4. Non-interacting electrons in a crystal

In this chapter, we return to the general solid state Hamiltonian of chapter 2

$$\mathcal{H} = \mathcal{H}_{el} + \mathcal{H}_{ion} + \mathcal{H}_{el-ion}$$

In the spirit of the adiabatic approximation, we now want to consider the purely electronic problem for fixed positions of the ions, i.e. the eigenvalue problem for electrons in step I of the adiabatic approximation.

We will start analyzing this electronic problem in this chapter with an approximation that looks like an oversimplification - we will neglect all electron - electron interactions. This is an a priori unjustified approximation since the Coulomb repulsion between electrons is large (several eV). However, due to the screening of the Coulomb interaction (see later chapters) the non-interacting electron approximation turns out to be a very good effective description of the electronic subsystem.

4.1 Single electron in a periodic potential

In the absence of electron - electron interactions, it is sufficient to study the Schrödinger equation for a single electron

$$\mathcal{H}\psi(\vec{r}) = \varepsilon\,\psi(\vec{r}) \qquad \text{with} \quad \mathcal{H} = -\frac{\hbar^2\nabla^2}{2m} + \underbrace{U(\vec{r})}_{\hookrightarrow \text{ ionic potential}}$$

where spin-orbit coupling effects are neglected (non-relativistic limit).

The ionic potential possesses the discrete translation symmetry of the Bravais lattice

$$U(\vec{r}) = U(\vec{r}+\vec{R}) \qquad \text{for all } \vec{R} \in \text{Bravais lattice}$$

From Bloch's theorem (see chapter 3.1) follows that the eigenstates $\psi(\vec{r})$ can be chosen as

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

with $\vec{k} \in$ 1. BZ and the Bloch function satisfies $u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$ for all $\vec{R} \in$ Bravais lattice.

Let's show this explicitly for this case by making a Fourier expansion

$$\psi(\vec r) = \sum_{\vec q} e^{i\vec q\vec r} c_{\vec q} \qquad\qquad U(\vec r) = \sum_{\vec G \in \text{reciprocal lattice}} e^{i\vec G\vec r} U_{\vec G}$$

The potential only has Fourier components $U_{\vec G}$ due to the discrete translational symmetry $U(\vec r+\vec R) = U(\vec r)$ with $e^{i\vec G\vec R} = 1$.
Inserting this Fourier expansion into the Schrödinger equation gives

$$\left[-\frac{\hbar^2\nabla^2}{2m} + U(\vec r)\right]\psi(\vec r) = \sum_{\vec q} e^{i\vec q\vec r}\frac{\hbar^2 q^2}{2m} c_{\vec q} + \sum_{\vec q,\vec G} \underbrace{e^{i(\vec q+\vec G)\vec r} U_{\vec G} c_{\vec q}}_{= e^{i\vec q\vec r} U_G c_{\vec q-\vec G}}$$

$$\overset{!}{=} \varepsilon \sum_{\vec q} e^{i\vec q\vec r} c_{\vec q}$$

substitution $\vec q \to \vec q - \vec G$
allowed since we sum over all $\vec q$

This brings us to the Schrödinger equation in momentum space

$$\boxed{\frac{\hbar^2 q^2}{2m} c_{\vec q} + \sum_{\vec G} U_{\vec G}\, c_{\vec q-\vec G} = \varepsilon c_{\vec q}}$$

Now rewrite $\vec q = \vec k + \vec K$ with $\vec k \in 1.$ BZ and reciprocal lattice vector $\vec K$

$$\frac{\hbar^2(\vec k+\vec K)^2}{2m} c_{\vec k+\vec K} + \sum_{\vec G} U_{\vec G}\, c_{\vec k+\vec K-\vec G} = \varepsilon c_{\vec k+\vec K}$$

For each $\vec k \in 1.$ BZ the eigenfunctions are $c_{n,\vec k+\vec K}$ with eigenvalues $\varepsilon_{n,\vec k}$ where n labels the quantum number

$$\to \psi_n(\vec r) = \sum_{\vec q} e^{i\vec q\vec r} c_{n\vec q} = \sum_{\vec K} e^{i(\vec k+\vec K)\vec r} c_{n,\vec k+\vec K} = e^{i\vec k\vec r} u_{n\vec k}(\vec r)$$

with the Bloch function $\quad u_{n\vec k}(\vec r) = \sum_{\vec K} e^{i\vec K\vec r} c_{n,\vec k+\vec K}$

Consequences:

- $\psi_{n\vec{k}}(\vec{r})$ is not an eigenstate of the momentum operator $\vec{p} = -i\hbar\vec{\nabla}$ as

$$-i\hbar\vec{\nabla}\,\psi_{n\vec{k}}(\vec{r}) = \hbar\vec{k}\,\psi_{n\vec{k}}(\vec{r}) - i\hbar\, e^{i\vec{k}\vec{r}}\,\vec{\nabla}\,u_{n\vec{k}}(\vec{r})$$

In fact, $\hbar\vec{k}$ is the crystal momentum or the quasi-momentum that is conserved modulo a reciprocal lattice vector $\vec{G}$ as $e^{i\vec{G}\vec{R}} = 1$.

- The effective Schrödinger equation obeyed by the Bloch function reads

$$\boxed{\left[\frac{\hbar^2}{2m}\left(-i\vec{\nabla}+\vec{k}\right)^2 + U(\vec{r})\right] u_{n\vec{k}}(\vec{r}) = \mathcal{E}_{n\vec{k}}\, u_{n\vec{k}}(\vec{r})}$$

with the boundary condition $u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$.

Due to the periodicity of $u_{n\vec{k}}(\vec{r})$ and the potential $U(\vec{r})$ we can restrict ourselves to solving this equation only within a single primitive unit cell. Such an eigenvalue problem in a fixed volume V_{uc} will give rise to discretely spaced energy levels that will be labeled by the band index n.

The Bloch functions $u_{n\vec{k}}(\vec{r})$ will form a basis for each $\vec{k}$ for continuous, square-integrable functions defined in the volume V_{uc}:

$$\sum_n u^*_{n\vec{k}}(\vec{r})\cdot u_{n\vec{k}}(\vec{r}\,') = V_{uc}\cdot\delta(\vec{r}-\vec{r}\,') \qquad \text{Completeness}$$

$$\longrightarrow \int_{1.BZ}\frac{d\vec{k}}{(2\pi)^3}\sum_n \psi^*_{n\vec{k}}(\vec{r})\cdot\psi_{n\vec{k}}(\vec{r}\,') = \underbrace{\int_{1.BZ}\frac{d\vec{k}}{(2\pi)^3}}_{1/V_{uc}}\ \underbrace{e^{i\vec{k}(\vec{r}\,'-\vec{r})}}_{=1}\ \underbrace{\sum_n u^*_{n\vec{k}}(\vec{r})\,u_{n\vec{k}}(\vec{r}\,')}_{V_{uc}\,\delta(\vec{r}-\vec{r}\,')}$$

$$= \delta(\vec{r}-\vec{r}\,')$$

Such a basis contains infinitely many functions $u_{n\vec{k}}(\vec{r})$, i.e. there are infinitely many energy bands $n = 0, 1, 2, 3, \ldots$ This should be contrasted to the phonon problem where only a finite number of bands were obtained.

- The eigenstates and eigenvalues are periodic functions of $\vec{k}$ in the reciprocal lattice

$$\boxed{\psi_{n,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r}) \quad \text{and} \quad \varepsilon_{n,\vec{k}+\vec{G}} = \varepsilon_{n\vec{k}}}$$

This represents the electronic band structure of the crystal. As an energy band $\varepsilon_n(\vec{k})$ for a given n is periodic and, for $V \to \infty$, continuous in $\vec{k}$ it has an upper and lower bound.

4.2 Electron in a weak periodic potential

To warm up and get some qualitative understanding, let us consider a weak periodic potential, i.e. assume that Fourier components $U_{\vec{G}}$ with $\vec{G} \neq 0$ are small.

The zero component $U_{\vec{G}=0}$ can be absorbed in the choice of the offset (zero) on the energy axis $\varepsilon \to \varepsilon + U_{\vec{G}=0}$ so that the Schrödinger equation becomes

$$\frac{\hbar^2(\vec{k}+\vec{K})^2}{2m} c_{\vec{k}+\vec{K}} + \sum_{\vec{G}\neq 0} U_{\vec{G}}\, c_{\vec{k}+\vec{K}-\vec{G}} = \varepsilon\, c_{\vec{k}+\vec{K}}$$

shift $\vec{K}' = \vec{K} - \vec{G}$ or $\vec{G} = \vec{K} - \vec{K}'$

$$\frac{\hbar^2(\vec{k}+\vec{K})^2}{2m} c_{\vec{k}+\vec{K}} + \sum_{\vec{K}'\neq \vec{K}} U_{\vec{K}-\vec{K}'}\, c_{\vec{k}+\vec{K}'} = \varepsilon\, c_{\vec{k}+\vec{K}}$$

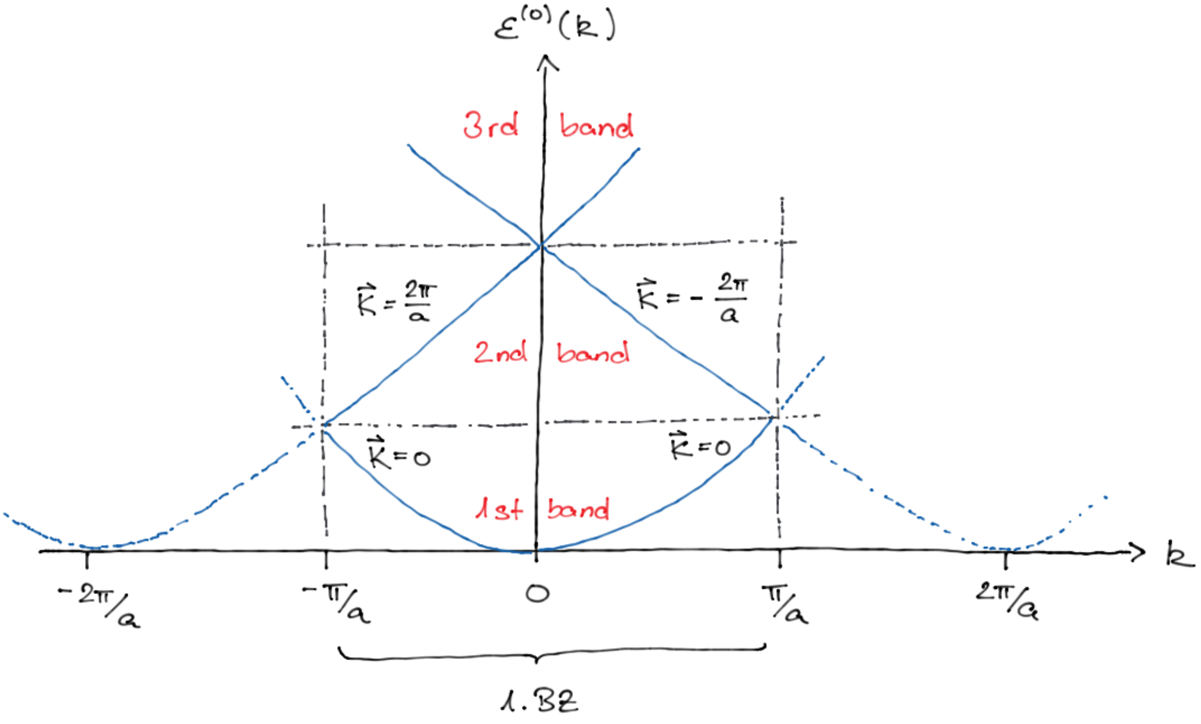
zeroth order in $U_{\vec{G}}$ with $\vec{G} \neq 0$

eigenenergies $\quad \varepsilon^{(0)}(\vec{k}+\vec{K}) = \dfrac{\hbar^2(\vec{k}+\vec{K})^2}{2m}$

eigenfunctions $\quad \psi^{(0)}_{\vec{k}+\vec{K}}(\vec{r}) = e^{i(\vec{k}+\vec{K})\vec{r}}$

Example: energy band in one spatial dimension (chain of electrons)

$\vec{R}_n = na \qquad \vec{K}_m = \frac{2\pi}{a} m$



The reciprocal lattice vector $\vec{K}$ plays the role of a band index.

Perturbative correction due to $U_{\vec{G}}$

For most of the values of $\vec{k} \in$ 1. BZ we can apply standard perturbation theory to evaluate the effect of $U_{\vec{G}}$ on the electronic band structure. However, there are special values of $\vec{k}$ where two or more electron bands are degenerate. We then need to apply the method of degenerate perturbation theory.

For such a degeneracy point $\vec{k}_d$ in the Brillouin zone we can restrict ourselves in lowest order to the subspace spanned by the eigenfunctions with degenerate eigenvalues at zeroth order in $U_{\vec{G}}$:

for n-degenerate point $\varepsilon^{(0)}(\vec{k}_d + \vec{K}_1) = \varepsilon^{(0)}(\vec{k}_d + \vec{K}_2) = \ldots = \varepsilon^{(0)}(\vec{k}_d + \vec{K}_n)$

The reduced Schrödinger equation with $\vec{k} = \vec{k}_d$ then reads

$$\varepsilon^{(0)}(\vec{k}+\vec{K}_i)\, c_{\vec{k}+\vec{K}_i} + \underbrace{\sum_{j\neq i}}_{} U_{\vec{K}_i-\vec{K}_j}\, c_{\vec{k}+\vec{K}_j} \cong \varepsilon\, c_{\vec{k}+\vec{K}_i}$$

restricted sum over $j = 1, 2, \ldots, n$ only

and corresponds to an <u>$n\times n$ matrix equation</u> for n-degenerate states.

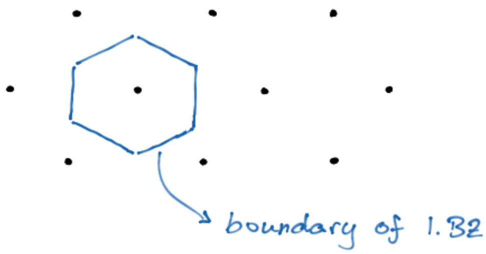
<u>Where do these degeneracies occur?</u>

$$\varepsilon^{(0)}(\vec{k}+\vec{K}_1) = \varepsilon^{(0)}(\vec{k}+\vec{K}_2) \iff |\vec{k}+\vec{K}_1| = |\vec{k}+\vec{K}_2| \quad \left(\begin{matrix}\text{elastic}\\ \text{scattering}\end{matrix}\right)$$

Furthermore, the difference $(\vec{k}+\vec{K}_1)-(\vec{k}+\vec{K}_2) = \vec{K}_1 - \vec{K}_2 \in$ reciprocal lattice vector

→ the two vectors $\vec{k}+\vec{K}_1$ and $\vec{k}+\vec{K}_2$ must fulfill the Bragg or van-Laue condition for constructive interference!

These conditions are fulfilled, for instance, on all boundaries of 1. BZ



Most important case: only <u>two degenerate levels</u>
→ 2×2 matrix equation

$$\varepsilon^{(0)}(\vec{k}+\vec{K}_1)\, c_{\vec{k}+\vec{K}_1} + U_{\vec{K}_1-\vec{K}_2}\, c_{\vec{k}+\vec{K}_2} = \varepsilon\, c_{\vec{k}+\vec{K}_1}$$

$$\varepsilon^{(0)}(\vec{k}+\vec{K}_2)\, c_{\vec{k}+\vec{K}_2} + U_{\vec{K}_2-\vec{K}_1}\, c_{\vec{k}+\vec{K}_1} = \varepsilon\, c_{\vec{k}+\vec{K}_2}$$

written in matrix form

$$\begin{pmatrix} \varepsilon^{(0)}(\vec{k}+\vec{K}_1) & U_{\vec{K}_1-\vec{K}_2} \\ U_{\vec{K}_2-\vec{K}_1} & \varepsilon^{(0)}(\vec{k}+\vec{K}_2) \end{pmatrix} \begin{pmatrix} c_{\vec{k}+\vec{K}_1} \\ c_{\vec{k}+\vec{K}_2} \end{pmatrix} = \varepsilon \begin{pmatrix} c_{\vec{k}+\vec{K}_1} \\ c_{\vec{k}+\vec{K}_2} \end{pmatrix}$$

with $U_{-\vec{K}} = U_K^*$ the eigenvalues are given by

$$\boxed{\varepsilon = \frac{\varepsilon^{(0)}(\vec{k}+\vec{K}_1) + \varepsilon^{(0)}(\vec{k}+\vec{K}_2)}{2} \pm \sqrt{\frac{\left(\varepsilon^{(0)}(\vec{k}+\vec{K}_1) - \varepsilon^{(0)}(\vec{k}+\vec{K}_2)\right)^2}{4} + \left|U_{\vec{K}_1-\vec{K}_2}\right|^2}}$$

The interaction $U_{\vec{K}_1-\vec{K}_2}$ generically leads to a <u>level repulsion</u>.

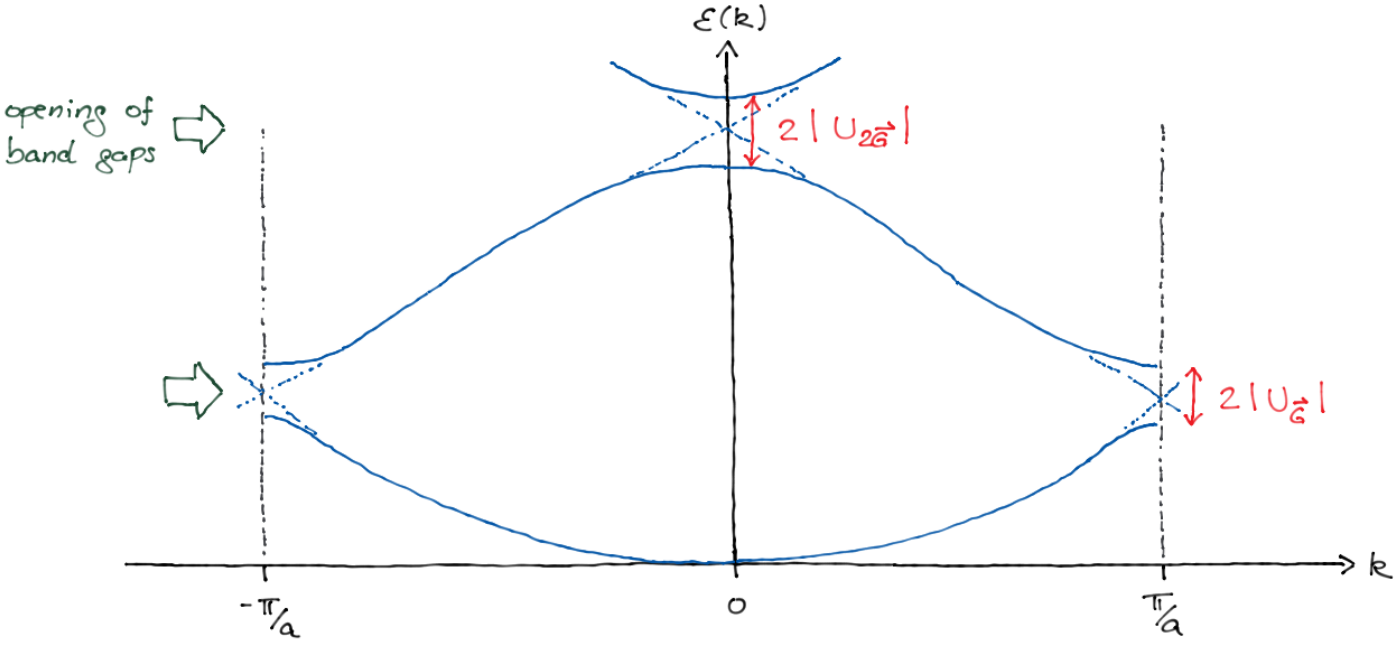
At the degeneracy point $\vec{k} = \vec{k}_d$ we have $\varepsilon^{(0)} = \varepsilon^{(0)}(\vec{k}_d + \vec{K}_1) = \varepsilon^{(0)}(\vec{k}_d + \vec{K}_2)$

$$\boxed{\varepsilon = \varepsilon^{(0)} \pm \left|U_{\vec{K}_1-\vec{K}_2}\right|}$$

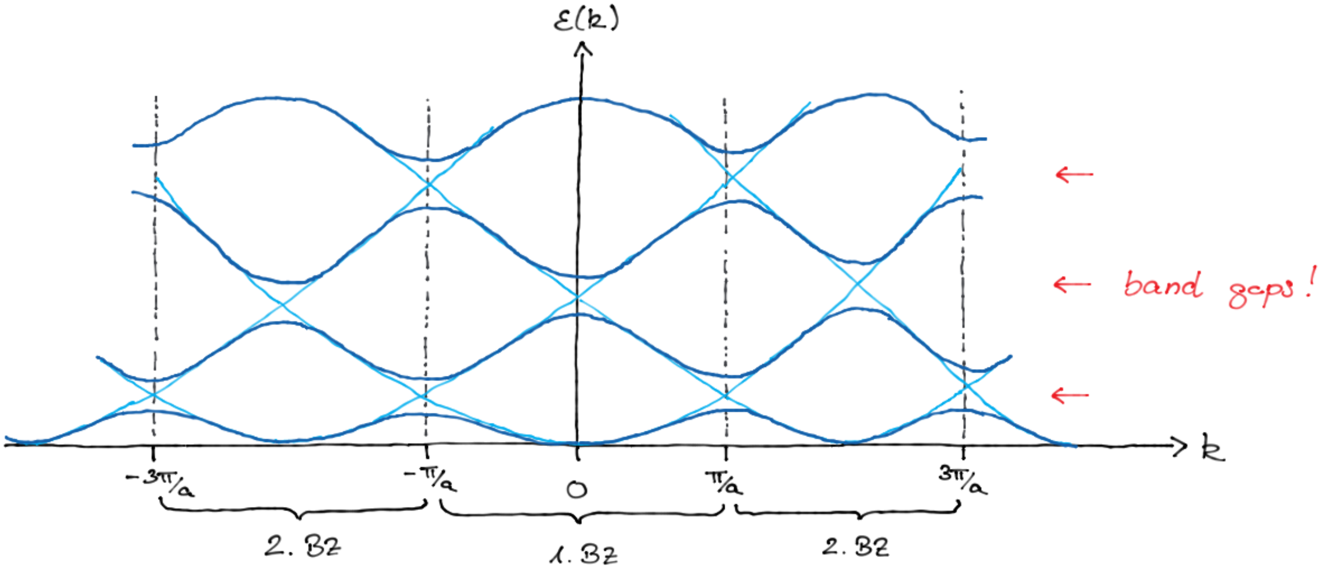
The <u>splitting</u> of the bands is <u>linear</u> in $|U_{\vec{K}_1-\vec{K}_2}|$ due to <u>Bragg reflection</u>!

Example: One-dimensional system

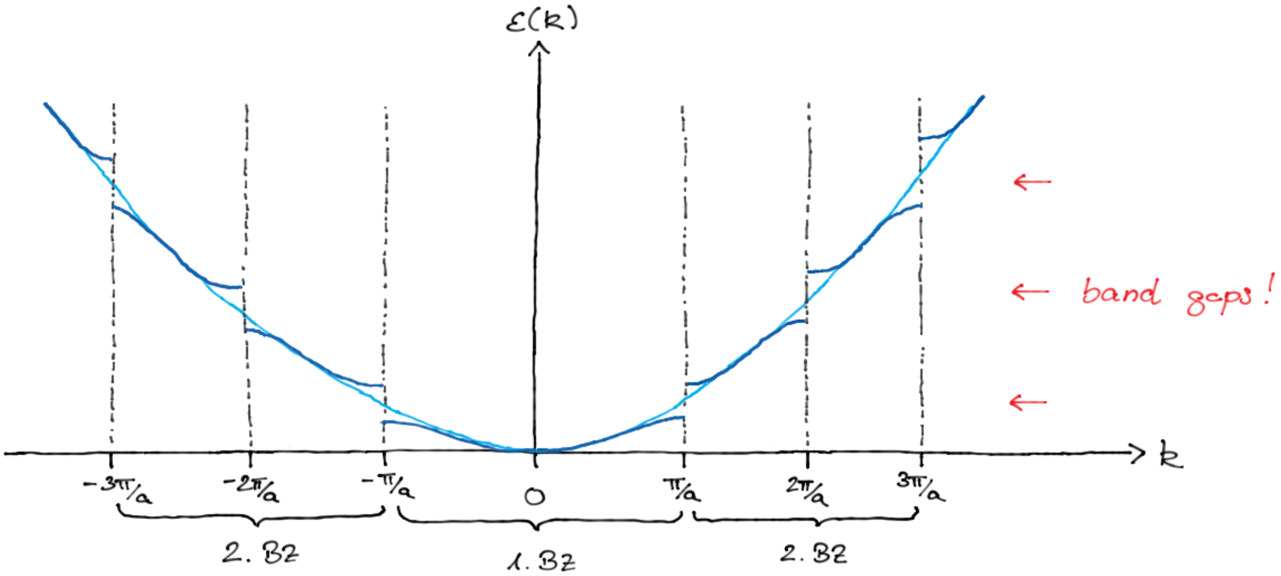
" reduced zone scheme "



"repeated zone scheme" — bands periodically continued for all k



"extended zone scheme"



Energy band gaps

Generically, a weak periodic potential introduces energy gaps by splitting degeneracies due to Bragg reflection. Energy bands then become separated by a finite energy gap $\Delta \simeq 2 \, | U_{\vec{K}_1 - \vec{K}_2} |$

4.3 Fermi surfaces

Ground state of non-interacting electrons in a periodic potential in the absence of a magnetic field:

> Occupy all states with $\vec{k} \in 1.$ BZ and band index n with $\varepsilon_{n\vec{k}} \leq \varepsilon_F$, once with a spin-up and once with a spin-down configuration. ε_F is the Fermi energy. (Pauli principle)

The Fermi energy is determined by the total number of electrons N_e:

$$\boxed{\sum_{s=\uparrow,\downarrow} \sum_{\substack{n,\vec{k}\in 1.BZ \\ \text{with } \varepsilon_{n\vec{k}} \leq \varepsilon_F}} \xrightarrow{V\to\infty} \underbrace{\sum_{s=\uparrow,\downarrow}}_{=2} \sum_{n} V \int_{\substack{1.BZ \\ \varepsilon_{n\vec{k}} \leq \varepsilon_F}} \frac{d^3\vec{k}}{(2\pi)^3} \overset{!}{=} N_e}$$

with the volume V.

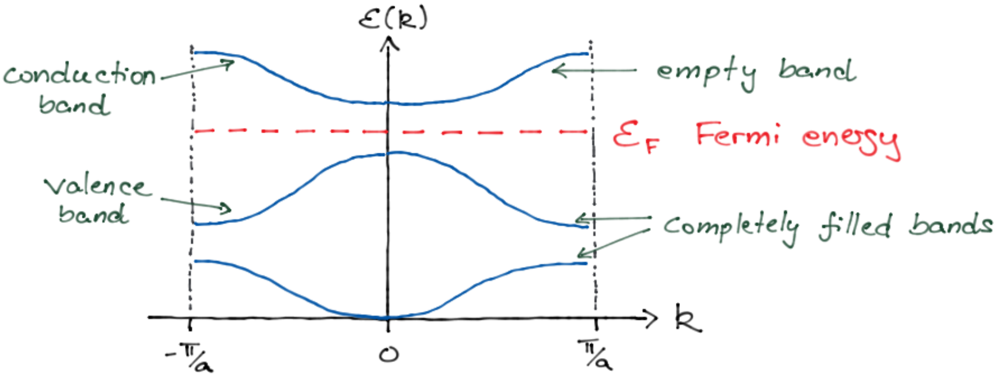
How many electrons can occupy a single band?

With $\sum_{\vec{k}\in 1.BZ} \xrightarrow{V\to\infty} V \int_{1.BZ} \frac{d^3\vec{k}}{(2\pi)^3} = N \longrightarrow$ number of Bravais lattice sites

$\rightarrow$ Each band can be occupied by $2N$ electrons (N with spin $\uparrow$, N with spin $\downarrow$)

One distinguishes two important cases:

I. All bands are either completely filled or completely empty

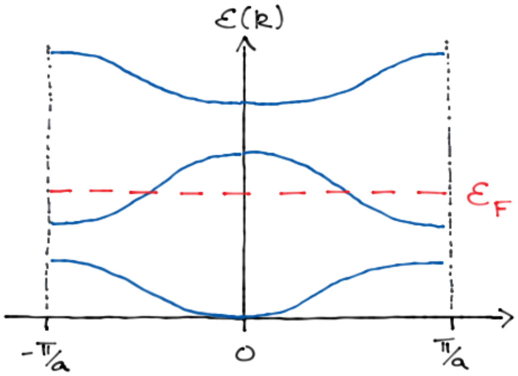


The Fermi energy is located within the band gap.
Further, the density of (non-interacting) electrons corresponds to an even number of electrons per unit cell as

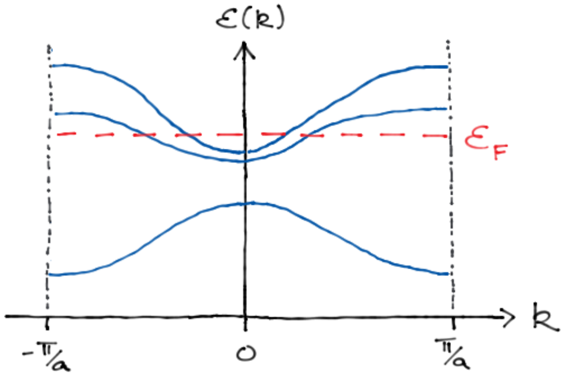
$$N_e = 2 \sum_n V \int \frac{d^3\vec{k}}{(2\pi)^3} = \underset{\substack{\uparrow \\ \text{spin}}}{2} \cdot \underset{\substack{\uparrow \\ \text{number of} \\ \text{occupied bands}}}{n_{\text{bands}}} \cdot \underset{\substack{\uparrow \\ \text{number of unit cells}}}{N}$$

The most upper filled band is the valence band and the first empty band is the conduction band.
In order to excite electrons out of the ground state, an energy larger than the band gap is required – typical magnitude of the band gap is in the range of 1eV – 7eV.
Such materials are semiconductors or (band) insulators.

II. The Fermi energy is located within one or more partially filled bands.



a single band crosses the Fermi energy

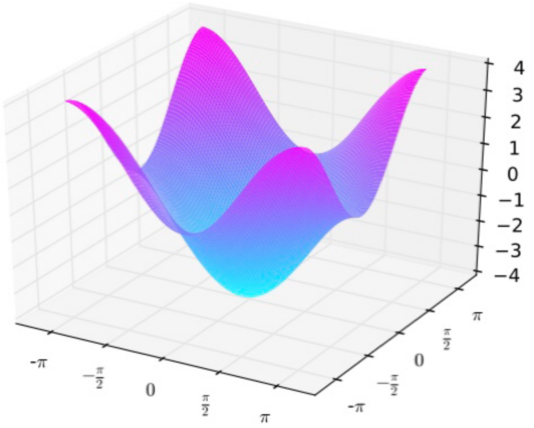


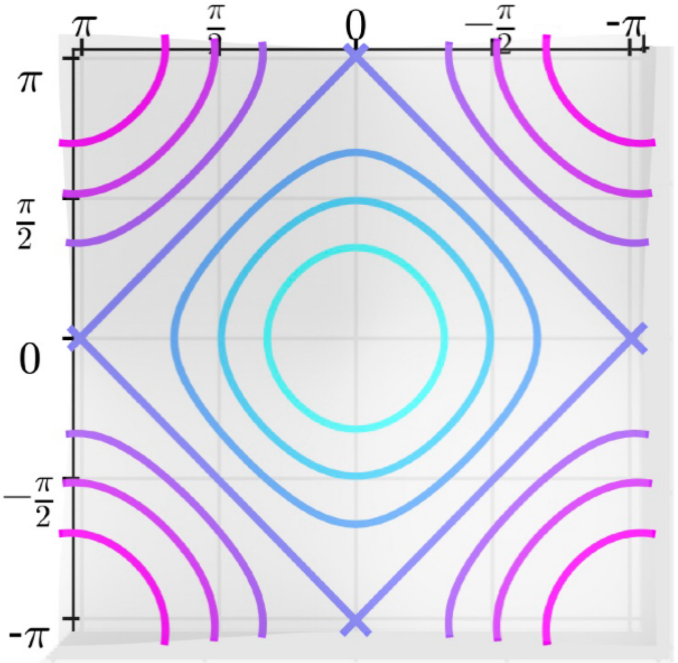
two bands cross the Fermi energy

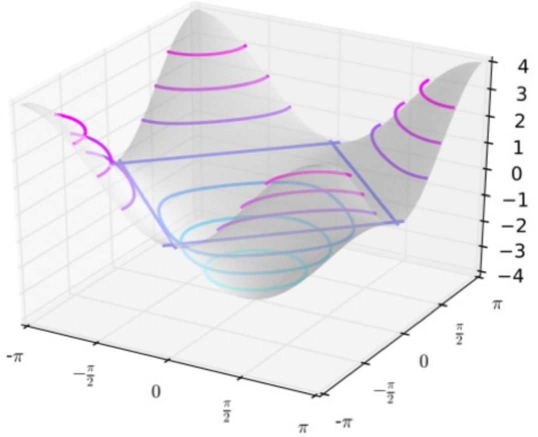
The partially filled bands are the conduction bands.
Around the Fermi energy electrons can be excited with very low energies
⟶ metal

The condition $\varepsilon_{n\vec{k}} \overset{!}{=} \varepsilon_F$ defines one or several $(d-1)$-dimensional manifolds within the 1. BZ that constitute the Fermi surface(s).

Example: One-dimensional Fermi surface of a single energy band with $\varepsilon(k_x, k_y) = -2t\,(\cos(k_x a) + \cos(k_y a)) \overset{!}{=} \varepsilon_F$







contour lines of the energy dispersion

Remarks

- typical values for Fermi energies: $\varepsilon_F \sim 1\text{-}10\,\mathrm{eV}$, $T_F \sim 10^4\text{-}10^5\,\mathrm{K}$
- Fermi surfaces can have different topologies (open or closed)
- The Fermi volume is the volume enclosed by the Fermi surface and is fixed by the electron density – even in the presence of interactions between the electrons (Luttinger theorem). Interactions, however, can change the shape and the topology of the Fermi surface.

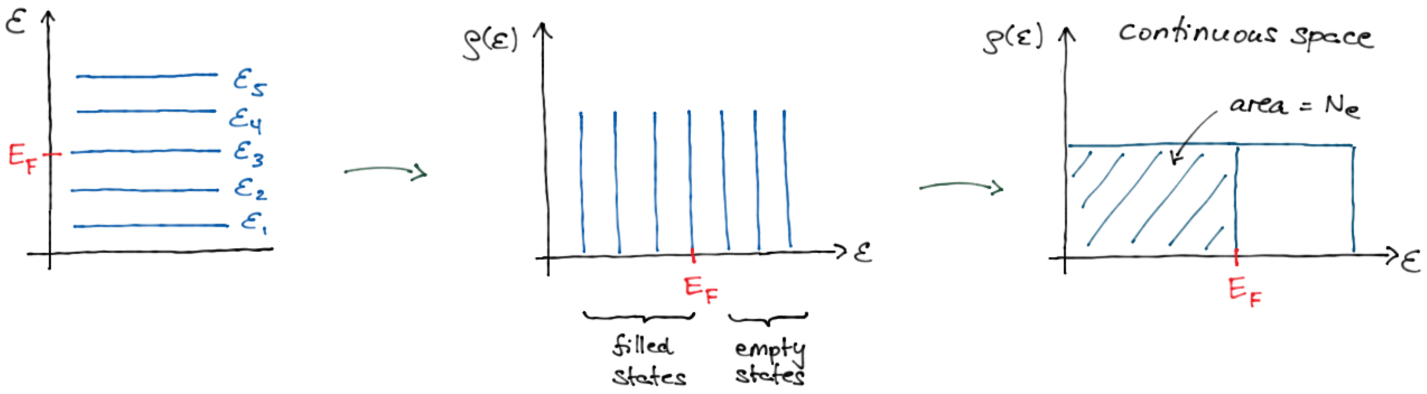
4.4 Density of states and van-Hove singularities

The electronic band structures provide full information on the dispersion of electrons in a given material. Oftentimes, however, one is not interested in this full information, but it suffices to know in which energy ranges there are electronic states, how many of those states exist and where there are energy gaps. To this end, one defines the density of electron states at a given energy as

$$\boxed{\varrho(\varepsilon) = \underset{\underset{\text{spin}}{\uparrow}}{2}\,\frac{1}{V}\sum_{n,\vec{k}\in 1.BZ}\delta(\varepsilon-\varepsilon_n(\vec{k}))}$$

If the band structure does depend on the spin (e.g. in the presence of spin-orbit coupling), one can consider the density of states per spin.

We can use the density of states to recast the definition of the Fermi energy.



→ Fermi energy E_F can be defined as

$$\boxed{\int_{-\infty}^{E_F} d\varepsilon\ \varrho(\varepsilon) = N_e}$$

Let's start with an example: density of states of free electrons in $d=3$

$$\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} \qquad \rho(\varepsilon) = \frac{2}{V}\sum_{\vec{k}} \delta(\varepsilon - \varepsilon(\vec{k}))$$

replace $\sum_{\vec{k}} \longrightarrow \frac{V}{(2\pi)^3}\int d^3\vec{k}$ and $\int d^3\vec{k} \longrightarrow 4\pi\int_0^\infty dk\, k^2$

$$\rightarrow \rho(\varepsilon) = 2\cdot\frac{4\pi}{(2\pi)^3}\underbrace{\int_0^\infty dk\, k^2\cdot\delta\left(\varepsilon - \frac{\hbar^2k^2}{2m}\right)}$$

$$= \int_0^\infty dk\, f(k)\cdot\delta(g(k)) = \frac{f(k_0)}{|g'(k_0)|}$$

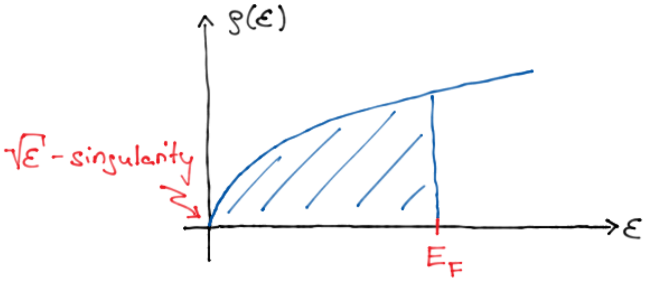
with $g(k_0)=0$
only one such root
with $k_0>0$

$$\rightarrow g(k) = \varepsilon - \frac{\hbar^2k^2}{2m}, \quad k_0 = \frac{1}{\hbar}\sqrt{2m\varepsilon}$$

$$f(k) = k^2, \quad f(k_0) = \frac{2m\varepsilon}{\hbar^2}$$

$$g'(k) = -\frac{\hbar^2}{m}k, \quad |g'(k_0)| = \frac{\hbar^2}{m}\cdot\frac{1}{\hbar}\sqrt{2m\varepsilon}$$

$$\rho(\varepsilon) = \frac{1}{\pi^2}\cdot\frac{2m\varepsilon}{\hbar^2}\cdot\frac{m}{\hbar}\cdot\frac{1}{\sqrt{2m\varepsilon}} \longrightarrow \boxed{\rho(\varepsilon) = \frac{m}{\pi^2\hbar^3}\cdot\sqrt{2m\varepsilon}}$$



→ calculate Fermi energy via

$$N_e = \int_0^{E_F} d\varepsilon\, \rho(\varepsilon) = \frac{1}{3\pi^2\hbar^3}(2mE_F)^{3/2}$$

$$\rightarrow \boxed{E_F = \frac{\hbar^2}{2m}\cdot(3\pi^2 N_e)^{2/3}}$$

Going back to the definition of the density of states we can introduce a <u>density of states per band</u> $\varrho(\varepsilon) = \sum_n \varrho_n(\varepsilon)$

$$\rightarrow \quad \varrho_n(\varepsilon) = 2 \cdot \int \frac{d\vec{k}}{(2\pi)^3}\, \delta(\varepsilon - \varepsilon_n(\vec{k}))$$

With $\int_{-\infty}^{\infty} d\varepsilon\, \varrho_n(\varepsilon) = 2 \int_{1.BZ} \frac{d\vec{k}}{(2\pi)^3} = 2\,\frac{N}{V} = 2\,\frac{1}{V_{uc}} \mathrel{\hat{=}} 2 \times$ density of unit cells

If the energy ε is located <u>within</u> the n^{th} band, i.e. $\min \varepsilon_n(\vec{k}) \le \varepsilon \le \max \varepsilon_n(\vec{k})$, the density of states $\varrho(\varepsilon)$ is finite and given by

$$\varrho_n(\varepsilon) = \frac{2}{(2\pi)^3} \cdot \int_{\varepsilon = \varepsilon_n(\vec{k})} dS \int \frac{d\varepsilon_n(\vec{k})}{|\vec{\nabla}_k \varepsilon_n(\vec{k})|}\, \delta(\varepsilon - \varepsilon_n(\vec{k})) = \frac{2}{(2\pi)^3} \int_{\varepsilon = \varepsilon_n(\vec{k})} dS\, \frac{1}{|\vec{\nabla}_k \varepsilon_n(\vec{k})|}$$

integration over surface of constant energy

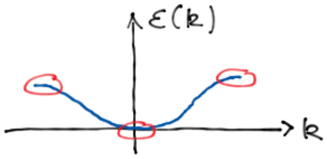
change of variables

$$\left.\begin{aligned} d^3\vec{k} &= dS\, dk_\perp \\ d\varepsilon &= |\vec{\nabla}_k \varepsilon_n(\vec{k})| \end{aligned}\right\} \rightarrow d^3\vec{k} = \frac{dS\, d\varepsilon}{|\vec{\nabla}_k \varepsilon_n(\vec{k})|}$$

The density of states is determined by an integral over constant energy surfaces weighted by the inverse of the <u>group velocity</u>

$$v_n(\vec{k}) = \frac{1}{\hbar}\, \vec{\nabla}_k\, \varepsilon_n(\vec{k}) \qquad \text{of the n-th band}$$

Whenever the group velocity <u>vanishes</u> on a surface of constant energy the density of states exhibits a <u>van-Hove singularity</u>.



In order to determine the nature of the singularity one expands around the singularity point $\vec{k}_0$ within the 1. BZ:

$$\varepsilon_n(\vec{k}) \cong \varepsilon_n(\vec{k}_0) + \frac{1}{2} \left.\frac{\partial^2 \varepsilon_n(\vec{k})}{\partial k_i\, \partial k_j}\right|_{\vec{k}_0} (\vec{k} - \vec{k}_0)_i\, (\vec{k} - \vec{k}_0)_j$$

with $i,j = x, y, z$

The matrix $\frac{\partial^2 \varepsilon_n(\vec{k})}{\partial \vec{k}_i \, \partial \vec{k}_j}$ describes the curvature of the spectrum and has eigenvalues λ_1, λ_2, and λ_3.

The energy spectrum has at $\vec{k}_0$

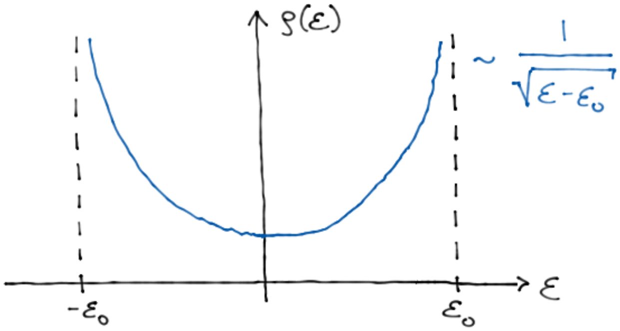
1) a minimum if $\lambda_i > 0 \quad \forall i = 1,2,3$
2) a maximum if $\lambda_i < 0 \quad \forall i = 1,2,3$
3) a saddle point in all other cases

Close to a van-Hove singularity in d spatial dimensions one obtains making a change of variables $\vec{k} = \vec{k}_0 + \sqrt{\varepsilon - \varepsilon_n(\vec{k})}\ \vec{x}$

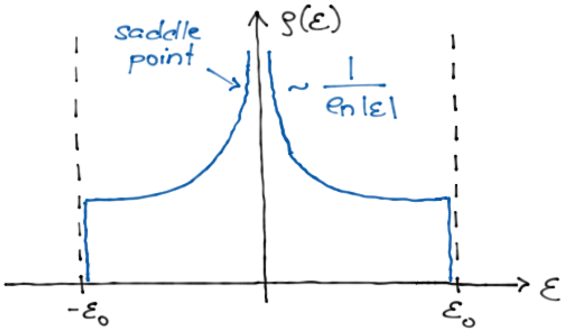
$$\rho_n(\varepsilon) \approx 2 \int \frac{d^d \vec{x}}{(2\pi)^d} \, (\varepsilon - \varepsilon_n(\vec{k}))^{d/2} \, \delta\Big((\varepsilon - \varepsilon_n(\vec{k})) \cdot \Big(1 - \frac{1}{2} \cdot \frac{\partial^2 \varepsilon_n(\vec{k})}{\partial \vec{k}_i \, \partial \vec{k}_j}\Big|_{\vec{k}_0} x_i x_j\Big)\Big)$$

$$\longrightarrow \boxed{\rho_n(\varepsilon) \propto (\varepsilon - \varepsilon_n(\vec{k}))^{d/2 - 1}}$$

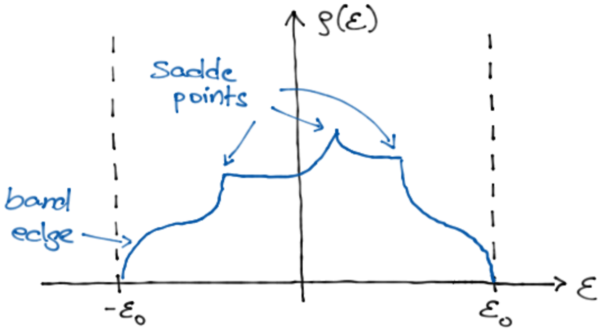
$d = 1$: $1/\sqrt{\varepsilon}$ divergence at band edges



$d = 2$: jump at the band edges and logarithmic singularity at saddle points



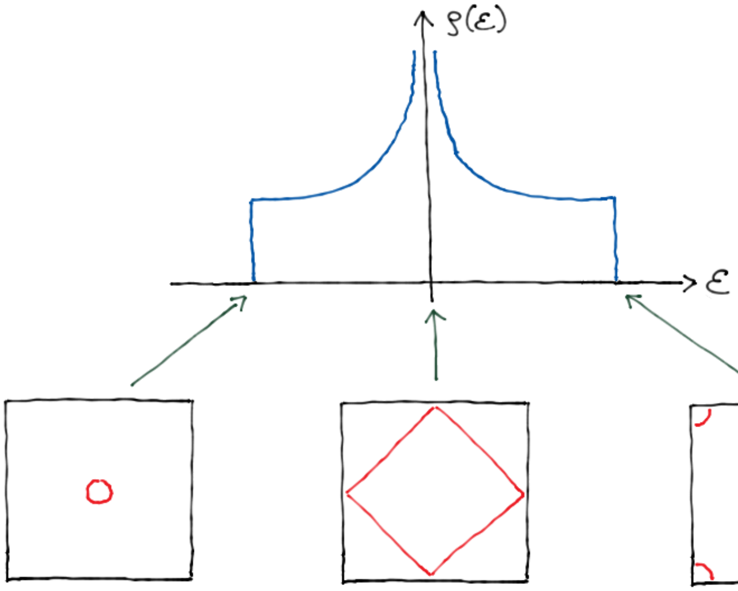
$d = 3$: $\sqrt{\varepsilon}$ - singularities



Since $\varepsilon_n(\vec{k})$ is a periodic function in $\vec{k}$, there always are a maximum, a minimum and in $d>1$ one or several saddle points.

Modern interpretation: A van-Hove singularity indicates a topological quantum phase transition, i.e. a point at which the topology of the Fermi surface changes as a function of the chemical potential μ at $T=0$.
In particular, we have the following correspondence

at a minimum – new Fermi surface emerges
at a maximum – Fermi surface vanishes
at a saddle point – Fermi surfaces merge



4.5 Effective mass

Let us go back to the Schrödinger equation for the Bloch function $u_{n\vec{k}}(\vec{r})$

$$\Big[\underbrace{\frac{\hbar^2}{2m}\left(-i\vec{\nabla}+\vec{k}\right)^2 + U(\vec{r})\Big]}_{} \, u_{n\vec{k}}(\vec{r}) = \varepsilon_{n\vec{k}} \, u_{n\vec{k}}(\vec{r})$$

$$h(\vec{k}) = \frac{\hbar^2}{2m}\left(k^2 - 2i\vec{k}\cdot\vec{\nabla} - \Delta\right) + U(\vec{r})$$

for $\vec{k}=\vec{0}$: $h(\vec{0}) = -\frac{\hbar^2}{2m}\Delta + U(\vec{r}) = \frac{\vec{p}^{\,2}}{2m} + U(\vec{r})$ with $\vec{p} = -i\hbar\vec{\nabla}$

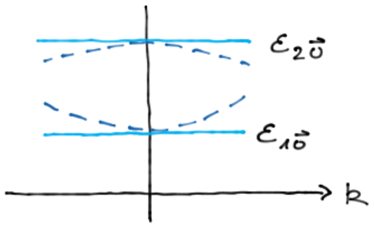
→ We can split the effective Hamiltonian as

$$\boxed{h(\vec{k}) = h(\vec{0}) + h_1(\vec{k})} \qquad \text{with} \qquad \boxed{h_1(\vec{k}) = \frac{\hbar^2 k^2}{2m} + \frac{\hbar}{m}\vec{k}\cdot\vec{p}}$$

Let us further assume that we can solve the above Schrödinger equation for $\vec{k}=\vec{0}$

$$\left(\frac{\vec{p}^{\,2}}{2m} + U(\vec{r})\right) u_{n\vec{0}}(\vec{r}) = \varepsilon_{n\vec{0}} \, u_{n\vec{0}}(\vec{r}) \quad \hat{=} \quad h(\vec{0})\,|n^{(0)}\rangle = \varepsilon_{n\vec{0}}\,|n^{(0)}\rangle$$

with a non-degenerate energy spectrum $\{\varepsilon_{n\vec{0}}\}$



→ treat $h_1(\vec{k})$ as a perturbation
(ok for small values of k, e.g. at Γ-point)
and calculate the $\vec{k}$-dependence of $\varepsilon_{n\vec{k}}$
in leading order perturbation theory

In standard Rayleigh-Schrödinger perturbation theory the energy is given to 2nd order in the perturbation as

$$\boxed{\varepsilon_n(\vec{k}) = \varepsilon_n(\vec{0}) + \langle n^{(0)}|\,h_1(\vec{k})\,|n^{(0)}\rangle + \sum_{n'\neq n}\frac{\langle n^{(0)}|\,h_1(\vec{k})\,|n'^{(0)}\rangle\langle n'^{(0)}|\,h_1(\vec{k})\,|n^{(0)}\rangle}{\varepsilon_n(\vec{0}) - \varepsilon_{n'}(\vec{0})}}$$

i) 1st order term

$$\langle n^{(0)}|\, h_1(\vec k)\,|n^{(0)}\rangle = \underbrace{\langle n^{(0)}|\frac{\hbar^2k^2}{2m}|n^{(0)}\rangle}_{=\frac{\hbar^2k^2}{2m}} + \frac{\hbar}{m}\underbrace{\langle n^{(0)}|\,\vec k\cdot\vec p\,|n^{(0)}\rangle}_{=0}$$

for potential with inv. symmetry $U(\vec r) = U(-\vec r)$ also $|n^{(0)}\rangle$ has inv. symmetry → no diagonal $\vec k\cdot\vec p$ matrix element

ii) 2nd order terms

$$\langle n^{(0)}|\, h_1(\vec k)\,|n'^{(0)}\rangle = \underbrace{\langle n^{(0)}|\frac{\hbar^2k^2}{2m}|n'^{(0)}\rangle}_{=0 \text{ for } n'\neq n} + \frac{\hbar}{m}\langle n^{(0)}|\sum_{\alpha=1}^{d} k_\alpha p_\alpha|n'^{(0)}\rangle$$

$$\longrightarrow \mathcal{E}_n(\vec k) = \mathcal{E}_n(\vec 0) + \frac{\hbar^2k^2}{2m} + \frac{\hbar^2}{m^2}\sum_{\alpha,\alpha'} k_\alpha k_{\alpha'} \sum_{n'\neq n}\frac{\langle n^{(0)}|p_\alpha|n'^{(0)}\rangle\langle n'^{(0)}|p_{\alpha'}|n^{(0)}\rangle}{\mathcal{E}_n(\vec 0)-\mathcal{E}_{n'}(\vec 0)}$$

This implies that for small k the energy dispersion $\mathcal{E}_n(\vec k)$ is quadratic in the k_α.

This lets us define the effective mass tensor

$$\boxed{\left(\frac{1}{m^*\underset{\underset{\text{band index}}{\uparrow}}{(n)}}\right)_{\alpha\alpha'} = \frac{1}{\hbar^2}\cdot\frac{\partial^2\mathcal{E}_n(\vec k)}{\partial k_\alpha\,\partial k_{\alpha'}}}$$

- the free electron part gives

$$\frac{1}{\hbar^2}\frac{\partial^2}{\partial k_\alpha\partial k_{\alpha'}}\frac{\hbar^2k^2}{2m} = \frac{1}{2m}\frac{\partial^2}{\partial k_\alpha\partial k_{\alpha'}}\left(k_xk_x + k_yk_y + k_zk_z\right) = \frac{1}{2m}\,2\delta_{\alpha\alpha'} = \frac{1}{m}\delta_{\alpha\alpha'}$$

→ the effective mass tensor of free electrons is diagonal, with diagonal matrix elements $\frac{1}{m^*} = \frac{1}{m}$ → $m^* = m$

- the 2nd order part gives

$$\frac{1}{\hbar^2}\frac{\partial^2}{\partial k_\alpha\partial k_{\alpha'}}\frac{\hbar^2}{m^2}\sum_{\beta\beta'} k_\beta k_{\beta'} f_{\beta\beta'} \qquad \text{with } f_{\beta\beta'} = \sum_{n'\neq n}\frac{\langle n^{(0)}|p_\beta|n'^{(0)}\rangle\langle n'^{(0)}|p_{\beta'}|n^{(0)}\rangle}{\mathcal{E}_n(\vec 0)-\mathcal{E}_{n'}(\vec 0)}$$

$\alpha = \alpha'$: $\frac{2}{m^2} f_{\alpha\alpha'}$ $\qquad$ $\alpha\neq\alpha'$: $\frac{1}{m^2}\left(f_{\alpha\alpha'} + f_{\alpha'\alpha}\right)$

In total, we can write

$$\boxed{\mathcal{E}_n(\vec{k}) = \mathcal{E}_n(\vec{0}) + \sum_{\alpha\alpha'} \left(\frac{1}{2m^*(n)}\right)_{\alpha\alpha'} \hbar^2 k_\alpha k_{\alpha'} + O(k^4)}$$

Remarks

- m^* can become negative, which is generally true for band maxima. This also applies for the edge of the Brillouin zone (for which this exp. around $\vec{k}=\vec{0}$ needs to be adjusted).
  Negative-mass electrons are called "holes".

- For cubic symmetry, the effective mass tensor is diagonal

$$\left(\frac{1}{m^*}\right)_{\alpha\alpha'} = \frac{1}{m^*}\delta_{\alpha\alpha'} \longrightarrow \mathcal{E}_n(\vec{k}) = \mathcal{E}_n(\vec{0}) + \frac{\hbar^2 k^2}{2m^*} + O(k^4)$$

  For alkali metals with bcc-lattice structure one finds

metall	Li	Na	K	Rb	Cs
band	2s	3s	4s	5s	6s
m^*/m	1.33	0.96	0.86	0.78	0.73

  In general, the effective mass m^* is of the same order of magnitude as the free electron mass.

- In some 4f and 5f compounds (rare earth materials) such as $CeRu_2Si_4$, $CeCu_6$, UPt_3 or $CeAl_3$ amongst others the ratio m^*/m is anomalously high with values up to $m^*/m \sim 100-1000$. These compounds are today referred to as heavy-fermion materials.
  While $CeAl_3$ was the first heavy-fermion compound to be discovered (1975 by Ott and coworkers), it was only shortly after in 1979 that Frank Steglich discovered heavy-fermion superconductivity in $CeCu_2Si_2$ at the II. Physikalische Institute in Cologne.

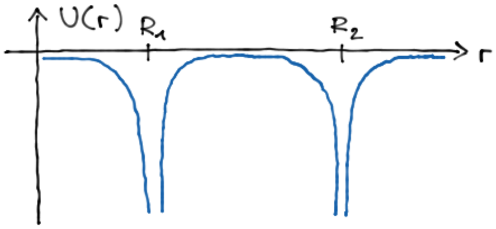
4.6 Almost localized electrons: tight-binding model

While the model of (nearly) free electrons has provided us with a qualitative understanding of the formation of energy bands, band gaps and van-Hove singularities for Bravais lattices, it often fails to allow for quantitative band structure calculations. The reason for this discrepancy arises from the simple fact that the periodic potential is not weak (as assumed in the perturbative treatment). In fact, the potential is often strong. This motivates an alternative approach starting from the limit of strongly bound, localized electrons. That is, one starts with isolated atoms, assumes that one knows its eigenenergies and -states, and then considers the modification of these states as one brings the atoms into spatial proximity.

Consider a strong periodic potential $U(\vec{r})$

$$U(\vec{r}) = \sum_{\substack{\vec{R} \in \\ \text{Bravais} \\ \text{lattice}}} V(\vec{r} - \vec{R})$$

→ sum over atomic potentials V (assuming monatomic Bravais lattice)



each atomic potential V decays rapidly with the distance to the ion positions $R_1, R_2, \ldots$
→ ΔU is small for small distances $\vec{r}$

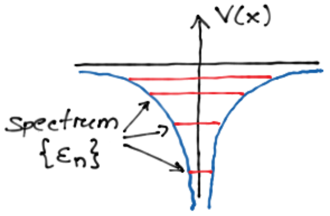
Hamiltonian for a single electron

$$\mathcal{H} = \frac{\vec{p}^{\,2}}{2m} + U(\vec{r}) = \mathcal{H}_{\text{atom},\vec{R}} + \Delta U(\vec{r})$$

with $\mathcal{H}_{\text{atom},\vec{R}} = \frac{\vec{p}^{\,2}}{2m} + V(\vec{r} - \vec{R})$ and $\Delta U(\vec{r}) = \sum_{\vec{R}' \neq \vec{R}} V(\vec{r} - \vec{R}')$

Starting point: electrons localized in atomic orbitals, i.e. eigenstates of $\mathcal{H}_{\text{atom},\vec{R}}$.
Let us assume that the atomic eigenvalue problem is solved:

$$\mathcal{H}_{\text{atom},\vec{R}}\, \varphi_n(\vec{r} - \vec{R}) = \varepsilon_n\, \varphi_n(\vec{r} - \vec{R})$$



where n represents the full set of atomic quantum numbers $n = (\bar{n}, \ell, m, s)$.

Our next step is to make an ansatz for the wavefunction of the full Hamiltonian including the complete, periodic potential. To this end, we construct a Bloch state of the form $\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \varphi_n(\vec{r}-\vec{R})$

This is a Bloch state because we have

$$\psi_{n\vec{k}}(\vec{r}+\vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}'} e^{i\vec{k}\vec{R}'} \varphi_n(\vec{r}+\vec{R}-\vec{R}') = \frac{1}{\sqrt{N}} e^{i\vec{k}\vec{R}} \sum_{\vec{R}'} e^{i\vec{k}(\vec{R}'-\vec{R})} \varphi_n(\vec{r}-(\vec{R}'-\vec{R}))$$

$$= \frac{1}{\sqrt{N}} e^{i\vec{k}\vec{R}} \sum_{\vec{R}''} e^{i\vec{k}\vec{R}''} \varphi_n(\vec{r}-\vec{R}'') = e^{i\vec{k}\vec{R}} \psi_{n\vec{k}}(\vec{r})$$

Let us show that these newly constructed Bloch states are eigenstates of the full multi-atom Hamiltonian. To do so, let us first ask whether the states $\varphi_n(\vec{r}-\vec{R})$ are eigenstates of $\mathcal{H}$.

$$\mathcal{H}\varphi_n(\vec{r}-\vec{R}) = (\mathcal{H}_{\text{atom},\vec{R}} + \Delta U(\vec{r}))\,\varphi_n(\vec{r}-\vec{R})$$

$$= \varepsilon_n \varphi_n(\vec{r}-\vec{R}) + \underbrace{\Delta U(\vec{r})\,\varphi_n(\vec{r}-\vec{R})}_{=g(\vec{r})}$$

We have an eigenstate if $g(\vec{r}) = 0$ (sufficient condition).

$g(\vec{r}) = 0$ if i) $\varphi_n(\vec{r}-\vec{R}) = 0$ for $\vec{r}$ outside the Wigner-Seitz cell at $\vec{R}$

and ii) $\Delta U(\vec{r}) = 0$ — " — inside — " —

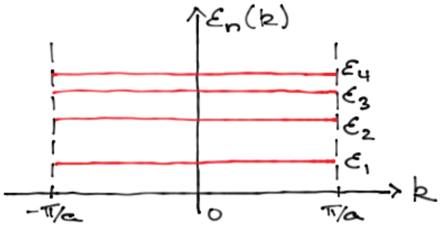
For the case of $g(\vec{r}) = 0$, we can then calculate the band structure of the full multi-atom Hamiltonian

$$\mathcal{H}\psi_{n\vec{k}}(\vec{r}) = \varepsilon_n(\vec{k})\,\psi_{n\vec{k}}(\vec{r})$$

$$\mathcal{H}\frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \varphi_n(\vec{r}-\vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \varepsilon_n \varphi_n(\vec{r}-\vec{R}) = \varepsilon_n \psi_{n\vec{k}}(\vec{r})$$

→ $\varepsilon_n(\vec{k}) = \varepsilon_n$

localized states give rise to dispersionless bands



The assumption of a rapid wavefunction decay (implying $g(\vec r)=0$ above) is justified only for the core electron states, but does not really hold for the valence electrons (whose wavefunction overlap constitutes the atomic binding). We can nevertheless apply the same Bloch wavefunction ansatz, though now appreciating that these Bloch states are not exact eigenstates of the crystal. In particular, the Bloch states $\psi_{n\vec k}(\vec r)$ are not normalized

$$\langle \psi_{n\vec k} | \psi_{n'\vec k} \rangle = \frac{1}{N} \sum_{\vec R_1} \sum_{\vec R_2} e^{i\vec k(\vec R_2 - \vec R_1)} \int d^3\vec r \; \varphi_n^*(\vec r - \vec R_1)\, \varphi_{n'}(\vec r - \vec R_2)$$

substitute $\vec r' = \vec r - \vec R_2$ $\quad \int d^3\vec r \longrightarrow \int d^3\vec r'$ integral over whole volume

$$= \frac{1}{N} \sum_{\vec R_1} \sum_{\vec R_2} e^{i\vec k(\vec R_2 - \vec R_1)} \int d^3\vec r' \; \varphi_n^*(\vec r' + \vec R_2 - \vec R_1)\, \varphi_{n'}(\vec r')$$

substitute $\vec R = \vec R_1 - \vec R_2$ $\quad \sum_{\vec R_2} \longrightarrow \sum_{\vec R}$

$$= \frac{1}{N} \sum_{\vec R_1} \sum_{\vec R} e^{-i\vec k\vec R} \int d^3\vec r' \; \varphi_n^*(\vec r' - \vec R)\, \varphi_{n'}(\vec r')$$

sum no longer depends on $\vec R_1$ $\longrightarrow$ $\sum_{\vec R_1}$ gives a factor of N

$$= \sum_{\vec R} e^{-i\vec k\vec R} \int d^3\vec r' \; \varphi_n^*(\vec r' - \vec R)\, \varphi_{n'}(\vec r')$$

with $\int d^3\vec r' \; \varphi_n^*(\vec r')\, \varphi_{n'}(\vec r') = \delta_{nn'}$

and $\alpha_{nn'}(\vec R) = \int d^3\vec r' \; \varphi_n^*(\vec r' - \vec R)\, \varphi_{n'}(\vec r')$ $\hat{=}$ atomic overlap

$$\boxed{\langle \psi_{n\vec k} | \psi_{n'\vec k} \rangle = \delta_{nn'} + \sum_{\vec R \neq 0} e^{-i\vec k\vec R}\, \underset{\uparrow}{\alpha_{nn'}(\vec R)}}$$

atomic overlap

So, for the valence electrons $\mathcal{H}\,\psi_{n\vec k}(\vec r) = \mathcal{E}_n(\vec k)\, \psi_{n\vec k}(\vec r)$ is no longer valid. Instead, we make an approximation for the energy eigenvalues $\mathcal{E}_n(\vec k)$ using the Ritz variational method

$$\boxed{\mathcal{E}_n(\vec k) = \frac{\langle \psi_{n\vec k} | \mathcal{H} | \psi_{n\vec k} \rangle}{\langle \psi_{n\vec k} | \psi_{n\vec k} \rangle}}$$

We are left with calculating the matrix element in the numerator.

$$\langle \psi_{n\vec{k}} | \mathcal{H} | \psi_{n\vec{k}} \rangle = \frac{1}{N} \sum_{\vec{R}_1} \sum_{\vec{R}_2} e^{i\vec{k}(\vec{R}_2 - \vec{R}_1)} \int d^3\vec{r} \; \varphi_n^*(\vec{r} - \vec{R}_1) \, \underset{\substack{\downarrow \\ \mathcal{H}_{\text{atom},\vec{R}} + \Delta U(\vec{r}) \\ \downarrow \\ \text{gives a factor } \mathcal{E}_n}}{\mathcal{H}} \, \varphi_n(\vec{r} - \vec{R}_2)$$

$$= \mathcal{E}_n \langle \psi_{n\vec{k}} | \psi_{n\vec{k}} \rangle + \frac{1}{N} \sum_{\vec{R}_1} \sum_{\vec{R}_2} e^{i\vec{k}(\vec{R}_2 - \vec{R}_1)} \int d^3\vec{r} \; \underline{\varphi_n^*(\vec{r} - \vec{R}_1)} \sum_{\vec{R}_3 \neq \vec{R}_2} \underline{V(\vec{r} - \vec{R}_3)} \, \underline{\varphi_n(\vec{r} - \vec{R}_2)}$$

these 3 functions are all <u>localized</u> at $\vec{R}_1$, $\vec{R}_2$ and $\vec{R}_3$, respectively

→ classify the contributions to the triple sum $\sum_{R_1}\sum_{R_2}\sum_{R_3}$ according to the number of equal $\vec{R}_i$'s

i) $\vec{R}_1 = \vec{R}_2 = \vec{R}_3$ is excluded

ii) two of the $\vec{R}_i$'s are equal: $\vec{R}_1 = \vec{R}_2 \neq \vec{R}_3$ or $\vec{R}_1 = \vec{R}_3 \neq \vec{R}_2$

iii) $\vec{R}_1 \neq \vec{R}_2 \neq \vec{R}_3 \neq \vec{R}_1$: these terms can be neglected as there is almost vanishing overlap for $\varphi_n^*(\vec{r} - \vec{R}_1) V(\vec{r} - \vec{R}_3) \varphi_n(\vec{r} - \vec{R}_2)$ for all values of $\vec{r}$

I. $\vec{R}_1 = \vec{R}_2 \neq \vec{R}_3$

$\sum_{R_1}\sum_{R_2} \longrightarrow \sum_{R_1}$ as $\vec{R}_2$ is fixed to $\vec{R}_1$

$$\frac{1}{N} \sum_{\vec{R}_1} e^{i\vec{k}\vec{0}} \int d^3\vec{r} \; \varphi_n^*(\vec{r} - \vec{R}_1) \, \Delta V_{\vec{R}_1}(\vec{r}) \, \varphi_n(\vec{r} - \vec{R}_1)$$

= expectation value of the potential of all other atoms considering the atomic state at $\vec{R}_1$

substitute $\vec{r}\,' = \vec{r} - \vec{R}_1$ $\quad \int d^3r \longrightarrow \int d^3r'$

and note that

$$\Delta V_{\vec{R}_1}(\vec{r}\,' + \vec{R}_1) = \sum_{\vec{R}_3 \neq \vec{R}_1} V(\vec{r}\,' + \vec{R}_1 - \vec{R}_3)$$

does not contain $V(\vec{r}\,')$

$$\overset{!}{=} \sum_{\vec{R} \neq 0} V(\vec{r}\,' - \vec{R}) = \Delta V_{\vec{0}}(\vec{r}\,')$$

$$\frac{1}{N} \sum_{\vec{R}_1} \underbrace{\int d^3\vec{r}\,' \; \varphi_n^*(\vec{r}\,') \, \Delta V_0(\vec{r}\,') \, \varphi_n(\vec{r}\,')}_{\text{does not depend on } \vec{R}_1} = \beta_n$$

→ gives a constant energy shift

II. $\vec{R}_1 = \vec{R}_3 \neq \vec{R}_2$

$$\frac{1}{N}\sum_{\vec{R}_1}\sum_{\vec{R}_2\neq\vec{R}_1} e^{i\vec{k}(\vec{R}_2-\vec{R}_1)} \int d^3\vec{r}\;\; \varphi_n^*(\vec{r}-\vec{R}_1)\, V(\vec{r}-\vec{R}_1)\, \varphi_n(\vec{r}-\vec{R}_2)$$

substitute $\vec{r}\,' = \vec{r}-\vec{R}_2$ $\qquad \int d^3\vec{r} \longrightarrow \int d^3\vec{r}\,'$

$\vec{R} = \vec{R}_1-\vec{R}_2$ $\qquad \sum\limits_{\vec{R}_2\neq\vec{R}_1} \longrightarrow \sum\limits_{\vec{R}\neq 0}$

$$\frac{1}{N}\sum_{\vec{R}_1}\underbrace{\sum_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}} \int d^3\vec{r}\,'\;\; \varphi_n^*(\vec{r}\,'-\vec{R})\, V(\vec{r}\,'-\vec{R})\, \varphi_n(\vec{r}\,')}_{\text{does not depend on } \vec{R}_1}$$

$$= \sum_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}}\, \lambda_n(\vec{R}) \qquad \text{with} \qquad \boxed{\lambda_n(\vec{R}) = \int d^3\vec{r}\;\; \varphi_n^*(\vec{r}-\vec{R})\, V(\vec{r}-\vec{R})\, \varphi_n(\vec{r})}$$

Alltogether, we arrive at the *tight-binding approximation*

$$\boxed{\mathcal{E}_n(\vec{k}) = \mathcal{E}_n + \frac{\beta_n + \sum_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}}\, \lambda_n(\vec{R})}{1+\sum_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}}\, \alpha_n(\vec{R})}}$$

with
$\alpha_n(\vec{R}) = \alpha_{nn}(\vec{R})$

Typically, one restricts the $\vec{R}$-sums to next and next-next nearest neighbors since the overlaps still become very small for any further neighbors.

For small overlaps, i.e. $\left|\sum\limits_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}}\, \alpha_n(\vec{R})\right| \ll 1$ we can further simplify

$$\mathcal{E}_n(\vec{k}) \approx \mathcal{E}_n + \Big(\beta_n + \underbrace{\sum_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}}\, \lambda_n(\vec{R})}\Big)\cdot\Big(1-\underbrace{\sum_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}}\, \alpha_n(\vec{R})}\Big)$$

neglect product
of these 2 sums

$$\approx \underbrace{\mathcal{E}_n + \beta_n}_{C_n} + \sum_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}} \underbrace{\big(\lambda_n(\vec{R}) - \beta_n\alpha_n(\vec{R})\big)}_{=\gamma_n(\vec{R})}$$

→ general form of the dispersion in tight-binding approximation

$$\boxed{\mathcal{E}_n(\vec{k}) = C_n + \sum_{\vec{R}\neq 0} e^{-i\vec{k}\vec{R}}\, \gamma_n(\vec{R})}$$

Example: One-dimensional lattice, $R_m = m \cdot a$

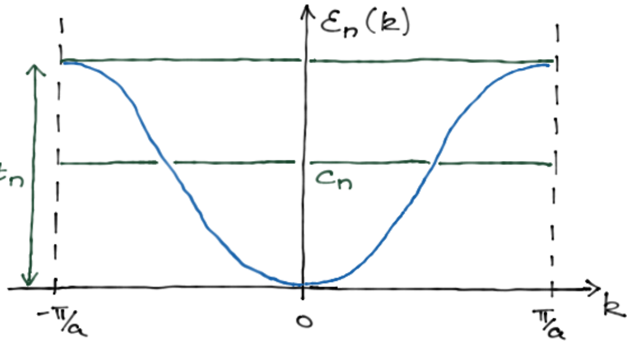
$$\longrightarrow \quad \mathcal{E}_n(k) = c_n + \sum_{m \neq 0} e^{-ikma} \gamma_n(R_m)$$

Now assume that $\gamma_n(R_m) = \begin{cases} -t_n & : \; |m| = 1 \\ 0 & : \; \text{otherwise} \end{cases}$

This means that we assume significant overlap of $\varphi_n(x - R_m)$ and $\varphi_n(x)$ only between a site and its two nearest neighbors.

$$\longrightarrow \quad \mathcal{E}_n(\vec{k}) = c_n - t_n\left(e^{ika} + e^{-ika}\right)$$

$$\boxed{\mathcal{E}_n(k) = c_n - 2t_n \cos(ka)}$$



bandwidth of the tight-binding band in d = 1: $W_n = 4t_n$

Now expand $\mathcal{E}_n(k)$ around band minimum at $k=0$

$$\mathcal{E}_n(k) \approx c_n - 2t_n\left(1 - \tfrac{1}{2}(ka)^2\right) = c_n - 2t_n + t_n a^2 k^2$$

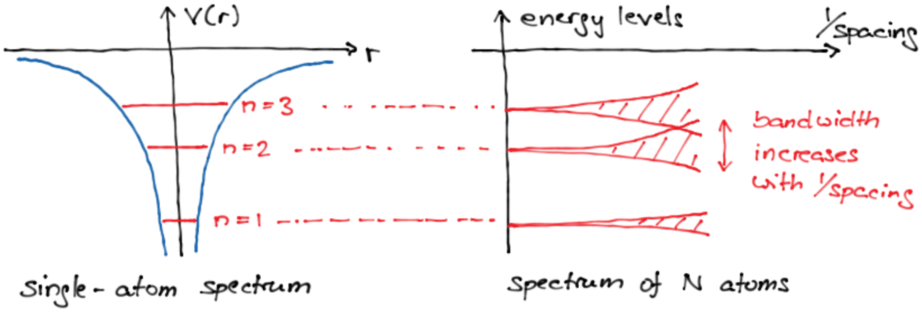
$$\rightarrow \text{effective mass:} \quad \frac{1}{m^*(n)} = \frac{1}{\hbar^2}\frac{\partial^2 \mathcal{E}_n(k)}{\partial k^2} = \frac{1}{\hbar^2} 2t_n a^2$$

$$\rightarrow \quad \boxed{m^*(n) = \frac{\hbar^2}{2a^2} \cdot \frac{1}{t_n}}$$

the effective mass diverges for $t_n \to 0$ ✓

Remarks

- Tight-binding bands are narrow bands. The bandwidth is determined by overlap γ.



small 1/spacing
→ tight-binding limit

large 1/spacing
→ limit of weakly periodic potential

4.7 Thermodynamics of non-interacting electrons

To discuss the thermodynamics of non-interacting electrons we consider their grand-canonical partition function

$$Z = \operatorname{tr} e^{-\beta \mathcal{H}} = \sum_{\{p_{n\sigma\vec{k}}\}} \exp\Big(- \overset{\beta = 1/k_B T}{\overset{\downarrow}{\beta}} \underset{\substack{\uparrow \\ \text{sum over} \\ \text{single-particle} \\ \text{states}}}{\sum_{\substack{n\sigma \\ \vec{k} \in 1.\mathrm{BZ}}}} \big(\varepsilon_n(\vec{k}) - \overset{\text{chemical potential}}{\overset{\downarrow}{\mu}} \big) \cdot \underset{\substack{\uparrow \\ =0,1 \\ \text{occupation of} \\ \text{single-particle state}}}{p_{n\sigma\vec{k}}} \Big)$$

$$= \sum_{\{p_{n\sigma\vec{k}}\}} \prod_{\substack{n,\sigma \\ \vec{k}}} \exp\left(-\beta \left(\varepsilon_n(\vec{k}) - \mu \right) p_{n\sigma\vec{k}} \right)$$

$$= \prod_{\substack{n,\sigma \\ \vec{k} \in 1.\mathrm{BZ}}} \left(1 + e^{-\beta(\varepsilon_n(\vec{k}) - \mu)} \right)$$

The free energy F is then given by

$$\boxed{F(T,\mu) = -k_B T \ln Z(T,\mu) = -k_B T \sum_{\substack{\sigma,n \\ \vec{k} \in 1.\mathrm{BZ}}} \ln\left(1 + e^{-\beta(\varepsilon_{n\vec{k}} - \mu)} \right)}$$

With the help of the density of states we can write the free energy density

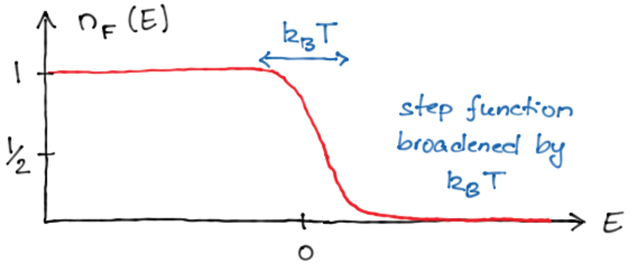
$$f(T,\mu) = \frac{F}{V} = -k_B T \int_{-\infty}^{\infty} d\varepsilon \; g(\varepsilon) \ln\left(1 + e^{-\beta(\varepsilon - \mu)} \right)$$

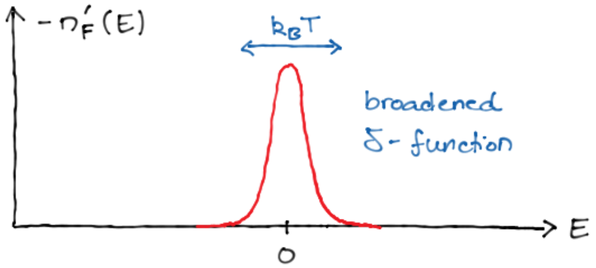
This, in turn, allows us to calculate the density of electrons $n = -\frac{\partial f}{\partial \mu}$

$$n(T,\mu) = \int_{-\infty}^{\infty} d\varepsilon \; g(\varepsilon) \frac{e^{-\beta(\varepsilon-\mu)}}{1 + e^{-\beta(\varepsilon-\mu)}} = \int_{-\infty}^{\infty} d\varepsilon \; g(\varepsilon) \, n_F(\varepsilon - \mu)$$

with the Fermi function

$$\boxed{n_F(E) = \frac{1}{e^{\beta E} + 1}}$$





$$\int_{-\infty}^{\infty} dE\,\left(-n_F'(E)\right) = -n_F(E)\Big|_{-\infty}^{\infty} = 1$$

At <u>zero temperature</u> we have $\quad n(0,\mu) = \int_{-\infty}^{\mu} d\epsilon\; g(\epsilon)$

→ at $T=0$ the chemical potential coincides with the Fermi energy

$$\boxed{\mu\big|_{T=0} = \mathcal{E}_F}$$

To evaluate <u>finite-temperature corrections</u> one uses the <u>Sommerfeld expansion</u>:

Consider some (smooth) function $a(\epsilon)$ with $a(\epsilon) \to 0$ for $|\epsilon| \to \infty$

$$\int_{-\infty}^{\infty} d\epsilon\; a(\epsilon)\cdot n_F(\epsilon-\mu) = \underbrace{A(\epsilon)}_{\substack{=0\\ \text{for } \epsilon\to-\infty}}\cdot\underbrace{n_F(\epsilon-\mu)}_{\substack{=0\\ \text{for } \epsilon\to\infty}}\Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} d\epsilon\; A(\epsilon)\left(-n_F'(\epsilon-\mu)\right)$$

with $\quad A(\epsilon) = \int_{-\infty}^{\epsilon} d\bar{\epsilon}\; a(\bar{\epsilon})$

Since $-n_F'(\epsilon-\mu)$ is only finite within a small intervall of width k_BT around $\epsilon-\mu \approx 0$ we can expand the function A in a Taylor series

$$A(\epsilon) = A(\mu) + \sum_{n=1}^{\infty} \frac{1}{n!}\,\frac{d^nA(\epsilon)}{d\epsilon^n}\Big|_{\epsilon=\mu}\,(\epsilon-\mu)^n$$

With this one obtains for the integral in the Sommerfeld expansion

$$\int_{-\infty}^{\infty} d\epsilon\; a(\epsilon)\cdot n_F(\epsilon-\mu) = \int_{-\infty}^{\mu} d\epsilon\; a(\epsilon) + \sum_{n=1}^{\infty} \frac{d^{n-1}a(\epsilon)}{d\epsilon^{n-1}}\Big|_{\epsilon=\mu} \int_{-\infty}^{\infty} d\epsilon\, \frac{(\epsilon-\mu)^n}{n!}\left(-n_F'(\epsilon-\mu)\right)$$

The last integral can be evaluated and yields

$$\int_{-\infty}^{\infty} d\varepsilon \; \frac{(\varepsilon-\mu)^n}{n!} \underbrace{\left(-n_F'(\varepsilon-\mu)\right)}_{\text{even function of } \varepsilon-\mu} = \begin{cases} (k_B T)^n \cdot C_{n/2} & \text{if } n \text{ is even} \\ 0 & \text{if } n \text{ is odd} \end{cases}$$

with coefficient $\boxed{C_n = \left(2 - \frac{1}{2^{2(n-1)}}\right) \cdot \zeta(2n)}$

Riemann's zeta function

in particular: $C_1 = \zeta(2) = \frac{\pi^2}{6}$, $\quad C_2 = \frac{7}{4}\zeta(4) = \frac{7\pi^4}{360}$

One finally obtains

$$\boxed{\int_{-\infty}^{\infty} d\varepsilon \; a(\varepsilon)\, n_F(\varepsilon-\mu) = \int_{-\infty}^{\mu} d\varepsilon \; a(\varepsilon) + \sum_{m=1}^{\infty} \left.\frac{d^{2m-1} a(\varepsilon)}{d\varepsilon^{2m-1}}\right|_{\varepsilon=\mu} (k_B T)^{2m}\, C_m}$$

In leading order, $m=1$, this becomes

$$\int_{-\infty}^{\infty} d\varepsilon \; a(\varepsilon)\, n_F(\varepsilon-\mu) = \int_{-\infty}^{\mu} d\varepsilon \; a(\varepsilon) + \left.\frac{d\,a(\varepsilon)}{d\varepsilon}\right|_{\varepsilon=\mu} (k_B T)^2 \, \frac{\pi^2}{6}$$

Let's use this result from the Sommerfeld expansion to calculate the <u>internal energy</u>

$$U = \int d\varepsilon \; \underbrace{g(\varepsilon)\cdot\varepsilon}_{a(\varepsilon)} \cdot n_F(\varepsilon-\mu)$$

$$= \int_{-\infty}^{\mu} d\varepsilon \; g(\varepsilon)\cdot\varepsilon + \frac{\pi^2}{6}(k_B T)^2 \left(g(\mu) + \mu\cdot g'(\mu)\right) + O(T^4)$$

Since the particle density n does not change with temperature (no particles leave or enter the system upon increasing T), the chemical potential must be temperature dependent, i.e. $\mu = \mu(T)$. We have for the particle density

$$n = \int_{-\infty}^{\infty} d\varepsilon \; g(\varepsilon)\, n_F(\varepsilon-\mu) = \int_{-\infty}^{\mu} d\varepsilon \; g(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 \, g'(\mu) + O(T^4)$$

For the integral $\int_{-\infty}^{\mu(T)} d\varepsilon\, g(\varepsilon)$ we assume that $\mu(T)$ is close to ε_F so that

$$\longrightarrow \int_{-\infty}^{\mu(T)} d\varepsilon\, g(\varepsilon) = \underbrace{\int_{-\infty}^{\varepsilon_F} d\varepsilon\, g(\varepsilon)}_{=n} + \underbrace{\int_{\varepsilon_F}^{\mu(T)} d\varepsilon\, g(\varepsilon)}_{\approx g(\varepsilon_F)\cdot(\mu-\varepsilon_F)}$$

So, we get for the particle density

$$\cancel{n} = \cancel{n} + (\mu-\varepsilon_F)\, g(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 \underbrace{g'(\mu)}_{\approx g'(\varepsilon_F)}$$

→ T-dependence of chemical potential given by

$$\mu(T) = \varepsilon_F - \frac{\pi^2}{6}\,\frac{g'(\varepsilon_F)}{g(\varepsilon_F)}\cdot(k_B T)^2 \qquad (*)$$

Back to <u>internal energy</u>

$$U = \underbrace{\int_{-\infty}^{\varepsilon_F} d\varepsilon\, g(\varepsilon)\cdot\varepsilon}_{\substack{U_0 \\ \text{internal energy for} \\ T=0}} + \underbrace{(\mu-\varepsilon_F)}_{\text{insert } (*)}\, g(\varepsilon_F)\cdot\varepsilon_F + \frac{\pi^2}{6}(k_B T)^2\left(g'(\varepsilon_F)\cdot\varepsilon_F + g(\varepsilon_F)\right)$$

$$\boxed{U = U_0 + \frac{\pi^2}{6}\, g(\varepsilon_F)\cdot(k_B T)^2}$$

This result immediately allows us to calculate the electronic contribution to the <u>specific heat</u>

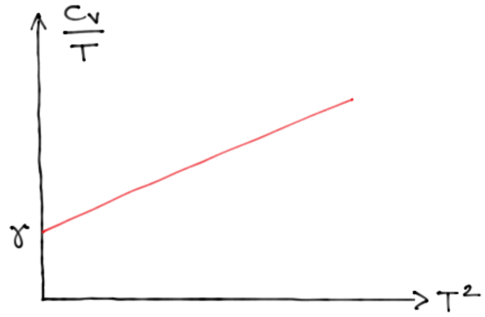
$$\boxed{c_V(T) = \frac{\partial U}{\partial T} = \frac{\pi^2}{3}\, g(\varepsilon_F)\, k_B^2\, T = \gamma\cdot T}$$

The electronic specific heat of a metal grows <u>linearly</u> in temperature.

The total specific heat of a metal at low temperatures has the form

$$c_V(T) = \underset{\text{electrons}}{\underset{\uparrow}{\gamma \cdot T}} + \underset{\text{phonons}}{\underset{\uparrow}{A \cdot T^3}}$$

often plotted as $\frac{c_V}{T}$ vs. T^2 → linear function



Remarks

- More generally, the power-law dependence of the electronic specific heat depends on the co-dimension d_c of the Fermi surface, i.e.

$$c_V(T) \propto T^{d_c} \qquad \text{with} \quad d_c = \underset{\substack{\text{spatial}\\\text{dimension}}}{\underset{\swarrow}{D}} - \underset{\substack{\text{dimensionality}\\\text{of Fermi surface}}}{\underset{\searrow}{d}}$$

- In particular, we have in $D=2$ spatial dimensions

nodal line → $c_V(T) \propto T$ (metal)
Dirac cone → $c_V(T) \propto T^2$ (semi-metal)

and in $D=3$ spatial dimensions

$$\begin{aligned} &\text{Fermi surface} \longrightarrow c_V(T) \propto T \\ &\left.\begin{aligned} &\text{nodal line} \longrightarrow c_V(T) \propto T^2 \\ &\text{Weyl nodes} \longrightarrow c_V(T) \propto T^3 \end{aligned}\right\} \text{semi-metals} \end{aligned}$$