Karlsruher Institut für Technologie

Vorlesungsmitschrieb

TKM I

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Mitschrieb von
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Wintersemester 2019/20
letzte Bearbeitung: November 5, 2020

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1 Solids

fundamental states of matter: solid, liquid, gas

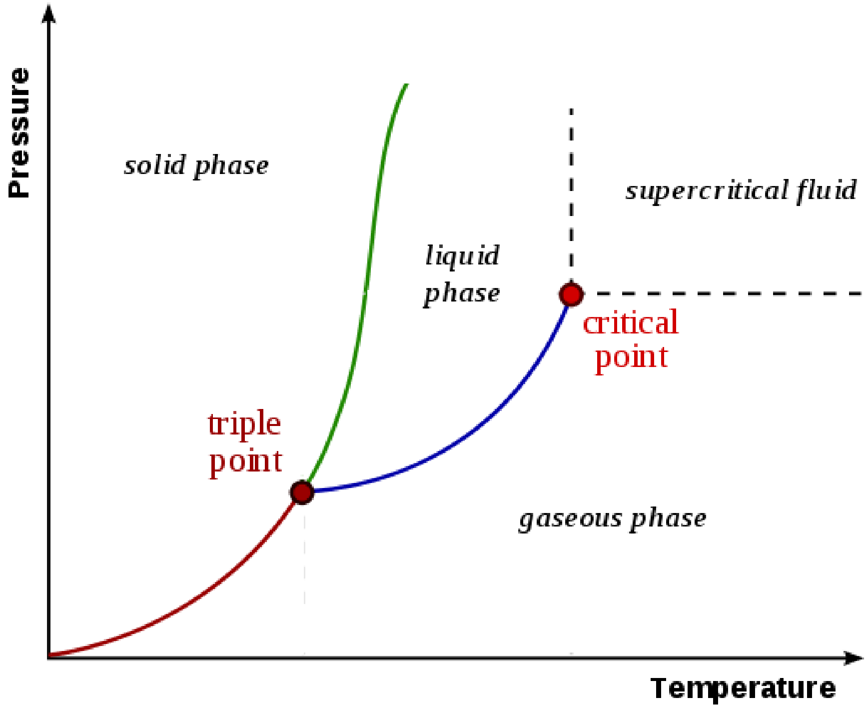

Figure 1: Phase diagram

At sufficiently low temperatures matter almost always assumes a *solid state*. Exception: for example Helium (He) → superfluid state

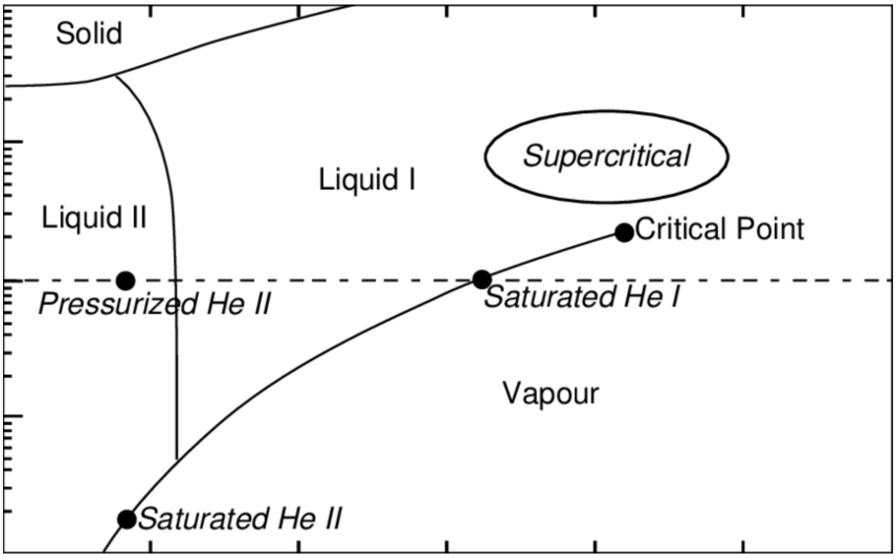

Figure 2: Phase diagram Helium

1.1 Crystalline Solids

Most solids are *crystals* characterized by a periodic arrangement of its constitutes e.g. atoms in contrast to amorphous solides like gases. Solid crystals break the translation and rotation invariance.
Consequences:

- a solid state is separated from liquid and gas state by a *symmetry-breaking phase transition.* A liquid or a gas cannot be continuously transformed into a solid. When a liquid freezes and solidifies it usually does not lead to a macroscopic solid composed of a *single crystal.* It often consists of a large number of smaller crystals generally known as domains, that have broken the symmetries in different fashions. Such a material is a *poly-crystal.*

- solids possess as a symmetry-broken state a *rigidity* (Steifigkeit), structural rigidity allows long distance transmission of forces and shear forces (Scherkräfte), i.e. dissipationless momentum and angular momentum flow (similar to superconductor that allows for dissipationless charge flow)

- a solid crystal is characterized by low-energetic excitations (Goldstone Modes) that are the *acoustic phonons.* Phonon velocities are determined by the elastic moduli like bulk and shear modules that quantify the rigidity of the crystal.

1.2 Crystal Structure

Geometrical properties of a periodic structure are characterized by the *Bravais lattice.*

Bravais lattice

A (three-dimensional) Bravais lattice consists of all points with position vector $\vec{R}$ of the form

$$\boxed{\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3}$$

with $n_i \in \mathbb{Z}$. The *primitive vectors* $\vec{a}_i$ are linearly independent. The choice of primitive vectors is not unique.

1.2.1 Theorem (Auguste Bravais 1848)

There exist only 14 Bravais lattice types in 3 dimensions.
Examples:

- simple cubic (sc)
$$\vec{a}_1 \perp \vec{a}_2 \perp \vec{a}_3 \quad \text{with } |\vec{a}_1| = |\vec{a}_2| = |\vec{a}_3|$$
- body-centered cubic (bcc)
$$\vec{a}_1 = a\hat{x},\ \vec{a}_2 = b\hat{y}, \quad \vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})$$
  sc plus an additional point at the center of each cube
- face-centered cubic (fcc)
$$\vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{z}), \quad \vec{a}_2 = \frac{a}{2}(\hat{z} + \hat{x}), \quad \vec{a}_2 = \frac{a}{3}(\hat{x} + \hat{z})$$
  sc plus an additional point at each centre of square faces

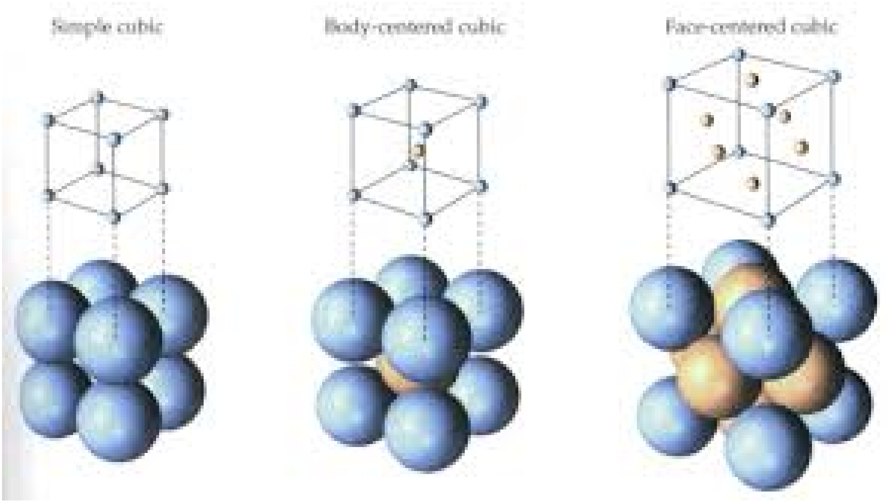

Figure 3: cubic Bravais lattices

1.2.2 Coordination number z

The coordination number z is the number of *nearest neighbors* of each lattice point, whereas the nearest neighbors are the points in the Bravais lattice that are nearest to a given point:

	sc	bcc	fcc
z	6	8	12

The bcc and fcc Bravais lattices are very important as an enormous variety of solids crystallize in these forms with an atom or ion at each lattice site. Usually, the fcc lattice is preferred at lowest temperatures since it possesses the larger coordination number z (dichtest gepackt). In contrast, the sc lattice is very rarely realized.

1.2.3 Unit cell (UC)

The unit cell describes the volume of space, when translated through a subset of the vectors of the Bravais lattice, which just fills all space without overlap itself or leaving voids.

1.2.4 Primitive unit cell (PUC)

The primitive unit cell is a UC containing exactly a single lattice point. Note: there does not exist a unique way of choosing a PUC for a given Bravais lattice. However, its volume is fixed by the density of points in the Bravais lattice n:

$$V_{\text{PUC}} = \frac{1}{n}$$

A possible choice is:

$$\text{PUC} = \{x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3 \mid 0 \leq x_i < 1,\ i = 1, 2, 3\}$$

For a given PUC an arbitrary vector $\vec{R}$ is uniquely defined:

$$\vec{R} = \vec{R}_n + \vec{x} \quad \text{with } \vec{x} \in PUC \quad \text{and } \vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

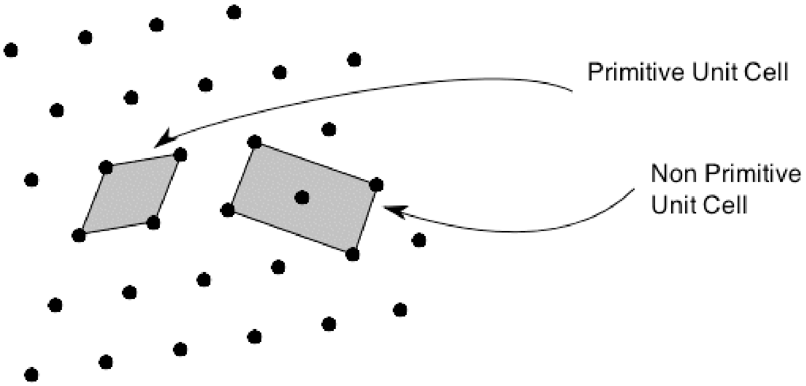

Figure 4: (primitive) unit cell

1.2.5 Wigner-Seitz primitive cell

The Wigner-Seitz primit primitive cell is a primitive unit cell about a lattice point containing the region of space that is closer to that point than to any other lattice point. The Wigner-Seitz cell possesses the full symmetry of the Bravais lattice.
Examples of a two-dimensional Bravis lattice are the triangular or the hexagonal lattice.

n in Figure 15.

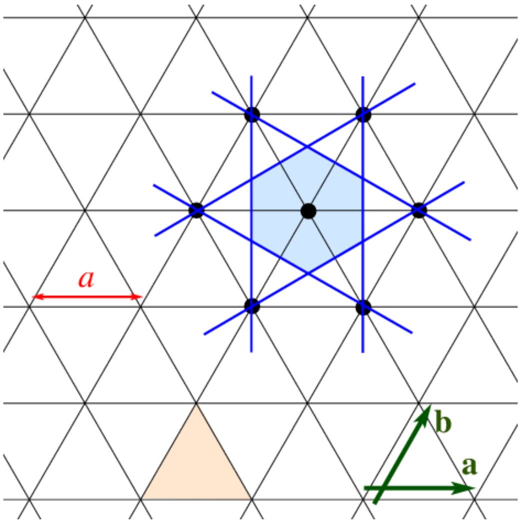

Figure 5: Wigner-Seitz cell of a triangular lattice

1.2.6 Crystal structure

The Crystal structure consists of identical copies of the same physical unit, called the *basis*, located at all points of the Bravais lattice. In particular, the basis specifies the position of atoms within a unit cell.
Examples:

- mono-atomic Bravais lattice crystal structure with a basis consisting of a simple atom or ion positioned for example at the point of the Bravais lattice. E.g. crystal structure of Cr(bcc), Fe(bcc), Xl (fcc), Au(fcc)
- two-dimensional honeycomb (realized in Graphene), which is not a Bravais lattice

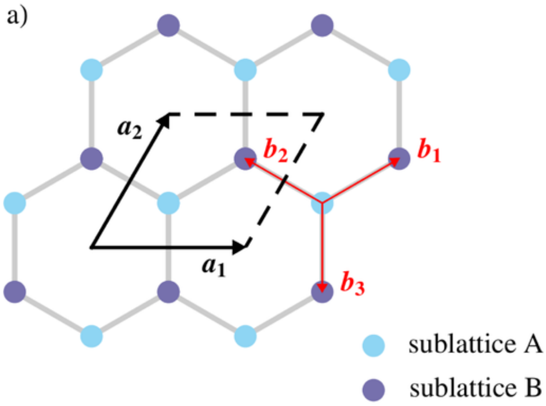

Figure 6: Honeycomb lattice

Its basis contains two points

$$\left\{\frac{1}{3}(\vec{a}_1+\vec{a}_2),\ \frac{2}{3}(\vec{a}_1+\vec{a}_2\right\}$$

- diamond structure
fcc lattice with two point basis

$$\left\{0,\ \frac{a}{4}(x+y+z)\right\}$$

- hexagonal close-pack structure
simple hexagonal lattice = stated two dimensional primitive vectors

$$\vec{a}_1 = ax, \quad \vec{a}_2 = \frac{a}{2}x + \frac{\sqrt{3}}{2}ay, \quad \vec{a}_3 = az,$$

with two point basis:

$$\left\{0,\ \frac{1}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3\right\}$$

This structure is of similar importance as the mono-atomic bcc and fcc lattice.

- structures that are necessarily described by a basis because two types of ions/ atoms are present:
  - NaCl (sodium chloride)
    fcc lattice, basis: Na at $(0, 0, 0)$ and Cl at $(\frac{a}{2}, \frac{a}{2}, \frac{a}{2})$
  - CsCl (cesium chloride)
    bcc lattice, basis: Cs at $(0, 0, 0)$ and Cl at $(\frac{a}{2}, \frac{a}{2}, \frac{a}{2})$
- Zincblende structure (Zns)
  diamond structure but the two positions specified by the basis are occupied by different atoms/ions.

18.10.2019

1.2.7 Classification of crystal structure

Crystal structures are classified according to their symmetries. One distinguishes

Point group

The point group is composed of all symmetry operations that leave a particular ion/ atom of the crystal fixed like reflection, inversion, rotation, combined rotation-reflection, rotation-inversion. There are in total 32 crystallographic point groups. Symmetries of the point group are important to determine the number of independent components of tensor quantities that characterize properties of the crystal for example conductivity σ_{ij}, polarizability α_{ij}, susceptibility ξ_{ij} or the piezoelectric tensor d_{ijk}.

Space group

The space group is composed of the symmetry operations of the point group in addition

- translation through Bravais lattice vector
- combined translation-rotation (screw axis) and translation-reflexion (glide planes) symmetry operations

and combinations thereof. There are in total 230 space groups.

1.2.8 Reciprocal lattice

Consider a function eg. a potential with a periodicity of Bravais lattice $V(\vec{r}+\vec{R}_n) = V(\vec{r})$ with $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$. The Fourier transformation of the potential is given by:

$$V(\vec{r}) = \sum V_{\vec{G}_m} e^{i\vec{G}_m\vec{r}}$$

where due to the periodicity the momenta $\vec{G}_m$ have the properties

$$\boxed{e^{i\vec{G}_m\vec{R}_n} = 1}$$

or alternatively

$$\vec{G}_m \vec{R}_n = 2\pi N \quad \text{with } N \in \mathbb{Z}.$$

The momenta are given by

$$\boxed{\vec{G}_m = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3, \quad m \in \mathbb{Z},\ i = 1,2,3}$$

with

$$\boxed{\vec{a}_i \vec{b}_j = 2\pi\delta_{ij}}$$

Explicitly:

$$\vec{b}_1 = \frac{2\pi}{V_{\text{PUC}}}(\vec{a}_2 \times \vec{a}_3), \quad \vec{b}_2 = \frac{2\pi}{V_{\text{PUC}}}(\vec{a}_3 \times \vec{a}_1), \quad \vec{b}_3 = \frac{2\pi}{V_{\text{PUC}}}(\vec{a}_1 \times \vec{a}_2)$$

with the volume of the primitive cell which is given by the scalar triple product of the basis vectors

$$V_{\text{PUC}} = \vec{a}_1(\vec{a}_2 \times \vec{a}_3)$$

The $\vec{b}_i$ are the primitive vectors of the *reciprocal lattice*. It is a Bravais lattice in Fourier space.
Examples:

Bravais lattice	sc	fcc	bcc	simple hexagonal
reciprocal lattice	sc	bcc	fcc	simple hexagonal

1.2.9 First Brillouin Zone

The *first Brillouin Zone* (1BZ) is the Wigner Seitz primitive cell of the reciprocal lattice. An arbitrary vector in wave-vector space is given by

$$\vec{k} = \vec{G}_m + \vec{p} \quad \text{with } \vec{p} \in \text{ 1BZ}$$

The volume of the 1BZ is given by the scalar triple product of the reciprocal basis vectors and is directly related to the volume of the primitive unit cell of the lattice in position-space

$$V_{1BZ} = \vec{b}_1(\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{V_{\text{PUC}}}$$

Conventions:

- directions in the Bravais lattice: $[n_1, n_2, n_3]$ direction specified by $n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$
- planes in the Bravais lattice (Miller indices): (m_1, m_2, m_3) plane that is normal to vector $m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$.

1.3 Scattering from a crystal

Typical inter-atomic distances in a solid are of order: $a \sim 1\,\text{Å} = 1 \times 10^{-10}\,\text{m}$. Typical energies needed for scattering can be calculated easily by the energy dispersion relation: $\hbar\omega = \frac{hc}{\lambda} \sim \frac{hc}{1\,\text{Å}} \approx 12\,\text{keV}$.

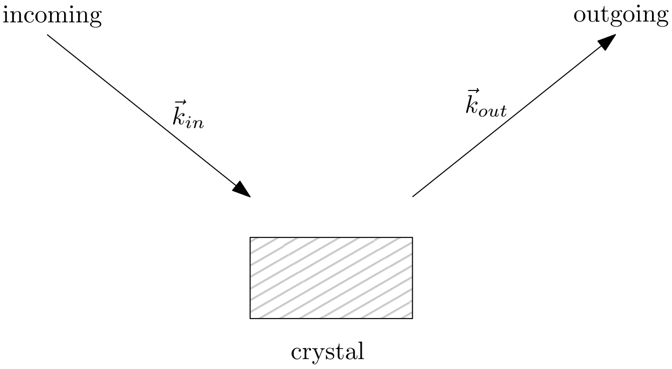

Figure 7: Scattering experiment

Now, consider the matrix element of the scattering potential $V(\vec{r})$

$$\begin{aligned} |\langle \vec{k}_{\text{out}}| V(\vec{r})\, |\vec{k}_{\text{in}}\rangle| &= \frac{1}{V}\int \mathrm{d}\vec{r} e^{-i\vec{k}_{\text{out}}\vec{r}} V(\vec{r}) e^{i\vec{k}_{\text{in}}\vec{r}} \\ &= \frac{1}{V}\int \mathrm{d}\vec{r} \sum_m V_{\vec{G}_m} e^{i(\vec{k}_{\text{in}}+\vec{G}_m-\vec{k}_{\text{out}})\vec{r}} \\ &= \sum_{\vec{G}_m} V_{\vec{G}_m} \delta_{\vec{k}_{\text{in}}+\vec{G}_m-\vec{k}_{\text{out}}} \end{aligned}$$

so we obtain the selection rule

$$\boxed{\vec{k}_{\text{out}} = \vec{k}_{\text{in}} + \vec{G}_m}$$

with a reciprocal lattice vector $\vec{G}_m$.

1.3.1 Geometric interpretation

Consider two ions / atoms in the crystal separated by a Bravais lattice vector R_n that both scatter in the incoming wave.

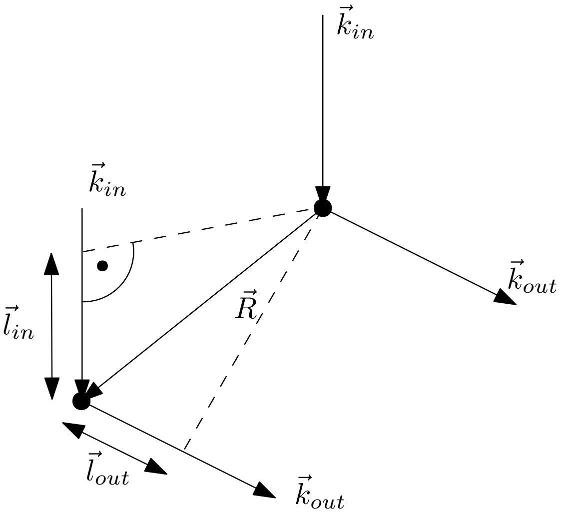

Figure 8: Scattering on two adjacent lattice points resulting in path differences between the wave vectors

Von Laue condition for constructive interference:
The two scattering events interfere constructively if the path difference Δl is an integer multiple of the wavelength λ.

$$\Delta l = l_{\text{in}} + l_{\text{out}} = \lambda N \quad \text{with } N \in \mathbb{Z}, \quad l_{\text{in}} = \vec{R}\hat{k}_{\text{in}}, \quad l_{\text{out}} = -\vec{R}\hat{k}_{\text{out}}$$

and assuming elastic scattering:

$$\vec{k}_{\text{in}} = \frac{2\pi}{\lambda}\hat{k}_{\text{in}}, \quad \vec{k}_{\text{out}} = \frac{2\pi}{\lambda}\hat{k}_{\text{out}}$$

It follows

$$\vec{R}(\vec{k}_{\text{in}} - \vec{k}_{\text{out}}) = \vec{R}(\hat{k}_{\text{in}} - \hat{k}_{\text{out}})\frac{2\pi}{\lambda} = (l_{\text{in}} - l_{\text{out}})\frac{2\pi}{\lambda} = 2\pi N \quad \text{with } N \in \mathbb{Z}$$

Also $\vec{k}_{\text{in}} - \vec{k}_{\text{out}}$ is a reciprocal lattice vector.
Scattering examples allow for example to

- determine the Bravais lattice of a solid (Deye-Scherrer-method)
- orient the crystal (Laue method)
- obtain information about the basis of a crystal via the *geometrical structure factor* and the *atomic form factor*.

2 Solid as a quantum system

In general, a solid consists of ions, i.e. nuclei and the tightly bound electrons of the inner shells, and valence electrons. Note that the separation of the core and the valence electrons is not unique and depends on the context, material, etc.
The Hamiltonian of this many-particle system then reads (in non-relativistic limit)

$$\begin{aligned} H &= H_{\text{el}} + H_{\text{ion}} + H_{\text{interaction}} \\ H_{\text{el}} &= \sum_i \frac{p_i^2}{2m_e} + \sum_i \sum_{j<i} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \text{spin-orbit correction} \quad \text{(Gaussian System)} \\ H_{\text{ion}} &= \sum_n \frac{p_n^2}{2M_n} + \sum_{n<m} \frac{Z_n Z_m e^2}{|\vec{R}_n - \vec{R}_m|} + \text{correction from core electrons} \\ H_{\text{int}} &= -\sum_{i,n} \frac{Z_n e^2}{|\vec{r}_i - \vec{R}_n|} \end{aligned}$$

The Hamiltonian is quite well-known but too complicated to solve exactly! Even numerically on a supercomputer only few particles can be treated but not 10^{23}! Hence, approximations and understanding of relevant degrees of freedom are essential! But how can we identify the relevant degrees of freedom?
First of all we need to proceed from the classical Hamiltonian to the Hamilton operator.

$$H \to \hat{H} \begin{bmatrix} \vec{r} \to \hat{r} = \vec{r} \\ \vec{p} \to \hat{p} = -i\hbar\partial_{\vec{r}} \end{bmatrix}$$

Consider the stationary Schrödinger equation

$$H\phi = E\phi$$

with wavefunction

$$\phi = \phi(\underbrace{\vec{r}_1, \vec{r}_2, \ldots}_{N_{\text{el}}}, \underbrace{\vec{R}_1, \vec{R}_2, \ldots}_{N_{\text{ion}}})$$

This gives a $3(N_{\text{el}} + N_{\text{ion}})-$dimensional space where the number of electrons and ions is around $N_{el,ion} = 10^{23} - 10^{25}$.
Consider the Hamiltonian in atomic units (CGS-units: $4\pi\varepsilon \to 1$):

- [length] $= a_0 = \frac{\hbar^2}{me^2}$ Bohr radius
- [energy] $= \frac{e^2}{a_0} = 2Ry$, with the Rydberg energy $Ry = \frac{e^2}{2a_0} \approx 13.6\,\text{eV}$.

Now, we want to write the Hamiltonian in quantum mechanical form with the units from above.

$$
\begin{aligned}
H_{\mathrm{el}} &= \sum_i \frac{-\hbar^2}{2m}\partial^2_{\vec r} + \sum_{j<i}\frac{e^2}{|\vec r_i - \vec r_j|} = \left|\tilde{\vec r} = \tfrac{1}{a_0}\vec r\right| = -\sum_i \underbrace{\frac{\hbar^2}{2m}\frac{1}{a_0^2}}_{\frac{\hbar^2 m e^2}{2m a_0 \hbar^2}}\partial^2_{\vec r} + \frac{e^2}{a_0}\sum_{j<i}\frac{1}{|\vec r_i - \vec r_j|} \\
&= \frac{e^2}{a_0}\left(-\sum_i \frac{1}{2}\partial^2_{\vec r} + \sum_{ij}\frac{1}{|\vec r_i - \vec r_j|}\right) \\
H_{\mathrm{ion}} &= \frac{e^2}{a_0}\left(\sum_n\left(-\frac{1}{2}\frac{m}{M_n}\right)\partial^2_{\vec R_n} + \sum_{n<m}\frac{Z_n Z_m}{|\vec R_n^2 - \vec R_m^2|}\right) \\
H_{\mathrm{int}} &= -\frac{e^2}{a_0}\sum_{i,n}\frac{Z_n}{|\vec r_i - \vec R_n|}
\end{aligned}
$$

Apart from the atomic numbers Z_n the Hamiltonian only involves a single parameter i.e. the mass ratio between masses of electrons and ions

$$
\boxed{\frac{m}{M_n} \cong 10^{-3} \text{ to } 10^{-5}}
$$

Strategy: develop a systematic expansion in the small parameter $\frac{m}{M_n}$ by treating the kinetic part of the ions, T_{ion}, as a perturbation:

$$
H = H_0 + T_{\mathrm{ion}}
$$

with

$$
T_{\mathrm{ion}} = \sum_n \frac{m}{M_n}\frac{-\nabla^2}{2}
$$

2.1 Adiabatic approximation (Born-Oppenheimer) 1927

The definition of the terms adiabatic/ diabatic in thermodynamics (greek: unable/ able to be crossed) is: an adiabatic process is a transfer of work without transfer of heat ie. at constant entropy. Usage in Quantum mechanics: a gradually, slowly changing of conditions allows the system to adapt as a function of time. If the system starts in an eigenstate of the initial Hamiltonian, it will end in the corresponding eigenstate of the final Hamiltonian (also „adiabatic theorem“of quantum mechanics and Landau-Zener problem).

Here: electrons possess a smaller mass and are thus much faster than the ions. Hence, electrons practically follow instantaneously the movement of the ions. It follows that the dynamics of electrons and ions are decoupled and we can apply adiabatic approximation systematically in the small parameter $\frac{m}{M_n}$.

$$
H = H_{\mathrm{el}} + H_{\mathrm{int}} + T_{\mathrm{ion}} + V_{\mathrm{ion}}
$$

→ perturbative calculation with T_{ion}

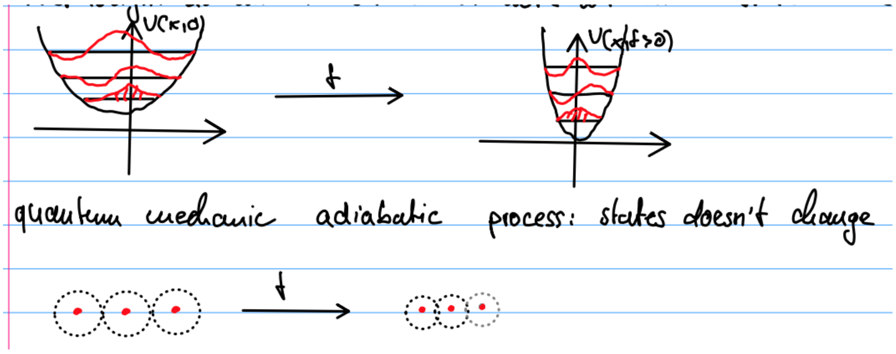

Figure 9: The system changes due to the changing conditions

Step 1: zero order approximation in $\frac{m}{M_n}$
Consider an electronic subsystem in the presence of a fixed ion configuration $\{R_1, R_2, ..., R_m\}$ described by the electronic many-particle wave function

$$\psi_a = \psi_a(\{r_1, r_2, ..., r_N\}, \{R_1, R_2, ..., R_m\})$$

where ψ_a is a complete system of orthogonal functions.
The ground state Hamiltonian is given by

$$H_0 = H_{\text{el}} + H_{\text{int}} + V_{\text{ion}}$$

and the eigenvalue problem for the adiabatic motion of electrons is

$$\boxed{H_0\psi_a(\{\vec{r}_i\}, \{\vec{R}_n\}) = \varepsilon_a(\{\vec{R}_n\})\psi_a(\{\vec{r}_i\}, \{\vec{R}_n\})}$$

with electronic quantum numbers $\varepsilon_a \in \mathbb{R}$. The exact solution of this equation is in general not possible, thus, further approximations are necessary (see later chapters). With the help of the (approximate) ground state energy $\varepsilon_0(\{R_n\})$ one obtains the crystal structure $\{R_n^{(0)}\}$ by minimizing with respect to the ion configuration

$$E_0 = \min_{\{R_n\}} \varepsilon_0(\{R_n\}) = \varepsilon_0(\{R_n^{(0)}\})$$

Step 2: Adiabatic corrections represent the full wave function in the eigenbasis

$$\phi(\{\vec{r}_i\}, \{\vec{R}_n\}) = \sum_a \phi_a(\{\vec{R}_n\})\psi_a(\{\vec{r}_i\}, \{\vec{R}_n\})$$

The full stationary Schrödinger equation now reads

$$\begin{aligned} E\sum_a \phi_a(\{\vec{R}_n\})\psi_a(\{\vec{r}_i\}, \{\vec{R}_n\}) &= (H_0 + T_{\text{ion}})\sum_a \phi_a(\{\vec{R}_n\})\psi_a(\{\vec{r}_i\}, \{\vec{R}_n\}) \\ &= \sum_a [\varepsilon_a(\{\vec{R}_n\}) + T_{\text{ion}}]\phi_a(\{\vec{R}_n\})\psi_a(\{\vec{r}_i\}, \{\vec{R}_n\}) \end{aligned}$$

Idea: derive an effective Hamiltonian for the „expansion parameters“ϕ_a by using the orthogonality of of $\psi_a(\{\vec{r}_i\},\{\vec{R}_n\})$, ie. by projection:

$$\int \mathrm{d}(\{\vec{r}_i\})\psi_a(\{\vec{r}_i\},\{\vec{R}_n\})\cdot\psi_b^*(\{\vec{r}_i\},\{\vec{R}_n\}) = \delta_{a,b}$$

Multiplying $\int \mathrm{d}\{r_i\}\psi_b^*(\{\vec{r}_i\},\{\vec{R}_n\})$ on both sides of the equation from the left one obtains

$$E\phi_b(\{\vec{R}_n\}) = \varepsilon_a\phi_b + \int \mathrm{d}(\{\vec{r}_i\})\psi_b^* T_{\mathrm{ion}}(\psi_a\phi_a)$$

with

$$\begin{aligned} T_{\mathrm{ion}}\phi_a\psi_a &= \sum_n \frac{\hbar^2}{2M_n}(-\nabla_n^2)\phi_a\psi_a \\ &= -\sum_n \frac{\hbar^2}{2M_n}\left[(\nabla_n^2\phi_a)\psi_a + \phi_a(\nabla_n^2\psi_a) + 2(\nabla_n\phi_a)(\nabla_n\psi_a)\right) \end{aligned}$$

where we made use of

$$\partial_x^2(f(x)g(x)) = f''g + g''f + 2g'f'$$

The Schrödinger equation finally becomes

$$E\phi_b(\{\vec{R}_n\}) = [\varepsilon(\{\vec{R}_n\}) + T_{\mathrm{ion}}]\phi_b + \sum_a C_{ab}(\{\vec{R}_n\})\phi_a$$

with the operator

$$C_{ab}(\{\vec{R}_n\}) = \int d(\{\vec{r}_i\})\sum_n\left(-\frac{\hbar^2}{2M_n}\right)\psi_b^*[\partial_{\vec{R}_n}^2\psi_a + 2(\partial_{\vec{R}_n}\psi_a)\partial_{\vec{R}_n}]$$

The off-diagonal part of this operator, in particular, induces transitions i.e. diabatic processes between electronic states. However, at lowest order, this operator can be neglected.

So, one arrives at an effective eigenvalue problem for the ions only

$$\boxed{E\phi_b = (\varepsilon_b + T_{\mathrm{ion}})\phi_b}$$

In particular for the electronic ground state this reads

$$E\phi_0 = (\varepsilon_0 + T_{\mathrm{ion}})\phi_0$$

What is about the neglected term C_{ab}?

$$\begin{aligned}
C_{ab}(\{\vec{R}_n\})\phi_a &= \int d\{r_i\}\sum_n \frac{\hbar^2}{2M_n}[\psi_b^*\partial^2_{\vec{R}_n}\psi_a + 2\psi_b^*(\partial_{\vec{R}_n}\psi_\alpha)\partial_{\vec{R}_n}]\phi_\alpha \\
&\sim \frac{m}{M}\langle T_{\text{el}}\rangle + \frac{1}{M}\langle P_{\text{el}}\rangle\langle P_{\text{ion}}\rangle \\
&\sim \frac{m}{M}E_{\text{el}} + \frac{1}{M}\sqrt{mE_{\text{el}}}\sqrt{ME_{\text{ion}}} \\
&\sim \frac{m}{M}E_{\text{el}} + \frac{1}{M}\sqrt{mE_{\text{el}}}\sqrt{M\sqrt{\frac{m}{M}}E_{\text{el}}} \\
&= E_{\text{el}}\left[\frac{m}{M} + \left(\frac{m}{M}\right)\right]^{\frac{3}{4}}
\end{aligned}$$

Since $C_{ab} \ll \sqrt{\frac{m}{M}}E_{\text{el}} = E_{\text{ion}}$ it can indeed be neglected.
The potential $\varepsilon_0(\{R\})$ is minimized by the particular crystal structure of the material. In order to estimate the correction to the ground-state energy attributed to the kinetic term T, one consider small deviations from the equilibrium configuration

$$\delta T_n = R_n - R_n^{(0)}$$

Taylor expanding the potential in δR gives

$$\varepsilon_0(\{\vec{R}_n\}) \approx \varepsilon_0(\{\vec{R}_n^0\}) + \frac{1}{2}\sum_{nm}\delta R_n D_{nm}\delta R_m$$

with

$$(D_{nm})^{ij} = \left.\frac{\partial\varepsilon(\{\vec{R}_n\})}{\partial(\vec{R}_n)^i\partial(\vec{R}_m)^j}\right|_{R_{nm}=R^0_{nm}}$$

One arrives at

$$E\phi_0 = (\varepsilon_0(\{\vec{R}_n^{(0)}\} + H_{\text{eff}})\phi_0$$

with the effective Hamiltonian (with $P_n = -i\nabla_n$)

$$H_{\text{eff}} = \sum_n \frac{1}{2}\frac{m}{M_n}\vec{P}_n^2 + \sum_{n,m}\frac{1}{2}\delta R_n D_{nm}\delta R_m$$

corresponding to a higher-dimensional harmonic oscillator. The kinetic and the potential term in H_{eff} are of equal importance which becomes manifest by rescaling

$$\delta R_n = \left(\frac{m}{M_n}\right)^{\frac{1}{4}}u_n, \quad P_n = \left(\frac{m}{M_n}\right)^{-\frac{1}{4}}p_n$$

and we get for a mono-atomic crystal ($M_n = M$):

$$H_{\text{eff}} = \left(\frac{m}{M}\right)\frac{1}{2}\left(\sum_n \frac{1}{2}\vec{p}_n^2 + \sum_{n,m}\frac{1}{2}u_n D_{nm}u_m\right)$$

The zero-point motion leads to a adiabatic correction to the groundstate energy of the order

$$\boxed{\delta E = E - \varepsilon_0(\{R^{(0)}\}) = \mathcal{O}\left(\sqrt{\frac{m}{M}}\right)}$$

The next-to leading order correction derives from the C_{ab} operator that can be estimated as follows

$$C_{ab} \cong \int \mathrm{d}\{r\} \sum_n \frac{m}{2M_n} 2(\psi_b^* \nabla_n \psi_a)\vec{P}_n = \int \mathrm{d}\{r\} \sum_n \left(\frac{m}{M_n}\right)^{\frac{3}{4}} (\psi_b^* \nabla_n \psi_a)\vec{p}_n$$

so that

$$\frac{C_{ab}}{\delta E} \sim \mathcal{O}\left(\left(\frac{m}{M_n}\right)^{\frac{1}{4}}\right)$$

The adiabatic approximation is controlled in the parameter

$$\boxed{\alpha = \left(\frac{m}{M}\right)^{\frac{1}{4}}}$$

with $\left(\frac{m}{M}\right) \sim 10^{-5}$ to 10^{-3} follows $\alpha \sim 10^{-2}$ to 10^{-1}.
If α is too large the crystal structure will melt due to zero-point fluctuations (superfluid ^{3}He and ^{4}He).

$$E_{\text{ion}}^2 = \hbar^2\omega^2 \sim \hbar^2 \frac{D}{M} \sim \hbar^2 \frac{E_{\text{el}}}{a_0^2 M} = \frac{m}{M} E_{\text{el}} \frac{me^4}{\hbar^2} = \frac{m}{M} E_{\text{el}}^2$$

$$\rightarrow E_{\text{ion}} \sim \sqrt{\frac{m}{M}} E_{\text{el}}$$

with

$$M\ddot{x} + Dx = 0.$$

Remember 25.10.2019

$$E_{\text{el}} = \frac{e^2}{a_0} = \frac{e^4}{\hbar^2 m}, \quad a_0 = \frac{\hbar^2}{me^2}$$

2.2 Cohesive energy of crystals

The crystal structure is obtained by minimizing the electronic ground state energy $\varepsilon_0(\{\vec{R}_n\})$ with respect to the ion configuration $\{R\}$. The energy at the equilibrium configuration $\{\vec{R}_n^{(0)}\}$

$$\varepsilon_0(\{\vec{R}_n\}) = V_{\text{eff}}(\{\vec{R}_n\}) = \sum_{n<m} V(|\vec{R}_n - \vec{R}_m|) = \frac{1}{2} \sum_{n \neq m} V(|\vec{R}_n - \vec{R}_m|)$$

carries information about the *cohesive energy* or binding energy ie. the energy required to disassemble it into its constituents.
The function $\varepsilon_0(\{\vec{R}_n\})$ is in general unknown. However, there are certain limits where the origin of the cohesive energy can be identified.

2.2.1 Phenomenological classification of bonding in crystals

Van-der-Waals bonding

Examples are molecular crystals consisting of the noble gases with closed electronic shells (no valence electrons) like Ne, Ar, Kr, ... The atoms interact *pair-wise* via the weak, attractive van-der-Waals interaction due to fluctuation.

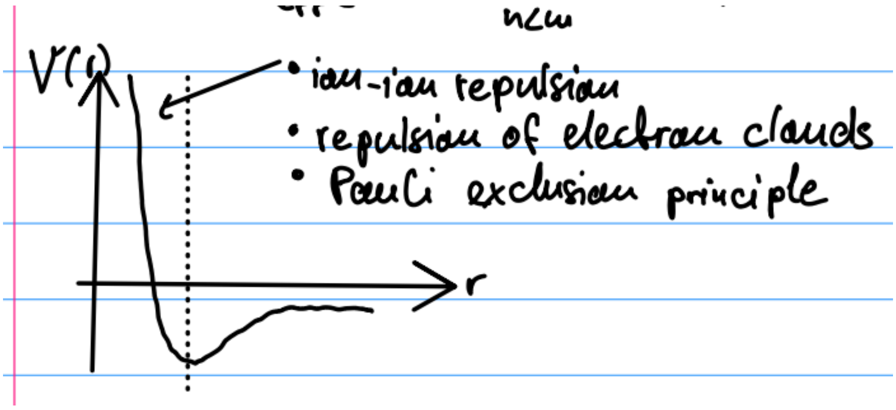

Figure 10: Groundstate

The zero-point fluctuation of the dipole moment is often described by the Lennard-Jones potential

$$V(\vec{r}) = 4\varepsilon \left[\underbrace{\left(\frac{\sigma}{r}\right)^{12}}_{\text{repulse}} - \underbrace{\left(\frac{\sigma}{r}\right)^{6}}_{\text{attract}} \right] \qquad \varepsilon, \sigma \in \mathbb{R}$$

$$V'(r_0) = 0$$

$$\rightarrow r_0 = 2^{\frac{1}{6}}\sigma$$

Therefore

$$V_{\text{eff}}(\{\vec{R}_n\}) = \frac{1}{2}\phi\varepsilon \sum_{n\neq m} \left[\left(\frac{\sigma}{|\vec{R}_n - \vec{R}_m|} \right)^{12} - \left(\frac{\sigma}{|\vec{R}_n - \vec{R}_m|} \right)^{6} \right]$$

Respect the crystal structure by

$$|\vec{R}_n - \vec{R}_m| = aP_{nm}$$

and remember the double sum

$$\sum_{n\neq m} = \sum_{n=1}^{N} \sum_{m\pm n}$$

so

$$V_{\text{eff}} = 2\varepsilon N \left[\left(\frac{\sigma}{a}\right)^{12} C_{12} - \left(\frac{\sigma}{a}\right)^{6} C_6 \right] \underbrace{=}_{\text{equilibrium}} -\frac{1}{2} N\varepsilon \frac{C_6^2}{C_{12}}$$

with a_0 at equilibrium and C_α:

$$a_0 = \sigma \left(2\frac{C_{12}}{C_6} \right)^{12}, \quad C_\alpha = \sum_{m\neq n} \frac{1}{P_{nm}^{\alpha}}$$

For example fcc:

$$\begin{aligned} C_{12} &\approx 12.13 \\ C_6 &\approx 14.45 \end{aligned}$$

Ionic bonding

In ionic crystals consisting of oppositely charged ions those ions attract each other pairwise by means of the strong Coulomb interaction. Here, crystal structures with a large coordination number z are preferred. Examples: NaCl, CsCl, ZnS.

$$\begin{aligned} V(r) &= -\frac{Q^2}{r} + \underbrace{\frac{\beta}{r^{\sigma}}}_{\lambda e^{\frac{-r}{\sigma}}} \\ V_{\text{eff}} &\approx \frac{1}{2}\sum_{n}^{N} \left[\sum_{m\neq n} \frac{-Q^2}{|\vec{R}_n - \vec{R}_m|} + zV_{\text{repulsive}(P_{12})} \right] \\ &= \frac{N}{2} ZV_{\text{rep}}(P_{12}) - N\frac{Q}{a} C_M \\ \text{with } C_M^{3D} &= \frac{1}{2}\sum_{m\neq n}\frac{1}{P_{nm}} = \frac{1}{2}\sum_{i\neq j\neq l} \frac{1}{\sqrt{i^2+l^2+j^2}} \approx 1.74 \end{aligned}$$

Covalent bonding

Covalent crystals are characterized by a distribution of valence electrons and substantially differ from the isolated atoms/ions. The covalent bonding is similar to the chemical bonding in molecules like H_2 (Heitler-London theory). The bonding is spatially oriented for example along the links of the diamond crystal structure of C, Si, Ge. The bonding is due to exchange interaction (quantum mechanical corrections due to the spin interactions).

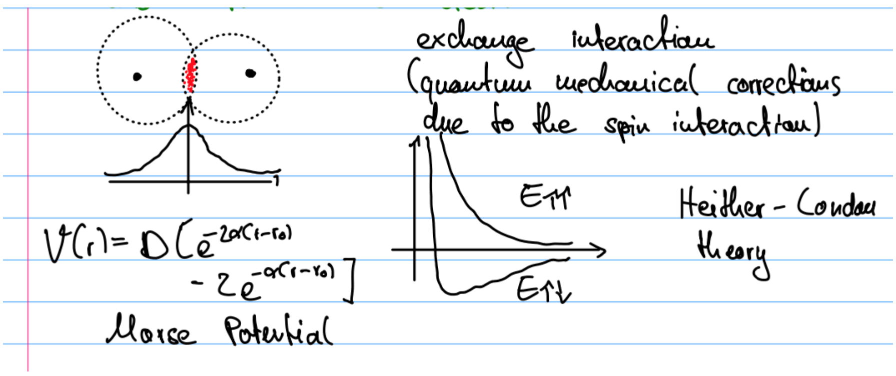

Figure 11: ions with valence electrons

Metallic bonding

The metallic bonding is mediated by valence electrons. The valence electrons are delocalised from the ion cores and become conduction electrons. The bonding is not spatially oriented in contrast to the covalent case.

3 Harmonic lattice vibrations: phonons

The effective n-th ion Hamiltonian derived in the adiabatic approximation reads:

$$H_{\text{eff}} = -\sum_n \frac{m}{M_n}\frac{\nabla_n^2}{2} + \sum_{n,m}\frac{1}{2}\delta^i_{\vec{R}_n} D^{ij}_{nm}\delta^j_{\vec{R}_m}$$

where n, m ist the label of the ion, i, j the vector component, $\delta_{\vec{R}_n} = \vec{R}_n - \vec{R}_n^{(0)}$ and

$$D^{ij}_{nm} = \frac{\partial}{\partial \vec{R}^i_n}\frac{\partial}{\partial \vec{R}^j_m}\varepsilon_0(\{\vec{R}\})\bigg|_{\{\vec{R}^{(0)}\}}$$

derives from the potential in the harmonic approximation and is the *dynamical matrix.* The Hamiltonian H_{eff} describes a system of coupled harmonic oscillators and can be diagonalised by standard means. This identifies the normal modes of the lattice vibrations similar as in molecules. For the characterization of the normal modes in a crystal however, one exploits the translation symmetry of the crystal.
We can label the ions with the help of a Bravais lattice vectors $\vec{l},\ \vec{m}$ that specify a specific primitive unit cell (PUC) of the crystal and an index $\lambda,\ \mu$ that counts the ions within the PUC ($\lambda,\ \mu = 1, 2, \dots, r$) for r ions in the unit cell.

$$D^{ij}_{nm} \to D^{ij}(\underbrace{\vec{l},\lambda}_{n\text{-th ion}}\ ;\ \underbrace{\vec{m},\mu)}_{m\text{-th ion}}$$

Due to the translation symmetry of the Bravais lattice we have

$$D^{ij}(\vec{l},\lambda;\vec{m},\mu) = D^{ij}(\vec{l}-\vec{n},\lambda;\vec{m}-\vec{n},\mu) = D^{ij}(\vec{l}-\vec{m},\lambda;\vec{0},\mu)$$

for any $\vec{n}$ of the Bravais lattice. Choosing $\vec{m} = \vec{n}$ one finds that D only depends on the difference $\vec{l}-\vec{m}$. In order to proceed further we will make use of the Bloch's theorem.

3.1 Bloch's theorem

Consider a translation operator $T_{\vec{R}}$ defined for a Bravais lattice vector $\vec{R}$ that acts on a wavefunction as

$$T_{\vec{R}}\psi(\vec{r}) = \psi(\vec{r}+\vec{R})$$

Translation operators commute

$$[T_{\vec{R}}, T_{\vec{R}'}] = 0$$

as

$$T_{\vec{R}}T_{\vec{R}'}\psi(\vec{r}) = T_{\vec{R}'}T_{\vec{R}}\psi(\vec{r}) = \psi(\vec{r}+\vec{R}'+\vec{R}) = T_{\vec{R}+\vec{R}'}\psi(\vec{r}) \tag{1}$$

Furthermore, consider an operator H that commutes $[H, T_{\vec{R}}] = 0$ for all $\vec{R}$ of the Bravais lattice. We can then choose simultaneous eigenstates ψ_α of H and of $T_{\vec{R}}$ for all $\vec{R}$:

$$H\psi_\alpha = \varepsilon\psi_\alpha$$
$$T_R\psi_\alpha = C_\alpha(\vec{R})\psi_\alpha$$

From equation (1) follows

$$C_\alpha(\vec{R})C_\alpha(\vec{R}') = C_\alpha(\vec{R}+\vec{R}') \quad \text{and } C_\alpha(\vec{R})C_\alpha(-\vec{R}) = 1$$

Moreover, from the normalization condition follows

$$1 = \int d\vec{r}|\psi_\alpha(\vec{r})|^2 = \int dr|\psi_\alpha(\vec{r}+\vec{R})|^2 = \int dr|\psi_\alpha(\vec{r})|^2|C_\alpha(\vec{R})|^2 = |C_\alpha(\vec{R})|^2$$

That in total implies

$$C_\alpha(\vec{R}) = e^{i\vec{k}\vec{R}}$$

where the wave vector $\vec{k}$ is specific for the ψ_α state. The eigenfunctions therefore obey

$$\boxed{\psi_\alpha(\vec{r}+\vec{R}) = e^{i\vec{k}\vec{R}}\psi_\alpha(\vec{r})}$$

Bloch's theorem.
As $e^{i\vec{G}\vec{r}} = 1$ for $\vec{G}$ of the reciprocal lattice, the wave vector $\vec{k}$ will be restricted to the first Brillouin zone.
Identifying α with a set of quantum numbers containing $\vec{k} \in$ 1BZ; $\alpha = \{\vec{k}, n\}$, we can alternatively express $\psi_\alpha(\vec{r}) = \psi_{n,\vec{k}}(\vec{r})$ in the following form:

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

where the *Bloch function* $u_{n\vec{k}}(\vec{r})$ obeys $u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$ for all $\vec{R}$ of the Bravais lattice.
Note: for systems that are invariant under arbitrary translations the momentum is conserved and a good quantum number. In contrast, for systems that are invariant with respect to discrete translations only, the quasi-momentum $\vec{k}$ is conserved, ie. the momentum modulo a reciprocal lattice vector, $\vec{k} \in$ 1BZ.

3.2 Diagonalization of the phonon Hamiltonian

We can use Bloch's theorem to diagonalize the dynamical matrix

$$\tilde{D}_{ij}(\vec{l},\lambda;\vec{m},\mu) = \frac{m}{\sqrt{M_\lambda M_\mu}}D^{ij}(\vec{l},\lambda;\vec{m},\mu)$$

for later convenience.
Consider the eigenvalue problem

$$\sum_{j,\mu,\vec{m}} \tilde{D}^{ij}(\vec{l},\lambda;\vec{m},\mu)\psi^j_\alpha(\vec{m},\mu) = d_\alpha\psi^i_\alpha(\vec{l},\lambda)$$

with eigenvalue d. Due to the discrete translation symmetry of the Bravais lattice we have:

$$T_R\psi^i(\vec{m},\mu) = \psi^i(\vec{m}+\vec{R},\mu)$$

and

$$T_R\tilde{D}^{ij}(\vec{l},\lambda;\vec{m},\mu) = \tilde{D}^{ij}(\vec{l}+\vec{R},\lambda;\vec{m}+\vec{R},\mu)T_R = \tilde{D}^{ij}(\vec{l},\lambda;\vec{m},\mu)T_R$$

that is $\tilde{D}$ commutes with T_R where $\vec{R}$ is a Bravais lattice vector. So it follows from Bloch's theorem that the eigenstates take the form

$$\psi^j_{\vec{k}n}(\vec{m},\mu) = e^{i\vec{k}\vec{m}}u^j_{\vec{k}n}(\vec{m},\mu) = e^{i\vec{k}\vec{m}}\vec{e}^j_{\vec{k}n}(\mu)$$

where the *polarization vector*

$$\vec{e}^j_{\vec{k}n}(\mu) = u^j_{\vec{k}n}(\vec{m},\mu) = u^j_{\vec{k}n}(\vec{0},\mu)$$

is the corresponding Bloch function.
We use the set of quantum numbers $\{\vec{k},n\}$ with $\vec{k}\in$ 1BZ for the eigenvalue problem:

$$\sum_{j,\mu,\vec{m}} \tilde{D}^{ij}(\vec{l},\lambda;\vec{m},\mu)\psi^j_{\vec{k}n}(\vec{m},\mu) = d_{\vec{k}n}\psi^i_{\vec{k}n}(\vec{l},\lambda)$$

Using the so-called Born- von Karmann boundary conditions

$$V_{\text{PUC}} \sum_{\vec{R}\,\in\,\text{Bravais}} e^{i\vec{k}\vec{R}} = V\delta_{\vec{k},0} \overset{V\to\infty}{\to} (2\pi)^3\delta(\vec{k})$$

and

$$\sum_{\vec{k}\in 1BZ} e^{i\vec{k}\vec{R}} = N\delta_{\vec{R},0}$$

with number of lattice sites $N = \frac{V}{V_{\text{PUC}}}$ and for $V\to\infty$ points in the 1BZ become dense, so that

$$\int_{1BZ} \frac{d\vec{k}}{(2\pi)^3} e^{i\vec{k}\vec{R}} = \frac{1}{V_{\text{PUC}}}\delta_{\vec{R},0}$$

Reminder $\frac{(2\pi)^3}{V_{\text{PUC}}}$ = volume of 1BZ.
We get for the Fourier transformation (multiplying $V_{\text{PUC}}\sum_{\vec{l}} e^{-i\vec{k}\vec{l}}$ from left) of the eigenvalue problem

$$\sum_{j,\mu,\vec{m}} V_{\text{PUC}} \underbrace{\sum_{\vec{l}} e^{-i\vec{k}\vec{l}}\tilde{D}^{ij}(\vec{l},\lambda;\vec{m},\mu)e^{i\vec{k}\vec{m}}}_{\tilde{D}^{ij}_{\vec{k}}(\lambda,\mu)} \hat{e}^j_{\vec{k}n}(\mu) = d_{\vec{k}n} \underbrace{V_{\text{PUC}}\sum_{\vec{l}} e^{-i\vec{k}(\vec{l}-\vec{l})}}_{V} \hat{e}^i_{\vec{k}n}(\lambda)$$

as $\tilde{D}^{ij}$ only depends on $\vec{l}-\vec{m}$.
With $\sum_{\vec{m}} V_{\text{PUC}} = V$ follows

$$\boxed{\sum_{j,\mu} \tilde{D}^{ij}_{\vec{k}}(\lambda,\mu)\hat{e}^j_{\vec{k}n}(\mu) = d_{\vec{k}n}\hat{e}^i_{\vec{k}n}(\lambda)}$$

This is an eigenvalue problem that determines polarization vectors $\hat{e}_{kn}$, which corresponds to diagonalizing a $3r \times 3r$ matrix with $\lambda, \mu = 1, 2, 3, \ldots, r$ and r are the numbers of atoms/ions per unit cell. The eigenvectors are labeled by the quantum number $n = 1, 2, \ldots, 3r$. The eigenvalue problem has to be solved for each vector $\vec{k}$ of the 1. Brillouin zone → evolution of eigenvalues $d_{\vec{k}n}$ as a function of $\vec{k}$. 5.11.2019

Orthonomally condition:

$$\sum_{\lambda i} \hat{e}^{i*}_{kn}(\lambda) e^{i}_{km}(\lambda) = \delta_{n,m}$$

Completeness relation:

$$\sum_{n} \hat{e}^{i*}_{kn}(\lambda) \hat{e}^{j}_{kn}(\mu) = \delta_{ij}\delta_{\lambda,\mu}$$

The dynamical matrix is real and symmetric:

$$\tilde{D}^{ij}_{nm} = \tilde{D}^{ji}_{mn}$$

Its Fourier transformation is thus hermitian:

$$\tilde{D}^{ij}_{k}(\lambda, \mu) = \left(\tilde{D}^{ji}_{k}(\mu, \lambda)\right)^*$$

and the eigenvalues d_{kn} are *real*. In addition, stability of the crystal requires positive eigenvalues $d_{kn} \geq 0$.

Moreover,

$$\left(\tilde{D}^{ij}_{k}(\lambda, \mu)\right)^* = \tilde{D}^{ij}_{-k}(\lambda, \mu)$$

so that we can choose the quantum numbers in n such that $d_{kn} = d_{-kn}$ and eigenvectors $\hat{e}^*_{-kn} = \hat{e}_{kn}$.

3.2.1 Expansion in normal modes

We expand position and momentum in normal coordinates q_{kn} and p_{kn}:

$$\begin{aligned}
\delta\vec{R}^i(\vec{m}, \mu) &= \frac{1}{\sqrt{N}} \sum_{\vec{k}n} \sqrt{\frac{m}{M_\mu}} e^{i\vec{k}\vec{m}} \hat{e}^{i}_{\vec{k}n}(\mu) q_{\vec{k}n} \\
\vec{P}^i(\vec{m}, \mu) &= \frac{1}{\sqrt{N}} \sum_{\vec{k}n} \sqrt{\frac{M_\mu}{m}} e^{-i\vec{k}\vec{m}} \hat{e}^{i*}_{\vec{k}n}(\mu) p_{\vec{k}n} = -i\nabla_{\{m,\mu\}}
\end{aligned}$$

with N is the number of Bravais lattice sites. And

$$\begin{aligned}
&[q_{kn}, q_{k'n'}] = [p_{kn}, p_{k'n'}] = 0 \\
&[q_{kn}, p_{k'n'}] = i\delta_{kk'}\delta_{nn'}
\end{aligned}$$

This ensures in particular that the commutator is obeyed:

$$\begin{aligned}
[\delta R^i(\vec{m},\mu), P^j(\vec{l},\lambda)] &= \frac{1}{N}\sum_{knk'n'} e^{i\vec{k}\vec{m}-i\vec{k}'\vec{l}}\hat{e}^i_{kn}(\mu)\hat{e}^{j*}_{k'n'}(\lambda)[q_{kn},p_{k'n'}] \\
&= \underbrace{i\,\frac{1}{N}\sum_k e^{ik(m-l)}}_{\delta_{m,l}}\underbrace{\sum_n \hat{e}^i_{kn}(\mu)\hat{e}^{j*}_{kn}(\lambda)}_{=\delta_{\mu,\lambda}\delta_{ij}} \\
&= i\delta_{\vec{m},\vec{l}}\delta_{\mu,\lambda}\delta_{i,j}
\end{aligned}$$

The effective ionic Hamiltonian (diagonalized):

$$H_{\text{eff}} = \sum_{\vec{m},\mu}\frac{m}{M_\mu}\frac{1}{2}\vec{P}^2(\vec{m},\mu) + \sum_{\vec{m},\vec{l},\mu,\lambda}\frac{1}{2}\delta R^i(\vec{l},\lambda)D^{ij}(\vec{l},\lambda;\vec{m},\mu)\delta R^j(\vec{m},\mu)$$

becomes

$$\begin{aligned}
H_{\text{eff}} &= \frac{1}{2}\sum_{\vec{m},\mu}\frac{1}{N}\sum_{knk'n'}\underbrace{e^{-i\vec{k}\vec{m}-i\vec{k}'\vec{m}}}_{N\delta_{\vec{k},-\vec{k}'}}\hat{e}^{i*}_{kn}(\mu)\hat{e}^{i*}_{k'n'}(\mu)p_{kn}p_{k'n'} \\
&\quad + \frac{1}{2}\frac{1}{N}\sum_{knk'n'}\sum_{\vec{m}\vec{l}\mu\lambda} e^{i\vec{k}\vec{l}+i\vec{k}'\vec{m}}\hat{e}^i_{kn}(\lambda)\underbrace{\sqrt{\frac{m^2}{M_\mu M_\lambda}}D^{ij}(\vec{l}\lambda;\vec{m},\mu)}_{\frac{1}{N}\sum_{\vec{q}\in 1BZ} e^{i\vec{q}(\vec{l}-\vec{m})}\tilde{D}^{ij}_q(\lambda,\mu)}\hat{e}^j_{k'n'}(\mu)q_{kn}q_{k'n'}
\end{aligned}$$

after summation over $\vec{m}$ and $\vec{l}$

$$\rightarrow N^2\delta_{\vec{k}+\vec{q},0}\delta_{\vec{k}',\vec{q}}$$

$$H_{\text{eff}} = \frac{1}{2}\sum_{\mu,n,n',\vec{k}}\hat{e}^{i*}_{kn}(\mu)\hat{e}^{i*}_{-kn'}(\mu)p_{kn}p_{-kn'} + \frac{1}{2}\sum_{n,n',\lambda,\mu,\vec{k}}\hat{e}^i_{kn}(\lambda)\underbrace{\tilde{D}^{ij}_{-k}(\lambda,\mu)\hat{e}^j_{-k,n'}(\mu)}_{d_{-kn'}\hat{e}^i_{-kn'}(\lambda)}q_{kn}q_{-kn'}$$

using $\hat{e}^{i*}_{-kn} = \hat{e}^i_{kn}$, and orthonormality

$$\boxed{H_{\text{eff}} = \frac{1}{2}\sum_{\vec{k}\in 1BZ}\left[p_{\vec{k}n}p_{-\vec{k}n} + d_{\vec{k}n}q_{\vec{k}n}q_{-\vec{k}n}\right]}$$

with $n = 1, 2, \ldots 3r$.
We introduce annhilation and creation operators ($d_{kn} \geq 0$):

$$q_{kn} = \frac{1}{\sqrt{2\sqrt{d_{kn}}}}(b^\dagger_{kn} + b_{-kn}), \quad p_{kn} = i\sqrt{\frac{\sqrt{d_{kn}}}{2}}(b^\dagger_{kn} - b_{-kn})$$

exercise

$$[b_{kn}, b^\dagger_{k'n'}] = \delta_{kk'}\delta_{nn'}, \quad [b_{kn}, b_{k'n'}] = [b^\dagger_{kn}, b^\dagger_{k'n'}] = 0.$$

Use $d_{kn} = d_{-kn}$:

$$\begin{aligned} H_{\text{eff}} &= \frac{1}{2}\sum_{kn}\left[(-1)\frac{\sqrt{d_{kn}}}{2}(b^\dagger_{kn} - b_{-kn})(b^\dagger_{-kn} - b_{kn}) + d_{kn}\frac{1}{2\sqrt{d_{kn}}}(b^\dagger_{kn} + b_{-kn})(b^\dagger_{-kn} + b_{kn})\right] \\ &= \frac{1}{2}\sum_{kn}\sqrt{d_{kn}}[b_{-kn}b^\dagger_{-kn} + b^\dagger_{kn}b_{kn}] \end{aligned}$$

with $\omega_{kn} = \omega_{-kn} = \sqrt{d_{kn}}$ and $b_{kn}b^\dagger_{kn} = b^\dagger_{kn}b_{kn} + 1$. It follows a harmonic oscillator Hamiltonian

$$\boxed{H_{\text{eff}} = \sum_{\vec{k}n}\omega_{\vec{k}n}\left(b^\dagger_{\vec{k}n}b_{\vec{k}n} + \frac{1}{2}\right) \quad \text{Phonon Hamiltonian}}$$

Remarks:

- $\omega_{kn} = \omega_n(k)$ define the phonon dispersions with $\vec{k} \in 1BZ$
- there are $n = 1, 2, \dots, 3r$ *bands* where r is the number of atoms/ ions in the unit cell
- three of the $3r$ bands have the property $\omega_n(k) \to 0$ for $\vec{k} \to 0$, these types of phonons can be excited with very long wavelengths $\lambda \sim \frac{2\pi}{|\vec{k}|}$, they are responsible for the propagation of sound in the crystal (e.g. concert pitch A with 440 Hz and sound velocity of gold $v \sim 3200\,\frac{\text{m}}{\text{s}} \to \lambda \sim 7\,\text{m}$; in air $v \sim 340\,\frac{\text{m}}{\text{s}} \to \lambda \sim 0.8\,\text{m}$))

We have *acoustic phonon branches.* Their existence is a consequence of the spontaneous symmetry breaking of continuous translation symmetry by the crystal structure. In general, the breaking of a continuous symmetry implies the presence of low-energetic gapless excitations, so-called Goldstone bosons. The acoustic phonons are the Goldstone bosons of the crystal.
Consider a constant translation of the crystal in any of the three directions in space

$$\delta\vec{R}^i(\vec{l}, \mu) = \delta R^i$$

with $i = x, y, z$. This translation should not cost any energy as a rigid translation does not generate a restoring force of the crystal. Thus, there are 3 acoustic phonon branches.
For small $\vec{k}$:

$$\boxed{\omega_n(\vec{k}) \approx c_n(\hat{k})|\vec{k}|}$$

with the *sound velocities* $c_n(\hat{k})$ that depend on the orientation

$$\hat{k} = \frac{\vec{k}}{|\vec{k}|}$$

. 8.11.19

They are related to the *elastic constants* of the crystal like bulk and shear modules.
Note: a liquid/ gas in contrast only possesses a single longitudinal sound mode, no shear modules!

- other phonon branches are known as *optical phonon branches* because they can often be excited by light
- dispersion relations $\omega_n(\vec{k})$ possesses the full symmetry of the point group
- anharmonic corrections $\varepsilon_0^{(3)}(\{\vec{R}\}) = \frac{1}{3!} A_{nml} \delta R_n \delta R_m \delta R_l$ result in an interaction between phonons $b^\dagger bb$ etc.
  This is necessary to explain e.g. thermal expansion and finite thermal phonon conductivity

3.3 Measuring phonon dispersions: neutron scattering

Phonon dispersion $\omega_n(\vec{k})$ can be measured by neutron scattering.

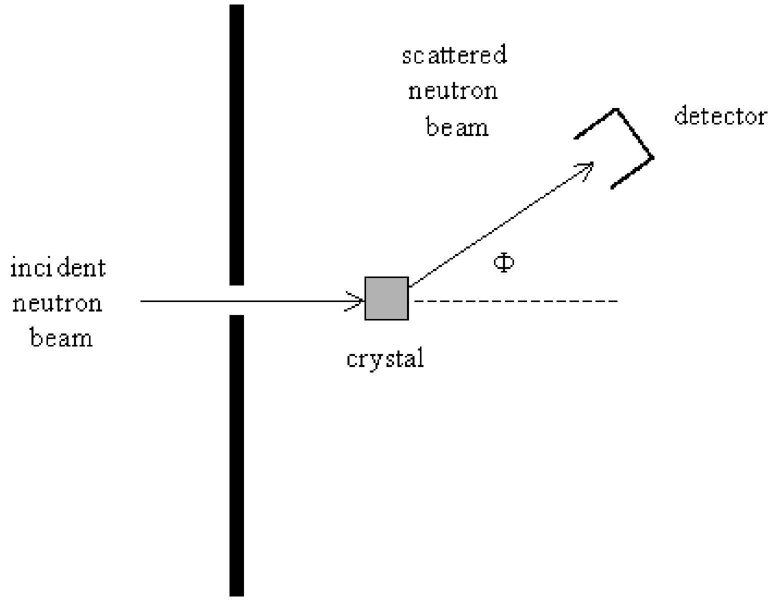

Figure 12: neutron scattering on crystal

Neutrons are neutral particles and interact mainly with the atomic nuclei and thus with phonons (neutrons also interact with magnetic moments that is used for the investigation of magnetism e.g. determination of magnetic order, spin wave dispersions etc.)
Neutron-ion interaction:

$$V(\vec{r}) = \sum_{\vec{l} \in \text{Bravais}} \sum_{\lambda \in \text{Basis}} \nu_\lambda(\vec{r} - \vec{R}(\vec{l}, \lambda))$$

the interaction potential ν_λ is very short ranged, its range being of order of typical nuclear dimensions, $10 \times 10^{-15}\,\mathrm{m} \sim 1\,\mathrm{fm}$. With respect to the typical length scale of crystal lattice constants $\sim 10 \times 10^{-10}\,\mathrm{m} \sim 1\,\mathrm{\mathring{A}}$ the potential can be approximated by delta functions

$$V(\vec{r}) \cong \sum_{\vec{l},\lambda} \nu_\lambda \delta(\vec{r} - \vec{R}(\vec{l},\lambda))$$

The probability per unit time for the neutron to scatter from $\vec{k}_{\mathrm{in}}$ to $\vec{k}_{\mathrm{out}}$ in lowest order perturbation theory is given by Fermi's Golden rule:

$$P_i = \sum_f \frac{2\pi}{\hbar} \left| \left\langle f, \vec{k}_{\mathrm{out}} \middle| V(\hat{\vec{r}}) \middle| i, \vec{k}_{\mathrm{in}} \right\rangle \right|^2 \delta(E_f - E_i + \hbar\omega)$$

where the sum runs over f which are all possible final states of the crystal, $\vec{k}_{\mathrm{out}}$ is the final momentum of the neutron as detected by the detector, $E_{i,f}$ are the initial and final energy of the crystal, $\hbar\omega = \frac{(\hbar\vec{k}_{\mathrm{out}})^2}{2m_n} - \frac{(\hbar\vec{k}_{\mathrm{in}})^2}{2m_n}$ is the energy gained by the neutron in the scattering process and m_n is the mass of the neutron. This formula can be simplified in the following way with usage of plane waves:

$$P_i = \sum_f \frac{2\pi}{\hbar} \left| \frac{1}{V} \int \mathrm{d}\vec{r} e^{-i\vec{k}_{\mathrm{out}}\vec{r}} \langle f | V(\vec{r}) | i \rangle e^{i\vec{k}_{\mathrm{in}}\vec{r}} \right|^2 \delta(E_f - E_i + \hbar\omega)$$

whit volume V and final and initial states of the crystal $\langle f|$ and $|i\rangle$. Now use the transferred wave vector

$$\vec{q} = \vec{k}_{\mathrm{out}} - \vec{k}_{\mathrm{in}}$$

now we have

$$P_i = \sum_f \frac{2\pi}{\hbar} \left| \frac{1}{V} \sum_{\vec{l},\lambda} \nu_\lambda \langle f | e^{-i\vec{q}\vec{R}(\vec{l},\lambda)} | i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega)$$

Usually the crystal is not in a definite eigenstate $|i\rangle$ but rather the states are thermally populated. So, we use the thermally averaged transition rate

$$P = \langle P_i \rangle = \sum_i \frac{1}{Z} e^{-\beta E_i} P_i$$

with partition function

$$Z = \sum_i e^{-\beta E_i}$$

The transition rate P is related to the measured scattering cross section

$$\begin{aligned} \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}\omega} \mathrm{d}\Omega \mathrm{d}\omega &= \frac{P \times \text{number of final states of neutron}}{\text{incoming flux density of neutrons}} = \frac{PV\frac{\mathrm{d}\vec{k}_{\mathrm{out}}}{(2\pi)^3}}{\frac{|\hbar\vec{k}_{\mathrm{in}}|}{m_n}\frac{1}{V}} \\ &= PV^2 \frac{m_n}{\hbar|\vec{k}_{\mathrm{in}}|} \frac{k_{\mathrm{out}}^2 \mathrm{d}k_{\mathrm{out}} \mathrm{d}\Omega}{(2\pi)^3} \end{aligned}$$

with the solid angle Ω

$$\frac{\mathrm{d}\omega}{\mathrm{d}|k_{\text{out}}|} = \frac{\hbar|k_{\text{out}}|}{m_n}$$

It follows

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega} = P\frac{V^2}{(2\pi)^3}\frac{|k_{\text{out}}|}{|k_{\text{in}}|}\frac{m_n^2}{\hbar^2}$$

For a mono-atomic Bravais lattice this simplifies further to

$$\boxed{\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega} = \frac{|k_{\text{out}}|}{|k_{\text{in}}|}\frac{m_n^2\nu_0^2}{(2\pi)^3\hbar^4}NS(\vec{q},\omega)}$$

where N is the number of lattice sites and S is the *dynamic structure factor*

$$S(\vec{q},\omega) = \sum_{f,i}\frac{e^{-\beta E_i}}{Z}\frac{1}{N}\sum_{\vec{l},\vec{m}}\langle i|\, e^{i\vec{q}\vec{R}(\vec{l})}\,|f\rangle\,\langle f|\, e^{-i\vec{q}\vec{R}(\vec{m})}\,|i\rangle\cdot 2\pi\hbar\delta(E_f - E_i + \hbar\omega)$$

where $\vec{l},\vec{m}$ are Bravais lattice vectors. With

$$\int \mathrm{d}te^{i\omega t} = 2\pi\delta(\omega)$$

and

$$e^{-i\frac{Ht}{\hbar}}\,|i\rangle = e^{-i\frac{E_i}{\hbar}t}\,|i\rangle$$

etc where H is the ionic Hamiltonian. This gives

$$\begin{aligned} S(\vec{q},\omega) &= \sum_{f,i}\frac{e^{-\beta E_i}}{Z}\int_{-\infty}^{\infty}\mathrm{d}te^{i\omega t}\frac{1}{N}\sum_{\vec{l}\vec{m}}\langle i|\, e^{i\vec{q}\vec{R}(\vec{l})}\,|f\rangle\,\langle f|\, e^{\frac{iHt}{\hbar}}e^{-i\vec{q}\vec{R}(\vec{m})}e^{-i\frac{Ht}{\hbar}}\,|i\rangle \\ &= \exp(-i\vec{q}\vec{R}(\vec{m},t)) \end{aligned}$$

which is an operator in the Heisenberg picture. Using the completeness relation

$$\sum_f |f\rangle\,\langle f| = \mathbb{1}$$

this gives with Fourier transformation

$$S(\vec{q},\omega) = \int \mathrm{d}te^{i\omega t}S(\vec{q},t)$$

where

$$S(\vec{q},t) = \frac{1}{N}\sum_{\vec{m},\vec{l}}\sum_i\frac{1}{Z}\langle i|\, e^{-\beta H}e^{i\vec{q}\vec{R}(\vec{l},t=0)}e^{-i\vec{q}\vec{R}(\vec{m},t)}\,|i\rangle$$

for a mono-atomic Bravais lattice:

$$\vec{R}(\vec{m},t) = \vec{m} + \delta\vec{R}(\vec{m},t)$$

with the deviation $\delta\vec{R}$ from the equilibrium by the phonons.

$$S(\vec{q},t) = \frac{1}{N}\sum_{\vec{m},\vec{l}} e^{i\vec{q}(\vec{l}-\vec{m})} \left\langle e^{i\vec{q}\delta\vec{R}(\vec{l},0)} e^{-i\vec{q}\delta\vec{R}(\vec{m},t)} \right\rangle$$

which is a thermal average.
If the phonons are treated in the *harmonic approximation* the thermal average simplifies to (without proof):

$$S(\vec{q},t) \cong \frac{1}{N}\sum_{\vec{l},\vec{m}} e^{i\vec{q}(\vec{l}-\vec{m})} \exp\left[-\frac{1}{2}\langle(\vec{q}\delta\vec{R}(\vec{l},0))^2\rangle - \frac{1}{2}\langle(\vec{q}\delta\vec{R}(\vec{m},t))^2\rangle + \langle(\vec{q}\delta\vec{R}(\vec{l},0))(\vec{q}\delta\vec{R}(\vec{m},t))\rangle\right]$$

using that

$$\langle(\vec{q}\delta\vec{R}(\vec{l},0))^2\rangle = \langle(\vec{q}\delta\vec{R}(\vec{m},t))^2\rangle \equiv 2W$$

is independent of lattice site and time and

$$\langle(\vec{q}\delta\vec{R}(\vec{l},0))(\vec{q}\delta\vec{R}(\vec{m},t))\rangle = \langle(\vec{q}\delta\vec{R}(\vec{0},0))(\vec{q}\delta\vec{R}(\vec{m}-\vec{l},t))\rangle$$

due to discrete translation invariance of the Bravais lattice. Now we get

$$\boxed{S(\vec{q},t) = e^{-2W}\sum_{\vec{m}} e^{-i\vec{q}\vec{m}} \exp\left[\langle(\vec{q}\delta\vec{R}(\vec{0},0))(\vec{q}\delta\vec{R}(\vec{m},t))\rangle\right]}$$

with *Debye-Waller factor* e^{-2W} (temperature dependent) and $\vec{m}$ is element of the Bravais lattice. Where 12.11.19

$$W = \langle(\vec{q}\delta\vec{R}(0,0))^2\rangle.$$

The time dependence is determined by the last factor that is treated in perturbation theory using

$$e^x = \sum_{n=0}^{\infty}\frac{x^n}{n!}$$

Zero-phonon contribution $n = 0$

$$S^{(0)}(\vec{q},\omega) = \int_{-\infty}^{\infty} \mathrm{d}t e^{i\omega t} e^{-2W}\sum_{\vec{m}} e^{-i\vec{q}\vec{m}}$$

where the index 0 of S refers to the state $n = 0$. Performing the integral and using the reciprocal lattice and Fourier transformation gives:

$$S^{(0)}(\vec{q},n) = 2\pi\delta(\omega)e^{-2W}\frac{(2\pi)^3}{V_{\text{PUC}}}\sum_{\vec{G}}\delta(\vec{q}-\vec{G})$$

where $\vec{q}$ is not necessarily within the first Brillouin zone. We get delta functions in frequency and momentum space. Thus, the scattering *Bragg peaks* remain sharp. Only the weight of the delta functions is reduced by the Debye-Waller factor.

Single-phonon contribution $n = 1$

needed expectation value

$$\left\langle \delta R^i(0,0)\delta R^j(\vec{m},t)\right\rangle = \left\langle \frac{1}{N}\sum_{\substack{\vec{k},\vec{k}'\\ n,n'}} e^{i\vec{k}'\vec{m}}\hat{e}^i_{kn}\hat{e}^j_{k'n'}q_{kn}(t=0)q_{k'n'}(t)\right\rangle$$

where the sum runs over $\vec{k},\vec{k}'$ in the first Brilluoin zone.

$$\begin{aligned}\langle q_{kn}(0)q_{k'n'}(t)\rangle &= \frac{1}{2}\frac{1}{\sqrt{\omega_{kn}\omega_{k'n'}}}\langle (b^\dagger_{kn}+b_{-kn})(b^\dagger_{k'n'}(t)+b_{-k'n'}(t))\rangle\\ &= \frac{1}{2}\frac{1}{\sqrt{\omega_{kn}\omega_{k'n'}}}\langle b^\dagger_{kn}b_{-k'n'}e^{-i\omega_{k'n'}t}+b_{-kn}v^\dagger_{k'n'}e^{i\omega_{k'n'}t}\rangle\end{aligned}$$

The last term can be written by the commutator relation:

$$b_{-kn}b^\dagger_{k'n'} = b_{k'n'}\dagger b_{-kn}+\delta_{k',-k}\delta_{nn'}$$

This gives

$$\langle q_{kn}(0)q_{k'n'}(t)\rangle = \frac{1}{2}\frac{1}{\omega_{kn}}\delta_{-k,k'}\delta_{n,n'}\left[n_B(\omega_{kn})e^{-i\omega_{kn}t}+(1+n_b(\omega_{kn}))e^{i\omega_{kn}t}\right]$$

with $\omega_{-kn}=\omega_{kn}$, $\hat{e}_{-k,n}=\hat{e}^{i*}_{kn}$. Thus, it follows:

$$\begin{aligned}S^{(1)}(\vec{q},\omega) = e^{-2W}\sum_{\vec{m}}e^{-i\vec{q}\vec{m}}\frac{1}{N}\sum_{\vec{k}n}\frac{m}{M}e^{i\vec{k}\vec{m}}|\vec{q}\hat{e}_{kn}|^2\frac{1}{2\omega_{kn}}\\ \cdot\left[n_B(\omega_{kn})2\pi\delta(\omega-\omega_{kn})+(1+n_B(\omega_{kn}))2\pi\delta(\omega+\omega_{kn})\right]\end{aligned}$$

and finally using

$$\frac{1}{N}\sum_{\vec{m}}e^{-i(\vec{q}+\vec{k})\vec{m}} = \sum_{\vec{G}}\delta_{\vec{q}+\vec{k},\vec{G}}$$

this gives

$$\boxed{S^{(1)}(\vec{q},\omega) = e^{-2W}\frac{m}{M}\sum_n|\vec{q}\hat{e}_{kn}|^2\frac{1}{2\omega_{qn}}\cdot\left[n_B(\omega_{qn})2\pi\delta(\omega-\omega_{qn})+(1+n_B(\omega_{qn}))2\pi\delta(\omega+\omega_{qn})\right]}$$

The factor $n_B(\omega_{qn})$ in the last term refers to absorption of phonons and the factor $1+n_B(\omega_{qn})$ refers to spontaneous and stimulated emission of a phonon.

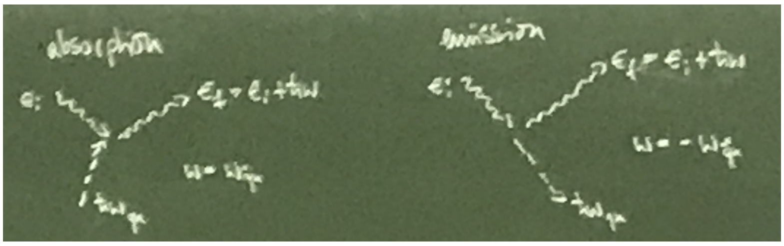

Figure 13: neutron scattering: emission and absorption

The absorption and emission of a phonon during the scattering process results in *additional sharp peaks* at finite energy

$$\hbar\omega = \pm\hbar\omega_{\vec{q}n}$$

this allows for the measurement of the phonon dispersion by *inelastic neutron scattering.*

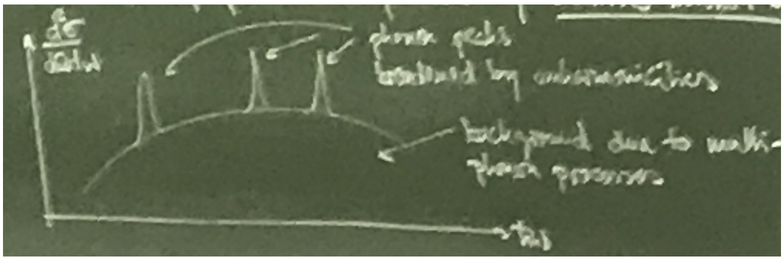

Figure 14: neutron scattering: phonon peaks produced by anharmonicities, background due to multiphonon processes

Remarks:

- neutron scattering is the method of choice for measuring of phonon spectra. X-rays are much less suitable due to linear dispersion of photons which gives difficulty in energy resolution.
- photons in the visible range can be used to probe phonons with a small momentum $\vec{k} \approx 0$ (Γ point)

  Brillouin scattering for acoustic phonons

  Raman scattering for optical phonons
- phonon emission and absorption result in Stokes/ anti-Stokes components of scattered radiation

3.4 Thermodynamics of phonons

(see exercise for more details)
Consider the specific heat $C = \frac{\partial E}{\partial T}$ with energy density E and temperature T.

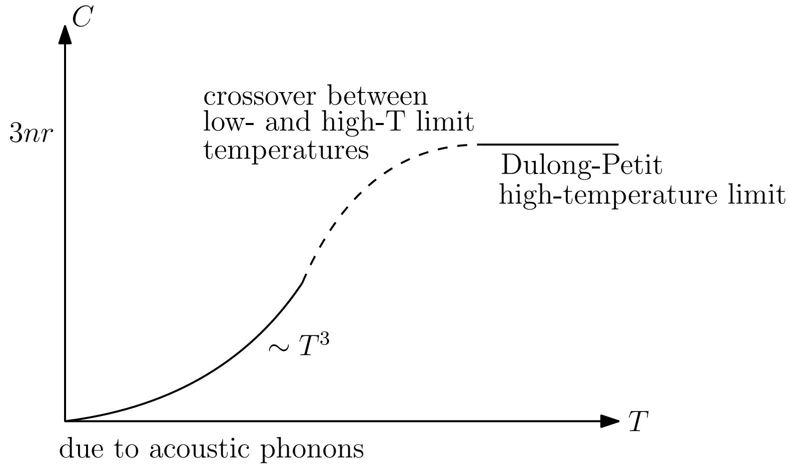

Figure 15: Contribution from phonons

A particular modelling of the crossover is provided by the *Debye-model* where the crossover occurs at the *Debye temperature* θ_D.
Typical values:

$\theta_D \sim 160\,\mathrm{K}$	Au
$\theta_D \sim 350\,\mathrm{K}$	Cu
$\theta_D \sim 470\,\mathrm{K}$	Fe
$\theta_D \sim 1860\,\mathrm{K}$	diamond

4 Non-interacting electrons in a crystal

Consider now an eigenvalue problem for electrons of step I in the adiabatic approximation (chapter 2.1.). Here, we neglect the electron-electron interactions a priori unjustified approximation because Coulomb repulsion energy 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 Electron in a periodic potential

The eigenvalue problem of a single effective particle in the ionic potential is given by

$$H\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

with

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

with spin-orbit coupling effects neglected (non-relativistic limit). The potential possesses the discrete translation symmetry of the Bravais lattice

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

for all $\vec{R} \in$ the Bravais lattice. From Bloch's theorem (chap. 3.1.) follows that the eigenstates $\psi(\vec{r})$ can be chosen as

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

with $\vec{k} \in 1.BZ$ and the *Bloch function* satisfies $u_{nk}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$ for all $\vec{R}$ in the Bravais lattice. 15.11.2019

Explicit proof in the present case:

Fourier expansion:

$$\psi(\vec{r}) = \sum_q e^{i\vec{q}\vec{r}}c_{\vec{q}}$$

so

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

where $\vec{G}$ is the reciprocal lattice vector.
The potential only has Fourier components $U_{\vec{G}}$ due to the discrete translation symmetry $U(\vec{r}) = U(\vec{r}+\vec{R})$ with $e^{i\vec{G}\vec{R}} = 1$.
This leads to

$$\begin{aligned}\left(\frac{-\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\psi(\vec{r}) &= \sum_q e^{i\vec{q}\vec{r}}\frac{\hbar^2\vec{q}^2}{2m}c_{\vec{q}} + \sum_{\vec{q},\vec{G}} e^{i(\vec{q}+\vec{G})\vec{r}}U_{\vec{G}}c_{\vec{q}}\\ &= \sum_q e^{i\vec{q}\vec{r}}\frac{\hbar^2\vec{q}^2}{2m}c_{\vec{q}} + \sum_{\vec{q}',\vec{G}} e^{i\vec{q}\vec{r}}U_{\vec{G}}c_{\vec{q}-\vec{G}}\\ &\overset{!}{=} \varepsilon\sum_{\vec{q}} e^{i\vec{q}\vec{r}}c_{\vec{q}}\end{aligned}$$

In the second last step, the index shift $\vec{q} \to \vec{q}-\vec{G}$ has been applied. Now, from this equation follows the Schrödinger equation in the Fourier space:

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

with $\vec{q} = \vec{k} + \vec{K}$ with $\vec{k} \in$ 1BZ and reciprocal lattice vector $\vec{K}$ follows

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

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

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

with the Bloch function

$$u_{n,\vec{k}}(\vec{r}) = \sum_{\vec{K}\in 1\mathrm{BZ}} e^{i\vec{K}\vec{r}} c_{n,\vec{k}+\vec{K}}, \qquad u_{n,\vec{k}}(\vec{R}+\vec{r}) = u_{n,\vec{k}}(\vec{r})$$

Consequences:

- $\psi_{n,\vec{k}}(\vec{r})$ is not an eigenfunction of the momentum operator $\vec{p}$ as

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

  thus $\hbar\vec{k}$ is not a momentum but the *crystal momentum* or quasi momentum. It is only 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

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

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

Due to the periodicity of the Bloch function $u_{n\vec{k}}$ and the potential $U(\vec{r})$ we can restrict ourselves solving this equation only within a single primitive unit cell. Such an eigenvalue problem in a fixed volume V_{PUC} will give rise to *discretely spaced energy levels* that will be labeled with *band index n*. The functions $u_{n\vec{k}}(\vec{r})$ will form a basis for each $\vec{k}$ for continuous square-integrable functions defined in the primitive cells of volume V_{PUC}.
Completeness

$$\sum_n u^*_{n\vec{k}}(\vec{r}) u_{n\vec{k}}(\vec{r}') = V_{\mathrm{PUC}}\delta(\vec{r}-\vec{r}')$$

and orthogonality

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

Such a basis contains infinitely many functions $u_{n\vec{k}}(\vec{r})$. Thus, there are *infinitely many energy bands* $n = 0, 1, 2, ...$ (In contrast 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.

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

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

4.2 Electron in a weak, periodic potential

Assume that the Fourier components $U_{\vec{G}}$ with $|\vec{G}| \neq 0$ are small. This is useful for a qualitative understanding. The zero component $U_{\vec{G}=0}$ can be absorbed in the choice of the zero point 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 $\vec{k}' = \vec{K} - \vec{G}$:

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

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

eigenenergies:

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

eigenfunctions:

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

for example: energy bands in one dimension ($\vec{R}_n = na, \vec{K}_m = \frac{2\pi}{a}m$)

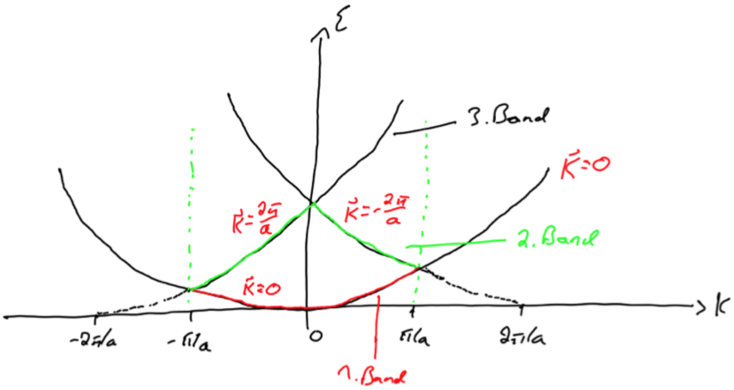

Figure 16: energy bands in one dimension

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

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

For most of the values of $\vec{k} \in$ 1BZ 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 bands are degenerate. We then need to apply the method of *degenerate perturbation theory*.
For such a degeneracy point $\vec{k}_d$ in the 1BZ we can restrict ourselves in lowest order to the 19.11.19
subspace of the Hilbert space spanned by the eigenfunctions with degenerate eigenvalues at zero order in $U_{\vec{G}}$:
For a *n-degenerate point*

$$\varepsilon^{(0)}(\vec{k}_d+\vec{K}_1)=\varepsilon^{(0)}(\vec{k}_d+\vec{K}_2)=\varepsilon^{(0)}(\vec{k}_d+\vec{K}_3)=\ldots=\varepsilon^{(0)}(\vec{k}_d+\vec{K}_n)$$

reduce the Schrödinger equation with $\vec{k}\approx\vec{k}_d$:

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

with a restricted sum over $j=1,2,\ldots,n$ and $i=1,2,\ldots,n$. This corresponds to a $n\times n$ *matrix equation* for n-degenerate eigenstates!
Where do degeneracies occur?

$$\varepsilon^{(0)}(\vec{k}+\vec{K}_1)=\varepsilon^{(0)}(\vec{k}+\vec{K}_2)\ \Leftrightarrow |\vec{k}+\vec{K}_1|=|\vec{k}+\vec{K}_2|$$

The energies are equal, therefore, no energy is transmitted: we have elastic scattering. Furthermore, the difference

$$(\vec{k}+\vec{K}_1)-(\vec{k}+\vec{K}_2)=\vec{K}_1-\vec{K}_2\in\ \text{reciprocal lattice vector}$$

is again a reciprocal lattice vector. The two vectors $\vec{k}+\vec{K}_1$ and $\vec{k}+\vec{K}_2$ must fulfill the Bragg or von-Laue condition for constructive interference.
For example: on all boundaries of the 1BZ

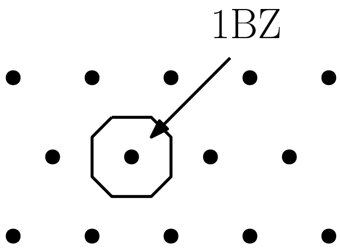

Figure 17: 1BZ

Most importantly is the case with only two degenerate levels (2 × 2 matrix equation):

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

eigenvalues with $U_{-\vec{k}} = U^*_{\vec{k}}$:

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

The interaction $U_{\vec{K}_1-\vec{K}_2}$ leads to a *level repulsion* $|U_{\vec{K}_1-\vec{K}_2}|^2$. At the degeneracy point $\vec{k}=\vec{k}_d$:

$$\varepsilon^{(0)}(\vec{k}_d+\vec{K}_1) = \varepsilon^{(0)}(\vec{k}_d+\vec{K}_2)$$

and

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

splitting of the bands *linear* in $|U_{\vec{K}_1-\vec{K}_2}|$ due to *Bragg reflection.*

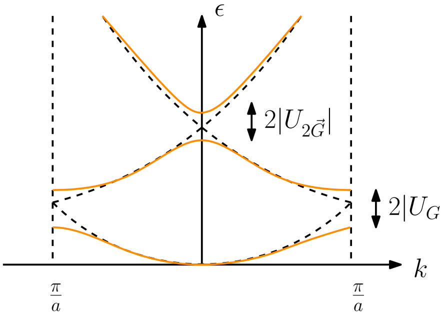

Figure 18: Reduced zone scheme (1D): opening of band gaps in 1BZ

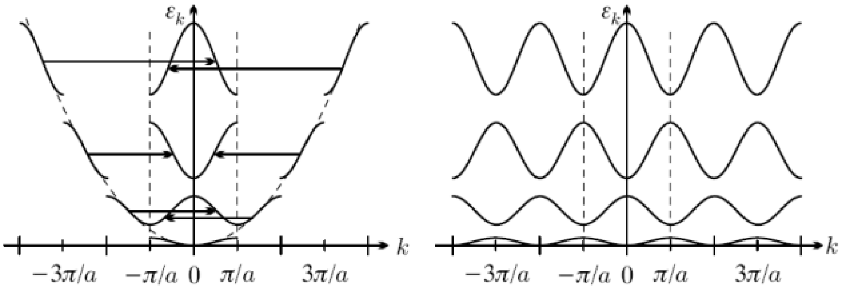

Figure 19: extended (and reduced) and repeated zone scheme

Energy band gap

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

4.3 Fermi surfaces

The ground state of non-interacting electrons in a periodic potential (in zero magnetic field) can be described in the following way:
all states with $\vec{k} \in 1BZ$ and band index n with $\varepsilon_{n\vec{k}} \leq \varepsilon_F$ are occupied once with a spin-up and a spin-down configuration, where ε_F is the Fermi energy. The Fermi energy is determined by the total number of electrons N_e:

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

How many electrons can occupy a single band?
with

$$\sum_{\vec{k}\in 1\text{BZ}} \overset{V\to\infty}{\to} V\int_{1\text{BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3} = N$$

the number of Bravais lattice sites N follows that each band can be occupied by $2N$ electrons (N with spin up and N with spin down).
One distinguishes two important cases:

1. All bands are either completely filled or completely empty

   The Fermi energy is then located within a bandgap. The density of (non-interacting) electrons corresponds then to an *even number of electrons per unit cell* as

$$N_e = 2\sum_{n} V\int_{1\text{BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3} = 2n_{\text{bands}}N$$

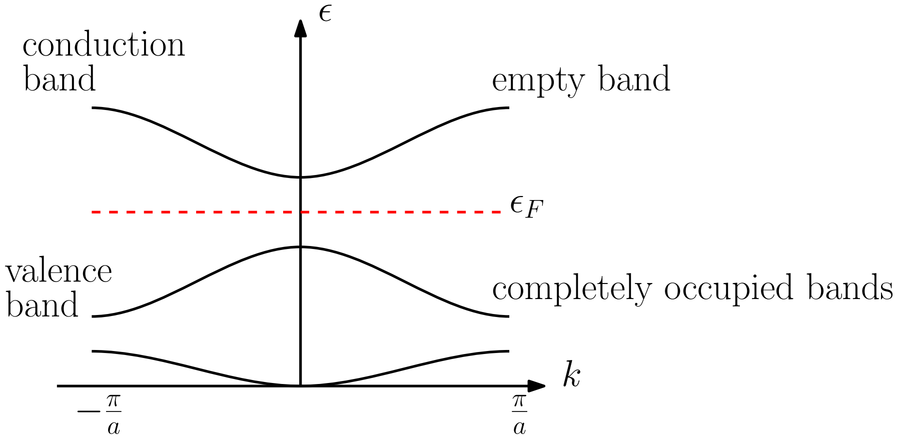

Figure 20: all bands are either completely filled or empty

where the factor 2 is from the different spins, n_{bands} is the number of occupied bands and N the number of unit cells. So, if the number of electrons per unit cell is known, this gives information about the occupation of bands.
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 whose magnitude is in the range of 1 eV to 7 eV. Such materials are *semiconductors* or *insulators*. In the case of semiconductors the room temperatures is in general large enough to excite electrons into the conduction band.

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

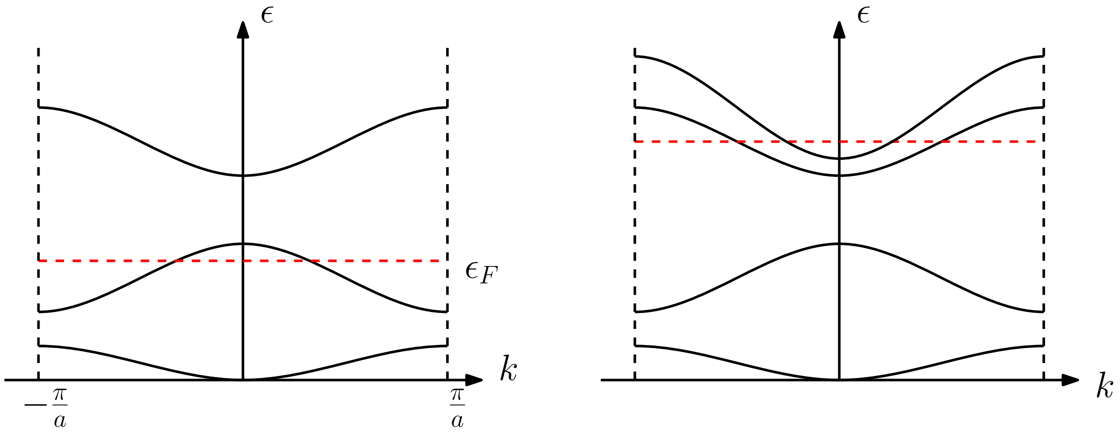

Figure 21: left: single band crosses the Fermi energy, right: two bands cross the Fermi energy

The partially filled bands are here the *conduction bands*. Around the Fermi energy

electrons can be excited with very low energies: metals:
The condition $\varepsilon_{n\vec{k}} \hat{=} \varepsilon_F$ defines one or several $D-1$ dimensional manifolds within the first Brillouin zone that are the *Fermi surface(s)*, respectively.

Example: two dimensional Fermi surface of single energy band with

$$\varepsilon_k = -2t(\cos k_x a + \cos k_y a) \overset{!}{=} \varepsilon_F$$

Remarks:

- typical values for Fermi energies: $\varepsilon_F \sim$ 1- 10 eV, $T_F \sim 10^4$- 10^5 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 (Luttinger's theorem). Interactions, however, can change the shape and the topology of the Fermi surface.

22.11.19

4.4 Density of states and van-Hove-singularities

The density of electron states at a given energy ε is defined by

$$\boxed{\nu(\varepsilon) = 2\frac{1}{V}\sum_{n,\vec{k}\in 1\mathrm{BZ}} \delta(\varepsilon - \varepsilon_{n\vec{k}})}$$

where the factor 2 is due to the spin configuration. Sometimes also the density of states per spin is considered. Introducing the density of states of a band

$$\nu(\varepsilon) = \sum_n \nu_n(\varepsilon)$$

for $V \to \infty$ we get

$$\nu_n(\varepsilon) = 2\int_{1\mathrm{BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\delta(\varepsilon - \varepsilon_{nk})$$

with

$$\int_{-\infty}^{\infty} \mathrm{d}\varepsilon \nu_n(\varepsilon) = 2\int_{1\mathrm{BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3} 1 = 2\frac{N}{V} = 2\frac{1}{V_{\mathrm{PUC}}}$$

This is two times the density of the primitive unit cell. If the energy ε is located within the n-th band, with $\min(\varepsilon_{nk}) \le \varepsilon \le \max(\varepsilon_{nk})$, the density of states $\nu(\varepsilon)$ is finite and given by

$$\nu_n(\varepsilon) = \frac{2}{(2\pi)^3}\int_{\varepsilon_{nk}=\varepsilon} \mathrm{d}S \int \frac{\mathrm{d}\varepsilon_{nk}}{|\nabla_k \varepsilon_{nk}|}\delta(\varepsilon - \varepsilon_{nk}) = \frac{2}{(2\pi)^3}\int_{\varepsilon=\varepsilon_{nk}} \mathrm{d}S \frac{1}{|\nabla_k \varepsilon_{nk}|}$$

Here, we integrated over the surface in k-space of constant energy and performed a change of variables by substituting $\vec{k}$ with ε_{nk}.

The density of states is determined by the integral over constant energy surfaces weighted by the inverse of the *group velocity*

$$v_{nk} = \frac{1}{\hbar} \nabla_k \varepsilon_{nk}$$

of the n-th band.
Compare with the density of states of free electrons

$$\varepsilon_k = \frac{\hbar^2 \vec{k}^2}{2m}, \quad \vec{v}_k = \frac{\hbar \vec{k}}{m}$$

that is given by

$$\nu(\varepsilon) = \frac{2}{(2\pi)^3} \underbrace{\int_{\varepsilon=\varepsilon_k} \mathrm{d}S}_{4\pi k^2} \int_0^\infty \frac{\mathrm{d}\varepsilon}{|\hbar^2 \frac{\vec{k}}{m}|} \delta(\varepsilon - \varepsilon_k) = \frac{1}{\pi^2} \frac{km}{\hbar^2} = \frac{1}{\pi^2} \frac{m}{\hbar^3} \sqrt{2m\varepsilon}$$

Whenever the group velocity vanishes on the surface of constant energy the density of states exhibits a *van-Hove singularity.* In order to determine the nature of the singularity one expands around the singularity point $\vec{k}_0$ within the 1BZ.

$$\varepsilon_{n\vec{k}} = \varepsilon_{n\vec{k}} + \frac{1}{2} \frac{\partial^2 \varepsilon_{nk}}{\partial \vec{k}_i \partial \vec{k}_j} \bigg|_{k_0} (\vec{k} - \vec{k}_0)_i (\vec{k} - \vec{k}_0)_j$$

The matrix $\frac{\partial^2 \varepsilon_{nk}}{\partial \vec{k}_i \partial \vec{k}_j}$ describes the curvature of the spectrum and has 3 eigenvalues $\lambda_1, \ \lambda_2, \ \lambda_3$.
The spectrum at $\vec{k}_0$ has

1. a minimum if $\lambda_i > 0, \ \forall \ i = 1, 2, 3$
2. a maximum if $\lambda_i < 0, \ \forall \ i = 1, 2, 3$
3. a saddle point else

Close to the van-Hove singularities in d spatial dimensions with the change of variables $\vec{k} = \vec{k}_0 + \sqrt{\varepsilon - \varepsilon_{n\vec{k}_0}} \vec{x}$ one obtains

$$\nu_n(\varepsilon) = 2 \int \frac{\mathrm{d}^d \vec{x}}{(2\pi)^d} (\varepsilon - \varepsilon_{n\vec{k}_0})^{\frac{d}{2}} \delta \left((\varepsilon - \varepsilon_{n\vec{k}_0}) \left(1 + \frac{\partial^2 \varepsilon_{nk}}{\partial \vec{k}_i \partial \vec{k}_j} \bigg|_{k_0} x_i x_j \right) \right)$$

Thus we obtain the relation $\boxed{\nu(\varepsilon) \propto (\varepsilon - \varepsilon_{n\vec{k}_0})^{\frac{d}{2}-1}}$

In the following, we will look at the 3 lowest cases:

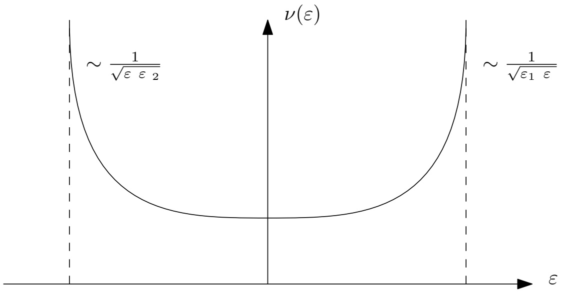

Figure 22: $d = 1$: $\frac{1}{\sqrt{\omega}}$ divergence at the band edges

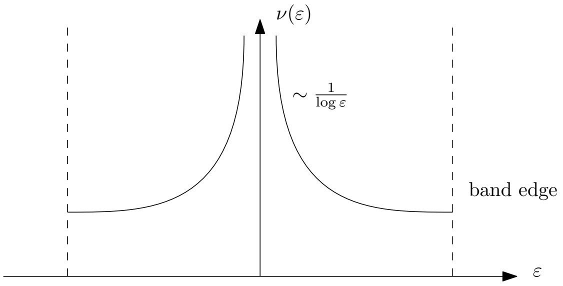

Figure 23: $d = 2$: jump at band edges and logarithmic singularity at saddle points

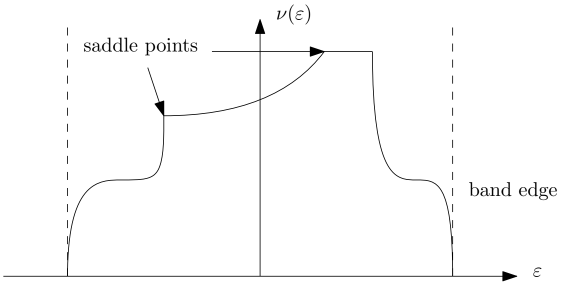

Figure 24: $d = 3$: $\sqrt{\varepsilon}$- singularities

As ε_{nk} is a periodic function in $\vec{k}$ a maximum, a minimum and in $d > 1$ one or more saddle points have to exist.

Modern interpretation

Van-Hove singularities are *topological quantum phase transitions.* The topology of the Fermi surface changes as a function of the chemical potential μ at $T = 0$.

- at the minimum: new Fermi surface energies
- at the maximum: Fermi surface vanishes

- at saddle points: Fermi surfaces merge

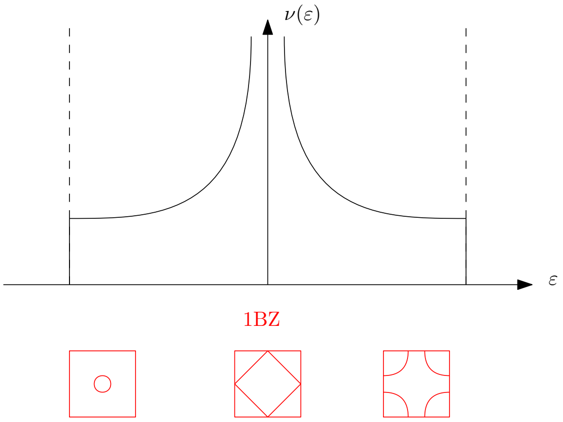

Figure 25: Fermi surface at different positions in $d = 2$

4.5 Thermodynamics of non-interacting electrons

Grand canonical partition function of non-interacting electrons:

$$Z = \mathrm{tr}(e^{-\beta\mathcal{H}}) = \prod_{n,\sigma,k\in 1\mathrm{BZ}} (1 + e^{-\beta(\varepsilon_{nk}-\mu)})$$

with $\mathcal{H} = H - \mu N$, $\beta = \frac{1}{k_B T}$ and the chemical potential μ.
The free energy is given by

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

The free energy density $f(T,\mu) = \frac{F}{V}$ reads with help of the density of states

$$f(T,\mu) = -k_B T \int_{-\infty}^{\infty} \mathrm{d}\varepsilon \nu(\varepsilon) \ln(1 + e^{-\beta(\varepsilon-\mu)})$$

The density of electrons $n = -\frac{\partial f}{\partial \mu}$ follows

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

with the *Fermi-function*

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

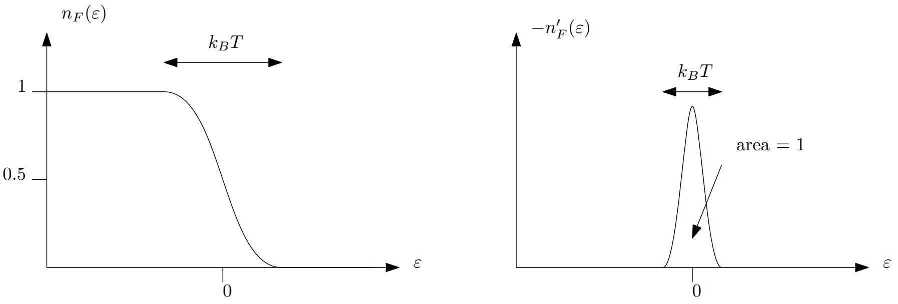

Figure 26: Fermi function (step function broadened by k_BT and its derivative (broadened delta function).

The derivative of the Fermi function is normalized

$$\int_{-\infty}^{\infty} \mathrm{d}\varepsilon(-n'_F(\varepsilon)) = -n_F(\varepsilon)\,|_{-\infty}^{\infty} = 1$$

At zero temperature $T = 0$:

$$n(0,\mu) = \int_{-\infty}^{\mu} \mathrm{d}\varepsilon\nu(\varepsilon)$$

the chemical potential coincides with the Fermi energy:

$$\mu(T=0) = \varepsilon_F$$

26.11.19

Sommerfeld expansion

In order to evaluate finite temperature corrections one uses the Sommerfeld expansion. Consider some smooth function $a(\varepsilon)$ with $a(\varepsilon) \to 0$ for $|\varepsilon| \to \infty$:

$$\int_{-\infty}^{\infty} \mathrm{d}\varepsilon a(\varepsilon) n_F(\varepsilon-\mu) = \int_{-\infty}^{\infty} \mathrm{d}\varepsilon A(\varepsilon)(-n'_F(\varepsilon-\mu))$$

where integration by parts has been used, and with

$$A(\varepsilon) = \int_{-\infty}^{\varepsilon} \mathrm{d}\varepsilon' a(\varepsilon').$$

As $-n'_F(\varepsilon-\mu)$ is only finite within a small interval of width k_BT around $\varepsilon-\mu \approx 0$ we can expand the function $A(\varepsilon)$ in a Taylor series:

$$A(\varepsilon) = A(\mu) + \sum_{n=1}^{\infty} \frac{1}{n!} \left.\frac{\mathrm{d}^n A(\varepsilon)}{\mathrm{d}\varepsilon^n}\right|_{\varepsilon=\mu} (\varepsilon-\mu)^n$$

One obtains for the integral the Sommerfeld expansion

$$\int_{-\infty}^{\infty} \mathrm{d}\varepsilon a(\varepsilon) n_F(\varepsilon-\mu) = \underbrace{\int_{-\infty}^{\mu} \mathrm{d}\varepsilon a(\varepsilon)}_{A(\mu)} + \sum_{n=1}^{\infty} \left.\frac{\mathrm{d}^{n-1} a(\varepsilon)}{\mathrm{d}\varepsilon^{n-1}}\right|_{\varepsilon-\mu} \int_{-\infty}^{\infty} \frac{(\varepsilon-\mu)^n}{n!}(-n_F'(\varepsilon-\mu))$$

The last integral can be evaluated and yields:

$$\int_{-\infty}^{\infty} \mathrm{d}\varepsilon \frac{(\varepsilon-\mu)^n}{n!}(-n_F'(\varepsilon-\mu)) = \begin{cases} (k_B T)^n C_{n/2} & \text{if } n \text{ is even} \\ 0 & \text{else} \end{cases}$$

due to symmetry as $(-n_F'(\varepsilon-\mu)$ is an even function. The coefficient C_n is given by

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

in particular:

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

One finally obtains:

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

The *specific heat* per volume (at constant volume) can thus be expressed by

$$C_V = -T\frac{\partial^2 f}{\partial T^2} = T\int_{-\infty}^{\infty} \mathrm{d}\varepsilon \nu(\varepsilon)\left(\frac{\varepsilon-\mu}{T}\right)^2 (-n_F'(\varepsilon-\mu))$$

with

$$\nu(\varepsilon) \cong \nu(\mu) + \nu'(\mu)(\varepsilon-\mu) + \ldots$$

away from fan-Hove singularities.

$$C_V \cong T\nu(\mu) 2\frac{\pi^2}{6}k_B^2$$

For $T \to 0$ the electronic specific heat vanishes linearly with temperature

$$\boxed{C_V = \gamma T}$$

with the so-called *Sommerfeld coefficient*

$$\boxed{\gamma = \frac{\pi^2}{3}k_B^2 \nu(\varepsilon_F)}$$

The total specific heat at low temperatures $T \ll T_F,\ \theta_D$ in a metal has the form

$$C_V = \gamma T + AT^3$$

where the first term corresponds to electrons and the second to phonons. This formula is often plotted as $\frac{C_V}{T}$ vs. T^2 which gives a linear function

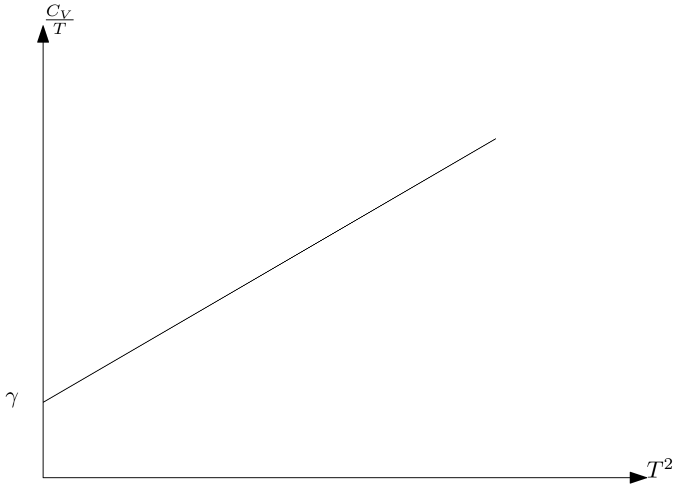

Figure 27: specific heat in Sommerfeld expansion

4.6 Almost localized electrons: tight-binding method

Consider the opposite limit: a strong periodic potential $U(\vec{r})$

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

where the sum runs over the atomic potentials assuming a mono-atomic Bravais lattice.

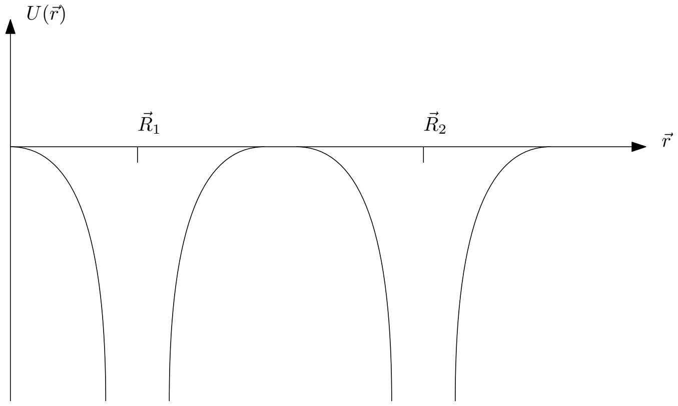

Figure 28: mono-atomic Bravais lattice potential

Each atomic potential V decays rapidly with the distance to the ions positions, thus ΔU is small in between.
Consider now, a Hamiltonian for a single electron:

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

with

$$H_{\text{atom},\vec{R}} = \frac{\vec{p}^2}{2m} + V(\vec{r} - \vec{R})$$

and

$$\Delta U(\vec{r}) = \sum_{\vec{R}' \neq \vec{R}} V(\vec{r} - \vec{R}')$$

Starting point: electrons located in atomic orbitals, i.e. eigenstates of $H_{\text{atom},\vec{R}}$; assume that the atomic eigenvalue problem is solved:

$$H_{\text{atom},\vec{R}} \phi_n(\vec{r} - \vec{R}) = \varepsilon_n \phi_n(\vec{r} - \vec{R})$$

where n represents the full set of atomic quantum numbers. With the help of ϕ_n we can construct an Ansatz for a wave function that obeys Bloch's theorem

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}'} e^{i\vec{k}\vec{R}'} \sum_n a_n \phi_n(\vec{r} - \vec{R}')$$

This Ansatz is a linear combination of atomic orbitals (LCAO) with coefficients a_n. Now, we can test whether this wave function indeed obeys Bloch's theorem

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

Full stationary Schrödinger equation

$$H\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\psi_{\vec{k}}(\vec{r})$$

projection onto eigenstates of $H_{\text{atom},\vec{R}}$ using

$$\int \mathrm{d}\vec{r} \phi_n^*(\vec{r}) \phi_{n'}(\vec{r}) = \delta_{n,n'}$$

Investigate the two terms of the Hamiltonian separately:

1.

$$\begin{aligned}\int \mathrm{d}\vec{r} \phi_m^*(\vec{r} - \vec{R}) H_{\text{atom},\vec{R}} \psi_{\vec{k}}(\vec{r}) &= \varepsilon_m \int \mathrm{d}\vec{r} \phi_m^*(\vec{r} - \vec{R}) \psi_{\vec{k}}(\vec{r}) \\ &= \varepsilon_m \left(a_m e^{i\vec{k}\vec{R}} + \sum_n a_n \underbrace{\sum_{\vec{R}' \neq \vec{R}} e^{i\vec{k}\vec{R}'} \int \mathrm{d}\vec{r} \phi_m^*(\vec{r} - \vec{R}) \phi_n(\vec{r} - \vec{R}')}_{A_{mn}} \right)\end{aligned}$$

A_{mn} is the so-called overlap integral which decays rapidly as function of the distance. It is only relevant for nearest neighbors as the atomic orbitals are strongly confined.

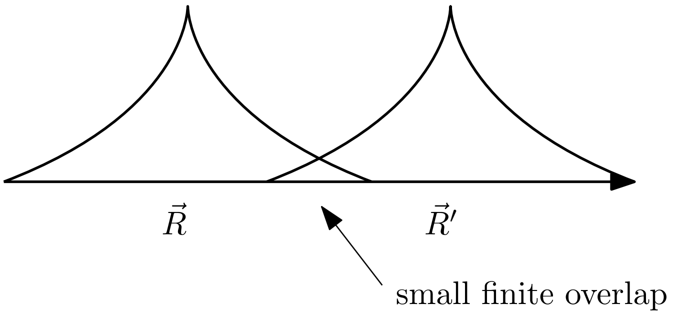

Figure 29: small finite overlap between two wave functions

2.

$$\int \mathrm{d}\vec{r}\phi_m^*(\vec{r}-\vec{R})\Delta U(\vec{r})\psi_{\vec{k}}(\vec{r}) = \sum_n a_n \underbrace{\sum_{\vec{R}'} e^{i\vec{k}\vec{R}'} \int \mathrm{d}\vec{r}\phi_m^*(\vec{r}-\vec{R})\Delta U(\vec{r})\phi_n(\vec{r}-\vec{R}')}_{B_{mn}}$$

The coefficient B_{mn} is small because either ΔU is small or the product $\phi^*\phi$ is small

The Schrödinger equation setting $\vec{R}=0$ becomes without loss of generality:

$$(E(\vec{k})-\varepsilon_m)(a_m+\sum_n a_n A_{mn}) = \sum_n a_n B_{mn}$$

this can be written as a matrix equation:

$$((E(\vec{k})-\varepsilon_m)(\delta_{mn}+A_{mn})-B_{mn})a_n = 0$$

with small coefficients A and B.
In practice, this equation is solved by considering only a restricted number of orbitals, $n, m = 1, 2, 3, \ldots, N$ so that only a $N \times N$ matrix equation is to be solved.

Application: single s-orbital

Consider a single non-degenerate orbital (s-wave). This gives a 1×1 equation:

$$(E(\vec{k})-\varepsilon)(1+A)-B = 0$$

The dispersion of the arising s-band

$$E(\vec{k}) = \varepsilon + \frac{B}{1+A}$$

with

$$A = \sum_{\vec{R}'\neq 0} e^{i\vec{k}\vec{R}'} \int \mathrm{d}\vec{r}\phi^*(\vec{r})\phi(\vec{r}-\vec{R}')$$

and

$$B = \sum_{\vec{R}'} e^{i\vec{k}\vec{R}'} \int \mathrm{d}\vec{r}\phi^*(\vec{r})\Delta U(\vec{r})\phi(\vec{r}-\vec{R}')$$

this sum rapidly decays with increasing distance $\vec{R}'$. Thus, the sums can be restricted to keeping only contributions up to nearest neighbors $\vec{R}_n$:

$$B \cong \underbrace{\int \mathrm{d}\vec{r}\phi^*(\vec{r})\Delta U(\vec{r})\phi(\vec{r})}_{-\beta} + \sum_{\mathrm{nn}\ \vec{R}_n} e^{i\vec{k}\vec{R}_n} \underbrace{\int \mathrm{d}\vec{r}\phi^*(\vec{r})\Delta U(\vec{r})\phi(\vec{r}-\vec{R}_n)}_{-\gamma(\vec{R}_n)}$$

and

$$A \cong \sum_{\mathrm{nn}\ \vec{R}_n} e^{i\vec{k}\vec{R}_n} \underbrace{\int \mathrm{d}\vec{r}\phi^*(\vec{r})\phi(\vec{r}-\vec{R}_n)}_{\alpha(\vec{R}_n)}$$

For an s-orbital wave function α can be chosen to be real: $\alpha(\vec{R}_n) = \alpha(-\vec{R}_n)$ (substitution 29.11.19 $\vec{r} \to \vec{r} + \vec{R}_n$). From the inversion symmetry of the Bravais lattice follows $\gamma(\vec{R}_n) = \gamma(-\vec{R}_n)$. The dispersion of the s-band then becomes:

$$\boxed{E(k) = \varepsilon - \frac{\beta + \sum_{nn}\gamma(R_n)\cos\vec{k}\vec{R}_n}{1+\sum_{nn}\alpha(R_n)\cos\vec{k}\vec{R}_n}} \approx \varepsilon - \beta - \sum_{nn}\gamma(\vec{R}_n)\cos\vec{k}\vec{R}_n$$

For example: simple cubic Bravais lattice:

$$\vec{R}_1 = a(\pm 1, 0, 0), \quad \vec{R}_2 = a(0, \pm 2, 0), \quad \vec{R}_3 = a(0, 0, \pm 1)$$

with

$$\gamma(R_n) \equiv \gamma$$

Remarks:

- Tight binding bands are narrow bands. The *bandwith* ie. $\max(E(k)) - \min(E(k))$ is determined by the small overlap integral γ.

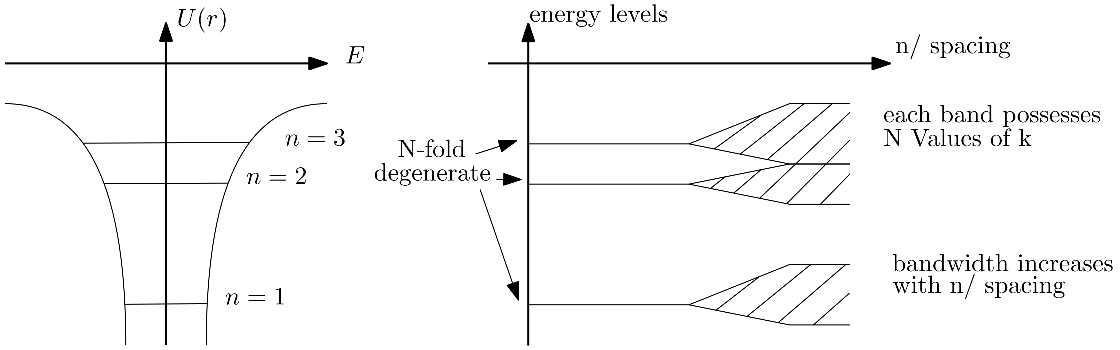

Figure 30: Left: spectrum of non-degenerate s-levels in an atomic potential. Right: Energy levels of N such atoms forming a lattice as a function of inverse interatomic spacing.

Small 1/ spacing: tight binding limit
large 1/ spacing: limit of weak periodic potential

- interpretation of overlap integral γ: hopping amplitude of electrons from atom to atom (often denoted as t).

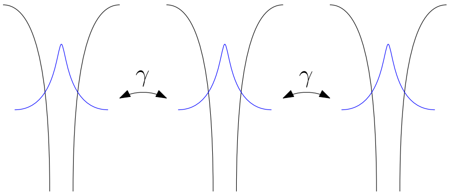

Figure 31: Overlap integral γ

- for solids with more atoms per unit cell: generalize the Ansatz to a linear combination of atomic orbitals centered at Bravais lattice point *and* basis points
- spin orbit coupling will be important for d- and f- electrons. Those can be included in the tight-binding method
- For an electron band deriving from well-localized atomic orbitals with small overlap integral the interaction between electrons is strong. Thus, this has to be included on top of the tight-binding method. This leads to the *Hubbard model.*

4.6.1 Wannier functions

The wave function can always be written in the form

$$\psi_{n\vec{k}}(\vec{r}) = V_{\text{PUC}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} w_n(\vec{r}-\vec{R})$$

that is used in the tight binding method where an Ansatz for $w_n(\vec{r}-\vec{R})$ is made in terms of a LCAO. The function w_n is the *Wannier function* and given by the inverse Fourier transform:

$$\boxed{w_n(\vec{r}-\vec{R}) = \int_{\text{1BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3} e^{-i\vec{k}\vec{R}} \psi_{n\vec{k}}(\vec{r})} = \int_{\text{1BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3} e^{i\vec{k}(\vec{r}-\vec{R})} u_{n\vec{k}}(\vec{r})$$

where

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

Wannier functions are *orthogonal*:

$$\begin{aligned}\int \mathrm{d}\vec{r} w_n^*(\vec{r}-\vec{R}) w_{n'}(\vec{r}-\vec{R}) &= \int_{\text{1BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3} \int_{\text{1BZ}} \frac{\mathrm{d}\vec{k}'}{(2\pi)^3} e^{i\vec{k}\vec{R}-i\vec{k}'\vec{R}'} \underbrace{\int \mathrm{d}\vec{r} \psi^*_{n\vec{k}}(\vec{r}) \psi_{n'\vec{k}'}(\vec{r})}_{\delta_{nn'}(2\pi)^3\delta(\vec{k}-\vec{k}')} \\ &= \delta_{nn'} \int_{\text{1BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3} e^{i\vec{k}(\vec{R}-\vec{R}')} = \delta_{nn'} \frac{1}{V_{\text{PUC}}} \delta_{\vec{R}\vec{R}'}\end{aligned}$$

and form a *complete basis.*

The choice of a complete set of Wannier functions is *not unique.* The Bloch function

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

is only defined up to a $\vec{k}$ dependent phase.

$$u_{n\vec{k}}(\vec{r}) \to e^{i\varphi(\vec{k})} u_{n\vec{k}}(\vec{r})$$

giving rise to a U(1) gauge freedom with $\varphi(\vec{k}+\vec{G}) = \varphi(\vec{k})$. (Additional freedom arises at positions within the 1BZ where different bands cross.) This freedom can be exploited to ensure that the $\vec{k}$-dependency of $u_{n\vec{k}}(\vec{r})$ is as smooth as possible so that the Wannier functions are *maximally localized.*

$$w_n(\vec{r}-\vec{R}) = \int_{\text{1BZ}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3} e^{i\vec{k}(\vec{r}-\vec{R})} u_{n\vec{k}}(\vec{r}) \to \frac{1}{V_{\text{PUC}}} \delta_{\vec{r}-\vec{R},0} u_n(\vec{R})$$

for a $\vec{k}$-independent $u_{n\vec{k}}(\vec{r}) = u_n(\vec{r})$, so the Wannier functions would be perfectly localized.

Exceptions: *Topological insulators* for which a smooth choice of $u_{n\vec{k}}(\vec{r})$ is not possible.

5 Electronic transport in solids

5.1 Drude theory of metals (1900)

5.1.1 Introduction

- electrons - classical gas of non-interacting particles

- electrons scatter on ions (immediately)
- scattering time $= 0$
- the scattering directions are randomly oriented, thermal equilibrium
- relaxation time τ is main parameter of Drude theory which is the average time interval between two scatterings. This relaxation time generates also the free path $l = |\sigma|\tau$

The probability of scattering during $\mathrm{d}t$:

$$\frac{\mathrm{d}t}{\tau}$$

is given by the momentum

$$\vec{p}(t+\mathrm{d}t) = \left(\vec{p}(t) + \vec{f}(t)\mathrm{d}t\right)\left(1 - \frac{\mathrm{d}t}{\tau}\right) + \frac{\mathrm{d}t}{\tau}(\vec{p}_0 + \vec{f}(t)\mathrm{d}t)$$

In average $\vec{p}_0$ is zero. We restrict ourselves to linear terms

$$\vec{p}(t+\mathrm{d}t) = \vec{p}(t) - \frac{\vec{p}(t)}{\tau}\mathrm{d}t + \vec{f}(t)\mathrm{d}t$$

The time derivative of the momentum is

$$\dot{\vec{p}}(t) = \vec{f}(t) - \frac{\vec{p}(t)}{\tau}$$

Now, consider some simple cases, eg. an external electrical field $\vec{E}$ that accelerates the electrons

$$\vec{f} = -e\vec{E}, \quad \vec{E} > 0$$

In stationary regime we have

$$\frac{\vec{p}(t)}{\tau} = \vec{f}$$

We introduce the conductivity of electrons

$$\frac{m}{\tau}\vec{\sigma} = -e\vec{E}$$

and the current density

$$\vec{j} = -en\vec{\sigma}$$

so

$$-\frac{m}{\tau}\frac{\vec{j}}{en} = -e\vec{E}$$

and finally

$$\boxed{\vec{j} = \frac{e^2 n\tau}{m}\vec{E} = \sigma_0\vec{E}}$$

with the Drude conductivity

$$\sigma_0 = \frac{e^2 n\tau}{m}$$

Are we able to measure the relaxation time?

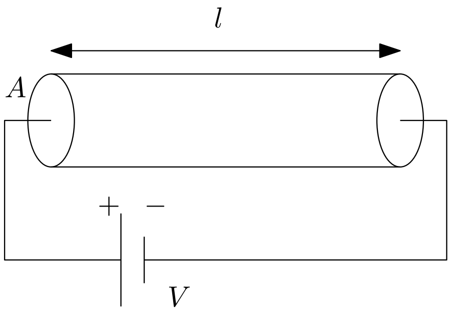

Figure 32: measurement of the relaxation time

here

$$\begin{aligned} V &= IR \\ El &= jAR \\ j &= \frac{l}{AR}E = \sigma_0 E \\ \tau &= \frac{\sigma_0 m}{e^2 n} \end{aligned}$$

5.1.2 Hall effect

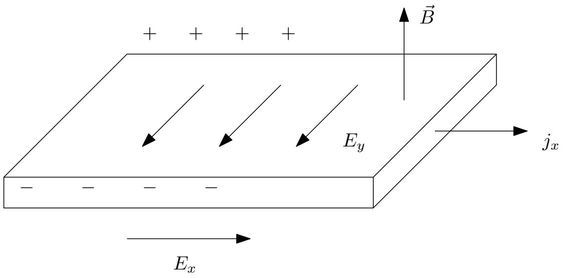

Figure 33: Hall effect

$$\vec{f} = -e\left(\vec{E} + \frac{1}{mc}\vec{p}\times\vec{B}\right)$$

the first term is the electric force and the second the Lorentz force. So

$$\dot{\vec{p}} = -e\left(\vec{E} + \frac{1}{mc}\underbrace{\vec{p}\times\vec{B}}_{\hat{x}p_yB-\hat{y}p_xB}\right) - \frac{\vec{p}}{\tau}$$

and take the current density into account

$$\vec{j} = -e\frac{n}{m}\vec{p}$$

we can write the equation for $\dot{\vec{p}}$ into matrix form

$$-\frac{m}{en}\partial_t \begin{pmatrix} j_x \\ j_y \end{pmatrix} = \begin{pmatrix} \frac{1}{\tau}\frac{m}{en} & \frac{eB}{mc}\frac{m}{en} \\ \dots & \dots \end{pmatrix} \begin{pmatrix} j_x \\ j_y \end{pmatrix} - e\begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

We set the left part of the equation to zero, so we are left with

$$\begin{pmatrix} 1 & \omega_c\tau \\ -\omega_c\tau & 1 \end{pmatrix} \begin{pmatrix} j_x \\ j_y \end{pmatrix} = \sigma_0 \begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

with the cyclotron frequency

$$\omega_c = \frac{eB}{mc}$$

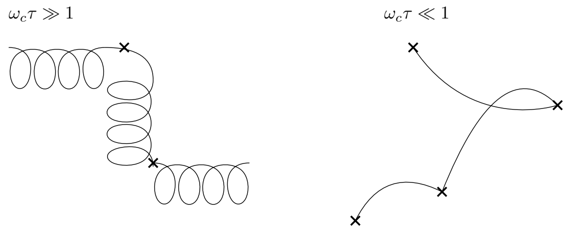

Figure 34: low and high limit of cyclotron frequency

Now look at the case $j_y = 0$. The matrix equation gives two equations:

$$j_x = \sigma_0 E_x, \qquad -\omega_c\tau j_x = \sigma_0 E_y$$

inserting ω_c and σ_0 explicitly

$$-\frac{eB}{mc}\tau j_x = \frac{e^2 n\tau}{m}E_y$$

gives equations for the Hall resistance R_H

$$R_H = \frac{E_y}{Bj_x} = -\frac{1}{enc}$$

and the time variable τ

$$\tau = -\frac{mc}{e}\frac{E_y}{E_x}\frac{1}{B}.$$

Now we want to determine the electric field $\vec{E}(t)$ in the case $\lambda \gg L$. The impulse $\vec{p}$ can be represented in time space

$$\vec{p}(t) = \int \mathrm{d}\omega \vec{p}(\omega) e^{-i\omega t}$$

and as its Fourier transformed version

$$\vec{p}(\omega) = \int \frac{\mathrm{d}t}{2\pi} \vec{p}(t) e^{i\omega t}$$

from before we know

$$\dot{\vec{p}} = -e\left(\vec{E} + \frac{1}{mc}\vec{p} \times \vec{B}\right) - \frac{\vec{p}}{\tau}$$

so it follows

$$-i\omega\vec{p}(\omega) = -e\vec{E}(\omega) - \frac{1}{\tau}\vec{p}(\omega)$$

now we insert

$$\vec{j} = -e\frac{n}{m}\vec{p}$$

which gives

$$-\frac{m}{en}\vec{j}(\omega)\left(-i\omega + \frac{1}{\tau}\right) = -e\vec{E}(\omega)$$

finally this gives

$$j(\omega) = \underbrace{\underbrace{\frac{e^2 n\tau}{m}}_{\sigma_0} \frac{1}{1 - i\omega\tau}}_{\sigma(\omega)} \vec{E}(\omega)$$

So we obtain

$$\boxed{\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}}$$

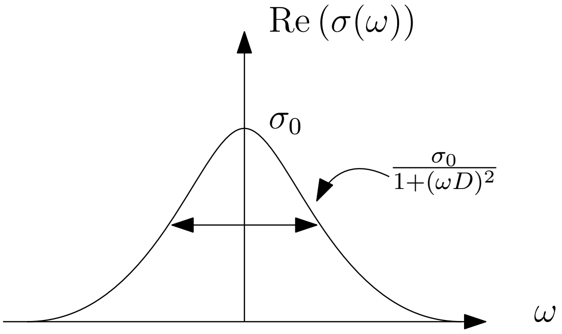

Figure 35: real part of the frequency

Using

$$E = E_0 e^{-i\omega t}$$

We get

$$\boxed{j(t) = \frac{E_0\sigma_0}{\sqrt{1 + (\omega\tau)^2}} e^{-i(\omega t + \arctan(\omega\tau))}}$$

5.1.3 Maxwell equations

Now we take a look at the Maxwell equations

$$\begin{aligned}
\nabla \times \vec{E} &= -\frac{1}{c}\partial_t \vec{B} \\
\nabla \times \vec{H} &= \frac{4\pi}{c}\vec{j} + \frac{1}{c}\partial_t \vec{D} \\
\nabla \vec{D} &= 4\pi\rho \\
\nabla \vec{B} &= 0
\end{aligned}$$

With the electric displacement field $\vec{D}$ and electric permittivity ϵ

$$\vec{D} = \epsilon \vec{E}$$

and magnetic permittivity μ and magnetic induct

$$\vec{B} = \mu \vec{H}$$

We use the relation

$$\Delta \vec{F} = \nabla(\nabla \vec{F}) - \nabla \times (\nabla \times \vec{F})$$

In the case of $\rho = 0$ ($\nabla \vec{E} = 0$) we get

$$\nabla \times (\nabla \times E) = \nabla \underbrace{(\nabla E)}_{=0} - \Delta E = -\Delta E = -\frac{\mu}{c}\partial_t \left(\frac{4\pi}{c}\vec{j} + \frac{\epsilon}{c}\partial_t \vec{E} \right)$$

Using the Fourier transformation of $\vec{E}$

$$\vec{E}(\vec{r}, t) = \int \vec{E}(\omega, \vec{k}) e^{i(\vec{k}\vec{r} - \omega t)} \mathrm{d}\omega \mathrm{d}\vec{k}$$

we get

$$\begin{aligned}
k^2 \vec{E}(\omega, \vec{k}) &= -\frac{\mu}{c} \left(\frac{4\pi}{c}(-i\omega) \underbrace{\vec{j}(\omega, \vec{k})}_{=\sigma \vec{E}} - \frac{\epsilon}{c}\omega^2 \vec{E}(\omega, \vec{k}) \right) \\
&= \frac{\omega^2}{c^2} \mu \underbrace{\left(\frac{4\pi i}{\omega}\sigma(\omega) + \epsilon \right)}_{:=\epsilon(\omega)} \vec{E}(\omega, \vec{k}) \\
&= \frac{\omega^2}{c^2} \mu \epsilon(\omega) \vec{E}(\omega, \vec{k})
\end{aligned}$$

with

$$\epsilon(\omega) := \frac{4\pi i}{\omega}\sigma(\omega) + \epsilon_S$$

We get a dispersion relation for k

$$k = \frac{1}{c}\omega\sqrt{\mu\epsilon(\omega)} = \frac{1}{c}\omega\tilde{n}(\omega)$$

With the frequency dependent refractive index

$$\tilde{n}(\omega) = n(\omega) + i\chi(\omega)$$

Now, we take a look at the limits:
$\omega\tau \ll 1$:

$$\epsilon(\omega) \approx \underbrace{\epsilon_S}_{\approx 1 \ll} + 4\pi i \underbrace{\frac{\sigma_0}{\omega}}_{\gg \text{ for metals}} \approx i\frac{4\pi\sigma_0}{\omega}$$

The result is totally imaginary. The refractive index follows to be

$$n(\omega) = \sqrt{\frac{4\pi\sigma_0}{\omega}} \cdot \sqrt{i} = \sqrt{\frac{4\pi\sigma_0}{\omega}}\frac{1+i}{\sqrt{2}}, \quad \chi(\omega) = \sqrt{\frac{2\pi\sigma_0}{\omega}}$$

The current density becomes

$$j \approx j_0 e^{i(kz-\omega t)} = j_0 e^{i(\dots)t} e^{-\alpha t)}$$

with

$$\alpha = \frac{\omega}{c}\sqrt{\frac{2\pi\sigma_0}{\omega}} \sim \sqrt{\omega}$$

finally

$$j = \frac{1}{\alpha} \sim \frac{1}{\sqrt{\omega}}$$

In the case $\omega\tau \gg 1$:

$$\epsilon(\omega) = \epsilon_S - \frac{\omega_p^2}{\omega^2}$$

with the *plasma frequency*

$$\omega_p^2 = \frac{4\pi n e^2}{m}$$

6.12.19

5.1.4 Plasma oscillations

The electron gas can sustain charge density oscillations with the frequency ω_p known as *plasma oscillations* which is a collective oscillation of all electrons.
The continuity equation for charge density is given by

$$\delta_t \rho + \nabla\vec{j} = 0$$

Thus

$$-i\omega\rho(\vec{k},\omega) + i\vec{k}\underbrace{(\sigma(\omega)\vec{E}(\vec{k},\omega))}_{=\vec{j}(\vec{k},\omega)} = 0$$

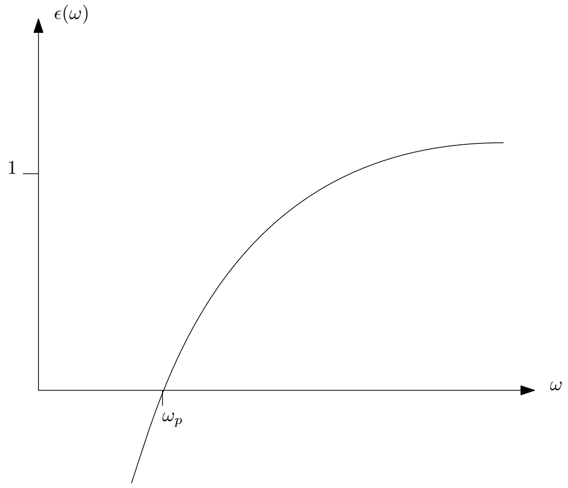

Figure 36: Energy $\epsilon(\omega)$

with Gauß' law:

$$\nabla\vec{E} = 4\pi\rho \;\Leftrightarrow\; i\vec{k}\vec{E} = 4\pi\rho$$

we obtain a solution if

$$-i\omega + 4\pi\sigma(\omega) = 0$$

so

$$\epsilon(\omega) = 1 + i\frac{4\pi}{\omega}\sigma(\omega) = 0$$

and finally

$$\omega = \omega_p \text{ for } \omega_p\tau \gg 1$$

.

5.2 Semi-classical model for electron dynamics

Consider a wave packet consisting of Bloch wave functions. Semi-classical model: effective equations of motion for the center of mass $\vec{r}$ of the wave packet and its momentum $\vec{k}$. The first equation corresponds to the sound velocity.

$$\boxed{\begin{aligned} \dot{\vec{r}} &= \vec{v}_n(\vec{k}) = \frac{1}{\hbar}\frac{\partial\epsilon_n(\vec{k})}{\partial\vec{k}} \\ \hbar\dot{\vec{k}} &= -e(\vec{E}(\vec{r},t) + \frac{1}{c}\vec{v}_n(\vec{k}) \times \vec{B}(\vec{r},t)) \end{aligned}}$$

Remarks:

- band index n is constant of motion. Inter-band transitions are neglected

- $\hbar\vec{k}$ is the crystal momentum which is defined up to additive reciprocal lattice vectors $\vec{G}$.
- in order to have a well-defined $\vec{k}$ located within the first Brillouin zone the spatial width of the wave packet must be much larger than the size of a primitive unit cell
- in order to treat the fields $\vec{E}$ and $\vec{B}$ classically their wavelength must be much larger than the width of the wave packet
- to neglect inter-band transitions the amplitude of the fields must be sufficiently small, otherwise electric or magnetic breakdown.
- *anomalous velocity*: the velocity $\vec{v}_n(\vec{k})$ can obtain a correction from the Berry curvature of Bloch function $\vec{\Omega}$

  $$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\frac{\partial \epsilon_n(\vec{k})}{\partial \vec{k}} - \hbar\dot{\vec{k}} \times \vec{\Omega}$$

  where

  $$\vec{\Omega} = \nabla_k \times \vec{A}(\vec{k}) \quad \text{with} \quad \vec{A}(\vec{k}) = -i \langle u_{n\vec{k}} | \nabla_k | u_{n\vec{k}} \rangle$$

  effective vector potential in $\vec{k}$-space. This plays a big role in the topology of oscillators because there the Berry curvature is important. This is analogous to electrodynamics in the $\vec{k}$-space. This correction is important in ferro-magnets where it contributes to the *anomalous Hall effect.*

5.2.1 Effective charge and heat carriers

The charge density of the nth band at $T = 0$ is given by

$$\vec{j}_n = 2(-e)\int_{1BZ,\text{occ. st.}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\vec{v}_n(\vec{k}) = 2(-e)\int_{1BZ,\text{occ. st.}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\frac{1}{\hbar}\frac{\partial \epsilon_n(\vec{k})}{\partial \vec{k}}$$

where the factor 2 corresponds to the spin degree of freedom and it is only integrated above occupied states.
The energy current density at $T = 0$ is given by

$$\vec{j}_{n\epsilon} = 2\int_{1BZ,\text{occ. st.}} \frac{\mathrm{d}\vec{k}}{(2\pi^3)}\epsilon_n(\vec{k})\vec{v}_n(\vec{k}) = 2\int_{1BZ,\text{occ. st.}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\frac{1}{2\hbar}\frac{\partial \epsilon_n(\vec{k})}{\partial \vec{k}}$$

Completely occupied (filled) bands are *inert*, so, they do not contribute to the current densities, as the integrand in both cases is a total derivative of a periodic function $\epsilon_n(\vec{k}) = \epsilon(\vec{k}+\vec{G})$, only surface terms contribute, so in this case, both integrals vanish. It follows that, conduction is only due to electrons within partially filled bands. If all bands are either completely filled or empty we have an electrical and thermal band insulator.

Holes

As a completely filled band does not contribute to the charge current density, we have

$$\begin{aligned}
\vec{j}_n &= 2(-e)\int_{1BZ,\text{occ. st.}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\vec{v}_n(\vec{k}) \\
&= 2(-e)\underbrace{\int_{1BZ} \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\vec{v}_n(\vec{k})}_{=0} - 2(-e)\int_{1BZ,\text{unocc. st.}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\vec{v}_n(\vec{k}) \\
&= 2e\int_{1BZ,\text{unocc. st.}} \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\vec{v}_n(\vec{k})
\end{aligned}$$

The current produced by occupied states with electrons of charge $-e$ is equal to that of fictitious particles, *holes*, with charge $+e$ filling all those states left unoccupied by the electrons.

The temporal evolution of states under influence of applied fields is fixed by the equations of motion irrespective whether they are occupied or not. When is it convenient to consider the current to be carried by holes?

Consider states close to the band maximum at $\vec{k}_0$.

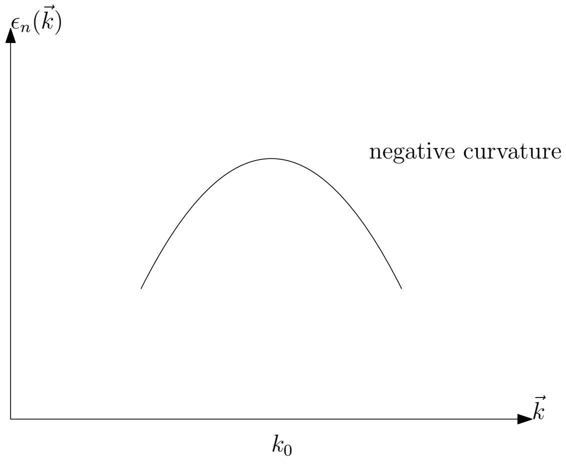

Figure 37: Energy $\epsilon(\vec{k})$ near band maximum

Expanding gives

$$\epsilon_n(\vec{k}) = \epsilon_n(\vec{k}_0) - \frac{\hbar^2(\vec{k}-\vec{k}_0)^2}{2m^*}$$

with a negative *effective mass* $-m^* < 0$. The equation of motion is now

$$\ddot{\vec{r}} = \frac{\mathrm{d}}{\mathrm{d}t}\vec{v}_n(\vec{k}) = -\frac{\hbar\dot{\vec{k}}}{m^*}$$

The acceleration is anti-parallel to $\vec{k}$. In the $\vec{E}$-field it is

$$\ddot{\vec{r}} = \left(-\frac{1}{m^*}\right)(-e)\vec{E} = \frac{e}{m^*}\vec{E}$$

The equation of motion for states close to the band maxima can be viewed as those of negatively charged particles with negative mass ($-e < 0,\ -m^* < 0$) or, more intuitively, as those of positively charged particles with positive mass ($e > 0,\ m^* > 0$). If the Fermi energy is close to a band maximum, in this case, it is conveniently to describe the transport in terms of holes with positive mass $m^* > 0$ and positive charge $e > 0$.

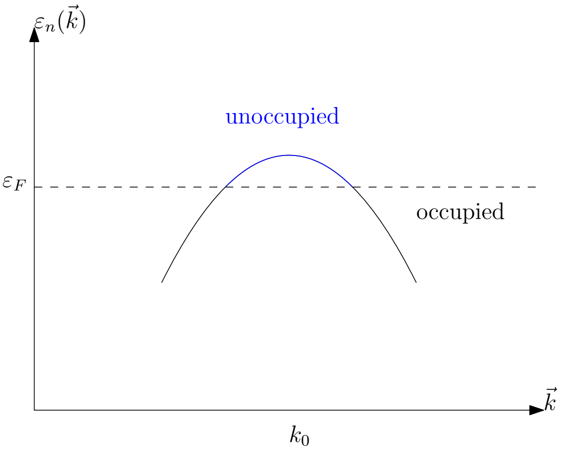

Figure 38: Fermi energy near the band maximum

More generally, we can introduce the *effective mass tensor*

$$\frac{1}{\hbar^2}\frac{\partial^2 \epsilon_n(\vec{k})}{\partial k_i \partial k_j}$$

which describes the curvature of the band. One of the applications are *semiconductors* that are at $T = 0$ band insulators with empty conduction band and completely filled valence band.

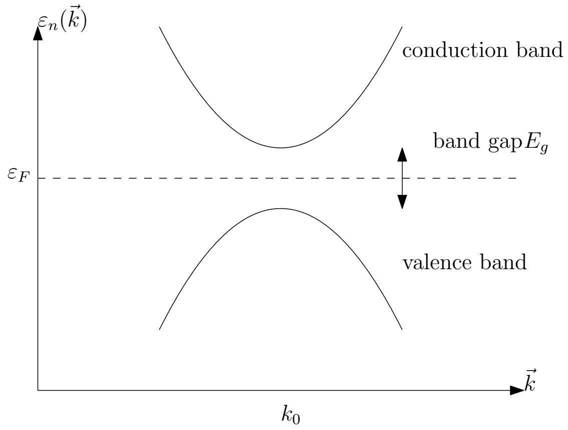

Figure 39: bands of a semiconductor

At $T > 0$ the intrinsic electronic properties determined by electrons are thermally excited from the valence band to the conduction band with exponentially small density $\propto \exp(-\frac{E_g}{k_B T})$ and for $E_g \gg k_B T$ typical band gaps are at $T = 300\,\mathrm{K}$:
Si: $E_g = 1.12\,\mathrm{eV}$, $\frac{E_g}{k_B T} \approx 43$
Ge: $E_g = 0.67\,\mathrm{eV}$, $\frac{E_g}{k_B T} \approx 26$
A parabolic approximation is applied. In the case of the valence band this gives 10.12.19

$$\begin{aligned}\varepsilon_v(\vec{k}) &\cong \varepsilon_v(0) + \frac{1}{2}\frac{\partial^2 \varepsilon_v}{\partial k_i \partial k_j}|_{\vec{k}=0} k_i k_j \\ &= \varepsilon_v(0) - \frac{\hbar^2}{2}\left(\frac{k_1^2}{m_{1h}} + \frac{k_2^2}{m_{2h}} + \frac{k_3^2}{m_{3h}}\right)\end{aligned}$$

and for the conduction band

$$\begin{aligned}\varepsilon_v(\vec{k}) &\cong \varepsilon_v(0) + \frac{1}{2}\frac{\partial^2 \varepsilon_c}{\partial k_i \partial k_j}|_{\vec{k}=0} k_i k_j \\ &= \varepsilon_v(0) + \frac{\hbar^2}{2}\left(\frac{k_1^2}{m_{1c}} + \frac{k_2^2}{m_{2c}} + \frac{k_3^2}{m_{3c}}\right)\end{aligned}$$

Diagonalizing the curvature tensor yields eigenvalues that correspond to inverse masses along three principal axes. They are negative for the valence band and positive for the conduction band. Thus, the transport within the valence and conduction band are described in terms of holes and electrons, respectively. Warning: For each band one can choose whether to describe the transport in terms of electrons or holes, but never mix the two pictures within a single band!

5.2.2 Bloch oscillations in electrical fields

Consider a uniform electric field $\vec{E}$:

$$\hbar\dot{\vec{k}} = -e\vec{E} \;\Rightarrow\; \vec{k}(t) = \vec{k}(0) - \frac{e\vec{E}t}{\hbar}$$

this we can insert into the velocity term

$$\dot{\vec{r}} = \vec{v}_n(\vec{k}(t)) = \vec{v}_n\left(\vec{k}(0) - \frac{e\vec{E}t}{\hbar}\right)$$

The wavevector changes linearly in time and as the velocity

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\frac{\partial\varepsilon(\vec{k})}{\partial\vec{k}}$$

We know that ε is a periodic function in $\vec{k}$, thus, also its derivative is periodic in $\vec{k}$. As $\vec{k}$ is linear in time, ε and $\vec{v}_n$ become periodic functions of time (for $\vec{E}$ parallel to a reciprocal lattice vector). These are called *Bloch oscillations*.

For example 1D:

$$\varepsilon(k) = -\frac{w}{2}\cos ka, \quad v(k) = \frac{wa}{2\hbar}\sin(ka)$$

it follows that

$$\begin{aligned} r(t) &= r(0) + \int_0^t \mathrm{d}t' v\left(k(0) - \frac{eEt}{\hbar}\right) \\ &= r(0) + \frac{wa}{2\hbar}\frac{\hbar}{eEa}\left(\cos\left(k(0)a - \frac{eEta}{\hbar}\right) - \cos\left(k(0)a\right)\right) \\ &= r_0 + \frac{w}{2eE}\cos\left(k_0 - \frac{eEta}{\hbar}\right) \end{aligned}$$

The Bloch electron oscillates in space with an amplitude given by

$$\Delta r = \frac{w}{eE}$$

and a frequency

$$\omega = \frac{eEa}{\hbar}$$

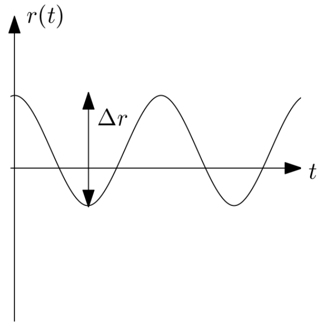

Figure 40: Bloch oscillation

This oscillation is difficult to observe in solids. An estimate of the amplitude can be made, e.g. $E \sim 10\,\frac{\mathrm{V}}{\mathrm{mm}}$, $w \sim 1\,\mathrm{eV}$:

$$\Delta r \sim 0.1\,\mathrm{mm} \approx 10 \times 10^6\,\text{Å}$$

The problem is, that electrons scatter from lattice defects before completing an oscillation $\omega\tau \ll 1$.
Bloch oscillations were observed in

- superlattices in semiconductores (artificially large a)
- optical lattices

But why do the Bloch electrons oscillate?
Consider the energy

$$\varepsilon = \varepsilon_n(\vec{k}(t)) + eEr(t)$$

where the first term is the kinetic energy of the Bloch electrons and the second term is the potential energy of the field.

$$\varepsilon = -\frac{w}{2}\cos\left(k_0 a - \frac{eEta}{\hbar}\right) + eE\left(r_0 + \cos\left(k_0 a - \frac{eEta}{\hbar}\right)\right) = eEr_0 = \text{const.}$$

The oscillating terms cancel out and the resulting total energy is constant. In order to conserve the energy, electrons can not escape to ±∞.

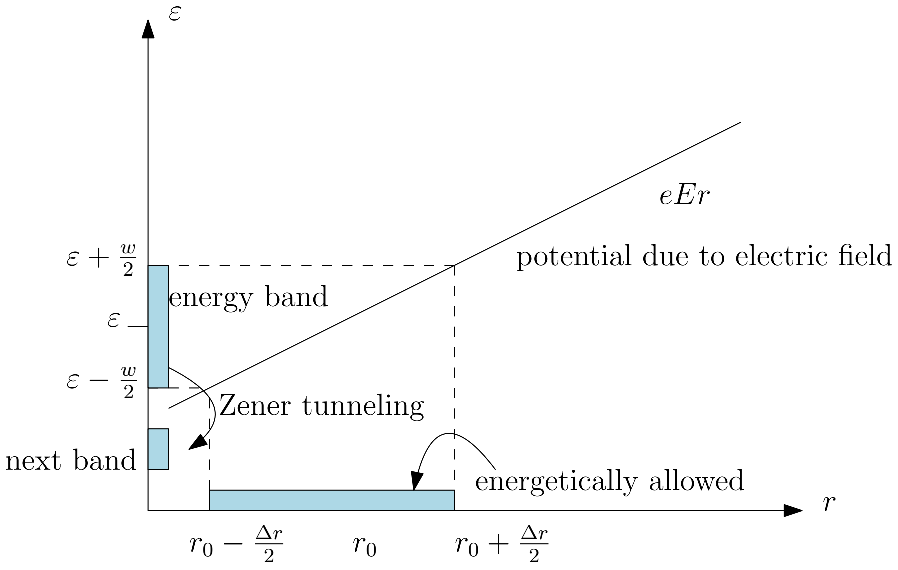

Figure 41: Energy as function of r with energy bands and Zener tunneling

For a single band the electron is electrically confined to a region in space. It can, however, escape via an inter-band transition i.e. *Zener tunneling.*

5.2.3 Semi-classical motion in a magnetic field

The semi-classical equation of motion in the presence of a $\vec{B}$ field is given by

$$\dot{\vec{r}} = \vec{v}_n(\vec{k}), \quad \hbar\dot{\vec{k}} = -\frac{e}{c}\vec{v}_n(\vec{k}) \times \vec{B}$$

The component of $\vec{k}$ parallel to $\vec{B}$ is conserved

$$\dot{k}_{\|} = 0$$

and also the electronic energy $\varepsilon_n(\vec{k})$ is conserved

$$\dot{\varepsilon}_n(\vec{k}) = \frac{\partial \varepsilon_n}{\partial \vec{k}} \cdot \vec{k} = \vec{v}_n(\vec{k})\hbar\dot{\vec{k}} = 0$$

because $\dot{\vec{k}}$ is perpendicular to $\vec{v}_n(\vec{k})$ and $\vec{B}$.

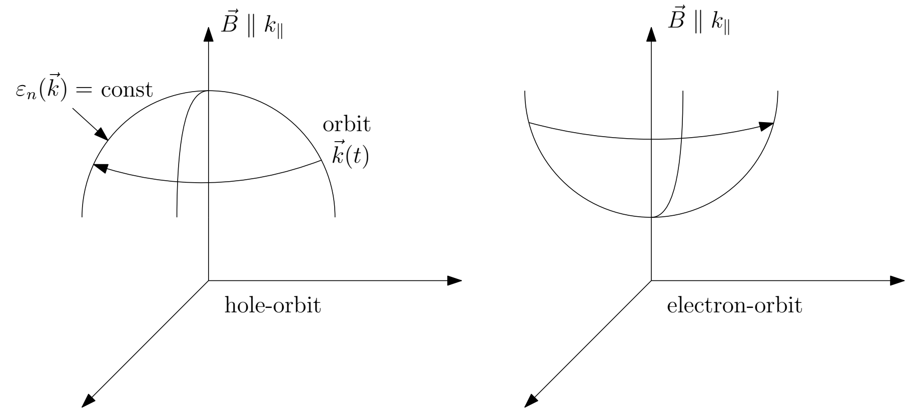

Figure 42: We can define a orbit in $\vec{k}$-space that is an intersection of a constant energy surface (e.g. sphere) with planes perpendicular to $\vec{B}$. The sense of the orientation depends on the sign of $\vec{v}$. We obtain electron/hole-like orbits.

One distinguishes between closed and open orbits similar to the discussion of fermi surfaces.

Closed orbits

Orbits closed in $\vec{k}$-space with a period

$$T = \int_0^T \mathrm{d}t = \oint_{\text{closed orbit}} \frac{\mathrm{d}\vec{k}}{|\dot{\vec{k}}|}$$

and

$$|\dot{\vec{k}}| = \frac{e}{\hbar c} |\vec{v}_{n,\perp}(\vec{k})||\vec{B}| = \frac{eB}{\hbar^2 c} \left| \left(\frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}} \right)_\perp \right|$$

where we use the component perpendicular to $\vec{B}$.

$$T = \frac{\hbar^2 c}{eB} \oint \frac{\mathrm{d}k}{\left| \left(\frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}} \right)_\perp \right|} = \frac{\hbar^2 c}{eB} \frac{\partial A}{\partial \varepsilon_n}$$

There is a geometrical interpretation: We have an area A on the plane perpendicular to $\vec{B}$ that is enclosed by the orbit

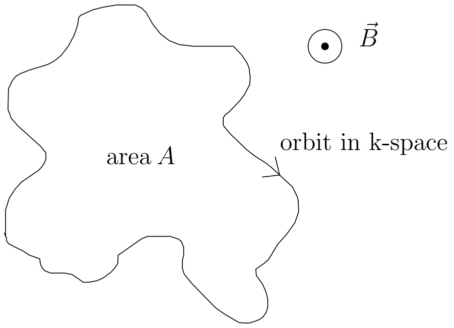

Figure 43: geometrical interpretation: We have an area A on the plane perpendicular to $\vec{B}$ that is enclosed by the orbit

$$A = \int \mathrm{d}k_\perp \oint dk = \oint dk \left| \frac{\mathrm{d}k_\perp}{\mathrm{d}E} \right| \mathrm{d}E$$

where the closed integral is a closed orbit for a given $k_\perp$.
A change in the area upon changing the energy is given by E: $\frac{\mathrm{d}A}{\mathrm{d}E}$. Consider a cyclotron frequency

$$\omega_c = \frac{2\pi}{T} = \frac{eB}{cm^*}$$

with the *cyclotron mass*

$$m^*(\varepsilon) = \frac{\hbar^2}{2m} \frac{\partial A}{\partial \varepsilon}$$

that is determined by a property of constant energy surfaces.

Open orbits

Open orbits in $\vec{k}$-space are possible for open constant energy surfaces.

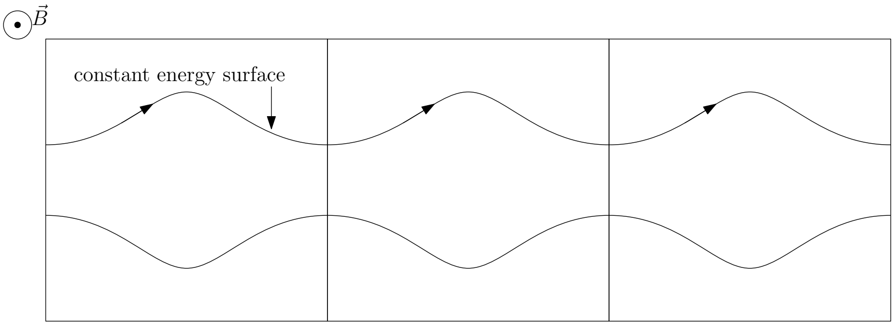

Figure 44: Extended zone scheme (3 Brillouin zones): constant energy surfaces connected, this leads to open orbits

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5.2.4 Quantized levels of Bloch electrons in a magnetic field

Reminder: free electron in a magnetic field: quantized Landau levels $E_n = \hbar\omega_c\left(n+\frac{1}{2}\right)$ with $\omega_c = \frac{eB}{mc}$.
Consider closed orbits, according to Bohr's correspondence principle:

$$E_{n+1} - E_n = \hbar\omega_c = \frac{2\pi eB}{\hbar c}\frac{\partial\varepsilon}{\partial A} \approx \frac{2\pi eB}{\hbar c}\frac{\Delta E}{\Delta A}$$

with the identification $E_{n+1} - E_n \cong \partial E$ follows

$$\boxed{\Delta A = \frac{2\pi eB}{\hbar c}}.$$

The are of orbits in k-space adjacent in energy differ by a fixed amount ΔA, so we get an area on which an electron travels in k-space that is also quantized:

$$A(E_n) = (n + \text{const})\frac{2\pi eB}{\hbar c}$$

for $n \gg 1$ (semi-classical limit).
Particular important are extremal orbits on the Fermi surface

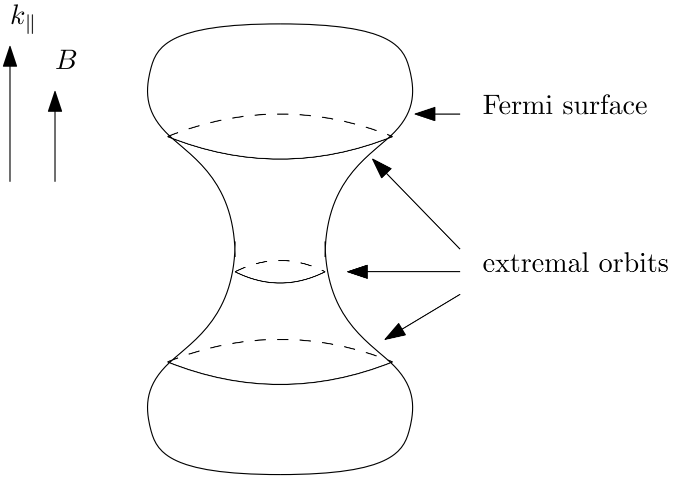

Figure 45: The area at fixed energy E_F varies as a function of longitudinal momentum $k_\|$

$$A(E_F, k_\|) = (n + \text{const})\frac{2\pi eB}{\hbar c}$$

with $k_\| = k_\|(n)$ for an extremal orbit at $k_{\|,e}$:

$$\left.\frac{\partial A}{\partial k_\|}\right|_{k_{\|,e}} = 0$$

with

$$A_e = A(E_F, k_{\|,e}).$$

There will be a singular contribution to the density of states whenever the value of the magnetic field B causes an extremal orbit on the Fermi surface to satisfy the quantization condition

$$A_e = (n + \text{const})\frac{2\pi eB}{\hbar c} = (n + \text{const})\Delta A$$

It follows that the density of states $\nu(E_F)$ is singular at regular spaced intervals of the inverse field $\frac{1}{B}$.

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{\hbar c}\frac{1}{A_e}$$

This suggests oscillatory behavior of many observables as a function of $\frac{1}{B}$:

- deHaas-van Alpen effect: periodic oscillation in magnetization $M(B)$
- Stubnikov-deHaas effect: periodic oscillation in electrical resistance $\rho(B)$

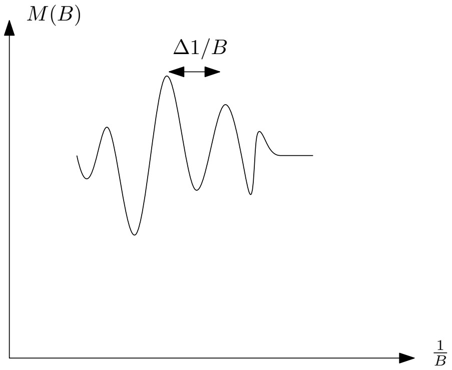

Figure 46: quantitative measurement of the shape of the Fermi surface is possible!

5.3 Boltzmann equation

We combine the semi-classical dynamic with a statistical approach. Consider an average number of electrons at position $\vec{r}$ with crystalline momentum $\hbar\vec{k}$ in the band n at time t:

$$f_{n\vec{k}}(\vec{r}, t)$$

This is semi-classical as both, position and impulse are fixed and do not obey Heisenberg's uncertainty principle. In equilibrium the average occupation is given by the Fermi function

$$f^{(0)}_{n\vec{k}}(\vec{r}, t) = \frac{1}{e^{\frac{\varepsilon_{n\vec{k}} - \mu}{k_B T}} + 1}$$

out of equilibrium f becomes time dependent:

$$\frac{\mathrm{d}f_{n\vec{k}}(\vec{r},t)}{\mathrm{d}t} = \frac{\partial f_{n\vec{k}}(t)}{\partial \vec{r}}\dot{\vec{r}} + \frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial \vec{k}}\dot{\vec{k}} + \frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial t}$$

Usage of the semi-classical equations of motion leads to

$$\frac{\mathrm{d}f_{n\vec{k}}(\vec{r},t)}{\mathrm{d}t} = \frac{\partial f_{n\vec{k}}(t)}{\partial \vec{r}}\vec{v}_{n\vec{k}} + \frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial \vec{k}}\frac{1}{\hbar}\vec{F} + \frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial t}.$$

The first term corresponds to a flow of particles and the second term to external forces $\vec{F}$. The time dependence is balanced by collisions of the electrons e.g. with defects, phonons, other electrons, etc. which eventually leads to a relaxation to equilibrium:

$$\frac{\mathrm{d}f_{n\vec{k}}(\vec{r},t)}{\mathrm{d}t} = \left.\frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial t}\right|_{\text{collisions}}.$$

This leads to the *Boltzmann equation*

$$\boxed{\frac{\partial f_{n\vec{k}}(t)}{\partial \vec{r}}\vec{v}_{n\vec{k}} + \frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial \vec{k}}\frac{1}{\hbar}\vec{F} + \frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial t} = \left.\frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial t}\right|_{\text{collisions}}}$$

We have discussed the left hand side of the Boltzmann equation as partial derivatives. In the following, the right hand side will be discussed.

5.3.1 Collision terms

Consider various sources for the collision term

I. Disorder

transition from $\vec{k} \rightarrow \vec{k}'$ with a scattering rate $W_{k'k}$ (read from right to left) due to impurities of the crystal

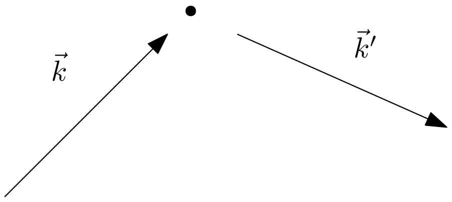

Figure 47: This transition is only possible if $\vec{k}$ is occupied and $\vec{k}'$ empty in the beginning

$$\left.\frac{\partial f_{n\vec{k}}(\vec{r},t)}{\partial t}\right|_{\text{collisions}} = -\sum_{\vec{k}'}\Big(\underbrace{W_{k'k}f_k(1-f_{k'})}_{\text{scattering out of } \vec{k}\text{-state}} - \underbrace{W_{kk'}f_{k'}(1-f_k)}_{\text{scattering into } \vec{k}\text{-state}} \Big)$$

We want to determine the scattering rate $W_{k'k}$ for weak impurity potentials at impurity positions $\vec{R}_i$

$$H_{\text{imp}} = \sum_{R_i} V_{\text{imp}}(\vec{r} - \vec{R}_i).$$

Therefore, we use Fermi's Golden rule

$$W_{k'k} = \frac{2\pi}{\hbar} | \langle \vec{k}' | H_{\text{imp}} | \vec{k} \rangle |^2 \delta(\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}'})$$

The elastic impurity scattering conserves the energy $\varepsilon_{\vec{k}}$. Insert the Hamiltonian:

$$W_{k'k} \cong \frac{2\pi}{\hbar} n_{\text{imp}} | \langle \vec{k}' | V_{\text{imp}} | \vec{k} \rangle |^2 \delta(\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}'})$$

where we only used the diagonal terms of the double sum and introduced the density of impurities n_{imp}. We can express the matrix element by an integral

$$\langle \vec{k}' | V_{\text{imp}} | \vec{k} \rangle = \int \mathrm{d}\vec{r} \psi^*_{n\vec{k}'}(\vec{r}) V_{\text{imp}} \psi_{n\vec{k}}(\vec{r})$$

The position of the impurities is constant, so it does not make any difference in which direction the time-evolution is performed. From the unitarity of the time-evolution follows that the scattering rate is symmetrical in k and k'

$$W_{k'k} = W_{kk'}$$

This symmetry is valid beyond perturbation theory. So, we can simplify the collision integral

$$\left.\frac{\partial f_k}{\partial t}\right|_{\text{collision}} = -\sum_{k'} W_{k'k}(f_k - f_{k'})$$

Sometimes the transition rates $W_{kk'}$ are treated as phenomenological parameters and (or the dependencies on k and k' are neglected (s-wave)). 17.12.19

II. Electron-electron scattering

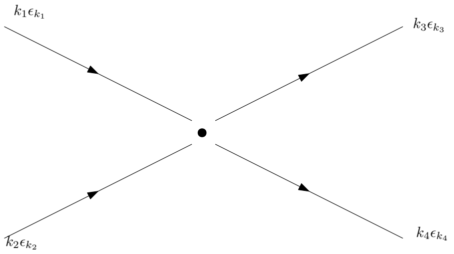

Figure 48: Scattering of two elements. Left momenta and energies before the collision and right after the collision

The scattering rate of this process is given by

$$W_{k_3k_4;k_1k_2} = \sum_{\vec{G}} \Gamma^G_{k_3k_4;k_1k_2} \delta_{k_1+k_2,k_3+k_4+G} \delta(\varepsilon_{k_1} + \varepsilon_{k_2} - \varepsilon_{k_3} - \varepsilon_{k_4})$$

Both, the energy and the momentum are conserved up to a reciprocal lattice vector $\vec{G}$. We get

$$\left.\frac{\partial f_k}{\partial t}\right|_{\text{collision}} = -\sum_{k_2k_3k_4} \left[W_{k_3k_4;kk_2} f_k f_{k_2}(1-f_{k_3})(1-f_{k_4}) - W_{kk_2;k_3k_4} f_{k_3} f_{k_4}(1-f_k)(1-f_{k_2})\right]$$

From time-reversal symmetry follows, that the transition rates are symmetric $W_{k_3k_4;kk_2} = W_{kk_2;k_3k_4}$.

III. Electron-phonon scattering

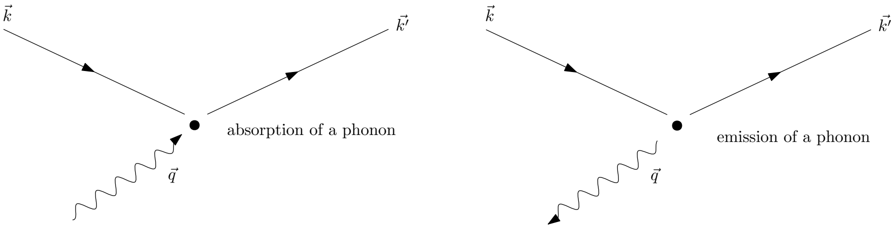

Figure 49: Emission and absorption by electron-phonon scattering

$$\begin{aligned}\left.\frac{\partial f_k}{\partial t}\right|_{\text{collision}} = -\sum_{\vec{k'}\vec{q}} &[W^A_{k'k;q} f_k(1-f_{k'})n_q - W^A_{kk';q} f_{k'}(1-f_k)n_q \\ &+ W^E_{k'k;q} f_k(1-f_{k'})(1+n_q) - W^E_{kk';q} f_{k'}(1-f_k)(1+n_q)]\end{aligned}$$

The first two terms corresponds to absorption and the second two terms to emission of a phonon. n_q is the phonon distribution function, where 1 corresponds to spontaneous and n_q to stimulated emission in the emission term.

5.3.2 Linearized Boltzmann equation and relaxation time approximatino

Collisions result in relaxation to a (local) equilibrium. The collision terms for disorder scattering and electron-electron scattering vanish for a local Fermi distribution

$$f_k^{(0)}(\vec{r}, t) = \frac{1}{e^{\frac{\varepsilon_k - \mu(\vec{r},t)}{k_B T(\vec{r},T)}} + 1}$$

with time and space dependent chemical potential $\mu = \mu(\vec{r}, t)$ and temperature $T = T(\vec{r}, t)$. Check for electron-electron scattering:

$$\left. f_k^{(0)} f_{k_2}^{(0)} (1 - f_{k_3}^{(0)})(1 - f_{k_4}^{(0)}) - f_{k_3}^{(0)} f_{k_4}^{(0)} (1 - f_k^{(0)})(1 - f_{k_2}^{(0)}) \right|_{\varepsilon_k + \varepsilon_{k_2} = \varepsilon_{k_3} + \varepsilon_{k_4}} = 0$$

The collision terms are only finite for a finite deviation from the local Fermi distribution:

$$\delta f_k(\vec{r},t) = f_k(\vec{r},t) - f_k^{(0)}(\vec{r},t)$$

We consider a simple, heuristic approximation of the collision term

$$\boxed{\frac{\partial f_k}{\partial t}\,|_{\text{collision}} \approx -\frac{\delta f_k}{\tau_k}}$$

the so-called *relaxation-time approximation* with k-dependent relaxation time τ_k. This allows for a simple solution of the Boltzmann equation. However, this approximation violates certain conservation laws. Furthermore, for small deviations from equilibrium linearization of the left-hand side of the Boltzmann equation in gradients ∇T, $\nabla\mu$, the forces $\vec{F}$ and δf is possible. For $\delta_t T = \delta_t \mu = 0$ one then obtains

$$\frac{\partial f_k}{\partial \vec{r}}\vec{v}_k + \frac{\partial f_k}{\partial \vec{k}}\frac{1}{\hbar}\vec{F} + \frac{\partial f_k}{\partial t} \cong \frac{\partial f_k^{(0)}}{\partial \vec{r}}\vec{v}_k + \frac{\partial f_k^{(0)}}{\partial \vec{k}}\frac{1}{\hbar}\vec{F} + \frac{\partial \delta f_k}{\partial \vec{r}}\vec{v}_k + \frac{\partial \delta f_k}{\partial t}$$

$$= \boxed{-\frac{\partial f_k^{(0)}(\vec{r})}{\partial \varepsilon_k}\left[\frac{\varepsilon_k - \mu(\vec{r})}{T(\vec{r})}\frac{\partial T}{\partial \vec{r}} + \frac{\partial \mu}{\partial \vec{r}} - \vec{F}\right]\vec{v}_k + \frac{\partial \delta f_k}{\partial \vec{r}}\vec{v}_k + \frac{\partial \delta f_k}{\partial t} = -\frac{\partial f_k}{\tau_k}}$$

This is called the *linearized Boltzmann equation* in the relaxation-time approximation. The best approximation for $\frac{1}{\tau_k}$ depends on the problem and the quantity of interest (heat/ charge transport etc.). One distinguishes in particular between a *single-particle relaxation-time* that is the typical time between two scattering events and the *transport relaxation-time* that is the typical time between two scattering events which relax a transport current.

5.3.3 Conductivity and transport relaxation time

For a homogeneous electrical field $\vec{F}(t) = -e\vec{E}(t)$ we can set $\nabla T = \nabla\mu = 0$ as the field is homogeneous and we obtain

$$-\frac{\partial f_k^{(0)}}{\partial \varepsilon_k}e\vec{E}(t)\vec{v}_k + \frac{\partial \delta f_k}{\partial t} = -\frac{\delta f_k}{\tau_k}$$

We perform a Fourier transform:

$$\delta f_k(t) = \int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega t}\partial f_k(\omega)$$

and obtain

$$\delta f_k(\omega) = \frac{-\frac{\partial f_k^{(0)}}{\partial \varepsilon_k}e\vec{E}(\omega)\vec{v}_k}{-\frac{1}{\tau_k} + i\omega}$$

The charge current density is given by

$$\vec{j} = -2e\int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} f_k \vec{v}_k = -2e\int \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\delta f_k \vec{v}_k$$

with the factor of 2 corresponding to the particle spin and no contribution in equilibrium. The *conductivity tensor* is given by

$$j_i(\omega) = \sigma_{ij}(\omega) E_j(\omega)$$

with

$$\boxed{\sigma_{ij}(\omega) = 2e^2 \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} v_k^i v_k^j \frac{\left(-\frac{\partial f_k^{(0)}}{\partial \varepsilon_k}\right)\tau_k}{1 - i\omega\tau_k}}$$

As $\frac{\partial f_k^{(0)}}{\partial \varepsilon_k}$ is sharply peaked only states close to the Fermi energy contribute for $T \to 0$:

$$-\frac{\partial f_k^{(0)}}{\partial \varepsilon_k} \approx \delta(\varepsilon_k - \mu)$$

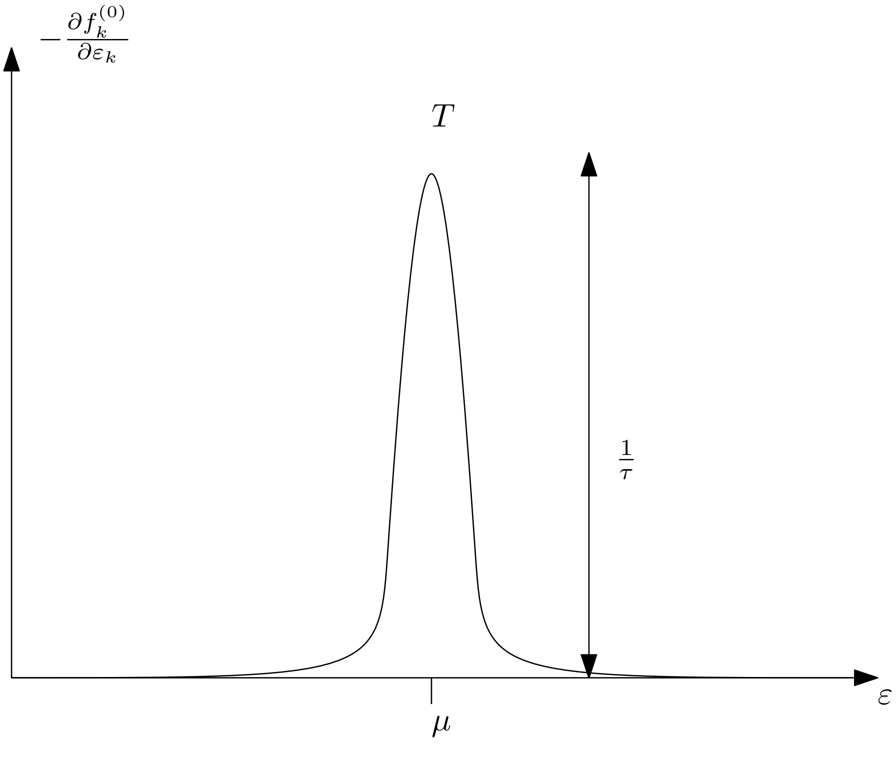

Figure 50: delta peak of$-\frac{\partial f_k^{(0)}}{\partial \varepsilon_k}$

Comparison with Drude formula

$$\sigma(\omega) = \frac{\frac{e^2 n\tau}{m}}{1 - i\omega\tau}$$

approximate $\tau_k \approx \tau$:

$$\sigma_{ij} = \frac{e^2\tau}{1-i\omega\tau} 2 \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} v_k^i \underbrace{v_k^j \left(-\frac{\partial f_k^{(0)}}{\partial \varepsilon_k}\right)}_{=-\frac{1}{\hbar}\frac{\partial f_k^{(0)}}{\partial k_j}}$$

$$= \frac{e^2\tau}{1-i\omega\tau} 2 \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} \underbrace{\frac{1}{\hbar^2}\frac{\partial \varepsilon_k}{\partial k_i \partial k_j}}_{m_{ij}^{-1}} f_k^{(0)}$$

where we performed integration by parts and introduced the effective mass tensor m_{ij}^{-1}. Finally, we obtain

$$\sigma_{ij}(\omega) = \frac{e^2 n\tau}{1-i\omega\tau} \langle m_{ij}^{-1} \rangle$$

with the density

$$n = 2 \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} f_k^{(0)}$$

and the inverse effective mass averaged over the Fermi volume:

$$\langle m_{ij}^{-1} \rangle = \frac{2 \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_k}{\partial k_i \partial k_j} f_k^{(0)}}{2 \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} f_k^{(0)}}$$

For an isotropic system with $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$ we obtain the classical solution:

$$\langle m_{ij}^{-1} \rangle = \frac{1}{m} \delta_{ij}$$

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Interpretation of the relaxation time τ_k entering the conductivity as a *transport scattering time*:
For impurity scattering:

$$-\frac{\delta f_k}{\tau_k} = -\int \frac{\mathrm{d}\vec{k}'}{(2\pi)^3} W_{k'k}(f_k - f_{k'}) = -\int \frac{\mathrm{d}\vec{k}'}{(2\pi)^3} W_{k'k}(\delta f_k - \delta f_{k'})$$

An analytical solution is possible if

- we have a isotropic system

$$\varepsilon_k = \varepsilon(|\vec{k}|) \quad \Rightarrow \quad \vec{v}_k = v_k \hat{k}$$

- scattering only depends on the angle between $\vec{k}$ and $\vec{k}'$:

$$W_{k'k} = \Gamma(\hat{k}\hat{k}')\delta(\varepsilon_k - \varepsilon_{k'})$$

We use the ansatz:

$$\delta f_k = \hat{k}\vec{E}\phi(\varepsilon_k)$$

with

$$\phi(\varepsilon_k) = \frac{\partial f}{\partial \varepsilon_k}\frac{3v_k}{v_k\tau_k - i\omega}$$

and taking into account that $\tau_k = \tau(\varepsilon_k)$ this leads to

$$\frac{\hat{k}\vec{E}}{\tau_k}\phi(\varepsilon_k) = \phi(\varepsilon_k)\vec{E}\underbrace{\int \frac{\mathrm{d}\vec{k}'}{(2\pi)^3}W_{k'k}(\hat{k} - \hat{k}')}_{\parallel\, \hat{k} \text{ by symmetry}}$$

It follows the transport relaxation rate

$$\begin{aligned}
\frac{1}{\tau_k} &= \int \frac{\mathrm{d}k'}{(2\pi)^3}W_{k'k}(1 - \hat{k}'\hat{k}) \\
&= \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\delta(\varepsilon_k - \varepsilon_{k'})\Gamma(\hat{k}\hat{k}')(1 - \hat{k}\hat{k}') \\
&= \frac{\nu(\varepsilon_k)}{2}\frac{1}{2}\int_{-1}^{1} \mathrm{d}\cos\theta\Gamma(\cos\theta)(1 - \cos\theta)
\end{aligned}$$

with the density of states per spin

$$\nu(\varepsilon_k) = 2\int \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\delta(\varepsilon_k - \varepsilon_{k'})$$

Now, we want to interpret the extra factor $(1 - \hat{k}\hat{k}') = 1 - \cos\theta$: for small angle scattering ($\theta \ll 1$) there is little change in the current velocity and thus only little current relaxation! Only scattering events with large angle do substantially relax the current.

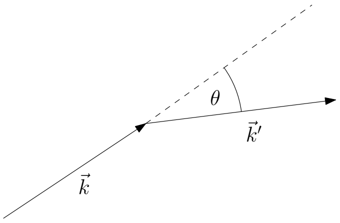

Figure 51: Scattering angle θ

Adding scattering events: Matthiessen's rule: Apart from impurity scattering, also electron-electron and electron-phonon scattering leads to relaxation. Within the relaxation time approximation: *add* scattering rates:

$$\frac{1}{\tau_k} = \frac{1}{\tau_{\text{disorder},k}} + \frac{1}{\tau_{\text{interaction},k}} + \frac{1}{\tau_{\text{phonons},k}}$$

If the $\vec{k}$ dependency can be neglected, contribution to resistivity $\rho = \frac{1}{\sigma} \propto \frac{1}{\tau}$ are additive.

$$\rho \approx \rho_{\text{disorder}} + \rho_{\text{interaction}} + \rho_{\text{phonons}}$$

which is called Matthiessen's rule.
This rule is frequently used to interpret experiments, but it is not valid for $\vec{k}$- dependent scattering and for strong disorders or interactions. Typically for metal at $T \ll T_F$:

$$\rho_{\text{dis}} = \text{const}, \quad \rho_{\text{int}} = AT^2, \quad \rho_{\text{phon}} \propto \begin{cases} T^5, & \text{low } T \ (T \ll \theta_D) \\ T, & \text{high } T \ (T \gg \theta_D) \end{cases}$$

5.3.4 Thermal conductivity and thermopower

Thermal current carries heat Q. Thermodynamic definition

$$\delta Q = T\mathrm{d}S + \mathrm{d}U - \mu \mathrm{d}N$$

In terms of currents:

$$\vec{j}_Q = \vec{j}_\varepsilon - \mu \vec{j}_N$$

where the first current corresponds to the heat, the second to energy and the last to particle current. If one neglects interaction effects and contributions from phonons etc. we can define the heat current density by

$$\vec{j}_Q = 2 \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} (\varepsilon_k - \mu) \vec{v}_k f_k$$

A finite electrical field and a thermal gradient ∇T will in general induce a thermal as well as an electrical current density

$$\vec{j}_c = 2(-e) \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} \vec{v}_k f_k = (-e) \vec{j}_k$$

For weak $\vec{E}$ and ∇T there will be a linear response

$$\boxed{\vec{j}_c = \mathbb{L}_{11} \vec{E} + \mathbb{L}_{12}(-\nabla T), \quad \vec{j}_Q = \mathbb{L}_{21} \vec{E} + \mathbb{L}_{22}(-\nabla T)}$$

where $\mathbb{L}_{\alpha\beta}$ with $\alpha, \beta = 1, 2$ are linear response matrices. They are related to transport coefficients under various experimental conditions:

- conductivity σ:
  for $\nabla T = 0$: $j_c = \sigma_{ij} E_j$ with $\sigma = \mathbb{L}_{11}$
- thermal conductivity k:
  heat current measured under the condition of a vanishing charge current

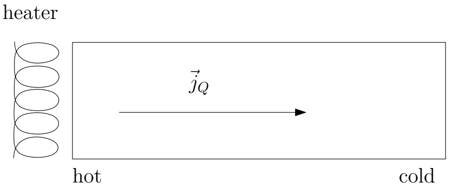

Figure 52: heat current measurement

$$\vec{j}_c = 0 \;\Leftrightarrow\; \vec{E} = -\mathbb{L}_{11}^{-1}\mathbb{L}_{12}(-\nabla T)$$

Hence,

$$\vec{j}_Q = (\mathbb{L}_{22} - \mathbb{L}_{21}\mathbb{L}_{11}^{-1}\mathbb{L}_{12})(-\nabla T) = \kappa(-\nabla T)$$

with thermal conductivity k

- Thermopower Q (Seebeck coefficient)
  Electrical field induced by the thermal gradient (thermoelectric effect)

  $$\vec{E} = -\mathbb{L}_{11}^{-1}\mathbb{L}_{12}(-\nabla T) = Q\nabla T$$

  with $Q = \mathbb{L}_{11}^{-1}\mathbb{L}_{12}$

- Peltier effect:
  Imposed electric current is accompanied by thermal current

  $$\vec{j}_Q = \pi\vec{j}_c$$

  with $\pi = \mathbb{L}_{21}\mathbb{L}_{11}^{-1}$. The Peltier coefficient π is related to the thermopower Q:

  $$\pi = TQ$$

  (Onsager relation)

Evaluation of $L_{\alpha\beta}$ with the help of the linearized Boltzmann equation

$$-\frac{\partial f^{(0)}}{\partial \varepsilon_k}\left(\frac{\varepsilon_k - \mu}{T}\nabla T + e\vec{E}\right)\vec{v}_k = -\frac{\delta f_k}{\tau_k}$$

gives

$$\delta f_k = -\tau_k\left(-\frac{\partial f^{(0)}}{\partial \varepsilon_k}\right)\left(\frac{\varepsilon_k - \mu}{T}\nabla T + e\vec{E}\right)\vec{v}_k$$

from which follows for the currents

$$\begin{aligned}\begin{pmatrix}\vec{j}_c^{\,i}\\ \vec{j}_Q^{\,i}\end{pmatrix} &= 2\int\frac{d\vec{k}}{(2\pi)^3}\begin{pmatrix}-e\\ \varepsilon_k-\mu\end{pmatrix}\vec{v}_k^{\,i}\delta f_k\\ &= 2\int\frac{d\vec{k}}{(2\pi)^3}\begin{pmatrix}-e\\ \varepsilon_k-\mu\end{pmatrix}\vec{v}_k^{\,i}\vec{v}_k^{\,j}\tau_k\left(-\frac{\partial f^{(0)}}{\partial \varepsilon_k}\right)\left(-e, \frac{\varepsilon_k-\mu}{T}\right)\begin{pmatrix}E^j\\ -\nabla^j T\end{pmatrix}\end{aligned}$$

and thus for the linear response coefficients

$$\boxed{(\mathbb{L}^{ij}_{\alpha\beta)} = 2\int \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\left(-\frac{\partial f^{(0)}}{\partial \varepsilon_k}\right)\varepsilon_k v^i_k v^j_k \begin{pmatrix} e^2 & -e\frac{\varepsilon_k-\mu}{T} \\ -e(\varepsilon_k-\mu) & \frac{(\varepsilon_k-\mu)^2}{T}\end{pmatrix}}$$

One finds the *Onsager relation:*

$$\mathbb{L}_{21} = T\mathbb{L}_{12}$$

The expression simplifies for an *isotropic system*:

$$v^i_k v^j_k \to v^i_k v^j_k \delta_{ij} \to \frac{1}{3}\vec{v}^2\delta_{ij}$$

and, hence, the matrix is diagonalized

$$\boxed{\mathbb{L}^{ij}_{\alpha\beta} = L_{\alpha\beta}\delta_{ij}}$$

with

$$(L_{\alpha\beta}) = \int \mathrm{d}\varepsilon \nu(\varepsilon)\left(-\frac{\partial f^{(0)}}{\partial \varepsilon}\right)\tau(\varepsilon)\frac{1}{3}\vec{v}^2_\varepsilon \begin{pmatrix} e^2 & -e\frac{\varepsilon_k-\mu}{T} \\ -e(\varepsilon_k-\mu) & \frac{(\varepsilon_k-\mu)^2}{T}\end{pmatrix}$$

where we used that for an isotropic system the relaxation time and the square of the velocity $\vec{v}^2$ will only depend on the energy ε. This expression can be evaluated for small 7.1.20
T using the *Sommerfeld expansion.* We need the following expressions

$$\int \mathrm{d}\varepsilon g(\varepsilon)\left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon-\mu) \cong g'(\mu)\int \mathrm{d}\varepsilon\left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon-\mu)^2 = g'(\mu)\frac{\pi^2}{3}(k_B T)^2$$

where we used that $g(\varepsilon) \cong g(\mu) + g'(\mu)(\varepsilon - \mu)$. The first term vanishes because of multiplication of a symmetric with an anti-symmetric term in the integral. Furthermore, we need to know the following integral

$$\int \mathrm{d}\varepsilon g(\varepsilon)\left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon-\mu)^2 \cong g(\mu)\frac{\pi^2}{3}(k_B T)^2$$

One obtains for low temperatures $T \to 0$ $(\mu = \varepsilon_F)$ with $g(\varepsilon) = \nu(\varepsilon)\tau(\varepsilon)\frac{1}{3}\vec{v_\varepsilon}^2$

$$(L_{\alpha\beta)} \cong \begin{pmatrix} e^2 g(\varepsilon_F) & -g'(\varepsilon_F)\frac{\pi^2}{3}k_B^2 T \\ -eg'(\varepsilon_F)\frac{\pi^2}{3}(k_B T)^2 & g(\varepsilon_F)\frac{\pi^2}{3}k_B^2 T\end{pmatrix}$$

For the transport coefficients one obtains:

thermal conductivity

$$\kappa = L_{22} - L_{21} L_{11}^{-1} L_{12} = L_{22} + \sigma(T^3) \cong g(\varepsilon_F) \frac{\pi^2}{3} k_B^2 T$$

comparing this with the electrical conductivity $\sigma = e^2 g(\varepsilon_F)$ one finds the the *Wiedemann-Franz law*

$$\boxed{\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \frac{k_B^2}{e^2}}$$

Thus, the ratio between thermal and electrical conductivity is predicted to be constant and only to dependent on nature constants for low temperatures. It is equal to the Lorenz number

$$L_0 = \frac{\pi^2}{3} \frac{k_B^2}{e^2}$$

The physical interpretation is that the typical excitation has charge $|e|$ and energy $k_B T$. This leads to charge and heat transport. The Wiedemann-Franz law is exact for purely elastic scattering. Inelastic processes might relax energy but not charge current, hence, this law might be violated.

thermopower Q

$$Q = L_{11}^{-1} L_{12} = \frac{\pi^2}{3} \frac{k_B^2 T}{-e} \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} = \frac{\pi^2}{3} \frac{k_B^2 T}{-e} \frac{\partial}{\partial \varepsilon} \ln g(\varepsilon) \,|_{\varepsilon_F} = \frac{\pi^2}{3} \frac{k_B^2 T}{-e} \frac{\partial}{\partial \varepsilon} \ln \sigma(\varepsilon) \,|_{\varepsilon_F}$$

This is the so-called *Mott formula* with energy dependent conductivity $\sigma(\varepsilon) = e^2 g(\varepsilon)$ and its derivative (remember: $g(\varepsilon) = \nu(\varepsilon)\tau(\varepsilon)\frac{1}{3}\vec{v_\varepsilon}^2$)

$$\begin{aligned}
\sigma'(\varepsilon_F) &= \frac{\partial}{\partial \varepsilon_F} \left(e^2 \tau(\varepsilon) \nu(\varepsilon) \frac{1}{3} \vec{v}_\varepsilon^2 \right)_{\varepsilon_F} \\
&= e^2 \tau'(\varepsilon_F) \nu(\varepsilon_F) \frac{1}{3} \vec{v}_{\varepsilon_F}^2 + e^2 \tau(\varepsilon_F) \frac{\partial}{\partial \varepsilon_F} \underbrace{2 \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} \delta(\varepsilon_F - \varepsilon_k) \frac{1}{3} \vec{v}_k^2}_{= \nu(\varepsilon_F) \frac{1}{3} \vec{v}_{\varepsilon_F}^2} \\
&= \frac{\tau'(\varepsilon_F)}{\tau(\varepsilon_F)} \sigma(\varepsilon_F) + 2e^2 \tau(\varepsilon_F) \int \frac{\mathrm{d}k^3}{(2\pi)^3} \qquad \underbrace{\frac{\partial}{\partial \varepsilon_F} \delta(\varepsilon_F - \varepsilon_k) \vec{v}_\varepsilon}_{= \left(-\frac{\partial}{\partial \varepsilon_k} \delta(\varepsilon_F - \varepsilon_k) \right) \frac{1}{\hbar} \frac{\partial \varepsilon_k}{\partial \vec{k}} = -\frac{1}{\hbar} \frac{\partial}{\partial \vec{k}} \delta(\varepsilon_F - \varepsilon_k)} \qquad \vec{v}_k \frac{1}{3} \\
&= \frac{\tau'(\varepsilon_F)}{\tau(\varepsilon_F)} \sigma(\varepsilon_F) + 2e^2 \tau(\varepsilon_F) \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3} \delta(\varepsilon_F - \varepsilon_k) \frac{1}{3\hbar^2} \frac{\partial^2 \varepsilon_k}{\partial \vec{k} \partial \vec{k}}
\end{aligned}$$

The effective mass tensor $\frac{\partial^2 \varepsilon_k}{\partial \vec{k} \partial \vec{k}}$ does only act on the Fermi surface. If the energy dependence of the relaxation time can be neglected $\tau'(\varepsilon_F) \approx 0$, then the sign of the thermopower Q is determined by the sign of the effective mass averaged over the Fermi surface.

6 Beyond the independent electron approximation

In step I of the adiabatic approximation of chapter 2.1 one has to solve the eigenvalue equation for electrons $H\psi = E\psi$ with $\psi = \psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, ..., \vec{r}_N\sigma_N)$ where $\vec{r}_i$ and σ_i are position and spin ($\sigma_i = \uparrow, \downarrow$) of the i-th electron, respectively. The Hamiltonian reads

$$H = \underbrace{\sum_i \frac{p_i^2}{2m}}_{\text{cinetic energy}} \underbrace{-\sum_{i,n} \frac{Ze^2}{|\vec{r}_i - \vec{R}_n|}}_{\text{ionic potential}} + \underbrace{\sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{e-e interaction}} + \text{spin-orbit coupling corrections}$$

In chapter 4 the e-e interaction was neglected and the eigenvalue problem was treated in the independent electron approximation.

6.1 Hartree-Fock approximation

For non-interacting electrons $H_{\text{non-int}} = \sum_i H_0(\vec{r}_i, \sigma_i)$ the many-particle wavefunction is totally anti-symmetric and given by a slater determinant

$$\psi_{\text{slater}}(\vec{r}_1\sigma_1, ..., \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_1(\vec{r}_1\sigma_1) & \phi_2(\vec{r}_1\sigma_1) & \dots & \phi_N(\vec{r}_1\sigma_1) \\ \phi_1(\vec{r}_2\sigma_2) & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \phi_1(\vec{r}_N\sigma_N) & \dots & \dots & \phi_N(\vec{r}_N\sigma_N) \end{pmatrix}$$

where $\{\phi_1, \phi_2, ..., \phi_N\}$ is a set of N orthonormal one-electron eigenfunctions of H_0. The anti-symmetry of the wavefunction is required by the Pauli principle that demands

$$\psi(\vec{r}_1\sigma_1, ..., \vec{r}_i\sigma_i, ..., \vec{r}_j\sigma_j, ..., \vec{r}_N\sigma_N) = -\psi(\vec{r}_1\sigma_1, ..., \vec{r}_j\sigma_j, ..., \vec{r}_i\sigma_i, ..., \vec{r}_N\sigma_N)$$

a sign change upon interchanging arguments.

Strategy: use ψ_{slater} as a variational Ansatz for the interacting problem by minimizing the energy

$$\boxed{E_0 \leq \min \frac{\langle\psi_{\text{slater}}|H|\psi_{\text{slater}}\rangle}{\langle\psi_{\text{slater}}|\psi_{\text{slater}}\rangle} = E_0^{\text{HF}}}$$

This is the *Hartree-Fock approximation*, where E_0^{HF} is the ground state energy within this HF approximation. The expectation value reads explicitly:

$$\begin{aligned}
\frac{\langle\psi_{\text{slater}}|H|\psi_{\text{slater}}\rangle}{\langle\psi_{\text{slater}}|\psi_{\text{slater}}\rangle} &= \langle H\rangle_{\text{slater}} \\
&= \sum_{i=1}^{N} \sum_{\sigma=\uparrow,\downarrow} \int \mathrm{d}\vec{r} \phi_i^*(\vec{r}, \sigma) \left(\frac{p^2}{2m} + V_{\text{ion}}(\vec{r})\right) \phi_i(\vec{r}, \sigma) \\
&+ \frac{1}{2} \sum_{i,i'}^{N} \sum_{\sigma\sigma'} \int \mathrm{d}\vec{r}\mathrm{d}\vec{r}' \frac{e^2}{|\vec{r} - \vec{r}'|} (|\phi_i(\vec{r}, \sigma)|^2 |\phi_{i'}(\vec{r}'\sigma')|^2 - \delta_{\sigma\sigma'} \phi_i^*(\vec{r}\sigma)\phi_{i'}^*(\vec{r}'\sigma')\phi_i(\vec{r}'\sigma')\phi_{i'}(\vec{r}\sigma))
\end{aligned}$$

The energy is minimized under the condition of normalized single particle functions $\langle\phi_i|\phi_j\rangle = \delta_{ij}$. So one considers the functional

$$F[\phi_i] = \langle H\rangle_{\text{slater}} - \sum_i \varepsilon_i(\langle\phi_i|\phi_i\rangle - 1)$$

where ε_i are Lagrange multipliers. Minimization

$$\frac{\delta}{\delta\phi_i^*(\vec{r},\sigma)}F[\phi] = 0$$

yields the *Hartree-Fock equations*:

$$\boxed{\left(-\frac{\hbar^2\nabla^2}{2m}V_{\text{ion}}(\vec{r})\right)\phi_i(\vec{r},\sigma) - e\int \mathrm{d}\vec{r}'\,\frac{\varrho^H(\vec{r}') - \varrho_{i\sigma}F}{|\vec{r}-\vec{r}'|}\phi_i(\vec{r},\sigma) = \varepsilon_i\phi_i(\vec{r},\sigma)}$$

This is a modified Schrödinger equation for a single particle plus an additional non-linear interaction potential term. 10.1.20

The *Hartree density*

$$\boxed{\varrho^H(\vec{r}) = -e\sum_{j\sigma'}|\phi_j(\vec{r},\sigma')|^2}$$

gives rise to an effective Coulomb potential generated by the electron and is the so-called *direct term.*

The *Fock density*

$$\varrho^F_{i\sigma}(\vec{r},\vec{r}') = -e\sum_j \frac{\phi_j^*(\vec{r}'\sigma)\phi_i(\vec{r}'\sigma)\phi_j(\vec{r}\sigma)}{\phi_i(\vec{r}\sigma)}$$

arises from the indistinguishability of electrons and is also called the *exchange term.* Now, the task is to solve the Hartree-Fock equations, which is *difficult*, because the exchange term gives rise to an integral operator and the equation is strongly non-linear. A numerical solution is practically impossible for solids and large molecules.

So, we need *a further approximation*: we replace $\varrho^F_{i\sigma}$ by its average over i, which is independent of the index i:

$$\varrho^F_{i\sigma}(\vec{r},\vec{r}') \cong \varrho^F_{\sigma}(\vec{r},\vec{r}') = \frac{\sum_i \phi_i^*(r\sigma)\phi_i(r\sigma)\varrho^F_{i\sigma}(r,r')}{\sum_i \phi_i^*(r\sigma)\phi_i(r\sigma)}$$

In this case one can find a solution by applying an iterative algorithm:

1. Find an Ansatz for $\phi_i(\vec{r}\sigma)$ (e.g. plane waves, Bloch functions,...)
2. Evaluate the potential $U_\sigma(\vec{r}) = V_{\text{ion}}(\vec{r}) - e\int \mathrm{d}\vec{r}'\,\frac{\varrho^H(\vec{r}')-\varrho^F_\sigma(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}$
3. Solve the Schrödinger equation with potential $U_\sigma(\vec{r})$ and obtain the eigenfunctions $\phi_i(\vec{r},\sigma)$. Go back to 2.

6.1.1 Hartree-Fock approximation for free electrons

Progress can be made by neglecting the periodic potential of the ions. More precisely: we represent the ions by a uniform distribution of positive charge in order to maintain charge neutrality.
For free electrons:

$$\phi_i(\vec{r}\sigma) = \frac{e^{i\vec{k}_i\vec{r}}}{\sqrt{V}} \times \text{ spin wavefunction}$$

The Hartree density is then uniform and is exactly canceled by the uniform positive charge density due to the ions. The Hartree-Fock equations then reduce to the following

$$\left[-\frac{\hbar^2\nabla^2}{2m} + e\int \mathrm{d}\vec{r}'\,\frac{\varrho^F_{i\sigma}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\right]\phi_i(\vec{r},\sigma) = \varepsilon_i\phi_i(\vec{r},\sigma)$$

For plane waves

$$\varepsilon_i = \frac{\hbar^2 k_i^2}{2m} + \varepsilon_i^{\text{ex}}$$

where the exchange correction is given by

$$\varepsilon_i^{\text{ex}} = -e^2\sum_j \int \mathrm{d}\vec{r}'\,\frac{1}{|\vec{r}-\vec{r}'|}\frac{1}{V}e^{-i\vec{k}_j\vec{r}'+i\vec{k}_i\vec{r}'+i\vec{k}_j\vec{r}-i\vec{k}_i\vec{r}}$$

with the Fourier transformation

$$\frac{1}{|\vec{r}-\vec{r}'|} = 4\pi\frac{1}{V}\sum_{\vec{q}}\frac{1}{q^2}e^{i\vec{q}(\vec{r}-\vec{r}')}$$

This gives

$$\varepsilon_i^{\text{ex}} = -4\pi e^2\frac{1}{V^2}\sum_j\sum_q\frac{1}{q^2}\underbrace{\int \mathrm{d}\vec{r}'\,e^{i(\vec{q}+\vec{k}_j-\vec{k}_i)(\vec{r}-\vec{r}')}}_{=V\delta_{\vec{q}+\vec{k}_j,\vec{k}_i}} = -4\pi e^2\frac{1}{V}\sum_j\frac{1}{|\vec{k}_i-\vec{k}_j|^2}$$

where we used that the integral can be substituted by a Dirac delta in the case of an infinite volume V, thus we get a independence of $\vec{r}$. The summation extends over all occupied states: $|k_j| \leq k_F$

$$\begin{aligned}
\varepsilon^{\text{ex}}(\vec{k}) &= -4\pi e^2\int_{|\vec{k}|\leq k_F}\frac{\mathrm{d}\vec{k}'}{(2\pi)^3}\frac{1}{|\vec{k}-\vec{k}'|^2}\\
&= -\frac{4\pi e^2}{(2\pi)^3}\int_0^{k_F}\mathrm{d}k'k'^2 2\pi\int_{-1}^{1}\mathrm{d}\cos\theta\,\frac{1}{k^2+k'^2-2kk'\cos\theta}\\
&= -\frac{e^2}{\pi}\int_0^{k_F}\mathrm{d}k'k'^2\ln\left(\frac{k^2+k'^2-2kk'}{k^2+k'^2+2kk'}\right)\frac{1}{(-2kk')}\\
&= -\frac{2e^2}{\pi}k_F F\left(\frac{k}{k_F}\right)
\end{aligned}$$

where we defined the function

$$F(x) := \frac{1}{2}\int_0^1 \mathrm{d}y \frac{y}{2x} \ln\left(\frac{(x+y)^2}{(x-y)^2}\right) = \frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|$$

Using this result one can calculate the *total energy* of the electron system in the Hartree-Fock approximation

$$E_{\mathrm{HF}} = 2\sum_{|\vec{k}|\leq k_F}\left(\frac{\hbar^2 k^2}{2m} + \varepsilon^{\mathrm{ex}}(\vec{k})\right) = 2V\int_0^{k_F}\frac{\mathrm{d}k k^2}{(2\pi)^3}4\pi\left(\frac{\hbar^2 k^2}{2m} + \varepsilon^{\mathrm{ex}}(k)\right)$$

with the *Fermi energy*

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

and the number of electrons

$$N = 2\sum_{|\vec{k}|\leq k_F} = \frac{k_F^3 V}{3\pi^2}$$

we obtain the total energy of the electron system per number of electrons

$$\boxed{\frac{E_{\mathrm{HF}}}{N} = \frac{3}{5}E_F - \frac{3}{4}\frac{e^2 k_F}{\pi}}$$

The first term is the a non-interacting term and the second the exchange correction. This can also be expressed in terms of the Rydberg energy $\frac{e^2}{2a} = 1\,\mathrm{Ry} = 13.6\,\mathrm{eV}$ and the Bohr radius $a = \frac{\hbar^2}{me}$:

$$\frac{E_{\mathrm{HF}}}{N} = \frac{e^2}{2a}\left[\frac{3}{5}(k_F a^2 - \frac{3}{2\pi}k_F a\right]$$

The Hartree-Fock correction is the leading correction in the high density limit, ie, in the small parameter $\frac{1}{k_F a}$ which is dimensionless due to the introduction of the Rydberg energy. One can show that the next-to-leading correction is of order $\ln(k_F a)$, ie, the energy per particle is given by

$$\frac{E}{N} = \frac{e^2}{2a}\left[\frac{3}{5}(k_F a)^2 - \frac{3}{2\pi}k_F a + \mathcal{O}(\ln k_F a)\right]$$

The parameter $\frac{1}{k_F a}$ is also often discussed in terms of the r_s *radius* of a sphere defined by the volume $\frac{1}{n}$

$$\frac{1}{n} = \frac{V}{N} = \frac{3\pi^2}{k_F^3} = \frac{4\pi}{3}r_s^3$$

Now, we can alternatively express the small parameter $k_F a$ by the radius

$$\frac{1}{k_F a} = \sqrt[3]{\frac{4}{9\pi}}\frac{r_s}{a}$$

6.2 Density functional theory (DFT)

For this theory the nobel prize in Chemistry was given to W.Kohn in 1998. It is based on the *Hohenberg-Kohn theorem* (1964):
The grand state energy E_0 of electrons in an arbitrary potential $V(\vec{r})$ is a functional of the local particle density $n(\vec{r})$:

$$E_0 = E_0[n(\vec{r})] = \underbrace{T[n(\vec{r})]}_{\text{kinetic energy}} + \underbrace{\int \mathrm{d}\vec{r} V(\vec{r}) n(\vec{r})}_{\text{potential energy}} + \underbrace{U[n(\vec{r})]}_{\text{interaction energy}}$$

where the functionals T and U are independent of the potential V.
Remarks

- idea of proof: $E_0 = E_0[V(\vec{r})]$ is a functional of the potential V. So, it is possible to use Legendre transformation to show that $E_0[n(\vec{r})]$
- the functionals T and U are not known and likely to be highly non-local and non-linear.
- the interaction energy possesses a long-range (non-local, can be seen by the integral over r and r') Hartree term

$$U[n(\vec{r})] = \underbrace{\frac{e^2}{2} \int \mathrm{d}\vec{r} \mathrm{d}\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|}}_{\text{Hartree term}} + \underbrace{E_{\text{ex}}[n(\vec{r})]}_{\text{rest}}$$

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Approximation of the kinetic term:

$$T[n(\vec{r})] = 2 \int \mathrm{d}\vec{r} \sum_i \varphi_i^*(\vec{r}) \left(-\frac{\hbar^2 \nabla^2}{2m} \right) \varphi_i(\vec{r})$$

where $\varphi_i(\vec{r})$ are complex systems but can be interpreted as hypothetical single-particle wavefunctions.They have to obey

$$n(\vec{r}) = \sum_{i,occ} |\varphi_i(\vec{r})|^2$$

Minimizing the energy functional E_0 with the constraint

$$\int \mathrm{d}\vec{r} |\varphi_i(\vec{r})|^2 = 1$$

for each i by introducing Lagrange multipliers ε_i then yields

$$\boxed{\left(-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{eff}}(\vec{r}) \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})}$$

with effective potential

$$\boxed{V_{\text{eff}}(\vec{r}) = V(\vec{r}) + \int \mathrm{d}\vec{r}' \frac{e^2 n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\partial E_{\text{ex}}[n(\vec{r})]}{\delta n(\vec{r})}}$$

Those equations are called *Kohn-Sham equations.*
remarks

- the problem is reduced to solve an effective single-particle Schrödinger equation self-consistently as functional $V_{\text{eff}} = V_{\text{eff}}[n]$
- the approximation allows to determine the groundstate energy E_0 which is useful to determine positions of atoms in molecules/ crystals by minimizing $E_0(\{R_n\})$ (step II of adiabatic approximation)
- strictly speaking: there is no direct physical meaning of ε_i and $\varphi_i(\vec{r})$. However both are often interpreted as energies and wavefunctions of electrons
- Now, we also need an approximation for the exchange term $E_{\text{ex}}[n]$

Local density approximation (LDA)

We neglect all non-local contributions and replace the functional with a function:

$$E_{\text{ex}}^{\text{LDA}}[n(\vec{r})] = \int \mathrm{d}\vec{r}\varepsilon_{\text{ex}}(n(\vec{r}))$$

so also the derivative reduces to

$$\frac{\delta E_{\text{ex}}^{\text{LDA}}}{\delta n(\vec{r})} = \frac{\partial \varepsilon_{\text{ex}}}{\partial n(\vec{r})}$$

The function ε_{ex} is often approximated by the free-electron expression:

$$E_{\text{ex}}^{\text{LDA}} = -N\frac{3}{4}\frac{e^2 k_F}{\pi} = V\varepsilon_{\text{ex}}$$

with exchange density

$$\varepsilon_{\text{ex}} = -n\frac{3}{4}\frac{e^2 k_F}{\pi} = -\frac{3}{4\pi}e^2 n(3\pi^2 n)^{\frac{1}{3}}$$

It follows

$$\boxed{\frac{\partial \varepsilon_{\text{ex}}}{\partial n} = -\frac{e^2}{\pi}(3\pi^2 n)^{\frac{1}{3}}}$$

remarks:

- improvements to LDA by including also dependencies on gradients ∇b. This approximation is known as generalized gradient approximation (GGA)
- implementation of LDA etc. available in the form of (commercial) ready-to-use software packages
- LDA fails sometimes completely if interactions are strong. Modern development, combination with field theoretic methods (LDA+U, LDA+DMFT, etc.)

6.3 Screening

In chapter 6.1 und 6.2 we have focused on an effective ionic potential modified by electron-electron interaction. Now, consider a positively charged particle rigidly fixed at a certain position. Mobile electrons get attracted creating surplus of negative charge in its vicinity reducing its field. This effect is called *screening.* If ϱ^{ext} is the positive charge density of the particle we have

$$-\nabla^2 \phi^{\text{ext}} = 3\pi \varrho^{\text{ext}}$$

which is the Poisson equation for the associated potential ϕ^{ext}.
For the full potential

$$-\nabla^2 \phi = 4\pi \varrho$$

with

$$\varrho = \varrho^{\text{ext}} + \varrho^{\text{ind}}$$

where ϱ^{ind} is the charge density induced in the electron gas. We define the *dielectric function* ε

$$\phi^{\text{ext}}(\vec{r}) = \int \mathrm{d}\vec{r}' \varepsilon(\vec{r}, \vec{r}') \phi(\vec{r}')$$

For a translationary invariant system (for simplicity) is is only dependent on the space difference

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

With the Fourier transform

$$\varepsilon(\vec{q}) = \int \mathrm{d}V r e^{-i\vec{q}\vec{r}} \varepsilon(\vec{r})$$

we finally get

$$\boxed{\phi(\vec{q}) = \frac{1}{\varepsilon(\vec{q})} \phi^{\text{ext}}(\vec{q})}$$

How does the induced charge density ϱ^{ind} depend on ϕ? For weak ϕ we expect a linear relation.
Definition:

$$\varrho^{\text{ind}}(\vec{q}) := \chi_0(\vec{q}) \phi(\vec{q})$$

with suszeptibility χ_0. We relate ε and χ via the Poisson equations

$$\phi(\vec{q}) = \frac{4\pi \varrho(\vec{q})}{4\pi^2} = \frac{4\pi \varrho^{\text{ext}}(\vec{q})}{q^2} + \frac{4\pi \chi_0(\vec{q}) \phi(\vec{q})}{q^2} = \phi^{\text{ext}}(\vec{q}) + \frac{4\pi \chi_0(\vec{q}) \phi(\vec{q})}{q^2}$$

This gives

$$\boxed{\varepsilon(\vec{q}) = 1 - \frac{4\pi}{q^2} \chi_0(\vec{q})}$$

For the evaluation of χ_0 and ε one needs to employ approximations.

6.3.1 Thomas-Fermi theory of screening

We consider the Schrödinger equation of free electrons in the Hartree approximation

$$\left(-\frac{\hbar^2\nabla^2}{2m} - e\phi(\vec{r})\right)\psi_i = \varepsilon_i\psi_i$$

where the potential $\phi(\vec{r})$ is due to positive charge and induced by rearrangement in the electron system.The potential modifies locally the chemical potential μ. For a function $\phi(\vec{r})$ that is slowly varying on the scale of inverse Fermi wavevector $\frac{1}{k_F}$, one can employ the semi-classical approximation and define a local density of electrons

$$n(\vec{r}) = n(\mu + e\phi(\vec{r})$$

This leads to a locally induced charge density

$$\varrho^{\text{ind}}(\vec{r}) = -e(n(\vec{r}) - n_0) = -e(n(\mu + e\phi(\vec{r})) - n(\mu)) = -e^2\frac{\partial n_0}{\partial\mu}\phi(\vec{r}) + \mathcal{O}(\phi^2)$$

From which follows

$$\chi_0(\vec{q}) = -e^2\frac{\partial n}{\partial\mu}$$

which is independent of $\vec{q}$ that gives $\varepsilon(\vec{q})$ in the *Thomas-Fermi approximation*

$$\boxed{\varepsilon(\vec{q}) = 1 + \frac{k_{\text{TF}}^2}{q^2}}$$

with the Thomas-Fermi wavevector

$$k_{\text{TF}}^2 = 4\pi e^2\frac{\partial n_0}{\partial\mu}$$

From the expression for the density

$$n_0 = 2\int\frac{\mathrm{d}\vec{k}}{(2\pi)^3}f(\varepsilon_k - \mu) = \int \mathrm{d}\varepsilon\nu(\varepsilon)f(\varepsilon - \mu)$$

follows for low temperatures $T \ll T_F$.

$$\frac{\partial n_0}{\partial\mu} = \int \mathrm{d}\varepsilon\nu(\varepsilon)(-f'(\varepsilon - \mu)) \cong \nu(\varepsilon_F)$$

where $\nu(\varepsilon_F)$ is the density of states of the Fermi level. For free electrons

$$\varepsilon_k = \frac{\hbar^2k^2}{2m}, \qquad \nu(\varepsilon_F) = \frac{mk_F}{\hbar^2\pi^2}$$

we get

$$k_{\text{TF}}^2 = 4\pi e^2\frac{mk_F}{\hbar^2\pi^2} = \frac{4}{T}\frac{k_F}{a}$$

with Bohr radius $a = \frac{\hbar^2}{me^2}$. Usually for metals $k_F a \sim \mathcal{O}(1)$, hence, $k_{\mathrm{TF}} \sim k_F$ and $\frac{1}{k_F} \sim \mathcal{O}(1\,\text{Å})$.
Illustration of the significance of k_{TF}: Consider a point charge

$$\phi^{\mathrm{ext}}(\vec{r}) = \frac{Q}{|\vec{r}|} \quad \Rightarrow \quad \phi^{\mathrm{ext}}(\vec{q}) = \frac{4\pi Q}{q^2}$$

The total potential is given by

$$\phi(\vec{q}) = \frac{1}{\varepsilon(\vec{q})}\phi^{\mathrm{ext}}(\vec{q}) = \frac{4\pi Q}{q^2 + k_{\mathrm{TF}}^2}$$

In real space we get the *screened Coulomb potential*

$$\boxed{\phi(\vec{r}) = \int \frac{\mathrm{d}\vec{q}}{(2\pi)^3} e^{i\vec{q}\vec{r}} \phi(\vec{q}) = \frac{Q}{|\vec{r}|} e^{-k_{\mathrm{TF}}|\vec{r}|}}$$

that decays exponentially on the length scale of the inverse Thomas-Fermi wavevectors $\frac{1}{k_{\mathrm{tF}}}$. Hence, electrons are highly effective in screening the external charge! 17.1.20

21.1.20

$$\boxed{\omega_{\mathrm{ion}}^2(q) = \frac{\Omega_p^2}{\varepsilon_{\mathrm{el}}}}$$

with ionic plasma frequency $\Omega_p^2 = \frac{Zm}{M}\omega_p^2$. With the Thomas Fermi result $\epsilon_{\mathrm{el}}(\vec{q}) = 1 + \frac{k_{\mathrm{TF}}^2}{q^2}$ one obtains

$$\omega_{\mathrm{ion}}^2(\vec{q})^2 = \frac{\Omega_p^2}{q^2 + k_{\mathrm{TF}}^2} q^2 \overset{|\vec{q}| \to 0}{\approx} \frac{\Omega_p^2}{k_{\mathrm{TF}}^2} q^2$$

with the sound velocity $e^2 = \frac{\Omega_p^2}{k_{\mathrm{TF}}^2}$. Using the free electron

$$k_{\mathrm{TF}}^2 = 4\pi e^2 \frac{mk_F}{\pi^2\hbar^2}$$

we get

$$c^2 = \frac{Zm}{M}\frac{\omega_p^2}{k_{\mathrm{TF}}^2} = \frac{Zm}{M}\frac{4\pi n_0 e^2}{m}\frac{\pi^2\hbar^2}{4\pi e^2 m k_F} = \frac{Zm}{M}\frac{n_0}{m}\frac{\pi^2\hbar^2}{mk_F}$$

We can simplify this further by using the electron density $n_0 = \frac{k_F^3}{3\pi^2}$ and the Fermi velocity $v_F = \frac{\hbar k_F}{m}$:

$$\boxed{c^2 = \frac{1}{3}\frac{Zm}{M} v_F^2}$$

this is the so-called *Bohm-Staver relation.* This predicts in particular $\frac{c}{v_F} \sim \sqrt{\frac{m}{M}} \sim \frac{1}{100}$ in agreement with values observed in many materials (note that $\frac{c}{v_F} \sim \frac{\theta_D}{T_F}$).
Using the Lindhord result for $\epsilon_{\mathrm{el}}(\vec{q})$ the above considerations also predict (weak) singularities at $|\vec{q}| = 2k_F$ in the phonon spectrum. These are known as *Vohn anomalies.* Thus, the positions of Kohn anomalies reflect the geometry of the Fermi surface (obtained eg. from de Haas-van-Alphen oscillations).

6.4 6.5. Dieletric function of a metal and effective electron-electron interaction

In a metal screening occurs by all charged particles, electrons and ions. Consider now an additional ionic source for screening. An external potential ϕ^{ext} induces a total potential ϕ via the dielectric function:

$$\varepsilon\phi = \phi^{\text{ext}}$$

The total potential consists of:

$$\phi = \phi^{\text{ext}} + \phi^{\text{ion}} + \phi^{\text{el}}$$

with the potential due to the positively charged ions, ϕ^{ion}, and the negatively charged electrons, ϕ^{el}. We can define a dielectric function describing the response of the electronic and ionic subsystem alone, ε^{el} and ε^{ion}, respectively.
The electronic system responds to the sum of potentials

$$\phi^{\text{ext}} + \phi^{\text{ion}}$$

so that

$$\varepsilon^{\text{el}}\phi = \varepsilon^{\text{ext}} + \phi^{\text{ion}}.$$

The ionic system responds to $\phi^{\text{ext}} + \phi^{\text{el}}$:

$$\varepsilon^{\text{ion}}\phi = \phi^{\text{ext}} + \phi^{\text{el}}$$

Summing the two equations:

$$(\varepsilon^{\text{el}} + \varepsilon^{\text{ion}})\phi = \phi^{\text{ext}} + \underbrace{(\phi^{\text{ext}} + \phi^{\text{ion}} + \phi^{\text{el}})}_{=\phi}$$

So we obtain

$$\boxed{\varepsilon = \varepsilon^{\text{el}} + \varepsilon^{\text{ion}} - 1}$$

We use the simplest expression for ε^{el} and ε^{ion}:

- treat the electrons in the Thomas-Fermi approximation

  $$\varepsilon^{\text{el}}(\vec{q}) = 1 + \frac{k_{\text{TF}}^2}{q^2}$$

- treat the ions as a gas of charged particles:

  $$\varepsilon^{\text{ion}}(\omega) = 1 - \frac{\Omega_p^2}{\omega^2}$$

  with the Plasma frequency $\Omega_p^2 = \frac{4\pi n_{\text{ion}}(Ze)^2}{M}$ (see chap. 5)

The frequency and momentum are dependent on the dielectric function

$$\boxed{\varepsilon(\vec{q},\omega) = 1 + \frac{k_{\text{TF}}^2}{q^2} - \frac{\Omega_p^2}{\omega^2}}$$

Alternative interpretation

The potential after screening by the electrons is given by

$$\phi^{\text{el, screend}} = \frac{1}{\varepsilon^{\text{el}}}\phi^{\text{ext}}$$

the full potential is then obtained when $\phi^{\text{el, screened}}$ is in addition shielded by the ions which are themselves screened i.e. dressed by the electrons

$$\phi = \frac{1}{\varepsilon^{\text{ion}}_{\text{dressed}}}\phi^{\text{el, screend}} = \frac{1}{\varepsilon^{\text{ion}}_{\text{dressed}}}\frac{1}{\varepsilon^{\text{el}}}\phi^{\text{ext}}$$

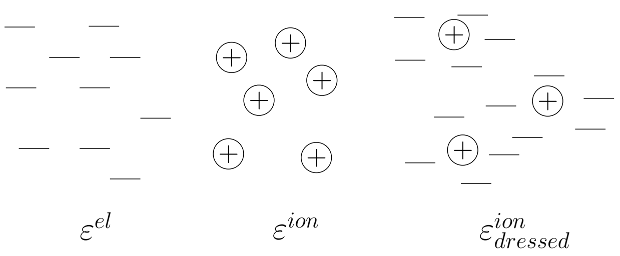

Figure 53: Ions dressed by electrons

Identification with ε yields $\frac{1}{\varepsilon} = \frac{1}{\varepsilon^{\text{ion}}_{\text{dressed}}}\frac{1}{\varepsilon^{\text{ el}}}$ gives

$$\varepsilon^{\text{ion}}_{\text{dressed}} = \frac{\varepsilon}{\varepsilon^{\text{el}}} = 1 + \frac{\varepsilon^{\text{ion}} - 1}{\varepsilon^{\text{el}}}$$

Finally we obtain

$$\boxed{\varepsilon^{\text{ion}}_{\text{dressed}}(\vec{q},\omega) = 1 - \frac{\frac{\Omega_p^2}{\varepsilon^{\text{el}}(\vec{q})}}{\omega^2} = 1 - \frac{\omega^2_{\text{ion}}(\vec{q})}{\omega^2}}$$

The screening has consequences for the effective electron-electron interaction. The bare electrons interact via the *Coulomb potential* in momentum space

$$V(\vec{q}) = \frac{4\pi e^2}{q^2}$$

The screening by electrons and ions yields the effective interaction

$$\boxed{V_{\text{eff}}(\vec{q},\omega) = \frac{4\pi e^2}{q^2\varepsilon(\vec{q},\omega)} = \underbrace{\frac{4\pi e^2}{q^2 + k_{\text{TF}}^2}}_{\text{screened by el.}} \cdot \underbrace{\frac{1}{1 - \frac{\omega^2_{\text{ion}}(\vec{q})}{\omega^2}}}_{\text{add. screened by dr. ions}}}$$

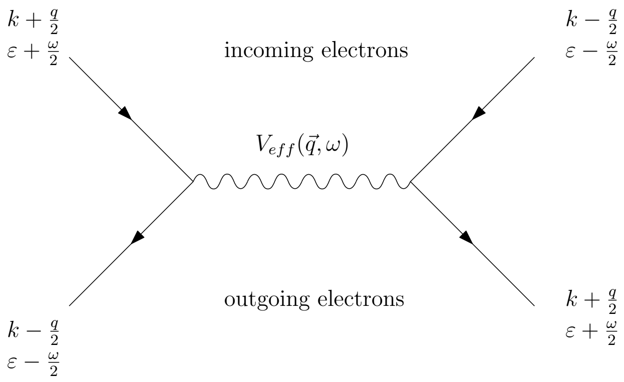

Figure 54: Exchange of energy $\hbar\omega$ and momentum $\hbar q$

Remarks:

- phonon frequencies are bounded by the Debye frequency: $\omega_{\text{ion}}(\vec{q}) \lesssim \omega_D$. The interaction possesses a substantial ω-dependence only for frequencies $\omega \lesssim \omega_D$. As the Fermi energy $E_F \gg \hbar\omega_D$ only electrons close to the Fermi energy are affected.
- for small energy transfer the effective interaction for $\frac{\omega_{\text{ion}}(\vec{q})}{\omega} > 1$ changes sign and becomes *attractive* (overscreening)! This is important for the theory of superconductivity.
- rigorous theory for the effective interaction V_{eff} requires advanced field theoretical methods.

6.5 Cooper instability

Due to overscreening by phonons the interaction between electrons becomes attractive. Do electrons form bound pairs? Consider the scattering of two electrons with a constant attractive interaction

$$V_{\text{eff}}(\vec{q},\omega) = -g$$

with $g > 0$. It is characterized by the scattering T-matrix which is obtained by summing up repeated scattering events.

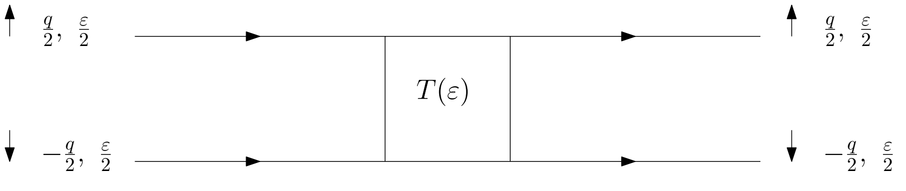

Figure 55: We consider two electrons with opposite sign configurations, vanishing total momentum and total energy ε measured with respect to ε_F

. The energy-dependent T-matrix is given by the summation of repeated scattering 24.1.20

events:

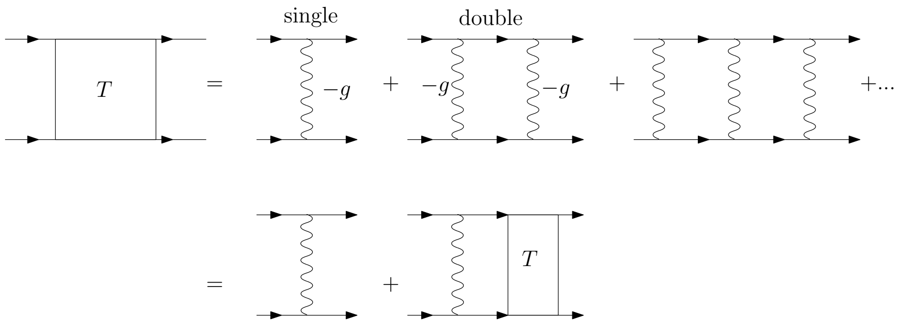

Figure 56: Summation of repeated scattering events

From scattering theory follows

$$T(\varepsilon) = -g + (-g)\frac{1}{\nu}\sum_q \frac{T(\varepsilon)}{\varepsilon - (\xi_{\frac{q}{2}} + \xi_{-\frac{q}{2}}}((1 - f_{\frac{q}{2}})(1 - f_{\frac{-q}{2}}) - f_{\frac{q}{2}} f_{\frac{-q}{2}})$$

Here, ε is the energy of the intermediate state, $\xi_{\frac{q}{2}} + \xi_{-\frac{q}{2}}$ is the dispersion. The intermediate state needs to be unoccupied in case of particles $((1 - f_{\frac{q}{2}})(1 - f_{\frac{-q}{2}}))$ and the last term is needed in case of holes. For $\xi_{-k} = \xi_k$ we get

$$T(\varepsilon) = (-g) + (-g)T(\varepsilon)\frac{1}{\nu}\sum_q \frac{1 - 2f_{\frac{q}{2}}}{\varepsilon - 2\xi_{\frac{q}{2}}}$$

In the *absence* of a Fermi sea:

- The problem reduces to a two-particle scattering problem that can be solved by elementary methods
- effective single-particle problem for wavefunction dependent on relative coordinate
- The T-matrix is obtained by setting $f_{\frac{q}{2}} = 0$, no other particles are present and $E_F = 0$

  $$T(\varepsilon) = (-g) + (-g)T(\varepsilon)\underbrace{\int \frac{\mathrm{d}\vec{q}}{(2\pi)^3}\frac{1}{\varepsilon - 2\xi_{\frac{q}{2}}}}_{\propto\sqrt{\varepsilon}}$$

  The approximation is valid for quadratic dispersion
- in order to obtain a bound state the attractive interaction must be sufficiently strong

However in the *presence* of a Fermi sea

$$\begin{aligned} T(\varepsilon) &= (-g) + (-g)T(\varepsilon)\nu \int \mathrm{d}\xi \frac{1}{\varepsilon - 2\xi} \underbrace{(1 - 2f(\xi))}_{=\mathrm{sgn}\xi \text{ at } T=0} \\ &= (-g) + (-g)T(\varepsilon)\nu \underbrace{\int_{-\hbar\omega_D}^{\hbar\omega_D} \frac{\mathrm{sgn}\xi}{\varepsilon - 2\xi}}_{\cong -\ln\frac{2\hbar\omega_D}{\varepsilon} \text{ for } \varepsilon \ll \hbar\omega_D} \end{aligned}$$

It follows that

$$T(\varepsilon) = \frac{-g}{1 + (-g\nu)\ln\frac{2\hbar\omega_D}{\varepsilon}}$$

possesses a bound state ie. a pole at

$$1 - gr\ln\frac{2\hbar\omega_D}{\varepsilon} = 0$$

Thus,

$$\boxed{\varepsilon = 2\hbar\omega_D \exp\left(-\frac{1}{g\nu}\right)}$$

Remarks:

- the bound state energy is non-perturbative in gr and present even for infinitesimal attractive interaction!
- in the presence of a Fermi sea electrons form a bound state and lower the total energy. Hence, the Fermi sea becomes unstable: *Cooper instability*

7 Superconductivity

The cooper instability indicated that the Fermi sea in the presence of an attractive e-e interaction is unstable with respect to the formation of bound e-e pairs. The resulting state is a so-called superconductor characterized by perfect conductivity and perfect diamagnetism (Meissner effect).

7.1 BCS theory of superconductivity

J. Bordeen, L. Cooper and R. Schrieffer (BCS) proposed 1957 a theory of superconductivity (nobel prize 1972).
Consider the BCS Hamiltonian

$$H_{\mathrm{BCS}} = \sum_{k\sigma} \xi_k c^\dagger_{k\sigma} c_{k\sigma} - g\frac{1}{V}\sum_{kk'} c^\dagger_{k\uparrow} c^\dagger_{-k\downarrow} c_{-k'\downarrow} c_{k'\uparrow}$$

It is implicitly assumed that the attractive interaction $g > 0$ is only active for electron energies $\xi_k = \varepsilon_k - \mu$ within an energy shell $|\xi_k| \lesssim \hbar\omega_D$.
The formation of bound states is reflected in finite expectation values

$$\langle c^\dagger_{k\uparrow} c^\dagger_{-k\downarrow}\rangle \neq 0$$

and

$$\langle c_{-k'\downarrow} c_{k'\uparrow}\rangle \neq 0$$

In order to find a mean-field description of the superconducting state, a mean-field decoupling of the interaction according to

$$AB = \underbrace{(A - \langle A\rangle)(B - \langle B\rangle)}_{\text{fluctuations are neglected}} + \langle A\rangle B + A\langle B\rangle - \langle A\rangle\langle B\rangle \overset{\text{MF}}{\approx} \langle A\rangle B + A\langle B\rangle - \langle A\rangle\langle B\rangle$$

This yields the mean-field BCS Hamiltonian

$$H^{\text{MF}}_{\text{BCS}} = \sum_{k,\sigma} \xi_k c^\dagger_{k\sigma} c_{k\sigma} - \frac{g}{\nu}\sum_{kk'}(\langle c^\dagger_{k\uparrow} c^\dagger_{k\downarrow}\rangle c_{-k'\downarrow}c_{k'\uparrow} + c^\dagger_{k\uparrow}c^\dagger_{-k\downarrow}\langle c_{-k'\downarrow}c_{k'\uparrow}\rangle - \langle c^\dagger_{k\uparrow}c^\dagger_{-k\downarrow}\rangle\langle c_{-k'\downarrow}c_{k'\uparrow}\rangle)$$

Introducing the abbreviation for $|\xi_k| \lesssim \hbar\omega_D$

$$\Delta = \frac{g}{\nu}\sum_k \langle c_{-k\downarrow}c_{k\uparrow}\rangle$$

and

$$\Delta^* = \frac{g}{\nu}\sum_k \langle c^\dagger_{k\uparrow}c^\dagger_{-k\downarrow}\rangle$$

we finally get

$$\boxed{H^{\text{MF}}_{\text{BCS}} = \sum_{k\sigma} \xi_k c^\dagger_{k\sigma}c_{k\sigma} - \sum_k(\Delta^* c_{-k\downarrow}c_{k\uparrow} + c^\dagger_{k\uparrow}c^\dagger_{-k\downarrow}\Delta) + \nu\frac{|\Delta^2|}{g}}$$

It is convenient to introduce the two-component *Nambu spinor* operators

$$\vec{\psi}_k = \begin{pmatrix} c_{k\uparrow} \\ c^\dagger_{-k\downarrow}\end{pmatrix}, \quad \vec{\psi}^\dagger_k = \begin{pmatrix} c^\dagger_{k\uparrow} & c_{-k\downarrow}\end{pmatrix}$$

Using that $c^\dagger_{k\downarrow}c_{k\downarrow} = 1 - c_{k\downarrow}c^\dagger_{k\downarrow}$ we can rewrite

$$H^{\text{MF}}_{\text{BCS}} = \sum_k \vec{\psi}^\dagger_k h_k \vec{\psi}_k + \sum_k \xi_k + \nu\frac{|\Delta|^2}{g}$$

with the matrix

$$h_k = \begin{pmatrix} \xi_k & -\Delta \\ -\Delta^* & -\xi_{-k}\end{pmatrix}$$

where we will assume $\xi_{-k} = \xi_k$ in the following. The eigenvalues of h_k come in pairs $\pm E_k$ with $E_k = \sqrt{\xi_k^2 + |\Delta|^2}$ due to the particle-hole symmetry

$$\tau^y h_k^* \tau^y = -h_k$$

with

$$\tau^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

The eigenvectors can be chosen to be of the form

$$h_k \begin{pmatrix} u_k \\ v_k \end{pmatrix} = E_k \begin{pmatrix} u_k \\ v_k \end{pmatrix}$$

and

$$h_k \begin{pmatrix} -v_k^* \\ u_k^* \end{pmatrix} = -E_k \begin{pmatrix} -v_k^* \\ u_k^* \end{pmatrix}$$

In order to diagonalize the Hamiltonian we perform a *Bololinbor* transformation and introduce new fermionic operators $a_{k\sigma}$

$$\vec{\psi}_k = U_k \begin{pmatrix} a_{k\uparrow} \\ a^\dagger_{-k\downarrow} \end{pmatrix}$$

with

$$U_k = \begin{pmatrix} u_k & -v_k^* \\ v_k & u_k^* \end{pmatrix}$$

or explicitely

$$\begin{aligned} c_{k\uparrow} &= u_k a_{k\uparrow} - v_k^* a^\dagger_{-k\downarrow} \\ c^\dagger_{-k\downarrow} &= v_k a_{k\uparrow} + u_k^* a^\dagger_{-k\downarrow} \end{aligned}$$

For the fermionic anticommutation relations follows

$$\{c_{k\uparrow}, c^\dagger_{k\uparrow}\} = |u_k|^2 \underbrace{\{a_{k\uparrow}, a^\dagger_{k\uparrow}\}}_{=1} + |v_k|^2 \underbrace{\{a^\dagger_{-k\downarrow}, a_{-k\downarrow}\}}_{=1} = |u_k|^2 + |v_k^2| = 1$$

and analogue

$$\{c_{k\uparrow}, c_{-k\downarrow}\} = ... = u_k v_k^* - v_k^* u_k = 0$$

which is equivalent to

$$U_k U_k^\dagger = U_k \dagger U_k = 1$$

, ie. the matrix U_k is unitary. As the matrix U_k is unitary this yields the conditions 28.1.20

$$|u_k|^2 + |v_k|^2 = 1 \qquad n_k v_k^* - v_k^* u_k = 0$$

An explicit calculation yields for the coefficients:

$$|u_k|^2 = \frac{1}{2}\left(1 + \frac{\xi_k}{E_k}\right), \quad |v_k|^2 = \frac{1}{2}\left(1 - \frac{\xi}{E_k}\right)$$

and

$$u_k v_k^* = -\frac{\Delta}{2E_k}$$

For the Hamiltonian we obtain

$$\boxed{H_{\text{BCS}}^{\text{MF}} = \sum_k \begin{pmatrix} a_{k\uparrow}^\dagger & a_{-k\downarrow} \end{pmatrix} \begin{pmatrix} E_k & 0 \\ 0 & -E_k \end{pmatrix} \begin{pmatrix} a_{k\uparrow} \\ a_{-k\downarrow}^\dagger \end{pmatrix} + \sum_k \xi_k + V\frac{|\Delta|^2}{g} = \sum_{k\sigma} E_k a_{k\sigma}^\dagger a_{k\sigma} + \varepsilon_0 V}$$

where we used $E_{-k} = E_k$. The ground state energy density is obtained as

$$\begin{aligned}
\varepsilon_0 &= \frac{1}{V}\sum_k (\xi_k - E_k) + \frac{|\Delta|^2}{g} \\
&= \int \frac{\mathrm{d}\vec{k}}{(2\pi)^3}(\xi_k - \sqrt{|\Delta|^2 + \xi_k^2} + \frac{|\Delta|^2}{g} \\
&\cong \nu \int_{-\hbar\omega_D}^{\hbar\omega_D} \mathrm{d}\xi(\xi - \sqrt{|\Delta|^2 + \xi^2}) + \frac{|\Delta|^2}{g} \\
&= -\nu\left[\frac{1}{2}\sqrt{|\Delta|^2 + \xi^2} + \frac{|\Delta|^2}{2}\ln(\xi + \sqrt{|\Delta|^2 + \xi^2}\right] \sqrt{-\hbar\omega_D}^{\hbar\omega_D} + \frac{|\Delta|^2}{g} \\
&= -\nu\hbar\omega_D\sqrt{|\Delta|^2 + (\hbar\omega_D)^2} - \nu\frac{|\Delta|^2}{2}\ln\left(\frac{\hbar\omega_D + \sqrt{|\Delta|^2 + (\hbar\omega_D)^2}}{-\hbar\omega_D + \sqrt{|\Delta|^2 + (\hbar\omega_D)^2}}\right) + \frac{|\Delta|^2}{g}
\end{aligned}$$

in the limit $|\Delta|^2 \ll \hbar\omega_D$ using

$$\sqrt{|\Delta|^2 + (\hbar\omega_D)^2} \approx \hbar\omega_D\left(1 + \frac{1}{2}\frac{|\Delta|^2}{(\hbar\omega_D)^2}\right)$$

it follows

$$\boxed{\varepsilon_0 \cong \text{const.} \; - \nu\frac{|\Delta|^2}{2} - \nu|\Delta|^2\ln\frac{2\hbar\omega_D}{|\Delta|} + \frac{|\Delta|^2}{g}}$$

Minimizing the ground state energy with respect to $|\Delta|$:

$$\frac{\partial\varepsilon_0}{\partial|\Delta|} = -\nu|\Delta| - 2\nu|\Delta|\ln\frac{2\hbar\omega_D}{|\Delta|} + \nu|\Delta| + \frac{2|\Delta|}{g} \overset{!}{=} 0$$

trivial solution: $|\Delta| = 0$ with energy $\varepsilon_0 = \text{const} = \varepsilon_0(|\Delta| = 0)$
non-trivial solution: $\Delta \neq 0$:

$$-\nu\ln\frac{2\hbar\omega_D}{|\Delta|} + \frac{1}{g} = 0$$

Thus

$$\boxed{|\Delta| = 2\hbar\omega_D e^{-\frac{1}{g\nu}}}$$

possesses the lower energy

$$\varepsilon_0 = \varepsilon_0(|\Delta| = 0) - \frac{\nu}{2}(2\hbar\omega_D)^2 e^{-\frac{2}{g\nu}}$$

So, if we have an attractive interaction, the supra state is energetic preferable.

7.1.1 BCS groundstate wavefunction

The Bogolinbov annihilation operator $a_{k\sigma}$ acting on the BCS groundstate wavefunction $|BCS\rangle$ gives:

$$a_{k\sigma}\,|BCS\rangle = 0 \quad \forall\ k, \sigma$$

where the transformation

$$a_{k\uparrow} = u_k^* c_{k\uparrow} + v_k^* c_{-k\downarrow}^\dagger, \quad a_{-k\downarrow} = u_k^* c_{-k\downarrow} - v_k^* c_{k\uparrow}^\dagger$$

relates $a_{k\sigma}$ to the original creation/annihilation operators. This can be solved with an Ansatz involving the superposition of states with different number of particles

$$|BCS\rangle = \prod_k (u_k - v_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger)\,|0\rangle$$

where the product runs over wavevectors within a finite shell close to $|\vec{k}| \approx k_F$.
The equation $a_{k\sigma}\,|BCS\rangle = 0$ follows from certain terms of the product yielding:

$$\begin{aligned}
a_{k\uparrow}(u_k - v_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger)\,|0\rangle &= (u_k^* c_{k\uparrow} + v_k^* c_{-k\downarrow}^\dagger)(u_k - v_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger)\,|0\rangle \\
&= (|u_k|^2 c_{k\uparrow} + v_k^* u_k c_{-k\downarrow}^\dagger - u_k^* v_k \underbrace{c_{k\uparrow} c_{k\uparrow}^\dagger}_{=1 - c_{k\uparrow}^\dagger c_{k\uparrow}} c_{-k\downarrow}^\dagger - |v_k|^2 c_{-k\downarrow}^\dagger c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger)\,|0\rangle \\
&= (v_k^* u_k c_{-k\downarrow}^\dagger - u_k^* v_k c_{-k\downarrow}^\dagger)\,|0\rangle = 0
\end{aligned}$$

Where we used that all annihilation operators $c_{k\uparrow}$ acting on the groundstate $|0\rangle$ vanish and the result is 0 because of the unitarity condition. We get as well in a similar way

$$a_{-k\downarrow}(u_k - v_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger)\,|0\rangle = \ldots = 0$$

7.1.2 Gap equation at finite temperature

The gap is defined as (with condition $|\xi_k| \le \hbar\omega_D$

$$\begin{aligned}
\Delta &:= \frac{g}{V}\sum_k \langle c_{-k\downarrow} c_{k\uparrow}\rangle = \frac{g}{V}\sum_k \langle (v_k^* a_{k\uparrow}^\dagger + u_k a_{-k\downarrow})(u_k a_{K\uparrow} - v_k^* a_{-k\downarrow}^\dagger)\rangle \\
&= \frac{g}{V}\sum_k [u_k v_k^* \langle a_{k\uparrow}^\dagger a_{k\uparrow}\rangle - u_k v_k^* \langle a_{-k\downarrow} a_{-k\downarrow}^\dagger\rangle - v_k^{*2} \underbrace{\langle a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger\rangle}_{=0} + u_k^2 \underbrace{\langle a_{-k\downarrow} a_{k\uparrow}\rangle}_{=0}]
\end{aligned}$$

When the expectation values are evaluated with respect to $H_{\mathrm{BCS}}^{\mathrm{MF}}$ this simplifies to

$$\Delta = \frac{g}{V} \sum_k u_k v_k^* (\langle a_{k\uparrow}^\dagger a_{k\uparrow} \rangle - 1 + \langle a_{-k\downarrow}^\dagger a_{-k\downarrow} \rangle)$$

Under the assumption of symmetry we get

$$\Delta = \frac{g}{V} \sum_k u_k v_k^* (2f(E_k) - 1)$$

with the Fermi function

$$f(x) = \frac{1}{e^{\frac{x}{k_B T}} + 1}$$

and

$$E_k = \sqrt{|\Delta|^2 + \xi_k^2}$$

Using that $u_k v_k^* = -\frac{\Delta}{2E_k}$ this simplifies for $|\Delta| \neq 0$ to

$$\boxed{1 = \frac{g}{V} \sum_k \frac{1 - 2f(E_k)}{2E_k} \qquad |\xi_k| \leq \hbar\omega_D}$$

At zero temperature $T = 0$ this just recovers

$$|\Delta| = 2\hbar\omega_D e^{-\frac{1}{g\nu}}$$

At finite T we obtain

$$1 = g\nu \int_{-\hbar\omega_D}^{\hbar\omega_D} \mathrm{d}\xi \frac{\tanh\left(\frac{\sqrt{\xi^2 + |\Delta|^2}}{2k_B T}\right)}{2\sqrt{\xi^2 + |\Delta|^2}}$$

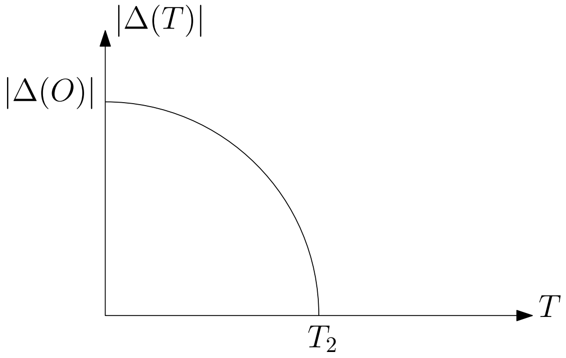

Figure 57: Temperature dependence of the gap $\Delta(T)$

This yields the temperature dependence of the gap $\Delta(T)$. Above the critical temperature $T \geq T_c$, the gap vanishes $\Delta = 0$ and the normal conductore is recovered. To determine T_c we take the limit $|\Delta| \to 0^+$:

$$\begin{aligned} 1 &= g\nu \int_{-\hbar\omega_D}^{\hbar\omega_D} \mathrm{d}\xi \frac{\tanh \frac{|\xi|}{2k_BT_c}}{2|\xi|} = g\nu \int_0^{\hbar\omega_D} \mathrm{d}\xi \frac{\tanh \frac{\xi}{2k_BT_c}}{\xi} \\ &\overset{x=\frac{\xi}{k_BT_c}}{=} g\nu \int_0^{\frac{\hbar\omega_D}{kBT_c}} \mathrm{d}x \frac{\tanh \frac{x}{2}}{x} \end{aligned}$$

In order to obtain the asymptotic behavior for $\frac{\hbar\omega_D}{k_BT_c} \gg 1$ we integrate by parts

$$\begin{aligned} 1 &= g\nu \left[\ln x \tanh \frac{x}{2}\right]_0^{\frac{\hbar\omega_D}{k_BT_c}} - gV \int_0^{\frac{\hbar\omega_D}{k_BT_c}} \mathrm{d}x \ln x \left(\tanh \frac{x}{2}\right) \\ &\overset{\hbar\omega_D \gg k_BT_c}{\approx} g\nu \left[\ln \frac{\hbar\omega_D}{k_BT_c} - \left(-\gamma + \ln \frac{\pi}{2}\right)\right] \end{aligned}$$

with the Euler's constant $\gamma \cong 0.0577$. This yields

$$\boxed{k_BT_c = \frac{2e^\gamma}{\pi} \hbar\omega_D e^{-\frac{1}{g\nu}}}$$

Comparing this with the gap at $T = 0$, $\Delta(0) = 2\hbar\omega_D e^{-\frac{1}{g\nu}}$ gives

$$\frac{2\Delta(0)}{k_BT_c} = \frac{2\pi}{e^\gamma} \approx 3.528$$

This result is well-obeyed by simple BCS superconductors. 31.1.20

7.1.3 Heat capacity of BCS superconductors

The heat capacity is given by

$$C_V = 2\sum_k E_k \frac{\partial f(E_k)}{\partial T}$$

with energy

$$E_k = \sqrt{\xi_k^2 + |\Delta|^2}$$

where $\xi_k = \varepsilon_k - \mu$.

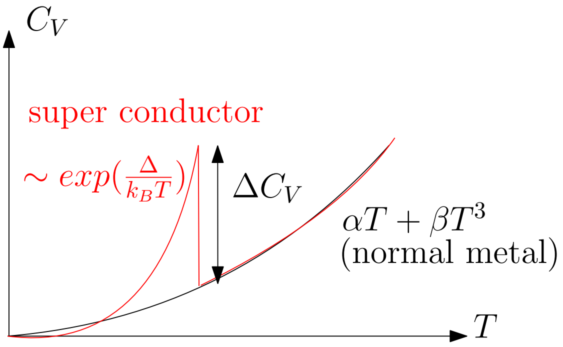

Figure 58: Temperature dependence of the heat capacity C_V

$$\frac{\Delta C_V}{C_V(T_C)} = \frac{12}{7\rho(3)} \approx 1.43$$

7.1.4 Isotope effect (1950)

$$T_C\sqrt{M} = \text{const.}$$

Thus

$$T_C \propto \frac{1}{\sqrt{M}}$$

and

$$\omega_D \propto \frac{1}{\sqrt{M}}$$

So

$$T_C \sim \Delta \sim \hbar\omega_D$$

7.1.5 Density of states of superconductors

$$\begin{aligned}\omega_{\text{tot}} &= \frac{1}{V}\sum_k (\delta(\varepsilon - E_k) + \delta(\varepsilon + E_k)) \\ &= \int \frac{d^3k}{(2\pi)^3}(\delta(\varepsilon - \sqrt{|\Delta|^2 + (\varepsilon-\mu)^2}) + \delta(\varepsilon + \sqrt{|\Delta|^2 + (\varepsilon - \mu)^2})\end{aligned}$$

Now, we perform a substitution with $\xi = (\varepsilon_k - \mu)$ and $d\xi = \partial_k\varepsilon_k dk$ and introduce $v = \frac{4\pi k_F^2}{(2\pi)^3\partial_k\varepsilon_k|_{k_F}}$

$$\begin{aligned}\omega_{\text{tot}} &\approx v\int_{-\xi_0}^{\xi\approx\hbar\omega_D} (\delta(\varepsilon - \sqrt{|\Delta|^2 + \xi^2}) + \delta(\varepsilon + \sqrt{|\Delta|^2 + \xi^2}))d\xi \\ &= 2v\int_0^{\varepsilon_0} (\delta(\varepsilon - \sqrt{|\Delta|^2 + \xi^2}) + \delta(\varepsilon + \sqrt{|\Delta|^2 + \xi^2})))d\xi\end{aligned}$$

Using another substitution of the form $\varepsilon' = \sqrt{|\Delta|^2 + \xi^2} \Rightarrow \varepsilon' > |\Delta|$ and $\xi = \sqrt{\varepsilon'^2 - |\Delta|^2} \Rightarrow d\xi = \frac{\varepsilon' d\varepsilon'}{\sqrt{\varepsilon'^2 - |\Delta|^2}}$ we get

$$\begin{aligned}\omega_{\text{tot}} &= 2v \int_{|} \Delta|^{\varepsilon_0} (\delta(\varepsilon - \varepsilon') + \delta(\varepsilon + \varepsilon')) \frac{\varepsilon' d\varepsilon'}{\sqrt{\varepsilon'^2 - |\Delta|^2}} \\ &= 2v \left(\frac{\varepsilon}{\sqrt{\varepsilon^2 - |\Delta|^2}} \theta(\varepsilon - |\Delta|)\theta(\varepsilon_0 - \varepsilon) + \frac{-\varepsilon}{\sqrt{\varepsilon^2 + |\Delta|^2}} \theta(-\varepsilon + |\Delta|)\theta(\varepsilon_0 + \varepsilon) \right) \\ &= 2v \frac{|\varepsilon|}{\sqrt{\varepsilon^2 - |\Delta|^2}} \theta(\varepsilon^2 - |\Delta|^2)\end{aligned}$$

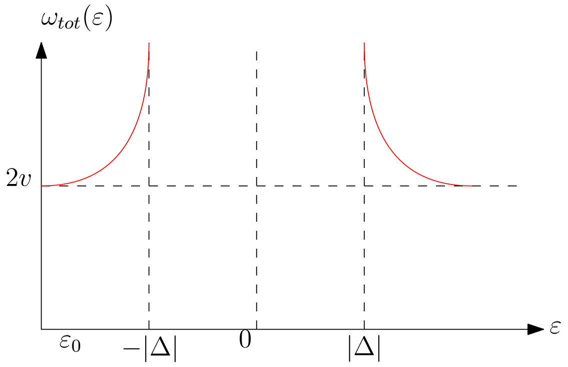

Figure 59: Density of states of superconductors

7.2 Ginzburg-Landau-Theory

$$L = \frac{1}{2m^*} |(-i\nabla - e^* \vec{A})\Delta|^2 + r|\Delta|^2 + \frac{u}{2}|\Delta|^4 + \frac{(\nabla \times \vec{A})^2}{2\mu_0}$$

for $|T - T_c| \ll T_c$, $\Delta \in \mathbb{C}$, $e^* = 2e$, $u > 0$, $r \propto T - T_c$, $\vec{A} = 0$ and the potential

$$U = r|\Delta|^2 + \frac{U}{2}|\Delta|^4$$

with $|\Delta_\infty| = -\frac{r}{u}$ and $V_\infty = -\frac{r^2}{2u}$.

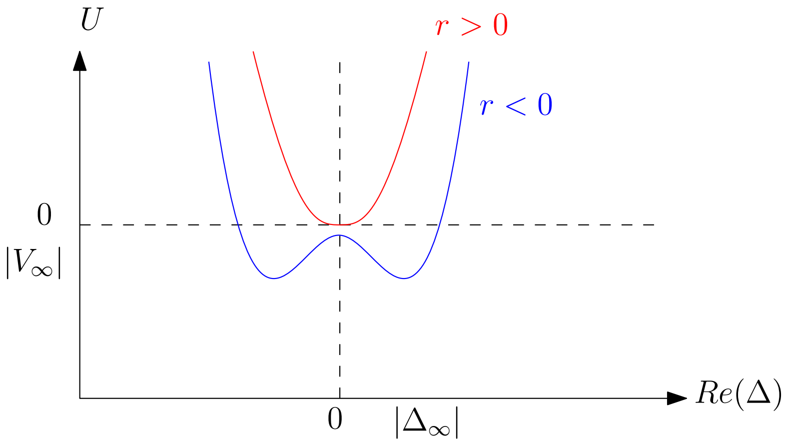

Figure 60: Ginzburg-Landau potential

The corresponding action is given by

$$S = \int dt d\sqrt{s} L$$

and

$$\frac{\partial S}{\partial \Delta^*} = \frac{\partial S}{\partial \Delta} = 0$$

Therefore, we have ($\Delta = \Delta(r)$)

$$r\Delta - \frac{\nabla^2}{2m^*}\Delta + u|\Delta|^2\Delta = 0.$$

And obtain for the wave function $\psi(\vec{r}) = \frac{\partial(\vec{r})}{\partial_\infty}$:

$$-\psi - \xi^2\nabla^2\psi + |\psi|^2\psi = 0$$

with the Ginzburg-Landau coherence length

$$\xi^2 = \frac{1}{2m^*|\Delta|}$$

and

$$\xi(T) \sim \frac{1}{\sqrt{T_c - T}}.$$

The Lagrangian has $U(1)$ symmetry for $\Delta \to \Delta e^{i\theta}$ and

$$\vec{J} = e^* \left(-i\frac{1}{2m^*}(\Delta^*\nabla\Delta - \Delta\nabla\Delta^*) - \frac{e^*}{m^*}|\Delta|^2\vec{A} \right)$$

is the conserved Noether current for this symmetry where the conserved Noether charge is the total number of Cooper pairs. Comparing this with Amperes law

$$\vec{J} = \frac{1}{4\pi}\nabla \times \vec{B} = \frac{1}{4\pi}\nabla \times (\nabla \times \vec{A})$$

this gives the same as above with an alternative derivation where $\vec{A}$ is found with $\frac{\partial S}{\partial \vec{A}} = 0$.

$$\vec{J} = -\frac{e^*}{m^*} n_s \vec{A}, \quad n_s = |\Delta|^2$$

with concentration of Cooper pairs n_s.
∂_t..., $\vec{E} = -\partial \vec{A}$ leads to

$$\partial_t \vec{J} = \frac{e^*}{m^*} n_s \vec{E}$$

the 1. Londons equation (1935)
and $\nabla \times$ ..., $\vec{B} = \nabla \times \vec{A}$ to

$$\vec{B} = -\frac{m^*}{n_s e^{*2}} \nabla \times \vec{J}$$

the 2. Londons equation (1935).
Drude model

$$\frac{d(m\vec{v})}{dt} = e\vec{E} - \frac{m\vec{v}}{\tau}$$

and $\tau \to \infty$ for a perfect conductor. $\vec{j} = en\vec{v}$ hence

$$\partial_t \vec{j} = \frac{e^2}{m} n \vec{E}$$

With $\nabla \times \vec{H} = \vec{j}$:

$$\nabla \times (\nabla \times \vec{A}) = -\nabla^2 \vec{H} = \nabla \times \vec{j} \overset{2.}{=} -\frac{n_s e^{2*}}{m^*} \mu_0 \vec{H}$$

or short

$$\nabla^2 \vec{H} = \frac{1}{\lambda^2} \vec{H}$$

with London penetration depth

$$\lambda = \sqrt{\frac{m^*}{n_s e^{*2} \mu_0}}$$

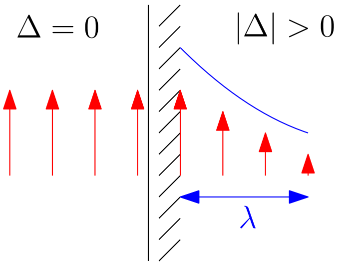

Figure 61: London penetration depth

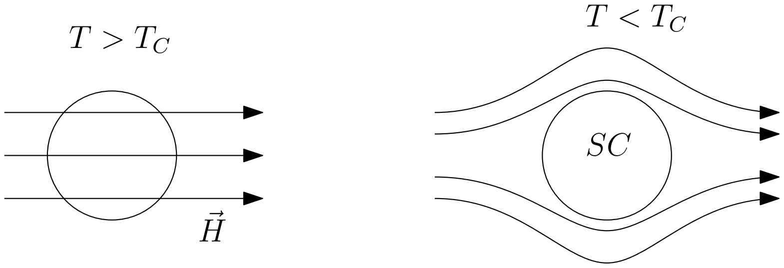

Figure 62: Magnetic field in super conductor at above and below the critical temperature

We get the energy of the magnetic field that is pushed out

$$\varepsilon_H = V\frac{1}{2}\mu_0 H^2$$

and the energy gain of the superconducting state

$$\varepsilon_\Delta = -\frac{r(T)^2}{2u}V$$

with $\varepsilon_H + \varepsilon_\Delta = 0$ 4.2.20

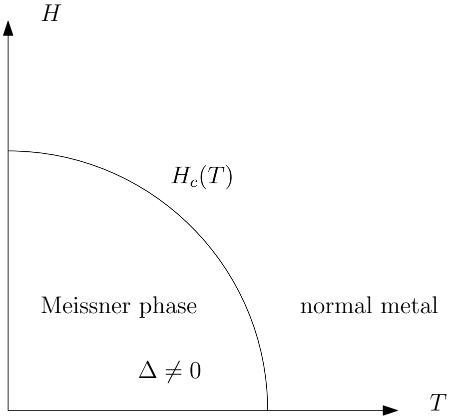

Figure 63: Type 1 superconductor

7.3 Type II superconductors

Consider the limit of large fields H. How does the superconductor order nucleate upon decreasing H? The Euler Lagrange equation in this rescaled form (for $r < 0$) is

$$-\psi + \xi^2(-i\nabla - e^*\vec{A})^2\psi + |\psi|^2\psi = 0$$

For small values of ψ the last term can be neglected. Choose $\vec{A} = B \times \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \to \vec{B} = B\hat{z}$.

The magnetic field is along the z axis. Hence,

$$\left(-i\nabla - e^* B \times \begin{pmatrix}0\\1\\0\end{pmatrix}\right)^2 = \frac{1}{\xi^2}\psi$$

$$(-\nabla^2 + 2ie^* Bx\partial_y + e^{*2}B^2x^2)\psi = \frac{1}{\xi^2}\psi$$

We choose the following ansatz:

$$\psi(\vec{r}) = e^{ik_y y + ik_z z} f(x)$$

and insert it

$$(-\partial_x^2 + k_y^2 + k_z^2 - 2e^* Bxk_y + e^{*2}B^2x^2)f(x) = \frac{1}{\xi^2}f(x)$$

We can rescale this with $x_0 = \frac{k_y}{e^* B}$ and by multiplying by $\frac{1}{2m^*}$

$$-\frac{1}{2m*}f''(x) + \frac{m^*\omega_c^2}{2}(x - x_0)^2 f(x) = \frac{1}{2m^*}\left(\frac{1}{\xi^2} - k_z^2\right)f(x)$$

with the cyclotron frequency $\omega_c = \frac{e^* B}{m^*}$. This Schrödinger equation describes a particle in a harmonic oscillator potential. We get an energy equation

$$\left(n + \frac{1}{2}\right)\omega_c \overset{!}{=} \frac{1}{2m^*}\left(\frac{1}{\xi^2} - k_z^2\right)$$

for the harmonic oscillator quantum number $n = 0, 1, 2, ...$ Especially, this yields

$$B(n, k_h) = \frac{\frac{1}{\xi^2} - k_z^2}{2e^*\left(n + \frac{1}{2}\right)}$$

The field is maximal for $k_z = 0$ and the ground state $n = 0$: $\mu_0 H_{c2} = B(0, 0)$. We get the critical field for a non-trivial solution $f(x) \neq 0$:

$$\boxed{H_{c2} = \frac{1}{\mu_0 e^*}\frac{1}{\xi^2}}$$

Comparison with $H_c = \sqrt{\frac{r^2}{2u}\frac{2}{\mu_0}}$ ($\xi = \frac{1}{\sqrt{2m^*|r|}}$):

$$\frac{H_{c2}}{H_c} = \frac{1}{\sqrt{\frac{r^2}{u\mu_0}}\mu_0 e^* \xi^2} = \sqrt{\frac{2m^*|r|}{\frac{r^2}{u\mu_0}\mu_0^2 e^{*2}}}\frac{1}{\xi} = \sqrt{2}\sqrt{\frac{m^*}{m_s\mu_0 e^{*2}}}\frac{1}{\xi}$$

With the penetration depth λ we get the following result

$$\boxed{\frac{H_{c2}}{H_c} = \sqrt{2}\frac{\lambda}{\xi} \equiv \sqrt{2}\kappa}$$

with $\kappa = \frac{\lambda}{\xi}$.

- for $H_{c2} < H_c \Leftrightarrow \kappa < \frac{1}{\sqrt{2}}$ a Meissner phase with a finite Δ appears at H_c: type 1 superconductor (and homogenous)
- for $H_{c2} > H_c \Leftrightarrow \kappa > \frac{1}{\sqrt{2}}$ superconducting order nucleates locally. Especially, looking at the harmonic oscillator wavefunction for $n = 0, k_z = 0$:

  $$\psi(x, y) = e^{ik_y y} e^{-\frac{(x-x_0)^2}{2\xi^2}}$$

  → *Shubnikov phase*!
- By closer inspection one finds that the magnetic flux penetrates the superconductor in the form of vortices each carrying a flux quantum $\phi = \frac{hc}{e^*}$. The repulsion of those vortices leads to the Abrikosov vortex lattice (1957).

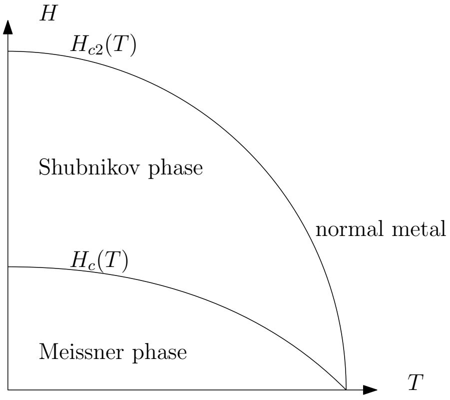

Figure 64: Phase diagram of a type II superconductor

7.4 Josephson effect

We consider a junction between two superconductors

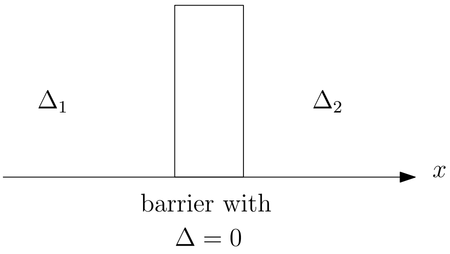

Figure 65: Two superconductors separated by a barrier

The Josephson effect predicts that there is a supercurrent across the junction that obeys

$$\boxed{\begin{aligned} I_s &= I_c \sin \Delta\phi \\ \frac{\mathrm{d}\Delta\phi}{\mathrm{d}t} &= \frac{2e}{\hbar} V \end{aligned}}$$ Josephson (1962), nobel prize 1973

where $\Delta\varphi = \varphi_2 - \varphi_1$ is the phase difference of the order parameters $\Delta_{1,2} = |\Delta| e^{i\phi_{1,2}}$. The critical current I_c is the maximal current that the junction can support.
In the absence of a voltage $V = 0$ and for a finite $\Delta\varphi$ there is a finite supercurrent I_s flowing across the junction. This is the so-called *dc Josephson effect.*
For a finite voltage $V \neq 0$ there is an oscillating supercurrent with frequency $\omega = \frac{2eV}{\hbar}$. The energy $\hbar\omega = 2eV$ equals the energy change of a Cooper pair with charge $e^* = 2e$ transferred across the junction → *ac Josephson effect.*

7.4.1 The Josephson cricital current for a short metallic link

Consider a short link between two superconductors of length $L \ll \xi$ that can be described by the Ginzburg-Landau equation

$$-\psi - \xi^2 \partial_x^2 \psi + |\psi|^2 \psi = 0$$

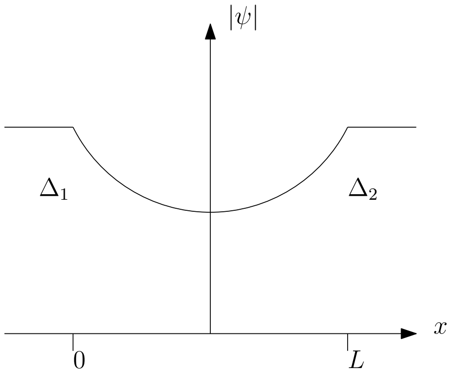

Figure 66: Short link between two superconductors

The two superconductors impose the boundary conditions

$$\psi(x=0) = e^{i\varphi_1} \quad \text{and} \quad \psi(x=L) = e^{i\varphi_2}$$

with $|\Delta_1| = |\Delta_2|$. For a short link $L \ll \xi$ the GL equation for ψ is dominated in the range of $0 \leq x \leq L$ by the gradient term:

$$\xi^2 \partial_x^2 \psi \approx 0$$

with the general solution $\psi(x) = a + bx$. The coefficients a and b are fixed by the boundary condition

$$\psi(x) = \left(1 - \frac{x}{L}\right) e^{i\varphi_1} + \frac{x}{L} e^{i\varphi_2}$$

for $0 < x < L$. The first term corresponds to the spread from Δ_1 and vice versa. Assuming a constant amplitude he wavefunction yields for the current (with $\Delta(x) = |\Delta|\psi(x)$)

$$\begin{aligned}
J &= -i\frac{2e\hbar}{2m^*}(\Delta^*\partial_x\Delta - \Delta\partial_x\Delta^*) \\
&= \frac{2e\hbar}{2m^*}|\Delta|^2\left(\left(-i\left(1-\frac{x}{L}\right)e^{-i\varphi_1} + \frac{x}{L}e^{-i\varphi_2}\right)\left(-\frac{1}{L}e^{i\varphi_1} + \frac{1}{L}e^{i\varphi_2}\right) + h.c.\right) \\
&= \frac{2e\hbar}{2m^*}|\Delta|^2\left(-i\left(\left(1-\frac{x}{L}\right)\frac{1}{L}e^{-i\varphi_1+i\varphi_2} - \frac{x}{L^2}e^{-i\varphi_2+i\varphi_1}\right) + c.c.\right) \\
&= \frac{2e\hbar}{2m^*}|\Delta|^2\left(\left(1-\frac{x}{L}\right)\frac{1}{L} + \frac{x}{L^2}\right)2\sin\Delta\varphi \\
&= \frac{2e\hbar}{m^*}|\Delta|^2\frac{1}{L}\sin\Delta\varphi
\end{aligned}$$

with $\Delta\varphi = \varphi_2 - \varphi_1$. The non-mixing terms vanish by usage of the complex conjugated terms.
For a link with cross-sectional area $\mathcal{A}$ within the yz plane one obtains a current of the following form

$$I_s = I_c \sin\Delta\varphi \quad \text{with } I_c = \frac{2e\hbar}{m^*}|\Delta|^2\frac{\mathcal{A}}{L} \tag{7.2.20}$$

7.5 Andreev reflections

Derive Joesphson relations microscopically by solving inhomogeneous wave equation for the Nambu spinor. The solutions will involve the concept of Andreev reflections.
Consider the one-dimensional wave equation for $\vec{\psi} = (c_{k\uparrow}c^\dagger_{-k\downarrow})^T$:

$$i\partial_t\vec{\psi} = \begin{pmatrix} \xi_{-i\partial_x} & -\Delta(x) \\ -\Delta^\dagger(x) & -\xi_{-i\partial_x} \end{pmatrix}\vec{\psi}$$

with $\xi_{\vec{k}} = \epsilon_k - \mu$ so that $\xi_{k_F} = 0$.
Introduce right- and left-moving fields

$$\vec{\psi}(x,t) = e^{ik_Fx}\vec{\psi}_+(x,t) + e^{-ik_Fx}\vec{\psi}_-(x,t)$$

where $\vec{\psi}_\pm(x,t)$ depend only weakly on x:

$$\xi_{-i\partial_x} \to \xi_{\pm k_F - i\partial_x} \cong \pm v_F(-i\partial_x)$$

with Fermi velocity $v_F > 0$. This yields the effective wave equation after Fourier transform ($\Delta(x) = \Delta$):

$$\begin{pmatrix} -\omega + \sigma v_F k & -\Delta \\ -\Delta^\dagger & -\omega - \sigma v_F k \end{pmatrix}\vec{\psi}_\sigma(k,\omega) = 0$$

for $\sigma = 1$ for right-movers and $\sigma = -1$ for left -movers.

I. Normal metal $\Delta = 0$

eigenfunctions $\vec{\psi}_\sigma(k,\omega) = (1,0)^T$ with $\omega = \sigma v_F k$

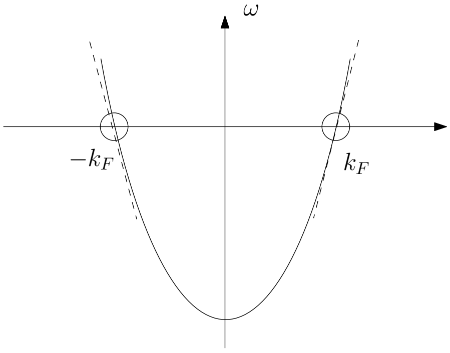

Figure 67: particle-branch

$\vec{\psi}_\sigma(k,\omega) = (0,1)^T$ with $\omega = -\sigma v_F k$

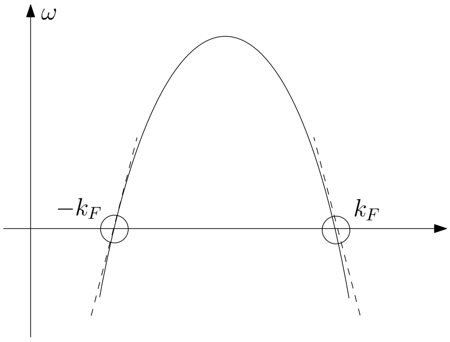

Figure 68: hole-branch

eigenfunctions $\vec{\psi}_\sigma(k,\omega) = (1,0)^T$ with $\omega = \sigma v_F k$

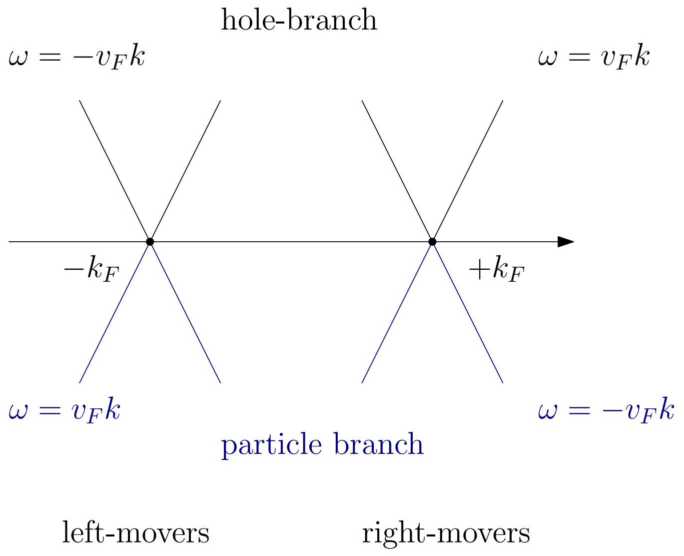

Figure 69: Both branches for left- and right-movers

II Superconductor $|\Delta| \neq 0$

For energies larger than the gap $|\omega| \geq |\Delta|$:

$$\vec{\psi}_\sigma(k,\omega) = \begin{pmatrix} \omega + \sigma v_F k \\ -\Delta^* \end{pmatrix} \quad \text{with} \quad \omega = \sqrt{(v_f k)^2 + |\Delta|^2}$$

and

$$\vec{\psi}_\sigma(k,\omega) = \begin{pmatrix} -\Delta \\ \omega - \sigma v_F k \end{pmatrix} \quad \text{with} \quad \omega = -\sqrt{(v_f k)^2 + |\Delta|^2}$$

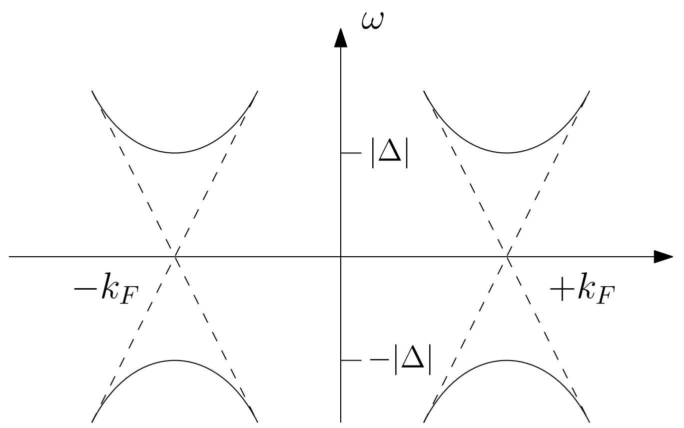

Figure 70: Superconductor

For energies smaller than the gap $|\omega| < |\Delta|$ there exists no propagating solutions but only solutions with imaginary wavevector $k = i\kappa$. Thus, $e^{ikx} = e^{-\kappa x}$ wavefunctions decay or grow exponentially for $\kappa \lesseqgtr 0$. Eigenvalues are then given by $\omega = \pm\sqrt{|\Delta|^2 - (v_F\kappa)^2}$ with $(v_F\kappa)^2 \le |\Delta|^2$.

7.6 Normal metal-superconductor interface

Consider an interface between a normal metal, $\Delta = 0$,and a superconductor $|\Delta| > 0$ that we model with a step function

$$\Delta(x) = \begin{cases} 0 & x < 0 \\ \Delta & x > 0 \end{cases}$$

Consider a wavefunction for energies $0 < \omega < |\Delta|$. General Ansatz for right-moving field $\vec{\psi}_+$:
For $x < 0$ with $\omega = v_F k$ and $k > 0$:

$$\vec{\psi}_+(x, \omega) = a \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ikx} + b \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-ikx}$$

We consider only backscattering processes with changes of momenta $|\Delta k| = |2k| \ll 2k_F$ ie. right- and left-moving fields do not mix.
For $x > 0$ with $\omega = \sqrt{|\Delta|^2 - (v_F\kappa)^2}$ with $\kappa > 0$

$$\vec{\psi}_+(x, \omega) = \frac{c}{|\Delta|} \begin{pmatrix} \omega + v_F i\kappa \\ -\Delta^* \end{pmatrix} e^{-\kappa x}$$

The wavefunction has to fulfill continuity at the junction $x = 0$:

$$\begin{pmatrix} a \\ b \end{pmatrix} = \frac{c}{|\Delta|} \begin{pmatrix} \omega + v_F i\kappa \\ -\Delta^* \end{pmatrix}$$

for an incoming particle $a = 1$. We get the Andreev reflection amplitude $r_A = b = -\frac{\Delta^*}{|\Delta|} c = -\frac{\Delta^*}{\omega + v_F i\kappa}$ and obtain

$$\boxed{r_A = -\frac{\Delta^*}{\omega + i\sqrt{|\Delta|^2 - \omega^2}}}$$

with $|r_A|^2 = 1$. The particle can not penetrate the superconductor but gets reflected. r_A can be interpreted as a phase.

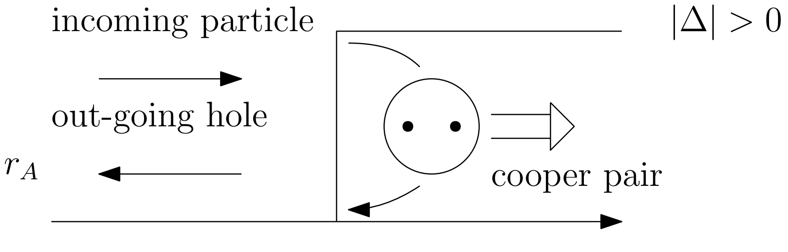

Figure 71: Cooper pair at metal-superconductor interface

The electron is fully reflected as a hole with amplitude r_A and $|r_A|^2 = 1$. The total charge $2e$ is transferred to the superconductor in the reflection process.
In superconductor-normal metal-superconductor (SNS) junctions the Josephson effect can be understood as the repeated Andreev reflection at the interfaces

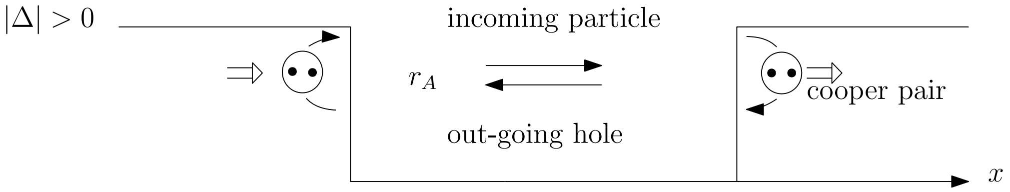

Figure 72: Cooper pair at SNS

In each cycle a charge of $2e$ is transferred across the junction.

7.7 Anderson-Higgs mechanism

Consider the Ginzburg-Landau theory for $Delta(\vec{r})$

$$\mathcal{L} = \frac{1}{2m^*}|(-i\nabla - e^*\vec{A})\Delta|^2 + r|\Delta|^2 + \frac{u}{2}|\Delta|^4$$

within the superconducting phase $r < 0$, with equilibrium solution $\Delta_0 = \sqrt{-\frac{r}{u}}$ chosen to be positive and real. Consider small fluctuations around the equilibrium value

$$\Delta = \Delta_0 + \phi_1 + i\phi_2 i$$

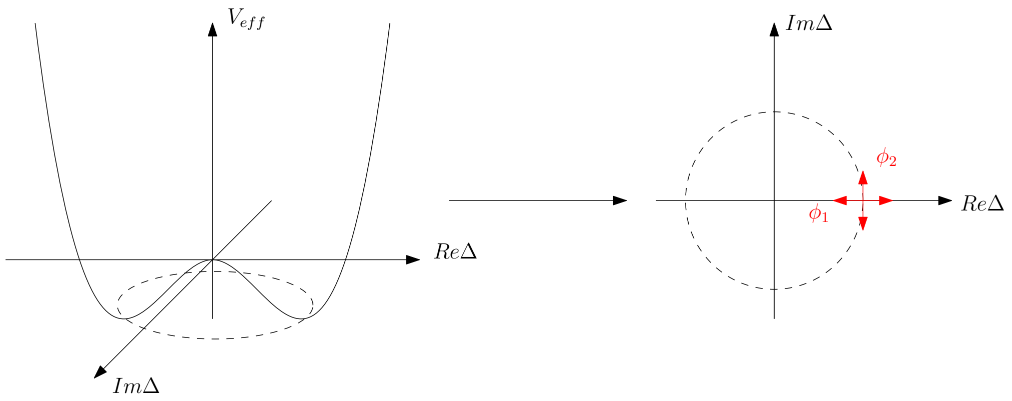

Figure 73: degenerate ground state manifold (circle)

The components ϕ_1 and ϕ_2 describe radial and tangential fluctuations of the order parameter. Expansion up to second order in $\vec{A}$ and $\phi_{1/2}$ gives:

$$\delta\mathcal{L} = \frac{1}{2m^*}((\nabla\phi_1)^2 + (\nabla\phi_2)^2 - 2e^{*2}\Delta_0\vec{A}\nabla\phi_2 + e^*\nabla_0^2\vec{A}^2) + \underbrace{r(\phi_1^2 + \phi_2)^2 + u\Delta_0^2\phi_2^2 + 3u\Delta_0^2\phi_1^2}_{2u\Delta_0^2\phi_1^2}$$

The last three terms corresponds to a potential. This potential for the tangential field ϕ_2 vanishes! This reflects the degenerate ground state manifold! → *Goldstone mode.* The gapless mode ϕ_2 can be absorbed however by a gauge transformation

$$\vec{A}' = \vec{A} + \nabla\chi \quad \text{and} \quad \Delta' = \Delta e^{ie^*\chi}$$

for small χ:

$$\Delta' \cong \Delta(1 + ie^*\chi) = \Delta_0 + \phi_1 + i\underbrace{(\phi_2 + e^*\Delta_0\chi)}_{=\phi_2'} + \mathcal{O}(\phi_1\chi, \phi_2\chi)$$

We can always find a gauge transformation χ so that $\phi_2' = 0$. The Goldstone mode is „eaten up“by the gauge transformation. The effective fluctuating part thus reads (dropping the prime).

$$\delta\mathcal{L} = \underbrace{\frac{1}{2m^*}(\nabla\phi_1)^2 + 2u\Delta_0^2\phi_1^2}_{\text{Higgs mode}} + \underbrace{\frac{e^{*2}}{2m^*}\Delta_0^2\vec{A}^2}_{\text{photon mass}}$$

The longitudinal fluctuation field ϕ_1 corresponds to the Higgs mode that has an excitation gap (we need a finite energy for excitation). The last term corresponds to a photon mass (Meissner effect). This generation of a photon mass is known as *Anderson-Higgs mechanism.* This mechanism is not only relevant for explanation of superconductors but is also invoked in the standard model of particle physics (nobel prize 2013, Englert & Higgs). The photon mass prevents the B field from penetrating the superconductor.