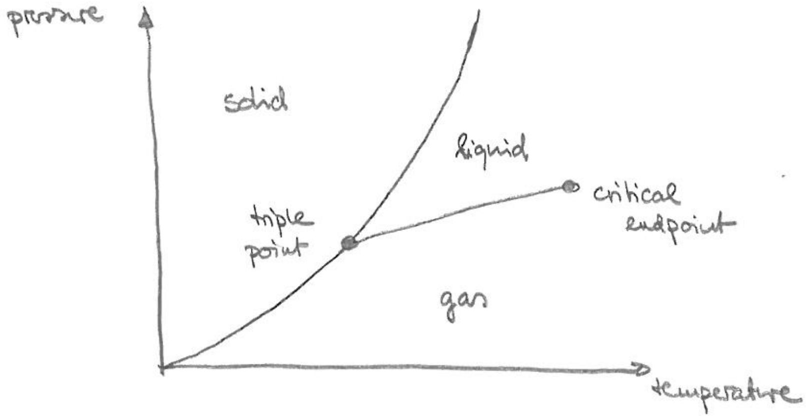
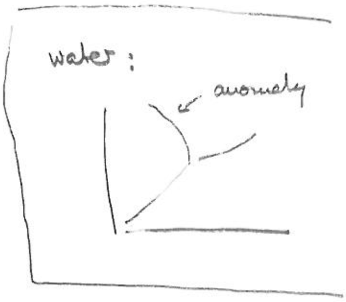
1. SOLIDS

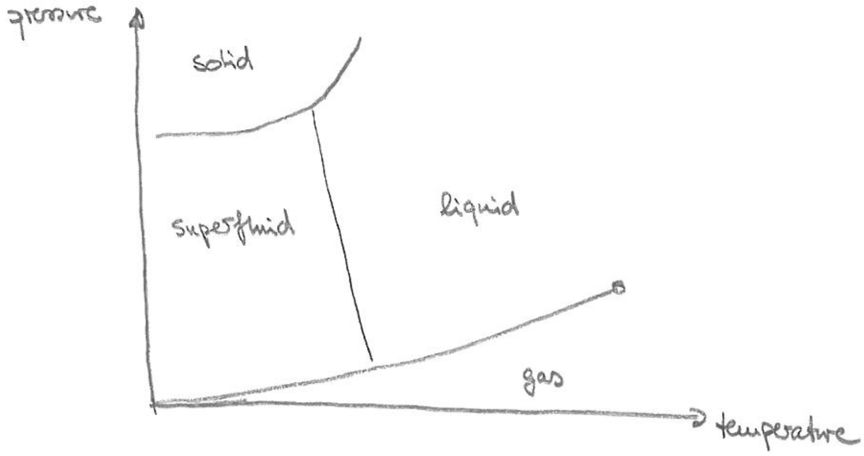
fundamental states of matter : solid, liquid, gas





at sufficiently low temperature matter almost always assumes a solid state.

exception : for example Helium (He) → superfluid state



1.1. Crystalline solids

most solids are crystals characterized by a periodic arrangement of its constituents, ie., the atoms.

in contrast to amorphous solids like glasses

solid crystals break the translation and rotation invariance symmetry of space

consequences :

→ solid state is seperated from the 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 *polycrystal*

→ solid possesses as a symmetry-broken state a rigidity

structural rigidity allows for long-distance transmission of forces and shear forces, i.e. dissipationless momentum and angular momentum flow

[similar to a superconductor that allows for dissipationless charge flow]

→ solid crystal is characterized by low-energy excitations (Goldstone modes) that are the acoustic phonons

phonon velocities are determined by the elastic moduli like bulk and shear modulus that quantify the rigidity of the crystal

1.2. Crystal structures

[crash course, for more details consult exp. lecture & books]

geometrical properties of a periodic structure is characterized by the

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.

Note: choice of primitive vectors is not unique.

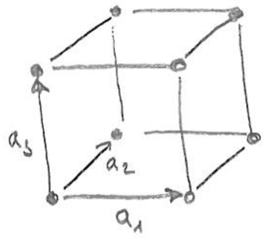
Theorem (Auguste Bravais 1848):

There exist only 14 Bravais lattice types in three dimensions

Examples

- simple cubic (sc)

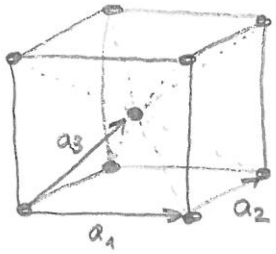
$\vec{a}_1 \perp \vec{a}_2 \perp \vec{a}_3$ with $|a_1| = |a_2| = |a_3|$



- <u>body-centered cubic</u> (bcc)

  $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, $\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$

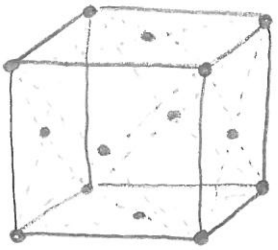
  sc plus an additional point at the centre of each cube



- <u>face-centered cubic</u> (fcc)

  sc plus an additional point at the centre of each square face

  $\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z})$, $\vec{a}_2 = \frac{a}{2}(\hat{z}+\hat{x})$, $\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$



<u>coordination number z</u>

number of nearest neighbors of each lattice point,

nearest neighbors : points in the Bravais lattice that are closest 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 prefered at lowest temperatures since it possesses the larger coordination number z.

In contrast, the sc lattice is very rarely realized.

<u>unit cell</u> (uc)

a volume of space that, when translated through some subset of the vectors of the Bravais lattice, just fills all of space without overlapping itself or leaving voids.

primitive unit cell (PUC)

a unit cell containing exactly a single lattice point

Note: there does not exist a unique way of choosing a primitive unit cell for a given Bravais lattice. However, its volume is fixed by the density of points in the Bravais lattice n : $V_{PUC} = \frac{1}{n}$.

A possible choice is

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

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

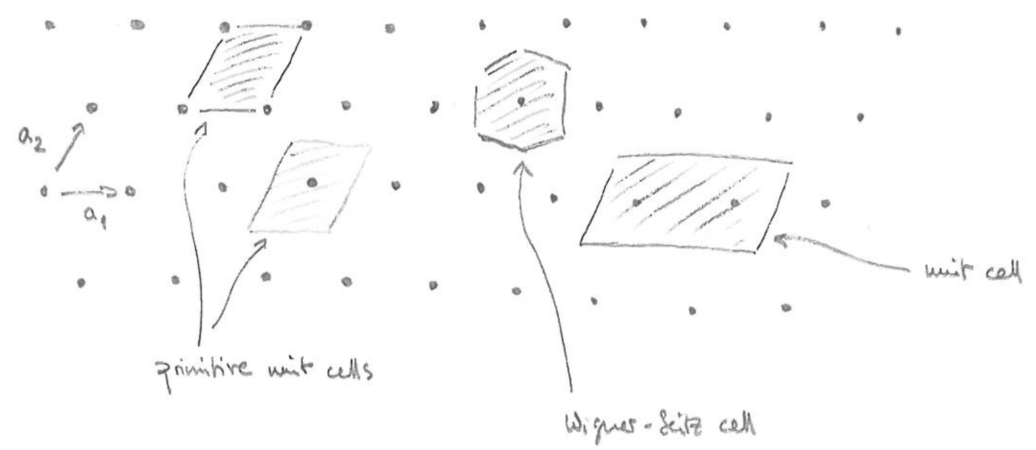
$$\vec{R} = \vec{R}_n + \vec{x} \quad \text{with} \quad \vec{x} \in PUC \quad \text{and} \quad \vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

Wigner-Seitz primitive cell

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 for a two-dimensional Bravais lattice:



crystal structure

consists of identical copies of the same physical unit, called the basis, located at all the points of a Bravais lattice. ("lattice with a basis")

In particular, the basis specifies the position of atoms within a unit cell.

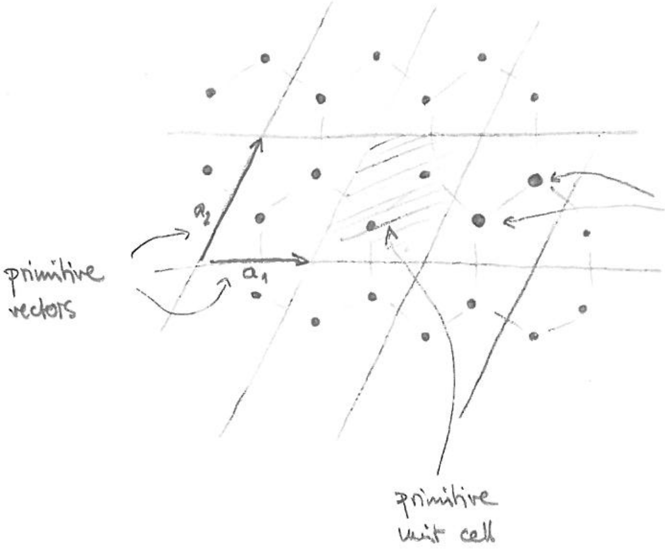
Examples

- monatomic Bravais lattice

  crystal structure with a basis consisting of a single atom or ion positioned for example at the points of the Bravais lattice

  Examples: crystal structure of Cr (bcc), Fe (bcc), Al (fcc), Au (fcc)

- two-dimensional honeycomb (realized in Graphene)



basis contains two points located at

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

honeycomb itself is not a Bravais lattice

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- diamond structure

  fcc lattice with two-point basis $\{\vec{0}, \frac{a}{4}(\hat{x}+\hat{y}+\hat{z})\}$

- hexagonal close-pack structure

  simple hexagonal Bravais lattice $\hat{=}$ stacked two-dimensional triangular lattices

  primitive vectors $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y}$, $\vec{a}_3 = c\hat{z}$

  with two-point basis $\{\vec{0}, \frac{1}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3\}$

  This structure is of similar importance as the monatomic bcc and fcc lattice

- Structures necessarily described by a basis because two types of ions/atoms are present:

  - sodium chloride (NaCl)

    fcc lattice, basis: Na at $\vec{0}$ and Cl at $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$

  - cesium chloride (CsCl)

    bcc lattice, basis: Cs at $\vec{0}$ and Cl at $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$

- Zincblende structure (sphalerite, zinc sulfide ZnS)

  diamond structure but the two positions specified by the basis are occupied by different ions/atoms.

Classification of crystal structures

subject of crystallography, here only very superficial

crystal structures are classified according to their symmetries

one distinguishes:

Point group

is composed of all symmetry operations that leave a particular ion/atom of the crystal fixed like reflections, inversion, rotations, combined rotation-reflection, rotation-inversion.

There are in total 32 crystallographic point groups.

(*)

Space group

is composed of the symmetry operations of the point group and in addition

- translations through Bravais lattice vectors
- combined translation-rotation (screw axis) and translation-reflection (glide planes) symmetry operations.

and combinations thereof.

There are in total 230 space 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 χ_{ij},
piezoelectric tensor d_{ijk}

1.3. Reciprocal lattice

consider a function eg. a potential with the periodicity of a Bravais lattice $V(\vec{r}+\vec{R}_n) = V(\vec{r})$ with $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

Fourier transform: $V(\vec{r}) = \sum_m V_{\vec{G}_m} e^{i\vec{G}_m\vec{r}}$

where the momenta $\vec{G}_m$ have the property: $\boxed{e^{i\vec{G}_m\vec{R}_n} = 1}$

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

Momenta are given by:

$$\boxed{\begin{array}{l} \vec{G}_m = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3 \quad , \quad m_i \in \mathbb{Z},\ i = 1,2,3 \\ \text{with} \quad \vec{a}_i\vec{b}_j = 2\pi\delta_{ij} \end{array}}$$

Explicitly:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1(\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1(\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1(\vec{a}_2 \times \vec{a}_3)}$$

with volume of the primitive unit cell $V_{PUC} = \vec{a}_1(\vec{a}_2 \times \vec{a}_3)$

$\vec{b}_i$ 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 latice	sc	bcc	fcc	simple hexagonal

First Brillouin zone

Wigner - Seitz primitive cell of the reciprocal lattice

Arbitrary vector in momentum space : $\vec{k} = \vec{G}_n + \vec{p}$ with $\vec{p} \in$ 1. BZ

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

Conventions

- directions in the Bravais lattice :

  $[n_1 \, n_2 \, n_3]$ direction specified by the vector $n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$

- planes in the Bravais lattice : Miller indices

  $(m_1 \, m_2 \, m_3)$ plane that is normal to the vector $m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3$

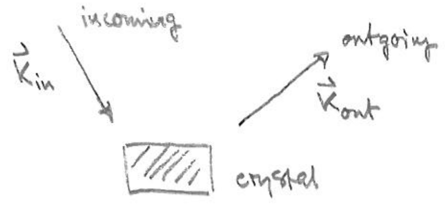
1.4. Scattering from a crystal

typical interatomic distances in a solid : $a \sim 1\,\text{Å} = 10^{-10}\,\text{m}$

typical energies needed for scattering : $\hbar\omega = \frac{hc}{\lambda} \sim \frac{hc}{1\,\text{Å}} \approx 12 \cdot \text{keV}$

→ X-ray energies

scattering experiment



consider matrix element of the scattering potential $V(\vec r)$

$$\langle K_{out} | V(\vec r) | K_{in} \rangle = \frac{1}{Vol} \int d\vec r \; e^{-iK_{out}\vec r} \, V(\vec r) \, e^{i\vec k_{in}\vec r}$$

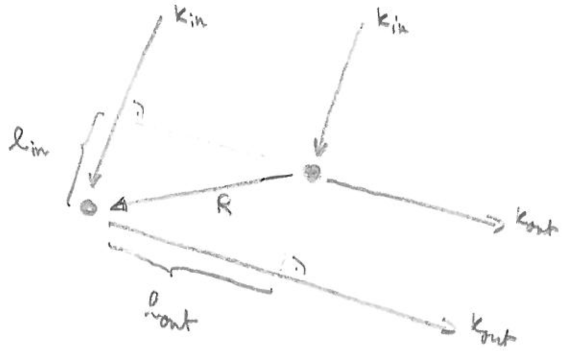
$$= \frac{1}{Vol} \int d\vec r \sum_{G_m} V_{G_m} \, e^{i(K_{in}+G_m-K_{out})\vec r} = \sum_{G_m} V_{G_m} \, \delta_{K_{in}+G_m,\, K_{out}}$$

so we obtain the selection rule

$$\boxed{\vec K_{out} = \vec k_{in} + \vec G_m} \quad \text{with a reciprocal lattice vector } \vec G_m$$

geometric interpretation :

consider two ions/atoms in the crystal separated by a Bravais lattice vector $\vec R_n$ that both scatter an incoming wave



von-Laue condition for constructive interference :

the two scattering events interfere constructively if the path difference is an integer multiple of the wavelength λ

$$l_{in} + l_{out} = \lambda \cdot N \quad \text{with } N \in \mathbb{Z}$$

with $l_{in} = \vec R \cdot \hat k_{in}$, $l_{out} = -\vec R \hat k_{out}$

and assuming elastic scattering $\vec k_{in} = \frac{2\pi}{\lambda} \hat k_{in}$, $\vec k_{out} = \frac{2\pi}{\lambda} \hat k_{out}$

$$\Rightarrow \quad \vec R \left(\vec k_{in} - \vec k_{out} \right) = 2\pi N \quad \text{with } N \in \mathbb{Z}$$

$$\Rightarrow \quad \vec k_{in} - \vec k_{out} \text{ is a reciprocal lattice vector}$$

Scattering experiment allow for example to

- determine the Bravais lattice of a solid (Debye-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, ie, nuclei and the tightly bound electrons of the inner shells, and valence electrons.

note that seperation of core and valence electrons is not unique and depends on context, material etc..

The Hamilton operator of this many-particle system then reads (in the non-relativistic limit)

$$H = H_{el} + H_{ion} + H_{el-ion}$$

where

$$H_{el} = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} \frac{e^2}{|r_i - r_j|} + \text{spin-orbit correction}$$ electron mass m

$$H_{ion} = \sum_n \frac{P_n^2}{2M_n} + \sum_{n<m} V_{ion}(\vec{R}_n - \vec{R}_m)$$ ion masses M_n,

$$V_{ion}(\vec{r}) = \frac{Z^2e^2}{|r|} + \text{correction from core electrons}$$ potential for ions V_{ion}

$$H_{el-ion} = -\sum_{i,n} \frac{Ze^2}{|\vec{r}_i - \vec{R}_n|}$$ interaction

Ze charge of ion

Hamilton quite well-known but too complicated to solve exactly!

even numerically on a supercomputer only few particles can be treated but not 10^{23}!

→ approximations & understanding of relevant degrees of freedom essential!

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How can we identify the relevant degrees of freedom ?

consider the Hamiltonian in atomic units : (CGS-units $4\pi\varepsilon_0 \to 1.$)

measure length in units of Bohr radius $a_0 = \frac{\hbar^2}{me^2} \approx 0.5 \cdot \mathring{A}$

and energies in units of $2\times$ Rydberg (energy) $2Ry = \frac{me^4}{\hbar^2} = \frac{e^2}{a_0} = 2 \cdot 13{,}6 \text{ eV}$

$$H = \underbrace{\sum_i \frac{-\nabla_i^2}{2} + \sum_{i<j} \frac{1}{|r_i - r_j|}}_{H_{el}} + \underbrace{\sum_n \frac{m}{M_n} \frac{-\nabla_n^2}{2} + \sum_{n<m} \frac{Z_n Z_m}{|R_n - R_m|}}_{H_{ion}} + \underbrace{\sum_{i,n} \frac{-Z_n}{|r_i - R_n|}}_{H_{el-ion}} + \dots$$

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

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

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

$$H = H_0 + T \quad \text{with} \quad T = \sum_n \frac{m}{M_n} \frac{-\nabla_n^2}{2}$$

2.1. Adiabatic approximation (Born-Oppenheimer)

definition : adiabatic / diabatic

etymology : greek , unable / able to be crossed

usage in thermodynamics : adiabatic process $\hat{=}$ transfer of work without transfer of heat
i.e. at constant entropy

usage in quantum mechanics :

adiabatic process $\hat{=}$ gradually, slowly changing conditions allow 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

(cf. also "adiabatic theorem" of quantum mechanics and Landau-Zener problem)

here : electrons possess a smaller mass and are thus much faster than the ions;

electrons practically follow instantaneously the movement of ions

→ dynamic of electrons and ions decouple

→ adiabatic approximation systematic in the small parameter $\frac{m}{M_n}$

Step I : zeroth order in $\frac{m}{M_n}$

consider electronic subsystem in the presence of a fixed ion configuration $\{R_1, R_2, \dots, R_M\}$

described by the electronic many-particle wavefunction $\Psi = \Psi(\{r_1, r_2, \dots, r_N\};\{R_1, \dots, R_M\})$

eigenvalue problem for the adiabatic motion of electrons :

$$\boxed{H_0 \Psi_\alpha = \varepsilon_\alpha(R_1, R_2, \dots, R_M)\, \Psi_\alpha} \qquad (I)$$

where $H_0 = H_{ee} + H_{el\text{-}ion} + V_{ion}$

with electronic quantum numbers $\{\alpha\}$

The exact solution of (I) is in general not possible

→ 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

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

<u>Step II</u> : adiabatic correction

represent the full wavefunction in the eigenbasis of (I)

$$\Phi(\{r_i\},\{R_n\}) = \sum_\alpha \varphi_\alpha(\{R\})\, \Psi_\alpha(\{r\};\{R\})$$

full stationary Schrödinger equation

$$E\Phi = H\Phi = \sum_\alpha \left[\varepsilon_\alpha(\{R\}) + T \right] \varphi_\alpha(\{R\})\, \Psi_\alpha(\{r\},\{R\})$$

idea : derive an effective Hamiltonian for the "expansion parameters" φ_α

by using the orthogonality of Ψ_α ie. by projection

apply $\int d\{r\}\, \Psi_\beta^+(\{r\};\{R\}) \times$ one obtains

$$E\varphi_\beta(\{R\}) = \varepsilon_\beta(\{R\})\, \varphi_\beta(\{R\})$$

$$+ \sum_\alpha \int d\{r\}\, \Psi_\beta^+(\{r\},\{R\})\, T\, \varphi_\alpha(\{R\})\, \Psi_\alpha(\{r\},\{R\})$$

with

$$T\varphi_\alpha \Psi_\alpha = \sum_n \frac{m}{2M_n} (-\nabla_n^2)\, \varphi_\alpha \Psi_\alpha =$$

$$= -\sum_n \frac{m}{2M_n} \left[(\nabla_n^2 \varphi_\alpha)\Psi_\alpha + \varphi_\alpha(\nabla_n^2 \Psi_\alpha) + 2(\vec\nabla_n \varphi_\alpha)(\vec\nabla_n \Psi_\alpha) \right]$$

the Schrödinger equation becomes

$$E\,\varphi_\beta(\{R\}) = \Big(\varepsilon_\beta(\{R\}) + T\Big)\varphi_\beta(\{R\}) + \sum_\alpha C_{\beta\alpha}(\{R\},\{P\})\,\varphi_\alpha(\{R\})$$

with the operator

$$C_{\beta\alpha}(\{R\},\{P\}) = -\int d\{r\}\sum_n \frac{m}{2M_n}\Big[\Psi^+_\beta\,\vec{\nabla}^2_n\,\Psi_\alpha + 2\big(\Psi^+_\beta\,\vec{\nabla}_n\Psi_\alpha\big)\vec{\nabla}_n\Big]$$

The off-diagonal part of this operator, in particular, induce 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

$$\boxed{E\,\varphi_\beta(\{R\}) = \Big(T + \varepsilon_\beta(\{R\})\Big)\varphi_\beta(\{R\})} \qquad (\mathrm{II})$$

In particular for the electronic ground state this reads

$$E\,\varphi_0(\{R\}) = \Big(T + \varepsilon_0(\{R\})\Big)\varphi_0(\{R\})$$

The potential $\varepsilon_0(\{R\})$ is minimized by the particular crystal structure of the material.

In order to estimate the correction to the groundstate energy attributed to the kinetic term T, one consider small deviation from the equilibrium configuration

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

Taylor expanding the potential in δR

$$\varepsilon_0(\{R\}) = \varepsilon_0(\{R^{(0)}\}) + \frac{1}{2}\,\delta R_n D_{nm}\,\delta R_m$$

one arrives at

$$E\,\varphi_0 = \left(\varepsilon_0(\{R^{(0)}\}) + \mathcal{H}_{eff}\right)\varphi_0$$

with the effective Hamiltonian (with $\vec{P}_n = -i\vec{\nabla}_n$)

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

corresponding to a higher-dimensional harmonic oscillator.

The kinetic and the potential term in $\mathcal{H}_{eff}$ are of equal importance which becomes manifest by rescaling

$$\delta R_n = \left(\frac{m}{M_n}\right)^{1/4} u_n$$

$$P_n = \left(\frac{m}{M_n}\right)^{-1/4} p_n$$

and we get for a monatomic crystal $(M_n = M)$:

$$\mathcal{H}_{eff} = \left(\frac{m}{M}\right)^{1/2}\left[\sum_n \frac{1}{2}\vec{p}_n^{\,2} + \sum_{n,m}\frac{1}{2}\,u_n D_{nm}\,u_m\right]$$

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 correction derives from the C_{BK} operator :

that can be estimated as follows

$$C_{\beta\alpha} \cong \int d\{r\} \sum_n \frac{m}{2M_n} 2 \left(\Psi_\beta^+ \vec{\nabla}_n \Psi_\alpha \right) \vec{P}_n = \int d\{r\} \sum_n \left(\frac{m}{M_n} \right)^{3/4} \left(\Psi_\beta^+ \vec{\nabla}_n \Psi_\alpha \right) \vec{p}_n$$

so that $\frac{C_{\beta\alpha}}{\delta E} \sim \mathcal{O}\left(\left(\frac{m}{M_n} \right)^{1/4} \right)$

$\Rightarrow$ The adiabatic approximation is controlled in the parameter

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

with $\left(\frac{m}{M} \right) \sim 10^{-5} \sim 10^{-3}$ follows $\kappa \sim 10^{-2} - 10^{-1}$

If κ is too large the crystal structure will melt due to zero-point fluctuations

$\rightarrow$ superfluid ^3He and ^4He

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2.2. Cohesive energy of crystals

The crystal structure is obtained by minimizing the electronic ground state energy $\mathcal{E}_0(\{R\})$ with repect to the ion configuration $\{R\}$.

The energy at the equilibrium configuration $\{R^{(0)}\}$, $\mathcal{E}_0(\{R^{(0)}\})$, carries information about the cohesive energy or binding energy i.e. the energy required to disassembled it into its constituents.

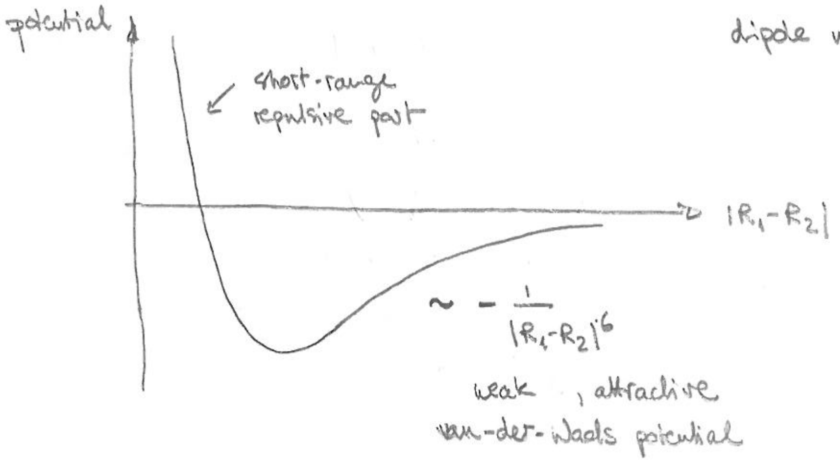
The function $\mathcal{E}_0(\{R\})$ is in general unknown. However, there are certain limits where the origin of the cohesive energy can be identified. →

Phenomenological classification of bonding in crystals

- van-der-Waals bonding

Molecular crystals consisting of the noble gases with closed electronic shells (no valence electrons) like Ne, Ar, Kr, ...

atoms interact pair-wise via the weak, attractive van-der-Waals interaction due to fluctuating dipole moments



often modeled by Lenard-Jones potential

- ionic bonding

  ionic crystals consististing of oppositely charged ions

  ions attract each other pair-wise by means of the strong Coulomb interaction

  crystal structures with a large coordination number z are prefered.

  Examples: NaCl, CsCl, ZnS

- covalent bonding

  covalent crystals characterized by a distribution of valence electrons that substantially differs from that found in the isolated atoms|ions.

  similar to the chemical bonding in molecules like H_2 (Heitler-London theory)

  bonding spatially oriented for example along the links of the diamond crystal structure of C, Si, Ge

- metallic bonding

  mediated by valence electrons,
  valence electrons delocalized from the ion cores and become conduction electrons.

  bonding not spatially oriented in contrast to the covalent case.

3. Harmonic lattice vibrations; phonons

The effective ion Hamiltonian derived in the adiabatic approximation reads

$$\mathcal{H}_{eff} = \sum_n \frac{m}{M_n} \frac{-\vec{\nabla}_n^2}{2} + \sum_{n,m} \frac{1}{2}\, \delta\vec{R}_n^{\,i}\, \underline{\underline{D_{nm}^{ij}}}\, \delta\vec{R}_m^{\,j}$$

← vector component

← label of ion

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

$$D_{nm}^{ij} = \frac{\partial}{\partial \vec{R}_n^{\,i}} \frac{\partial}{\partial \vec{R}_m^{\,j}} \mathcal{E}_0(\{R\}) \Big|_{\{R^{(0)}\}}$$

derives from the potential in the harmonic approximation and is the dynamical matrix.

The Hamiltonian $\mathcal{H}_{eff}$ describes a system of coupled harmonic oscillators and can be diagonalized by standard means. This identifies the normal modes of 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 vector $\vec{l}$ that identifies a specific primitive unit cell of the crystal and an index λ that counts the ions within the unit cell ($\lambda = 1, 2, \ldots, r$ for r ions in the unit cell).

$$D_{nm}^{ij} \longrightarrow D^{ij}(\underbrace{\vec{l}, \lambda}_{\substack{\text{specifies} \\ \text{the } n^{th} \text{ ion}}} ; \underbrace{\vec{m}, \mu}_{\text{the } m^{th} \text{ ion}})$$

where $\vec{l}$ and $\vec{m}$ are Bravais lattice vectors, and $\lambda, \mu = 1, 2, \ldots, r$

Due to the translational 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 $\vec{n}=\vec{m}$ for example one finds that D only depends on the difference $\vec{l}-\vec{m}$.

In order to proceed further we will make use of 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 $[T_R, T_{R'}] = 0$

as

$$T_{\vec{R}}T_{\vec{R}'}\Psi(r) = \Psi(r+R+R') = T_{R'}T_R\Psi(r) = T_{R+R'}\Psi(r) \quad ⊛$$

Furthermore, consider an operator H that commutes $[H, T_R] = 0$ for all $\vec{R}$ of the Bravais lattice.

We can then choose simultaneous eigenstates Ψ_α of H and T_R for all R:

$$H\Psi_\alpha = \varepsilon_\alpha\Psi_\alpha$$

$$T_R\Psi_\alpha = c_\alpha(R)\,\Psi_\alpha$$

From ⊛ follows

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

Moreover, from the normalization condition

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

That in total implies

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

where the momentum $\vec{k}$ is specific for the ψ_α state.

The eigenfunction 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 momentum $\vec{k}$ will be restricted to the 1. BZ.

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

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

where the Bloch function $u_{nk}(\vec{r})$ obeys $u_{nk}(r+R) = u_{nk}(\vec{r})$ for all $\vec{R}$ of the Bravais lattice

Note: for systems that are invariant under arbitrary translation the momentum is conserved and a good quantum number.

in contrast, for systems that are only invariant 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

use Bloch's theorem to diagonalize the dynamical matrix $\tilde{D}^{ij}(\vec{l},\lambda;\vec{m},\mu) = \frac{m}{\sqrt{M_\lambda M_\mu}} D^{ij}(\vec{l},\lambda;\vec{m},\mu)$

consider eigenvalue problem

$$\sum_{j,\mu,\vec{m}} \tilde{D}^{ij}(\vec{l},\lambda;\vec{m},\mu)\,\Psi^{j}(\vec{m},\mu) = d\,\Psi^{i}(\vec{l},\lambda)$$

← for later convenience

due to the translational 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 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

$$\Psi^{j}_{kn}(\vec{m},\mu) = e^{i\vec{k}\vec{m}}\,u^{j}_{kn}(\vec{m},\mu) = e^{i\vec{k}\vec{m}}\,\vec{e}^{\,j}_{kn}(\mu)$$

where the polarization vector $\vec{e}_{kn}(\mu) = u^{j}_{kn}(\vec{m},\mu) = u^{j}_{kn}(0,\mu)$ is the corresponding Bloch function and the set of quantum numbers $\{\vec{k},n\}$ with $\vec{k}\in 1BZ$:

$$\sum_{j,\mu,\vec{m}} \tilde{D}^{ij}(\vec{l},\lambda;\vec{m},\mu)\,\Psi^{j}_{kn}(\vec{m},\mu) = d_{kn}\,\Psi^{i}_{kn}(\vec{l},\lambda)$$

using $$V_{uc}\sum_{\substack{\vec R \in \text{Bravais}\\ \text{lattice}}} e^{i\vec k\vec R} = \underset{\uparrow \text{ total volume}}{V}\,\delta_{\vec k,0} \xrightarrow{V\to\infty} (2\pi)^3\,\delta(\vec k)$$ (Born-von Karman boundary conditions)

$$\sum_{K\in 1BZ} e^{i\vec k\vec R} = N\,\delta_{\vec R,0}$$ with N # of lattice sites $= \frac{V}{V_{uc}}$

and for $V\to\infty$ points in the 1BZ become dense so that

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

we get for the Fourier transform:

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

$= \tilde D^{ij}_k(\lambda,\mu)$ as D^{ij} only depends on $\vec l-\vec m$

with $\sum_{\vec m} V_{uc} = V$

$$\to \boxed{\sum_{j,\mu}\tilde D^{ij}_k(\lambda,\mu)\,\hat{\vec e}^{\,j}_{kn}(\mu) = d_{kn}\,\hat{\vec e}^{\,i}_{kn}(\lambda)}$$

eigenvalue problem that determines the polarization vectors $\vec e_{kn}$;

corresponds to diagonalizing a $3r\times 3r$ matrix with $\lambda,\mu = 1,2,\dots,r$ and r are the numbers of atoms per unit cell;

the eigenvectors are labeled by the quantum number $n = 1,2,\dots,3\cdot r$

eigenvalue problem to be solved for each vector $\vec k$ of the 1. Brillouin zone

→ evolution of eigenvalues d_{kn} as a function of $\vec k$

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

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

the dynamical matrix is real and symmetric, $\tilde{D}^{ij}_{nm} = \tilde{D}^{ji}_{mn}$.

→ its Fourier transform 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 $\underline{d_{Kn} > 0}$

Moreover, $\left(\tilde{D}^{ij}_{K}(\lambda,\mu)\right)^{*} = \tilde{D}^{ij}_{-K}(\lambda,\mu)$ so that we can choose the quantum numbers n such that $d_{K,n} = d_{-K,n}$ and eigenvectors $\vec{e}^{\,*}_{-Kn} = \vec{e}_{Kn}$.

Expansion in normal modes

we expand position and momentum in normal coordinates q_{Kn} and p_{Kn}

$$\delta\vec{R}^{i}(\vec{m},\mu) = \frac{1}{\sqrt{N}} \sum_{Kn} \sqrt{\frac{m}{M_\mu}}\, e^{i\vec{K}\vec{m}}\, \vec{e}^{\,i}_{Kn}(\mu)\, q_{Kn}$$

$$\vec{P}^{i}(\vec{m},\mu) = \frac{1}{\sqrt{N}} \sum_{Kn} \sqrt{\frac{M_\mu}{m}}\, e^{-i\vec{K}\vec{m}}\, \vec{e}^{\,i*}_{Kn}(\mu)\, p_{Kn} \quad = -i\vec{\nabla}_{\{\vec{m},\mu\}}$$

with N # of Bravais lattice sites

and $[q_{Kn}, q_{K'n'}] = [p_{Kn}, p_{K'n'}] = 0$ and $[q_{Kn}, p_{K'n'}] = i\,\delta_{KK'}\delta_{nn'}$.

This ensures in particular that the commutator is obeyed:

$$\left[\delta\vec{R}^{i}(m,\mu), \vec{P}^{j}(\vec{\ell},\lambda)\right] = \frac{1}{N}\sum_{\substack{Kn\\K'n'}} e^{i\vec{K}\vec{m} - i\vec{K}'\vec{\ell}}\, \vec{e}^{\,i}_{Kn}(\mu)\, \vec{e}^{\,j*}_{K'n'}(\lambda)\, [q_{Kn}, p_{K'n'}]$$

$$= i \underbrace{\frac{1}{N}\sum_{K} e^{i\vec{K}(\vec{m}-\vec{\ell})}}_{=\delta_{\vec{m},\vec{\ell}}} \underbrace{\sum_{n} \vec{e}^{\,i}_{Kn}(\mu)\, \vec{e}^{\,j*}_{Kn}(\lambda)}_{=\delta_{\mu\lambda}\delta_{ij}\ \text{completeness}} = i\,\delta_{\vec{m},\vec{\ell}}\,\delta_{\mu,\lambda}\,\delta_{ij}$$

effective ionic Hamiltonian:

$$\mathcal{H}_{eff} = \sum_{\vec{m},\mu} \frac{m}{M_\mu} \frac{1}{2} \vec{P}^{2}(\vec{m},\mu) + \sum_{\substack{\vec{m},\vec{\ell}\\ \mu,\lambda}} \frac{1}{2}\, \delta\vec{R}^{i}(\vec{\ell},\lambda)\, D^{ij}(\vec{\ell},\lambda;\vec{m},\mu)\, \delta\vec{R}^{j}(\vec{m},\mu)$$

becomes

$$\mathcal{H}_{eff} = \frac{1}{2}\sum_{\vec m,\mu}\frac{1}{N}\sum_{\substack{k,n\\k'n'}} \underbrace{e^{-i\vec k\vec m - i\vec k'\vec m}}_{\to N\delta_{\vec k,-\vec k'}} \vec e^{\,i*}_{kn}(\mu)\,\vec e^{\,i*}_{k'n'}(\mu)\; p_{kn}\, p_{k'n'}$$

$$+\frac{1}{2}\frac{1}{N}\sum_{\substack{kn\\k'n'}}\sum_{\substack{\vec m,\vec l\\\mu,\lambda}} e^{i\vec k\vec l + i\vec k'\vec m}\;\vec e^{\,i}_{kn}(\lambda)\underbrace{\sqrt{\frac{m}{M_\lambda M_\mu}}\,D^{ij}(\vec l,\lambda;\vec m,\mu)}_{\frac{1}{N}\sum_{\vec q\in 1BZ} e^{i\vec q(\vec l-\vec m)}\tilde D^{ij}_{q}(\lambda,\mu)}\vec e^{\,j}_{k'n'}(\mu)\quad q_{kn}\, q_{k'n'}$$

$$\underbrace{\frac{1}{N}\sum_{\vec q\in 1BZ} e^{i\vec q(\vec l-\vec m)}\tilde D^{ij}_{q}(\lambda,\mu)}_{\text{sum over } \vec l \text{ and } \vec m \;\to\; N^2\delta_{\vec k+\vec q,0}\,\delta_{\vec k',\vec q}}$$

$$= \frac{1}{2}\sum_{\mu,n,n'} \vec e^{\,i*}_{kn}(\mu)\,\vec e^{\,i*}_{-k,n'}(\mu)\; p_{kn}\, p_{-kn'}$$

$$+\frac{1}{2}\sum_{n,n',\mu,\lambda} \vec e^{\,i}_{kn}(\lambda)\underbrace{\tilde D^{ij}_{-k}(\lambda,\mu)\,\vec e^{\,j}_{-k,n'}(\mu)}_{=\, d_{-k,n'}\,\vec e^{\,j}_{-kn'}(\mu)}\; q_{kn}\, q_{-kn'}$$

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

$$\boxed{\mathcal{H}_{eff} = \frac{1}{2}\sum_{\substack{k\in 1BZ\\ n=1,2,\dots 3r}}\Big[\, p_{kn}\, p_{-kn} + d_{kn}\, q_{kn}\, q_{-kn}\Big]}$$

introducing annihilation and creation operators (remember $d_{kn} > 0$)

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

$$\rightarrow \quad [b_{kn}, b^+_{k'n'}] = \delta_{k,k'}\delta_{n,n'} \quad , \quad [b_{kn}, b_{k'n'}] = [b^+_{kn}, b^+_{k'n'}] = 0 \qquad \text{exercise !}$$

$$\Rightarrow \quad \mathcal{H}_{eff} = \frac{1}{2}\sum_{k,n}\left[-\frac{\sqrt{d_{kn}}}{2}\left(b^+_{kn} - b_{-kn}\right)\left(b^+_{-kn} - b_{kn}\right) + \frac{\sqrt{d_{kn}}}{2}\left(b^+_{kn} + b_{-kn}\right)\left(b^+_{-kn} + b_{kn}\right)\right]$$

$$= \frac{1}{2}\sum_{k,n}\sqrt{d_{kn}}\left[b_{-kn}b^+_{-kn} + b^+_{kn}b_{kn}\right]$$

with $\omega_{kn} = \sqrt{d_{kn}}$ and $\omega_{-kn} = \omega_{kn}$ and $b_{kn}b^+_{kn} = b^+_{kn}b_{kn} + 1$

$$\hookrightarrow \quad \boxed{\mathcal{H}_{eff} = \sum_{kn}\omega_{kn}\left[b^+_{kn}b_{kn} + 1/2\right]} \qquad \text{Phonon Hamiltonian}$$

Remarks :

- $\omega_{kn} = \omega_n(\vec{k})$ define the phonon dispersions with $\vec{k} \in$ 1BZ.
- there are $n = 1, 2, \ldots, 3r$ bands where r is the number of atoms in the unit cell
- Three of the $3r$ bands have the property $\omega_n(\vec{k}) \rightarrow 0$ for $\vec{k} \rightarrow 0$, these type 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 (cf. concert pitch A with 440 Hz and sound velocity of gold $v \cong 3200 \frac{m}{s}$ $\rightarrow \lambda \cong 7\,m$; in air $v \cong 340 \frac{m}{s} \rightarrow \lambda \simeq 0.8\,m$.)

  → acoustic phonon branches

  Their existence is a consequence of the spontaneous breaking of translation symmetry by the crystal structure

  In general, the breaking of a continuous symmetry imply the presence of low-energy 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 direction of space

$$\delta\vec{R}^i(\vec{\ell},\mu) \equiv \delta R^i \quad \text{with } i = x,y,z$$

this should not cost any energy as rigid translation does not generate a restoring force of the crystal $\Rightarrow$ 3 acoustic phonon branches

For small $\vec{k}$:

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

with the sound velocities $c_n(\hat{k})$ that depend on the orientation $\hat{k} = \frac{\vec{k}}{|\vec{k}|}$.

They are related to the elastic constants of the crystal like bulk and shear modulus.

Note: a liquid in contrast only possesses a single longitudinal sound mode, no shear modulus!

- Other phonon branches are known as optical phonon branches because they can often be excited by light

- dispersion relations $\omega_n(\vec{k})$ possess the full symmetry of the point group.

- anharmonic corrections $\varepsilon_0^{(3)}(\{R\}) = \frac{1}{3!} A_{nml}\,\delta R_n \delta R_m \delta R_l$

  results in an interaction between phonons b^+bb etc.

  → necessary to explain eg. thermal expansion

3.3. Measuring phonon dispersions : neutron scattering

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

neutrons are neutral particles and interact mainly with the atomic nuclei and thus also with phonons

(neutrons also interact with magnetic moments that is used for the investigation of magnetism eg. determination of magnetic order, measurement of spin waves etc.)

neutron - ion interaction:

$$V(\vec{r}) = \sum_{\vec{l} \in \text{Bravais lattice}} \; \sum_{\lambda \in \text{basis}} v_\lambda(\vec{r} - \vec{R}(\vec{l},\lambda))$$

the interaction potential v_λ is very short ranged, its range being of order of typical nuclear dimensions, 10^{-15} m = 1 fm.

With respect to the typical length scale of crystal lattice constants ~ 10^{-10} m = 1 Å the potential can be approximated by delta functions:

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

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

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

sum over all possible final states of the crystal

final momentum of neutron detected by detector with E_f : final energy of the crystal

E_i : initial energy of the crystal

$\hbar\omega = \frac{(\hbar\vec{k}_{out})^2}{2m_n} - \frac{(\hbar\vec{k}_{in})^2}{2m_n}$: energy gained by the neutron in the scattering process

m_n : mass of neutron

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

final & initial state of crystal

with $\vec{q} = \vec{k}_{out} - \vec{k}_{in}$ transfered wavevector

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

usually the crystal is not in a definite eigenstate $|i\rangle$ but rather the states are thermally populated → thermally averaged transition rate

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

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

$$\frac{d^2\sigma}{d\Omega\, d\omega} d\Omega\, d\omega = \frac{P \times \text{number of final states for neutron}}{\text{incoming flux density of neutrons}}$$

$$= \frac{P \cdot Vol \frac{d\vec{k}_{out}}{(2\pi)^3}}{\frac{|\hbar\vec{k}_{in}|}{m_n} \frac{1}{Vol}} = P\, Vol^2 \frac{m_n}{\hbar|\vec{k}_{in}|} \frac{k_{out}^2\, dk_{out}\, \overset{\text{solid angle}}{d\Omega}}{(2\pi)^3}$$

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

$$\rightarrow \quad \frac{d^2\sigma}{d\Omega\, d\omega} = P \cdot \frac{|V_0|^2}{(2\pi)^3} \frac{|k_{out}|}{|k_{in}|} \frac{m_n^2}{\hbar^2}$$

for a monatomic Bravais lattice this simplifies further to

$$\boxed{\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{|k_{out}|}{|k_{in}|} \frac{m_n^2 V_0^2}{(2\pi)^3 \hbar^4} \underset{\substack{\uparrow \\ \text{number of lattice sites}}}{N} S(\vec{q},\omega)}$$

with the <u>dynamic structure factor</u>

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

ionic Hamiltonian

with $$\int_{-\infty}^{\infty} dt\, e^{+i\omega t} = 2\pi\delta(\omega)$$ and $$e^{-\frac{iHt}{\hbar}} |i\rangle = e^{-\frac{iE_i t}{\hbar}} |i\rangle$$ etc.

$$\hookrightarrow \quad S(\vec{q},\omega) = \sum_{f,i} \frac{e^{-\beta E_i}}{Z} \int_{-\infty}^{\infty} dt\, e^{+i\omega t} \frac{1}{N} \sum_{\vec{\ell},\vec{m}} \langle i | e^{i\vec{q}\vec{R}(\vec{\ell})} | f \rangle \langle f | \underbrace{e^{\frac{iHt}{\hbar}} e^{-i\vec{q}\vec{R}(\vec{m})} e^{-i\frac{Ht}{\hbar}}}_{= \exp[-i\vec{q}\vec{R}(\vec{m},t)]} | i \rangle$$

↑ operator in the Heisenberg picture

using $\sum_f |f\rangle\langle f| = 1$ completeness

$$\hookrightarrow \quad S(\vec{q},\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}\, S(\vec{q},t)$$

where

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

for a monatomic Bravais lattice : $\vec{R}(\vec{m},t) = \vec{m} + \underset{\uparrow\ \text{deviations from equilibrium} \to \text{phonons!}}{\delta\vec{R}(\vec{m},t)}$

$$S(\vec{q},t) = \frac{1}{N}\sum_{\vec{\ell},\vec{m}} e^{i\vec{q}(\vec{\ell}-\vec{m})}\, \underset{\uparrow\ \text{thermal average}}{\langle e^{i\vec{q}\,\delta\vec{R}(\vec{\ell},0)}\, e^{-i\vec{q}\,\delta\vec{R}(\vec{m},t)}\rangle}$$

If the phonons are treated in the harmonic approximation the thermal average simplifies

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

↑
harmonic
approximation
exercise !

using that $\langle(\vec{q}\,\delta\vec{R}(\vec{\ell},0))^2\rangle = \langle(\vec{q}\,\delta\vec{R}(\vec{m},t))^2\rangle \equiv 2W$ independent of lattice site and time

and $\langle(\vec{q}\,\delta\vec{R}(\vec{\ell},0))(\vec{q}\,\delta\vec{R}(\vec{m},t))\rangle = \langle\vec{q}\,\delta\vec{R}(0,0)\;\vec{q}\,\delta\vec{R}(\vec{m}-\vec{\ell},t)\rangle$ due to discrete translation invariance of the Bravais lattice

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

with <u>Debye-Waller factor</u> e^{-2W} (temperature dependent)

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 $n=0$

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

Note: $\vec{q}$ not necessary within 1. Brillouin zone!

$$= 2\pi\delta(\omega) \, e^{-2W} \, \frac{(2\pi)^3}{V_{uc}} \sum_{\vec{G} \in \text{reciprocal lattice}} \delta(\vec{q}-\vec{G})$$

Delta functions in frequency and momentum space

=> scattering Bragg peaks remain sharp

Only their weight is reduced by the Debye-Waller factor e^{-2W}.

7.11.2013

Single-phonon contribution $n=1$

needed expectation value

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

and

$$\langle q_{kn}(0)\, q_{k'n'}(t) \rangle = \frac{1}{2} \frac{1}{\sqrt{\omega_{kn}\omega_{k'n'}}} \langle (b^+_{kn} + b_{-kn})(b^+_{k'n'}(t) + b_{-k'n'}(t)) \rangle$$

$$= \frac{1}{2} \frac{1}{\sqrt{\omega_{kn}\omega_{k'n'}}} \langle b^+_{kn} b_{-k'n'} e^{-i\omega_{k'n'}t} + \underbrace{b_{-kn} b^+_{k'n'}}_{b^+_{k'n'} b_{-kn} + \delta_{k',-k}\delta_{n,n'}} e^{i\omega_{k'n'}t} \rangle$$

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

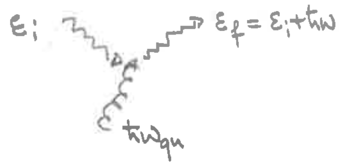
with
$\omega_{-kn} = \omega_{kn}$
$\hat{e}^i_{-kn} = \hat{e}^{i*}_{kn}$

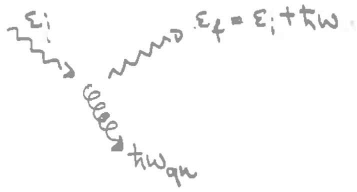
$$S^{(1)}(\vec{q},\omega) = e^{-2W} \sum_{\vec{l}} e^{-i\vec{q}\vec{l}} \frac{1}{N} \sum_{k,n} \frac{m}{M} e^{-i\vec{k}\vec{l}} |\vec{q}\hat{e}_{kn}|^2 \frac{1}{2\omega_{kn}}$$

$$\times \left[n_B(\omega_{kn})\, 2\pi\delta(\omega-\omega_{kn}) + (1+n_B(\omega_{kn}))\, 2\pi\delta(\omega+\omega_{kn}) \right]$$

and finally using $\frac{1}{N}\sum_{\vec{l}} e^{-i(\vec{q}+\vec{k})\vec{l}} = \sum_{\substack{\vec{G}\in \\ \text{reciprocal} \\ \text{lattice}}} \delta_{\vec{q}+\vec{k},\vec{G}}$

$$\boxed{S^{(1)}(\vec{q},\omega) = e^{-2W}\,\frac{m}{M}\sum_{n} |\vec{q}\,\hat{e}_{qn}|^2\,\frac{1}{2\omega_{qn}}\Big[\underbrace{n_B(\omega_{qn})}_{\substack{\text{absorption} \\ \text{of a phonon}}}\,2\pi\delta(\omega-\omega_{qn}) + \underbrace{\big(1+n_B(\omega_{qn})\big)}_{\substack{\text{spontaneous \& stimulated emission} \\ \text{of a phonon}}}\,2\pi\delta(\omega+\omega_{qn})\Big]}$$

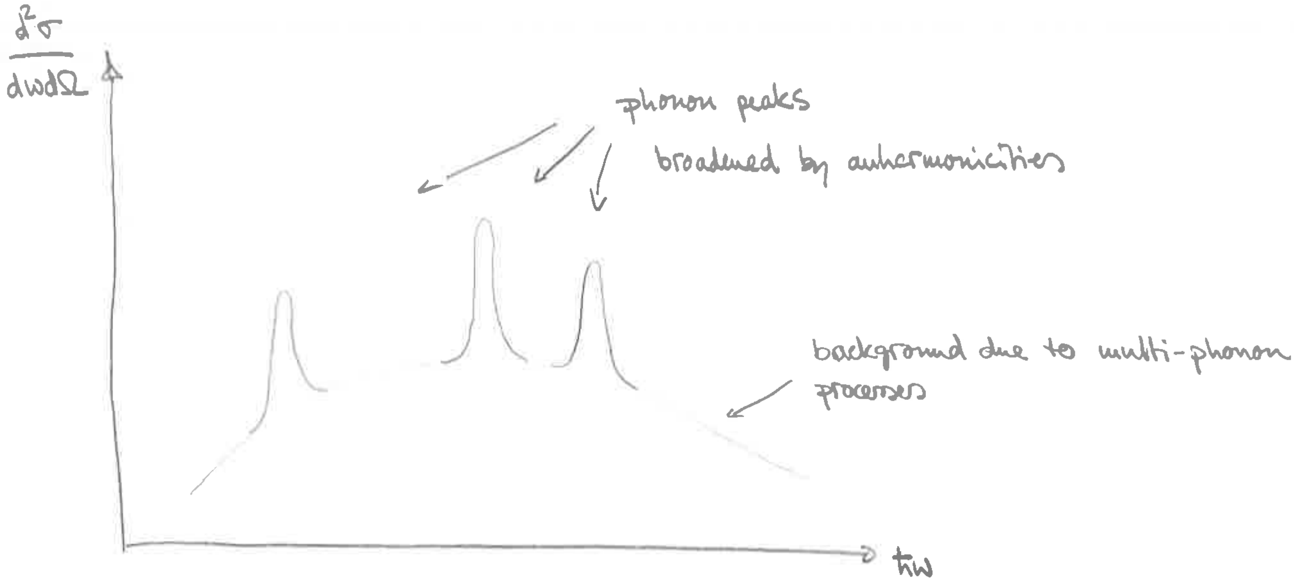




with $\varepsilon_{i/f} = \frac{|\hbar\vec{k}_{i/out}|^2}{2m_n}$

The absorption and emission of a phonon during the scattering process results in <u>additional sharp peaks</u> at finite energy $\hbar\omega = \pm\hbar\omega_{qn}$

→ measurement of phonon dispersion by <u>inelastic neutron scattering</u>.



<u>Remarks</u>

- neutron scattering method of choice for measuring phonon spectra.
  X-rays much less suitable due to linear dispersion of photons → difficulty in energy resolution.
- photons in the visible range can be used to probe phonons with $\vec{k} \approx 0$ (Γ point)
  → Brillouin scattering if phonon involved is acoustic
  Raman scattering if phonon is optical.

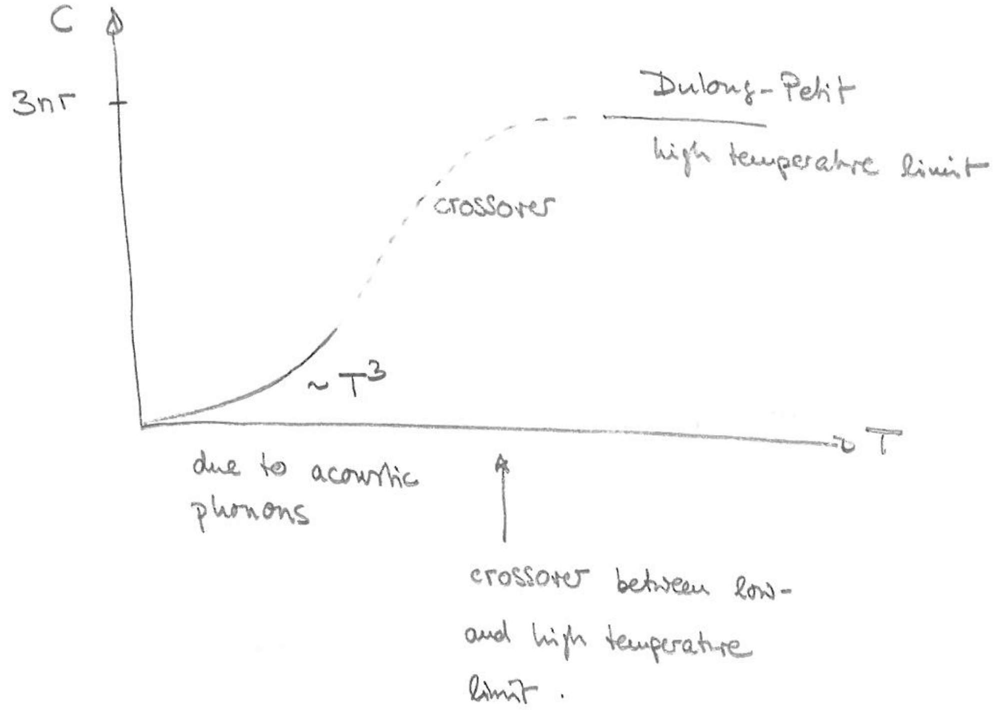
phonon emission/absorption results in Stokes/anti-Stokes component of scattered radiation.

3.4. Thermodynamics of phonons

→ see exercise for more details

specific heat $C = \frac{\partial E}{\partial T}$ with energy density E and temperature T

contribution from phonons



A particular modeling of the crossover is provided by the Debye-model where the crossover occurs at the Debye temperature Θ_D

typical values :

$\Theta_D \sim 160$ K Au.

$\Theta_D \sim 350$ K Cu

$\Theta_D \sim 470$ K Fe

$\Theta_D \sim 1860$ K diamant

4. Non-interacting electrons in a crystal

Consider now eigenvalue problem for electrons, cf. step I in the adiabatic approximation of chapter 2.1.

Here: neglect 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

eigenvalue problem of a single effective particle in the ionic potential

$$H \psi(\vec{r}) = \varepsilon \psi(\vec{r}) \quad \text{with} \quad H = -\frac{\hbar^2 \nabla^2}{2m} + U(\vec{r})$$

with spin-orbit coupling effects neglected (non-relativistic limit)

The potential possesses the discrete translation symmetry of the Bravais lattice

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

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

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

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

Explicit proof in the present case:

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

$$U(\vec r) = \sum_{\substack{G \in \text{reciprocal} \\ \text{lattice}}} e^{i\vec G\vec r}\, U_{\vec G}$$

The potential only has Fourier components $U_{\vec G}$ due to the discrete translational symmetry $U(r+R) = U(r)$ with $e^{iGR} = 1$.

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

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

From which follows the Schrödinger equation in momentum space

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

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

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

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

$$\to \psi_n(\vec r) = \sum_q e^{i\vec q\vec r} c_{nq} = \sum_K e^{i(\vec k+\vec K)\vec r} c_{n(\vec k+\vec K)} = e^{i\vec k\vec r} u_{nk}(\vec r)$$

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

Consequences:

- $\psi_{nk}(\vec{r})$ is not an eigenstate of the momentum operator $\vec{p}$ as

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

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

- The effective Schrödinger equation obeyed by the Bloch function reads

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

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

Due to the periodicity of $u_{nk}(\vec{r})$ 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_{uc} will give rise to disretely spaced energy levels that will be labeled by the band index n.

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

$$\sum_n u^*_{nk}(\vec{r})\,u_{nk}(\vec{r}\,') = V_{uc}\,\delta(\vec{r}-\vec{r}\,') \qquad \text{completeness}$$

$$\rightarrow \int_{1BZ}\frac{d\vec{k}}{(2\pi)^3}\sum_n \psi^*_{nk}(\vec{r})\,\psi_{nk}(\vec{r}\,') = \underbrace{\int_{1BZ}\frac{dk}{(2\pi)^3}}_{\frac{1}{V_{uc}}}\ \underbrace{\sum_n u^*_{nk}(\vec{r})\,u_{nk}(\vec{r})}_{V_{uc}\,\delta(\vec{r}-\vec{r}\,')} = \delta(\vec{r}-\vec{r}\,')$$

Such a basis contains infinitely many functions $u_{nk}(\vec{r})$

→ there are infinitely many energy bands $n = 0, 1, 2, 3, \ldots$

(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

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

This represents the electronic band structure of the crystal.

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

42. Electron in a weak periodic potential

Assume that Fourier component $U_{\vec{G}}$ with $\vec{G} \neq 0$ are small

→ useful for a qualitative understanding

The zero component $U_{G=0}$ can be absorbed in the choice of the zero on the energy axis $\varepsilon \to \varepsilon + U_{G=0}$ 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 $\vec{K}' = \vec{K} - \vec{G}$, $\vec{G} = \vec{K} - \vec{K}'$

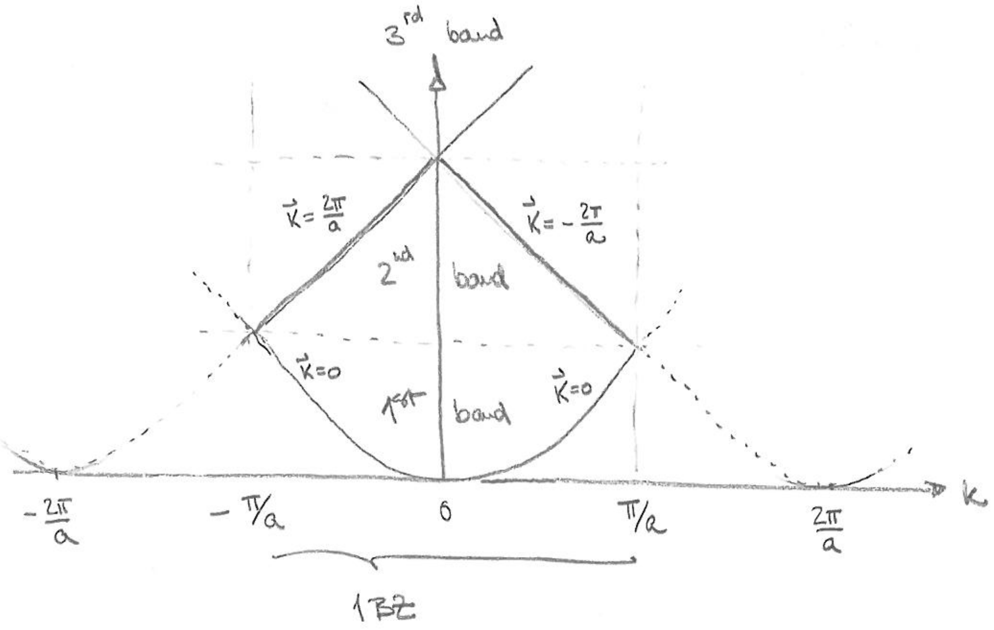
$$\frac{\hbar^2 (\vec{k}+\vec{K})^2}{2m} c_{\vec{k}+\vec{K}} + \sum_{\vec{K}' \neq \vec{K}} U_{\vec{K}-\vec{K}'}\, c_{\vec{k}+\vec{K}'} = \varepsilon\, c_{\vec{k}+\vec{K}}$$

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

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

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

for example: energy band in one dimension, $\vec R_n = na$, $\vec K_m = \frac{2\pi}{a} m$



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 electron bands are degenerate. We then need to apply the method of degenerate perturbation theory.

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

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

reduced Schrödinger equation with $\vec{k} \approx \vec{k}_d$

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

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

corresponds to <u>$n \times n$ matrix equation</u> for n-degenerate eigenstates!

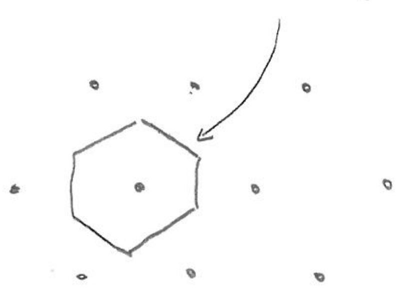
Where do degeneracies occur?

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

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

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

for example: on all boundaries of the 1BZ



Most importantly : only two degenerate levels

→ 2x2 matrix equation

$$\varepsilon^{(0)}(\vec{k}+\vec{K}_1)\, C_{K+K_1} + U_{K_1-K_2}\, C_{K+K_2} = \varepsilon\, C_{K+K_1}$$

$$\varepsilon^{(0)}(K+K_2)\, C_{K+K_2} + U_{K_2-K_1}\, C_{K+K_1} = \varepsilon\, C_{K+K_2}$$

eigenvalues : with $U_{-K} = U_K^*$

$$\boxed{\varepsilon = \frac{\varepsilon^{(0)}_{K+K_1} + \varepsilon^{(0)}_{K+K_2}}{2} \pm \sqrt{\frac{\left(\varepsilon^{(0)}_{K+K_1} - \varepsilon^{(0)}_{K+K_2}\right)^2}{4} + |U_{K_1-K_2}|^2}}$$

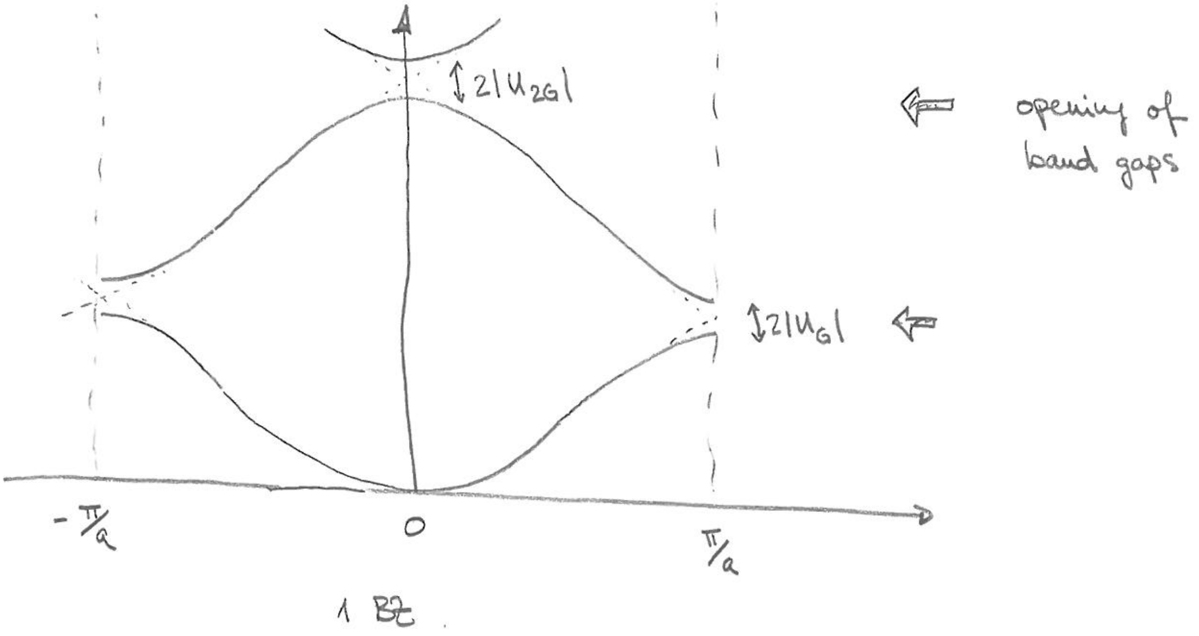
The interaction $U_{K_1-K_2}$ leads to a <u>level repulsion</u>.

at the degeneracy point $\vec{k} = \vec{k}_d$: $\varepsilon^{(0)} \equiv \varepsilon^{(0)}(\vec{k}_d+\vec{K}_1) = \varepsilon^{(0)}(\vec{k}_d+\vec{K}_2)$

$$\boxed{\varepsilon = \varepsilon^{(0)} \pm |U_{K_1-K_2}|}$$

<u>splitting</u> of the bands <u>linear</u> in $|U_{K_1-K_2}|$ due to <u>Bragg reflection</u> !

one-dimensional example : "reduced zone scheme"



opening of band gaps

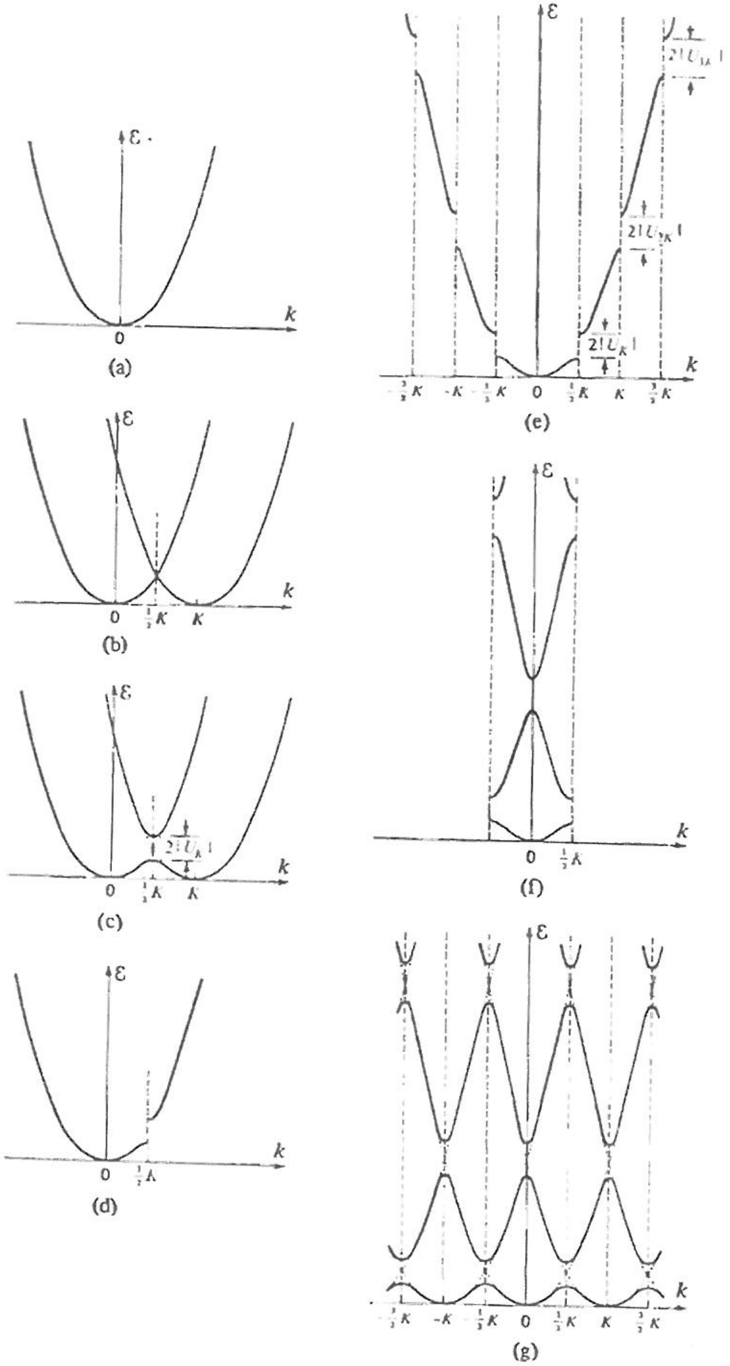
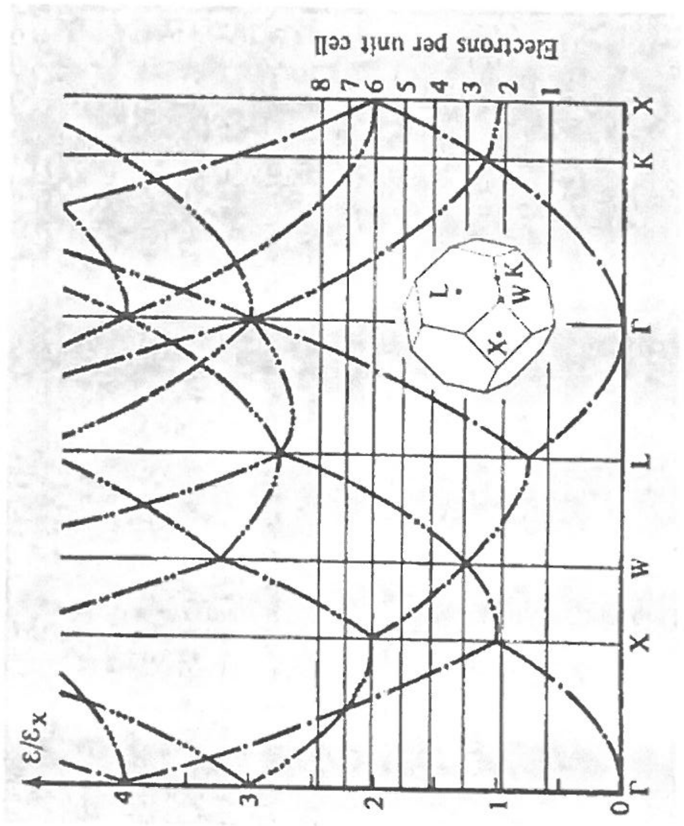


Figure 9.4

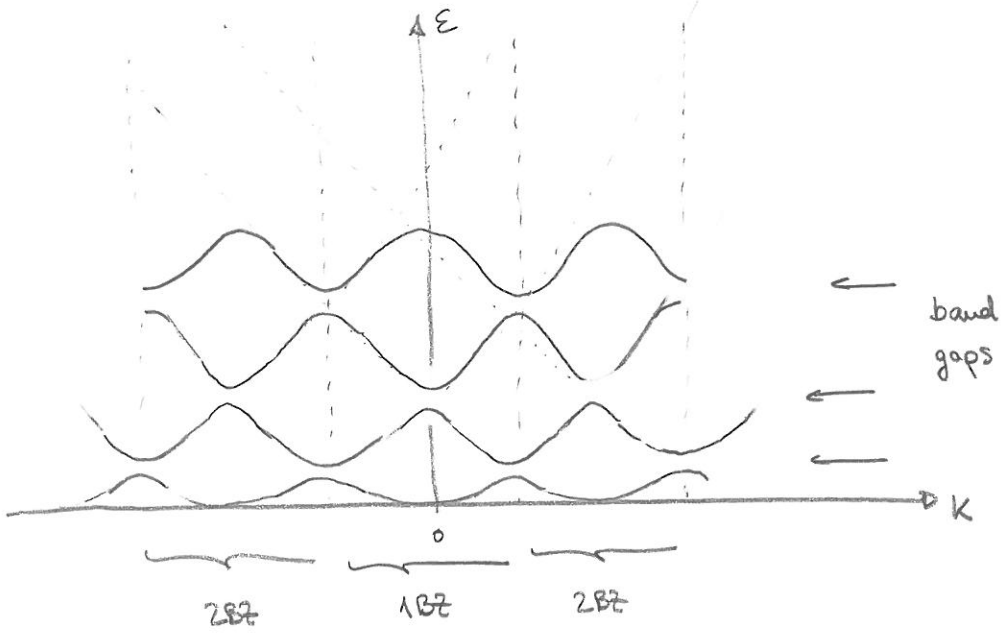
(a) The free electron $\mathcal{E}$ vs. k parabola in one dimension. (b) Step 1 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane," due to a weak periodic potential. If the Bragg "plane" is that determined by K, a second free electron parabola is drawn, centered on K. (c) Step 2 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane." The degeneracy of the two parabolas at $K/2$ is split. (d) Those portions of part (c) corresponding to the original free electron parabola given in (a). (e) Effect of all additional Bragg "planes" on the free electron parabola. This particular way of displaying the electronic levels in a periodic potential is known as the *extended-zone scheme.* (f) The levels of (e), displayed in a *reduced-zone scheme.* (g) Free electron levels of (e) or (f) in a *repeated-zone scheme.*

Figure 9.5

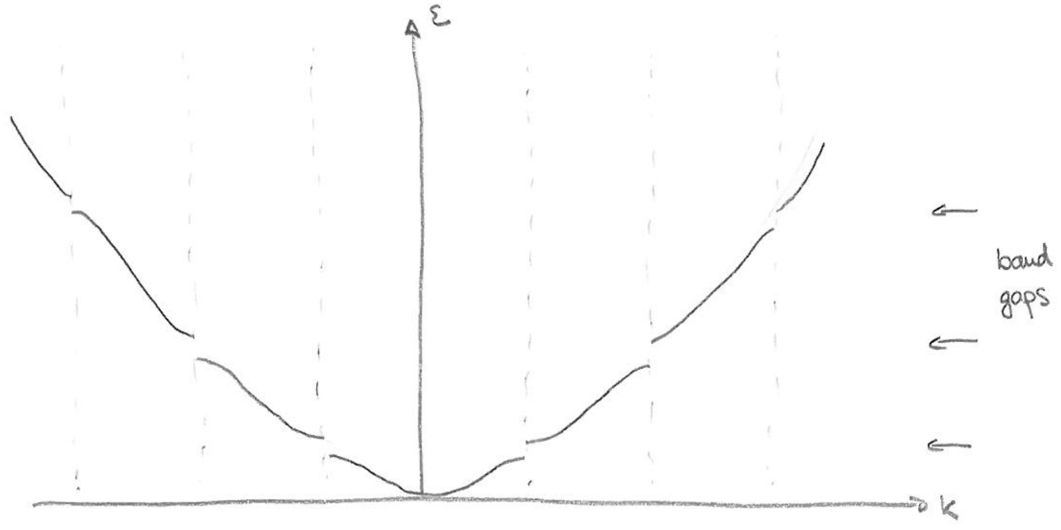
Free electron energy levels for an fcc Bravais lattice. The energies are plotted along lines in the first Brillouin zone joining the points $\Gamma(\mathbf{k} = 0)$, K, L, W, and X. $\mathcal{E}_x$ is the energy at point X ($[\hbar^2/2m][2\pi/a]^2$). The horizontal lines give Fermi energies for the indicated numbers of electrons per primitive cell. The number of dots on a curve specifies the number of degenerate free electron levels represented by the curve. (From F. Herman, in *An Atomistic Approach to the Nature and Properties of Materials,* J. A. Pask, ed., Wiley, New York, 1967.)



"repeated zone scheme": bands periodically continued for all k.



"extended zone scheme":



Energy band gap:

Generally, a weak periodic potential introduces energy gaps by splitting degeneracy due to Bragg reflection. Energy bands then become separated by a finite energy gap $\Delta \simeq 2|U_{K_1-K_2}|$

The Fermi energy is then located within a bandgap.

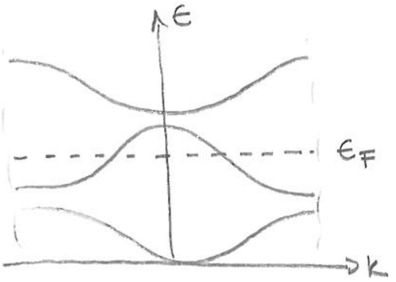
The density of (non-interacting) electrons corresponds then to an <u>even number of electrons per unit cell</u> as

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

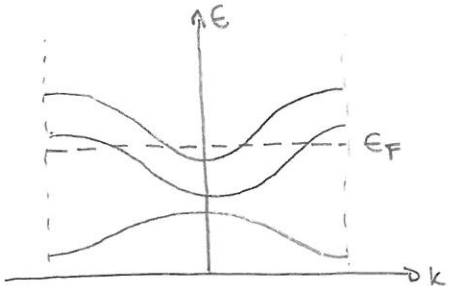
The most upper filled band is the <u>valence band</u> and the first empty band is the <u>conduction band</u>.
In order to excite electrons out of the groundstate an energy larger than the band gap is required whose magnitude is in the range of 1 eV ~ 7 eV.

Such materials are <u>semiconductors</u> or <u>insulators</u>.

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



single band crosses the Fermi energy



two bands cross the Fermi energy

The partially filled bands are here the <u>conduction bands</u>.

Around the Fermi energy electrons can be excited with very low energies.

→ <u>metal</u>

The condition $\epsilon_{n\vec{k}} \overset{!}{=} \epsilon_F$ defines one or several d-1 dimensional manifolds within the first Brillouin zone that are the <u>Fermi surface</u> or <u>Fermi surfaces</u>, respectively.

4.3. Fermi surfaces

Groundstate of non-interacting electrons in a periodic potential (in zero magnetic field):

> occupy all states with $\vec{k} \in 1BZ$ and band index n with $\epsilon_{nk} \leq \epsilon_F$
>
> once with a spin-up and once with a spin-down configuration.
>
> ϵ_F is the <u>Fermi energy</u>.

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

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

with the volume V.

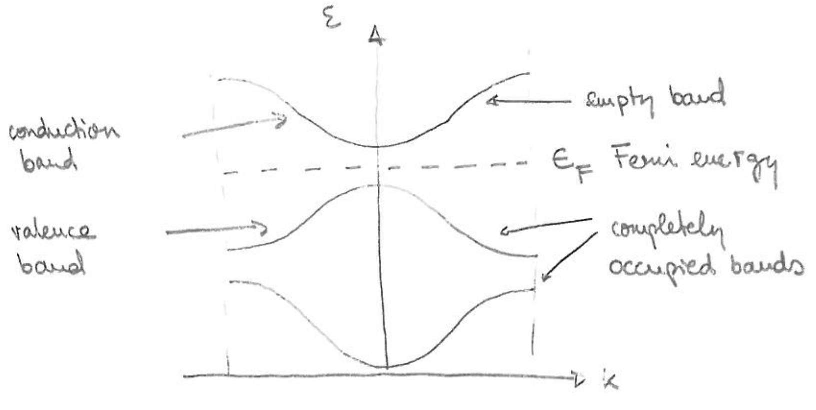
How many electrons can occupy a single band?

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

$\longrightarrow$ each band can be occupied by $2N$ electrons (N with spin $\uparrow$ and N with spin $\downarrow$)

One distinguishes two important cases:

I.) All bands either completely filled or completely empty



Example: two-dimensional Fermi surface of single energy band

with $\epsilon_k = -2t\left(\cos k_x a + \cos k_y a\right) \overset{!}{=} \epsilon_F$

$\rightarrow$ contour plot in Mathematica

Remarks

- typical values for Fermi energies: $\epsilon_F \sim 1 - 10$ eV, $T_F \sim 10^4 - 10^5$ K
- Fermi surface can have different topologies (open or closed)
- 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.

4.4. Density of states and van-Hove singularities

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

$$\boxed{\nu(\varepsilon) = \underset{\substack{\uparrow \\ \text{spin}}}{2}\,\frac{1}{V}\sum_{n,k\in 1BZ}\delta(\varepsilon - \varepsilon_{nk})}$$

sometimes also the density of states per spin is considered.

Introducing the density of states per band $\nu(\varepsilon) = \sum_n \nu_n(\varepsilon)$

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

with $\displaystyle\int_{-\infty}^{\infty} d\varepsilon\, \nu_n(\varepsilon) = 2\int_{1BZ}\frac{d\vec{k}}{(2\pi)^3} = 2\cdot\frac{N}{V} = 2\,\frac{1}{V_{uc}} \hat{=} 2\times$ density of unit cells if the energy ε is located within the n^{th} band, $\min \varepsilon_{nk} \le \varepsilon \le \max \varepsilon_{nk}$, the density of states $\nu_n(\varepsilon)$ is finite and given by

$$\nu_n(\varepsilon) = \frac{2}{(2\pi)^3} \int\limits_{\varepsilon_{nk}=\varepsilon} dS \int \frac{d\varepsilon_{nk}}{|\vec{\nabla}_k \varepsilon_{nk}|} \, \delta(\varepsilon - \varepsilon_{nk}) = \frac{2}{(2\pi)^3} \int\limits_{\varepsilon_{nk}=\varepsilon} dS \, \frac{1}{|\vec{\nabla}_k \varepsilon_{nk}|}$$

integration over surface of constant energy

change of variables

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

$$v_{nk} = \frac{1}{\hbar} \vec{\nabla}_k \varepsilon_{nk} \qquad \text{of the } n^{th} \text{ band}$$

compare: density of states of free electrons $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$, $\vec{v}_k = \frac{\hbar \vec{k}}{m}$

$$\nu(\varepsilon) = \frac{2}{(2\pi)^3} \underbrace{\int\limits_{\varepsilon_k=\varepsilon} dS}_{4\pi k^2} \int_0^\infty \frac{d\varepsilon_k}{(\hbar^2 k/m)} \, \delta(\varepsilon - \varepsilon_k) = \frac{1}{\pi^2} \frac{mk}{\hbar^2} = \frac{1}{\pi^2} \frac{m}{\hbar^3} \sqrt{2m\varepsilon}$$

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

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

$$\varepsilon_{nk} \cong \varepsilon_{nk_0} + \frac{1}{2} \left. \frac{\partial^2 \varepsilon_{nk}}{\partial \vec{k}_i \partial \vec{k}_j} \right|_{\vec{k}_0} (\vec{k} - \vec{k}_0)_i (\vec{k} - \vec{k}_0)_j$$

The matrix $\frac{\partial^2 \varepsilon_{nk}}{\partial \vec{k}_i \partial \vec{k}_j}$ describes the curvature of the spectrum and has eigenvalues λ_1, λ_2 and λ_3. The spectrum has at $\vec{k}_0$

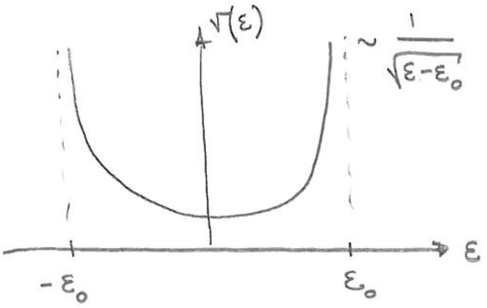
1) a minimum if $\lambda_i > 0 \quad \forall i = 1,2,3$
2) a maximum if $\lambda_i < 0 \quad \forall i = 1,2,3$
3) a saddle point if else

One obtains close to a van-Hove singularity in d spatial dimensions with the change of variables $\vec{k} = \vec{k}_0 + \sqrt{\varepsilon - \varepsilon_{nk_0}}\, \vec{x}$

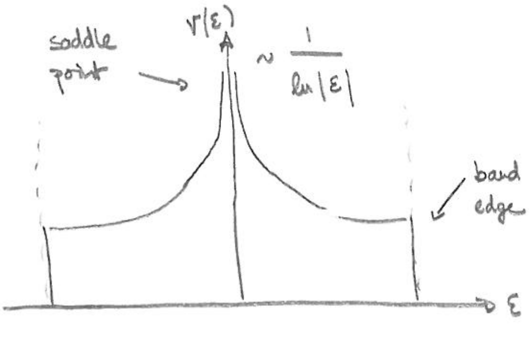
$$\nu_n(\varepsilon) \approx 2 \int \frac{d^d \vec{x}}{(2\pi)^d} \left(\varepsilon - \varepsilon_{nk_0}\right)^{d/2} \delta\left((\varepsilon - \varepsilon_{nk_0}) \left(1 + \left. \frac{\partial^2 \varepsilon_{nk}}{\partial \vec{k}_i \partial \vec{k}_j} \right|_{k_0} x_i x_j \right) \right)$$

$$\rightarrow \quad \boxed{\nu_n(\varepsilon) \propto \left(\varepsilon - \varepsilon_{nk_0}\right)^{d/2 - 1}}$$

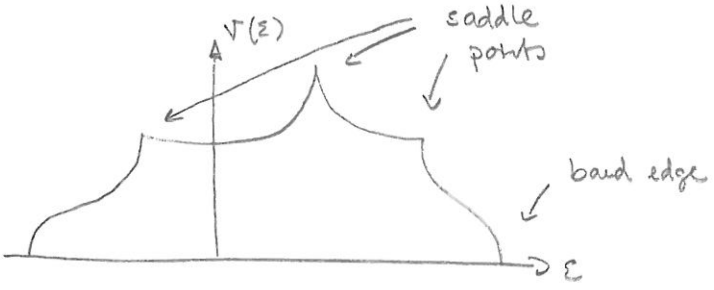
$d = 1$: $1/\sqrt{W}$ divergence at the band edges



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



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



As ε_{nk} is a periodic function in $\vec{k}$

$\Rightarrow$ a maximum, a minimum and in $d>1$ one or several saddle points have to exist.

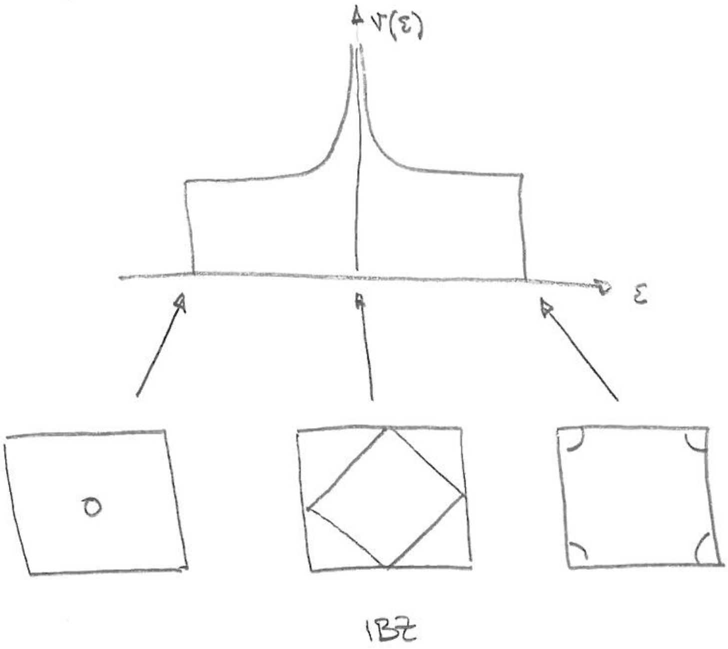
Modern interpretation : van-Hove singularity $\hat{=}$ topological quantum phase transition

the topology of the Fermi surface changes as a function of the chemical potential μ at $T=0$

at a minimum : new Fermi surface emerges

at a maximum : Fermi surface vanishes

at a saddle point : Fermi surfaces merge



4.5. Thermodynamics of non-interacting electrons

grand canonical partition function of non-interacting electrons

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

with $\beta = \frac{1}{k_B T}$ and the chemical potential μ.

Free energy F :

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

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

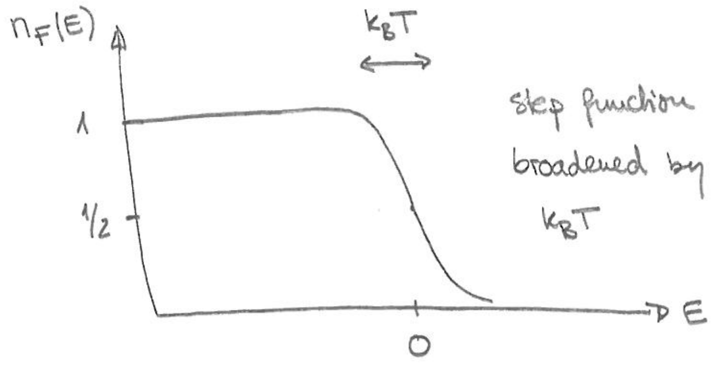
$$f(T,\mu) = -k_B T \int_{-\infty}^{\infty} d\varepsilon \, \nu(\varepsilon) \ln\left(1 + e^{-\beta(\varepsilon - \mu)}\right)$$

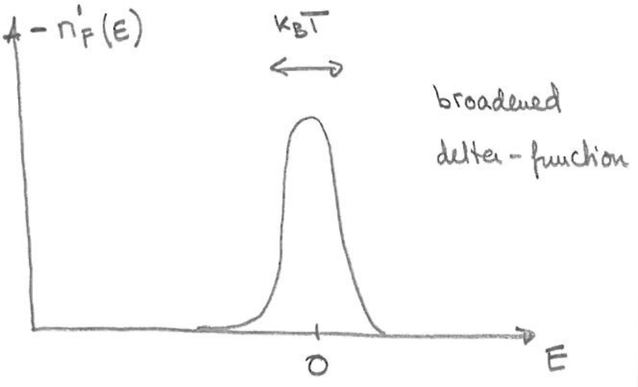
Density of electrons : $n = -\frac{\partial f}{\partial \mu}$

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

with the Fermi function

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





$$\int_{-\infty}^{\infty} d\varepsilon \left(-n_F'(\varepsilon)\right) = -n_F(\varepsilon)\Big|_{-\infty}^{\infty} = 1$$

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

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

$$\boxed{\mu \Big|_{T=0} = \varepsilon_F}$$

in order to evaluate finite temperature corrections one uses the

Sommerfeld expansion

consider some (smooth) function $a(\varepsilon)$ with $a(\varepsilon) \to 0$ for $|\varepsilon| \to \infty$

$$\int_{-\infty}^{\infty} d\varepsilon \, a(\varepsilon) \, n_F(\varepsilon - \mu) \underset{\uparrow}{=} \int_{-\infty}^{\infty} d\varepsilon \, A(\varepsilon) \left(-n_F'(\varepsilon - \mu) \right)$$

integration by parts

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

As $-n_F'(\varepsilon - \mu)$ is only finite within a small intervall of width $k_B T$ around $\varepsilon - \mu \approx 0$ we can expand the function A in a Taylor series:

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

so one obtains for the integral the Sommerfeld expansion

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

The last integral can be evaluated and yields

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

even function of $\varepsilon - \mu$

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

where ζ is the Riemann's Zeta function.

in particular : $c_1 = \zeta(2) = \frac{\pi^2}{6}$, $c_2 = \frac{7\pi^4}{360}$

one finally obtains

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

Specific heat per volume (at constant volume)

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

with $\nu(\varepsilon) \cong \nu(\mu) + \nu'(\mu)(\varepsilon-\mu) + \dots$

$$\rightarrow \quad C_V = T\,\nu(\mu)\, 2 \cdot \frac{\pi^2}{6} k_B^2$$

for T → 0 the electronic specific heat vanishes linearly with temperature

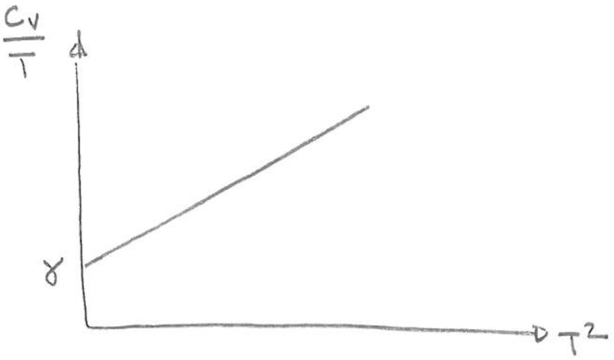
$$\boxed{C_V = \gamma \cdot T}$$

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 in a metal has the form

$$C_V = \gamma T + A \cdot T^3$$

$\uparrow$ electrons $\uparrow$ phonons



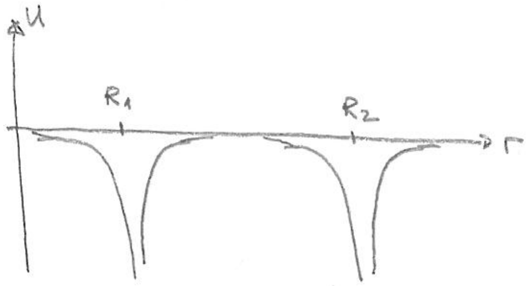
often plotted as $\frac{C_V}{T}$ vs. T^2 → linear function.

4.6. Almost localized electrons; tight-binding method

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

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

sum over atomic potentials assuming monatomic Bravais lattice



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

Hamiltonian for a single electron

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

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

starting point: electrons localized in atomic orbitals, ie, eigenstates of $H_{\text{atom},R}$

assume that atomic eigenvalue problem is solved:

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

where n represents the full set of atomic quantum numbers.

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

$$\left(E(k)-\varepsilon_m\right)\left[a_m+\sum_n a_n A_{mn}\right] = \sum_n a_n B_{mn}$$

matrix equation :

$$\Big[\left(E(k)-\varepsilon_m\right)(\delta_{mn}+\underset{\substack{\uparrow\\ \text{small}}}{A_{mn}}) - \underset{\substack{\uparrow\\ \text{small}}}{B_{mn}}\Big] a_n = 0$$

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)

$$\longrightarrow \quad \left(E(k)-\varepsilon\right)(1+A) - B = 0$$

dispersion of the arising s-band

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

with $$A = \sum_{R'\neq 0} e^{ikR'} \int dr\, \phi^*(r)\,\phi(r-R')$$

$$B = \underset{\substack{\uparrow\\ \text{sum rapidly decays with increasing distance } |R'|}}{\sum_{R'}} e^{ikR'} \int dr\, \phi^*(r)\,\Delta U(r)\,\phi(r-R')$$

with the help of ϕ_n we can construct an Ansatz for a wavefunction that obeys Bloch's theorem :

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

linear combination of atomic orbitals (LCAO) with coefficients a_n

Full stationary Schrödinger equation : $H\psi_k(\vec r) = E(k)\,\psi_k(\vec r)$

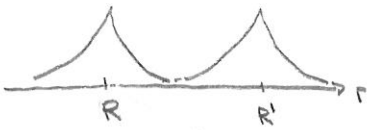
projection onto eigenstates of $H_{atom,R}$: $\left(\int d\vec r\, \phi_n^*(\vec r)\,\phi_{n'}(\vec r) = \delta_{n,n'} \right)$

(I) $$\int d\vec r\, \phi_m^*(r-R)\, H_{atom,R}\, \psi_k(\vec r) = \varepsilon_m \int d\vec r\, \phi_m^*(r-R)\, \psi_k(\vec r)$$

$$= \varepsilon_m \Big(a_m e^{ikR} + \sum_n a_n \underbrace{\sum_{R'\neq R} e^{ikR'} \int d\vec r\, \phi_m^*(r-R)\, \phi_n(r-R')}_{\equiv A_{mn}} \Big)$$

overlap integral

rapidly decays, only relevant for nearest neighboors as the atomic orbitals are strongly confined



small finite overlap

(II) $$\int d\vec r\, \phi_m^*(r-R)\, \Delta U(\vec r)\, \psi_k(\vec r) = \sum_n a_n \underbrace{\sum_{R'} e^{ikR'} \int d\vec r\, \phi_m^*(r-R)\, \Delta U(r)\, \phi_n(r-R')}_{\equiv B_{mn}}$$

coefficients are small because either ΔU is small or product $\phi^*\phi$ is small keeping only contribution up to nearest neighbors $\vec{R}_n$

$$B \cong \underbrace{\int dr\, \phi^*(r)\, \Delta U(r)\, \phi(r)}_{= -\beta} + \sum_{\substack{\text{nearest}\\ \text{neighbors}}} e^{i\vec{k}\vec{R}_n} \underbrace{\int dr\, \phi^*(r)\, \Delta U(r)\, \phi(r-\vec{R}_n)}_{= -\gamma(R_n)}$$

$$A \cong \sum_{\substack{\text{nearest}\\ \text{neighbors}}} e^{i\vec{k}\vec{R}_n} \underbrace{\int dr\, \phi^*(r)\, \phi(r-R_n)}_{= \alpha(R_n)}$$

for an s-wave orbital wavefunction can be chosen to be real → $\alpha(-R_n) = \alpha(R_n)$

from the inversion symmetry of the Bravais lattice follows further → $\gamma(-R_n) = \gamma(R_n)$

The dispersion of the s-band then becomes

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

for example : simple cubic Bravais lattice

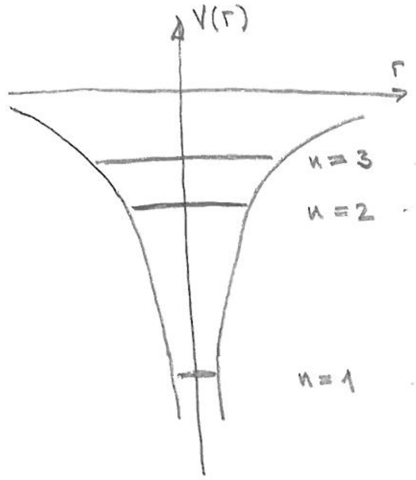
$$\vec{R}_1 = a(\pm 1, 0, 0)\,,\ \vec{R}_2 = a(0, \pm 1, 0)\,,\ \vec{R}_3 = a(0, 0, \pm 1)$$

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

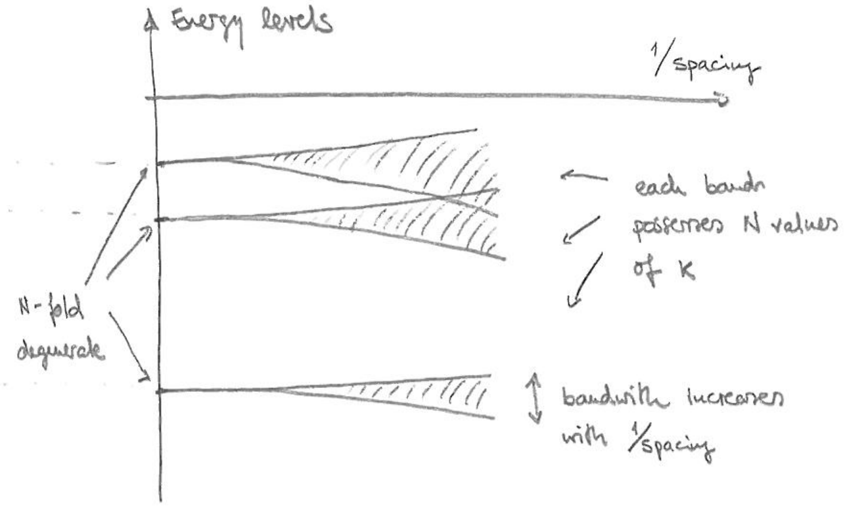
→ Mathematica

Remarks

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



spectrum of non-degenerate s-levels in an atomic potential



Energy levels of N such atoms as a function of inverse interatomic spacing

small $\frac{1}{\text{spacing}}$: tight-binding limit

large $\frac{1}{\text{spacing}}$: limit of weakly periodic potential

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

- for solids with more atoms per unit cell : generalize the Ansatz to a linear combination of atomic orbitals centered at Bravais lattice point <u>and</u> basis points.

- spin-orbit coupling will be important for d- and f-electrons → possible to include 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
  → to be included on top of the tight-binding description.
  This leads to the Hubbard model, see later.

Wannier functions

The wave function can always be written in the form

$$\Psi_{nk}(\vec{r}) = V_{uc} \sum_{R} e^{i\vec{k}\vec{R}} \, w_n(\vec{r}-\vec{R})$$

that is used in the tight-binding method where an Ansatz for $w_n(r-R)$ is made in terms of a LCAO.

The function w_n is the Wannier function and given by inverse Fourier transform

$$\boxed{w_n(r-R) = \int_{1BZ} \frac{d^3k}{(2\pi)^3} \, e^{-ikR} \, \Psi_{nk}(\vec{r})} = \int_{1BZ} \frac{d^3k}{(2\pi)^3} \, e^{-i\vec{k}(\vec{R}-\vec{r})} \, \underset{\substack{\uparrow \\ \text{Bloch function}}}{u_{nk}(\vec{r})}$$

Wannier functions are orthogonal

$$\int d\vec{r} \; w_n^*(r-R) \, w_{n'}(r-R') = \int_{1BZ} \frac{d^3k}{(2\pi)^3} \frac{d^3k'}{(2\pi)^3} \, e^{+ikR} \cdot e^{-ik'R'} \underbrace{\int d\vec{r} \; \Psi_{nk}^*(r) \, \Psi_{n'k'}(r)}_{\delta_{n,n'} (2\pi)^3 \delta(k-k')}$$

$$= \delta_{n,n'} \int_{1BZ} \frac{d^3k}{(2\pi)^3} \, e^{+ik(R-R')}$$

$$= \delta_{n,n'} \, \frac{1}{V_{uc}} \, \delta_{R,R'}$$

and form a complete basis.

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

The Bloch function $\psi_{nk}(r) = e^{ikr} u_{nk}(r)$ is only defined up to a k-dependent phase $u_{nk}(r) \to e^{i\phi(k)} u_{nk}(r)$ giving rise to a U(1) gauge freedom with $\phi(k+G) = \phi(k)$. (Additional freedom arises at positions within the 1BZ where different bands cross.)

This freedom can be exploited to ensure that the k-dependence of $u_{nk}(r)$ is as smooth as possible so that the Wannier functions are maximally localized :

$$w_n(r-R) = \int_{1BZ} \frac{d^3k}{(2\pi)^3}\, e^{-ikR}\, e^{ikr}\, u_{nk}(r) \underset{\uparrow}{\longrightarrow} \frac{1}{V_{uc}} \delta_{r-R,0}\, u_n(R)$$

for a k-independent $u_{nk}(r) \approx u_n(r)$ Wannier function would be pefectly localized

Exceptions : topological insulators

for which a smooth choice of $u_{nk}(r)$ is not possible.

5. Dynamics of electrons

5.1. Drude theory of metals

simplest model for conduction in metal put forward by Drude in 1900 shortly after the discovery of the electron by Thomson in 1897.

phenomenological classical approach :

current density $\vec{j} = -en\vec{v}$

charge of electron $-e$ with $e>0$

density of electron n

average electronic velocity $\vec{v}$

At any time t, the velocity $\vec{v} = \frac{\vec{p}}{m}$ where $\vec{p}$ is the total momentum per electron. obeys the equation of motion

$$\boxed{\frac{d\vec{p}}{dt} = \vec{f}(t) - \frac{\vec{p}(t)}{\tau}}$$

The force acting on the electrons is $\vec{f}$, and the last term is a phenomenoligal frictional damping term that leads to a decay of the momentum $\vec{p}$ on the time-scale of the relaxation time τ. and on the length-scale of the mean-free path $\ell = |\vec{v}| \cdot \tau$.

5.1.1. AC electrical conductivity

In the presence of an electric field $\vec{E}(t)$, the electrons experience a force $\vec{f} = -e\vec{E}$.

Fourier transform of the equation of motion:

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

From which follows the optical or AC conductivity $\vec{j}(\omega) = \sigma(\omega)\vec{E}(\omega)$

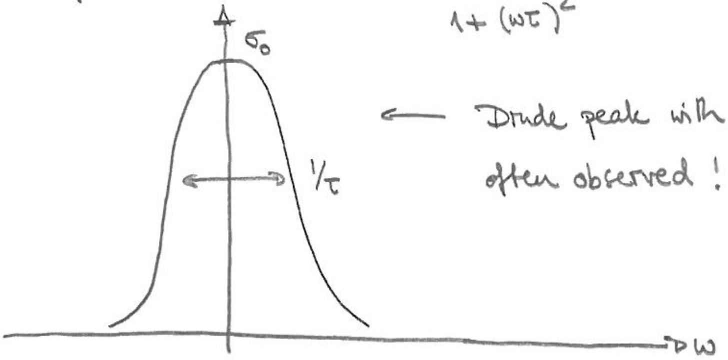
with

$$\boxed{\sigma(\omega) = \frac{\sigma_0}{1-i\omega\tau} \quad , \quad \sigma_0 = \frac{ne^2\tau}{m}}$$

In particular, the response to a static electric field is determined by the

<u>Drude conductivity</u> $\sigma(\omega=0) = \sigma_0 \longrightarrow$ resistivity $\rho = \frac{1}{\sigma_0} = \frac{m}{ne^2\tau}$.

As a function of ω : $\quad \mathrm{Re}\,\sigma(\omega) = \frac{\sigma_0}{1+(\omega\tau)^2}$



← Drude peak with width $1/\tau$, often observed !

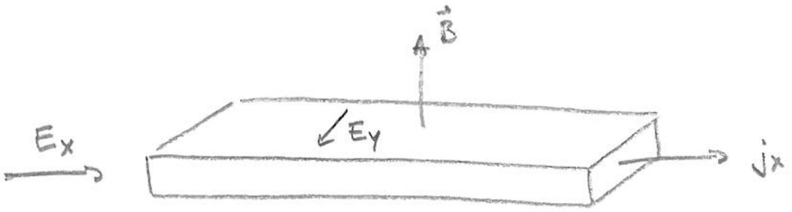
5.1.2. Hall effect and magnetoresistance

in the presence of electric and magnetic field :

$$\vec{f} = -e\left(\vec{E} + \frac{1}{mc}\,\vec{p}\times\vec{B}\right) \qquad (\text{in CGS units})$$

$$\longrightarrow \quad \frac{d\vec{p}}{dt} = -e\left(\vec{E} + \frac{1}{mc}\,\vec{p}\times\vec{B}\right) - \frac{\vec{p}}{\tau}$$

consider a Hall experiment (E.H. Hall 1879)



$$\Rightarrow \quad \frac{d}{dt}\begin{pmatrix} p_x \\ p_y \end{pmatrix} = -e\left[\begin{pmatrix} E_x \\ E_y \end{pmatrix} + \frac{B}{mc}\begin{pmatrix} p_y \\ -p_x \end{pmatrix}\right] - \frac{1}{\tau}\begin{pmatrix} p_x \\ p_y \end{pmatrix}$$

introducing the cyclotron frequency $\omega_c = \frac{eB}{mc}$

and using $\vec{j} = -en\cdot\frac{1}{m}\vec{p}$ one obtains in the steady state $\dot{\vec{p}} = 0$

$$0 = -e\begin{pmatrix}E_x\\E_y\end{pmatrix} - \omega_c\frac{m}{en}\begin{pmatrix}-j_y\\j_x\end{pmatrix} + \frac{m}{en\tau}\begin{pmatrix}j_x\\j_y\end{pmatrix}$$

and finally with $\sigma_0 = \frac{ne^2\tau}{m}$

$$\boxed{0 = -\sigma_0 \begin{pmatrix}E_x\\E_y\end{pmatrix} - \omega_c\tau\begin{pmatrix}-j_y\\j_x\end{pmatrix} + \begin{pmatrix}j_x\\j_y\end{pmatrix}}$$

under the condition of a Hall experiment : $j_y = 0$

one obtains a field-independent magnetoresistance :

$$\rho(B) = \frac{E_x}{j_x} = \frac{1}{\sigma_0}$$

and a transverse electric field

$$E_y = -\frac{\omega_c\tau}{\sigma_0}\, j_x = -\left(\frac{B}{nec}\right) j_x \equiv R_H\cdot B\cdot j_x$$

with the Hall coefficient

$$\boxed{R_H = -\frac{1}{nec}}$$

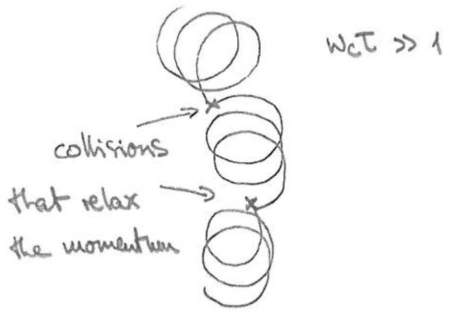
R_H is independent of τ ! It only depends in this approximation on the <u>charge e</u> and the <u>density n</u> of the charge carriers

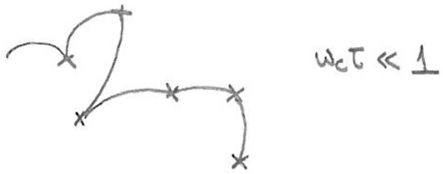
$\longrightarrow$ measurement of charge and density possible

($R_H > 0$ for hole transport, cf later)

The parameter $\omega_c\tau$ is an important dimensionless measure of the strength of magnetic field with respect to the relaxation time τ.

classical trajectories :





no full cyclotron orbit completed between collisions

5.1.3. Dielectric function $\varepsilon(\omega)$

application : propagation of electromagnetic radiation in a metal

for wavelengths much larger than the mean-free path $\lambda \gg \ell$

one can neglect the position dependence of conductivity : $j(\vec{r},\omega) \approx \sigma(\omega)\, E(\vec{r},\omega)$

moreover, neglect the modification of $\sigma(\omega)$ due to the Lorentz-force :

$-e\frac{\vec{p}}{mc}\times\vec{B}$ that is suppressed by a factor $\frac{v}{c}$ compared to $-e\vec{E}$

$\longrightarrow$ use $\sigma(\omega) = \dfrac{\sigma_0}{1-i\omega\tau}$

Maxwell-equations (CGS)

$$\vec{\nabla} \times \vec{E} = -\frac{1}{c} \partial_t \vec{B} \qquad \vec{\nabla} \vec{D} = 4\pi \rho$$

$$\vec{\nabla} \times \vec{H} = \frac{4\pi}{c} \vec{j} + \frac{1}{c} \partial_t \vec{D} \qquad \vec{\nabla} \vec{B} = 0$$

consider a wave which does not induce a charge density $\rightarrow \rho = 0$

furthermore $\vec{D} \cong \varepsilon \vec{E}$ with static $\varepsilon \approx 1$ and $\vec{B} = \mu \vec{H}$ with $\mu \approx 1$

$$\Rightarrow \quad \vec{\nabla} \times \left(\vec{\nabla} \times \vec{E} \right) \underset{\vec{\nabla}\vec{E}=0}{=} -\vec{\nabla}^2 \vec{E} = -\frac{\mu}{c} \partial_t \left(\frac{4\pi}{c} \vec{j} + \frac{\varepsilon}{c} \partial_t \vec{E} \right)$$

Fourier transform :

$$\vec{k}^2 \vec{E}(\vec{k},\omega) = -\frac{\mu}{c} (-i\omega) \left(\frac{4\pi}{c} \vec{j}(\vec{k},\omega) + \frac{\varepsilon}{c} (-i\omega) \vec{E}(\vec{k},\omega) \right)$$

$$\overset{!}{=} \frac{\omega^2}{c^2} \mu \varepsilon(\omega) \cdot \vec{E}(\vec{k},\omega)$$

using $\vec{j}(\vec{k},\omega) = \sigma(\omega) \vec{E}(\vec{k},\omega)$ we obtain for the dielectric function

$$\boxed{\varepsilon(\omega) = 1 + i \frac{4\pi}{\omega} \sigma(\omega) = 1 + i \frac{4\pi}{\omega} \frac{\sigma_0}{1 - i\omega\tau}}$$

The dispersion of the wave is determined by $(\mu \approx 1)$

$$\boxed{c^2 k^2 = \omega^2 \; \varepsilon(\omega)} \longrightarrow \quad k = \frac{\omega}{c} \tilde{n}(\omega)$$

with the complex index of refraction $\tilde{n}(\omega) = n(\omega) + i\kappa(\omega) = \sqrt{\varepsilon(\omega)}$

where $n(\omega)$ and $\kappa(\omega)$ are real functions of ω.

An imaginary part $\kappa(\omega)$ leads to damping of the wave ie. it cannot penetrate the metal → the wave gets reflected

→ absorption coefficient $\alpha = 2\kappa(\omega) \frac{\omega}{c}$ describes decay of energy density and Poynting vector

Limit of small frequencies $\omega\tau \ll 1$: $\varepsilon(\omega) \cong 1 + i\,\frac{4\pi}{\omega}\,\sigma_0$

for good metals $\frac{4\pi\sigma_0}{\omega} \gg 1$: $\tilde{n}(\omega) \cong \sqrt{\frac{4\pi\sigma_0}{\omega}}\,\sqrt{i} = \sqrt{\frac{2\pi\sigma_0}{\omega}}\,(1+i)$

penetration depth of the electromagnetic wave

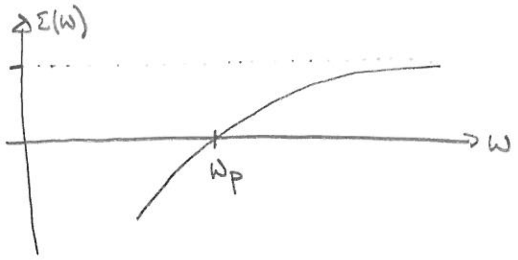
$$\delta = \frac{c}{\omega\kappa} = \frac{c}{\omega}\sqrt{\frac{\omega}{2\pi\sigma_0}} = \frac{c}{\sqrt{2\pi\sigma_0\omega}} \propto \frac{1}{\sqrt{\omega}}$$

normal Skin effect

Limit of high-frequencies $\omega\tau \gg 1$: $\varepsilon(\omega) \cong 1 - \frac{\omega_p^2}{\omega^2}$

where ω_p is the Plasma frequency

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



as long as $\omega_p > \omega$, $\varepsilon(\omega) < 0$ yielding a finite κ so that the wave still cannot penetrate the metal

however, for $\omega > \omega_p$ radiation can propagate and metal should become transparent

5.1.4. Plasma oscillation

The electron gas can sustain charge density oscillations with the frequency ω_p known as plasma oscillations $\hat{=}$ collective oscillation of all electrons

continuity equation for charge density : $\partial_t \rho + \vec{\nabla}\vec{j} = 0$

$$\Rightarrow \quad -i\omega\,\rho(\vec{k},\omega) + \sigma(\omega)\,\vec{\nabla}\vec{E}(\vec{k},\omega) = 0$$

with Gauß' law $\vec{\nabla}\vec{E} = 4\pi\rho$ $\quad(\varepsilon \approx 1)$

we obtain a solution of

$$-i\omega + \sigma(\omega)\,\frac{1}{4\pi} \overset{!}{=} 0 \quad \Leftrightarrow \quad \varepsilon(\omega) = 1 + i\,\frac{4\pi}{\omega}\,\sigma(\omega) \overset{!}{=} 0$$

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

5.2. Semiclassical model of electron dynamics

consider a wavepacket consisting of Bloch wavefunctions

semiclassical model : effective equation of motion for the centre of mass $\vec{r}$ of the wavepacket and its momentum $\vec{k}$

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

Remarks

- bandindex n is constant of motion. Interband transitions are negleted
- $\hbar\vec{k}$ is the crystal momentum, it is only defined to within an additive reciprocal lattice vector $\vec{G}$
- in order to have a well-defined $\vec{k}$ located within the 1 BZ the spatial width of the wavepacket must be much larger than the size of a primitive unit cell
- in order to be able to treat the fields $\vec{E}$ and $\vec{B}$ classically their wavelength must be much larger than the width of the wavepacket.
- to neglect intraband transitions the amplitude of the fields must be sufficiently small; otherwise electric or magnetic breakdown
- anomalous velocity : the velocity $\vec{v}_n(k)$ can obtain a correction from the Berry curvature of Bloch functions $\vec{\Omega}$

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

where $\vec{\Omega} = \vec{\nabla}_k \times \vec{A}(\vec{k})$ with $\vec{A}(k) = -i \langle u_{nk} | \vec{\nabla}_k | u_{nk} \rangle$

effective vector potential in $\vec{k}$ space.

This correction is important in ferromagnets where it contributes to the

<u>anomalous Hall effect</u>.

5.2.1. Effective charge and heat carriers

- charge and energy current density of the n^{th} band (at $T=0$)

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

$$\vec{j}_{n\varepsilon} = \underset{\text{spin}}{2} \int_{\substack{\text{1BZ}\\ \text{occupied}\\ \text{states}}} \frac{d\vec{k}}{(2\pi)^3}\, \varepsilon_n(\vec{k})\, \vec{v}_n(\vec{k}) \;=\; 2 \int_{\substack{\text{1BZ, occ.}\\ \text{states}}} \frac{d\vec{k}}{(2\pi)^3}\, \frac{1}{2}\, \frac{1}{\hbar}\, \frac{\partial \epsilon_n^2(k)}{\partial \vec{k}}$$

Filled bands are inert

Completely occupied bands do not contribute to the current densities!

As the integrand in both cases is a total derivative of a periodic function

$\varepsilon_{n\,k+G} = \varepsilon_{nk}$ both integrals vanish in this case

→ conduction is only due to electrons within partially filled bands

if all bands are completely filled or empty → electrical and thermal band insulator

Holes

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

$$\vec{j} = (-e)\int_{\substack{1BZ,\\ \text{occupied states}}} \frac{d\vec{k}}{(2\pi)^3}\,\vec{v}_n(\vec{k}) = \underbrace{(-e)\int_{1BZ} \frac{d\vec{k}}{(2\pi)^3}\,\vec{v}_n(\vec{k})}_{=0} + e\int_{\substack{1BZ\\ \text{unoccupied}\\ \text{states}}} \frac{d\vec{k}}{(2\pi)^3}\,\vec{v}_n(\vec{k})$$

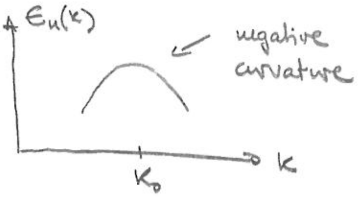
$$= e\int_{\substack{1BZ\\ \text{unoccupied}\\ \text{states}}} \frac{d\vec{k}}{(2\pi)^3}\,\vec{v}_n(\vec{k})$$

Current produced by occupying states with electrons of charge $(-e)$ is the same as that of fictitious particles, <u>holes</u>, with charge $e>0$ filling all those states left unoccupied by the electrons.

Evolution of states under the influence of applied fields is fixed by the equation of motion irrespective whether they are occupied by electrons or not.

When it is convenient to consider the current to be carried by holes?

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



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

with a negative <u>effective mass</u> $-m^* < 0$.

$\longrightarrow$ equation of motion $\quad \ddot{\vec{r}} = \dfrac{d}{dt}\vec{v}_n(t) = -\dfrac{\hbar\dot{\vec{k}}}{m^*}$ $\qquad$ acceleration antiparallel to $\dot{\vec{k}}$!

in an $\vec{E}$ field: $\quad \ddot{\vec{r}} = \left(-\dfrac{1}{m^*}\right)(-e)\vec{E} = \dfrac{e}{m^*}\vec{E}$

Equation of motion for states close to band maxima can be viewed as those of a negatively charged particle with negative mass, $-e < 0$ and $-m^* < 0$, or, more intuitively, as those of positively charged particles with positive mass, $e > 0$ and $m^* > 0$.

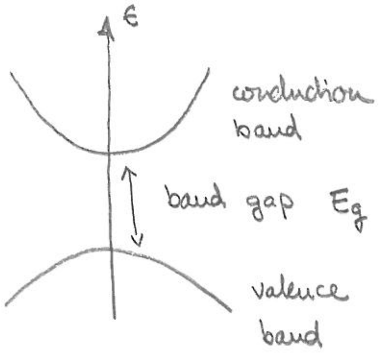
If the Fermi energy is close to a band maxima

→ transport is conveniently described in terms of holes with positive mass $m^* > 0$ and positive charge $e > 0$.

More generally: <u>effective mass tensor</u>

$$\frac{1}{\hbar^2}\frac{\partial^2 \epsilon_n(k)}{\partial k_i \partial k_j}$$ curvature of the band

application: <u>semiconductors</u>



at $T=0$: band insulator
empty conduction band and completely filled valence band

at $T>0$: (intrinsic) electronic properties determined by electrons thermally excited from the valence band to the conduction band with exponentially small density $\propto e^{-E_g/k_BT}$ for $E_g \gg k_BT$

band gaps: Si $E_g = 1.12$ eV, $\frac{E_g}{k_BT} \cong 43$ @ 300 K

Ge $E_g = 0.67$ eV, $\frac{E_g}{k_BT} \cong 26$

Parabolic approximation

valence band $$\varepsilon_v(k) \cong \varepsilon_v(0) + \frac{\hbar^2}{2} \left.\frac{\partial^2 \varepsilon_v}{\partial k_i \partial k_j}\right|_{k=0} k_i \cdot k_j$$

$$= \varepsilon_v(0) - \frac{\hbar^2}{2}\left(\frac{k_1^2}{m_{1h}} + \frac{k_2^2}{m_{2h}} + \frac{k_3^2}{m_{3h}}\right)$$

conduction band $$\varepsilon_c(k) \cong \varepsilon_c(0) + \frac{\hbar^2}{2} \left.\frac{\partial^2 \varepsilon_c}{\partial k_i \partial k_j}\right|_{k=0} k_i k_j$$

$$= \varepsilon_c(0) + \frac{\hbar^2}{2}\left(\frac{k_1^2}{m_{1e}} + \frac{k_2^2}{m_{2e}} + \frac{k_3^2}{m_{3e}}\right)$$

diagonalizing the curvature tensor its eigenvalues correspond to inverse masses along three principal axes that are negative for the valence band and positive for the conduction band.

→ description of transport within the valence and conduction band in terms of holes and electrons, respectively.

Warning: For each band one can choose whether to describe transport in terms of electrons or holes, but never mix the two pictures within a single band!

5.2.2. Bloch ostillations

uniform electric field $\vec{E}$:

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

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

The wavevector changes linearly in time. As the velocity $\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\frac{\partial \epsilon_n}{\partial \vec{k}}$ is a periodic function of $\vec{k}$, it becomes a periodic function of time (for $\vec{E}$ parallel to a reciprocal lattice vector) ⟶ Bloch ostillations

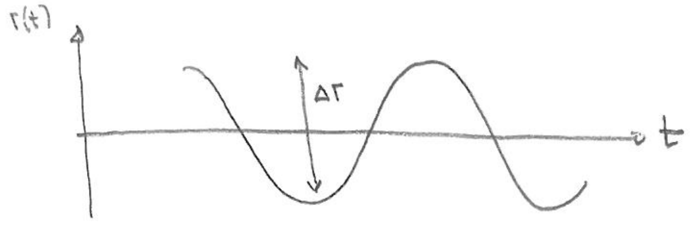
for example : $\epsilon(k) = -\frac{W}{2}\cos ka$, $v(k) = \frac{Wa}{2\hbar}\sin ka$

$$\longrightarrow r(t) = r(0) + \int_0^t dt'\, v_n\left(k(0) - \frac{eEt}{\hbar}\right) = r(0) + \frac{Wa}{2\hbar}\frac{\hbar}{eEa}\left(\cos\left(k(0)\cdot a - \frac{eEta}{\hbar}\right) - \cos(k(0)a)\right)$$

$$= r_0 + \frac{W}{2eE}\cos\left(k_0 a - \frac{eEta}{\hbar}\right)$$

Bloch electron oscillates in space with amplitude $\Delta r = \frac{W}{eE}$ and frequency

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



very difficult to observe in solids

estimate of amplitude : field $E \sim \frac{10V}{mm}$, $W \sim 1eV \Longrightarrow \Delta x \sim 0.1\text{ mm} = 10^6$ Å

problem: electrons scatter from lattice defects before completing oscillation $\omega\tau \ll 1$.

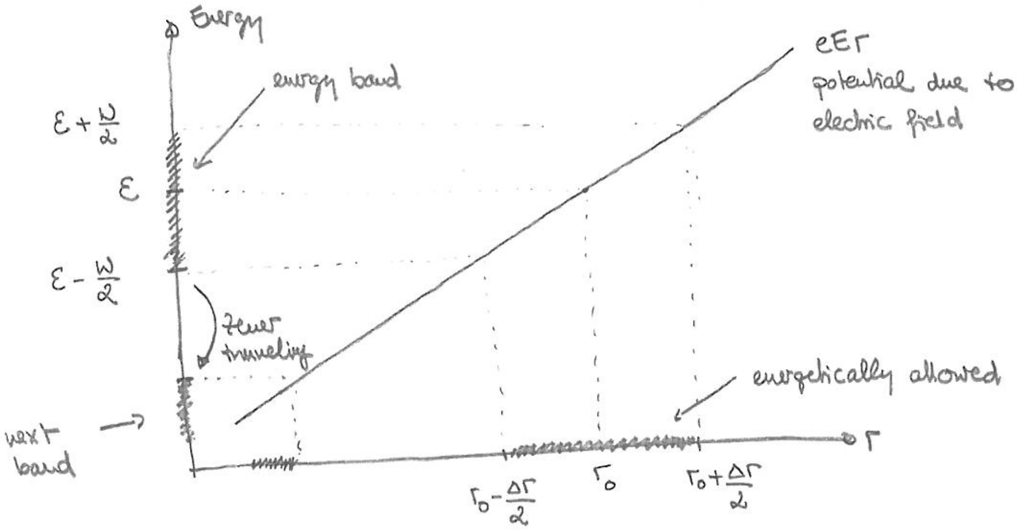
Bloch ostillations were observed in :
- superlattices in semiconductors (artificially large a)
- in optical lattices with atoms

Why does the Bloch electron oscillate ?

consider the energy $$\mathcal{E} = \underset{\substack{\uparrow \\ \text{kinetic energy of} \\ \text{Bloch electrons}}}{\mathcal{E}_n(k(t))} + \underset{\substack{\uparrow \\ \text{potential} \\ \text{energy}}}{eE\,r(t)}$$

$$\Rightarrow \quad \mathcal{E} = -\frac{W}{2}\cos\left(k_0 a - \frac{eEta}{\hbar}\right) + eE\left(r_0 + \frac{W}{2eE}\cos\left(k_0 a - \frac{eEta}{\hbar}\right)\right) = eE\cdot r_0 \quad \text{const}$$

in order to conserve energy electron cannot escape to ± ∞



for a single band the electron is energetically confined to a region in space.

It can however escape via an interband transition ie. Zener tunneling

5.2.3. Semiclassical motion in a magnetic field

semiclassical equation of motion in the presence of $\vec B$ field

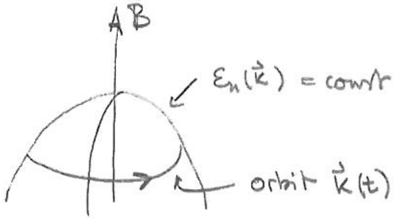
$$\dot{\vec r} = \vec v_n(\vec k) \quad , \quad \hbar\dot{\vec k} = -\frac{e}{c}\,\vec v_n(k)\times\vec B$$

⇒ component of $\vec k$ parallel to $\vec B$ is conserved, $\dot{\vec k}_\parallel = 0$

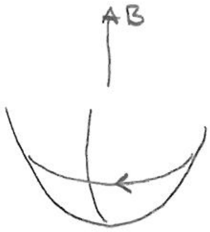
and electronic energy $\varepsilon_n(\vec k)$ is conserved, $\dot\varepsilon_n(\vec k) = \frac{\partial\varepsilon_n(\vec k)}{\partial\vec k}\,\dot{\vec k} = \vec v_n(k)\,\hbar\dot{\vec k} = 0$

as $\dot{\vec k}$ is perpendicular to $\vec v_n(k)$ and $\vec B$.

⇒ orbit in $\vec k$-space: intersection of constant energy surfaces with planes perpendicular to $\vec B$



hole-orbit



electron-orbit

sense of orientation depends on the sign of $\vec v$ → hole/electron-like orbits

one distinguishes between

Closed orbits

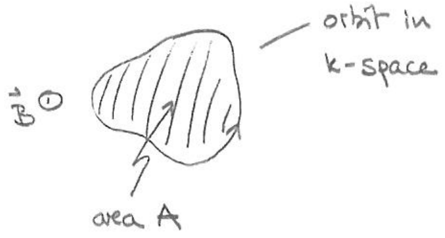
orbits closed in $\vec k$-space with period $T = \int_0^T dt = \oint_{\substack{\text{closed}\\\text{orbit}}} \frac{dk}{|\dot{\vec k}|}$

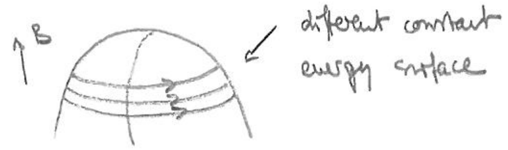
with $|\dot{\vec k}| = \frac{e}{\hbar c}\,|\vec v_{n\perp}(\vec k)|\cdot|\vec B| = \frac{eB}{\hbar^2 c}\left|\left(\frac{\partial\varepsilon_n(k)}{\partial\vec k}\right)_\perp\right|$

component $\perp$ to $\vec B$

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

geometrical interpretation : area A on the plane ⊥ to $\vec{B}$ that is enclosed by the orbit





$$A = \int dk_\perp \underbrace{\oint dk}_{\text{closed orbit for given } k_\perp} = \oint dk \left|\frac{dk_\perp}{dE}\right| dE$$

$\frac{dA}{dE}$ change in area upon changing energy E

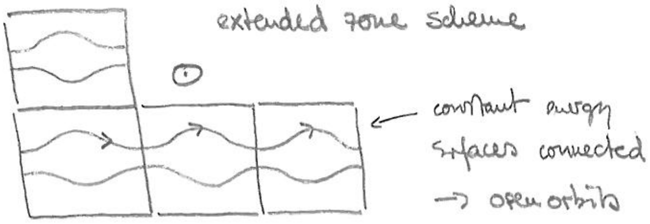
→ cyclotron frequency $\omega_c = \frac{2\pi}{T} = \frac{eB}{cm^*}$

with <u>cyclotron mass</u> $m^*(\mathcal{E}) = \frac{\hbar^2}{2\pi}\frac{\partial A}{\partial \mathcal{E}}$ determined by a property of constant energy surfaces !

<u>Open orbits</u>

open orbits in $\vec{k}$-space

possible for open constant energy surfaces



5.2.4. Quantized levels of Bloch electrons in a magnetic field

reminder : free electrons in a magnetic field

→ quantized Landau levels $E_n = \hbar\omega_c(n+1/2)$ with $\omega_c = \frac{eB}{mc}$

consider closed orbits, according to Bohr's correspondence principle

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

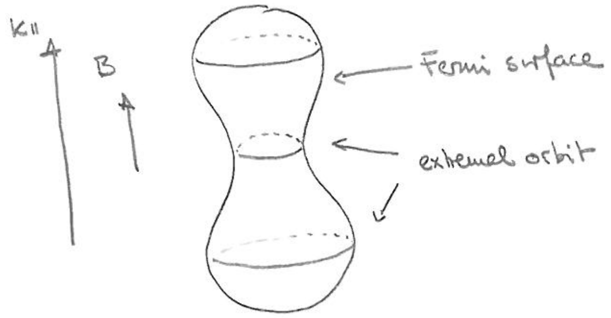
with the identification $E_{n+1} - E_n \cong \partial E$ follows $\boxed{\Delta A = \frac{2\pi eB}{\hbar c}}$

area of orbits adjacent in energy differ by a fixed amount

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

for $n \gg 1$ semiclassical limit

Particular important: extremal orbits on the Fermi surface



area at fixed energy E_F varies as a function of longitudinal momentum $k_\parallel$

$$A(E_F, k_\parallel) = (n + \text{const}) \frac{2\pi e B}{\hbar c} \qquad \text{with} \quad k_\parallel = k_\parallel(n)$$

for an extremal orbit at $k_{\parallel e}$: $\left.\frac{\partial A}{\partial k_\parallel}\right|_{k_{\parallel e}} = 0$ with A_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.

$$A_e = (n + \text{const}) \cdot \frac{2\pi e B}{\hbar c} = (n + \text{const})\, \Delta A$$

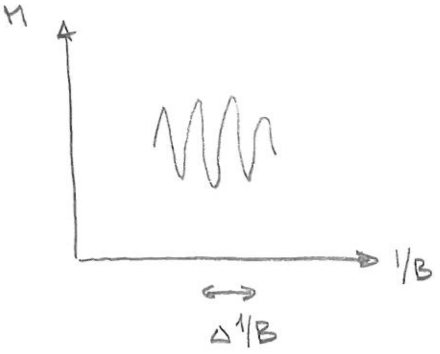
→ The density of states $\nu(E_F)$ will be singular at regularly spaced intervals of inverse fields $1/B$

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

⇒ oscillatory behavior of many observables as a function of $1/B$

<u>de Haas-van Alphen effect</u> : periodic oscillations in magnetization $M(B)$

<u>Shubnikov-de Haas effect</u> : " in resistivity $\rho(B)$



→ quantitative measurement of the shape of the Fermi surface possible!

5.3. Boltzmann equation

combine semiclassical dynamics with statistical approach

consider average number of electrons at position $\vec{r}$ with crystalline momentum $\hbar\vec{k}$ in band n at time t : $f_{nk}(\vec{r},t)$

in equilibrium the average occupation is given by the Fermi function

$$f^{(0)}_{nk}(\vec{r},t) = \frac{1}{e^{\frac{\varepsilon_{nk}-\mu}{k_BT}}+1}$$

out of equilibrium → f time dependent

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

$$\overset{\text{semiclassical equation of motion}}{=} \frac{\partial f_{nk}(\vec{r},t)}{\partial \vec{r}}\underbrace{\vec{v}_{nk}}_{\text{flow of particles}} + \frac{\partial f_{nk}(\vec{r},t)}{\partial \vec{k}}\frac{1}{\hbar}\underbrace{\vec{F}}_{\text{external forces}} + \frac{\partial f_{nk}(\vec{r},t)}{\partial t}$$

The time-dependence is balanced by collisions eg. with defects, phonons, other electrons, ... which eventually leads to relaxation to equilibrium

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

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

Boltzmann equation

5.3 1. Collision terms

consider various sources for the collision term

I. Disorder

transition from $\vec k \to \vec k'$ with scattering rate $W_{k'k}$ due to impurities

only possible if k occupied and k' empty

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

determination of scattering rate $W_{k'k}$:

for weak impurity potentials $H_{imp} = \sum\limits_{R_i} V_{imp}(r - \underset{\uparrow\ \text{position of impurities}}{R_i})$

use Fermi's golden rule

$$W_{k'k} = \frac{2\pi}{\hbar} \left| \langle k' | H_{imp} | k \rangle \right|^2 \underset{\uparrow\ \text{elastic impurity scattering conserves energy}}{\delta(\varepsilon_k - \varepsilon_{k'})}$$

$$= \frac{2\pi}{\hbar} n_{imp} \left| \langle k' | V_{imp} | k \rangle \right|^2 \delta(\varepsilon_k - \varepsilon_{k'})$$

with density n_{imp} of impurities and matrix element

$$\langle k' | V_{imp} | k \rangle = \int d\vec{r}\; \psi^*_{nk'}(\vec{r})\, V_{imp}(\vec{r})\, \psi_{nk}(\vec{r})$$

from uniterity of time-evolution follows $\boxed{W_{k'k} = W_{kk'}}$

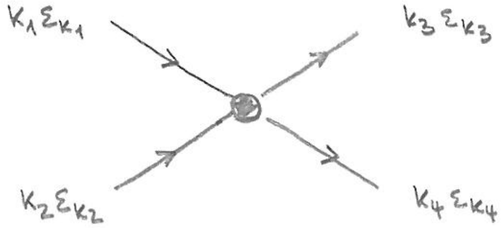
valid beyond perturbation theory

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

Sometimes transition rates $W_{k'k}$ are treated as phenomenological parameters and/or the dependences on k' and k are neglected.

II. Electron-electron scattering

scattering of two electrons :



momenta and energy before the collision

and after the collision

scattering rate
$$W_{k_3k_4;k_1k_2} = \sum_G \Gamma^G_{k_3k_4;k_1k_2} \underset{\substack{\uparrow \\ \text{momentum conserved} \\ \text{up to reciprocal lattice} \\ \text{vector } G}}{\delta_{k_1+k_2,\, k_3+k_4+G}} \underset{\substack{\uparrow \\ \text{energy conserved}}}{\delta(\varepsilon_{k_1}+\varepsilon_{k_2}-\varepsilon_{k_3}-\varepsilon_{k_4})}$$

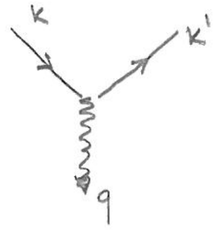
$\downarrow$

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

from time-reversal symmetry $W_{k_3k_4;kk_2} = W_{kk_2;k_3k_4}$

III. Electron-phonon scattering

absorption of a phonon



emission of a phonon

$$\begin{aligned}\left.\frac{\partial f_k}{\partial t}\right|_{\text{collision}} = - \sum_{k'q} \Big[& W^{A}_{k'k;q}\, f_k (1-f_{k'})\, \overset{\substack{\text{phonon distribution function}\\ \downarrow}}{n_q} - W^{A}_{kk';q}\, f_{k'}(1-f_k)\, n_q & \text{absorption} \\ & + W^{E}_{k'k,q}\, f_k(1-f_{k'})(\underset{\substack{\uparrow\\ \text{spontaneous}}}{1}+\underset{\substack{\nwarrow\\ \text{stimulated}}}{n_q}) - W^{E}_{kk',q}\, f_{k'}(1-f_k)(1+n_q) \Big] & \text{emission}\end{aligned}$$

5.3.2. Linearized Boltzmann equation and relaxation time approximation

Collisions result in relaxation to a (local) equilibrium.

The collision terms for disorder scattering and electron-electron scattering <u>vanish</u> for the local Fermi distribution

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

with time and space dependent chemical potential $\mu = \mu(\vec r,t)$ and temperature $T = T(\vec r,t)$.

check eg. for e-e scattering:

$$\left. f^{(0)}_k f^{(0)}_{k_2} \left(1-f^{(0)}_{k_3}\right)\left(1-f^{(0)}_{k_4}\right) - f^{(0)}_{k_3} f^{(0)}_{k_4}\left(1-f^{(0)}_k\right)\left(1-f^{(0)}_{k_2}\right)\right|_{\substack{\varepsilon_k+\varepsilon_{k_2} = \varepsilon_{k_3}+\varepsilon_{k_4}\\ \text{energy conserving}}} = 0$$

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

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

Simple, heuristic approximation of the collision term:

$$\boxed{\left.\frac{\partial f_k}{\partial t}\right|_{\text{collision}} \approx -\frac{\delta f_k}{\tau_k}}$$ relaxation-time approximation

with k-dependent relaxation time τ_k.

allows for simple solutions of the Boltzmann equation

However: it violates certain conservation laws.

Furthermore, for small deviations from equilibrium linearization of the left-hand side of the Boltzmann equation in gradients $\vec{\nabla}T, \vec{\nabla}\mu$, the force F, and δf.

For $\partial_t T = \partial_t \mu = 0$ one then obtains

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

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

Linearized Boltzmann equation in the relaxation time approximation

Best approximation for $1/\tau_k$ depends on the problem and the quantity of interest (heat / charge transport)

One distinguishes in particular a <u>single-particle relaxation time</u> that is the typical time between two scattering events and, for example, a <u>transport relaxation time</u> that is the typical time between two scattering event which relax a transport current.

5.3.3. Conductivity and transport relaxation time

For a homogeneous electric field $\vec{F}(t) = -e\vec{E}(t)$

we can set $\vec{\nabla}T = \vec{\nabla}\mu = 0$ and obtain

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

than can solve by Fourier transform: $\delta f_k(t) = \int \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \delta f_k(\omega)$

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

From the current density $\vec{j} = \underset{\substack{\uparrow \\ \text{spin}}}{-e\cdot 2} \int \frac{d\vec{k}}{(2\pi)^3}\, \vec{v}_k f_k \underset{\substack{\uparrow \\ \text{no contribution in} \\ \text{equilibrium}}}{=} -2e \int \frac{d\vec{k}}{(2\pi)^3}\, \vec{v}_k\, \delta f_k$

follows for the conductivity tensor:

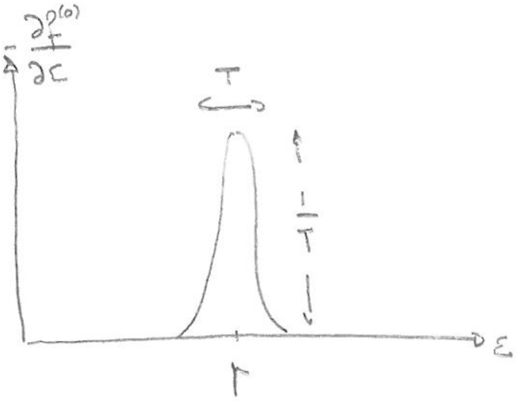
$$j_i(\omega) = \sigma_{ij}(\omega)\, E_j(\omega)$$

ith

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

as $\frac{\partial f^{(0)}}{\partial \varepsilon_k}$ is sharply peaked only states close to the Fermi energy contribute

for $T \to 0$: $-\frac{\partial f^{(0)}}{\partial \varepsilon_k} \simeq \delta(\varepsilon_k - \mu)$



comparison with Drude formula $\sigma(\omega) = \dfrac{e^2 n \tau / m}{1 - i\omega\tau}$:

approximate $\tau_k \approx \tau$:

$$\sigma_{ij}(\omega) = \frac{e^2\tau}{1-i\omega\tau}\, 2\int \frac{d\vec{k}}{(2\pi)^3}\, v_k^i \underbrace{v_k^j \left(-\frac{\partial f^{(0)}}{\partial \varepsilon_k}\right)}_{= -\frac{1}{\hbar}\frac{\partial f_k^{(0)}}{\partial k_j}} \overset{\text{integration by parts}}{\downarrow}{=} \frac{e^2\tau}{1-i\omega\tau}\, 2\int \frac{d\vec{k}}{(2\pi)^3}\, \underbrace{\frac{1}{\hbar^2}\frac{\partial^2 \varepsilon_k}{\partial k_i \partial k_j}}_{\substack{\text{effective mass tensor}\\ m^{-1}_{ij}}} f_k^{(0)}$$

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

with $$\langle m^{-1}_{ij}\rangle = \frac{2\int \frac{d\vec{k}}{(2\pi)^3} \frac{1}{\hbar^2} \frac{\partial^2\varepsilon_k}{\partial k_i \partial k_j} f_k^{(0)}}{2\int \frac{d\vec{k}}{(2\pi)^3} f_k^{(0)}}$$ inverse effective mass averaged over Fermi surface

for isotropic system $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$: $\langle m^{-1}_{ij}\rangle = 1/m\, \delta_{ij}$

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

for impurity scattering : $$-\frac{\delta f_k}{\tau_k} = -\int \frac{d\vec{k}'}{(2\pi)^3} W_{k'k}\left(f_k - f_{k'}\right) = -\int \frac{d\vec{k}'}{(2\pi)^3} W_{k'k}\left(\delta f_k - \delta f_{k'}\right)$$

analytic solution possible if

(i) isotropic system where $\varepsilon_k = \varepsilon(|\vec{k}|) \Rightarrow \vec{v}_k = v_k \cdot \hat{k}$

(ii) scattering only dependent on angle between $\vec{k}$ and $\vec{k}'$: $W_{k'k} = \Gamma(\hat{k}\hat{k}')\, \delta(\varepsilon_k - \varepsilon_{k'})$

Ansatz : $\delta f_k = \hat{k}\vec{E}\, \phi(\varepsilon_k)$ with $\phi(\varepsilon_k) = \dfrac{\frac{\partial f^{(0)}}{\partial \varepsilon_k} e v_k}{1/\tau_k - i\omega}$ and $\tau_k = \tau(\varepsilon_k)$

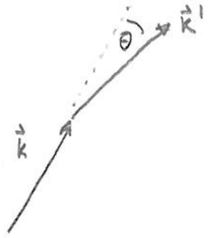
$$\longrightarrow \quad \frac{\hat{k}\vec{E}}{\tau_k}\phi(\varepsilon) = \phi(\varepsilon)\, \vec{E} \underbrace{\int \frac{d\vec{k}'}{(2\pi)^3} W_{k'k}\left(\hat{k} - \hat{k}'\right)}_{\parallel \hat{k} \text{ by symmetry}}$$

$$\Rightarrow \boxed{\frac{1}{\tau(\varepsilon_k)} = \int \frac{d\vec{k}'}{(2\pi)^3} W_{k'k} \left(1 - \hat{k}\hat{k}'\right)} = \int \frac{d\vec{k}'}{(2\pi)^3} \delta(\varepsilon_k - \varepsilon_{k'}) \Gamma(\hat{k}\hat{k}') \left(1 - \hat{k}\hat{k}'\right)$$

$$= \underbrace{\frac{\nu(\varepsilon_k)}{2}}_{\text{density of states per spin}} \frac{1}{2} \int_{-1}^{1} d\cos\theta \; \Gamma(\cos\theta) \left(1 - \cos\theta\right)$$

transport relaxation rate

interpretation of 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!

$\longrightarrow$ only scattering events with large angle θ do substantially relax the current!

Adding scattering processes: Matthiessen's rule

Apart from impurity scattering, also electron-electron and electron-phonon scattering lead to relaxation.

Within the relaxation-time approximation: add scattering rates

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

if $\vec{k}$-dependence can be neglected contributions to resistivity $\rho = \frac{1}{\sigma} \propto \frac{1}{\tau}$ are additive

$$\boxed{\rho \cong \rho_{\text{disorder}} + \rho_{\text{interaction}} + \rho_{\text{phonons}}}$$

Matthiessen's rule

frequently used to interpret experiments

but not valid for $\vec{k}$-dependent scattering and/or strong disorder / strong interactions.

typically for a metal:

$$\rho_{disorder} = \text{const} \; , \quad \rho_{interaction} = A \cdot T^2 \; , \quad \rho_{phonon} \propto \begin{cases} T^5 & \text{low } T \\ T & \text{high } T \end{cases}$$

5.3.4. Thermal conductivity and thermopower

Thermal current carries heat. Q

Thermodynamic definition : $dQ = T\,dS = dU - \mu\,dN$

in terms of currents : $\underset{\substack{\text{heat}\\ \text{current}}}{j_Q} = \underset{\substack{\text{energy}\\ \text{current}}}{j_\varepsilon} - \mu \underset{\substack{\text{particle}\\ \text{current}}}{\vec{j}_n}$

if one neglects interaction effects and contributions from phonons etc.

we can define the heat current density

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

A finite electric field $\vec{E}$ and a thermal gradient $\vec{\nabla} T$ will in general

induce a thermal as well as an electric current density

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

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

$$\boxed{\begin{aligned} \vec{j}_c &= \mathbb{L}_{11} \vec{E} + \mathbb{L}_{12} \left(- \vec{\nabla} T \right) \\ \vec{j}_Q &= \mathbb{L}_{21} \vec{E} + \mathbb{L}_{22} \left(- \vec{\nabla} T \right) \end{aligned}}$$

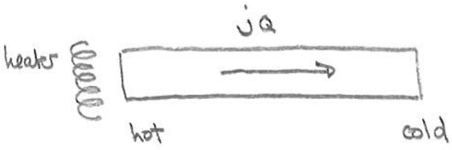
where $\mathbb{L}_{\alpha\beta}$ with $\alpha,\beta = 1,2$ are linear response matrices . They are related to transport coefficients under various experimental conditions :

i) <u>conductivity σ</u>

for $\vec{\nabla}T = 0$; $\vec{j}_c^{\,i} = \sigma_{ij}\vec{E}^j$ with $\sigma = L_{11}$

ii) <u>thermal conductivity κ</u>

heat current measured under the condition of a vanishing charge current



$$\vec{j}_c = 0 \quad \Leftrightarrow \quad \vec{E} = -L_{11}^{-1}L_{12}(-\vec{\nabla}T)$$

$$\Rightarrow \quad \vec{j}_Q = \left(L_{22} - L_{21}L_{11}^{-1}L_{12}\right)\left(-\vec{\nabla}T\right) \equiv \kappa\left(-\vec{\nabla}T\right)$$

with the thermal conductivity κ

iii) <u>thermopower Q</u> (Seebeck coefficient)

electric field $\vec{E}$ induced by the thermal gradient → thermoelectric effect

$$\vec{E} = -L_{11}^{-1}L_{12}\left(-\vec{\nabla}T\right) \equiv Q\,\vec{\nabla}T \quad \text{with} \quad Q = L_{11}^{-1}L_{12}$$

iv) <u>Peltier effect</u>

imposed electric current is accompanied by thermal current

$$\vec{j}_Q = \Pi\,\vec{j} \quad \text{with} \quad \Pi = L_{21}L_{11}^{-1}$$

The Peltier coefficient Π is related to the thermopower

$$\Pi = TQ. \qquad \text{(Onsager relation)}$$

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

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

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

from which follows for the currents

$$\begin{pmatrix} \vec{j}^{\,i}_c \\ \vec{j}^{\,i}_Q \end{pmatrix} = 2\int\frac{d\vec{k}}{(2\pi)^3}\begin{pmatrix} -e \\ \varepsilon_k-\mu \end{pmatrix}\vec{v}^{\,i}_k\,\delta f_k$$

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

and thus for the linear response coefficients

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

One finds the <u>Onsager relation</u> : $L_{21} = T\,L_{12}$

The expressions simplify for an isotropic system for which we can substitute $v_k^i v_k^j = v_k^i v_k^i \delta_{ij} = \frac{1}{3} \vec{v}_k^2 \delta_{ij}$

and $L^{ij}_{\alpha\beta} = L_{\alpha\beta} \delta_{ij}$ with

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

where we used that for an isotropic system the relaxation time and $\vec{v}^2$ will only depend on energy ε.

The resulting expression can be evaluated for small T using the Sommerfeld expansion:

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

$$g(\varepsilon) \cong g(\mu) + g'(\mu)(\varepsilon-\mu)$$

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

So one obtains at low temperatures with $g(\varepsilon) \equiv \nu(\varepsilon)\tau(\varepsilon)\frac{1}{3}\vec{v}_\varepsilon^2$

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

For the transport coefficients one obtains

<u>thermal conductivity</u>:

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

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

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

ratio $\kappa/\sigma T$ is predicted to be constant and equal to the Lorenz number $L_0 = \frac{\pi^2}{3} \frac{k_B^2}{e^2}$.

physical interpretation: typical excitation has charge $|e|$ and energy $k_B T$

The Wiedemann-Franz law is exact for purely elastic scattering.

Inelastic processes might relax energy but not current and this law might then be violated.

Thermopower Q:

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

$$= \frac{\pi^2}{3} \frac{k_B^2 T}{-e} \frac{\partial}{\partial \varepsilon} \ln \sigma(\varepsilon) \Big|_{\varepsilon_F} \qquad \text{Mott formula}$$

with energy dependent conductivity $\sigma(\varepsilon)$

with

$$\sigma'(\varepsilon_F) = e^2 \int d\varepsilon' \frac{\partial}{\partial \varepsilon_F} \delta(\varepsilon_F - \varepsilon') \frac{1}{3} \vec{v}_{\varepsilon'}^{\,2} \tau(\varepsilon') \nu(\varepsilon')$$

$$= \frac{\tau'(\varepsilon_F)}{\tau(\varepsilon_F)} \sigma(\varepsilon_F) + 2 e^2 \tau(\varepsilon_F) \int \frac{d\vec{k}}{(2\pi)^3} \underbrace{\frac{\partial}{\partial \varepsilon_F} \delta(\varepsilon_F - \varepsilon_k) \vec{v}_\varepsilon}_{\begin{array}{l} - \frac{\partial}{\partial \varepsilon_k} \delta(\varepsilon_F - \varepsilon_k) \frac{1}{\hbar} \frac{\partial \varepsilon_k}{\partial \vec{k}} \\ = - \frac{1}{\hbar} \frac{\partial}{\partial \vec{k}} \delta(\varepsilon_F - \varepsilon_k) \end{array}} \vec{v}_\varepsilon \frac{1}{3}$$

$$= \frac{\tau'(\varepsilon_F)}{\tau(\varepsilon_F)} \sigma(\varepsilon_F) + 2 e^2 \tau(\varepsilon_F) \int \frac{d\vec{k}}{(2\pi)^3} \delta(\varepsilon_F - \varepsilon_k) \frac{1}{3\hbar^2} \frac{\partial \varepsilon_k}{\partial \vec{k} \partial \vec{k}}$$

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 $\Psi = \Psi(r_1\sigma_1, r_2\sigma_2, \ldots, r_N\sigma_N)$ where r_i and σ_i are position and spin of the i^{th} electron, respectively. The Hamiltonian reads

$\sigma_i = \uparrow, \downarrow$

$$H = \underbrace{\sum_i \frac{p_i^2}{2m}}_{\text{kinetic energy}} - \underbrace{\sum_{i,n} \frac{Ze^2}{|r_i - R_n|}}_{\text{ionic potential}} + \underbrace{\sum_{i<j} \frac{e^2}{|r_i - r_j|}}_{\text{e-e interaction}} + \text{spin-orbit coupling corrections}$$

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 $H_{\text{non-interacting}} = \sum_i H_0(r_i, p_i)$ the many-particle wavefunction is totally antisymmetric and given by a Slater determinant

$$\Psi_{\text{Slater}}(r_1\sigma_1, \ldots, r_N\sigma_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_1(r_1\sigma_1) & \phi_2(r_1\sigma_1) & \ldots & \phi_N(r_1\sigma_1) \\ \phi_1(r_2\sigma_2) & & & \vdots \\ \vdots & & & \\ \phi_1(r_N\sigma_N) & \ldots & & \phi_N(r_N\sigma_N) \end{pmatrix}$$

where $\{\phi_1, \phi_2, \ldots, \phi_N\}$ is a set of N orthonormal one-electron eigenfunctions of H_0.

The antisymmetry of the wavefunction is required by the Pauli principle that demands

$$\Psi(r_1\sigma_1 \ldots r_i\sigma_i \ldots r_j\sigma_j \ldots r_N\sigma_N) = - \Psi(r_1\sigma_1 \ldots r_j\sigma_j \ldots r_i\sigma_i \ldots r_N\sigma_N)$$

a sign change upon interchanging arguments.

Strategy: use Ψ_{slater} as an variational Ansatz for the interacting problem by minimizing its energy

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

Hartree-Fock approximation

where E_0^{HF} is the ground state energy obtained within this HF approximation.

The expectation value reads explicitly

$$\frac{\langle \Psi_{\text{slater}} | H | \Psi_{\text{slater}} \rangle}{\langle \Psi_{\text{slater}} | \Psi_{\text{slater}} \rangle} = \langle H \rangle_{\text{slater}} =$$

$$= \sum_{i=1}^{N} \sum_{\sigma=\uparrow,\downarrow} \int d\vec{r}\; \phi_i^*(\vec{r},\sigma) \left(\frac{\vec{p}^2}{2m} + V_{\text{ion}}(\vec{r}) \right) \phi_i(\vec{r},\sigma)$$

$$+ \frac{1}{2} \sum_{ii'=1}^{N} \sum_{\sigma\sigma'=\uparrow\downarrow} \int d\vec{r}\, d\vec{r}\,' \frac{e^2}{|\vec{r}-\vec{r}\,'|} \left(|\phi_i(r\sigma)|^2 |\phi_{i'}(r'\sigma')|^2 - \delta_{\sigma\sigma'} \phi_i^*(r\sigma) \phi_{i'}^*(r'\sigma) \phi_i(r'\sigma) \phi_{i'}(r\sigma) \right))$$

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

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

where ε_i are Lagrange multipliers.

Minimization $\quad \dfrac{\delta}{\delta \phi_i^*(r\sigma)} F[\phi] = 0 \quad$ yield

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

Hartree-Fock equations.

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

gives rise to an effective Coulomb potential generated by the electrons. → <u>direct term</u>

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

arises from indistinguishability of electrons → <u>exchange term</u>

The Hartree-Fock equations are <u>difficult</u> to solve because the exchange term gives rice to an integral operator. Numerical solution practically impossible for solids and large molecules.

<u>Further approximation</u>: replace $\rho^F_{i\sigma}$ by average over i:

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

independent of index i

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

1. Ansatz for $\phi_i(r\sigma)$ (for example plane waves, Bloch functions, ...)

2. evaluate potential $$U_\sigma(\vec{r}) = V_{ion}(\vec{r}) - e\int d\vec{r}\,' \frac{\rho^H(\vec{r}\,') - \rho^F_\sigma(r,r')}{|r-r'|}$$

3. solve Schrödinger equation with potential $U_\sigma(\vec{r})$ and obtain eigenfunctions $\phi_i(r\sigma)$ → back to 2.

6.1.1. Hartree-Fock approximation of free electrons

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

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

→ Hartree-density is then uniform and is exactly canceled by the uniform positive charge density attributed to the ions.

Hartree-Fock equations then reduce to

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

with $\varepsilon_i = \frac{\hbar^2 k_i^2}{2m} + \varepsilon_i^{ex}$ where the exchange correction is given by

$$\varepsilon_i^{ex} = -e^2\sum_j\int d\vec{r}\,' \frac{1}{|\vec{r}-\vec{r}\,'|}\frac{1}{V}e^{-ik_jr' + ik_ir' + ik_jr - ik_ir}$$

with $$\frac{1}{|r-r'|} = 4\pi\frac{1}{V}\sum_q\frac{1}{q^2}e^{iq(r-r')}$$

$$\rightarrow \quad \varepsilon_i^{ex} = -4\pi e^2 \frac{1}{V^2}\sum_j \sum_q \frac{1}{q^2} \underbrace{\int d\vec{r}\,' \, e^{i(q+k_j-k_i)(r-r')}}_{V\delta_{q+k_j,k_i} \quad \text{independent of } \vec{r} \; !}$$

$$= -4\pi e^2 \frac{1}{V}\sum_j \frac{1}{|k_i-k_j|^2}$$

summation extends over all occupied states : $|k_j| \le k_F$

$$\varepsilon^{ex}(\vec{k}) = -4\pi e^2 \int\limits_{|\vec{k}'|\le k_F} \frac{d\vec{k}'}{(2\pi)^3}\frac{1}{|\vec{k}-\vec{k}'|^2} = -\frac{4\pi e^2}{(2\pi)^3}\int_0^{k_F} dk'\, k'^2\, 2\pi \int_{-1}^{1} d\cos\theta \, \frac{1}{k^2+k'^2+2kk'\cos\theta}$$

$$= -\frac{e^2}{\pi}\int_0^{k_F} dk'\, k'^2 \frac{1}{2kk'} \ln\left[\frac{k^2+k'^2+2kk'}{k^2+k'^2-2kk'}\right] = -\frac{2e^2}{\pi} k_F\, F\left(\frac{k}{k_F}\right)$$

where $F(x) = \frac{1}{2}\int_0^1 dy\, \frac{y}{2x} \ln\left(\frac{(x+y)^2}{(x-y)^2}\right) = \frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|$

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

$$E_{HF} = \underset{\substack{\uparrow \\ \text{spin}}}{2} \sum_{|\vec{k}|\le k_F}\left[\frac{\hbar^2 k^2}{2m} + \varepsilon^{ex}(\vec{k})\right] = 2V \int_0^{k_F} \frac{dk\, k^2}{(2\pi)^3} 4\pi \left[\frac{\hbar^2k^2}{2m} + \varepsilon^{ex}(k)\right]$$

with Fermi energy $E_F = \frac{\hbar^2 k_F^2}{2m}$ and number of electrons $N = 2\sum_{k\le k_F} = \frac{k_F^3 V}{3\pi^2}$

$$\boxed{\frac{E_{HF}}{N} = \frac{3}{5}E_F - \frac{3}{4}\frac{e^2 k_F}{\pi}}$$

$$\underbrace{\qquad\qquad}_{\text{non-interacting}} \quad \underbrace{\qquad\qquad}_{\text{exchange correction}}$$

in terms of $\frac{e^2}{2a} = 1\,\mathrm{Ry} = 13{,}6\,\mathrm{eV}$ and the Bohr radius $a = \frac{\hbar^2}{me^2}$

$$\frac{E_{HF}}{N} = \frac{e^2}{2a}\left[\frac{3}{5}(k_F a)^2 - \frac{3}{2\pi}(k_F a)\right]$$

The Hartree-Fock correction is the leading correction in the high-density limit ie. in the small parameter $\frac{1}{k_F a}$. 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 defined by

$$\frac{1}{n} = \frac{V}{N} = \frac{3\pi^2}{k_F^3} \equiv \frac{4\pi}{3} r_s^3$$

r_s : radius of sphere with the volume of $1/n$

$$\Rightarrow \quad \frac{1}{k_F a} = \sqrt[3]{\frac{4}{9\pi}}\,\frac{r_s}{a}$$

5.2. Density functional theory (DFT)

nobel prize in Chemistry 1998
to W. Kohn

based on the

Hohenberg - Kohn theorem (1964)

The ground state energy E_0 of electrons in an arbitrary potential $V(\vec{r})$ is a functional of the local particle density $n(\vec{r})$:

$$E_0 = E_0[n(r)] = \underbrace{T[n(r)]}_{\substack{\text{kinetic}\\ \text{energy}}} + \underbrace{\int d\vec{r}\, V(\vec{r})\, n(\vec{r})}_{\substack{\text{potential}\\ \text{energy}}} + \underbrace{U[n(\vec{r})]}_{\substack{\text{interaction}\\ \text{energy}}}$$

where the functionals T and U are independent of the potential V.

remarks :

- idea of proof : $E_0 = E_0[V(r)]$ is functional of potential V $\rightarrow$ use Legendre transformation to show that $E_0[n(r)]$
- the functionals T and U are not known, likely to be highly non-local, non-linear...
- interaction energy possesses a long-range Hartree term

$$U[n(\vec{r})] = \underbrace{\frac{e^2}{2}\int dr\,dr' \frac{n(r)\,n(r')}{|r-r'|}}_{\text{Hartree term}} + \underbrace{E_{ex}[n(r)]}_{\text{rest}}$$

Approximation of the kinetic term :

$$T[n(r)] = 2\int d\vec{r} \sum_i \varphi_i^*(r)\left(-\frac{\hbar^2\nabla^2}{2m}\right)\varphi_i(r)$$

where $\varphi_i(r)$ are hypothetical single-particle wavefunctions

that obey $$n(\vec{r}) = \sum_{\substack{i \\ \text{occupied}}} |\varphi_i(\vec{r})|^2$$

minimizing the energy functional E_0 with the constraint $\int d\vec{r}\, |\varphi_i(\vec{r})|^2 = 1$ for each i

by introducing Lagrange multipliers ε_i then yield the

$$\boxed{\begin{aligned} &\left(-\frac{\hbar^2\nabla^2}{2m} + V_{eff}(\vec{r})\right)\varphi_i(\vec{r}) = \varepsilon_i\,\varphi_i(\vec{r}) \\ &V_{eff}(\vec{r}) = V(r) + \int d\vec{r}\,' \frac{e^2 n(r')}{|r-r'|} + \frac{\delta E_{ex}[n]}{\delta n(r)} \end{aligned}}$$

Kohn-Sham equations

remarks

- problem is reduced to solve an effective single-particle Schrödinger equation self-consistently as $V_{eff} = V_{eff}[n]$.
- allows to determine the groundstate energy E_0, useful to determine position of atoms in molecules/crystal by minimizing $E_0(\{R_n\})$ (step II of adiabatic approx.)
- strictly speaking: no direct physical meaning of ε_i and $\varphi_i(r)$ however: often interpreted as energies and wavefunctions of electrons.
- needed: approximation for $E_{ex}[n]$

Local density approximation (LDA)

replace functional by function: $E_{ex}^{LDA}[n] = \int d\vec{r}\ \varepsilon_{ex}(n(r))$

$$\Rightarrow \quad \frac{\delta E_{ex}^{LDA}}{\delta n(\vec{r})} = \frac{\partial \varepsilon_{ex}}{\partial n}$$

The function ε_{ex} is often approximated by the free electron expression

$$E_{ex}^{LDA} = -N\frac{3}{4}\frac{e^2 k_F}{\pi} = V\,\varepsilon_{ex}$$

with $$\varepsilon_{ex} = -n\frac{3}{4}\frac{e^2 k_F}{\pi} = -\frac{3}{4\pi}e^2 n\left(3\pi^2 n\right)^{1/3}$$

$$\Rightarrow \quad \boxed{\frac{\partial \varepsilon_{ex}}{\partial n} = -\frac{e^2}{\pi}\left(3\pi^2 n\right)^{1/3}}$$

remarks

- improvements to LDA by including also dependencies on gradients $\vec{\nabla} n$
  → generalized gradient approximation (GGA)

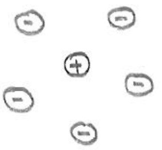
- implementations of LDA etc. available in the form of (commercial) ready-to-use software packages.

- LDA fails sometimes completely if interactions are strong → modern development: combination with field-theoretic methods.

6.3. Screening

chapter 6.1 and 6.2.: effective ionic potential modified by e-e interaction.

consider positively charged particle rigidly fixed at a certain position



mobile electrons get attracted creating surplus of negative charge in its vicinity thus reducing its field → screening

if ρ^{ext} is the positive charge density of the particle, we have

Poisson equation: $-\vec{\nabla}^2 \phi^{ext} = 4\pi \rho^{ext}$

for the associated potential ϕ^{ext}.

For the full potential: $-\vec{\nabla}^2 \phi = 4\pi\rho$ with $\rho = \rho^{ext} + \rho^{ind}$

where ρ^{ind} is the charge density induced in the electron gas.

definition: dielectric function ε

$$\phi^{ext}(\vec{r}) = \int d\vec{r}\,' \, \varepsilon(\vec{r},\vec{r}\,') \, \phi(\vec{r}\,')$$

for a translationary invariant system (for simplicity) : $\varepsilon(r,r') = \varepsilon(r-r')$

Fourier transform : $\varepsilon(\vec{q}) = \int d\vec{r}\, e^{-i\vec{q}\vec{r}}\, \varepsilon(\vec{r})$

$$\rightarrow \quad \boxed{\phi(\vec{q}) = \frac{1}{\varepsilon(\vec{q})}\phi^{ext}(\vec{q})}$$

real potential ϕ
similar as in dielectrics

How does the induced charge density ρ^{ind} depend on ϕ ?

for weak ϕ expect linear relation $\rightarrow$

definition : $\rho^{ind}(\vec{q}) = \chi_0(\vec{q})\,\phi(\vec{q})$ with the susceptibility χ_0

relate ε and χ via Poisson equations :

$$\phi(\vec{q}) = \frac{4\pi\rho(\vec{q})}{\vec{q}^2} = \underbrace{\frac{4\pi\rho^{ext}(\vec{q})}{\vec{q}^2}}_{=\phi^{ext}(\vec{q})} + \frac{4\pi\chi_0(\vec{q})\phi(\vec{q})}{\vec{q}^2}$$

$$\Rightarrow \quad \boxed{\varepsilon(\vec{q}) = 1 - \frac{4\pi}{q^2}\chi_0(\vec{q})}$$

For the evaluation of χ_0 and thus ε one needs to employ approximations.

6.3.1. Thomas-Fermi theory of screening

consider Schrödinger equation of free electrons in the Hartree approximation

$$\left(-\frac{\hbar^2\nabla^2}{2m} - e\phi(\vec{r})\right)\psi_i = \varepsilon_i\psi_i$$

$\uparrow$ potential due to the positive charge and the induced rearrangement in the electron system

The potential $\phi(\vec{r})$ modifies locally the chemical potential μ.

For a function $\phi(\vec{r})$ that is slowly varying on the scale of the inverse of Fermi wavevector $1/k_F$ one can employ the semiclassical approximation and define a local density of electrons:

$$n(\vec{r}) = n(\mu + e\phi(\vec{r}))$$

→ locally induced charged density

$$\rho^{ind}(\vec{r}) = -e\left(n(\vec{r}) - n_0\right) = -e\left(n(\mu + e\phi(\vec{r})) - n(\mu)\right)$$

$$= -e^2 \frac{\partial n_0}{\partial \mu} \phi(\vec{r}) + \mathcal{O}(\phi^2)$$

From which follows: $\chi_0(\vec{q}) = -e^2 \dfrac{\partial n_0}{\partial \mu}$ independent of $\vec{q}$

that gives $\varepsilon(\vec{q})$ in the Thomas - Fermi approximation

$$\boxed{\varepsilon(\vec{q}) = 1 + \frac{k_{TF}^2}{q^2}}$$

with the Thomas - Fermi wavevector k_{TF}: $k_{TF}^2 = 4\pi e^2 \dfrac{\partial n_0}{\partial \mu}$

From the expression for the density:

$$n_0 = 2 \int \frac{d\vec{k}}{(2\pi)^3} f(\varepsilon_k - \mu) = \int d\varepsilon\, \nu(\varepsilon) f(\varepsilon - \mu)$$

follows for low temperatures $T \ll T_F$

$$\frac{\partial n_0}{\partial \mu} = \int d\varepsilon\, \nu(\varepsilon)\left(-f'(\varepsilon - \mu)\right) \cong \nu(\varepsilon_F)$$ density of states at the Fermi level

for free electrons $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$, $\nu(\varepsilon_F) = \frac{m k_F}{\hbar^2 \pi^2}$

$\rightarrow$ $k_{TF}^2 = 4\pi e^2 \frac{m k_F}{\hbar^2 \pi^2} = \frac{4}{\pi}\frac{k_F}{a}$ with Bohr radius $a = \frac{\hbar^2}{me^2}$

usually for metals $k_F a \sim \mathcal{O}(1)$ $\Rightarrow$ $k_{TF} \sim k_F$ and $\frac{1}{k_{TF}} \sim \mathcal{O}(1\,\text{Å})$

Illustration of the significance of k_{TF}:

consider point charge $\phi^{ext}(\vec{r}) = \frac{Q}{|\vec{r}|}$ $\rightarrow$ $\phi^{ext}(\vec{q}) = \frac{4\pi Q}{q^2}$

total potential $\phi(\vec{q}) = \frac{1}{\varepsilon(\vec{q})}\phi^{ext}(\vec{q}) = \frac{4\pi Q}{q^2 + k_{TF}^2}$

in real space:

$$\boxed{\phi(\vec{r}) = \int \frac{d\vec{q}}{(2\pi)^3} e^{i\vec{q}\vec{r}} \phi(\vec{q}) = \frac{Q}{|\vec{r}|} e^{-k_{TF}\cdot|\vec{r}|}}$$

screened Coulomb potential decays exponentially on the length scale of the inverse Thomas-Fermi wavevector $1/k_{TF}$.

$\rightarrow$ electrons are highly effective in screening the external charge!

6.3.2. Lindhard theory of screening

going beyond the Thomas-Fermi approximation

perturbation theory in the potential ϕ for the wave function

$$|\psi_k\rangle = |\psi_k^{(0)}\rangle + \sum_{k' \neq k} \frac{|\psi_{k'}^{(0)}\rangle\langle\psi_{k'}^{(0)}| -e\phi(\vec{r}) |\psi_k^{(0)}\rangle}{\varepsilon_k - \varepsilon_{k'}}$$

for plane waves $|\psi_k^{(0)}\rangle$:

$$\langle\psi_{k'}^{(0)}| -e\phi(\vec{r}) |\psi_k^{(0)}\rangle = -\frac{e}{V}\int dr\, e^{-i\vec{k}'\vec{r} + i\vec{k}\vec{r}} \phi(\vec{r}) = -e\frac{\phi(\vec{k}'-\vec{k})}{V}$$

so that one obtains for the density in lowest order in ϕ

$$n(\vec{r}) = 2\sum_k f_k\, |\psi_k(r)|^2 = 2\sum_k f_k\, |\psi_k^{(0)}(r)|^2 +$$

$$+\, 2\sum_k f_k \sum_{k'\neq k} \frac{-e}{v}\, \frac{\psi_k^{(0)*}(r)\,\psi_{k'}^{(0)}(r)\,\phi(k'-k) + \phi^*(k'-k)\,\psi_{k'}^{(0)*}(r)\,\psi_k^{(0)}(r)}{\varepsilon_k-\varepsilon_{k'}}$$

induced charge density (with $\phi^*(q)=\phi(-q)$ as $\phi(r)$ is real)

$$\rho^{ind}(\vec{r}) = 2\,\frac{e^2}{v^2}\sum_k\sum_{k'\neq k} f_k\, \frac{e^{-ikr+ik'r}\,\phi(k'-k) + \phi(k-k')\,e^{-ik'r+ikr}}{\varepsilon_k-\varepsilon_{k'}}$$

Fourier transform

$$\rho^{ind}(\vec{q}) = \int dr\, e^{-iqr}\,\rho^{ind}(\vec{r}) =$$

$$= 2\,\frac{e^2}{v}\sum_k f_k\,\phi(q)\left(\frac{1}{\varepsilon_k-\varepsilon_{k+q}} + \frac{1}{\varepsilon_k-\varepsilon_{k-q}}\right)$$

from which follows for the susceptibility

$$\boxed{\chi_0(\vec{q}) = 2e^2\,\frac{1}{v}\sum_k \frac{f_{k-q/2}-f_{k+q/2}}{\varepsilon_{k-q/2}-\varepsilon_{k+q/2}}}$$

in the limit $|\vec{q}|\to 0$:

$$\chi_0(\vec{q}\to 0) = 2e^2\,\frac{1}{v}\sum_k f'(\varepsilon_k-\mu) = -e^2\,\nu(\varepsilon_F)$$

one recovers the Thomas-Fermi result.

for finite $\vec q$ and quadratic dispersion $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$

$$\chi_0(\vec q) = 2e^2 \frac{1}{V}\sum_k f_k \left(\frac{1}{\frac{\hbar^2}{2m}\left(k^2-(\vec k+\vec q)^2\right)} + \underbrace{\frac{1}{\frac{\hbar^2}{2m}\left(\vec k^2 - (\vec k - \vec q)^2\right)}}_{\vec k \to -\vec k} \right)$$

$$= 4e^2 \int_0^{k_F} \frac{dk\,k^2}{(2\pi)^3} \cdot \int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta \, \frac{1}{\frac{\hbar^2}{2m}\left(-2kq\cos\theta - q^2\right)}$$

$$= -\frac{4e^2}{(2\pi)^2}\frac{2m}{\hbar^2}\int_0^{k_F} dk\,k^2 \underbrace{\int_{-1}^{1} d\cos\theta \, \frac{1}{q^2+2qk\cos\theta}}_{\frac{1}{2qk}\ln\frac{q^2+2qk}{q^2-2qk}}$$

$$\overset{y=k/k_F}{=} -\frac{4e^2}{(2\pi)^2}\frac{2mk_F}{\hbar^2}\underbrace{\int_0^1 dy\, \frac14 \, \frac{2k_F}{q}\cdot y \ln\left(\frac{\frac{q}{2k_F}+y}{\frac{q}{2k_F}-y}\right)}_{=\frac12 F\left(\frac{q}{2k_F}\right)}$$

with the Lindhard function known from chap. 6.1.1

$$F(x) = \frac12 + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right| \qquad \text{with} \quad F(0) = 1$$

So one obtains an additional $\vec q$-dependence of $\varepsilon(\vec q)$ in the Lindhard approximation:

$$\boxed{\varepsilon(\vec q) = 1 + \frac{4\pi}{q^2}\frac{e^2}{\pi^2}\frac{mk_F}{\hbar^2}F\left(\frac{q}{2k_F}\right)} = 1 + \left(\frac{k_{TF}}{q}\right)^2 F\left(\frac{q}{2k_F}\right)$$

Lindhard function possesses logarithmic singularity at $|\vec{q}| = 2k_F$:

$$\varepsilon(\vec{q}) \underset{|\vec{q}| \approx 2k_F}{\approx} 1 + \left(\frac{k_{TF}}{2k_F}\right)^2 \left[\frac{1}{2} + \frac{1}{2}\left(1 - \frac{q}{2k_F}\right) \ln \left| \frac{2}{1 - \frac{q}{2k_F}} \right| \right]$$

<u>$2k_F$ - singularity</u>

consequences in real space :

consider eg. modified Coulomb potential

$$\phi(\vec{r}) = \int \frac{d\vec{q}}{(2\pi)^3} e^{i\vec{q}\vec{r}} \frac{1}{\varepsilon(\vec{q})} \frac{4\pi Q}{q^2} = \frac{2\pi}{(2\pi)^3} \int_0^\infty dq\, q^2 \underbrace{\int_{-1}^{1} dx\, e^{iqrx}}_{\frac{1}{iqr}\left(e^{iqr} - e^{-iqr}\right) = \frac{2}{qr} \sin qr} \frac{4\pi Q}{\varepsilon(q)\, q^2}$$

$$= \frac{2Q}{\pi r} \int_0^\infty dq \frac{\sin qr}{q\, \varepsilon(q)}$$

the presence of the logarithm in $\varepsilon(q)$ changes the analytical properties in the complex q plane $\longrightarrow$ $\phi(\vec{r})$ does <u>not</u> decay exponentially

instead :

$$\boxed{\phi(\vec{r}) \propto \frac{\cos 2k_F r}{r^3} \quad \text{for} \quad r = |\vec{r}| \to \infty}$$

<u>Friedel oscillation</u>

6.4. Elementary theory of phonon dispersion relation

in chap. 5.1.4. we learned that the electron gas can sustain density oscillations at the plasma frequency:

continuity equation for charge density $\partial_t \rho + \vec{\nabla}\vec{j} = 0$

with $\rho = -en$, $\vec{j} = -en \frac{\vec{p}}{m}$

Newton : $\partial_t \vec{p} = -e\vec{E}$ (neglecting collisions)

Gauß : $\vec{\nabla}\vec{E} = 4\pi\rho$

$$\Rightarrow \quad \partial_t^2 \rho + \vec{\nabla}\partial_t \vec{j} \cong \partial_t^2 \rho + \underbrace{\frac{-en_0}{m}(-e)\,4\pi}_{\equiv \omega_p^2} \rho = 0 \qquad \text{harmonic oscillator}$$

$$\longrightarrow \quad \text{plasma frequency } \omega_p^2 = \frac{4\pi n_0 e^2}{m}$$

The positively charged ions can similarly sustain plasma oscillations at the ionic plasma frequency:

$$\boxed{\Omega_p^2 = \frac{4\pi n_{ion} (Ze)^2}{M} = \frac{Zm}{M}\,\omega_p^2}$$

with $n_{ion} = n_0 / Z$ due to charge neutrality.

How is this related to the results for phonon dispersions obtained in chap 3? In particular, where is the acoustic phonon modes whose frequencies vanish linear with momentum?

More carefully : Gauß law $\vec{\nabla} \vec{D} = 4\pi \rho_{ion}$

taking into account the screening of the ionic charges by the electrons : $\vec{D}(\vec{q}) = \varepsilon_{el}(\vec{q}) \vec{E}(\vec{q})$

$$\Rightarrow \quad \partial_t^2 \rho_{ion}(\vec{q},t) + \partial_t (i\vec{q}) \vec{j}_{ion}(\vec{q},t) =$$

$$\partial_t^2 \rho_{ion}(\vec{q},t) + \frac{(eZ)^2 n_{ion}}{M} \underbrace{i\vec{q}\vec{E}(\vec{q})}_{\frac{4\pi \rho_{ion}(\vec{q},t)}{\varepsilon_{el}(\vec{q})}} = 0$$

one obtains a momentum dependent eigenfrequency for the ions

$$\boxed{\omega_{ion}^2(\vec{q}) = \frac{4\pi n_{ion} (Ze)^2}{M} \frac{1}{\varepsilon_{el}(\vec{q})} = \frac{\Omega_p^2}{\varepsilon_{el}(\vec{q})}}$$

with the Thomas-Fermi result $\varepsilon_{el}(\vec{q}) = 1 + \left(\frac{k_{TF}}{q}\right)^2$ one obtains

$$\omega_{ion}^2(q) = \frac{\Omega_p^2}{q^2 + k_{TF}^2} q^2 \underset{q \to 0}{\approx} \frac{\Omega_p^2}{k_{TF}^2} q^2$$

with the sound velocity $c^2 = \Omega_p^2 / k_{TF}^2$

using the free electron value : $k_{TF}^2 = 4\pi e^2 \frac{m k_F}{\pi^2 \hbar^2}$

$$\rightarrow \quad c^2 = \frac{Zm}{M} \frac{\omega_p^2}{k_{TF}^2} = \frac{Zm}{M} \frac{\cancel{4\pi} n_0 \cancel{e^2}}{m} \frac{\pi^2 \hbar^2}{\cancel{4\pi} \cancel{e^2} m k_F} = \frac{Zm}{M} \frac{n_0}{m} \frac{\pi^2 \hbar^2}{m k_F}$$

with the electron density $n_0 = \frac{k_F^3}{3\pi^2}$, Fermi velocity $v_F = \frac{\hbar^2 k_F^2}{m}$

$$\rightarrow \quad \boxed{c^2 = \frac{1}{3} \frac{Zm}{M} v_F^2}$$ 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.

$\left(\text{Note that } \frac{c}{v_F} \sim \frac{\Theta_D}{T_F} \right)$

using the Lindhard-result for $\varepsilon_{ee}(\vec{q})$ the above consideration also predict (weak) singularities at $|\vec{q}| = 2k_F$ in the phonon spectrum. These are known as Kohn anomalies.

→ position of Kohn anomalies reflect the geometry of the Fermi surface (obtained eg. from de Haas-van Alphen oscillations)

6.5. Dielectric function of a metal and effective electron-electron interaction

in a metal screening occurs by all the charged particles, electrons and ions,

consider now additional ionic sorce for screening

an external potential ϕ^{ext} induces a total potential ϕ via the dielectric function

$$\varepsilon \phi = \phi^{ext}$$

The total potential on the other hand consists of

$$\phi = \phi^{ext} + \phi^{ion} + \phi^{el}$$

ϕ^{ext} and in addition of 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 system alone, ε^{el} and ε^{ion}, respectively.

The electronic system responds to the sum of potentials $\phi^{ext} + \phi^{ion}$ so that

$$\varepsilon^{el} \phi = \phi^{ext} + \phi^{ion}$$

The ionic system responds to $\phi^{ext} + \phi^{el}$:

$$\varepsilon^{ion} \phi = \phi^{ext} + \phi^{el}$$

Summing the two equations gives

$$(\varepsilon^{el} + \varepsilon^{ion}) \phi = \phi^{ext} + \underbrace{(\phi^{ext} + \phi^{ion} + \phi^{el})}_{= \phi}$$

$$\Rightarrow \boxed{\varepsilon = \varepsilon^{el} + \varepsilon^{ion} - 1}$$

Use the simplest expressions for ε^{el} and ε^{ion}:

- treat electrons in the Thomas-Fermi approximation: $\varepsilon^{el}(\vec{q}) = 1 + \left(\frac{k_{TF}}{q}\right)^2$
- treat ions as a gas of charged particles: $\varepsilon^{ion}(\omega) = 1 - \frac{\Omega_p^2}{\omega^2}$

  with the plasma frequency $\Omega_p^2 = \frac{4\pi n_{ion} (Ze)^2}{M}$ (see chap 5)

→ frequency and momentum dependent dielectric function

$$\boxed{\varepsilon(\vec{q},\omega) = 1 + \left(\frac{k_{TF}}{q}\right)^2 - \left(\frac{\Omega_p}{\omega}\right)^2}$$

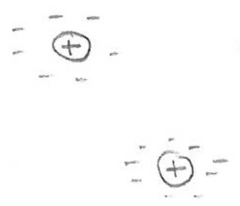
alternative interpretation:

the potential after screening by the electrons is given by

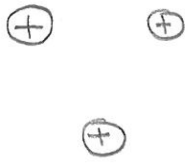
$$\phi_{el,\,screened} = \frac{1}{\varepsilon_{el}}\,\phi^{ext}$$

the full potential is then obtained when $\phi_{el,\,screened}$ is in addition shielded by the ions which are themselves screened ie dressed by the electrons

$$\phi = \frac{1}{\varepsilon^{ion}_{dressed}}\,\phi_{el,\,screened} = \frac{1}{\varepsilon^{ion}_{dressed}}\,\frac{1}{\varepsilon^{el}}\,\phi^{ext}$$



$\varepsilon^{ion}_{dressed}$



ε^{ion}

ε^{el}

identification with ε yields $\dfrac{1}{\varepsilon} = \dfrac{1}{\varepsilon^{ion}_{dressed}}\,\dfrac{1}{\varepsilon^{el}}$

$$\varepsilon^{ion}_{dressed} = \frac{\varepsilon}{\varepsilon^{el}} = 1 + \frac{\varepsilon^{ion} - 1}{\varepsilon^{el}}$$

$$\Rightarrow \boxed{\varepsilon^{ion}_{dressed}(\vec{q},\omega) = 1 - \frac{\Omega_p^2/\varepsilon^{el}(\vec{q})}{\omega^2} = 1 - \frac{\omega_{ion}^2(\vec{q})}{\omega^2}}$$

with the dressed phonon frequency $\omega_{ion}(\vec{q})$.

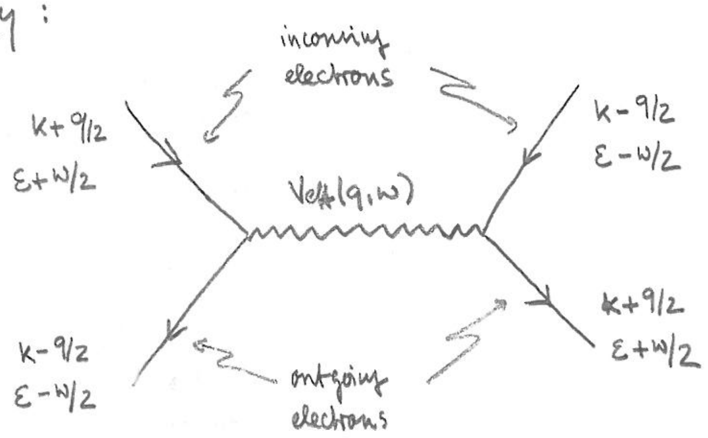
The screening has consequences for the effective electron-electron interaction. The bare electrons interact via the Coulomb potential

$$V(\vec{q}) = \frac{4\pi e^2}{q^2} \qquad \text{Coulomb potential}$$

The screening by electrons and ions yields the effective interaction

$$\boxed{V_{\text{eff}}(\vec{q},\omega) = \frac{4\pi e^2}{q^2\,\varepsilon(\vec{q},\omega)} = \underbrace{\frac{4\pi e^2}{q^2 + k_{TF}^2}}_{\substack{\text{screened by}\\ \text{electrons}}} \; \underbrace{\frac{1}{1 - \frac{\omega_{ion}^2(\vec{q})}{\omega^2}}}_{\substack{\text{additionally screened}\\ \text{by dressed ions}}}}$$

pictorially :



exchange of energy $\hbar\omega$ and momentum $\vec{q}$

remarks

- phonon frequencies are bounded by the Debye frequency: $\omega_{ion}(\vec{q}) \lessapprox \omega_D$ The interaction possesses a substantial ω-dependence only for frequencies $\omega \lessapprox \omega_D$. As the Fermi energy $E_F \gg \hbar\omega_D$ only electrons close to the Fermi energy are affected.

- For small energy transfers $\omega < \omega_D$ the effective interaction for $\omega_{ion}(q)/\omega < 1$ changes sign and becomes attractive! (overscreening)

  $\longrightarrow$ important for the theory of superconductivity

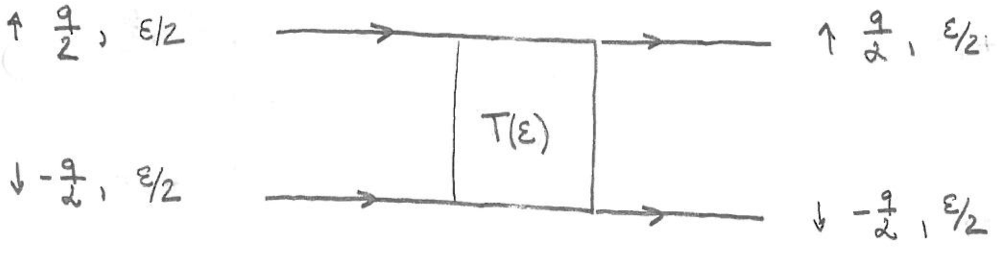
- rigorous theory for the effective interaction V_{eff} requires advanced field-theoretic methods.

6.6. Outlook: Cooper instability and superconductivity

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 $V_{eff}(q,\omega) = -g$ with $g > 0$. It is characterized by the scattering T-matrix which is obtained by summing up repeated scattering events.

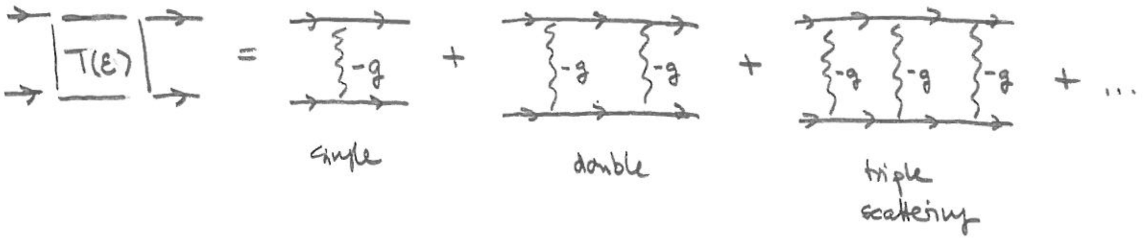
pictorially

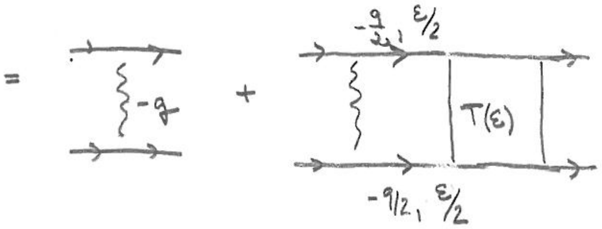


we consider two electrons with opposite spin configurations, vanishing total momentum and total energy ε measured from the Fermi surface ie wrt ε_F.

(Electrons with equal spins do not interact locally due to Pauli principle.)

The frequency-dependent T-matrix is given by





from scattering theory follows

$$T(\varepsilon) = (-g) + (-g)\frac{1}{V}\sum_q \frac{T(\varepsilon)}{\underbrace{-(\xi_{q/2}+\xi_{-q/2})}_{\text{dispersion of intermediate state}} + \underbrace{\varepsilon}_{\text{energy of intermediate state}}}\left[\underbrace{(1-f_{q/2})(1-f_{-q/2})}_{\text{two particles}} - \underbrace{f_{q/2}f_{-q/2}}_{\text{two holes}}\right]$$

$$\overset{\xi_{-k}=\xi_k}{=} (-g) + (-g)\,T(\varepsilon)\frac{1}{V}\sum_q \frac{1-2f_{q/2}}{-2\xi_{q/2}+\varepsilon}$$

in the <u>absence</u> of a Fermi sea :

→ problem reduces to a two-particle scattering problem that can be solved by elementary methods

→ effective single-particle scattering problem for the wavefunction dependent on relative coordinate.

→ T-matrix obtained by setting $f_{q/2}=0$, no other particles present, and $E_F=0$

$$T(\varepsilon) = (-g) + (-g)\, T(\varepsilon) \underbrace{\int \frac{d\vec{q}}{(2\pi)^3} \frac{1}{-2\xi_{q/2} + \varepsilon}}_{\propto \sqrt{\varepsilon} \text{ for quadratic dispersion } (E_F = 0)}$$

→ in order to obtain a bound state the attractive interaction must be sufficiently strong

however: in the presence of a Fermi sea

$$T(\varepsilon) = (-g) + (-g)\, T(\varepsilon)\, \nu \int d\xi \frac{1}{-2\xi + \varepsilon} \underbrace{(1 - 2f(\xi))}_{= \operatorname{sgn} \xi \text{ at } T=0}$$

$$= (-g) + (-g)\, T(\varepsilon)\, \nu \underbrace{\int_{-\hbar\omega_D/2}^{\hbar\omega_D/2} d\xi \frac{\operatorname{sgn}\xi}{-2\xi + \varepsilon}}_{\approx -\ln \frac{\hbar\omega_D}{\varepsilon}}$$

interaction only attractive within a shell $\hbar\omega_D$ near the Fermi surface

$$\Rightarrow \quad T(\varepsilon) = \frac{-g}{1 + (-g\nu) \ln \frac{\hbar\omega_D}{\varepsilon}}$$

possesses a bound state ie a pole at $1 - g\nu \ln \frac{\hbar\omega_D}{\varepsilon_b} = 0$

$$\Leftrightarrow \quad \boxed{\varepsilon_b = \hbar\omega_D\, e^{-1/g\nu}}$$

remarks

- bound state energy is non-perturbative in gV, present even for infinitesimal attractive interaction !

- in the presence of a Fermi sea electrons form a bound state and lower the total energy → Fermi sea becomes unstable

  → Cooper instability

- The resulting state is a so-called superconductor characterized by perfect conductivity and perfect diamagnetism.

7. Superconductivity

The Cooper instability indicates that the Fermi sea in the presence of an attractive electron-electron interaction becomes 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. Bardeen, L. Cooper and R. Schrieffer (BCS) proposed 1957 a theory for superconductivity (Nobel prize 1972).

Consider the BCS Hamiltonian

$$H_{BCS} = \sum_{k\sigma} \xi_{k\sigma} c^+_{k\sigma} c_{k\sigma} - g \frac{1}{V} \sum_{k,k'} c^+_{k\uparrow} c^+_{-k\downarrow} c_{-k'\downarrow} c_{k'\uparrow}$$

It is implicitly assumed that the attractive interaction $g > 0$ is only active for electron energies $\xi_{k\sigma} = \varepsilon_{k\sigma} - \mu$ within an energy shell $|\xi_{k\sigma}| \leq \hbar\omega_D$.

The formation of bound states is reflected in finite expectation values

$$\langle c^+_{k\uparrow} c^+_{-k\downarrow} \rangle \neq 0 \quad \text{and} \quad \langle c_{-k'\downarrow} c_{k'\uparrow} \rangle \neq 0 .$$

In order to find a mean-field description of the superconducting state, a mean-field decoupling of the interaction is performed according to

$$AB = \underbrace{(A - \langle A \rangle)(B - \langle B \rangle)}_{\text{fluctuations are neglected}} + \langle A \rangle B + A \langle B \rangle - \langle A \rangle \langle B \rangle$$

$$\approx \langle A \rangle B + A \langle B \rangle - \langle A \rangle \langle B \rangle .$$

This yields the mean-field BCS Hamiltonian

$$H^{MF}_{BCS} = \sum_{k\sigma} \xi_{k\sigma} c^+_{k\sigma} c_{k\sigma} - g \frac{1}{V} \sum_{kk'} \Big(\langle c^+_{k\uparrow} c^+_{-k\downarrow} \rangle c_{-k'\downarrow} c_{k'\uparrow} + c^+_{k\uparrow} c^+_{-k\downarrow} \langle c_{-k'\downarrow} c_{k'\uparrow} \rangle$$

$$- \langle c^+_{k\uparrow} c^+_{-k\downarrow} \rangle \langle c_{-k'\downarrow} c_{k'\uparrow} \rangle \Big)$$

Introducing the abbreviation

$$\Delta = \frac{g}{V} \sum_{\substack{k \\ |\xi_k| \leq \hbar\omega_D}} \langle c_{-k\downarrow} c_{k\uparrow} \rangle \quad \text{and} \quad \Delta^* = \frac{g}{V} \sum_{\substack{k \\ |\xi_k| \leq \hbar\omega_D}} \langle c^+_{k\uparrow} c^+_{-k\downarrow} \rangle$$

we get

$$\boxed{H^{MF}_{BCS} = \sum_{k\sigma} \xi_k \, c^+_{k\sigma} c_{k\sigma} - \sum_k \left(\Delta^* c_{-k\downarrow} c_{k\uparrow} + c^+_{k\uparrow} c^+_{-k\downarrow} \Delta \right) + V \frac{|\Delta|^2}{g}}$$

It is convenient to introduce two component Nambu spinor operators

$$\vec{\Psi}_k = \begin{pmatrix} c_{k\uparrow} \\ c^+_{-k\downarrow} \end{pmatrix} \quad \text{and} \quad \vec{\Psi}^+_k = \left(c^+_{k\downarrow} \quad c_{-k\downarrow} \right)$$

Using that $c^+_{k\downarrow} c_{k\downarrow} = 1 - c_{k\downarrow} c^+_{k\downarrow}$ we can rewrite

$$H^{MF}_{BCS} = \sum_k \vec{\Psi}^+_k h_k \vec{\Psi}_k + \sum_k \xi_k + V \frac{|\Delta|^2}{g}$$

with the matrix $$h_k = \begin{pmatrix} \xi_k & -\Delta \\ -\Delta^* & -\xi_{-k} \end{pmatrix}$$

where we 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

$$\tau^y h_k^* \tau^y = -h_k \quad \text{with} \quad \tau^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

The eigenvectors can be chosen to be of the form

$$h_k \begin{pmatrix} u_k^* \\ -v_k^* \end{pmatrix} = E_k \begin{pmatrix} u_k^* \\ -v_k^* \end{pmatrix} \quad \text{and} \quad h_k \begin{pmatrix} v_k \\ u_k \end{pmatrix} = -E_k \begin{pmatrix} v_k \\ u_k \end{pmatrix}$$

In order to diagonalize the Hamiltonian we perform a Bogoliubov transformation and introduce new fermionic operators $a_{k\sigma}$

$$\vec{\Psi}_k = U_k \begin{pmatrix} a_{k\uparrow} \\ a^+_{-k\downarrow} \end{pmatrix} \qquad \text{with} \qquad U_k = \begin{pmatrix} u_k^* & v_k \\ -v_k^* & u_k \end{pmatrix}$$

or explicitly

$$c_{k\uparrow} = u_k^* a_{k\uparrow} + v_k a^+_{-k\downarrow}$$

$$c^+_{-k\downarrow} = -v_k^* a_{k\uparrow} + u_k a^+_{-k\downarrow}$$

From the fermionic anticommutation relations follows

$$\{c_{k\uparrow}, c^+_{k\uparrow}\} = |u_k|^2 \underbrace{\{a_{k\uparrow}, a^+_{k\uparrow}\}}_{=1} + |v_k|^2 \underbrace{\{a^+_{-k\downarrow}, a_{-k\downarrow}\}}_{=1} = |u_k|^2 + |v_k|^2 = 1$$

which is equivalent to $UU^+ = U^+U = \mathbb{1}$, i.e. the matrix U is unitary

An explicit calculation yields for the coefficients

$$|u_k|^2 = \frac{1}{2}\left(1 + \frac{\xi_k}{E_k}\right), \qquad |v_k|^2 = \frac{1}{2}\left(1 - \frac{\xi_k}{E_k}\right)$$

and $u_k v_k^* = \dfrac{\Delta^*}{2E_k}$

For the Hamiltonian we obtain

$$\boxed{\begin{aligned} H^{MF}_{BCS} &= \sum_k \begin{pmatrix} a^+_{k\uparrow} & a_{-k\downarrow} \end{pmatrix} \begin{pmatrix} E_k & \\ & -E_k \end{pmatrix} \begin{pmatrix} a_{k\uparrow} \\ a^+_{-k\downarrow} \end{pmatrix} + \sum_k \xi_k + V \frac{|\Delta|^2}{g} \\ &= \sum_{k\sigma} E_k a^+_{k\sigma} a_{k\sigma} + \varepsilon_0 V \end{aligned}}$$

where we used $E_k \doteq E_{-k}$.

The ground state energy density is obtained as

$$\mathcal{E}_0 = \frac{1}{V}\sum_{k}\left(\xi_k - E_k\right) + \frac{|\Delta|^2}{g}$$

$$= \int \frac{d\vec{k}}{(2\pi)^3}\left(\xi_k - \sqrt{|\Delta|^2+\xi_k^2}\right) + \frac{|\Delta|^2}{g}$$

$$\cong \underset{\uparrow}{\nu} \int_{-\hbar\omega_D}^{\hbar\omega_D} d\xi \left(\cancel{\xi} - \sqrt{|\Delta|^2+\xi^2}\right) + \frac{|\Delta|^2}{g} =$$

DOS per spin at the Fermi level

$$= -\nu\left[\frac{1}{2}\,\xi\sqrt{|\Delta|^2+\xi^2} + \frac{|\Delta|^2}{2}\ln\left(\xi+\sqrt{|\Delta|^2+\xi^2}\right)\right]_{-\hbar\omega_D}^{\hbar\omega_D} + \frac{|\Delta|^2}{g}$$

$$= -\nu\,\hbar\omega_D\sqrt{|\Delta|^2+(\hbar\omega_D)^2} - \nu\frac{|\Delta|^2}{2}\ln\frac{2\hbar\omega_D}{\underbrace{\sqrt{|\Delta|^2+(\hbar\omega_D)^2}}_{\approx\,\hbar\omega_D\left(1+\frac{1}{2}\frac{|\Delta|^2}{(\hbar\omega_D)^2}\right)} - \hbar\omega_D} + \frac{|\Delta|^2}{g}$$

for $|\Delta| \ll \hbar\omega_D$ follows:

$$\boxed{\mathcal{E}_0 \cong \text{const} - \nu\frac{|\Delta|^2}{2} - \nu|\Delta|^2\ln\frac{2\hbar\omega_D}{|\Delta|} + \frac{|\Delta|^2}{g}}$$

Minimizing the ground state energy with respect to $|\Delta|$

$$\frac{\partial\mathcal{E}_0}{\partial|\Delta|} = -\nu\cancel{|\Delta|} - 2\nu|\Delta|\ln\frac{2\hbar\omega_D}{|\Delta|} + \nu\cancel{|\Delta|} + \frac{2|\Delta|}{g} \overset{!}{=} 0$$

trivial solution $|\Delta| = 0$ with energy $\mathcal{E}_0 = \text{const}$

non-trivial solution $|\Delta| \neq 0$

$$-\nu\ln\frac{2\hbar\omega_D}{|\Delta|} + \frac{1}{g} = 0 \quad \Longrightarrow \quad \boxed{|\Delta| = 2\hbar\omega_D\, e^{-\frac{1}{g\nu}}}$$

possesses the lower energy

$$\mathcal{E}_0 = \mathcal{E}_0(\Delta=0) - \frac{\nu}{2}\left(2\hbar\omega_D\right)^2 e^{-\frac{2}{g\nu}}$$

BCS groundstate wavefunction

The Bogoliubov annihilation operator $a_{k\sigma}$ acting on the BCS groundstate $|BCS\rangle$ gives

$$a_{k\sigma}|BCS\rangle = 0 \quad \text{for all } k \text{ and } \sigma.$$

where the transformation (exercise)

$$a_{k\uparrow} = u_k c_{k\uparrow} - v_k c^+_{-k\downarrow}$$

$$a^+_{-k\downarrow} = v_k^* c_{k\uparrow} + u_k^* c^+_{-k\downarrow}$$

relates $a_{k\sigma}$ to the original fermionic creation and annihilation operators.

This can be solved with an Ansatz involving the superposition of states with different numbers of particles

$$|BCS\rangle = \prod_k \left(u_k + v_k c^+_{k\uparrow} c^+_{-k\downarrow}\right)|0\rangle$$

where the product runs over wavevectors within a finite shell close to $|\vec{k}| \approx k_F$.

This follows from certain terms of the product yielding

$$a_{k\uparrow}\left(u_k + v_k c^+_{k\uparrow} c^+_{-k\downarrow}\right)|0\rangle = \left(u_k c_{k\uparrow} - v_k c^+_{-k\downarrow}\right)\left(u_k + v_k c^+_{k\uparrow} c^+_{-k\downarrow}\right)|0\rangle$$

$$= \Big(\underbrace{u_k^2 c_{k\uparrow}}_{\to 0} - v_k u_k c^+_{-k\downarrow} + u_k v_k \underbrace{c_{k\uparrow} c^+_{k\uparrow}}_{= 1 - \underbrace{c^+_{k\uparrow} c_{k\uparrow}}_{\to 0}} c^+_{-k\downarrow} - v_k^2 \underbrace{c^+_{-k\downarrow} c^+_{k\uparrow} c^+_{-k\downarrow}}_{\to 0}\Big)|0\rangle$$

$$= \left(- v_k u_k c^+_{-k\downarrow} + u_k v_k c^+_{-k\downarrow}\right)|0\rangle$$

as well as

$$a_{-k\downarrow}\left(u_k + v_k c^+_{k\uparrow} c^+_{-k\downarrow}\right)|0\rangle = \left(v_k c^+_{k\uparrow} + u_k c_{-k\downarrow}\right)\left(u_k + v_k c^+_{k\uparrow} c^+_{-k\downarrow}\right)|0\rangle$$

$$= \left(v_k u_k c^+_{k\uparrow} + u_k v_k c_{-k\downarrow} c^+_{k\uparrow} c^+_{-k\downarrow}\right)|0\rangle \quad = 0$$

Gap equation at finite temperatures

The gap was defined as

$$\Delta \equiv \frac{g}{V}\sum_{\substack{k\\|\xi_k|\le\hbar\omega_D}} \langle c_{-k\downarrow} c_{k\uparrow}\rangle = \frac{g}{V}\sum_{\substack{k\\|\xi_k|\le\hbar\omega_D}} \langle \left(-v_k a^+_{k\uparrow} + u^*_k a_{-k\downarrow}\right)\left(u^*_k a_{k\uparrow} + v_k a^+_{-k\downarrow}\right)\rangle$$

$$= \frac{g}{V}\sum_k \left[-u^*_k v_k \langle a^+_{k\uparrow} a_{k\uparrow}\rangle + u^*_k v_k \langle a_{-k\downarrow} a^+_{-k\downarrow}\rangle - v_k^2 \langle a^+_{k\uparrow} a^+_{-k\downarrow}\rangle + u^{*2}_k \langle a_{-k\downarrow} a_{k\uparrow}\rangle\right]$$

When the expectation values are evaluated with respect to H^{MF}_{BCS} this simplifies to

$$\Delta = \frac{g}{V}\sum_k \left(-u^*_k v_k\right)\left(\langle a^+_{k\uparrow} a_{k\uparrow}\rangle - 1 + \langle a^+_{-k\downarrow} a_{-k\downarrow}\rangle\right)$$

$$= \frac{g}{V}\sum_k \left(-u^*_k v_k\right)\left(2 f(E_k) - 1\right)$$

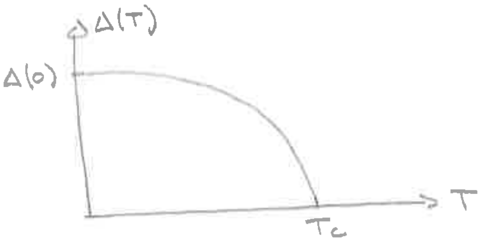
with the Fermi function $f(x) = \dfrac{1}{e^{x/T}+1}$ and $E_k = \sqrt{\xi_k^2 + |\Delta|^2}$.

Using $-u^*_k v_k = -\dfrac{\Delta}{2E_k}$ this simplifies for $|\Delta| \neq 0$ to

$$1 = \frac{g}{V}\sum_{\substack{k\\|\xi_k|\le\hbar\omega_D}} \frac{1-2f(E_k)}{2E_k}$$

At zero temperature $T=0$ this just recover $|\Delta| = 2\hbar\omega_D\, e^{-\frac{1}{g\nu}}$. At finite T we obtain

$$1 = g\nu \int_{-\hbar\omega_D}^{\hbar\omega_D} d\xi \, \frac{\tanh\left(\frac{\sqrt{\xi^2+|\Delta|^2}}{2k_BT}\right)}{2\sqrt{\xi^2+|\Delta|^2}}$$



This yields the temperature dependence of the gap $\Delta(T)$. It is expected that above the critical temperature $T \geq T_c$, the gap vanishes $\Delta = 0$ and the normal conductor is recovered. To determine T_c we take the limit $|\Delta| \to 0^+$:

$$1 = gv \int_{-\hbar\omega_D}^{\hbar\omega_D} d\xi \, \frac{\tanh\frac{|\xi|}{2k_BT_c}}{2|\xi|} = gv \int_0^{\hbar\omega_D} d\xi \, \frac{\tanh\frac{\xi}{2k_BT_c}}{\xi}$$

$$\overset{x=\frac{\xi}{k_BT_c}}{=} gv \int_0^{\hbar\omega_D/k_BT_c} dx \, \frac{\tanh\frac{x}{2}}{x}$$

In order to obtain the asymptotic behavior for $\frac{\hbar\omega_D}{k_BT_c} \gg 1$ we integrate by parts

$$1 = gv \Big[\underbrace{\ln x \tanh\frac{x}{2} \Big|_0^{\hbar\omega_D/k_BT_c}}_{} - \int_0^{\hbar\omega_D/k_BT_c} dx \, \ln x \left(\tanh\frac{x}{2}\right)' \Big]$$

$$\overset{\hbar\omega_D \gg k_BT_c}{\approx} gv \Big[\ln\frac{\hbar\omega_D}{k_BT_c} - \left(-\gamma + \ln\frac{\pi}{2}\right) \Big]$$

with Euler's constant $\gamma \cong 0{,}577$. This yields

$$\boxed{k_BT_c = \frac{2e^\gamma}{\pi} \hbar\omega_D e^{-\frac{1}{gv}}}$$

Comparing this with the gap at zero temperature $\Delta(0) = 2\hbar\omega_D e^{-\frac{1}{gv}}$ gives

$$\boxed{\frac{2\Delta(0)}{k_BT_c} = \frac{2\pi}{e^\gamma} \approx 3{,}528}$$

This result is well-obeyed by certain simple superconductors.

For temperatures $T < T_c$ and $|T-T_c| \ll T_c$ one can show that

$$\Delta(T) = \sqrt{\frac{8\pi^2}{7\zeta(3)}} \, k_BT_c \sqrt{1 - T/T_c} \cong 3{,}06 \, k_BT_c \sqrt{1 - T/T_c}$$

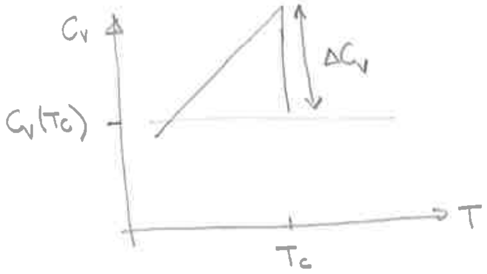
Heat capacity of a BCS superconductor

The specific heat of a BCS superconductor is given by

$$C_V = 2 \sum_k E_k \frac{\partial f}{\partial T}$$

where the Fermi function $f(E)$ has an explicit temperature dependence and an implicit dependence via the gap $\Delta = \Delta(T)$. The latter dependence $\Delta(T) \propto \sqrt{1 - T/T_c}$ leads to a mean-field jump ΔC_V of the specific heat at the transition temperature T_c.

An explicit calculation gives



$$\frac{\Delta C_V}{C_V(T_c)} = \frac{12}{7\,\zeta(3)} \approx 1{,}43$$

At low temperatures $T \ll T_c$ one obtains $C_V \propto e^{-\frac{\Delta}{k_B T}}$ an exponentially small specific heat.

Isotope effect

The proportionality $T_c \propto \Delta \propto \omega_D \propto \sqrt{M}$, where M is the ionic mass, can be experimentally confirmed by considering materials with different isotope content. It was one of the major arguments in favour of the phonon-mediated attractive interaction.

Density of states of the superconductor

Density of states for $|\Delta| \neq 0$ is given by

$$\nu(\varepsilon) = \frac{1}{V}\sum_k \Big(\underbrace{\delta(\varepsilon - E_k)}_{\text{positive}} + \underbrace{\delta(\varepsilon + E_k)}_{\text{negative}} \Big) =$$

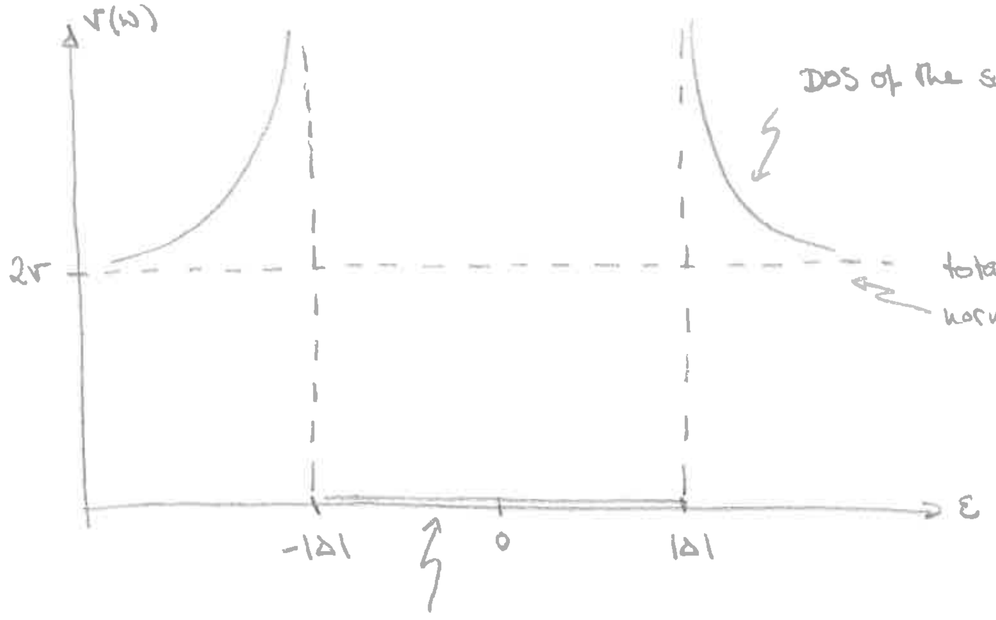
eigenenergies

$$= \nu \int d\xi \left(\delta\left(\varepsilon - \sqrt{|\Delta|^2 + \xi^2}\right) + \delta\left(\varepsilon + \sqrt{|\Delta|^2+\xi^2}\right) \right)$$

↳ DOS per spin of the normal state

$$= \nu \left(2 \frac{\sqrt{|\Delta|^2+\xi^2}}{|\xi|} \Bigg|_{\varepsilon = \sqrt{|\Delta|^2+\xi^2}} + 2 \frac{\sqrt{|\Delta|^2+\xi^2}}{|\xi|} \Bigg|_{\varepsilon \overset{-}{=} \sqrt{|\Delta|^2+\xi^2}} \right)$$

$$= 2\nu \frac{|\varepsilon|}{\sqrt{|\varepsilon|^2 - |\Delta|^2}} \Theta\left(\varepsilon^2 - |\Delta|^2\right)$$



DOS of the superconductor

total DOS of the normal metal

no DOS in a window $\pm|\Delta|$ around the Fermi level

$\nu(\omega)$ is directly accessible in tunneling experiment (I. Giaever, Nobel prize 1973)

7.2. Ginzburg-Landau theory of superconductivity

Phenomenological theory for the superconducting order parameter $\Delta(\vec{r})$ valid close to the transition temperature T_c and smoothly varying $\Delta(\vec{r})$;

useful for the description of inhomogeneous situations and treatment of macroscopic behavior of superconductors;

it can be derived from microscopic BCS Hamiltonian using field-theoretical techniques

Effective Lagrange density for order parameter field $\Delta(\vec{r}) \in \mathbb{C}$

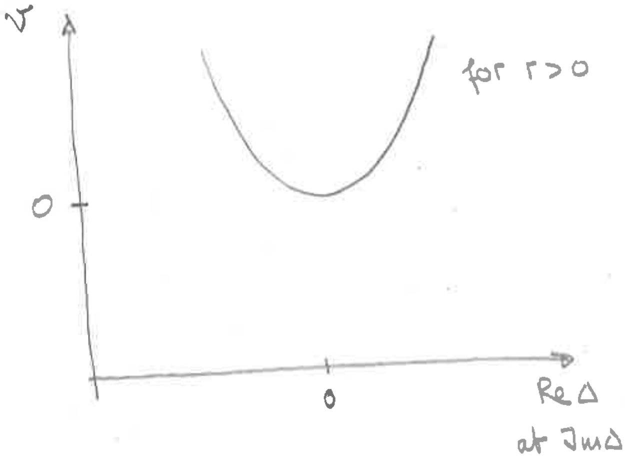
$$\mathcal{L} = \frac{1}{2m^*} \left| \left(-i\vec{\nabla} - e^* \vec{A} \right) \Delta \right|^2 + r|\Delta|^2 + \frac{u}{2} |\Delta|^4$$

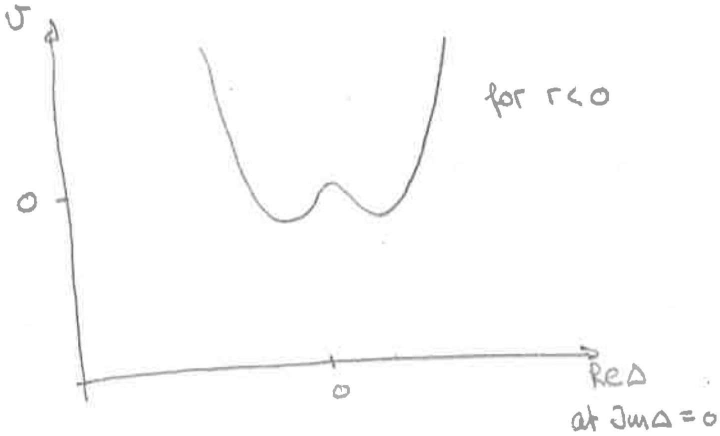
with $r \propto T - T_c$, mass m^* and charge $e^* = 2e$ of a Cooper pair, and $u > 0$.

Phase transition

neglecting fluctuations of $\vec{A} = 0$ and assuming a spatially constant $\Delta(\vec{r}) \equiv \Delta$

$\longrightarrow$ effective potential $\quad \mathcal{V} = r|\Delta|^2 + \frac{u}{2}|\Delta|^4$





on the mean-field level: second-order phase transition at $r = 0$

for $r < 0$: finite order parameter $|\Delta_0|^2 = -\frac{r}{u}$ with $\mathcal{V}(\Delta_0) = -\frac{r^2}{2u}$

Euler-Lagrange equations for spatially varying $\Delta(\vec{r})$ (at $\vec{A} = 0$)

$$r\Delta - \frac{\vec{\nabla}^2}{2m^*}\Delta + u|\Delta|^2\Delta = 0$$

for $r < 0$: reduced wavefunction $\Psi(\vec{r}) = \frac{\Delta(\vec{r})}{\Delta_\infty}$ with $\Delta_\infty = \sqrt{-\frac{r}{u}}$

$$-\psi - \xi^2 \nabla^2 \psi + |\psi|^2 \psi = 0$$

with $\boxed{\xi^2 = \frac{1}{2m^*|r|}}$ Ginzburg-Landau coherence length

characteristic length for variation of wavefunction

close to T_c : $\xi^2(T) \sim \frac{1}{T_c - T}$

London equations

$U(1)$ symmetry of $\Delta(r)$ ⟶ charge conservation

○ charge current $\vec{j} = e^* \left[-i \frac{1}{2m^*} \left(\Delta^* \vec{\nabla} \Delta - \overset{\curvearrowleft}{\Delta^* \vec{\nabla}} \Delta \right) - \frac{e^*}{m^*} \Delta^\dagger \Delta \vec{A} \right]$

in the superconducting ground state $\Delta(r) = \Delta_\infty$ and $\vec{\nabla} \Delta_\infty = 0$

$$\longrightarrow \boxed{\vec{j} = -\frac{e^{*2}}{m^*} n_s \vec{A}}$$

with $n_s = |\Delta_\infty|^2$ superconducting density

applying ∂_t and $\vec{\nabla} \times$ $\left(\text{with } \vec{E} = -\vec{\nabla}\phi - \partial_t \vec{A} \, , \; \vec{B} = \vec{\nabla} \times \vec{A} \right)$

○
$$\boxed{\begin{aligned} \partial_t \vec{j} &= \frac{e^{*2}}{m^*} n_s \vec{E} && (1) \\ \vec{B} &= -\frac{m^*}{n_s e^{*2}} \vec{\nabla} \times \vec{j} && (2) \end{aligned}}$$

London equations (1935)

- London equation (1) describes a <u>perfect conductor</u>

compare Drude theory for metals :

$$\frac{d(m\vec{v})}{dt} = e\vec{E} - \frac{m\vec{v}}{\tau}$$ with relaxation time τ

perfect conductor $\frac{1}{\tau} = 0$: charge current $\vec{J} = env$ $\Rightarrow$ $\partial_t \vec{J} = \frac{e^2 n}{m}\vec{E}$

- London equation (2) describes Meissner - Ochsenfeld effect : <u>perfect diamagnetism</u>

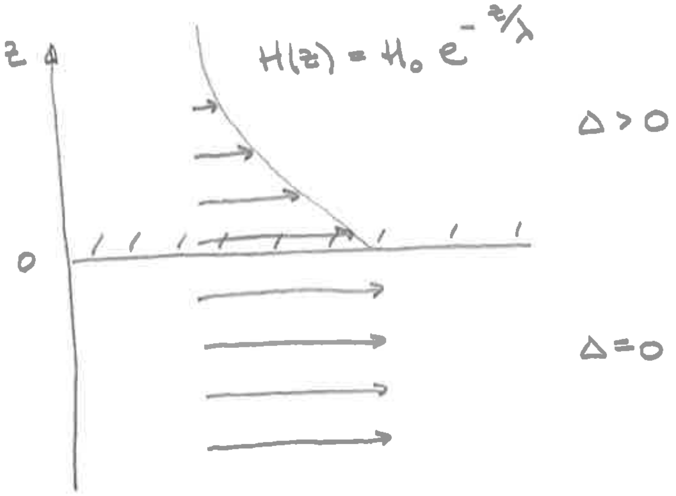
Maxwell equation $\vec{\nabla}\times\vec{H} = \vec{J}$

$$\Rightarrow \vec{\nabla}\times(\vec{\nabla}\times\vec{H}) \underset{\vec{\nabla}\vec{H}=0}{=} -\vec{\nabla}^2\vec{H} = \vec{\nabla}\times\vec{J} \overset{(2)}{=} -\frac{n_s e^{*2}}{m^*}\mu_0\vec{H}$$

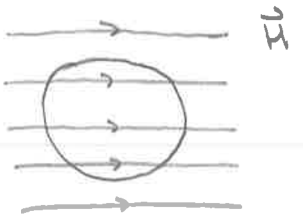
with $\vec{B} = \mu_0\vec{H}$.

$$\Rightarrow \quad \vec{\nabla}^2\vec{H} = \frac{1}{\lambda^2}\vec{H} \quad \text{with} \quad \boxed{\lambda = \sqrt{\frac{m^*}{n_s e^{*2}\mu_0}}}$$ London penetration depth

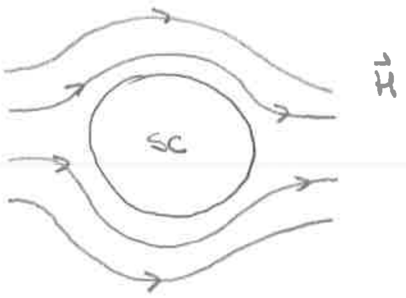
static magnetic fields do not penetrate the superconductor, they are screened on the length scale λ



Meissner-Ochsenfeld effect : expulsion of magnetic flux



$T > T_c$



$T < T_c$

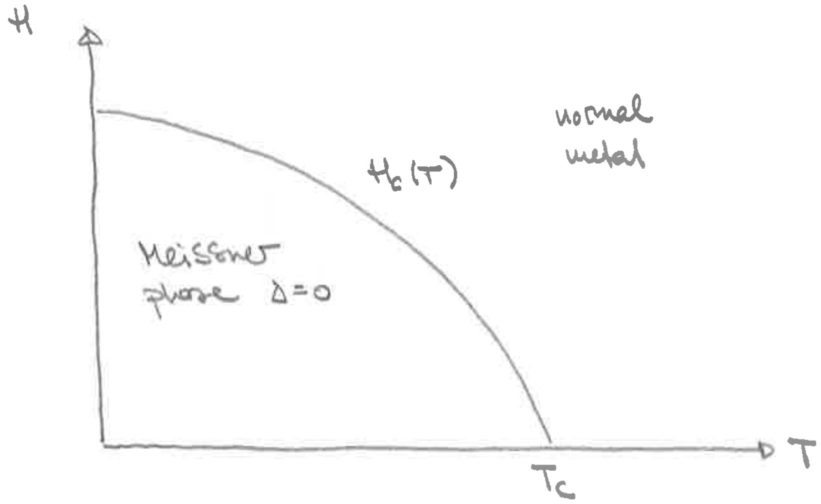
energy cost of expelling the magnetic flux $\varepsilon_H = \frac{1}{2}\mu_0 \vec{H}^2$

energy gain due to finite $\Delta > 0$ $\varepsilon_\Delta = -\frac{r^2}{2u}$ for the Ginzburg-Landau model

magnetic flux is expelled by developing a finite Δ as long as $\varepsilon_H + \varepsilon_\Delta > 0$

→ thermodynamic critical field H_c : $\frac{1}{2}\mu_0 H_c^2 = -\varepsilon_\Delta$

phase diagram of a type I superconductor



Type II superconductor

consider the limit of large fields H. How does superconducting order nucleate upon decreasing H?

Euler-Lagrange equation (for $\tau<0$):

$$-\psi + \xi^2\left(-i\vec{\nabla} - e^*\vec{A}\right)^2\psi + \underbrace{|\psi|^2\psi}_{\text{neglect this term for small } \psi} = 0$$

choose $\vec{A}(\vec{r}) = Bx\begin{pmatrix}0\\1\\0\end{pmatrix} \rightarrow \vec{B} = B\hat{z}$ magnetic field along $\hat{z}$

$$\Rightarrow \left(-i\vec{\nabla} - e^*Bx\begin{pmatrix}0\\1\\0\end{pmatrix}\right)^2\psi = \frac{1}{\xi^2}\psi$$

$$\left(-\vec{\nabla}^2 + i2e^*Bx\,\partial_y + e^{*2}B^2x^2\right)\psi = \frac{1}{\xi^2}\psi$$

Ansatz: $\psi(\vec{r}) = e^{ik_y y + ik_z z} f(x)$

$$\left(-\partial_x^2 + k_y^2 + k_z^2 - 2e^*Bxk_y + e^{*2}B^2x^2\right)f(x) = \frac{1}{\xi^2}f(x)$$

with $x_0 = \frac{k_y}{e^*B}$ and multiplying by $\frac{1}{2m^*}$

$$-\frac{1}{2m^*}f''(x) + \frac{m\omega_c^2}{2}(x-x_0)^2 f(x) = \frac{1}{2m^*}\left(\frac{1}{\xi^2} - k_z^2\right)f(x)$$

particle in a harmonic oscillator potential

with the cyclotron frequency $\omega_c = \frac{e^*B}{m^*}$

$$\Rightarrow \left(n + 1/2\right)\omega_c \overset{!}{=} \frac{1}{2m^*}\left(\frac{1}{\xi^2} - k_z^2\right)$$

for $n = 0, 1, 2, \ldots$ harmonic oscillator quantum number

$$\Rightarrow \quad B(n,k_z) = \frac{1}{2(n+1/2)e^*}\left(\frac{1}{\xi^2} - k_z^2\right)$$

field is maximal for $k_z = 0$ and $n = 0$ $\quad \mu_0 H_{c2} \equiv B(0,0)$

$$\rightarrow \quad \boxed{H_{c2} = \frac{1}{\mu_0 e^*}\frac{1}{\xi^2}}$$

comparison with H_c : $\quad \left(H_c = \sqrt{\frac{r^2}{2u}\frac{2}{\mu_0}} \ , \ \xi = \frac{1}{\sqrt{2m^*|r|}} \right)$

$$\frac{H_{c2}}{H_c} = \frac{1}{\sqrt{\frac{r^2}{u}\frac{1}{\mu_0}}}\frac{1}{\mu_0 e^*}\frac{1}{\xi^2} = \sqrt{\frac{2m^*|r|}{\frac{r^2}{u}\mu_0 e^{*2}}}\frac{1}{\xi} = \sqrt{2}\sqrt{\frac{m^*}{n_s \mu_0 e^{*2}}}\frac{1}{\xi}$$

$$\rightarrow \quad \boxed{\frac{H_{c2}}{H_c} = \sqrt{2}\frac{\lambda}{\xi} \equiv \sqrt{2}\,\kappa} \qquad \text{with } \kappa = \frac{\lambda}{\xi}$$

- for $H_{c2} < H_c \iff \kappa < 1/\sqrt{2}$ a Meissner phase with a constant Δ appears at H_c → type I superconductor
- for $H_{c2} > H_c \iff \kappa < 1/\sqrt{2}$ superconducting order nucleates locally

  harmonic oscillator wavefunction for $n=0, k_z=0$:

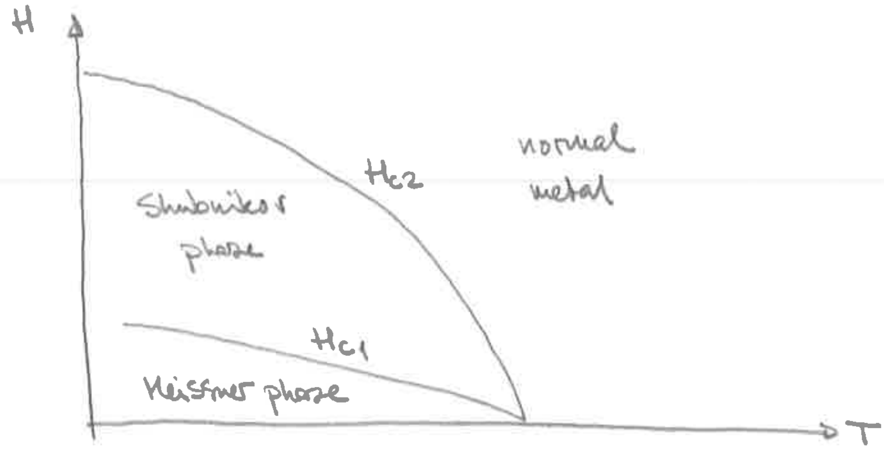
$$\psi(x,y) = e^{ik_y y}\, e^{-\frac{(x-x_0)^2}{2\xi}}$$

→ <u>Shubnikov phase</u>

closer inspection : magnetic flux penetrates the superconductor in the form of vortices each carrying a flux quantum $\phi = \frac{hc}{e^*}$

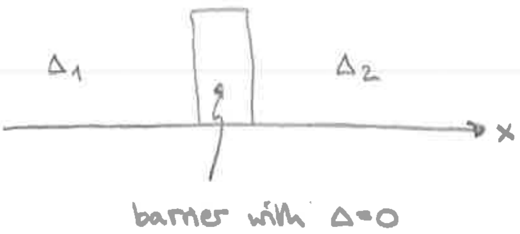
repulsion of vortices → Abrikosov vortex lattice (1957)

phase diagram of a type II superconductor



Josephson effect

consider a junction between two superconductors



There is a supercurrent across the junction that obeys

$$\boxed{\begin{aligned} I_s &= I_c \sin \Delta\varphi \\ \frac{d\Delta\varphi}{dt} &= \frac{2e}{\hbar} V \end{aligned}}$$

Josephson (1962)

Nobel prize 1973

where $\Delta\varphi = \varphi_2 - \varphi_1$ is the phase difference of the order parameters : $\Delta_{1,2} = |\Delta| e^{i\varphi_{1/2}}$

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 → dc Josephson effect

For a finite voltage V 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

Josephson critical current for a short metallic weak link

consider a short link between two superconductors of length $L \ll \xi$ that can be described by the Ginzburg-Landau equation

$$-\psi - \xi^2 \partial_x^2 \psi + |\psi|^2 \psi = 0$$

The two superconductors impose the boundary conditions

$$\psi(x=0) = e^{i\varphi_1} \quad \text{and} \quad \psi(x=L) = e^{i\varphi_2} \qquad \text{with } |\Delta_1| = |\Delta_2|$$

For a short link $L \ll \xi$ the GL equation for ψ is dominated in the range $0 \leq x \leq L$ 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 conditions

$$\rightarrow \quad \psi(x) = \underbrace{\left(1-\frac{x}{L}\right) e^{i\varphi_1}}_{\text{spread from } \Delta_1} + \underbrace{\frac{x}{L} e^{i\varphi_2}}_{\text{spread from } \Delta_2} \qquad \text{for } 0 < x < L$$

The wavefunction yields for the current $J = -i \frac{2e\hbar}{2m^*}\left(\Delta^* \partial_x \Delta - \Delta \partial_x \Delta^*\right)$

$$J = \frac{2e\hbar}{2m^*}|\Delta|^2 \left(-i\left[\left(1-\frac{x}{L}\right)e^{-i\varphi_1} + \frac{x}{L}e^{-i\varphi_2}\right]\left[-\frac{1}{L}e^{i\varphi_1} + \frac{1}{L}e^{i\varphi_2}\right] + \text{h.c.}\right)$$

$$= \frac{2e\hbar}{2m^*}|\Delta|^2 \left(-i\left[\left(1-\frac{x}{L}\right)\frac{1}{L}e^{i(\varphi_2-\varphi_1)} - \frac{x}{L^2}e^{-i(\varphi_2-\varphi_1)}\right] + \text{h.c.}\right)$$

$$= \frac{2e\hbar}{2m^*}|\Delta|^2 \left(\left(1-\frac{x}{L}\right)\frac{1}{L} + \frac{x}{L^2}\right) 2 \sin\Delta\varphi$$

$$= \frac{2e\hbar}{m^*}|\Delta|^2 \frac{1}{L} \sin\Delta\varphi \qquad \text{with } \Delta\varphi = \varphi_2 - \varphi_1$$

For a link with a cross-sectional area A within the y-z plane one obtains a current

$$I_S = I_c \sin \Delta\varphi \qquad \text{with} \qquad I_c = \frac{2e\hbar}{m^*} |\Delta|^2 \frac{A}{L}$$

Andreev reflections

One can also derive the Josephson relation microscopically by solving an inhomogeneous wave equation for the Nambu spinor.

The solution will involve the concept of Andreev reflections.

Consider the one-dimensional Schrödinger equation for the Nambu spinor $\vec{\Psi}$

$$i\partial_t \vec{\Psi} = \begin{pmatrix} \xi_{-i\partial_x} & -\Delta(x) \\ -\Delta^*(x) & -\xi_{-i\partial_x} \end{pmatrix} \vec{\Psi}$$

with $\xi_k = \epsilon_k - \mu$ and $\epsilon_{-k} = \epsilon_{+k}$ with $\xi_{k_F} = 0$.

Introduce right- and left-moving fields

$$\vec{\Psi}(x,t) = e^{ik_F x}\, \vec{\Psi}_+(x,t) + e^{-ik_F x}\, \vec{\Psi}_-(x,t)$$

where $\vec{\Psi}_\pm(x,t)$ depend only weakly on x: $\xi_{-i\partial_x} \longrightarrow \xi_{\pm k_F - i\partial_x} \approx \pm v_F(-i\partial_x)$ with the Fermi velocity $v_F > 0$.

This yields the effective wave equation after Fourier transform (for $\Delta(x) = \Delta$)

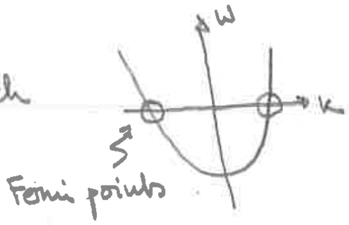
$$\begin{pmatrix} -\omega + \sigma v_F k & -\Delta \\ -\Delta^+ & -\omega - \sigma v_F k \end{pmatrix} \vec{\Psi}_\sigma(k,\omega) = 0$$

for right movers $\sigma = +1$ and left movers $\sigma = -1$.

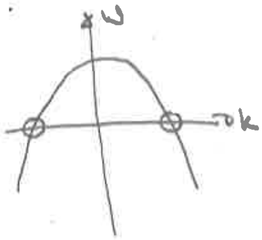
1. Normal metal $\Delta = 0$

eigenfunctions

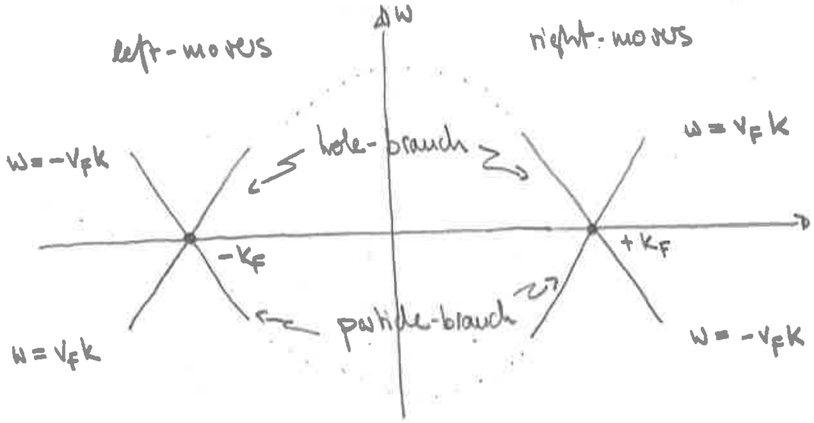
$$\vec{\psi}_\sigma(k,\omega) = \begin{pmatrix}1\\0\end{pmatrix} \quad \text{with} \quad \omega = \sigma v_F k \quad \text{particle branch}$$



$$\vec{\psi}_\sigma(k,\omega) = \begin{pmatrix}0\\1\end{pmatrix} \quad \text{with} \quad \omega = -\sigma v_F k \quad \text{hole branch}$$



focusing on the vicinity of k_F:



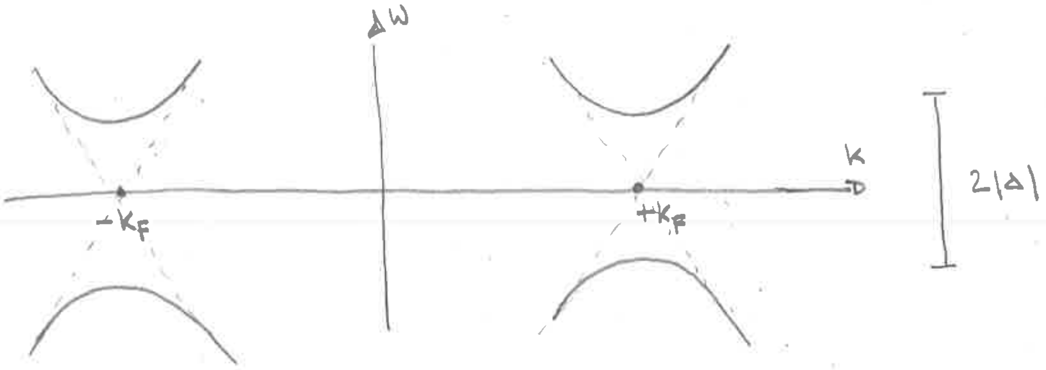
2. Superconductor $|\Delta| > 0$

for energies larger than the gap $|\omega| \geq |\Delta|$

eigenfunctions (not normalized)

$$\vec{\psi}_\sigma(k,\omega) = \begin{pmatrix}\omega + \sigma v_F k\\ -\Delta^*\end{pmatrix} \quad \text{with} \quad \omega = \sqrt{(v_F k)^2 + |\Delta|^2}$$

$$\vec{\psi}_\sigma(k,\omega) = \begin{pmatrix}-\Delta\\ \omega - \sigma v_F k\end{pmatrix} \quad \text{with} \quad \omega = -\sqrt{(v_F k)^2 + |\Delta|^2}$$



There are not any propagating solutions for energies smaller than the gap $|\omega| < |\Delta|$. There exists only a solution for imaginary wavevektors $k = i\kappa \rightarrow e^{ikx} = e^{-\kappa x}$ wavefunction decays or grows exponentially for $\kappa \gtrless 0$. The eigenvalues are then given by $\omega = \pm\sqrt{|\Delta|^2 - (v_F \kappa)^2}$ with $(v_F\kappa)^2 < |\Delta|^2$,

Normal metal - superconductor interface

consider the interface between a normal metal, $\Delta = 0$, and a superconductor with $|\Delta| > 0$ that we model by a step function

$$\Delta(x) = \begin{cases} 0 & \text{for } x < 0 \\ \Delta & \text{for } x > 0 . \end{cases}$$

consider the wavefunction for energies $0 < \omega < |\Delta|$.

The general Ansatz for a right-moving field $\vec{\psi}_+$ is then given by

for $x < 0$ and $\omega = v_F k$ with $k > 0$

$$\vec{\psi}_+(x,\omega) = e^{ik_F x} \left[a \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ikx} + b \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-ikx} \right]$$

we consider only backscattering processes with changes of momenta $|\Delta k| = |2k| \ll 2k_F$ ie. right- and left-movers do not mix because we assume the interface to vary smoothly on the scale of $1/k_F$.

for $x > 0$ and $\omega = \sqrt{|\Delta|^2 - (v_F \kappa)^2}$ with $\kappa > 0$

$$\vec{\psi}_+(x,\omega) = e^{ik_F x} \, c \begin{pmatrix} \omega + i v_F \kappa \\ -\Delta^* \end{pmatrix} e^{-\kappa x}$$

the exponentially growing solution $e^{\kappa x}$ is here not allowed.

Continuity at the junction $x = 0$ requires

$$\begin{pmatrix} a \\ b \end{pmatrix} = c \begin{pmatrix} \omega + v_F i \kappa \\ -\Delta^* \end{pmatrix}$$

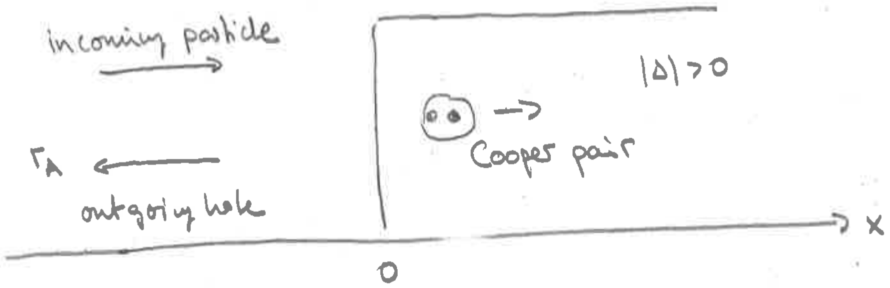
for an incoming particle $a = 1$:

Andreev reflection amplitude

$$r_A = b = -c\Delta^* = -\frac{\Delta^*}{\omega + i v_F \kappa} = -\frac{\Delta^*}{\omega + i\sqrt{|\Delta|^2 - \omega^2}}$$

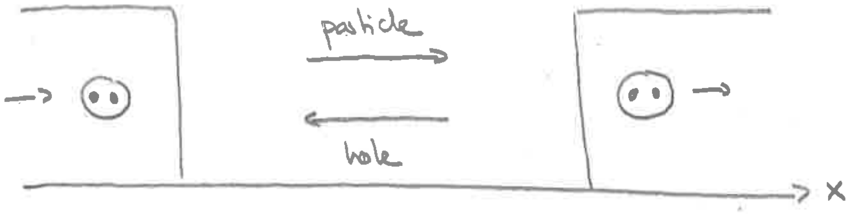
$$= -\Delta^* \frac{\omega - i\sqrt{|\Delta|^2-\omega^2}}{\omega^2 + (|\Delta|^2 - \omega^2)} = -\frac{\Delta^*}{|\Delta|}\left(\frac{\omega}{|\Delta|} - i\sqrt{1 - \frac{\omega^2}{|\Delta|^2}}\right)$$

electron is fully reflected as a hole with amplitude r_A and $|r_A|^2 = 1$



total charge of 2e is transfered to the superconductor in the reflection process.

In a superconductor - normal metal - superconductor (SNS) junction the Josephson effect can be understood as the repeated Andreev reflection at the two interfaces.



In each cycle of reflection a charge of 2e is transfered across the junction.

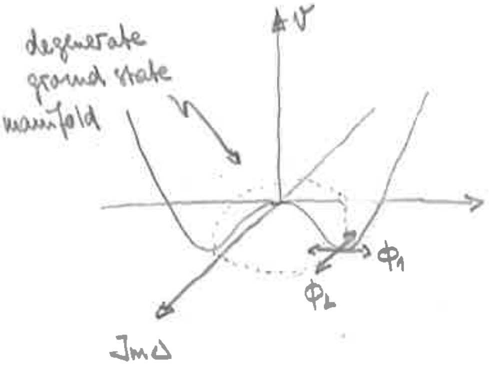
Anderson-Higgs mechanism

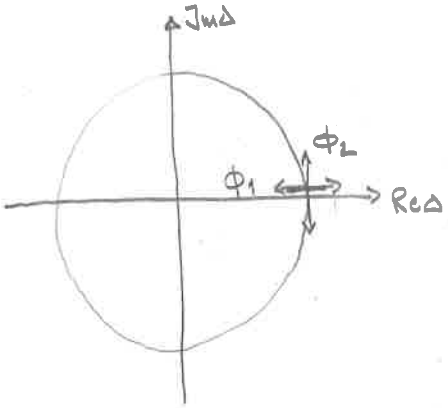
consider the Ginzburg-Landau theory for the order parameter field $\Delta(\vec r)$

$$\mathcal{L} = \frac{1}{2m^*}\left|\left(-i\vec\nabla - e^*\vec A\right)\Delta\right|^2 + r|\Delta|^2 + \frac{u}{2}|\Delta|^4$$

within the superconducting phase, $r<0$, with equilibrium solution $\Delta_0 = \sqrt{-\frac{r}{u}}$ chosen to be real and positive.

Consider small fluctuation around the equilibrium value $\Delta = \Delta_0 + \phi_1 + i\phi_2$





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 $\phi_{1/2}$:

$$\delta\mathcal{L} = \frac{1}{2m^*}\left[(\vec\nabla\phi_1)^2 + (\vec\nabla\phi_2)^2 - 2e^*\Delta_0\vec A\vec\nabla\phi_2 + e^{*2}\Delta_0^2\vec A^2\right] +$$

$$+ \underbrace{r\left(\phi_1^2 + \cancel{\phi_2^2}\right) + u\cancel{\Delta_0^2\phi_2^2} + 3u\Delta_0^2\phi_1^2}_{= 2u\Delta_0^2\phi_1^2} \quad \leftarrow \text{potential}$$

The potential for the tangential fluctuation 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

$$\vec{A}' = \vec{A} + \vec{\nabla}\chi \quad \text{and} \quad \Delta' = \Delta e^{i2e^*\chi}$$

for small χ :

$$\Delta' \cong \Delta(1+i2e^*\chi) = (\Delta_0+\phi_1+i\phi_2)(1+i2e^*\chi)$$

$$\cong \Delta_0 + \phi_1 + i(\underbrace{\phi_2 + 2e^*\Delta_0\chi}_{\phi_2'}) + \mathcal{O}(\phi_1\chi, \phi_2\chi)$$

We can always find a gauge transformation χ so that the transformed field component ϕ_2' vanishes. Goldstone mode "eaten up" by the gauge transformation.

The effective fluctuating part thus reads (dropping the prime)

$$\delta\mathcal{L} = \underbrace{\frac{1}{2m^*}(\vec{\nabla}\phi_1)^2 + 2u\Delta_0^2\phi_1^2}_{\text{Higgs mode}} + \underbrace{\frac{e^{*2}}{2m^*}\Delta_0^2\vec{A}^2}_{\text{photon mass}}$$

It consists of the longitudinal fluctuation field, ie. the Higgs mode ϕ_1 whose characteristic length is the coherence length ξ

The last term corresponds to a mass term for the photons which accounts for the Meissner effect. This generation of a photon mass is known as the Anderson-Higgs mechanism. This mechanism is also invoked in the standard model of particle physics (nobel prize 2013, Englert & Higgs)

Excursion : Second quantization

Hilbert space for many particle systems : Fock space

states characterized by occupation numbers : $|\{n_\lambda\}\rangle$; quantum number λ

eigenstates of the particle counting operator $\hat{N}$:

$$\hat{N}\,|\{n_\lambda\}\rangle = \sum_{\lambda'} \hat{n}_{\lambda'}\,|\{n_\lambda\}\rangle = \sum_{\lambda'} n_{\lambda'}\,|\{n_\lambda\}\rangle$$

for bosons : $n_\lambda = 0, 1, 2, \dots$

fermions : $n_\lambda = 0, 1$ (Pauli principle)

representation of $\hat{N}$ in terms of creation and annihilation operators

$$\hat{N} = \sum_\lambda a_\lambda^+ a_\lambda$$

bosons

$$[a_\lambda, a_{\lambda'}] = [a_\lambda^+, a_{\lambda'}^+] = 0 \,, \quad [a_\lambda, a_{\lambda'}^+] = \delta_{\lambda,\lambda'}$$

$$a_\lambda^+ |\dots n_\lambda \dots\rangle = \sqrt{n_\lambda + 1}\,|\dots n_\lambda + 1 \dots\rangle$$

$$a_\lambda |\dots n_\lambda \dots\rangle = \sqrt{n_\lambda}\,|\dots n_\lambda - 1 \dots\rangle$$

fermions

$$\{a_\lambda, a_{\lambda'}\} = \{a_\lambda^+, a_{\lambda'}^+\} = 0 \,, \quad \{a_\lambda, a_{\lambda'}^+\} = \delta_{\lambda,\lambda'}$$

with anticommutator $\{A, B\} = AB + BA$

$$a_\lambda^+ |\dots n_\lambda \dots\rangle = \begin{cases} (-1)^{\sum_{i<\lambda} n_i}\,|\dots 1 \dots\rangle & \text{if } n_\lambda = 0 \\ 0 & \text{if } n = 1 \end{cases}$$

$$a_\lambda |\ldots n_\lambda \ldots\rangle = \begin{cases} (-1)^{\sum_{i<\lambda} n_i} |\ldots 0 \ldots\rangle & \text{if } n_\lambda = 1 \\ 0 & \text{if } n_\lambda = 0 \end{cases}$$

$\downarrow$

$a_\lambda |0\rangle = 0$ with vacuum $|0\rangle$ empty of any particles

$$|\{n_\lambda\}\rangle = \prod_\lambda \frac{(a_\lambda^+)^{n_\lambda}}{\sqrt{n_\lambda!}} |0\rangle$$

representation of a many-particle Hamiltonian

in real space :

$$H = \sum_{\sigma=\uparrow,\downarrow} \int d\vec{r}\, \psi_\sigma^+(\vec{r}) \left[-\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_\sigma(\vec{r}) +$$

$$+ \frac{1}{2} \sum_{\sigma,\sigma'} \int d\vec{r}\, d\vec{r}\,'\, U(\vec{r}-\vec{r}\,')\, \psi_\sigma^+(\vec{r})\, \psi_{\sigma'}^+(\vec{r}\,')\, \psi_{\sigma'}(\vec{r}\,')\, \psi_\sigma(\vec{r})$$

in momentum space

$$H = \frac{1}{V} \sum_{k\sigma} \epsilon_k c_{k\sigma}^+ c_{k\sigma} + \frac{1}{V^2} \sum_{kk'\sigma} V(\vec{k}-\vec{k}\,')\, c_{k\sigma}^+ c_{k'\sigma}$$

$$+ \frac{1}{2} \frac{1}{V^3} \sum_{\substack{kk'q \\ \sigma\sigma'}} U(\vec{q})\, c_{k\sigma}^+ c_{k'\sigma'}^+ c_{k'+q\sigma'} c_{k-q\sigma}$$