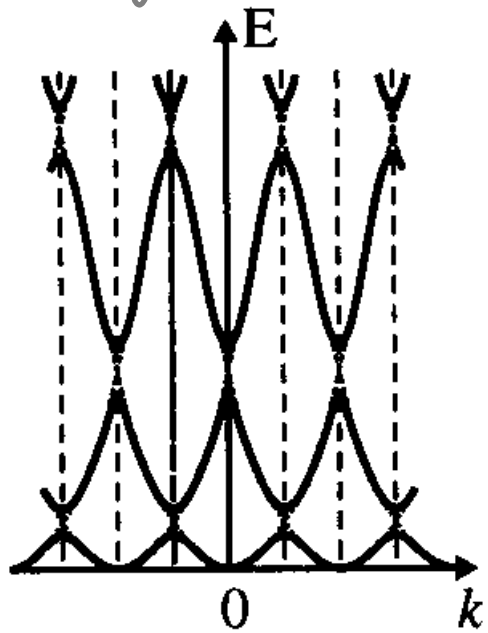
these 3 schemes represent the same :



Extended zone scheme

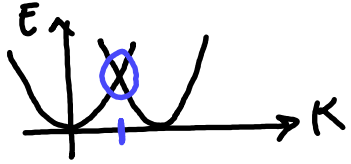


Reduced zone scheme



Periodic-zone scheme.

Why a gap?



If free e^- energy is degenerate at 2.B $\Rightarrow$ Schr. eq solution is superposition of 2 waves

$$\begin{cases} \Psi_1(r) = c_{q-G_1} e^{i(q-G_1)\bar{r}} \\ \Psi_2(\bar{r}) = c_{q-G_2} e^{i(q-\bar{G}_2)\bar{r}} \end{cases}$$

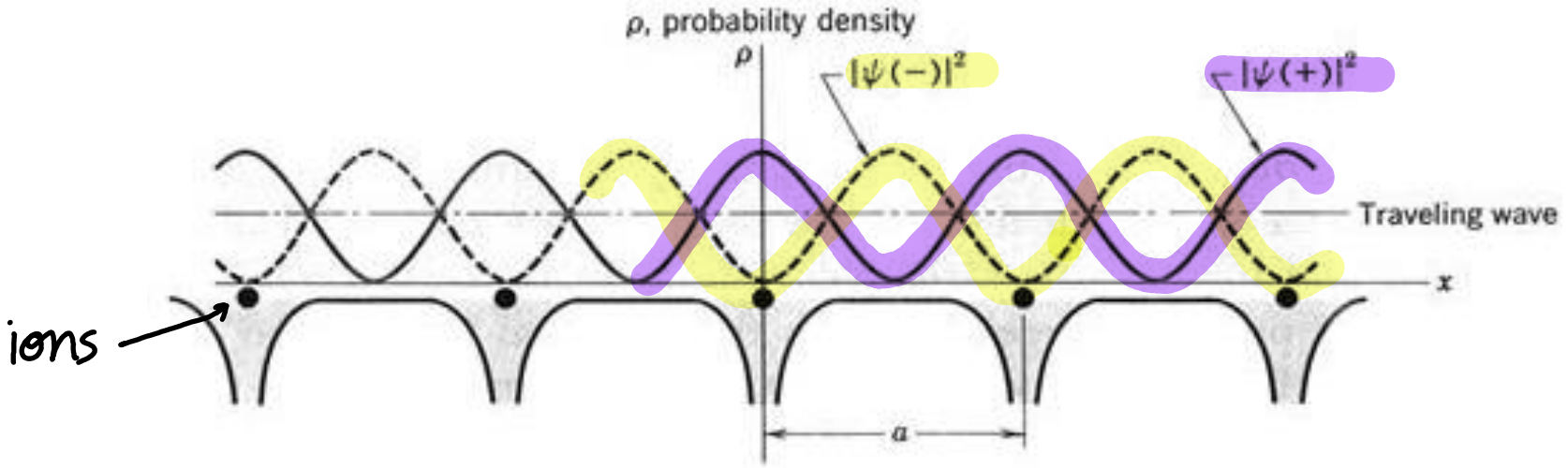
Probability density functions of the 2 superimposed waves:

$$|\Psi_\pm(\vec{r})|^2 = |\Psi_1(r) \pm \Psi_r(\bar{r})|^2$$

to simplify $c_{q-G_1} = c_{q-G_{12}} = c$

$$|\Psi_\pm(\bar{r})|^2 = \dots = \underbrace{2|C|^2 (1 \pm \cos(\bar{G}_1 - \bar{G}_2)\vec{r})}_{\text{standing wave.}}$$

$$|\Psi_\pm(\vec{r})|^2 = 2|C|^2\left(1 \pm \cos\left[(G_1 - G_2)\cdot\vec{r}\right]\right)$$

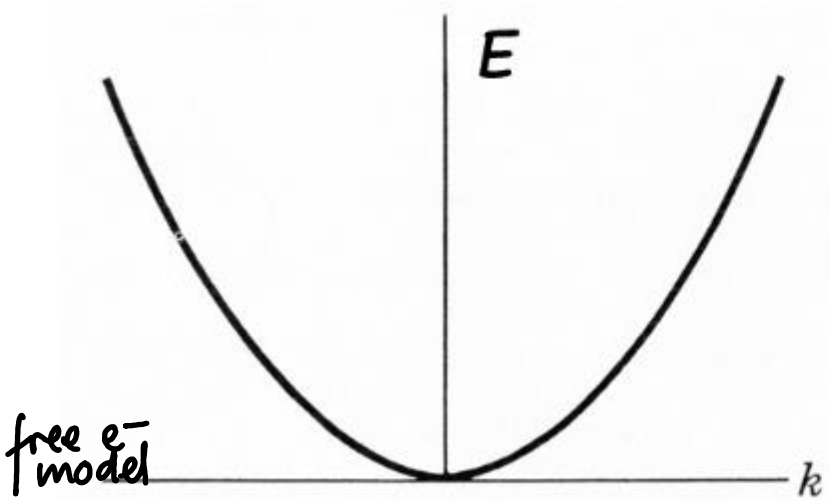


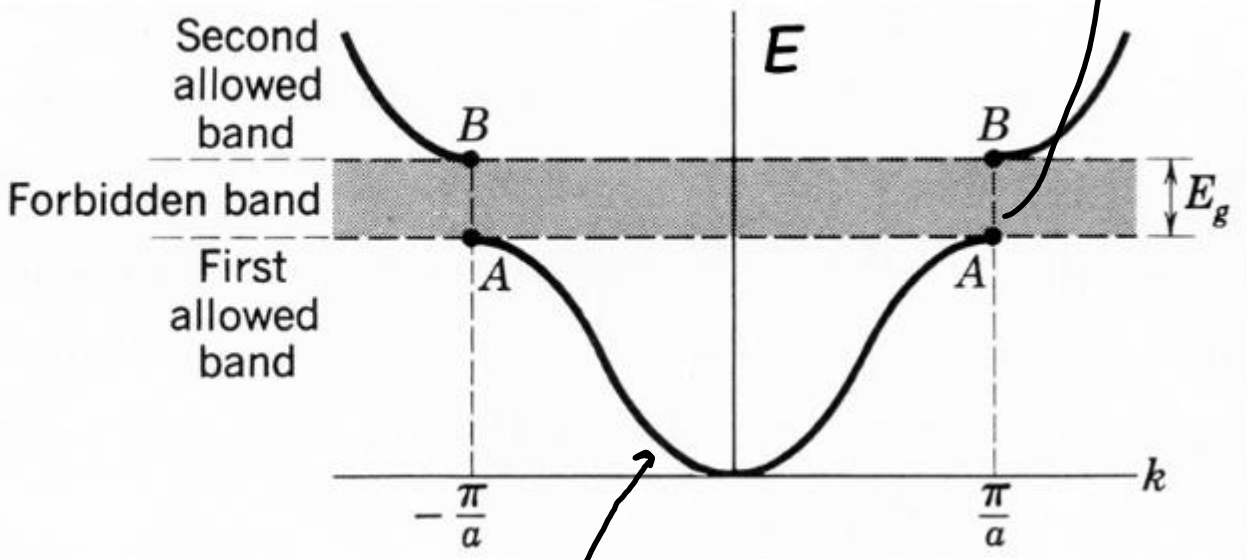
1D $\quad G_1 - G_2 = n\dfrac{2\pi}{a}$

Ψ_+ tends to concentrate e- probability density close to ionic cores (lower E)

Ψ_- : concentrates it between ionic cores

Recap of the consequences of the nearly free e⁻ model so far :





② Forbiden bands of energy whenever E(K) surfaces cross

① Far from Σ.B. : E(K) similar to free e⁻ model

i.e. dispersion relationships energy bands

! Remember : each band in the Brillouin zone can contain 2N electrons

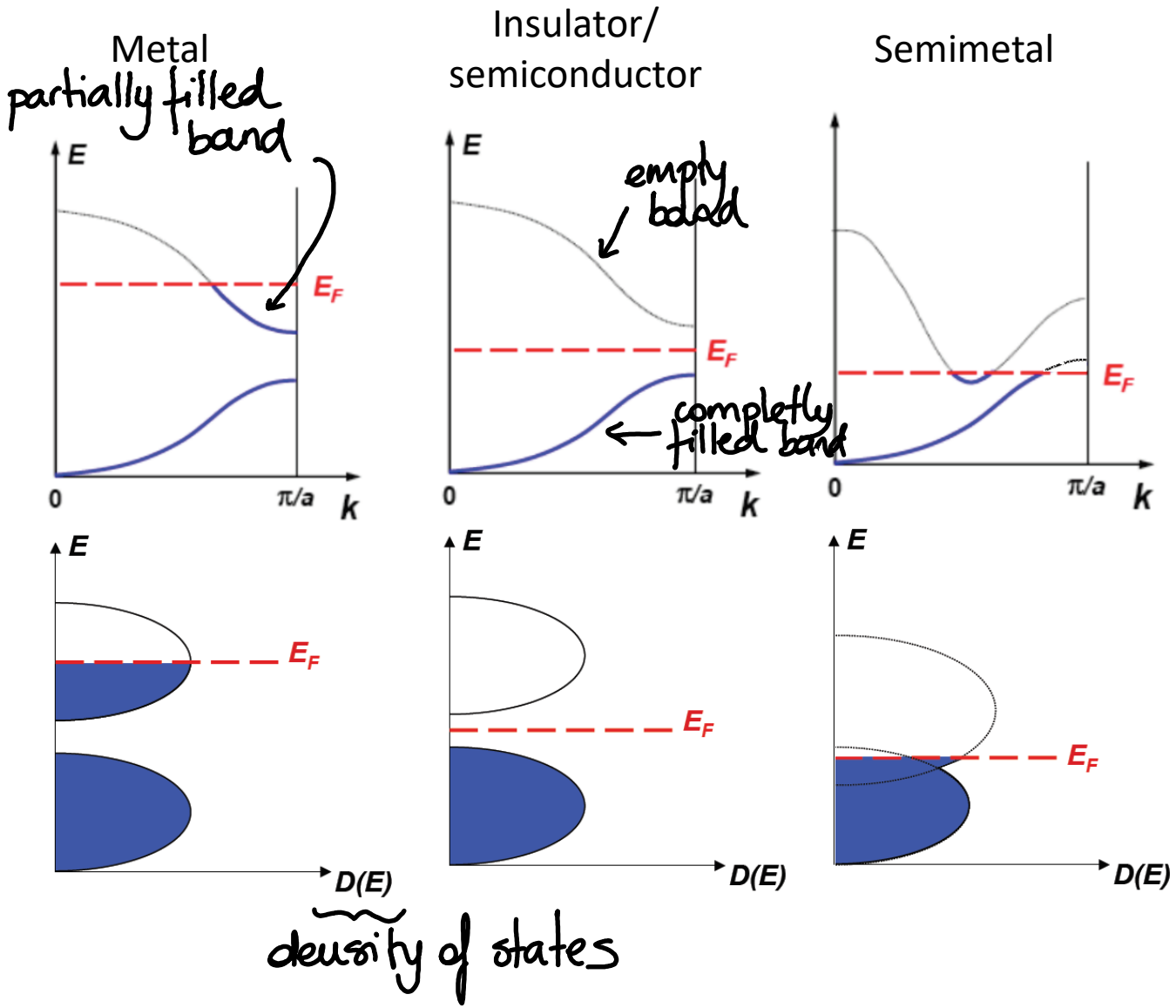
↑ # primitive u.c. in the crystal

Metals and Insulators ⇒ Criteria to distinguish them based on how bands are filled

electric current flows under $\vec{E}$

no current flows

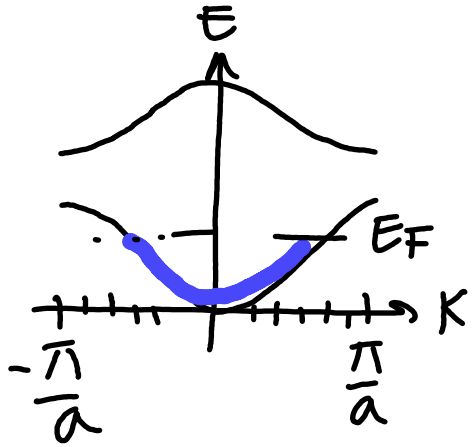
T=0K



Alkali metals

Alkali metals (body-centered cubic)	
Li:	$1s^2 2s^1$
Na:	$[Ne]3s^1$
K:	$[Ar]4s^1$
Rb:	$[Kr]5s^1$
Cs:	$[Xe]6s^1$

$\Rightarrow$ monovalent : 1 e⁻ per primitive u.c. $\Rightarrow$ N conduction e⁻ in the crystal

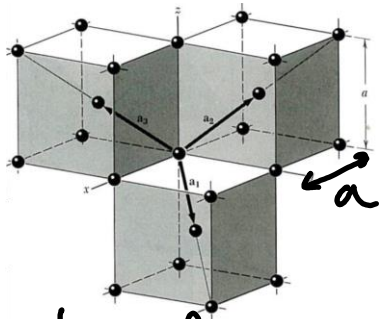


$\Rightarrow$ Fermi surface volume = half of the 1rst B.Z. vol (includes N e⁻) (can host 2N e⁻)

- Fermi wavevector $K_F = (3\pi^2 n)^{1/3} \sim 1.24\ \pi/a$
- Shortest distance between origin and boundary of B.Z.

$$\frac{1}{2} b_i = \frac{1}{2}\left(\frac{2\pi}{a}\right)(1^2+1^2+0)^{1/2} \sim 1.41\ \frac{\pi}{a}$$

real lattice

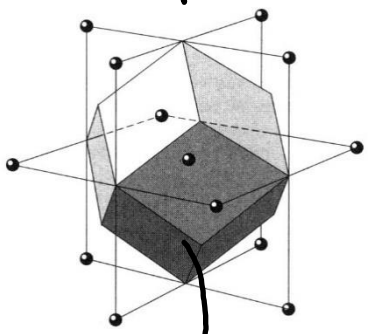


Conventional u.c.

bcc : 2 atoms basis

$n = \frac{2}{a^3}$

Reciprocal lattice



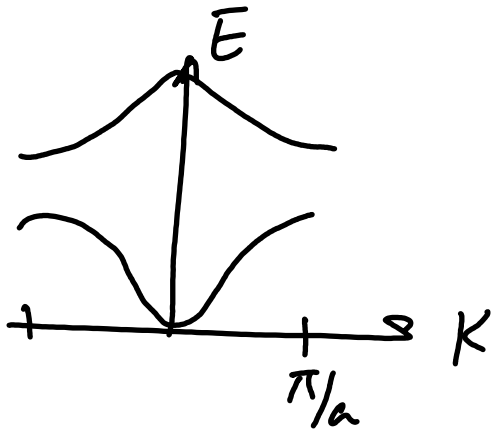
1rst Brillouin zone

$\Rightarrow$ Fermi surface reaches $\left(\frac{1.24}{1.41}\right) \simeq 88\%$ of the closest point to the zone boundary.

$\Rightarrow$ No gap distortions and the Fermi surface remains almost spherical.

(Properties similar to free e⁻ model)

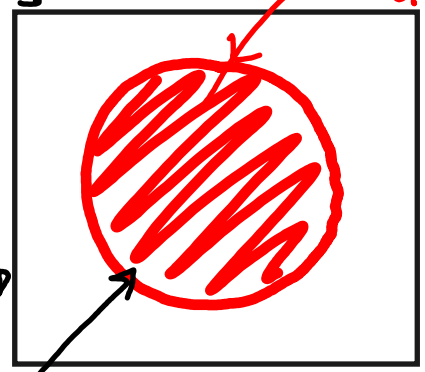
Half-filled Fermi surface (Ne⁻)



Note that in all 3 examples the area of the Fermi surface is the same (and $= \frac{1}{2}$ B.Z.)

Square B.Z.

Fermi surface enclosing states occupied by the e⁻

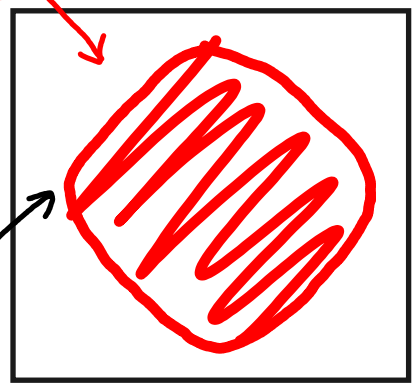


B.Z Boundaries

Weak periodic potential

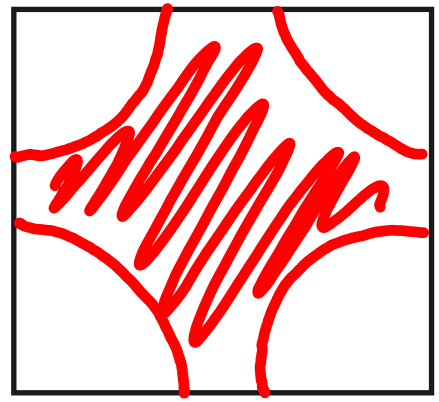
Fermi sea is circular

Alkali metals: properties close to free e⁻ model



As potential increases gap opens at B.Z.

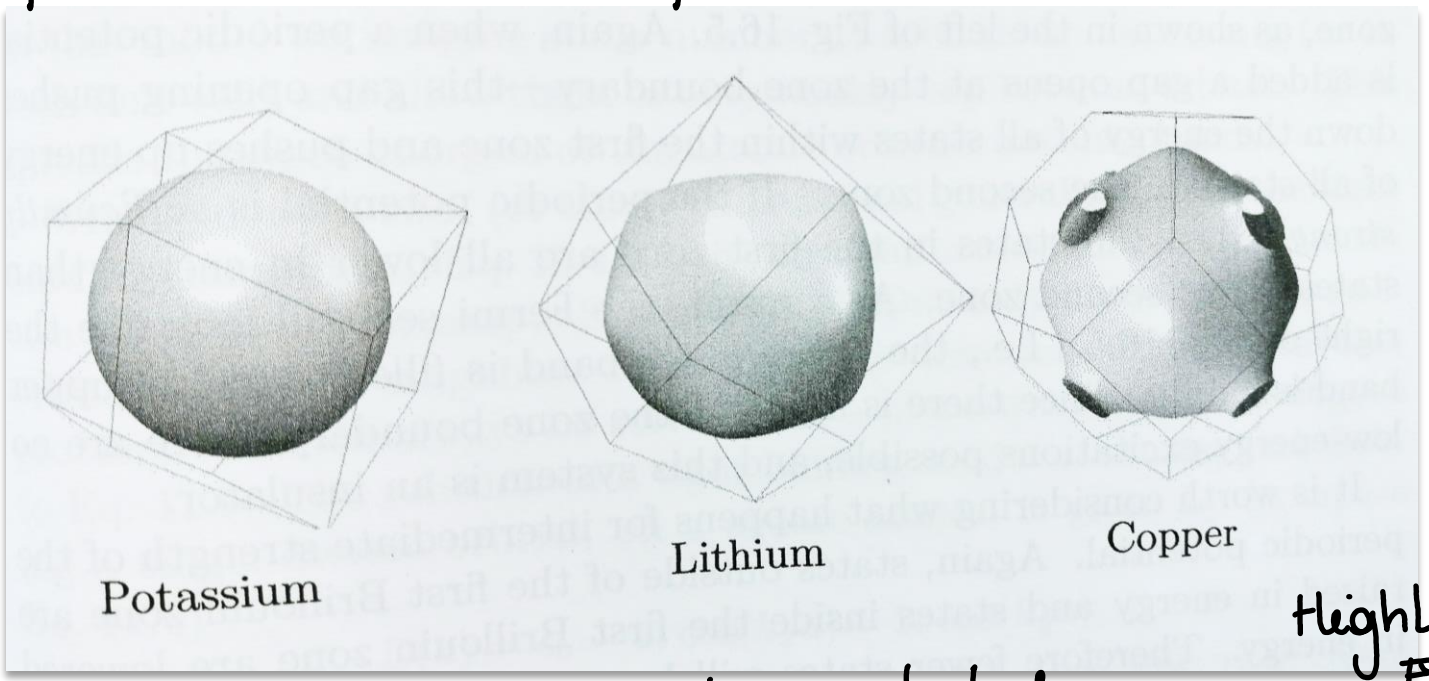
⟹ states close to zone boundary are pushed down in Energy and they will be more filled ⟹ Fermi surface is deformed



very strong potential

Fermi surface touches the boundaries

Fermi surfaces (in all cases, half filling)



(almost ideal free e- model)

slightly distorted Fermi surface

highly distorted Fermi surface